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B.S. Levine

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Volume 12

A SURVEY

by B. S. Levine, Ph. D.

I - 80 AIR POLLUTION CONTROL AND PREVENTION REPORTS WHICH APPEARED IN GIGIENA I SANITARIYA VOLUME 28, 1963

II - SUPPLEMENT - A NEW TYPE OF INTERNAL COMBUSTION ENGINE

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VOLUME 12

A SURVEY

by

B. S. Levine, Ph. D.

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1966

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GIGIENA I SANITARIYA, VOLUME 28, 1963

AIR POLLUTION AND RELATED OCCUPATIONAL DISEASES

NO. 1 JANUARY

Spectrophotometric Determination of Benzene, Isopropylbenzene, and α-Methylstyrol in the Air

pp. 31-36

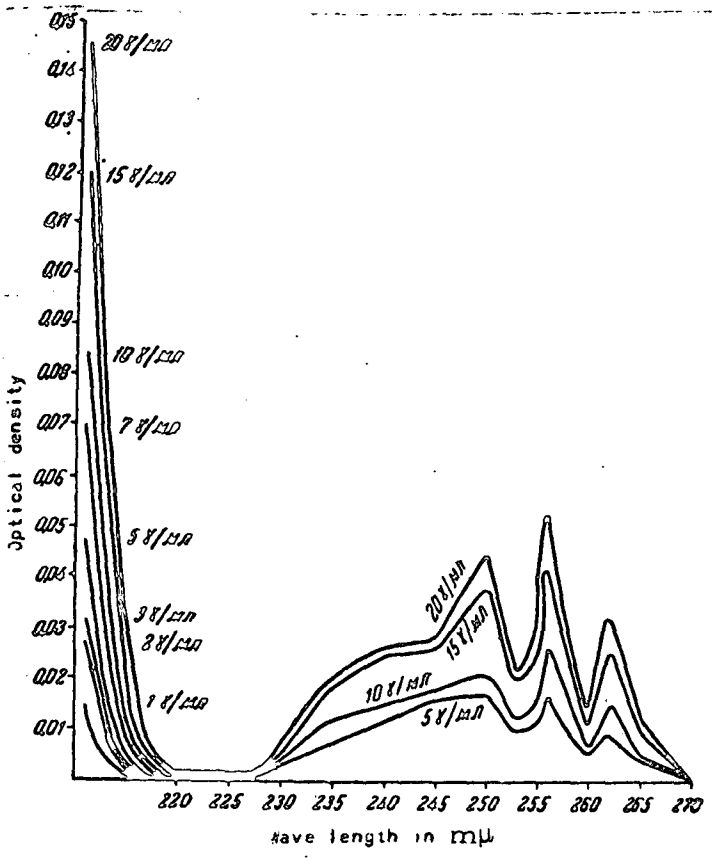
M. V. Alekseeva, N. A. Krylova and V. A. Khrustaleva
(From the F. F. Erisman Moscow Scientific - Research Institute of Hygiene)

Chemoanalytical procedures frequently fall short of making possible the determination of organic substances in mixtures. In such instances it may be necessary to resort to the use of methods based on the principles of molecular spectral analysis, and specifically to the method of ultraviolet absorption spectroscopy. This method is characterized by specificity, accuracy, and in the case of some substances by high sensitivity.

The present authors were faced with the following two problems: 1) determination of small amounts of benzene, isopropylbenzene and α-Methylstyrol in the air, and 2) selection of a solvent medium for the collection of samples of the above substances, which might make possible the quantitative determination of the substances. In this connection the spectrophotometric method is based on the determination of the optical density of the investigated substance in solution at wave length corresponding to its maximum absorption. An essential requisite of this method is that the investigated substance must behave in the selected solution in accordance with Beer's law. Ethanol was finally selected as the solvent in the study here described using spectrophotometer SF-4.

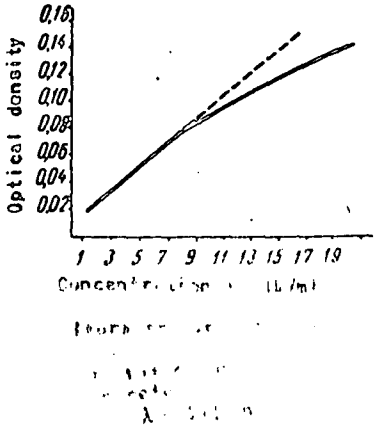
Determination of benzene. The absorption spectrum of benzene in solution is basically located in two ultraviolet light regions. At 198 mμ absorption intensity is very great ($\Sigma = 8000$), where Σ is the molecular absorption coefficient, and at 230-270 mμ the absorption intensity is considerably less ($\Sigma = 230$). Spectrophotometer SF-4 used in this study was limited to spectra beginning with $\lambda = 210$ m, therefore wave length $\lambda = 211$ was selected for the determination of benzene. The spectral characteristics were established using anhydrous distilled benzene for the preparation of standard ethanol solutions containing 1 to 20 γ/ml of the benzene. Fig. 1 represents curves of benzene spectral characteristics.

Fig. 1.



Spectral characteristics of benzene

Fig. 2.



A calibrated curve was constructed, as shown in Fig. 2 for the determination of benzene at λ = 211 mμ. It can be seen from this curve that benzene in ethanol solution behaved according to Beer's law within concentration limits of 1 - 7 γ/ml. Between concentration of 7 - 20 γ/ml the curves gradually deviate from the curves characterizing the law of Beer. However, the curve in Fig. 2 can serve as a calibrated nomogram for the determination of benzene in ethanol solution. Data in Table 1 show results of benzene determination in ethanol solution with the aid of the nomogram at λ = 211μ. The data show that the calibrated curve can be used reliably for the determination of benzene in ethanol solution 1 - 20 γ/ml. On the other hand, the nomogram shows that the spectrophotometric method was insufficiently sensitive for the determination of benzene.

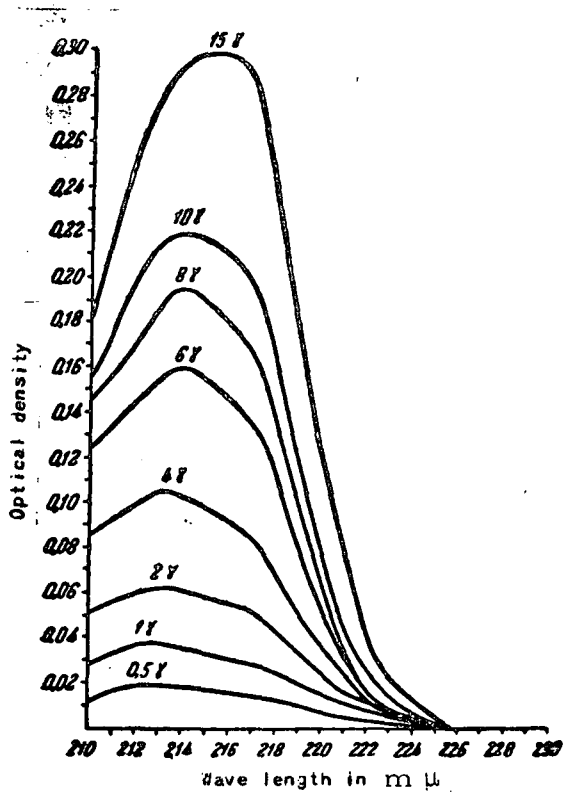
Table 1.

Benzene determination in ethanol solution λ = 211 mμ as in curve

Benzene in γ/ml	Found γ/ml	Error γ/ml	Error %	Remarks
1,0	1,0	0	0	Each value represents an
2,5	2,3	0,2	—8	
3,0	3,0	0	0	
	5,3		6	determination

Determination of isopropylbenzene. Pure redistilled isopropylbenzene was prepared, from which 0.5 to 15 γ/ml solutions in ethanol were made, and the spectral characteristics established on the basis of absorption intensity in the 210 - 350 mμ ultraviolet region. Resulting absorption curves are presented in Fig. 3. By means of numerous experiments it was established that maxi-

Fig. 3.



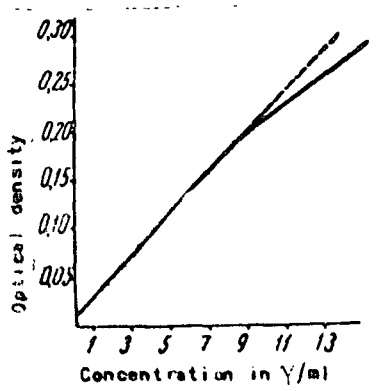
Special characteristics of isopropyl benzene

mum absorption for isopropylbenzene occurred at λ = 215 mμ, where solutions of isopropyl in ethanol behaved according to Beer's law. At isopropylbenzene concentrations 9 - 15 γ/ml the curve deviated from the curve characterizing Beer's law. However, as in the case of benzene, the calibrated curve in Fig. 4 was adequate for the determination of isopropylbenzene with a sensitivity of 0.5 γ/ml. Using spectrophotometer SF-4 laboratory determinations had been made of many standard isopropylbenzene solutions prepared in the laboratory. Some of the results are presented in Table 2.

Determination of α-methylstyrol.

The general study procedure was the same as described for the benzene compounds, i. e., absorption characteristics had been established first, as shown in Fig. 5. Ethanol solutions of pure redistilled α-methylstyrol were used. In this case maximum absorption of light occurred in the ultraviolet region of wave length λ =213 and 243 - 245 mμ, with a basic maximum at λ = 245 mμ, which was used in this investigation. It was estab-

Fig. 4.



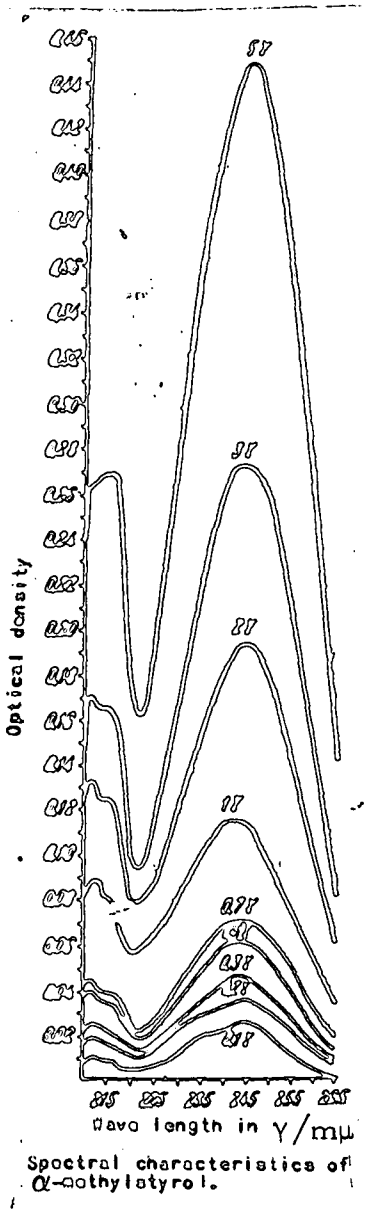
Calibrated curve for the determination of isopropyl benzine at λ = 215 mμ.

Table 2.

Determination of isopropyl benzene by calibrated curve at λ = 215 mμ

Isopropyl benzene used in γ/ml	Determined in γ/ml	Error γ/ml	Error %	Remarks
0,5	0,5	0	0	
1,0	0,9	0,1	—10	Values
2,5	2,7	0,2	+8	represent
5,0	4,7	0,3	—6	averages
7,0	7,2	0,2	+3	of 4
9,0	9,0	0	0	detins.
10,0	10,0	—	—	
15,0	15,4	0,4	+2,6	
20,0	20,4	0,4	+2	

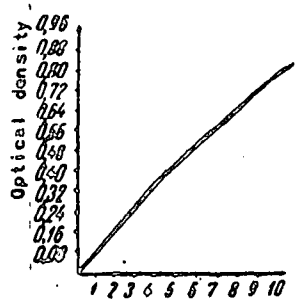
Fig. 5.



Spectral characteristics of α-methylstyrol.

lished experimentally that solutions of α-methylstyrol in ethanol reacted according to the law of Beer at λ = 245 mμ and that the determination sensitivity was within the limit of 0.1 γ/ml. Results of determinations made in the laboratory with ethanol solutions of α-methylstyrol, using the calibrated curve shown in Fig. 6 are presented in part in Table 3. The data obtained show that the spectrophotometric method can be used for the quantitative determination of small amounts of the substance under investigation.

Fig. 6.



Calibrated curve for the det'n of methyl styrol at λ = 245 mμ.

Table 3.

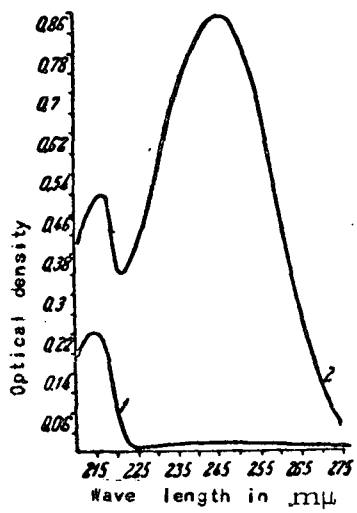
Det'n of α-methylstyrol by calibrated curve at λ = 245 mμ

α-methyl styrol used in γ/ml	Determined in γ/ml	Error γ/ml	Error %	Remarks
0,1	0,1	0	0	
0,4	0,4	0	0	
0,7	0,7	0	0	
1,0	1,0	0	0	Averages of 4 det'ns
1,6	1,5	0,1	—6	
2,0	2,0	0	0	
5,0	4,9	0,1	—2	
8,0	7,85	0,15	—2	
12	11	1,0	—8	

Determination of simultaneously present isopropylbenzene and α-methylstyrol. The differential determination of isopropylbenzene and of α-methylstyrol simultaneously present in a medium is based on the determination of the optical density of α-methylstyrol solution at λ = 225 mμ. Solution of isopropylbenzene is transparent in this light region, while α-methylstyrol solution intensely absorbs the light passing through it. Spectral characteristics are presented in Fig. 7. Fig. 8 presents a calibrated curve for α-methylstyrol concentration of 0 [illegible] 10 γ/ml. Fig. [illegible] presents a calibrated curve for same [illegible]. The differential determination of the two substances is carried out as follows: first the optical density of the solution at λ = 225 mμ; assume it to be 0.[illegible]. This optical density corresponds with α-methylstyrol, since isopropylbenzene is transparent in this light region. Find on curve in Fig. 8 the corresponding amount of α-methyl styrol, which in the assumed case is 2 γ/ml. Then, determine the optical density of the solution at λ = mμ, which is the optical density of the mixture of the two substances. Assume it to be 0.140. According

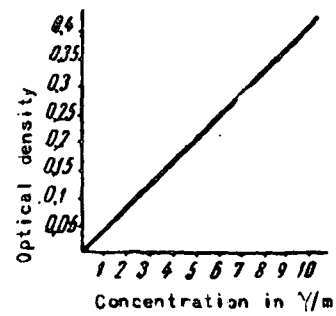
to calibrated curve in Fig. 9 the optical density for 2 γ/ml of α-methylstyrol at γ = 215 mμ is 0.15 (This must be a typographical error, it should be 0.115 BSL). Accordingly, the optical density of isopropylbenzene at λ = 215 is 0.140 - 0.115 = 0.025, which corresponds with 0.8 γ/ml of isopropylbenzene Hence, the mixture contained 2 γ/ml of α-methylstyrol and 0.8 γ/ml of isopropylbenzene.

Fig. 7.



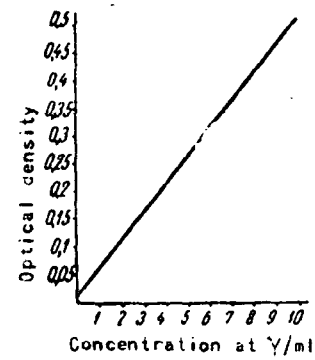
Spectral characteristics of isopropyl benzene and α-methylstyrol in 10 γ/ml concentrations.

Fig. 8.



Calibrated curve for the determination of α-methylstyrol at λ = 225 mμ.

Fig. 9.



Calibrated curve for the determination of α-methylstyrol at λ = 215 mμ.

Mixtures of α-methylstyrol and isopropylbenzene in methanol solution were prepared in the laboratory and differential quantitative determinations were made on the basis of the calibrated curves shown in Figs. 8 and 9. Some of the results are listed in Table 4. Data in that Table show that the spectrophotometric method offered the possibility of making separate differential determinations of α-methylstyrol and isopropylbenzene simultaneously present in solution. Procedures were also developed for the collection of air samples containing benzene, isopropylbenzene and α-methylstyrol, using methanol as the absorption medium. Experience indicated the necessity of using three successively connected Zaitsev aspirators for the aspiration of air samples. The apparatus must contain 10 ml of ethanol and must be submerged into ice-cooled water, the air sample is aspirated through the ethanol at the rate of 0.5 li/min. Some results of check tests made by the collection procedure and the tests described are listed in Table 5. See next page for Tables 4 and 5.

Table 4.

Graphic quantitative determination of isopropyl benzene and α/methyl-styrol simultaneously present in a medium

Isopropyl benzene				α-methylstyrol			
		Error				Error	
Used in γ/ml	Detn'd in γ/ml	γ/ml	%	Used in γ/ml	Detn'd in γ/ml	γ/ml	%
0,5	0,55	0,05	+10	3	3,1	0,1	+3,3
1,0	0,9	0,1	−10	5	5,4	0,4	+8
2,0	1,9	0	0	0,7	0,8	0,1	+14
5,0	4,7	0,3	−6	7,0	7,0	0	0
6,0	6,4	0,4	+6,6	2,0	2,0	0	0
8,0	7,8	0,2	−2,5	4,0	4,4	0,4	+10
10,0	9,5	0,5	−5	2	2,2	0,2	+10

Table 5.

benzene, isopropyl benzene and α-methylstyrol adsorption by ethanol at 0.5 l/min. aspiration rate

Substance	γ/m³ of air	Found			
		1st absorber	2d absorber	3d absorber	% in 2d absorber
Benzene	5	21,5	2,5	0	10
	8	36	5	0	12
	20	36	3	0	8
	30	75	16	0	17
	45	120	16	0	11
Isopropyl benzene	0,5	2,5	0	0	0
	1,7	8,5	0	0	0
	3,2	24	0	0	0
	5,0	23,7	3	0	4
	7,0	19	2	0	10
α-methylstyrol	0,1	0,5	0	0	0
	2,0	10	0,3	0	3
	4,0	29,5	1,25	0	4
	6,4	62,5	1,75	0	2,7
	9,0	29	0,9	0	3

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[illegible] Инструментальные методы химического анализа [illegible]

Absorption of Gaseous and Vaporous Harmful Air Pollutants by means of a "Turbulent" Layer of Hard Sorbents

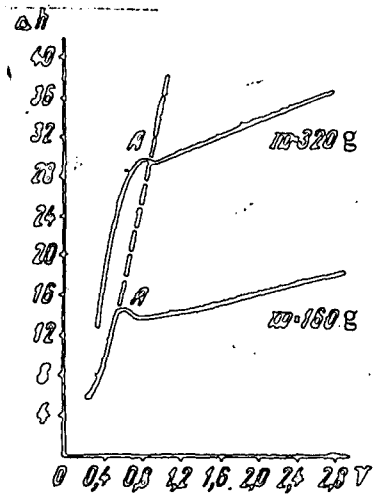
pp. 36-38

S.F. Yavorovskaya
(From the Institute of Labor Hygiene and Occupational Diseases of the U.S.S.R. Academy of Medical Sciences)

The determination of toxic substances in the air of working premises frequently requires large volumes of air. Many gaseous and vapor substances, mostly organic, are well absorbed from air currents by solid granular sorbents, such as different types of silicagel, activated charcoal, and the like. In such cases the sorbent is used in the granular or powdered form contained in straight or V-shaped tubes in columns of different lengths, held in position by the insertion of cotton or metallic wool wads at each end of the sorbent layer. Arranged in such a way, the sorbent presents some resistance to the flow of the air to be studied, the force of which increased with the increase in the rate of air aspiration. Under such conditions, and depending upon the length and diameter of the sorbent column and upon the size of the sorbent granules, the rate of air aspiration seldom exceeds 2-3 li/min., and frequently only fractions of a liter. Because of such limitations in the rate of air aspiration, the collection of desired air volumes is frequently protracted, and the analytical results do not reflect the characteristics of a given process at the given moment with adequate accuracy. This clearly points to the need of developing a set of conditions which would completely trap the specific pollutants by aspirating the tested air through the solid sorbents at an accelerated rate.

The present author developed an air sample collection procedure according to which the air to be investigated is aspirated through a layer of sorbent in constant agitation, generally referred to as a "turbulent" sorbent. Many industrial processes require high rates of gas flow and an almost complete contact with the surfaces of particulate matter; under such conditions, use is made of layers of powdered or granular substances in "turbulent" suspension; such, for instance, in the case of catalytic reactions in drying processes, or in calcination, etc. The "turbulent" condition of the sorbent suspension is further enhanced by creating circulating movements of the air, gas or vapor. The rate of air flow at which the entire mass of the solid sorbent acquires an even up and down movement, here designated as a "turbulent" movement, is usually referred to as the "critical rate". The "turbulent" character of the sorbent suspension layer possesses some advantages over the immovable layer. Fig. 1 presents experimental curves which illustrate the relationship between the linear air velocity (v) in m/sec. and the sorbent suspension layer resistance (Δh) in ml. In the case of a "non-turbulent" sorbent suspension layer this relationship is expressed in the form of a sharply rising straight line curve, as indicated by the dotted line in Fig. 1. In the

Fig. 1.



Relation between air flow rate and sorbent layer resistance. A - point of transition from quiescent layer to layer of turbulence.

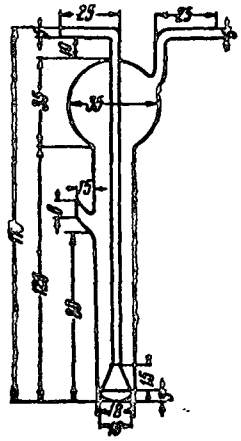
case of a "turbulent" sorbent suspension layer the curve of relationship between the suspension layer resistance and the rate of passing air sharply drops after it reaches the point of "critical flow", as shown at point A in Fig. 1.

Fig. 1 presents curves obtained with sorbent quantities of 160 and 320 g. The curves show that resistance of the "turbulent" suspension layer did not depend upon the sorbent mass. Due to the continuous and effective sorbent intermixing, its absorption capacity is utilized almost in full. The fact that the suspended sorbent is in a continuous state of agitation permits the passage of greater air volume in shorter time periods, and the air samples can be collected by aspirating the air at the rate of 10-12 li/min. without any loss of sorbent. This condition is of considerable advantage in analyzing air containing low concentrations of specific harmful substances.

It is not possible to create a condition of sorbent suspension "turbulence" in tubes. Therefore, the present author developed two types of adsorbers which are illustrated in Figs. 2 and 3. Both adsorbers consist of cylindrical glass tubes, the upper parts of which are in the form of spherical widenings. In the first adsorber the studied air enters via an inside tube which ends in a funnel-shaped opening, and in the second adsorber the air enters through a perforated glass plate. Both have lateral openings through which the solid sorbent can be introduced. Similar rates of air sample aspiration can be attained with either of the tubes and perhaps some higher rates can be attained with the second type of absorption tube at a more effective state of sorbent particles agitation. No loss of the suspended absorber had been noted in the case of absorber (1) when the sorbent granule diameters were small. The absorption of large gaseous molecules can be best attained with silicagel trademarked MSK and ShSk which have relatively large pores, and in the case of low molecules best results were obtained with silicagel trademarked ASM and ShSM. In the case of activated charcoal, the one trademarked BAU is recommended. The optimal granule diameter range should be between 0.25-0.5 mm.

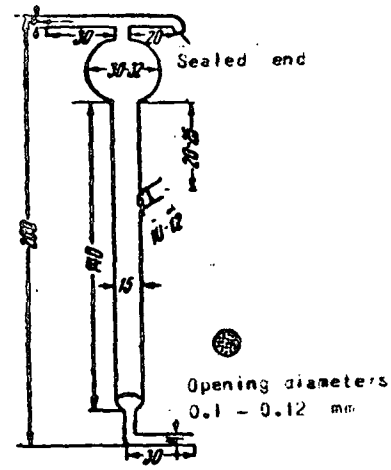
Best results were obtained with absorber No. 1 built so that the distance between the edge of the funnel-shaped opening and the glass bottom of the absorber was at a minimum; in the case of glass absorber No. 2 the pore in the porcelain plate should be within the range of 0.1-0.12 mm. The method of "turbulent" solid sorbent suspension in conjunction with absorber tubes here described has been in use in many industrial and sanitary chemical laboratories. See next page for Figs. 2 and 3.

Fig. 2.



Absorber apparatus for turbulent sorbent layer Ya-1

Fig. 3



Absorber apparatus for turbulent sorbent layer Ya-2

Purification of Gases Generated in Phthalic Anhydride Production

pp. 66-68

M. Kh. Tsipenyuk and Yu. E. Tsipenyuk
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Expansion in the chemical industry outlined in the general seven-year plan for USSR national economy demands that more attention be given to the improvement of hygienic conditions which prevailed in or resulted from the chemical industry. This applies particularly to industrial wastes discharged into the atmospheric air and national open water bodies. In this connection there arises the problem of improving the means of trapping tail gases, and in particular phthalic anhydride, the production of which must be greatly increased according to the seven-year economic development plan. Solution of this sanitary problem becomes especially urgent, since workers employed in this branch of industry may come in contact with such toxic substances as phthalic anhydride, malonic anhydride, 1-4-napthoquinone, etc., which at one time have been regarded as harmless. All technological processes used at present in the production of phthalic anhydride are based on the principle of napthalene and at times o-xylol oxidation by air oxygen catalytically. Under such production conditions the tail gases contain numerous admixtures after the phthalic anhydride concentration even under the most favorable waste gas trapping conditions. These admixtures pollute the atmospheric air, and can unfavorably affect man, animals and plants.

Many attempts had been made to purify the tail gases from the harmful substances. Fugler of Canada (1960) expressed the opinion that freezing

of the tail gases at 60° was the best procedure for their purification, burning of the tail gases with or without catalyzer was regarded by Fugler as another effective method of phthalic anhydride tail gas purification. These two methods are, indeed, highly effective. However, they are costly and difficult of accomplishment. In the USSR such tail gases are trapped by means of wet scrubbers of different types. It is important that the right type of wet scrubber be selected in order to bring about the maximal degree of exhaust gas purification. Scrubbers of several types had been tested at the Rubezhansk chemical combine. Scrubbers packed with Raschig rings had been tested first and were found adequately efficient. However, the Raschig rings soon became clogged with solid particles, while at the same time the pressure drop markedly rose thereby lowering the efficiency of the packed scrubbers. Table 1 presents data from the files of the central plant laboratory of the Rubezhansk Chemical Combine. The data clearly reflect the unfavorable effects mentioned above.

Table 1.

Performance efficiency of scrubber packed with Raschig rings (1960)

Date of sampling	Before scrubber treatment		After scrubber treatment	
	Total acidity	Naphthoquinone	Total acidity	Naphthoquinone
	g/l			
5/IV	0,0045	0,00025	0,00180	0,000002
12/IV	0,0016	0,00011	0,00034	0,0000012
15/IV	0,0021	0,00011	0,00044	0,0000044
22/IV	0,0032	0,00035	0,00011	0,0000060
14/VI	0,0035	0,00060	0,00058	0,0000160

For the past several years wet scrubbers had been used, inside of which fine spray devices had been installed, instead of Raschig ring packing; the spray was very fine and the devices were installed so as to insure maximum contact between the water and the air or gases. Results obtained with such scrubber types are presented in Table 2. The efficiency of packed and free spray scrubber types had been investigated by N. A. Pitelin in 1957. The present author compared the efficiency of the above mentioned scrubber types with the efficiency of presently used foam type scrubbers. The NIOP&K developed, and the Rubezhansk combine put into operation, a system for the purification of gases generated in the production of phthalic anhydride using foam scrubbers. Literature describing the operation of foam scrubbers is an extensive one. M. E. Posine and others (1959) described the results of their evaluation of foam scrubbers. Essentially such scrubbers consist of a hollow cylinder equipped with an inside grate. Water, or some other fluid, is run over the grate, while the gases generated during phthalic anhydride production entered the hollow cylinder below the grate. The grate perforations were made in such a way that the purifying fluid passed through them at the rate of 8-13 m/sec., while the gases entered the scrubber at the rate of 0.7 - 0.8

Table 2.

Performance efficiency of plain (no packing) scrubber (1961)

Sampling date	Prior to scrubber treatment		After scrubber treatment	
	Total acidity	Napthoquinone	Total acidity	Naphthoquinone
	g/li			
19/VI	0,0020	0,00028	0,000027	Trace
20/IV	0,0018	0,00070	0,00004	»
30/VI	0,0032	0,00033	0,00016	»
1/VII	0,0024	0,000023	0,00031	»

m/sec. The water, or other purifying fluid, entered the scrubber at the rate of 100 m^3/hr. Under such conditions an abundant layer of foam formed above the fluid surface above the grate, resulting in an intimate contact between the gases and the foam, which in turn brought about a high degree purification of the gases from harmful substances.

Table 3 presents results of foam scrubber purification of gases generated in the department of phthalic anhydride production. During the foam scrubber operation the slit perforations of the grate become filled with particulate material, which is removed continuously by a steadily operated special solid material removing device.

Table 3.

Performance efficiency of foam scrubbers (1961)

Sampling date	Before scrubber treatment		After scrubber treatment	
	Total acidity	Naphthoquinone	Total acidity	Naphthoquinone
	g/li			
30/III	0,00364	0,00122	0,0000240	Trace
1/IV	0,00126	0,00126	0,0000247	»
3/IV	0,00564	0,00127	0,0000350	»
4/IV	0,00320	0,00135	0,0000279	»
6/IV	0,00641	0,00110	0,0000309	»

The used scrubber fluid can be filtered for the removal of the solid material and other impurities and recirculated for repeat tail gas purification. Gases leaving the foam scrubbers contain a negligible residual of organic substances which are imperceptible by odor even at close proximity. It should be added at this point that in the case of packed or free spray wet scrubbers, frequent cleaning of the packing or of the sprayers is required for their continuous effective operation; this is costly and time consuming. Data presented on the operation of such scrubbers were taken immediately after the packed or spray scrubbers had been cleaned, as the packing in one scrubber or the spray apertures in the other type, become gradually clogged

with solid matter, the efficiency of their operation rapidly falls, and may become practically negligible. The foam scrubbers operated at high efficiency for long periods, and have to be cleaned or washed less frequently. Experience has indicated that in the case of gases containing solid particles which fall out during purification at the rate of 8-10 kg/hr and with the use of fresh or well filtered purification fluid, foam scrubbers can operate without cleaning interruptions up to 6 months.

Results of this investigation indicated that gases generated in the production of phthalic anhydride can be purified most efficiently by foam scrubbers. Their use in all departments of plants engaged in the production of phthalic anhydride is here recommended.

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Sanitization of Iron Pyrites Grinding at the M. B. Frunze Sulfuric Acid Plant

pp. 77-79

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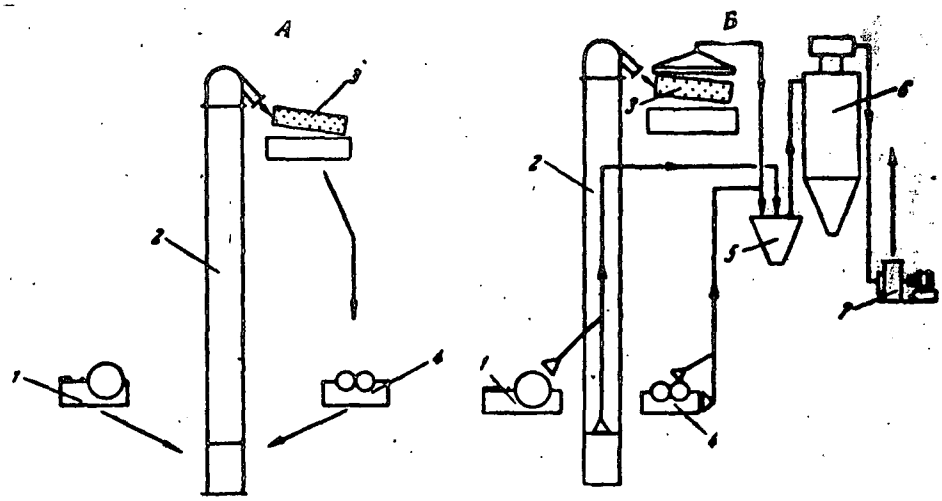
The iron pyrite grinding department at the M. F. Frunze sulfuric acid plant was an intense source of fine air-suspended dust which was coming from the transportation, unloading, grinding, and loading of the ground ore unto the small transfer cars. The entire pyrite grinding process was accomplished in an inclosed brick building, and consisted of the following operations: the raw ore was delivered to the plant's grinding territory in open railroad gondolas from which it was unloaded by means of a crane into brick or stone-lined excavations for storage. Whenever needed, the raw pyrite was picked up by means of Greifer cranes, loaded upon small transfer cars, and wheeled to and dumped into the grinding department's bunker, below which there was stationed a box-like "transporter". Again, whenever necessary, the box-like "transporter" was filled with the raw pyrite ore and wheeled into the ore crushing section located on the first floor,and discharged into a squirrel-wheel-shaped first step crusher. The crushed pyrite was picked up by a bucket-shaped elevator and was delivered into a sifting drum located on the third floor. Fragments of 8 mm or larger were separated and run by gravity into a roller mill located on the first floor, where the pyrite was ground finally

to the desired diameter particles. The material was then again picked up by the bucket elevator and again delivered to the third floor into the revolving sifting drums. Material consisting of particles less than 8 mm in diameter was then transported and dumped into the bunker storing the finely ground pyrite, from which it was taken to the furnace department when required.

Fine dust was intensely liberated into the surrounding air at each step of the above described procedure. The density of the air-suspended pyrite dust was inversely proportional to the moisture content of the raw ore, but the temperature of the air generally reduced the initial moisture of the raw pyrite by 65 - 70%, and under the prevailing ore grinding conditions it was not possible to raise the moisture content of the material artificially. Attempts to sanitize the working conditions had to be limited to encasing points of dust generation and to establish a suitable system of leak-proof ventilation. The old system of pyrite ore grinding also discharged a considerable amount of fine ore dust into the atmospheric air. This had also been taken into consideration when planning a new and appropriate system of indoor and outdoor air sanitization.



Schematic plan of pyrites grinding process

A - grinding prior to dust abating; B - grinding with dust abatement
1 - jawbreaker crusher; 2 - elevator; 3 - sifting drum; 4 - roller grinder
5 - coarse dust receiving bunker; 6 - cyclone; 7 - exhaust fan.

The above schematic figure presents the original conditions prevailing during raw pyrite grinding, and the scheme proposed for remedying the old unsanitary conditions. The schematic illustration shows that before the encapsulation of some intense dust discharging points and instituting local dust exhaust devices, all dust-generating apparatuses had been installed in the open, and the dust freely and abundantly was thrown into the surrounding air of the premises and of the atmosphere. After the sanitizing measures had been introduced, the dust was trapped at the squirrel-wheel-shaped [illegible] by a local dust catcher where the crushed ore ran out of the drum [illegible].

clined screen and by gravity was delivered into a "jawbreaker". The roller mill was inclosed (4) and suitably ventilated. The air from the sifting drum (3) was exhausted from a local inclosure which also took care of elevator air (2). All individual ventilator conduits opened into a main ventilator conduit. The dust-laden air was drawn off by suction into the ore receiving bunker (5). where the heavier dust particles were picked up; the air then passed through a cyclone (6) and picked up the finer dust particles. The air of the entire ventilation system was set into motion by a centrifugal ventilator (7), carrying the heavier and finer dust particles into the bunker containing the finally ground pyrite ore, and the air free from 96-97% of the dust was discharged into the atmosphere.

The investigation included medical examinations of persons engaged in work connected with pyrite-dust creating operations. Two of the examined individuals showed symptoms of dust disease diagnosed as silicosis of first degree. Analysis of conditions surrounding the specific functions performed by the two individuals made the diagnoses of doubtful value. Data in the table below show that the intensity of dust suspended in the air of the ore crushing chamber varied with the season of the year; it was 10 times as great during the hot season as in the cold periods. Data in the table also show that the air dust density was greater in the proximity of the roller mill, due to the considerably higher degree of particles dispersion. Lower air dust concentrations were found in the proximity of the sifting drum due to the fact that this apparatus was completely inclosed. Introduction of the air santization measures, as described, lowered the air dust density in the iron pyrites grinding mill to permissible levels specified in the official sanitary code. No cases of suspected silicosis had been found by medical examination conducted after the introduction of sanitary improvements during the period of 1958-1961.

Dust concentration in the air of working zone in mg/m^3

Place of air sample collection	Before installation of exhaust ventilation		After ventilation installation
	Febr.-March	June-July	June-July
At crusher "Belka"	23,6—24	261,6—261,9	6,9—7,2
At roller mill	27,6—27,8	281,4—294,9	4—4,1
At center of first floor	25,5—26,3	263,1—263,4	5,4—5,5
At sifting drum	10,1—10,8	122,5—123,2	2—2,2

Conclusions

1. Before the above described sanitary improvements in the process of iron pyrites grinding have been instituted the density of the generated and air suspended pyrite dust was great and constituted a serious sanitary problem.

2. The density of the iron pyrite dust in the air surrounding the pro-

cess was to a degree inversely proportional to the moisture content in the raw ore.

3. The sanitary improvements consisted basically in leak-proof encasing of strategic dust generating production points and in instituting an arterial ventilation system.

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Experimental Sanitary Improvement of Working Conditions in the Ya. M. Sverdlov Superphosphate Plant
pp. 80-82

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The Vinitsy superphosphate plant was built in 1912; its capacity is 10,000 tons of superphosphate per anum. For the past 30 years it has been gradually expanded, and in many phases reconstructed; at present it is one of the USSR most advanced chemical enterprises. New departments have been added, and old departments rebuilt along modern plans and principles for grinding superphosphate, tricalcium phosphate, sodium fluoride and sodium silicofluoride and phosphates; experimental departments had been equipped for the production of white soot and for the production of oxygen; an electric heat and power station and a waste water purification and disinfection installation have been added. Superphosphate production increased 50-fold in volume and in variety, while the number of employed increased by 150%. Mechanization is being annually modernized and sanitary working conditions are continually improved. Density of suspended dust and concentration of harmful gases in the surrounding air have been gradually abated. Along with the above plant improvements, there was gradual progressive improvement in the living conditions and welfare of the workers who resided in a nearby village. Money alloted to labor protection has been annually increased from 43,500 rubles in 1951 to 351,500 rubles in 1961. New construction, reconstruction and production department activation are all done in accordance with and under the supervision of authoritative sanitary bodies. A 100 meter smokestack was erected at the order of the sanitary organization equipped with gas purifying devices which abated atmospheric air pollution by 80 to 85%, and resulted in the recovery of

3.5 - 5 tons of sulfuric acid daily. Below are brief descriptions of the most significant sanitary measures instituted in the plant's basic production departments:

At the apatite stockyard. The atmospheric air dust density became considerably reduced after the grounds had been asphalt covered and spraying equipment installed. The apatite unloading from the railroad gondolas and loading onto small delivery cars was changed from manual to electric crane shovels or buckets, which lowered the stockyard air dust density by 80 - 90%. Manual cleaning of the bunker grates, from which the apatite was picked up by the elevator, was replaced by automatically operated electric scrapers, which also lowered the air dust density by 80 - 90%.

At the superphosphate department. The acid diluting, dosing, and temature regulating in the operating section had been automated, the conduits made leakproof, and the exhaust ventilation was operated at 30 mm of mercury or below; all this lowered the department's air dust density to 17 - 12% of the original. Fluorine elimination with the urine of workers ranged between 4 - 5 mg, whichis below the level at which development of fluorosis may set in. Other sanitary improvements had also been instituted.

At the silico-fluoride department. Sanitary working conditions had been especially unfavorable at the department for milling and packing raw sodium silicofluoride ore, where the air dust density ranged between 30 - 40 mg/m^3, and at times reached a density of 115 mg/m^3; workers inhaling air having such a concentration of suspended sodium silicofluoride suspended dust suffered of respiratory mucous membrane ulceration, nose bleeding, dermatitis and otosclerosis. Employees of this department eliminated 12 - 16 mg of fluorine daily. The sanitary authorities had ordered that the old type milling process be replaced by one of roller grinding, and that manual packaging of the final product be replaced by an automatic filling, dosing and sealing device; a more powerful local exhaust ventilation had been installed and all conduit leaks were carefully sealed. No occupational diseases had occurred among employees of this department after the above described sanitary improvements had been instituted, and the elimination of fluorine with the urine of such employees never exceeded 2 - 4 mg per day. The use of coal for drying-oven heating was replaced by natural gas, and the oven had been heat insulated, which eliminated the presence of coal dust in the air and lowered the intensity of heat radiation by the drying ovens from 0.5 to 0.2 $cal/cm^2/min$.

At the sodium fluoride department. Serious sanitary shortcomings had been noted at this department when it was first set into operation in 1956; the density of air-suspended sodium fluoride was high at the point of material mixing; in the proximity of the tubular furnace the air temperature rose to 42°, and the noise at the ball mill reached 120 decibels, etc. Conditions have been considerably improved since then: the general operation technology has been changed, which resulted in the elimination of the ball mill and the dis-

turbing noise its operation created; the soda dosing step has been changed from dry to wet, which completely obviated the dust previously generated by the dosing device, etc. A new ammonium fluoride-bifluoride department is now in project along the lines of up-to-date sanitary requirements.

At the powdered silicagel department. An experimental installation is now in operation; it is being constantly perfected with a view to improving working conditions. The basic technological process has been mechanized.

At the department of granulated superphosphate. The following had been the basic sanitary shortcomings in the old and, during the early period, in the new departments: a heavy air dust concentration in the proximity of the screening machine, transportation of the final product, drying drums, and fire holes; a fluorine air concentration range of 0.04 - 0.08 mg/li, and unsanitary atmosphere (microclimate) in the proximity of the drying drums and in the cinder section. The following improvements have been instituted: natural gas instead of coal is burned in heating the drying drums, a two-step air purification from fluorine and superphosphate dust has been installed, all ventilation conduits have been examined and made absolutely leak-proof, etc. The tail gases discharged into the atmosphere now contain only 0.18 g/m^3 of dust and 0.002 g/m^3 of fluorine.

At the tricalcium phosphate department (phosphate defluoridation). The phosphate defluoridation department heavily polluted the atmospheric air of the plant's grounds. The local sanitary authority ordered that the work in this department be conducted in two stages: the first stage, or step, consisted of production of intermediates, which were sent into the second technological stage for final production of tricalcium phosphate. Tail gases from the packing drum of the first processing stage were subjected to a two-stage purification from dust and fluorine. Fluoride tail gases from the first processing stage were sent into the absorption towers of the superphosphate department, and the SO_2 gas was piped into the sulfuric acid production department. Introduction of these improvements in the tricalcium phosphate department completely cleared the air over the plant's grounds from dust and fluorine pollution.

At the sulfuric acid production department. The following can be regarded as the determining sanitary measures instituted in this department: mechanized delivery of the iron pyrites into the cintering furnaces, and unloading of the cintered material; installation of dust-catching funnels and conduits for the automatic removal of dust from strategic dust generating production points. However, basic as such means of improvement in working conditions actually were, they did not suffice for adequate sanitization of conditions surrounding the location of the furnaces. It was necessary to widen the tower section, to institute automatic controlled aeration, and to install new and more powerful exhaust ventilators for the removal of tail gases from the new automatically operated cooler pump, etc. The amount of sulfuric acid aerosol and sulfuric acid spray discharged into the atmos-

pheric air had been reduced by the parallel installation of two PM-15 and one MT-184 electric precipitators.

At the sodium tripolyphosphate production department. The production process was completely mechanized. The exhaust tail gases from the cintering furnaces were passed through a three-stage purification in a cyclone-scrubber combination.

At the thermo-electric station. The plant's Th-E-S used coal and natural gas in its furnace; work is now in progress to convert the operation to natural gas only. Jalousie and battery cyclone catchers have been installed for the purification of the flue gases from ash, but their operation proved of low efficiency. Therefore, beginning with 1962, all Th-E-S boilers have been rebuilt for the combustion of natural gas only.

At the therapeutic-prophylactic service. The plant has its own polyclinic located in a cubically shaped two-story building of 2542 m^3 capacity. The clinic staff consists of an officer in charge, a therapist, otolarygologist, stomatologist, neuropathologist, obstetrician-gynecologist, and rentgenologist. The plant has well equipped rentgenological, oxygen, physiotherapeutic and hydrotherapeutic facilities, an inhalation apparatus and a clinical laboratory. All plant personnel undergo regular and systematic medical examinations in a specially equipped dispensary. The plant has a labor protection and occupational safety division the personnel of which sees that all safety regulations are observed; it has its own laboratory where working space air and gas samples collected from different plant departments are being analyzed as control and prophylactic measures. Study of the plant's personnel medical and work records indicated that due to the above described system of sanitary, therapeutic, general medical and prophylactic services the rate of morbidity and loss in work days have been steadily declining in this plant.

Determination of Maximal Allowable Strontium-90 Concentrations in Food Products

pp. 83 - 89

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It is known now that long lived isotopes such as strontium-90, oesium-137, cerium-144, settling in the form of radioactive fall-out upon the earth's surface find their way into the animal and human organism. Table 1 presents a list of radioactive isotopes regarded as most important from the viewpoint of radiation hygiene. Of these, strontium-90 is of greatest importance in relation to man. Sr is a chemical analogue of Ca; the two elements participate together in the synthesis and growth of bone tissue. It is generally consider-

Table 1

Radioactive isotopes of importance from the viewpoint of radioactive hygiene

Name of isotopes	Yield in % at Uranium – 235 splitting	Irradiation	Effective half-life period in the human organism in days	Critical organ	Isotope fractions entering from gastro intestinal tract of man into critical organs.	Isotope MAC in the critical organ in μc	MAC in open natural water bodies in c/l
Carbon-14	—	β	12	Fatty tissue	0,5	300	$2 \cdot 10^{-7}$
Strontium-89	4,6	β	50,4	Bones	0,21	4	$3 \cdot 10^{-9}$
Strontium-90	5,0	β	6400	"	0,09	2	$3 \cdot 10^{-11}$
Yttrium-91	5,0	β	58	"	$7,5 \cdot 10^{-5}$	5	$8 \cdot 10^{-9}$
Zirconium-95	6,4	β, γ	55,5	Entire Body	10^{-4}	20	$2 \cdot 10^{-8}$
Niobium-95	6,4	β, γ	33,5	"	10^{-4}	40	$3 \cdot 10^{-8}$
Iodine-131	2,8	β, γ	7,6	Thyroid gland	0,3	0,7	$6 \cdot 10^{-10}$
Cesium-137	6,2	β, γ	40	Entire body	1,0	30	$1 \cdot 10^{-9}$
Barium-140	6,0	β, γ	10,7	Bones	0,035	4	$7 \cdot 10^{-9}$
Cerium-144	5,3	β, γ	243	"	$3 \cdot 10^{-5}$	5	$3 \cdot 10^{-9}$
Promethium-147	2,6	β	570	"	$3,5 \cdot 10^{-5}$	60	$6 \cdot 10^{-8}$
Plutonium-239	—	α	72 000	"	$2,4 \cdot 10^{-5}$	0,04	$5 \cdot 10^{-11}$

Note Data pertaining to the yield of different isotopes resulting from the splitting of Uranium-35 and the nature of irradiation are cited from W. Langham and E. Anderson, pertaining to the effective periods, the critical organs, isotope fractions entering from the gastrointestinal tract into the critical organs, and the MAC levels of radioactive isotopes in critical organs are cited from ICRP of 1959; and data pertaining to MAC in open natural water bodies are cited from USSR Sanitary Regulations No. 333-60.

that 99% of strontium-90 deposited in the organism becomes firmly fixed in the bone tissue, where it forms characteristic deposition foci of radioactivity. Sr^{90} can enter the human organism in the following three ways: through inhalation of air polluted with Sr^{90}, through the intake of water similarly polluted, and through the ingestion of vegetables grown on strontium-90 polluted soil. Thus, Sr^{90} can enter the living organism through one, combination of two, or all three channels simultaneously. In this connection it must be noted that the amount of isotopes entering the organism differed with the path of their original entrance. The inhalation path is the least significant, since the concentration of Sr^{90} in the atmospheric air is negligibly slight and is tens of times below the established maximal levels. The same can be said of this isotope entering the organism with water. According to Bryant and others such an amount constituted only 10% of the total Sr^{90} which finds its way into the organism with food products, which is of greatest significance from the viewpoint under consideration. Sr^{90} can find its way into the human organism in the following succession chains: soil-vegetables-man, soil-vegetables-animals-animal food products-man, water-animals-animal food products-man, etc.

Hawthorn, Bryant, Chamberlain and other English investigators found that strontium-90 concentration in milk from farms in Great Britain examined during 1959 averaged 9.6 μμcurie per 1 g of Ca, or 10 μμ per one li of milk. Highest Sr^{90} concentration was found in the milk of Central Wales, where it reached 32 μμ curie per 1 g of calcium. Nezu and Asano of Japan analyzed samples of food products collected in Mito city and found that Sr^{90} concentration in milk was 10.9 μμcurie per 1 g of calcium, while the average for other food products was 19.5 per 1 g of calcium. A correct hygienic appraisal of radiochemical and radiometric determinations of strontium-90 concentration in food products can be made only on the basis of comparison with adopted maximal limits. At the same time, it must be borne in mind that rate of radioisotope accumulation in the human organism, and the consequent radiation activity, bear a direct relation to the reliability with which the adopted allowable concentration limits have been established.

Data presented in the literature on the subject of allowable radioactive concentration limits of different isotopes are contradictory. Thus, prior to 1960 the USA adopted the Sr^{90} allowable concentration limit recommended by the National Committee on Protection Against Radioactivity, which was 80 μμcurie per kg of food product, or per 1 li of milk. Other data recorded in the literature indicated that 100 μμcurie was the recommended maximal concentration. The Committee of the USA National Academy of Science presented a report in which it was recommended that the maximal concentration be set at 100 μμcurie per 1 g of calcium; the same report mentions 50 μμcurie per 1 g of calcium. In its report of April 1958 the California Health Department proposed that the maximal allowable strontium-90 concentration in food products including milk and vegetables, be set at 2×10^{-10} per kg. In February 1959 it was unofficially recommended by a USA Subcommittee that the previously recommended level be lowered from 80 to 60, and even to 16 μμcurie per li.

of milk. Similar lack of uninanimity in this respect existed in England.

According to USSR Sanitary Code of Regulations, No. 333-60, the total radioactivity entering the organism with the daily ration, including water, must not exceed 2.2 MAC curie per 24 hours, where 2.2 is the amount of water in li taken in per day on the MAC basis, and where MAC is the maximal allowable concentration of radioactive isotope activity in water.

In 1959 the Muenchen Committee for Protection Against Radioactivity recommended that $1x10^{-10}$ curie per liter of water be accepted as Sr^{90} MAC for drinking water used by the population residing in the proximity of the so-called "control zone" and $3x10^{-11}$ curie per li of drinking water for all other residents. The analyzed data indicated that the maximal permissible Sr^{90} intake with food products, including water, must not exceed 212×10^{-10} curie per day for persons residing in the so-called "control zone", and for all other residents it must not exceed 616×10^{-11} per day. The Chief USSR Sanitary Inspector and the Chairman of the Government Committee of the USSR Soviet of Ministers stipulated in regulations code No. 333-60, dealing with the use of atomic energy, that MAC of Sr^{90} be set at 3×10^{-11} curie per li of water. In accordance with such stipulation, the limit of allowable daily strontium-90 intake was set at $212 \times 3 \times 10^{-11} = 6.6 \times 10^{-11}$ curie. Table 2 presents data on maximal permissible strontium-90 doses entering the human organism adopted by different international organizations, national committees and by the USSR Sanitary Inspection Authority.

Table 2. Maximal permissible strontium-90 doses contained in 24-hour population rations adopted by different organizations

Information source	Maximal permissible strontium-90 intake with 24-hour ration	
	In c per day	In C-E per day
Recommended by the Council of Medical Studies of Great Britain for regions polluted with radioactive fall-out	$2 \cdot 10^{-9}$	2 000
Recommended by the ICRP in 1959 for persons residing in proximity of control zones . .	$2{,}2 \cdot 10^{-10}$	220
Recomended by the ICRP in 1959, and by the NCRP in 1960 and by Sanitary Regulations No. 333-60, approved by USSR State Sanitary inspector for the entire population. . . .	$6{,}6 \cdot 10^{-11}$	66

Note: Strontium-90 dose entering the organism in 24 hours was computed in terms of strontium units on the basic assumption that the amount of calcium entering the organism with all daily rations did not exceed 1 g.

It is regretted that the sanitary regulations code No. 333-60 presents no concrete method for the determination of the maximal permissible concentration of isotopes in food products. The regulations merely state that the MAC of different isotopes in food products of animal and vegetable origin determined, taking into consideration local conditions, on the basis of total 24 hour radioactivity contained in the daily ration, which must not exceed

2.2 MAC in curie per day. This is accompanied by a reservation which stipulates that the recommendation was based on an approximate calculation or estimation, and that in each concrete case a special examination or analysis was required involving more precise calculations. In summarizing it can be stated that methods of approach to the basic factors underlying the maximal permissible determination of radioisotope concentrations in food products differed with each investigator or group of investigators.

It appears ill-founded and irrational to adopt MAC of the same value for all types of food products regardless of their nutritional values and mineral composition. The heterogeneity of the chemical composition of different food products, especially the trace elements composition, presents a serious obstacle to the determination of a basic strontium-90 MAC in food products. Strontium belongs to the group of alkaline earth metals, and in its chemical properties is an analogue of calcium, barium and radium. It is precipitated together with calcium in the form of phosphates or carbonates, and upon permeating into the organism accumulates with Ca in the bone tissue. Strontium follows calcium in its path of biological nutritional chain of entrance into the human organism from the biosphere. The metabolic part played by strontium-90 varies considerably with the amount of calcium contained in the daily ration. In view of the above presented data, it appears more appropriate, if not more correct, to base the calculation of strontium-90 MAC in food products on their calcium content. Daily rate of calcium entrance into the human organism in different global regions varies between 0.24 and 1.87 g. According to B. I. Zbarskii and G. Sherman infants required a daily intake of not less than 1 g of calcium, regardless of their considerably smaller body.

Calcium belongs to the group of elements assimilated by the human organism with some difficulty. Its assimilation depends considerably on the content of other elements in the ration, foremost among which are phosphorus, magnesium, also proteins and fats. In this connection the daily norm of calcium is determined not so much by its absolute concentration in the foods as by its ratio in relation to other food ingredients, such as phosphorus and others. According to B. I. Zbarskii the daily intake of calcium was 0.8 g under conditions of optimal ratios with other basic ration ingredients. The calcium content in daily ration of inhabitants of most RFSFR, the Ukraine, and Belorusiya is of an adequately high level. Inhabitants of USSR regions, the local food products of which have a low calcium content, can compensate such deficiency by consuming calcium rich products brought in from other USSR sections, or by artificially adding calcium to bread during baking, etc. On the basis of a rough average, the present authors regard 1 g as the basic calcium amount taken in with a daily ration. Based on data presented in Table 2, and taking into consideration data obtained by I. S. Popov, M. F. Tomme and others relative to calcium content in different food products, the present authors estimated the strontium-90 MAC for different food products. Results are presented in Table 3.

Table 3.

Maximal allowable strontium-90 concentrations in food products in c/kg or c/l

Food Product	Ca content in g/kg	Maximal allowable Sr-90 concn. in different food products in c/kg or c/l computed according to recommendations		
		British Med. Council, for radioactive fall-out polluted regions	ICRP, 1960 for persons residing near control zones	ICRP-1960, NCRP-1960, USSR Sanit. Regul. No. 333-60
Milk	1,20	$2,4 \cdot 10^{-9}$	$2,7 \cdot 10^{-10}$	$7,9 \cdot 10^{-11}$
Curds	3,00	$6,0 \cdot 10^{-9}$	$6,6 \cdot 10^{-10}$	$2,1 \cdot 10^{-10}$
Cheese	9,30	$1,9 \cdot 10^{-8}$	$2,1 \cdot 10^{-9}$	$6,6 \cdot 10^{-10}$
Potatoes	0,14	$2,8 \cdot 10^{-1}$	$3,1 \cdot 10^{-}$	$1,0 \cdot 10^{-11}$
Grains	0,60	$1,2 \cdot 10^{-9}$	$1,3 \cdot 10^{-10}$	$4,2 \cdot 10^{-11}$
Cabbage	0,45	$9,0 \cdot 10^{-10}$	$1,0 \cdot 10^{-10}$	$3,2 \cdot 10^{-11}$
Beets	0,40	$8,0 \cdot 10^{-10}$	$0,9 \cdot 10^{-10}$	$2,8 \cdot 10^{-11}$
Carrots	0,60	$1,2 \cdot 10^{-9}$	$1,3 \cdot 10^{-10}$	$4,2 \cdot 10^{-11}$
Apples	0,07	$1,4 \cdot 10^{-10}$	$1,5 \cdot 10^{-11}$	$5,0 \cdot 10^{-12}$
Beef	0,12	$2,4 \cdot 10^{-10}$	$2,7 \cdot 10^{-11}$	$7,9 \cdot 10^{-12}$
Pork	0,06	$1,2 \cdot 10^{-10}$	$1,3 \cdot 10^{-11}$	$4,2 \cdot 10^{-12}$
Any Product	K	$2 \cdot 10^{-9}$ K	$2,2 \cdot 10^{-10}$ K	$6,6 \cdot 10^{-11}$ K

Such an approach to the determination of maximal permissible strontium-90 content in different food products appears to the present authors as more rational or basic, because it offers a basic concept of the role played by food products as sources of strontium-90 entering the human organism, and of their significance in relation to the total strontium-90 radioactivity in a daily ration; it also presents a basis for regulating the amount of strontium-90 entering the human organism with the food. The rationale of the proposed method for the determination of maximal permissible radioactivity in food products rests also on the possible radioactivity accumulation in the human organism. Under balanced metabolic conditions strontium-90 concentration in human bone tissue can be estimated with the aid of the following formula:

$$Q_{bone} = \alpha Q_{food}$$

where Q bone - denotes strontium-90 concentration in newly formed bone tissue in Sr Units; α - is the coefficient of "food-bone" discrimination; Q_{food} - denotes average level of strontium-90 in the daily ration in Sr Units.

It has been generally accepted that under normal conditions of mixed diets $\alpha = 0.25$. It is easy to show with the above formula that as the result of prolonged ingestion of food products which introduce into the gastro-intestinal

tract a total not exceeding 0.66×10^{-10} (66 SrU - the limit of permissible amount for the entire population) and 2.2×10^{-10} curie per day (220 SrU - the limit of permissible amount for a population residing in the proximity of a "control zone") the organisms of such inhabitants will accumulate, under conditions of balanced concentrations, not more than 16.5 and 55 SrU on the average. At the same time, according to recommendations made by MCRP in 1959, the maximal permissible strontium-90 concentration in the organisms of large population groups should be 67 SrU and of those residing in the proximity of "control zones" should be 200 SrU.

The USSR Sanitary Code No. 333-60 specifies no concrete values for MAC of different radioelements, including strontium-90, in the organism or any vital organ of man. However, with the aid of data presented in Table 2 related to maximal permissible dose of internal and external radiation for different population groups taken from Appendix 2 of Sanitary Code No. 333-60, it can be shown that isotope "loads" of 200 and 67 SrU are permissible correspondingly for persons residing in "sanitary protection zones" (class B) and those residing elsewhere. Indeed, according to the regulations the permissible internal radiation dose for vital organs of group III, including bones, can be 3 rem/anum for category B and 1 rem/anum for category C. (rem = roentgen equivalent for man) It has been agreed for the present to assume that 1 SrU under conditions of unequal Sr^{90} distribution in bone tissue generated a dose of 0.015 rem/anum (N. G. Gusev, Morgan). The ratio between the permissible internal annual radiation dose and the dose elicited by strontium-90 present in bone tissue of specific SrU concentration makes possible the determination of values sought for maximal "organism loads" of 200 SrU for category B and 67 SrU for category C. A comparison of the 200 and 67 SrU values with the probable "organism loads" computed with the aid of data on permissible strontium-90 concentrations in the population's rations according to Regulation Code No. 333-60, indicated that the strontium-90 MAC specified for rations by the regulations had a, so-called, built in quadruple safety factor.

In conclusion it should be noted that in presenting the above discussion the present authors did not wish to imply that the magnitude of permissible strontium-90 intake by the organism, or the specific levels of strontium-90 content in food products, must necessarily be expressed in terms of SrU units. The authors merely wished to emphasize that the method of computing strontium-90 MAC in food products on the basis of calcium content in such foods appeared to be more rational.

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Mine Dust Abatement by Preliminary Forced Coal Bed Moistening

pp. 108-110

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Air in the proximity of coal beds becomes polluted with dust not only as the result of coal dust generated by the coal mining machines, but also through the liberation of highly dispersed coal dust present in the cracks of coal beds. Such coal dust liberation into the air can be prevented by moistening the coal beds prior to beginning the mining machines' operation. M. V. Ratner, G. S. Grodel and others stated that preliminary moistening of coal beds lowered the Donbass mine air dust density by 60-69%. A. I. Xenophontova made a similar investigation in the Karagadin coal basin and found that preliminary coal bed moistening lowered the mine air dust density by 50-80%. Similar results were obtained by E. I. Ontin and L. Ya. Likhachev in 1961; V. N. Shilenkov, L. I. Ryzhikh, and A. P. Posluev obtained similar reduction in the air dust density after coal bed moistening in mines in which they conducted their investigations in 1960. Reports presented at the 1952 Geneva conference on the subject of dust abating during mine operation also affirmed that preliminary coal bed moistening lowered the mine air dust density by 60-75%. Preliminary coal beds moistening also softened the coal strata which enhanced the mining productivity by 25%, and lowered the amount of dead rock particles in the suspended dust. Coal bed moistening has its effect predominently on the smaller dust fraction. Experiments conducted in France and Belgium demonstrated that forced strata moistening lowered suspended dust particles of less than 10 μ in diameter by 60-70%, and of larger particles by 40-60%. The water sprayed into the coal strata cracks forced the methane out during the preliminary mining shift, thereby creating more sanitary mining conditions. The method of coal bed moistening should prove of particular sanitary benefit in abating suspended dust in mining steeply dipping faces and thin coal beds where the application of other dust abating means presented come difficulties.

This paper describes attempts made by the present authors to evaluate the effectiveness of forcing water into coal beds aimed at lowering the dust density of underground mining spaces. A study was made of the dust density in the air of mines having gently or sharply sloping coal strata of 0.7 - 0.8 meters thick, which generally consisted of anthracite or coke coal. The study was conducted in mines belonging to Rostovugol and Vorkutugol combines where mining was done by the usual mining method and by force-wetting the

coal strata first. Effectiveness of preliminary force-wetting as a method of dust abatement was studied and evaluated also at "Donbass" and LOD-1 combines and also at mines Yugozapadnaya No. 1 (faces 101 and 406) and Kapital-'naya No. 1 (face No. 7), where the pneumatic hammer mining method was used. Water was forced between the coal faces with the aid of apparatus RPP-2 under pressure of 60 - 80 atmospheres through holes 1.8 - 2.0 meters deep drilled in the coal strata 3 - 4 meters apart perpendicular to the slope of the coal face.

Mining in longwall 101 of combine "donbass" was done by the air method. Air dust density was investigated at the location of mining machine operation. Results of the investigation showed that air-suspended dust concentrations averaged 673.3 mg/m^3, with a maximum of 900 mg/m^3, where mining was done by the usual method, without forcing water into the coal beds; moistening the coal strata as described above lowered the dust concentration in the air to an average of 109 mg/m^3, with a maximum of 177 mg/m^3; the dust concentration at the point of the air jet emergence also dropped from 156 to 97.7 mg/m^3. Dust concentration at the point of air jet inflow, i. e. at the location of loaders-timberers remained unaffected and retained its usual concentration range of 12-20 mg/m^3. The high dust concentration of the air entering the longwall most probably resulted from shale and coal dust introduced into the air by air currents generated by the movement of the transportation and delivery equipment. Dust suspended in the inflowing air and in the air surrounding the coal mining machines operating under wet or usual dry methods was highly dispersed and contained 86% of particles 4 μ or less in diameter.

Results of the investigation indicated that the procedure of forcing water into the coal bed at the time of the mining combine operation lowered the concentration of the dust suspended in the air at the working location to 16%, which was still considered high and required additional or different means for further and more efficient dust abatement.

Dust concentrations in the air of Yugozapadnaya mine No. 1, managed by the Donetsugol trust at longwall No. 406, where mining was done manually, with or without pneumatic drills, were conducted next under conditions of wet and dry mining. Air samples were collected at points of drilling and loading and also at the approach to and exit from the longwall or long working face. Results of analyses showed that concentrations of dust suspended in the air where coal mining was done manually without preliminary strata wetting averaged 455.3 mg/m^3. Forcing water into the coal strata reduced the concentration of the suspended dust to an average of 90-92 mg/m^3; however, dust concentrations of 88.6 mg/m^3 frequently occurred, showing the inadequate safety the strata wetting method yielded under such conditions. Pneumatic coal drilling also reduced the effectiveness of forced water wetting as a method for lowering suspended coal dust density; under such mining conditions suspended dust concentrations averaged 59.9 mg/m^3, and the generated dust contained 92% of particles less than 4 μ in diameter.

Dust density investigation, similar to the one described above, was

conducted at Vorkut mine Kapital'naya No. 1, which was the source of soft and also medium hard coal, containing 19% of ash and approximately 5% of moisture, and which was used in the production of coke. Mining was done with a combine trade named "Donbass". The forced water process considerably lowered the concentration of coal dust suspended in the air in the location of the combine operator and his assistant. Thus, combine coal mining by the dry process created an average air dust density of 434 mg/m^3, which forced water wetting reduced to an average of 157 mg/m^3, or to 35% of the dust created by the dry mining process. Preliminary forced water wetting of coal strata was used in mine Artem-2 Glubokaya at longwalls 203 and 205; the hard anthracite of this mine had a moisture content of 2.98-4.30% and an ash content of 16-30%. Here pressure apparatus RPP-2 was used according to the above described system, and coal was mined with combine LGD-1 equipped with a spryaing arrangement. Results indicated that concentrations of air suspended dust at the location of the coal digging machine were 393.1 mg/m^3 when the dry mining process was used, and 311.2 mg/m^3 when the wet process was used or practically the same, because of the highly dust polluted incoming air currents.

In summary it can be stated that water forcing into coal strata of different hardness and structure of Vostochnyi Donbass and Pechora coal basin effected a considerable reduction in the air dust concentration where relatively soft coal was mined for use in coke ovens; however, in mining hard anthracite the effect of water forcing into the coal bed was insignificant. In the words of V.A. Golutvin and A.D. Kolomyisev, the beneficial effect of coal bed moistening with forced water differed with the softness of the coal, the structure of the coal layer and with its cracks or fissure pattern, etc. It must be added that much depended upon the method of water-forcing into the coal faces, a phase of work which calls for thorough investigation. Another factor which must be taken into consideration is the pollution density of the air supplied to the long working face areas, the dust effect of which can not be counteracted by coal strata moistening, and accordingly, must be abated or eliminated by some supplemental sanitary means.

Data presented by different investigators point to the feasibility of enhancing the dust abating effect of coal strata wetting by the forced water method through the simultaneous application of other supplemental dust abating menas. Thus, A. I. Zenophontova, A. I. Burchakova and G. E. Panova demonstrated that air spraying lowered the air concentration from 850-950 to 500-600 mg/m^3 during the operation of the "Donbass" coal mining combine, while combined air spraying and forced water strata wetting brought down the air dust concentration in the same location to 120-250 mg/m^3; by supplementing the above combination with an appropriate ventilation system it was possible to reduce the dust concentration from the previously mentioned 850-950 to 40 - 100 mg/m^3. By adding wetting agents to the forced water the sanitary effectiveness of this method can be enhanced to a considerable degree. This was demonstrated by experimental results obtained by E. I. Ontina, L. Ya. Likhacheva, A. I. Ivanov, E. M. Dubrovskii, and others.

The data presented in this paper emphasize the need of applying a complex of sanitary means for the abatement of mine air dust where coal is mined by pneumatic drilling, or by coal digging combines; the central or basic component of such a complex must be coal strata wetting by water forcing. This should be done not only at chosen strategic, but at all points of coal mining.

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NO. 2 FEBRUARY

Experimental Basis for the Determination of Allowable Acetophenone Limits in Atmospheric Air

pp. 3-8

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Acetophenone (C_8H_8O) belongs to the simplest fatty aromatic ketones in the molecule of which the carbonyl group is connected with one aryl and one fatty radical-alkyl. Under normal conditions it is a colorless or yellowish fatty fluid which turns into easily fusible leaf-life crystals at room temperature. The substance possesses a specific bird-cherry odor. Acetophenone is used in the chemopharmaceutical industry in the production of therapeutic agents, in the aniline dye industry and in the synthesis of organic substances. Chloroacetophenone, a product of acetophenone chlorination, belongs to the group of toxic substances. Acetophenone is used in chemopharmaceutical, aniline dye and organic synthesis industries. For this reason such industries constitute potential sources of atmospheric air pollution with acetophenone. The basic sources of air pollution are production of acetone and of phenol by the cumene method of which acetophenone is a side product. According to M. I. Fongauz (1961), this side product entered the air in disproportionally large

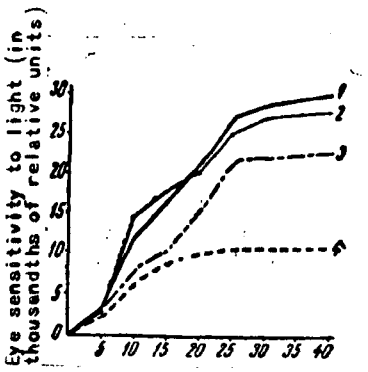
quantities in comparison to the primary and intermediate reaction products. Information found in the literature regarding the toxicity of acetophenone is limited and contradictory. Reports on this subject first appeared at the end of the 19th Century and dealt with the effect of acetophenone in large doses. No reports have been found in the literature describing the effects of low acetophenone vapor concentrations or with the effects of short duration contact with the substance; chronic effects of acetophenone have not been studied experimentally, and no experimental investigations have been conducted for the determination of maximal allowable acetophenone concentration in the atmospheric air, or in the air of working premises.

Experiments for the determination of acetophenone in the atmospheric air were conducted by the method of V. A. Khrustaleva in 1960. This method was based on the reaction between acetophenone and m-dinitrobenzene which resulted in the production of a rose-colored substance, the intensity of which was proportional to the concentration of acetophenone; the test color is compared with a freshly prepared color scale. Benzene, isopropylbenzene, isopropylbenzene hydroperoxide, α-methylstyrol, phenol and other such substances did not interfere with the determination of acetophenone, acetone interfered with the determination when present in quantities exceeding 100 γ. The method sensitivity has been established at 1 γ in 1 ml. Solid sorbent silicagel is used as the absorbed agent contained in a modified Zaitsev absorbers. The air should be aspirated at the rate of 4 li/min. After the acetophenone sample has been collected it is extracted with alcohol and determined colorimetrically. Under laboratory conditions low acetophenone concentrations can be determined by the spectral absorption method using spectrophotometer SF-4; the method was developed in the physico-chemical laboratory of the M. D. Manit Post Graduate Institute. The method sensitivity was 0.25 γ/ml.

Samples for the determination are collected the same as for simple colorimetric determinations. Maximal single dose of acetophenone in atmospheric air was determined by the threshold of acetophenone odor perception method, and by the effect of low acetophenone concentration on eye sensitivity to light, and by the electroencephalographic method. The average 24 hour limit of allowable acetophenone concentration was determined on the basis of acetophenone effect on experimental animals under chronic experimental conditions. The threshold of acetophenone odor perception was determined with the cooperation of 18 normal healthy adults 18 - 60 years of age using the procedure recommended by V. A. Ryazanov, K. A. Bushtueva and Yu. V. Novikov in 1957. A total of 455 observations were made in this way. Results indicated that the minimal perceptible acetophenone concentration was within the range of 0.027 - 0.01 mg/m^3. The latter concentration characterized the perceptibility of the more sensitive test persons. None of the test persons sensed any odor of acetophenone at 0.008 mg/m^3 concentration. Effect of low acetophenone concentrations on reflex changes in eye sensitivity to light was determined by the method of dark adaptation in three persons, using adaptometer ADM. Fresh air and the experimental mixtures of air and of

acetophenone in different concentrations were run into the inhalation tubes for ten minutes prior to actual determination of eye sensitivity to light. In this way the following ranges of acetophenone concentrations in air had been investigated: 0.018-0.020, 0.014-0.015, 0.01-0.011 and 0.007 mg/m^3. Triplicate tests were made with each concentration range. Results indicated that 0.014-0.015 mg/m^3 of acetophenone in the air elicited changes in the dark adaptation curve of all test individuals; 0.01-0.011 mg/m^3 elicited a change in only one female. Acetophenone in 0.007 mg/m^3 concentration in air had no effect on the course of the dark adaptation curve as shown in Fig. 1.

Fig. 1.



Changes in dark adaptation curve of female T. after acetophenone vapor inhalation

1-fresh Air. 2-0.007 mg/m^3 of acetophenone, 3-0.01-0.011 mg/m^3 of acetophenone 4-0.014-0.015 mg/m^3 of acetophenone

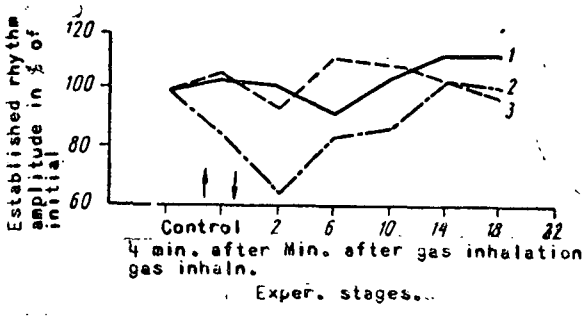
The determinations of threshold changes in the electric activity of the human brain as a result of acetophenone inhalation in different concentrations were made by a modification of the method developed in the Department of Community Hygiene of the Central Post-Graduate Institute. The modification was designed especially for use in functional electroencephalography to study the effect of nonperceptible pollutant concentrations in atmospheric air. The method is based on the capacity of the central nervous system to manifest rhythmic responses to rhythmic stimulation as described by V.S. Rusinov in 1954, by N. V. Golikov in 1956, and others. The administration of different acetophenone concentrations simultaneously with rhythmic light stimulation of different intensities offers a means of studying the nature of nerve processes during short time intervals. Such investigations had been conducted with five individuals whose state of upper respiratory passages had been checked and found normal. Results were recorded by means of an 8-lead electroencephalograph and photostimulator of the Kaizer type. Prior to making the actual tests 5-minute duplicate or triplicate check tests were made to obtain the background rhythm amplitudes of the test individuals. Actual testing lasted 46 minutes. During the first 5 minutes the test person inhaled nasally a given acetophenone concentration in air. No records were made during the first four minutes of the experimental vapor inhalation. Thereafter the individual was subjected to eye-light stimulation

mg/m^3. The first acetophenone concentration elicited a [illegible] control rhythm amplitude in all test individuals after 2-6 min. of light stimulation. The 0.003 mg/m^3 concentration had no effect on the background rhythm amplitude. However, the time record of the electrocardiogram and of the respiration rhythm manifested no specific regularity in their changes.

Thus, results obtained show that of three physiological methods tested for the determination of the allowable single acetophenone concentration

limit in the air, the most sensitive for the group of test individuals was the method of functional state of brain evaluation by means of electroencephalographic curves of rhythm adaptation. Thresholds of acetophenone reflex effect on the human organism were as follows: odor perception threshold, -0.01 mg/m^3; threshold of eye sensitivity to light - 0.01 mg/m^3; threshold of effect on electric brain activity - 0.007 mg/m^3. The 0.003 mg/m^3 concentration proved inactive by each of the three methods; accordingly, it is suggested that it be designated as the limit of allowable single acetophenone concentration in atmospheric air.

Fig. 2.



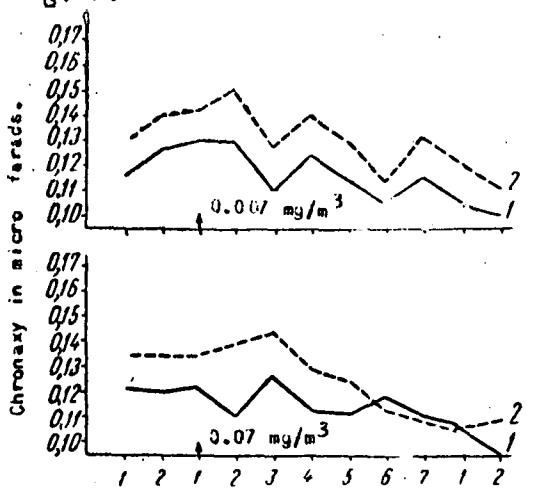
Effect of acetophenone on amplitude of established rhythm of test person A.

1-fresh air, 2-0.003/m^3, 3-0.007 mg/m^3 of acetophenone.

The limit of allowable 24-hour concentration of acetophenone in the air was determined in experiments with white mice subjected to continuous 24-hour inhalation of acetophenone in 0.07 and 0.007 mg/m^3 concentrations respectively for 70 days. The 0.007 mg/m^3 concentration was chosen as the one which manifested no effect on the eye sensitivity to light, as shown by results of electroencephalographic tests conducted later on a chronic basis. The second, or 0.07 concentration was merely 10 times the first. Air concentration fluctuations in the first exposure chamber averaged 0.008 ± 0.0008 mg/m^3, and in the second chamber - 0.076 ± 0.002 mg/m^3. Tests were conducted with 45 young white male rats, in groups of 15. Observations were made of the rats' general condition, changes in their weight, etc. Throughout the entire period of experimental observation rats of all groups were normally active, and experimental and control animals showed the same type of weight curves.

A study was then made of low acetophenone concentration effect on the functional state of the central nervous system; this was done by recording changes in the chronaxy ratios of the rats' muscle antagonists of the right hind leg. Chronaxy determinations were made in five rats of each group under similar conditions once every 10 days at the same time of the day. Prolonged administration of 0.07 mg/m^3 of acetophenone elicited changes in the chronaxy ratios of the flexor and extensor muscles. On the 7th to 8th week the two muscle antagonists' chronaxies in two of the five rats became equal and on the 10th week this happened in all five rats. Rats number 27 and 29 showed inverse chronaxy ratios of the flexors and extensors as shown by curves in Fig. 3. The 0.007 mg/m^3 concentration elicited no motor chronaxy changes in the muscle antagonists. Changes in the rheobase manifested no regular pattern.

Fig. 3.

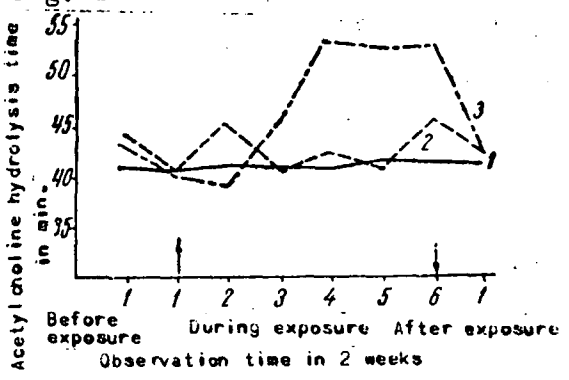


Acetophenone effect on muscle antagonists chronaxy in rats.

1-flexor, 2-extensor

Records were kept of the possible effect of low acetophenone concentration on changes in whole blood cholinesterase activity. Cholinesterase determination was made by the A. P. Martynov modification (1957) of the A. A. Pokrovski method of 1953. The principle of the method is based on changes in the indicator color due to shifts in the pH which occurred during acetylcholine hydrolysis. Cholinesterase activity determinations were made fortnightly. The 0.07 mg/m^3 concentration of acetophenone inhalation lowered the level of cholinesterase activity in all rats, except number 19, by 22% as shown in graph of Fig. 4. It sharply rose in rat number 19, especially at the end of the second month of the vapor inhalation. During the recovery period cholinesterase activity returned approximately to its original level, that is, to the level of the control group. The chronic inhalation of 0.007 mg/m^3 of acetophenone by the rats had no recordable effect on their cholinesterase activity.

Fig. 4

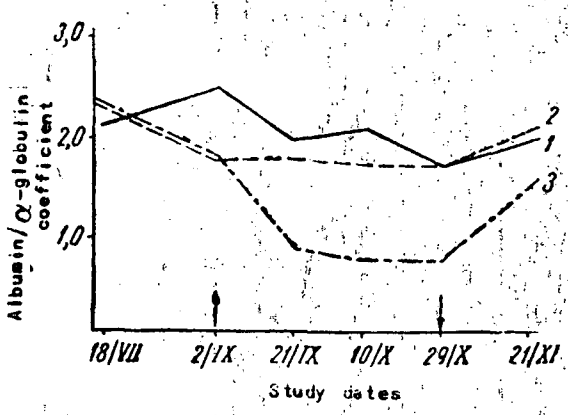


Acetophenone effect on whole blood cholinesterase activity in experimental animals

1-Control, 2-0.007 mg/m^3, 3-0.07 mg/m^3 of acetophenon

According to many authors the prolonged action of chemical substances changed the total amount of animals' blood protein as well as its fractional composition; therefore, such studies were included in the present investigation. Total protein was determined refractometrically every 20 days in five rats of each of the above mentioned groups. No changes in the rats of the experimental groups as compared with the controls were noted in any of the animals. The fractional blood serum protein composition was determined by paper electrophoresis, and elution of the obtained foregram with 0.1 normal solution of NaOH. Analysis of the foregram showed the following: rats exposed to the inhalation of the higher acetophenone concentration had a reduced albumin and a correspondingly increas. globulin content at the end of the first exposure month. Particularly indicative was the change in the albumin-alpha-globulin index from the 2.8-2.1 range to 1.2-0.6 at the end of the first month, as shown in curves of Fig. 5.

Fig. 5.



Acetophenone effect on the albumin/α-globulin coefficient of experimental animals.

1-Control, 2-0.007 mg/m^3, 3-0.07 mg/m^3 of acetophenon

Thus, result of chronic experiments lead to the conclusion that acetophenone in 0.007 mg/m^3 concentration had no effect on the animals of that group. Accordingly, it is recommended that the average 24-hour limit of allowable acetophenone concentration in the air should be set at 0.003 mg/m^3, which is at the level recommended for the single acetophenone concentration.

In order to obtain a picture of the atmospheric air pollution with acetophenone, observations had been made in the vicinity of a plant producing synthetic alcohol; in this plant acetone and phenol were obtained by the cumen method, and acetophenone resulted as a side product. The source of atmospheric air pollution with acetophenone was a department in which isopropylbenzene hydroperoxide was produced, and a department in which the isopropylbenzene hydroperoxide was hydrolyzed into the acetone and phenol, and also a department which processed the end or so-called waste products. The pollution was caused by departments which exhausted their polluted indoor air directly into the atmosphere. In June and July of 1962 single air samples were collected at distances of 100-200 meters from the source of air pollution. Results of analyses are listed in the Table below. Data in the Table show that only at 2,000 m from the source of air pollution were all the pollutant concentrations below the limits of the colorimetric method sensitivity for the determination of acetophenone, which means the concentrations were below 0.007 mg/m^3.

Different acetphenone concentrations in the air around the synthetic alconol plant

Meters from source of discharge	Number of samples		Maximal aceto-phenone concn., in mg/m^3	Distribution of acetophenone concentrations			
	Total	Above 0.007 mg/m^3		0,1—0,2	0,014—0,10	0,014—0,007	Less than 0.007 mg/m^3
100	3	3	0,023		2	1	
200	32	32	0,12	1	24	7	1
400	26	25	0,028		11	14	10
800	28	18	0,016		6	12	14
1 200	25	11	0,007			11	20
1 600	26	6	0,007			6	25
2 000	25	0					

Conclusions

1) The threshold of acetophenone threshold odor perception for most se

persons was determined as 0.01 mg/m^3, and the maximal nonperceptible concentration (subthreshold concentration) was determined as 0.01 mg/m^3.

2) The threshold of acetophenone reflex activity on eye sensitivity to light was determined as 0.01 mg/m^3.

3) Inhalation of 0.007 mg/m^3 acetone-air mixture for a short time elicited changes in the electrical brain activity but was inactive at 0.003 mg/m^3 concentration.

4) Chronic 24-hour inhalation of 0.07 mg/m^3 of acetophenone under chronic experimental conditions elicited no detected changes in the above mentioned indexes.

5) It is recommended that 0.003 mg/m^3 be adopted as the maximal single and 24-hour concentration limit for acetophenone in atmospheric air.

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Effect of Stabile Strontium Traces on Mineral Metabolism and on Radioactive Strontium-90 Accumulation in the Skeleton of Rats

pp. 19-24

V. A. Knizhnikov and P. F. Burgyshev (Moscow)

Reports found in the literature on the toxicology of stabile strontium deal with its effect on the organism in doses hundreds of times greater the amount of strontium which entered the organism with the food and water rations under natural conditions. Excessively high stabile strontium doses had been administered to experimental animals in an attempt to prevent the accumulation of radioactive strontium-90 in the organism. It was hoped that stabile strontium might act as a "diluent" for strontium-90 and that it might enter into "competition" with it, lowering the rate of strontium-90 assimilation and accumulation in the organism. However, it was soon realized that stabile strontium elicited strontium rickets and other grave disturbances in the experimental animals. No data had been found in the literature on the ef-

fect of stabile strontium traces on the organism's metabolism and, particularly, the mineral metabolism under chronic conditions. Despite persisting opinions regarding the, so-called, stabile strontium background, the concentration of the latter in natural waters was found to be considerable, which gives the problem of stabile strontium as a trace element a considerable degree of urgency in relation to general and especially mineral metabolism.

The present authors conducted their experiments with 245 adult white male rats. Stabile strontium was used in the form of its chloride in drinking water. Three sets of experiments had been conducted. The same strontium chloride was added to bread in the fourth set of experiments. The amount of strontium chloride added to the drinking water did not exceed concentrations of the element normally found in natural waters. Rats received Moscow City tap water having a strontium concentration not exceeding 0.2 mg/li. The animal rations were the same as indicated by the USSR Ministry of Health in Code No. 756 of September 11, 1953; the last experiment was an exception, since at this point, the rats received a simplified and reduced ration consisting of 10 g of rye bread per rat per day. Strontium-90 and calcium-45 were used in the chloride form. At the end of the experimental periods, the rats had been sacrificed, and their muscle-free thigh bones dried, weighed and ashed. Concentrations of strontium-90 and calcium-45 had been determined radiometrically as described in 1961 by V. A. Knizhnikov. Isotope accumulation in the skeleton was expressed in percent of the total dose administered, basing the calculation on the accepted assumption that the thigh isotopes amounted to 1/20 of the entire skeletal isotope content, and considering that the skeleton contained 99% of the strontium assimilated by the organism, The strontium-90 doses have been corrected according to calculations made on the basis of the mother product without yttrium-90. The first experiment was organized so as to simulate actual conditions; the effect of chronic consumption of water with a high content of stabile strontium on the accumulation of strontium-90 and calcium-45 had been studied. Results shown in Table 1 indicate that ingestion of drinking water having a high stabile strontium content actually lowered the accumulation of strontium-90 in the skeleton, and also the accumulation of calcium-45, which possessed similar chemical and metabolic properties. In another experiment the rats were kept on a reduced ration (see Table 1) and received bread containing 20 mg/kg of strontium, or the equivalent of 15 mg of strontium per 1 li of water.

For a more detailed and precise determination of the mechanism under investigation a supplementary experimental series was conducted with 138 rats which received the isotope through different routes, as shown in Table 2. Data of this series show that rats which received perorally water containing 15 mg of the stabile strontium per li of water accumulated during the first two hours strontium-90 and calcium-45 in their skeleton at approximately the same rate as did the animals of the corresponding control group, and possibly even at a higher rate. Later, the situation reversed itself, and the radioisotope concentration in the experimental animals fell to levels below those of the control animals, so that in the course of 168 hours the difference acquired a substantial

value. It has been estimated that at the end of 168 hours, the radioisotope content in the skeleton of the experimental animals amounted to only 1/3 and even 1/4 of that found in the control animals, which again verified the previously noted phenomenon. Following intraperitoneal isotope administration to rats of groups No. 11 and 14, the rate of isotope accumulation in the skeleton was greater in the control than in the experimental animals; however, 16 hours after the isotope administration, the picture became reversed to the one noted in experimental rats which received the isotopes perorally. It is of interest that prolonged administration of stable strontium in trace quantities had no effect on the usual concentration of stable calcium in bone ash as shown by data in Table 3. On the other hand, the 225 ± 5.6 g average weight of 59 experimental rats was lower than the 246 ± 5.1 g average weight of the 68 control rats. The different between the two average values was found statistically significant since $P < 0.05$.

Table 1.

Accumulation in the organism of Sr-90 and Ca-45 chronically entering the gastrointestinal tract with drinking water containing a high concentration of stabile strontium

Animal group No.	Number of group animals	Mg/li of stabile Sr. in the water	Accumulation in the skeleton in % of dose entered		Drop in skeleton accumulated Sr in % of initial control		Probability of accidental difference	
			Sr-90	Ca-45	Sr-90	Ca-45	Sr-90	Ca-45
With usual (balanced) ration								
1	11	15,0	12,7±0,5	22,6±1,5	—21	—35	<0,01	<0,01
2к	11	0,2	16,1±1,0	31,8±2,3	—	—	—	—
With unbalanced ration								
1	11	20	14,2	32.0	—28	—29	<0,05	<0,05
2к	18	0	19,7	45,2	—	—	—	—

Notes: 1. Weight of experimental rats which received the usual ration remained within the initial range of 135-10 g; in the course of 60 days of the experiment the rats received perorally 30 administrations of 1 ml solution containing the equivalent of 2.5×10^{-9} c of Sr-90 and 5×10^{-6} c of Ca-45

2. Rats which received non-balanced ration weighed 165 g to begin with; in the course of 60 days of experimentation they received per os 44 administrations of 1.2×10^{-7} c of Sr-90 and 2.0×10^{-6} c of Ca-45

Results of the last experiment are shown in Table 3. In this experiment, the authors attempted to arrive at an approximate stabile strontium threshold concentration for drinking water, which could elicit changes in the accumulation of calcium and of strontium under chronic conditions. Data in Table 3 show that strontium-90 and calcium-45 concentrations in the skeleton of animals which drank water containing 30 mg/li of strontium for 10 days following the administration of the radioisotopes, fell to levels below those of the control animals. Drinking water containing 10 and

Table 2

Effect of chronic and acute intake of correspondingly increased and very high quality Sr concentrations on the accumulation rates of Sr-90 and Ca-45 in bones

Expt. animal Group No. at end of experiment	No. of animals in group 4	Av. animal wt. in g at exprmnt. end	Mg/li of stabile Sr in the drinking water	Route of Sr-90 and Ca-45 administration	Hours after isotope administration	Percent of administered does retained by the skeleton		Percent of control in rat's skeleton		Probability of accidental difference (P)		Ca in the bones mg per 1 g of raw wt.	Percent of ash in bones
						Strontium-90	Calcium-45	Sr-90	Ca-45	Sr-90	Ca-45		
1a	5	268	150	Intraperitoneally	18	84,7±4,6	74,0±5,1	0	±3	>0,5	>0,5	146	52
1б	5	245	15	"	18	77,6±4,7	75,1±3,3	—9	±5	>0,25	>0,5	143	51
2	9	266	0,2	"	18	81,9±5,8	71,8±5,2	—	—	—	—	142	52
3	10	219	15	Per os	2	20,1±2,1	34,9±3,7	+14	±7	<0,5	<0,5	133	49
4	10	234	0,2	" "	2	17,7±1,7	32,7±3,7	—	—	—	—	138	50
5	10	238	15	" "	18	21,2±2,2	57,6±4,9	—16	—2	<0,25	<0,5	147	51
6	10	247	0,2	" "	18	25,2±1,6	58,7±3,2	—	—	—	—	143	50
7	10	210	15	" "	72	14,5±1,8	40,9±5,0	—12	—12	<0,5	<0,5	139	50
8	10	212	0,2	" "	72	16,4±1,2	46,4±6,0	—	—	—	—	143	52
9	10	232	15	" "	168	11,7±1,1	30,4±1,8	—25	—31	<0,1	0,01	143	49
10	10	260	0,2	" "	168	15,7±2,1	44,2±4,3	—	—	—	—	143	52
11	9	213	15	Intraperitoneally	2	86,6±5,5	56,6±2,7	+13	±5	<0,25	<0,5	143	51
12	9	227	0,2	"	2	76,4±4,2	54,0±4,1	—	—	—	—	143	50
13	10	236	15	"	18	80,5±4,2	55,2±2,4	—2	—11	>0,5	<0,1	143	51
14	10	247	0,2	"	18	81,3±3,6	62,2±2,8	—	—	—	—	144	52

Notes. 1. Weight of animals at beginning of experiment 130 ±10 g. 2. Animals of groups No. 1a and 1b received water with added stabile strontium 4 days before the isotope administration up to the time of their being sacrificed. 3. Animals of groups No. 3, 5, 7, 9, 11, and 13 received water with added Sr 2-1/2 months before radioisotope administration and up to the time of their being sacrificed. 4. Activity of administered solution: Sr-90, - 6.5×10^{-8} c, Ca-45 - 3.5×10^{-6} c.

Table 3

Effect of drinking water with different stabile strontium concentrations on rats' bone mineral metabolism.

No. of animal group	No. of animals in group	Average animal wt. in g: At beginning of experiment	Average animal wt. in g: At end of experiment	mg/li of stabile Sr in drinking water	Time between isotope administration and animal sacrifice	Content in skeleton in % of administered dose: Sr-90	Content in skeleton in % of administered dose: Ca-45	Drop in isotope content in experimental rats in percent of control: Sr-90	Drop in isotope content in experimental rats in percent of control: Ca-45	Probability of accidental difference (P): Sr-90	Probability of accidental difference (P): Ca-45	Percent of bone ash
1	10	200±10	251	30,0	2 hours	10,0±1,2	21,6±2,4	—43,5	—33,1	<0,01	<0,05	51,0
2к	9	200±10	256	0,2	2 "	17,7±1,9	32,3±3,2	—	—	—	—	52,2
3	9	200±10	254	30,0	10 Days	18,8±1,6	40,1±3,2	—22,0	—30,6	0,05	<0,01	51,7
4	8	200±10	243	10,0	10 "	20,9±2,1	48,2±4,1	—13,3	—16,6	0,25	>0,1	51,0
5	10	200±10	270	3,0	10 "	20,7±2,6	50,2±4,0	—14,1	—13,1	>0,25	<0,1	50,8
6к	10	200±10	280	0,2	10 "	24,1±2,0	57,8±3,7	—	—	—	—	52,2

Notes. 1. 40 days between beginning of experiment and radioisotope administration. Indicates stabile strontium concentrations in the drinking water consisted from beginning of experiment to the time of animals being sacrificed

2. Rats received 1.2×10^{-7} of Sr-90 and 2.5×10^{-6} of Ca-45

3 mg/li of stabile strontium gave similar results, but not as sharply expressed. An analysis of the results showed the following: reduction of strontium-90 and calcium 45 accumulation in the skeleton of animals which ingested same perorally in fractional amounts was reduced by the ingestion of water and bread containing added amounts of stabile strontium; this was equally true of rats which received full or partial diet rations. Reliability and significance of the differences had been verified by statistical analysis. Less clear cut and less significant results had been obtained from the series of experiments designed for the determination of the mechanism of action of such phenomenon.

Reliability of differences computed statistically on the basis of calcium-45 and strontium-90 for separate pairs of tests was of small magnitude in all cases. This is only natural; on the basis of experimental data, shown in Table 1, no great difference between the indexes could be expected; also, individual accumulation indexes of radioactive calcium and strontium in rats differed considerably as a rule. Data in Table 2 show that it might be more to the point to go beyond the limit of formal reliability evaluation of differences between individual indexes. The univalent character of changes in the investigated indexes in the order of animal groups, and particularly as noted on a parallel basis in the calcium-45 and strontium-90 isotopes, undoubtedly enhanced the reliability of data obtained by comparing individual tests. Differences between individual indexes are generally of low magnitudes, and cannot be used as reliable; consideration should also be given to the univalent character changes. In the light of all this, it may be possible to conclude that experimental animals which drank water containing 15 mg/li of stabile strontium eliminated both radioactive isotopes at a higher rate than did the

trol animals (Groups No. 9 and 10). It can also be assumed that stabile strontium stimulated not only the elimination but also to some degree the inclusion of the radioisotopes into the skeletons of the experimental animals. (Groups No. 3 and 4, 11 and 12)

The fact that stabile strontium ingested with water lowered the accumulation rate of calcium-45 and of strontium-90, should be regarded as additional evidence of the positive stabile strontium effect on the elimination of strontium-90, thereby adding some explanation to the mechanism of its action. (See Tables 1 and 2). The quantity of stabile strontium which brought about the above described effects was hundreds of times less than the amount of the same type of strontium which entered the organism with the daily solid and liquid rations. Under such conditions it cannot be assumed that stabile strontium acted as the "diluent" or as the "competitor" of calcium, which, incidentally, is assimilated with greater ease than strontium. This is substantiated by the fact that the addition of stabile strontium to rats' rations several days before the administration of the radioisotopes had no effect on the rate of their accumulation. (See Table 2, rats Groups No. 1 and 16) This is further substantiated by the following; peroral and intraperitoneal administration of radioactive isotopes showed the same changes in the rate of radioisotope accumulation in the experimental rats as in the control rats. (See Table 2) Finally, had "dilution" played a substantial part in the mechanism under discussion, then the rate of radioisotope accumulation in the experimental animals in the course of the first two hours should have been below the one found in the control animals; but this was not the fact. On the basis of above presented data and discussions it may be concluded that prolonged drinking of water containing 15 mg/li of stabile strontium changed the rats' mineral metabolism, as indicated in part by the fall in the rate of strontium-90 and calcium-45 accumulation in the skeleton. Similar changes had been noted in the leg bones of experimental animals after operative bone denervation (N. I. Kuznetsov in 1961). It is possible that the effect noted in the recorded experiment came about as the result of stabile strontium action on the nervous elements controlling the trophic processes of the bone system. It should be noted, as shown in Table 3, that animals which received water containing 30 mg/li of strontium manifested a lower rate of radioisotope accumulation in the skeleton two hours after administration of the latter. The same effect was noted at the end of 10 days experimentation. Apparently, unlike 15 mg/li, 30 mg/li of strontium did not act as a stimulator, but as a depressant of mineral metabolism. Such a phenomenon had been previously noted in connection with other trace elements.

It was not possible to determine the threshold concentration of stabile strontium with the desired degree of precision, because the statistical difference reliability obtained in the third series of experiments had been of low magnitudes in many instances. Therefore, it was assumed, on a purely orientation basis, that such a concentration was at the level of several mg/li.

In conclusion, it can be stated that the acceptability or expediency of enriching solid or liquid rations with stabile strontium as a metabolism stimulator or depressant for the prevention of strontium-90 accumulation in the skeleton, still remains undecided and requires additional and thorough investigation.

Conclusions

1. Prolonged ingestion of stabile supplemental strontium as a trace element reduced the rate of strontium-90 and of calcium-45 accumulations in the skeletons of experimental rats by 25-33%.

2. Reduction in strontium-90 and calcium-45 accumulation rate in the animal skeleton resulting from the administration of higher concentrations of stabile strontium was not the result of "dilution" or "competition" phenomena, but the result of changes induced in the mineral metabolism per se.

3. Changes in mineral metabolism and arrest in the rate of body weight gain occurred in rats which drank water containing stabile strontium in concentrations naturally found in water.

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Determination of Triethoxysilane and of Ethylester of Orthosilisic Acid (Tetraethoxysilane) in the Air

pp. 54-56

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The present author undertook to develop a rapid and sensitive test for the determination of tri- and tetraethoxysilane in the air of working premises which would not require the use of platinum dishes. In this connection

the author used data presented in the literature for the determination of silicon in easily hydrolyzed silicon containing compounds without preliminary oxidation, as described by A. P. Terent'ev and others in 1961. In order to obtain optimal determination conditions, the author used as his first step hydrolysis of the triethoxysilane - $SiH(OC_2H_5)_3$ and of tetraethoxysilane - $Si(OC_2H_5)_4$. Results showed that milligrams and decimilligrams of the two silicon compounds under investigation completely hydrolyzed in 0.05 N. solution of sulfuric acid. Optimal conditions have been developed for the production of silicomolybdenum-blue as a reagent for the quantitative determination of silicon in the presence of different reducers of yellow heteropolysilicates and of heteropolymolybdates. Optimal conditions have also been determined for the preparation of 3 standard comparison scales for use in the quantitative determination of silicon, using sodium sulfite, and other similar substances, as the reducing agent. Sensitivity of the method for the determination of tri- and tetraethoxysilane was 1γ in 5 ml of the solution. The standard scale ranged from 1-100 γ of the tri- or tetraethoxysilane. The standard scales kept well and results could be easily reproduced. Only chemically pure redistilled triethoxysilane was used which had a boiling range of 132-135°, and the tetraethoxysilane had a boiling range of 166.5-168.1°. The standard solution of either the tri- or the tetraethoxysilane contained 50 γ of the corresponding substance to 1 ml of the solution and could be used over a period of 3-4 days.

The next step was the development of an appropriate procedure for the collection of air samples containing tri- or tetraethoxysilane vapor. Results showed that 0.05 N. solution of sulfuric acid was most suitable for the absorption of either vapor. It was now necessary to establish the degree to which either of the two vapors had been absorbed by the 0.05 N. sulfuric acid solution in the course of air sample collection. This was done as follows: 3 drops of the tri- or tetraethoxysilane weighing 2-3 mg had been placed into a 15 liter dry glass flask. The flask was stoppered and the contents thoroughly mixed. The air in the bottles containing the vapor of either of the two compounds had then been aspirated through two successively connected absorbers, each containing 3 ml of 0.05 N. sulfuric acid at the rate of 1.5 and 2 li/min. Absorption of moisture was eliminated by first passing the air samples through tubes filled with calcium chloride. Absorber solution in the two successively arranged absorbers had been analyzed as shown below, and results presented in the following Table. Data listed in the Table show that where the tested air had been aspirated at the rate of 1 li/min. absorption was complete in the first absorber, since no vapor of either the tri- or tetraethoxysilane had been found in the second absorber at any time. The amount of determined triethoxysilane vapor amounted to 86.3-93.3%, and of the tetraethoxysilane to 80-83.3% of the actual amount aspirated. The average error of determination ranged between 11-19%. Aspiration of the air to be tested at the rate of 1.5 or 2 li/min. resulted in a 10-15% vapor slip-through.

Results of tests for trapping tri- and tetraethoxysilane for quantitative colorimetric determination (rate of air aspiration 1 li/min)

Expt. number	Substance	Mg taken	Mg found		
			In 1st absorber	In 2-d absorber	δ
1	Triethoxysilane . . .	0,12	0,105	None found	87,5
2	»	0,11	0,085	» »	86,3
3	»	0,09	0,084	» »	93,3
4	»	0,13	0,105	» »	80,7
5	»	0,12	0,10	» »	83,3
6	»	0,10	0,08	» »	80,0

Precision of the method for the determination of tri- or tetraethoxysilane by the silicon method and standard scale comparison was tested next. The standard scale was prepared with SiO_2 using the above mentioned reducing agent. Results of the check methods established determination errors between the actual amounts resulting from molecular triethoxysilane hydrolysis and the computed amount of silicon. In the case of tri- and tetraethoxysilane the amounts obtained by the determination amounted to 82.2 and 107.8% of the actual. The average relative determination error amount to 6.4%. Thus, the results convincingly showed that the standard scale method based on SiO_2 could be used in making quantitative determinations of tri- and tetraethoxysilane vapors in the air.

The following procedures are recommended for the collection and analysis of air samples containing tri- and tetraethoxysilane in working premises: use 1 glass absorber equipped with a porous glass plate which contained 3 ml of 0.05 N. sulfuric acid. Aspirate the air at the rate of 1 li/min. Now, take 2 ml of the solution through which the air had been aspirated and place into a colorimetric tube. Simultaneously prepare the standard scale in a series of 1 to 100 γ of the tri- and tetraethoxysilane. Add to each of the standard tubes 0.05 N. sulfuric acid solution to the volume of 2 ml. Place 2 ml of the 0.05 N. sulfuric acid solution only into the control tubes. Then add to the tube with the test sample and to the tubes of the standard scale 1 ml of 10% acetic acid solution, 1 ml of 10% ammonium molybdate solution; shake each tube carefully, but thoroughly, and leave rest for 5 minutes, after which make the quantitative color determinations. Where Mohr's salt is used as the reducing agent in the standard scale, add 1 ml of 1 M. sulfuric acid and 1 ml of 10% ammonium molybdate to the tubes, and allow to rest for 4 minutes; again add 1 ml of 5% Mohr's salt solution.

Where benzidine acetate is used as the reducing agent, the standard scale is prepared in series ranging from 1-60 γ of the tri- or tetraethoxysilane. After the volumes in the tubes have been brought to 2 ml by the addition of 0.05 N. sulfuric acid solution add 0.5 ml of 10% acetic acid solution and 1 ml of 10% ammonium molybdate solution; shake the tubes and let stand for 5 minutes. At the expiration of 5 minutes, add 0.1 ml of 0.5% benzidine acetate solution followed by 0.5 ml of 10% tartaric acid solution; mix

well and add 2 ml of ethylester.

Where tri- and tetraethoxysilane, as such, are not available, the standard scale can be prepared by using SiO_2, which contains 0.5-20 g of silicon. First prepare a standard SiO_2 solution, each ml of which contained 10 γ of Si; the remainder of the procedure is the same as previously described. In this case, the conversion coefficient for triethoxysilane is 5.85, and for tetraethoxysilane, the conversion coefficient is 7.43. The method is simple and does not require the use of platinum dishes. A single analysis can be performed in 20-30 minutes. In the presence of silicon tetrachloride and other easily hydrolyzed silicon containing compounds, the method is not specific for the substances under investigation. However, the presence of silicon dioxide in the air does not interfere with the determination of the vapors under study. The method has been tested under field and industrial conditions. Thus, a method has been developed for the determination of triethoxysilane and of tetraethoxysilane or ethylester of orthosilisic acid, based on the hydrolysis of the original substances to silisic acid, which is then determined on the basis of the blue silicomolybdic complex. The method sensitivity is 1 γ for tri- and tetraethoxysilane in 5 ml of solution. A single determination can be made in 20-30 minutes. The method had been tested under industrial and field conditions.

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Experimental Data as a Basis for the Determination of Maximal Permissible Xylol Concentration in Atmospheric Air

pp. 93-95

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Xylol is used as a solvent in the lacquer industry, in the production of synthetic rubber, and other similar industries. Therefore, it is possible that the atmospheric air surrounding such industries should be polluted with xylol; despite that, no maximal permissible xylol concentration in the atmospheric air had been established officially, and no investigation had been conducted for the determination of effects produced on the human organism by low xylol vapor concentrations. Results of previous studies, conducted for the determination of high xylol concentration effects under acute conditions, noted primarily shifts in the central nervous system, manifested as vertigo, fatigue, restlessness, loss of appetite, nausea, vomiting, irritation of upp

respiratory mucous membrances, etc. Under normal industrial production conditions, acute xylol poisoning occurs rarely. Descriptions of chronic poisoning recorded in the literature, in addition to central nervous system symptons, mentioned changes in the hemopoietic organs. Such description mentioned changes in the number, shape and size of the erythrocytes, the appearance of neutropenia, monocytosis, thrombocytopenia, etc. V. M. Retnev mentioned in 1907 the appearance in urine of protein and of cylinders in chronic poisoning with xylol. Henderson and Haggard (1930) called attention to the capacity of xylol to accumulate upon repeated exposure to the vapor. Under such conditions, chronic poisoning may result from the accumulation of oxidation products. Xylol as such is partly eliminated from the human organism through the lungs and partly as oxidation products in the form of toluol acids, which are eliminated via the urine as conjugated glycol compounds.

Studies of xylol effect on animals had been conducted only in large concentrations. After inhalation of air containing 43 mg/li of xylol vapor for 40 minutes, experimental animals became narcotized. Chronic exposure of rabbits and cats to the inhalation of air containing 5-10 mg/li of xylol vapor 4 hours daily for 55 days elicited a drop in the number of red blood cells, in the hemoglobin concentration, and in the appearance of lympho cytopenia in the early exposure stage, as shown by N. V. Lazarev in 1954. It is seen, that data thus far found in the literature were limited to the effect of high xylol concentration and that the effect of low concentrations had been neglected, which may explain the reason for which no attempts have been made thus far to determine the maximal permissible xylol concentration in atmospheric air. Therefore, the present author undertook to investigate this phase of air sanitation.

Procedures used in this investigation were the same as previously described by other investigators, namely, determining the concentration of xylol odor perception threshold and also the concentration of xylol threshold reflex effect on eye sensitivity to light using the dark adaptation method, as recommended by the Committee on Sanitary Protection of Atmospheric Air. Xylol determinations were made by the method of M. B. Alekseeva. By this method xylol is nitrated to trinitroxylol which is then extracted with butane. The addition of alkaline solution converted the trinitroxylol to orthoxylol, which is of a yellowish-orange color. The method is not specific, since other aromatic compounds interfered with the reaction; however, in the case under present consideration, all interfering aromatic compounds were absent. The sensitivity of the method is one μ in 2 ml of the solution, and the rate of air sample aspiration was limited to 1 li/min.

Threshold xylol odor perception was determined with the cooperation of 14 presumably normal test subjects, who had been previously familiarized with the odor of xylol. Xylol vapor concentration in the inhaled air had been checked before and after each investigation. Results showed that vapor concentration fluctuations were negligible. A significant difference had been

noted only once in the course of the entire investigation. Test subjects have been used once, at the most twice, a day at great time intervals to eliminate effects of possible adaptation. A total of 366 threshold odor perception determinations had been made with 6 xylol vapor concentrations ranging between 0.36 and 4.9 mg/m^3. Results obtained with 14 test subjects listed in Table 1 show that thresholds of xylol odor perception differed with each individual within the rage of 0.73 and 3.6 mg/m^3. The 0.73 mg/m^3 concentration was characteristic of most odor sensitive individuals. The maximal odor nonperceptible xylol vapor concentration was 0.36 mg/m^3. All test persons were cognizant of xylol vapor odor at 3.3-3.8 mg/m^3 concentrations. At xylol vapor concentration within the range of 1.38-1.90 mg/m^3, 4 persons stated that they were clearly cognizant of its odor. Several persons stated that they could barely perceive the odor, while 3 persons stated that they could not tell that they had been inhaling xylol vapor specifically. 0.82 mg/m^3 of xylol vapor was the subthreshold xylol odor perception concentration for 11 of the test persons.

Table 1.

Threshold of xylol odor perception

Number of test persons	Number of tests	Mg/m^3 of xylol	
		Minimal perceived	Maximal not perceived
2	56	0,73	0,36
1	35	0,82	0,73
1	32	1,14	0,73
1	35	1,19	0,82
6	156	1,64	1,14
3	53	3,60	1,64

Next step in the study was the determination of xylol vapor threshold reflex effect on the functional state of the cerebrum. This determination was made by the adaptometric method previously described by several other investigators, and recommended by the Committee on the Sanitary Protection of Atmospheric Air. By this method, it is possible to determine the effect of subthreshold odor perception concentrations in some instances. Determinations of xylol vapor effect on eye sensitivity to light had been conducted using adoptometer ABM, in cooperation with 3 test volunteers of normal vision and odor perception. Tests had been made daily under similar environmental conditions and at same hours of the day using only one concentration per day. Such tests had been conducted for 43 days. [illegible] few days had been devoted to the determination of, the [illegible] eye sensitivity to light, using clean air. Observations of changes in sensitivity to light were usually made after a 3 minute adaptation period. Determinations for eye sensitivity to light were made at 5 minute intervals for 40 minutes. Clean air or xylol vapor was run up to the test individual's nostrils for inhalation on the 15th minute of the investigation.

Results noted in the case of test person T., female, 26 years old, showed that the threshold of xylol odor perception coincided with 0.[illegible] and that after inhaling xylol in 0.2, 0.3 and in 0.32 and 0.37 mg/m^3 concentrations, there appeared some deviations from the background curve of adaptation, the magnitudes of which were within the limits of possible error.

Therefore, it was concluded that such xylol vapor concentrations had no effect on the curve of dark adaptation. However, inhalation of air containing 0.5-0.6 mg/m^3 of xylol vapor produced a statistically significant drop in the dark adaptation curve and in the curve of eye sensitivity to light, and only on the fortieth minute of testing did the eye sensitivity to light return to its normal level. Test person, female I., 20 years of age, exhibited a threshold xylol odor perception at 0.73 mg/m^3. Inhalation of xylol vapor in 0.2-0.3 and 0.5-0.6 mg/m^3 elicited in this test person no changes in the dark adaptation curve. However, inhalation of xylol vapor in 0.62-0.68 mg/m^3 concentrations began to manifest gradual rise in the curve of dark adaptation beginning with the twentieth test minute and reached greater heights towards the end of the test. Values were found statistically insignificant and reliable.

Female test person M., 19 years of age, manifested a threshold xylol odor perception at 1.19 mg/m^3 concentration. Changes in eye sensitivity to light in this test person showed that inhalation of xylol vapor in 0.62-0.68 mg/m^3 concentration elicited statistically significant changes in the curve of eye sensitivity to light. Sensitivity to light considerably increased on the twentieth minute, fell below the initial background curve on the twenty-fifth minute, followed by negligible fluctuations. Xylol vapor of 0.5-0.6 mg/m^3 elicited no statistically significant changes in this person's curve of eye sensitivity to light.

Based on the data presented in this paper the present author feels justified to conclude that xylol vapor concentrations below its threshold of odor perception affected eye sensitivity to light in all the test persons. A summary of the data obtained in the study of the threshold reflex xylol vapor effect is presented in Table 2.

Table 2.

Composite data for threshold of odor perception and reflex changes in eye sensitivity to light

Test person's initials	Minimal odor perceived concentration in mg/m^3	Minimal concn. affecting eye sensitivity to light
Т. К.	0,82	0,50
И. Н.	0,73	0,62
М. Л.	1,19	0,62

Conclusions

1. The concentration of threshold xylol vapor odor perception in most sensitive test individuals was found at 0.73 mg/m^3.

2. Reflex effect of xylol vapor on eye sensitivity to light had been noted at 0.5-0.6 mg/m^3.

3. Xylol vapor concentration not perceptible by odor produced observable changes in eye sensitivity to light.

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NO. 3 MARCH

Basic Experimental Data for the Determination of Maximal Permissible Concentrations of Carbon Disulfide and Hydrogen Sulfide Simultaneously Present in the Air

pp. 3-7

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Most maximal permissible concentrations of atmospheric pollutants have been adopted in the USSR on the basis of their individual presence in the air, despite the fact that under actual conditions the atmospheric air frequently contained two or more suspended harmful substances simultaneously; it has been established that where two or more substances are simultaneously present in a medium the effect of each component might be different than when the components are present individually. The most frequently occuring simultaneous presence of two harmful substances in the atmosphere is that of carbon disulfide and hydrogen sulfide, especially in air surrounding plants producing viscous fibers. The USSR State Sanitary Inspection approved the recommendation made by the Committee for the Sanitary Protection of Atmospheric Air regarding maximal permissible concentration of carbon disulfide and hydrogen sulfide individually present in the air. The Committee's recommendation was based on the carbon disulfide studies made by P. S. Gil'denskjold and hydrogen sulfide studies made by Duan Fyn-zhui.

No data were found in the literature on the effect of carbon disulfide and hydrogen sulfide vapors simultaneously present in the air in low conce

trations; accordingly, no recommendations had been made previously for maximal permissible concentrations of the two air pollutants simultaneously present in the air. Low concentrations of the individual components were determined by the method of Khritinina for carbon disulfide and by the Polezhaev method for hydrogen sulfide; sensitivity of the methods was 0.5 γ in 3 ml for carbon disulfide and 1 γ in 5 ml for hydrogen sulfide. Maximal permissible single concentrations had been established on the basis of threshold odor perception and reflex effect of eye sensitivity to light. Odor perception threshold was established with the cooperation of 14 presumably normal healthy individuals, 18-30 years of age, whose nasal and oral examinations were negative. Tests were made using only one concentration per day per individual; each test concentration was used 3 - 4 days in succession. Concentration constancy was checked analytically at the start and end of each test. Results of the tests showed that the threshold of odor perception for hydrogen sulfide corresponded to 0.014-0.03 mg/m^3 H_2S, and for carbon disulfide to 0.08-0.5 mg/m^3; practical consideration indicated that the difference between these concentration ranges was negligible.

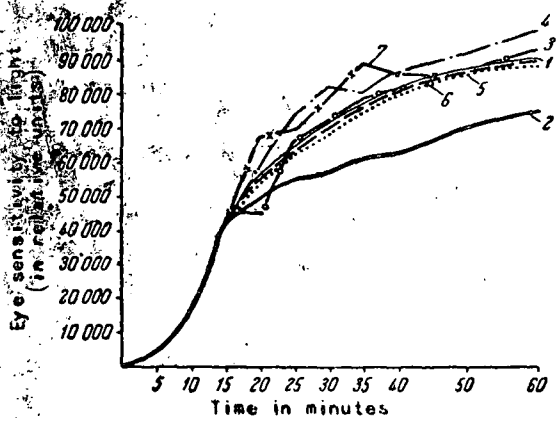
In studying the combined effect of the two vapors the concentration of each ingredient was expressed in fractions of its concentration corresponding to its threshold odor perception. If the sum of the fractions amounted to unity then the effect was believed to be one of physiological summation, and if the fractions added up to more than unity, then the physiological action was regarded as one of potentiation, or synergism, and where fractions added up to less than unity, then the physiological effect was regarded as one of antagonistic action. It was noted in the presently described investigation, conducted with 14 test persons, that where the sum of concentrations was within the range of 0.78-0.99, the test persons recorded no odor perception, indicating the absence of potentiation; where the sum of the concentrations was within the range of 1.07-1.055 test persons recorded perceptible odor, pointing to simple physiological summation; in the case of some test persons to incomplete odor summation.

Tests for changes in eye sensitivity to light had been conducted using adaptometer AD, testing three subjects ranging in age between 18 - 28 years. Tests had been conducted in a dark room at normal temperature and humidity, in complete absence of unrelated odors, and in absolute quiet. Preliminary tests were made first for the determination of reflex effect concentrations for each substance individually, then for the two components in combination. Tests with any specific concentration had been conducted at the same hour on 3 - 4 successive days. Tests were made between the 15th and 20th adaptation minute, and indexes were recorded in the course of 60 minutes adaptation every 5 minutes during the first 40 minutes, followed by two ten-minute intervals.

Fig. 1 illustrates curves of dark adaptation changes induced by the inhalation through the nose of carbon disulfide and hydrogen sulfide indiv...

ally, and Fig. 2 illustrates curves of dark adaptation changes induced by the inhalation through the nose of CS_2 and H_2S combined. Carbon disulfide in 0.05 mg/m^3 and hydrogen sulfide in 0.01 mg/m^3 concentrations individually had no effect on eye sensitivity; 0.06 mg/m^3 of CS_2 and 0.012 of H_2S, also individually, produced curves which deviated from the control curve to degrees statistically established as significant. The corresponding concentrations previously established by R. S. Gildenskjold and Duan Fyn-zhui were 0.04 and 0.01 mg/m^3, which are of the same order as the values obtained in the present investigation. In the simultaneous presence of the two pollutants the minimal concentrations of CS_2 and H_2S which effected changes in eye sensitivity to light were below the threshold levels, pointing to a partial physiological summation.

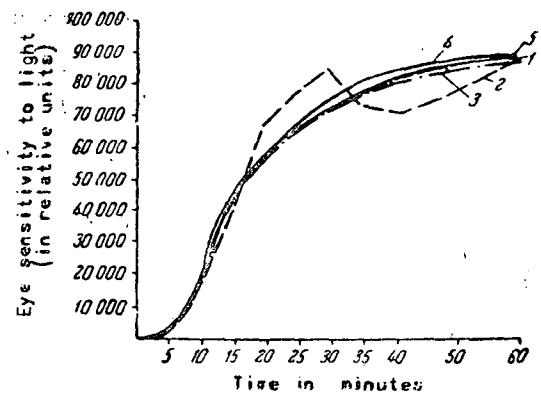
Fig. 1.



Effect of separate carbon bisulfide and hydrogen sulfide vapor inhalation on eye sensitivity to light

1-normal; 2-0.2 mg/m^3 of carbon bisulfide; 3-0.06 mg/m^3; 4-0.08 mg/m^3; 5-0.05 mg/m^3; 6-hydrogen sulfide vapor 0.01/m^3; 7-0.012 mg/m^3.

Fig. 2.



Effect of combined inhalation of carbon bisulfide and hydrogen sulfide vapors on eye sensitivity to light.

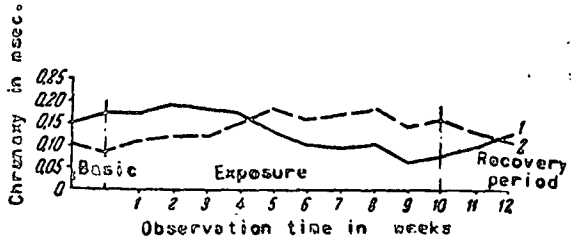
1-normal; 2-0.01 mg/m^3 of H_2S and 0.05 mg/m^3 of CS_2; 3-0.005 mg/m^3 of H_2S and 0.02 of CS_2; 4-0.005 mg/m^3 of H_2S and 0.03 mg/m^3 of CS_2; 5-0.008 mg/m^3 of H_2S and 0.02 mg/m^3 of CS_2.

In the next step tests were made to determine the effect on rats of chronic 24 hour exposure to the inhalation of different CS_2 and H_2S concentrations in the air. Rats were placed into specially constructed exposure chambers equipped with devices for the automatic pollutants' concentration control; so that the investigation required the attention of only one investigator. Experiments were conducted with 45 male rats weighing 110-150 g; animals had been subjected to uniterrupted inhalation of the pollutants in the chamber air for 70 days. Rats were divided into three groups of 15 each. Rats of group 1 inhaled air containing 10 mg/m^3 of CS_2, which corresponds to the maximal permissible concentration of this pollutant in the air of working premises. No such test was conducted with H_2S, since this has already been done by Duan Fyn-zhui in 1959. Rats of group 2 were subjected to the inhalation of air simultaneously containing 0,010 mg/m^3 of CS_2 and 0.008 mg/m^3 of H_2S, which corresponded to maximal permissible average 24 hour concentration of each pollutant correspondingly. Rats of group 3 served as

controls. During 70 days of chronic exposure records were kept of the rats' general behavior, changes in body weight, changes in motor chronaxy of muscle-antagonists, cholinesterase activity, number of sulfhydryl groups, total blood serum protein, and morphologic blood picture. At the end of the chronic poison inhalation, rats of all three groups had been examined pathoanatomically and histologically. Rats of groups 2 and 3 (control) appeared healthy throughout the 70 days of the chronic experiment, they behaved normally, were active and gained weight.

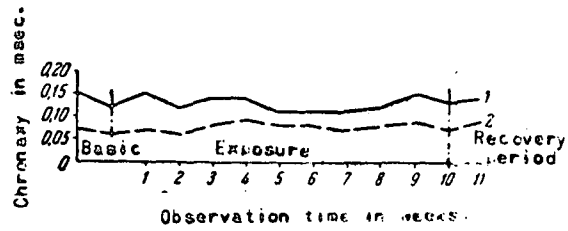
Effect of carbon disulfide individually and in combination with hydrogen sulfide on the functional state of the central nervous system was determined by recording changes in motor chronaxy of motor antagonist muscles, using electric impulse stimulator ISE 01-58. Tests made with rats of group 1, which inhaled air containing 10 mg/m^3 of CS_2, yielded the following results: beginning with the 4th week of exposure the normal chronaxy ratio between the flexor and extensor muscles became disturbed, as shown by curves in Fig. 3. No chronaxy ratio disturbance had been noted in rats of group 2, as illustrated by curves shown in Fig. 4. According to evidence found in the literature CS_2 and H_2S belonged to the group of substances which affected the blood cholinesterase activity. Therefore, cholinesterase activity was used as the effect index of the two air pollutants. Cholinesterase activity was determined by the colorimetric Fleisher and Pope method, based on changes in the solution color intensity depending on the formation of acetic acid by the hydrolytic enzyme action on acetylcholinechloride. The color intensity was determined photoelectrocolorimetrically. Tests had been made at 14 day intervals. Depressed cholinesterase activity appeared in rats of group 1 on the 5th inhalation week, as shown by curves in Fig. 5. Statistical analysis proved the results to be reliable. No changes in cholinesterase activity were noted in rats of Group 2.

Fig. 3.



Effect of carbon bisulfide vapor on muscle antagonists motor chronaxy in rats of Group 1.
1-extensor chronaxy; 2-flexor chronaxy

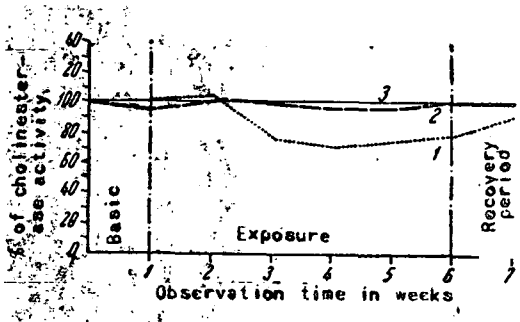
Fig. 4.



Combined effect of hydrogen sulfide and carbon bisulfide vapors on muscle antagonists motor chronaxy of Group 2 rats.
1-extensor chronaxy; 2-flexor chronaxy

The study of blood serum sulfhydryl groups yielded particularly interesting results. Kh. S. Koshtoyants, T. M. Turpaeva, V. A. Lebedeva, V. N. Chernigovskii, and others demonstrated that sulfhydryl groups played

Fig. 5.



Effect of carbon bisulfide vapor alone and in combination with hydrogen sulfide vapor on whole blood cholinesterase activity of rats.
1-inhaling air containing 10 mg/m^3 of CS_2 vapors; 2-air containing 0.018 mg/m^3 of H_2S vapor in combination with 0.01 mg/m^3 of CS_2; 3-control

a part in the life processes of the organism. According to M. S. Tolgskaya there existed a large known group of substances which bound free protein sulfhydryl groups. The number of sulfhydryl groups in blood serum can be determined iodometrically and by emperometric titration. The iodometric method was used in the present investigation. Blood was taken from the rats' tail vein at 20 day intervals. Results indicated that total sulfhydryl groups in the blood serum of rats of Group 1 dropped by 19%, and in some cases by 25% and free protein SH-groups dropped by 14% at the end of the exposure period. Reliability of results was verified statistically. No changes were noted in the total blood serum or the free protein sulfhydryl groups in rats of Group 2. No statistically significant changes were recorded in the total blood serum protein in any animals of any group. Autopsies of rats of Group 1 showed emphysema, athelectiasis, localized lung hemorrhages; practically all animals showed cardiac dilatation, dark-brown kidney discoloration, and a poor delineation between the cortical and brain tissues; stasis was noted in some animals; the liver and kidneys showed dark-brown discoloration, plethora and stasis. Localized enteritis was noted in all animals. No visible changes had been observed in other organs. No pathologic changes had been noted in the internal organs of rats of the second group.

Conclusions

1. Inhalation of air containing vapors of carbon disulfide and hydrogen sulfide simultaneously in maximal permissible average 24-hour concentrations had no noticeable adverse effect on rats under conditions of daily 24-hour chronic exposure.

2. Chronic 24-hour daily exposure of rats to inhalation of air containing 10 mg/m^3 of carbon disulfide elicited in the experimental animals changes in muscle antagonists chronaxy, in cholinesterase activity, in the concentrations of total blood serum protein, in the free SH-groups, and produced pathoanatomical changes in some internal organs.

3. Results of the present investigation also showed that the previously adopted maximal permissible CS_2 and H_2S maximal single average 24-hour concentrations were below the threshold summation effect; therefore, in evaluating the sanitary condition of atmospheric air polluted simultaneously by the two studied components the norms recommended by the Government

State Sanitary Inspector may prevail without correction factors.

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Experimental Data for the Determination of Maximal Permissible Phosphamide Concentrations in the Air of Working Premises

pp. 21-27

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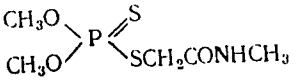
The new Phospho-organic insecticide and acaricide - phosphamide - which kills on contact or internally has been synthesized at the Ya. V. Samoilov Scientific-Research Institute for fertilizers and insecto-fungicides. It is an analogue of similarly acting compounds, rogor and dimetoat, synthesized in other countries. Phosphamide was studied by L. P. Bocharova, G. K. Shapovalova, A. S. Sedykh, T. A. Spirina, V. V. Shcherbakov, and P. I. Mitrofanov; they found it effective against fruit, berries and citrus fruits and cotton plant parasites, and for this reason phosphamide has found wide application in agriculture. Therefore, it is important that its harmful properties as an air pollutant be established, and its presence in the air be quantitatively standardized in terms of maximal permissible concentrations, which, is the aim of the present investigation.

Structurally phosphamide is O,O-dimethyl-S-methylcarbamidiomethyldithiophosphate:



In its pure form phosphamide is a white crystalline powder of an unpleasant

odor; its m. p. range is 49-50°, vapor tension 1 x 10^{-4} mm of mercury at 25°. Its technical preparation is a yellowish fluid of an unpleasant odor. It is synthesized from phosphorus pentasulfide, methanol and monochloracetic acid. Phosphamide is water-soluble up to 3%, and easily soluble in most organic solvents and in oils; it is not markedly hydrolyzed by water, but is easily hydrolyzed in alkaline solution.

Toxic properties of phosphamide were investigated using white mice, rats, cats and rabbits. Routes of phosphamide administration differed. Results indicated that phosphamide penetrated into the organism of warm blooded animals through the gastro-intestinal mucosa, through the mucosa of respiratory tracts, and through the intact skin. Administered perorally in single doses to mice, rats, and cats phosphamide manifested a less intense toxicity parameter than did such phospho-organic insecticides as mercaptophos, thiophos, metaphos, methylmercaptophos, and others. LD_{50} of chemically pure phosphamide was for white mice 135 (158-112) mg/kg, for white rats 230 (254-206) mg/kg; LD_{50} of technical phosphamide was for white mice 125 (152-98) mg/kg, for white rats 172 (205-139) mg/kg, and for cats 100 mg/kg. Results of phosphamide application to intact skin also indicated that its toxic potency was below that of the previously mentioned phospho-insecticide: here its lethal dose for rabbits was 1000 - 1500 mg/kg, and for rats 120 mg/kg of the technical preparation, without showing any signs of skin irritation. Administration of phosphamide LD_{100} induced the development of the following toxic effects: excitation of the muscarine, nicotine and choline reactive systems of the organism.

Cumulative properties of technical phosphamide had been investigated experimentally using rats and cats. Results showed that the preparation possessed only slight cumulative properties and depended generally on the fraction of the lethal dose administered daily. Thus, all five rats which received daily 1/5 LD_{100} doses died, three after receiving a total of 1.0-1.6 LD_{100} dose, and of 5 rats which received daily 1/10 LD_{100} of the technical phosphatide, 3 died after receiving a total of 7.2-11.0 lethal doses, and 2 had been still alive six months after having received a total of 15 lethal dos . All 5 rats which received 1/20 LD_{100} daily for six months survived, having received a total of 7.3 lethal doses. Experiments with cats yielded approximately similar results.

Determination of maximal permissible phosphamide concentration in the air can be most appropriately arrived at on the basis of results obtained in tests with experimental inhalation. Such tests had been performed with cats and rats which were placed into a special inhalation chamber the air of which contained given concentrations of technical phosphamide in the vapor and emulsion aerosol state. The latter was used to simulate conditions under which phosphamide was used under practical conditions in agriculture. Animals had been exposed to the phosphamide inhalation for 4 hours. Phosphamide concentrations in the exposure chamber air were checked every half-hour by the method of M. A. Klisenko based on phosphamide

reducing properties. Results of exposure experiments performed with 45 cats and 56 rats are listed in Tables 1 and 2.

Table 1.

Toxicity of technical phosphamide vapor upon one and several daily 4-hour inhalation exposures.

Concentration in mg/li	Animal	Observed effect
		Single exposure effect
0,025	Cats	No visible organism effects. Notably depressed blood serum and erythrocyte cholinesterase activity.
0,02	Rats	No visible toxicity effects.
0,01	Cats	25 - 30% drop in cholinesterase activity
0,01	Rats	40% drop in cholinesterase activity
0,005	Cats	13 - 18% drop in cholinesterase activity
0,002	Rats	Cholinesterase activity unchanged.
		Several inhalation exposures.
0,002 (2 months)	Rats	No visible toxicity effects. Average 26% drop in cholinesterase activity at the end of 2 months as compared with the control group.
0,005 (3 months)	Cats	No visible toxicity effects. 76 - 95% drop in cholinesterase activity in the early days of the experiment and 30 - 40% drop at the end of the experiment.

Table 2.

Toxicity of technical phosphamide in the form of liquid aerosol upon one and several 4-hour daily inhalation exposures of cats.

Concentration in mg/li	Observed effects
	One exposure
0,08	Some visible toxicity symptoms, cats became aggressive, profuse oral and nasal secretion, vomiting. Strongly depressed blood serum and erythrocyte cholinesterase activity.
0,06 0,05	Cats were aggressive; pronounced nasal and oral secretion; strongly depressed cholinesterase activity.
0,02	No visible toxicity symptoms; 0-66 % drop in cholinesterase activity (See foot-note)
0,008 0,007	Up to 56% drop in cholinesterase activity
0,006 0,005	7 - 30% drop in cholinesterase activity
0,003 0,002	Up to 20% drop in cholinesterase activity
0,0015	No recordable change in cholinesterase activity
	Several exposures
0,0015 ((45 days)	No visible toxicity manifestations. 40 - 72% drop in cholinesterase activity at the end of the experiment.

Footnote. Considerable fluctuations in cholinesterase activity changes may have been due to individual sensitivity of the experimental animals to phosphamide

Results show that effects of single inhalation exposure, as above described, were less toxic to the experimental animals than the other phosphoinsecticides, such as thiophos, mercaptophos, or methylmercaptophos. For example, 0.025 mg/li of phosphamide vapor killed none of the cats and failed to elicit any visible toxicity symptoms. No toxic manifestations had been exhibited by rats which had been exposed to a single 4-hour inhalation of air containing 0.02 mg/li of phosphamide. In similar experiments performed by Yu. S. Kagan with mercaptophos, inhalation of air containing 0.015-0.02 mg/li of the mercaptophos proved fatal to some of the experimental animals. Tests were also made to determine the effect of phosphamide inhalation by cats as above described, on the activity of cholinesterase in the blood serum and in the erythrocytes, and also on changes in the pattern of the animals' reflex activity. Cholinesterase activity was determined colorimetrically as described by Hestrin. Conditioned reflex studies were conducted on the basis of motor-nutritional behavior as described by Spinul in 1957. Single exposure of cats to 4 hours inhalation of air containing 0.025 mg/li of phosphamide vapor lowered the activity of cholinesterase in the blood serum by 28-80%, in the erythrocytes by 49-68%, but effect on the cats conditioned reflex activity was slight and poorly defined, the most marked symptom being a delay in eye accommodation to light. Two of the cats manifested an easy extinction of conditioned reflexes and an enhanced differentiation inhibition. Cats exposed to single 4-hour inhalation of air containing 0.01 mg/li of phosphamide vapor suffered a 25-35% loss in cholinesterase activity. Two of three cats with experimentally fixed conditioned reflex patterns manifested a delay in the latent period of response and in eye adaptation to light. Exposure to the inhalation of air containing 0.005 mg/li of phosphamide vapor lowered cholinesterase activity by 8-18%, which can also happen in control animals, and had no effect on the experimental animals' conditioned reflex activity pattern.

Rats exposed to the inhalation of air containing 0.01 mg/li of phosphamide vapor suffered a 40% loss in blood serum cholinesterase activity; no change in cholinesterase activity was noted in rats exposed to a single inhalation of air containing 0.002 mg/li of phosphamide vapor, nor were there any other symptoms of poisoning. Accordingly, 0.01 mg/li of phosphamide in the air was regarded as the single dose threshold concentration.

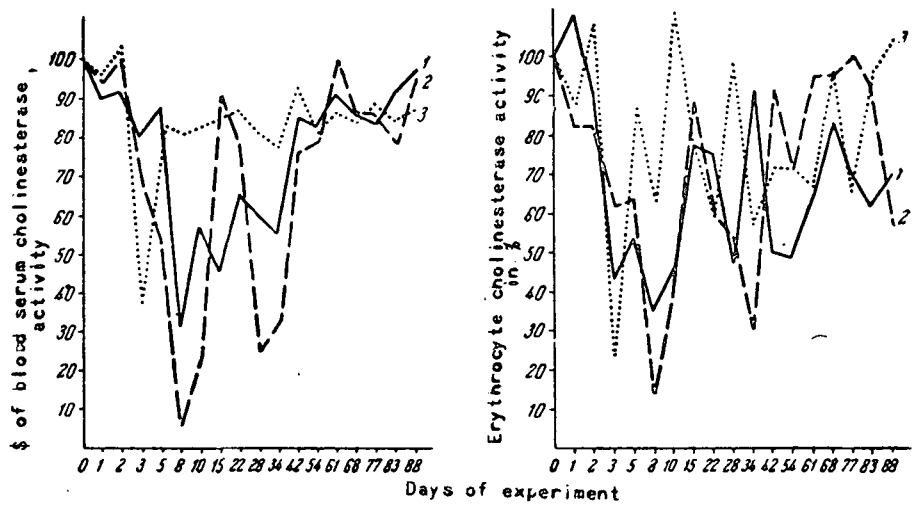
Tests with emulsified phosphamide aerosol in the air gave the following results: 0.08 mg/li killed none of the cats, whereas methylmercaptophos in the investigation of N. K. Statsek killed some of the experimental animals at 0.02-0.03 mg/li concentration in the air; there were no noteworthy changes in the activity of any type of cholinesterase activity. However, the behavior of the experimental animals appeared to have been affected: the cats became aggressive, they lost control over their oral and nasal secretions, and had vomiting attacks; activity of blood serum cholinesterase fell by 60-88%, and of the erythrocytes by 40-100%. Similar, but less intense symptoms of poisoning appeared in cats exposed to single 4-hour inhalation of air containing 0.05-0.06 mg/li of the phosphamide aerosol. No symptom

of poisoning had been noted in cats exposed to inhalation of air containing 0.02 mg/li of the aerosol. Accordingly 0.05 mg/li of the aerosol in the air was the minimal toxic dose. Single inhalation of 0.005 mg/li of phosphamide aerosol in the air elicited in cats a drop in the cholinesterase activity two days later, which amounted to 8-23% in the blood serum, and to 7-30% in the erythrocytes; 0.003 mg/li of the phosphamide elicited similar, but considerably less intense changes. Accordingly, 0.005 mg/li of aerosolized phosphamide in the air should be regarded as the threshold concentration of a single inhalation. Cats with experimentally developed conditioned reflex patterns and which had been exposed to a single inhalation of air containing 0.007 mg/li of aerosolized phosphamide manifested no changes in their conditioned reflex picture, but showed a drop of 9-12% in the blood serum cholinesterase activity, and of 17-26% in the cholinesterase activity of the erythrocytes. The results, thus, indicated that the toxic properties of phosphamide in aerosol form were more potent than in the vapor form.

Rats and cats had been subjected to repeated inhalation of air containing vaporized phosphamide in different concentrations. Forty rats were divided into two groups of 20 animals each; group 1 was the experimental and group 2 the control group. The experimental rats had been exposed repeatedly to the inhalation of phosphamide vapor for two months. Every fortnight 5 rats had been taken from each group, and cholinesterase activity of the blood serum, erythrocytes and the brain determined. The phosphamide vapor concentration in the exposure chamber stayed within the range of 0.0015 - 0.004, with an average of 0.002 mg/li. Observations throughout the entire 2 months period failed to disclose any signs of poisoning, and some of the rats gained weight (average 30%). Observation failed to disclose any difference between the behavior of the experimental and control animals. During the first 2 to 4 weeks of exposure activity of all cholinesterase types remained unchanged; at the end of the third fortnight activity of blood serum cholinesterase of the experimental rats dropped by 26%; a similar drop in the blood serum cholinesterase was recorded at the end of the two months' exposure. On the basis of results of these experiments it was concluded that 0.002 mg/li of phosphamide vapor in the air should be regarded as the threshold concentration of chronically inhaled phosphamide vapor.

Repeated (2 months) inhalation of 0.005 mg/li of phosphamide vapor had only a slight effect on the cholinesterase activity of cats, causing a drop within the range of 13-18%, a phenomenon observed also among individual cats of the control group. No changes of any kind could be elicited in the established conditioned reflex pictures of the cats. Therefore, chronic exposure was extended to another three months. Phosphamide vapor concentration in the exposure chamber fluctuated within the 0.002 - 0.008, with an average of 0.005 mg/li. On rare occasions the vapor concentrations fluctuated within the 0.0015 - 0.002 mg/li. Here, as during the first two months, experimental cats showed no outward ill effect produced by the prolonged exposure. Changes in cholinesterase activity are graphically presented in the

Figs. below. The curves show that activity of the blood serum and erythrocytes cholinesterase dropped by 65-95% on the 3rd to the 8th day of the secondary exposure, and thereafter fluctuated in an alternating rise and fall pattern. At the end of the last month of exposure cholinesterase activity returned to practically the original levels in the blood serum, but remained 30-40% below the normal level in the erythrocytes. Effects of the pattern of established conditioned reflexes were slight and not clearcut, with the exception of the latent period of response, which was of a clearly delayed character.



Changes in blood serum and erythrocyte cholinesterase activity of cats exposed to the inhalation of phosphomide vapor in 0.005 mg/li concentration for three months

1, 2, and 3 - numbers of experimental cats.

Single exposure of cats to the inhalation of air containing 0.0015 mg/li of aerosolized phosphamide elicited no changes in the activity of blood serum of erythrocyte cholinesterase. Therefore, three cats had been exposed to chronic inhalation of the aerosol in the exposure chamber, where the vapor concentration fluctuated between 0.0009 and 0.0017 with an average of 0.0015 mg/li for six weeks. Observation throughout the six weeks failed to detect any poisoning signs in the experimental cats. Drop in cholinesterase activity noted in two cats was within the range of occurrence in the control cats during the first half of the exposure period, but at the end of the exposure period activity of erythrocyte cholinesterase activity fell by 43-46%. The third cat proved highly sensitive to the effect of phosphamide: on the 6th day of experimental exposure erythrocyte cholinesterase activity fell by 40%, on the 9th and 16th days the drop in cholinesterase activity increased to 49-58%, and at the end of the experimental exposure it dropped by 72% of its normal level. No substantial changes had been noted in the established conditioned reflex picture. Four to twelve days after the termination of the experimental exposure all phases of cholinesterase activity returned to their normal levels.

A parallel investigation was conducted of actual working conditions under which phosphamide was applied in agriculture. In fruit trees spraying under pressure phosphamide was used in 0.05-0.1% concentration; the orchard air temperature ranged between 18 and 20°, with a prevailing relative humidity of 55-86%, and the surrounding air current did not exceed 0.2 m/sec. Phosphamide concentration in the air at the respiration level varied between 0.0004 and 0.001 mg/li. Hand, face, and glove wash-water analysis indicated a deposition of 0.024 - 0.52 mg of the phosphamide per 100 cm^2 of washed body area. Persons working with phosphamide generally used means of protection which differed with the individuals, such as gowns, gloves, respirators, etc. No changes in the activity of any of the cholinesterase forms, no significant shifts in the vegetative nervous activity system, and no shifts in the morphologic blood picture had been found in any of the examined workers. Hence, taking into account all previously presented and discussed results, it appears safe to conclude that phosphamide was less toxic to humans and other warmblooded animals than were mercaptophos, metaphos, thiophos, methylmercaptophos, etc; however, it possessed a relatively wide toxicity spectrum, and its toxic effects were slightly cumulative. Accordingly, phosphamide can be recommended as a substitute for many presently used phospho-organic compounds of high systemic toxicity.

0.0005 mg/li of phosphamide vapor or aerosol in the air of working locations is here recommended as the maximal permissible concentration of this preparation. This phosphamide vapor or aerosol concentration is 10 to 20 times below the threshold concentration established for single exposure to its inhalation, and 10 times below the phosphamide vapor concentration which under conditions of chronic experiments brought about a considerable loss in cholinesterase activity in the experimental cats, without eliciting any visible signs of toxicity. Exposure of rats and cats to the inhalation of air containing phosphamide vapor, or aerosol, in concentrations exceeding 3 - 4 times the concentrations recommended above as maximal permissible elicited no noticeable symptoms of toxicity in the experimental animals.

The recommended maximal permissible phosphamide concentration reflects the experimentally established toxicity parameter for this substance as compared with toxicity parameters of other phospho-organic insecticides. It has been officially accepted by the Committee on Limits of Allowable Concentrations by authority of the Chief USSR Government Sanitary Inspection.

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Method for the Determination of Ditolylmethane and the Differential Determination of Ditolylmethane and Styrol Simultaneously Present in the Air

pp. 48-52

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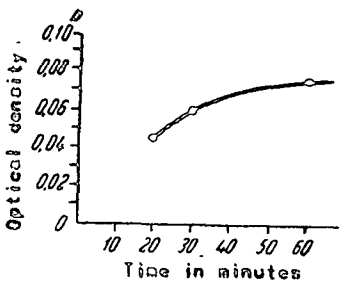
Use of the new heat carrier - ditolylmethane - for heating manufacturing equipment in industry, and a study of its toxicity, pointed to the necessity of its quantitative determination in air. No method has been found in the available literature for the determination of this preparation. Ditolylmethane-DTM-$CH_3C_6H_4CH_2C_6H_4OH_3$-is a light yellowish liquid having a specific weight of 0.98 at 20°, a b.p. of 293° at 760 mm of mercury. It is insoluble in water, easily dissolves in alcohol, ether, chloroform and other organic solvents. Based on the chemical and physical properties of ditolylmethane, the present author tested several methods for its determination. The luminescence method, based on the characteristic violet fluorescence of alcoholic DTM solutions upon exposure to ultraviolet radiation was not sensitive enough, -0.1 mg in 5 ml. The emulsion method, based on the different DTM solubility in ethyl alcohol and in water, also was not adequately sensitive. Results with the sulphuric formaldehyde reagent were also unsatisfactory. The possibility of determining DTM by the Yanowsky reaction was investigated (1891). Technical conditions for the determination of benzene were used as the basis. Standard solutions of DTM were prepared in nitro-mixture. The nitration was done at room temperature for 2 hours, which was followed by 30 minutes of heating over a boiling water bath. After nitrating, the solution was diluted with water and the formed poly-nitroso compounds were extracted with 10 ml of ethyl ether. The separated ether layer was washed with distilled water. Seven ml acetone and 1 ml 40% sodium hydroxide were then added to 3 ml of the ether solution, and thoroughly shaken. The ether-acetone solution acquired a rose color. It was found that the color developed more intensely if the nitrating was done over a boiling water bath. The sensitivity of the method was 10γ in the analyzed volume. The color was unstable, it faded noticeably after 15-20 minutes. The color was still less persistent when the reaction was carried out in ether-alcohol solution.

Later investigations were based on the reduction of DTM polynitro-compounds, and the resulting amine was determined in the azo-form. The nitro compounds were reduced as described by E.G. Kachmar with metallic zinc in diluted nitro-mixture solution - (0.5 ml nitro-mixture and 4.5 ml water). Diazotized sulphanilic acid and p-nitrophenyl diazonium were used as conjugation agents. Optical density of the colored solutions was determined using photo colorimeter FEK-M in 10 mm colorimetric tube at 400μ.

Results indicated that maximal light absorption could be attained by limiting the solution reduction reaction to 60 minutes (Fig. 1). P- nitrophenol diazonium, or diazotized sulphanilic acid, can be used as the azo-ingredient. The first indicator developed an orange and the second a yellow color. The color intensity increased slow in both cases, reaching maximal intensity after 12-15 hours. However, if the solutions were heated to 60° the color reached maximum intensity after 5 minutes and remained so for 5-6 hours. At 5 to 50γ in 10 ml, a linear relation becomes established between the optical density and concentration of DTM in solution (Fig. 2). Reproducible results can be obtained by maintaining strictly identical reduction and solution heating conditions. Benzene, toluol, styrene and other aromatic hydrocarbons interfere with the determination of DTM by this method. Ethylene glycol, caprolactam, hexamethylene diamine did not interfere with the determination.

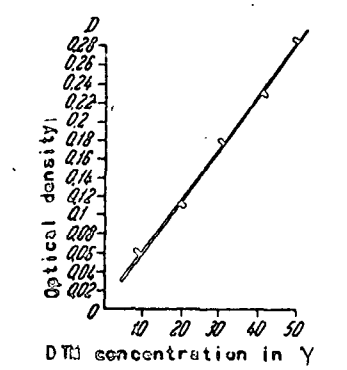
Fig. 1.



Effect of reduction time on solution optical density

The extent of DTM vapor absorption was studied by generating the substance in a vessel of 20 liter capacity. A bulb containing DTM was attached to the vessel and heated on a sand bath at 150°. Samples of air were run from the vessel into successively attached absorbers each containing 2 ml of the nitro-mixture. Results showed that about 80-90% of DTM was absorbed in the first absorber, and that its walls and the connecting tubes were covered with small liquid droplets. Therefore, it was important to determine whether some highly dispersed aerosol slipped through. For this purpose a perchlorvinyl filter FPP-15 was placed after the absorber. The filter was treated with the nitro-mixture, and the DTM determined in the solution. In no instance was DTM found on the filter. Hence, it can be concluded that DTM vapor and aerosol condensation were quantitatively retained in the absorber containing the nitro-mixture.

Fig. 2.

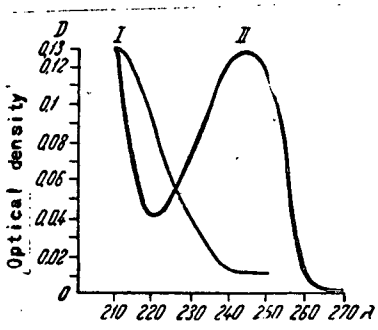


Calibrated curve of ditolylmethane

Additional investigations had been conducted to find a method for the separate determination of DTM and styrol present in combination. Best results were obtained with the ultraviolet spectrophotometric method of analysis. According to Filles and Stern, styrol had a high optical density at λ max. The molar absorption coefficient (Σmax.) is equal to 10,000. No data were found in the literature on DTM absorption spectra. Spectral characteristics of alcoholic extracts of DTM and of styrol were used in determining the wave lengths at which the maximal optical density of the solutions ($\lambda_{max.}$) was observed, as well as the range of concentrations which satisfy the Lambert-Beer law. The determination was made

with spectrophotometer SF-4, a colorimetric cup containing a 1 cm. layer of the solution in the wave length region of 210 and 260 mμ, using alcohol as the standard. Curves in Fig. 3 show that styrol had 2 absorption peaks: At $\lambda_{max.}$ equal to 211 and 244 mμ. The optical density was the same in both spectral regions. DTM has one absorption peak at $\lambda_{max.}$ equal to 211 mμ. At 1-5γ/ml concentration range a linear functional relationship exists between the optical density and DTM or styrol concentration in the solution.

Fig. 3.



Spectral characteristics of DTM and of styrol
I - DTM II - Styrol

The Firordt method was used in quantitative determinations. In this method two wave lengths are selected on the light absorption curve; in one the optical densities of both mixture components differed widely, while in the other, the optical densities of the two compounds were closely alike. By solving the equation with two unknowns, a calculation can be derived for determining the concentration of each mixture component. Alcoholic solutions of styrol and DTM at $\lambda_{max.}$ of 211 mμ, have optical densities of 0.12 and 0.13 respectively at a concentration of 1γ/ml; at λ equal to 244 mμ, the optical densities of these solutions differed widely and were for styrol 0.12 and for DTM 0.02. By solving the double equation system with two unknowns, a calculation formula can be derived for determining the concentrations of styrol and DTM in unknown solutions:

for DTM $x=(\Sigma^{\lambda_1}-\Sigma^{\lambda_2})/0.11$, for styrol $y=(0.13\Sigma^{\lambda_2}-0.22\Sigma^{\lambda_1})0.11$, where x is the concentration of DTM (in γ/ml; y- concentration of styrol (in γ/ml) Σ^{λ_1} is the optical density of the investigated solution at λ equal to 211 mμ; Σ^{λ_2} - the optical density of the investigated solution at λ equal to 244 mμ. Some analytical results of solutions containing given quantities of styrol and DTM are presented in the following Table. The data obtained show that ultraviolet spectrophotometric analysis is sufficiently accurate for separate determination of DTM and styrol simultaneously present in a solution. Experiments on styrol and DTM vapor absorption by ethyl alcohol showed that at 50 li/hr rate of air aspiration the condensation aerosol of DTM and of styrol can be completely absorbed in a single absorber containing 10 ml of ethyl alcohol and a porous glass plate.

It is recommended that the following procedure be used for the determination of DTM in air: Aspirate the air at 12-15 li/hr through two absorbers, each containing a porous glass plate and 2 ml of the nitro-mixture. Place the connected absorbers into boiling water for 30 min. Cool and take 0.5ml samples from each absorber; and place into colorimetric cups equipped with ground-to-fit stoppers containing 4.5 ml of distilled water. At the same time, and under similar conditions prepare a standard

scale using a series of test tubes containing 20, 30, 40 and 50γ of DTM. Place 0.3-0.4g granulated zinc into each test tube containing the standard solution and the sample; stopper the test tubes and leave stand for one hour. Decant the supernatant fluid from the precipitate, and add to each tube 0.5 ml 1% nitrophenyldiazonium solution, shake, heat on a water bath at 60° and cool: compare color intensity of the sample with the standard scale visually, or photocolorimetrically in 10 mm cups at λ equal 400 mμ. The method sensitivity is 5γ in the analyzed solution volume. Benzene, toluol, styrol and other aromatic hydrocarbons interfere with the determination. Ethylene glycol, capro-lactam and hexamethylene do not interfere with the reaction.

Separate DTM and styrol determination

γ taken		γ found			
		DTM		Styrol	
DPM	Styrol	in γ	in %	in γ	in %
1	5	1	100	4,6	92
1	3	1	100	3,0	100
4	5	0,9	90	5,0	100
1	3	0,8	80	3,0	100
5	5	3,9	78	5,1	102
2	2	2,17	108	1,96	98

For the separate determination of styrol and DTM the spectrophotometric method using the ultraviolet spectral region is recommended. The air sample is aspirated through 2 successively connected aspirators equipped with a porous glass plate and containing 10ml of ethyl alcohol. Aspirate the air at 40-50 li/hr with the absorbers submerged into ice water; determine the solution optical density at λ equal 211 and 244 mμ. First determine the optical densities of standard solutions containing from 1 to 5 λ/ml of styrol and DTM at the same wave lengths, then compute the average optical density for 1γ/ml; by solving the two equations with two unknowns, derive the computation formula for the determination of styrol and DTM concentration in the analyzed solution. The sensitivity of the method is 1γ/ml of styrol and DTM. Benzene and its homologues interfere with the determination. The method was checked under practical conditions in the production of styrol and DTM. Styrol and DTM in the air of industrial premises were determined separately as above described.

The spectrophotometric method was also used for the determination of DTM in the air of experimental animal exposure chambers. The optical density was measured at $\lambda_{max.}$ equal to 211 mμ, and the quantitative determination was made with the aid of a calibrated diagram.

Conclusions

1. It was established that DTM can be determined by the Yanowsky reaction in alkaline ether-acetone solution. The reaction sensitivity is 10γ

in the analyzed solution volume.

2. A method was developed for determination of DTM based on reduction of the polynitrocompound DTM and the conjugation of the resulting amine with p-nitrophenyldiazonium. The sensitivity of the method is equal to 5γ in the analyzed sample volume.

3. A spectrophotometric method was developed for the separate determination of DTM and styrol simultaneously present in air. The sensitivity of the method is 1 γ/ml of DTM and of styrol.

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Respiratory Organ Diseases Among Chromium Industry Workers

pp. 72-75

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Fisher in 1911 and Lehmsn in 1918 pointed out that morbidity was high among those employed in the manufacture of hexavalent chromium compounds, such as chromium anhydride, sodium and potassium chromates and bichromates, etc. Yet, no investigations had been conducted, specifically on the occurrence of respiratory diseases among such workers in general and the course followed by such diseases in particular. Reports found in the literature on this phase of occupational diseases presented contradictory opinions and conclusions. Thus V. A. Zamanskii in 1935, V. P. Lukanin in 1948, S. M. Gen'kin et al in 1948, I. G. Fridlyand in 1950 and many others emphasized the frequent occurrence among such workers of laryngotracheitis, bronchitis, pneumosclerosis, bronchoectasis, and bronchial asthma. On the other hand, investigators, such as A. Ge in 1882, R. L. Gol'dberg and V. N. Strelkova in 1949, Kober and Hanson in 1918, and many others, stated that they found no noteworthy changes in the lungs of workers they had examined. And again, such investigators as N. A. Vigdorovhik, N. V. Lazarev, Baetjer, Mancuso and Hueper pointed out that lung cancer frequently occurred among workers connected with different branches of the chromium manufacturing industry, a fact which indicated the importance of frequent X-ray lung examinations of such workers.

In this connection the present authors investigated work-time lost by workers of the chromium manufacturing industry due to morbidity of the respiratory organs, and compared their findings with those resulting from a similar investigation conducted among workers of the ferroalloy and construction industries. The investigation was begun in 1958, and was concluded in 1960; it covered 1000 workers in each respective field of employment. Results showed that the length of industrial service among the chromium manufacturing workers averaged 3 years, among the structural industry workers 5 years, and among the workers of the ferroalloy industry the average work period was 15 years.

According to data collected by the Sanitary-Epidemiological Station air pollution exceeded the maximal permissible concentration by 100-200%. Data collected from parallel studies on the occurrence of respiratory diseases and loss of work time are listed in Table 1. Results obtained with seasonal catarrhal and grippe morbidity were grouped apart from results obtained with pharyngeal and laryngo-tracheal morbidity. Analysis of data in Table 1 shows that the upper respiratory morbidity level among workers employed in the chromium production industry was lower than among workers employed in the ferroalloy industry, and that it was about the same as among workers employed in the construction industry. A rise in the morbidity level among workers of 3 chromium production plants occurred in 1959 due to a grippe epidemic. Polyclinic observations failed to establish any unfavorable effect of chromium intoxication on the course of the grippe. Data related to oral diseases and to rhinitis are not included in Table 1, since such pathological conditions occurred only among workers employed in the chromium production industry, and, as such, constituted material of a separate specific investigation. It should be noted in this connection that occupational chromium laryngitis manifested considerable resistance to clinical therapy and a tendency to run into the acute stage. One of the examined workers developed ulcerative laryngitis which affected the true vocal cord.

Data in Table 2 show that diseases of the accessory nasal sinuses, such as highmoritis, ethmoiditis, frontisis, sinusitis, etc. occurred among workers employed in the chromium production industry less frequently than among workers of the other two industries investigated on a parallel basis. However, supplemental roentgenological examination of the workers employed in the chromium production industry disclosed pathological changes of the nasal sinuses in seventy of 100 workers examined. The pathogenesis of nasal sinusitis under the conditions of the present investigation should be more thoroughly investigated. It should be established whether the sinusitis was a primary condition resulting from the effects of chromium, or developed as a secondary complication in workers with primary rhinitis.

Data in Table 3 show that no noteworthy tendency towards inflamatory pulmonary bronchitis was observed among workers of the chromium

Table 1

Comparative morbidity data of upper respiratory passages

Industrial plants	Morbidity per 100 employed: The grippe and catarrh of upper respiratory passages						Pharyngitis						Laryngitis					
	1958		1959		1960		1958		1959		1960		1958		1959		1960	
	Cases	Days	Cases	Days	Cases	Days	Cases	Days	Cases	Days	Cases	Days	Cases	Days	Cases	Days	Cases	Days
Producing chromium compounds	15.7	71.6	34.7	150.2	16.5	65.8	0.2	0.7	0.4	1.7	0.1	0.5	0.2	0.7	0.7	4.6	0.3	2.6
Ferroalloys plants	29.3	112.4	58.5	239.9	30.3	112.4	0.4	1.8	0.7	3.9	1.1	6.6	3.0	17.1	3.8	22.4	3.7	19.3
Bldg. & construction trust	11.8	65.1	33.2	193.7	16.5	79.7	0.3	2.6	0.5	3.8	0.1	0.5	0.8	8.0	0.6	4.9	0.5	2.4

industry, not even among workers of three year employment records. No significant rise in tuberculosis morbidity was noted among workers employed in the chromium production industry, as can be seen from the data presented in Table 4. Data in that Table were taken from an investigation conducted by V. P. Lukanin in 1930. It should be noted at this point that data obtained from a comparative analysis of diseases of the respiratory organs with data related to the simultaneous loss of work time can not be used as a basis from which to conclude that occupational pneumosclerosis was a pathologic consequence of chromium poisoning. This phase of the investigation must be studied more thoroughly. The investigation also showed that occasional cases of bronchial asthma, bronchoectasis and other similar diseases had occurred among workers employed in the chromium production industry. However, it can not be concluded on the basis of the present investigation only that these pathological conditions were sequeli of chromium intoxication. Lung cancer was not found among the examined workers; but here, again, no final conclusions can be drawn, since the employment period of the examined workers did not exceed 3 years.

Thus, the comparative analysis of respiratory organ diseases, such as catarrh of the upper respiratory passages, grippe, pharyngitis and laryngotracheitis, accessory nasal sinusitis, bronchitis lung inflammation, pulmonary tuberculosis, etc., and of lost work time failed to establish any morbidity increase among workers employed in the chromium production industry for a period of 3 years. This conclusion appears valid even for workers who had chromium rhinitis and pathological changes of the accessory nasal sinuses disclosed by roentgenologic examination.

See pages 66 and 67 for Tables 2, 3, 4 and Bibliography.

Table 2.

Comparative accessory nasal sinuses morbidity

Industrial enterprise	Morbidity per 100 employees					
	1958		1959		1960	
	Cases	Days	Cases	Days	Cases	Days
Production of chromium compounds	0,8	11,2	0,6	3,5	0,3	0,9
Ferroalloy plants	2,1	20,2	2,3	25,1	3,4	25,6
Bldg. & construction trust	0,2	1,0	0,5	5,5	0,5	3,4

Table 3.

Comparative bronchial and pulmonary inflamatory morbidity

Industrial enterprise	Morbidity per 100 employees											
	Bronchitis						Pulmonary inflamation					
	1958		1959		1960		1958		1959		1960	
	Cases	Days	Cases	Days	Cases	Days	Cases	Days	Cases	Days	Cases	Days
Production of chromium compounds	0,9	3,9	0,6	3,9	1,6	11,1	1,0	7,4	1,3	13,5	1,3	15,0
Ferroalloys plants	1,8	9,4	1,7	7,8	2,2	12,3	1,7	17,9	1,7	17,4	1,1	11,9
Bldg. & Construction Trust	2,4	19,5	2,1	13,5	2,0	17,2	0,3	3,2	0,6	9,7	0,6	8,8

Table 4.

Comparative pulmonary tuberculosis morbidity

Industrial enterprises	Morbidity per 100 employees					
	1958		1959		1960	
	Cases	Days	Cases	Days	Cases	Days
Production of chromium compounds	0,4	2,4	0,8	18,5	0,4	10,5
Ferroalloys	1,5	31,0	1,5	22,1	1,2	16,9
Bldg. & Construction trust	0,6	22,3	0,6	12,8	0,5	15,0

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Pollution of High School Physics Departments with Metallic Mercury

pp. 76-79

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Metallic mercury is used in high-school physics classes extensively in studying the Boyle-Mariotte and Gay-Lussac laws, the Torricelli experiment, etc. In this connection air pollution in high school physics departments with metallic mercury was investigated in 7 schools located in different sections of Dniepropetrovsk. Results revealed considerable mercury content in the air of such locations. Samples of air were collected at work desks, teachers' desks, in the middle of classrooms and in the preparation rooms where mercury was distributed into tubes for classroom exercises. The air samples were collected at the ground and breathing levels. Similarly, mercury was determined in wash water from surfaces of school furniture, floors and equipment. Mercury content in samples of air and wash water was determined by the Polezhaev method.

Analytical results of air samples collected in physics departments of different schools are listed in Table 1. The data show that only 25% of the investigated samples of air from physics departments contained no mercury, while in 23% of the samples the concentration of mercury exceeded the maximum permissible for air of industrial establishments (0.01 mg/m^3). No mercury was found in only 6% of air samples collected in the preparation rooms, while in 35% of all samples the mercury concentration exceeded the permissible maximum. Thus, the greatest pollution of air by mercury vapor was found in the preparation rooms, in which mercury has been distributed generally in open tubes and carried in and out without regard for specified hygienic safety requirements. It should be pointed out in this connection

Mercury Concentration in mg/m^3 in the Air of High Schools' Physics Laboratories — Table 1

Points of sampling / School No.	Lab. tables			Instructor's table			Room center			Preparation room					
										Center of room			Place of mercury distribution		
	Minimal	Maximal	Average	Minimal	Maximal	Average	Minimal	Maximal	Average	Minimal	Maximal	Average	Minimal	Maximal	Average
38	Trace	0,023	0,0112	Trace	0,006	0,0035	Trace	0,013	0,0048	Trace	0,06	0,0188	0,017	0,024	0,02
9	None found	0,096	0,0054	None found	0,004	0,003	None Found	0,004	0,007	0,0025	0,0133	0,0065	0,0205	0,0215	0,021
100	0,0054	0,011	0,0082	Ditto	0,0044	0,0022	Ditto	0,0053	0,0026	0,005	0,0073	0,0062	—	—	—
33	—	—	—	" "	None Found	None found	0,0055	0,006	0,0057	0,11078	0,008	0,0072	0,0082	0,011	0,0096
22	—	—	—	0,007	0,008	0,0075	0	0,0054	0,0027	0,006	0,0092	0,0076	0,011	0,0036	0,0023
81	None found	0,01	0,0044	0	0,04	0,0085	0,0056	0,0235	0,0156	0	0,0066	0,0039	0,0093	0,0152	0,0122

Mg/m^3 of mercury in wash water from physics laboratory — Table 2

Wash water source / School No.	Physics study room				Preparation room					
	Floor		Tables		Floor		Tables		Exhaust hood	
	Minimal	Maximal	Minimal	Maximal	Minimal	Maximal	Minimal	Maximal	Minimal	Maximal
38	0,036	2,16	0,0	0,096	0,024	1,68	0,036	0,144	0,036	0,144
9	0,0	0,432	0,0	Trace	0,012	1,68	Trace	0,0288	—	—
100	0,0	0,036	—	—	0,024	0,031	—	—	—	—
33	Trace	0,048	0,014	0,024	Trace	0,4	0,048	0,336	—	—
81	0,0	0,036	Trace	0,036	0,024	0,144	—	—	—	—

that 0.01 mg/m^3 of mercury vapor adopted by the Institute of General and Community Hygiene of the AMS USSR as the maximal permissible mercury concentration in the air of working premises was too high, since long exposure to the inhalations of a mercury concentration may elicit the development of early symptoms of chronic mercury poisoning. Consequently, the presently accepted maximal mercury level in the air of working premises must be reduced. Assuming that 0.0003 mg/m^3 adopted officially as the maximal permissible mercury concentration in atmospheric air was a rationally safe level, then mercury concentrations found in the air of high school physics departments were many times in excess of the adopted safety level.

Analyses of wash water from surfaces of different objects in physics departments (furniture, equipment, floors, etc.), showed considerable pollution of the entire surroundings with mercury (Table 2). The relatively high air temperature in high school physics departments (18-25°) contributed to the volatilization of mercury. The floors, work desks and equipment in the preparation rooms were highly mercury polluted, in fact 2-3 times greater than the air pollution in the physics departments. Results of the present investigation brought out the fact that students and teachers of the high school physics departments investigated were in danger of developing chronic mercury poisoning. In addition, work with equipment presents the possibility of mercury evaporation from open containers, of spilling mercury during pouring it from one container to another, accidental dropping and breaking mercury containing glassware, etc. Lack of proper ventilation enhanced the mentioned chances for the development of mercury poisoning.

Analysis of old plaster and of contents in the cellar immediately below the classroom showed that the plaster contained 0.044 mg of mercury per g. of plaster, and the objects in the cellar contained 0.0025 mg/g. Supplemental analyses showed considerable mercury content in the wash water of the corridor floor adjacent to the physics department. This intense mercury pollution of the surroundings was the cause of occupational mercury poisoning of teacher and laboratory technician working in the high school physics departments. This was confirmed by medical examination, which uncovered characteristic mercury poisoning symptoms: mercury and albumen in the urine, complaints of headache, dizziness, weakening of memory, etc.

Conclusions

1. Laboratory investigations showed that air and wash water from surface of floors, furniture and other objects in high school physics departments were intensely polluted with mercury and mercury vapor.

2. Basic causes of contamination with mercury in disregard for hygienic requirements for the sanitary maintenance of high school physics

departments, carless handling of mercury containing equipment, conducting experiments with mercury poured into open dishes or directly on desks, and lack of hoods and of proper ventilation.

3. The most radical measure for improvement of working conditions in high school physics departments is the substitution of mercury with other nonpoisonous substances, such as alcohol, kerosene, etc., providing visual demonstration of the experiments.

4. It is recommended that strict compliance with existing sanitary hygienic regulations be inforced in high school physics departments in the future as a prophylactic measure against acute and chronic mercury poisonings.

5. The air, equipment, and general environment of such departments should be inspected and checked periodically by competent sanitarians.

6. The physics department personnel should be instructed in the sanitary-hygienic and toxicological principles pertaining to their department.

Students in high school physics departments generally ranged between the ages of 13-17 years. For this reason the present authors regarded it more apropos, in fact, more rational to use the 0.0003 mg/m^3 M.A.C. adopted officially for mercury in atmospheric air and not the 0.01 mg/m^3 M.A.C. officially adopted for mercury vapor in the air of working premises.

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Experimental Data as a Basis for the Determination of Maximal Permissible Aniline Concentration in Atmospheric Air

pp. 3 - 11

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Aniline has the structural formula of $C_6H_5NH_2$ and is known as amino benzene or phenylamine; it is the simplest member of the aromatic amines and is a well known industrial toxic substance. In its pure form aniline is almost colorless and has an aromatic odor and a b.p. of 184.4°. Commercially aniline is prepared by reducing nitrobenzene with pig iron shavings and hydrochloric acid. Recently aniline has been manufactured in the U.S.S.R. predominately by the following new method: chlorobenzene and ammonia were heated to 340°, or nitrobenzene and hydrogen were brought into high pressure contact. Aniline is widely used in many industries as raw product from which aniline dyes are prepared for use in the textile and rubber industries and in the production of intermediates for the manufacture of medicinal products.

Aniline toxic properties have been studied basically by administering the preparation to experimental animals directly into the gastrointestinal track, by subcutaneous injection, and by direct application to the skin in relatively large doses. No records had been found in the literature which dealt with results of prolonged inhalation of air containing low aniline concentrations, nor had any records been found which dealt with aniline polluted atmospheric air. The only record found by the present author was one presented by M. K. Grodzovskii in 1925, who found the presence of aniline vapor on the grounds of the textile plant "Trekhgornaya Manufaktura". Aniline's wide use in industries, its high toxicity, the absence of information regarding its effect of chronic aniline inhalation in low concentrations and also the absence of information regarding atmospheric air pollution with aniline prompted the present author to make the study herein reported on, the chief aim of which was to determine the maximal permissible aniline concentration in atmospheric air of inhabited areas. The invesigation was conducted along channels previously recorded by other authors in connection with other atmospheric air pollutants. The methods used were specifically those of establishing the concentration of threshold odor perception and the threshold of aniline vapor reflex effect. Experimental animals had been exposed to the inhalation of air containing different aniline vapor concentrations for 24 hours; simultaneously, studies had been made of the sanitary condition of the air inside th

production plant with reference to its pollution with aniline vapor.

Many methods have been described in the literature for the determination of aniline; the method developed by M. V. Alekseeva in 1930, and improved in 1931 and in 1948, was most widely used in scientific and practical investigations. The method is a colorimetric one and is based on the indophenol reaction, which developed a violet color in akaline solution. With the aid of M. V. Alekseeva the method was modified, and its sensitivity has been considerably enhanced from one μ in ten ml to 0.25μ in 3 ml. In connection with this modification use was made of photoelectrocolorimeter FEK-M or FEK-N. A calibrated curve of functional relationship between the light flow intensity and the aniline concentration was constructed under standard conditions. As a result of many photocolorimetric standard scale check determinations it was established that maximal light absorption for the blue colored solution occurred when a red light filter was used in association with a solution layer 1 mm thick representing 0.25-10 μ of the aniline. Air samples taken from the animal exposure chambers had been analyzed by the locally revived Khokhlova method which was free from the effect of ammonia. The modification also enhanced the test sensitivity from 1 to 0.25 μ in 3 ml.

Threshold aniline odor perception was determined with the aid of a device recommended by the Committee for the Sanitary Protection of Atmospheric Air affiliated with the U.S.S.R. Sanitary Inspection. A total of 484 experimental tests had been performed on 17 practically normal persons with normal odor perception, in an aniline concentration range of 6.37 - 0.25 mg/m^3. Results indicated that the concentration of threshold odor perception of different persons ranged between 0.37 - 2.82 mg/m^3, and that the odor nonperceptible concentration for all persons was 0.35 mg/m^3. Results of aniline odor threshold perception tests are listed in Table 1.

Table 1.

Threshold of Aniline Odor Perception

Number of testers	Number of observations	Mg/m^3 of aniline	
		Minimal perceptible	Maximal non-perceptible
2	44	2.82	2.78
2	63	2.21	2.07
6	150	1.74	1.68
5	148	0.88	0.74
2	79	0.37	0.34

The effect of aniline on reflex activity of experimental testers was studied by the method of functional electroencephalography on the basis of effect on the acquired rhythm amplitude in response to stimulation by light. Subjects of this study were 6 persons with ostensibly normal organs of odor perception who manifested a clearcut α rhythm. Each of the test persons was given 11-16 tests with air containing 0.3, 0.15, 0.07 mg/m^3 of aniline vapor. These tests were made for control purposes and established the pattern of normal response of each test person. Values obtained were processed statistically comparing amplitudes of the acquired α rhythm manifested during the inhalation of fresh air containing the above indicated aniline concentrations. Data of this investigation are presented in

Table 2.

Ammonia Effect on the Amplitude of Established Biocurrent Rhythm of the Human Brain Cortex

Initials of testers	Aniline in mg/m^3		
	0,3	0,15	0,07
K	+	—	—
B	+	—	—
G	+	—	—
M.I.	+	+	—
G	+	+	—
M.V.	+	+	+

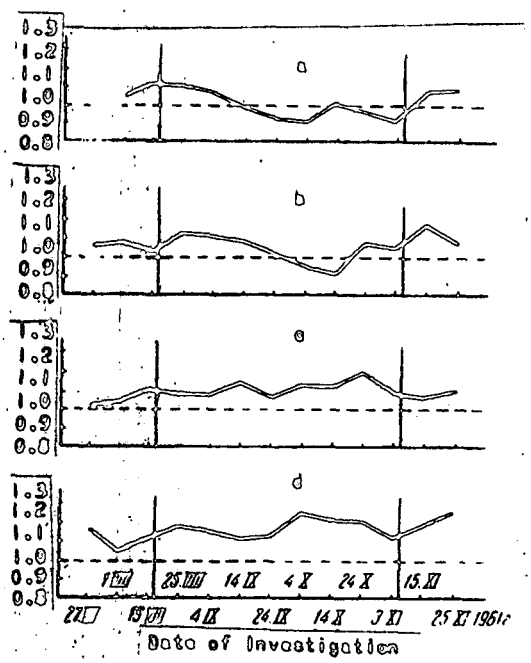
in Table 2. Statistically reliable changes in the direction of reduction in the acquired α rhythm amplitude following the inhalation of 0.3 mg/m^3 of aniline appeared in 6 test persons, and at 0.15 mg/m^3 in 3 of the test persons. In the case of test person MV (female) the changes appeared during the first minute of the recovery period in response to the inhalation of fresh air containing 0.07 mg/m^3 of the aniline vapor. This concentration was designated by the present author as the minimal active on the process of rhythm acquiring. The 0.05 mg/m^3 concentration for a brief time was assumed to be the subthreshold concentration; it is recommended as the maximal single permissible concentration for atmospheric air.

For the determination of average 24 hour aniline concentration in the atmospheric air, rats had been exposed to chronic inhalation of air containing different aniline vapor concentrations for 80 successive days. The experiments were conducted with 80 male rats weighing 90-150 g. Rats were divided into 4 groups of 20 animals. Rats of group 1 were placed into an exposure chamber the air of which contained 3 mg/m^3 of the aniline vapor, which is the level of maximal permissible aniline vapor concentration for working premises. Animals of group 2 were similarly exposed to the inhalation of air containing 0.3 mg/m^3 of aniline vapor, which is the concentration of threshold aniline odor perception. Animals of group 3 were similarly exposed to the inhalation of 0.03 mg/m^3, which is below the minimal dose acting on the process of rhythm adaptation. Animals of group 4 served as controls. Simultaneously observations had been made and records kept of the general behavior, external appearance and weight changes in the animals of the 3 experimental and one control groups. This included changes in the chronaxy of muscle antagonists, elimination of coproporphyrin with the urine, changes in blood serum and erythrocyte cholinesterase activity, hemoglobin, methemoglobin, blood morphology picture and histopathological changes of internal organs. Such studies had been conducted 30 days before the inhalation exposure, continued throughout the period of inhalation exposure and up to the twentieth day of the recovery period. The experimental study extended over 130 days. Check tests for aniline concentration in the air of the exposure chambers had been made daily with the following results: in chamber No. 1 (animals of group 1) the aniline vapor concentration averaged 3.02 ± 0.31 mg/m^3; in chamber No. 2 (rats of group 2) the average aniline vapor concentration was 0.31 ± 0.036 mg/m^3, and in chamber No. 3 (rats of group 3) the aniline vapor concentration averaged 0.031 ± 0.0047 mg/m^3. Throughout the entire period of confinement in the exposure chambers rats of all groups appeared healthy, active, and showed moderate gain in weight.

R. V. Borisenkova in 1952, Duan Fyi-Jui and Chjao Chjen-Zi in 1959,

A. Gofmakler, Yu. G. Fel'dman in 1960, and R. Ubaidulaeva, Li Shen in 1961, demonstrated that chronic poisoning of white rats with harmful substances affected muscle antagonists chronaxy, which reflected changes in the subordinate function of the central nervous system. Disturbed balance in muscle antagonists chronaxy supposedly reflected arrest or inhibition in the brain, which in turn reflected the development of defense processes resulting from the effect of harmful substances in low concentrations, as was shown by V. A. Ryazanov in 1961. Muscle antagonists chronaxy and rheobase tests were made with 5 rats of each group using electronic impulse stimulator I S E-01. Tests had been conducted under the same conditions for 10 days. Changes in the muscle antagonists chronaxy ratios are presented graphically in Figure 1.

Fig. 1.



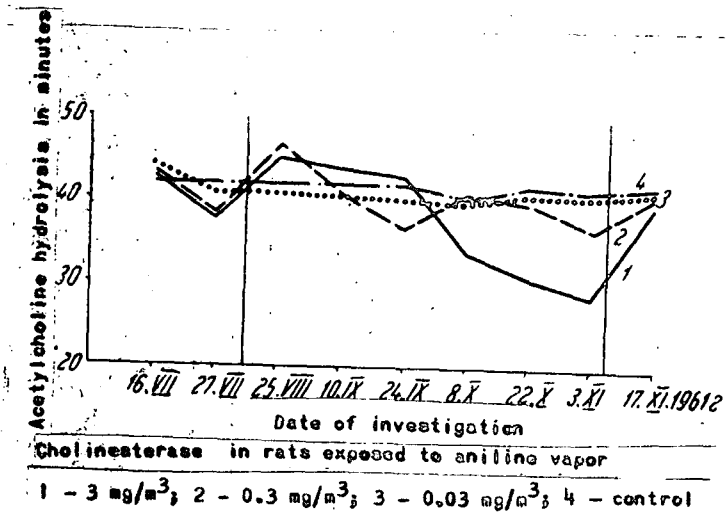
Muscle antagonists chronaxy ratio in rats exposed to the inhalation of aniline

a - first clinical group, 3 mg/m³; b - second group, 0.3 mg/m³; c - third group, 0.03 mg/m³; d - control group

Data plotted in curves of Fig. 1 show that inverse chronaxy ratios appeared in rats of Group 1 exposed to inhalation of air containing 3 mg/m^3 of aniline vapor during decade III of the poison inhalation and returned to normal during the first decade of the recovery period. Reverse chronaxy ratio appeared in rats of Group 2 exposed to inhalation of air containing 0.3 mg/m^3 of aniline vapor between the V - VII decades of the aniline vapor inhalation in a less manifested form than in rats of Group 1. No deviations in muscle antagonists chronaxy ratios had been noted in rats of Group 3 exposed to inhalation of air containing 0.03 mg/m^3 of the aniline vapor, or in the rats of the control group throughout the entire experimental period.

A. P. Martynov in 1958, R. F. Ozerov in 1960, G. I. Slonim in 1961, and others had demonstrated that changes in blood serum and erythrocyte cholinesterase activity reflected the effects of toxic substances on the mediator processes which are associated with changes in the vegetative and central nervous systems. Since then the method of detecting changes in cholinesterase activity has been used widely in investigations similar to the one under present discussion. Blood serum and erythrocyte cholinesterase activity was determined by the A. A. Pakrovskii method, and modified by A. P. Martynova in 1958. Cholinesterase activity determinations had been made in 5 rats of each group at two week intervals. Results have been plotted in curve form as shown in Fig. 2. Data had been processed statistically and found to be reliable. Curves in Fig. 2 clearly show that significant increase in cholin-

Fig. 2.



Cholinesterase in rats exposed to aniline vapor

1 - 3 mg/m^3; 2 - 0.3 mg/m^3; 3 - 0.03 mg/m^3; 4 - control

esterase activity occurred only in rats which had been exposed to the inhalation of air containing 3 mg/m^3 of the aniline vapor. This is in agreement with results obtained by V. K. Navrotskii, V. I Lukashev, N. M. Nikolaeva, and M. M. Tiraspol'skii in 1958. M. I. Gusev and Yu K Smirnov in 1960, G. I. Solomin, R. Ubaidulaev and Li Shen in 1961, and others studied the rate of coproporphyrin elimination with the urine in experimental animals subjected to the inhalation of air containing low concentrations of toxic substances. Z. A. Il'ina, N. S. Pravdin and S. B. Shakhnovskaya found that aniline depressed tissue respiration and particularly enzymic processes. This and the fact that most oxidizing enzymes are complex hemoporphyrin entities prompted the present author to include in his studies an investigation of coproporphyrin elimination with urine of rats exposed to experimental inhalation of air containing different aniline vapor concentrations. Coproporphyrin was determined by the Fisher method; the coproporphyrin was extracted from the urine with ether and determined spectrophotomatically as porphyrinhydrochloride. Before exposing the rats to the inahalation of air containing aniline vapor and during the recovery period of rats of all groups, and also in the course of actual aniline vapor inhalation by rats of groups 2 and 3, which inhaled correspondingly air containing 0.3 and 0.03 mg/m^3 of the aniline vapor, the rate of coproporphyrin elimination ranged between 0.39 - 0.03 μ per 100 g of rat body weight. Rats of the first group, which inhaled air containing 3 mg/m^3 of the aniline vapor, showed an increase in the rate of coproporphyrin elimination with the urine up to 1.11 μ per 100 g of animal body weight, rats of this group continued to eliminate coproporphyrin with the urine at a higher level than rats of the other two groups. In the course of exposure to the inhalation of air containing aniline vapor, rates of coproporphyrin elimination with the urine were as follows: in rats of the first group the average was 0.78 ± 0.19 μ, in rats of the second group - 0.58 ± 0.15 μ, in rats of group 3 - 0.48 ± 0.19 μ, and in rats of group 4 - 0.47 ± 0.10 μ. On the basis of the above data it appeared reasonable to assume that aniline vapor in 3 mg/m^3 concentration in the air elicited in the experimental animals a moderate coproporphyrinuria; this was verified by statistical processing of the experimental results.

It has been known that aniline easily combined with blood proteins forming methemoglobin and Heinz bodies; therefore, the present author analyzed the blood serum electrophoretically. Results presented in Table

3 show that the direct addition of aniline in the indicated concentrations elicited no reliable changes in the total blood serum protein. Statistically reliable changes in the blood albumin concentrations of rats of group 3, which inhaled air containing 3 mg/m^3 of aniline vapor, appeared on the 10th day of exposure; on the thirtieth day of exposure the albumins slightly receded, while the globulins increased. The changed blood serum albumin concentration persisted to the end of the exposure period, while the changed blood serum globulin concentration was still noted on the 22nd day of the recovery period. Particularly sharp changes in the blood serum protein fractions had been noted in rat number 3 of group 1, in which the albumin concentration fell from the original 39.7% to 15.5% during the period of experimental inhalation. Only slight albumin and globulin concentration changes had been noted in rats of group 2; the blood serum protein fractions in animals of group 3 remained indistinguishable from those of the control rats.

Table 3.

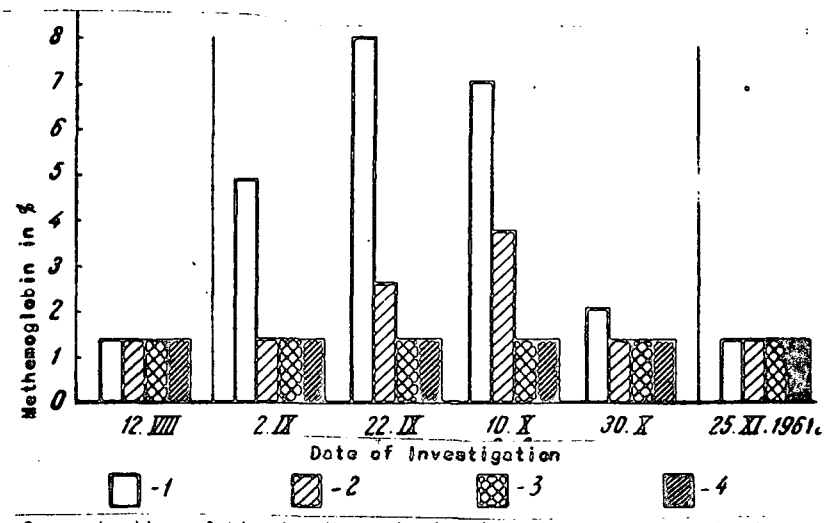
Changes in Blood Serum Protein Fractions in % in rats exposed to the Inhalation of Aniline Vapor

Animal Group	Background				Exposure				Recovery Period			
	Albumins	Globulins			Albumins	Globulins			Albumins	Globulins		
		α	β	γ		α	β	γ		α	β	γ
First	46,4	19,2	21,3	13,0	31,3	23,7	30,5	14,1	34,4	27,7	26,9	11,3
Second	43,3	18,4	24,4	13,8	38,6	18,5	26,4	16,4	43,1	18,2	24,1	14,4
Third	43,9	19,2	22,5	14,2	37,6	19,1	26,1	17,0	35,9	20,1	27,6	16,2
Control	45,	20,7	20,7	12,1	39,2	19,7	26,3	14,5	38,6	17,7	27,6	15,9

The fact that aniline converted hemoglobin to methemoglobin has been known for some time. In the present study methemoglobin determinations had been made in 5 rats of each group at 20 day intervals by the Gorin method. The sensitivity of the method used was 1.68%. The method was modified to raise its sensitivity. (Author does not indicate how this was done B.S.L.) Before exposing the experimental rats to the inhalation of air containing different aniline vapor concentrations, typical curves were constructed representing light absorption by solutions of oxy- and methemoglobin in 43 normal healthy rats. Results of the preliminary test had shown that the concentration of the naturally occurring methemoglobin in the blood of all 43 test rats did not exceed 1.39%; accordingly, 1.39% of methemoglobin was taken as the initial and orientation concentration with which results obtained in the course of the experimental exposure had been compared. Because 1.39% of methemoglobin had been used as the orientation level, the sensitivity of the Gorin test had to be raised so as to be able to determine 1.39% of hemoglobin. This was done in cooperation with M.B. Manite; the 0.4 ml of blood required for the determination was reduced to 0.2 ml. The methemoglobin determinations had been made using spectrophotometer S. F-5. Results obtained with

the methemoglobin determinations in the experimental rats are presented in Figure 3. Graphs in that Figure show that methemoglobin concentration of 4.86% was found in the blood of rats belonging to group 1 on the 15th day of exposure, which rose to 8.06% on the 35th day of exposure; in rat no.63 of this group the methemoglobin concentration rose to 13.9% which gradually receded at the end of the exposure period. Methemoglobin concentration of 2.64% was found in rats of group 2 on the 35th day of exposure, which rose to 3.82% on the 55th day of exposure; thereafter it fell to and persisted at 1.39%. Methemoglobin concentrations in rats of group 3 were below the established sensitivity of the modified test, i. e. below 1.39%.

Fig. 3.



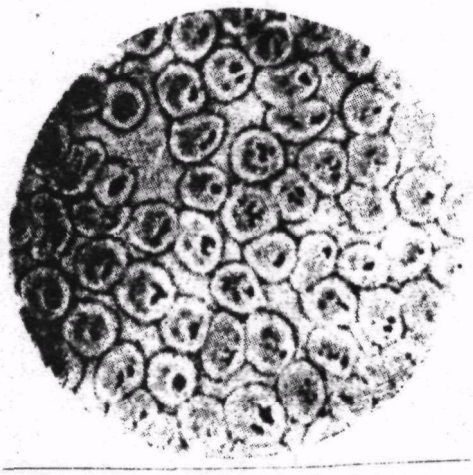
Concentration of blood methemoglobin in rats exposed to the inhalation of aniline vapor
1 - 3 mg/m^3; 2 - 0.3 mg/m^3; 3 - 0.03 mg/m^3; 4 - control. Method sensitivity - 1.39%

It has been established that the presence of Heinz bodies in the blood reflected acute or chronic intoxication with aniline of some gravity. However, prior to diagnosing such cases it is necessary to eliminate the presence of other toxic substances, which are equally conducive to the formation of Heinz bodies. Heinz bodies were detected microscopically using ultravital stain consisting of 1% methylviolet solution. A considerable number of Heinz bodies were noted in the blood of rats belonging to group 1 on the 55th day of exposure (see Fig. 4) and a reduced number on the 55th day of exposure. Isolated Heinz bodies had been observed in rats belonging to group 2 as shown in Fig. 5. No Heinz bodies were found in the blood in rats belonging to the control group.

A study was also made of the blood morphology and hemoglobin of the experimental rats. Statistically significant changes were found in rats belonging to group 1, and less pronounced similar results were found in rats belonging to group 2. Animals belonging to this group had a reduced number

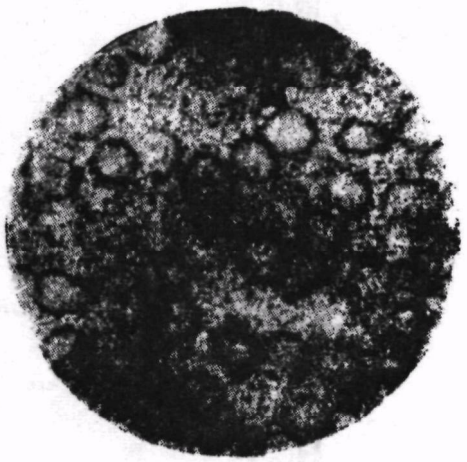
of erythrocytes and a lowered hemoglobin concentration. On the 55th day of exposure these changes in animals of groups 1 and 2 appeared more pronounced. Anisocytosis, poikilocytosis, and slight reticulocytosis appeared in the blood of some rats. However, these changes were transient, and on the 20th day of recovery the blood picture in all the experimental rats returned to normal. Results obtained in this investigation lead to the assumption that 0.03 mg/m^3 of aniline chronically inhaled by the experimental animals elicited no reliable changes in the rats' indexes used in this investigation, and that, accordingly, such aniline concentration could be denoted as the maximal permissible average 24 hour aniline vapor concentration in the air surrounding inhabited areas.

Fig. 4



Heinz bodies. Rat No. 18 of Group 1, 3 mg/m^3

Fig. 5



Heinz bodies. Rat No. 35 of Group 2, 0.3 mg/m^3

The next step in the investigation was a study of existing atmospheric air pollution with aniline vapor. In this connection observations were made on the grounds of and general vicinity surrounding the Novomoskovsk Phenol Plant, where aniline was used for the production of neozone D (phenylnaphthylamine) which this plant used at the rate of 6.5 - 7.0 tons per day. It was not possible to establish by computation the amount of aniline vapor discharged by the plant into the atmospheric air, because some of the aniline entered into the composition of the final product, another part was regained and recirculated, while the third part was discharged with the plant's waste water. Neozone D is produced by the plant periodically and under highly unfavorable sanitary-hygienic conditions. Despite the fact that most of the rooms in which aniline was stored were equipped with ventilators, and that the plant was equipped with means for the recovery of unused aniline vapor, many of the processes discharged large volumes of aniline vapor into the atmospheric air. This condition was aggravated by the high temperature

surrounding certain installations used in different methods of aniline processing. Aniline vapor found its way into the atmosphere during loading and unloading of the reagents and by leakage from faulty conduits, etc.

Air samples were collected for analysis during the spring and summer months at different hours of the day, 100, 300, 500, 750 and 1000 m from the source of aniline discharge on the lee side of the plant. A total of 188 air samples were collected and analyzed by the method of Alekseeva and Khokhlova which eliminated the effect of ammonia on the analytical results. Analytical data presented in Table 4 clearly indicate that at 750 m from the source of aniline discharge 3 of 35 air samples contained aniline vapor in concentrations exceeding the recommended maximal single dose. Aniline concentrations in all 44 air samples collected at 1000 m from the source of aniline discharge contained the vapor in concentrations below the maximal permissible single dose. Data in Table 4 also show that aniline vapor in the air possesses a high stability; even when discharged in low concentrations aniline vapor became distributed over great distances. On the basis of the data presented it is recommended that a sanitary clearance zone of not less than 1000 m wide be organized around the neozone D department of the Novomoskovsk Phenol Plant.

Table 4.

Maximal Single Aniline Concentrations in Atmospheric Air Around the Novomoskovsk Phenol Plant during the 1962 Summer-Winter Season

Meters from the discharge source	Number of collected samples	Aniline concentrations		Distribution of sample concentrations		
		Mg/m^3				
		Maximal	Minimal	0,5—0,11	0,1—0,05	Less than 0.05
100	33	0,5059	0,02°3	14	12	7
300	40	0,1344	0,0048	1	11	28
500	36	0,0956	0,0070	—	14	22
750	35	0,0795	Trace	—	3	32
1 000	44	0,0324	Trace	—	—	44

Conclusions

1. The minimal odor perceptive aniline concentration for most sensitive persons was 0.37 mg/m^3, and the maximal non perceptible concentration by odor was 0.34 mg/m^3.

2. The concentration of aniline vapor threshold reflex effect on the brain cortex adaptation process to the rhythm of light flashes, as obtained by the method of functional electroencephalography, was 0.07 mg/m^3.

It was previously shown that 0.05 mg/m^3 of aniline vapor elicited no changes in the animal organism; accordingly, it is recommended that 0.05 mg/m^3 be adopted as the maximal single permissible aniline vapor concen-

tration in the atmospheric air.

3. Results of the investigation showed that 3.0 and 0.3 mg/m^3 under similar conditions was entirely inactive.

4. It is recommended that 0.03 mg/m^3 of aniline vapor in the atmospheric air be adopted as the maximal 24 hour average concentration.

5. It is also recommended that the department which produced neozone D be surrounded by a sanitary clearance zone of not less than 1000 m wide; this recommendation does not take into account other possible harmful atmospheric air discharges.

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Industrial Tungsten, Molybdenum and Rhenium Condensates and Their Hygienic Evaluation

pp. 24 - 28

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The present author studied working conditions prevailing in industries which received or processed tungsten, molybdenum, and rhenium. Results indicated that many of the technological processes in which the metals were heated to 1000 - 6000°, or higher, were accompanied by the formation of aerosols in different degrees as a result of metal vapor condensation. The investigation had shown that in smelting different quality steel containing tungsten and molybdenum, aerosols were generated which consisted of oxides of the metals at the workers respiration level the density of which varied from negligible to 2.4 mg/m^3, depending upon the character of the technological process, and other accompanying operations. In the case of molybdenum and its products the density of its oxide aerosol was in the range of 4.0 - 79.9 mg/m^3. In the case of tungsten the oxide aerosol density was in the range of 100 - 240 mg/m^3. Some processes connected with these metals may be accompanied by even higher metal aerosol concentrations.

The present author made a detailed parallel study of the morbidity and loss of work time among respective employees of the above mentioned industries. Preliminary results pointed to frequent sickness among workers who

inhaled aerosols of the rare metals which affected mostly the upper respiratory tracts, the bronchial system, etc. Physiological observations made directly in the plant under actual working conditions indicated that many workers in such industries as are mentioned above developed some functional respiratory disturbance manifested as respiratory insufficiency. Thus, 44 of 57 examined worker patients had pulmonary hyperventilation, 52 showed a lowered maximal pulmonary ventilation (15 - 20%), and in 23 of the examined workers the vital lung capacity was reduced by more than 15%. O. Ya Mogilevskaya showed in 1956 that some employees with work records of many years developed pneumoconiosis as the result of inhaling highly dispersed molybdenum aerosol particles and its oxides. Surveys made at the I. M. Sechenov Institute and other research institutes showed that many employees of the metallurgical industries showed signs of, what appeared as, process of pneumoconiosis. This could only be verified by further and more detailed clinical examination.

Investigations conducted by the present author indicated that there existed many industrial and manufacturing processes which generated rare metal aerosol condensates, the inhalation of which produced in the workers, especially under certain conditions, functional disturbances of the respiratory organs. However, the above recorded observations failed to firmly establish whether condensation aerolsols of tungsten, molybdenum and rhenium affected the organism in a manner different from aerosol particles of the same metals generated as a result of friction or grinding. Rational sanitary hygienic standardization of air polluted with aerosols of the three rare metals required additional detailed information on the degree of the aerosols dispersion and their physiological effect on the organism. N. V. Mezemtseva in 1957 and O. Ya. Mogilevskaya in 1950 and 1952 arrived at reliable data on tungsten and molybdenum aerosol effects on the organism, on the basis of which the office of the U.S.S.R. Chief Sanitary Inspector adopted maximal allowable tungsten and molybdenum aerosol concentrations in the air. This served as a sound basis for the present authors investigations along similar lines.

No information relative to the toxicity of rhenium aerosol in the air has been found in the literature; therefore, this phase of the investigation had to be initiated individually. Investigations have been conducted on the basis of animal experimentation. The object of the investigation was to obtain data regarding the comparative pathogenicity of the different aerosol types under conditions which would insure complete comparability of experimental results with previously obtained results and with the results found in the literature. To attain this, investigations have been conducted with white male rats weighing 180-250 g using the blood-free method of intratracheal administration of the metallic particles suspended in saline. The usual dose of 50 mg was used at first, but this proved too toxic with the molybdenum trioxide condensation aerosol, which killed most of the test animals during the first few hours of the experiment. Microscopic examination of the lungs of the dead animals showed wide spread hemolysis, hyperemia, extensive

localized atelectasis. Following this, molybdenum trioxide aerosol was administered to new rats twice at the rate of 16 mg 10 days apart. Here, as in the case of the condensed aerosol, and as in the case of highly dispersed rhenium, morphologic changes developed in the internal organs of the experimental rats. The administration of rare metals, as above described, developed bronchitis and chronic interstitial pneumonia accompanied by diffuse sclerosis of the pulmonary tissues in all experimental animals. Histologic examinations indicated that sclerosis was well defined in all cases. A well defined protein dystrophy was observed in all the parenchymatous organs. In the case of rats administered rhenium aerosol, there also appeared a hepatic and renal fatty distrophy.

Administration of tungsten condensation aerosol elicited more clearly expressed changes than in the two previous experiments with molybdenum and rhenium aerosols. This was particularly true of the reticuloendothelial system and of the connective tissue elements. Results of general tissue and organ examinations 2, 4 and 6 months after the metallic aerosols administration showed that the condensation aerosols had a considerably higher toxic potency than the metallic disintegration aerosols. The morphologic changes produced by the two types of rare metal aerosols were of similar character. Results clearly indicated that tungsten and molybdenum condensation aerosols possessed fibrogenic properties, especially in relation to lung tissue, and had toxic effects on the parenchymatous organs of the experimental animals. Tests were, then, conducted to determine whether aerosols of these rare metals had an unfavorable effect in concentrations adopted as maximal permissible for coarsely dispersed tungsten and molybdenum. Accordingly, parallel with morphologic investigations more refined experimental procedures were used. The pathogenic effect of rhenium has been established and previously described; therefore, the same concentration was used in the new experiment.

In the hope of simulating practical conditions, experiments were conducted on a chronic inhalation basis, as described on numerous occasions by other authors for similar investigations. The rare metals condensate aerosols were prepared by burning pure metallic electrodes in a voltaic arc for 2 hours every other day for 18 weeks. The aerosol concentration was maintained at approximately 6 mg/m^3, with fluctuations within the limits of 10% and with $p = 0.05$, which corresponded to the maximal permissible tungsten and molybdenum condensation aerosol concentration in atmospheric air. Ten animals were subjected to the inhalation of air containing tungsten aerosol. Two of these died after two months. Ten white rats were exposed to the inhalation of molybdenum and 10 to the inhalation of rhenium aerosols. All 20 animals survived. Animals were observed between exposure periods; nothing noteworthy was observed in their behavior or general appearances; however, their body weight fell below that of the control rats. No substantial changes had been noted in the blood indexes during this phase of the study, except for slight drop in blood hemoglobin concentration in rats which had been exposed to the inhalation of air containing aerosols of molybdenum and

rhenium.

Paper electrophoretic studies of the blood serum proteins of the experimental animals were conducted to determine what effect, if any, the inhaled rare metal aerosols had on the intracellular biochemical reactions, and in what manner have they interacted, if at all, with the blood serum proteins. A dysproteinemia was noted towards the end of the inhalation tests, expressed as a drop in the total protein and a parallel rise in the α- and γ-globulins. These changes were more clearly defined in rats exposed to the inhalation of air containing molybdenum aerosol, as can be seen from the data presented in Table 1. The dysproteinemia was not associated with sulfhydryl group blocking; in fact, a reverse tendency appeared as a rise in the number of sulfhydryl groups, which in the case of tungsten aerosol inhalation amounted to 41.5%. The rate of amino nitrogen elimination via the urine of rats which inhaled molybdenum aerosol increased to twice that found in the control rats, indicating that the normal course of protein metabolism was disturbed.

Table 1.

Average Blood Serum Protein and Protein Fractions Content and Albumin/Globulin Coefficient

Index	WO_3		MoO_3		Re_2O_7		Control	
	Before exprt.	After exprt	Before exprt.	After exprt	Before exprt.	After exprt	Before exprt.	After exprt
% of total protein	6,93	7,84	8,28	8,88	8,28	7,68	7,26	7,80
% of total albumin	35,6	32,4	45,1	31,9	39,6	36,2	38,2	37,0
% of total globulin	64,4	67,6	56,9	68,1	60,4	63,8	61,8	43,0
α	24,6	25,9	17,9	27,2	25,3	23,7	24,0	22,5
β	23,4	19,6	25,1	18,3	19,4	20,9	19,2	23,4
γ	16,5	22,0	11,9	22,5	15,7	19,2	19,7	17,1
Albumin/globulin coefficient	0,576	0,488	0,864	0,482	0,684	0,580	0,622	0,614

Having obtained information regarding disturbed protein metabolism in the organism as the result of tungsten, molybdenum and rhenium aerosol inhalation, as shown by the results of previously discussed morphologic studies, the investigation was directed into a study of protein regeneration, which pertained to the total and reduced glutathione level in the blood serum. Results showed that normal levels of total and reduced blood serum glutathione remained undisturbed in the experimental animals, which was in favor of the protein biosynthesis processes, creating tissue protein resources. In addition, a drop in alkaline phosphatase activity was noted in all experimental animals, especially in rats exposed to the inhalation of molybdenum aerosol. This is significant, since alkaline phosphatase is an enzyme associated with vital liver activity. The morphological studies disclosed a chronic interstitial pneumonia accompanied by a progressing sclerosis, which was more pronounced in rats which inhaled air containing tungsten aerosol, and which was also accompanied by a tension in the reticulo-endothelial system and in

the connective tissue elements. A mild protein dystrophy was noted in the parenchymal organs. Generally speaking, the intensity of rare metals' toxic effects accorded their solubility in fluids of different pH, as shown by the data presented in Table 2.

Table 2.

Solubility of finely dispersed WO_3 MoO_3 and Re in Liquid Media of Different pH (Concentration of the Metal in 10 ml of the solvent)

Solvent	After 3 days exposure			After 30 days exposure		
	MoO_3	WO_3	Re	MoO_3	WO_3	Re
Distilled water (pH - 6.8)	0.013 mg	5 μ	0.5 mg	1.82 mg	5 μ	1.25 mg
0.22% soln. (pH - 7.8)	4.6 »	5 »	0.75 «	4.59 »	10 »	3 »
0.3% soln. (pH - 1.2)	2.4 »	5 »	0.5 «	2.35 »	5 »	1.25 »

Results of the investigation illuminated the true nature of the toxic effect exerted by highly dispersed aerosol of molybdenum, tungsten and rhenium, which could not be brought into light by the histo-morphological investigation of the experimental animals' tissues and organs. Results of the investigation led the present author to an important practical conclusion, namely, that high dispersion of molybdenum, tungsten, and rhenium aerosols considerably enhanced their toxic properties. The investigation also demonstrated that inhalation of air containing highly dispersed aerosols of molybdenum, tungsten and rhenium in maximal permissible concentrations adopted for coarsely dispersed particles of the same metals may prove toxic to the organism.

Conclusions

1. Many metallurgical industrial processes generated tungsten, molybdenum and rhenium condensation aerosols resulting from high temperatures to which ground granules and powders of these metals are heated.

2. Inhalation of air containing highly dispersed molybdenum, tungsten and rhenium aerosols under certain conditions disturbed the normal functional state of the respiratory organs. Inhalation of tungsten, molybnum and rhenium condensation aerosols developed chronic interstitial pneumonia accompanied by pneumosclerosis, tension of the endothelial system and dystrophic changes in the parenchymal organs.

3. Condensation aerosol of molybdenum and rhenium elicited morphologic changes in the body organs, disturbed the process of protein metabolism, eliciting dysproteinemia, and a rise in the rate of amino nitrogen elimination with the urine towards the end of the experimental period, and lowered the activity of alkaline phosphatase.

4. Inhalation of air containing equivalent concentrations of mechanical and condensation aerosols showed that the latter had a higher toxicity parameter. Therefore, the maximal permissible tungsten, molybdenum and rhenium crude aersol concentrations cannot be applied to the condensate aerosols of the same rare elements.

5. In attempting to determine the maximal permissible rhenium dust concentration in the air consideration must be given the fact that rhenium in its metallic form, or in solution, is less toxic than tungsten or molybdenum in the form of mechanical dust; at the same time it was shown that in the form of the condensate aerosol rhenium was more toxic than aerosols of either of the other two rare metals. Therefore the maximal permissible concentration in the air of rhenium in the form of its condensate aerosol must be set below the ones set for tungsten and molybdenum. Accordingly, it is recommended that such concentration for rhenium condensate aerosol be set at 4 mg/m^3.

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Toxic Properties of Manganese Cyclopentadienyltricarbonyl Antiknock Substance

pp. 29 - 32

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Manganese cyclopentadienyltricarbonyl has the chemical formula of $C_5H_5Mn(CO_3)$. It has been used as an antiknock substance for internal combustion engines instead of tetraethylead. No reports have been found in the literature dealing with the toxicity of this compound. This new antiknock agent exists in the form of a bright yellow crystalline powder which sublimates at 75-77°. It is water insoluble, and is soluble in alcohol, benzene, and oil. The antiknock property of this compound is stronger than that of tetraethylead. At the same time, it is more easily manipulated and is less harmful than tetraethylead. In the course of its production the new antiknock substance finds its way into the organism through inhalation and through the oral route by ingesting food inadvertently contaminated by careless handling, and by inhaling air-suspended dust. Therefore, the toxic properties of the new antiknock compound were studied by the method of direct gastrointestinal

administration. Changes in the state of the nervous system in the peripheral blood circulation, as well as in the functional state of the liver and kidneys, were determined pathomorphologically by examining internal organs of experimental animals. Manganese cyclopentadienyltricarbonyl was administered to the animals by a gastric tube in 1 ml quantities in sunflower-seed-oil solution. Control animals were administered sunflower-seed-oil alone.

Results of the tests indicated that gastrointestinal administration of 200 mg/kg of the preparation killed all the animals and constituted the absolute lethal dose, while the administration of 150 mg/kg killed 60% of the experimental white mice and was regarded as close to the L D_{50} dose. Occasionally experimental white mice died following the administration of 100 mg/kg. None of the experimental white mice died which received doses below 100 mg/kg. White rats proved the most sensitive to the effects of the new antiknock substance, as shown by the fact that 120 mg/kg proved to be the L D_{100} dose; 80 mg/kg killed 60% of the experimental animals; 40 mg/kg was the minimal lethal dose, and 20-30 mg/kg was the maximum tolerance dose. It should be noted at this point that animal experimental tests made with samples of 4 batches of the antiknock substance yielded identical results, showing that they possessed identical toxic properties.

Experimental animals which survived the test several days manifested the following symptoms of intoxication: bloody exudation from the nasopharynx, the animals appeared sluggish and indifferent to some types of external stimulation. In the later periods of intoxication and shortly before death the animals developed clonic spasticity. Some of the experimental animals developed paralysis of the hind legs 5-7 days after the antiknock substance administration. As previously mentioned, mice proved less sensitive to the effects of the new antiknock substance than rats. Autopsies performed on white rats which perished within 24 hours after the antiknock substance administration disclosed that the blood was of a raspberry color, and the liver and kidneys acquired a brownish tinge. Histological examination of the internal organs of autopsied animals showed sharply defined vascular disturbance in the form of extreme plethora, brain hemorrhages, perivascular and pericellular edema. There also appeared localized necrotic gastritis and fatty liver cell dystrophy.

Autopsy of white rats which perished 24 hours after the antiknock substance administration in lethal doses showed changes basically identical with those previously described. Experimental animals which had been subjected to the acute effect of the new antiknock substance had been tested for the threshold of electric neuro-muscular stimulability. No deaths had occurred among white mice which received 70 and 50 mg/kg of the new antiknock substance; however, the threshold of electrostimulability dropped from 9-10 mA with an average of 9.6 mA to 5-7 mA with an average of 5.5 mA. It was, thus shown that a single administration of the new antiknock substance elicited changes in the activity of the nervous system manifested as spasticity and lo-

wered threshold of electric neurostimulability; the latter was also noted in experimental animals which received the new antiknock compound in doses not otherwise visibly toxic.

The occurrence of unusual changes in the blood color led to the assumption that the new toxic substance possessed erythrocyte lytic properties which induced hemosiderin accumulation in the tissues. Several crystals of the new antiknock substance had been injected into the blood system of fresh animals. Observations showed that the new antiknock substance possessed some hemolytic activity which could result from the effect of the primary substance or from its conversion products, basically from the cyclopentadiene which split off from the original molecule. This observation led to the determination of the osmotic erythrocyte resistance in white rats. Results showed that following the administration of the new antiknock substance in 40 mg/kg dose the red blood cell resistance dropped. Under normal conditions red blood cell hemolysis began at NaCl 0.49%, and complete hemolysis occurred at NaCl 0.38%. Red blood cells of rats which received the new antiknock substance showed beginning hemolysis at 0.73% NaCl, and complete hemolysis at 0.48% NaCl.

A single administration of the new antiknock substance to rats in lethal doses increased the animals' permeability, which resulted in punctate and infarctlike bleeding, and in acute and uneven plethora of the internal organs, and also in the appearance of periovascular edema. The total picture of results obtained, as above described, clearly indicated that manganese cyclopentadienyltricarbonyl belonged to the group of substances possessing polytropic toxic properties. Experiments were conducted with white mice and rats to determine the effect of repeated injections of doses which upon single administration produced no toxic results. The antiknock substance was administered to the experimental animals repeatedly intragastrically in the form of its sunflower-seed-oil solution in doses of 25 mg/kg. The manganese compound was thus administered to white mice on 18 successive days in 0.5 ml of its oily solution. No toxic manifestations appeared in the mice during the first 3 days of the repeated administration. On the fourth day some of the animals perished and at the end of the repeated administration 8 of the 20 mice died. In a similar series of experiments, rats had been administered daily 10 mg/kg doses of the manganese compound. Two of the rats died after the 5th administration of the poison while the remaining rats were still alive at the end of the second week. The external appearance of the animals, their general behavior and gradual loss of weight indicated that the animals were unfavorably affected by the toxic properties of the new antiknock substance. Results of these experiments clearly indicated that the new antiknock substance, or the products of its conversion, accumulated in the organism upon repeated injection, resulting in the intoxication and death of the experimental animals which received doses, a single administration of which produced no death and no intoxication symptoms.

Chronic intoxication experiments extending over considerably long

period of time were then conducted with the experimental animals administering 5 mg/kg of the organic manganese compound. Experiments were conducted with 20 white rats which received the above mentioned dose of the manganese antiknock substance as described in previous experiments for 2 month periods. Fourteen control rats received 0.5 ml of sunflower-seed-oil only daily for the same period of time. Determinations of the neuromuscular stimulability threshold showed that it dropped slightly below the normal level. Blood tests showed fluctuations of positive and negative values in the hemoglobin concentration and in the number of erythrocytes. Shifts in the red blood cell osmotic resistance were of more significant values. Thus, under normal conditions the minimal resistance of rats' red blood cells were within the range of 0.52-0.48% of NaCl, and the maximal within the range of 0.36 and 0.4%. After repeated administration of the manganese antiknock substance, erythrocyte hemolysis appeared at 0.6-0.56% of NaCl, and in some cases even at 0.7%; in the animals administered the antiknock compound the NaCl concentration range was 0.38-0.42%. Evaluating the data of the above experiments, it can be stated that repeated administration of the antiknock substance to the experimental animals lowered the osmotic resistance of red blood cells.

Repeated administration of low doses of the new antiknock substance lowered the animals resistance to infection as a result of inflamation which developed at points of subcutaneous administration, where purulent processes develop as a rule. No such phenomena had been observed in experimental animals which received single skin injections of the new antiknock substance. Results of daily subcutaneous injection of the antiknock substance in small doses for a period of two months indicated that 20 mg/kg could be regarded as the maximal tolerance dose under the conditions of the experiment. Control animals received a single 20 mg/kg dose without the preliminary injection of the small doses. Following the injection of the provocative dose the experimental animals began to lose weight rapidly. They appeared slovenly and dirty, showed external signs of intoxication, and died within 10 - 12 days. Histologic examinations disclosed signs of acute gastric polyemia, lymphocitic infiltration of the submucous membrane, and a marked eosinophilia; processes of catarrhal desquamation appeared in the duodenum; necrotic changes, bleeding, polyneuclear infiltration, granular tissue proliferation appeared in the cutaneous and subcutaneous layers. Peritoneal wall muscles showed necrotic spots surrounded by leucotytic infiltration. Brain neurocells became edematous in the cortical and subcortical regions; the neurocell protoplasm showed signs of vacuolization, karyolization accompanied by the appearance of neuronophagia. The lungs showed signs of acute polyemia and of catarrhal bronchitis. Some vascular lumens showed leucytic stasis, and the blood vessels were surrounded by round cell infiltration. The spleen appeared acutely polyemic and showed disappearance of lymphoid tissue pulp, and deposition of a brown pigment. There were also many hepatic and renal pathologic manifestations. Histologic examinations of gastrointestinal tissue showed signs of pathology similar to the ones described above for other body

organs. Results of the above investigation indicated generally that the administration of the new antiknock substance to experimental animals in low doses elicited no noted changes in any of the organism's functional systems; however, they seriously upset the organism's biological balance.

The total picture resulting from the study warrants the conclusion that the investigated new antiknock compound was actually a toxic substance. Samples taken from different batches of the new antiknock substance showed different types of toxicity which most likely was due to differences in its purification. This fact should be given special attention and should be taken into serious consideration when making standard sanitary and hygienic evaluation of this product. Emphasis is placed on the fact that acute and subacute intoxication stages showed the predominance of symptoms related to damage done to the neurovascular system and to the gastrointestinal tract. It should be remembered that dystrophic changes had also been noted in other organs and that the compound manifested marked cumulative and hemolytic properties.

Determination of Small Thorium Quantities in Biological Specimens

pp. 48 - 52

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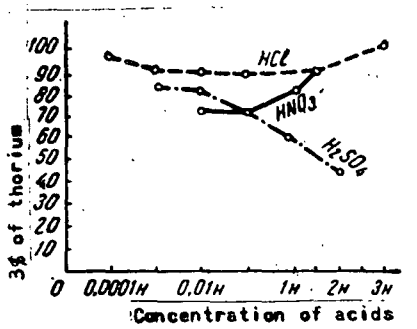
The use of thorium in the USSR national economy has been progressively increasing. Therefore, the present authors undertook to develop a method for the determination of small thorium quantities in biological specimens. The existing methods for the determination of small amounts of thorium frequently fail to serve the basic purpose of the analysis. In 1948 S. V. Tokmakova and A. D. Turkin presented a, so-called, emanation method; however, this method could not be applied to determination of thorium in biological specimens, where a high degree of sensitivity was required. The spectrometric and spectroscopic methods for the determination of thorium in biological specimens proposed by Hursh in 1957, by Tilton and Perkins in 1956, and by others are characterized by insufficient sensitivity, or they require almost complete removal of other metallic salts present in the analyzed specimen; this considerably complicated the analytical procedure and made it prohibitively time consuming. In 1959 B. N. Belousov and S. A. Potapova proposed a highly sensitive method based on the extraction of thorium from the solution with mesityl oxide after each mineralization, which was

then followed by nephelometric estimation. However, the presence of titanium and zirconium interfered with this determination, and the fact that the extraction of thorium must be done with freshly prepared mesityl oxide made this method cumbersome and inapplicable to the determination of titanium in biological specimens.

In developing the method for the determination of small thorium quantities in biological specimens the present authors chose thoron and arsenazo III, which were first recommended by V. I. Kuznetsov and S. B. Savvin in 1961 for the determination of thorium in ore. Thorium combined with arsenazo III to form a stable complex substance of an emerald greenish color; the newly formed substance remained stable in a 6 N solution of hydrochloric acid. The complex resulting from the combination of thorium with "thoron" was less stable; therefore, determinations had to be made in 0.05 - 0.09 N solution of hydrochloric acid. The reaction sensitivity of thorium with "thoron" is 0.5 μ of thorium in 1 ml. The reaction beteen thorium and arsenazo III proved more sensitive, amounting to 0.02 μ of thorium in 1 ml. Preliminary tests showed that the presence of phosphates, sulfates, titanium, zirconium, and large quantities of iron interfered with thorium determination, whereas in the case of thorium and arsenazo III only titanium, zirconium and fluorides interfered with the determination. Thus, thorium with arsenazo III can be determined by the fractional method in the fluid obtained after mineralization of the biological specimen. Separation from admixtures may become necessary only when the biological material is suspected to contain admixtures of titanium, zirconium or fluorides. Preliminary separation of coexisting ions is required in all cases of thorium determination by the "thoron" method. Thorium can be separated from the interfering elements chromatographically with the aid of cation K U-2, as recommended by Yu. A. Chernikhov, V. F. Luk'yanov and A. B. Kozlov in 1960, or by the ionoexchange, using the highly acid resin No. 1 tested by the present authors. As shown in Figure 1, it was brought out that thorium could be separated quantitatively by ionoexchange resin only in hydrochloric acid solution in which thorium precipitated up to 90%, or more, regardless of its concentration. Thorium separated from nitric and sulfuric acids, by precipitation only within the range of 30 - a maximum of 80%, independent of acid concentration. It was also shown that the presence of Ti^{4+} and PO_4^{3-} ions in 100:1 ratio to thorium and Zr^{4+} And Fe^{3+} in 1000:1 ratio to thorium did not interfere with the adsorption of thorium by ionoexchange resin No. 1, nor did it interfere with its final determination.

Thus determination of small thorium quantities in mineralized biological specimens can be made by the differential method with arsenazo III, or by the preliminary chromatographic separation of the admixtures, followed by the determination of thorium by the "thoron" or arsenazo III methods. The biospecimens to be analyzed, such as muscle tissue, internal organs, blood, urine, feces, in quantities of 50-200 g should be mineralized by a mixture of concentrated H_2SO_4 and HNO_3. The mineralized light yellow fluid is placed

Fig. 1



Effect of hydrochloric, nitric and sulfuric acids concentrations on the quantity of thorium separated by ionoexchange rosin No. 1.

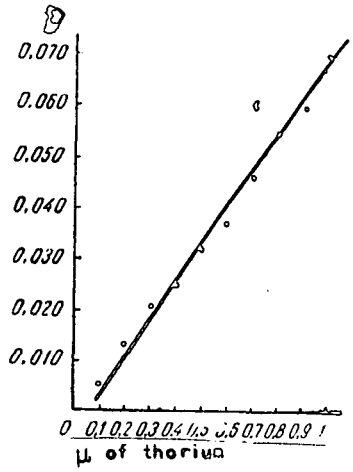
into a Erlenmeyer flask followed by the addition of twice the volume of distilled water. It is then neutralized with concentrated NH_4OH which is added at first drop at a time until the reaction range is between pH 6.0 - 7.0. The precipitated hydroxides are filtered off and washed clean of SO_4^{2-} until no turbidity develops upon the addition of $BaCl_2$. In the course of this step part of PO_4^{3-} is lost in the form of $(NH_4)_3PO_4$ which interferes with the chromatographic partitioning of thorium. The washed precipitate is then dissolved in 10-20 ml of 6 M. hydrochloric acid solution. Further determination of thorium can be made in one of the three ways.

Thorium determination by the fractional method is based on the formation of a stable thorium-arsenazo III complex in a 6 N HCl solution. The determination can be made colorimetrically or photoelectrocolorimetrically. The colorimetric procedure is as follows: prepare a standard scale consisting of 10 colorimetric test tubes by placing into the tubes in successive order, 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0 ml of a standard solution containing 10 μ of the thorium per ml of 6 N HCl solution; add 6 N HCl solution to the tubes to make a volume of 4.8 ml, then add 0.2 ml of 9.05% arsenazo III solution to a final volume of 5 ml in each tube of the series.

Prepare the solution to be analyzed as follows: add 1-2 ml of the solution to be tested to a standard colorimetric test tube; add 6 N HCl solution to make 4.8 ml, then add 0.2 ml of the arsenazo III solution. Appearance of a yellowish color indicates the presence of Fe^{3+}, in which case add 5-10 mg of ascorbic acid. Compare the color of this tube with the colors of the standard scale. The sensitivity of the colorimetric method is 0.5 μ of thorium in 5 ml.

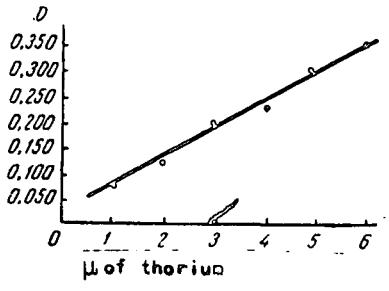
Less time consuming determinations can be made with the aid of a photoelectrocolorimeter, in which case the final estimation is made with the aid of a calibrated normogram constructed on the basis of a previously prepared standard scale. Two such calibrated curves should be prepared, one for solutions ranging from 0.1 to 1 μ and another for solutions ranging from 1 to 6 μ, as shown in Figs. 2 and 3. Both scales are prepared similarly. Determinations are made in 10 ml colorimetric cups at 680 μμ wave length using a red light filter. The thorium determination solution is prepared as previously described for the colorimetric method. Sensitivity of the test is 0.1 μ in 5 ml. The lowest thorium amount which can be determined by the colorimetric method is 2.5 μ, and by the photocolorimetric method is 0.5 μ. In either case the determination error is below 15%.

Fig. 2.



Thorium calibrated curve, from 0.1 to 1.0 μ

Fig. 3.



Calibrated thorium curve from 1.0 to 6.0 μ

The colorimetric method is adequately sensitive, possesses a low experimental error, and is interfered with only by the presence of titanium, zirconium or fluorides in ratios of 10:1 to thorium.

The second and third thorium determination methods are based on the chromatographic partitioning of thorium from the co-existing ionic admixtures and differ from one another with respect to the ionoexchange resins used (K U-2 and highly acid resin I). The fluid obtained after dissolving the precipitated hydroxides is diluted in both instances with twice the volume of distilled water to obtain a 20% HCl solution by volume and 5 ml of 20% tartaric acid is passed through the ionoexchange resin column.

Before using cationite KU-Z resin it must be thoroughly purified and placed into a special glass cylinder 15 cm high and 0.5 cm in diameter. The solution to be analyzed is passed through the resin column twice at a rate not exceeding 30 drops per minute. This will insure a more thorough separation of thorium from the solution. The column is then washed with 20% by volume of HCl and the acid wash water is discarded.

The thorium adsorbed by the resin column is eluted with a saturated solution of $(NH_4)_2C_2O_4$. The eluate is evaporated to dryness and is treated with 4 ml of concentrated HNO_3, and again evaporated to dryness over a water bath. The dry residue is then dissolved by the addition of 2 ml of 0.05 N HCl solution and determined colorimetrically by the "thoron" method. The residue can also be dissolved by adding 5 ml of 6 N HCl solution and determined colorimetrically or photocolorimetrically by the arsenazo III method, as described above. The lowest amount of thorium which can be determined in this way is 1 μ. In this case titanium, zirconium, fluorides and phosphorus did not interfere with the thorium determination. The de-

termination error is 20% or less.

In the case of the highly acid ionoexchange resin I it is necessary to use a cylinder 3 cm high and 3 cm in diameter. The fluid exchange rate should not exceed 20-30 drops per minute. The test solution diluted to contain 20% HCl by volume is passed through the ionoexchange column three times. This is followed by passing 15 ml of 20% tartaric acid solution mixed with 5 ml of 20% by volume of HCl solution through the ionoexchange column, which is then washed with 15 ml of distilled water until the pH of the wash water becomes neutral. The thorium is eluted from the ionoexchange material by aspirating through a solution of $(NH_4)_2C_2O_4$ at 60 - 70° to which strong HCl of 1.17 sp. g. has been added, or at the rate of 20 ml of the $(NH_4)_2C_2O_4$ per 5 ml of the HCl. The elution is done 3 times. The alternate use of ammonium oxalate and of hydrochloric acid brings about an almost complete elution of the thorium from the resin column. The eluate is then treated with the cationic KU-2. The lowest amount of thorium determined by the "thoron" method is 1 μ and by the arsenazo III method is 0.05 μ, with a loss of less than 25%. The tests have been checked by making thorium determinations in muscles, internal organs, blood and feces. Results are presented in the Table following and show that the procedures proposed for the determination of thorium in biological specimens yielded satisfactory results.

Determination of thorium in biological specimens (muscles, internal organs, experimental, blood

Th^{4+} added	Th^{4+} found in μ		
	Fractional method	Using resin KU-3	Using resin No. 1
1	0,8	0,8	1,6
5	3,4	4,0	4,0
10	9	9	8
50	46	45	40
200	180	170	180
500	475	425	450
2 000	2 000	1 800	1 800
4 000	3 800	3 200	—
Control	0	1	1

In the case of thorium determinations in amounts ranging from 1-4,000 μ by the described differential method the error stayed within the range of 10-15%, and by the chromatographic method within the range of 20-25%, with the minimal determinable amount being 1 μ in 100 g of the biological specimen. Thorium determination in 100 g of a biological specimen by the differential method consumed 9-10 hours, as compared with 12-14 hours consumed by the chromatographic thorium partitioning. An efficient analyst can make 8-10 simultaneous tests. All control tests were positive indicating the presence of 1-3 μ of thorium; human feces in many instances contained as much as 20 mg in 100 g of the substrate. Organs of rats which received thorium dioxide intratracheally have also been analyzed by the above methods. Thorium was found in the lungs, trachea, spleen, lymphatic nodes, gastrointestinal tract, urine, and in the blood. A comparison of results obtained by the three analytical methods indicated a satisfactory closeness between them.

Conclusions

1. The following 3 methods for thorium determination in biological specimens have been described: the differential method with the aid of arsenazo III, and 2 methods based on chromatographic partitioning of thorium from admixtures on cationic reagent KU-2 and strongly acid ionoexchange resin No. 2, followed by final colorimetric or electrophotocolorimetric determinations.

2. The lowest amount of thorium which could be determined by the differential method was 2.5 μ using the colorimetric method, and 0.5 μ using the photoelectrocolorimetric method. The lowest amount of thorium that can be determined in a biological specimen with the aid of cationic resin KY-2 was 1 μ, and with the aid of the highly acid ionoexchange I it was 0.5 μ using the "thoron" reagent; it was 0.1 μ when arsenazo III reagent was used.

3. The error in determining thorium by the differential method was within the range of 10-15%. Interfering factors in this method were zirconium, titanium and fluorides. Determination of thorium in biological specimens with the aid of ionoexchanges resins I and KY-2 following specimen mineralization was free from titanium and zirconium interference.

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Prevention of Air Pollution in Gas Equipped Apartments (With reference to the Proposed Sanitary Regulations for Gas Equipped Residences)

pp. 60 - 62

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Gas is gradually replacing hard fuel in the USSR, which affects favorably the population's living conditions. On the other hand, lack of develop-

ment or improvement in gas burners has resulted in frequent air pollution in houses and apartments which had been equipped with gas. This was noted in 1945 by L.I. Los and 1949 by D. N. Kalyuzhnyi, and by many others. Gas burning generates such air polluting products as carbon monoxide, carbonic acid, hydrocarbons, etc; it also raises the surrounding air temperature and humidity, easily detected even after the gas has been used for 1 hour. Thus, rise in air temperature up to 10° and rise in relative humidity up to 20-30% have been noticed by the investigators above referred to. As a result of such conditions, Kh. V. Storoshchuk (in 1951), M. N. Troitskaya in 1958, S. F. Sorokina (in 1960) and many others found cases of chronic carbon monoxide poisoning upon examining inhabitants of gas equipped houses and apartments.

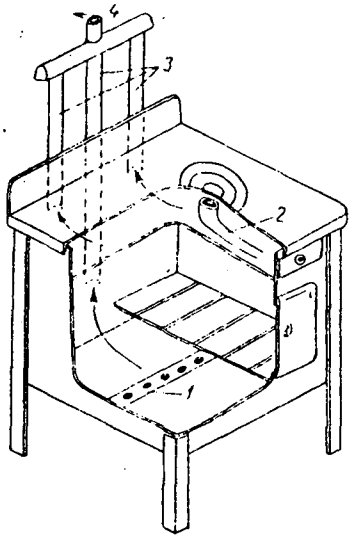
The above clearly points to the need of regular sanitary inspections for the purpose of establishing the factors which caused air pollution in gas equipped homes. In this connection past examinations have indicated that imperfect gas burners and gas plates used for cooking constituted a basic factor in the pollution of indoor air in gas-equipped dwellings. Another important factor is the complete lack of organized ventilation, imperfect construction, installation, and operation of existing ventilation systems, of the improperly planned room arrangements. S. P. Sladkova demonstrated in 1955 that the imperfect gas burners were responsible for breaks in the continuity of gas burning and in the consequent appearance of incomplete combustion products in the indoor air. She also noted that the exhaust ventilation system installed in the average present-day residential house or apartment was either faulty or inadequate to bring about complete removal of the gas combustion products. D. G. Devyatka noted in 1959 that the operating ventilation system in gas-equipped residences lowered the carbon monoxide concentrations in the kitchen air by only 22%. Kh. A. Zarivaiskaya found in 1962 that the usually planned and installed exhaust ventilation system brought about kitchen air exchange in one-room apartments to the extent of 60.4% of the required minimum, and only to the extent of 31% of the required minimum in two and three room apartments.

Comparative studies conducted in differently planned gas-equipped living quarters indicated that where living rooms were connected directly with the kitchen, intensity of air pollution with carbon monoxide, and other products of gas combustion, was greater in apartments in which the kitchen was isolated from the living room. The above indicated facts clearly point to the channels along which modern engineers, planners, architects, and hygienists must direct their attention for the rational solution of the air pollution problem in future construction of gas equipped residential houses and apartments. Present day attainments in sanitary technique and in the perfection of typical residence plans offer a basis for the solution of this important problem, and urgently call for the formulation of mandatory regulations and specifications applicable to the planning of gas installation in residential homes. In this connection complete gas combustion by home utilities or gas

installations is a basic requisite. This presupposes a steady and even gas flow of homogeneous composition under a regulated, constant pressure into properly computed and constructed gas burning utilities. K. N. Pravoverov and others have developed gas burners and kitchen gas plates which produced a, so-called, flameless or invisible combustion with an overhead flue which removed the gas combustion products including the resulting water (humidity) and the increased air temperature directly into the atmospheric air.

L. M. Pinchuk, N. M. Porubinovskaya of the Moscow City Sanitary - Epidemiological Station demonstrated that carbon monoxide concentration in the air of premises where the, so-called, flameless burners have been used did not exceed 2 mg/m^3. According to S. P. Slabkova carbon monoxide concentration in the kitchen using the flameless gas plate was reduced by several times and according to F. F. Lampert and V. E. Konstantimova (1959) no carbon monoxide presence could be detected in the other living rooms. Naturally, most efficient from the viewpoint of carbon monoxide and other gas combustion products elimination was the direct exhaust ventilation of such products through a properly constructed flue. M. N. Troitskaya found in 1962 no carbon monoxide in the air of kitchens which used the P. Akuz'min gas burning plate. Under such conditions of gas combustion no increase in the humidity of the apartment house air could be detected. This shows that proper gas burning utilities are at present obtainable and that proper plans for their installation can be proposed. Therefore, it is urged that construction and planning engineers in sanitary organizations should make proper use of the available home gas equipment. It is also suggested that for the purposes of proper sanitary safety gas burning utilities, particularly those used for water heating, should be equipped with automatic safety devices which would stop the gas flow as soon as unfavorable conditions developed in the exhaust flue. Naturally, the same applies to gas burners used in water heated houses.

Installation of boilers directly under living quarters, and especially under institutions for children, must be mandatorily forbidden. Particular attention should be paid to the properly planned and properly functioning ventilation systems. Official sanitary hygienic and engineering specifications should be formulated as guides for the calculation, construction, and proper installation of the gas-equipped dwelling ventilation system according to principles outlined by L. B. Chernin, Kh. A. Zarevaiskaya, and others. Generally speaking, the hygenic requisites and specifications related to the volume and dimensions of gas operating rooms, such as kitchens, etc. vary with the type and dimensions of the apartment or other dwelling, with the character of kitchen equipment, and with the nature of other house facilities. It is recommended that an air exchange of 5 m^3 should be provided for each plate gas burner. Wherever possible the kitchen, equipped with gas burning cooking facilities, should be completely isolated from the rest of the living space. A general educational campaign must be instituted along these lines and a rational sanitary hygienic inspection and control



Schematic plan of gas plate L-15 OPS

concentration had increased. No substantial improvements in the temperature-humidity conditions had been noted. However, the fact that experiments conducted with gas burning plate L-15 OPS yielded no desirable results should not discourage other investigators from continuing this type of work. It is possible that the principle of using direct carbon monoxide removing devices, which in our opinion is basically rational, may yield favorable results in future appropriately planned experiments.

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NO. 5, MAY

Experimental Data as a Basis for the Determination of the Maximal Permissible Amylenes (Pentenes) Concentration in Atmospheric Air

pp. 3 - 8

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Amylenes, or as they are generally known, pentenes, represent a mixture of 6 olefin isomers. Olefins are saturated hydrocarbons which consist of carbon and hydrogen. They contain a single double bond. Olefins

make up the homologous order of ethylenes. Amylenes are synthesized basically by the dehydration of amyl alcohol with aluminum oxide at 380-450°, or by a 65% sulfuric acid solution at 90-110°, or by the pyrolysis of amyl acetate at 500-700°. Amylenes can also be synthesized by dehydrating amyl alcohol solutions of fusel oils by means of zinc chloride. They are also contained in the light amyl distillates, mostly in the low boiling fraction of petrolic ether obtained in cracking or pyrolysis of crude oil. Technically, amylene has a b.p. of 39-40.5° d_4^{20} 0.6509, p_d^{20} 1.3783 and is, a mixture of all amylene isomers including isopentene. The main source of air pollution with olefins is exhaust of automobile gases. According to data presented by Hutchenson and Holdane of Los Angeles, California, automobile exhaust gases contained 88% of olefin. Other investigators of Los Angeles found the percentages to range between 70 and 80, and those of San Francisco found the olefin concentration to be 60%.

Olefin poisoning appears in the form of narcosis accompanied by profuse salivation, a considerable drop in arterial pressure, tachycardia, renal disturbance, such as uremia, proteinemia and appearance of cylinders, also spasticity of the glottis. 100-120 mg/li of olefins constituted a narcotic dose, if inhaled for 2 hours; 140-250 mg/li constituted a lethal dose. Rabbits exposed to the inhalation of air containing up to 0.15 mg/li of olefin for 7 hours daily for 20 days developed marked leucocytosis and paralysis of the hind legs. No noteworthy anatomical abnormalities had been noticed by N. V. Lazarev upon autopsy, as reported by him in 1954. Lately, olefins, (especially pentenes and hexenes) attracted investigators' attention by the fact that they were factors in the formation of smogs, as noted in Los Angeles.

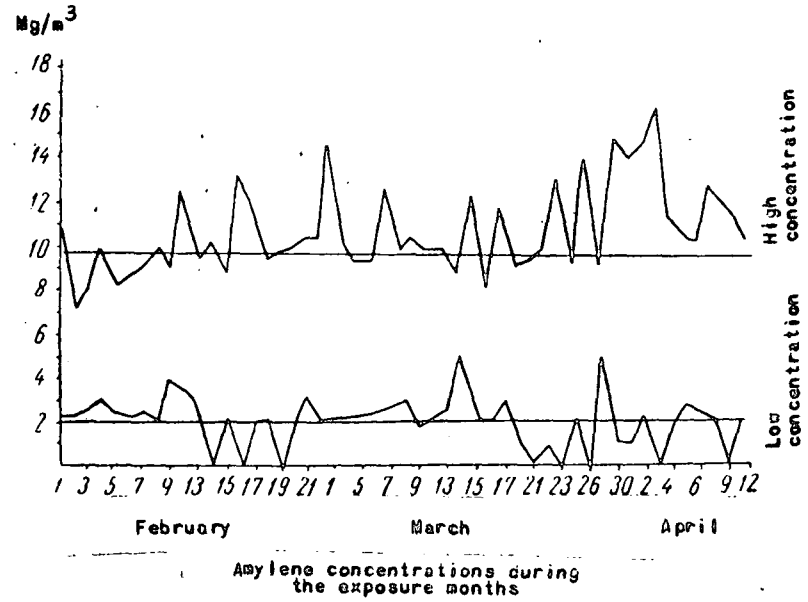
The present authors investigated the affect of low amylene (pentene) concentrations on animals in chronic experiments, and also conducted some observations on the affect of amylene on man. Amylenes were determined in the air by the Morozov method, which is based on the fact that unsaturated hydrocarbons reacted with bromine at the double bond, as shown by the following formula:

$$CH_3—CH=CH_2+Br_2 \rightarrow CH_3—CHBr—CH_2Br.$$

The amount of bromine entering into reaction is used as the basis for the determination of the unsaturated hydrocarbon concentration, and computed as pentenes according to M. V. Alekseeva.

The threshold odor perception of amylenes was determined by the method recommended by the Committee on Sanitary Protection of Atmospheric Air affiliated with the Government Sanitary Inspection of the USSR. Test volunteers were students of the medical institute, 20-36 years of age. Before beginning the experiment, the students were familarized with the specific odor of the preparation under investigation. Students were examined for possible disturbances of the odor perception organs. Tests were con-

ducted for 10 days. Results of the first 3 days investigation showed that 3.58 mg/m^3 represented the average minimal olefin concentration perceptible to all the testers. The following set of odor perception tests indicated that at 1.79 mg/m^3 of the olefin, the odor was still perceptible. However, at 0.75 mg/m^3 the olefin odor was perceived by none of the student testers.



Amylene concentrations during the exposure months

The next step of the investigation was devoted to experiments with rats. Thirty young white rats weighing 94-160 g were divided into 3 groups of 10 animals. The investigation was conducted on the basis of chronic experiments. Rats were exposed to the inhalation of the olefin-containing air 24 hours daily for 75 days. Work was conducted in exposure chambers of 100 li capacity. As indexes of toxic effect the authors used the animal's general conditions of behavior, changes in their body weight, coproporphyrin elimination with the urine, in blood serum and in erythrocyte colinesterase activity, the number of luminescent leucytes, changes in reflex activity, and results of pathoanatomical examination of the internal organs of autopsied animals.

To facilitate the maintenance of constant amylene concentrations in the exposure chambers, the tube through which the amylene entered the chamber was submerged into a constant temperature waterbath of 29-31°. Fluctuations in the concentration of amylene vapor in the exposure chamber during the chronic experiments are graphically plotted in the following Figure. The average amylene concentration in the air of chamber No. 1 was 9.8±, 0.51 mg/m^3. The amylene concentration in the air of the second exposure chamber was 1.9±, 0.22 mg/m^3, with a maximum of 4.86 and a minimum of 0.0 mg/m^3. Experimental animals of Chamber No. 1 began to show deviations from their normal behavior pattern 10-12 days after the beginning of the exposure period, which was supposed to last 15 days. The experimental

animals appeared highly agitated. At the same time, animals in exposure Chamber No. 2 presented a general behavior picture which in no way differed from the behavior pattern of the control animals. The agitation noted in animals in exposure Chamber No. 1 gradually abated, and the rats appeared to have adjusted themselves to their environmental conditions, as shown by the fact that their behavior returned to normal. Body weight records of all animals kept in the course of the inhalation exposure experiments showed no significant deviations; therefore, it was concluded that the inhalation of air containing olefins had no effect on weight gaining in animals of the two experimental groups. Observations conducted during the recovery periods showed that rats of Groups 1 and 2 began or continued to gain weight, at the same time the weight of rats belonging to the control group remained constant. The reliability of the observations was confirmed by statistical analysis. The general impression was that inhalation of low amylene vapor concentrations enhanced the rate of weight gain in experimental animals.

The effect of amylene inhalation on porphyrin metabolism, as a means of determining maximal permissible concentration of the substance in atmospheric air, was studied by procedures of M. I. Gusev, G. I. Solomin and T. M. Shul'ga (1961) and Li-Shen (1962). This type of investigation was conducted with rats exposed to the inhalation of air containing different amylene concentrations under conditions of chronic experiments. Twenty-four hour urine specimens were collected once every week. Corproporphyrin was extracted from the urine by the Fisher method, and qualitative and quantitative determinations were made spectrophotometrically using electrospectrophotometer SF-5. In this way 10 tests were made with the urine of animals exposed to the poison inhalations, and 3 urine specimens were tested during the recovery period. Results are listed in Table 1. Data in that table show that chronic 24 hour exposure of white rats to the inhalation of air containing 9.8 mg/m^3 of amylene vapor resulted in increased porphyrin metabolism, computed on the basis of 100 g of rat body weight. The increase in the porphyrin metabolism amounted to 25%, which statistical analysis established as reliable. Increased coproporphyrin elimination with the urine continued for more than 30 days after exposure inhalation was stopped. No changes in porphyrin metabolism had been noted among rats chronically exposed to the inhalation of air containing 1.9 mg/m^3 of amylene vapor.

Effect of inhaling air containing different amylene concentrations on blood serum and erythrocyte cholinesterase activity in rats was determined by procedures previously described by G. I. Solomin, R. Ubaidulaev, Li-Shen, and others. The analytical procedure was described in detail by A. A. Pokrovskii in 1953, and modified by A. P. Martynova in 1958. Cholinesterase activity control determinations were made once before inhalation exposure, at 6 intervals during the period of inhalation, and twice during the recovery period. Results are listed in Table 2. Reliably significant drops in cholinesterase activity appeared beginning with the 23rd exposure day in rats of Group 1, which persisted through the entire period of exposure to chronic inhalation. Cholinesterase activity returned to normal in rats of

Table 1

Gamma of coproporph elimination with the urine in 24 hrs. per rat and per 100 g of animal body weight

	Exposure period										Recuperation period		
	10/II	19/II	26/II	5/III	12/III	19/III	26/III	2/IV	9/IV	16/IV	25/IV	8/V	22/V
Control													
Coproporphyrin per rat	1,81	1,79	1,99	2,56	2,42	3,09	3,72	3,54	2,86	3,51	2,54	3,60	3,65
Coproporphyrin per 100 g of body weight	1,17	1,04	1,05	1,28	1,18	1,43	1,66	1,55	1,20	1,44	1,02	1,39	1,42
Concentration 1,9±0,22 mg/m³													
Coprophyrin per rat	1,76	2,03	2,31	2,80	1,84	2,50	3,22	3,45	3,13	3,05	2,37	3,70	3,31
Coproporphyrin per 100 g of body weight	1,11	1,20	1,27	1,31	1,20	1,03	1,29	1,36	1,21	1,17	0,82	1,27	1,07
Concentration 9,8±0,51 mg/m³													
Coproporphyrin per rat	1,98	2,55	2,29	2,76	2,34	2,88	3,70	3,41	2,50	3,28	4,68	3,66	3,58
Coproporphyrin per 100 g of rat body weight	1,31	1,62	1,42	1,55	1,28	1,48	1,89	1,74	1,25	1,61	2,08	1,57	1,39

this group only on the 25th day of the recovery period. No statistically reliable or significant results have been obtained indicating either a rise or fall in the activity of this enzyme. Accordingly, an average 1.9 mg/m³ amylene concentration in the air elicited no changes in the blood serum cholinesterase activity of the experimental animals.

A. D. Semenenko was the first to apply the principle of leucocyte luminescence analysis to the standardization of harmful substances in atmospheric air. He conducted his experiments at the Central Institute of Post-Graduate Medicine. The present authors used this method in connection with the investigation herein reported. Blood specimens were taken periodically from the experimental rats, and the percentage of luminescent leucocytes determined as described by A. D. Semenenko. Results are listed in Table 3. Statistical processing of the attained results indicated that 37 days after inhalation initiation the blood of rats belonging to Group 1 showed an increase in the number of luminescent leucocytes, as compared with the control animals. This condition persisted for 30 days, after which the number of luminescent leucocytes gradually returned to normal and remained at that level to the end of the inhalation period and through one month of the recovery period. No changes in the number of luminescent leucocytes had been noted in the blood of rats belonging to the second group.

Effect of chronic amylene inhalation in different concentrations on the established pattern conditioned reflexes was conducted by the method of Yu. V. Novitov, N. F. Ismerov and others. Experiments were conducted with 10 white male rats weighing 10-160 g. Four white rats were placed into ex-

posure chamber No. 1, the air of which contained a low concentration of amylene. Similarly 4 white rats were placed into Chamber No. 2, the air of which contained amylene in high concentration, while 2 control white rats were placed into Chamber No. 3 containing clean air. Conditioned reflexes had been developed by the L. E. Kotlyarevskii rapid method, as described by Ya G. Dvoskin. A sterotype conditioned reflex pattern was developed in the experimental rats, which consisted of responses to two positive signals, bell-light, light and bell. Slight changes in the conditioned reflex activity were noted only in the rats which inhaled air containing 9.8 mg/m^3 of amylene. Disturbance in the higher nervous activity appeared as slightly prolonged latent periods of response to the sound of a bell and to the flash of light. Occasionally, a falling out of reflex in response to light, and the appearance of phase states had been noted. These changes in the conditioned reflex activity began to appear on the 5th week of the poisonous vapor inhalation. The functional activity of the brain cortex returned to normal in the experimental rats 2 weeks after discontinuation of exposure to amylene inhalation.

Table 2.

Whole blood cholinesterase activity in rats (in minutes)

mg/m^3	Before exposure 25/I	Exposure period						Recovery period	
		13/II	23/II*	8/III	3/III	4/IV	17/IV	27/IV	10/V
Control	38,4	38,6	38,3	39,7	39,5	39,0	40,2	40,0	41,0
1,9	38,0	39,0	39,5	40,7	41,0	40,4	41,0	40,6	39,4
t	0,44	0,84	1,68	0,92	1,23	2,15	1,43	0,78	2,08
9,8	39,4	38,5	40,4	46,0	48,0	57,0	60,0	43,4	40,0
t	1,30	0,32	2,73a	4,70b	6,54c	12,15c	8,15c	5,15c	2,0

Note. reliability degrees a-95%, b-99%, c-99.9%

Table 3.

Percent of luminescent leucocytes

mg/m^3	Before exposure	Exposure period						Recovery period	
	24/I	12/II	22/II	7/III	22/III	3/IV	17/IV	27/IV	10/V
Control	4,5	3,4	4,2	2,8	2,6	2,3	2,8	3,4	2,6
1,9	3,4	4,0	3,5	3,2	2,3	1,6	2,2	1,9	1,8
t	0,90	1,36	0,65	0,49	0,26	0,50	0,40	1,07	1,29
9,8	3,6	2,8	5,1	11,6	7,5	5,6	2,2	1,7	1,9
t	0,47	0,57	0,64	5,30c	5,30c	2,68a	0,39	1,43	1,13

Autopsies had been performed on some of the animals, and their internal organs examined macroscopically and microscopically. No macroscopic changes had been noted in any of the animals. Pathohistologic changes

were noted in the organs of rats which chronically inhaled air containing 9.8 mg/m^3 of the amylene vapor; most clearly defined were signs of bronchitis, perybronchitis, localized and confluent catarrhal and interstitial pneumonia, emphysema accompanied by minor bleeding and vascular plethora.

Conclusions

1. It was established that 1.8 mg/m^3 of amylene in the atmospheric air represented the concentration of threshold odor perception of the substance.

2. Continuous 24 hour exposure of white rats to the inhalation of air containing 9.8± of 0.51 mg/m^3 of amylene for 75 days elicited statistically significant enhanced porphyrin metabolism, lowered cholinesterase activity, and increased number of luminescent leucocytes. In addition, the animals' pattern of established reflex responses had become disturbed. Some microscopic histologic changes had been noted in the organs and tissues of autopsied rats, most noteable among which were pathologic lung changes.

3. Exposure of rats to the inhalation of 1.9±, 0.22 mg/m^3 of amylene under similar experimental conditions elicited none of the above enumerated changes, with very slight postmortem exceptions.

On the basis of the above discussed results, it is recommended that the maximal permissible amylene concentration in atmospheric air be set at 1.9 mg/m^3.

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Effect of Combined Radiation and High Air Temperature on Animals

pp. 24 - 29

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A study of hygienic working conditions with radioactive substances in the petroleum industry must not be limited to the effect of ionizing radia-

tions, but must take into consideration other environmental factors, such as temperature increase of the surrounding air. According to N. I. Rykov (1958), P. A. Milonov (1959), and others one single total exposure of animals to X-ray of 250-600r at increased surrounding air temperature enhanced the gravity of acute radiation sickness.

The present author studied the effect of increased surrounding air temperature on the appearance and development of radiation sickness caused by exposure to rapid neutrons radiation. The investigation was conducted with 20 male rabbits, divided into four groups; the first group consisted of 8 rabbits; the second, third, and fourth of 4 rabbits each. During the initial 6 weeks (January - February) the normal physiological patterns of all animals had been established. During the following 20 weeks (February - July) the animals had been irradiated and studied on definite days and at definite hours. The months of July and October constituted the recovery period, during which experimental and control rabbits had been kept in the animal room under usual conditions.

Animals of group 1 had been irradiated by fast neutrons of polonium-beryllium at normal surrounding air temperature; (15-17°). Animals were transferred to special radiation cages where they were kept in a fixed position. Four rabbits had been irradiated at the same time. The posterior-anterior longitudinal body axis of the irradiated rabbits was in accommodation with the radial direction of the fast neutrons emanation. The distance between radio-emanation source and the closest point of each animal exposed surface, that is the hind part, was kept at a constant 8 cm. Each experiment lasted 2 hours. Irradiation lasted about 59 minutes during the initial period of the experiment, when the activity of the source was approximately 1.10^7 neutr/sec.

Subsequently the exposure time was in proportion to the drop in activity of the source. Irradiation was made every other day attaining a maximal weekly tissue dose of 0.4rd. The total dose of radiation for each rabbit was 8.6 rd. The radiation dose was controlled by means of a portable radiometer which measured the emanation of fast neutrons (KPN-2, RPN-1), and by calculation. The instruments had been calibrated in a special laboratory using a polonium-beryllium source of known activity; the measurement error averaged 20% of the nominal scale value.

Rabbits of the second group had been irradiated similarly at surrounding air temperature raised to 37-39°. This was done in an exposure chamber specially constructed for such studies. The rabbits were kept at the increased temperature for 2-30 min. before being irradiated. Rabbits were kept at the increased air temperature for a total of 2 hours, after which they were returned to the laboratory animal room.

Rabbits of the third group had been placed into a chamber, the air of

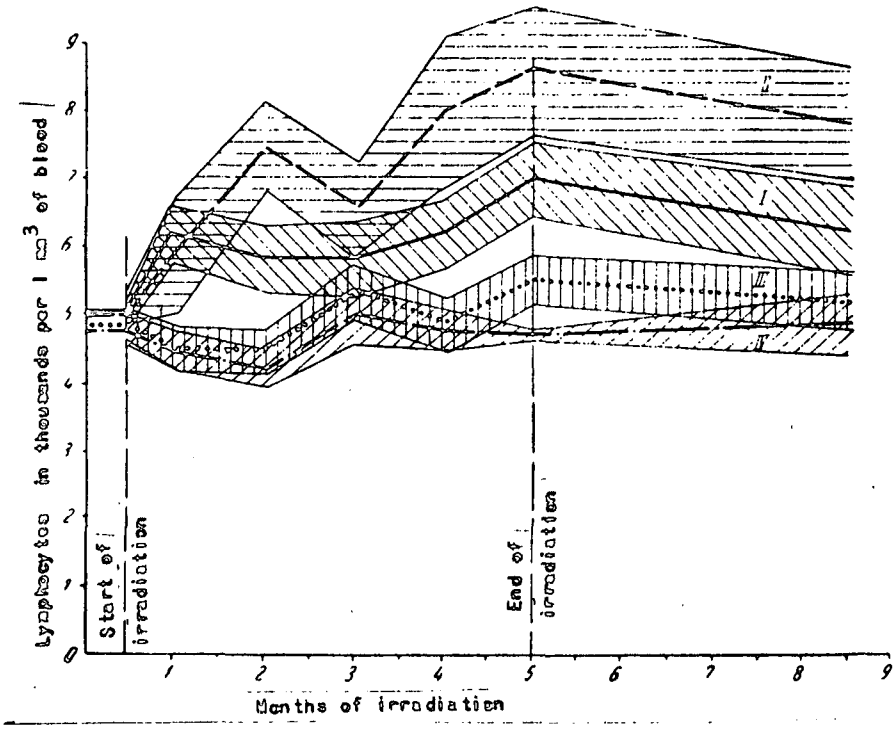
which was raised to 37-39° without being irradiated. Rabbits of the fourth group served as controls. Records were kept of all animals general condition, behavior, appearance, appetite, and changes in body weight. Determinations were made of the following: 1) number of erythrocytes 2) hemoglobin content 3) number of reticulocytes and thrombocytes 4) ratio of morphologic blood and plasma elements and their volumes, 5) osmotic resistance stability of erythrocytes 6) sedimentation rate 7) catalase activity 8) total leucocyte number 9) leucocytic formula 10) phagocytic leukocyte activity 11) blood coagulation time 12) prothrombin time and 130 heparin tolerance. Erythrocyte and leucocyte counts and the leucocyte formula were determined weekly. All the other indicators were checked fortnightly. Resulting data were analyzed statistically.

No external signs of radiation sickness appeared during the entire time (4-1/2 months) of irradiation and during the 3 months of recovery. All rabbits appeared healthy and lively; they fed normally and gained weight. Some blood indexes declined as compared with the initial values and with those of the controls. This decline was lowest in the erythrocytes. All irradiated rabbits showed a wider fluctuation range in the number of erythrocytes and reticulocytes in the 13-15th week of the test as compared with these indicators in the controls. Changes were more pronounced in rabbits irradiated at higher surrounding air temperature. At the end of the irradiation the color index decreased by 15-20%, as compared with the initial data, while it changed only slightly in rabbits of the first group. The average erythrocyte volume, the red blood cell resistance and their sedimentation rate changed only slightly in irradiated and control animals. The number of thrombocytes decreased slightly in some rabbits by the middle of the irradiation period; the decrease was most pronounced in some animals of the second group (up to 70,000 in 1 mm^3 of blood) at the end of the irradiation. The number of such cells rapidly increased later and reached the initial level 45 days after irradiation discontinuation. All animals manifested during the experiment significant catalase number fluctuations, which were more pronounced in rabbits irradiated at increased temperature. The catalase index was considerably reduced toward the end of irradiation in rabbits of the second group. The number of leucocytes, the leucocyte formula, the phagocytic activity of leucocytes, and some blood coagulation indexes showed greatest changes.

Number of leucocytes began to increase during the first weeks in all irradiated animals of groups 1 and 2. Leucocytosis was more pronounced in rabbits under the action of neutrons at the higher temperature, amounting to 13,000- 17,000 leucocytes in 1 mm^3 of blood (the average control number for this group was 7400 leucocytes). The number of leucocytes increased mainly at the expense of the increase of the relative and absolute quantity of lymphocytes (Fig. 1). These indexes did not change substantially in control animals throughout the entire experimental period. Animals of groups 1 and 2 showed an increased number of leucocytes at the end of the ninth week of irradiation, a shift to the left in the nuclear leucocytes, which were more pronounced in rabbits irradiated at increased temperature (Fig. 2). This shift to the left

was caused mainly by the increase in the number of neutrophiles with rod-shaped nuclei and decrease in the number of young forms.

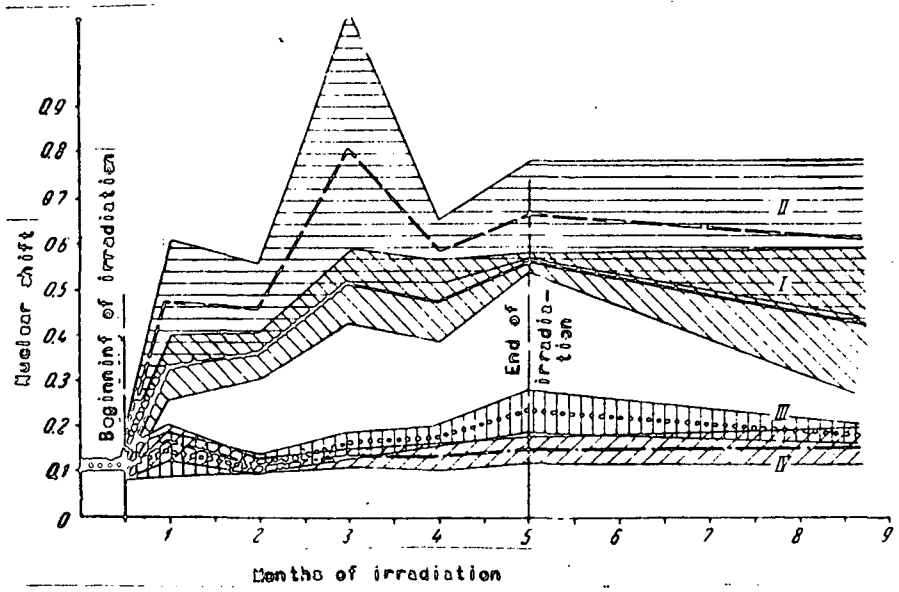
Fig. 1.



Course of changes in the absoluto number of lymphocytes in the peripheral blood of the animals (fluctuation limits of average statistical values $P < 0,05$).

I–Ave. number of lymphocytes in animals irradiated at normal temperatures; II–ditto in animals irradiated at the higher temperature of the surrounding air; III – ditto in animals kept at same temperature of the surrounding air but not irradiated; IV – controls.

Fig. 2.

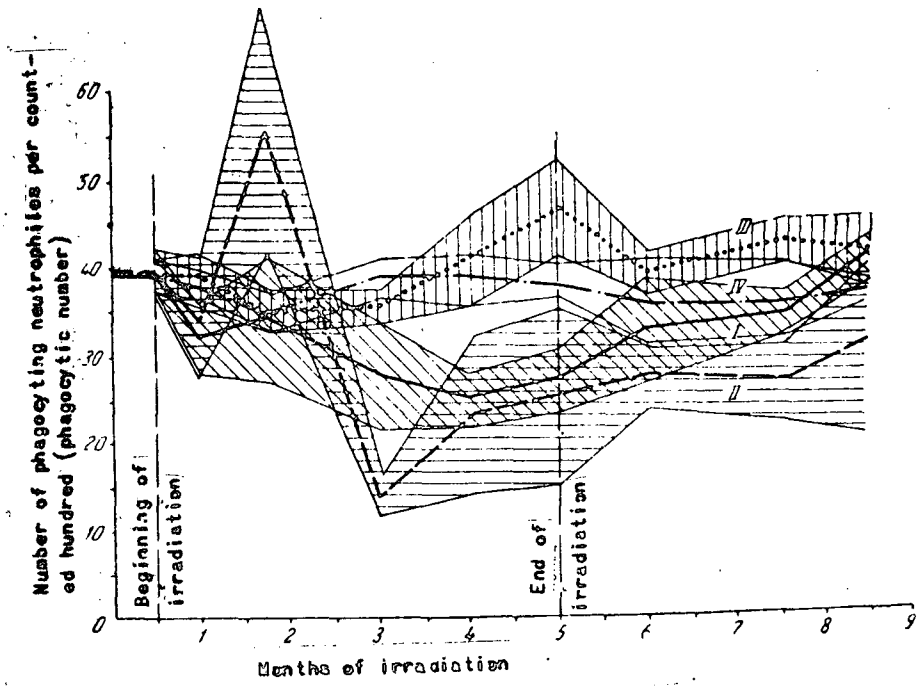


Course of changes in leucocyte phagocytic activity in animals of all groups (fluctuation limits in average statistical values $P < 0.05$).

I–Nuclear shift in animals irradiated at normal temperature; II – ditto in animals irradiated at higher temperature of surrounding air; III – ditto in animals at higher temperature of surrounding air, but not irradiated; IV–ditto in animals of the control group

Values of nuclear shifts to the left amounted to unity or more in some rabbits as compared with 0.1 - 0.15 of the controls and 0.3 - 0.35 of nonirradiated rabbits kept at increased room temperature. Phagocytic leukocyte activity was studied by the Platonov method. Results showed that the irradiation of rabbits by fast neutrons at normal temperature gradually decreased the number of phagocytic neutrophiles beginning with the fifth week of irradiation (Fig. 3). This index decreased up to the 9-13th irradiation week by 50% of the control level. The combined effect of fast neutrons and increased surrounding air temperature resulted at first in a decrease in the phagocyte number, followed by a sharp increase in the 5th irradiation week which was again followed by a gradual decrease up to the 13-15th irradiation week. The phagocyte number partly returned to normal in animals of group 1 at the end of irradiation, and during the restoration period rose to the initial values. Number of phagocytic neutrophiles in rabbits of group 2 returned to their initial normal level at a considerably slower rate.

Fig. 3.



Course of changes in leucocyto phagocytic activity in animals of all groups (fluctuation limits in average statistical values $P < 0,05$).

I - Average value of phagocytic number in animals irradiated at normal temperature; II - Ditto in animals irradiated at higher temperature of surrounding air; III - Ditto in animals at higher temperature of surrounding air, but not irradiated; IV - Ditto in animals of the control group.

Recalcification time, determined by the Bergerhof and Rock method fluctuated in all irradiated and control rabbits within normal limits noted during the preirradiation period. Prothrombin time, determined by the Quick method failed to disclose any changes from the initial normal values. Heparin tolerance, as determined by the Poller method, was of a relatively constant value in the control rabbits, but differed notably from the ini-

tial and control values in the irradiated rabbit. Most substantial changes had been observed in rabbits irradiated by rapid neutrons at increased surrounding air temperature, that is, in rabbits of the second group, in which heparin tolerance time increased by 50% and more as compared with their initial normal time, and with time of the control rabbits. Irradiation of rabbits at normal temperature extended heparin tolerance time by 25-30% as compared with the initial background values. The fact that the discussed index changes manifested in rabbits of the first and particularly of the second group tended to return to their initial normal values during the recovery period is of particular significance and interest.

Conclusions

1. Changes of several indexes in the red and white blood cells and in the blood coagulation time had been observed in rabbits irradiated by fast neutrons with the maximal tissue dose of 0.4 rd weekly to a total of 8.6 rd irradiation.

2. These changes appeared more defined in rabbits chronically irradiated by fast neutrons at increased surrounding air temperature (37-39°). The effect of increased surrounding air temperature intensified the harmful effects of fast neutrons.

3. In planning means for the protection of employees working at processes connected with sources of fast neutron emanation, serious consideration should be given to the possibility of a rise in the temperature of the working premises.

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The Toxicity of Low Styrol Vapor Concentrations

pp. 29 - 35

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Styrol is used extensively in the production of high molecular compounds such as synthetic rubber and different types of plastic materials. It is a benzene homologue with one unsaturated bond (C_6H_5 $CH=CH_2$); it is a

colorless liquid having a characteristic odor, a specific weight of 104.14, a b.p. of 146°; it is soluble in water up to 0.03% by weight. Styrol is an unsaturated hydrocarbon which easily polymerizes and copolymerizes. According to reports found in the literature styrol, a benzene homologue, belonged to the group of narcotic hydrocarbons which irritate the respiratory passages. According to H. S. Faustova the concentration of a single styrol dose for rabbits was 0.62 mg/li, and according to M. L. Rylova 0.25-2 mg/li. According to the latter author 0.02 mg/li was also the concentration of threshold mucous membrance irritating effect, while Li Shen (1961) established it at 0.00002 mg/li.

The concentration of chronic styrol vapor effect was investigated by L.F. Larionov and E. I. Nusel'man (1936). They exposed white mice and rabbits to the inhalation of air containing 3-15 mg/li of styrol for 10-45 days. Records were kept of inhalation effect on the cardiovascular system, on the peripheral blood, on the liver and kidney functions, and on the hemopoietic system.

Results of M. L. Rylova's tests with 3 mg/li of styrol showed a loss of resistance in rats to unfavorable environmental effects and a drop in physical work capacity in white mice. Microscopic examination of the internal organs showed the presence of abscesses and pneumonia in the lungs, and of hyperplasia in the spleen. T. A. Blinova exposed rabbits to air containing 1 mg/li of styrol vapor and detected changes in the peripheral blood. The chronic action of 2 mg/li styrol vapors (A.S. Faustova, 1961) elicited functional liver disturbance. Spencer, Irish, Adams, (1942) of the USA studied the lasting effects of different styrol vapor concentrations on several animal species. Most sensitive were Guinea pigs; inhalation of air containing styrol vapor severely irritated the eyes, nose and mucous membranes; the animals became sluggish, their fur became ruffled, and 10% of the animals died. At 9.3 mg/li styrol concentration the above condition became more aggravated. Patho-morphologic liver and kidney changes were found in guinea pigs which inhaled air containing 11.6 mg/li of styrol vapor. The above presented literature survey clearly shows that all previous studies of styrol effect on the organism had been conducted with high concentrations.

Reports found in the literature on the health of workers coming in contact with styrol vapor showed that inhalation of air containing 42.5 mg/li of styrol vapor was harmful and even fatal. (Lefaux, 1955). The concentration of 3.4 mg/li produced irritation of the mucous membranes of eyes and upper respiratory passages, apathy and somnolence (Carpenter, 1944). Workers temporarily exposed to the inhalation of 1.85 - 2.97 mg/li styrol concentrations developed signs of "styrol sickness", such as nausea, general weakness and loss of appetite (Rodgers, 1955). Barsotti and others found in 1952 that 0.8 mg/li of styrol applied externally produced skin irritation.

In 1961 V.A. Pokrovskii examined 100 persons exposed to the inhala-

tion of air containing 0.6 mg/li of styrol vapor. Clinical examinations disclosed functional central nervous system disturbance, atrophic and hypertrophic changes in the mucous membranes of the upper respiratory tracts, changes in the genital system and in the blood. Employees with long work records in styrol plants developed toxic hepatitis, the gravity of which became intensified. Development of pathological liver changes was also observed at 0.1 mg/li concentration (N.I. Shumskaya, 1956).

Liver function disturbance and toxic hepatitis, as a liver syndrome, were found during the clinical observation in workers exposed to the permissible maximal concentration or close to it. (E. I. Drogichina, 1959). Arterial pressure dropped to 100 mm, and below, in 33% of the examined workers, and the gastric secretory function was disturbed in some, accompanied by complaints of dyspeptic disorders. Blood changes appeared in the form of moderate leukopenia, lymphocytosis, and a type of thrombocytopenia and reticulocytosis. Results of the clinical examinations indicated that most characteristic manifestations of styrol vapor effect resulted from its hepatotropic action, changes in the central nervous system, and in the blood and the cardio-vascular system. Irritation of mucous membranes of the eyes and of the upper respiratory tract were caused by higher styrol in air concentrations.

Results of the above described investigations, particularly the clinical examinations of workers exposed to the inhalation of low styrol vapor concentrations prompted the present author to study the effect of low styrol-in- air concentrations, notably those below the permissible maximum concentration limit. The studies were centered on the block and emulsion polystyrol production, where styrol vapor was the predominant harmful factor in the surrounding atmosphere. The studies had been conducted for several years. Results indicated that the stvrol vapor content in the air fluctuated in the range of thousandths of milligrams in 1 m^3, which is below the permitted maximum of 0.05 mg/li. Observations showed that styrol concentrations during the winter and summer months of 1962 (about 1000 analyses) ranged in the block polystyrol production department from 0.002 to 0.0093 mg/li and in the polystyrol emulsion production department from 0.0004 to 0.0068 mg/li. Styrol vapor concentrations were equal to or exceeded the 0.05 mg/li permitted maximal concentration in some air samples collected in the polymerization sections during apparatus cleaning as a prophylactic inspection measure.

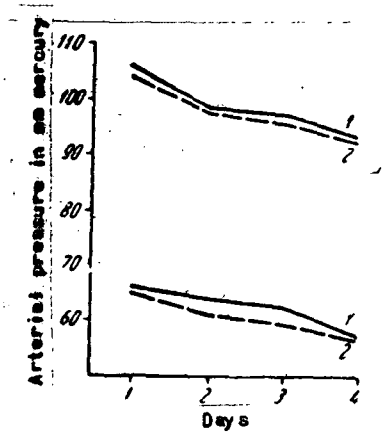
Thus, the above sanitary hygienic survey of the plant established that styrol vapor concentrations in the air of the working premises were below the 0.05 mg/li adopted maximum. In this connection a statistical study was made of morbidity types which occurred among the workers of the entire plant and loss of work time. Some of the data are listed in the Table below, which show highest morbidity in hepatic and gall bladder diseases. Half of the workers in the block and emulsion polystyrene production department

Indexes of Liver and Gall Bladder Ducts Morbidity (Form 3-1)

	Morbidity per 100		
	1959	1960	1961
In the plant generally	1,7	2,7	2,1
In polystyrol block production	6,7	9,7	7,5
In emulsion polystyrol production	2,9	6,4	5,5

complained of frequent headaches, subcostal pains on the right side (38%), irritation of the mucous membranes of the upper respiratory tract (dryness, rasping feeling, aches - 44%), pains in the heart region (21%), and in the epigastric region (19.5%). Arterial blood pressure determined in non-selected workers (20 from the block and 20 from the emulsion polystyrol departments) was as follows: the pressure level fell in workers connected with the polystyrene emulsion production from 105/65.7 to 93/57.5 mm, (Fig. 1). It returned to normal during off days. No such arterial blood changes were noted in workers of the control group, according to E. A. Kapkaev. Relative peripheral blood albumin fell below the normal level in some workers of long contact with styrol vapor. Thus, characteristic changes appeared in employees of long contact with low styrol vapor concentrations, indicating that the concentrations of styrol vapors occurring in the investigated industry unfavorably affected the workers' health.

Fig. 1.



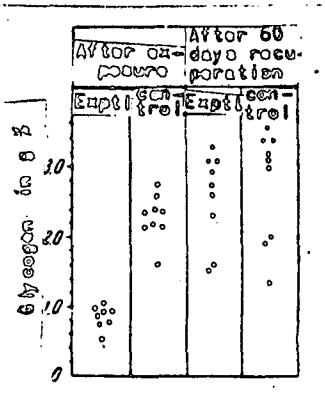
Blood pressure in workers producing polystyrol
1 - Block polystyrol production;
2 - Emulsion polystyro production

The above conclusion had to be confirmed experimentally. Accordingly, toxicological tests had been conducted with two groups of white rats. Rats of the first group were exposed to the inhalation of styrol vapor concentrations averaging 0.049 mg/li. within the range of 0.046 to 0.070 mg/li. Rats of group 2 were exposed to the inhalation of styrol vapor ranging between 0.004-0.0072 mg/li, with an average of 0.0055 mg/li. The two experimental and control groups consisted of 15 rats each. The rats were exposed to the styrol vapor in 100 liter chambers 5 hours daily for 6 months. Effect of styrol vapor inhalation on the rats was determined by examining changes brought about in the following indexes: glycogenic function, changes in blood serum albumin fractions, pathoanatomic changes, states of cardiovascular and nerve systems, changes in body weight, weight ratio of body organs, rate of coproporphyrine elimination with the urine, and histology of post-mortem internal organs. No significant changes were noted in the animals' behavior during the exposure to styrol inhalation. Hyperemia of the nasal and eye mucous membranes developed in rats of group 1 during the early days of exposure to styrol vapor inhalation; rats of group 2 became sluggish towards the end of the experimental styrol vapor inhalation; epidermal and subcutaneous abscesses de-

veloped in 5 rats of the first group, toward the end of the exposure. The wounds healed slowly, pointing to lowered resistance. Dynamics of the weight increase in rats of the first and second group remained unaffected and unchanged.

The effect of 0.05 mg/li styrol vapor inhalation on the glycogenic liver function of rats was studied next. Quantitative liver glycogen determinations were made in the experimental rats at the end of the styrol vapor inhalation, and 30-60 days of the recovery period. Results showed that the initial 2.32% of glycogen was reduced to 0.82% after the period of styrol vapor inhalation. Return of glycogen to its original normal levels occurred at the end of two months, amounting to 2.52% in the test rats and to 2.62% in the control animals (Fig. 2).

Fig. 2.



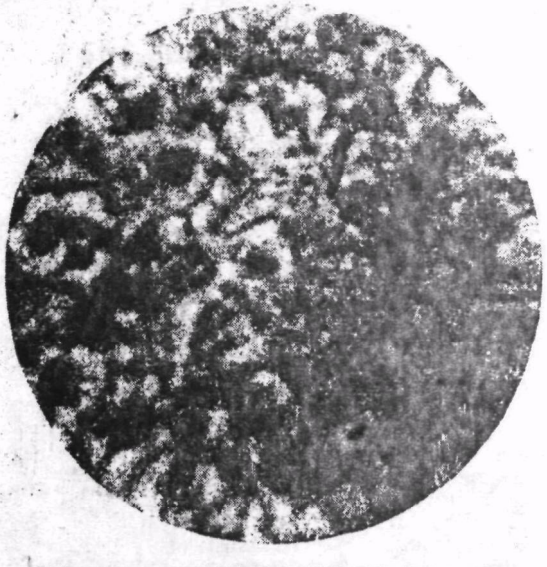
Liver glycogen in rats of group 1

Blood serum albumin fractions were determined monthly by the method of paper electrophoresis. Results showed a relative albumin decrease and a corresponding globulin increase in rats of groups 1 and 2 on the third month of exposure. Peripheral blood albumin fell at the end of the inhalation exposure period from 41.8 to 31.7% in rats of group 1, and from 39.5 to 33.2% in rats of group 2, while it rose to higher levels in the control rats. Results of serum globulin fraction analysis presented no clearcut change regularity except for a relatively persistent increase in the γ-globulin in rats of groups 1 and 2. One month after the end of exposure to styrol vapor inhalation the relative blood albumin fraction returned to its original level in rats of group 1. Macroscopically, the liver in rats of group 1 appeared flabby and of yellowish-brown color. The microscopical examination disclosed turbid edema, granularity, and vacuolization. Similar, although less pronounced changes appeared in rats of group 2. Autopsy examinations performed at the end of the experimental styrol vapor inhalation showed increased weight and enlargement of the liver. Thus, the study indicated that the chronic effect of low styrol vapor concentrations produced toxic changes of pathologic character in the experimental rats as described in the preceding paragraphs.

Effect of styrol vapor inhalation on the activity of the central nervous system was determined by the chronaximetric method establishing the rheobase and the chronaxy ratio of the right hind leg muscle antagonists before and after styrol vapor inhalation. Rheobase changes presented no consistently regular pattern. Changes in the chronaxy ratios of the muscle antagonists appeared to be of a compensatory character and occurred at the same time without substantial difference. Before exposure and during the first three exposure months chronaxy fluctuated between 0.08 and 0.09

m/sec. in rats of all groups. Chronaxy ratio changes were most pronounced in rats of group 1. Beginning with the third exposure month occasional rats of this group manifested delayed chronaxy, while in all other rats such manifestations appeared during the 5th-6th month, reaching average values of 0.21 - 0.22 m/sec. Delayed chronaxy was manifested occasionally among rats of group 2 on the 5th and 6th month of exposure, attaining a maximum value of 0.15 m/sec.

Fig. 3.



Degenerative liver changes in the rats

Effect of styrol vapor inhalation on the vascular system was determined from records made of arterial blood pressure, before, during and after rats' exposure. Arterial pressure began to drop one month after the start of the exposure in animals of the first group and decreased from an average of 99 to 69 mm. Blood pressure continued to drop sharply during the months following. The blood pressure began to fall later in rats of group 2, and the drops were less pronounced. Return to normal blood pressure proceeded slowly in rats of group 1 and 2, reaching their initial normal values at the end of the second month of the recovery period.

Rate of coproporphyrin elimination with the urine was determined in 5 rats of each group. Daily urinary voidings of each of 5 rats were collected and the coproporphyrin extracted by the Fisher method and determined spectrophotometrically. Accumulated data were irregular and of inconclusive character. Histologic examinations of internal organs of both test group rats disclosed pathologic liver and spleen changes such as hyperplasia and lymphoid folliculitis. Thus, results of clinical examinations of plant workers and results of experimental animal tests verified the previously expressed assumption that the officially adopted maximal permissible styrol vapor concentration was too high and should be revised downward.

Conclusions

1. Statistical comparative evaluation of morbidity and work time loss records of workers employed in plants producing polystyrol disclosed high rates of liver and gall bladder morbidity, fall in arterial blood pressure and a variety of complaints characteristic of systemic intoxication with styrol vapor. Since the prevailing styrol vapor concentration in the air of the plant was below the permitted 0.5 mg/li concentration, it was assumed that the official limit was set too high.

2. Chronic experiments with animals exposed to the inhalation of 0.05 mg/li of styrol vapor impaired the glycogenic liver function, the liver parenchyma and brought about many other pathologic functional and morphologic changes in the experimental animals. Some of the pathologic changes were reversible, others were permanent.

3. Results of tests performed with rats indicated that 0.005 mg/li of styrol vapor concentration constituted its threshold of harmful effect for rats.

It is recommended that 0.005 mg/li of styrol vapor be adopted as the maximal permissible concentration in the air of working premises.

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A Photoelectrometric Method for the Determination of Low 3,4-Benzpyrene Concentrations

pp. 47-49

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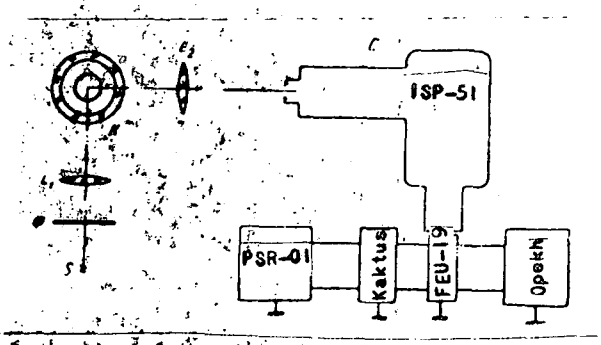
(From the Ukrainian Research Institute of Community Hygiene).

The report published by P. P. Dikun in 1961 contains a quantitative spectrophotometric method for the determination of low 3,4-benzpyrene concentrations. The sensitivity of the method makes possible the determination of 10^{-8} μ of 3,4-benzpyrene in 1 ml of solution. The quantitative analytical procedure previously recommended by the same author which was based on fluorescent 3,4-benzpyrene spectra at low temperatures and on the use of a photometer as described by F. Weigart in 1934; V. K. Prokof'ev, 1951; by that procedure 1,12-benzperylene was used as the inside standard. The spectra were recorded photographically. The present authors increase the method sensitivity and rapidity by recording spectral intensities photo-

electrically. The plan of the photoelectric spectrometer is schematically presented in Fig. 1.

Fig. 1.



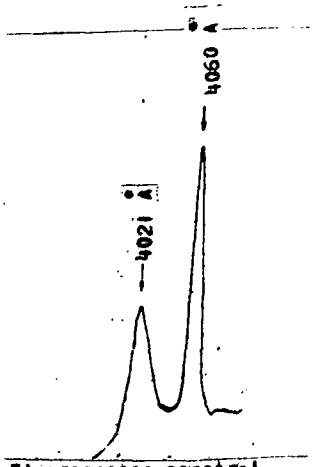
Basic plan of the photoelectric spectrophotometer

Source of U-V radiation which elicited fluorescence in the tested specimens; using PRK-4; F - Light filter of UFS-3; L_1 - quartz illuminating lense; K - Dewara flask with liquid Nat temp. 77° into which is placed the tube containing the 3,4-benzpyrene and 1,12- benzperylene solns; L_2 - projecting glass lense; S - spectrograph ISP-51 with a 270 mm camera

The outlet aperture was placed in the focal plan of the camera objective. The photoelectronic multiplier FEU-19 (N.O. Checkik and co-workers, 1954), served as the receiver of light. The photoelectric multiplier was fed by the electronic stabilizer of the type "Orekh". The photomultiplier signal was conveyed to the entrance of the amplifier of the direct current. A micro-roentgenometer of the type "Kaktus", having the sensitivity of 3.10^{-12} amps (division at which the ionization chamber receded) served as an intensifier, while the signal was conveyed on the screen of the double electrometric lamp 2E2P. The continuous recording of the signal was carried out by the self-recording electronic potentiometer. The shifting of the spectrum was accomplished with the help of the mechanical revolving of the little prismatic tube of the spectrograph, syncronously with the unrolling of the potentiometer roller.

Fig. 2 shows the recording of the fluorescence spectrum of the solution of 0,1 microgram per ml 3,4-benzpyrene and 1 microgram per ml 1,12-benzperylene in n-hexane in the spectral intervals of 4000-4100 A. The solution was frozen in liquid nitrogen.

Fig. 2.



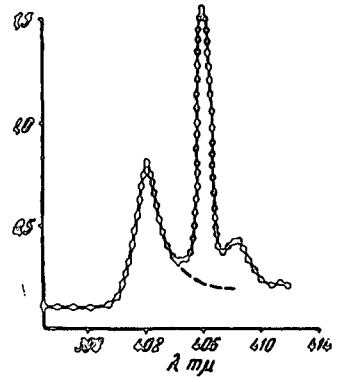
Fluorescence-spectral tracing of a soln. containing 0.1 γ/ml of 3,4-benzpyrene and 1.0 γ/ml of benzperylene in n-hexane at 20°

The maximum λ_2 = 4060 Å the line of the 1,12 benzperylene. The recorded response corresponds to the spectral slit width of 1,9 Å. The spectrum in question is slightly altered by the spreading of the spectral sensitivity of the photomultiplier. The spectrum of the same solution, together with the recording of the spectral sensitivity of the photomultiplier is shown in Fig. 3. The computations show that the recording of the spectral activity deforms the curve represented in Fig. 2 within 4-5%, because the registered spectral section is rather narrow. Hence, in the farther measurements, the selectivity of the spectral sensitivity of the photomultiplier can be henceforth neglected.

The determination of the 3,4-benzpyrene is carried out from the comparison of intensities in the maxium of the line λ_1 = 4021 Å of the 3,4-benzpyrene and λ_2 = 4060

Å of the 1,12-benzperylene (see Fig. 2). The reading of the intensity in the maximum of the line of the 3,4-benzpyrene $J_{3,4}$ is made from the short wave ground of the intensity, which depends on the spectral width of the slit. To determine accurately the intensity of the line of the 1,12 benzperylene, it is necessary to consider the contribution given by the fluorescency of the 3,4-benzpyrene under the maximum λ_2 = 4060 Å of the 1,12-benzperylene (see Fig. 3). The carried out measurements of the fluorescence spectrum of the pure 3,4-benzpyrene, frozen at 77° K, in concentrations from 3 to 0.01 γ/ml showed that this contribution amounts to 11% of the intensity maximum λ_1 = 4021 Å at the spectral width of the slit of 1.9 Å. Its magnitude changes slightly with the change of the spectral width.

Fig. 3.



Fluorescence spectrum of solution containing 0.1 γ/ml of 3,4-benzpyrene and 0.1 γ/ml of benzperylene, taking spectral photomultiplier sensitivity into consideration. Circles indicate distribution of the fluorescence spectral intensity of 3,4-benzpyrene at maximal line λ2 = 4060 Å of 1,12 benzperylene

For determination of unknown concentrations of the 3,4-benzpyrene, it is necessary to know in advance the intensities $J_{3,4}$ and $J_{1,12}$ of the fluorescence line λ_1 = 4021 Å of the 3,4-benzpyrene, and λ_2 = 4060 Å of the 1,12-benzperlene, reduced to the unit of concentrations. For this purpose measurements were carried out at wide intervals of concentrations of 3,4-benzpyrene and 1,12-benzperylene (between 10 and 0.005 γ/ml.) The results are contained in the table. See next page for table.

The data in the table show that at the indicated interval of concentrations we do not encounter any concentration extinguishing of the fluorescence. Therefore, the intensity of the fluorescence of the 3,4-benzpyrene and 1,12-benzperylene is proportional with the respective concentrations.

The relation of the intensities $J_{3,4}/J_{1,12}$ of the photometrically measured fluorescence lines of the 3,4-benzpyrene and 1,12-benzperylene was found to be 4.55 for equal concentrations. The obtained result agrees with the data of the photographical method of P. P. Dikun (1961).

To determine the unknown concentration of C_x of the 3,4 benzpyrene at known content $C_{1,12}$ benzperylene in a solution, it is necessary to measure the intensities $J_{3,4}$ and $J_{1,12}$ of the respective lines λ_1 = 4021 Å and λ_2 = 4060 Å. Then the sought for concentration of the 3,4 benzpyrene can be computed from the relation

$$C_x = \frac{C_{1,12}}{4,55} \cdot \frac{J_{3,4}}{J_{1,12}} = 0,22\, C_{1,12} \frac{J_{3,4}}{J_{1,12}}$$

The sensitivity of the photoelectric method was equal to 5.10^{-10}

γ/ml. The accuracy of the analysis is not less than 12%.

Determination results of unknown 3,4-benzpyrene concentrations

Concns. of 3,4 benz-pyrene $C_{3,4}$	Concns. of 1,12-benzpery-lene $C_{1,12}$	Max. fluorescence intensity ratios of photometric lines (See note below)	Concns. of 3,4 benz-pyrene $C_{3,4}$	Concns. of 1,12-benzpery-lene $C_{1,12}$	Max. fluorescence intensity ratios of photometric lines (See note below
In γ/ml (10^{-6} g/ml)			In γ/ml (10^{-6} g/ml)		
2	1	4,4:1	0,1	1,0	5,1:1
2	2	4,5:1	0,01	0,01	4,0:1
2	4	4,0:1	0,01	0,02	5,0:1
2	10	4,2:1	0,01	0,05	5,1:1
0,5	0,5	4,0:1	0,01	0,1	4,9:1
0,5	1	4,0:1	0,005	0,01	4,1:1
0,5	2,5	4,1:1	0,001	0,005	5,9:1
0,5	10	4,3:1	Avg. intensity ratios of max. fluorescent lines. (See note below)		
0,1	0,1	5,2:1			
0,1	0,2	5,0:1			
0,1	0,5	5,0:1			4,55:1

Note: on the basis of 3,4-benzpyrene and 1,12 benzperylene unit concentrations. (This note was introduced by us to cut the corresponding insertions shorter BSL)

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Colorimetric Method for Total Alkyl Amines Determination

pp. 50-53

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Specific methods have been developed for the quantitative determination of primary and secondary aliphatic amines in air containing small amounts of ammonia, but not for the quantitative determination of tertiary amines. For this reason it is not possible to determine directly the total content of amines, which is essential in making chemical investigations of polluted air in some industrial establishments. Therefore, total content of mono-, di-, trialkyl amines and of ammonia in the air is determined parallel with the determination of ammonia alone, and total of the three amines

computed by subtracting results of the second determination from the results of the first determination.

For this purpose O. D. Khalizova and L. S. Chemodanova (1953) developed a method by which the bases are absorbed by a sulfuric acid solution, then broken down by the Kjeldahl method, and the formed ammonia determined colorimetrically by the Nessler method. E. A. Peregud and B. S. Boikina in 1954 and L. A. Mokhov and B. A. Malyshkin in 1959 proposed titrimetric methods, based on the binding of amines by a standard solution of sulfuric acid, and the excess of the latter determined by idometric or alkaline solution titration, using a suitable indicator.

Picric acid has been proposed for the colorimetric determination of amines in biological products by Richter in 1941, Dyer in 1945 and in sewage by Yu. Yu. Lure in 1961. Other nitro-compounds have been used for this purpose by Inekova in 1954, Mathewson in 1955, and others. The present author studied different indicators, including tri-, di-, and mononitrophenols. Best results were obtained with o-nitrophenol, which has been recommended for the determination of total aliphatic amines in air. The method is simple and highly sensitive. Aqueous solution of o-nitrophenol in 0.1% has a narrow absorption band and a maximum at 420 mμ. In the presence of amines the maximum shifts in the direction of the longer waves. The spectral characteristics are represented in Fig. 1. In making colorimetric determinations it was found advantageous to select a light filter having a narrow transmission band at 440-450 mμ to avoid large loss of light as the result of light absorption by the nitrophenol solution. Use distilled water in making the absorptive solution, since mono-, di, and trimethyl and ethyl amines contained in the air are easily absorbed by water. Tests made with three amines and ammonia established that o-nitrophenol formed colors of same optical density with solutions of the investigated bases in equal molecular concentrations. Therefore, in analyzing a mixture of lower amines, their total molar quantity can be determined, regardless of their composition (See Fig. 2, curve 1). For Figs. 1 and 2 see next page.

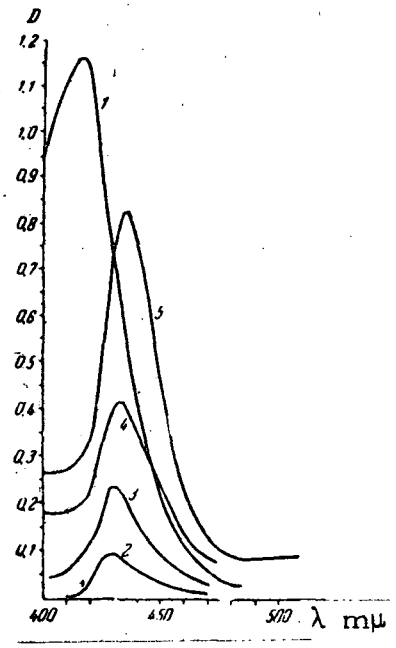
Since O-nitrophenol is the indicator, the presence of acid gases and vapors and also of ammonia, interferes with the analysis. Acidic impurities can be eliminated by aspirating the test air through ascarite or a 5-30% alkaline solution. It was experimentally established that aliphatic amines passed through these absorbents quantitatively. Absorbents, such as soda lime, KhPI, or barium hydroxide cannot be used in this case, since they adsorbed microquantities of amines.

Ammonia is determined in parallel samples by the Nessler method and the results obtained subtracted from the results of the total determination. Aromatic amines do not interfere with the determination.

The optical sensitivity of o-nitrophenol reaction with the bases is only

negligibly affected by changes in its concentration within the limits of 0.1 and 0.25%, and only slightly by temperature, differing in this respect from many other indicators which change color upon reaction with amines, including p-nitrophenol. The o-nitrophenol solution is stable. It reacts with bases instantaneously and the formed color does not change with time.

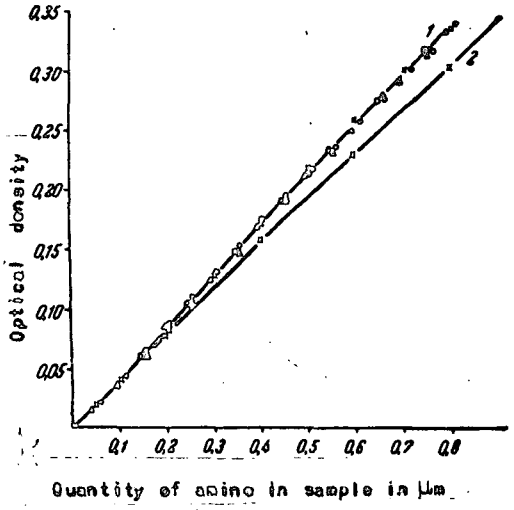
Fig. 1.



Spectral characteristics

1-0.1% solution of o-nitrophenol in 1:2; 1:3, 1:4, 1:5 ratios in relation to water - solutions of o-nitrophenol derivatives in relation to o-nitrophenol at layer thickness of 50 mm were as follows: 2 - 10 μM/li; 3 - 20 μ M/li; 4 - 50 μ M/li; 5 - 100 μM/li

Fig. 2.



Calibrated curves

1 - Colorimetric determination of ammonia and amines in the o-nitrophenol solution using FEC-N-57 at 50 mm layer thickness and with light filter 3; 2 - colorimetric ammonia determination with the Nessler-Folin reagent using colorimeter FEC-N-57, at 50 mm layer thickness and using light filter 3; circular black discs - monomethylamine, square black disks - dimethylamine, triangular black discs - trimethylamine; circle - monoethylamine, square - diethylamine; triangle-triethylamine; X - ammonia

Accordingly the recommended reagent can be used for ordinary single determinations and for continuous or periodic determinations in automatic liquid photocolorimetric gas analyzers, developed in the USSR by M. T. Borok in 1961, B. G. Vtorov and V.N. Kalmanovskiy in 1961. The recommended reagent can be used also in analyzing individual fractions of alkyl amines by paper chromatography.

The following reagents are used in determining amines in the air:
1) Ammonia-free distilled water; remove ammonia and acid by boiling the distilled water for 1-1/2 to 2 hours; keep in a bottle with a stopper through which insert an absorber tube containing activated charcoal and ascarite; store so as to prevent contact with air containing ammonia or acid vapor;

2) 0.1% solution of O-nitrophenol prepared at 40-50° with intermittent stirring; 3) Nessler-Folin solution, prepared from potassium iodide, iodine, mercury, and alkali, as described by D.T. You in 1935; 4) standard 0.1 millimolar (0.1μ mole/ml) solutions of aliphatic amine and ammonia, prepared by hundredfold dilution of 0.01 M stock solutions, using ammonia-free water; check by titrating 100 ml of the 0.01 M amine solution with a standard 0.1N HCl solution using methyl red as the indicator; 5) ascarite granular 2-4 mm in diameter.

Photoelectrocolorimeter FEK-N-57 was used in performing the analysis. Determinations were made using light filter 3, having a narrow transmission band and a maximum at 453 mμ. Now proceed as follows; set up a series of 16 photo colorimetric cups 30 mm high. Place into the first cup 0.5 ml of the 0.1 millimolar amine solution, 1.0 ml into the second cup, 1.5 into the third cup; continue to progressively increase the values until cup 16 will contain 8.0 ml; add ammonia-free distilled water to the first 15 cups to make a volume of 8.0 ml. Add 4 ml of 0.1% standard o-nitrophenol solution to all 16 cups and shake gently. Make colorimetric determinations and plot the results as shown in the curve of Fig. 2.

Set up another series of 16 colorimetric cups 30 mm high; place into the first tube 1.0 ml of the 0.1 millimolar ammonia solution; continue to progressively increase the volume by 1.0 ml until cup 16 will contain 16 ml of the standard ammonia solution. Add ammonia-free water to the first 15 cups to make a volume of 16 ml; add 4 ml of Nessler-Folin reagent; make colorimetric determinations and plot results as shown in curve 2, Fig. 2.

Make air tests as follows: aspirate 2-5 li of the air successively through a 5 ml U-shaped tube filled with ascarite and through a coiled absorber containing 40 ml of ammonia-free water, or through two successively connected Richter absorbers, each containing 16 ml of ammonia-free distilled water. Pour the contents of the coil or Richter absorbers into a glass flask. Remove 8 ml of the water from the flask, place into a colorimetric cup, add 4 ml of the Nessler-Folin reagent and proceed as above described.

On the basis of the optical density data, and with the aid of the standard curve, and of Formula 1 compute the total concentration ($C_{tot.}$) of the amines and ammonia in the air in moles per liter. Take 16 ml of the sample and place into a colorimetric cup, add 4 ml of the Nessler-Folin reagent; make colorimetric determination; on the basis of the data and with the aid of the corresponding standard curve compute ammonia concentration (C_{NH_3}) in moles per liter, using the same formula.

$$C_{tot}\,(\text{or } C_{NH_3}) = a \cdot b/v_o \cdot d$$

where $(a)^-$ denotes μ moles of total bases in terms of ammonia found by using curve 1 or 2 corresponding to optical density data; $(b)^-$ denotes ml of volume

of solution in the absorbers (in the given case 40 or 32 ml); (d) denotes ml of the sample taken for colorimetric determination (in this case 8 ml for the total bases and 16 ml for the ammonia); $(V_o)^-$ denotes li of air aspirated through the absorbers, reduced to standard temperature and pressure.

Concentration of amines in the air was computed on the basis of total bases minus ammonia concentration. To convert ml to li of a given amine multiply by M/1000, where M is the molecular weight of the given amine.

$$C_{amine} = (C_{tot} - C_{NH_3}) \cdot M/1000 \text{ mg/li}$$

The value of M/1000, in the case of methyl amine is 0.031; for dimethyl or ethyl amine it is 0.045, and for triethyl amine, 0.101. The method is accurate to 0.02 μ mole in the colorimetrically analyzed volume; for methyl amines and ethyl amine it corresponds to about 1γ, for di- and triethylamine 2γ, and for ammonia 0.4γ per sample volume.

The method was applied in practice and yielded satisfactory results in determining content of aliphatic amines in the air of working premises and in experimental animal exposure chambers.

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The Accuracy of a Colorimetric Method for Determining Toxic Dinitrophenols in Biological Matter

pp. 53 - 58

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The use of dinitrophenol (DNP), dinitro-o-cresol (DNOC), dinitro-sec-butylphenol (DNSBP), and dinitro-iso-propylphenol (DNPP) in agriculture as insecticides and herbicides is progressively increasing. These preparations are highly toxic to man and farm animals, and continuous contact with them can induce acute and chronic poisoning. Therefore, a method had to be developed for the detection of dinitrophenols in biological specimens.

Such a method must be highly sensitive, satisfactorily reproducible and easy to perform. In this connection the present author examined the following reactions:

1. Anger's drop reaction for nitrobenzene derivatives (1960). The authors stated that 2,4-dinitrophenol also produced this reaction. Tests were made to determine the possibility of applying this method to a study of the toxicity of dinitro derivatives, particularly DNP and of DNOC. A blue color appeared as soon as diphenylbenzidine was dissolved in 80% sulphuric acid; the color disappeared during subsequent stages of the reaction and did not reappear upon boiling even in the presence of large amounts of tested substances.

2. Meyer's reaction (L. Devern, 1934) was modified and described by Petrascu and Grou in 1955. Check tests made by the present author showed that this reaction gave positive results only in the presence of 50μ/g or more. Therefore, this reaction was also unsuitable for the purpose.

3. Lead dichloride reaction (L. Devern, 1934) This reaction was tested with all four preparations. Its sensitivity was very low. A faint, yellowish color appeared in the test tube in the presence of 20μ/g or more of the preparation, which was not sensitive enough for the purpose.

4. In 1956 Zeumer described the Yanovskii and Bose methods for the determination of dinitro-compounds. A check of these methods showed that only Bose's reaction yielded positive results in the presence of 100 to 500 μ/g of the toxic preparations. Yanovskii's reaction failed to produce colored solutions even with 100μ/g of the preparations. Therefore, these methods were not suitable for the determination of dinitrophenols in biological specimens.

Table 1.

Extinction of DNPh, DNOC, DNSBPh and DNPPh solutions in 3 ml of the test sample of different μg content

μg of the substance	Extinction E			
	Substance			
	DNPh	DNOC	DNSBPh	DNPPh
0,5	0,002	0,002	0,001	0,002
1,0	0,005	0,005	0,007	0,006
2,5	0,015	0,010	0,015	0,010
5,0	0,035	0,020	0,030	0,020
10,0	0,067	0,037	0,055	0,042
12,5	0,080	0,046	0,071	0,053
15,0	0,092	0,053	0,084	0,063
20,0	0,120	0,069	0,108	0,080
25,0	0,140	0,088	0,138	0,097
50,0	0,237	0,152	0,244	0,157

5. Parker's method for the determination of DNOC in urine (1949). This method was described by M. P. Slyussar and I. B. Kogan in 1958.

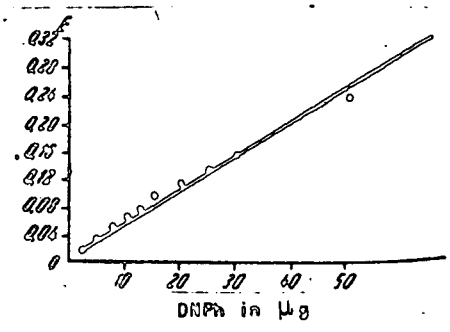
6. Harvey (1952) developed a method for the determination of DNOC in 0.1 ml of blood serum. This method was based on the principle of Parker's method. Drops of finger blood were collected in a weighted 5-10 ml centrifuge tube equipped with a ground- to- fit stopper containing an anticoagulant. The centrifuge tube was then weighed again. Blood traces on the centrifuge tube walls were washed down by a piece of filter paper saturated with a 1% physiological solution. The filter paper was then placed into the centrifuge tube containing the blood, and 2 ml of methyl ethyl ketone and an excess of physiological solution added. The entire contents was shaken well for five minutes. The methyl ethyl ketone extract turned yellow in the presence of DNOC in the blood serum. Other steps of the investigation were carried out by means of a spectrophotometer.

The aim of the study was: 1) to investigate the possibility of using the Harvey method for the determination of DNP, DNOC, DNSBP, and DNPP in biological specimens; 2) to find optimum conditions for the determination of the above-mentioned substances in urine, feces, blood serum and internal organs and tissues; and 3) to determine the sensitivity and accuracy of the proposed method. Results of check tests showed that the reaction could be used in determining toxic dinitrophenols in biological specimens. The accuracy of the Harvey method was determined by introducing known quantitites of DNP, DNOC, DNSBP, and DNPP into specimens of urine, feces, blood serum, and internal organs and tissue.

Determinations in urine: Use 3 ml of the urine; add 50 μ/g of the test substance, 1 g anhydrous sodium sulfate, and 3 ml of methyl ethyl ketone. Shake the contents vigorously and centrifuge for 10-15 minutes. Examine the upper yellow colored methyl ethyl ketone layer for color intensity using a photoelectrocolorimeter. Evaluate the concentration of DNP, DNOC, DNSBP, or DNPP with the aid of a calibrated curve, previously plotted as follows: let the abscissa represent μ of the preparation per unit volume of the urine, and the ordinate the solution extinction (E) as shown in Table 1.

Sensitivity of the method is 0.001 mg per sample volume. Curve in the figure below exemplifies the procedure used in constructing a calibrated curve for the determination of dinitrophenol in urine. Calibrated curves for the determination of other dinitrophenolic derivatives in biological specimens are constructed similarly. The figure is on the following page.

Accuracy of the method was checked by introducing known quantities of DNP, DNOC, DNSBP, and DNPP into urine specimens. Results were processed statistically by the M. L. Belen'ki method and expressed in percent. Data in Table 2 show the accuracy to which DNP can be determined in urine. The accuracy of the method for other dinitrophenol derivatives is as follows:



Curve for DNPh determination in urine

for DNOC - 78.3 ± 2.57%; for DNBP, -88.1± 2.02; for DNPP - 72.8± 3.93% per specimen volume.

Determination in feces. Prepare a 1:1 mixture of feces and anhydrous Na_2SO_4. To 1 g of this mixture ad 50 μ of the preparation to be tested and 1-2 drops of ammonia to alkalinize the mixture. Add 5 ml of methyl ethyl acetone, extract for 10-15 min. and irradiate with UV rays for 50 min. until the solution develops a yellow color. Compare color intensity with a standard color scale prepared so that 5 ml of the solution will contain successively 0.5, 1.0, 40.0 and 50.0 μ of the preparation. Sensitivity of the method for each of the 4 derivatives is 0.002 mg in the test specimen. Accordingly, presence of 0.002 mg or more of the dinitro derivatives in a fecal test specimen can be detected by this test visually.

Table 2.

Accuracy of method for the determination of DNPh in urine

μg of substance taken	Substance found		X	$X-\bar{X}$	$(X-\bar{X})^2$
	μg	%			
12,5	13,75	110,0		+22,5	506,30
12,5	10,50	83,7		--3,8	14,44
12,5	10,75	86,0	n=14;	—1,5	2,25
12,5	10,75	86,0	X=87,5	—1,5	2,25
12,5	10,50	83,7		—3,8	14,44
25,0	25,00	100,0		+12,5	156,30
25,0	21,50	86,2		—1,3	1,69
25,0	24,00	96,0		+8,5	72,25
25,0	23,50	94,2		+6,7	44,89
25,0	24,25	97,0		+9,5	90,25
50,0	34,50	69,2		—18,3	334,90
50,0	37,25	74,6		—12,9	166,40
50,0	41,00	82,0		—5,5	30,25
50,0	38,25	76,4		—11,1	123,20
		1225,0			1559,81

The accuracy of the method was determined as follows: 50μ of a dinitro derivative was added to a fecal specimen, and completness of its extraction by methyl ethyl ketone was determined. Accuracy of the method for DNP is 84.6±7.12%, for DNOC - 92.0±5.92% for DNSBP - 92.0±5.54% and for DNPP - 101.0±4.22%, per specimen before making corrections. However, corrections based on control tests were necessary, since some fecal control specimens were of a slight yellow color.

Determination in blood serum. Add the test substance to 0.1 ml of blood serum, add 0.1 g anhydrous Na_2SO_4, and 0.2 ml methyl ethyl ketone. Shake for 10 - 15 min., and centrifuge. Wash sediment with 0.1 ml methyl ethyl ketone and centrifuge three times. Determine the concentration of the toxic

derivatives using a calibrated curve constructed as usual and a photoelectrocolorimeter. Data in Table 3 show that the method sensitivity was 0.0005 mg for DNP, DNOC, and DNSBP, and O.002 mg for DNPP in 0.1 ml blood serum.

$$S = \pm\sqrt{\frac{(X-\overline{X})^2}{n-1}};$$

$$S = \pm\sqrt{\frac{1559,81}{13}} = \pm\sqrt{120,0} = \pm\ 10,95;$$

$$S_{\overline{X}} = \pm\frac{S}{\sqrt{n}} = \pm\frac{10,95}{3,742} = \pm\ 2,39;$$

$$\overline{X} = 87,5 \pm 2,93.$$

Table 3.

Extinction readings of DNPh, DNOC, DNSBPh, and DNPPh solutions of blood serum samples having different concentrations of the substances

Amount in μg	Extinction E			
	Substance			
	DNPh	DNOC	DNSBPh	DNPPh
0,5	0,007	0,003	0,004	0,003
1,0	0,010	0,005	0,006	0,003
1,5	0,012	0,007	0,0085	0,003
2,0	0,013	0,008	0,009	0,005
2,5	0,015	0,010	0,010	0,007
5,0	0,025	0,018	0,015	0,010
7,5	0,032	0,025	0,020	0,0125
10,0	0,041	0,033	0,028	0,018
12,5	0,050	0,040	0,030	0,020

Accuracy of the method was determined by adding 12.5 or 25μ of test derivative to the blood serum specimen. Statistical data processing showed the following degrees of the method sensitivity: for DNP- 77.6 ± 3.16%; for DNOC - 70.8 ± 3.82%; for DNSBP - 61.6 ± 2.58%; and for DNPP - 77.6 ± 5.15%, per blood serum specimen.

Determination in internal organs. To a weighed amount of tissue or organ add an equal amount by weight of anhydrous Na_2SO_4 and grind to complete homogeneity. Place 2 g of the homogenate into a test tube; add the dinitro derivative, followed by the addition of 0.4 ml of methyl ethyl ketone, extract for 10-15 min. and separate by centrifuging the sediment 4-5 times with 0.2 ml of methyl ethyl ketone. Determine the concentration of the test substance in the supernatant methyl ethyl ketone, using a photoelectrocolorimeter and a calibrated curve constructed on the basis of data in Table 4.

Data in Table 4 show that the method sensitivity in the case of in-

internal organs was 0.0005 mg for all four dinitro substances.

Table 4.

Extinction of DNPh, DNOC, DNSBPh, and DNPPh solutions depending upon their concentration in internal organs

µg of substance	Extinction E			
	Substance			
	DNPh	DNOC	DNSBPh	DNPPh
0,5	0,004	0,005	0,002	0,003
1,0	0,006	0,007	0,0025	0,005
1,5	0,008	0,009	0,0045	0,008
2,0	0,010	0,010	0,007	0,009
2,5	0,012	0,011	0,012	0,010
5,0	0,022	0,014	0,016	0,016
10,0	0,040	0,020	0,026	0,021
20,0	0,070	0,040	0,046	0,032
50,0	0,152	0,095	0,095	0,060

Data in Table 5 show that contents of any dinitroderivative in internal organs and tissues can be determined accurately. It was previously shown that this was equally true of dinitroderivatives in urine, feces, and in blood serum.

Table 5.

Accuracy of method for the determination of DNPh, DNOC, DNSBPh, and DNPPh in internal organ tissues

Tissue or organ	Accuracy of method			
	Substance			
	DNPh	DNOC	DNSBPh	DNPPh
Liver	72,3±4,52	95,1±2,74	74,6±4,55	88,4±5,17
Kidneys	75,4±4,67	90,7±1,87	73,9±4,08	82,6±4,99
Adrenals	82,1±6,04	97,0±2,72	83,8±3,37	91,5±2,41
Spleen	78,9±4,78	93,1±2,54	72,0±5,59	85,4±5,37
Lungs	84,8±5,82	92,8±3,24	78,5±4,38	83,6±6,28
Heart	69,8±4,44	95,5±2,30	72,3±4,58	81,4±4,49
Brain	84,7±6,90	94,1±2,89	82,2±4,63	88,8±4,59
Muscles	82,2±6,15	94,8±3,69	70,3±5,90	85,9±4,48

Conclusions

1. The sensitivity and accuracy of the proposed method for the determination of toxic dinitrophenol derivatives in biological substrate had been investigated.

2. Accuracy of the proposed method for the determination of DNP,

DNOC, DNSBP, and DNPP in living organisms ranged between 0.005 and 0.002 mg per specimen, which is considered high.

3. Accuracy of the proposed method for the determination of dinitro-derivatives ranged between 61.6 ± 2.58% and 95.5 ± 2.3%.

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Mine Waters Use for Dust Abatement
pp. 91-94

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Data available regarding the water resources and water supplies in the Novoshakhtinsk administrative region of the Rostov oblast, where the mines of coal trust "Nesvetal-Antratzit" are located, suggest that in approaching the problem of dust abastement in the mines, the possibility of utilizing the mine waters should be given first consideration, provided that such mine water can satisfy some important technological and sanitary basic requirements. In this connection the Novocherkask Polytechnic Institute investigated the conditions under which the dust was generated in the mines and the type of dust and character of the mine waters in the Institute's Ventilation and Mine Dust Laboratory. First under investigation were the V.I. Lenin, A.M. Gor'kii and No. 5 mines, where the problem of dust abatement was most acute. The cleaning and preparatory faces in these mines had no provisions for dust abatement, and the dust density in the air was frequently between 10 and 100 times in excess of the permissible maximum. The i_z^v coal vein of the mines is only 0.55-0.65 m wide; therefore, in working it, it became necessary to break up, load and deliver to the surface a considerable amount of surrounding rocks, of which approximately 75% are sandstones and aleurites, which contain 20-70% of free silicon dioxide. It was hoped that results of analyses of the V.I. Lenin, A.M. Gor'kii and No. 5 mine waters could serve as reasonable bases for the judgment of water quality of other Nesvetaev region mines of considerably heavier coal veins.

It was mentioned above that only water which fulfils certain sanitary

and technological requirements should be used in dust abatement. The technological requirements pertain to qualitative indexes which might affect the dust catching capacity of the water and also the water distribution system, such, for instance, as the presence of mechanically suspended matter, hardness, etc. The sanitary requirements pertain to such qualitative indexes as pollution which may be harmful to health, or factors which may unfavorably affect the atmosphere in mine shafts and mining spaces; the pollution may be of a bacteriological, toxicological, or organoleptic character, especially in relation to odor. Mechanical suspensions in the water are regarded as an obstacle, since they can cause clogging and obstructions in the spraying system and in the water flow regulating device. It was also noted that certain types of particles suspended in rapidly flowing water had abrasive effects on the distribution system pipes and their fittings. Data presented by N.I. Kurenkov indicated that suspended particles of less than 0.05 μ in diameter had no destructive effect on the water distribution system, nor did they cause sediment deposits or clogging of even small orifices through which the water passed, as, for instance, in the case of spraying or sprinkling equipment. In accordance with Kurenkov's observations, it is recommended that the presence in water used for dust abatement of suspended particles the diameters of which exceeded 0.15 μ should be regarded as undesirable and prohibited.

Water hardness had no substantial effect on its dust abating properties, however, the use of such water for dust abatement should be restricted in the presence of certain wetting agents. It is recommended that in the presence of iron compounds in the water, its pH should be kept within the 6.0-8.5 range, if it is to be used for mine dust abating purposes by sending it through the mine water pipes and into the spray distribution system; it is also recommended that the water Fe concentration should not exceed 1 mg/li. Careful determinations should be made of the free silicon dioxide in the mineral sediment of the water, and its content should be taken into consideration in regulating the water quality with respect to its suspended mineral matter content in order to avoid erroneous conclusions. For example, the temporary directives applicable to humidification of underground working spaces issued in 1952 specified unconditionally that the water used for mine dust abatement must contain not more than 50 mg/li of suspended mineral matter; actually this limitation should be instituted only for water the mineral suspended matter of which contained 10% of free silicon dioxide; for waters in which the silicon dioxide content is below 10% the above specified limitation is excessive. This statement is verified as follows: the maximal mineral suspended matter in water used for dust abatement can be determined by the following expression:

$$n = 1000\ p:q \quad mg/li$$

where p represents the permissible sanitary norm of mine atmosphere dust density in mg/m^3

q represents the maximal permissible content of atomized water in the mine air in ml/m^3

As a rule the value of (q) never exceeds 40 ml/m^3; actually under present conditions of mine air humidification the value of (q) is below 12 ml/m^3. Assuming that (q) had the value of 40 ml/m^3 substitute for (p) and (q) in the above expression their values, find that the permissible norm of suspended mineral matter in the above cases could be assumed equal to 250 mg/li. Accordingly, depending upon the percent of free silicon dioxide contained in the water-suspended mineral matter two limiting suspended matter norms should be set, one at 50 and one at 250 mg/li. The need for limiting the water bacterial density in such cases is self evident. And yet, even in this respect the existing sanitary specifications were also excessive. According to the same 1952 temporary directive not more than one E.coli organism per 300 ml must be present in the water used for underground dust abatement.

Determination of the mine water quality in places where the coal vein i_z^v was being worked was based on the following indexes: 1) the water pH; 2) mg/li of mechanical suspended matter; 3) mg/li of suspended mineral matter; 4) % of free silicon dioxide in the suspended mineral matter; 5) percent of fractions with diameter greater than 0.05 μ, as determined by the Sobanin method, and 6) Fe^{3+} and H_2S content in mg/li. Water samples for the above enumerated determinations had been collected in the spring season from central and gradient water collecting points, and from troughs which delivered water to points of drift mining. In addition, summer pH determinations were made of the A.M. Gor'kii and No. 5 mines. Results showed that the summer pH ranged between 6.4-6.8 and the winter pH between 6.6-8.7 H_2S traces were found in isolated samples of water collected from the A.M. Gor'kii mine. Data related to the mechanical water suspended matter are presented in the table. See Table next page. Records of the Sanitary-Epidemiological Station showed that the bacterial pollution of the mine waters was on the level of river Don pollution during the summer months.

The present authors concluded that mine waters having up to 250 mg/li of suspended mineral matter and a coli titre of 0.1 could be used for the purpose of mine dust abatement.

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Characteristics of mine water pollution indexes with mechanical admixtures

Mine	Points of water sample collection	Mechanical suspension content (in mg/l)	Mineral suspension content (in mg/l)	Percent of 0.05 mm fraction	Percent of silicon oxide: in total suspension	Percent of silicon oxide: in mineral precipitate
V.I.Lenin Mine	Second thousand water accumulator	663,1	216,5	12,4	12,14	6,6
Ditto	Drive face	111,9—550,0	62,7—240,0	4,3—13,1	1,9—4,8	5,8—10,6
A.M. Gor'kii Mine	Central water accumulator	386,4	189,3	20,1	7,20	14,7
Ditto	Drive face	389,1—842,6	82,0—519,0	7,2—16,4	2,3—8,3	7,2—12,3
Mine No. 5	Central water accumulator	693,4	201,0	18,9	2,26	7,8
Ditto	Other water accumulators	263,8—780,0	89,9—308,6	18,6—31,2	2,0—4,13	5,9—9,7

Experimental Data as a Basis for the Determination of Maximal Permissible Toluylene Diisocyanate Concentration in Atmospheric Air

pp. 8-15

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Toluylene diisocyanate has the chemical formula of $CH_3C_6H_3(NCO)_2$. It is a light yellowish fluid having a sharp unpleasant odor, a b.p. of 246°, and solidified at 4-6°. It is used as raw material in the manufacture of polyurethane foam-like plastic materials. It is synthesized by interaction between toluylene-diamine dissolved in chlorobenzene and phosgene. Most frequently used in the national economy and in industry is a mixture of 2,4 and 2,6 isomeres of toluylene diisocyanate known abroad as "desmodur T". Industrial plans which use or produce toluylene diisocyanate may become sources of atmospheric air pollution with this compound. Little information has been found in the literature concerning the toxicity of toluylene diisocyanate, and practically no information was found regarding it as an air pollutant or its effect on the human and animal organisms in low concentrations. Acute toluylene diisocyanate poisoning has been encountered and described by several investigators as an irritant of the conjunctiva and mucosa of the upper respiratory tract. Toxic effects of the preparation have been described as cumulative. Some authors believed that toluylene diisocyanate possessed active allergic properties.

Tests for the determination of toluylene diisocyanate concentrations in the air had been conducted by the present author by the method described by Tubina in 1960, and modified by M. V. Alekseeva of the F. F. Erisman Institute. Sensitivity of the method is 2 μ in the studied sample volume. The method is based on interaction between toluylene diisocyanate with sodium nitrate. In the presence of toluylene diisocyanate, a dark-orange color appears which reached maximum intensity in 60 minutes, and persisted for another 60 minutes. Acute affect of this product in low concentrations on the human organism was studied beginning with the concentration of threshold odor perception. Zapp found that 0.4 ppm in the air, or its equivalent 2.8 mg/m^3 was the concentration of toluylene diisocyanate odor perception threshold. The present author conducted experimental toluylene diisocyanate threshold odor determinations according to the procedure recommended by the Committee for the Sanitary Protection of Atmospheric Air. Three-hundred ninety-five (395) determinations have been made with 13 different toluylene diisocyanate concentrations. Results presented in Table 1 show

that 0.2 mg/m^3 was the concentration of minimal perception for most odor sensitive individuals, and 0.15 mg/m^3 was the maximal nonperceptible toluylene diisocyanate concentration.

Table 1.

Determination of toluylenediisocyanate threshold odor perception

Number of observations	mg/m^3 of the substance	
	Minimal perceptible	Maximal nonperceptible
2	0,2	0,15
3	0,3	0,2
3	0,35	0,3
5	0,45	0,35
5	0,6	0,45
2	1,0	0,6
1	2,6	2,0

The next step in this study was to determine the effect of low toluylene diisocyanate concentrations on electric brain activity. This was done with the aid of an 8-lead Kaiser electroencephalograph by the usual procedure employed in electroencephalography and adapted to the study of maximal permissible concentrations of harmful substances in atmospheric air.

The procedure is briefly as follows: An electroencephalographic record is made of the test individual's response to rhythmic stimulation with light; the electroencephalographic record thus produced enables the investigator to study the character of the tested person's adaptation to the stimulating light rhythm during the entire experiment. Several control experiments are made first with the person inhaling clean air; then, without the test person's awareness known concentrations of the pollutant are introduced into the inhaled air and experimental encephalographic records made with the different concentration of the pollutant. Results of such tests made with toluylene diisocyanate are shown in Table 2. Data in Table 2 show that 5 minutes inhalation of low toluylene diisocyanate concentrations affected the electric brain activity of different individuals differently. Thus, in the case of female A. I. statistically significant changes in the electrocencephalogram were obtained only upon the inhalation of air containing 0.2 mg/m^3 of the tested pollutant, as shown in Fig. 1. In the case of 2 other test individuals the concentration was 0.15 mg/m^3, and for 2 others it was 0.10 mg/m^3. It should also be noted that in the experiments here described, changes in adaptation to the rhythm of light stimulation extended in the direction of increased and decreased adaptation rhythm amplitudes. 0.2 mg/m^3 toluylene diisocyanate concentration depressed the brain electric activity in every case, while in 0.1 mg/m^3 concentration most test persons manifested a brief rise in the adopted rhythm amplitude, followed by a depression. Each test individual was given to inhale toluylene diisocyanate in 4 different concentrations, making a total of 100 experimental tests. All concentrations were below the threshold of toluylene diisocyanate odor perception. Based on the results of this investigation the present author proposes 0.05 mg/m^3 of toluylene diisocyanate as its maximal permissible single concentration in atmospheric air. The maximal permissible 24 hour toluylene diisocyanate concentration in atmospheric air under chronic experimental conditions was determined by exposing white rats to the toluylene diisocyanate containing air daily for 24 hours. Sixty male rats weighing 110-130 g were divided into 4 groups of

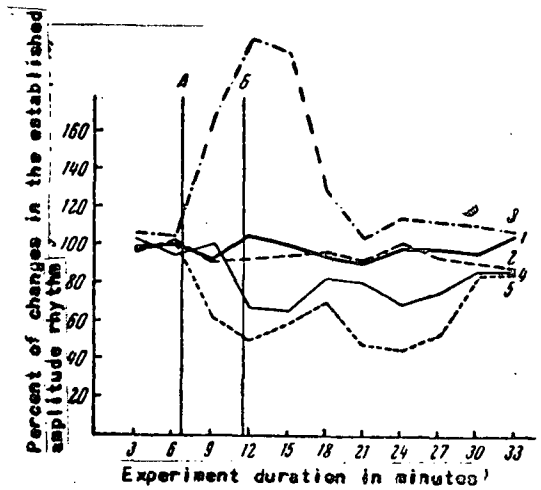
15 specimens. Rats of group No. 1 inhaled air containing 2 mg/m^3, rats of group No. 2 - 0.2 mg/m^3, and rats of group No. 3 - 0.02 mg/m^3 of the toluylene diisocyanate, while rats of Group No. 4 served as controls. Checks for the toluylene diisocyanate concentrations in the exposure chambers were made 3-4 times daily in exposure Chamber No. 1, and 1-2 times daily in Chambers Nos. 2 and 3. The average toluylene diisocyanate concentration was 1.951±0.223 mg/m^3 in Chamber No. 1, 0.2036±0.18 mg/m^3 in Chamber No. 2, and 0.0207±0.038 mg/m^3 in Chamber No. 3. Chronic experiments under conditions described extended over 84 days. Evaluation of effects was based on changes noted in the behavior of the animals, their general state of well being, favorable or unfavorable changes in body weight, changes in muscle-antagonists motor chronaxy, cholinesterase activity, blood serum protein composition, and in rats of coproporphyrin elimination with the urine.

Table 2

Determination of toluylenediisocyanate threshold effect on olectrical brain activity

Number of test Persons	Mg/m^3 of the compound	
	Eliciting activity changes	Eliciting no changes
2	0,10	0,05
2	0,15	0,10
1	0,20	0,15

Fig. 1.



Changes in the established amplitude rhythm in test persons. A. I. upon inhalation of different t luyldiisocyanate concentrations 1 - response reaction - pure air; 2 - ditto 0.05 mg/m^3; 3 - 0.10 mg/m^3; 4 - 0.15 mg/m^3; 5 - 0.20 mg/m^3 of the cyanate vapor. A and B cyanate vapor administration

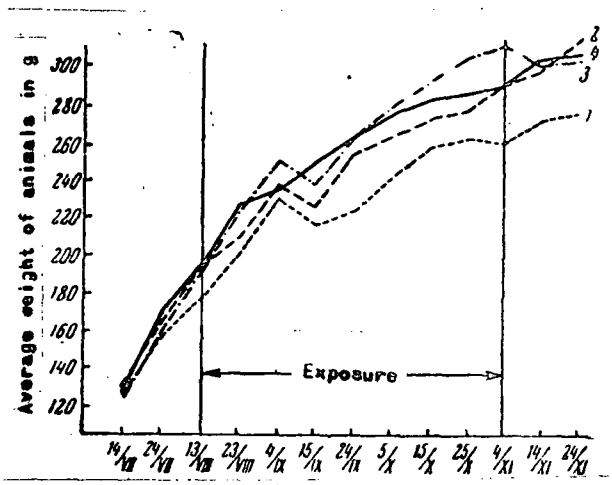
Results of chronic toluylene diisocyanate exposure experiments showed that the general condition, appearance and weight of rats belonging to group 1 have been unfavorably affected. Rats of Groups 2 and 3 behaved and appeared like the control group rats. Rats belonging to Group 1, which inhaled air containing an average of 1.951 mg/m^3 of toluylene diisocyanate manifested changes in their general behavior beginning with the first few days of inhalation; the rats were restless, irritable, and showed signs of nasal mucous membrane irritation. The negative signs abated after a few days. However, the signs reappeared in a more aggravated form after the second half of the inhalation exposure. The rats became sluggish, indifferent to food, and consumed less of it. Their nasal mucosa and conjunctiva were irritated, the fur became shaggy, and one of the rats died before the termination of the experimental period. Resistance to experimental starvation became considerably reduced in rats of group 1 which inhaled air containing 2 mg/m^3 of the pollutant. (Fig. 2).

Many authors believed that motor chronaxy size depended upon the state of the cortical regulatory function and that chronaxy changes served as an objective and sensitive indicator of functional disturbance in the central nervous system; among such investigators are Yu. M. Uflan'd (1941), A.N. Magnitskii (1934), A.F. Makarchenko (1952) and many others. This served as a basis for the application of this method in many toxic or dynamic investigations. Accordingly, study was made of hind leg muscle antagonist motor chronaxy of 5 rats in each group, once every 10 days, at the same hours of the day, and under similar experimental conditions. Results indicated that rats of group 1 showed reverse muscle antagonist chronaxy ratios at the end of the first month. Similar manifestations appeared in rats of Group 3 later in the inhalation exposure. Return of normal muscle antagonist chronaxy ratio appeared during the recovery period first in rats of Group 2. No statistically significant or reliable changes in the motor chronaxy ratio had been noted in rats of Group 3 and in the control rats. All results were statistically processed and found reliable.

Cholinesterase activity was determined by the method described by A.A. Pokrovskii in 1953 and revised by A.P. Martynova in 1957. The method is based on determination of time required for the hydrolysis of added acetylcholine, which changed the medium pH, as shown by color changes in the experimental test tubes. Such tests had been conducted at 15 day intervals. Animals of Group 1, which inhaled air containing 2 mg/m^3 of toluylene diisocyanate, showed 35-40% increase in cholinesterase activity. Cholinesterase activity of rats belonging to Group 2 increased to a lesser extent. In both groups the cholinesterase activity levels rapidly returned to normal. (Fig. 3).

Many authors noted that animals exposed to the chronic effects of some harmful substances developed changes in protein metabolism, as indicated by lowered albumin concentration and increased concentrations in the blood serum globulin fractions. This was particularly true of animals which had been exposed to the chronic effect of low furfural concentrations. Therefore, studies had been conducted by the method of electrophoresis to determine what effect, if any, toluylene diisocyanate had on the blood serum protein picture in 5 rats of each group. This was done at 20 day intervals. No changes had been detected in the blood serum protein concentration of any rat during the entire observation period. Because of the highly dispersed character of the values obtained, the data had been processed statistically in a preliminary manner; the results confirmed the validity of the above recorded impression. Data in Table 3 show that albumin fractions showed greatest changes; this was followed by changes in β-globulins. No changes of any kind had been noted in the γ-globulin fractions. Changes in the above indicated protein metabolism phases of the rats were most expressed in animals of Group 1, and less so in rats of Group 2. The protein metabolism picture of rats belonging to Group 3 was practically the same as of rats belonging to the control group. Maximal changes in the different phases of protein metabolism appeared at the end of the exposure period, the levels of which persisted throughout the recovery period.

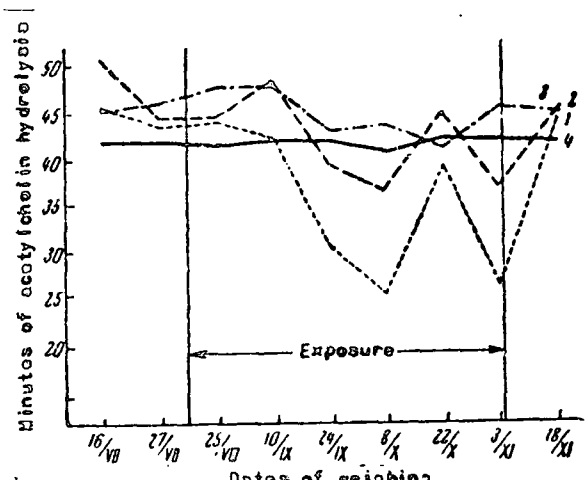
Fig. 2.



Changes in animal weights in the course of chronic exposure to toluylidiisocyanate

1 - Animals of Group 1; 2 - Group 2; 3 - Group 3; 4 - Control; 5 - Exposure

Fig. 3.



Effect of toluylidiisocyanate on blood cholinesterase activity of the rats

1 - Rats of Group 1; 2 - Group 2; 3 - Group 3; 4 - Control group

Table 3

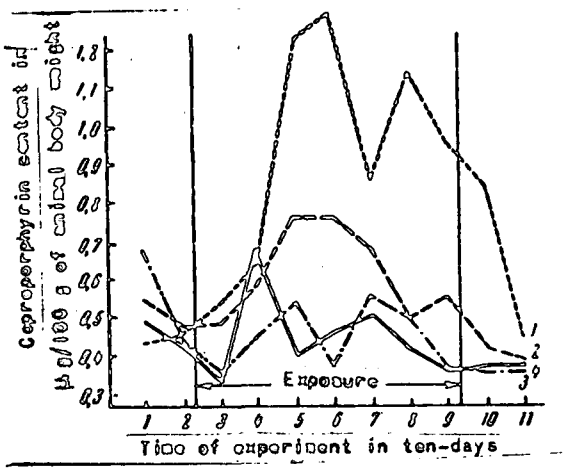
Blood serum protein fractions of changes of rats exposed to the effect of toluylidiisocyanate

Blood protein fraction	Time of Determination	Animal Group			
		One	Two	Three	Control
Albumins	Before exposure	40,83	40,83	40,83	40,83
	During exposure	32,11	36,69	37,14	39,19
	During recovery period	34,75	39,25	38,38	38,40
α-Globulins	Before exposure	18,45	18,45	18,45	18,45
	During exposure	21,16	17,46	18,84	19,67
	During recovery period	20,30	21,80	18,11	18,16
β-Globulins	Before exposure	24,81	24,81	24,81	24,81
	During exposure	29,11	27,47	26,22	26,0
	During recovery period	27,97	24,65	26,0	27,80
γ-Globulins	Before exposure	16,10	16,10	16,10	16,10
	During exposure	18,0	18,41	17,77	15,0
	During recovery period	16,95	14,28	17,45	15,60

Tests were then conducted to determine possible changes in coproporphyrin elimination with the urine. The mechanism by which harmful substances affected the rate of coproporphyrin elimination under conditions of chronic experiment had not been clearly understood. Many suggestions have been offered in the way of explanation, but none has been verified. In the present study, 5 rats of each group had been set aside for the coproporphyrin elimination investigation. Tests were made with 24 hour urine specimens of

rats which were kept in cages specially constructed for the collection of urine. Porphyrin had been extracted from the urine by the Fisher method; qualitative and quantitative determinations of coproporphyrin were made spectrophotometrically in the region of 400-410 mμ wave length. Beginning with the fourth week of experimental inhalation exposure, the rate of coproporphyrin elimination with the urine increased in rats of Group 1; this increase persisted throughout the entire exposure period, and returned to normal only at the end of the recovery period. Slight, but statistically significant changes in the rate of coproporphyrin elimination with the urine had been noted in rats of Group 2. However, enhanced levels of coproporphyrin elimination with the urine noted in rats of Group 2, rapidly returned to normal, as shown in Fig. 4. No statistically significant changes in the rate of coproporphyrin elimination with the urine had been noted in rats of Group 3.

Fig. 4.



Effect of toluylindiisocyanate on the rate of coproporphyrin elimination with the urine of experimental white rats

1 - Rats of Group 1; 2 - Group 2; 3 - Group 3; 4 - Control groups; Coproporphyrin eliminated per 24 hours

In summary, it can be stated that continuous chronic exposure of white rats to the effects of toluylene diisocynate of 2.0 and 0.2 mg/m^3 concentrations for 84 days elicited toxic symptoms in the experimental animals, such as loss of body weight, increase in cholinesterase activity, changes in muscle antagonists motor chronaxy ratios, changes in some phases of protein metabolism, and in the rate of porphyrin elimination via the urine. As previously mentioned, no such changes occurred in experimental rats which chronically inhaled toluylene diisocyanate in 0.02 mg/m^3 concentration. Accordingly, the present author recommends that 0.02 mg/m^3 of the air pollutant be accepted as its maximal permissible average 24 hour concentration in atmospheric air.

In the next step of the investigation the present author attempted to obtain a general picture of existing atmospheric air pollution with toluylene diisocyanate. This was done in the vicinity of a plant which used toluylene diisocyanate as the raw product in its manufacturing processes. The investigation was conducted in September, 1962 when 107 single test air samples had been collected. The plant around which the studies had been conducted lacked the necessary purification installations, and all harmful side products had been discharged into the atmosphere without preliminary purification. The plant operated in two shifts, and was organized so that the final product had been completed during the first shift, whereas the second shift made all necessary preparatory operations. Data in Table 4 show that toluylene

diisocyanate concentrations in the atmospheric air surrounding the plant under investigation became rapidly dispersed, reducing the pollutant concentration as it floated away from the plant in the higher atmospheric layers, so that 300 m from the plant the concentration of this air pollutant did not exceed the maximal single average 24 hour permissible concentration. It must be noted, however, that under different conditions of technology or different arrangements in the working shifts, and especially with an increase in the production volume, the situation may change, so that the density of air pollution with toluylene diisocyanate may rise to levels exceeding the one just indicated. It is suggested that the investigated plant should be surrounded by a sanitary clearance zone the width of which should be determined on the basis of dominant and important factors.

Table 4.

Atmospheric air pollution with toluylidiisocyanate

Meters from source of discharge	No. of collected Air samples		Concentration in mg/m^3		Sample concentration distribution in mg/m^3		
	Total	Samples with concen. above method sensitivity	Maximal	Minimal	Above 0.05	0.05—0.02	Below 0.02
75	25	18	0,075	—	6	10	2
200	50	22	0,024	—	—	4	18
300	32	1	0,006	—	—	—	1

Conclusions

1. The concentration of toluylene diisocyanate threshold odor perception for most sensitive persons was experimentally established as 0.2 mg/m^3 and the maximal odor nonperceptible concentration was established at 0.15 mg/m^3.

2. The concentration of toluylene diisocyanate threshold effect on electric brain activity was established at 0.1 mg/m^3, while 0.05 mg/m^3 concentration elicited no changes in the electric brain activity.

3. The maximal single permissible toluylene diisocyanate concentration in atmospheric air should be set at 0.05 mg/m^3.

4. Exposure of white rats to the inhalation of air containing 2.0 or 0.2 mg/m^3 of toluylene diisocyanate 24 hours daily for 84 days caused the animals to lose weight, brought about increased cholinesterase activity, changed muscle antagonists motor chronoxy, and disturbed the protein fraction ratios, and the process of porphyrin metabolism. In 0.02 mg/m^3 con-

centration, toluylene diisocyanate had no observable unfavorable effects on the organism of the exposed experimental rats.

5. Based on the results of the present investigation, it is recommended that 0.02 mg/m^3 be accepted as the maximal average 24 hour toluylene diisocyanate concentration in atmospheric air.

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Labor and Sanitary Health Conditions in Phthivazide Manufacturing Plants

pp. 24-28

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Pharmaceutical products such as PASC, phthivazide, metazide, larusan, and others are now being manufactured on a commercial scale. Literature contains insufficient information regarding the processes used in the production of anti-tuberculous pharmaceuticals, especially in relation to sanitary hygienic labor conditions. In this paper, the author reports on a study conducted in plants producing phthivazide with special emphasis on sanitary-hygienic labor conditions. The report presents observations made in a plant producing isonicotinic acid, which is an intermediate product of phthivazide manufacture. Phthivazide results from the reaction of isonicotinic acid with thionyl chloride which forms first chloranhydro-isonicotinate hydrochloride which is converted into ethyl-nicotinate-hydrochloride; the reaction mass is neutralized by an alkaline solution, which yields amyl nicotinate; from which hydrazide of isonicotinic acid is formed upon the addition of hydrazine hydrate. Hydrazide of isonicotinic acid is

used in the final synthesis of phthivaside. The resulting mass is centrifuged, desiccated, sifted and filtered. In the production of isonicotinic acid and phthivaside the air in the working premises may become polluted with vapors of picolines and of hydrazine hydrate; in some cases the air may also contain nitrogenous gases, sulfur dioxide, and fine particles of phthivaside and nicotinic acid. Table 1 presents concentrations in which the above mentioned pollutants can be found in the surrounding air. The method described by Dolgopolva and ogloblina in 1961 was used in this investigation. Picoline vapor was found in the air of the room in which γ-methylolpicoline was synthesized from components of β-picoline fractions used in the production of the intermediate products. Results of 8 analyses showed the presence of 0.012-0.032 mg/li of picoline, which is 2-6 times in excess of the maximal allowable concentration of this substance, and in one instance the concentration was 0.058 mg/li, or 12 times in excess of the maximal allowable concentration. A thorough investigation disclosed that picoline vapor was generated where β-picoline fraction components had been utilized in synthesizing the final product. Employees working at such points complained of continuous coughing. To obtain some relief the workers opened the doors which helped to disseminate the harmful substance and disturbed the temperature and humidity conditions in the working premises, especially during the fall and winter months.

Table 1.

Concentrations of poisonous gases and vapors in the air of working premises

Harmful components	No. of samples	Samples within MAC limits	Concentrations in mg/li		
			Maximal	Minimal	MAC
Picoline vapor	10	0	0,007	0,058	0,005
Hydrazine hydrate vapor	19	0	0,00016	0,008	0,0001
Nitrogases	24	17	0	0,03	0,005
Sulfur dioxide	20	17	0	0,06	0,02

Air pollution with hydrazine hydrate vapor was noted in the room where hydrazide-nicotinate had been synthesized. Analytical results indicated that most air samples contained the hydrazine hydrate pollutant in concentrations considerably exceeding the maximal permissible limits. Further inspection showed that the technological organization of some intermediary production stages was faulty; it was equipped with leaky vapor conduits, and constituted the main cause of surrounding air pollution with hydrazine hydrate vapor exceeding the maximal permissible concentration limit 10-25 times. This was further aggravated by the fact that the entire system of hydrozideisonicotinate production was antiquated and primitive. This was particularly true of the hydrazine-isonicotinate paste unloading which was done manually. This was equally true of the paste centrifugation.

Nitrogenous gases were formed as side products in the process of

γ-methylol picoline mixture oxidation which was done in a properly isolated installation. Most of the generated nitrogenous gases were trapped by passing them through a special absorption installation and the nonabsorbed residue was discharged into the atmosphere through a stack 50 m high, which adequately dispersed the original pollutant gas concentration. Chances for vapor leakage into the atmospheric air appeared during sample collection, loading of the activated charcoal, etc. Results of analyses established that where such operations had been performed the nitrogenous gas concentration in the immediate air ranged between 0.01-0.03 mg/li, or 2-6 times in excess of the maximal permissible concentration. Results of some analyses showed nitrogenous gas concentrations not exceeding the maximal permissible limit. Sulfur dioxide was generated during halogenation of the isonicotinic acid with thionyl chloride and during the thionyl chloride hydrolysis. It was present in 3 of 20 analyzed air samples in 0.03-0.06 mg/li, or 2-3 times in excess of the established norm. In all the instances observed, sulfur dioxide leakage occurred through the aggitator vacuum boxes. Generally speaking, making the production techology leakproof had a favorable effect and only on rare occasion was serious leakage noted.

Air pollution with particulate matter was noted mostly during the final stages of the antibiotic production. Analytical results showed that the particulate matter concentration in the surrounding air ranged between 8.2-20 mg/m^3 when the dry isonicotinic acid was poured from the drying pans into the collecting bags. Such a dust density prevailed only during the pouring of the final product which usually lasted between 15 to 20 minutes; when operation time was prolonged, the dust density in the air reached the concentration of 72.1 mg/m^3. Phthivaside dust concentration in the drying room air ranged between 9.1-33.5 mg/m^3, in the sifting room between 5.1 and 60.1 mg/m^3, and in the packing room between 7.8-37.5 mg/m^3. Highest phthivaside dust concentrations were found in the air during manual unloading of the driers, which usually lasted up to 30 minutes. Other operations, although manually performed, generated lower dust densities, probably due to the fact that the final product under those conditions contained considerable moisture. Where the open manual operations were of very short duration, phthivaside dust density in the air was also slight. Phthivaside dust of considerable density was found in the room of the shaker sifters where its range was 20.6-60.1 mg/m^3. The sifting operation in the plant under investigation was done manually in the open. In some instances the sifters were jacketed. This somewhat reduced the phthivaside dust concentration in the air, but added little to the solution of the basic problem.

Effect of phthivaside and isonicotinic acid dust on mucosae of the upper respiratory tract was studied next by examining some female employees who worked in the drying and packing rooms. Examinations consisted of anterior rhinoscopy, of the oral cavity, of the glottis, and of laryngoscopy. All workers were tested for taste and odor acuity. Results are shown in Table 2. Data in that Table show that no hypertrophic changes of the nasal, oral and throat mucosa had been noted in any of the examined workers; on

the other hand, subatrophic rhinopharyngitis was found in practically all women who worked in the plant 3-6 years. Six of the women workers had a lowered odor perception. The data here presented and discussed are not sufficient to warrant final conclusions, but they can be used as orientation values for more detailed future investigations. Picoline and hydrazine hydrate were the most toxic of the vapors generated in the phthivaside production complex. Picoline vapor toxicity is rated as high as that of pyridine vapor, and, as was indicated by M. L. Rylov in 1951, it also unfavorably and irreversibly affected the central nervous system. Hydrazine hydrate vapor produced anemia, hypocholesterolaemia and changes in the arterial blood pressure. The vapor also caused inflamatory processes in the conjunctiva and in the nasal pharyngeal mucosa, and occasionally produced temporary blindness. The above presented data and their discussion clearly point to the urgent need of adopting and introducing means of sanitization in the working conditions of the industry, aimed primarily at the prevention of air pollution with picoline and hydrazine hydrate vapors.

Table 2.

Mucous membrane changes in the upper respiratory and nasal passages of women working in an atmosphere of phthivazide and nicitinic acid dust

Initials	Age (Years)	Work Record (Years)	Nature of Dust	Mucous Membrane Changes: Nasal	Mucous Membrane Changes: Pharyngeal	Mucous Membrane Changes: Laryngeal	Odor Perception
Ch	32	6	Isonicotinic Acid Dust	c	c		Normal
I	45	6		a	c	c	Hyposmia
Z	47	4		c	c	—	"
B	46	3		c	c	—	"
P	56	6	Phthivazide dust	c	—	—	Normal
K	44	3		a	a	—	" "
K	32	3		c	c	c	Hyposmia
U	38	2		—	—	—	"
D	30	2		—	—	—	"
I	20	2		—	—	—	Normal

Note. a - atrophic changes c - subatrophic changes

In conclusion it is suggested that the crystalizer installations in the hydrazide isonicotinic acid synthesis room should be metallically encased and connected by means of conduits to the local ventilation system. It is also suggested that the presently existing general ventilation system be thoroughly modified and improved to accord with the latest principles of modern type of industrial space ventilation.

Repeated analyses had shown that hydrazine hydrate vapor concentrations in the air could be considerably reduced by improving the existing system of local ventilation. However, such reduction still failed to satisfy the official standards of air condition in working premises. Therefore, it

is suggested that the following basic changes be instituted in the phthivaside producing plant with undue delay: 1. Isolation and encasing of equipment used in the utilization of β - picolinic fraction components used in the intermediate steps of phthivaside production; 2. Installation of an interdepartmental pneumatic system for the distribution of isonicotinic acid and soda; 3. Introduce the use of automatic packaging machines in the final phthivaside production operations.

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Hygienic Aspects of Methylmercaptophos Spraying by Airplanes

pp. 28-34

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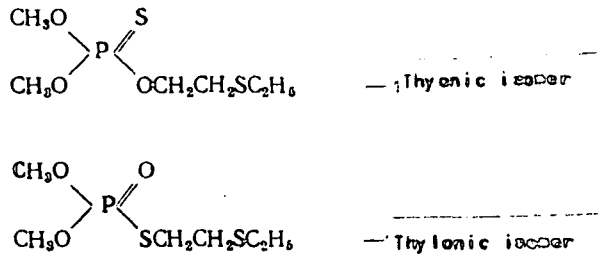
Mercaptophos, a highly toxic insecticide, has been used as a cotton plant insecticide spray since 1955. In most instances the cotton crops have been sprayed with mercaptophos from the air by specially equipped airplanes. Mercaptophos is a member of the phospho-organic group of compounds which includes metaphos, thiophos, carbophos, octametphyl, M-81, M-82, phosphacol, acetylurate, and many others. According to some USSR and foreign investigators mercaptophos is a neurotropic poison which attacked particularly the parasympathetic system. It was hoped that methylmercaptophos would possess effective insecticide properties and lower the general toxicity to man and animals; and, indeed, many investigators proved that this was the case.

In 1961 the present author studied the hygienic aspects of crop spraying with methylmercaptophos by means of specially equipped airplanes. The studies had been conducted during the months of April and May, which is the period of orchard spraying in the Crimean region, and in July and August, which is the cotton crop spraying time in central Asia. Methylmercaptophos, similar to mercaptophos, is a mixture of two isomeres, - thionic and thiolic, the formulas of which are as follows.



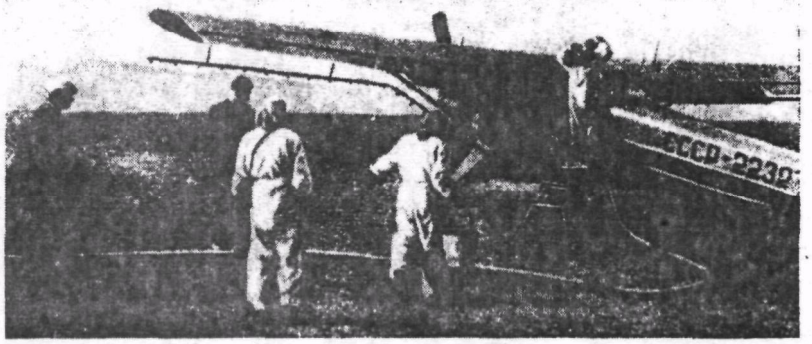
The technical concentrate of methylmercaptophos is a light to dark-brown fluid which emulsifies in water. It contains 30% of the thiolic and thionic isomeres and 70% of a surface active substance trade-named OP-7. In the process of isomerization the thionic isomer becomes converted to the more toxic thiolic isomer; isomerization proceeds much faster in methylmercaptophos than in mercaptophos. Temperature increase and polar catalytic agents markedly enhance the rate of methylmercaptophos polymerization. Methylmercaptophos concentrate is distributed by the chemical industry in 20 li containers.

Methylmercaptophos crop spraying is done by airplanes An-2 and Yak-12 and by helicopter Mi-1. The airplanes have been equipped with 2 types of spraying systems. In system No. 1 the spraying is done with the insecticide previously prepared for the purpose. In the second system insecticide mixture preparation and the spraying are done simultaneously in the air. Investigations made by the present author (1958-61) showed that the second method of atomized spraying was the more sanitary and offered more protection to the airplane and helicopter operating personnel. Orchard and cotton field spraying was usually done during the morning hours of 6 - 9, and in the evening during the hours of 17 - 20, when the wind velocity was below 4 m/second. The working emulsion contained 0.2-0.3% of active methylmercaptophos and was applied at the rate of 100 li per hectare, or the equivalent of 700-1000 g of the methylmercaptophos per ha. The airplane and helicopter tanks were filled with the spray material by motor driven pumps. Other tank filling operations were done manually in the airplanes and in the helicopters. (See Fig. 1)

Flights over the sections to be sprayed extended between 5 to 15 minutes, depending upon the distance from the aerodrum to the field to be sprayed. All personnel which participated in the crop spraying had been supplied with means for protection against spray inhalation; however, only the laborers made complete use of such protection equipment (see Fig. 2). Pilots and aviation technical personnel did not take advantage of the protection facilities because such equipment has been designed without taking into consideration specific work conditions. The rubber gloves were crudely designed and were too large. They lacked elasticity, and could not be used in finer operations usually performed by pilots and technical aviation personnel. Respirator F-46 was poorly designed and markedly reduced the pilot's field of vision. Technicians and manual workers were in contact with

the insecticide most intimately and for longer time in the course of a work day. Methylmercaptophos could enter the workers' system through inhalation or through skin absorption. The same routes of the insecticide entrance into the organism applied to the pilots, though to a lesser degree.

Fig. 1.



Filling the stationary (fixed) spray tank of aeroplane An-2 with methylmercaptophos and water

Fig. 2.

Filling the portable (removable) spray tank of aeroplane An-2 with methylmercaptophos and water

Determinations had been made also of the methylmercaptophos vapor concentrations in the air of the airplane and helicopter cabins and in the air surrounding other technical aero workers. One hundred and eighty test flights had been made, during which 300 air samples had been collected. Face and hand skin wash water samples had also been collected and tested for the amount of the insecticide deposited per unit area of the face and hand skin. Skin wash water samples had been collected before and after the air had been degased by spraying with an alkaline solution. Determinations were also made of the amount of methylmercaptophos which may have settled upon the compartment floors of the airplane or of the helicopter. This was done before and after the floors had been degased with a suspension of chloride of lime.

Twelve pilots, 10 aviation technicians and 10 manual workers had been examined clinically and physiologically. Tests included reviews of previous illnesses, complete opthalmological examination, sensitivity to light and to convergence, changes in the dermographic reaction, in body

temperature, in arterial blood pressure, and in the Aschner eyeball-heart reflex phenomenon, and other pertinent tests. Complete determinations were made of the morphologic and chemical blood pictures, including checks for prothrombin and cholinesterase activities. Chemical analyses of the air samples showed that the air in the airplane and helicopter cabins contained methylmercaptophos in concentrations exceeding the maximal permissible 0.0001 mg/li. The actual concentration of mercaptophos in the air depended upon the temperature, as seen from data presented in Table 1. Results also showed that mercaptophos concentration in the air depended to a considerable degree upon the velocity of the flight, especially so in the case of the helicopter. Thus, when the helicopter flew at the rate of 30 km/hr, the methylmercaptophos concentration in the cabin ranged between 0.00006 and 0.00979 mg/li, and when its flight velocity ranged between 50-60 km/hr, the methylmercaptophos concentration in the helicopter cabin ranged between 0.00019 and 0.00041 mg/li, as shown in Table 1. Methylmercaptophos vapor concentrations found in the air of the actual workroom are listed in Table 2. The data show that in 77% of the tests the mercaptophos concentration in the air of the airplane and helicopter operating rooms exceeded the concentration in the cabins by 150 - 860%, and in one case it was 460 times as high. This was probably due to the nature of the operation which required opening of the canisters containing the insecticide. Other contributing factors may have been complete absence of mechanization and of leakage preventing improvements.

Data yielded by analyses of the face and hand wash water showed that methylmercaptophos was present in all such samples in concentrations ranging from hundredths to thousandths of mg. Amounts of mercaptophos found per unit of face or hand skin surface indicated that the material settled upon the skin not as a result of careless handling of the toxic material, but as a result of methylmercaptophos vapor condensation upon the skin. A certain amount of mercaptophos was found in the wash water even before the airplane and helicopter began actual spraying. Wash water of external and internal airplane and helicopter surfaces and from instrument and panel surfaces contained tenths of mg of methylmercaptophos. Protecting devices failed to completely protect some surfaces from becoming polluted with condensed mercaptophos vapor, although the concentrations of the insecticide were somewhat reduced.

Work ground surfaces contained 0.00039-0.01560 mg of mercaptophos per 1 cm^3 of soil. Greatest insecticide concentrations were found on grounds where methylmercaptophos was stored and loaded into the airplane and helicopter. Soil samples collected at one of the insecticide storage grounds 15 days after degasing contained 0.00073 - 0.04953 mg per 1 cm^3 of soil.

Most aviation air spraying workers complained of headaches, vertigo, general weakness, heavy sensation in the head, restlessness, irritability,

Table 1.

Methylmercaptophos concentration in the air of aeroplane and helicopter cabins during orchard and cotton field spraying from the air

Type of aeroplane or helicopter	Methylmercaptophos in mg/li		Number of dates.		% of air samples with indicated concns.	Region and reason for air spraying
	Cabin					
	Pilot	Spray operator	Pilot's Cabin	Operator's Cabin		
Aeroplane An-2 equipped with a removable spray tank	0,00023—0,00056	0,00015—0,00244	9	9	100	Air spraying of Crimean orchards
Aeroplane An-2 equipped with a stationary spray tank	0,00020—0,00679	0,00014—0,00114	11	11	100	Air spraying of Crimean orchards
Aeroplane An-2 equipped with a removable spray tank	0,00011—0,00098	0,00045—0,00134	14	11	100	Air spraying of central Asian cotton plantations
Aeroplane Yak-12 equipped with removable spray tank	0,00018—0,00034	0,00017—0,00042	12	11	52	Air spraying of Crimean orchards
Aeroplane Yak-12 equipped with stationary spray tank	0,00016—0,00471	0,00018—0,00570	35	25	57	Air spraying of Crimean orchards
Aeroplane Yak-12 equipped with removable spray tank	0,00013—0,00044	0,00022—0,00058	25	10	100	Air spraying of central Asian cotton plantations
Helicopter Mi-1	0,00006—0,00979	—	33	—	100	Air spraying of Crimean orchards
" "	0,00019—0,00041	—	10	—	100	Air spraying of central Asian cotton plantations

Table 2.

Methylmercaptophos concentrations in the air of working grounds during air spraying of orchards and cotton fields

Points of air sample collection	Mg/li of methylmercaptophos		No. of determinations
	Minimal	Maximal	
Methylmercaptophos storage grounds	Trace	0.0460	13
Aeroplane parking grounds	»	0,00862	3
Methylmercaptophos loading	»	0,00273	6
Methylmercaptophos loading grounds when methylmercaptophos is poured into aeroplane spray tanks	»	0,00416	12

uncontrolled salivation, sleeplessness, loss of appetite, nausea, abdominal pains, sharp pains in the eyes, skin scaling and many other similar symptoms. The complaints were more persistent and more constant among workers using methylmercaptophos than among workers similarly employed in field and crop spraying with mercaptophos. Results of clinical and physiological examinations of the workers, as previously described, showed that most of the examined personnel had a drop in their maximal arterial blood pressure by 10-30 mm, and in the minimal by 10-15 mm. The pulse rate was reduced by 2-18 beats per minute, and body temperature dropped by 0.1-0.8 degrees. Localized dermographic reaction became more persistent; there appeared symptoms of increased stimulability of the sympathetic nervous system, and a lowering in the stimulability threshold of the parasympathetic branch of the nervous system. The total symptom-complex yielded by the clinical and physiological investigation indicated that workers employed in the airplane and helicopter spraying of crop fields with methylmercaptophos showed some pathologic changes in their central and vegetative nervous systems. Morphological and physical chemical blood changes were as follows: increase in the number of erythrocytes, in hemoglobin concentration, and in the color index; number of reticulocytes increased in some and decreased in others; the number of blood platelets also increased. The number of stab-form neutrophiles and of segmented nuclear neutrophiles increased in most of the pilots and aviotechnicians, and the number of leucocytes and lymphocytes decreased. In employees engaged in the aviochemical phase of field-crop spraying the symptoms became reversed, i.e., the number of stab-form and segmented neutrophiles were reduced, while the leucocytes and lymphocytes increased numerically. Blood coagulation time was shortened in most of the examined persons, accompanied by an increase in the prothrombin concentration. Red blood cell sedimentation time was shortened. Cholinesterase activity fell by 10-30%.

Conclusions

1. Noncompliance with safety regulations in field work with methylmercaptophos may lead to intoxication of the central and vegetative nervous systems accompanied by changes in the morphologic blood composition and in its physico-chemical properties. Accordingly, those who work with methylmercaptophos must be provided with, and must be compelled to wear, devices of individual protection against occupational intoxication.

2. Medical examination of pilots and chemical and technical workers

engaged in crop spraying must include blood cholinesterase activity determinations. No one should be assigned to work in chemical field and crop aerospraying with methylmercaptophos from the air without a preliminary medical examination.

3. Air field and crop spraying with methylmercaptophos should be done from airplane A-2 and YAK-12 which must be equipped with removable tanks containing the insecticide concentrate. All equipment of airplanes used in field and crop spraying must be mechanized and made leakproof.

4. During field and crop aviospraying the kolkaoz and sovkhoz administrations must provide workers employed on the chemical storage and distribution grounds with properly fitting individual devices for their protection against the toxic effects of the insecticide spray or vapor.

5. Airplanes and helicopters built for field and crop spraying with insecticides must be equipped with air conditioned systems for the removal or neutralization of the toxic insecticide vapor.

6. R A-59 is at present the best type of apparatus or respirator designed for the protection of workers against the inhalation of active chemical poisons.

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Separation of Ethylamine Traces from Ammonia Traces in the Air

pp. 49 - 53

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This paper is a report on attempts to develop a rapid quantitative method for the separation of ethylamine vapor traces from ammonia traces simultaneously present in the air. The method must be applicable to individual and continuous alkylamine determinations using direct colorimetry. Previously reported chemical methods for the separation of primary, second-

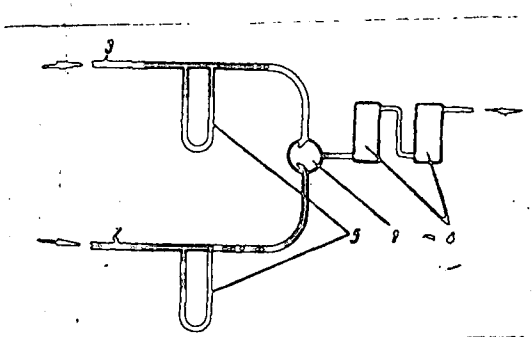
ary, tertiary amines from ammonia were developed specifically for the identification of large ammonia quantities. Thus, Francois developed a method in 1901 which was revised by other chemical investigators; the method was based on the property of yellow mercuric oxide to bind ammonia. However, it was found later that ammonia absorption by yellow oxide of mercury was accompanied by secondary factors which gave rise to considerable determination errors. For this reason, present attempts to use yellow oxide of mercury in the separation of ammonia traces were unsuccessful. Leone proposed in 1925 that ammonia be precipitated with sodium cobalto nitrate. This method was perfected by K. G. Mizuch and A. Ya. Savchemko in 1940. However, the precipitate thus obtained had to be washed, which made the procedure cumbersome and time consuming. Guinot, Bellier, and Isham in 1954 developed a method for the separation of primary and secondary methylamines from ammonia based on the property of formaldehyde to react in solution with primary and secondary amines, but not with tertiary amines. Ammonia was precipitated as hexamethylenetetramine and the trimethylamine and dimethylamine aldehyde derivatives were removed by distillation ever, monomethylamine formed a practically nonvolatile compound with formaldehyde which could not be separated from ammonia. In this connection S. Kolosov showed in 1936 that hexamethylenetetramine was formed in a mixture of gaseous formaldehyde and ammonia.

The present author found that inactive tertiary ethylamine was not the only one which failed to react with formaldehyde vapor on short contact; primary and secondary ethylamines, if present in the air in traces, also failed to react with formaldehyde vapor present in the air in high concentrations. Under similar conditions ammonia reacted with formaldehyde quantitatively. This property of differential reaction with formaldehyde formed the basis of the method here described for the separation of alkylamines from ammonia. The schematic drawing in Fig. 1 illustrates the principle of the method. By this method the air to be analyzed entered the apparatus at (2) and continued in the direction indicated by the arrow, while formaldehyde vapor entered the apparatus at (3) and also in the direction indicated by the arrow. The two gases entered mixing chamber (1). This converted ammonia present in the air into hexamethylenetetramine. As the reaction mixture passed through absorbers (4), containing an alkaline solution, the formaldehyde excess and acid air vapors became trapped and the ammonia containing air entered the air analyzers. Purification of ethylamine from ammonia and other air admixtures is accomplished in an apparatus schematically illustrated in Fig. 2. The air to be analyzed entered the T-shaped tube, divided into two currents flowing in opposite directions, - one part to be analyzed, and the other to react with formaldehyde.

The air to be analyzed moved at the rate of 70-80 ml/min. along channel (1) then through flowmeter (3), through capillary (4) entered gas mixing bulb (5) of 30 mm diameter. Capillary resistance at (4) helped to maintain the required ratio of flows. The air which was to react with formaldehyde was aspirated at the rate of 150-180 ml/min, through channel

(2), through flowmeter (6) and column (7) filled with silicagel, where it was freed from ammonia. It then entered glass tube (8) equipped with a porous glass plate 40 mm in diameter, and was bubbled through 35-40% formaldehyde solution; here it becamed absorbed by or mixed with the formaldehyde and entered mixing bulb (5). From mixer (5) the ammonia-free gas mixture was aspirated through spiral shaped absorber (9) filled with 300-400 ml of 30-40% sodium hydroxide solution; it then entered another cylindrically shaped ascarite-filled container 30 mm in diameter and 70 mm high. After passing through stopcock (1) it entered absorber (12), containing water, for final analysis. Air samples were collected as follows: the air was drawn through the stopcock and glass container (13) for 5-10 minutes. The air may be analyzed directly, quantitatively, for the amines by mixing it with a solution of o-nitrophenol, and making final determinations coloratometrically.

Fig. 1.

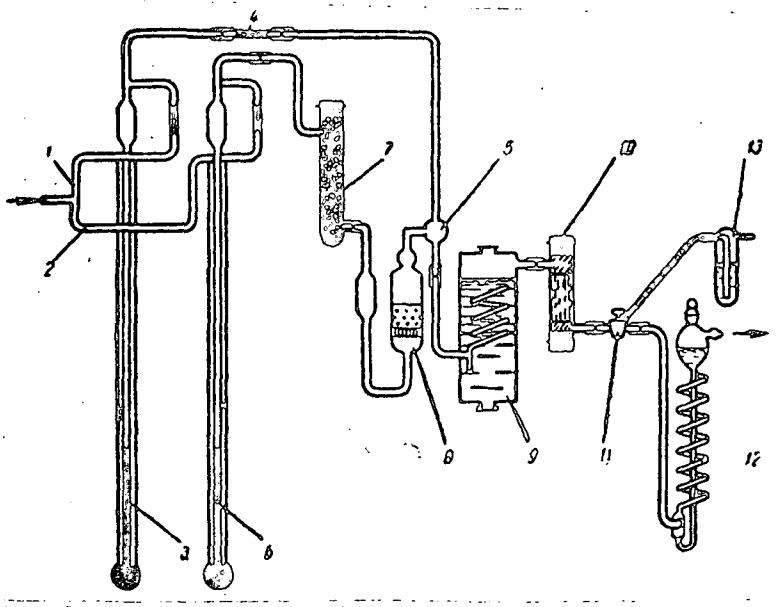


General plan of continuous purification of ethylamine traces from traces of ammonia and said gases in air currents.
1 - Gas mixer; 2 - tube for the delivery of analyzed air; 3 - tube for the delivery of formaldehyde; 4 - absorbers filled with alkaline substances; 5 - flow meters.

Indoor air samples should be collected with the aid of an air pressure device installed at the outgoing end of the apparatus connected via a T-shaped tube to absorber (12) and glass tube (13) in which the entire system is under air pressure. The special air pressure device may not be required. All parts of the apparatus should be made of glass or transparent plastic material, and the entire assembly must be absolutely leakproof. The flowmeters should be filled with mercury or with sodium hydroxide. Application of lubricating material must be scrupulously avoided. If all described specifications of apparatus construction and assembly have been complied with, then the time necessary for collection and analysis of an air sample should not exceed 5 minutes; in plants which operated on the basis of single shifts, reagents in the analytical apparatus should be changed only once, or at the most twice a month. Absorber (12) can be replaced by an automatic colorimetric gas analyzer constructed by M. T. Borok in 1957, replacing the working fluid with 0.1% solution of o-nitrophenol. In this way continuous control determinations can be conducted for amine concentrations in the air. Air purification check tests should be made with the aid of specially prepared gas-air mixtures containing mono-, di-, triethylamines and ammonia. The mixtures must be prepared with pure chemicals (gases) kept in steel cylinders. All precautions and preliminary surface drying and cleansing steps must be taken to ensure proper storage of the prepared gas-air mixtures. Amines are easily adsorbed by metallic surfaces; therefore, an excess of the gas-air mixture should be run into the cylinder upon first filling. Desorption of the amines will become noticeable when the pressure in the steel cylinder will drop to 20-10 atm. Concentration of amines and ammonia released

from the steel cylinders at 100-20 atm. pressure remained constant regardless of storage duration. Each gas-air mixture was analyzed by the combined and direct methods after passing through the purification installation.

Fig. 2.



Plan of laboratory apparatus for the purification and sample collection for the determination of the air contained ethylamines

1 - Delivery of air for analysis; 2 - delivery of air carrying formaldehyde; 3 - flow meter; 4 - capillary tube; 5 - gas mixer; 6 - flow meter; 7 - cylinder containing silicagel; 8 - a bubbler containing formaldehyde; 9 - alkali containing absorbers; 10 - ascarite containing cartridge; 11 - a 3-way stopcock; 12 - absorber for amines; 13 - a glass container

Samples had been taken from the compression steel cylinders by carefully opening the fine regulating petcock and by releasing the examined air at a slow rate for 60-90 minutes, thereby avoiding errors caused by the adsorption of amines and of ammonia by the valve surfaces. Air samples intended for combined analysis were released from the steel cylinders through U-shaped glass tubes filled with ascarite, and then through absorbers containing distilled water. Total quantity of bases was determined colorimetrically with the aid of o-nitrophenol; ammonia concentration was determined by the Nessler method, and the amines were determined by difference.

In making direct analysis the steel cylinder was connected to the previously described analyzer and the gas-air mixture was passed through it in the direction of glass container (13) for 10 minutes. Then stopcock (11) was turned so that the gas flow passed through absorber (12) which was filled with ammonia-free distilled water. At that time the timer recording seconds was switched into the system. The amount of analyzed air was recorded by the flowmeter and the stop watch. It amounted to 2-5 li; 6-15 li of air was passed at the same rate through absorber (12). Then petcock (11) was again turned so that the air flow passed through glass tube (13), or through an absorber installed in the place of it, and the time was recorded in seconds.

Concentration of amines in the absorber was determined colorimetrically in 8 ml of the sample to which 4 ml of 0.1% o-nitrophenol was added. Results obtained by the direct and combined analysis of the same gas-air mixture consisting of monoethylamine, ammonia, and air are listed in Table 1.

Table 1.

Monoethylamine determination in air containing ammonia

Sample No.	Combined analysis without the apparatus: μM/l of bases — Total bases colorimetrically with o-nitrophenol	Total by Nessler method	Amines by difference	Direct analysis upon emergence from the apparatus: Sample No.	μM/l of amine, colorimetrically with o-nitrophenol
1	0,60	0,18	0,42	1	0,42
2	0,62	0,19	0,43	2	0,40
3	0,62	0,20	0,42	3	0,41
4	0,63	0,20	0,43	4	0,43
5	0,61	0,21	0,40		
6	0,63	0,22	0,41		
7	0,64	0,22	0,42		
Averages . . .	,62	0,20 (0,0034 mg/l)	0,42 (0,019 mg/l)		0,42 (0,019 mg/l)

Data listed in Table 1 show that deviations in separate direct colorimetric determination magnitudes yielded by the combined analysis; in either case the magnitudes were within the limits of experimental error. Average values of 4-8 analyses made by both methods in each of the investigations are listed in Table 2.

Table 2. Ethylamine determination in air containing ammonia

Composition of bases in the air	Concentration of bases in the air (averages of 4 - 8 analyses): Combined analysis of the mixture — Total bases (μM/l)	Ammonia (μM/l)	Amines by difference (μM/l)	Direct analysis after purification by apparatus (μM/l or (mg/l))	Error: Absolute in μM/l	Relative %
$C_2H_5NH_2+NH_3$ . . .	3,28	0,08	3,20	3,23 (0,144)	+0,03	+0,9
$C_2H_5NH_2+NH_3$ . . .	0,62	0,20	0,42	0,42 (0,019)	0,00	0,0
$(C_2H_5)_2NH+NH_3$ . .	1,36	0,03	1,33	1,32 (0,096)	−0,01	−0,8
$(C_2H_5)_2NH+NH_3$ . .	0,88	0,39	0,49	0,50 (0,037)	+0,01	+2,0
$(C_2H_5)_3N$	0,23	0,00	0,23	0,23 (0,023)	0,00	0,0
$(C_2H_5)_3N$	1,02	0,00	1,02	1,01 (0,102)	−0,01	−1,0
$(C_2H_5)_3N+NH_3$ . . .	2,43	1,61	0,82	0,86 (0,87)	+0,04	+4,9
NH_3	1,17	1,17	—	0,00 (0,00)	0,00	
NH_3	—	10,7	—	0,01 —	+0,01	

Data in that Table show that ammonia present in the air alone and in combination with amines in 0.03 - 10.7 μM/li (0.0005 - 0.182 mg/li) was quantitatively absorbed during the air sample aspirations while the three ethylamines, including the most active primary member, passed through the apparatus quantitatively and could be determined colorimetrically when present in the air in 0.42 - 3.20 μM/li (0.019 - 0.144 mg/li concentrations. In one instance only did the difference between the direct and combined determination procedures amount to 4.9%.

Conclusions

1. The brief simultaneous presence in the air of low ammonia concentrations and of formaldehyde vapor excess elicited an interaction between the two substances which resulted in the formation of hexamethylenetetramine. No interaction occurred between mono-, di- and triethylamine and formaldehyde gases simultaneously present in the air.

2. On the basis of the above described differential reaction a procedure and a laboratory apparatus have been developed for the continuous quantitative purification of the examined air and for the separation of ethylamine from ammonia simultaneously present in the air.

3. Direct single or continuous automatic ethylamine determinations in the air can be made by the new analytical procedure and apparatus.

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Method for the Determination of Carbon Tetrachloride in Intestinal Juice

pp. 55-56

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Carbon tetrachloride (CCl_4) is a heavy colorless fluid which has a sp. gr. of 1.594 and a b.p. of 76.7°; it is widely used in the chemical in-

dustry. N. V. Lazarev described carbon tetrachloride as a toxic substance which caused grave damage to the liver and kidneys. Carbon tetrachloride frequently contained admixtures of carbon disulfide, hydrogen sulfide, hydrochloric acid, and organic sulfides. The toxicity of carbon tetrachloride and its accumulation in the animal organism are reasons for its frequent determination in biological specimens. In this paper the author reports on attempts to develop a method for the determination of carbon tetrachloride in intestinal juices. A search of the literature indicated that no such method has been developed and described.

It is well known that chlorinated hydrocarbons reacted with pyridine in acetone at alkaline pH, producing a colored compound. This reaction formed the basis of the present investigation. Intestinal juice has been obtained from animals in which an experimental intestinal fistula had been produced. The intestinal juice was filtered and centrifuged to remove adventitous material. The procedure was as follows: 3 ml, or less, of intestinal juice was placed into a test tube to which 1 g of NaCl was added, and the test tube vigorously shaken until the NaCl saturated the intestinal juice. Then 3 ml of acetone was added, and the test tube centrifuged for 5 minutes at 3000 rpm, or the tube was allowed to stand for 60 minutes until complete separation had taken place. The upper acetone layer was then carefully poured into another test tube to which 2 ml of 20% NaOH and 2 ml of pyridine were added. The test tube was then heated to 70° in a water bath. After the solution has cooled and the rose color has developed, the intensity of the color was compared with a standard color scale. The standard six-tube scale was prepared from a stock solution of 10% CCl_4 in acetone. The first tube contained no CCl_4; the second tube contained 0.005, the third 0.01, the fourth 0.02, the fifth 0.04 and the sixth 0.06 mg of CCl_4. The sensitivity of the reaction was 0.005 mg CCl_4 in one ml of acetone. Chloroorganic compounds interfered with the reaction. The standard color scale should be prepared by using as the diluent an analogue of gastrointestinal juice free from carbon tetrachloride and from other chlorinated hydrocarbons.

Conclusions

1. A method has been developed for the determination of carbon tetrachloride in gastrointestinal juice, based on a reaction the sensitivity of which is 0.005 ml of CCl_4 in 1 ml of acetone.

2. Chlorinated hydrocarbons interfered with the reaction.

3. The test can be performed with 3 ml of the gastrointestinal juice. Carbon tetrachloride should be extracted from the juice with acetone and NaCl; the formed precipitate should be removed by centrifugation.

Experimental Study of Atmospheric Air Pollution with 3, 4-Benzpyrene in Industrial Sections

pp. 65-69

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Recently atmospheric air has been investigated for the presence of cancerogenic hydrocarbons by the fluorescent-spectral analysis. Such studies have been conducted mostly for the detection of 3,4-benzpyrene in the air. The earliest studies for the detection of 3,4-benzpyrene in atmospheric air had been conducted in the USSR in 1948 by B. P. Gurinov and others. In the winter of 1954-1955 P.P. Dikun, L.M. Shabad, and V. N. Norkin conducted similar detailed investigations in Leningrad. However, these investigators restricted their studies to the detection of 3,4-benzpyrene in sedimented air dust samples. Results of tests previously conducted by the fluorescent-spectral method showed that the concentration of 3,4-benzpyrene ranged between 0.018 and 0.08 γ per 100 m^3 of atmospheric air.

The purpose of the present investigation was to obtain more complete and up-to-date information on the state of Moscow atmospheric air pollution with 3, 4-benzpyrene, on the basis of which rational sanitation means could be developed for the protection of atmospheric air against pollution with 3,4-benzpyrene. The work was conducted under the supervision of Prof. L.M. Shabed. The first investigation was centered around industrial enterprises which had been only slightly surveyed with regard to the presence of 3, 4-benzpyrene in the air and which, by the nature of their processing and production, lent themselves to the introduction of appropriate sanitization measures. 3, 4-benzpyrene determinations were made by the P. P. Dikun fluorescent spectral method in the following order: in the primary raw material, in the intermediate and final products, in dust settled from the atmospheric air, and in dust collected by aspiration. Analyses were conducted in the physico-chemical laboratory of the Moscow Sanitary Epidemiological Station.

The raw material used in the investigated plants contained different quantities of tarry substances and presumably contained 3,4-benzpyrene in varying concentrations. Tests for the presence of 3,4-benzpyrene were made with pitch, crude oil bitumens, different types of soot, crude oil coke, heat processed anthracite, many other intermediates, by-and end-products of the plants under investigation. The number of examined products amounted to 31. Samples of coal tar and pitch collected at different plants contained 3, 4-benzpyrene in the range of 0.1 - 1.2%. No 3,4-benzpyrene was detected by the analytical method in the crude oil bitumen. Ten types of soot had been examined, and it was found that 6 types contained 3,4-benzpyrene in the

range of 0.005 - 0.0003%, which included lamp black, gas soot, and furnace soot. No. 3,4-benzpyrene was detected by the method in the remaining 4 types of industrial soot. 3, 4-benzpyrene was also found in the crude oil coke, in pyrolyzed anthracite, and in several other by-products. Results also showed that crude oil coke of different trademarks used in the same industrial plant contained 3,4-benzpyrene ranging between 0.0008 and 0.007%. The same was true of 3,4-benzpyrene content in differently labeled soot of the same plant.

The above results caused the present authors to assume that the plants under investigation discharged into the atmospheric air some concentrations of 3,4-benzpyrene. Maximal 3,4-benzpyrene concentrations were found in the dust discharged by one of the plants into the atmospheric air. Survey was made of atmospheric air pollution with 3,4-benzpyrene at different city sections, where dust sedimentation samples had been collected in locations of the "Tol'prom" electrode plant, the "Krasnyi Bogatyr" rubber plant, and the like. Settled samples had been collected during the months of April and May, 1960, from cracked windows and other breaks and openings of nearby dwellings. Most samples had been collected inside the dwelling rooms.

Results showed that greatest air pollution with 3,4-benzpyrene occurred in the proximity of processing and production plants which used coal tar and crude oil coke as their raw materials. It was found that the maximal 3,4-benzpyrene concentration was contained in dust settled from the atmospheric air in the vicinity of plants which used the above mentioned products in their production and manufacture. Thus, the dust settled in the proximity of the "Tol'prom" plant contained 0.009 - 0.049% of 3,4-benzpyrene, and the dust settled in the vicinity of the elctrode plant contained 0.0013 - 0.01% of 3,4-benzpyrene. Concentrations of 3,4-benzpyrene were considerably lower in dust which penetrated into the Moscow Sanitary Epidemiological Station, probably due to the fact that no production or manufacturing plants of the above described character existed where the Station was located. In summary, it can be stated that 3,4-benzpyrene concentrations varied in the settled dust samples from thousandths to hundredths of per cent, depending upon the nature of the existing air pollution sources. On the basis of the first investigation stage sanitization measures have been recommended for some of the plants which had been instituted by order of the Chief Physician of the Moscow Sanitary Epidemiological Station. As a result, the "Tol'prom" plant discontinued the use of 3,4-benzpyrene-containing raw products, replacing them with 3,4-benzpyrene-free raw materials. Other air pollution protection measures have also been instituted.

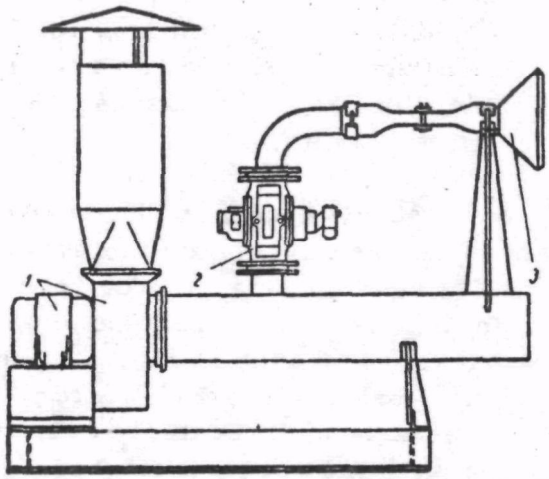
In the second stage of the investigation tests have been conducted for the direct determination of 3,4-benzpyrene in the air. Investigations conducted in England in 1949-1951 had shown that annual 3,4-benzpyrene concentrations in the air ranged between 1.3 and 4.6 γ per 100 m^3 of air. At

such concentrations the quantitative determination of 3,4-benzpyrene in the air by the fluorescent-spectral analysis required the aspiration of thousands of cubic meters of air for a single analysis. It was also necessary to catch the most highly dispersed air dust which contained 3,4-benzpyrene. This could not be done with the usual type of cotton or filter paper aspirators, and required the preliminary testing of many samples of synthetic tissues. A specimen labeled FPA-15 gave the desired positive results.

A special aspirator was installed in the Moscow Electrode Plant for the collection of highly dispersed dust. This plant used pyrolyzed anthracite, crude oil coke, soot, coal tar and graphite as its raw materials. The technological procedures consisted in grinding the anthracite or the crude oil coke. The ground material was then calcined in gas heated furnaces at 1300°. The dust formed in this process was caught by a filter-bag installation. After the heated crude-oil coke had cooled to 80° it was ground repeatedly to a fine powder. Dust generated in this process was trapped by a filter bag installation. The fine coal powder was mixed with other materials to form the final production mixture. The air in this production department was passed through a purification system consisting of a cyclone and bag filter or electric precipitator. The previously prepared basic powder was then mixed with thick coal tar or coal pitch at 120°, and was then directed into the hydraulic press department for final manufacture of the electrodes. After this the electrodes were calcined at 200-1300°, and coated by a layer of finely ground coke. The assembly in which the foundry coke powder was prepared was equipped with a bag filter installation. Dust and sublimated tar particles formed in the furnaces were trapped by 4 electrostatic precipitators. The final electrode shaping was done mechanically. The dust thus generated was trapped by a two-stage cyclone and bag filter installation or by wet scrubbers and returned to the production department.

The aspiration installation is schematically shown in Fig. 1 and photographically in Fig. 2. As mentioned before, the Petryanov filter tissue FPA-15 was used in this dust trapping apparatus. Its filter area is 314 cm^2, and the air is aspirated at the rate of 10-20 m^3/hr, or at the rate of 0.5-1 li/min. per 1 cm^2. I.I. Gusarov and V.K. Lyapidevskii found in 1948 that at air aspiration rate of 12.1-12.8 li/min. per 1 cm^2 through filter tissue FPA-15 there occurred an 8.4% slip-through of the air suspended dust. In the present investigation the air was aspirated through the synthetic tissue at a rate of 0.5-1 li/min. per 1 cm^2, so that the amount of slip-through dust was negligible. The installation used in this investigation possessed the advantages of uninterrupted operation over long periods of time usually required for the aspiration of great air volumes even at higher temperatures with a high degree of reliability. It was necessary to aspirate 2000-3000 m^3 of air over a period of 5 days in order to obtain an adequate sample for a reliable quantitative 3,4-benzpyrene determination in the aspirated air. The amount of dust collected during such an aspiration ranged beteen 0.2 and 1 g.

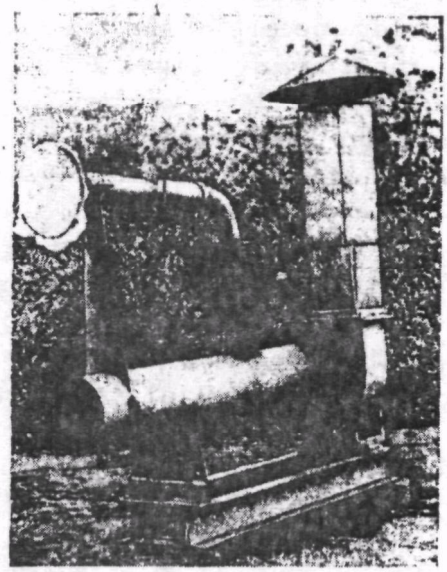
Fig. 1.



Plan of apparatus for the collection of air samples polluted with 3,4-benzpyrene

1 - Electric ventilating fan; 2 - Gas meter PS - 40; 3 - Funnel shaped air blower

Fig. 2.



General view of apparatus for air sample collection.

During the months of August-November of 1961, 13 samples had been collected as above described. Data in the Table show that 3,4-benzpyrene concentrations were within the range of 0.4 and 2.33 γ per 100 m^3 of air. Data in the Table also show that in only 4 of the 13 samples was the 3,4-benzpyrene concentration below 1 γ per 100 m^3 of air. In most cases the 3,4-benzpyrene range was between 1 and 2.33 γ per 100 m^3 of air. It is significant that the increase in percent of tar was paralleled by an increase in the amount of 3,4-benzpyrene in most samples. The 0.4-2.33 γ of 3,4-benzpyrene per 100 m^3 of air considerably exceeded the 0.018 - 0.08 γ per 100 m^3 found by B. P. Gurinov in 1957 in Moscow air. This can be explained by the fact that the sample collecting device used in the present investigation was of higher performance efficiency.

Results of aspiration collected atmospheric air samples

Sample No.	Time of Air sample collection	γ100 M^3 of 3,4-benzpyrene in the air	% of tar in the atmospheric air dust
1	21/VII—2/VIII	1,10	—
2	2/VIII—10/VIII	0,94	3,20
3	10/VIII—19/VIII	0,54	1,80
4	19/VIII—24/VIII	1,59	4,30
5	24/VIII—29/VIII	0,40	1,00
6	29/VIII—4/IX	2,10	5,20
7	4/IX—15/IX	1,10	—
8	21/IX—26/IX	1,60	—
9	26/IX—2/X	1,90	9,50
10	2/X—7/X	1,90	7,54
11	7/X—12/X	0,52	—
12	18/X—24/X	0,10	8,46
13	24/X—31/X	2,33	9,30

Note. Range of air sample collection time 120 - 215 hours. Range of aspirated air 735 - 2987 m^3

Conclusions

1. It has been established that some raw materials, intermediate and final products used or manufactured by the investigated industrial plant contained detectable quantities of 3,4-benzpyrene; samples of settled dust collected in the proximity of the investigated plants also contained detectable quantities of 3,4-benzpyrene.

2. Samples of aspirated atmospheric air collected on the electrode plant grounds during August-November of 1961, contained 3,4-benzpyrene in 0.4-2.33 γ per 100 m^3 of air.

3. On the basis of this orientation investigation and sanitary-hygienic examinations, certain sanitization and air pollution protection means have been recommended and instituted in the investigated plants. The present report presents results of the first stage of a general investigation to be conducted in the future on a broader and profounder scale.

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The Toxicology of Refrigerant Freon - 12

pp. 95-97

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Freon-12, which is dichlorodifluoromethane (CF_2Cl_2), is widely used as a refrigerant. The advantage which this reagent possesses from a practical viewpoint lies in the fact that in addition to its thermodynamic properties it is characterized by chemical inertness and noninflammability, as shown by G. Z. Yakovkin in 1956. Freon-12 is a gas which possesses a slight specific odor. It becomes odor perceptible in concentrations of 20% or more by volume, or 1080 mg/li. Freon-12 decomposes at a temperature exceeding 400° with the formation of hydrogen chloride, hydrogen fluoride, and a small quantity of carbonyl chloride, as shown by O. D. Khalizova and E. I. Vorontsova in 1952. It is generally believed that freon-12, being an inert gas, possessed no toxic properties under normal conditions of use, but in concentrations exceeding 30% by volume, or 1620 mg/li it manifested early signs of intoxication, not as the result of its own toxicity, but as the result of created oxygen insufficiency in the surrounding air. At the same time, some reports appeared in the literature pointing to some toxic properties of freon-12. Lester, Greenberg and others reported in 1950 that freon possessed certain narcotic properties, while Brenner in 1937 concluded, on the basis of his experiments, that freon-12 was a central nervous system depressant. Dalhamm in 1958 and Mendelhof in 1952 reported on cases of intoxication with products of freon-12 decomposition which resulted in fatalities. This may have been caused by some source of temperature rise which resulted in the

decomposition of freon-12 into the previously mentioned components. Freon poisoning also occurred during the repair of freon operated refrigerators, during the use of acetylene torches, and during the use of insecticide bombs in which freon-12 was used as the spraying agent.

The aim of the present study was to investigate the toxicity of freon-12 in the absence of oxygen insufficiency. For this purpose experimental conditions have been created under which oxygen concentration had been maintained at 20-22% by volume. White male mice weighing 20 g were placed into 100 liter exposure chambers. The oxygen and carbon dioxide concentrations in the exposure chambers were kept under control at 19.5-22.3 and 0.38-0.8% correspondingly. The air in the exposure chambers was kept in constant motion by small fans. Mice were exposed to freon-12 vapor for 3 hours in experiments designed for the determination of its lethal concentration, and for the determination of its threshold effect concentration, as indicated by the loss of conditioned defense reflexes during exposure to inhalation. Early signs of poisoning appeared in the experimental mice at freon-12 concentration 30% by volume, or 1620 mg/li. Freon-12 inhalation in concentration of 30% for 15 to 20 minutes elicited in the experimental animals motor stimulation followed by immobility. The animals became placid, and respiration became rapid. At freon-12 concentration 40-60% by volume, or 2160-3240 mg/li, the clinical picture of poisoning became sharply defined. The stimulation period was shortened to 1-3 minutes. The experimental mice soon developed a tremor, and fell into a narcotic sleep which persisted to the end of the experiment. At 61% by volume, or 3294 mg/li of freon the animals died. LD_{50} at 3 hours exposure amounted to 62% by volume, or 3348 mg/li; under similar conditions 66% by volume, or 3564 mg/li of freon was the LD_{100} dose. Results of these experiments clearly showed that freon-12 per se possessed toxic properties and proved lethal to experimental animals even in the presence of oxygen sufficiency in the surrounding air.

Effect of freon inhalation on positive and negative conditioned reflexes was tested by the procedures described on numerous occasions by previous investigators. Results showed that in 10-20% by volume, or 540-1080 mg/li, freon-12 elicited clearcut disturbance in the experimental animals conditioned reflex activity, as shown by the lowered percentage of response to conditioned stimulation. At 5% by volume, or 270 mg/li, no break was noticed in the conditioned reflex activity of the exposed experimental animals.

Conclusions

1. Information found in the technical literature regarding the biological inertness could not be confirmed scientifically. Experiments with white mice showed that freon-12 elicited shifts in the organism's functions following a single exposure to the inhalation of air containing 6% by volume, or 324 mg/li, of freon or more, even in the presence of complete oxygen sufficiency.

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NO. 7, JULY

Hygienic Determination of Sanitary Clearance Zones Between Residential Developments and Animal Husbandry Farms

pp. 7 - 11

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Agricultural industries, including extensive animal husbandry farms have been recently moving into residential regions. Some kolkhozes and sovkhozes have already begun to construct facilities for the maintenance of 800-1000 cows and 5000-15000 hogs. The present 200/m standard is applicable to sanitary hygienic clearance zones between residential developments and animal husbandry farms is based on a maximum of 400 heads of cattle. Therefore, it becomes imperative to define new standards for sanitary clearance zones in relation to animal husbandry farms of the size and capacity which are now in the process of development and organization. It is reasonable to assume that the increase in size and capacity of animal husbandry farms will be followed by worsening in the environmental conditions. A. A. Kirpichnikov noted in 1957 that the unpleasant specific odor emanating from large swine-breeding farms extended over an area of 700 m radius. M. M. Uvarov and L. F. Tulyakova noted in 1961 that the sanitary clearance zones for large animal breeding farms should not be less than 500-1000 m wide. In searching for a solution of the problem related to rural sanitary clearance zones factors of economics and convenience must be taken into consideration. It cannot be doubted that the localized development of a village has its positive aspects since the shortening of water supply, sewage, and other engineering systems of roads and other communication means add to the comfort, convenience and efficiency of village dwellers. The fact that it is mo-

difficult to manage and operate distantly located farms, especially in bad weather, should also be given serious consideration. Nevertheless, the width of a sanitary clearance zone must be based primarily on basic sanitary hygienic considerations.

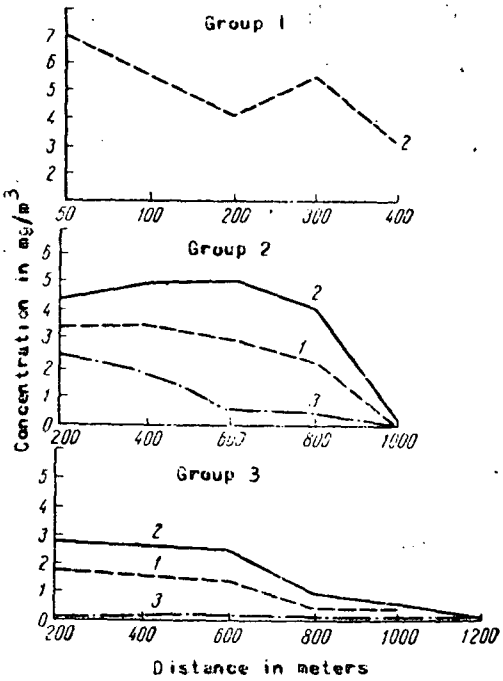
In this connection it was felt that recommendations made regarding the width of sanitary hygienic clearance zones for farms of different profile and different numbers of cattle heads must be based on a knowledge of the zonal air and soil pollution distribution in the proximities of hog breeding and dairy farms organized within the last several years. Such investigations had been conducted in 24 animal husbandry farms in the Saratov, Volgograd, and Moscow regions. Soil samples and air samples had been collected at distances ranging between 50 and 1000 m for the determination of maximal single ammonia concentrations. Sample collection and analytical procedures were conducted by the usual methods. Records were kept of the temperature, wind direction and velocity; simultaneously organoleptic tests were made to determine distances to which perceptible ammonia odor spread over the entire neighborhood.

Bacteriological studies of the air had been conducted by the Krotov aspiration method and by the open Petri dish method. A total of 156 bacterilogical air tests had thus been made. Soil samples collected at the same points were analyzed for the presence of ammonia, nitrites, nitrates, and chlorides. At the same time, special questionaires had been distributed among 500 persons residing in the vicinity at different distances from the farm. Distances to which flies migrated from the farm were determined by the luminescent method. Flies were trapped inside of village residences with the aid of strategically placed fly paper. The investigated stock farms were divided into 4 groups. Hog breeding farms of up to 100 heads belonged to group 1, farms of 1000 to 3000 heads belonged to Group 2, and those of 4000 -13000 heads belonged to Group 3. Cattle breeding farms usually pastured 200-800 heads and were classed in Group 4. It was noted that farms of Groups 3 and 4 were well-organized, well-mamaged, and the animals were kept in a relatively clean and sanitary condition. However, sovkhozes "Krasnokutskii" and "Vol'novsk" made no special provision for manure disposal; it was merely piled up close to the cattle barn. The pasture grounds of hogsovkhozes "Temp" and "Vydvizhenets" were heavily covered with hog manure and flies freely proliferated in the farm surroundings.

Analyses of atmospheric air showed that within a radius of 400 m of farms belonging to Group 1 ammonia concentration was considerable. Maximal concentrations in the air of farms belonging to Group 2 were found in the 400-600 m zone, while in farms belonging to Group 3 maximal ammonia concentrations were found in the 600 m zone, as shown by curves in Fig. 1. Lowest ammonia concentration in the air was found in the vicinity of the sovkhozes "Belaya Dacha", which was the most extensive, the best managed and the most sanitarily maintained. As the distance from the farm increased, the ammonia concentration in the air decreased, so that at a distance o

800-1000 m from the farm only a trace of the ammonia could be detected. But the specific odor of ammonia was still perceptible at 1000 m from the farm.

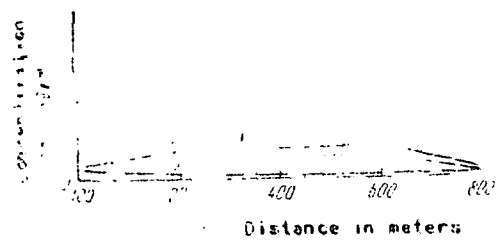
Fig. 1.



Ammonia concentration in atmospheric air near the hog farm.
I Farms and territories maintained in poor sanitary condition; 2 - Sanitary conditions better than in 1; 3 - Good sanitation and cleanliness

In the case of farms classed as Group 4 slight concentrations of ammonia had been found in air samples collected at a distance of 200 m, from the well maintained dairy farm "Zarya Kommunizma". On the other hand, the manure piles accumulated in the sovkhozes "Vol'novskii" and "Krasnokutskii" seriously affected the sanitary condition of the atmospheric air, as shown by curves in Fig. 2. Air samples were collected in some sovkhozes along 2 radii from the farm. One of the radii crossed the green sanitary clearance zone. Analysis of air samples showed that air pollution seldom extended beyond the green zone. Organoleptic tests showed no perceptible traces of odor coming from the animal breeding farms. A. A. Kirpichnikov showed in 1957 that the presence of a sufficiently wide green clearance zone reduced the specific farm odors by 17-20%. Residents of sovkhozes verified the positive effect of green sanitary clearance zones and stated that the unpleasant odor became non-perceptible as soon as the planted trees reached sufficient height. Results of the tests and observations, also answers to questionnaires clearly indicated that the proper management, cleanliness, and general maintenance of a farm, plus the introduction of a green sanitary clearance zone, played a substantial role in lowering the air pollution around the residential area.

Fig. 2.



Ammonia concentration in atmospheric air in the proximity of milk farms.
Designations are the same as in Fig. 1 above

As previously mentioned, bacteriological investigations had been conducted in the atmospheric air surrounding the animal breeding farms by the aspiration and sedimentation methods. Results showed that within a radius of 800 m from the large hog breeding farm "Zarya Farms" the air contained thousands and even tens of thousands of microorganisms per 1 m^3 air, as shown by the aspiration method, and per 1 m^2 area, as shown by the sedimentation method. The suspended bacterial counts became lower at 800 m from the farm. Results of similar bacte-

iological tests conducted in surroundings of smaller hog breeding farms showed the presence of hundreds and thousands of microorganisms in the air. In the case of poorly managed and improperly maintained hog breeding farms bacterial air contamination extended even beyond 1000 m. Counts of thousands and tens of thousands of microorganisms per 1 m^3 of air had been recorded at distances of 100-200 m from the dairy farms. However, in the case of well-managed and sanitarily maintained dairy farms the bacterial air density dropped considerably at a distance of 400 m from the farms. No such reduction in the bacterial air population was noted 400-600 m from farms in which the manure was stored improperly.

Atmospheric air pollution with microorganisms, with ammonia, and other unpleasant odors caused especially by poorly maintained hog breeding farms created unsanitary and unpleasant living conditions to the surrounding urban population, a condition which must be corrected by instituting appropriate sanitary hygienic measures. Answers to the previously mentioned questionnaires contained many complaints of unpleasant odor and fly infestation coming from the animal breeding farms. Such complaints came from practically 100% of persons residing 200-400 m from the investigated farms. Number of complaints became reduced with increase in the distance from the farms under consideration. Fluorescent-marked flies were found in large numbers in the 400-600 m zone and occasionally fluorescent-marked flies were found within a radius of 800 m from the animal breeding farm.

Chemical analyses of soil samples collected on the animal breeding farms showed high concentrations of chlorides, ammonia, nitrites, and nitrates, clearly pointing to intense soil contamination with fecal matter. The intensity of such soil pollution abated as the distance from the farm increased. At 1000 m from the hog breeding farm the soil contamination became negligible. It should be noted at this point that the radius of soil contamination in the well kept and properly managed hog farms of sovkhozes "Belaya Dacha" and "Petrovsk" was relatively limited. In the case of the dairy farms substantial soil pollution reduction was noted at 50-100 m from the farm, and beyond 200 m the soil showed practically no signs of unusual contamination.

Conclusions

1. Animal breeding farms are sources of regional atmospheric air and soil pollution: (a) small farms with an animal population not exceeding 1000 heads and which are improperly managed and poorly maintained caused intense air and soil pollution within a radius of 400 m, while farms with an animal population of 3000-6000 heads under similar conditions showed intense soil and air pollution in the 1000 m zone; (b) in farms with a hog population of 4000-13000 heads which were relatively well managed and sanitarily maintained the above mentioned types of air and soil pollution were noted within the zone of 600-800 m; (c) in properly maintained dairy farms air and soil pollution, as above described, was noted in the limited radius of 200 m.

2. It is recommended that 600 m be adopted as the absolute minimal sanitary clearance zone for large well managed and properly maintained hog farms.

3. It is recommended that 200 m be specified as the minimal sanitary clearance zone for large dairy farms which are well managed and properly maintained from the sanitary viewpoint.

4. The above recommendations mandatorily imply forestation of the sanitary clearance zones.

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Experimental Data as a Basis for the Determination of Maximal Permissible Porophore ChKh 3-5 Concentration in the Air of Working Premises

pp. 18-23

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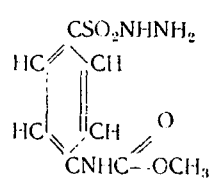
Light porous or foamy synthetic materials are being used on an increasing scale by different brances of USSR industries. Porous or foam rubber and plastic materials are produced with the aid of gas formers of an organic or inorganic nature. Best results for the production of evenly distributed pores and materials of lowest specific gravity are obtained with the organic pore or foam formers known as porophores. Organic porophores of varying chemical structure are being synthesized by many institutions by different chemical processes. A sulfohydrazide preparation known as porophore ChKh 3-5 is widely used in the USSR; it is a p-methylurethanebenzylsulfohydrazide of the following structural formula:



It is a light crystalline powder practically insoluble in water, soluble in acids, ethanol acetone and in NaOH solutions. At 160-170° one g of the porophore decomposes generating approximately 115 ml of gas, known as its gas number.

Working conditions under which ChKh3-5 is produced were studied at plant Mosplastkozh and at combine Iskozh of Kalinin City. The commercial product is in the form of a coarse powder; contains considerable moisture; it must be dried, reground and sifted before being used in the production of foam rubber or porous plastic material. In the process of drying and grinding to a fine powder, much of the material becomes suspended in the air of the production premises, mostly due to grinding and sifting on shaker screens, especially those manually operated. Work with finely powdered porophore is of short duration, amounting generally to 2-25% of the sifter's operating time, and depends largely on the rate of its daily consumption. The workers use gauze masks, or other types of masks over their mouth and nostrils as protection against inhalation of the porophore powder.

The commercial use of the porophore preparation is gradually increasing, yet practically nothing is known concerning its effect on the organism. The present author conducted special experiments for the determination of the porophore toxicity parameter by administering same to white mice and rats intragastrically. Experiments had been conducted in ten series of acute tests, using 100 experimental animals which received different doses of porophore powder suspended in water and starch medium. Results of the investigation established the following toxicity parameters to both animal species: LD_{100} was 0.5 g/kg, and LD_{50} - 0.35 g/kg, while the maximal tolerance dose was 0.2 g/kg. Experimental data had been processed by the Miller and Teintner method. Administration of lethal porophore doses elicited in the animals profound convulsion states followed by death several hours after the porophore administration. Some of the animals died two days after the substance administration. Application of an aqueous porophore paste to the skin of rabbits had no unfavorable effect on the organisms. Under industrial working conditions the air-suspended porophore dust entered the workers' organisms basically through the respiratory route; accordingly, 4 series of experiments had been conducted in which white male rats had been exposed to the inhalation of air containing different concentrations of suspended porophore dust. A total of 82 white male rats had been exposed to inhalation of the porophore preparation in the following concentrations: 20-30, 7-10, 2-4, and 0.6 mg/m^3. Experiments had been conducted in inhalation exposure chambers of 100 li capacity, into which air containing porophore dust was supplied on a constantly exchanged basis. Results of the first 2 series of inhalation tests with high porophore concentrations produced grave intoxication pictures and established the upper toxicity parameters. Each group of the two series consisted of 12 male rats. Control groups consisted of 10 rats. The rats were exposed to the inhalation of lower porophore concentrations for 4 hours, while exposure to the higher concentrations was limited to 1 hour.

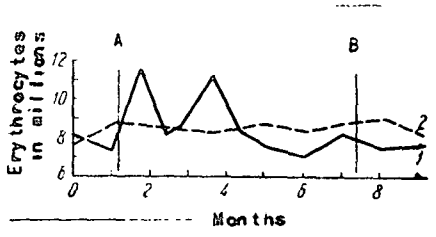
During exposure to the porophore dust inhalation the rats became restless, and some remained lying in a lateral position. Respiration rate of all experimental animals rose to 60-90 per minute, and all animals showed signs of hyperhidrosis. At the end of the exposure period clonic and chronic spasticity appeared in the animals accompanied by disturbed motor coordination, restlessness and motor stimulation. Between states of convulsion animals fell into a state of collapse. Death ensued within several hours after the onset of convulsions or collapse. Five of the 12 rats exposed to inhalation of air containing 7-10 mg/m^3 of the porophore and 8 of the 12 rats which inhaled 20-30 mg/m^3 perished. The surviving rats showed changes in the nervous system expressed as convulsions, slight or complete paralysis of the hind legs; the blood showed an increased number of Heinz bodies, which was still in evidence 2 months after the brief exposure to the polluted air. Thus, a single exposure to inhalation of 20-30 and 7-10 mg/m^3 of the porophore killed 13 of the 24 rats and developed signs of toxicity in the surviving experimental rats.

The purpose of the third series of exposure tests was to determine the effects of longer exposure to the action of porophore at concentrations of 2-4 mg/m^3. These were subacute experiments. During these experiments a test was developed for the colorimetric estimation of decomposed porophore ChKh3-5 molecules in the air. Twelve white rats had been exposed to the inhalation of the porophore dusts 4 hours daily for 45 days. Between inhalation periods rats were kept in individual specially constructed metallic cages to obviate the possibility of inhaling porophore dust during intermittent or rest periods. Appropriate controls had been conducted as previously described. Rats began to die on the 3rd or 4th day following exposure to the porophore containing air. All test animals died during 45 days of the experimental period. Observations conducted through the experimental exposure period showed gradual loss of weight with a final loss of 30-95 g, which pointed to profoundly disturbed metabolic processes. Five of the 12 experimental rats showed an increase in their erythrocytes from 11 million to 17 million per 1 mm^3 of blood. Osmotic erythrocyte resistance fell to considerably lower levels, and the number of Heinz bodies in the erythrocytes markedly increased. The leucocyte formula shifted as a result of increased number of neutrophiles. Incomplete and complete paralysis set in; latent period of conditioned reflex response became shortened. Some rats showed signs of urine retention and hyperhidrosis. Rats died manifesting grave symptoms usually noted in acute poisoning experiments. Macroscopic examination of autopsied animals showed acute plethora of all organs which appeared of raspberry color. The liver and other organs developed acute pathology signs; signs appeared of other anatomical disturbances. Thus, inhalation of 2-4 mg/m^3 of porophore ChKh3-5 for 45 days killed all experimental animals as a result of profound functional and morphological pathology.

An analysis of symptoms elicited in the rats exposed to inhalation of air containing concentrations of porophore ChKh3-5 clearly indicated that ex-

perimental animals developed a pathologic picture of hypoxia, and animals apparently died as a result of oxygen hunger. To verify this conclusion, a fourth series of experiments had been conducted for the purpose of determining the chronic effect of low porophore ChKh3-5 dust concentrations on the organism, and to obtain data on which to base recommendations for maximal permissible porophore dust concentrations in the air of working premises. Experiments had been conducted with 36 white male rats 12 of which served as controls. A regulating system was established by means of which it was possible to maintain an average 0.63 mg/m^3 porophore concentration in the exposure chamber with maximal/minimal fluctuation 0.3-0.9 mg/m^3. This experiment extended over 6 months, and was followed by a recovery period of 45-90 days. The general technique of these experiments was identical with one previously described. At the end of each 30 days, the experimental animals' functional state was tested, by procedures usually employed in similar investigations. Changes in the red blood picture began to appear during the first and second inhalation months. As in the case of the subacute experiments, substantial fluctuation in the number of erythrocytes began to appear, as shown by the fact that in 8 of the 12 animals the number of red blood cells rose to 10 - 13 million per mm^3 during the first 2 months of exposure. The color index and hemoglobin per cent also rose periodically in the control group. Curves in Fig. 1 show changes in the number of erythrocytes in experimental rat No. 9, as comparted with a control rat. As the number of erythrocytes increased, their diameters decreased. Heinz bodies were seen in the erythrocytes of some experimental rats. No progressing changes were noted in the erythrocyte inclusions during the remaining 4 or 5 months of the chronic low dose porophore inhalation experiments.

Fig. 1.

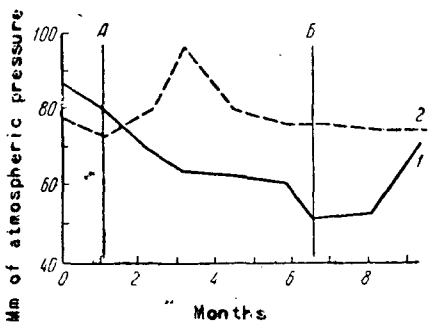


Changes in erythrocyte numbers. A,B - Exposure, 1 - Experimental, 2 - control

Osomotic erythrocyte resistance dropped to 0.62-0.7% of NaCl during the first 60 days, but the upper maximum limit remained unchanged. At the end of the experimental exposure period, erythrocyte resistance rose to higher levels, the minimal ranging between 0.56-0.46, and the maximal between 0.38-0.30% of NaCl. These changes point to the hemolytic porophore effect and to the appearance of young erythrocytes, which possessed a higher osmotic resistance. The number of reticulocytes in the blood of experimental rats fluctuated within the range of 10-40%, pointing to some periodic stimulation in the production of erythrocytes by the brain marrow. Microscopic slide examinations indicated that at the end of the porophore inhalation period the experimental animals exhibited slight increase in the red cell elements which returned to normal at the end of the exposure period. No clearcut changes have been noticed in the number of leucocytes or in the peripheral blood picture. Changes in the cardiovascular system appeared during the 1st month as a drop in the arterial blood pressure in the experimental animals, which persisted throughout

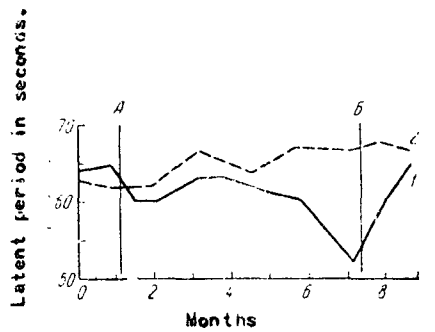
the exposure period in all the experimental rats. (Fig. 2). Blood serum and red blood cells cholinesterase activity rose to higher levels which persisted in all experimental animals through the entire exposure period. The latent period of the motor reflex response became slightly shortened during the first 5 months of exposure, but returned to almost normal on the 6th month, as shown by curves in Fig. 3. No substantial changes had been noted in the weight and general behavior of the experimental rats. Recovery of the different functions occurred at different periods in the experimental animals. Longest recovery period of 3 months was noted in the arterial blood pressure. Other functions returned to normal within 30-45 days.

Fig. 2.



Average changes in arterial pressure. Other designations as in Fig. 1 preceding.

Fig. 3.



Average changes in latent period of motor reflex response
Other designations as in Fig 1 preceding.

According to results of this investigation, most pronounced changes occurred in the red blood cells and in the arterial blood pressure. However, in evaluating the true effect of the concentrations used in the current study, consideration must be given to the time in which the animals recovered their initial indexes. Accordingly, 0.6 mg/m^3 of porophore should be regarded as a near threshold concentration. Changes in the nervous system, as indicated by shifts in the latent period of the motor reflex response and by the cholinesterase activity, were slight and returned to normal within a short time. Histologic weight, and behavior changes showed no substantial deviations from those in rats of the control group.

Taking into consideration the high toxicity of porophore dust, its limited toxic parameter, the development of shifts in the functions of erythrocytes and arterial pressure under conditions of chronic experiments, the present author decided to introduce a substantial safety coefficient of 12. The 0.05 mg/m^3 porophore ChKh3-5 concentration in the air of working premises recommended by this author as the maximal permissible norm was accepted by the committee of the USSR Ministry of Health.

Conclusions

1. Toxicity parameter of porophore ChKh3-5 was determined by administering the substance to experimental animals intragastrically. Results showed that LD_{100} equalled 0.5 g/kg, LD_{50} equalled 0.35 g/kg, and the maximal tolerance dose equalled 0.2 g/kg. The closeness between the tolerance and lethal dose characterizes porophore as a substance having a narrow toxic activity zone.

2. Experimental inhalation of porophore in 20 - 30 and in 7 - 10 mg/m^3 concentrations for a short time, and in 2 - 4 mg/m^3 concentrations for a long time killed the experimental animals, clearly indicating that porophore ChKh 3-5 was a highly toxic preparation.

3. Results of the investigation brought out the dominant effect of porophore ChKh 3-5 on the erythrocytes and on the central nervous system, the first being in the nature of hypoxia and the second in the nature of profound pathomorophologic changes in experimental animals which died as a result of the porophore administration.

4. Chronic effect of porophore dust inhalation in average concentration of 0.6 mg/m^3 elicited reversible functional shifts in the red blood cells and in the arterial blood pressure; slight functional changes in the nervous system and in cholinesterase activities were trancient.

5. Based on the experimental data it is recommended that 0.05 mg/m^3 of porophore ChKh 3-5 in the air of working premises be adopted as its maximal permissible concentration.

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Labor Conditions Prevailing in Spraying Cotton Crops with Phospho-organic Insecticides

pp. 24-27

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Phospho-organic compounds have been recently used as insecticides on an increasing scale regardless of the fact that they were highly toxic to man and warm blooded animals. Many reports have appeared in foreign literature describing cases of poisoning with phospho-organic insecticides during their application in agriculture. I. A. Kryuchkova reported in 1959 several cases of phospho-organic poisoning in the UzbekSSR. Kh. Z. Lynbetskii and T. M. Efendiev reported in 1961 on similar cases in other USSR regions. The present author made a direct study of the sanitary hygienic labor conditions prevailing in the application of phospho-organic insecticides to agriculture in different climatic USSR regions. The first stage of the investigation was concerned with the application of phospho-organic insecticides to cotton crops and was conducted at the Kurgan-Tuvin, Ordzhonikidzabad and in the Khodzhantsk regions of the Tadzhik SSR. Local conditions in the Tadzhik SSR, in some instances, are not favorable to the insecticide treatment of cotton crops by airplanes, so that crop spraying has to be done from the ground using tractors. In some cases the spraying was done entirely manually. Agricultural workers came in contact with the insecticide (a) during its transportation, (b) during the preparation of the aqueous insecticide emulsion, (c) during the cotton crop spraying,(d) in repairing and adjusting and cleaning the spraying equipment.

Table 1. Phospho-organic insecticide concentration in the air of working zones of different methods of cotton field spraying (average data)

Spraying method and working zone	Mercaptophos		Methyl Mercaptophos		Intratnion	
	No. of samples	Mg/li	No. of samples	Mg/li	No. of samples	Mg/li
Air Spray Method						
Aeroplane cabin	29	0.00025	25	0.0003	33	0.0003
Insecticide distribution point	76	0.0007	28	0.0003	18	0.0008
Dispatcher's breathing level	78	0.0009	19	0.001	31	0.0006
Treated sections	5	0.0003	24	0.0003	10	0.0005
Inhabited points	--	--	18	0.0002	25	0.0001
Ground Spraying Method						
Tractor workers' breathing level	---	--	27	0.0007	16	0.0016
Breathing level of workers using back carrying spray pumps		--	-		13	0.0009

Data in Table 1 show that insecticide concentrations in the air of all investigated areas exceeded the maximal permissible norms. High insecticide concentrations were found in the air at the breathing level of most agricultural workers connected with cotton crop spraying during opening the in -

secticide pressure containers, measuring and preparing the reagent, filling the airplane and tractor insecticide containers, etc.; the insecticide spray fell on the worker's face, eyes, hands and clothing, and skin of other open body parts.

The airplane method was the most advantageous from a hygienic and economic viewpoint because it enabled the operator to spray crops within a relatively short time with few workers. However, under present local conditions, the airplane cotton crop spraying had certain limitations. The temporary airplane landing was below standard from a sanitary viewpoint; the spraying was done mostly during the hottest part of the day accompanied by enhanced insecticide evaporation, and resulted in plugging and stopping up of the sprayers. Cotton crop spraying was done usually with insecticide doses of 1.5 and 2 kg per 1 ha, which created high insecticide concentrations in the air of working areas. The treatment of cotton crops growing in close proximity to residential areas heavily polluted the surrounding air with the phospho-organic insecticides.

The present author noted that methylmercaptophos and intrathion concentrations in the air surrounding residential areas did not exceed the maximal permissible concentrations. Cotton crop spraying from the ground resulted in an intense pollution of the air at the working level, and in addition the sprayed insecticide became deposited on the workers' unprotected skin and on their garments. In addition, the manual spraying method required considerable physical exertion during the hottest hours of the day. This was considerably aggravated by the lack of individual means of protection against high air temperature effects. The rate of phospho-organic insecticide evaporation from the sprayed crops had to be determined. This was of considerable importance, since Tadzhikistan fields had been usually irrigated the day following the spraying. This raised the content of the phospho-organic insecticide suspended in the air to concentrations exceeding the permissible maximum; thus, during 6-12 hours after spraying the insecticide concentration in the air was within the range of 0.0001 and 0.001 mg/li, and only after 2-3 days did the insecticide concentration abate to traces. The personnel connected with the phospho-organic insecticide spraying of cotton crops during 1960 and 1961 had been examined medically on a parallel basis. Under observation were 77 workers. It had been previously established that phospho-organic insecticides possessed cholinergic properties; therefore, particular attention had to be given to the determination of the vegetative nervous system condition and to the blood cholinesterase activity which was determined before, during and after the workers' contact with the insecticide. Results in Table 2 show that cholinesterase activity was lower in 11 of 16 investigated summer personnel 20 days after contact with the poison. In 7 of these cholinesterase activity was lowered by 22-33%, and in the remaining 4 the drop ranged between 5 and 16%. The average drop amounted to 24%.

Table 2.

Average concentrations of phospho-organic insecticides in the air of working zones at diferent methods of cotton field spraying

Personnel	No. of analyses	Cholinesterase activity		
		Before exposure	In the course of exposure	At the end of spraying
Aviation	29	4 440±166 (100%)	3 391±162 (74%)	3 560± 80 (80%)
Service	54	4 349±136 (100%)	3 874±143 (89%)	3 988±121 (92%)
Signalmen	54	4 118±121 (100%)	3 986±121 (96%)	4 134±112 (100%)
Tractor workers	30	4 150±152 (100%)	3 250±134 (77%)	4 020±156 (96%)
Persons operating "Automax" Manual sprayers	45	3 998±123 (100%)	2 810± 82 (70%)	3 925±150 (100%)

It should be noted that summer spraying was usually done with the more toxic mercaptophos preparation. Blood cholinesterase activity was reduced in 8 of 18 tank filler workers. The reduction ranged between 20 and 30% in 5 workers and 31 and 41% in 3 workers. These workers had been in contact with the insecticide for 10 to 15 days. Three of the 5 workers who showed a 20- 30% reduction in blood cholinesterase activity worked with mercaptophos. Four of 18 examined signal workers showed 11-25% cholinesterase activity reduction. Results obtained with the remaining 14 signal workers were statistically analyzed and found not significant or not reliable. The signal workers generally had been in contact with the insecticide for 2-5 days, which was too brief for the development of significant functional changes under the prevailing working conditions. Blood cholinesterase activity in tractor workers associated with the ground method of insecticide crop spraying fell by an average of 23%,and in workers who operated sprayer "Automax", the average cholinesterase drop was 30%. Seven of 10 examined tractor workers showed a 15-37% range of reduction in cholinesterase activity. Cholinesterase activity dropped by 34-37% in 3 workers exposed to the effects of mercaptophos for 24 days. Blood cholinesterase activity was determined in 15 workers who applied the insecticide manually; lowered cholinesterase activity was found in 13, of whom 5 showed a reduction of 17 - 28%, 4 showed a reduction of 30-40%, and 1 showed a reduction of 50%. All such workers had been engaged in the intrathion crop spraying. Results of the investigation showed that maximal reduction in blood cholinesterase activity was found in workers associated with the ground method of spraying, and during the hot summer months in workers associated with the airplane method of cotton crop spraying.

Data in Table 3 show that cholinesterase activity was affected negatively to different degrees by different phospho-organic insecticides. Maximal effects were noted in persons working with mercaptophos in whose cholinesterase activity drop averaged 19%, as compared with an average of 12.5% in workers handling methylmercaptophos and intrathion. Eight to 10 days after contact with phospho-organic insecticides, cholinesterase began to rise gradually; recovery was considerably slower in workers exposed to the effects of mercaptophos than in workers exposed to the other two insecti-

cides. Recovery of cholinesterase activity to normal levels was generally complete in persons exposed to the effects of insecticides other than mercaptophos. Most examined workers showed a persistent red dermographia and a slight hypotonia. Some workers complained of headaches, thirst, hyperhidrosis and a sensation of heat. Skin temperature determination showed a rise in the skin parallel with increase in the atmospheric air temperature. At 24-25° air temperature the skin temperature was 32.1°; at 38-39° of surrounding air temperature the upper temperature limit of skin of the forehead, the back of the head, of the hands, the chest, and etc. rose to 35°. No changes were noted in the general body temperature.

Table 3.

Average results of cholinesterase hydrolyzed acetylcholine per 1 ml of whole blood in 30 min. in employees working with different types of phospho-organic insecticides

Insecticides	No. of analyses	Prior to exposure		In the course of exposure		At the end of work	
		In µg	In %	In µg	In %	In µg	In %
Mercaptophos. . . .	82	4 338 ±76	100	3 581 ±65	81	3 784 ±134	86
Methyl mercaptophos	40	3 771 ±46	100	3 330 ±57	87	3 966 ±126	100
Intrathion.	90	4 020 ±87	100	3 550 ±134	88	3 990 ±95	99

Conclusions

1. Cotton crop spraying with phospho-organic insecticides created a considerable insecticide concentration in the air at working level. Results of most analytical tests showed an insecticide air concentration exceeding the maximal permissible limit. Most appropriate method from the viewpoint of lower air pollution was the airplane method of crop spraying.

2. Studies had been conducted for the determination of negative effects produced by air suspended insecticide on physiological indexes of workers engaged in cotton crop spraying with phospho-organic insecticides; results established that workers connected with cotton crop treating by manually operated sprayers were more vulnerable to the effect of the insecticides. The same can be said of tractor-hose spray workers, of signal workers, and of the repair men employed in the aviation method of insecticide crop spraying.

3. Some of the physiological changed noted among the workers, such as hypotonia, thirst, hyperhidrosis, etc., may have been the result of high air temperature or other environmental causes. It is suggested that under climatic Tadzhik SSR conditions, coupled with high temperature and excessive solar radiation, the combined effect of the insecticide and of the high air temperature should be taken into consideration in making final sanitary hygienic evaluations.

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Experimental Study of Grain Dust Harm

pp. 28-32

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Labor and health conditions of workers engaged in the grain industry have been investigated only slightly. Morbidity due to bronchitis and neuralgia is rather high among grain elevator workers. In fact, such morbidity rates are higher among grain elevator workers than among other personnel connected with the grain industry, as was shown by M. I. Karpova in 1962. Investigations conducted by the present authors in 1958-1961 on working conditions in grain elevators and at mechanized grain conveyors in the Saratov region showed that the laborers were subjected to the effects of high grain dust concentration which in many instances amounted to hundreds of mg per 1 m^3 of air. The installation of grain cleaning machines in electrically operated and mechanized grain conveyors considerably improved working conditions due to the fact that grain cleaning installations reduced the grain dust density in the air to 82-86 mg/m^3, as was shown by M. I. Karpova.

It was shown that air grain-dust density in Saratov region grain elevators exceeded the maximal permissible dust concentrations 9-120 times. The highly dispersed fraction, particles of less than 1 μ in diameter, constituted 11.2-38.9%, while the fraction of particles measuring 1-5 μ in diameter amounted to 59-98.8%, and the fraction of particles above 5 μ in diameter ranged between 2.4-17.4%. Meteteorological conditions during the winter months were unfavorable in the grain elevators; the air temperature inside the elevators was practically the same as the outside air. The air of the grain drying rooms contained carbon monoxide which came from the gas burning room. Carbon monoxide concentration was 13 times above the maximal permissible limit. According to the previously mentioned author, the noise at the working levels of the grain elevators also exceeded the maximal permissible decibel intensity. Analysis of settled dust collected at different grain elevator working levels showed the presence of vegetable particles in large quantities. Amorphous loam clay and coal particles were practically absent, and when present in an occasional sample, did not exceed 20%. Chemical analysis showed that the grain dust contained 62-70% of organic substances and 3.5-17% of free silicon dioxide. In addition the dust con-

tained large quantities of fungal spores. Mycological sprouting tests made with the grain dust yielded an abundant growth of different fungi.

The effect of grain dust on respiratory organs of animals was studied experimentally. As shown above, grain dust contained large quantities of fungal spores, some of which might have been pathogenic to man. Therefore, the experimental study also included a determination of pathogenic changes which the grain-dust and the fungal spores could produce in the organism.

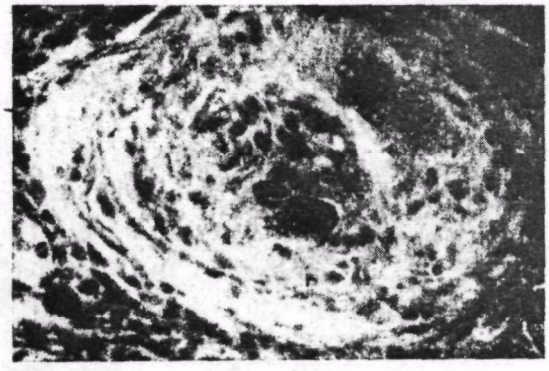
Settled grain dust was collected in the Saratov region grain elevators and sterilized to kill all fungal spores. The dust was sifted through a series of sieves followed by partitioning in N. I. Smetanin separator. The highly dispersed dust fraction, of particles less than 5 μ in diameter, was then used in the experiment. White rats were administered the dust intratracheally by the Gorodenska method and also by the V. B. Latushkina inhalation method. The grain dust was triple steam sterilized at normal pressure. Fifty mg of the dust was then suspended in 6 ml of physiological solution and stirred until the suspension became evenly distributed. Forty-nine white rats were used in the first series of experiments; 50 mg of the sterilized grain dust was carefully administered intratracheally to each rat under narcosis. Ten of the 49 rats died of pulmonary inflamation two days after the intratracheal administration of the sterilized grain dust. Surviving rats were killed 10 days, 4 and 6 months after the dust administration. In the second series of experiments, 12 white rats had been exposed to the inhalation of air containing 200 mg/m^3 of the sterilized grain dust in suspension for 2-1/2 hours; such a dust concentration corresponded roughly to the average concentration of grain dust in the air of grain elevators. Four and 6 months after the dust inhalation, the rats were decapitated. Lung tissue was studied histologically and histochemically using a polarizing microscope. The chest cavity was opened under sterile conditions and material was taken to determine the presence of fungi. The incubated plates developed a growth of monotype fungi cultures similar to those previously mentioned. Thirty-two plate innoculations made from rats of the control group yielded penicillia in only 4 of the inoculated plates.

Outwardly, no difference could be detected between the behavior and general appearance of the experimental rats and the control rats. It must be noted, however, that during the first 10 days following the grain dust inhalation, experimental animals began to lose weight. Later, all rats gained weight steadily over a period of 2 months, after which the rats again began to lose weight.

Microscopic tissue examinations showed that 10 days after the dust inhalation and intratracheal dust administration pulmonary ceulluar granulomas developed around the anchored mineral and vegetable dust particles. The granulomas measured 10-30 μ in diameter and were distributed predominantly subpleurally, at times within the bronchial walls and around the

bronchi and vessels. They consisted of large cells with engulfed dust particles, of epthelioid, lymphoid and polynuclear giant cells, as shown in Fig. 1. There appeared signs of subpleural interstitial pneumonia in the form of indurated alveolar septi, disturbed alveolar lung tissue structure and an increased number of histiocytes in the septi. The differentiation of vegetable from mineral particles, which permeated into the lung tissue, was made by the microscopic examination of stained sections for the detection of polysaccharides with the aid of a polarizing microscope. Vegetable particles normally showed the presence of polysaccharide stained red-violet by the Schiff stain. Fungal hyphae isolated from grain dust and from the lungs of experimental animals could also be stained by the Schiff reagent

Fig. 1.

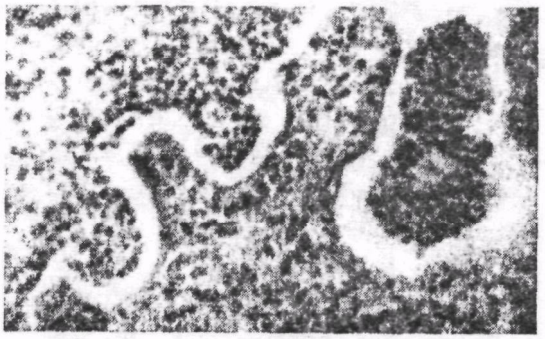


Cellular granuloma which developed around the foreign particles
Hematoxylin-eosin stain. Obj. 40, Ocul. 6

It has been known that some organic substances and mineral particles such as corundum crystals became illuminated under polarized microscopic examination, but they did not stain by the Schiff reagent. On this differential basis it was possible to establish that the cellular reaction in lung tissue, in the form of granules conglomenated around mineral and vegetable particles and around fungal spores and hyphae. The bronchial mucosa showed signs of catarral desquamation in the early stages of the experiment, which later developed into chronic and purulent bronchitis. Similar, and more clearly expressed, lung changes were noted in rats sacrificed 4 months after the grain dust administration. Cellular granulomas occurred more frequently in tissues of rats belonging to this experimental basis. Parallel sclerotic changes were more clearly expressed in animals of this group. Rats sacrificed 6 months after intratracheal grain dust administration showed localized peribronchial pneumonia, accompanied by purulent bronchitis, bronchiectasis and abscess forming pneumonia, as shown in Fig. 2. The presence of foreign particles on the bronchial mucosa elicited in the early and late stages following the dust inhalation, proliferation of the cylindrical epithelium, lymphoid infiltration of the bronchial walls, and considerable constrictions of their lumens. The finer bronchi became obliterated.

Lung tissue of rats sacrificed during the early and late periods following the intratracheal administraion of the sterilized grain dust showed monotypical changes; however, suppurative bronchitis, bronchiectasis, and abscesses were noted frequently. Lung changes in the rats which inhaled grain dust were less clearly defined than in the rats which received the grain dust intratracheally. In this case, changes were characterized by the presence of cellular granulation, interstitial pneumonia, pulmonary emphysema, catarrahl desquamation of the bronchial mucosa.

Fig. 2.



Bronchopneumonia and abscesses developed after six months of intratracheal administration of raw grain dust.
Hematoxylin-eosin stained Obj. 10 Ocul. 8

Thus, intratracheal administration and inhalation of grain dust by the experimental animals elicited pulmonary lung changes which were more clearly defined and more sharply expressed in the rats which received grain dust intratracheally. In the early stages these changes resulted from the formation of cellular granulation around the vegetable and mineral particles, interstitial pneumonia, pulmonary emphysema, and catarrhal desquamation. In the later stages, the above changes became superimposed by purulent lung processes, such as purulent bronchitis, bronchiectasis and abscess forming pneumonia. The enumerated pathological processes were not the results of fungal action. Such changes, including the purulent processes, had been observed frequently in rats which had been administered or inhaled sterilized grain dust, although the changes occurred less frequently and were less clearly defined. Nevertheless, consideration must be given to the fact that it was possible to cultivate monotypical cultures of fungi from smears taken under sterile conditions from surface cuts of lungs. Fragments of hyphae and fungal spores had also been seen in lung tissue sections, which were accompanied by the formation of cellular nodules. There appeared some evidence that the effect of grain dust on respiratory organs, and the formation of cellular granules in lung tissue differed with the grain dust composition, its origin, with the type of mineral and organic particles, and with the fungal spores and hyphae present in the dust. The morphologic changes noted in the lungs of the experimental rats cannot be effects of mycotic flora only. On the other hand, the effect on the animal organism of toxic fungal products cannot be entirely excluded.

Conclusions

1. Grain dust is composed of approximately 70% organic and inorganic substances and 17% of free silicon dioxide; it also contains spores of different fungi. Grain dust suspended in the air of grain elevators and of mechanized conveyors consists mostly of high dispersion particles measuring less than 5 μ in diameter. Actual concentration of the latter, according to analytical results, varied between 82.6 and 97.6%.

2. Experiments with rats showed that the effect of grain dust on respiratory organs was due to the presence in the dust of mineral and organic admixtures, and to the presence of fungal spores and hyphae.

3. Intratracheal and inhalation administration to rats of natural and sterilized grain dust elicited in the animals catarrhal and purulent bronchi-

tis, interstitial, peribronchial and abscess forming pneumonia, and the formation of nodular granules consisting of epitheliod, histioid, lymphoid and giant cells.

4. Progressively changing mechanization of technological processes in grain moving and storing increased the air pollution intensity in grain elevators and in mechanized conveyors creating an urgent need for a thorough hygienic evaluation of labor conditions and a study of morbidity among workers employed in the grain industry. Results of such investigations should serve as a basis for the recommendation of sanitary hygienic improvements in working conditions of the grain industry.

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Colorimetric Methods for the Determination of Sulfamate in the Air

pp. 45 - 46

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Sulfamate has the formula of $NH_4SO_3NH_2$. It is a herbicide used in the forest industry. It is a white or yellowish crystalline substance having a m.p. of 125°; it decomposes at 160° or above. It is hygroscopic and is easily soluble in water. It can be stored for a long time in a dry atmosphere at normal temperature. It is not inflammable, not explosive, but possessed corrosive properties. The development of a method for the determination of sulfamate in the air was conducted on the basis of 2 color reactions which characterize the NH_4^+ : (a) with Nessler reagent, as described in GOST 5606-50, Group Zh-29; (b) with phenol and sodium hypochlorite, as described by M.I. Poletave and N.A. Andreev in 1959. In the presence of sulfamate, the Nessler reagent produces a complex of a yellowish-brown color. The reaction sensitivity is 6.7 μ of sulfamate in 10 ml of solution. The reaction between phenol and sodium sulfamate in the presence of hypochlorite yields a substance of a blue color. A minimum of 3.35 μ of sulfamate in 5 ml can be determined by this method. In both determination methods the intensity of the color produced is directly proportional to the amount of sulfamate present. In the elimination of brush wood the latter is sprayed with a sulfamate solution which may remain suspended in the air as a yellowish aerosol. Air samples for the determination of sulfamate

aerosol are best collected with the aid of fabric filter FPP-15 fastened inside a metallic holder. The filter is placed into a small glass beaker washed several times with small volumes of ammonia-free distilled water for the removal of the trapped sulfamate aerosol. The filter paper is then pressed by means of a glass rod to remove the residual sulfamate solution; all the wash fractions are poured into a cylinder graduate.

For analysis with the Nessler reagent, proceed as follows: place 10 ml of the sample containing absorber solution obtained as above described, into a colorimetric cup; prepare the standard scale as follows: set up a series of 11 test tubes; place none into Tube No. 1, into tube No. 2-0.1, tube No. 3-0.2, tube No. 4-0.3, tube No. 5-0.4, tube No. 6-0.5, tube No. 7-0.6, tube No. 8-0.7, tube No. 9-0.8, tube No. 10-0.9 and tube No. 11-1.0 ml of standard sulfamate solution, each 1 ml of which contained 67.13 μ of the reagent. In this way, the standard scale will cover a range of 6.7-67.13 μ of sulfamate, as shown in the Table below. Now, add ammonia-free distilled water to each of the 11 tubes to the 10 ml mark. Then add to all tubes, including the one to be tested, 0.5 ml of the Nessler reagent. Mix the tubes, and after 10 minutes make the colorimetric determination.

Standard scale for the determination of sulfamate

Tube no.	1	2	3	4	5	6	7	8	9	10	11	12
Standard solution in ml	0	0,05	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1,0
Ml of ammonia-free water	5	4,95	4,9	4,8	4,7	4,6	4,5	4,4	4,3	4,2	4,1	4
4% of aqueous phenol solution	Add 1 ml to all test tubes											
Sodium hypochlorite	» 0,5 » » » »											
μg of sulfamate	0	3,35	6,7	13,4	20,1	26,8	33,56	40,27	46,99	53,7	60,4	67,13

For the determination of sulfamate, by the phenol and sodium hypochorite method, collect the sample as described under the Nessler method. Remove the trapped sulfamate from the tissue filter FPP-15 as described for the Nessler method. Then place 5 ml of the air sample solution into a colorimetric cup. Prepare the standard sulfamate solution so that each 1 ml contains 67.13 μ of the sulfamate. Then add to the tube containing the 5 ml of the air sample solution 1 ml of 4% phenol solution and 0.5 ml of the sodium hypochorite solution previously prepared by the method described by Poletaeva and Andrdeva. Shake, and after 10 minutes compare the intensities of the blue color with the intensity of blue colors developed in the standard scale.

Check tests were conducted as follows: samples of air containing given sulfamate aerosol concentrations were collected from experimental animal exposure chambers and tested on a parallel basis by the 2 described methods. The difference in the results of the 2 methods ranged between

0.001 and 0.006 mg of sulfamate, indicating that the 2 methods were of nearly equal sensitivity. In view of such results, it is felt that either of the methods could be used for the determination of sulfamate aerosol concentration in the air under conditions of agricultural application.

Micro Dose Gas Delivery Apparatus

pp. 46 - 48

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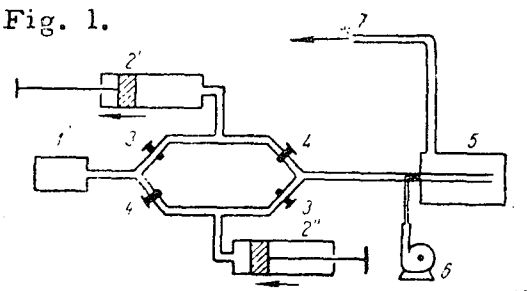
In conducting toxicological studies based on the continuous supply of gas into an exposure chamber there arises the need for delivering small gas doses at one minute intervals; this applies in particular to studies conducted with gases and vapors under chronic experimental condictions. The present author developed a simple micro dose gas delivering apparatus which operated on a continuous basis delivering 100 ml of the tested gas up to tens of thousands ml per minute. The apparatus consists of a medical type syringe which intermittently sucked in and forced gas out. This pneumatically closed system is schematically illustrated in Fig. 1. The studied gas is first collected into a suitable collapsible container from which it passes through a T-shaped connection into a system of tubes equipped with valves or pinch-cocks, which automatically control the flow direction of the gas. Valves marked (3) and (4) are arranged so that when piston of syringe (2') is moved in the direction of the arrow, valves (3) open and valves (4) close. This brings two processes into simultaneous action: in process No. 1 air is sucked into syringe (2') from the collapsible container and is forced out from syringe (2'') into the mixer. As the pistons of the two syringes touch the bottom of the cylinders, valves (3) automatically close, while valves (4) open so that the gas is forced out of syringe (2') and is sucked into syringe (2'').

Fig. 1.



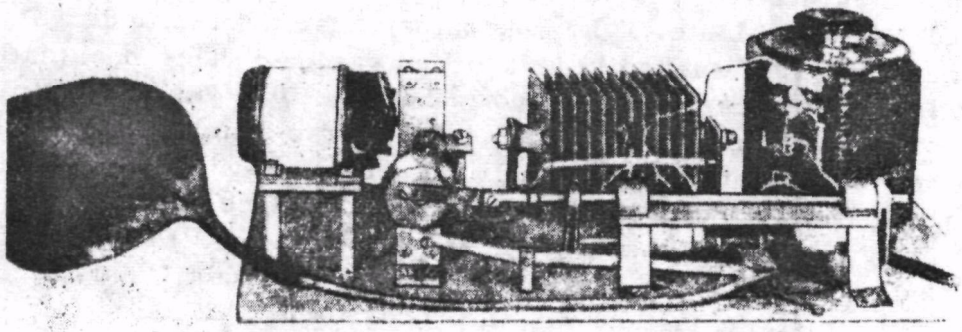
Plan of the pneumatic microdose gas delivery apparatus

1 - Container with the gas under analysis; 2' and 2'' - Medical syringes; 3 - Open valves; 4 - Closed valves; 5 - Mixer; 6 - Air blower; 7 - Outflow tube leading to the gas chamber.

The apparatus is mounted on a metallic plate as shown in Fig. 2; it consists of a direct current motor SL-281 of 24v and 26w; it is equipped with a selenium rectifier, a laboratory regulating autotransformer LATP-2, a reducing gear 23:1 ratio, a crank gear and a valve-type connecting mechanism, and 2 syringes. By means of a reducer and a crank gear connecting rod the original motor rotation is transmitted as a transformed motion to a horizontal rod which passes through two

two hollow trunions fixed to a special frame. At the lower end of the frame two syringes are firmly attached parallel to the horizontal rod, but in opposite positions; syringes of different sizes can be inserted whenever required. Two holders are affixed to each end of the horizontal rod into which the piston handles can be firmly inserted and through which the horizontal rod transmitted its in and out movements to the syringe pistons. One crank brings about a complete piston cycle during which given volume of gas is sucked into and forced out of the syringe cylinder. The valve containing apparatus part is in the form of an unevenly balanced water carrying beam, one end of which contacts the circumference of the crank gear and the other extends into the metallic frame between the two parts of the tubes as shown in Fig. 2. The long shoulder of the beam is attached to the base or metallic plate by means of a small spring. In such position the valves of one pair of the tubes are closed. The first end of the beam rolls along the inside of a peripheral semi-circular groove on the crank gear. When the extending part of the crank gear comes close to this end, the position of the unevenly shoulder beam becomes reversed and the previously open valves close. As the crank gear makes a 180° turn the unevenly shouldered beam returns to its original position.

Fig. 2.



General view of the gas microanalyzer

The speed at which the small gas-dosing apparatus operates depends upon the speed of the motor and the size of syringes used at the time. The speed of the motor can be regulated by means of a laboratory autotransformer. Maximal rate can be obtained with the autotransformer set at 24 v. With this apparatus it is possible to vary the rate of gas supply within a wide range. Gas supply rate can be reduced or increased by using a poly staged reducer instead of the monostage. The apparatus construction is a simple one. It has no complex detail parts and can be assembled in any laboratory, and can be easily set to deliver any desired gas volume at any desired time intervals. The model here described has been used in the author's laboratory in studying the chronic effect of toxic gases on experimental animals.

Dust Discharged by Plants Producing "Cold Asphalt", and its Effect on the Sanitary Conditions of Residential Localities

pp. 62 - 64

O. B. Perov and D. M. Boris
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The large scale production of improved road paving materials began in the USSR in 1927. This led to a substantial increase in the production of asphalt, including the preparation of "cold asphalt". In 1931-1932 plants for the production of road paving materials made of asphalt and cement had been opened up in Leningrad, Moscow, and later in the Ural Mountain region, in Povolzh'e, in the Ukraine, and in many other regions. Plants which produced "cold asphalt" operated through the year.

"Cold asphalt" is a viscous mixture of finely ground rock and bitumen or asphalt. "Cold asphalt" is manufactured in stationary plants or production departments which use the same production methods; this type of asphalt can also be prepared in the open, creating unfavorable sanitary hygienic working and living conditions in nearby residential and industrial areas.

The mineral filler used in the production of "cold asphalt" can be sedimented deposits or crushed or ground igneous rock. Limestone and dolomites are usually most suitable for the manufacture of "cold asphalt". The filler particles must not be larger than 8 mm in diameter, and can be as fine as 74 μ in diameter, usually obtained by grinding the original filler material to a powder. Such filler material is generally prepared in advance and is kept in the open until needed. In the final operation, the mineral powder is poured into the dose supplying installation from which it is taken in given quantities and poured into the mixer containing the asphalt. The temperature of the mixture is then raised to 90-100°. The powder and the asphalt are mixed to homogeneity and the mass transported to the storage place. In the process of rock crushing and grinding a considerable amount of dust is generated which permeates into the surrounding air. Where "cold asphalt" is prepared in the open, the mineral dust persists in the atmospheric air for a long time, and is also carried with the air currents to distant and extended areas. The dust pollution pattern of any given territory can be studied by the combination of aspiration and sedimentation methods.

Data obtained in connection with studies at asphalt processing plants show that in dry weather the density of dust in the air over the rock crushers and dryers amounted to 1360-1550 mg/m^3. The air over the mixers at times contained 2400 mg/m^3 rock dust. The air of territories surrounding plants producing dry asphalt were severely affected by the generated filler dust. Data obtained by the present authors show that through the year, and depend-

ing upon the wind pattern, the greater part of sedimented dust was found in the 100-500 m zone. Data obtained from dust distribution studies made in the proximity of the Skala-podol'sk asphalt plant are listed in the Table below.

Dust distribution of the Skala-Podol'sk Asphalt plant
(averages of 5-6 determinations)

In the direction of	g/m^3 of dust in 24 hours							
	Fall-Winter period				Spring-Summer period			
	Meters from the source of dust formation							
	100	200	500	1000	100	200	500	1000
East	4,6	4,0	3,7	2,7	12,0	9,3	8,0	6,0
Northeast	6,1	4,7	4,3	3,1	7,0	6,0	5,8	4,0
North	3,2	2,9	2,0	1,2	6,3	3,1	2,3	1,8
Northwest	4,2	3,0	2,0	1,5	7,1	5,4	4,5	3,0
West	6,3	3,1	3,0	2,7	7,9	7,8	7,8	7,6
Southwest	11,2	6,6	6,2	4,7	17,3	12,5	12,3	5,8
South	7,8	4,5	2,3	2,0	15,7	10,8	7,8	6,3
Southeast	7,8	4,7	3,1	2,3	20,4	16,6	11,0	7,1

Data in the Table show that in the 100 m zone surrounding the asphalt plant the dust settled during the dry season of the year on the windy side of the plant and amounted on the average to 12 g per 1 m^2 per day; the rate of dust sedimentation per day per m^2 of area amounted to 20.4 on the windy side of the plant. At a distance of 200 m from the plant the corresponding rates of dust sedimentation were 9.3 g and 16.6 g per 1 m^2 per day. At 500 m from the asphalt plant, dust concentration in the air was still high, and its sedimentation rate reached 12.3 g per 1 m^2 of area. At 1000 m from the dust pollution source the sedimentation rate was still within the range of 1.2-4.7 g per 1 m^2 per day during damp seasons of the year, and 1.8-7.6 g during dry seasons of the year.

The high dust concentrations generated by plants producing "cold asphalt" and the extensive spread of the dust over the plant territory and neighboring residential areas created the following unpleasant conditions: the workers' bodies and their clothing became heavily covered with dust; the sanitary condition of many residential sections in the proximity of the "dry asphalt" producing plant were negatively affected by the dust; the yards and even the inside of residences suffered heavily of heavy dust settling; domestic wash hung out to dry in the open air became coated with the filler dust, and seriously affected, and in some instances even killed, ornamental and other vegetation.

The following recommendations have been proposed as means for improving the above mentioned deteriorated sanitary conditions. It was recommended, first, that rock crushing and filler grinding by the dry method should be discontinued during the spring and summer months and replaced by a wet process. Observations have shown that this change had not

affected the technological aspects of this project, while it had considerably lowered the dispersion of the mineral filler and its spread over the territory. At the point of crushing and grinding air dust density was reduced by 50%, and its rate of sedimentation over the working platform did not exceed the one usually prevailing during the fall and winter seasons. It was recommended next that the crushing and grinding installations should be enclosed in leak-proof metallic housings, and that the ground material should be stored in dugouts. Observation indicated that encasing the crushing and grinding installations failed to completely stop dust dissemination; on the other hand storing of the ground mineral filler in dugouts proved effective and prevented the stored material from becoming dispersed by air currents. It was also noted that the metal or other material used for the encasement of the crushing and grinding installations rapidly deteriorated, and the air dust density gradually returned to the original level. Therefore, it was recommended that the asphalt-cement plant should be moved to a location more distant from residential areas, and that it be surrounded by a sanitary clearance zone not less than 500 m wide. However, the most rational way appeared to be to discontinue production of "cold asphalt" in the open, and to move all its operations inside of an appropriately planned and constructed building equipped with necessary dust abating or eliminating installations and adequate fresh air circulating ventilation systems. It was also recommended that the sanitary clearance zone be implanted with leaf bearing trees.

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NO. 8, AUGUST

Correlation between 3,4-Benzpyrene and Carbon Monoxide Concentrations in Automobile Exhaust Gases

pp. 3 - 8

V. A. Gofmekler, M. D. Manita, Zh. V. Manusadzhants and L. L. Stepanov
(From the Community Hygiene Department of the Central Institute of Automotive Transportation)

One of the most widely occurring cancerogenic substances in ambient air, 3,4-benzpyrene, is also a component of automobile exhaust gases. K-

tin and his collaborators demonstrated in 1954 that highest 3,4-benzpyrene concentrations were discharged by slow moving auto vehicles. This is also true of carbon monoxide; seemingly, there exists a correlation between the formation and discharge of 3,4-benzpyrene and carbon monoxide, as both may result from incomplete liquid fuel combustion. It was hoped that a better understanding of this 3,4-benzpyrene and carbon monoxide correlation might be of value in dealing with the problem of sanitary protection of atmospheric air.

Concentrations of 3,4-benzpyrene in auto exhaust gases were determined by the spectral-fluorescent method which consists of the following 4 steps: extraction, chromatographic partitioning, qualitative determination by fluorescent spectra, and quantitative determination by absorption spectra, as described by P. P. Dikun in 1955. Many authors, namely Sawick and others, demonstrated in 1960 that 3,4 benzpyrene was found in the air in the solid phase of exhausts. Accordingly, samples of automobile exhaust soot were collected using synthetic fabric filter FPA-15, which is an acetylcellulose product of low pressure drop and high filter retention. It is insoluble in organic solvents such as benzene, dichloroethane and the like. Two types of filter holders were used. The first type was conically shaped and had a base diameter of 12 cm. The above mentioned filtering material was placed between two copper wire screens and fastened into the filter holder. The smaller end of the conically shaped holder was fastened to the automobile exhaust pipe. For sample collecting convenience the exhaust pipe can be extended into the automobile interior. By this method, samples of soot had been collected from an automobile truck trade marked ZIL-164 as it travelled over a distance of 24000 km; the automobile was equipped with a carburetor marked ZIL-120. Second grade gasoline A-66, of the same batch, was used in all experiments. Gas analysis was performed using the Orsa apparatus. The pressure drop created by the filtering assembly was 80-100 mm at the testing speed, and exceeded 600 mm during idling. However, this difference in pressure drop was not accompanied by any noteable change in the carbon monoxide content of the exhaust gases at the time of soot sample collection; immediately after, the filtering assembly had been disconnected with the engine running at the same speed.

Three series of samples had been collected as above described. The amount of soot collected per sample varied between 50 and 300 mg. The determined 3,4-benzpyrene ranged between 0.24 and 45 μ per sample. 3,4-benzpyrene concentration in the exhaust soot of an idling automobile ranged between 9.00015 and 0.0022%. The color of the filter after sample collection varied from yellow to deep velvety black. The first series consisted of 6 samples collected while the auto truck was idling at 400-1200 rpm. During the collection of samples for this series the carburetor was under control and performed evenly and efficiently so that in the 10 minutes of sample collection only a slight greyish soot deposit accumulated, which gave either very slight or no positive tests for 3,4-benzpyrene.

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Table 1.

3,4-benzpyrene and carbon monoxide concentrations in automobile exhaust gases

Engine operation			No. of tests	3,4-benzpyrene		Carbon monoxide	
Transmission	Speed km/hr	rpm		$\mu g/m^3$	mg/min	Abs.	g/m^3
Idling engine							
First series with carburetor in good condition							
		400	1	0,00	—	0,8	10,0
		600	1	0,00	—	0,8	10,0
		800	2	0,00	—	0,6	7,5
		1 000	1	0,80	0,60	0,4	5,0
		1 200	1	0,89	1,07	0,3	3,75
Second series Carburetor at cruising speed							
		400—500	1	0,00	—	0,4	5,0
		600	1	0,06	0,02	1,0	12,5
		800	2	0,41	0,22	2,8	35,0
		1 000	2	0,04	0,03	5,0	62,5
		1 200	2	2,22	1,80	2,2	27,5
		1 400	2	0,10	0,09	1,0	12,5
		1 600	2	0,00	—	0,8	10,0
		1 800	2	0,06	0,06	1,0	12,5
		2 000	2	0,00	—	0,5	7,5
		2 200	2	0,00	—	0,5	6,3
		2 400	2	0,05	0,10	2,2	26,9
		2 600	1	0,55	1,10	2,8	35,0
In motion							
Third series with carburetor at cruising speed							
II	0—15	400—2 500 Accelerated	1	26,70	75,00	4,9	61,3
III	10—30	1 400—2 800 Accelerated	1	8,57	31,30	2,7	33,8
IV—V	30	1 000—1 200	2	3,90	2,90	1,6	19,4
Ditto	40	1 400—1 600	2	1,80	2,50	1,2	14,4
» »	50	1 800—2 000	2	1,30	2,50	0,7	8,8
» »	60	2 200—2 400	2	0,50	1,50	0,9	10,7

Twenty-one samples were collected in the second series of tests under all auto truck operation systems. Two samples were collected with the engine operating at each of the following speeds: 400, 600, 800, 1000, 1200, 1400, 1600, 1800, 2000, 2200, 2400 and 2600 rpm. Concentration (C) of the 3,4-benzpyrene was computed with the aid of the following formula,

$$C = \frac{S}{G}\ \text{мкг/м}^3;\quad G = \frac{15 \cdot P \cdot 0,74}{1000}\ \text{м}^3,$$

in which S- denotes 3,4-benzpyrene concentration in the sample in μ; G denotes the volume of exhaust gases in m^3; 15- is the conversion coefficient; 0.74- is the sp. gr. of the fuel; P- is ml of fuel consumed.

Carbon monoxide concentration was computed by the following formula:

$$C = a \cdot 1,25 \cdot 10\ \text{г/м}^3,$$

in which (a)- denotes volume percent of carbon monoxide; 1.25- is the weight of 1 ml of CO; 10- is the conversion coefficient. Determination data of the series are presented in Table 1. Data in the Table show that changes in 3,4-benzpyrene concentrations in the exhaust gases were accompanied to a degree by corresponding changes in the carbon monoxide concentrations, which, as shown in the Table, ranged between 5 and 62.5 g/m^3. The correlation coefficient of 3,4-benzpyrene and carbon monoxide concentrations amounted to 0.42, which was twice the value of the average experimental error.

Twelve soot samples were collected in the third series at different motor speeds, using the same carburetor as in the second series. Two summary samples had been collected under different motor operation conditions during a 1 km drive. The different operations included the start, even motion and use of brakes. The 3,4-benzpyrene concentrations in the two samples were correspondingly 3.28 and 3.87 μ/m^3, which from the practical viewpoint, can be regarded as identical. Higher 3,4-benzpyrene concentrations were obtained when the motor operated in second gear; as the motor speed increased, the 3,4-benzpyrene concentration gradually abated to a mere trace, as shown by the data listed in Table 1.

The carbon monoxide concentrations expressed in g/m^3 practically paralleled the 3,4-benzpyrene concentration curve. The correlation coefficient between 3,4-benzpyrene and carbon monoxide concentration in this series of experiments amounted to 0.96 and was 32 times greater than the average experimental error, which indicated high reliability of the correlation coefficient. However, the working area of the soot collecting filter used under above described conditions was relatively small and created a high pressure drop. For this reason, following series of experiments had been performed with a soot collecting filtering apparatus of a considerably lower pressure drop. The filter holder was in the form of an elongated cylinder. One end of it was tightly sealed. Synthetic tissue FPA-15, measuring 30 x 94 cm, or of 2820 cm^2 working area, was wrapped around the cylinder. The tissue was held in place by a wide gauge copper netting. This assembly, together with a water cooling device, was attached directly to the exhaust pipe of an automobile truck of mark GAZ-51A. Soot samples were collected as the motor truck was driven 122-127 km along a level section of the Leningrad highway.

Records were kept of gas fuel consumption, time of sample collecting, conditions of motor operation, partial vacuum created in the air sucking tube, resulting pressure drop, and carbon monoxide concentration in the exhaust gases, as indicated by a device developed at the Scientific Research Institute of Autotransportation, known as NIIAT, with 0.1% accuracy. This filtering device created a pressure drop of 30-40 mm of water column at low motor speed, not exceeding 140-160 mm at high rpm, and at 60 km/hr speed as shown in Table 2. Such a low pressure drop had no effect on the normal motor operation. It had no effect on the initial carbon monoxide content in

the exhaust gases, nor did it have any effect on the degree of negative pressure developed in the air sucking pipe, or collector, which is a true reflection of the condition of the motor operation.

Table 2.

Effect of soot sample taking on the operating efficiency of motor GAS-51

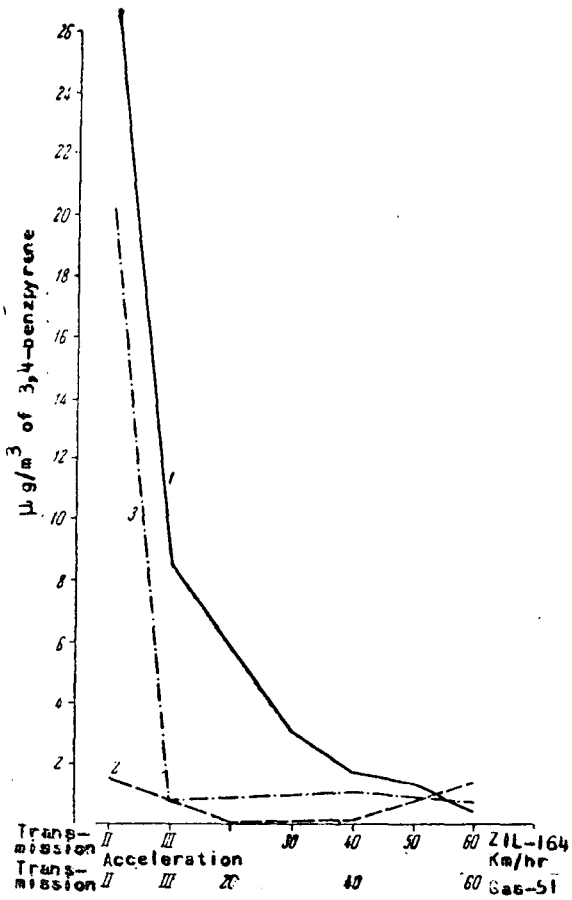
Operating conditions	Resistance (pressure drop) in mm of water column	Discharge in suction collector		CO in g/m³	
		With filter device	Without the device	With the device	Without the device
Carburetor well regulated					
Load 2.5 ÷ 3.0 ton IV transmission 20 km/hr	30	270—280	280	<1,25	<1,25[1]
» » 40 »	40	200—220	200—220	<1,25	<1,25
» » 60 »	70	70—80	70—80	<1,25	<1,25
Carburetor poorly adjusted (cruising)					
Load 2.5 — 3.0 ton IV transmission 20 km/hr	(increases as soot accumulates)	290	280—300	150	150
» » 40 »	80—90	200—230	230	58	56
» » 60 »	Up to 160	180—190	180—190	50	38

(1) Below sensitivity of the method

Two soot sample series had been collected under the above described conditions from exhaust gases of auto truck Gaz-51 carrying a load of 2.5-3.0 tons. The first series consisted of 7 samples, during the collection of which the carburetor was in an excellent condition; 12 soot samples were collected when the carburetor worked under favorable carburetor conditions, as shown in curves illustrated in the Fig. below. As in the preceeding series of collected samples, the color of the filter varied from light brown to dark velvety black. The time required for the collection of a single sample with the motor operating in second gear at a rate of 60 km/hr varied from 5-6 seconds to 10-15 minutes, with the motor operating at a speed equivalent to 20 km/hr; 2-3 filters operating under identical conditions of sample collection were analyzed together as shown in Table 3. Changes in carbon monoxide concentrations in the exhaust gases resulting from automobile operation under different conditions corresponded with changes in 3,4-benzpyrene concentrations in the exhaust gases under identical engine operation. The correlation coefficient between the two exhaust components was 0.83, and nearly 6 times as great as the average experimental error, pointing to a high reliability.

Results presented and discussed in this paper agreed with the data presented by Kotin and his collaborators. Discharge of 3,4-benzpyrene per unit time abated with increase in the speed of the engine operation from 4.35 μ/min to traces during the early stages of the automobile operation and

with the carburetor properly adjusted, and from 88.2 to 2 μ/min in the second period of experiments in which the carburetor had not been well adjusted, as shown in Table 2.



Exhaust of 3,4-benzpyrene by different automobiles at different operation conditions
1 – ZIL-164 with carburetor poorly adjusted;
2 – GAS-51 with carburetor well adjusted;
3 – GAS-51 with carburetor poorly adjusted

Conclusions

1. Carbon monoxide concentration in automobile exhaust gases ran in correlation with the concentration of simultaneously occurring 3,4-benzpyrene; accordingly, CO concentration can be used as an indicator of the rate at which 3,4-benzpyrene is discharged into the atmosphere with the automobile exhaust gases.

2. Automobiles with properly adjusted carburetors generated and discharged into the atmospheric air less carbon monoxide and less 3,4-benzpyrene.

3. The highest concentration of 3,4-benzpyrene and of carbon monoxide was discharged with exhaust gases coming from automobiles operated at low rpm, usually at the time of starting or accelerating.

4. Atmospheric air pollution with 3,4-benzpyrene and carbon monoxide can be reduced substantially as follows: by controlled carburetor operation at all times, particularly when starting and moving into line with the traffic, and most of all by keeping the carburetor clean and well adjusted; by reducing to a minimum the number of stops and starts at cross sections and light signals. This can be done by proper manual and signal traffic regulations and by instituting overhead and underground auto routes which would allow automobiles to travel without making many stops.

See page 193 for Table 3.

Table 3.

3,4-benzpyrene and CO concentrations in exhaust gases of automobile GAZ 51A

Operating conditions: Transmission	Operating conditions: Speed Km/hr	No. of samples	3,4-benzpyrene: μg/m³	3,4-benzpyrene: μg/min.	Carbon monoxide: Abs. %	Carbon monoxide: g/m³
	First series; carburetor well adjusted					
II	0—20 Acceleration	2	1,45	4,35	—	—
III	15—35 Acceleration	1	0,83	0,47	—	—
III	Ditto	1	Traces	Traces	—	— Filter tests
IV	20	1	»	»	<0,1	<1,25
IV	40	1	»	»	<0,1	<1,25
IV	60	1	1,52	4,40	<0,1	<1,25
	Second series; carburetor poorly adjusted					
II	0—20 Acceleration	2	20,20	88,20	10,0	125
III	15—35 Acceleration	2	0,83	3,20	From 6 To 10 At the end	100
IV	20	2	None found	None found	12	150
IV	40	2	1,04	2,10	4,5—5,0	58
IV	60	3	0,81	2,00	4,0	50

(1) Below the method sensitivity

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Effect of Hexachlorocyclohexane (HClCH) γ-Isomer on the Organism's Immunobiological Reactions

pp. 29 - 33

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Chemical poisons used in combatting crop damaging and infecting pests may unfavorably affect the health of farm workers under certain conditions. It can be assumed that the toxic properties of such pesticides in many instances are of an occult character and can be detected only by special means, as was indicated by B. A. Kiryachko in 1957, by V. K. Navrotskii in 1959, etc. Changes in the organism's reactions produced by the above me-

tioned pesticides may unfavorably affect the organism's resistance to different diseases, thereby raising the rate of different morbidity types among workers coming in contact with such pesticides; and in fact, E. N. Burkatskaya, G. A. Voitenao, E. P. Krasnyuk and others have shown that morbidity of different types was more frequent among workers engaged in the production of chemical pesticides.

The present author studied the effect of HClCH γ-isomer, a component of hexaclorane, on the immunobiological properties of the animal organism. Hexaclorane, a trade name for HClCH, is widely used in agriculture as an insecticide; it consists of several stereoisomers of which only the γ-isomer is of practical value. Technical hexaclorane contained 12-13% of γ-isomer. However, the production of hexaclorane containing 60-90% of γ-isomer and its application are gradually increasing. The γ-isomer of HClCH is a polytropic poison which acts on the central nervous and vegetative nervous systems. LD_{50} of this isomer for rats is 120/mg/kg, according to some authors, and 190 - 200 mg/kg, according to other investigators. It possesses no well defined cumulative properties; however, daily administration of this preparation in oily solution to rats at the rate of 20 mg/kg for 22 days resulted in the rats' loss of weight and appetite, drop in the liver glycogen level, and in fatty liver degeneration.

The clinical picture of γ-isomer HClCH poisoning, is as follows: stimulated central nervous system, hypersalivation, tremor, convulsions, emaciation, blood picture changes, etc. The maximal permissible γ-isomer concentration in the atmospheric air was set at 0.00005 mg/li. The effect of γ-isomer HClCH on the immunobiological reactivity was studied using rabbits and cats as experimental animals. The preparation was administered to the rabbits daily, for 3 months at the rate of 10 mg/kg. Experimental cats were exposed to the inhalation of air containing 0.002 mg/li of the toxic substance in specially constructed chambers four hours daily for 2 months. Of 4 such experimental series 2 were performed with the HClCH γ-isomer, using 5 rabbits and 5 cats, and 2 control experiments of 5 rabbits and 3 cats. Experimental animals of all series were triple immunized with typhoid vaccine containing 1 milliard micro-organisms per ml. The vaccine was administered subcutaneously to a total of 2.5 ml in the following order: 0.5 ml the first injection, and 1.1 ml each of 2 following injections at weekly intervals. Seventy-five days after the exposure, the animals were revaccinated subcutaneously with 1 ml of the vaccine. Tests for the determination of the animals' immunobiological reactions were as follows: agglutination titer after the typhoid vaccination, blood complement titer and leucocyte phagocytic titer. The latter was checked for phagocytosis intensity based on the average number of phagocytized microorganisms per phagocyte, and by establishing the ratio between phagocytically active and nonactive polynuclear leucocytes. The phagocytic activity of leucocytes was determined as follows: using a micro-pipette, 0.1 ml of 2% sodium citrate solution was placed into a centrifuge tube followed by 0.2 ml of whole blood and 0.2 ml of typhoid

fever diagnostic agent which contained 2 milliard microorganisms per ml. The centrifuge tube was rotated between the hand palms for 2-3 minutes until the suspended bacteria became evenly distributed. The centrifuge tube was then incubated for 30 minutes and centrifuged. The leucocytes separated into a layer were drawn off with the aid of a Pasteur pipette, deposited on a microscopic slide, spread, fixed with ethanol, stained by the Giemsa method, and examined microscopically under the oil immersion lens.

As indexes of γ-isomer HClCH effect on the animal organism the present author used body weight and temperature, appetite, general animal behavior; blood sedimentation changes were noted and recorded in the case of cats. Results showed that the above indexes were practically the same in the experimental as in the control animals which were immunized by the typhoid vaccine but not exposed to the effects of the γ-isomer. The study indicated that immunobiological indexes of cats and rabbits possessed species specific characteristics.

The aggultination titers of the experimental and control rabbits, prior to having been immunized, varied between 1:20 and 1:40, as shown in Table 1. One week after the first immunization, the aggultination titer in the experimental rabbits increased 12 fold, and only 8 fold in the control rabbits. Following the second immunization the aggultination titer rose 80-fold in the experimental animals and 18-fold in the control animals. Continued administration of the toxic γ-isomer to the rabbits had no effect on the blood aggultination, which retained its final enhanced titer. This indicated that rabbits subjected to the action of low γ-isomer concentrations during the first stage of poisoning became immunologically more reactive and produced larger quantities of antibodies in response to typhoid vaccine. Following revaccination the aggultination titer rapidly rose in the control rabbits to an average quadruple intensity of the original. At the same time the post-revaccination aggultination titer remained practically the same in the experimental rabbits. The complement titer dropped to lower levels during rabbits chronic exposure to the effects of the HClCH γ-isomer to the same degree as in the control rabbits. However, 7 days after revaccination there appeared a notable fall in the complement titer of the experimental rabbits and a considerably lesser drop in the control rabbits; in the experimental rabbits the drop amounted to 50%, and in the control rabbits only to 12%.

On the basis of the results it can be assumed that prolonged exposure to HClCH γ-isomer after the first period of defense mechanism activation in the living organism elicited the appearance of depressed immunobiological activity in the form of arrested agglutination titer increase, and in a drop in the complement titer. Aa B. Sakhnovskii noted similar changes in lead poisoning. He observed that the organism's defense functions in lead poisoning could be expressed so intensely as to conceal from observation the phenomenon of bactericidal depression. However, long exposure to lead poisoning brought about changes in the phases of bactericidal activity, pointing to a rise in the organism's defense properties. No changes have been

noted in the indexes of weight, body temperature, appetite, general animal behavior, etc. This led to the assumption that changes in the immunibiological reactivity of rabbits exposed to the toxic effect of HClCH γ-isomer under chronic conditions appears as the only early symptom of intoxication. It should also be noted that no changes appeared in the phagocytic activity of leucocytes under conditions of the experiment, and no visible signs of intoxication appeared in the animals exposed to the action of HClCH γ-isomer for 3 months. The total amount of HClCH γ-isomer received by all the experimental rabbits amounted to 8 lethal doses (LD_{100}).

Table 1.

Agglutination titres of rabbits exposed to chronic inhalation of hexachlorocyclohexane γ-isomer vapor

Animals	Animal No.	Initial data	7 days after 1st immunization	7 days after 2d immunization	7 days after 3d immunization	60 days after 3d immunization	7 days after revaccination	14 days after revaccination
Immunized and exposed to inhalation of HClCH γ-isomer vapor inhalation	24	1:40	1:320	1:1 600	1:600	1:1 400	1:1 600	1:1 600
	25	1:2	1:320	1:1 600	1:3 200	1:800	1:1 600	1:1 600
	26	1:20	1:80	1:800	1:100	1:1 600	1:800	1:1 600
	27	1:20	1:240	1:2 400	1:1 600	1:1 600	1:800	1:2 400
	28	1:20	1:240	1:1 600	1:1 600	1:1 6'0	1:1 600	1: 800
Averages		1:20	1:240	1:1 600	1:1 600	1:1 600	1:1 600	1:800
Controls	17	1:40	1:400	1:320	1:600	1:600	1:2 400	1:2 400
	18	1:40	1:240	1:320	1:400	1:200	1:800	1:1 600
	19	1:20	1:3'0	1:640	1:400	1:200	1:1 600	1:1 600
	22	1:40	1:3-)	1:1 600	1:1 600	1:600	1:1 600	1:2 400
	23	1:40	1:3	1:800	1:800	1:400	1:1 600	1:1 600
Averages		1:40	1:320	1:730	1:760	1:360	1:1 600	1:1 900

Agglutination titer changes in experimental cats exposed to the inhalation of HClCH γ-isomer were similar to those manifested in the experimental rabbits. The initial 1:40 titer of the control cats rapidly rose to an average of 1:6400, while in the experimental cats the titer rose from initial 1:60 to 1:1280. In two of the five experimental cats the agglutination titer dropped to 1:100 before they died. The complement titer of the experimental cats did not differ significantly from that of the control rats. In the light of the present findings blood serum complement cannot be used as the determining indicator of the organism's state of immunoreactivity. V. K. Navrotskii studied the effect of low SO_2 concentrations on the immunobiological reactivity of rabbits; he also noted that changes in complement titers were poorly defined and insufficiently characteristic. The phagocytic activity rose significantly in 4 experimental cats, as shown by pertinent averages listed in Table 2. Comparison of the results showed that the phagocytic number rose by 0.04 in the control cats as compared with 0.35 in the experimental cats, or more than 4 times as high as in the control cats. Phagocytosis in the experimental cats was also four times as extensive as in the control cats.

Table 2.

Average phagocytic activity values in cats exposed to chronic inhalation of HClCh γ-isomer inhalation

Animals	No. of animals	Index	Initial data	7 days after 1st immunization	7 days after 2d immunization	7 days after 3d immunization	30 days after 3d immunization	7 days after revaccination	14 days after revaccination
Immunized and exposed to HClCH γ-isomer inhalation	5	Phagocytic number	0,78	1,13	1,26	1,29	1,14	1,16	1,0
		Phagocytic extensiveness. . . .	0,27	0,33	0,35	0,39	0,3	0,39	0,35
Controls	3	Phagocytic number	0,8	0,84	0,94	1,09	1,11	1,14	1,0
		Phagocytic extensiveness. . . .	0,3	0,32	0,32	0,31	0,3	0,40	0,36

Phagocytic activity rose to higher levels in the experimental cats with each successive immunization, a phenomenon not noted in the control cats. The rise in the phagocytic activity of the experimental animals seemingly reflected stimulated activity and development of the defense processes. No further clearly defined phagocytic activity changes had been noted in either the control or experimental animals during the remaining 45 days of the experiments. At the end of the experimental period there appeared a rise in the erythrocytes and leucocytes sedimentation rates of the cats. Two cats, which died two months after exposure to the inhalation of the poisonous γ-isomer, developed symptoms of apathy, loss of appetite, loss of weight, tremor and convulsions.

Conclusions

Prolonged effect of HClCH γ-isomer in the doses used elicited changes in the organism's immunobiological activity, particularly in the agglutination titer. The latter first rose to higher and then dropped to lower levels. The agglutination titer dropped to lower levels as the result of HClCH γ-isomer effect only after revaccination of the experimental animals, which points to the phase character of the changes, namely, a rise in the immunobiological organism reactivity during the early intoxication period followed by activity depression.

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Colorimetric Method for the Determination of Monoisoprophydiphenyl in the Air

pp. 40 - 41

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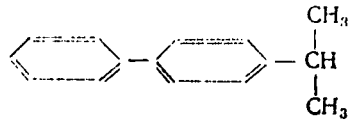
Monoisopropyldiphenyl (MIPD)



is a transparent liquid of a yellowish color, having a characteristic aromatic odor. Its m.p. is 270°-297°, sp. gr. at 20° is 0.9865, and its flash point is 117°. Ninety-five per cent of the final product consists of isomers ortho-, meta-, para-, and 5% of diphenyl. It is used as a heat carrier and in the production of snythetics in many branches of the USSR industry. The purpose of the present paper is to report on attempts to develop a method for the determination of MIPD in the air of working premises. This author used the method based on the colorimetric determination of MIPD by the Yanovskii reaction. Air samples were collected by the aspiration method using the Polezhaev microabsorber which contained 1 ml of a nitro mixture consisting of 10 g of ammonium nitrate in 100 ml of sulfuric acid of 1.82-1.84 sp. gr.; the air was aspirated through this medium at the rate of 0.2-0.4 li/min. Where the concentration of MIPD is suspected to be high, air samples can be collected by the vacuum method into special containers of 100-200 ml capacity. Two ml of the nitro mixture is added to the air sample containing vessel, and let stand for 1 hour periodically washing the walls of the sample container with the nitro mixture.

Perform the analysis as follows: remove 1-2 ml of the nitro mixture absorber and place into a separatory funnel marked at 50 ml to which 2 ml distilled water had been previously added; wash the absorber with 4 ml of distilled water and add to the separatory funnel. Further procedure of the MIPD determination can be accomplished either by extracting the polynitro compounds with acetone from alkaline solution, or by ether from the acid nitro mixture. In the first case, proceed as follows: neutralize the content in the separatory funnel with 30% NaOH to slight alkalinity, using litmus as the indicator. Then add 0.5-1.0 ml more of the alkaline solution, add 3 ml of acetone, and shake vigorously several times. Allow the mixture to separate into layers. Remove the upper aqueous-acetone layer into a colorimetric tube with a ground-to-fit stopper, which should yield 5.5-6.0 ml. If at this point there occurs a separation of salts in crystalline form, heat the separatory funnel in hot water up to 40-45°. Use a previously prepared

scale of MIPD preferably produced at the plant the indoor air of which is being investigated.

Place about 15-20 ml of the nitro mixture into a 25-50 ml volumetric flask and weigh on an analytical balance; add 1 drop of the MIPD and weigh again. The difference between the two weights represents the weight of the added MIPD. Mix the solution and leave rest for 1 hour, then add the nitro mixture up to the mark. Compute the amount of MIPD contained in each 1 ml of the final solution. Now, adjust the solution by the well-known analytical procedure, so that each 1 ml of the nitro mixture will contain 0.1 mg of the MIPD. Prepare the standard scale as follows: set up a series of colorimetric tubes 120 mm high and 15 mm in diameter. Add to the first tube 0.03, to the second 0.06, to the third 0.1, to the fourth 0.2, to the fifth 0.5, and to the sixth 1.0 of the standard MIPD solution; add to each of the tubes enough of the nitro mixture to make a final volume of 1 ml. Use a control tube which contains only 1 ml of the nitro mixture. Now, treat the tubes of the scale series the same as above described for the sample containing tube. After 30 min. standing compare the intensity of the developed yellowish-brown color with the intensity of the sample in the usual manner.

Prior to final extraction of the polynitro compound from the acid solution of the nitro mixture cool the separatory funnel under running tap water; add 5 ml of ethyl ether and thoroughly shake several times. This phase of the work should be done preferably under a chemical hood, and away from open flames. Remove the top ether layer and place into a colorimetric tube equipped with a ground-to-fit glass stopper. Add an equal volume of acetone, then add a 1:1 ether-acetone mixture to make a volume of 9 ml. Finally add 1 ml of 40% NaOH. Make colorimetric comparison 20 minutes after the addition of the alkaline solution. Prepare a standard scale from the same MIPD solution which was used in the extraction of the nitro compounds in the alkaline medium, i.e. 1 ml of which contained 0.1 mg of the MIPD.

Add to a series of colorimetric tubes 0.02, 0.05, 0.1, 0.2, 0.5, and 1.0 of the standard solution and bring volume in each tube to 1 ml by adding nitro mixture. Treat the series the same as the air sample. The control tube should contain 1 ml of the nitro mixture alone. The scale range extends over 2-100 μ of MIPD. Make final comparison of color intensities visually or photocolorimetrically using a green light filter of 450-600 mμ wave length.

Experiences indicated that the first extraction removed 92-95% of the nitro compound by the described procedure. It is felt that a second extraction would not add materially to the determination precision. The minimal amount of MIPD determined by the acetone-alkaline medium extraction was 3 μ in colorimetric volume, and by the ether extraction in acid medium, the minimum was 2 μ. In the presence of other aromatic substances, the method is nonspecific.

Experimental Hygienic Evaluation of Combustion Products Discharged into the Atmospheric Air by the Smelting Department of a Metallurgical Plant

pp. 58 - 59

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The smelting department of the plant is located in a residential block. It has one smelting furnace which burns 7 tons of fuel and produces 20 tons of pig iron per day. The hygienic investigation included a sanitary inspection of the territory over which the discharged smoke extended, and laboratory examinations of atmospheric air samples collected at given intervals. Air samples had been collected beginning with the month of May and ending with the month of December, a period during which the north-western and north-eastern winds prevailed in the vicinity. Air samples were tested for dust, soot and sulfur trioxide. Samples were collected in yards bordering on the plant grounds at the time the smoke plume spread over the yard at a distance of 12-30 m from the pollution origin. Sample collection was made by the aspiration method. Analytical results are presented in the Table below.

Dust, soot, and SO_2 concentrations in atmospheric air on the lee side of the plant

Meters from source of discharge	No. of air samples	Concentration in mg/m³	
		Maximal	Minimal
	Dust		
12–20	17	9,0	1,6
22—30	30	8,9	2,6
	Soot		
12–20	22	0,42	0,21
22–30	15	0,43	0,1
	Sulfur Dioxide		
12—20	18	0,94	0,12
22—30	24	0,32	0,15

Data listed in the Table show that maximal single soot concentration was 2.8 times as high as the maximal permissible concentration in atmospheric air at a distance of 12-30; the dust concentration at 12-30 was 18 times as high at its maximal permissible concentration. Minimal single dust concentration at 12-20 m was 3.2 times as great, and at 22-30 m distance 5.2 times as great as the maximal permissible concentration in atmospheric air. The discharged smoke contained predominately fractions exceeding

10 μ in diameter.

The maximal single CO_3 concentration at 12-30 m was 212 times as high as the maximal allowable concentration for atmospheric air. The minimal single concentration of CO_3 was within the permissible limits. Answers to questionnaires distributed among the residents contained complaints of headaches, general ill feeling, and a burning sensation in the throat. Leaves of trees growing at points of sample collection appeared wilted, yellowish and of stunted growth. Results of this investigation caused the sanitary authorities to order the smelting department to move outside the city limits. In compliance with such order, the plant administration began to move the smelting department in 1962 with the expectation of its complete removal from its old location to the new one in 1963.

Radioactivity of Some Building Materials
pp. 94 - 95

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B. Hultkvist and A. I. Shafir investigated 6 types of radioactivity in 14 types of building materials. According to data presented by them, highest radioactivity was emanated by clay, loam, granite, clinkers or slags, and bricks; lowest radioactivity came from chalk and chalky materials and from limestone. The present authors investigated the α- and β-activities of 16 types of building materials generally used in Moscow and its surroundings. The materials studied had been ground and sifted. α- activity was determined by a B-2 installation equipped with a scintilating device; β-activity was determined using same installation B-2, but one equipped with an end-counter, and a parallel cylindrical counter AC-1. When the end-counter was used 0.5 g of the investigated material was evenly distributed over a round target and placed into a lead housing. Ten samples of each material had been thus tested and the results averaged.

β-activity determinations with counter AC-1 were made with the aid of a special cylindrical double walled paper container. The inside wall of this container fitted closely over the counter surface with the outside wall creating an 0.5 air space. In this way the studied material was distributed around the counter in an even layer 0.5 cm thick. The entire material under study, depending upon its sp.gr., weighed between 20 and 35 g. Determinations of individual samples of the same material made by this method were identical so that only 2 determinations were made and averaged by this method. Each determination lasted one hour. The radioactive background was

determined immediately prior to making the material determination and lasted 30 minutes instead of 1 hour, and immediately after the experimental determination also for 30 min. Absolute activity of the investigated samples was determined by comparison with the activity of a standard irradiator, such as KCl, under identical conditions; results were processed statistically.

A comparison of results obtained in determining the radioactivity of the building material samples by the cylindrical and end-counters leads to the assumption that orientation determinations of building material activities could be made by either count method, but that the results of the cylindrical method were more precise, as shown in the Table below.

Radioactivity of Structural Materials

Materials	Obtained from	α-activity 10^{-12}	β-activity by radio-counter 10^{-12}	β-activity by cylindrical counter 10^{-12}
		Curie/g		
Cement BT	Nikolaev factory, L'vov	0,44	15,2	4,0
Reinforced concrete		0,42	2,7	5,5
Porous clay and pebble concrete	Karacharovo, Moscow Region	0,63	8,0	11,4
Portland cement		0,61	12,5	10,2
Crushed granite	Factory Gigant, Voskresensk	2,10	23,3	26,2
Crushed stone	Ukraine	0,60	17,9	2,4
»	Venevsk Region, Moscow Oblast			
	Akademicheskii karʹer, Moscow Oblast	0,55	8,2	6,0
Ceramic clay		0,64	30,5	30,0
Sand	Tuchkovsk Region, Moscow Oblast	0,56	10,8	6,9
Gypsum	Danilov Alabaster Plant of Moscow	0,21	9,8	1,3
Bricks		0,43	21,8	21,3
Floor tile		0,70	18,8	17,5
Glazed tile		0,63	10,9	14,0
Slag	Govardovo	2,49	26,5	31,5
»	Serpukhov	1,38	43,7	46,1
Cement mixture with ground slag	—	1,37	25,1	18,0

Data in the Table show that cinder materials possessed higher radioactivity than any of the other type materials, which is due probably to the enhanced concentration of the radioactive substances originally present in hard coal. Relatively high radioactivity was noted in gravel and in porous clay used as cement, also in bricks and in facing and floor tiles. The relatively high radioactivity of the mentioned building materials may be due to the fact that they were products of processed clay, which is one of the natural materials possessing high radioactivity. Lowest radioactivity was found in gypsum and in sand; relatively low activity was found in pure cement. However, with the addition to the cement of high radioactive components the activity of the cement naturally rose. Data in the Table show that materials possessing high α-activity also possessed high β-activity. Therefore, it can be assumed that granite and brick buildings emanated a relatively high

radioactivity as compared with buildings constructed of wood materials and concrete. In the light of above statements, consideration should be given to type of components added to the cement base.

A study of α-activity emanated by building materials may lead to information regarding the effect of building material dust inhalation on the health of workers engaged in processing building materials. In this connection, the present authors computed the radioactivity emanated by the combustion of coal originally possessing high α-activity. Results showed that air containing such cinder dust in 10 mg/m^3 concentration emanated a radioactivity equivalent to 2.49×10^{-17} curie/li, which is considerably below the maximal permissible radioactivity for working premises processing α-activity emanating raw building materials. The maximal permissible concentration of α-activity for working premises is 2×10^{-18} curie/li. It should be noted at this point that the combined α- and β-activities under similar conditions would amount to 3.4×10^{-16} curie/li. According to data presented by G. I. Rumyantsev in 1961, radioactive dust concentrations in the air under some working conditions may be as high as 210 mg/m^3, and the intensity of radioactivity would be equal to 7.14×10^{-15} curie/li, which is considerably above the permissible concentration limit. In other words, the radioactivity intensity emanated by 59 mg/m^3 air dust concentration would exceed the maximal permissible concentration. Therefore, it is suggested that in processing building materials which generated considerable amounts of radioactivity into the air of working premises the sanitary inspectors should take these factors into consideration, particularly in making recommendations for the introduction of rational sanitary protective measures.

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NO. 9, SEPTEMBER

Radioactivity Level of Moscow Ambient Atmospheric Air in 1957-1961

pp. 5 - 11

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Nuclear armament tests have been polluting the atmospheric air, the soil, plants, food products, etc. Considerable data have been accumulated during the past few years on the intensity of radioactive fallout at different seasons of the year. V. P. Shvedov and his collaborators (1959) Hvinden (1960), Martel (1959), and others found that the amount of radioactivity has been gradually increasing, reaching maximum in 1959; thereafter the amount of radio fallout was significantly reduced. Considerable data have also been accumulated showing that concentrations of β-active fallout have been changing. Peirson and his collaborators (1960) presented data which show that concentrations of β-active substances in the atmosphere paralleled the intensity of radioactive fallout. A drop in the level of radioactive fallout and in the concentration of radioactive substances in the air was noted beginning with the second half of 1959 following the moratorium on nuclear test explosions in 1958.

The present authors followed and recorded the amount of radioactive fallout and concentration of radioactive substances in the air surrounding Moscow during 1957-1961. Determinations of radio fallout intensity in relation to long-lived β-active aerosols were made by the snow sample method and by the open pan method. The first method was used during the month of March, when the snow began to fall. Snow samples had been collected every year at the same 20 points. The snow was melted and the water evaporated. The residue was ashed, and the ash placed upon the counter target and determined by means of B-2 apparatus equipped with counters T-25, BFL and SI-2B by the thin layer method. The count error did not exceed ±20% and the final results were expressed in terms of millicurie per 1 km^2. Quantitative twenty-four hour determinations of atmospheric radioactive fallout were made by the open collection method using containers 50 x 10 cm. The containers were lined with filter paper for better aerosol retention. Samples were collected at twenty observation points continuously in the region under study. Radioactive fallout catch containers were changed every 10 days at all points. Radioactive material accumulating upon the filter paper was processed as previously outlined and determined by the method described for snow samples.

Samples intended for the quantitative determination of long-lived

radioactive aerosol in the atmospheric air layer close to the ground were collected by the aspiration method, using filter FPP-15 and aspirating at the rate of 100-150 li/min through a 140 cm^2. The total aspirated air ranged between 100-180 m^3. The filter paper with the radioactive fallout material was ashed in a muffle furnace at 300-400°. An average of 4-6 samples had been thus collected per month, and between May of 1957 and December of 1962 the total of samples amounted to 237. Strontium-90 was determined by a method of precipitation with fuming nitric acid, as described by E. I. Orlova in 1959. Cesium-137 was determined by the method of isomophic precipitation in the form of a practically insoluble cesium phospho-molymbdate salt as described by E. N. Belyaeva in 1959. The group of rare earth radioactive isotopes were determined by the method of precipitation with oxalic and hydrofluoric acids with a consequent formation of practically insoluble oxolates and fluorides, also as described by E. N. Belyaeva in 1959. Cesium-144 was determined by isolating it from the mixture of rare earth isotopes by the carrier separation method, in the form of cesium iodate, after preliminary oxidation of trivalent cesium to tetravalent, as described by E. N. Belyaeva in 1959.

Ground snow samples were studied annually during 1956-1957, including winter of 1960 and 1961. Radiometric determinations showed that, despite careful adherence to prescribed steps of technical procedures, results varied considerably. This may have been due to uneven thickness of snow layers at sample collection points, resulting from drifts which carried the snow from place to place. Under such conditions, reliable results could be obtained only from an adequately large number of samples collected at many points. Data presented in Table 1 are averages, which characterize intensity of β-active substances in the snow samples collected during 1956-1961. Results show that the amount of radioactive fallout increased each succeeding year up to and including 1959, after which the fallout sharply dropped to 1/8-1/12 during the period of 1959-1960, and to 1% of the original during 1958-1959.

Table 1.

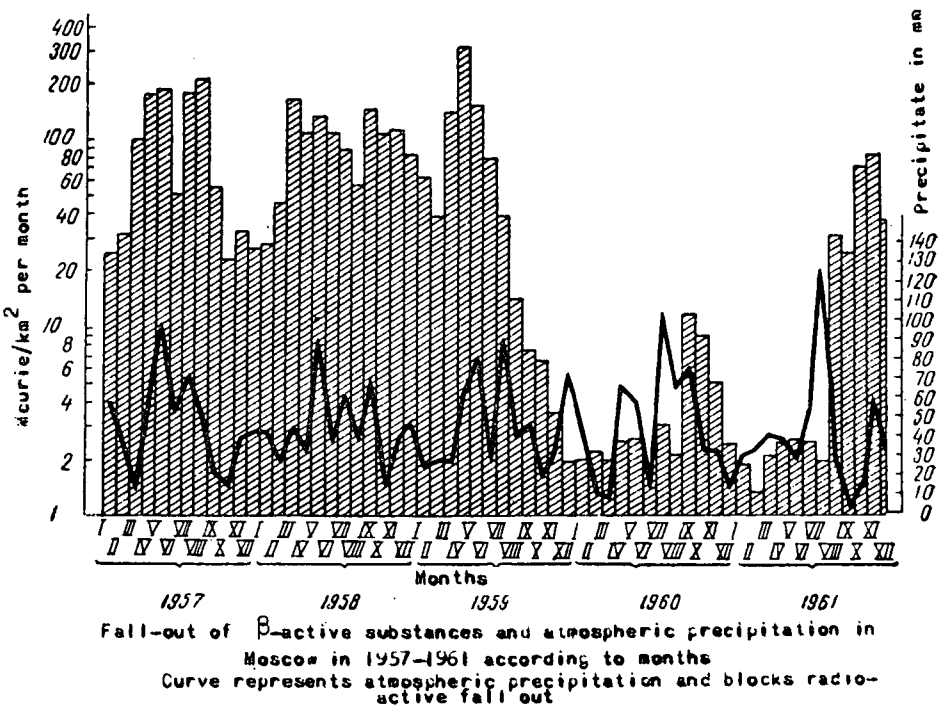
Amount of β-active substances in snow samples

Year	No. of samples	Amount of β-active substances in mcurie/km^2		
		Maximal	Minimal	Average
1956—1957	16	17	150	49±0,83
1957—1958	17	28,5	118	58,5±5,8
1958—1959	19	35	120	73,0±7,9
1959—1960	19	2,9	12	6,2±0,6
1960—1961	17	0,15	1,56	0,56±0,097

Rate of β-active fallout was determined by the collection method from February, 1957 to January, 1962, amounting to 59 months. Sample

collecting distribution was as follows: 541 during 11 months in 1957; 674 during 12 months in 1958; 783 during 12 months in 1959; 655 during 12 months in 1960, and 674 during 12 months in 1961, making a total of 3327 samples in 59 months. Final results indicated that the total fallout of long-lived β-active substances amounted to 1047 microcurie/km^2 for the 11 month period in 1957; it amounted to 1114 microcurie/km^2 for the 12 month period in 1958; 998 microcurie/km^2 for the 12 months in 1959; 45.88 microcurie/km^2 during the 12 months of 1960; and 220 microcurie/km^2 for the period of 12 months of 1961. Curves in Fig. 1 graphically represent the quantitative course followed by the long-lived β-active fallout substances. The curves show that during 1957, 1958, and 1959 there appeared 2 maxima annually, one during the spring-summer period of April-May, and the other during the fall period of September - October. No fall maxima had been noted in 1959 or during the spring of 1960 and 1961. Absolute values and the character of radioactivity fall curves during 1960 and 1961 differed markedly from those recorded the previous years.

Fig. 1.



Fall-out of β-active substances and atmospheric precipitation in Moscow in 1957-1961 according to months
Curve represents atmospheric precipitation and blocks radioactive fall out

Beginning with January and through September of 1960, and from January through August of 1961 the monthly radioactive fallout had been practically the same, ranging from 1.3 to 3 microcurie/km^2. In September of 1961, coincident with the resumption of nuclear bomb tests, the amount of radioactiive fallout rose sharply, reaching 30 microcurie/km^2. The rise continued during the following months, and rose to 80 microcurie/km^2 in December. Thus, 92% of the radioactive fallout of 1961 occurred during the last 4 months of the year. Maximum radioactive fallout of 300 microcurie/km^2 was noted during May of 1959, and minimum of 1.3 microcurie/km^2 was noted during March of 1961. A parallel study of monthly radioactive

fallout with simultaneous atmospheric precipitation, pointed to a degree of correspondence between the two indexes, particularly during the months of April-August and October-November, 1957-1959, as illustrated by curves in Fig. 1. The total picture appeared different in 1960 and 1961. For example, the amount of radioactive fallout during January, February, March and April of 1960 was approximately the same, while the amount of atmospheric precipitation during January-February was 7 times as high as during March-April, showing that the correlation between radioactive fallout and the atmospheric precipitation was not of a definitive quantitative character. It was noted that the amount of radioactive fallout depended not only upon the absolute amount of atmospheric precipitation, but also on its general character and duration, etc.

Some of the samples collected by the open pan method during 1959-1961 were analyzed radiochemically. Records were kept of radioisotopes playing a part in biological investigations, such as strontium-90, cesium-137, and the rare earth elements. Twenty radiochemical analyses were performed in 1959, the results of which are listed in Table 2. Atomic weapon tests had been resumed in 1961. As a result, the amount of strontium-90, cesium-137, and of rare earth metals falling out from the atmosphere had increased as compared with those found in 1960. The ratio between cesium-137 and strontium-90, according to the data obtained in this investigation averaged 2.1 in 1960 and 1.6 in 1961. These results coincide with values found in the literature. Average monthly concentrations of radioactive substances found in the atmospheric air during 1957-1961 listed in Fig. 2 show that radioactive substance concentrations in most instances had been found in the limits of $n \times 10^{-15}$ curie/li. Maximal radioactive substances were found during the spring and fall, which is in agreement with observations made by the open collection method. Highest radioactive substance concentrations were found in the air in March, 1958, when it reached 9×10^{-15} curie/li. Beginning with July, 1959 the level began to drop, and in 1961, the concentration fell to 9.2×10^{-17} curie/li which amounted to a hundred-fold drop. Results of air samples collected and analyzed during each month of 1960-1961 are presented in Table 3.

Table 2.

Amount of radioactive substances in samples collected by the open dish method (in acurie/км^2)

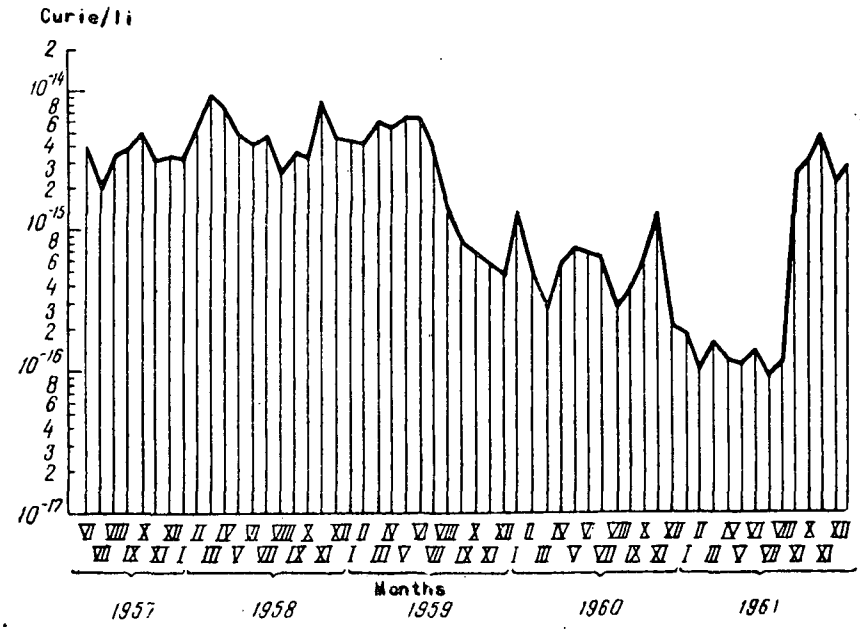
Sample collection date	Strontium-90		Cesium-137		Total of radioactive elements	
	During collection period	Average 24 hours	During collection period	During collection period	за период отбора	Average 24 hours
7—23/VIII 1958	0,14	0,0088	0,194	0,012	5,06	0,32
9—25/X 1958 г.	0,145	0,0085	0,1	0,059	3,7	0,28
17/XII—2/I 1959	0,044	0,0028	0,085	0,053	1,28	0,08
13—29/I 1959	0,066	0,0041	0,092	0,058	2,14	0,134

Table 3.

Amount of radioactive fall-out during 1960 and 1961 in mcurie/km^2

Months	Strontium-90		Cesium-137		Ratio of Cs-137/Sr-90		Cerium-144 Praseodymium 144	
	1960	1961	1960	1961	1960	1961	1960	1961
January	0,067	0,021	0,04	0,043	0,6	2,0	0,48	0,177
February	0,146	0,021	0,022	0,037	0,15	1,8	0,85	0,2
March	0,037	0,047	0,072	0,113	2,0	2,4	0,41	0,161
April	0,032	0,047	0,16	0,093	5,1	2,0	1,05	0,26
May	0,077	0,084	0,16	0,203	2,0	2,4	1,0	0,33
June	—	0,166	—	0,27	—	1,6	—	0,411
July	0,093	0,05	0,255	0,083	2,6	1,6	1,86	0,17
August	0,08	0,075	0,218	0,171	3,6	2,3	1,56	0,42
September	0,031	0,22	0,065	0,17	1,6	0,8	1,14	2,95
October	0,047	0,111	0,046	0,089	1,0	0,8	0,7	2,7
November	0,063	0,45	0,119	0,37	2,2	0,8	0,53	8,67
December	0,056	0,39	0,083	0,29	2,6	0,7	0,75	18,35
Totals	0,73	1,68	1,24	1,93			10,33	35,0

Fig. 2.



Concentration of β-active fall-out from the air over Moscow in 1957 - 1961

Average annual radioactive substance concentrations in the atmospheric air, based on results of 31 samples collected in 1957, amounted to $3.5 \pm 0.30 \times 10^{-15}$ curie/li, and in 1958 based on 52 samples, it amounted to $4.8 \pm 0.45 \times 10^{-15}$ curie/li; in 1960, 52 samples had been collected which gave an average of $0.64 \pm 0.086 \times 10^{-15}$. Finally the 51 samples collected in 1961 gave an average of $1.1 \pm 0.01 \times 10^{-15}$ curie/li. Average concentrations during the period of January - August, 1961 (34 samples) amounted to 0.13×10^{-5}, and during the period of September-December (17 samples, the average amounted to 3.1×10^{-5}. Thus, the average annual radioactive substance concentration in the atmospheric air for the 3 years of 1957-1959 remained practically the same, which ranged between 3.2×10^{-15} curie/li. This level dropped to one-fifth of the one given for 1960.

The hygienic atmospheric air pollution evaluation during 1961 must take into consideration not only average annual concentrations, but also average concentrations determined during January-August, prior to the resumption of atomic weapon tests, and during September-December, following the resumption of such tests. Average radioactive substance concentration in the atmospheric air during January-August of 1961 amounted to 0.13×10^{-15} curie/li, indicating that it continued to fall from the levels of previous years. The average radioactive substance concentration in the atmospheric air sharply rose with the resumption of the atomic weapons test in September of 1961 and amounted to 3.1×10^{-15} curie/li. Thus, atmospheric air pollution with radioactive substances was of the same level at the end of 1961 as it was during the period of 1957-1959.

Conclusions

1. The present investigation extended over 6 years and yielded data which illuminated the course of changes in the levels of Moscow atmospheric air radioactivity. Highest level of radio activity was recorded during 1957-1959 in the first 6 months of 1959 and at the end of 1961. Results showed that the radioactive substance concentrations in the air in the fall of 1958 retained their high levels after the resumption of nuclear weapon tests in the fall of 1958 for 6-7 months. This was followed by a substantial fall in the radioactivity level, reaching a minimum at the end of 6 months. Average monthly radioactive substance concentrations in the atmospheric air ranged between 1×10^{-16} and 1×10^{-14} curie/li during the period of observation.

2. Results of radiochemical analyses showed that 0.73 microcurie of strontium-90, 1.24 microcurie of cesium-137 fell per 1 km^2 of ground surface in 1960; 1.68 microcurie of strontium-90 and 1.93 microcurie of cesium-137 fell per 1 km^2 of ground in 1961.

3. Results of the present investigation point to the occurrence of spring and fall maxima of radioactive substance fallout from the atmospheric air. A degree of correlation appeared to exist between the amount of radio-

active fallout and atmospheric precipitation.

4. Results of atmospheric air investigation made by the method of snow samples, open pan collection procedure, and aspiration method were in good agreement and reflected the course followed by atmospheric air pollution with radioactive substances in Moscow environs during the 1957-1961 period.

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Labor Hygiene Problems in Plants Manufacturing Construction Glass

pp. 23-30

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The state of labor hygiene in glass making factories was first investigated by Ya. Kuritskii and by A. P. Flerovskii in 1927, by I. I. Matusevich and E. A. Peregud in 1933, and again by Matusevich in 1934. Many reports have appeared of late which presented some data regarding labor conditions in the glass making industry and dealing with the state of health and morbidity among the workers. Among the authors of such reports were Milev (1957), Berdan, Pafnote, and Vaida (1959), E. E. Vishnevskaya (1960), R. Sh Samitova (1961), V. S. Bodyako, G. I. Pashkovskaya, N. S. Irger (1961), Z. S. Gavrik, I. G. Gulitz, and M. Ya Suponitskii (1959) and K. K. Vrochinskii (1961). Reports of the above authors dealt primarily with labor conditions in glass packing and glass bottle making plants. None of the above mentioned authors included in their investigation the study of labor conditions in construction glass making plants. The present paper is a report of labor conditions and morbidity noted among workers of several construction glass making plants.

Construction glass making consists of the following steps or stages: preparation of the glass making mixture in the composition department, mixture smelting in the glass furnace, vertical drawing out of the glass or horizontal glass blowing, glass cutting into given sizes, sorting and packing. The

above steps in making construction glass have been largely mechanized within recent years. This applies particularly to the loading and unloading of the raw materials, their grinding, drying, sifting and mixing of the components for the preparation of the final mixture, which is also mechanically loaded into the glass smelting furnaces. Many plants have also mechanized the control of the smelted glass mass levels in the furnaces, the furnace temperature, and several other production steps. The mechanization and automation of the basic construction glass making steps led to considerable improvement in the working conditions of the employed personnel. Nevertheless, there still remained some phases of the work which have been and still are conducted under favorable labor conditions from a hygienic and strictly physical viewpoint. The most important of these is the suspended dust in the air of some working premises, unfavorable temperature, humidity, noise and vibration. Data in Table 1 show that dust density in the air of the composition, dose measuring and mixing departments was 10-fold and hundred-fold as great as the maximal permissible dust concentration limit. High air dust concentrations had also been noted during loading and conveying of the individual components and of the final mixture. Cleaning of the work premises was done manually using a broom which also created air dustiness of high densities. In such instances, the dust was of a highly mixed character. Dispersion determinations, showed that 86.4-100% of the dust particles measured up to 5 μ in diameter, of which 51-92.2% measured up to 1.3 μ in diameter.

Table 1.

Mg/m^3 of dust in the air of compound departments working points at different production operations

Production processes and working points	Mg/m^3 of dust: Maximal	Minimal
Unloading of coal, sulfate mixture, soda, kaolin, etc.	610	10
Crushing and sifting of components (dolomite, chalk, etc.)	555	30
Loading and unloading of drying drums	72	2
Sieve sifting of components	227	72
Mixing of components	620	2

Air dust concentrations between 16-66 mg/m^3 had also been noted in other production departments, and an air dust concentration between 100 and 103 mg/m^3 was noted at loading of glass plates onto the transportation wagons, due to glass breakage. Air dust concentrations at other sections of the mechanized vat department did not exceed the maximal permissible concentration. The dust in this department consisted entirely of particles measuring up to 5 μ in diameter, 82.4-91.6% of which measured up to 1.3 μ in diameter. Temperature and humidity conditions of the construction glass production department were the most unfavorable from the viewpoint of labor hygiene. Data in Table 2 show that the air temperature at all points of this department was high during the warm season of the year.

Table 2. Air temperature and relative humidity in the machine and the melting vat departments

Production space	Outdoor temperature 19 - 28°				Outdoor temperature -6 to +2°			
	Temperature in degrees		% of relative humidity		Air temp. in degrees		% of relative humidity	
	Maximal	Minimal	Maximal	Minimal	Maximal	Minimal	Maximal	Minimal
Glass melting furnace control panel	38,0	26,0	52	23	20,0	7,0	43	20
At thin layer charging	43,0	26,0	52	20	22,0	8,0	44	17
At furnace burners	43,4	29,0	43	14	21,0	6,0	54	21
At VVS machines working points								
Lower platform	48,0	22,0	47	15	23,0	4,0	61	11
Automatic cutting and breaking off section	50,0	26,4	40	15	39,0	17,0	39	7
Position of glass cutters	31,0	20,4	59	31	19,0	5,0	53	17

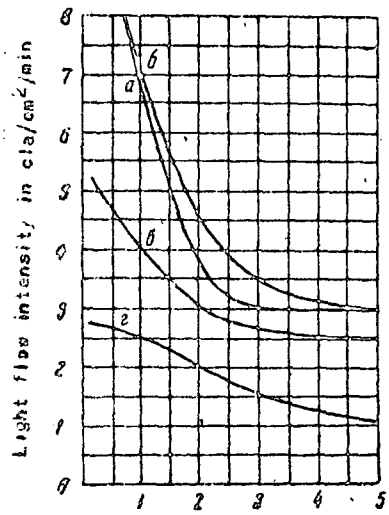
The maximal air temperature at certain points exceeded the maximal outdoor temperature by 3-22°; particularly high air temperature had been noted close to the glass smelting furnace and to the vertical glass drawing-out. The air temperature in this department fluctuated considerably at different points during the cold period of the year: at some points the temperature was the same as it was outdoors, at other points it varied from the outdoor air temperature by 10-18°, whereas at other points, it was uncomfortably high even during cold winter months, as shown in Table 2. In addition, considerable air temperature fluctuations have been noted at one and the same department sections on different days. Air temperature fluctuations at different sections of the department varied with the distance of the working spaces from the heat generating sources.

Operational periodicity of heat producing processes also played a part in the temperature fluctuation. Thus, during the summer months the indoor air temperature fluctuated between 10-33° at the same working point, while the outside air temperature fluctuation did not exceed 8°. During the winter months, when the outdoor temperature fluctuation stayed within the range of 6-8°, the indoor temperature at such working points fluctuated in the range of 7-30°. The glass melting furnace and the vertical glass drawing-out machine constituted sources of high temperature radiation. The radiation intensity coming from the melting furnace reached 7 cal/cm^2/ min at 1 m, and 3-1 cal/cm^2/min 5 m from the glass melting furnace. (see curves in Fig. 1). The extensive insulated furnace surface radiated heat of 90-190°. The heat radiating from the furnace surface at a distance of 1 m amounted to 0.75-2.5 cal/cm^2/min, and at 4 m from the furnace it amounted to 0.3-0.6 cal/cm^2/min as shown by curves in Fig. 2.

The walls, ceiling and floor of the building housing the plant acted as secondary sources of heat emanation, and the temperature of such surfaces ranged between 40-68°. The inside wall temperatures of the building ranged

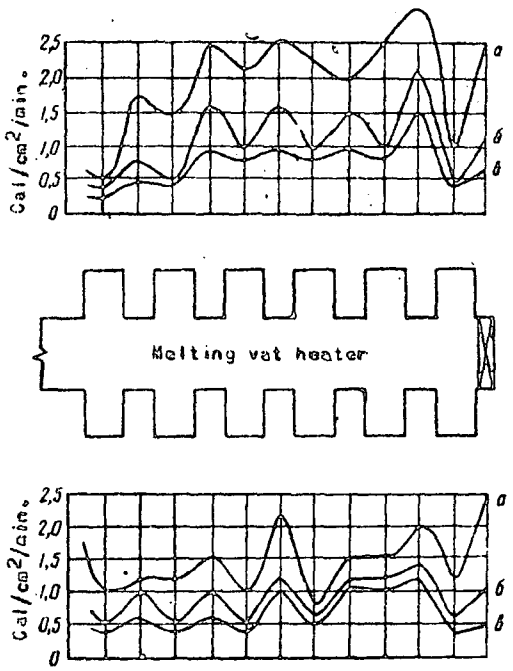
between 43-55° during summer months. Intensive heat also radiated from the vertical glass drawing machine pits; thus, the heat radiation 1 m from the machine pit ranged between 1.5-2 cal/cm^2/min. Intensive heat came from the final glass plates and glass fragments accumulated during glass cutting.

Fig. 1.



Infrared radiation intensity between the melting vat burners (System No. 1)
a – between 1st, 2d, 3d, and 4th burners; b – between 4th and 5th burners; c – between 2d and 3d burners; d – between 5th and 6th burners with passage closed.

Fig. 2.



Infrared radiation intensity at the working space of the mechanized melting department in the proximity of each melting vat burner (System 1)
a – one meter from the burner; b – 2 meters from the burner; c – 3 meters from the burner

The glass plate had a temperature of 100-140° as it entered the vertical glass drawing machine, and 1 m from the machine it radiated heat ranging between 0.6-1.26 cal/cm^2/min. Heat also emanated within the department confines during the glass plates transportation to the cutting tables. All such sources of heat emanation contributed to the formation of the heat and moisture character of the local department micro climate. Production noise is an important factor which affected general working conditions. Measurements established that the general noise prevailing in the glass making department ranged between 60-67 decibels. The noise intensity created during loading of the crushed material into the thin layer loader ranged between 95-97 decibels. Dropping of broken or cracked glass into the bunker produced a noise of 100-108 decibels, while loading the plate glass upon the transport wagons produced a noise of 110-115 decibels. The exhaust fan and motors in the composition and melting departments produced a noise of 80-82 decibels. Thus, the conclusion is that the general noise in the glass producing department was of a high decibel intensity.

Examination of workers' physiological functions disclosed a lowered sense of odor perception caused by dust accumulated on the nasal mucosa. Workers employed at points of unfavorable temperature and humidity conditions developed tension of the thermo-regulation function, particularly during the summer months, as shown by increased temperature of the forehead and the chest skin by 2.5-3°, of the palms by 2-4.5°, and by excessive perspiration. It was estimated that glass smelters lost between 2.8-5.9 kg of weight through perspiration, including water taken in during the working hours. Workers employed at the vertical glass drawing machine lost between 3 and 5 kg of weight, and the glass cutter between 2-5.8 kg of weight through perspiration during working hours. The pulse rate rose by 16-24 beats per minute, especially during physical exertion at high air temperatures. The systolic blood pressure frequently dropped by 10-15 mm at the end of a working day. Not withstanding the high heat elimination, particularly caused by intensive perspiration, the organism retained enough heat to cause a body temperature rise by 0.3-1°, or higher in some cases. Increase in skin temperature and in cardiac contractions were less pronounced during the winter months. Loss in body weight due to profuse perspiration was also less pronounced during the winter months, ranging between 1-4.3 kg among workers employed at different production processes. Sharp temperature fluctuations noted in the machine-bath departments elicited drops in the organism temperature, especially during winter months. Glass smelters, machinists, and other workers stated that they preferred to spend most of the time close to the glass furnace and machines during the winter months to avoid the cold.

An estimation of the heat balance by the formula of W. K. Vitte showed the following: if the heat radiation in the immediate proximity of a heat emanation source exceeded the heat lost by the body, then the air temperature will be 7.7°, radiation will be nill, and the air current rate will be 0.95 m per second, the heat balance will be 2.5 cal/cm^2/min, and at a distance of 8 m the air temperature will be 2°, the air current rate will be 1.7 m/sec, and the heat balance will be 4.36 cal/min. Workers operating the glass drawing machines, and their helpers, generally move from points of high heat emanation to points at which loss of body heat increases; they usually subject their organisms to sudden cooling which is conducive to frequent common cold development.

A thorough study was made of the morbidity rate and of loss of work time among workers of construction glass producing plants. Results indicated that the high morbidity and loss of work time noted during the investigation was closely related to unfavorable labor conditions. Elaborate statistical analysis verified this conclusion. Morbidity rate among workers of specific occupational groups had been compared with average morbidity rate among all workers of the glass producing plant. Results showed that average morbidity of workers operating at most unfavorable working conditions was higher than the average morbidity of the plant's total working personnel.

The differences were noteworthy and significant. Thus, average morbidity among workers employed under conditions of high temperature and heat radiation exceeded the average morbidity among the workers of the entire plant by 65%, and among workers employed at points of dust generation, the morbidity rate exceeded the average morbidity rate of the plant as a whole by 75%, etc. Rates of morbidity also varied with the length of employment at a particular occupation.

A clinical study was made of 570 workers connected with the high temperature and high dust generating phases of construction glass manufacture. Results clearly pointed to a direct connection between the employees' state of health and the sanitary-hygiene of labor conditions. Medical examination of workers engaged in the high temperature occupations showed a lowered arterial blood pressure more often than an increase in the blood pressure. Such workers also showed symptoms of myocardial dystrophy as a result of unfavorable working conditions, particularly high air temperatures. Chronic bronchitis was found frequently among workers operating under conditions of continuous high temperature heat radiation and high air dust density. The same was true of gastrointestinal and digestive morbidity. Fifty-three per cent of such workers showed disturbance of the peripheral nervous system in the form of radiculitis, neuritis, neuralgia, neuromyositis, etc. Affected conjunctivae were noted in 15% of workers engaged in dust generating phases of the work, and in 18% of workers operating under conditions of high air temperature. Considerable eye, ear, nose and throat changes had been noted in 60% of workers operating under unfavorable air temperature and humidity conditions, and in 50% of workers operating under conditions of high air dust density.

An important phase of the present investigation was the development of means suggested for the sanitization of working conditions in the construction glass making plants. Some of the suggestions have already been instituted in some plants. The developed and recommended suggestions can be outlined as follows: (1) it was recommended that the transportation, loading and unloading of the components used in the final mixture should be completely mechanized and properly enclosed to prevent any dust from getting into the air; in this connection, the vacuum transportation system or, the so-called, pneumotransportation, was regarded as the most efficient from the sanitary-hygienic viewpoint; moistening the crushed material intended for transportation was recommended as a temporary sanitization measure; (2) it was also recommended that the crushing and grinding machines should be equipped with appropriate dust catching and dust aspirating installations; it was noted that the presently existing equipment was inadequate and ineffective to accomplish the intended purpose; (3) it was recommended that sifting of the ground components and of the final product should be done under leakproof housing, and that opening of the housing whenever necessary should be done after proper care had been taken to prevent any dust from getting into the surrounding air; (4) it was recommended that the dosing apparatus and the component mixer should be enclosed by a leakproof housing; from the

sanitary viewpoint, mixing apparatus C-10, or the like, appeared to be the most rational; (5) manual cleaning of the working premises and dust blowing off or dusting with the aid of brooms or similar equipment must be forbidden, and mechanized up-to-date cleaning and dust removing apparatuses should be installed throughout the plant; (6) appropriate measures should be taken at the recommendation of experienced engineers for the control of humidity and heat emanated by some of the production processes; this can be attained by the use of heat insulating materials, by appropriate ventilation systems, and the like; as stated above, this should be done at the recommendation and direction of experienced engineers in the pertinent field of sanitation; (7) measures should be introduced for the prevention of sudden temperature drops in the winter and undue temperature rise in the summer; the existing construction glass manufacturing technology should be thoroughly examined and analyzed by trained industrial construction engineers and production specialists and where necessary should be improved or replaced so as to create more favorable labor conditions from the physical and physiological viewpoints.

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Acetylene Determination in the Air by Infrared Spectroscopy

pp. 51 - 54

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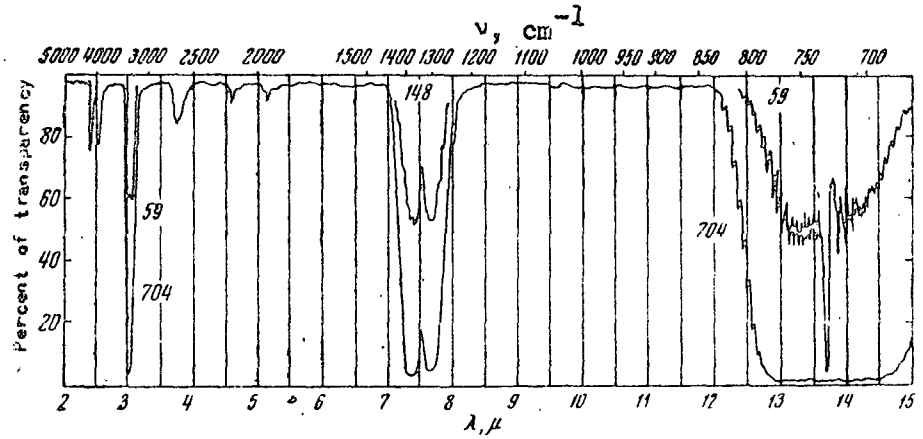
Acetylene vapor is present in the air of working premises in the production of calcium carbide, in the air of acetylene stations and of plants which use acetylene in their production processes. No maximal permissible concentration of acetylene vapor in the air has as yet been established. The All-Union Congress dealing with problems of industrial ventilation recommended that 0.5 mg/li (0.043% by volume) of acetylene vapor in the air should be adopted as its maximal permissible concentration. A colorimetric method for the determination of acetylene in the air has been developed by M. S. Bykhovskaya, S. L. Ginzburg, O. D. Khalizova in 1904 which enabled the de-

tection of 0.003 mg/ml of the tested solution. However, determination of very low concentrations of acetylene vapor in the air by this method required the collection of large volume air samples, which is time consuming. In addition different samples are characterized by different color shades which makes precise determination at times difficult, if not impossible. By the method here described it is possible to determine minute quantities of acetylene in the air with the aid of infrared microscopy.

Fig. 1 shows that the acetylene spectrum has a wide absorption band at 730 cm^{-1} due to the fluctuations in the H-C triple bond group, as shown by G. Gertsberg in 1949. With the aid of a single illumination infrared spectrophotometer and using a standard gas tube of 16.8 cm thickness it is possible to determine 0.023 mg/li or 0.002% by volume of acetylene concentration. Spectroanalysis was made in the region of 700-800 cm^{-1} using a sodium chloride prism. The gas containing window was also made of sodium chloride. The working width of the slit was 400 microns. The effective spectral width of the slit was 3.4 cm^{-1}. Dispersed light in the 730 cm^{-1} region was accounted for by measuring the intensity of the dispersed light which passed through a film of lethium fluoride and which was equal to 7.5%. Correction factor for light dispersion was also determined by making a spectrum for pure acetylene (p = 766 mm of mercury) in this region. In this instance the light dispersion amounted to 4%. The latter method appeared more reliable, since the lethium fluoride incompletely absorbed rays of the given wave length.

Fig. 1.

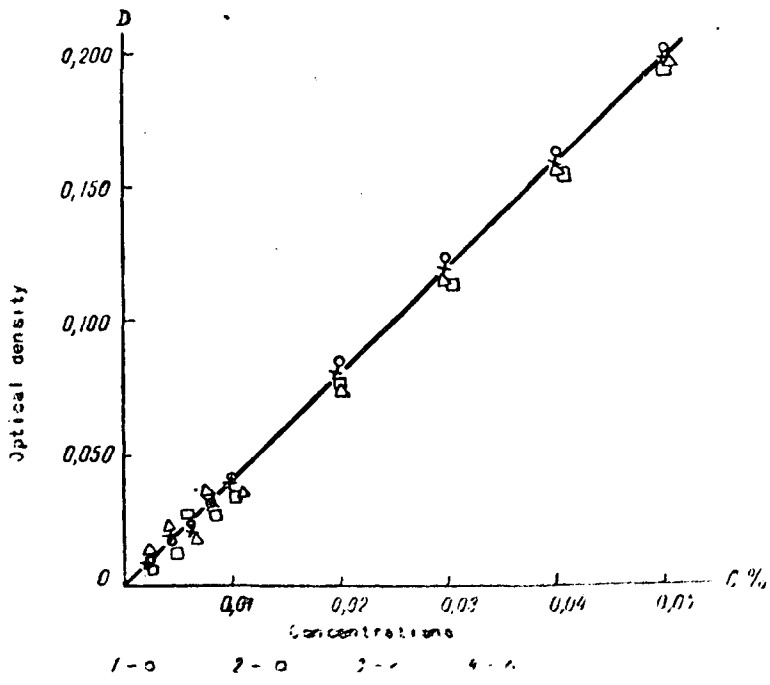


Infrared spectrum of acetylene. Pressure in mm of mercury, as indicated at curves

Impurities were removed from the acetylene by passing the sample through solutions of sodium bichromate in concentrated sulfuric acid and dried by passing it through concentrated sulfuric acid containing calcium chloride. A graduated standard curve was constructed by obtaining spectra of gas mixtures containing 0.050, 0.040, 0.030, 0.020, 0.010, 0.008, 0.006, 0.004, and 0.002% of acetylene by volume. Prepare acetylene concentration gas mixtures as follows: fill the gasometer with dry nitrogen gas and add a given volume of acetylene. Raise the pressure in the gasometer to 2

atmospheres by adding nitrogen gas. The acetylene concentration thereby becomes equal to 5% by volume. Reduce the pressure to 76 mm of mercury and again raise the pressure in the gasometer to 2 atmospheres, which will reduce the acetylene concentration in the air mixture to 0.25% by volume. Again reduce the pressure in the gasometer to 400 mm of mercury, and again raise it to 2 atmospheres by adding dry nitrogen gas, which produces a 0.05% by volume of C_2H_2. Force this gas mixture into the gas pipette up to a pressure of 1 atmosphere. After the spectrometric determination of this mixture has been made pump a part of it out from the pipette and replace by dry nitrogen gas which again lowers the acetylene concentration in the gas mixture container. In this way, spectra can be prepared for reduced acetylene concentrations down to 0.02% by volume. Determinations of acetylene band intensity at 730 cm^{-1} was made by the Wright basic line method (1941). Straight line curve in Fig. 2 is a calibrated curve of ratios between optical density in the band of minimum absorption at 730 cm^{-1} and acetylene concentration in the air. The straight line character of the curve shows that in this instance the Lambert-Beer law prevailed. The value of molar extinction coefficient (ε) at a given band is equal to 529 li/cm x mol. The relative error of acetylene determination in the concentrations interval of 0.002-0.050 by volume is characterized by the data shown in Table 1. Comparative determinations of different acetylene concentrations were made by the spectral and colorimetric methods; results are listed in Table 2. Acetylene concentration in the initial gas was determined by the method of A. E. Volkov (1953) using gas analyzer VTI, and determination of acetylene concentration in the gas mixture was made by the method of M. I. Bogdanov (1959).

Fig. 2.



Calibrate curve for the determination of acetylene in the air.
1 - First experimental series; 2 - second experimental series;
3 - third experimental series; 4 - fourth experimental series.

Table 1.

Precision of acetylene determination in the air

Acetylene concentrations during mixture preparation	Acetylene concentrations as determined by calibrated curve	Deviation	% of relative error
Absol.%			
0,006	0,006	0,000	0
0,010	0,012	0,002	20,0
0,020	0,023	0,003	15,0
0,030	0,030	0,000	0
0,0354	0,034	0,0014	4,0
0,040	0,041	0,001	2,5
0,047	0,048	0,001	2,1

Table 2.

Results of spectral and colorimetric determinations in absolute %

Acetylene concentrations during mixture preparation	Results of spectral detns.	Results of colorim. detns.
0,005	—	0,003
0,037	0,036	0,028
0,041	0,041	0,028
0,042	0,0425	0,028
0,050	—	0,021

Data presented in Table 2 show that the colorimetric method yielded somewhat lower results. However, a detailed comparison of the characteristics of the 2 methods in relation to acetylene trace quantities in the air is now in the process of study. Thus, in this paper a method was described for the quantitative determination of low acetylene concentrations in the air; it was developed on the basis of infrared spectrophotometry and is sufficiently sensitive to determine acetylene vapor in the air within the limits of 0.002-0.05% by volume.

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Some Principles Underlying the Determination of Maximal Permissible Dust Concentrations in the Air of Working Premises

pp. 88 - 94

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In 1960 the Soviet Union adopted a new list of maximal allowable concentrations for poisonous gases, vapors and dust in the air of working premises. According to the old concept, air polluting dust was classed as toxic and nontoxic, for which two corresponding maximal permissible pollution con-

centration had been adopted. Only dust containing free silicon dioxide was regarded as toxic. At present there exists an extended list of maximal permissible concentrations for dusts of different kinds. In establishing the new list of maximal dust concentrations, the Committee on Maximal Limits had taken into consideration not only the presence of free silicon dioxide but also other factors. The most important factor was percent of free silicon dioxide in the dust. On that basis the Committee established three grades of pneumonoconiosis potentialities, depending upon the amount of free silicon dioxide contained in the dust. The Committee had also lowered the maximal allowable concentration of silicon dioxide containing dust up to 1 mg/m^3, and established lower maximal permissible concentrations for some silicates, including asbestos, and considerably lowered the number of instances in which 10 mg/m^3 could be regarded as the maximal permissible concentration in the air of working premises.

Comparison between results obtained by the gravimetric and the particles' count methods can be only of an approximate nature, nevertheless, results presented by Elkins in 1961 may prove of considerable interest. Elkins had analyzed the count coefficients of Drinker and of Hatch and came to the conclusion that the maximal allowable concentrations recommended in the USA for different mineral dusts were 2-9 times as high as those correspondingly adopted in the Soviet Union. The recommendations made by USA investigators have been in use in many other industrially developed countries which had adopted the principle of hygienic air standardization. This clearly indicates that the maximal allowable dust concentrations in the air of working premises adopted in the USSR insured safer hygienic conditions for the workers. On that point, the present authors express no difference of opinion; however, they believe that the principle underlying the classification of dust as "nontoxic" [1] or "toxic to varying degrees", should be discussed more thoroughly. In fact, many investigators of this phase of sanitization are still analyzing the principles upon which the new classification is based.

In the first place, doubt arises in the minds of the present authors regarding the necessity of excessive breaking up into many standards of the interval between present concepts of maximal and minimal permissible concentrations of different dusts, thereby introducing fine distinctions between the degree of dust "harmfulness". It is, indeed, difficult to select a single principle on which to base such interval breaking up. On the one hand, different maximal permissible concentrations have been adopted for groups of dust which were of almost the same degree of pneumonoconiosis potentiality. Such, for instance, as artificially abrasive dusts for which 5 mg/m^3 was adopted as the maximal permissible concentration, and loam cement and other mineral dusts which are free from silicon dioxide, and for which 6 mg/m^3 was adopted as the maximal permissible concentration in the air of working premises. On the other hand, the same 2 mg/m^3 concentration was adopted as the maximal permissible concentration for dusts con-

taining 10-70% free silicon dioxide, despite the fact that dusts containing 15-65% of quartz possessed high fibrogenosis potentialities, indeed, higher than those possessed by the dusts mentioned just above. The fact that the new list of standards contained maximal permissible dust concentrations of 1, 2, 3, 4, 5, 6, 8, 10 mg/m^3 creates the impression that medical science is in possession of precise quantitative data on which to base such fine differentiations between the effect of, so-called, nontoxic dusts on the organism. It may give rise to the idea that the task of establishing maximal permissible concentrations for some, so-called, nontoxic dusts is in a more advantageous position than poisonous gases and vapors, in as much as the latter differ from one another most frequently only by the order of magnitude, as is shown by the fact that 115 of the 168 inacted or adopted maximal permissible concentrations fall within the range of 1×10^{-n} and 5×10^{-n} mg/li.

The present authors believe that such impressions are erroneous. It is well known that degrees of toxicity as determined by experimental data, and on which the adoption of maximal permissible concentration is based did not agree with the results obtained by experimental studies of pneumonoconiosis. Dust inhalation by experimental animals produced visible changes in the lungs only when dust concentration in the air of the experimental chamber was substantially above the adopted maximal permissible concentration limit. Intratracheal dust administration to experimental animals, which is the most frequently used method of evaluating the effect of different substances on the organism, cannot by its very nature yield data for the direct or computed determination of maximal permissible dust concentrations in the air of working premises. Finally, data obtained as a result of medical examination and general observation of large groups of workers, who had been exposed to the effects of low dust concentrations for many years, could be obtained only in exceptional cases and with considerable difficulty. It should be noted, however, that maximal permissible concentrations of 1 and 2 mg/m^3 have been arrived at by just such a method in the case of quartz containing dusts.

It is only natural that under such unavoidable conditions all new maximal permissible concentration values adopted in the new list should be based on qualitative and semiquantitative comparisons of the nature and degree of dust effect on the organism, whether experimentally or clinically arrived at. Although, this approach to the standardization of dust concentrations in the air of working premises appears to be the only possible one, it must be admitted that it can not be used as a rational basis for the fine distinctions in the standards adopted in the new list. Despite that, the present practice in developing "precise" sanitary dust standards follows basically the precedent established by those who recommended and adopted the new list of investigated dust concentrations. In fact, it is sometimes extremely difficult to decide which of the dusts elicited simulating pathosymptomatic pictures on the basis of which maximal permissible dust concentration of 5 or 6 mg/m^3 should be adopted. Such difficulty presents itself even after a complex histopathologic picture has been obtained for a dust of low toxicity experimental

It should also be born in mind that such a procedure of determining maximal permissible dust concentrations is basically oriented around previously described evaluations of the organism's reactions as seen by other investigators and not as presented by the direct observation of the studied material. By the above described procedure of sanitary dust concentration standardization the quantitative evaluation of the fibrosis reaction, elicited by the dust under experimental conditions, is not given due consideration. The present authors found this to be particularly true with regard to many experimental investigations which had been used as bases for the adoption of the new maximal permissible dust concentrations in the air of working premises. On the other hand, it would be erroneous to expect that other methods, such as biochemical evaluation of the degree of experimental fibrosis, should yield basic results applicable to the differentiation between dusts requiring 4 and 5, or 5 and 6 mg/m^3 as the maximal permissible air concentrations, since even the results of most carefully controlled biochemical experiments are reliable only within certain limits. Results obtained by the gravimetric method of dust concentration determination in the air also show that the fine differentiation in maximal permissible dust concentrations incorporated into the new list were not based on rational foundation. Thus, in making duplicate air-dust concentration determinations by the aspiration method, one test may yield a concentration of 5 mg/m^3 and a duplicate concentration of 6 mg/m^3. According to GOST specifications the maximal allowable dust concentrations should be a single one but according to the new list the determinations require 2 levels of maximal permissible dust concentrations. In addition, it is well known that dust density in the air of working premises at any particular point may vary within wide limits in short time periods. For instance, a dust concentration fluctuation between 4 and 6 mg/m^3 frequently occurs in many plants without any apparent cause, but under the system presented by the new list such variations in air dust concentrations cover 3 levels of the newly adopted maximal permissible air dust concentrations in working premises. In this connection, it is of interest to note, that only 3 maximal concentration levels have been established in the USA for 16 types of mineral dust in the air, namely, 5, 20, and 50 million parts per cubic foot of air. It should be added, however, that, whereas the present authors regard the levels of maximal permissible dust concentrations adopted in the USA as inadequate for the sanitary protection of workers, they, nevertheless, agree with the basic principle of 3 levels.

On the basis of the above discussion, the present authors suggest that the new list of maximal permissible dust concentrations be reviewed and revised in the following way: that 1 of 3 permissible dust concentrations, namely 2, 5, and 10 mg/m^3 be adopted as the maximum for nontoxic mineral organic or metallic dust, with the exception of dust containing more than 70% of free silicon dioxide, for which the present 1 mg/m^3 maximal permissible concentration should be retained. The present authors base their reasoning on the fact that 1 and 2 mg/m^3 concentrations have been adopted as maximal for dust containing a considerable amount of silicon dioxide, and

that no evidence had been presented requiring positive or negative changes in the upper (10 mg/m^3) limit of dust concentrations. Finally, the above stated considerations present reasons for the selection of only 1 intermediate level between 2 and 10 mg/m^3 as the maximal permissible concentration. For the same reason the present authors suggest that the selection of maximal permissible limits of all types of dust; as recommended in the newest lists, be limited. This suggestion has no relation to dust possessing frankly toxic and irritating properties, nor to dust possessing radioactive and cancerogenic properties. It is suggested that in establishing maximal permissible limits of dust concentrations in the air of working premises the following be taken into consideration:

(1) that 2 mg/m^3 be adopted as the maximal permissible concentration of dust possessing clear-cut fibrogenic properties, as evidenced by results of laboratory experiments or clinical and microscopic examinations;

(2) that 5 mg/m^3 be adopted as the maximal permissible concentration of dust possessing some degree of fibrogenisis, as shown by experimental data, but the intensity of which was below that possessed by quartz and / or dusts which elicited development of pneumonoconiosis in persons exposed to such dust for long periods of time, but the intensity of which was lower and the occurrence less frequent as compared with the development of silicosis;

(3) that 10 mg/m^3 be adopted as the maximal permissible concentration for dusts which experimentally produce only slight cellular reactions or a barely perceptible reticular fibrosis around points of dust accumulation, but which produced no fibrosis even in as long a period as 18-24 months after intratracheal or inhalation administration of high dust concentrations; this includes dusts which after the inhalation of high concentrations over a period of many years under working conditions produced symptoms of pneumonoconiosis and of pneumosclerosis in only occasional well established and properly diagnosed cases.

The present list of maximal permissible dust concentrations rests on dusts grouping on the basis of silicon dioxide and silicate per cent they contained; such a grouping limits the criterion of standardization to the capacity of dust to elicit pneumonoconiosis of predominantly interstitial and fibroplastic characters. However, it is known that "Instructions for the Application of the List of Occupational Diseases" approved by the USSR Ministry of Health in 1956 permits to class as occupational diseases cases of chronic diffuse bronchitis and pulmonary emphysema, which develop in persons of long work records under conditions of intense air-dust pollution even in the absence of roentgenological evidence of pneumosclerosis. The present authors regard this position taken by the Ministry of Health as of great significance and as basically rational. Records accumulated in the Sverdlovsk Institute, and pertinent references found in the literature, clearly indicate that pneumonoconiosis was not only the effect of dust, but that

it was also an occupational disease accompanied by the development of bronchitis and symptoms of pulmonary emphysema. This disease [2] was noted among workers who had roentgenologic symptoms of dust pneumonoconiosis, which may be lacking in some cases. In any case, such workers must be diagnosed as having an occupational disease frequently accompanied by considerable functional disturbances. It should be remembered that considerable bronchial changes had been seen in persons exposed to dusts of low fibrogenic potency, or in the absence of any fibrogenisis, as the case may be in persons exposed to the inhalation of dust consisting of elemental silicon. In the light of what was said above, the determination of maximal permissible limits of dust concentrations should be based not only on the previously mentioned criterion of fibrogenisis, but must also take into consideration their effect on the bronchi, since statements regarding the etiology of occupational diseases have been officially recognized as pertinent documents.

In this connection the following must be recognized assuming that the differential approach to dusts of different chemical origin as factors in the etiology of pneumonoconiosis was a correct one, then dust as a factor in the production of bronchitis is still looked upon as undifferentiated. Proper dust differentiation in relation to chronic bronchitis etiology must be based on data derived from extensive clinical and experimental investigations pertinent to this problem. In this connection the present authors wish to emphasize the urgent need for such investigations. At the moment, and in the absence of the necessary data, the present authors suggest that 5 mg/m^3 be adopted as the maximal permissible concentration of dust which causes undoubted wide spread occurrence of dust bronchitis. Included in this category should be dusts which produced low intensity fibrogenosis. If this viewpoint should be adopted, then 10 mg/m^3 as the maximal permissible concentration for some dusts of vegetable and animal origin, even when free from silicon dioxide, could not be accepted as rational. The adoption of a single theoretical approach to the standardization of maximal permissible air dust concentrations presupposes the use of unified and standardized methods for the study of dust effects, on the organism, particularly in experiments with animals. Such methods can be developed only with the participation of workers engaged in different phases of laboratory investigations. In arriving at unified and standardized methods for the study of maximal permissible limits of air suspended dusts special consideration should be given to the following phases of the investigation: species and age of the experimental animals, their number, dose, concentration and route of dust administration, dust dispersion, duration of exposure and observation periods, minimal parameters of morphological investigation, means for quantitative determination of dust accumulation in the lungs, chances of fibrosis formation and statistical data processing. The adoption of unified investigation methods should not preclude the freedom to conduct supplementary investigational procedures, and should be regarded as the minimum necessary for securing an adequate basis for the determination of maximum permissible dust

concentrations in the air.

The discussion would not be complete without defining the maximal permissible concentration as the maximal single concentration indicated in the introductory part of the latest list. Such an approach to the concept of maximal permissible concentration elicited controversies even with regard to toxic substances. The controversies become profounder and more acute when the above mentioned concept is applied to dusts which elicit pathological conditions only upon chronic exposure to their effect. Theoretical considerations and experimental evidence indicated that the accumulated dust deposits in the lungs over a long period of time are determined, all other conditions being equal, not so much by the dust concentration in the air, as by the duration of daily exposure to dust inhalation. Therefore, it is suggested that maximal permissible nontoxic dust concentrations should be regarded as average concentrations prevailing at specific processing positions during the work day. Where the air dust density significantly fluctuated during the day, due to changes in technology or other similar causes, the maximal permissible dust concentration must be compared with the average of the fluctuating daily concentrations. This means that air dust concentration determinations must be made in a processing room or department every time the technological procedure is changed. Neither the duration of the changes, nor brief peaks of dust concentration will have any significant effect on the value of the, so-called, maximal single concentration.(39)

The above discussion does not exhaust the many problems which may arise in arriving at maximal permissible dust concentration limits. There are also other factors, such as volume and rate of air inspiration and the problem of simultaneous presence of dust and gas, etc. But for the present the authors prefer to limit their discussion to the above presented points. The problems raised by the present authors and their concrete suggestions are controversial; it is not expected that they will be treated as proposed; however, it is hoped that the discussion will lead to the development of unified and standardized theoretical and practical methods of approach to the problem of standardizing maximal permissible dust concentrations in the air.

Notes:

(1)
The term in quotes, "nontoxic", has been officially adopted by sanitary code N 101-54; like many such terms in biology it represents an arbitrary designation. However, it serves its purpose from a practical viewpoint. For this reason, the authors continue to use it in discussing the subject of maximal permissible concentration limits.

(2)
Many authors designate this disease by the term of "miner's" disease and believe it to be widespread. Some authorities do not regard it as an occu-

pational disease.

(3)

Assume that there has occurred a 10-minute rise in quartz dust concentration MAC/mg/m^3. Assume also that during a 6 hour work day the basic dust concentration was 0.5 mg/m^3. Solve equation $(10 \times 350 \times 0.5)/ 360 = 1$ and find that the permissible concentration during the 10 minutes would be only 18.5 mg/m^3. Under practical conditions and longer periods of dust concentration the permissible maximum would be of even lower value.

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Effect of Natural Climatic Conditions on Atmospheric Air Pollution Near Seashore Cities

pp. 95 - 96

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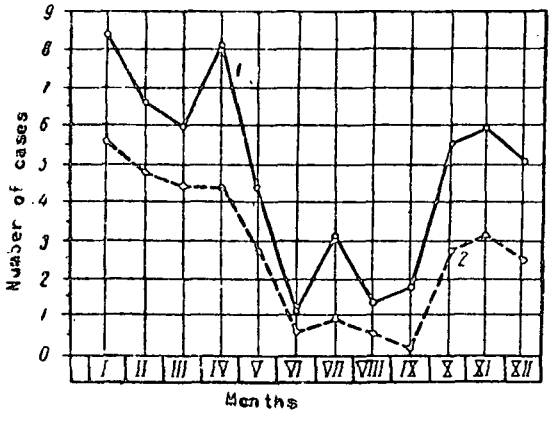
It is known that some cities located close to the seashore which had no definite sources of atmospheric air pollution had a considerable air pollution fallout amounting to 730-900 tons per 1 km^2 annually, and single air pollution concentrations 7 times as great as the specified maximal permissible air pollution concentration. This paradoxical phenomenon can be explained by specific natural local climatic conditions. The topography complex of near seashore cities has a considerable effect on the city's local climatic conditions. Cold air masses descending along the hill slopes produced disturbances in the vertical temperature gradient, as a result of which smoke failed to rise and extended horizontally over the city, creating heavy smogs consisting of gaseous vapor and solid particulate substances. These conditions become considerably aggravated in the presence of temper-

ature inversion.

The vertical temperature gradient was analyzed on the basis of data accumulated for the past 5 years at two meteorological stations located in strategic positions favoring such analysis. Distortions in the vertical temperature gradient had been observed monthly throughout the year at different recurrent frequencies. Highest recurrence frequency was noted during the winter and spring months, that is during the heating period when the smoke discharge into the atmospheric air was greatest, as shown by the curves in the figure below.



Repeated cases of vertical temperature gradient inversion in seashore cities ambient air in 1954 - 1959

1 - Total number of inversions;
2 - Cases of temperature inversion

The topography of city territories under observation was complex in each case, so that the mouths of industrial smoke stacks and of residential chimneys were frequently on the level with streets and windows of residences located at the higher slope levels. Under such conditions the smoke plume axis reached the breathing level immediately after its discharge, that is at a time when the smoke pollution was at its maximum. For this reason, the measure adopted for the protection of the city's atmospheric air by raising the height of the residential chimneys and industrial smoke stacks proved ineffective near seashore cities of a complex geological topography. In places of complex topography, points of contact between the smoke plume and the ground surface depended, not only upon the smoke stack height and the horizontal distance from it, but also on the steepness of slopes surrounding the locality; for this reason the usual standard maximal permissible pollution regulations were inadequate for the protection of atmospheric air cleanliness in cities located in regions under present discussion.

Historically developed plans for the construction of near-shore cities are characterized by inflexibility. In one such city more than 52.11% of the [illegible] slopes had a 12° slope. Slopes of many other streets varied between 2° and 7°. Automobiles traveling through such streets operated under conditions of increased load while ascending and descending such slopes, and required the continuous use of brakes, especially during winter months. The gases exhausted by automobiles under such conditions contained an increased number of incomplete combustion products, and an increased concentration of toxic substances. The characteristic distribution of atmospheric precipitation according to annual seasons, constituted one of the factors which in the case of near-seashore cities impeded the successful process of air self purification. Thus, the amount of atmospheric precipitation

during the cold winter months was 45-65% below that of the centrally located cities, despite the fact that at such time the atmospheric precipitation in seashore regions was supposed to be at its maximum. Climatic conditions of cities located within the immediate proximity of the Pacific Ocean were characterized by constant trade wind patterns which blew in the northerly direction from the south during the summer months, and in the reverse direction during the winter months. Such seasonal changes in the wind direction presented additional difficulties to rational planning of industrial regions in relation to residential sites.

Present code Sn 41-58, p. 101 specifies that the average annual wind pattern, particularly during warm months should be the determining factor in planning cities and their direction of expansion. However, such a specification could not properly apply to construction of cities under above described seasonal wind direction changes. Atmospheric air pollution concentrations are affected by natural climatic conditions, particularly when the fog season and consequent reduced natural ultraviolet radiation density persisted for many days. Under such conditions the prevailing climatic condition strongly intensified concentrations of atmospheric air pollution.

Analysis of meteorological observations made during the last 18 years in the vicinity of near-seashore towns under study indicated that during 1924-1941 the number of foggy days increased from 21 to 28%. Examination of meteorological data accumulated by the city under investigation and by a nearby meteorological station showed that the city lost annually 13-56, with an average of 26, clear days. The effect of atmospheric pollution on sanitary living conditions was studied in 1962 by the questionnaire method specially prepared for this investigation. The total number of questionnaires distributed among inhabitants residing under different air pollution conditions at different city regions was 829. The questionnaires were distributed among residents of 9 city regions. Results obtained in regions No. 1 and No. 9 are briefly presented below. Region 1 was the site of a harbor and of some industrial plants. Inhabitants of this region (17.5%) complained of damage and soiling caused by the air pollution to their upper clothing; 92.2% of the answers complained of the impossibility to dry the washed clothing in the open air. Region No. 9 had the appearance of a well-managed section, and its air pollution was of a low intensity. Accordingly, their complaints came from about 35 - 22% of the questioned residents. Among the predominant complaints, were unpleasant odor, headaches, nausea, cough, and during the still winter months also dense fogs. Generally, the unfavorable climatic conditions occurred simultaneously, which enhanced the unfavorable effect of the atmospheric pollution on the city residents.

Answers to the questions also showed that outdoor air pollutants penetrated inside the residences even with the doors and windows closed, a condition which most obviously must not be tolerated. Row houses facing south or north suffered most intensely from the above mentioned dust pene-

tration into the dwellings. This was especially true with regard to apartments of the first and second building stories. Under any set of atmospheric and air pollution conditions the situation was generally more favorable in region No. 9 than in region No. 1.

Summarizing, it can be stated that natural climatic conditions of cities located in close proximity to seashores contributed to the formation of high pollution concentrations even when pollution discharges were relatively low. This fact makes the problem of atmospheric air protection more pressing in cities located in close proximity to seashores. The facts discussed in this paper must be taken into consideration by authoritative bodies concerned with the planning and construction of near seashore cities.

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Radiation Danger Presented by Surfaces Contaminated with Alpha-Active Substances

pp. 101 - 103

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Radioactivity intensity in premises assigned to work with radioactive substances is affected to a considerable degree by radioactive contamination of the walls, ceilings, installations and instruments. Such surface contamination with α-active substances seldom, if ever, affects the exterior surroundings, but is harmful to the health of persons employed inside such radio polluted premises, affecting particularly exposed body parts. There exists a definite connection between surface radio contamination and the concentration of radioactive substances in the air, depending upon the character of the protecting coverings, the rate of air ventilation, the general dustiness of the premises, and the chemical and physical condition of the α-active substances. The rate at which radioactive substances entered the air also depended upon the volume of air which passed over the contaminated surface. Surface contamination with α-active substances under similar conditions is accompanied by a greater entrance of radioactive aerosols into the air than in contamination with β and γ-active substances. This is particularly true of such α-emanators as Po, Ro, and Pu, which are characterized by aggregate emanation. In addition, the chemical composition of

the contamination also plays an important part, since it has been shown that the volatility intensity of the same compound, or of the same radioactive element, may differ. This was shown by K. Bengal in 1960, who noted different degrees of air pollution in the laboratory when working with Polonium dioxide and Polonium halide, which he explained on the basis of high volatility of polonium halides.

Effect of surface contamination with α-active substances on ambient air has been studied by many investigators. It was shown that in the presence of a given surface contamination, and in the absence of known air contamination sources the formed air aerosol concentration was at the level of its maximal permissible concentration. Data presented in the Table below show that intensity of surface contamination effect on the condition of air was practically the same for different α-emanating substances, especially if differences in the maximal permissible concentrations in the air were taken into consideration. Data obtained by Aizenbad did not support such an opinion. This can be explained by the fact that Aizenbad and other investigators did not have at their disposal data related to the rate of air ventilation in the investigated premises, a fact which prevented them from obtaining quantitative relationships between the degree of surface radio contamination in the working premises and its concentration in the air. The present author found that by complying with the specified maximal surface contamination level (500 α-particles per 150 cm^2 per min.) and by insuring an 8-fold to 10-fold air ventilation per hour, the air aerosol concentration could be reduced to below the maximal permissible level. Under such conditions a "reserve" was created between the contaminated surfaces which conditioned the maximal permissible air aerosol concentration and the maximal permissible contamination levels specified by sanitary regulations.

Загрязненность рабочих поверхностей, обусловливающая предельно допустимую концентрацию α-активных веществ в воздухе

Active substance	MAC in the air of working premises in cu/li	α-particles per 150 cm^2 which determine the MAC in the air	Authors
Polonium-210	$1 \cdot 10^{-14}$	4 000—10 000	G. M. Parkhomenko, 1961
Radium-226	$3 \cdot 10^{-14}$	10 000	G. M. Parkhomenko, G. Ya. Zolotukhina, 1960
Radium-226	$3 \cdot 10^{-14}$	100 000	Eisenbud, Beatz, and Barry, 1954
Plutonium-239	$2 \cdot 10^{-15}$	3 300	Dunster, 1955
Plutonium-239	$2 \cdot 10^{-15}$	6 600	Chamberlain and Stanbury, 1955

(1) Cited from R. Sherwood, 1961

The present author is of the opinion that such a "reserve", or safety factor, was practical from the hygienic viewpoint. It would be erroneous to establish the maximal permissible surface contamination

at a level requiring a maximal permissible air pollution. It must be remembered that work with radioactive substances is generally accompanied by other atmospheric air polluting causes which cannot be completely disregarded. In addition, it has also been shown that a connection existed between radioactive surface contamination and degree of workers' skin of arms and of clothing surface contamination, which must also be taken into consideration in establishing surface contamination standards. Determination of maximal permissible limits for radioactive surface contamination must give consideration to the possibility of attaining same technically. Experience indicated to the present author that laboratory work with α-active substances can be conducted so as to avoid intensity of surface contamination exceeding the permissible level. Radioactive surface deactivation can be markedly facilitated by rational planning of the work, selection of suitable equipment, and installations, and many other sanitary protective steps. Present sanitary contamination controlling regulations specify that intensity of contamination be determined before and after cleaning operations, It is obvious that such a radioactivity standardization procedure must apply to clothes of employees whose work was directly connected with radioactive substances. Radio contamination of surfaces should not exceed 500 α-particles/150 cm^2. In this connection, it appears more rational to standardize surface contamination not on the basis of 150 cm^2, as has been done before, but on the basis of 1 cm^2, since many of the apparatuses used in measuring contamination have different transmitter unit areas, and adopting the 1 cm^2 basis would simplify measurement calculations. The terms of fixed and non-fixed contamination, and the need for standardizing same are frequently mentioned. In the opinion of the present author, these are ill defined concepts.

A review of the literature shows that radioactivity contamination levels have been adopted by many countries. In work with α-radiating substances the permissible surface contamination varies within 3300 and 33300 α-particles per 100 cm^2/min. Different standards have been suggested for surface contamination in different laboratory sections and for different contaminated surfaces. The present author is of the opinion that limited contamination areas should be restricted to low contamination levels. It has been demonstrated that localized radioactive contamination frequently served as a source of radioactive substance dispersion over the entire working premises; a gradual averaging of contamination has been observed in instances of poorly organized deactivation due to the carry over and spread of contamination to and over the entire surfaces of the floors or equipment during manual cleaning of the premises. This is particularly true of floor installations, and apparatus surfaces. In the light of what has been said above, different maximal levels of surface contamination should be established for different zones of some laboratories. In other laboratories, where work with radioactive substances was conducted at infrequent and short time intervals it is possible to set a limit of permissible surface contamination 5-6 times as high as in other places. Under presently prevailing conditions it can be safely stated that strict observance of surface contamination limits for radioactive substances adopted in the USSR reduces the effects of sur-

face radiation to safe levels.

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NO. 10, OCTOBER

Toxic Properties and Biotransformation of Benzotrichloride

pp. 30 - 34

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Benzotrichloride ($C_7H_5Cl_3$) is a transparent yellowish fluid which is insoluble in water, partly soluble in alcohol, benzene and ether. Its. M. W. is 194.48, sp. gr. is 1.37 and b.p. 214-220. It is used in the production of plastics and in the rubber industry as a vulcanizing catalyzer and as an intermediate product in the synthesis of organic substances. Knowledge of its toxic properties is incomplete. N. V. Lazarev, of the USSR, merely states that it elicited eczema.

The present authors studied the toxic properties of benzotrichloride by the methods of vapor inhalation and skin application. Experiments were conducted with white rats and white mice placed into special chambers of 100 li capacity where they had been subjected to single, and also daily 2 hour inhalations of different benzotrichloride vapor concentrations. The daily inhalation exposure lasted 60 days. Concentrations of benzotrichloride in the air of the exposure chambers was determined by a procedure developed in cooperation with Z. M. Pimenova. The benzotrichloride was decomposed

in acid medium and the Cl determined with the aid of $AgNO_3$. Air samples were collected by aspiration using an aspirator devised by the institute; the aspirator was filled with 10 ml of alcohol. Upon completing the sample collection 1 ml of the alcohol was dilluted with 5 ml of distilled water to which 1 ml of 10% HNO_3 were added. A standard solution was prepared by dissolving benzotrichloride in alcohol. Sensitivity of the method was 0.005 mg in a given volume. Results indicated that air containing 1 mg/li of the benzotrichloride vapor was lethal to the experimental animals. Results of acute toxic experiments produced the following clinical picture: mucous membrane irritation, dyspnea and general excitability. These symptoms appeared almost immediately following benzotrichloride inhalation and was followed by delayed motor activity. No complete narcosis was observed. Higher concentration of the vapor produced extensive dilatation of the peripheral vessels of the tail, paws and ears at the end of the experiment. Upon return to fresh air inhalation the delayed motor reaction disappeared, and the experimental animals entered into a brief stage of excitation. Inhalation of large doses elicited partial narcosis which lasted 2-3 days. Benzotrichloride concentrations up to 0.1 mg/li elicited irritation and stimulation.

Death of white mice caused by the inhalation of benzotrichloride in lethal concentration was paralleled by the appearance of sharp vascular disturbances and irritation of the mucous membrane in the upper respiratory tracts. Autopsies of the perished animals showed vascular disturbances such as plethora of the lungs, liver, kidneys and intestinal tract, brain bleeding of varying degrees; liver cells showed signs of diffuse fatty dystrophy; kidney tissue appeared dull and the adrenals were enlarged and swollen. Histologic examination of internal organs of white mice and rats which died following a single 2 hour inhalation of air containing benzotrichloride also showed plethora of internal organs, extensive and small brain bleeding, swelling of cortical brain cells, of the subcortical nodes and of the trunk. The lungs showed signs of swelling and of catarrhal and desquamative bronchitis; micro droplet type diffuse fatty dystrophy appeared in the liver; the kidneys showed a faintly defined protein dystrophy of the convoluted tubular epithelium. Thus, results of single benzotrichloride vapor effect in different concentrations showed that it possessed narcotic properties and elicited considerable irritation of the conjunctiva and of the lining of the upper respiratory tract; it also elicited vascular dilatation and morphologic changes in the lungs, liver and kidneys.

The chronic effect of benzotrichloride on white rats was determined by exposing the experimental animals to the inhalation of air containing benzotrichloride in 2 concentrations in the exposure chambers for 2 hours daily: the first concentration was 0.03 mg/li which elicited no toxic manifestations in the experimental animals upon a single inhalation exposure; the other concentration 0.01 mg/li elicited general irritation and some delay in the animal's motor activity after a single inhalation exposure; the effect

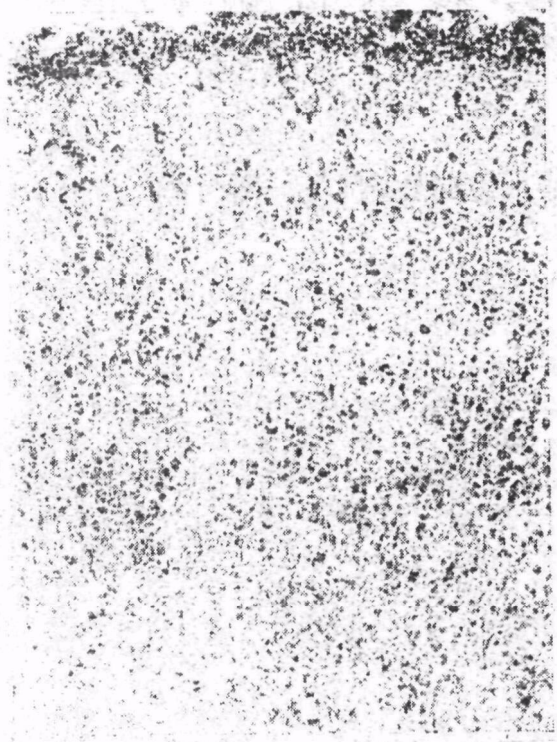
was transient and of short duration. Chronic experiments had been conducted with 30 rats of 170-200 g, of which 10 were kept as controls. The general behavior and appearance of the experimental rats at first differed in no way from those of the control animals. However, at the end of the first week, rats subjected to the inhalation of air containing 0.1 mg/li of the benzotrichloride began to lose weight, showed signs of malnutrition and their external appearance reflected internal pathology. Animals became aggressive towards their cell mates and towards the laboratory service personnel. They refused to eat the food normally supplied to them but devoured rats which died in the exposure chamber. Rats subjected to repeated inhalation of air containing 0.03 mg/li of the benzotrichloride also showed signs of malnutrition and loss of weight, and at the end of the experiment, loss of weight in individual rats ranged between 35-76 g. No such signs developed among the control rats which, in fact, gained weight. Despite the developed unusual aggressiveness among the experimental rats, an investigation of their threshold of neuromuscular stimulability showed no signs of unusual changes.

Benzotrichloride is a derivative of benzene and chloroform and is a CO-trichlorotoluol. Accordingly, the present authors made a thorough study of the experimental rats' peripheral blood picture. Results showed that generally the number of erythrocytes remained within the normal limits of 6×10^6 - 624×10^3; hemoglobin also remained practically normal, ranging between 12.8-11.9 g%. On the other hand, the number of leucocytes dropped considerably to the range of 8,600-14,400, and some of the rats which originally had a leucocyte count of 12,000 showed a count of 5,200 per 1 mm^3. Results of the Quick test showed a loss in the liver function activity. As previously mentioned, a single acute exposure to the toxic effect of benzotrichloride inhalation elicited liver vascular dilatation and repeated inhalation of the poisonous vapor lowered the blood pressure considerably. Thus, rats with a maximal arterial pressure of 90/110 mm manifested a blood pressure of 60 mm after 2 months of daily benzotrichloride inhalation, and in some individual rats the arterial blood pressure dropped to 30-25 mm. Repeated benzotrichloride vapor inhalation elicited considerable changes in the mucous membranes of the bronchi, brought about development of mucous bronchitis and of focal purulent pneumonia; internal organs showed occult bleeding; there appeared some liver cell fatty degeneration, fatty degeneration of the convoluted tubule epithelium and also depletion of the superenal cortex.

Extensive changes were noted in the nervous system, especially in the cortex and in the thalamo-hypothalamic region. Darkly stained cells were noted in the cortex, and there were also wrinkled cells, most of the pyramidal type. These were surrounded by cells with vacuolized protoplasm and cariocytolyzed cells as shown in Fig. 2. Sharply defined vacuolized protoplasm and cariocytolysis were noted in cells of the thalamo-hypothalamic region. These signs may explain the appearance of clinical intoxication in the form of hyperstimulability and aggressiveness of the experimental

animals, while changes which appeared in the cells of the hypothalamic region may be regarded as the cause of drop in the animals' blood pressure. The investigation of benzotrichloride toxicity and of its toxical dynamic properties have next been studied by a follow up of its physical, chemical conversion in the organism and the nature of its metabolites eliminated by the organism. Some data indicated that toluol in the organism underwent changes similar to benzoic acid, and that it was eliminated with the urine as hippuric acid.

Fig. 1.



Rat adrenal; depletion of cortical lipoid (magnif. 8 x 10)

Fig. 2.

Rat brain; caryocytolysis of cortical cells

It was indicated in one of the preceding paragraphs that benzotrichloride was a CO-trichlorotoluol; therefore, the present authors worked on the assumption that benzotrichloride might also be changed in the organism chemophysiologically similar to toluol, and that it, too, might be eliminated with the urine as hippuric acid. On the basis of such an assumption the following experiments were performed: the rate of hippuric acid elimination via the urine under normal conditions was determined in a group of 10 rats. This was done by the Quick method as described by M. Ya. Savina. The animals were then placed into an exposure chamber 2 hours daily for 20 days and were subjected to the inhalation of air containing 0.03 mg/li of benzotrichloride vapor. The amount of hippuric acid eliminated by the experimental rats prior to exposure to the inhalation of benzotrichloride vapor containing

air ranged between 14-20 mg/day. After exposure to the inhalation of air containing 0.03 mg/li of the toxic vapor for 20 days, the daily hippuric acid elimination with the urine rose in individual cases to 47 mg as a result of inhaled benzotrichloride conversion in the organism; one of the conversion products was identified as sodium benzoate which became converted to hippuric acid. It should be noted at this point that the possible formation of other benzotrichloride metabolites cannot be excluded. Thus, Stekol found, in 1938, that chlorinated toluols having a haloid in their side chain, could be transformed into benzylmercapturic acid. In the next stage of the investigation, a study was made of benzotrichloride effect on the skin and its possible penetration through the intact skin. In this case, experiments were connected with rabbits; benzotrichloride was applied to fur-free skin at the rate of 1 ml, 3 times daily for 7 days. Records were kept of local skin effects, effects on the peripheral blood picture, such as hemoglobin, leucocytes, erythrocytes, reticulocytes and also on red blood cell resistance. After the third benzotrichloride application to the depilated skin there developed bleeding skin erosions and cracks which later became covered with scar tissue. Rabbits showed signs of pain sensation upon pressure application to such points. The affected skin spots healed slowly, but developed new scar tissue after a second application of the benzotrichloride to the same spots. The fur, surrounding points of the benzotrichloride application, fell out and the bare skin acquired a dark pigmented color. The effects of above described benzotrichloride application were not limited to the skin; leucocytes fell from the original 14,000 to 8-9,000 per mm^3, and the osmotic red blood cell resistance fell to lower levels.

Conclusions

1. Benzotrichloride is a toxic substance. Air containing 1 mg/li of benzotrichloride vapor was lethal to white mice and rats.

2. Experimental animals subjected to acute benzotrichloride poisoning developed irritated conjunctiva and mucous membrances of the upper respiratory tract, dyspnea and disturbances of the nervous system. A single exposure to the toxic effects of benzotrichloride elicited in the experimental animals vascular disturbance in the internal organs and in the brain, catarrhal desquamative bronchitis and focal purulent pneumonia, also dystrophic liver dysfunction.

3. Repeated benzotrichloride inhalation possessed the potentiality of eliciting chronic intoxication paralleled by loss of weight, leucopenia, and fall in arterial blood pressure.

Repeated benzotrichloride inhalation elicited in the experimental animals changes at the point of its entrance, of which purulent bronchitis and pneumonia were the gravest along with changes which indicate general resorption of the substance and its capacity to disturb the blood circulation system, to produce dystrophic liver, kidney and suprarenal changes, as well

as profound changes in the cortical layers of nerves, and in the thalamo, hypothalamic region.

4. Benzotrichloride is partly eliminated with the urine as hippuric acid.

5. Benzotrichloride penetrated through intact skin, and elicited symptoms of poisoning, such as leucopenia and alopecia. Damage done to intact skin by the direct application of benzotrichloride healed very gradually.

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Comparative Efficiency of Bacteria Catching Devices Used in Determining Bacterial Aerosol Concentrations

pp. 45 - 48

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Existing methods for the determination of aerosols are time consuming, cumbersome, and are subjective, thereby yielding unreliable results. The present authors attempted to use an objective method for the determination of bacterial aerosols using a continuous flow ultramicroscope, to which a special highly sensitive photoelectronic device and an electromechanical counter were attached, making possible automatic counting and recording of aerosol particulates passing through the tube of the continuous flow phot microscope. Using this method, the present authors compared the effectiveness of different bacterial catching devices including cotton filters soaked in 3% gelatin solution or liquid vaseline. All investigated devices and methods were based on aerosol filtration through liquid or soluble solid filters and also on aerosol precipitation by a highly dispersed fluid. The technique in which such devices have been prepared and used accorded with the descriptions and specifications described by the original authors. Experiments were conducted by the drop and solid aerosol fractions of Chromobacterium prodigiosum strain No. 266 with particulate dispersion range of 0.6 and 3.4 μ, and with Bac. subtilis, strain No. 8236 aerosol of 3 μ average diameter. The bacterial suspensions contained 0.5 milliards of microbial cells per ml.

and were prepared with distilled water and physiological saline containing a mixture of 15% of glycerol and 5% saccharose. The chromobacterium prodigiosum suspension contained a gelatin-phosphate buffer prepared as follows: gelatin-2g, Na_2PO_4-4g, distilled water-1000 ml, with pH adjusted to 7.0. A spore containing Bac. subtilis suspension was heated to 70-80° and vigorously shaken for 5-10 minutes as described by Tyler and Shape. Samples were collected simultaneously by four bacteria catching devices. Ten li of air was passed through each bacteria catching device and the air flow rate checked with an air flow meter of R.S.-5 type. Air samples collecting time was 1-3 minutes. Results are shown in Table 1.

Table 1.

Comparative evaluation of bacteria trapping apparatus efficiency based on averages of 32 experimental series

Bacteria trapping apparatus	Average number of bacterial per li of air	
	Bact. prodigiosum, blood	Hay bacillus
Construction of apparatus:		
V. S. Kiktenko	5 581	6 286
S. S. Rechmenskii	3 189	4 281
P. P. D'yakonova	3 081	3 862
N. M. Rudenko	1 859	2 303
A. E. Vershigory	1 451	2 402
Soluble gelatin foam filters	152	1 922
Fiber filters:		
Dry cotton fiber filters	21	861
Dry glass wool filters	42	893
Dry cotton filters saturated with 3% gelatin solution and vaseline oil	37 218	42 680
Cotton fibers saturated with 3% gelatin solution and vaseline oil	26 534	31 871

Data presented in Table 1 show that highest number of microorganisms per 1 li of air was yielded by the impregnated cotton filter. The nonimpregnated cotton and glass wool filters trapped the lowest number of micro-organisms, probably as a result of rapid dying off of the B. prodigiosum. The same was true of B. Subtilis. Consideration should also be given to the fact that "micro-organisms" are incompletely removed from cotton and glass wool fibers and with considerable difficulty. Data presented in Table 1 were verified by results obtained in studying the retention capacity of the devices by the oil aerosol method and by the retention capacity of B. prodigiosum. The dispersion of the oil aerosol ranged between 0.31-0.34 μ. Results of the investigation are presented in Table 2.

Data in Table 2 show that the greatest number of slip through particles was found in the bacteria retaining devices of different construction and that lowest particulate retention capacity was possessed by the soluble gelatin foam filters which showed a slip through coefficient of 92-98%. The de-

vice suggested by S.S. Kikenko had a slip through of 42-48%. Simultaneously counts were made by the photoelectronic device. Results are shown in Table 3.

Table 2.

Oil aerosol particles and bacterial aerosol slip-through coefficient in different apparatuses

Filter made of	Amount of substance	Slip-through coefficient in %	
		Oil Aerosol	Bacterial aerosol
Glass wool (per g)	10	2,1	5,5
Cotton filter (per g)	5	0,08	1,05
Glass wool (per g) sat'd with 3% sol'n of gelatin and vaseline oil (ml)	10 12	8,1	0,35
Cotton fiber (in g) sat'd as above (in ml)	5 12	0,1	0,025
Bacterial trapping apparatus of different construction		From 42 to 98	—

The aerosol concentration was computed by the following formula: $n = N/V = d \times N/W$, where N- represents the number of counted particulates; W- represents the aerosol volume; d- represents the constant of a given diaphragm aperture in a given optical system, and V- represents the aerosol volume in which the particulates were counted.

Data presented in Table 3 show that the aerosol concentration in the counting chamber dropped to lower values 10 minutes after its dispersion by only 5% of the original concentration as determined immediately following the aerosol dispersion. It can be concluded, therefore, that no noteworthy change occurred in the aerosol concentration during the sample collection. Counts made by the photoelectronic counter could conceivably contain some aerosols particles free from micro-organisms; therefore, the present authors considered it desirable to determine the approximate count of bacteria containing particles per unit volume. This was done by desiccating the drop phase of a bacterial aerosol by a silicagel desiccating column. In such instance the bacterial suspension was free from glycerol particles. The concentration of bacterial particles in an aerosol; that is the hard core drop-nuclear fraction, determined by the photoelectronic particle counter, amounted to 43,250 per l li of chamber air during the period of air sample collection by the devices, amounting to 3% of the total number of aerosol particles.

By determining the number of particles in a microorganism containing aerosol by the method described, and by considering the results obtain-

Table 3.

Aerosol particulate concentration in the chamber in the course of the air sample collection (Averages of 18 experimental series)

Immediately after dust dispersing	Photoelectrical particulate counts						
	3 min. later	5 min. later	10 min. later	15 min. later	20 min. later	25 min. later	30 min. later
1 441 700	1 438 286	1 396 018	1 106 321	1 028 046	987 654	967301	804 206

from a comparison of the effectiveness of the bacteria catching devices, it is possible to determine the approximate efficiency of the bacteria catching devices under investigation. Thus, by examining data in Table 1, it will be found that the bacteria catching device based on the principle of cotton filter impregnated with the 3% mixture of dissolved gelatin and vaseline oil, amounted to 89% of all micro-organisms present per unit of chamber air volume. The bacteria catching capacity of the other devices fluctuated within the limits of 0.3-14%. In conclusion, it must be noted that the per cent of microorganisms which lost their viability during the process of dispersion and at the moment of sample collection had not been taken into consideration in this study.

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Fluorine and Hydrogen Fluoride Determination in the Air with a Solid Sorbent

pp. 48 - 50

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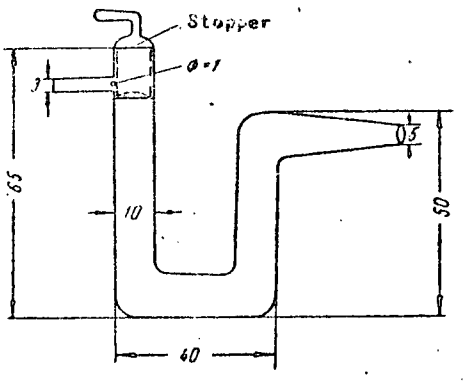
(Moscow)

No simple and adequately sensitive methods have been described for the determination of fluorine and hydrogen fluoride. Therefore, the first step in this investigation was to select a substance which might completely absorb both components. Tests were made with water, solutions of alkalies, carbonates, sodium sulfite, hydrazine, hydroxylamine, and other substances. After some preliminary tests the following absorber solution was selected; $Na_2S_2O_3$-7, KI-4, and methyl (p-methylaminophenol sulfate) 0.1 per cent by weight. However, successive determinations of the fluorine-ion in this absorber mixture by highly sensitive procedures proved very complicated. In addition, the liquid absorber presented some difficulties when used in the field under conditions of low temperature. For this reason, the present authors decided to use solid absorbers. The first absorber thus tested was silicagel trademarked MSK of granule sizes ranging between 260 and 300 mg, which were impregnated with an aqueous solution of triethanolamine. The silicagel was clarified and decolorized by boiling it in 6 N solution of hydrochloric acid. It was then washed in distilled water, dried at 100-120°, cooled and saturated with a 3% aqueous solution of triethanolamine in a 1:1 ratio by weight, and again dried at room temperature. The silicagel thus prepared was then placed into a ground-to-fit glass stoppered bottle. The silicagel thus prepared can be stored for a long time. Best results were obtained with 2 g of the silicagel in a Yavorov or in a U-shaped tube as shown in the Figure below.



U-shaped HF absorber

Preliminary tests were then made to determine the effect of aspiration rate on the complete fluorine or hydrogen fluoride absorption by the silicagel. Some results are presented in Tables 1 and 2. For the determination of possible fluorine or hydrogen fluoride slip through a second Yavorov or u-shaped absorber was attached to the first one. Fluorine determinations were made colorimetrically by the thorium-thoron method after it had been extracted from the silicagel.

Data in Table 2 show that complete fluorine absorption varied with its original concentration in the air. At fluorine concentration in the air of 0.02 mg/li, its slip through began to appear at 0.6 li/min. aspiration; at

fluorine concentration in the air of 0.003 mg/li its slip through was noted at aspiration rate of 2 li/min. Such data indicate that in instances where the fluorine concentration in the air was only slightly above the maximal permissible level, the air could be aspirated through the silicagel as described at the rate of 2 li/min. However, since the method sensitivity is 0.0001 mg of fluorine in the test volume the aspiration rate can be reduced further. Additional tests showed that temperature changes within the range of 25-30°, had no effect on the original absorption properties of the silicagel.

Table 1.

Effect of aspiration rate on the completeness of HF absorption by silicagel

Concentration in mg/li	Aspiration rate in ml/min	Min. of aspiration	Theoretical amount in mg	Observed amount in mg	Remarks
0,020	100	10	0,02	0,019	
0,020	250	4	0,02	0,020	
0,020	500	2	0,02	0,020	
0,020	600	1,6	0,02	0,018	Slip through 10%
0,020	1 000	1	0,02	0,017	» 15%
0,015	2 000	5	0,150	0,135	» 10%
0,015	3 000	5	0,225	0,191	» 15%
0,015	5 000	5	0,375	0,170	» 55%
0,003	1 000	5	0,015	0,015	
0,003	2 000	5	0,030	0,027	» 10%
0,003	5 000	5	0,075	0,045	» 40%

Table 2.

Absorption rate of F and HF mixture by silicagel at 0.5 li/min. aspiration rate

Amount of F_2 in the mixture	Amount of HF in the mixture	Total HF and F	Found F^- as HF
	in ml		
0,014	0,003	0,017	0,017
0,012	0,004	0,016	0,016
0,010	0,005	0,015	0,015
0,010	0,006	0,016	0,016
0,010	0,007	0,017	0,017
0,009	0,010	0,019	0,020
0,008	0,010	0,018	0,019

Simultaneously present fluorine and hydrofluoric acid in the air are determined as follows: place 2 g of the silicagel saturated with 3% solution of triethanolamine into a Yavorov or U-shaped absorber. Aspirate the air at the rate of 0.5- 2 li/min. The volume of air to be aspirated and the rate at which it is to be aspirated vary with the anticipated fluoride and hydrogen fluoride mixture concentration in the air. If only elemental fluoride is to be determined then the air can be aspirated through a separator containing sodium fluoride. The fluorine-ion is eluted from the silicagel with distilled water. This is accomplished by placing the silicagel into a test tube coated

on the inside with parafin; 5 ml of water is then added. Leave stand for 20 minutes and remove 1 ml of the solution and place into a colorimetric cup. Simultaneously, prepare the standard scale as follows: set up a series of 11 colorimetric tubes and place into the second tube a volume of NaF standard solution containing 0.0002 mg of the fluorine. Now, add to the third tube the standard solution of NaF containing 0.004, to the fourth containing 0.006, 0.008 mg of the fluorine, etc. continue adding so that the volume added to the last tube contained 0.002 mg. of the fluoride. Add to all tubes 0.02 triethanolamine solution so as to make a final volume of 1 ml. Then add to all the tubes of the standard scale and to the tubes containing the samples, 1 ml of thorium nitrate, 0.25 ml of 1 N HCl and 3 drops of 0.05% thoron solution. The thorium nitrate solution should contain 0.024 mg/ml of the reagent. Leave stand for 5 minutes and make colorimetric determinations. As stated above, the method sensitivity is 0.0001 mg of fluorine-ion per test volume.

Characteristic of Natural Ultraviolet Radiation in Vladivostok

pp. 58 - 61

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Prevention and elimination of ultraviolet insufficiency symptoms or consequences presupposes a thorough knowledge of natural ultraviolet radiation under different climatic zones on the basis of which hygienists can arrive at and formulate zonal, or local, standards of hygiene. A knowledge of natural ultraviolet radiation in zones of prevailing sunshine is also of considerable importance to hygienists. In this connection V. S. Svarichevskii and O. Ya. Khomeriki observed in Tashkent and in Tbilisi (formerly Tiflis), for example, considerable losses in ultraviolet radiation, which was reflected in the development of ultraviolet insufficiency symptoms among some population groups. It is only natural that the problem of ultraviolet radiation and consequent compensatory processes should appear most acute in the northern latitudes of USSR, as was noted by N. F. Galanin and also by N. M. Kaikov. A survey of the literature made by this author failed to find any records dealing with ultraviolet radiation of Vladivostok or other regions of the USSR extending along the shore of the Pacific Ocean.

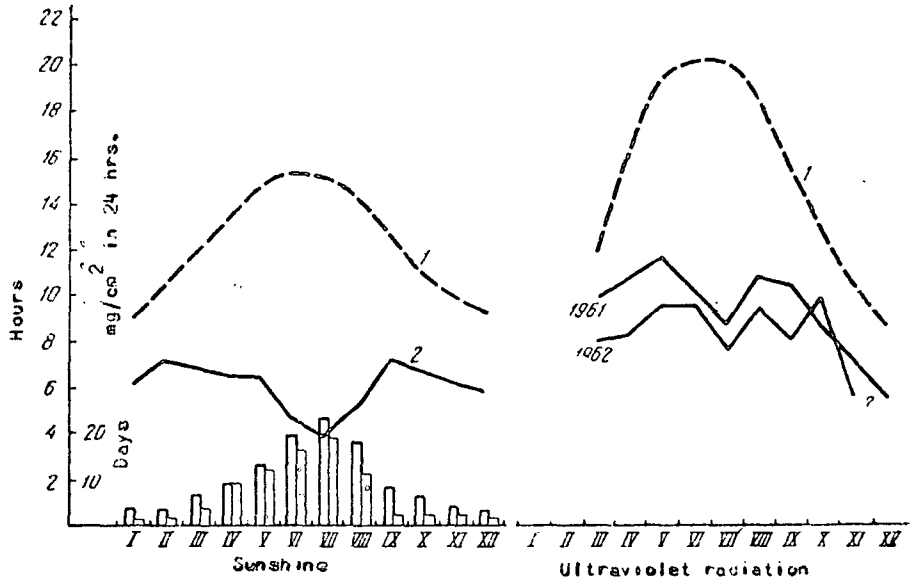
The latitude location of Vladivostok is much the same as the location of populated areas extending along the Caucasian Black Sea shoreline, for instance, Sukhumi and Sochi. Maximal solar altitude recorded locally, according to months were as follows: January - 25.4°, February - 33.5°, March - 44.2°, April - 56°, May - 64.8°, June - 69.3°, July - 67.5°, Au-

gust - 60°, September - 49.1°, October - 37.6°, November - 27.6°, and December - 23°. Duration of solar radiation in most of the inhabited areas of the Northern hemisphere changes in proportion with the solar position, so that maximum solar radiation duration prevails during the summer solar period and minimal during the month of December. The average annual solar radiation duration of Vladivostok differs only slightly from other regions of approximately the same latitude, but the pattern of solar radiation distribution according to months has its specific characteristics. The present author studied the data accumulated at the Vladivostok meteorological observatory for 15 years, between 1945 and 1959, and found that the shortest solar radiation hours occurred in the months of June, July and August, amounting correspondingly to 30, 26, and 37% of the possible maximum. It was also noted that during the month of June, which is theoretically the month of longest solar radiation, actual solar radiation duration was 1.2 - 1.8 times less than the solar radiation hours during the other months of the year. Longest solar radiation hours prevailed during the month of September, with an average of 57% of the possible maximum.

These specific characteristics can be explained by the distribution of seasonal foggy and cloudy days. Thus, during the months of June, July, and August the foggy and cloudy days ranged between 60 and 90%, according to meteorological records of many years, as compared with only 10% during the other months of the years. Total cloudiness during the summer months as a rule measured 7-10 balls (arbitrary units), while during all other months' cloudiness rarely exceeded 6 balls. Maximum number of cloudy days occurred during May, June, and July, amounting to 43-57%; minimum occurred during January and February, amounting to 2-3%. Such data, taken from the meteorological observatory records explain why the duration of solar radiation in Vladivostok is greater during the winter instead of the summer months.

Natural U-V radiation prevailed in Vladivostok during September in 1960. Intensity of U-V radiation was determined by the oxalic acid method proposed by N. M. Danzig, and Z. N. Kulichkova. Despite the shortcomings noted by A. A. Generalov, this method is the easiest to perform. Determinations were carried out at three points in the city during the frost-free period. Data had been obtained on the courses of seasonal and daily U-V radiations, half-daily radiation, short-wave and dispersed radiation, total daily radiation, and loss of U-V radiation due to smoke and dust. A total of 1000 determinations have thus been collected and processed. The data indicated that highest average daily total U-V radiation during 1961 prevailed during May (11.57 mg/cm^2). During June and July U-V radiation fell to 10.04 and 8.77 mg/cm^2 correspondingly. During the winter months, when the solar altitude is lower, U-V radiation fell to 6 mg/cm^2; it was generally lower in 1962 than in 1961. It was noted that seasonal U-V radiation course generally ran parallel to the solar radiation duration, as shown in the following diagram. Curves in that diagram show the characteristic difference between the actual course of U-V radiation and radiation prevail-

ing during cloudless days: under prevailing Vladivostok conditions maximum U-V radiation had not been noted during summer months at highest solar altitude. It is of interest to note in this connection that monthly U-V radiation in Moscow, Kazan, Kiev, L'vov, Gurzufe, and Tashkent changed with the height of the sun, i. e. its maximum occurred in June and minimum in the winter months, a condition which had not been noted in Vladivostok for the above mentioned reasons. Considerable U-V radiation fluctuations were noted here on different days of the same month. Thus, recorded data show that in 1961 daily U-V radiation fluctuated in the range of 7 - 12 mg/cm^2 in March, 3 - 7.5 in April, 3.5 - 18.5 in May, 6.5 - 17.8 in June, 2.5 - 13.8 in July, 3.0 - 16.5 in August, 3.1 - 15.7 in September, 5.5 - 14 in October, and 2.6 - 10.7 mg/cm^2 in December.



Hours of sunshine and intensity of ultraviolet radiation per cm^2 per day in Vladivostok

1 – Hours of sunshine and computed ultraviolet radiation intensity during clear atmosphere; 2 – Hours of sunshine computed on the basis of data of many years, and actual ultraviolet intensity in 1961 – 1962.

Number of cloudy days Number of foggy days

A study of daily U-V radiation course had shown that the oxalic acid test begins to be positive about 60 to 90 minutes before sunrise, and continues for about 90 minutes after sunset. Maximum U-V radiation was recorded during midday hours, amounting each midday hour to 10 - 13% of total daily radiation, and summarily to more than 50% of total daily radiation. Dispersed U-V radiation amounted to 30 - 50% of total daily radiation during bright sunny days, total daily U-V radiation dropped considerably during cloudy days, while dispersed U-V radiation rose to 70 - 90%. A study of the specific intensity of short wave U-V radiation (290-350 mμ) led to the conclusion that it diminished as the height of the sun receded. Thus, in July the short wave radiation constituted 33.8%, in August 28.5%, in September

27.3%, and in October 25.2% of total daily radiation; average absolute daily short wave U-V radiation values during the same months were correspondingly as follows: 3.4, 2.4, 2.9, and 2.2 mg/cm^2. Results of U-V radiation determinations made in different Vladivostok sections yielded information on radiation loss caused by air suspended dust and smoke. The air was cleanest in region close to the city limits, where industrially operating plants were few and, consequently, sources of smoke were few. Compared to such regions U-V radiation of the city center was on the average 23 - 25% below, the radiation loss fluctuating between 8 - 70%; the data here presented ran a close parallel to the number of smoke and dust sources existing in the city's central sections, U-V radiation losses in the southend and eastend of the city were intensified by fogs most frequently coming from the southeast.

Analyses of seasonal changes in U-V radiation and of such meteorological factors as fogs and cloudiness, indicated that lowered U-V radiation which prevailed in Vladivostok the greater part of the year created conditions not conducive to the development of resistance to rickets. During the winter months the U-V radiation intensity was low and the winter apparel allowed only 5% of the body to be exposed to solar radiation. During the summer months more of the human body surface was exposed to solar radiation and hours of exposure were markedly prolonged. However, during each month the number of gloomy, cloudy and foggy days noticeably increased, considerably lowering the intensity of the U-V radiation. Thus, the, so-called, period of low U-V radiation level in Vladivostok prevailed through the longest part of the year. Therefore, it is only natural to assume that under such conditions some population groups, namely children, workers employed indoors and in mines, etc. could easily develop symptoms of U-V radiation insufficiency. Accordingly, the entire problems of U-V radiation in Vladivostok must be investigated systematically and thoroughly from the clinical viewpoint and prophylactic measures should be developed and instituted for the prevention of rickets and similar clinical conditions among Vladivostok inhabitants and other similar regions of the Southern Seashores.

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The December Fog in England

pp. 71 - 72

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USSR newspapers reported that in December 1962 a dense fog spread over the country which seriously affected that Country's life; but the report contained no information regarding the degree of the fog toxicity. The report which appeared in the journal "Smokeless Air" No. 125, 1963 threw some light on the subject. The fog persisted through 3 - 7 of December 1962, varying in its intensity through the 5 days in different regions of Great Britain. Similar to the fog of 1952, the South-Eastern part of the island was affected most seriously, especially London and the Thames valley. The fog soon turned into a smog, similar to the one which occurred in 4 - 9 of December 1952. The 1962 fog lasted longer than the one of 1952, it also was denser and more consistent. The inversion height was approximately the same, ranging between 300 - 400 feet, or 9 - 12 meters. Tall buildings, such, for instance as the Royal Military Academy (College), appeared as though they were piercing through the fog coat, but the air temperature was somewhat below the temperature of 1952.

The fog density was great enough to bring to a stop all interurban transportation. Transportation over the roads of England in general suffered 20,000 automotive accidents in 5 days. More than 100 large seagoing ships were anchored in the London harbor due to inability to sail out into the open sea. Air communications also came to a complete stop. Aviation companies lost 500,000 pounds sterling.

Air analyses showed that density of suspended soot in the air during the 1962 fog amounted to only 60% of the air suspended soot observed during the 1952 fog. This was due to basic changes which had taken place in the interim in the methods of home and house heating in England, such as central community heating systems, use of smokeless fuel in the place of coal, etc. Despite that, maximal soot concentrations in the air during the fog days reached 2.8 mg/m^3, which was 7 times in excess of soot concentration in the air prevailing during winter days in normal times. The SO_2 concentration in the atmospheric air of London during the 1962 fog exceeded the maximum concentration recorded during the 1952 fog. Thus, during the 1952 London fog it amounted to 3.8 mg/m^3, while during the 1962 fog SO_2 concentration in the atmospheric air was 4.2 mg/m^3. The Journal in which the report appeared explained it by the fact that the 1962 winter was considerably colder and, therefore, more fuel was burned. It should be noted in this connection that modernization of combustion chambers does not lead to a drop in SO_2 formation; on the contrary, more of the fuel containing sulfur becomes oxi-

dized, so that less of the sulfur remains in the slag and more of it is converted to SO_2 thrown into the atmospheric air.

Analysis of total inhabitants' mortality occurring during the fog prevailing days showed an increase of approximately 340 cases; persons below 70 constituted 33.4%, and persons older than 70 years constituted 66.6% of the dead. The mortality curve crest was recorded on the third day of the prevailing fog, 5/XII/1962. Statistical study showed this increase was due primarily to increase in bronchitis cases. Rate of general morbidity also increased. Thus, records showed that during the period of foggy days morbidity, as the cause of loss in working days, rose to levels exceeding those of preceding and following periods by 50%. However, morbidity rate during the 1962 foggy days was below that of the 1952 foggy incidence, despite the fact that intensity of atmospheric air pollution with SO_2 was greater in the 1952 days. The report in the English Journal ascribed that to the facts that atmospheric air pollution with soot and dust in the fog days of 1962 was considerably below that of 1952, and that conditions of personal hygiene in 1962 were on a higher level than in 1952, and also to the propaganda conducted by the Society for the Protection of Clean Air.

These assumptions deserve attention, since experimental studies, especially those of M. Amdur in the USA indicated that aerosol adsorbed gases, specifically sulfur dioxide, manifested enhanced toxic activity, in comparison with free gases. Accordingly, it is reasonable to assume that the lowered soot concentration in the atmospheric air in 1962 lowered the total toxicity of adsorbed SO_2 in the air. However, this is a mere assumption, since no data had been collected on the amount of SO_2 present in London air during the fog of 1962. This is to be regreted for it might have proved of considerable help in the search for an explanation of this or other similar phenomena. K. A. Bushtueva of the USSR demonstrated that the transition of free SO_2 to the aerosol state depended upon meteorological conditions. It can be reasonably supposed that under conditions of identical SO_2 concentrations, the H_2SO_4 aerosol concentration or dispersion in the air over London in 1962 profoundly differed from the same in 1952, which may have been the reason for the lowered fog toxicity. Reports of medical authorities indicate that the latest December fog had seriously affected many industrial centers of England. Thus, an increased respiratory organ morbidity was reported in Birmingham during the period of the last fog. The latest fog was especially dense in Leeds, where respiratory organ morbidity also rose, although not as high as in Birmingham. In Glasgow where the fog lasted only one day (5/XII), increased pneumonia and bronchitis morbidity was noted among the oldsters. The toxic smog of England elicited many comments in the press and was the subject of parliamentary discussion. As for us, in the USSR, the following is clear: measures taken in England for the ten years between 1952 and 1962 proved to be far from adequate to bring to a stop the periodic occurrence of toxic fogs which carry off large numbers of human lives.

Maximal Permissible Concentration of Hexavalent Chromium in Atmospheric Air

pp. 9 - 16

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It has been established by many toxicologists in the USSR and abroad that hexavalent chromium compounds were the most toxic of chromium compounds. The toxic properties of hexavalent chromium had been studied most frequently under experimental conditions of brief inhalation of air containing comparatively low concentrations of the compound; some tests have been made by the intragastric, intravenous administration and by skin application. A review of the literature failed to disclose reports dealing with the effects of chronic hexavalent chromium inhalation in low concentrations. Little information was found in the literature regarding air pollution with hexavalent chromium compounds. The present author knows of only one report presented by Bourne of the USA in 1950, which dealt with such ambient air pollution in the vicinity of a chromium processing plant.

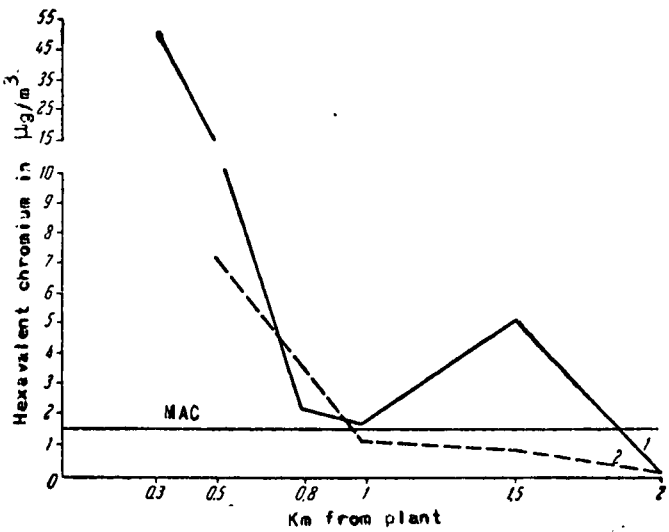
The present author conducted his studies of air pollution with hexavalent chromium in the proximity of two largest USSR plants producing chromium compounds. A study of the technological processes and of the ventilation systems showed that the plants discharged into the atmospheric air monochromates, bichromates, chromyl chlorides, and the like, in the form of gases, vapors, and aerosol condensates. Much of such pollution also came from sources commonly designated as "nonorganized". The exhaust air of one of the plants was subjected to preliminary 70% scrubber purification. It has been estimated that between 700 and 800 kg of hexavalent chromium compounds had been discharged by the plants into the atmospheric air at a height of 10-15 m.

Chromium oxide was produced in the other plant by the sulfur-chromium method. By such a method hexavalent chromium could be used only in solution, which reduces the discharge of the hexavalent chromium into the air from 700-800 kg to 150-200 kg per day. Air samples were collected within a radius of 2 km from the plants, usually on the side of the wind direction. The air was aspirated through membrane filter No. 2, or through textile filter FBP-15 fastened inside of a "dust cartridge". A single sample required the aspiration of 30 li of air at the rate of 1 li/min. Hexavalent chromium in the air was determined by the method of Gurvits and Sergeeva,

modified by the present authors to make possible the collection of small air samples and to increase the sensitivity of the test to 0.0001 mg/li.

Curves in Fig. 1 graphically represent results of hexavalent chromium determinations in the atmospheric air surrounding the investigated plants.

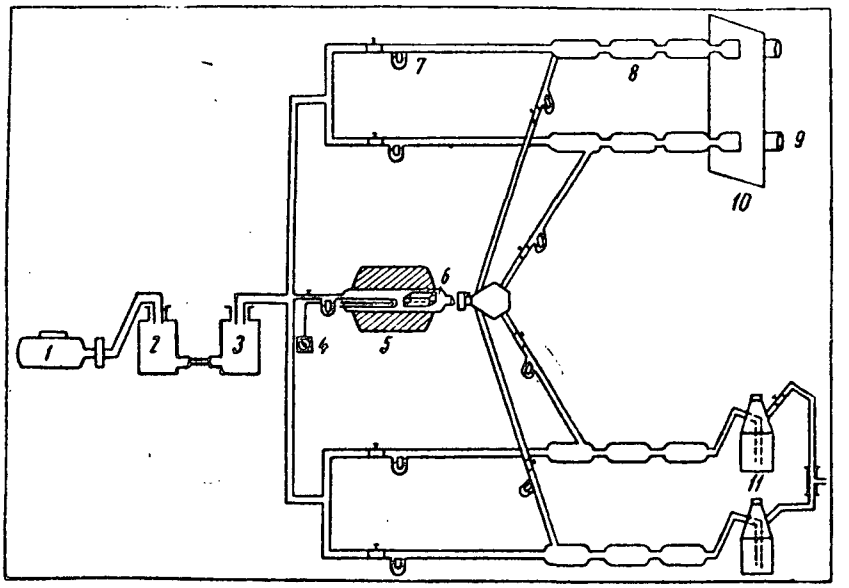
Fig. 1.



Maximal single concentration of hexavalent chromium in the air surrounding the plant producing chromium compounds
1 – Pervoural chromium plant; 2 – Aktubin chromium plant

Procedures used in the determination of maximal permissible hexavalent concentrations in the atmospheric air were those described and recommended by the Committee for the Sanitary Protection of Atmospheric Air. Hexavalent chromium condensation aerosols were obtained by heating portions of chromic anhydride in a tubular electric furnace, schematically illustrated in Fig. 2. The gas mixture containing a given aerosol concentration was run into inhalation cylinders installed inside a special exposure chamber. Determinations were made of concentrations producing irritation, and also concentrations representing the threshold of hexavalent chromium reflex effect on the functional state of the cerebral cortex. The concentration of chromium threshold irritating properties was determined by the usual method described by many investigators testing ten practically normal volunteers. Two hundred and fifty determinations were made with 12 different chromium aerosol concentrations in the range of 1.5 and 40 μ/m^3. Results indicated that inhalation of air containing 10-24 μ/m^3 of chromium, even for a brief period of time, elicited the sensation of sharp irritation in the nostrils; inhalation of lower chromium concentrations elicited slight irritation of the upper respiratory tract. Lowest perceptible chromium concentrations for the entire group of test volunteers ranged between 4-2.5 mg/m^3. For most sensitive of the volunteers 2.5 μ/m^3 of chromium represented the concentration of threshold perception; 1.5 μ/m^3 was below the perception threshold of the entire group of test volunteers.

Fig. 2.



Plan of the experimental apparatus

1 – Air blower; 2 – silicagel; 3 – activated charcoal; 4 – electronic potentiometer; 5 – electric oven; 6 – a quartz boat; 7 – flowmeter; 8 – mixer; 9 – odor testing cylinder; 10 – screen; 11 – exposure chamber

Tests for chromium concentration of threshold reflex effect on sensitivity to light were conducted by the method of dark adoptation using adaptameter ADM. Results are shown in the Table below:

Average values of eye sensitivity to light in the course of inhaling different chromium vapor concentrations, in – on the 15th minute

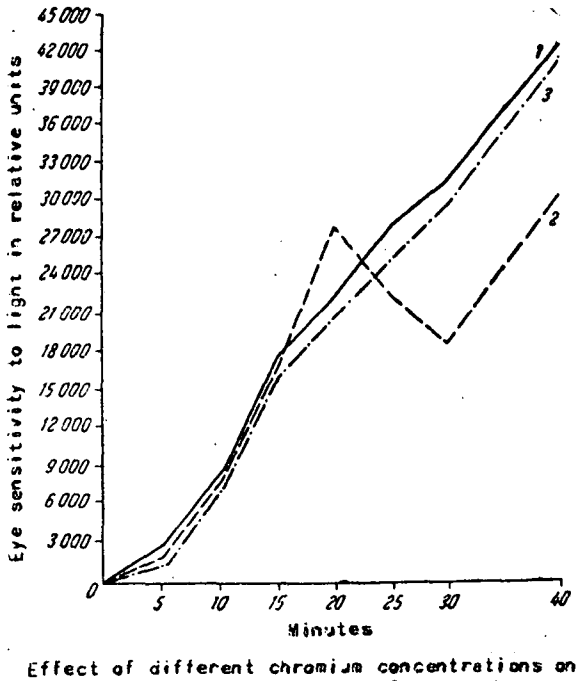
Tester's initials	20th min.			25th min.		
	Clean air	Chromium in $\mu g/m^3$		Clean air	Chromium in $\mu g/m^3$	
		2.5	1.5		2.5	1.5
A	150	198	149	205	184	205
G	118	266	118	149	238	129
L	129	152	124	160	128	153

Tests were conducted with 3 volunteers whose threshold of chromium irritation effect had been previously determined. Two courses of dark adaptation were tested first with clean air for control purposes and then with air containing 2.5 and 1.5 μ/m^3 of chromium aerosol. The fresh air and the aerosol air mixtures were tested at 15 minute intervals for 4.5 minutes, making triplicate tests for each concentration. A total of 60 dark adaptation tests have thus been made.

Inhalation of 2.5 μ/m^3 of hexavalent chromium for a short time considerably enhanced eye sensitivity to light in all test persons on the 20th

minute. Adaptation to the dark failed to return to normal even on the fortieth minute. Statistical processing of experimental data showed that the adaptometric changes elicited by the inhalation of 2.5 μ/m^3 of chromium were significant and reliable. Chromium aerosol concentration on 1.5 μ/m^3 had no effect on the process of eye adaptation to the dark or on the eye sensitivity to light. This is shown by curves presented in Fig. 3.

Fig. 3.



Effect of different chromium concentrations on eye sensitivity to light of tester L
1 - Clean air, 2 - 2.5 $\mu g/m^3$ of chromium; 3 - 1.5 $\mu g/m^3$

Thus, experimental results indicated that the threshold reflex effect of chromium on the functional state of the cerebral cortex, as determined by the adaptometric method, coincided with the concentration representing the threshold of its irritating effect, which is characteristic of substances affecting the trigeminal perception apparatus. In summary it can be stated that 1.5 μ/m^3 (0.0015 mg/m^3) of hexavalent chromium was a subthreshold concentration as established by each of the two methods. This concentration is recommended as the maximal single permissible concentration of hexavalent chromium in atmospheric air. It was adopted by the GSI of the USSR November 14, 1961 in code No. 221-61.

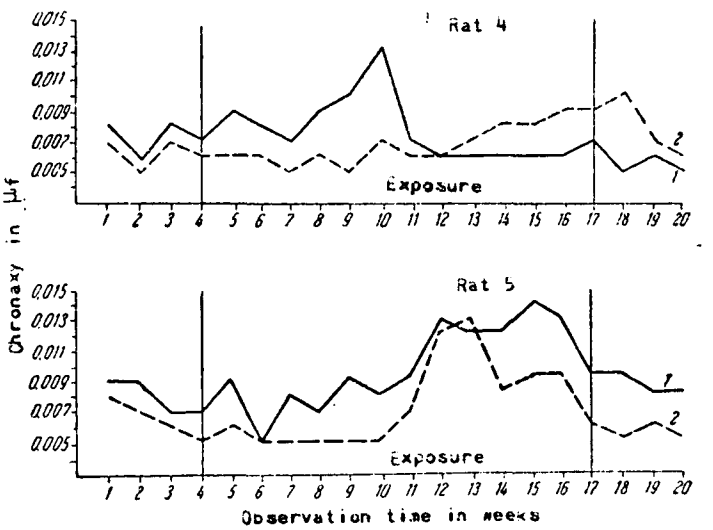
Chronic experiments for the determination of prolonged inhalation of hexavalent chromium in low concentrations were conducted by exposing laboratory animals to continuous 20 hour inhalation daily for a period of 90 days. Experiments were conducted with 45 white male rats weighing 90-120 g which were divided into 3 groups of 15 rats each. Rats of group 1 inhaled air containing 30 μ/m^3 of the hexavalent chromium, which is only 33-35% of the maximal permissible concentration of hexavalent chromium in working premises; rats of group 2 inhaled air containing 1.5 μ/m^3 of hexavalent chromium, which is on the same level as the recommended maximal single concentration limit; animals of group 3 served as controls. Air in the exposure chambers was tested four times daily. The average hexavalent chromium concentration in the chamber occupied by rats of group 1 averaged 29± 0.3 μ/m^3. In chamber No. 2 the average hexavalent chromium concentration was 1.31±, 0.026 μ/m^3. The hexavalent chromium aerosol concentration in the air mixture consisted of particles 90% of which measured 1 μ in diameter. All through the exposure

period, records were kept of the animals weight, changes in muscle antagonists motor chronaxy, activity of blood enzymes, such as carbonic anhydrase, and of the blood morphology picture. No changes were noted in the external appearance of the animals, except for a slight loss of activity in the animals of group 1.

Changes in the chronaxy and rheobase of the extensor and flexor muscles of the rats right hind leg were measured by the GIF chronaxymetric condenser daily under similar conditions. Rats of group 1 which inhaled air containing 30 μ/m^3 of the chromium aerosol showed delayed chronaxy of the extensor and flexor muscles two weeks after exposure to chronic chromium inhalation. At the end of the second recovery week, the chronaxy returned to its original level. The effect of chronic hexavalent chromium inhalation by rats presented a more clearly expressed picture when the animals had been observed individually, and not as a group. Under such conditions it was noticed that some animals manifested paradoxical and reverse chronaxy ratios. No changes in the chronaxy ratios were noted in any of the rats belonging to group two, throughout the course of continuous hexavalent chromium inhalation. This conclusion was verified by statistical processing of the experimental data of this group. See Fig. 4.

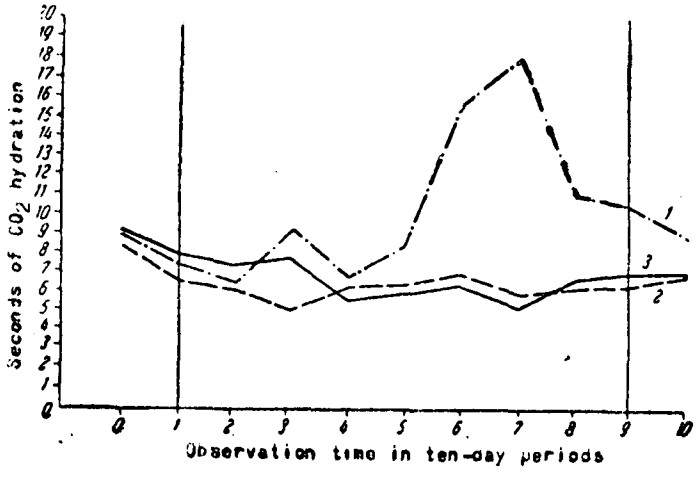
It has been demonstrated repeatedly that many toxic substances strongly inhibited blood carbonic anhydrase. The present author used the colorimetric method for the determination of carbonic anhydrase in whole blood. The method was originally developed by N. E. Ponomarenko and is based on the determination of CO_2 hydration rate in the presence of bicarbonate and sodium carbonate. Carbonic anhydrase activity was determined in 3 rats of each group, and the results graphically presented in Fig. 5.

Fig. 4.



Muscle antagonists motor chronaxy in rats Nos. 4 and 5 of Group I (30 μg/m³) before exposure, during exposure and during the recovery period. 1 – Extensor; 2 – flexor.

Fig. 5.



Whole blood carbonicannhydrase activity of rats before and during exposure and during the recovery period. 1 – Rats of Group 1, 30 $\mu g/m^3$, 2 – rats of Group 2, 2.5 $\mu g/m^3$; 3 – control rats

Prior to hexavalent chromium inhalation, the carbonic anhydrase activity average of the 9 rats was 8-9 sec. As the experimental exposure to the inhalation of hexavalent chromium extended, the time of carbonic anhydrase activity gradually became longer and at the mid-point of the experiment, the time of CO_2 hydration extended to 15-20 sec. in rats of group 1. The carbonic anhydrase activity time of rats belonging to group 2 (1.5 mg^3) were practically identical with the carbonic anhydrase time manifested by rats of the control group.

No changes were noted in the number of erythrocytes, leucocytes or in the hemoglobin concentration; however, the blood leucocyte formula in rats belonging to group 1, which inhaled 30 μ/m^3 of the hexavalent chromium, showed an increase in the number of stabnuclear neutrophiles up to 6-8%, paralleled by the appearance of young forms. There also appeared a small number of neutrophilic myelocytes. These changes pointed to a decided shift to the left of the leucocytes reflecting an irritation in the hemopoetic organs produced by the hexavalent chromium. No blood changes were noted in the rats of group 2 which inhaled air containing 1.5 μ/m^3 of hexavalent chromium. At the end of the 3 months continuous exposure to the inhalation of air containing hexavalent chromium, the rats were autopsied and their organs examined histomorphologically by the usual staining procedures. Tissues of rats which inhaled air containing 30 μ/m^3 of hexavalent chromium, showed many changes, particularly in tissue of the respiratory organs. Tissue of the trachea showed lymphoid infiltration into the cells of the mucosa paralleled by intensive hyperemia. The sinuses were dilated, and hemorrhages appeared in the paratracheal lymphatic nodes. There was also thickening of interalveolar septa and signs of emphysematous processes and of perivascular and peribronchial diffuse sclerosis. There were some clearcut changes in the parenchymal organs.

The absence of complete changes in the nasal septa in many of the animals is of particular interest in this case. This was also noted by V. P. Lukanin in his experimental rabbits, which were exposed to the inhalation of sodium bichromate. In the experiments conducted by the present

author, absence of such changes in the nasal septa of the experimental rats may have been due to the fact that they were exposed to the inhalation of lower chromium concentrations, and also to the fact that the aerosol was of a high dispersion and more easily penetrated into the higher sections of the respiratory apparatus. No noteworthy histopathelogical changes were observed in tissues of rats belonging to group 2 which inhaled 1.5 μ/m^3 of hexavalent chromium. In fact, their tissue pictures were indistinguishable from tissue pictures of the experimental animals. A study of chromium accumulation and distribution in organs of the experimental animals showed that in rats belonging to group 1, which inhaled air containing 30 μ/m^3 of chromium, the chromium-ion content in the lungs determined by the spectral method was 1%, computed as ash, which is 30 times in excess of chromium similarly determined in the lungs of the control rats. The same trend, though at lower levels, appeared in the kidneys, the spleen, the liver, and in the cerebrum.

Based on the data yielded by the chronic experiments, it can be recommended that the maximal permissible average daily concentration of hexavalent chromium in the atmospheric air should be the same as the maximal permissible single concentration previously recommended, which is 1.5 μ/m^3. This concentration of hexavalent chromium in the air elicited no functional changes in the organism of man or laboratory animals. The experimental data which point to the harmful effect of 30 μ/m^3 of hexavalent chromium in the air, strongly point to the need of restudying the concentration of this toxic component in the air of working premises with a view to lowering the present maximal permissible concentration of 100 μ/m^3.

A comparative analysis of hexavalent chromium concentrations found in the atmospheric air surrounding the investigated plants with the proposed maximal concentration limit indicated that at a distance of 0.5 km from plant No. 1, hexavalent chromium concentration in the air was 10-30 times as high as its maximal permissible limit. At 1.5 km its concentration in the atmospheric air was still 3 times as high as the maximal permissible concentration limit. At 2 km, the air contained a lower hexavalent chromium concentration than the one now officially enforced, as shown by results of all analyzed air samples. In the case of air surrounding plant No. 2 the hexavalent chromium pollution was even of greater intensity. Hygienic evaluation of conditions surrounding the two chromium processing plants as sources of air pollution suggest that a sanitary clearance zone 1-2 km wide should be established around each plant.

Conclusions

1. A concentration of 2.5 μ/m^3 of hexavalent chromium in the air represented its threshold of irritation action; the same 2.5 μ/m^3 concentration represented the threshold of reflex chromium aerosol effect on the functional state of the cerebral cortex, as determined by the adaptometric method for persons of highest perception sensitivity.

2. 1.5 μ/m^3 of chromium, as determined by the above mentioned procedure, produced no unfavorable effects on the organism, and should be regarded as the nonactive or subthreshold concentration.

3. Hexavalent chromium in 30 μ/m^3 concentration chronically inhaled for a period of 90 days, as described in the text, elicited in the experimental animals, changes in their motor chronaxies, in the carbonic anhydrase activity, and in the morphologic component of the blood. Some definite histologic changes were noted in the tissue of internal organs.

4. Under similar chronic conditions, inhalation of air containing 1.5 μ/m^3 of the hexavalent chromium produced no statistically significant changes.

5. The concentration of 1.5 μ/m^3 computed as CrO_3 can be adopted as the maximal single, and also as the 24 hour, hexavalent chromium concentration in atmospheric air.

6. The following sanitary clearance zones are recommended for chromium processing plants: for plants which discharged 200 kg of hexavalent chromium into the air, the sanitary clearance zone should be not less than 1000 m, and for plants which discharged 1000 kg of hexavalent chromium into the air daily, the sanitary clearance zone should be not less than 2000 m wide.

7. The existing maximal permissible hexavalent chromium concentration in the air of working premises, now 0.1 mg/m^3, is regarded, in the light of the present investigation, as too high and should be revised to a lower level.

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Orientation Data for the Determination of Maximal Permissible DDT Concentration in the Air of Working Premises

pp. 36 - 39

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DDT, which is 4,4-dichlorodiphenyltrichlorethane, also known as pentachlorine, is a pesticide widely used in agriculture. It is also used as a pesticide in homes. Its use is progressively increasing; yet the toxicity of DDT to the organism upon entering via the respiratory route has not been adequately investigated. Literature reports a number of DDT poisoning cases occurring in the production of the pesticide which contradict the heretofore existing notion of this pesticide's low toxicity. During its application, DDT can be inhaled by the worker or by persons close by causing intoxication of different intensities. Some authors also believe that the effect of DDT is cumulative. Other authors expressed the opinion that persons working with DDT in many instances become sensitized to the effect of the preparation. There have also been noted effects of species and of individual sensitivity to the effects of DDT. Results of numerous investigations established that man was more sensitive to the effects of DDT than laboratory animals. Thus, according to tests, the lethal dose of DDT to animals was in hundreds of mg per kg, whereas, in man, the lethal dose measured in tenths of mg per kg.

DDT inhalation experiments were conducted with cats which, according to S. G. Serebryabnaya and others, are the most sensitive of all laboratory animals to the effects of this preparation. Twenty cats were used in two series of experiments. The first series was used to study DDT toxicity under acute experimental conditions, and consisted of 13 cats exposed to DDT inhalation for 6 hours. Seven cats of the second series were used in determining the toxic DDT effect under conditions of chronic experiments, in which the cats were exposed to the inhalation of the DDT 6 hours daily for 75-90 days. Experimental animals were exposed to the inhalation of DDT in 2 exposure chambers. In one, the preparation was introduced into the air in the form of finely particulate talc containing 10% of the DDT; in the other chamber, the DDT was introduced into the air in the form of a 1-5% highly pulverized aqueous DDT emulsion. At the conclusion of the acute and chronic experiments, the animals were kept under observation for 2 weeks, after which they were sacrificed and their organs studied histopathologically. Results showed that 0.0007 mg/li of DDT elicited no visible intoxication in the acute experiments. At DDT concentrations of 0.005 mg/li in dust form, the animals began to lose activity, became indifferent to the surroundings, their hemoglobin concentration fell and they developed a slight leucocytosis. Cats exposed to the effect of 0.02 mg/li DDT suspended in the air in the emulsion form for 6 hours developed symptoms of toxicity such as salivation, sluggishness, muscular convulsions, vomiting, nausea, ataxia, tremor, frequent defecation, and urination. Animals ate only part of their daily rations. The

blood picture showed leucocytosis, rapid red blood cell sedimentation, and hyperglycemia. The urine contained albumin, and urobilin. Inhalation of air containing 0.08 mg/li of DDT dust clinically showed the same signs of intoxication as in the case of inhalation of lower DDT concentrations in the air, but the severity of the symptoms was considerably greater. Experimental animals subjected to the acute inhalation of DDT in 0.005-0.08 mg/li concentration, in addition to the clinical intoxication manifestations, showed morphorlogical changes in the cerebrum and in the internal organs. There appeared slight blood circulation disturbances and slight dystrophic changes in the brain, the liver, the kidneys and in the heart muscles. Hemodynamic changes developed in the lungs. All above symptoms were paralleled by swelling of the argyrophilic fibers. The enumerated symptoms increased in gravity with increase in the DDT concentration in the air. Chronic inhalation of 0.008 mg/li of DDT by the 3 experimental cats for 3 months, developed well defined pictures of intoxication at the end of the second experimental week. Two of the cats showed blood in the fecal matter and in the vomitus beginning with the fourth week. All cats showed the presence of albumin and urobilin in their urine at the end of 2 weeks. The albumin concentration rose progressively as the experimental period progressed. The blood picture showed reduced number of erythrocytes, lowered hemoglobin concentration, rapid red blood cell sedimentation and hypoglycemia. The body temperature of 2 cats considerably dropped at the midpoint of the experimental period, and one cat developed spasticity of some muscles, general tremor and ataxia.

Following the discontinuation of inhalation the toxic manifestations began to abate, but the flabbiness and general indifference, as well as loss of appetite persisted. The presence of albumin and urobilin in the urine, the reduced number of erythrocytes and increased rate of red blood cell sedimentation persisted. Macroscopically, autopsies showed discolored swelling venous plethora of the internal organs, and uneven pulmonary blood distribution, localized emphysema and occasionally small hemorrhagic foci. Four cats were exposed to the inhalation of 0.015 mg/li of DDT dust in the air for 75 days. The cats developed signs of grave intoxication, the clinical picture of which in its character and gravity was similar to the one developed by cats which inhaled DDT emulsion in 0.008 mg/li concentration. Results of above investigations led the present authors to conclude that inhalation of DDT produced in the experimental animals general intoxication. Thus, results of the above described experiments verified the observations made by V. A. Kaganovich and others (1956) under actual working conditions in plants producing DDT regarding the effect of DDT inhaled in 0.001 mg/li concentration.

The present authors also investigated the sanitary-hygienic working conditions prevailing in the synthesis of DDT and in making the insecticide mixtures of this preparation. Results showed that the air of premises where DDT has been synthesized and mixed contained DDT vapor in concentrations

ranging between 0.0017-0.0085 with an average of 0.003 mg/li, and that the suspended DDT dust in the form of a 10% mixture ranged between 13 and 272 mg/m^3, with an average of 23 mg/m^3 which was the equivalent of 0.0023 mg/li of the DDT proper. Workers exposed to the inhalation of air containing DDT in the form of vapor or dust in the above indicated concentrations manifested clearly discernable disturbances of their general health; the central nervous system developed an asthenic syndrome and vegetative dystonia. The nervous system disturbance was of a diffuse character, but pathological processes were localized predominately in the region of the cerebellum and its sinuses, usually paralleled by arterial hypotonia. The above picture was frequently associated with disturbance in the peripheral nervous system as polyneuritis, which agreed with observations recorded in the literature.

Changes in the internal organs appeared frequently as myocardial distrophy, physical liver changes, chronic gastritis and, less frequently, as changes in the respiratory organs. Examined workers also showed the presence of hypochromic anemia, leucopenia, eosino-and neutropenia, a moderate lymphocytosis, throbocytopenia, and changes in carbohydrate metabolism. It was noted, unmistakably, that the above conditions increased in gravity with length of employment. This is particularly true of myocardial dystrophic liver changes and of toxic polyneuritis.

On the basis of above presented experimental data and observations under conditions of actual production and processing, and taking into consideration data found in the literature regarding the toxic effects of DDT, the present authors arrived at the following conclusions and recommendations regarding the maximal permissible DDT concentration in the air of working premises; the threshold DDT concentration in inhaled air was 0.05 mg/li and its toxic concentration was 0.02 mg/li. The toxic zone of perorally administered DDT was a narrow one; the lethal 200 mg/kg dose exceeded the 100 mg/kg minimal toxic dose only by 100%. DDT is a strongly cumulative poison. The ratio between the total amount of cumulative DDT administered daily and which resulted in the death of the animal and its lethal dose, as determined by acute experiments, was 0.75 and pointed to a super accumulation of the DDT. Results of chronic inhalation tests conducted by the present investigators verified the above statement. Intensity of DDT toxicity was the same whether administered as dust or emulsion. In other words, it varied only with its concentration in the air. Under industrial production conditions the inhalation of air containing an average of 0.003 mg/li of DDT produced frequent disturbance of the central and peripheral nervous system, of the cardio-vascular system, of the gastrointestinal tract, of the liver and kidney functions, and of the blood morphology and enzymic activity. Based on the results of the present investigation, the authors recommended that 0.0001 mg/li or 0.1 mg/m^3 of DDT in the air of working premises should be regarded as its maximal permissible concentration. This recommendation was officially inacted by the Chief State Sanitary USSR Inspection Office, and was incorporated into code No. 388-61 December 30, 1961.

Conclusions

1. DDT inhalation proved toxic to warm blooded animals. The minim toxic DDT concentration in the air under conditions of acute experiments was 0.005 mg/li for cats and toxic effects were produced by 0.02 mg/li. In chronic experiments 0.008 mg/li of DDT in the air elicited sharp symptoms of intoxication and 0.15 mg/li proved to be the LD_{50} for cats.

2. Inhalation of air containing an average of 0.003 mg/li of DDT was harmful to workers' health, the gravity of the poisonous effect increased with the DDD employment record.

3. It is recommended that the maximal permissible DDT concentration in the air of working premises be set at 0.0001 mg/li or 0.1 mg/m^3.

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The Toxicology of Metallic Antimony

pp. 39 - 44

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Antimony is used in the manufacture of high quality steel to which it imparts the property of antifriction important in the production of ball bearing. The property of antimony to expand with the lowering of temperature, accompanied by its hardness, makes it of considerable value in typography. Antimony is also used in the preparation of lead antimonate, of babbit, of battery plates, in the rubber industry, in the preparation of enamel paints, of fire resistant fabrics, and in many other industrial processes. As a result of the wide antimony use in the national production and processing industry many workers are exposed to the inhalation of antimony vapor and dust.

Fairhall and Hyslop of the USA showed in 1947 that the number of workers connected with the production and processing of antimony and its compounds was nearly 100,000 prior to the Second World War. Despite that, the toxic antimony properties have not been adequately investigated. Most reports dealing with the subject have been devoted to the study of easily soluble organic antimony compounds used primarily in the medical and veterinary practices. Only few studies have been devoted to the determination of biological effects of inorganic antimony compounds, and only 1 report was found in the literature which dealt with the toxic effect of antimony. This was a report by Bradley and Frederick which appeared in 1941 in the foreign literature. No report of this type was found in the USSR literature.

Investigators who studied the toxicity of antimony compounds always inserted notes pertaining to the role played by arsenic, lead, bismuth, iron, and other constant antimony admixtures, always emphasizing the importance of arsenic and lead; other investigators are inclined to ascribe no particular significance to such antimony admixtures. However, the opinions of either group of investigators are not based on any experimental evidence, and, as such, were mere suppositions. The present author undertook to determine the toxic properties of metallic antimony and the effect which the above enumerated admixture elements had on the basic toxicologic properties of metallic antimony. The present study was conducted with metallic antimony of 3 different trademarks, - Sb_{000}, Sb_0 and Sb_3, which differed only in the degree of their purity. Metallic antimony of the highest purity - Sb_{000} - contains admixtures in thousandths of a per cent and includes lead and arsenic, the total amount of which is equal to 0.0008%; this can be completely disregarded, since the amount of antimony present in the human body varies between 50 and 200 mg/kg of body weight. According to N. V. Lazarev (1954) the toxic doses of the admixture elements are in the tenths of mg for arsenic and tens of mg for lead. Antimony of trademark Sb_0 contains approximately 0.5% of admixtures including 0.4% of lead and 0.016% of arsenic. In the case of Sb_3 the admixtures amount to 2.3%, half of which is lead and only one tenth is arsenic. Tests were made for the determination of metallic Sb_0 solubility in different media. Results are presented in Table 1 as averages of ten successive tests in buffer solutions, and of 50 successive tests in each of the other media.

Data in Table 1 show that antimony is readily soluble particularly in body fluids of neutral and alkaline reactions despite the fact that up to the present investigation, antimony was regarded as an insoluble metal. Toxic antimony properties were investigated using white rats weighing between 230 and 320 g. Experimental groups of animals consisted of 20 rats of which 10 were male and 10 female. The toxic properties of the above specified metallic antimony products were tested in the following doses: 50, 100, 150, and 200 mg/kg. The material was administered intraperitoneally as a fine antimony powder suspended in apricot oil. Control animals similarly received equivalent volumes of sterile apricot oil. The antimony powder

was of the following fractional dispersion: up to 1 μ - 51%, 1-2 μ - 37%, above 2 - 2%. Diameters of the largest particles measured 8 μ. The antimony powder of the above indicated dispersion was obtained by grinding the metal in an agate mortar followed by thorough washing. Spectrographic studies of the 3 antimony types before and after washing showed that their physico-chemical properties were not affected by the washing step. Results of the experiments had shown that administration of 50 mg/kg of the dispersed antimony by the route described killed none of the experimental animals by any of the 3 trademarked antimony metals; on the other hand, 200 mg/kg was absolutely lethal in the case of any of the trademarked antimony metals. Results also showed that dose for dose experimental rats which had been administered the purest (Sb_{000}) antimony died quicker than experimental animals receiving similar doses of other antimony types. Administration of 150 mg/kg also showed that Sb_{000} was the most toxic judged by the greater number of animals killed within a shorter period of time. Results thus indicated that the toxicity of Sb_{000} was greater than the toxicity of Sb_3 which had the greatest amount of admixtures.

Table 1.

Solubility of metallic antimony in mg% at 37° (averages)

Time in minutes	Type of medium										
	Buffered solvents – medium pH						Dist. water	Physiol. soln.	Blood serum	Gastric Juice	Urine
	1,4	2,0	5,0	7,0	7,2	8,2					
10	3,10	3,36	4,44	5,38	5,70	6,04	5,02	4,00	5,07	3,91	2,63
30	3,98	3,94	5,58	7,34	6,54	6,74	6,30	5,95	6,85	5,08	4,84
60	4,28	4,30	5,92	8,54	7,85	8,04	8,04	6,77	9,38	5,92	6,58
360	4,52	4,40	7,86	10,80	8,00	8,87	7,06	8,48	18,08	7,78	11,07
1440	4,52	4,80	7,80	9,66	6,08	6,26	5,50	7,49	23,20	8,04	—

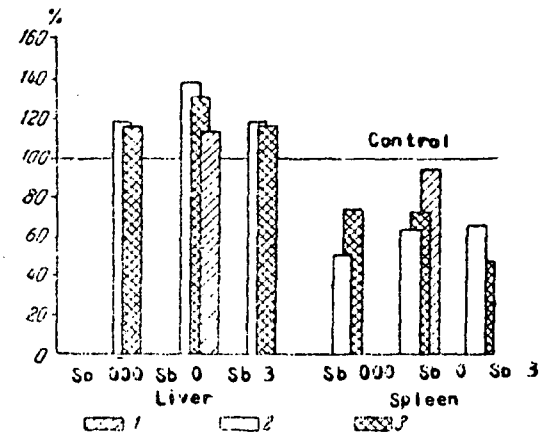
Data obtained in experiments for the determination of LD_{50} were processed for each type of metal by the statistical method of G. N. Pershin. All methods yielded the same results. LD_{50} for Sb_{000} was 115 mg/kg, for Sb_0 - 110 mg kg, and for Sb_3 - 130 mg/kg. Bradley and Frederick administered powdered metallic antimony to experimental animals and found 100 mg/kg as the LD_{50} dose. It was not possible to establish clearcut toxicity differentials between the 3 types of antimony metal on the basis of clinical observations. Experimental animals became somewhat excited between the 6 and 8 hours following the antimony powder administration. They lost their avidity for food and drank much water; simultaneously, they developed a state of anuria which led to body swelling noted particularly over the head so

that their eyes became almost completely closed. Six to 8 hours later, there appeared a state of depression and a simultaneous lack of mobility and reactivity to external stimuli, superimposed later, by disturbed motor coordination, as shown by lateral body locomotion. Respiration became labored and less frequent, and the stool of many animals became liquid. Death ensued as a result of respiratory arrest with the experimental animals in a convulsive state. It was noted however, that animals receiving Sb_3 were not as profoundly affected by the metal administration as were experimental animals which had been administered Sb_{000} or Sb_0. Autopsy observation showed marked vascular hyperemia especially in the skin mesentery and in the internal organs. Vascular blood stasis varied with the antimony dose. The liver was enlarged, swollen, soft and flabby. Macroscopic dystrophic changes had also been noted in the kidneys, lungs, mesentery and especially in the small intestine.

Surviving rats were kept under observation for an additional 30 days. At the end of this period, the rats were decapitated. Livers, kidneys, spleens, hearts, lungs, and brains of the dead and decapitated animals were weighed, after which sections were made for histologic study. It was noted that the surviving animals lost much of their fur during the 30 days observation. A hemorrhagic rash spread over the skin which became wrinkled and covered with scar tissue. Changes in body weight of the control animals throughout the observation period were within the limits of normal fluctuation. Curves plotted on the basis of weight changes in experimental rats which received antimony of different purity manifested similar characteristics. In every case there was an initial loss in body weight followed by a progressive rise in body weight. However, rats which received dust of antimony Sb_3 gained weight after their original loss of weight at a very low rate, reaching the initial weight 22 days after the administration of 100 mg/kg, and 24 days after the administration of 150 mg/kg. Generally, however, the data indicated that antimony contributed to the increase in the animals' body weight throughout the observation period. This agrees with data found in literature and explains the long standing practice of hog and geese breeders who added antimony to the rations of their animals and birds.

It has been known for some time that internal animal organs, particularly the parenchyma, were highly sensitive to the effects of many poisons. Such effects appeared as changes in the weight of the different organs in a specific manner, and, therefore, in specific ratios. Most pronounced changes, which are also most indicative, occurred in the weights of the liver and kidneys, as shown by graphs in the Fig. In such experiments the weight of control animals is regarded as 100%. Data obtained from weighing organs of the experimental animals were statistically processed and showed firstly that changes in the weight of organs in animals administered 50 mg/kg of the antimony were not statistically significant and/or reliable; secondly, that organs weight changes were more significant in the animals which died early in the experimental period, as shown by the weight coeffi-

cients; and thirdly, that the increase in the liver weight and fall in the weight of the kidneys followed a regular pattern.



Ratio of organ in body weight in animals poisoned with Sb of different purity degree 1 - 50 mg/kg of Sb; 2 - 100 mg/kg; 3 - 150 mg/kg

Profound changes in the liver and spleen were paralleled by corresponding differences in the antimony distribution, which is clearly indicated by data presented in Table 2. Analysis of such data showed that most of the antimony accumulated in the liver and in the spleen and that during the early days of observation the amount of antimony accumulated in the liver was twice as great as the amount accumulated in the spleen. Whereas 30 days later, or at the end of the observation period, the spleen contained 6 times as much antimony as did the liver. Antimony accumulation was also noted in the gastro-intestinal tract. Data in Table 2 also show that the rate of antimony accumulation in the body organs varied with the degree of the metal purity, and intensity of toxicity. This was shown by the fact that organs of experimental animals which received Sb_3 accumulated 50-75% less of the metal than was found in the organs of experimental animals which received Sb_{000}, and also in organs of animals which died during the early days of the experiment, and also animals which had been sacrificed at the end of the observation period. The large antimony accumulation in the bifurcated lymph glands may have been the result of mechanical carrying over of metallic antimony by the lymph flow. See next page for Table 2.

Conclusions

1. Metallic antimony possesses highly toxic properties as shown by the fact that the Sb_{000} was more toxic to the animal organism than the dust of the less pure antimony, such as Sb_0 and Sb_3.

2. The belief that toxic properties of antimony were due to lead or arsenic impurities was not substantiated by the present investigation.

3. Metallic antimony is easily soluble in different body fluids. Highest solubility was noted in human blood serum (23.2 mg%) at 37° in the course of a day. Solubility of metallic antimony increased directly with increase in the fluid alkalinity and vice versa.

4. Antimony poisoning produced dystrophic changes in the parenchymatous organs which explains the reason for increase in the weight of liver and loss in the weight of spleen in the experimental animals. Antimony

accumulated in the liver and in the spleen. Changes in weight coefficient of other organs in the experimental animals were of lesser magnitude.

Table 2.

Distribution of Sb000, Sb0, and Sb3 in organs and tissues of white rats which died during the early days of the experiment and rats sacrificed and autopsied 30 days from beginning of experiment

Organ	Averages in mg/100 g of organ					
	Rats dead within 5 - 8 days			30 days from beginning of experiment		
	Sb000	Sb0	Sb3	Sb000	Sb0	Sb3
Spleen	7,62	6,97	2,86	6,07	13,40	1,88
Liver	16,02	11,69	6,88	1,34	1,51	0,54
Kidneys	4,43	3,48	2,42	0,43	0,17	0,08
Adrenals	Not studied	1,28	Not studied	Not studied	0	Not Studied
Heart	2,34	1,11	0,47	0,03	Trace	0
Lungs	13,32	1,23	0,98	0,42	0,12	0,03
Small intestine	Not studied	1,66	1,93	1,33	0,33	Not studied
Large intestine	4,20	1,44	1,20	2,41	1,45	0,70
Stomach	6,66	4,02	1,97	14,95	2,23	1,19
Brain	0,98	0,71	0,24	0,34	0	0
Muscles	9,13	2,08	Not studied	Trace	Not studied	Not studied
Skin and fur	Not studied	0,61	Not studied	0,29	Not studied	0,14
Bone marrow	Not studied	Not studied	5,85	1,33	0,72	0
Lymphatic gland	5,86	Not studied	7,69	102,14	133,15	68,36

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3,4-Benzpyrene in Crude Oil and in Bitumenous Products

pp. 71 - 73

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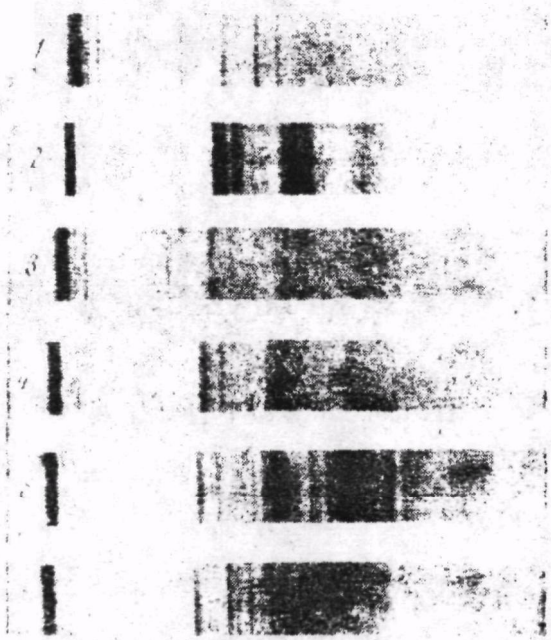
The task of cancer prevention can be considerably advanced by the elimination or significant reduction of cancerogenic products widely used in the nation's daily life. Among such products are coal brickettes which are used as a convenient fuel, especially in rural districts. The present technology used in making brickettes from coal dust is based on the use of coal pitch as the binding material; the cancerogenic properties of coal pitch have been well demonstrated. L. M. Shabad and P. P. Dikun showed in 1959 that coal pitch content of cancerogenic 3,4-benzpyrene can be as high as 1.5%. Data close to the above were found by the present authors during their investigation of pitch products produced by different Ukrainian coke-chemical plants. The present authors found that the 3,4-benzpyrene concentration in different coal pitch products ranged between 0.98-1.4%. By order of the Chief Government Sanitary Inspector of the R.S.F.S.R. the use of brickettes in which coal tar pitch was the binder, for the population's daily needs was forbidden. In the place of coal-tar crude oil binders had been recommended. Evidence found in the USSR and foreign literature indicated that blastomogenic activity of crude oil products was of a considerably lower intensity than of hard coal products. Lately, however, many investigators found the presence of 3,4-benzpyrene in crude oil products. A study of the Groznesk and of Lyuberetsk crude oil tars failed to discover the presence of 3,4-benzpyrene. It should be noted in this connection that such studies had been conducted by spectrofluorescent method at room temperature.

The present authors investigated the 3,4-benzpyrene concentrations in crude oil tars of different trademarks. The investigation aimed at finding which of the products contained the least amount of 3,4-benzpyrene so their use could be recommended in the place of other products which contained higher cancerogenic hydrocarbon concentrations. The investigation included crude oil, tar and pitch products trademarked BN-IV and BN-V, obtained from cracking residuals BN-V produced by the Kherson plant. This plant processed crude oil coming from the Ukraine and partly from Povolzh'ya. Samples for the investigation came in a variety of forms of processed crude oil, such as crude oil asphalt resulting from direct vertical crude oil distillation, and cracking residuals resulting from processing crude oil break down products. The composition of products resulting from direct vertical crude oil distillation depended largely upon the nature of the crude oil, and the composition of cracking products characterized by high content of aromatic polycyclic hydrocarbons is determined basically by the production technology. Trademarked crude oil bitumens are distinguished by their melting point and viscosity.

Samples of crude oil-bitumen products weighing 0.1-0.5 g were dissolved in 2.5 ml of benzene and poured into a partitioning column of activated aluminum oxide. Chromatographic partitioning was made at first with petrolic ether and then with a mixture of petrolic ether and benzene and ending with pure benzene. The fluorescent fractions were collected under ultraviolet lamp PRK-4, the light of which was passed through light filter UFS-3. 3,4-benzpyrene was identified by comparing fine structure fluorescent spectra of different fractions with the spectrum of 3,4-benzpyrene solution. N-hexane was used as the solvent. Quantitative analysis was made using 3,4-benzpyrene spectrofluorescence at a temperature of liquid nitrogen using 1,12-benzpyrene as the inside background. The fluorescent spectra were recorded by the photoelectric method developed in the laboratory of the institute by N. N. Serzhantova, V. B. Timofeev and P. A. Korotkova. Sensitivity of this photoelectric method was 5×10^{-10} g/ml and the accuracy was within 12%. At first the spectralfluorescent analysis of the crude oil bitumen was conducted at room temperature, and no 3,4-benzpyrene could be detected in any of the 20 investigated samples. Later, 3,4-benzpyrene determinations were made at the temperature of liquid nitrogen. Using this method it was possible to establish that, contrary to the prevailing opinion, crude oil bitumen products contained 3,4-benzpyrene, as can be seen in the spectra presented in the Figure.



Fluorescent spectra of crude oil fractions recorded at temperature of liquid nitrogen.
2 - Standard 3,4-benzpyrene solution 1, 3, 4, 5, 6, - crude oil benzpyrene fractions.

Quantitative results of the investigation are presented in the Table.

Bitumen trademarked BN-V, prepared from crude oil tar residue also contained 3,4-benzpyrene. However, in the present study only 1 tested sample contained the cancerogenic hydrocarbon in a considerably lesser quantity than in the crude oil cracking residues. This is in agreement with information found in the literature which indicated that products of distructive crude oil processing contained more groups of aromatic compounds than the products of vertical crude oil distillation, as was shown by B. T. Brooks and his collaborators in 1959. Results of the presented investigation make it possible to determine the cancerogenic properties of different crude oil tar residues by determining the quantitative content of 3,4-benzpyrene. Results indicated that even the maximal 3,4-benzpyrene concentrations found in the crude oil tar residues were considerably below the maximal concentrations of 3,4-benzpyrene found in coal pitch. Therefore, it appears that replacing the coal tar pitch

as a binder by crude oil tar residue should reduce considerably the amount of cancerogenic coal products in coal dust brickettes. It should be remembered, however, that crude oil tar residue binders may contain cancerogenic substances other than 3,4-benzpyrene, the concentration of which may be different in different types of the crude oil binders. In view of this, final recommendations for the use of the safest crude oil residue binders of different trademarks should be based on experimental studies with animals.

3, 4-benzpyrene concentration in crude oils processed by the Kherson plant

Crude oil trade mark	No. of samples	% of 3,4-benzpyrene in samples
BN IV of cracking residue	9	0.0004 – 0.0075
BN V of cracking residue	4	0.0071 – 0.0272
BN V of crude oil tar residue . .	3	None found — 0.00005

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Blastomogenic Properties of Crude Oils From Different Oil Fields

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The machine building industry extensively uses lubricating and cooling fats and oils of crude oil origin. During machine operation the lubricating materials fly into the air of the working premises or become deposited on the exposed skin and clothing of the workers in the form of a fine spray. The droplets finally permeate through the clothing, come in contact with the skin of the trunk and appendages. The oils generally possess irritating and photodynamic properties. Prolonged repeated skin contamination with the lubricating oils and fats frequently results in the appearance on the workers'

skin of wart-like growths. This justifies the search of blastomogenic potentialities in crude oil proper.

O. G. Prokof'eva experimented with white mice (1938) and found that sulfurized mineral oils possessed cancerogenic properties. She applied the sulfuric oil to the skin of the white mice for 4 and one-half months, at the end of which some of the experimental mice developed papillomas and some developed cancers. R. I. Verkhovskaya performed similar experiments with emulsol and concluded that the substance contained slight blastomogenic properties, if any, since none of her experimental mice developed cancer growths. Lubricating and cooling oils used in the machine building industry are derivatives of crude oil. Therefore, it is reasonable to determine first whether crude oil as such possessed blastomogenic properties. A clearcut answer to this question will predetermine the expediency of further investigations with respect to blastomogenicity of crude oil derivatives, such as lubricating and cooling oils. The investigation herein reported included crude oil specimens coming from 5 different oil fields. Experiments were conducted with groups of 6 rabbits, by coating their outer ear skin every other day with crude oil samples selected for the investigation. Application of the oils to the outer skin of the rabbits was continued for 10-17 months. The skin of the experimental rabbits' ears developed slight erythematosis scaling, follicular hyperkeratosis, and falling out of the fur. The rabbits developed isolated nodules around the ear periphery the size of a poppy seed, and some of the rabbits, developed small flat isolated warts the size of a millet seed. Such growth generally remained stationary and in some instances expanded at a very slow rate, while in other cases the warts became reabsorbed. Warts resulting from the application of the Bitkov and Gozhansk oil fields were generally more numerous and of larger dimension and their development could be easily detected.

Histologic examination of skin sections with wart development presented a picture of varying pathology, such as papillomatosis, acanthosis, and predominately focal wart-like epithelial protrusions. According to results of the investigation, most pronounced changes, as above described, were produced by crude oil coming from the Bitkov oil field; next in order of intensity was the oil from the Gozhansk oil fields, then came the crude oil from the Radchenkov, the Romashkin, and lastly from the Kokhanov oil fields. The samples selected for the present investigation contained different concentrations of paraffin, tar, and sulfur, as shown in the Table below.

Percent of paraffin, sulfur, and tar in different types of crude oil

Substances	Bytkof	Gozhansk	Romash-kin	Radchen-kov	Kok-hanov
Paraffin	14	4	3	1,6	1
Sulfur	0,5	3,67	1,3	0,17	6,2
Tar	35	39	36	0,17	52

Results indicated that tar and sulfur in themselves could not explain the cancerogenic properties of the crude oils, since the Kokhanov crude oil, which possessed highest concentrations of the two substances, manifested the slightest blastomogenic properties. On the other hand, the Bitkov crude oil which had the lowest tar concentration, manifested blastomogenic properties of intensity greater than did the crude oil from the Kokhanov oil fields which contained 14% paraffin. The data indicated that the intensity of blastomogenic properties of the investigated crude oils abated with the reduction in the paraffin concentration.

Supplemental tests were conducted with white mice and crude oil coming from the Kokhanov, Bitkov, and Gozhansk oil fields. That is crude oils which contained highest concentrations of tar, paraffin and sulfur. Experiments were performed with groups of 30 mice. Experimental animals received crude oil applications twice weekly over the skin covering the backbone area in the neighborhood of the blades. The applications were continued 10 months, amounting to a total of 80 applications. Mice, the skin of which was treated with the Kokhanov crude oil, developed alopecia and localized hyperkeratosis. One of the experimental mice treated with the Bitkov crude oil developed a malignancy the size of an Italian plum on the ninth month of the crude oil application. Upon incision of the malignant growth a bluish bloody fluid oozed out. One of the mice treated with the Gozhansk crude oil developed a malignancy the size of an average plum on the tenth month of the crude oil application. Macroscopically, it appeared as a nodular grayish blue malignant growth which easily separated from the animals skin and muscles. Histologic studies showed that the two malignant growths consisted of polymorphic cellular elements, the nuclei of which were of different developmental stages and different maturity periods. There was a large number of polynuclear and giant mononuclear cells. There were signs of nuclear and protoplasmic cell degeneration. The stroma consisted of connective tissue fibers visible in small numbers between the accumulation of cellular elements. The inside surface of the blood vessels was frequently covered with a layer of sarcomatous cells, and the malignant growths penetrated into the intravascular spaces accompanied by thrombosis. Based on the paranchyma and stroma appearances, the developed malignancy was classed as angiosarkoma. Supplemental experiments for the determination of the role played by paraffin in crude oil blastomogenisis were conducted with white mice and crude oil tar-pitch products and cracking residues of Dolinsk-Bitkov and Tuimazinsk crude oil. Crude oil from the Dolinsk oil fields contained 0.37% of sulfur, 20% of tar, and 11.55% of paraffin; crude oil coming from the Bitkov oil field, as noted previously, contained 0.5% of sulfur, 35% of tar, and 14% of paraffin. The Tuimazin crude oil contained 1.47% of sulfur, 40% of tar, and 5.9% of paraffin. Cancers developed in two of the 20 mice, the skin of which was treated with the Dolinsk crude oil tar-pitch product. The mice ultimately died. On the basis of histologic investigation, the cancers were classed as angiosarcomas. Twelve of the 28 mice, the skin of which was treated with the Dolinsk crude oil cracking residue, developed neoplastic growths. Histologic examination showed that 8 of the

12 neoplastic growths were of a true cancerous nature. Observation of mice, the skin of which was treated with Bitkov crude oil cracking residue, showed that 8 of the 13 surviving animals showed wart-like formations of different dimensions. No wart-like or cancerous growth developed in the white mice, the skin of which was treated with the Tuimazin crude oil cracking residue.

Results of experiments conducted with mice by treating their skins with cracking residues of Bitkov, Dolinsk and Tuimazin crude oil generally agreed with the results in experiments with rabbits and verify the assumption that paraffin played an important part in the cancerogenicity of crude oil and of its processed derivatives.

Conclusions

1. Results of the above investigations show that crude oil coming from the Bitkov, Gozhansk, Romashkin, Radchenkov and Kokaanov oil fields possessed blastomogenic properties.

2. Results of the investigations, as reported in the present paper, show that the blastomogenic properties of the crude oils mentioned in Conclusion No. 1, and of their derivative products differed to some extent with the concentration of paraffin contained in them. The results showed that the greater was the paraffin concentration in the crude oil, the more intensive was its blastomogenic activity. The same was true of the crude oil tar-pitch and of the crude oil cracking residue.

3. The blastomogenic effects of crude oil derivative lubricating and cooling oils may be eliminated or greatly reduced; it is recommended that such oils be prepared from crude oil, the paraffin content of which originally was or was artificially reduced to less than 1%.

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The Role Played by Paraffin in the Blastomogenicity of Crude Oil

pp. 87 - 92

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(With reference to the paper of Prof. D. D. Shapiro and I. Ya Hetmanetz entitled "Blastomogenic Properties of Crude Oils from Different Oil Fields" which appeared in Gigiena i Sanitariya, 1962, No. 6)
pp. 38 - 41

Prof. D. D. Shapiro and scientific aide I. Ya Hetmanetz studied the properties of crude oil from 5 different oil fields and found them to possess blastomogenic properties. The question concerning the presence of blastomogenic properties in crude oil was not a new one. Results of many investigations showed that crude oil of some oil fields possessed blastomogenic properties of different intensities, as was shown by the investigations of Twort and Twort in 1928-1933, by Combes in 1954, and by others. Examination of workers engaged in oil mining in different oil fields showed that a direct connection existed between the nature of the crude oil, conditions of contact with same, and rate of skin cancer morbidity. According to data presented by Schwarts and his collaborator 146 of 743 workers engaged in the crude oil industry of California had keratosis of their hands, forearms, face and back of the neck, while 7 had general skin cancer. It is of interest that 5 of the workers who had skin cancer had been employed as underground oil well repairmen, which brought them into intimate contact with crude oil. Similar examination of 330 workers employed in the oil fields of Texas failed to disclose the presence of skin cancer among them.

The crude oil mined in the USSR has been regarded as practically free from blastomogenic properties. Thus, M. Yu Gol'denberg, Yu. I. Faer and M. D. Vesloguzova stated in the literature of 1956 that the USSR crude oil was generally free from skin cancer producing properties. However, this opinion was not held by all investigators. N. V. Lazarev stated in 1954 that as the mining of crude oil spread over different USSR territories some evidence appeared that the crude oil of some oil fields possessed blastomogenic properties. In this connection the position taken by M. I. Fongaus in 1962 regarding the approach to the hygienic evaluation of physical, chemical crude oil properties from the viewpoint of possible blastomogenesis is fully justified. Indeed, reports which appeared in the literature during the past several years indicated that crude oil of some new oil fields, unlike those of the Caucasus possessed blastomogenic properties. Finally D. D. Shapiro and I.Ya. Hetmanetz verified the fact that the crude oil from Bitkovsk, Gozhknsk, Romashkin, Radshekov and from Kokhanovsk oil fields possessed blastomogenic properties. It should be noted that the paper presented by Prof. Shapiro and Hetmanetz is of considerable interest, since it stimulated great interest

on the part of medical and technological and engineering workers in protecting the skin of workers employed in the crude oil industry. Nevertheless, it is not enough to establish the fact that one or another type of crude oil was free from or possessed blastomogenic properties. Attempts should also be made to identify the cancerogenic compounds specifically and to demonstrate the presence in crude oil of other compounds possessing blastomogenic potentialities.

It has been known that crude oil coming from different oil wells possesse different physical properties and chemical compositions. In addition to different hydrocarbons crude oil contained sulfur compounds, oxygen, nitrogen, etc. What are the compounds which supposedly possessed blastomogenic properties? Unfortunately, this question can not be answered categorically, and opinions in this respect differ. Generally speaking, no known cancerogenic substances have been detected in crude oil. On the other hand, Cook and his collaborators found several polycyclic hydrocarbons in crude oil of Kuwait, which supposedly possessed blastomogenic properties. P. A. Bogovskii expressed the opinion in 1960 that from the viewpoint of possible cancerogenicity the group of high molecular tarry substances, which are unsaturated heterocyclic compounds were of considerable interest. In our present state of knowledge it is difficult to say whether the above opinion was right or wrong.

It is an unfortunate fact that many of the investigators made no effort to correlate the results of their experiments on animals with the physical chemical characteristics of the crude oil. In this respect the work of D. D. Shapiro and I. Ya Hetmenetz is an exception, and advantageously differs from investigations of other authors. Shapiro and Hetmenetz found that blastomogenic properties of oils coming from different oil fields differed in their intensities. The above authors put in the first place crude oil coming from the Vitkovsk oil field and in the second place crude oil coming from the Gozhansk oil field, followed by oil coming from the Radchenkov and Romashkinsk fields, and finally crude oil coming from the Kokhknovsk oil field. They correlated such data with results of physical, chemical properties of the same crude oil samples and came to the following conclusion: in cases where the concentrations of tar and sulfur appeared of no importance, the paraffin concentration proved of exceptional significance. The correlative studies showed that crude oil from the Vitkovsk and from the Gozhansk oil fields, the paraffin content of which was greater, possessed more intensive blastomogenic properties. However, no such correlation was found by these authors in the case of crude oil coming from the Romashkinsk and Radchenkov oil fields. On the contrary, the Romashkinsk crude oil contained paraffin up to 3% and was below the Radchenko crude oil with regard to blastomogenic activity, despite the fact that its paraffin content was only 1.6% or 50% of that found in the Romashkinsk crude oil. The blastomogenic properties of all the 5 crude oils are studied by the authors using rabbits and in addition using rats in connection with the Brickov, Gozhansk and the Kokhanov crude oils. Results of experiments with the rabbits could be arranged in a specif-

ic succession (not specifically indicated by the authors) while the results of tests made with the rats were somewhat different. Essentially, the crude oil which contained approximately 4% of paraffin possessed a blastomogenic intensity similar to the Bitkov crude oil which contained 14% paraffin. Both types of crude oil elicited the same type of cancer.

It has been known for some time that paraffin is a skin damaging substance. In the second half of the preceding century, Grotovskii described a folliculitis type of skin disease developed among workers employed in the production of paraffin. At one time a "paraffin disease" has been recognized or spoken of as occurring among workers engaged in the production of paraffin. Reports of paraffin cancer have been found in the literature elicited in workers engaged in the production of paraffin and its products. N. N. Petrov (1931) listed paraffin cancer as an occupational disease. According to Hendricks and his co-workers cancer of the scrotum was frequently found among workers employed in paraffin purifying departments. This type of cancer occurred among the workers at no greater frequency than in the general population. However, among employees whose work record exceeded 10 years cancer of the scrotum was found at a higher frequency. On the other hand, some investigators believe that paraffin as such had no damaging effect on the skin, and that the above mentioned harmful effects were the result of some paraffin processing by-products. Wood stated in 1929 that pure paraffin was inert and harmless and that it produced no dermatitis of pholliculitis among employees working in the paraffin industry. B. T. Brooks expressed a similar opinion in 1959. He pointed to the fact that from the physiologic viewpoint, paraffin was inert and, as a rule, produced no irritating effects. He believed that the specific type of cancer which at times developed in workers connected with the production of paraffin was actually elicited by aromatic hydrocarbons. In this connection, it should be mentioned that some investigators established a clearcut connection between the concentration of aromatic hydrocarbons including other high molecular compounds, and the paraffin content in crude oil. Thus, E. A. Robinson noted in 1960 that an increase in the paraffin content was paralleled by a reduction in the amount of high temperature boiling aromatic hydrocarbons, and also a reduction in the cyclic nature of the molecules. The blastomogenic or cancerogenic substances well known to investigators belonged to different groups of chemical compounds foremost among which are the aromatic and heterocyclic compounds, as shown by L. M. Shabad in 1947, and by L. M. Shabad and P. P. Dikum in 1959, and by many others.

In their paper on the subject, D. D. Shapiro and I. Ya. Hetmanetz failed to indicate clearly whether or not they have taken the above mentioned circumstances into consideration. It is difficult to comprehend why Shapiro and Hetmanetz considered irrelevant data regarding contents of different hydrocarbon types in the studied crude oil samples, while they presented information concerning the contents of paraffin, tar and sulfur. It is pointed out above that crude oil coming from foreign oil fields could be arranged

in a definite consistent order. Thus, Combes noted in 1954 that crude oil coming from Venezula, Borneo, Rumania, and Iran possessed stronger blastomogenic properties than crude oils coming from California, Texas, Pennsylvania or from oil fields of the Soviet Union. According to data presented by some American investigators, Pennsylvania crude oil represented the classical type of so-called paraffin crude oil, while the Mid-Continental crude oil belonged to the same class, whereas, California crude oil contained less of the paraffin and the Borneo surface crude oil contained no hard paraffin and only as the depth of the wells increased the content of solid paraffin began to appear and rise. In this connection the following definitions are generally used. Crude oil containing up to 3% of paraffin is classed as paraffinic crude oil, and crude oil containing more than 3% is referred to as strongly paraffinic crude oil. Below 1% the crude oil is usually referred to as paraffin-free. E. A. Robinson pointed out in 1960 that crude oil coming from Pennsylvania and Borneo oil fields represented strong paraffinic as well as weak paraffinic crude oils. Crude oils coming from Venezuela and Oklahoma oil fields occupied an intermediate position, with Venezuela oil being closer to the Borneo oil, and Oklahoma oil resembling more the Pennsylvania crude oil. A. F. Dobryanskii found that Pennsylvania crude oil contained approximately 2.5% and Texas oil 1.5%, California oil 0.1-0.6% and Rumanian oil 6-7% of hard paraffin. A careful study of the above presented data clearly indicates that no direct connection existed between the paraffin content of a crude oil and its blastomogenic properties.

D. D. Shapiro and I. Ya. Hetmanetz made a more elaborate study of the role played by paraffin in relation to blastomogenic properties of crude oil. They investigated the blastomogenic properties of crude oil tar products and crude oil cracking residuals using white mice as the experimental animals. Experiments were limited to investigation of crude oils and their products coming from the Dolinsk, Bitkov, and Tuimazin oil fields. In their studies they paid particular attention to the contents of sulfur, paraffin, and tar in the crude oils. The present writer believes that such a scope of information was utterly inadequate, for the reason that crude oil consisted of many hydrocarbon groups. It is also believed that data presented by Shapiro and Hetmanetz regarding the quantities of paraffin, tar and sulfur in the original crude oil, failed to adequately reflect the true concentration of even these substances in the products of the crude oil processing, particularly in the tar or pitch and in the cracking residues. Up to the present, particular attention has been given to aromatic hydrocarbons in the crude oil. In this connection, Twort and Twort stated in 1928: "It has been stated at times that crude oil contained no aromatic compounds, or a small quantity of same, prior to its distillation, and that such products became synthesized during the process of distillation. Such a supposition is understandable, yet it can not be denied that some samples of crude oil are capable of eliciting cancer development in animals even though it may be to a small degree." Results of experimental series showed that high temperature crude oil processing brings about a recombination of the split products which results in

the formation of aromatic cancerogenic compounds. Kennaway (1925) tested some California crude oil by applying same to the skin of white mice for 515 days without eliciting cancer formation symptoms. He, then, heated the same oil to 880° in hydrogen atmosphere, after which the oil, which previously was presumably free from cancerogenic properties, possessed cancerogenic activity. Similar experiments had been performed by other investigators. There are no data which would clearly point to the origin of blastomogenic crude oil products; nevertheless, there are isolated indications of same. Thus, Twort and Ing (1929) expressed the opinion that blastomogenic effects were elicited by unsaturated aromatic hydrocarbons. According to data presented by Fischer and his collaborators in 1951, high boiling crude oil products may contain a considerable amount of different hydrocarbons. This should have been reason enough to prompt D. D. Shapiro and I.Ya. Hetmanetz to determine the exact chemical composition of each individual product with special reference to aromatic compounds. This should have been necessarily done for no other reason than for the fact that cracking residuals consisted of high condensation aromatic hydrocarbons, and some other compounds; yet, this was not done by Shapiro and his collaborators. It is generally known that values characteristic of paraffin concentrations, sulfur and other crude oil components did not always coincide with values characterizing their concentrations in other products. Thus, according to D. L. Nelson and his collaborators (1956) the ratio between sulfur concentration in cracking residuals and its concentration in crude oil ranged between 0.7 and 5.5% according to the original oil field. On the basis of their proposed conception D. D. Shapiro and his collaborator concluded at the end of their report that it was necessary to free crude oil from paraffin or to reduce it to 1%.

The present author believes that more convincing data regarding the part played by paraffin in the blastomogenic potentialities of crude oil should have been obtained. The indications are that the two authors continue to pursue their highly important studies. For if it were actually and undoubtedly established that paraffin played an important role in the blastomogenic potentialities of crude oil, then it would become necessary to concentrate all effort in the direction of complete and general mechanization and automation of crude oil treatment processes as well as their complete leak-proof encasement wherever necessary. M. I.Fongaus found in 1962 that the use of high temperature in connection with crude oil products may form vapors of heavy hydrocarbons which upon cooling condensed to aerosols of solid or liquid phases forming paraffin aerosols or oil fogs, both of which are acutely harmful to the organisms of workers. Such aerosols, consisting of heavy polynuclear aromatic hydrocarbons, act not only by way of the respiratory organs but by skin permeation as well.
N. M. Thompson showed in 1959 that the human organism eliminated through the skin 20 g of fat or oil per day, and under the protection of the skin such oil can catch and retain and even dissolve some substances present in the air as aerosols. The possibility of paraffin entering the organism in a similar manner can not be excluded.

D. D. Shapiro and his collaborator made an earnest attempt to explain the reason for or origin of blastomogenic properties of different types of crude oil. In their work, they made certain inaccurate assumptions which to some extent invalidate their results, or lead to incorrect evaluation ation of their results. It is hoped that the studies being conducted at the Ukrainian Institute of Labor Hygiene and Occupational Diseases in connection with the Ufa Institute of Hygiene and Occupational Diseases will produce data on the basis of which the problem attacked by Shapiro and Hetmanetz, and which is discussed in this paper, will be rationally resolved.

Editor's Remarks

Commenting on the remarks made by M. M. Gimadeev regarding the publication of D. D. Shapiro and I. Ya. Hetmanetz, M. I. Fongaus states at the request of the editor that the paper was justly evaluated by Gimadeev, both as regards its positive significance and shortcomings. The objections presented by M. M. Gimadeev are basically sound and convincing. The question of crude oil and crude oil products cancerogenicity is occupying the attention of increasingly larger circles of sanitary hygienic investigators. For this reason, the position adopted by Gimadeev in his evaluation of the paper by Shapiro and Hetmanetz acquires special significance, since it can prevent other investigators from taking the wrong positions in organizing and executing future investigations in crude oil mining and crude oil processing plants. On her part, M. I. Fongaus notes that M. M. Gimadeev failed to note and take into account some erroneous positions expressed in the paper by Shapiro and Hetmanetz. In her opinion, it is erroneous to regard all mineral oils as agents capable to produce warty growth on the skin. In this respect the authors contradict themselves. Thus, on two occasions they point to the fact that cancerogenicity of crude oil products raised the problem of blastomogenic potentialities of crude oil proper; but the cancerogenicity of raw crude oil is a problem by itself, and has no relation to the cancerogenicity of the crude oil products. Employees engaged in crude oil mining in underground repair of oil well casing and apparatuses, and in similar branches of the industry, come in contact with the crude oil only. The cancerogenicity of crude oil products likewise presents a problem of its own, which can not be disregarded even in instances in which the crude oil itself was devoid of cancerogenic properties, since in the course of its processing by destructive distillation cancerogenic substances may come into being. Under such conditions the position assumed by the original authors has a disorienting effect, on hygienists and sanitarians.

Bibliography next page.

Bibliography

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NO. 12, DECEMBER

Orientation Data for the Determination of Maximal Permissible α-Methyl Styrol Concentration in the Air of Working Premises

pp. 14 - 22

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Alpha-methyl styrol is widely used in industry in the production of divinyl methyl styrol, synthetic rubber of styrolated drying oils and of alkylated resins; it is an intermediary product in the production of synthetic phenol and acetone. According to information found in the foreign literature, alpha-methyl styrol is also used as a reaction-starter in the production of medicaments, plastic materials and acid-resistant rubber.

The structural formula of α-methyl styrol is

$$(C_6H_5 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} = CH_2)$$

it is a transparent, colorless, oily fluid having a characteristic odor of

napthalene. Its b.p. is 160-163°. It is water soluble and easily soluble in organic solvents. It belongs to the group of narcotics and possesses strongly irritating properties. Little information was found in the literature on the subject of α-methyl styrol toxicity, and what evidence has been found was of a contradictory nature. T. A. Blinova exposed several species of experimental animals to the inhalation of α-methyl styrol vapor in 1 mg/li concentration for 106 days. She reported in 1954 the following changes in the peripheral blood of the experimental animals: hyperchromic anemia, relative leucocytic reticulocytosis, which turned into reticulopenia at the end of the vapor inhalation exposure, and a shortened blood clotting time. N. L. Rylova (1955) exposed white rats to the inhalation of α-methyl styrol vapor in concentration of 3 mg/li for 9 months, and reported that the preparation irritated mucous membranes and lowered the experimental animals' capacity to perform difficult physical tasks. She found that 0.02 mg/li of the vapor constituted the concentration of threshold irritation to the conjunctiva and to mucous membranes of the respiratory tract, and also the concentration of α-methyl styrol odor perceptibility. Using the procedure of Zakusova-Lyablina, she determined that 0.06 mg/li of the α-methyl styrol vapor represented the concentration of threshold activity on the central nervous system of rabbits.

Experimental results obtained by T. A. Blinova and M. L. Rylova led them to the conclusion that prolonged exposure to the effects of α-methyl styrol vapor was toxicologically harmful. Wolf of the USA came to the opposite conclusion in 1956. He and his collaborators worked with white rats, guinea pigs, rabbits, and Macacus rhesus, male and female; these experimental animals were exposed to the inhalation of air containing 2.9 mg/li of α-methyl styrol vapor for 6 months, and found only slight changes in the form of arrested growth and increase in the liver and kidney weights; inhalation of air containing 0.97 mg/li of the tested vapor elicited no toxic symptoms in any of the experimental animals. Wolf and his collaborators were of the opinion that even under conditions of chronic exposure, α-methyl styrol failed to manifest notable toxic effects usually characteristic of compounds of the aromatic series. They emphatically denied that α-methyl styrol vapor possessed myelotoxic properties. Gerarde (1962), Browning (1958), Batchelor (1927), Spencer and his co-workers (1947), and other investigators expressed the same opinion in relation to the toxicity of benzene homologues.

Such contradictory conclusions may be explained by the fact that the authors used toxicity indexes of different natures. In addition, the cited USSR and foreign authors based their conclusions only on experimental data, whereas, the practice of establishing maximal permissible concentration of toxic substances must be mandatorily based on data obtained experimentally and under practical conditions including examinations of general health of persons exposed to the effects of the investigated toxic substance in different concentrations.

Investigations of conditions prevailing in the production of divinyl methyl styrol synthetic rubber in the Bashkir ASSR indicated that the basic harmful factor in the production of the preparation was air pollution of the working premises with α-methyl styrol vapor. Results of 1400 analyses of air samples collected during 1960-1963 showed that concentrations of α-methyl styrol were below the official permissible maximum of 0.05 mg/li ranging between 0.01 and 0.03 mg/li. At some points of the synthetic rubber production, such as rubber drying conveyors and other similar points, α-methyl styrol vapor concentration in the air ranged between 0.65-0.11 mg/li.

Investigators who studied the sanitary conditions prevailing in some branches of the organic synthetic industry noted that chronic exposure to the inhalation of benzene and some of its compounds elicited symptoms of cardio-vascular poisons. Therefore, it appeared important to determine what effect vapor of α-methyl styrol, which is a benzene homologue, had on the physiological functions of workers chronically exposed to the inhalation of air containing low concentrations of such vapor.

The physiological reactions of some employees was studied in the course of a work shift and a work week. Results pointed to a lowering in body temperature, a drop in the systolic and diastolic arterial blood pressure and a loss in eye sensitivity to light. A comparison of results obtained from above described investigations in 1960-1961 and 1962 indicated that there was a reduction in the values of index shifts according to reports in 1962. This may have been caused by the development of a peculiar intoxication characterized by a sharp drop in external manifestations of poisoning.

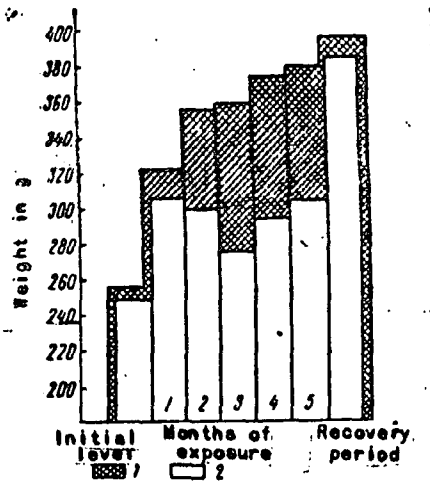
The observed shifts in the organism's functions basically accorded with the results of clinical observations and examinations made on 224 workers employed by the synthetic rubber producing plant. Some workers manifested disburbance in the functional state of the central nervous system, such as headaches, tremor of the fingers and eyelids, disseminated red dermography and a labile pulse; 24.8% of the observed and examined workers manifested atrophic changes of the nasal and glottis mucous membrances. Individual workers also developed leucopenia, thrombocytopenia, a rise in the pH of the gastric juice, and a loss in its digestive capacity. Some changes were noted in the liver of young workers, but no hepatotropic diseases; the liver size increased, and its antitoxic function was impared,as shown by the Quick test. A. A. Orlova, G. N. Mazunina, and E. A. Solov'eva studied the effect of α-methyl styrol in the Krasnoyarsk synthetic rubber plant; their results were similar to those cited above.

Results of the above physiological, hygienic and polyclinic investigations prompted the present author to study the biological effect of α-methyl styrol vapor under acute and chronic experimental condictions, in order to secure basic data for the determination of the maximal permissible α-methyl styrol vapor concentration in the air of production premises. Results ob-

tained under acute experimental conditions indicated that α-methyl styrol vapor possessed resorptive properties, and that it constituted no possible intoxication factor under industrial production conditions. Exposure of mice to a single 2-hour inhalation of the tested vapor failed to kill any of the experimental animals probably due to the insufficient exposure chamber air saturation with the α-methyl styrol vapor due to the low volatility of the oily preparation. Only slight sluggishness was noted in the mice at the end of the inhalation tests. Intragastric α-methyl styrol administration in oily solution in 1.5-9.0 g/kg doses irritated the gastrointestinal mucosa, elicited motor agitation and a state of narcosis. Experimental animals died within 1-2 days in a state of clonic convulsions, cyanosis, lowered body temperature, paralysis of the hind legs and uncontrolled urination. The absolute lethal dose was 7.0 g/kg, and LD_{50} was 4.5 g/kg. The maximum tolerance dose was 2.0 g/kg. Dipping the tails of the mice into α-methyl styrol for 2-4 hours produced results similar to the ones described above, strongly affected the blood vessels, and killed some of the mice. Autopsie showed acute hyperemia, areas of atelectasis and pulmona_ hemorrhagi injected blood vessels, cerebral swelling and minute kidney and liver hemorhages.

Chronic experiments were conducted with 33 male rats; they were exposed to the inhalation of air containing 0.05, 0.005 and 0.0001 mg/li of α-methyl styrol vapor. It should be noted that 0.05 mg/li was the concentration officially specified as the maximal permissible concentration in the air. Eleven rats were used as controls. Experimental animals were placed into exposure chambers the air of which contained the respective α-methyl styrol for 5.5 hours daily, excepting Sunday, for 5 months. Concentrations of the tested vapor were checked in the chambers by the method of optical density. Results of daily analysis indicated that fluctuation from the intended concentrations were statistically insignificant. Throughout the period of chronic intoxication, the experimental animals had been observed for their general behavior, body temperature, arterial blood pressure, muscle antagonist chronaxy, blood serum protein composition, the thymol test, whole blood cholinesterase activity, morphologic peripheral blood picture, and, oxygen consumption rate. At the end of the chronic experiment the animals became sluggish as compared with the control rats; rats which inhaled air containing 0.05 and 0.005 mg/li of α-methyl styrol vapor developed mucous membrane irritation and bloody nasal exudation. These symptoms became clearly discernible at the end of 30 days experimental inhalation exposure. At the end of 60 days chronic inhalation of air containing 0.05 mg/li of α-methyl styrol vapor, the experimental animals lost weight, as compared with the controls, the values of which were statistically significant. The loss of weight by rats of this group persisted to the end of the chronic vapor inhalation. Rats which inhaled air containing 0.005 mg/li of α-methyl styrol vapor lost weight statistically significant only at the end of 120 days of chronic inhalation. This loss in body weight was rapidly regained by rats of this group after the inhalation was discontinued. Rats which inhaled air containing 0.001 mg/li of the poisonous vapor showed no loss in body weight throughout the experiment. (see Figure 1)

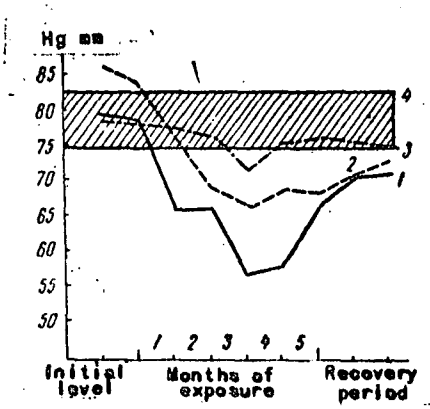
Fig. 1.



Animals' weight in the course of the chronic experiment
1 – Control rats; 2 – Rats of group 1, 0.05 mg/li

Rectal temperatures taken by the battery type electrothermometer showed drops only in rats of group 1. The drop in rat's rectal temperature was greatest at the end of the vapor inhalation period. Thus, the drop in rectal temperature during the second and third month, ranged between 0.68-106, with an average of 0.67°, as compared with the initial values, and between 0.44 and 0.80, with an average of 0.62° as compared with the control values. Such drop in the body temperature may have been a central nervous reaction, and the relative temperature stability may be ascribed to enhanced organism's tolerance to the active agent.

Alpha-methyl styrol had a considerable hypotensive effect on the level of arterial blood pressure. Statistically significant values in arterial blood pressure drop in rats of groups 1 and 2 appeared at the beginning ot the second inhalation exposure month. At the end of the chronic exposure period the arterial pressure drop ranged between 16.5-26.7 with an average of 21.6 mm in rats of group 1, and a range of 11.3-19.7 with an average of 15.5 mm in rats of group 2. It was noted that a rise in blood pressure occurred during the fourth and fifth months of experimental inhalation, a probable manifestation of the compensating mechanism expressed as a non-specific rise in the organisms resistance to the effects of a toxic agent. Arterial pressure returned to its original level rather slowly; 2 months after the discontinuation of the experimental inhalation it was still below the initial levels. Differences recorded in the blood pressure of rats inhaling air containing 0.001 mg/li, and those of the control rats, were statistically insignificant, as shown by curves in Fig. 2 below.

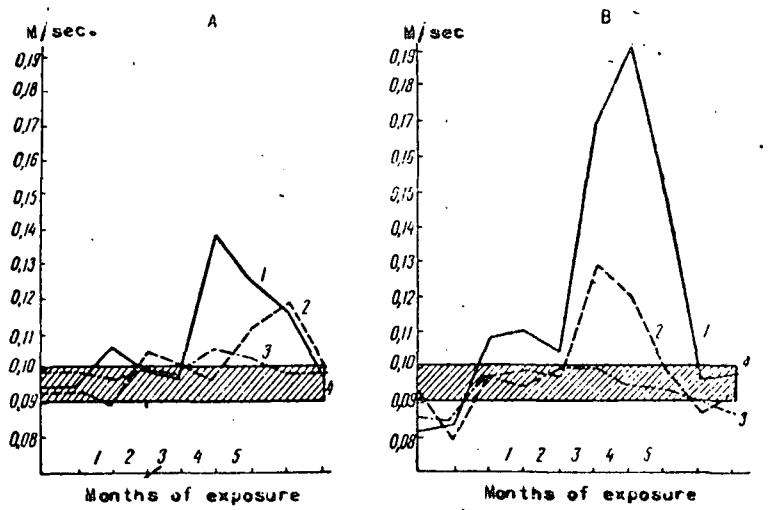


Rats' arterial pressure in the course of the chronic experiment. 1 – Rats of group 1, 0.05 mg/li; 2 – rats of group 2, 0.05 mg/li; 3 – rats of group 3, 0.001 mg/li; 4 – control rats

Effect of α-methyl styrol on the cerebral cortex, as reflected in muscle antagonist chronaxy changes was determined by electronic impulse stimulator ISE-01-58. Delay in muscle antagonists motor chronaxy appeared in some rats of Group 1 on the third exposure month; on the fourth and fifth months this phenomenon was noted in nearly all rats of this group. On the fifth exposure month the extensor chronaxy ranged between 0.01-0.179, with an average of 0.14; the flexor chronaxy ranged between 0.198-0.222, with an average of 0.190 m/sec., as compared with corresponding original values of 0.084-0.102 and average of 0.093, and 0.007-0.087 with an average of 0.82 m/sec.

Statistically verifiable muscle antagonist chronaxy prolongation appeared in rats of group 2 on the fifth exposure month less clearly defined and less general in character. In addition, the central nervous control over the neuromuscular apparatus was disturbed in rats of both experimental groups, as shown by the close approximation between the two chronaxies. Later the chronaxy ratio became reversed. Muscle antagonist chronaxies and their ratio returned to normal only at the end of the second recovery month. Curves in Fig. 3 show that 0.001 mg/li of the α-methyl styrol had no substantial effect on the muscle antagonist chronaxies. Accordingly, 0.05 and 0.005 mg/li of α-methyl styrol vapor affected the cerebral cortex, as evidenced by lowered response to electric stimulation.

Fig. 3.



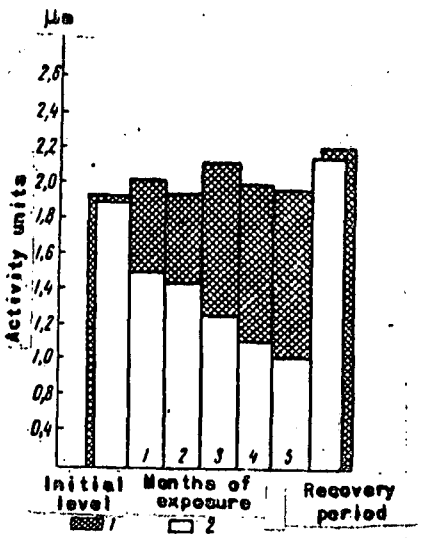
Courses of muscle antagonists chronaxies
A – Flexors Б – Extensors in the course of the chronic experiment.
Other designations as in Fig. 2

Recently accumulated data indicated that cholinesterase, which hydrolyzed acetylcholine, played an important role in transmitting stimulation from the central nervous system, from the ganglia apparatus of the vegetative nervous system, and from the neuromuscular synapses. The present author determined whole blood cholinesterase activity by the Ph-buffer method which is based on determining the amount of acetic acid liberated by acetylcholine hydrolysis, as shown by changes in the Ph-buffer solution. This method has been described in detail by M. V. Smitrieva. Cholinesterase activity of rats belonging to group 1 dropped from the original range of 1.80-2.36, with an average of 2.08, to 0.38-1.18, with an average of 1.78 units at the end of the experimental vapor inhalation as shown in Fig. 4. No statistically verifiable values in cholinesterase activity have been found in rats belonging to groups 2 and 3.

Effect of α-methyl stryol vapor on the hematological indexes was investigated next. Toxic vapor inhalation in 0.05 mg/li under chronic ex-

perimental conditions affected such indexes during the early vapor inhalation stages, as shown by the gradual rise in the number of erythrocytes from 6.89×10^6 - 6.91×10^6, with an average of 6.9×10^6, to 8.11×10^6 - 8.77×10^6, with an average of 8.44×10^6. This was paralleled by a slight rise in the number of leucocytes during the first two months of vapor inhalation, followed by a notable tendency to drop. Such fluctuations were more pronounced in animals of group 1 than in animals of groups 2 and 3, as shown by the data presented in the following Tables.

Fig. 4.



Cholinesterase activity in the rats in the course of the chronic experiment
1 - Control rats; 2 - Rats of Group 1, 0.5 mg/li

The rise in number of erythrocytes in the blood of rats of group 1, and the relative stability in the number of erythrocytes in the rats belonging to group 2 was paralleled in each case by a loss in the hemoglobin concentration. Thus, the hemoglobin percent in the blood of rats belonging to group 1 fell from 75.4-81.4, with an average of 78.4%, to 60.5-67.9, with an average of 64.2%. In rats belonging to group 2, the hemoglobin dropped from 76.3-97.7, with an average of 81%, to 66.3-72.9, with an average of 69.6%. No statistically verifiable data in hemoglobin changes were obtained in rats belonging to group 3. Such changes as had been described above are regarded by the present author as pointing to the development of hypochromic anemia. Rats of groups 1 and 2 also showed indications of developing reticulocytosis. Data of the present investigation accord with the opinion expressed by T. A. Blinova regarding the effect of α-methyl styrol on the general blood picture. Results of the experiments also show that the assumption made by Wolf and co-authors, and by Gerard and others, that α-methyl styrol possessed no myelotoxic activity could not be substantiated by the present author; it is true however, that the effect in the case of α-methyl styrol was less pronounced than in the case of benzene and some of its homologues.

Results of paper electrophoretic studies show that a fall in the blood serum albumin concentration from 40.9 to 35.98% occurred in rats belonging to group 1 during the fifth month of chronic vapor inhalation. This was paralleled by a slight rise in the concentrations of α- and β- globulins. Accordingly, the albumin-globulin coefficient dropped from 0.7 to 0.52. No changes were noted in the turbidity degree of the thymol test, and no significant histologic changes were noted in the liver tissue of the experimental rats; therefore, no study was made of possible hypoalbuminemia as an index of damage caused to the kidneys. The above blood serum protein fraction changes may have been caused by the direct α-methyl styrol effect

Effect of chronic exposure of rats to α-methylstyrol vapor on the white blood picture

Group of rats	Number of leucocytes in 1000s				
	Initial level	After 1 month exposure	2 months' exposure	3 months' exposure	4 months' exposure	5 months' exposure
Group 1, 0.05 mg/li	16.2±1.52	17.1±1.31	17,8±1.47	13.2±0.74	12.5±1.1	11.8±0.8
Group 2, 0.005 mg/li	9.8±0.6	13.3±1.1	11.9±0.6	12.7±1.31	11.6±0.85	9.6±0.35
Group 3, 0.001 mg/li	11,9±0,9	13,9±0.79	12,8±1,1	11,3±0,4	15.3±1,34	13,7±1

on the tissue and serum proteins. However, since the clinical symptoms pointed to liver damage, the possible effect of α-methyl styrol toxicity should be considered; workers connected with the production of processing α-methyl styrol should be checked periodically for the appearance of pertinent liver damage symptoms. Rate of oxygen consumption in rats of group 1 dropped to less than 50% at the end of the vapor inhalation period. No changes in the rate of oxygen consumption were noted in rats belonging to groups 2 and 3.

Pathologic studies of internal organs of rats belonging to group 1 showed changes in the lungs, kidneys, liver, and cerebrum. The lungs showed the presence of interstitial pneumonia, desquamative bronchitis, and a well defined emphysema; the kidneys showed epithelial degeneration of the convoluted tubules and dilated lumens. The interstitial tissue appeared friable, and the lumens of the convoluted tubules were filled with a pinkish mass. Some proliferation in the periportal connective tissue was seen in the liver and in Disse's spaces. Cells of the liver parenchyma were devoid of protoplasmic glycogen. The cerebrum showed the presence of cytopyknosis and karyocytolysis accompanied by the formation of shadow cells and small anemic areas. Acute swelling was seen in the region of subcortical ganglia, also gravely affected gangliar cells, presenting a picture of true neurophagia; the cerebellum showed falling out of Purkinje cells accompanied by acute light or pynknomorphic swelling of the Purkinje cells. The pathomorphologic changes in rats belonging to group 2 appeared as light pulmonary interstitial pneumonia and glycogen depleted liver. Histologic investigations conducted two months after discontinuation of the experimental vapor inhalation showed complete restoration of liver glycogen and of cell structure in the cerebrum. The lungs showed residuals of emphysema and points of resolving pneumonia.

Thus, the clearly expressed changes on the part of the central nervous system, of the peripheral blood, cholinesterase activity, arterial blood pressure, and protein-forming liver function evidenced in rats belonging to group 1, and the presence of organic changes in their internal organs incline the present author to regard the 0.05 mg/li α-methyl styrol concentration as an active one. Rats exposed to the inhalation of 0.005 mg/li of α-methyl styrol vapor manifested the above

described changes in a less gravely expressed form in only a part of the experimental rats, and in no instance did the picture of changes include all the investigated physiological systems; in addition, such changes rapidly regressed and returned to normal at the end of the experimental period. Therefore, 0.005 mg/li of α-methyl styrol vapor is regarded by the present author as the threshold concentration, while 0.001 mg/li was regarded as entirely inactive.

Results of the investigation showed that α-methyl styrol belonged to the group of poisons characterized by a wide zone of toxic effects. It has been established that in the case of substances characterized by a wide zone of toxic effects, the maximal permissible concentration could be adopted within the range of threshold concentrations. Results obtained from a comparative analysis of sanitary hygienic investigation, animal experimental studies, and of physiologic and polyclinic human observations led the present author to recommend 0.005 mg/li of α-methyl styrol vapor in the air as the maximal permissible concentration. The recommended concentration has been adopted by the official authorities and was included in the appropriate sanitary code.

Conclusions

1. Results of experimental, clinical and physiological studies had shown that α-methyl styrol had a definite effect on the central nervous and cardiovascular systems; its action on the peripheral blood produced mild polychromic anemia. Chronic exposure to the effects of α-methyl styrol may produce trophic and metabolic changes.

2. Examination of workers in contact with α-methyl styrol vapor should include arterial pressure, mucous membranes of the upper respiratory tracts, and the peripheral blood picture. The presence of some upper respiratory diseases in applicant workers should be regarded as contraindicative to their employment requiring contact with α-methyl styrol vapor.

3. Results of clinical observations conducted in the studies herein reported showed weakening of the liver function; wherever this is the case workers should be carefully examined as a prophylactic measure against any possibility of toxic hepatitis development.

4. It is recommended that 0.005 mg/li of α-methyl styrol be adopted as the maximal permissible concentration in the air of working premises.

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Hygienic Evaluation of Dust from Vanadium Containing Slag

pp. 23 - 29

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Bessemer, open hearth, and blast furnaces yield considerable quantities of slag. Slag can be defined as a chemically inert fusion mass of different metal oxides, the composition of which depends upon the composition of the original ore and on the smelting technology. Slags are frequently referred to as artificial minerals of great variety. Many slags represent conversion products which are used in additional future reprocessing. Slags of the ferrous metalurgic industry have found wide application in the preparation of many building materials and as base material in street and highway road construction. Some slags contain considerable amounts of phosphorous and are finding increasingly wider application to soil fertilizers, particularly the open hearth slags. Some Bessemer, Thomas and open hearth slags contain quantities of rare metals. This is particularly true of the Bessemer and

open hearth slags formed in processing pig iron obtained from the Ural iron ores. The latter contain titanium and vanadium. For the recovery of the rare metals the slags must be crushed and ground to a very fine powder for the complete removal of the rare metal. The crushing and grinding is usually conducted on a large scale, and it is natural that air suspended dust be generated in concentrations constituting a factor of occupational danger, such as blast furnace slag dust, or open hearth furnace slag dust, the factor of primary hygienic importance is the presence of highly dispersed free and combined silicon dioxide. On the other hand, in the case of slags, the composition of which is chemically complex, and which contain considerable quantities of highly toxic metallic oxides, free and combined silicon dioxide is not the only important factor from the hygienic viewpoint; a special and broader study of the toxic properties of the dust must be conducted, due to the presence of other toxic metallic components, without which the determination of maximal concentration limits would be incomplete and ineffective.

The literature contains reports of foreign authors dealing with the effect of Thomas slag on the human organism (Thomas slag pneumonia) due to the presence in such slag of phosphorus. Some investigators studied the pathogenic role played by individual Bessemer slag components in the development of bronchitis and pneumonia. However, all such reports lack detailed descriptions of the effect of metallic slags on the respiratory organs of the workers. Therefore, the present author conducted industrial-hygienic and experimental studies and also clinical observations to determine the mechanism of action on the organism of dust from Bessemer slag, from which vanadium is extracted in the USSR. The aim of the investigation was to find means for workers' protection against metallurgical occupational diseases.

The technology of slag processing consists first in crushing the large lumps of fused slag by means of a heavy steel block; the slag pieces thus obtained are then crushed and ground to a fine powder by means of tubular or ball-mill. The slag powder is then conveyed into rotating furnaces, where they are cinter oxidized in the presence of NaCl at 900°. At this stage the lower vanadium oxides become converted to vanadium pentoxide forming sodium salts of vanadium, which are easily water soluble and can be extracted from the powdered slag. It is easily seen that considerable dust is generated during the breaking up, crushing, grinding, loading, conveying and cintering of the raw material.

Air pollution studies were conducted in 1949, 1962. In 1961, the air dust concentrations were determined by Yu.V. Osipov. At other times, dust density determinations were made by the city sanitary epidemiological station. Results of 400 air sample analyses are presented in Table 1. Particular attention was centered on most frequently met concentrations which constituted more than 50%. The data show that dust concentrations

most frequently encountered at all production stages fluctuated within narrow limits. Processes of cold slag breaking up were not organized as a unit, but were widely scattered over the plant; this seriously hampered any attempt to institute a centralized leak-proof enclosed dust removing system.

Table 1.

Air dustiness and dust dispersion at basic operations of slag processing

Production processes	Mg/m^3 of dust			% of particles up to 5μ in diameter
	Minimal	Maximal	Occurring most frequently	
Slag crushing[1]	40,0	150,0	50—100	95—96
Loading of crushed slag	70,0	150,0	90—130	90—92
Unloading	17,0	300,0	90—100	92—92
Slag grinding	17,0	240,0	30—50	85—86
Slag milling to powder and magnetic separation	23,0	500,0	100—150	86—87
Calcining of powdered slag	6,0	75,0	20—40	95—96
Leaching	3,0	10,0	5—6	9

[1] These operations are done under one roof, other operations are done in different premises.

This was true of the crushing and grinding as well as of loading, unloading, conveyor transportation, and of cleaning the working premises. There were other factors which enhanced the danger to the workers' health, such as prolonged intimate exposure to high concentrations of highly dispersed dust. Results of chemical slag analyses are shown in Table 2.

Table 2.

Химический состав шлака (по данным анализов за 1958—1962 гг.)

Oxides	Contents in %				Remarks
	Ground charge		Calcined charge		
	Minimal	Maximal	Maximal	Minimal	
FeO	35,4	37,1	40,0	48,4	FeO converts to Fe_2O_3 during calcining
SiO_2	22,1	25,6	18,97	22,4	1 – 5% SiO_2 is found in free state, the remainder is bound
V_2O_5 (Computed as V_2O_5)	11,1	12,9	9,6	11,8	V_2O_3 converts to $NaVO_3$ after calcining
Cr_2O_3	9,0	11,3	8,50	9,52	
TiO_2	6,7	7,7	5,8	7,03	
MnO	3,7	5,8	3,07	5,08	
Al_2O_3	2,21	4,0	2,66	3,3	
MgO	0,8	1,6	0,72	1,3	
CaO	0,75	1,4	0,85	1,3	
Other component parts	1,9	3,2			Is found basically in the Fe components

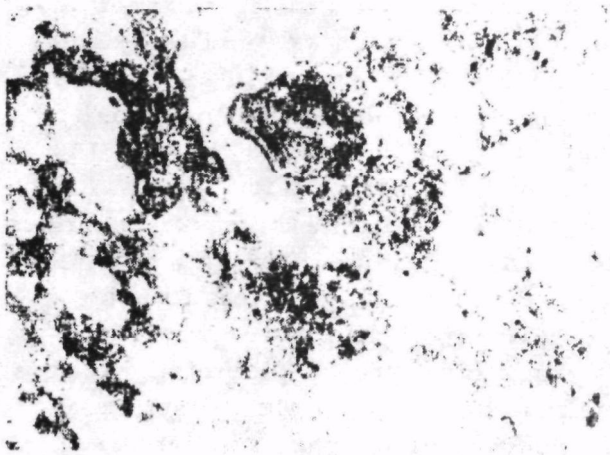
Data in the Table show that the slag dust contained oxides of vanadium, chromium, manganese, etc., all of which possessed well known toxic properties. Dust concentration in the air generally was considerable, yet, no specific symptoms characteristic of each toxic dust components had been noted in the workers probably due to the complex masking interaction between the metallic oxides. On the other hand, it should be remembered that hygienic evaluation of dust and its standardization can not be based on the toxic properties of individual elements.

Petrographic and roentgenostructural analyses of the slags made by Ya. S. Umanskii, Ya. E. Samchuk, A. Yu. Polyakov, and V. I. Kolpakova showed that vanadium was present in the slag in the form of a trivalent oxide. The slag contained approximately 67% of mineral spinel consisting of iron, chromium, and vanadium; 67% of the latter was in the form of vanadium trioxide. In addition, the spinel also contained oxides of aluminum and of manganese. No silicon was found in the mineral spinel. The iron, vanadium and chromium components were firmly embedded in the spinel which prevented the components from acting as free oxides. Silicon was present in the slag in the form of manganese, iron and calcium metasilicate; part of it was also in the form of fayalite. The total amount of silicon dioxide in the slag ranged between 15-20%, 1-5% of which was in the form of tridymite, cristobalite, plus silicon in the form of silicon dioxide. During cintering the mineral spinel oxidized to hematite and released pentavalent vanadium; the latter possessed toxicologic potentialities, which were imparted to the slag dust. Chromium and manganese, together with some other oxides, remained firmly bound and were unable to directly manifest their toxicologic effects.

Toxic slag dust effects were tested by administering intratracheally 50 mg of the dust to each of 20 white rats. At intervals of 3, 6, 12 and 15 months rats had been sacrificed and their organs studied pathohistologically. No clinical manifestations of poisonous dust effects on the experimental animals had been observed, and the experimental and control rats gained body weight steadily. Autopsies showed only subpleural slag dust accumulation. Pathologic changes in the respiratory organs appeared as serous-desquamative bronchitis, enlarged lymphatic folliculi, and thickening of the interalveolar septi as a result of round cell lymphoid and histiocyte infiltration. In addition, dust cell foci formed at the interalveolar septi and the vessels. There were also foci of epithelial cells and of coniophages with phagocytized dust. There were no giant cells and no signs of narcosis and no development of mature fibrous connective tissue. However, many of the animals developed concentrically distributed fibroblasts around the dust accumulated foci, as shown in Fig. 1. Van Gieson stained sections showed that the dust cell foci developed thickened interstitial tissue 6-15 months after the intratracheal dust administration (see Fig. 2). The dust cell foci appeared massive on the third month after the dust administration; their size appeared somewhat reduced 12-15 months after the dust administration.

It appeared as though the amount of dust in the lungs became reduced, but the hardening of the inactive tissue at the point of dust accumulation somewhat increased. All histological sections showed dust engulfing coniophages in the bronchial lumens, indicating that the dust had been systematically eliminated by the lungs. Accumulations of free and phagocytized dust was noted in the sectional lymphatic nodes.

Fig. 1.



Dust-cell nodes in interalveolar tissue with concentrically distributed fibroblasts in some small nodes. The rat was sacrificed 3 months after the dust injection. Magnif. 5 x 8

Fig. 2.

Dust-cell nodes in the lungs at points of dust accumulation — indurated connective tissue. Rat was sacrificed 11 months after dust injection. Magnif. 5 x 8

Detailed histologic investigation of pulmonary alveolar tissue frequently showed alveoli in which the epithileum regenerated in the form of glandular epithelium, probably as the result of prolonged chemical dust action. The coniophage protoplasm showed signs of fatty infiltration, a phenomenon which can be explained by the same fact as cited just above. Thus, the slag dust showed no clearly defined fibrogenic effects under experimental conditions; nevertheless, it possessed the capacity to elicit moderate development of productive changes. Pneumoconiosis developed on the basis of chronic desquamative bronchitis.

The slag dust affected the mucous membrane of the upper respiratory tract. This was shown by the fact that among 45 workers examined in the clinic hyperemia of the mucous membrane of the upper respiratory tract and hypertrophy of the nasal mucosa appeared in all the examined persons. Subatrophic rhinitis was noted in 11 workers of extensive employment records. Nasal mucous membrane erosion localized in the region of Locus kisselbachi was noted in 10 workers who had been in contact with slag dust for 10 years or longer. In some, the nasal mucous membrane appeared bloody. Some workers exposed to the effects of cintered slag dust had perforation nasal septi, others had developed extensive scar tissue. Thus, results of the

investigation showed that the toxic properties of cintered slag dust were more pronounced. Nasal septi perforations may have been caused by sodium vanadate, an assumption prompted by the occurrence of perforated nasal septi in several employees who worked with vanadium pentoxide; the perforations may have also been caused by the chromium oxide contained in the dust in low concentrations. Chronic bronchitis was found in 27 of 45 examined workers. Practically all workers with a record of 5 years employment had chronic bronchitis.

Clinical-roentgenological studies made by G. V. Bulychev, V. B. Usman, and by L. M. Markova confirmed the conclusion arrived at by the present author that the investigated slag dust could be regarded as a coniosis causative agent. Twenty-four of 45 examined employees with a work record of more than 10 years showed roentgenological changes; in 11 of the workers the changes were indicative of pneumoconiosis of I-II stage. An X-ray picture showed characteristic distribution of diffuse-sclerotic changes over the entire pulmonary lobes, and other changes characteristic of pneumoconiosis. Unlike in silicosis, no extensive damage was noted in the lower section of the lungs. Enhanced and delineated pulmonary deformation was seen in 13 examined workers with 10 years or more employment records; this observation should be regarded as indicating the possible presence of pneumoconiosis, or early manifestation of occupational pneumoconiosis. Thus, thorough observation of the workers brought out the fact that prolonged exposure to the inhalation of slag dust elicited pneumoconiosis which appeared and developed on the background of damaged mucous membrances of the upper respiratory tract complicated by the presence of chronic bronchitis. Pneumoconiosis belongs to the mixed diffuse sclerotic form of pulmonary diseases. The roentgenological manifestations of slag dust pneumoconiosis simulated in some respects the general picture found in literature dealing with silicosis, but differed from it by the presence of damage to the upper respiratory tract, not generally observed in other types of pneumoconiosis.

Additional clinical investigations have been in process which might elucidate more profoundly the characteristics of slag dust pneumonconiosis. It was shown that the changes enumerated above were well defined in persons who had been exposed to the inhalation of cintered slag dust, and it was assumed that the presence of free pentavalent vanadium was the causative agent. It was also shown that general health conditions of workers coming in contact with vanadium-containing slag dust accorded with the data obtained in experiments with animals. Results of the present general investigation clearly indicated that there was need for the determination of maximal permissible concentration of Bessemer slag dust generated in processing titano-magnetic ores from the Ural Mountains. It was noted during the investigation that the Bessemer slag dust contained low free silicon dioxide concentrations. This, and other observations and data, led the present author to conclude that the approach to the problem should be based not only on the free SiO_2 dust in the air, but that other factors should also be taken

into consideration. Measures adopted for the improvement in the production and processing technology are usually the most important factors in the prevention of dust disease. In this respect, the introduction of an integrated and leak-proof enclosed system in the slag grinding and calcining should be given primary consideration. The same applies to the conveyor system and to loading and unloading of the raw and ground materials. Fused slag should be delivered into the crushing machines in smaller chunks, so that the preliminary slag breaking up by a heavy block could be completely eliminated. All manual procedures should be replaced by automatic operations. Next in importance is the appropriate improvement in the system of local and overall ventilation.

Workers exposed to Bessemer slag dust inhalation should be mandatorily examined clinically periodically and systematically. The examining board should consist of an otolaryngologist, a therapist, a roentgenologist, and a general practitioner. Only persons found free from diseases of the respiratory tract and of the cardiovascular system should be employed in work which includes contact with vanadium containing slag dust.

Conclusions

1. It has been proven, experimentally, that Bessemer slag dust formed in processing Ural titano-magnatites chronically inhaled in concentrations of 30-100 mg/m^3 or more, may elicit pneumoconiosis. Productive changes developed only moderately and the process is a relatively benign one. Pneumoconiosis development is usually preceded by well defined changes in the mucous membrane of the respiratory tract, and by chronic bronchitis elicited by the slag dust. The coexistence of moderate roentgenological pneumoconiosis manifestations and of well defined damaged mucous membrane of the upper respiratory tract, creates a picture of variable subjective and objective systems which distinguished slag dust pneumoconiosis from other pneumoconiosis types.

2. Prevention of slag dust pneumoconiosis can be attained by a complex of special technical sanitary hygienic and therapeutic-prophylactic measures.

3. It is recommended that 4 mg/m^3 of Bessemer slag dust be adopted as its maximal concentration in the air.

Note from the Editor

It is regretted that the author failed to present data regarding the radioactivity of the investigated slag which lately had been regarded as one of the important hygienic factors.

Bibliography next page.

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A Method for the Determination of Industrial Aerosols of Antimony and of Its Compounds

pp. 50 - 54

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Existing methods for the determination of antimony proved inadequate for the study of atmospheric air pollution made by the present authors in the surroundings of an antimony industrial combine, because such methods were time consuming, cumbersome, and inaccurate for the purpose at hand. Therefore, the present authors investigated the possibility of applying diaminotriphenylmethane dyes to the determination of metallic antimony and its compounds in the air. In 1927, Eegriwe proposed that small antimony quantities should be determined by the rhodamine-B-reaction in the presence of chloride ions. V. I. Kuznetsov made a thorough study of the reaction mechanism in 1947-1949 and replaced rhodamine-B with methylviolet which was a considerable improvement in the procedure for the determination of antimony and its compounds. Further improvements in the reaction were made in 1956 by L. N. Lapin and V. O. Hein who replaced methylviolet with brilliant green, a member of the basic diaminotriphenylmethane dyes.
The pentavalent antimony ion ($SbCl_5$) turned brilliant green solution orange in the presence of strong HCl. The authors state that the chain of reaction will proceed only in the presence of HCl. After the orange color has formed, a small amount of toluol, or of its analogues, is added and thoroughly shaken; the toluol extracts the newly formed orange colored antimony complex which acquires a bluish green color. The test is highly sensitive and permits the determination of 0.05γ of the antimony. Any other type of antimony ion must be converted first to the $SbCl_5^-$ ion. The Sb complex must be converted first to $SbCl_3$, and then oxidized to $SbCl_5$ with the aid of strong HCl; in the course of this reaction the Sb combines with the brilliant green ion to form a complex which is ultimately converted to a toluol blue complex. Having made a series of check tests, the present authors recommend with confidence the following method for the determination of aerosols of antimony and its compounds:

Aspirate the air samples through cloth filter of trademark FPP-15

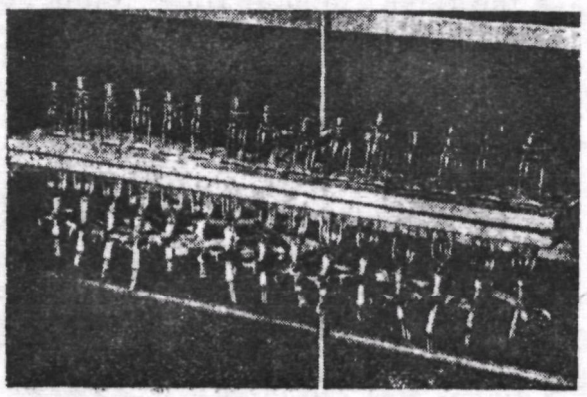
firmly held by a standard metallic filter device. Aspirate 200-400 li; and when necessary 1 m^3 of the air through the FPP-15 filter at the rate of 15-18 li/min. Weigh the filter before and after aspiration of the air, and determine the amount of trapped aerosols contained in the air by the difference in the two weights. The air volume must be adjusted to normal pressure and temperature. Then place the filter inside a 100 ml Kjeldhal flask containing 5 ml of concentrated hydrochloric acid and 10 ml of sulfuric acid. Heat the flask for about 15-20 minutes; the FPP-15 filter will turn into a small solid round lump. The double acid treatment has a dual purpose: first, the HCl prevents the cloth filter from becoming digested or charred by the sulfuric acid, and second, the sulfuric acid enhances the solution of the antimony and reduces its loss during heating. Two additional attempts were made to treat the FPP-15 filter with hot sulfuric acid without subsequent heating, and with aqua regia which completely dissolves antimony. The 3 methods produced approximately similar results.

Upon completion of the filter treatment cool the solution and transfer to a 100 ml volumetric flask; fill the flask to the 100 ml mark with a solution of 10% hydrochloric and 1% tartaric acid. Rinse the Kjeldhal flask several times with some of this solution and add the rinsings to the 100 ml volumetric flask. The FPP-15 filter residuals contain practically no antimony. Depending upon the suspected concentration of antimony, place between 1-5 ml of the solution into a 25 ml Erlenmeyer flask for final reaction. Add to the Erlenmeyer flask 5 ml of 5 N hydrochloric acid solution and 0.5 ml of 10% tin chloride solution in 5 N HCl. Leave the flask stand at room temperature for 5 minutes then shake thoroughly at 1 minute intervals. The pentavalent antimony will become reduced to trivalent; the trivalent antimony is then converted to its pentavalent ion of $SbCl_5$ by the addition of 0.5 ml of N sodium nitrite solution.

Leave the flask stand for another 5 minutes, while free brown vapor of nitrogen oxide is given off. Carry this step out under a chemical hood. Decompose excess of sodium nitrite by adding 1.5 ml of 10% urea in 5 N hydrochloric acid. In the presence of nitrite excess shake the flask for about 3-4 minutes. The reaction may be regarded as completed when formation of oxygen nitrite bubbles discontinue. Now, add 20 drops of 1% aqueous-alcoholic solution of brilliant green. Prepare the dye by dissolving 1 g of the substance in 25 ml of ethanol over a water bath. After the dye has completely dissolved make the volume up to 100 ml with distilled water. Pour the resulting orange-yellow solution into a separatory funnel to which add 10 ml of toluol and shake for 2-3 minutes. If the solution becomes colorless, add more of the dye since it is essential that the dye be present in the final product in an excess as shown by the persistence of the yellowish-orange color in the solution. The separation can also be accomplished in test tubes.

Where several such determinations are made simultaneously, the

separatory funnels can be suspended in a special rack as shown in the accompanying figure. Complete separation into layers of toluol and water usually requires 3-5 minutes. Remove the water phase and pour the bluish-green toluol into test tubes containing a small quantity of disodium phosphate, for the complete removal of any residual water. Make colorimetric determinations using photoelectriccolorimeter of trademark FEK-M, and colorimetric cups containing 5 ml of the solution and using a blue light filter. One liter of the standard solution should contain 0.2743 g of chemically pure potassium tartrate and 5 g of tartaric acid dissolved in 10% HCl solution. One ml of this standard solution should contain 100 γ of antimony. A graduated standard curve can be constructed by using 1 ml of this standard solution according to the generally adopted procedure. Place the colored toluol into a series of test tubes in the following quantities: 0.2, 0.5, 1.0, 1.5, 2.0, and 2.5 ml. Add chemically pure toluol to make 10 ml in each tube and make final colorimetric determinations. The colorimetric scale should be equivalent to 2.0, 5.0, 10.0, 15.0, 20.0, 25.0 μ of antimony. It should be pointed out that in making colorimetric determinations of high antimony concentrations, there may be a negative deviation from the Lambert-Beer law. Where the antimony concentration is expected to be high appropriate dilutions of the original solution should be made first. Sensitivity of the recommended method is 9.5 μ in 1 ml of the solution.



A holder with an assembly of separatory funnels ready for analyses

The method described had been tested first under laboratory conditions, then under mining engineering conditions at the antimony combine. Series of check tests have been appropriately made. Results of determinations made under above described conditions using cloth filter FPP-15 are presented in Table 1. Check tests were made under industrial conditions using triple layer of filter FPP-15. Final determinations were made with each of the filter layers individually for the purpose of determining traces of possible slip-through. Results are shown in Table 2. Differences in the results of duplicate check tests ranged between 10-15%. The method is specific. Arsenic did not interfere with the determination of antimony. Gold, gallium and iron yielded similar reaction. However, these metals can be removed by the addition of urea used to remove excess of sodium nitrite. As shown above, the method is highly sensitive, specific, and accurate. Therefore, it is recommended for use by industrial sanitarians during their air purity control examinations, especially in the air of plants engaged in the production or processing of antimony or its compounds. Laboratories which have no electrocolorimeters use a series of standard color tubes prepared as previously described.

Table 1.

Sb determinations on cloth filter FPP-15

Test No.	Mg of Sb deposited on filter	Sb found	
		Mg	%
1	7,9	8,1	102,5
2	16,0	16,0	100,0
3	16,0	14,0	88,0
4	16,0	15,0	93,8
5	16,0	14,7	92,0
6	16,0	14,2	88,8
7	12,5	12,0	96,0
8	19,4	18,9	97,4
9	14,2	14,2	100,0
10	15,4	15,2	98,7
	% of average accuracy		95,7±2,1

Table 2.

Results of Sb determination on FPP-15 cloth filters after aspirating 100 l of air at 15 l/min.

Test No.	Substance	Mg found		
		1st cloth layer	2d cloth layer	3d cloth layer
1	Metallic Sb	3.0	—	—
2	" "	9.6	Trace	—
3	" "	14.2	—	—
4	" "	12.8	—	—
5	Antimony trioxide	17.0	Trace	Trace
6	" "	11.1	—	»
7	Antimony pentoxide	18.0	Trace	»
8	" "	14,9	—	»

Conclusions

1. A method is proposed for the determination of aerosol antimony and its compounds in the air using a basic dye of the diaminotriphenylmethane series.

2. Filter fabric FPP-15 retained 99.9% of the antimony and its compounds contained in the aspirated air sample.

3. The method is precise, simple, comparatively rapid, and can be used in making industrial sanitary determinations in the air of various premises by plant laboratories.

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Methods for Lowering Solvent Concentrations in the Air of Plants Engaged in Dry Cleaning Clothes

pp. 71 - 73

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Dry cleaning of every day and working clothes is being used more and more extensively. The present authors investigated the sanitary hygienic conditions prevailing in 5 Moscow dry cleaning plants which used different types of equipment. The technological procedure used in dry cleaning clothes is generally as follows: (a) preliminary removal of unusually dirty spots; (b) first step of dry cleaning with trichlorethylene or with perchlorethylene in special wash drums, (c) when necessary second removal of persistent dirty spots, (d) ironing. An examination of the room in which the preliminary spot removal was done showed complete lack of standard equipment. Preliminary spot removal and cleaning was done by spreading the clothes over the usual type of ironing table; special tables for spot removing were seen in only one of the 5 examined plants. For the removal of specially dirty spots, the following organic solvents were used: acetone, gasoline, benzene, trichlorethylene, white spirits (a turpentine substitute). Spots are removed as follows: the suitable spot removing chemical is applied to the spot manually with a saturated cotton wad or saturated gauze. The spot is rubbed until it disappears. This is repeated using a clean solvent saturated cotton or gauze wad. This procedure of special spot removing was practiced in all the 5 plants heavily polluting the air of the working premises at the level of workers breathing solvent vapors. Direct contact between the solvent and the skin is frequent under the above described conditions. Trichlorethylene vapor permeates the air of other departments at the time clothes are delivered from one department to another. Results of air analyses made in all the plant's operating rooms verified this.

Ventilation in some spot removing departments consisted of the usual mechanical systems which exchanged the air 4-20 times. An exhaust fan usually installed close to the ceiling enhanced the ventilation of the work rooms. Air analysis made in such rooms found an average trichlorethylene concentration of 0.04 mg/li and higher, which is considerably above the adopted sanitary hygienic maximum. Thus, working conditions in the spot removing rooms of the dry cleaning plants were highly unfavorable from the sanitary hygienic viewpoint, due to the lack of efficient solvent vapor removing installations. Vapor concentrations in the air of such rooms can be lowered to the prescribed official level by installing ventilation equipment which would increase the air exchange rate. It is suggested that manual spot removing as above described be discontinued and that sponge-stopper flasks be used instead of saturated cotton or gauze wads. In addition to remodeling the general ventila-

tion system, local vapor exhaust devices should be installed close to workers engaged in spot removal as above described. Similar local vapor exhaust devices should be installed in other sanitarily strategic sections of dry cleaning plants.

The final step of clothes dry cleaning is done in tightly closed revolving drums containing trichlorethylene or perchlorethylene. The operator manually loads the revolving drum with 15-16 kg of clothes, tightly closes the drum and runs in the required amount of solvent through a specially connected inflow pet cock. Each drum is connected via a closed communication system with a distilling apparatus usually installed inside the operating room, and with a solvent supply tank installed outside the operating room, from which the required amount of solvent is run into the cleaning drum once a month. In the course of this month, the solvent circulates via the above mentioned closed solvent distilling system.

The worker who operates the clothes cleaning drum is stationed at the control panel and observes the dry cleaning process through an inspection window. A dry cleaning procedure may last 20-90 minutes depending upon the type of equipment used. The operator generally loads and unloads the rotating dry cleaning drum 3 to 10 times per working shift. In the case of drums SN-60 "Trilux" and "Spesima" the dry cleaned clothes are also dried before being released. The two mentioned machines are equipped with exhaust ventilation devices which begin to operate automatically as the drum is opened for unloading, and also when air is run into the drum during the clothes drying operation. Under such operation conditions the clothes come out from the dry cleaning drum free of solvent and have only a barely perceptible odor of trichlorethylene. In the case of USA dry cleaning machines the clothes drying and deodorizing is done in separate installations, and the operator unloads the solvent saturated clothes, loading them into the revolving drying drum manually. Air analysis made by different methods indicated that trichlorethylene and perchlorethylene concentrations in the air during unloading of clothes from the different types of drying cleaning revolving drums exceeded the maximal permissible limits; vapor concentrations amounted to 0.15 mg/li in the air surrounding Czechoslovakia built machines, 0.08 mg/li in the air surrounding German built machines and 0.81 mg/li in the air surrounding American built machines. The above data represent averages of 98 air sample analyses. The sanitary hygienic conditions of air in dry cleaning plants equipped with American machines was sanitarily the most unfavorable, due to the fact that the drum had to be unloaded 10 times during a single work shift, resulting in the increase of trichlorethylene or perchlorethylene vapor concentration in the air.

Analyses made of air samples collected at dry cleaning plants which used different equipment, and operated under different technological conditions had been compared, that is effects of different drying and airing periods had been compared. Results indicated that 30 minutes of clothes drying

followed by 4 minute aeration created a trichlorethylene vapor concentration in the air at the time of unloading which was 100% above the trichlorethylene vapor concentration resulting from a procedure of 40 minutes drying and 10 minutes aeration. Unorganized trichlorethylene air pollution was a contributing air pollution factor.

The general air exchange ventilation system in the working premises under consideration ranged between 6 and 22 times per hour as compared with the 13.5 times per hour originally planned. Exhaust fans operated at the upper and lower air levels with the final outlet close to the ceiling. On many occasions the air exchange rate was greater than the officially specified rate, yet results of air analysis indicated that frequently the solvent vapor concentrations exceeded the prescribed maximal level. This suggested that in some of the plants considerable leakage from vapor of the organic solvents came from the equipment, conduits, solvent pipes and from dry cleaned clothes. The amount of solvent vapor (trichlorethylene and perchlorethylene) released into the air of working premises was estimated at 737 - 931 g/hr as compared with the originally planned 80-100 g/hr. The removal of such a large solvent vapor volume from the air of working premises could be accomplished only with an air exchange rate of 284-233 times per hour, unattainable under practical conditions and for technical reasons, and also inadvisable for hygienic considerations.

Conclusions

1. Indoor air pollution with organic solvent vapors in dry cleaning plants constituted a hazard to the health of the workers.

2. The following air pollution sources were found in dry cleaning plants: open manual method of applying solvents in the spot removing department; non-observance of safety regulations, primitive and manual technological procedures in loading and unloading the rotating cleaning drums, unorganized leakage, etc.

3. The method used in unloading dry cleaned clothes from the solvent containing drums constituted a particularly hygienically unfavorable condition. Comparative evaluation of equipment and machines used showed that highest solvent vapor air pollution was noted in dry cleaning plants equipped with USA machines. Therefore, it is recommended that the use of American machines be discontinued.

4. Prevention of air pollution with solvent vapors in dry cleaning plants can be attained by the following means: (a) strict adherence to most advanced technological defatting processes; (b) elimination of all leakage sources, especially in the pipes and conduits; (c) installation of a properly planned up-to-date overall ventilation system supplemented by the installation of local exhaust devices at points of workers' exposure to the inhalation

of the solvent vapor polluted air.

5. The present practice of manual spot removing from clothes in the open should be unconditionally prohibited, appropriate local exhaust ventilation devices be installed; the rate of fresh air inflow should be increased.

6. Employees of dry cleaning establishments should be examined periodically by industrial medical personnel, and persons unfit for such occupation should be replaced.

Sanitization of Working Conditions in Chemical and Pharmaceutical Plants which use Mercury as a Catalyzer

pp. 73 - 76

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Metallic mercury and its salts have been recently used as catalyzers in the chemical and chemo-pharmaceutical industries. During the past decade the chemical and chemo-pharmaceutical industries, especially of the organosynthetic type, have been rapidly developing in the USSR. The tempo of such development will continue to progress, and with it will increase the use of metallic mercury and its compounds as catalyzers.

The present author investigated the effect of mercury and its compounds as catalyzers on working conditions in the above mentioned manufacturing industries. This particular phase of labor hygiene and sanitation has not been studied adequately. The aim of the present study was to determine the effect of mercury used as a catalyzer on the air of working premises, its absorption by wall, ceiling and equipment surfaces, and to develop measures for the sanitary improvement of labor conditions in the above mentioned industries.

Mercury was determined in the air, dust, and scraping samples by the Polezhaev colorimetric method. Hygienic investigations were conducted at the "Akriquin" chemo-pharmaceutical plants producing promedol, in which the hydration process proceeded in the presence of mercury as the catalyzer. A survey of sanitary working conditions prevailing in the production of promedol showed that mercury was one of the basic toxic substances which polluted the air of the working premises in which successive technological chemical steps were accomplished. Mercury concentration in the indoor air exceeded its maximal limit by 300-700%. Analytical results showed that mercury vapor was present not only in the air of the hydration room,

where yellow oxide of mercury was used as the catalyzer, but also in other seemingly isolated work rooms in which other types of production steps have been carried out, such as cyclization and piperitone vacuum distillation. No mercury vapor was found in any of the work rooms in which chemical synthesis was completed.

Mercury vapor was present in the air of the hydration room due to imperfect hydration in which manual procedures were used in introducing the mercury catalyzer and in other reaction phases, such as removing mercury from the accumulation wells, etc. For this reason the hydration room was equipped with a separate entrance which isolated it to a degree. In the opinion of the present writer, the emulsified mercury salts accumulated in the reaction mass, and which were partially reduced to the metallic state, and constituting the source of air pollution in the cyclization and vacuum distillation rooms, which were separated from the hydration room and from each other. Following the completion of the hydration process, the emulsified mercury salts failed to precipitate completely from the reaction mass.

Observation of the residue formed in distilling off methanol from the ketone mixture disclosed the presence of metallic mercury, indicating that mercury was carried over by the reaction mass and by the incomplete products of the nonprecipitated salts into the following technological stages. Thus, in the residues remaining after piperitone extraction and vacuum distillation, metallic mercury was noted periodically. This indicated that emulsified mercury salts present in the reaction mass became partially reduced to metallic mercury which was carried over into the succeeding technological stages; aided by the ketone and solvent vapors contained in the reaction mass, the carried over mercury permeated through the apparatus doors and the flange couplings polluting the air of the working premises. Mercury compounds, or metallic mercury, could also be carried over by the vapors of organic solvents used in processing the intermediary products containing mercury or mercury compounds. Mercury slurry and distillation residue are collected in asphalt coated metallic drums and are disposed of in the plant's dump.

Results of laboratory ambient air studies proved of particular interest from the hygienic viewpoint. Data of such a study are presented in Table 1 which show that mercury vapor concentrations in the air of the hydration, cyclization, and vacuum distillation rooms exceeded the maximal permissible concentration even hours after the reaction and distillations had been discontinued, and the apparatus, equipment, and rooms had been thoroughly cleaned. Mercury vapor concentrations were higher in the air of the cyclization and vacuum distillation than in the hydration room, which may have been due to the fact that no measures for the abatement of air pollution with mercury have been used in this room, because mercury carry over by the reaction had not been suspected. Thus, it must be assumed that pollution

of indoor air with mercury vapor occurred during the nonoperational period as a result of mercury desorption and evaporation from the building structural parts and from the equipment and installation surfaces which became polluted with mercury during the operation of the production processes.

Table 1.

Mercury vapor concentration in the air of production rooms of the promedol department 6 – 8 months after discontinuation of the process

Points of air sample collection	No. of samples	mg/m^3 of mercury vapor			Surrounding conditions
		Minimal	Maximal	Average	
Hydration room	5	0,0075	0,028	0,014	Exhaust ventilation operating
Cyclization room	7	0,012	0,03	0,022	
Vacuum distillation room	6	0,009	0,066	0,026	
Other rooms	6	None found			In the center of rooms at workers' breathing level

Data presented in Table 2 show the degree to which the walls, ceiling, and equipment and installation sufaces were polluted with mercury.

Table 2.

Mercury polluted walls, ceiling, apparatus and equipment surfaces after processing was stopped

Point of dust sample collection	No. of samples	Mg of Hg in 100 g of sample material				Conditions under which polluted material was collected and character of collected samples
		Minimal	Maximal	Average		
Hydration room	10	1,3	219	46,5		Two weeks after work was stopped. Oil painted and plastered walls 0.5, 1.5, and 3 m above the floor, white-washed and plastered ceiling sections. Oil painted apparatus covers.
Cyclization room	9	1,5	15	7,4	6 months after discontinuing operation	Oil painted walls at 1.5 m level; white-wash and plaster of walls at 2.0 and 2.5 m level; ceiling plaster and oil paint; oil paint from apparatus and equipment covers.
Vacuum distillation room	6	7,2	24 2	14,4		Walls: white-wash at 1.5, 3 and 4 m levels; oil paint from walls at 1 m level; also ceiling white-wash.
Other rooms	5	None found				White-wash from walls and ceiling

It should be noted that mercury was found not only on the external coating surfaces, but penetrated through the entire depth of the plastering, as shown by the fact that 100 g of the wall plastering contained 1.3-5.1 mg of mercury.

At the same height from the floor, more mercury was found on the surface of white washed than on the surface of oil painted walls. The following sanitization measures were recommended by the present author and have been adopted and executed by the plant managers:

1. Surfaces of walls, ceiling and equipment are to be cleaned and coated by a mercury nonpermeable paint.

2. The exhaust ventilation and fresh air intake systems are to be rebuilt in accordance with the latest principles of air ventilation for production premises. All work rooms in which mercury or mercury compounds were used should be equipped with individual local exhaust and fresh air intake ventilation systems. Where required, the ventilation system should be equipped with air conditioning apparatuses during the summer months.

3. Such apparatuses were placed in rooms where the production reaction masses contained mercury.

4. Demercurization systems were installed throughout the plant.

5. Based on the findings presented in this paper, official regulations, applicable to the production of promedol, have been revised, and new regulations and technological instructions have been issued. Final sanitary inspection of the plant showed marked improvement in the sanitary condition of the air in the plant's different processing rooms. It was also recommended, as a final thought, that special filters be installed for the trapping of mercury vapor discharged by the plant into the air.

Conclusions

1. Mercury vapor was found in the air of production rooms of the chemo-pharmaceutical industry producing synthetic drugs, and of the chemical industry producing technical organic synthetic substances.

2. The presence of mercury vapor was not limited to the air of work rooms in which metallic mercury or its compounds have been used as catalyzers, but also in the air of rooms assigned to the processing successive production phases, as a carry-over by the reaction mass, or by the intermediary half-products. In making sanitary evaluations of such plants this fact should be taken into consideration; it should also play an important part in making sanitary inspections of industrial production plants in which mercury and its compounds are used as catalyzers.

3. Mercury desorption from walls, ceiling, surfaces of equipment, etc. should be regarded as a significant factor in air contamination with mercury vapor in processing rooms of such production industries. Coating all surfaces, including those of equipment, with a mercury vapor nonpermeab

varnish or paint will markedly reduce the amount of adsorbed and permeated mercury vapor, the concentrations of which will be still further reduced by the introduction of demercurization of the working premises.

4. In planning new, or reconstructing and renovating previously existing industrial premises of the type under consideration, the location of technological processes should be arranged so as to reduce to a minimum air pollution with mercury vapor. Manual operations should be automated.

5. All production processes which used mercuric compounds as catalyzers, and all associated production states, must be evaluated from the sanitary hygienic viewpoint as industries which employ mercury and which must comply with corresponding sanitary specifications.

Biogeochemical Problems in Radiation Hygiene

pp. 81 - 86

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The level of radioactivity has been constantly rising in the environment due to the dispersion of nuclear explosion products and atomic industry waste products. This raises the need for the determination of possible consequences to future generations if the rise in atmospheric radioactivity should continue. It becomes necessary to ascertain the nature of somatic changes which such a rise in atmospheric radioactivity level may elicit in man of the present generation. Scientists differ in their opinions regarding the active microdose of ionized radiation on the organism. E. S. London in 1920, Yu. V. Sivintsev in 1950 and other investigators expressed the opinion that a natural radioactivity level is essential to the normal development of the animal organism, in support of which they point to the part played by radioactive substances in protein synthesis, carbohydrate metabolism, and in the processes of growth and proliferation. Opposed to that is a group of other scientists, predominately geneticists, who believe that any dose of ionized radiation was harmful. Results of experiments with animals exposed to known ionized radiation levels under experimental conditions should not be used as a basis for the correct evaluation of future consequences, nor should they be used as a basis for the interpretation of possible results on humans. The number of observations thus far made on human beings in radioactive polluted regions is too small and of too short duration

to be used as bases for the determination of a safe radioactive microdose, and for the determination of future consequences.

A possible means for the solution of this problem is presented by organized observations in regions of abnormal natural radioactive backgrounds, where man had been subjected to the effects of high level radiation for many generations, and where, as a result, definite somatic and genetic changes have accumulated. In this connection, V. I. Vernadskii initiated a science known as biogeochemistry, an original branch of geochemistry and biology which analyzes the role played by organisms in the migration of chemical elements in the external milieu, and of the effects which such elements had on the adoptive chemical or morphological changes in plants, animals and humans. In the words of V. I. Vernadskii, organisms did not exist outside the sphere of the earth's crust effects. It is possible to delineate territories over the earth's surface characterized by high or low content of natural radioactive substances. A. P. Vinogradov designated as "biogeochemical provinces" regions characterized by a high or inadequate content of naturally radioactive substances, or by other chemical elements which brought about reactions in the organism by their excess, or inadequacy. It is possible to speak of uranium, thorium, radon biogeochemical provinces, depending upon the element present in the province in quantities sufficient to produce biologic effects. However, the question of radioactive background effect on the health of a population must be examined more profoundly and not on the limited regional basis of known biological effects, since the latter may frequently be of an occult nonspecific character. Thus, the hygienic problem regarding the remote consequences of radioactivity and the problem of maximal permissible radioactive element concentrations in the external environment become intimately bound to the problem of biogeochemical provinces.

It has been known that γ radiation emanating from soils into the external environment, water radioactivity and radioactivity emanating from other substances into the external medium in some territories was 5-10 times in excess of the usual radiation emanation, and in some instances exceeded the maximal permissible radiation level. Studies devoted to the determination of uranium and radium contents in natural waters of some regions indicated that the concentration of such elements fluctuated widely depending upon the regional geologic characteristic of the locality, and also depending upon the general geoclimatic characteristics of the region. States of Travankur-kochin and Kerala on the eastern and western shores of India can serve as classical examples of extensive provinces, the territory of which is richly covered with placer deposits of monazite sand; the monazite contained 5-11% of thorium and 0.2-0.46% of uranium oxide and peroxide. Natural radioactive substances such as uranium, radium, thorium and others belong to the class of rare metals and organic formations. The natural radioactive effects under which the native population had lived for many centuries, and the short duration effect of the natural radioactivity on persons of relatively brief residence and persons coming from regions of biogeochem-

ical provinces having a high radioactivity background offer the possibility of establishing conditions and degrees of adaptation to a given level of radioactive background.

Of particular interest are biogeochemical provinces in which the content of uranium in sources of drinking water exceeded 5×10^{-5} g/li, and in the soil exceeded 1×10^{-3}%, and where the radium content in drinking water exceeded 5×10^{-11} g/li. The average γ radiation background of the central Soviet Union strip amounted to 8-15 m curie/hr. The level of the general atmospheric γ background in territories of radioactive biogeochemical provinces is 3-4 times greater, and in some regions reaches the level of 50-70 m curie/hr, and even higher. If the uranium content in sources of water supply of the Soviet Union black soil region is estimated as $n \times 10^{-6}$ g/li, and its contents in the soil at $n \times 10^{-5}$%, then it becomes clear that persons residing in the territories of radioactive biogeochemical provinces are continuously exposed, generation after generation, to the effects of radiation levels the dose of which per critical organ is several times, and in some instances 10 times, in excess of the usual level. The reason for this is in the following: as the uranium level of the environment rises, the content of other elements, which are offshoots of uranium radioactivity, also rises. That is, the content of radon and its decomposition products rises in the indoor air. Simultaneously, the soil γ emanation along with that of natural rocks and construction materials also rises. Therefore, under conditions of radioactive biogeochemical provinces, determination of uranium is not the only factor of importance, but also the determination of polonium, radium, radon, and other elements of the uranium-radon family. All these elements in their totality determined the radioactive radiation dose to which the organism was exposed under existing conditions.

The science of biogeochemistry rests on the concept of trace element migration in the system "water-soil-vegetables-animal organism-man". This constitutes a unique system in which the significance of any individual component can be understood only in connection with the other links of the migration chain. This system has now been generally accepted in radiation hygiene. In making recommendations for studies of an external environment, USSR hygienists emphasize the necessity of investigating all biosphere elements and a determination of the nutritional migration chains of radioactive substances from the environment into the human organism.

The special branch of ecology, known as geochemical ecology, represents the development of biochemistry which attempts to elucidate the interrelation between organisms and geochemical environment under different biogeochemical conditions, as was indicated by V. V. Koval'skii in 1958 and 1962. It has been established that organisms, including microorganisms, were capable of adaptating to different trace elements existing in the environment, such as a fall or rise in the concentration of cobalt, iodine, copper, molybdenum, boron, nickel, strontium, and lead. Such changes are usual-

ly accompanied by specific changes in the metabolic role played by any specific geochemical factor, as for instance, the effect of cobalt on the synthesis of vitamin B_{12}, or the effect of molybdenum on the synthesis of xanthine oxidase, etc. Geochemical ecology acquires practical significance in its application in radiation hygiene. It shows that the explanation of radiochemical connection between the radioactive environment and man presupposes the determination of the radioactive substances distribution in the organs and tissues under conditions prevailing in different biochemical provinces. Such an explanation will lead to the determination of interconnection between natural radioactive elements and such stable elements as strontium, calcium, cobalt and iron. The contents of such elements in the external environment and in the organism are interrelated. It is essential that a study be made of functional changes in those organs and systems, tissues and cellular organella such as nuclei, mitochondria, which concentrate the given element within themselves. It becomes necessary to determine with the aid of metabolic experiments the individual balance of the natural radioactive substances in different groups of residents living under conditions of high and low radiation.

Up to the present, effects on the organism of isolated external environmental factors had been explained, or studied, by classical hygienic methods, such as clinical and sanitary statistical studies, physiological experiments, etc. With the development of the concept discussed above, new methods developed by geochemical ecologists have been added to the old classical procedures. Investigations by methods of geochemical ecology include fine analyses of radioactive substances distribution in different sections of the same tissue and in individual biological entities, such as enzymes, hormones, vitamins, etc. Such investigational procedures result in the accumulation of materials on the basis of which it becomes possible to evaluate the physiological characteristics inherent in radioactive elements and their elimination from the organism in combination with stable elements. For instance, the present authors have been able to show that uranium accumulated more in the erythrocytes than in the leucocytes, and that its specific concentration in bile was greater than in urine. In this way, different branches of science using existing procedures and methods, and approaching a problem from different angles, reached a solution for the same leading problem.

At the same time, it must be realized that the radioactive background of any biogeochemical province was complex consisting of many components. The background determined by natural radioactive elements such as uranium, thorium, and calcium can be augmented by atmospheric fallout activity and by products of nuclear tests and of the atomic industry disseminated over the earth's surface. Effect of man on the redistribution of radioactive substances in nature is of considerable interest from the viewpoint of overall effect of the artificially changed environmental radioactive medium on the human organism.

V. I. Vernadskii calls man-changed biosphere "noosphere". Changes effected by industry in the earth's natural radioactive background present an example of man's influence on the earth's evolution. Under such conditions, new regions arise which can be regarded as artificial radioactive biogeochemical provinces. These come into being by man bringing to the surface natural radioactive minerals and organic compounds which are gradually decomposed through geochemical oxidation and other weathering factors and become converted into mobile substances. Such regions may develop in the proximity of radioactive element sources, such as mines, resulting in the accumulation of radioactive waste products. Radioactive element dissemination from points of waste product accumulation results from the presence of geochemical factors and of living organisms. The participation of living organisms in the redistribution of radioactive waste products is closely connected with the formation of the previously mentioned nutrition chains, which differ specifically in the soil, fresh water, or in the seas.

Geochemists in association with hygienists must first concretely investigate the forms of chemical compounds which make up the naturally radioactive substances present in individual objects of the environment; they obtain a clear picture of their mobility and the part they played in geochemical processes. For example, the different migration of compounds belonging to humic substances with the mineral soil layers has now been well established; it is known that organic acids eliminated by plants' root systems played an important part in the migration of chemical elements. Organic acids eliminated by plants' root systems combined with trace elements present in the soil to form complex compounds, the character of which depended upon the ratio existing between the acids and the trace elements. The degree of trace element assimilation by the plants depended upon such ratios. For this reason, the rate of radioactive element migration from the soil into plants differed with the character of the metal-organic complex which acted as the recipient of the radioactive element. Uranium formed firm complex compounds with organic substances in the soil, and, as a consequence, may accumulate in the soil in high concentrations in the course of time.

Distribution of radioactive elements over territories of non-natural biogeochemical provinces usually resulted from changes introduced by geological explorations, mining, and radio chemical industries. Radiation hygiene is basically concerned with such artificially created radioactive elements distribution. Basically, such artificial distribution of radiochemical elements follows the laws discovered by biogeochemists, although in individual cases there may be characteristics specific to local environmental conditions. Best results can be obtained by investigating the problem of biogeochemical provinces through cooperative studies of hygienists and biogeochemists. Radiation hygienists delineate territories of artificial biogeochemical provinces which resulted from environment pollution by radioactive by-products. Chemical reagents and technological impurity admixtures, together with changes in the aggregate state of the by-products can and do

affect the migration conditions in the external environment. The study of natural and artificial radioactive biogeochemical provinces must bring into light the following data on which to base rational conclusions and practical recommendations: (1) information on the concrete content of individual radioactive elements in the entire factor complex in the external environment of the investigated territory; (2) specific biological effects elicited by enhanced radioactive background in microorganisms, plants, animals, and man; (3) the specific fodder and nutrition changes under actual environmental conditions; (4) information relative to the internal distribution and accumulation of natural radioactive substances in the organs, tissues and cellular organella; (5) computed doses of internal radiation used in connection with metabolic experiments, as shown by survival and postmortem radioactivity analyses of the experimental animals' internal organs; computed doses of internal α-radiators concentrated in topographically delineated differential tissue and cell sections, such as nuclei, mitochondria, chloroplasts, etc.; (6) medical examination and statistically processed mortality data, birth and morbidity rates, anthropometric measurements, and results of special physiological and immunological tests. Field studies of biogeochemical provinces must make extensive use of topographical maps on 1:100,000 or 1:500,000 scale, as well as geological, soil, hydrological, geobotanical, and other large scale local maps, outlines, or plans. The investigation should also include detailed descriptions of landscape differences between the investigated and the control regions, differences in their water regimes, in types of industries, and in the population's living conditions. The investigators should outline courses for province investigations, which should, by necessity, include most typical regions. Soil samples should be collected by the pocket-profile method within the confines of the micro- and mezzo- relief of the locality, in pasture lands, in arable lands, and in hay growing fields. Soil samples should be collected from special drilled wells and soil dugouts. More detailed investigations should be conducted at points of highest exposed radioactive element concentrations. Plant and vegetation samples should be collected at known typical sections, with particular reference to morphological variability, appearance of deformed specimens and endemic species, time and character of development according to vegetation stages. A connection should be established between the radioactivity in the external environment and specific changes in the plants' metabolic processes resulting from adaptation to the new environment, or produced by pathological reactions. Reaction to geochemical factors is usually less clearly expressed in man than in animals, because social conditions lessen the effect of geochemical factors on the living process. For this reason, the direct effect of radiation on humans can be noticed more easily among the rural population, which depended predominantly on their own agricultural food products. The organism's adaptation to different radiation conditions should be studied on a comparative basis.

Data found in the literature on boron, cobalt, and copper in biogeochemical provinces may be of aid in solving individual specific questions related to the organization of hygienic studies in a radiation region. In studying

the effect of radiation backgrounds on the population's health, attention should be centered on the human organism; this has not been done in the usual biogeochemical investigations. Lately, biogeochemists accumulated some experience from studies of element concentrations in different tissues in the course of a life circle. It has been known for some time that a specific hair protein easily bound and concentrated different trace elements. Life studies can also be made with teeth obtained from stomatological and surgical clinics, as well as with urine and feces. Such studies might present data on the accumulation of radioactive substances inside organs and tissues of men and would make possible a correlative evaluation between radioactivity of external environment and similar data obtained in the study of man's internal radiation. In this connection, information supplied by section studies of radioactive organs might prove of considerable value. Investigations conducted in provinces of thorium, radium, and uranium must include determinations of radioactivity in the bones and parenchymal organs; similar determinations should be centered on the blood and expired air in radon provinces.

Studies of biogeochemical provinces must aim at the development of complete series of practical measures for the sanitary protection of nature, specifically rivers, lakes and seas with particular reference to fishing, to the utilization of algae, seaweeds, and other fresh water and sea water organisms. Such complex protective means must be based on the principle of prophylaxis with regard to the effect of high ionized radiation doses on the general population; it must include not only industries engaged in mining radioactive minerals but coal, nonferrous and rare metals, fuel materials, and construction materials, because such substances are frequently associated with radioactive minerals and other substances. The possibility of local rise in external environmental γ radiation, an increase in the concentrations of radon in the atmospheric and indoor air must be taken into consideration in planning and constructing residential areas and in planning water supply systems in localities where the water radon concentration amounted to hundreds of emans. The radon factor played an important role in occupational therapy not only of miners engaged in the recovery of radioactive minerals, but also in miners employed in the ordinary mines. Radon can accumulate in the air in concentrations exceeding the permissible maximum in poorly ventilated mines not connected with the radioactive elements. Radon enhanced the development of silicosis in miners. The amount of radioactive substances entering the organism can be reduced considerably by boiling, technological treatment during grain milling, bread baking, meat packing, dairy products processing, etc. Through the selection of special technical cultures, medicaments or edible vegetables and plants, it may be possible to arrive at a crop rotation and agricultural field working system under which the high content of naturally radiated substances contained in the soil and in irrigation water would be retained to a lesser degree by the human or animal organism.

Radioactive elements present in mining and industrial products frequently transported over long distances contaminated territories which had no detectable natural connection with geochemical provinces. In this way new migration paths come into being which hygienists must place under control. The biogeochemical concept of "noosphere" viewed from a biogeochemical angle makes possible to investigate the role played by man and industrial progress in the rise of new foci and zones of enhanced radioactivity, and of their effect on the organism. Therefore, a study of biogeochemical behavior or radioactive substances under "noosphere" conditions should be regarded regarded as a most important problem in radiation hygiene.

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The Problem of Sanitary Protection of Atmospheric Air in the USA

pp. 87 - 96

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Early in 1963 Soviet specialists in the field of sanitary protection of atmospheric air visited the USA in accordance with cultural and scientific exchange agreements between the USSR and the USA. USA specialists in different phases of air pollution visited the USSR in September-October of 1962. The visit of the USSR group was in the spirit of reciprocal courtesy. The visiting group included Professor D.N. Kalyuzhnyi, Director of the Ukrainian Institute of Community Hygiene, Candidate of Medical Sciences, O. P. Shalamberidze, Deputy Director of the Research Department of the Sanitary Hygienic Research Institute of the Georgian SSR Ministry of Health, and the authors of the present report. During the 30 days the group spent in the USA they visited 10 cities, which presented them with the opportunity to

become acquainted with activities of more than 30 scientific research centers, laboratories, universities, departments and bureaus engaged in the study of problems in the field of air pollution.

Making laws regulating the sanitary protection of atmospheric air in the USA is not a function of the Federal government. Such a function is within the immediate jurisdiction of each state. Planned and directed work in the field of atmospheric air protection began in 1955, after the U.S. Congress became aware of the need to investigate and study the causes of atmospheric air pollution, to offer assistance to the industry in work on this problem and in training pertinent technical and scientific personnel. A special study was made in 1955, the results of which indicated that atmospheric air pollution was found in 9500 populated localities in the USA. The same year the Federal Government appropriated five million dollars for the purpose of investigating the extent of the atmospheric air pollution problem, a P.H.S. Division for the study of air pollution was organized at the Robert A. Taft Engineering Center in Cincinnati, Ohio. Work in atmospheric air protection against pollution was conducted in 15 of the 50 USA states; these states had adopted legal codes for the protection of atmospheric air. Laws for the protection of atmospheric air have also been adopted independently by some individual municipalities.

Law-making in the USA can be divided into two basic categories: a) punitive laws, designed to eliminate atmospheric air pollution by way of penalizing those guilty of discharging polluting substances into the atmospheric air; and b) regulatory laws, the purpose of which is to lessen the intensity of atmospheric air pollution by precluding the discharge of pollutants into the atmospheric air. State laws, as a rule, assign the responsibility for compliance with the laws to districts or cities. Thus, in the state of California a law is in force which creates special "districts" for the control of atmospheric air pollution within different state regions; such "districts" existed in vicinities surrounding Los Angeles and Santa Clara. Discharge of "heavy smoke" (No. 2 by the Ringelman scale) in the state of California is limited to 3 minutes per hour. Regulations enacted in Los Angeles in 1948 specify that fly-ash concentration in smoke containing 12% of CO_2 must not exceed 0.4 grains per m^3, or the equivalent of 0.92 g/m^3. Maximal allowable limits have also been set for fly-ash or smoke discharged by industrial plants. The standard limits are: 0.11 kg/hr at production rate using an average of 22.68 tons/hr of raw material to 18.4 kg/hr at production rate using an average of 27.216 T/hr of raw material.

A "smoke alarm system was instituted in California in June 1955, the purpose of which was to forestall excessive accumulation of pollutants in the atmospheric air and to avoid catastrophic results from high concentrations of toxic substances in the air (Merril, 1956). The Table below lists concentrations of harmful substances calling for signals or alarms of caution, alert, and danger.

Substances	Max. allowable concentrations in ppm.		
	Caution	Alert	Danger
Oxides of nitrogen	3	5	10
Ozone	0.5	1	1.5
Sulfuric anhydride	3	5	10
Carbon monoxide	100	200	300

Alarm No. 1 is sounded when carbon monoxide concentration in the atmosphere exceeded 100 parts per million, nitrogen oxides 3 parts per million, oxides of sulfur 3 parts per million, and ozone 0.5 parts per million. Alarms Nos. 2 and 3 are sounded when these gases reach concentrations exceeding the above indicated limits correspondingly by 50 to 100 percent. These indexes are characterized as follows: alarm No. 1 indicated merely an approach to the maximal allowable concentrations which constituted no immediate danger to the population but were gradually approaching the danger levels. Thus, alarm No. 1 called for the immediate adoption of preventive measures; alarm No. 2 warned that the concentration level of an atmospheric air pollutant or pollutants constituted a health hazard (alert stage); alarm No. 3 sounded when the concentration of the air pollutant constituted a positive health hazard. Alarm No. 1 was in essence a call to voluntary curtailment in non-essential automobile traffic and a taboo sound against certain types of trash burning. Alarm No. 2 covered items mentioned under alarm No. 1, and, in addition, called for a stricter curtailment in automobile traffic and for halting the operation of certain specified industrial production processes. Regulation instructions advise that realization of the purpose of atmospheric air pollution protection, as called for by alarm No. 2, must be accomplished as much as possible without resorting to unduly harsh measures which might upset the normal course of local economic life, or cause financial loss to some branch of local industry or trade. The sound of alarm No. 3 called for action indicated by alarms No. 1 and No. 2 and in addition, the Governor of the State could declare a state of emergency, giving the proper authorities the right to effectuate preventive measures stipulated by the laws in catastrophies. Data presented in the preceding Table show that the maximal allowable limits adopted in the State of California for the protection of atmospheric air and which called for the sounding of Alarm 1 were 19 times as high as the corresponding allowable concentration limits adopted in the USSR. As stated previously in this report, discharge into the atmospheric air of smoke the density of which exceeded 2 Ringelman units for 3 or more minutes per hour was forbidden. Sulfur compounds could be discharged into the air in concentration not exceeding 0.2% by volume. Depending upon the amount of fuel used, the maximal discharge of dust or fly-ash could not exceed 18 kg/hr.

"Thick" or "heavy" smoke was defined in Pittsburgh as smoke of 2 Ringelman unit density. The use of fuel containing more than 20% of vola-

tile substances was allowed in Pittsburgh only where the fuel burning chambers were of the complete smokeless combustion type. The regulations also prescribed conditions for the discharge of soot, ash, harmful gases, vapors and fly-ash. Locomotives had to use hard smokeless fuel, or they had to be equipped with smokeless complete combustion type of fuel burners; the discharge of "thick" or "heavy" smoke by locomotives was limited to 1 minute per hour.

In 1/X/1950 New York adopted standard allowable limits for fly-ash discharged by boiler installations and by electric heat and power stations. According to these standards the allowable fly-ash concentration limit range was from 2.2 kg/T of steam in small boiler operated plants to 0.8 kg/T of steam in large electric power and heat generating stations; the range of corresponding total discharge equivalents was 10 - 1450 kg/hr, which in turn corresponded to a concentration range of 0.5 - 0.15 g/m^3. Maximal allowable concentration of dust in flue gases coming from boiler operated plants differed with the city municipalities within the range of 0.9 and 1.2 g/m^3. Some cities prohibited the burning of coal having a volatile substance content in excess of 20-25%, and of ash in excess of 12% by plants equipped with the usual (old) type fuel burners, unless such burners have been modernized by the addition of devices to insure complete smokeless fuel combustion.

In the Allegheny region, which is the center of extensive steel production, the maximal concentration of volatile substances was set at 23% for hard fuel burned in non-automatic combustion chambers, but there are some exceptions, especially with regard to some special technological processes or branches of the industrial production. Special maximal limits have also been set for the ash content in the smoke discharged by plants of some production and manufacturing branches.

Regulations adopted in St. Louis forbid the use of hard coal having a 23% content of volatile substances, or coal the lumps of which were less than 5 cm in diameter, if such coal contained more than 12% of ash and more than 2% of sulfur, except in plants equipped with complete combustion chambers of approved original or modernized construction. The discharge into the atmospheric air of smoke, the density of which exceeded 2 Ringelman units was forbidden, except when the chamber was being cleaned or during the start of furnace firing. However, even in such emergencies, the discharge of smoke the density of which exceed 2 Ringelman units, could not exceed 6 minutes per hour; in such instances the smoke discharge could be extended to not more than 9 minutes per hour if its density did not exceed 2 Ringelman units; even in such special instances the ash and dust concentrations in the discharged gases could not exceed 1 g per 1 m^3 of smoke. All newly designed combustion chambers and old combustion chambers in the process of repair or reconstruction had to be approved by the smoke inspector, who had the authority to stop operation of any production, manufacturing or processing plant in cases of non-compliance with the above regulations.

A basic shortcoming of the present day USA law-making procedure for the protection of atmospheric air against pollution is the lack of a uniform approach to the solution of the problem in relation to the Country as a whole, which results in the issuing of different codes, rules and regulations by different states, and frequently by different cities within the same state. Therefore, it frequently happened that sanitary efforts exerted by one city or state in the field of atmospheric air protection were negated by air pollutants coming from a neighboring city or state in which air purity protection means were either inadequate or entirely lacking.

Despite the fact that laws existed in the USA for the protection of atmospheric air purity, the air of its cities was notably polluted by industrial discharges, and more so by automobile exhaust gases and fumes. This was confirmed by numerous complaints which came from private individuals and from business people. In 1962 New York City authorities received 20,000 such complaints and California authorities received 25,000.

The structure and organization of the service in the field of atmospheric air protection. The Division of Atmospheric Air Protection is a component of State Services, an organization of the Public Health Service of the Department of Health, Education, and Welfare. The Division of Air Pollution was made up of the following sections: 1) scientific research and personnel training, the staff of which consisted of experts who examined requests for financing specific problems related to the study of atmospheric air pollution and for the training of technical and scientific personnel, etc.; these experts also dealt with problems of publications, disbursement of funds, and use of facilities granted to investigators; 2) laboratory for medical and biological research devoted to the study of related problems in farm economy, such as damage caused to crops by air pollutants, clinical, pharmacological and toxicological problems of routine and research character; 3) centers for the study of air pollution effects at chosen points, staffed by statisticians, epidemiologists, and biometricians; and 4) an aerometric subdivision; studies have also been initiated in morbidity caused by atmospheric air pollution, in the effect of meteorologic factors on air pollution and possible prognosis of same, etc.; 5) a laboratory for the study of engineering, scientific-physical and meteorological problems related to air pollution reduction or elimination; 6) a section for the study of physical chemical air qualities and related meteorological aspects; 7) a technical and technological section, the function of which was to assist states in training professional personnel, participate in consultations related to problems of atmospheric air pollution, etc.

This section of the Division of Air Pollution was located not in Washington, but in Cincinnati, Ohio at the Robert A. Taft Sanitary Engineering Center. The Division of Air Pollution has a personnel of 400 employees, including those assigned to states; of the 400 employees 20 are physicians, 25 meteorologists, about 60 engineers, approximately 60 chemists; then

there are physicists, mathematicians, statisticians, pathologists, etc.; 15% of the personnel were scientists who held different professional or scientific college or university degrees. The entire personnel was financed by the Department of Health, Education, and Welfare. The engineers were actively engaged in sanitary-hygienic investigations. Heads of the Division of Air Pollution believed that under conditions prevailing in present-day complex industry a technically adequate appraisal of the parameters of external environmental conditions could be made only by engineers trained to deal with problems of air pollution.

It was briefly mentioned in the preceding paragraphs that the USA had adopted the municipal form of organization in the control of atmospheric air pollution. Each town or city could arrive at its own maximal limits of air pollutant concentrations discharged from smoke stacks. Cities and towns of some states were guided by principles adopted by their state while municipalities of other states preferred to guard their air environment independently, and to establish their own standards of air purity, and to use their prerogative in adopting means for the control of the city air purity in accordance with their own regulations.

The Division of Air Pollution of the Public Health Service of the Department of Health, Education, and Welfare developed and offered recommendations to sanitary law-makers; such recommendations may or may not be adopted by the states' health departments. Furthermore the Division of Air Pollution of the Public Health Service had no inspection authority, except in cases governed by laws operating on a federal level. Money assigned to the Air Pollution Division by the Federal government was intended specifically for research purposes and for the training of technical and scientific personnel.

Scientific-research investigations in the fields of sanitary protection of atmospheric air was conducted in many universities, engineering centers, in research laboratories and in many USA Government bureaus. Local municipalities or State Departments of Health selected their research problems according to local conditions and assigned them to appropriately trained and experienced research investigators. Research grants alloted to selected research experts in 1963 amounted to 3 million dollars, which covered the cost of 90 research projects. This amount was raised to 4 million dollars for 1964. The Department of Health, Education, and Welfare financed 39 universities and 18 scientific research institutes; it also engaged other Government organizations such as the Weather Bureau, the Bureau of Mines, Bureau of Weights and Measures to conduct related investigations on a contract basis. The Division of Air Pollution also subsidized 2 experimental stations, one in Oklahoma and one in Pittsburgh, Pennsylvania. Most of the air pollution research was conducted and financed directly by the states. For example, the State of New York allotted 8 million dollars for air pollution research in 1963, which is more than twice the amount spent in the same year by the Division of Air Pollution of the Public Health Service for the

same general purpose. (I was informed that this statement was incorrect - BSL.) The division of Air Pollution of the Public Health Service also issued publications, such as results of scientific research studies, and pertinent state, county or municipal reports, etc.

San Francisco, Los Angeles, Cincinnati, Detroit, Pittsburgh, Harrisburg, Philadelphia and New York municipalities, and of other cities have organizations and equipment for the sanitary protection of atmospheric air which were in constant operation. Special regional and municipal bureaus have been organized whose functions were air pollution prevention through inspection and general watchfulness. State air pollution bureaus usually had a staff of approximately 20 to 24 employees, distributed as follows: one bureau chief, 6 engineers, 2 chemists, 10 inspectors, laboratory technician, and 4 laboratory helpers. Much of the responsible personnel's time was given to the study of complaints, applications, suggestions and similar correspondence. Non-compliance with the regulations was usually noted by the inspectors who traveled through regions assigned to them in automobiles equipped for field air analysis, making it possible to determine on the spot the type and extent of regulation violations, which they reported to their chiefs. Minor violations were reported immediately to the plant management and nothing more was done about it if the infraction was corrected; in more serious and stubborn cases authorities could resort to financial or other type of penalties; financial penalties usually ranged between 25 and 500 dollars, or jail confinement up to 2 months.

While making his, so-called, prophylactic observation the sanitary inspector had no authority to prevent industrial discharges into the atmospheric air; construction plans were examined in the blue print stage, and, as a rule, resulted in no changes. Generally the sanitary authorities did not participate in the planning or construction of industrial and community projects. The Division of Air Pollution of the U.S. Public Health Service offered no suggestions for the adoption of more rational technological production systems, or for the replacement of highly toxic raw material by materials of lower toxicity, since managements of the industrial enterprises were under no compulsion to accept or follow such suggestions if they should appear unprofitable.

Atmospheric air pollution investigations. The type and intensity of atmospheric air pollutions with industrial production and by-products discharges were investigated in stationary and mobile laboratories at designated points. Permanent or stationary laboratories at points of air sample collection and analysis were equipped with fully automatic or semi-automatic apparatuses. Air samples were examined simultaneously for NO, NO_2, CO, CO_2, SO_2, H_2S, organic substances, and hydrocarbons. In the State of New York air samples were also analyzed for HF and O_3. Air samples were collected and analyzed around-the-clock. Results were fixed on continuous recording paper or recording tape every 5 minutes, constituting a 24-hour control of the state of atmospheric air pollution. The fixed rec-

ords were then sent to the Air Pollution Division Laboratory in Cincinnati, Ohio, where the data were processed with the aid of electronic computers, written up, published in the form of reports and distributed among pertinent scientists, technicians, sanitarians, universities, research institutions, etc. Fully automatically operating sample collecting, analyzing and recording equipment was seen in centers located in New York, San Francisco, Washington, Harrisburg, Detroit, Los Angeles, and other cities. The number of air sample collecting points varied with the cities. Thus, New York had 4 fixed points, San Francisco had 2 fully automatically operating sample collecting points and 16 semi-automatically operating points. Forty air sample collecting points were seen in California, and 50 in Pennsylvania. The USA mobile laboratories generally were assigned to vicinities surrounding known sources of atmospheric air pollution. The mobile automobile laboratories of Los Angeles collect and analyze up to 2,000 air samples annually.

In 1960 the Air Pollution Laboratory of the Robert A. Taft Sanitary Engineering Center of the Public Health Service assumed the task of collecting and analyzing air samples at 50 stationary points equipped with fully automatic sample collecting devices. As was previously indicated, the Public Health Service, and consequently the Robert A. Taft Sanitary Engineering Center located in Cincinnati, are parts of the Department of Health, Education, and Welfare. The Center has a personnel of 150, which includes physicians, engineers, chemists, physicists, physiologists, biochemists, chemical analysts, mathematicians, veterinarians, minerologists, sanitary engineers, etc. The Center investigators visit cities in which they study the sources, character and extent of atmospheric air pollution, and suggest suitable ways for the reduction of such pollution. At the same time they instruct local personnel in methods of air sample collection and analysis. Up to the time of the visit herein reported, the Cincinnati Center fully investigated sources and extent of atmospheric air pollution in 11 states. On the average the Cincinnati Center conducts one extensive investigation per year and makes pertinent recommendations. However, as previously noted, compliance with or action indicated by such recommendations are in no way obligatory.

Training of specialists. Basic training of specialists and advanced courses are conducted at the Robert A. Taft Sanitary Engineering Center in Cincinnati, Ohio. The study and instruction programs must be approved by authorities of the Public Health Service in Washington, i.e., by pertinent authorities of the Department of Health, Education, and Welfare. Short courses usually last from 1 to 3 days; longer courses may last up to one year. State and municipal health departments send their qualified workers to the Cincinnati Center to attend such courses and pay all expenses. Courses offered in 1962 - 1963 covered 75 different programs which included the following specialized fields: air pollution, water pollution, radiology, food hygiene and city planning.

Scientific research and purification of industrial discharges. No internal combustion engine had been designed at present which could eliminate, neutralize or detoxify automobile exhaust gases by complete fuel combustion or by other means. For this reason the atmospheric air of USA cities, in particular, in the State of California, is intensely polluted; accordingly, a considerable volume of air pollution research is devoted to the study of automobile exhaust gases. Thus, in the San Francisco laboratory located near Berkeley, in Los Angeles, in San Bernardino, Bartlesville, Cincinnati, Detroit, and in New York intensive studies are conducted to find the factors and conditions which created smog, and to determine the effect which different exhaust gas components had on animals, man, vegetation, etc. Special experimental chambers had been constructed in which automotive exhaust gases are subjected to the action of artificial solar rays attempting to produce a laboratory photochemical smog. Many laboratories, especially in California, directed their fight against effects of automotive exhaust gases by experimenting with different designs of internal combustion engines or by incorporating afterburners. A mandatory law was passed in California in 1963 which required that all motor vehicles had to be equipped with specially constructed afterburners for the purpose of lowering the concentrations of toxic and harmful substances in exhaust gases. The afterburners now in use can reduce CO concentration to 1.5%, hydrocarbons to 275 parts per million; some types of afterburners reduced the concentration of hydrocarbons to 20 parts per million and CO to 1.0%. This law had not been faithfully complied with, and specific means of enforcing it had not been adopted.

The effect of smog on animals is being studied in special exposure chambers equipped with automatically regulated devices for the determination of the chamber air composition. Changes occurring in the experimental animals' organisms are also recorded automatically, and the results of numerous determinations and observations are processed by means of electronic computers. In the Cincinnati Laboratory of Professor Kehoe investigations were conducted on the effect of lead on man; the experiments were conducted in a special exposure chamber employing, as it appeared to the USSR observers, unusually high lead doses. Members of the Epidemiological Division of Cornell University in New York selected 1,000 inhabitants in 9 city blocks, the air pollution of which was approximately of the same type and intensity; selected persons belonged to different social groups of different financial levels. Once a week all test persons were asked to fill out a questionnaire of 150 questions related to their state of health, with special emphasis on the condition of their respiratory organs. This method of morbidity study seemed to lack scientific objectivity; no provision was made for a control group, and no objective studies were made of the test subjects' physiological systems and their functioning.

Studies were conducted at the University of Southern California in Riverside on air pollution effect on the general state of health of patients suffering of emphysema under clinical conditions. Two wards of the University's clinic, having only emphysematous patients, have been devoted

exclusively to the study of this problem. Patients of one ward inhaled natural outside air not previously purified; patients of the other ward inhaled air freed from all harmful components. It was hoped that a comparative study of the course followed by the disease in patients of the two wards and of their general state of health might lead to informative conclusions regarding the effect of air pollution on patients having emphysema. The study is still in progress.

Interesting studies were conducted on cancerogenic properties of some chemical substances at the Bethesda Cancer Institute of the National Institutes of Health. Similar studies were conducted at New York University. At the University of Southern California thorough and detailed animal experimental studies were conducted for the purpose of determining the effect of smog on chemical changes of the blood, tissues, physiology of the lungs, and on morphological tissue changes, paralleled by studies on the effect of smog on the psychology of the experimental animals. Problems related to the theory of smog formation were being studied in the laboratory of Professor Haagen-Smit at the University of California. Problems related to the presence of lead in atmospheric air were under study at the same University. The harmful effect of air pollutants on vegetation was under study at the University of Southern California. Studies were also conducted on the effects of ozone, PAN, ethylene, sulfuric anhydride and of fluorine. One of the University's air pollution laboratories was located amid California's orange groves. It should be noted in this connection that observations of smog effect on fruits and vegetations were limited to external damage and appearance without the application of finer biochemical and physiological methods of investigation, which lowered the usefulness and significance of the entire complex of studies and made the results less convincing.

At the Department of Industrial Medicine of Michigan University, located in Detroit, studies were conducted on the effect of atmospheric air pollutants on respiration, with special emphasis on the presence in the air of cyanides and mercury emitted by plants of the rubber producing and processing industry, using duplicate groups of rats and rabbits. One group, housed in three chambers, was exposed to the inhalation of natural city air; animals of the duplicate groups inhaled purified air. Throughout the animals' survival period records were kept of results of biochemical, physiological and pathomorphological tests, including enzyme tests. Tests were also conducted with the antibiotic tetracycline. At the Yeshiva University of New York studies were conducted to determine the causes of different levels of seasonal bronchial asthma morbidity in some New York regions, using hospital patient turnover data. Investigators believed that seasonal increase in bronchial asthma morbidity may be caused by the seasonal presence of microspores in the air, but this belief has not been decisively substantiated, and studies and observations are being continued.

Interesting experiments were also conducted in the same laboratory with mice and hamsters to establish the possible cancerogenic effect of the

inhalation of air polluted with SO_2 and simultaneously contaminated with influenza virus. At the same institution studies were being conducted to determine the cause of lung cancer in general, and with special reference to cancerogenic substances, which included hydrocarbon fractions, their behavior in the organism and elimination via the lungs. At the time of the visit the investigators were studying substances resulting from the oxidation of hydrocarbons. Synthetic cancerogens had been produced which, according to the investigators, elicited cancers in mice. Professor Laskin developed a procedure for the production of cancer by introducing into the organism a thread saturated with a cancerogenic substance, which elicited cancer development in 90% of the experiments. Investigators did not deny that cancer can be produced by a variety of methods, but they apparently concluded that cancer could not be produced in experimental animals by the inhalation route alone. Experiments were being conducted with pure cancerogens alone or in combination with other hydrocarbons.

The USA Bureau of Mines cooperated in the development and study of different problems and phases of atmospheric air pollution. Here attention was concentrated on the problem of removing sulfur from crude oil. The section of the Bureau which dealt with hard fuel, located in Pittsburgh, analyzed the composition of flue gases resulting from combustion of hard fuel, automotive exhaust gases, and during the removal of sulfur from hard fuel.

Investigations in the USA in the field of sanitary atmospheric air protection were conducted along the following channels: designing and building equipment, apparatuses and devices for continuous automatic recording of general atmospheric pollution; designing and building improved devices and apparatuses for the detection and determination of specific air pollutants, such as cancerogens; studying the photochemical conversion processes of air pollutants under atmospheric conditions; experimental animal toxicological studies, and determination of population morbidity related to atmospheric air pollution; studying the effect of industrial air discharges on vegetable life; studying meteorological aspects of air pollution; developing methods for limiting or reducing the volume of industrial discharges into the atmospheric air, including the discharge of automotive exhaust gases, smoke gases emitted by domestic combustion chambers, stoves or furnaces, etc. The procedures, equipment and installations recommended in all cases were much the same as those recommended and used in the USSR.

The USSR visiting delegation was presented with the opportunity to examine purification installations in two electric heat and power stations, one in Cincinnati, Ohio, and one in New York; in an asphalt-concrete plant in Cincinnati, a typographical plant in Philadelphia, and a crude oil processing plant also in Philadelphia; other forms of industrial purification equipment and installations were shown on the screen by means of moving films. On the basis of what the delegation had the opportunity to observe it can be stated that the problem of freeing flue and smoke gases from sulfur was far

from having been solved in the USA; the most probable means of combatting SO_2 discharged into the atmospheric air was limited to the removal of sulfur from the fuel. Ash was removed from the coke at electric heat and power stations by the two-stage methods, using multicyclones and electrostatic filters, the efficiency of which was 99%. Smoke stacks were equipped with teleinstallations which controlled the smoke density. Sleeve and bag filters, made of glass wool or orlon, were widely used for the removal of dust. Recovery installations and recovery systems were practically the same as in the USSR. The observed asphalt-concrete plant was equipped with two types of installations for gas afterburning, and concrete mixers were equipped with bag type filters for dust catching.

Domestic trash burning in smoke creating combustion chambers seriously aggravated the air pollution problem in the USA. The recommended paper filters in this connection had not been widely accepted. About 60 private USA business enterprises were engaged in the developement of different types of wet or dry operating electrostatic and other dust catchers, and gas afterburners, as well as other types of purification installations. Such manufacturing organizations issued catalogues widely used by municipal bureaus or divisions concerned with the practical control of atmospheric air pollution. Despite the fact that scientific studies in the field of atmospheric air protection were conducted on a broad scale in the USA, the attainment of practical results was not impressive.

It should be noted that the work of Soviet hygienists is widely know in the USA, from translations either in the abstract form or as full translations. The latter is particularly true of "sborniks" (collections) issued by the USSR Committee on Limits of Allowable Concentrations of Atmospheric Air Pollutants.

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SUPPLEMENT

A NEW TYPE OF INTERNAL COMBUSTION ENGINES

(Precombustion Chamber Flame Ignition)

A. S. Sokolik

(Vestnik Akademii Nauk SSSR, Vol. 31, No. 10, 1961, pp 78-90)

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USSR electrification is a basic instrumentality in the building of communism. However, in the USSR, as in other industrial countries, internal combustion engines (ICE) produced 90% of the country's energy supply for the past decade or two. This condition will persist as long as studies fail to develop new ways of converting fuel into energy which could replace the use of internal combustion engines in transportation automobiles and tractors. Automotive power generating engineers are now faced with the problems of radically improving the ICE, especially with respect to a more economic use of fuel.

Two Types of Internal Combustion Engines: All types of modern ICE used in motor vehicles can be divided into two categories, based on their methods of ignition, of initiating the combustion process, and methods of forming fuel-air mixtures: a) engines with spark ignition and external carburetion; and b) engines with compression ignition and internal carburetion by means of fuel injection into a cylinder, where it becomes mixed with compression heated air - the so-called "diesel" engines.

The differences in the ignition methods and carburetion are inherent in the fact that highest power concentration, i. e., power per liter of effective cylinder volume, can be achieved in spark-ignited engines with relatively poor economy. On the other hand, a more effective use is made of fuel combustion heat in diesels, but without full utilization of the effective cylinder volume.

It became apparent at the time of the First World War that the possibilities of improving the operating economy in spark-ignited engines and the pressure feeding in diesels were rigidly limited by the fact that one would have to interfere with the normal course of combustion. A detonation "knock" appeared when the thermodynamic efficiency of the operating cycle in a spark-ignited engine was increased by increasing the degree of compression. The exhaust became smoky when excess air in the air-fuel mixture in diesel engines was lowered, so that the fuel-air ratio approximated a theoretical (stoichiometric) composition. Combustion became explosive ("diesel knock") when a rotational feeding apparatus was used, and especially when the ignitability of the fuel deteriorated.

Engine and Fuel. Long before the complex physico-chemical nature of these phenomena was understood, their relationship to the chemical structure of hydrocarbons was discovered, - on the one hand an increased anti-knock stability characterized hydrocarbons having a branched hydrocarbon chain (isooctane being the highest standard), and, on the other hand, an increased combustibility characterized hydrocarbons having a straight hydrocarbon chain (cetane being the highest standard for diesel fuels). The opposite requirements for the chemical structure of the fuels in both classes of engines arose from the identical nature of detonation ignition in the spark-ignited engine and the initial ignition in the diesel.

However, even fuels having a high cetane number failed to eliminate smoke formation. Therefore, increasing the cetane number of diesel fuels played no decisive role in the technical progress of diesels as increasing the octane number of gasolines did in the development of carburetor engines. The 50-year history of spark-ignited engine development presents a continuous rivalry between petroleum industry achievements in increasing the octane number and the requirements of new engines for fuels having an increased antiknock stability. This rivalry became especially dramatic during the development of the aircraft piston engine, in which not only the permissible degree of compression and the improvement of engine economy was dependent on the available octane number, but also the possibilities of supercharging the engine and, thereby, the flight characteristics of the aircraft, - ceiling, maximum speed, take-off weight, range. It was specifically the race for supremacy in this basic World War II weapon that produced the most progress in increasing the octane number of aviation gasolines, which was based on new petroleum manufacturing processes and on the synthesis of isooctanes and other hydrocarbons with similar properties.

At end of the Second World War the high-octane aviation gasoline industry lost its chief consumer when first military and later civilian aviation began the transition to jet engines, since the octane number required at that time for automobile engines never exceeded 80. The problem of creating a new mass market for the vast resources of high-octane aviation gasolines arose in the United States. An intensive campaign was expressly developed during the post-war years for a sharp increase in the compression ratio of automobile engines so that high-octane gasolines could be used in them. C. Kettering of General Motors Corporation stated in his report "A More Effective Use of Fuel"[1] (explanation of all footnotes will be at the conclusion of this paper) that increasing the compression ratio in automobile engines from 6 to 12 would be a reality in the near future. D. Caris and E. Nelson[2] of the same firm discussed in their paper the possible effect of increasing compression ratio to 20. In this case it was assumed that the automobile engine would be converted in the near future to 100-octane gasolines and that certain ethyl liquid additives would

be used, which in themselves would create a number of additional problems, both in a sanitary-hygienic sense and with respect to reducing the lifetime of such vitally important parts of an ICE as spark plugs, valves, etc.

It is still not clear to what degree the improved fuel economy of the automobile attained by increasing the compression ratio justifies making the petroleum manufacturing process more complex, and especially the overall reduction of motor fuel resources, which is associated with increased antiknock stability of the gasolines. In other words, to what extent did the economic benefits of the consumer coincide with the interests of the national economy. There was also the additional problem in countries which had not developed a high-octane aviation gasoline industry as to what extent were capital expenditures justified in creating such an industry.

In examining these problems it is essential to know whether increasing the compression ratio was the only means of improving the economic characteristics of an automobile engine, and whether modern science could discover any other way of achieving the same aims, but without increasing the special requirements for a motor fuel or even by generally eliminating any kind of requirements for the chemical structure of the fuel, assuming, of course, that the efficiency of the fuel would be maintained at the level of modern gasolines. It is this problem in particular which is the subject of this paper.

How is the Economic Effect of the Compression Ratio Achieved?

The most prevailing opinion, including the basic assumptions in the previously mentioned Kettering paper, is that this effect was completely due to increase in the thermodynamic efficiency of converting heat into energy and to increase the temperature differential during expansion in accordance with the formula $\text{Eff} = 1 - 1/\varepsilon^{k-1}$, where ε is the compression ratio. However, engine economy increased in this way parallel with the compression ratio only when other invariable conditions were present. The economic effect actually achieved in increasing compression ratio of an automobile engine always significantly exceeded thermodynamic efficiency. Data of many researchers show that an increase in automobile engine efficiency caused by increasing compression ratio invariably considerably exceeded increase in thermodynamic efficiency. Thus, the economy of an automobile engine increased by 90% while its efficiency increased only by 25% when the compression ratio was changed from 6.25 to 12.[3] The research workers of General Motors Corporation have also come to a similar conclusion.[4]

To understand why the principle economic effect depended on raising the compression ratio, the following must be remembered: regulating the work an automobile engine accomplished in one cycle under a quickly changing load (the so-called average indicated pressure which deter-

mined engine power at a given r.p.m.) by altering the air-fuel mixture in the cylinder by throttling its flow, is a qualitative regulation of the load. In this case a certain amount of excess fuel, in contrast to the amount which corresponded to complete combustion, must be added to obtain completely stable engine operation under all loaded conditions. Thus, the degree to which the mixture became enriched by unburned fuel increased progressively as the load decreased. In this way an engine operated with a known incomplete use of fuel efficiency during the most prolonged medium and light loads, or especially during city driving.

Furthermore, as follows from the theory of the working process, it is most advantageous not to reduce the air-fuel mixture when lessening the load, but to gradually dilute it with air and thin out the mixture with fuel. In this case combustion temperature is reduced, heat losses from the burning gases to the cylinder walls are lessened, and index (k) approaches the adiabatic as the magnitude of thermodynamic efficiency increased (cf. formula). Therefore, despite the theory, quantitative regulation by throttle control, which requires reduced loads of progressive mixture enrichment and increasing unburned fuel losses, is being used in place of the more economic qualitative regulation by the mixture composition.

Experience showed that the necessity of maintaining stable combustion in an enriched mixture fell off with a sufficient increase in the compression ratio, and that it also became possible to use some degree of mixture impoverishment within a rather wide range. American statistical data show that the average enrichment of a mixture in automobile engines noticeably decreased with increase in the compression ratio.[5]

Therefore, it can be concluded that the greater part of the economic effect attained by increasing compression ratio in an automobile engine was an indirect effect of the enrichment reduction or complete enriched mixture elimination and of the use of lean mixtures during partial loads, i.e., by approximating an economic quantitative control of the mixture.

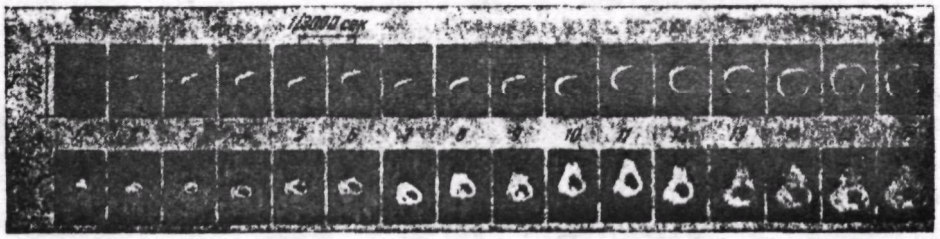
The problem presented earlier can be formulated now more specifically as follows: is increasing compression ratio in an automobile engine the only, or most effective, way of eliminating unburned fuel losses and of using qualitative control on partial engine loads? A definite answer can be given now to this problem. A physicochemical study of the combustion process in an engine yielded a more rational and effective solution to the problem of economic engine control than increasing the compression ratio. To understand the essence of the new solution examine what factors limit the steady combustion of lean mixtures in an engine, and why it is necessary to introduce excess fuel.

Spark Ignition and Combustion in an Engine. In order to completely convert the heat of combustion into work the combustion process must

begin during the terminal phase of the compression stroke to prevent piston drag and end during the start of the expansion stroke to fully utilize the power stroke. Duration of the combustion process does not exceed 1/10 of a revolution within this range, which in a high-speed engine is approximately 1/500 of a second. Such a rapid combustion is made possible only by the turbulent intermixing of the charge in the engine cylinder. The turbulent pulsations in an engine cylinder are generated during the filling process and increase in intensity with the number of revolutions, so that the factor which accelerated combustion became automatically enhanced with a decrease in combustion time.

There are no generally accepted viewpoints at present on the nature of turbulent combustion. Studies made by this author and his associates[5] show that this type of combustion should be represented as an envelopment of the fuel mixture by continuous combustion resulting from the disorderly intermixing of small fuel volumes and fresh gas. The following important conclusion is drawn from these concepts which is confirmed by experimental data: turbulent combustion occurred only in the presence of sufficiently developed flame sources. This fact is illustrated in Figure 1 by the two series of motion picture frames showing the development of a flame in a model engine combustion chamber, the first series shows the flame in a quiescent charge, while the second shows the same in an artificially turbulent charge. The photographs show that continuous ignition characteristic for turbulent combustion appears only after a certain critical volume of approximately 2 cm in diameter was attained. Accordingly, it is possible to distinguish two essentially different phases in an engine's combustion process: 1) formation of a flame source open to the effect of turbulence, and 2) turbulent combustion proper in which the basic charge mass is combused. In fact, it is the first stage where only about 1% of the cylinder charge combusted, which actually determined the use of economically advantageous poor mixtures.

Fig. 1



Two schlieren-cinematographic velocity exposure series of spherical flame development in (I) quiescent and (II) turbulent gas, at 1/3000 sec. intervals

The possibility of a flame arising from a spark was determined by a condition at which the rate of reaction released within the volume of the

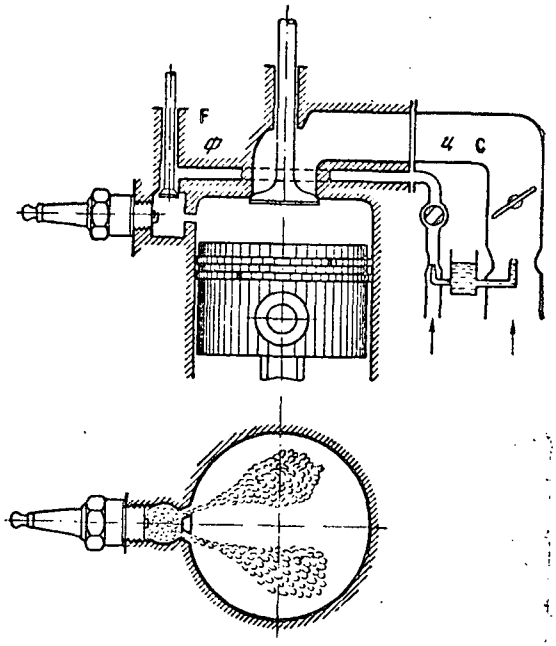
primary nidus exceeded the rate at which heat was transmitted to a fresh gas or to the spark plug electrodes. Because of this the charge agitation necessary for the accomplishment of combustion in an engine within the 1/500 of a second inhibited the development of the initial stage of the process. The more intensive was the turbulent charge motion, the more difficult it was for the charge to be ignited by a spark and to form the initial flame source. On the other hand, this process retarded the drop in the rate of heat liberation when the fuel mixture was thinned either by excess air or by inert combustion products. Even with a slight degree of leaning (10-20% excess air) the formation of a flame source was delayed to the entry of the first portions of a fresh mixture. This is how knocking appeared in a carburetor, which is the obvious sign of delayed combustion in an excessively leaned mixture. It is specifically this condition which makes it necessary to step up the fuel enrichment in proportion to throttling causing the appearance in the residual gases of incomplete combustion products, such as chemically active CO and H_2, which hasten flame formation. Enrichment of the mixture and unburned fuel losses in modern automobile engines at partial charge are not caused by faulty design in the control system, but by the necessity to insure flame formation at partial charge.

The same reasons, which inhibit this process during throttling, give rise to factors which enhance it when the compression ratio is increased. The rate of volume heat liberation in this case increased by reduction in the concentration of residual gases and by increase in the charge density. This explains the reason why increased compression ratio gradually lowered the necessity of resorting to mixture enriching at partial charge. In fact there arises a slight fuel leaning. Increasing the compression ratio enhanced the partial elimination of disadvantages inherent in a spark-ignition system at the expense of raising the requirements for antiknock fuel stability. In contrast to this, the system of precombustion chamber-flame (PCF) ignition eliminates these disadvantages, accompanied by a definite reduction in the requirements for the antiknock fuel stability.

Precombustion Chamber-Flame Ignition in Engines with External Carburetion. Two main principles form the basis of the PCF system. Principle one can be formulated as follows: To insure optimal conditions for the formation of an initial flame source in the cylinder of an engine independently of the mixture composition in conformance with regulating its charge the spark ignition has to be moved from the working cylinder to a precombustion chamber, the capacity of which is only 2-3% of the capacity of the combustion chamber. The precombustion chamber is connected with the cylinder by one or more valves (Fig. 2) and is equipped with a spark plug and a valve which opens simultaneously with the main intake valve. The precombustion chamber is filled with a mixture from the precombustion chamber carburetor simultaneously as the cylinder is filled with an air-fuel mixture from the main carburetor. These two car-

buretors are in fact two sections of a common carburetor and are regulated so that the excess air in the cylinder mixture accorded with the excess fuel in the precombustion chamber. The lean cylinder mixture entered through a valve in the precombustion chamber during the compression stroke and mixed with the rich precombustion chamber mixture, forming at ignition moment a mixture which easily ignited by a spark at any air-fuel mixture in the cylinder. Although control of the precombustion chamber mixture depended upon a specific ratio with the control of the cylinder mixture, it will be shown later that the mechanism of the PCF-ignition system itself makes this dependence very flexible. In addition to the mixture composition flame formation in the forechamber enhances the chamber purification from residual gases, lessened turbulence as compared with a cylinder and promotes the formation of a flame in the precombustion chamber.

Fig. 2



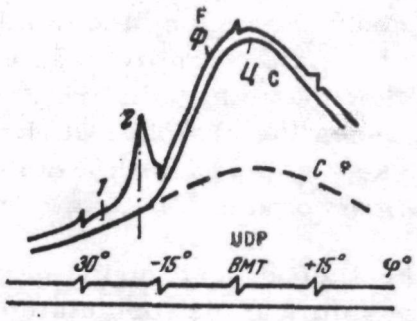
Basic plan of forechamber jet ignition
F - forechamber; C - mixture cylinder

The second basic principle of the PCF system can be formulated as follows: turbulent combustion of the main charge did not develop in the course of the continually-increasing turbulent motion effect of the charge on the flame after spark ignition, but developed as the result of the way in which this charge ignited from the hot gas stream ejected at a high rate through the precombustion chamber nozzle or nozzles. The pressure differential between the precombustion chamber and the cylinder required to eject the stream can be determined directly from pressure diagrams recorded simultaneously in the precombustion chamber and in the cylinder, as shown in Fig. 3. This differential is formed by the nozzle pressure drop against the gas outflow from the precombustiontion chamber, i. e., resulting from the fact that combustion occurred here under conditions of semi-enclosure.

Some concept pertaining to the cylinder charge ignition mechanism by the precombustion chamber stream can be illustrated by high-speed motion picture records of the precombustion stream development (Fig. 4) and by ionization current records (Fig. 5) which can trace the development of the chemical reaction itself at various distances from the nozzle. It has been established that this reaction was connected directly with the gas ionization in the flames. The motion picture records show that an igni-

tion nucleus appeared in the stream at some distance from the nozzle and then quickly enveloped the main charge.

Fig. 3

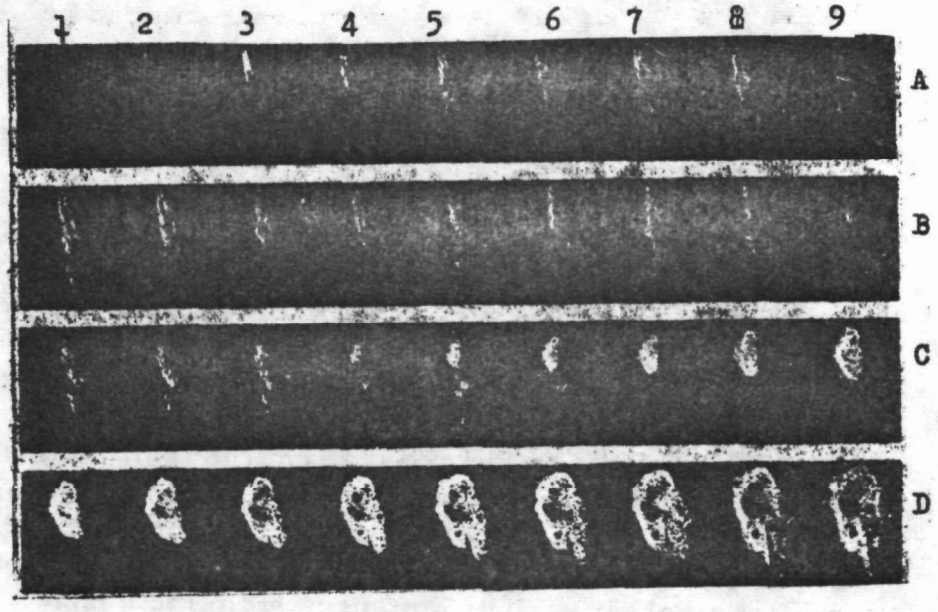


Pressure changes during combustion in (F) forechamber and in (C) cylinder P_o – pressure curve without combustion; φ^o – degrees of angular shaft; UDP – upper dead point; 1 – ignition moment; 2 – ejection of hot stream from forechamber

An analysis of ionized oscillograms showed that combustion in the precombustion chamber stream itself was pulsating at a frequency of approximately 5000 cps, which is considerably above the normal pulsation frequency of turbulent flame ignition. After combustion in the given zone is damped, the same analysis shows that following some delay secondary ignition occurred at normal frequency of conventional turbulent flames of approximately 1000 cps.

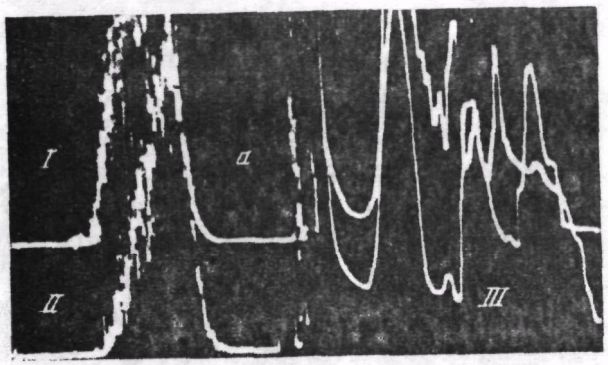
On the basis of the described observations it can be assumed that at this stage of the process in the precombustion chamber stream the following occurred according to laws governing a free stream: fresh gas was captured and underwent turbulent intermixing with the hot gas; after the primary flame of high-frequency pulsation is damped, a genuine autoignition of the trapped gas occurred which was identical with the pulsating ignition occurring during the propagation process of turbulent flames.

Fig. 4



Schlieren-cinematographic records of forechamber stream ejection (3000/sec.). At exposure C-3 the nucleus of turbulent ignition begins to appear.

Fig. 5



I - Oscillogram of ionization flow; II - ignition fluctuations in the forechamber flow; III - in the ignition nucleus
a - section of complete combustion extinction

Based on the identity of precombustion chamber ignition with the turbulent combustion mechanism it can be assumed that in such mixtures, e. g., with twice the excess air as against the theoretical value of possible turbulent combustion, rapid ignition from the precombustion chamber stream was possible. Precisely this completely removes the limitations of spark ignition in the basic PCF-ignition mechanism when difficult to ignite or totally unignitible mixtures with excess air are used.

Many technical details of the precombustion chamber system including the choice of nozzle or nozzles, which insure smooth combustion and provide sufficiently wide fuel leaning limits, will be temporarily disregarded and attention will be centered only on an important quality of the PCF system to regulate itself, or the extremely flexible control manifested by the precombustion chamber carburetor without loss of ignition effectiveness. This is a direct result of the PCF ignition mechanism itself, and results specifically from following: when the flame temperature in a precombustion chamber drops with increase in the fuel excess in the precombustion chamber mixture, the precombustion chamber stream combustibility associated with its heat control, decreases accordingly, even though the factors facilitating ignition increased simultaneously. The chemical activity of burning gases decreased as the combustion temperature in the precombustion chamber dropped, which is in accordance with the lowered concentration of active centers, such as H, O, OH in them. However, the concentration of unburned combustion products, i. e., H_2 and CO, which increased the ignitibility of fresh gas, rose simultaneously; pressure drop fell as the combustion temperature in the precombustion chamber decreased together with the velocity of the precombustion chamber stream and the volume of entrapped fresh gas. The precombustion chamber stream insensitivity controlled by the precombustion chamber mixture, which has been repeatedly checked by engine tests, considerably simplified the design of an efficient precombustion chamber carburetor.

The precombustion chamber ignition system can facilitate the ignition of lean mixtures down to idling; however such purely qualitative control is not the most economical, only because the mixture is being thinned with air. When the excess air is more than 150% of the theoretical value, a progressive drop in the economy appears caused by a drop in the rate of turbulent combustion with a drop in flame temperature. Thermal

losses caused by retarded combustion upon further leaning exceed the losses caused by flame temperature decreases. Beginning with this maximum leaning, it becomes more advantageous to reduce the power at a constant level of leaning, i.e., at constant flame temperature, by throttling, that is by applying a qualitative-quantitative combination control. Here, again, the profound difference between spark and precombustion chamber ignition systems is obvious. In the first system contamination of the air-fuel mixture by residual gases prevents the formation of a turbulent flame even with a slight degree of air excess; in the second system throttling has little effect on the initiating precombustion-chamber ignition stage of the charge, and less on the turbulent combustion propagation since both processes developed by intermixing fresh gas with combustion products.

Duration of the combustion process active stage in a maximum power course is reduced approximately 1 1/2 times in comparison with conventional spark ignition, since a turbulence created by precombustion-chamber ignition is superimposed on the natural turbulence created by filling. The significance of this factor is associated with the fact that, in accordance with the currently accepted theory of detonation "knock", it appeared primarily during the complex multi-stage process of autoignition which developed in the last portion of the charge preceding a turbulent flame front. Therefore, turbulent combustion acceleration can forestall detonation autoignition completion by creating, for example, the possibility of increasing compression under conditions of constant antidetonation fuel stability.

The idea of precombustion chamber ignition originated in the Institute of Chemical Physics in 1935 in the course of searching for a more effective method of preventing detonation ignition. Numerous experiments showed that precombustion-chamber ignition presented the possibility to increase compression ratio by 1-11/2 units without changing the full properties, or to decrease the required octane number by approximately 10 points at a given compression ratio. Accordingly, an increase in thermodynamic efficiency brought about by raising compression ratio augments the basic economic effect of the precombustion-chamber system which makes applicable the use of lean mixtures at partial charges.

The PCF-ignition system in a carburetor engine was subjected to a detailed study both in one-cylinder models[7] and in true engines[8]. A production model of a GAZ-52 automobile engine with a precombustion-chamber ignition system was built for a 3-ton truck jointly by the Gor'kii Automobile Plant and the Institute of Chemical Physics of the USSR Academy of Sciences (L. A. Gussak). The main characteristics of the engine are as follows: number of cylinders - 6; cylinder volume - 3.48 li; diameter - 82 mm; stroke length - 114 mm; compression ratio - 7.2; maximum power at 3000 rpm - 86 h.p.

Precombustion chambers with a volume of 3% of the compression chamber volume were equipped with two 2.4 mm diameter nozzles forming a 60° angle between their axes and mounted in an overhead-valve type head. The precombustion-chamber feed line was heated by exhaust gases to insure fuel vaporization. This engine did not differ outwardly or in control from a conventional engine, and did not create any additional manufacturing problems. Comparison tests were conducted with one-cylinder model engines having spark and precombustion-chamber ignition systems using 55-octane gasoline; maximum compression ratios in terms of detonation were 6.2 for the spark type and 7.2 for the precombustion-chamber ignition type. Minimal specific fuel consumption at 1200 rpm averaged 190 g/h. p. hr. for the spark-ignition and 160 g/h. p. hr for the precombustion-chamber ignition type. However, in this case the fact should be taken into consideration that the minimum consumption recorded for the precombustion-chamber engine was maintained through the entire range of partial charge. A corresponding minimum consumption recorded for the spark-ignition type was realized for a brief regime close to a maximum charge and sharply increased upon converting to throttled regimes and enriched mixtures.

Even when lean mixtures were used with spark ignition the effect was lowered to a considerable degree by the instability of the flame formation process. The dispersity caused by this in the record diagrams in subsequent cycles shown in Fig. 6 reflects the incomplete utilization of a nominal expansion degree. In contrast, the precombustion-chamber system regularly repeated the combustion course from cycle to cycle. An exhaust temperature drop to 600° or below in the precombustion-chamber engine coincided with the lower combustion temperature of lean mixtures beginning with a load of 70% of the maximum. The exhaust temperature in an engine with a spark-ignition system persisted at 900° through the entire charge range.

Precombustion Chamber-Flame Ignition in Engines with Internal Carburetion. This combination of precombustion-chamber ignition with the fuel spray injected into the cylinder presents the possibility of radically eliminating the principle disadvantages of the spark-and compression-ignited engines.

Fig. 6

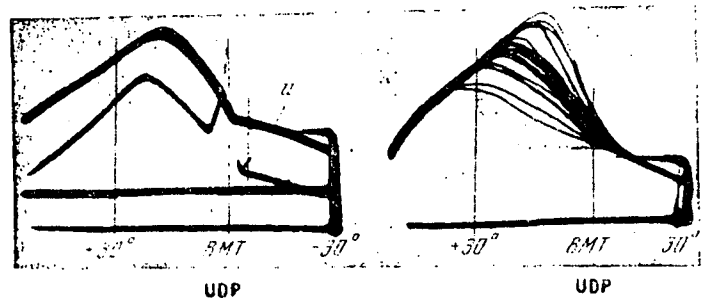


Diagram series of pressure in consecutive cycles of a motor with spark ignition and one with forechamber jet ignition operating with a mixture containing 120% air excess

Physico-chemical studies of the diesel combustion process found that it consisted of two essentially different autoignition stages and of the turbulent combustion proper; it will be shown later that the two stages were characterized by opposite requirements. Autoignition of a fuel stream occurred in a succession of "cold" flames, especially that type of chain ignition which liberated the fuel energy incompletely, and which was completed by the formation of one or more flame sources which enveloped the entire fuel charge present during the process of turbulent combustion.[9] The difference between these two stages is manifest primarily in the opposite condition requirements for fuel vaporization and mixing with the air.

Calculations showed that only about 5% vaporization of the injected fuel was necessary for the formation of the initial flame source. Vaporization of excess fuel and enhanced intermixing with air reduced the autoignition zone temperature and inhibited reaction development by prolonging the interval in autoignition period which increased the autoignition volume and formed shock waves thereby turning diesel autoignition into one approximating the type of detonation ignition in a spark-ignited engine. Vice versa, the stage of turbulent combustion depends upon the highest possible degree of fuel-gas intermixing. In fact, even with an overall excess air present there exist zones with a considerable lack of air when fuel droplets are unevenly distributed within a volume. The fuel does not burn in these zones, but undergoes pyrolysis with subsequent liberation of free carbon. In this way factors which contribute to "knocking" elimination during autoignition cause smokiness during the turbulent combustion process and vice-versa. An extremely high compression ratio or a high-octane fuel must be used in a diesel to prevent "knocking"; a considerable amount of excess air must be used to prevent smokiness; but this lowers the maximum power development.

All attempts to overcome this internal diesel process contradiction by changing ignition of the injected fuel from the autoignition type to the spark ignition type failed to yield the expected result. All proposed systems were unsuccessful, including the widely advertised systems of Hesselman engine[10] or the "Texaco process" design[11]; however, this was not due to faulty design but resulted from the very conditions created by spark ignition of a heterogeneous charge, and specifically from the fact that even very small fuel drops entering an initial ignition source sharply inhibited or made impossible the development of an ignition reaction. Calculations showed that vaporization of a fuel droplet 50-μ in diameter and raising the fuel vapor to the temperature of reaction initiation consumed 0.20 microjoule, or the equivalent of the energy of an igniting spark.

It can be stated that spark ignition was least advantageous particularly when a liquid fuel spray was present in the charge. The following

precombustion chamber system advantages becomes especially obvious here: the possible formation of a phase generating the flame source in a precombustion chamber filled with a completely vaporized fuel-air mixture coming from the precombustion-chamber carburetor accompanied by the formation of an easily-ignited combination of mixture and air from the cylinder; the possibility of igniting air and fuel spray from the precombustion chamber flow of hot gases, and of burning it in a turbulent flame. Turbulent ignition and propagation of a turbulent flame result from the intermixing of a fresh charge with the combustion products at maximum flame temperature; for this reason the presence of a drop of unvaporized fuel will have a negligible effect on the thermal balance and speed of these processes.

Accordingly, it is only with the aid of a precombustion chamber system that ignition can be effected before the beginning of any noticeable evaporation of fuel sprayed into the air immediately after being sprayed into the cylinder, thereby preventing the appearance of the pre-flame reactions of detonation ignition. In addition, this system produces completely smokeless combustion of the fuel-air mixture without excess air, leading to total cylinder volume utilization.

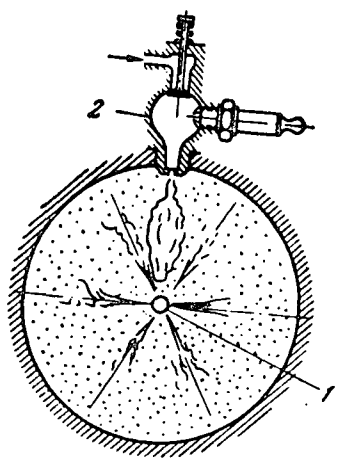
These possibilities of the precombustion chamber system used with internal carburetion have been fully realized in 102 X $114^{1\,2}$ [mm?] and 155 X $160^{1\,3}$ [mm?] one-cylinder models.

Smokeless combustion down to the theoretical fuel-air ratio can be successfully obtained with precombustion-chamber ignition by uniformly distributing the forced fuel-spray through the entire combustion chamber volume by a centrally-mounted atmomizer (cf. Fig. 7). The mean indicated pressure of 9.5 kg/cm^2 obtained with a compression ratio of 9 did not differ from the value obtained in the same cylinder operating on carbureted isooctane and spark ignition. Qualitative-quantative control yielded a minimum indicated specific fuel consumption of 140 g/h.p. hr, which approximated that of a diesel. Accordingly, judged by the maximal magnitude of indicated mean pressure and by the completeness of cylinder working volume the indexes here manifested were of a carburetor operated engine of spark ignition, but judged by fuel economy the index was one of a diesel engine. Detonation-free engine operation reduced to 25 is registered with octane number (the octane number required at compression ratio of 9 is at least 100) when ignition moments (ejecting the ignited stream from the cylinder) are sufficiently close and injection is completed.

On the other hand, the ignitibility effect is lost when the fuel is ignited from a precombustion chamber stream; the engine characteristics remain unaffected when the cetane number is changed within the range of 25 to 70; so does volatiling when the temperature of 90% fuel

evaporation changes the range of 150 to 420°. The possibility of doing away with the special requirements pertaining to the development of the "multifuel engine" realizable for the first time. In addition to the purely operational advantages of multifuel engines, their use in an automobile or tractor motor pool should result in a considerable saving in motor fuel up to 30% according to American data. The most important result of replacing existing engines with multifuel engines is probably the possibility of a more complete use of petroleum as a chemical raw material and as a source of motor fuel free from special requirements related to their chemical structure.

Fig. 7



Schematic presentation of a motor with forechamber jet ignition and internal mixture formation
1 - atomizer; 2 - forechamber

The PCF ignition system transcends the design perfection limits of existing spark ignition and diesel engines by their origin of development and by their purpose as scientific analytical extrapolations from the nature of combustion processes and from methods developed for the control of the operating process. This class of engines is based on a fundamentally new method of igniting homogeneous or heterogeneous charges in a cylinder from a stream of hot gas.

The industrial use of this class of carburetor engines, which is possible even now, will yield considerable savings in gasoline consumption without requiring increased compression ratio or the manufacture of high-octane fuel. Engines of this type with internal carburetion open possibilities of creating multifuel engines which have all the advantages of spark-ignited and compression-ignited engines, but without their disadvantages.

In conclusion it should be remembered that exhausts of engines equipped with precombustion chamber flame ignition contained no products of incomplete combustion and pyrolysis, such as carbon monoxide, carcinogens, smoke or other toxic gases, which is favorable from the viewpoint of air protection against pollution in cities saturated with automobile traffic.

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