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# U.S.S.R. LITERATURE ON AIR POLLUTION AND RELATED OCCUPATIONAL DISEASES

## Volume 7

A SURVEY

by

B. S. Levine, Ph. D.

INTRODUCTION BY VERNON G. MacKENZIE, CHIEF
DIVISION OF AIR POLLUTION, PUBLIC HEALTH SERVICE
DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE

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# U.S.S.R. LITERATURE ON AIR POLLUTION AND RELATED OCCUPATIONAL DISEASES

## Volume 7

A SURVEY

by

B. S. Levine, Ph. D.

U.S. Public Health Service
(Health, Education, and Welfare)
Research Grantee

Washington, D.C., U.S.A.

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Other pertinent conversion tables are presented on succeeding pages.

## RUSSIAN ALPHABET WITH TRANSLITERATION

| | | | | | |
|---|---|---|---|---|---|
| А | а | A a | Р | р | R r |
| Б | б | B b | С | с | S s |
| В | в | V v | Т | т | T t |
| Г | г | G g | У | у | U u |
| Д | д | D d | Ф | ф | F f |
| Е | е | E e | Х | х | Kh kh |
| Ж | ж | Zh zh | Ц | ц | Ts ts |
| З | з | Z z | Ч | ч | Ch ch |
| И | и | I i | Ш | ш | Sh sh |
| Й | й | I i | Щ | щ | Shch shch |
| К | к | K k | Ы | ы | Y y |
| Л | л | L l | Ь | ь | Mute soft sound |
| М | м | M m | Э | э | E e |
| Н | н | N n | Ю | ю | Iu iu or Yu yu |
| О | о | O o | Я | я | Ia ia or Ya ya |
| П | п | P p | | | |

# U.S.S.R. LITERATURE ON AIR POLLUTION AND RELATED OCCUPATIONAL DISEASES

## INTRODUCTION

This is the seventh in a series of English translations of the Russian literature on air pollution by Dr. Benjamin S. Levine. Through the medium of these publications and four special reports to date on "Limits of Allowable Concentrations of Atmospheric Pollutants", Dr. Levine has undertaken to make available to all who are interested in air pollution problems in this country a large resource of technical information on the subject which otherwise would not be readily available.

In this edition sixty papers deal with the medical, chemical, physical, engineering, instrumentation, and other aspects of the problem. A paper on "Carboxyhemoglobin in the Blood of Persons Directing City Traffic" reports the highest levels of blood COHb which have come to our attention. "City Street Air Pollution by Autotransport Using Ethylated Gasoline" concludes with the drastic recommendation that "the use of ethyl lead gasoline be discontinued." Volume 7 also covers a wide range of other subjects; it includes: "Effect of

Superphosphate Production Discharges on Children's Health"; "Electroencephalographic Determination of Threshold Reflex Effects of Atmospheric Pollutants", and several papers dealing with the control of pollutants from coke ovens and with techniques and instrumentation for the analysis of air pollutants.

The Public Health Service is appreciative of Dr. Levine's important contributions to the current literature on the subject of air pollution. I would recommend consideration and evaluation of this information by all concerned for possible application to their respective fields of interest.

V. G. MacKenzie

V. G. MacKenzie
Chief, Division of Air Pollution
Public Health Service
Department of Health, Education, and Welfare

## A C K N O W L E D G E M E N T.

By way of grateful acknowledgement each item in this collection is headed by the original title (in translation), name of the author or authors, institutional affiliation, and periodical or book from which the item was selected. The volume, issue number, year of publication, and inclusive pages are indicated for the convenience of those who may wish to consult the Russian original, or may wish to make reference to same.

I wish to express my grateful appreciation to Mr. Vernon G. MacKenzie, Chief of the Public Health Service Division of Air Pollution for the introduction he has written to this volume.

## F O R E W O R D.

This volume has been organized on the same basis as were Volume 5 and Volume 6 in that representation was given to a variety of phases of air pollution with emphasis on what might be designated as theoretical work of an engineering character. In his introduction Mr. MacKenzie briefly evaluated the material collected in this volume. He called attention to a few selected papers which typify the scientific awareness and directness with which U.S.S.R. scientists engaged in the field of environmental health approach the solution of some urgent and perplexing problems in air pollution. A translation of Book 5 of Professor V. A. Ryazanov's Committee is about to go to press. The material contained in that book illustrates the path-finding spirit of Professor Ryazanov's colleagues and coworkers, a tendency to self-criticism, and to a reevaluation of old values. Mr. MacKenzie quite appropriately concludes his introduction by saying: "I would recommend consideration and evaluation of this information by all concerned for possible application to their respective fields of interest." In addition to Mr. MacKenzie's recommendation the undersigned can only say that it expresses the purpose and intent of the translations past and future. In this connection it is the plan of the undersigned to conclude the series with an appropriate index volume for purposes of quick and convenient reference.

B. S. Levine, Ph. D.
3312 Northampton Street, N.W.
Washington 15, D.C.

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# Vapor Tension and Vaporization of Substances in Moving Air.

V. G. Matsak.

Gigiena i Sanitariya, No. 8, 35-41, 1957.

The purpose of this report is to place at the disposal of engineers and hygienists working in the field of sanitary technology concrete and basic data regarding vapor tension and rate of vaporization of different inorganic and organic substances in moving air. Particular emphasis is placed in this paper on substances, and especially toxic substances, most commonly used in industrial technology. Such information should allow hygienists to evaluate the potential danger associated with vaporization of toxic substances in relation to their physico-chemical and toxicological properties, and sanitary engineers to apply it in their computation of air ventilation in general and of quantitative determination of the degree of air charged with vapor of high-molecular substances, and in correctly distributing incoming and exhaust air, and in computing other means required for the sanitary improvement of labor conditions. Vapor tension of any substance within certain temperature limits can be expressed by the following logarithmic generalization:

$$\log P_n = \frac{A}{T} + B \qquad (1)$$

In which $P_n$ represents the tension of saturated vapor of a given substance in mm of mercury at absolute temperature T; A and B are constants characteristic of any substance. Handbooks dealing with such and similar phases of sanitation present tables of such constants. Determination of vapor tension by generalization (1) usually is accompanied by a tedious search for data in different handbooks and frequently leads to errors. Therefore, it is suggested that sanitary engineers use the nomograms presented in this paper, especially where a 5% error is permissible. One of the nomograms shown in Fig. 1 was proposed by Professor V. A. Kireev. In this nomogram hexane and water play the part of basic substances. The present author modified this nomogram by adding to it 16 new substances. For nitro- and amino-compounds this author constructed a special nomogram; included in the latter are also substances which follow a similar law of change in saturated vapor tension at different temperatures; this nomogram is shown in Fig. 2. A third nomogram, shown in Fig. 3, was constructed by this author for vapor tension of some melted metals and salts. Nitrobenzene and lead vapors were taken as standards in this nomogram.

Example for nomogram use: assume that it is necessary to determine saturated vapor tension of carbon tetrachloride at 20°. In the legend appended to Fig. 1 carbon tetrachloride is listed as No. 14a. Place ruler so that its edge passes through point 14a and the point corresponding to 20°. The point at which the ruler edge intersects the vertical line of vapor tension represents the vapor tension of carbon tetrachloride at 20°, it is equal very closely to 90 mm of mercury.

Assume again that it is necessary to determine the boiling temperature of methylamine; this substance is listed among the legend

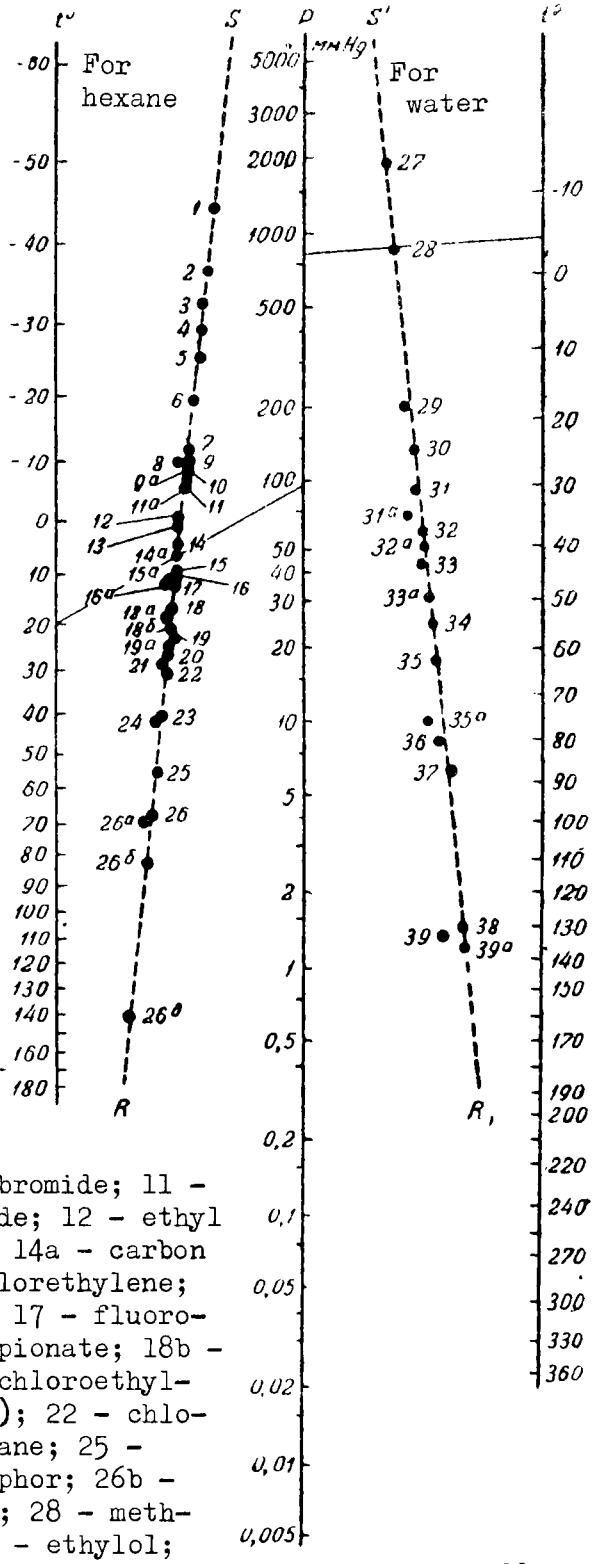
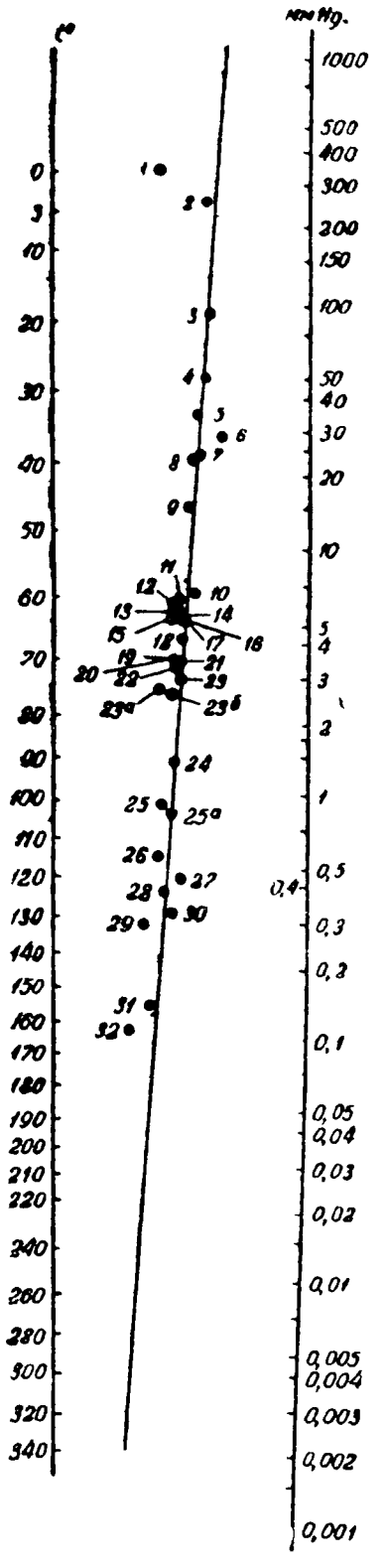



Fig. 1. Nomogram for saturated vapor tension of chemically pure substances, according to V. A. Kireev and the present author.

1 - methylsilicane; 2 - propadiene; 3 - methyl chloride; 4 - chlorovinyl; 5 - butadiene; 6 - ethyl chloride; 7 - isoprene; 8 - methyl formate; 9 - pentane; 9a - diethyl ether; 10 - ethyl bromide; 11 - methylene chloride; 11a - carbon bisulfide; 12 - ethyl formate; 13 - chloroform; 14 - n-hexane; 14a - carbon tetrachloride; 15 - benzene; 15a - trichlorethylene; 16 - ethyl acetate; 16a - dichlorethane; 17 - fluorobenzene; 18 - n-heptane; 18a - ethyl propionate; 18b - propyl acetate; 19 - toluol; 19a - tetrachloroethylene; 20 - n-octane (w); 21 - n-octane (l); 22 - chlorobenzene; 23 - bromobenzene; 24 - n-decane; 25 - iodobenzene; 26 - naphthalene; 26a - camphor; 26b - diphenyl; 26c - anthracene; 27 - ammonia; 28 - methylamine; 29 - acetone; 30 - methylol; 31 - ethylol; 31a - formic acid; 32 - water; 32a - propyl alcohol; 33 - acetic acid; 33a - butanol; 34 - propyonic acid; 35 - isobutyric acid; 35a - valeric acid; 36 - n-butylene glycol; 37 - ethylene glycol; 38 - glycerol; 39 - mercury; 39a - mercuric chloride.

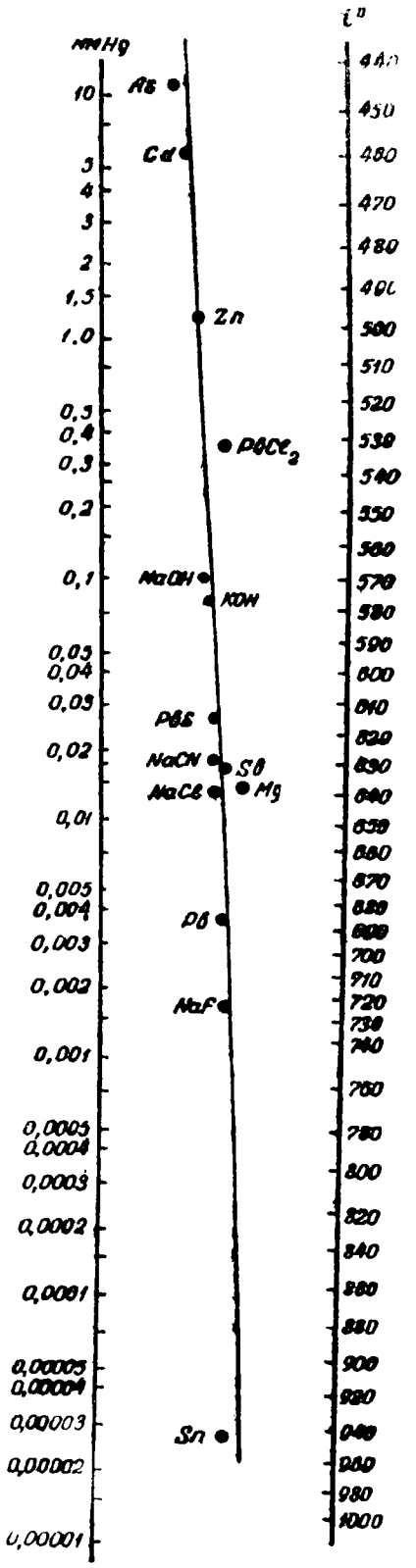
data as No. 28; place the ruler so that its edge passes through points 760 mm and point 28. It will be found that the boiling point of methylamine is $-4^{\circ}$.




The saturated vapor tension of lead at $500^{\circ}$, according to nomogram 3 amounts approximately to 0.00001 mm of mercury. This corresponds to a lead concentration of 0.0043 $mg/m^3$. However, premises in which melted lead is processed frequently contain higher lead concentrations in the air. This may be due to the fact that lead vapor condenses in the form of minute particles which gradually fall out of the air. The lead aerosol concentration depends upon the rate of such particles sedimentation and frequently exceeds the lead vapor concentration at the time of vaporization. It should be noted that some lead compounds, such as lead sulfide and lead chloride vaporize more easily than metallic lead; this can be seen in nomogram No. 3. In the air of industrial premises, where scrap lead is being melted, as in some chemical plants, the above condition may considerably enhance the concentration of lead or of lead compounds in the air. Methods presently used for the collection of air samples containing

Fig. 2. Nomogram for saturated vapor tension of chemically pure substances according to the present author.

1 - nitrogen tetroxide; 2 - isopentane; 3 - phosphorus trichloride; 4 - nitromethane; 5 - chloropicrin; 6 - sulfur chloride; 7 - tetranitromethane; 8 - arsenic trichloride; 9 - acetic anhydride; 10 - dimethylaniline; 11 - aniline; 12 - phenol; 13 - benzoyl chloride; 14 - o-toluidine; 15 - methylaniline; 16 - p-toluidine; 17 - ethylaniline; 18 - nitrobenzene; 19 - o-nitrobenzene; 20 - diethylaniline; 21 - antimony trichloride; 22 - m-nitrotoluol; 23 - p-nitrotoluol; 23a - dimethylparatoluidine; 23b - quinoline; 24 - phthalic anhydride; 25 - o-nitrotoluol; 25a - diphenyl; 26 - nitroglycerine; 27 - arsenic trioxide; 28 - dibenzylketone; 29 - n-nitroaniline; 30 - trinitrotoluol; 31 - mercuric chloride; 32 - anthraquinone.




lead are limited to the use of nitric acid as the absorber; this procedure may be satisfactory for purposes of total lead determination in the air regardless of its state - metallic or chemical compound. Knowledge of maximal vapor tension of a substance under usual meteorological conditions enables the hygienist to determine its concentration in the air. For this purpose use should be made of the generalization proposed by this author in cooperation with Professor A. K. Khotsyanov in 1944:

$$C = \frac{P_n M}{18.3} \qquad (2)$$

In this generalization C represents concentration in mg/li; M represents the molecular weight of the substance; $P_n$ represents saturated vapor density of the substance at 10 - 20° and standard atmospheric pressure.

Example: assume that vapor tension of acetic anhydride saturated at 20° = 2.7 mm of mercury, as shown in nomogram 2. It is necessary to determine its maximum possible concentration in the air. Use generalization 2, substitute 2.7 for P and 92 for M; calculation will show that maximal possible concentration of acetic anhydride at 20° amounts to 15.5 mg/li.

Where it is desired to know what concentration may form in a benzene tank after it has been drained at 10°, generalization 2 should be used as shown above.

As a rule the benzene tank is never drained completely. Some of the benzene remains in the tank, especially in the presence of rust, dust,

Fig. 3. Nomogram for saturated vapor tension of chemically pure substances according to the present author.

or other similar substances. For this reason "empty" tanks may contain saturated vapor of the original volatile substances. As the benzene vaporizes, the air temperature in the benzene tank at first drops; however, due to heat transmission by the tank walls the temperature rises and becomes equal to that of the outside air.

According to nomogram 1 saturated benzene vapor tension at $10^{\circ}$ equals 40 mm of mercury. Molecular weight of benzene is 78. To obtain corresponding concentration use generalization 2, as shown below:

$$C = \frac{P_n \cdot M}{18.3} = \frac{40 \cdot 78}{18.3} = 170 \text{ mg/li}$$

This benzene concentration is 3,400 times in excess of the limit of allowable benzene concentration specified in N 101-54. It is also in excess of its explosive concentration.

It is known that vaporization rate of water and other substances is proportional to the differences in the saturated vapor tension of the substances at the surface of the vaporized substance and its vapor tension in the surrounding area. In most instances under practical industrial conditions vaporization of non-aqueous substances in mobile air differs from water vaporization by the fact that the vaporization extends into air containing none, or only a slight amount, of the substance vapor. For instance, where benzene vaporized into air containing 1 mg of benzene per li; its vapor concentration in the air will be 20 times as great as the allowable concentration; at $20^{\circ}$ such a benzene concentration will represent only 0.3% of complete saturation.

The temperature of a substance vaporizing in moving air drops depending upon its volatility. In the case of easily volatilized substances, such as ether or carbon bisulfide, the temperature may drop by tenths of degrees. This phase of physical chemistry has been studied inadequately. The temperature drop of evaporating water has been well studied within the range of energetically moving air which approximates the temperature drop in a sling thermometer. In 1938 this author derived a generalization for the determination of temperature of evaporating water, and in 1951 he derived another generalization for the determination of temperature of surfaces of any vaporizing substance into mobile air. In instances where moving air into which a substance vaporized contained none or only negligible amounts of this substance vapor, the generalization becomes as follows:

$$0.24\ t_c = 0.24\ t_{lim} + (L + C_p \cdot t_{lit}) \frac{34.5\ P_n \cdot M}{(B - P_n)\ 1000} \qquad (3)$$

In which $t_c$ represents the temperature of the moving air at a given distance above the surface of the vaporized substance; $t_{lim}$ represents the limiting temperature toward which the surface of the vaporized substance tends; L represents the latent temperature of vaporization of the substance at 0 temperature in cal/kg; $C_p$ represents the specific heat under constant vapor pressure of a substance in cal/kg; $P_n$ represents tension of saturated vapor of the substance in mm mercury at $t_{lim}$; B represents atmospheric pressure in mm of mercury.

With the aid of this generalization determinations were made of temperatures toward which surfaces of different substances were tending during their vaporization into moving air. Determinations were then made as follows: the thermometer bulbs of the sling psychrometer were moistened with different substances, such as alcohol, chlorobenzene, aniline, etc., which have different boiling points. Results of the experiments are presented in Table 1.

TABLE 1.

Temperature of substances during evaporation into mobile air.

| Substance | Boiling point at 760 mm pressure | Air temperature | Temperature of evaporating substance | | Vapor tension in mm mercury at vaporization temperature of substance |
|---|---|---|---|---|---|
| | | | Calculated | Experimental | |
| Mercury | 360° | 20° | 19.997° | - | 0.0012 |
| Diphenyl | 255° | 20° | 19.95° | - | 0.03 |
| Naphthalene | 218° | 20° | 19.6° | 19.6° | 0.05 |
| Nitrobenzene | 210.8° | 20° | 19.1° | 19.1° | 0.22 |
| Aniline | 184° | 20° | 18.8° | 18.9° | 0.3 |
| Chlorobenzene | 132° | 20° | 12° | 13° | 6 |
| Amyl alcohol | 137.7° | 20° | 14° | 15° | 2 |
| Benzene | 80° | 20° | -5° | 0° | 17 |
| Ethyl alcohol | 78.7° | 20° | 2° | 5° | 11.6 |
| Dichlorethane | 83.7° | 20° | -2° | 1° | 16 |
| Acetone | 56.1° | 20° | -17° | - | 28 |
| Ethyl ether | 34.6° | 20° | -28° | - | 43 |

Analysis of the data in Table 1 shows the following:

a) The temperature drop during vaporization of substances having a b.p. above 250° in moving air and at standard atmospheric pressure is negligible;

b) For substances having a b.p. ranging between 184° (aniline) and 218° (naphthalene) the vaporization temperature drop ranged between 0.4 and 1.2°;

c) For substances having a b.p. ranging between 132 - 137.7°, the vaporization temperature ranged between 6 - 8°;

d) For substances having a b.p. of approximately 80° the vaporization temperature drop in dry air can be as high as 20 - 25°.

In case of low boiling substances the drop in vaporization temperature may approach computed values, if the air is dry. In the case of air containing moisture, the temperature cannot drop below the dew point.

Rate of water vaporization has been well studied. Of the many generalizations proposed for the calculation of rate of water vaporization in moving air, the one proposed by the All-Union Thermotechnical Institutes gives results most nearly approaching experimental values.

$$S = (22.9 + 17.4\ V)\ (P_n - P_1) \qquad (4)$$

In which S represents vaporization rate in $g/m^3/hr$; V represents air movement in m/sec.; $(P_n - P_1)$ represents the difference in vapor tensions of the vaporizing water and of the water vapor in the air immediately over the water surface.

The vaporization process of other substances differs from that of water vaporization in the following:

a) Vapor density of a substance differs from vapor density of water in proportion to its molecular weight. Thus, the density of benzene vapor at same atmospheric pressure is greater than that of water in the proportion of 78:18 = 4.3 in which 78 is the molecular weight of benzene and 18 is the molecular weight of water.

b) A substance normally vaporizes into air containing none or only negligible amounts of its vapor, i.e., considerably below saturation. Thus, in 1 mg/li concentration of benzene at 20° it will be only at the point of 0.3% saturation. Under such conditions the absolute value of $P_n - P_1$ approaches $P_n$, the tension of saturated vapor of the substance at its vaporization temperature.

This author hypothesized that vaporization rate of water and of other substances was similar to steam passing through openings at slight pressure

differences. Linear rate of steam passing as above described can be expressed by generalization 5.

$$Q = \sqrt{\frac{2g \cdot \Delta P}{\gamma}} \tag{5}$$

In which Q represents steam passage rate in m/sec.; g represents force of gravity acceleration which is equal to 9.8 m/sec.$^2$; $\Delta P$ represents pressure differences in kg/m$^3$; $\gamma$ represents weight of 1 m$^3$ of steam in kg.

From generalizations 4 and 5, generalization 6 was derived for the calculation of vaporization rates of substances in moving air.

$$S = (5.38 + 4.1\ V)\ P_n \sqrt{M} \tag{6}$$

In which M represents the molecular weight of the substance; other symbols have same designations as in equation (4). The correctness of this generalization was checked by tests made for the determination of vaporization rate of toluol with a b.p. 104°, chlorobenzene with a b.p. of 132°, aniline with a b.p. 184°, naphthalene with a b.p. 218° and water in air moving over the surfaces of such substances at the rate of 0.25 - 5 m/sec. Results of the tests are shown in Table 2. Analysis of data in Table 2 show that values computed by generalization 6 closely approximated experimental values. Therefore, it is suggested that gravimetric vaporization rates of substances in the air be determined using equation 6.

Temperature of vaporizing substances can be computed according to equation 3, or it can be determined approximately using Table 2 by analogy with some other substance.

Determination of saturated vapor tension at the substance's vaporization temperature can be determined with the aid of the proposed nomograms. Thus, if it is desired to determine vaporization rate of nitrobenzene spilled over an area of 2 m$^2$ at 20° air temperature with the air moving at the rate of 3 m/sec. in the absence of radiation heat, then it will be found in Table 1 that the surface vaporization temperature is 19.1°. The vapor tension of nitrobenzene at 19.1°, as indicated in nomogram No. 2, is equal to 0.22 mm of mercury. The molecular weight of nitrobenzene is 123. Substituting numerical values in equation 2 as shown below:

$$S = (5.38 + 4.1\ V)\ P_n \sqrt{M} = (5.38 + 4.1 \cdot 3)\ 0.22 \sqrt{123} = 43\ g/m^2/hr$$

TABLE 2.

Computed and experimental evaporation rate into mobile air.

| Dates | Substance | Air mobility in m per sec. | Evaporation surface in $cm^2$ | Air temperature | Temperature of wet surface | Evaporated substance in g per hour | | Difference between experimental and computed | Notes |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Experimental | Calculated | | |
| 22 June 1954 | Toluol | 5 | 12 | 22° | 7° | 3.01 | 2.98 | +1 | Air was dried in this experiment |
| | | 3 | 12 | 22° | 7° | 1.94 | 2.03 | -4.5 | |
| | | 1 | 12 | 22° | 7.1° | 1.16 | 1.09 | +6.4 | |
| | | 0.5 | 12 | 22° | 7.3° | 0.78 | 0.86 | -10 | |
| 18 - 20 May | Chlorobenzene | 5 | 12 | 17.2° | 13° | 1.92 | 1.95 | -1.5 | |
| | | 3 | 12 | 17.2° | 13° | 1.4 | 1.34 | +4.5 | |
| | | 1 | 12 | 17.2° | 13.2° | 0.775 | 0.725 | +6.9 | |
| | | 0.5 | 12 | 17.2° | 13.4° | 0.6 | 0.56 | +7.1 | |
| 27 May - 8 June | Aniline | 5 | 8 | 17.2° | 16° | 0.06 | 0.061 | -1.6 | Data of the second series of experiments are presented |
| | | 3 | 8 | 17.2° | 16° | 0.041 | 0.038 | +8 | |
| | | 1 | 8 | 17.2° | 16.2° | 0.018 | 0.02 | -10 | |
| | | 0.5 | 8 | 17.2° | 16.2° | 0.014 | 0.015 | -6.7 | |
| | | 0.25 | 8 | 17.2° | 16.2° | 0.014 | 0.013 | +6.7 | |
| 1 - 17 June | Naphthalene | 5 | 24.6 | 17.3° | 17° | 0.03 | 0.03 | 0 | By loss in weight |
| | | 5 | 24.6 | 17.3° | 17° | 0.031 | 0.03 | +3 | By analysis |
| | | 3 | 24.6 | 17.3° | 17° | 0.021 | 0.022 | -5 | By loss in weight |
| | | 3 | 24.6 | 17.3° | 17° | 0.023 | 0.022 | +5 | By analysis |
| | | 1 | 24.6 | 17.3° | 17° | 0.011 | 0.011 | 0 | By loss in weight |
| | | 1 | 24.6 | 17.3° | 17° | 0.01 | 0.011 | -10 | By analysis |
| | | 0.5 | 24.6 | 17.3° | 17° | 0.01 | 0.009 | +10 | By loss in weight |
| 25 June | Water | 5 | 12 | 22° | 11° | 0.75 | 0.76 | -1.30 | |

It will be found that the rate of nitrobenzene evaporation from an area of 2 $m^2$ amounted to 86 g/hr. Such an amount of vaporized nitrobenzene can pollute a considerable volume of air. According to N 101-54 the limit of allowable nitrobenzene concentration is 0.005 mg/li, or 1 $g/m^3$. At nitrobenzene evaporation 86 g/hr, the concentration created in the ventilated air volume will equal 17,200 $m^3$/hr.

# Deposition of Particles from a Gas Stream on an Isolated Cylinder. (Theoretical).

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The process of flowing aerosol onto a fixed obstruction is related to deposition of smoke, vapor and dust on filters made of fine-fibered materials, such as cotton, wool, mixtures of cellulose and asbestos, etc. [1]. Therefore, in theoretical deposition investigations, one usually studies the problem of aerosol particles deposition on a thin cylinder, localized in the stream and acting as fibrous material element. In spite of the numerous investigations, the process of aerosol filtration by means of fibrous materials can not be regarded as well understood from the empirical or theoretical standpoints. Experimental data in the field of filtration indicated that the process can not be explained on the basis of a single causative factor of deposition. Therefore, theoretical considerations are usually based on the effects of several causative factors, among which are: a) inertia deposition; b) deposition as a result of direct interception; c) diffusion deposition; d) gravitational or sedimentation deposition; and sometimes e) electrical deposition. The role of any one factor changes with the size of particles in any isolated section, with the flow velocity, the diameter of the filter fibers, and with other causes.

The present theoretical analysis deals with the effect of two factors: diffusion and direct interception; this is in accord with the simplest process of filtration of highly dispersed aerosols where the inertia and sedimentation deposition factors can be disregarded. The primary purpose of the present investigation is the determination of the relation between filtrational effectiveness and the size of aerosol particles. Knowledge of this is of importance since such dependence is especially characteristic of fiber filters, used in all filtration experiments. Notwithstanding certain disagreements among different authors, specific filter selectivity can be regarded as an established fact. Filters will retain (prevent the passage of) the finest and coarsest particles; on the other hand, the effectiveness of sedimentation is minimal even in the case of medium dispersal. A theory of particles deposition from an aerosol flow upon an isolated cylinder may be formed by regarding the phe-

nomenon as a special class of the orthokinetic coagulation of polydispersed sols in a state of flow. A similar theory of spherical particles coagulation was developed by Müller [3], who studied the motions of coarse aerosol particles suspended among fine particles. An analogous mechanism was in operation in the case of aerosol particle deposition on a stationary obstruction, such as a cylinder, which acts as an adsorption body.

Let us now investigate the viscous flow of gas around a cylinder of infinite length in the range of extremely small magnitudes of Reynolds numbers ($Re \leq 0.1$). This corresponds closely to practical conditions under which fibrous materials are used in most technical installations [4]. For simplicity the study will be limited to a case in which the cylinder is stationary and the linear velocity $v_o$ of the unbroken flow is constant. Assume that spherical particles of radius r of a monodispersed aerosol were carried by an air flow while they were simultaneously undergoing Brownian movement, the intensity of which was determined by diffusion coefficient D. Considering that the velocity vector $v_o$ was of constant magnitude and direction, place a cylinder of radius R perpendicular to the flow. Some particles, being carried in the direction of the flow while undergoing Brownian movement, approach the cylinder and eventually come in contact with its surface. In accordance with experimental data related to minute particles ($\leq 1 - 5\ \mu$) assume that any impact between the cylinder surface and the particles results in the adsorption of the latter [5]. The problem narrows down to the determination of the number of particles which settle in this manner per unit time and per unit length of the cylinder, given the particle and cylinder radii, the velocity of the constant flow, the concentration of aerosol particles $N_o$ at a distance from the cylinder, and the parameters of the dispersed medium characteristics.

The differential equation of forced diffusion in flow (in motion) is:

$$D \operatorname{div} \operatorname{grad} N + (v \operatorname{grad} N) = \frac{\partial N}{\partial t}$$

Under stationary conditions becomes:

$$D \operatorname{div} G + (vG) = 0 \qquad (1)$$

in which N is the particle concentration in the proximity of the cylinder and $G = \operatorname{grad} N$. It is known that in cylindrical coordinates:

$$\operatorname{div} G = \operatorname{div} \operatorname{grad} N = \frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial N}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2 N}{\partial \varphi^2} + \frac{\partial^2 N}{\partial z^2}$$

whereupon:

$$G = \text{grad } N = e_\rho \frac{\partial N}{\partial \rho} + e_\varphi \frac{1}{\rho} \frac{\partial N}{\partial \varphi} + e_z \frac{\partial N}{\partial z}$$

In this case $\partial^2 N/\partial z^2 = 0$ and $v_z = 0$. Therefore, equation (1) takes the form of:

$$D\left[\frac{1}{\rho} \frac{\partial}{\partial \rho} (\rho G_\rho) + \frac{1}{\rho} \frac{\partial}{\partial \varphi} G_\varphi\right] = - (G_\rho v_\rho + G_\varphi v_\varphi) \tag{2}$$

To solve the posed problem it is enough to establish the gradient in the immediate proximity of the cylinder. It is clear that a particle can approach the cylinder surface at a distance equal to its radius r; hence, interception takes place on a projected cylinder coaxial with the original radius a = R + r.

The present computation is limited to instances in which r < R, therefore, the range of values of $\rho$ are only slightly greater than R. Under such conditions one may assume that $G_\varphi = 0$, in which case equation (2) assumes the form of:

$$D \frac{1}{\rho} \frac{\partial}{\partial \rho} (\rho G_\rho) = - (G_\rho v_\rho)$$

or:

$$\frac{\partial}{\partial \rho} \text{In } (\rho G_\rho) = - \frac{v_\rho}{D} \tag{3}$$

Upon integration this equation becomes:

$$\text{In } (\rho G_\rho) = - \frac{1}{D} \int_R^\rho v_\rho d\rho + C \tag{4}$$

Here, a lower limit is assigned to $\rho = R$, since there is no flow on the cylinder surface and $v_\rho = 0$. Integration constant of C can be determined by examining the process of aerosol diffusion toward the cylinder in the absence of flow, N = 0 always on the surface of the cylinder and $N = N_o$ at an infinite distance from the cylinder surface. An analogous problem related to the theory of heat conductivity was solved by Carslaw and Jaeger [6] for an infinitely long cylindrical recess (void or hollow) in unlimited space. The solution is presented in the form of an integral with a Bessel function. However, its computation is cumbersome, therefore, a table of values was eventually prepared by Jaeger and Clarke [7] and by Perry and Berggren [8]. When applying the solution of the above mentioned authors to the solution of the problem of diffusion in the direction of a cylinder the following formula may prove of value:

$$\frac{dn}{dt} = DN_o LF(x)$$

in which dn/dt is the number of particles deposited per unit time and per section length L on the cylinder; $F(x)$ is a dimensionless function of argument $x = Dt/R^2$, the values of which can be found in the publications of the above mentioned authors. At $x \geq 3.0$ the process becomes static and $F(x) = \text{const.} = k$. Numerical values of constant k can be seen in a nomographic curve of the function $F(x)$. This value proved to be $k \approx 4.38$. The concentration gradient at the surface of a cylinder under static conditions can be determined easily by comparing the above solution with the usual expression for diffusion flow:

$$G_\rho = R = \frac{N_o b}{R}$$

in which $b = k/2w$. Accordingly the integration constant:

$$C = \text{In } (N_o b)$$

By substituting this expression in formula (4) the following expression is derived:

$$\text{In } (_\rho G_\rho) = -\frac{1}{D}\int_R^\rho v_\rho d\rho + \text{In } (N_o b)$$

or:

$$\frac{_\rho G_\rho}{N_o b} = \exp\left(-\frac{1}{D}\int_R^\rho v_\rho d\rho\right)$$

Accordingly:

$$G_\rho = N_o \frac{b}{\rho} \exp\left(-\frac{1}{D}\int_R^\rho v_\rho d\rho\right) \qquad (5)$$

Thus, the number of particles dn/dt settled per unit time from the flow onto the cylinder section of length L is equal to the number of particles diffused over the surface of the coagulation range. It is evident that with $\rho = a$ we have:

$$\frac{dn}{dt} = DL\int_0^{2\pi} G_\rho = a\, ad\varphi$$

Substituting $G_\rho$ at $\rho = a$ by its value as shown in formula (5):

$$\frac{dn}{dt} = DN_o Lb \int_0^{2\pi} \exp\left(-\frac{1}{D}\int_R^a v_\rho d\rho\right) d\varphi \qquad (6)$$

The deposition effectiveness $\eta$ represents the ratio between the number of particles desposited dn/dt and the number of particles carried by the flow per unit time in the direction of the projected cylinder surface perpendicular to vector $v_o$. I.e., for $\phi = 2R$, we have:

$$\eta = \frac{dn/dt}{N_o v_o \phi L} = \frac{Db}{v_o \phi} \int_0^{2\pi} \exp\left(-\frac{1}{D}\int_R^a v_\rho d\rho\right) d\varphi \qquad (7)$$

Formula (7) gives the general solution to the problem of particles deposition from a flow to a cylinder; however, it can be applied only if the species of the radial component velocity function $v_\rho$ is known. As a rule this function cannot be found around the cylinder, although it is possible to find an appropriate expression for it in a particular case. In instances of small Reynolds numbers, $v_\rho$ may be represented by Lamb's formula [9], which holds true for $Re \leq 0.1$ at $\rho < 2R$. Recently, Davies [10] used Reynolds values of 0.2, 20 and 2000, at great distances and derived a more precise expression. In the present study we are not investigating the deposition of large particles, for which $r \geq R$, and are limiting ourselves to the range of small Reynolds numbers and we need only avail ourselves of Lamb's formula for radial component of velocity, and formulate:

$$v_\rho = A \cos\varphi \left[\frac{1}{2}\left(1 - \frac{R^2}{\rho^2}\right) - \ln\frac{\rho}{R}\right] \qquad (8)$$

where:

$$A = v_o \left[0.5 + \ln\frac{8}{\gamma[Re]}\right]^{-1} \quad \text{and} \quad \gamma = 1.781072$$

Here, the Reynolds number has the value of $Re = v_o\phi/\nu$, where $\phi = 2R$ or the diameter of the cylinder, and $\nu$ is the kinematic medium viscosity. Substituting expression (8) into formula (7) and integrating, we find:

$$\eta = \frac{Db}{v_o\phi}\int_0^{2\pi} e^{-B\cos\varphi}\, d\varphi = \frac{2\pi Db}{v_o\phi} I_o(B) = \frac{2\pi b}{[Pe]} I_o(B) \qquad (9)$$

where Pe is Pekle's diffusion number; $Pe = v_o\phi/D$ and $I_o(B)$ is a Bessel function of the zero order of the first kind of imaginary argument. For the sake of brevity B in formula (9) is expressed as follows:

$$B = \frac{[Pe]}{4.0044 - 2\ \mathrm{In}\ [Re]}\left[\frac{3}{2}\beta - \frac{1}{2}\frac{\beta}{1+\beta} - (1+\beta)\ \mathrm{In}\ (1+\beta)\right] \qquad (10)$$

where $\beta = r/R$. By this procedure, the final expression characterizing deposition effectiveness is presented as an explicit function of non-dimensional criteria, Pe, Re and $\beta$.

$$\eta = f\ (Pe,\ Re,\ \beta)$$

Formula (9) can be simply expressed as:

$$\eta = kY$$

where $k = 4.38$ and:

$$Y = I_o(B)\ [Pe]^{-1}$$

A knowledge of this function helps to determine relation between the deposition effectiveness and the radius of the aerosol particles on the one hand and the flow velocity on the other.

Discussion of results. First, let us examine the variation range of individual components entering into formula (11) as applied to the actual conditions of filtrational action. Let us direct our attention to the fact that variable B, as shown in expression (10), can be represented as the product of two factors:

$$B = UV$$

In which:

$$V = \frac{3}{2}\beta - \frac{1}{2}\frac{\beta}{1+\beta} - (1+\beta)\ \mathrm{In}\ (1+\beta) \qquad (12)$$

is a function of $\beta$ only, whereas:

$$U = [Pe]\ (4.0044 - 2\ \mathrm{In}\ [Re])^{-1} \qquad (13)$$

involves two characteristics Pe and Re.

Let us examine the variation ranges of V and U resulting from the practical conditions of aerosol deposition and let us note the characteristics of variations in argument B. Some calculated values which can be regarded as typical are listed in the following table to which reference will be made later.

1. Function $V = V(\beta)$. Materials used in filtering aerosols are made of fibers generally of extremely small diameter (1 to 10 $\mu$ occasionally up to 20 $\mu$). Layers of such material assure good filtration of particles within diameter range of 0.04 - 0.08 $\mu$ and occasionally 1 - 3 $\mu$. More coarsely dispersed aerosols are separated by other methods. The indicated intervals for

$\Phi = 20\mu$; $v_o = 5$ cm/sec; Re = 0.07145

| d=2r μ | $D \cdot 10^7$ $cm^2/sec$ | β | $[V] \cdot 10^5$ | $Pe \cdot 10^{-3}$ | $U \cdot 10^{-3}$ | [B] | $I_o(B)$ | $Y \cdot 10^5$ |
|---|---|---|---|---|---|---|---|---|
| 0.04 | 380.0 | 0.002 | 0.000262 | 0.263 | 0.02835 | $7.43\ 10^{-8}$ | 1.0000 | 380 |
| 0.10 | 71.5 | 0.005 | 0.00414 | 1.399 | 0.15068 | $6.238\ 10^{-6}$ | 1.0000 | 71.5 |
| 0.40 | 8.47 | 0.020 | 0.260 | 11.806 | 1.2720 | $3.307\ 10^{-3}$ | 1.0000 | 8.47 |
| 1.00 | 2.75 | 0.050 | 3.914 | 36.36 | 3.9177 | 0.1533 | 1.0057 | 2.77 |
| 1.40 | 1.92 | 0.070 | 11.22 | 52.15 | 5.620 | 0.630 | 1.1017 | 2.12 |
| 2.00 | 1.28 | 0.100 | 29.55 | 78.28 | 8.4336 | 2.492 | 3.270 | 4.18 |
| 2.40 | 1.05 | 0.120 | 49.95 | 95.20 | 10.250 | 5.120 | 30.327 | 31.84 |
| 2.80 | 0.89 | 0.140 | 77.10 | 112.10 | 12.080 | 9.300 | 1451.40 | 1291.70 |
| 3.00 | 0.83 | 0.150 | 94.56 | 120.60 | 12.993 | 12.286 | 31620.0 | 26216.0 |

d and Φ determine the range of parameter β. Obviously, change in this magnitude generally lies within the range of 0.02 and approximately 10 and at times 20. In the present calculation we limited ourselves to the range of small β values, since for large β values Lamb's formula becomes inaccurate. Therefore, later on we will deal with cases in which particle diameters are less than the cylinder diameter, i.e., in the interval between 0.002 and 0.2. However, even values of this order cover a sufficiently wide field of filtration and formula (12) indicates that at $\beta > 0$, the value of V is negative. The absolute value of V increases with an increase in β, varying greatly in the interval of our present interest as can be judged by the above table. Here V increases by 6 orders of magnitude with an increase in β by 2 orders of magnitude.

2. Function U. The present problem is characterized by extremely large Pekle values which is a condition of the small diffusion coefficients which is an intrinsic property of aerosols. It is known that the magnitude of D can be determined by the generalization:

$$D = kTP$$

where P is the mobility for spherical particles:

$$P = \frac{\varphi(r)}{6\pi r\mu}$$

in which $\varphi(r)$ is a function of the particle radius, tending to approach unity in the case of large particles, when r is significantly greater than λ, the

length of the free path of an air molecule; $\mu$ is the air viscosity. Therefore, in a general case:

$$D = \frac{kT}{6\pi\mu} \frac{\varphi(r)}{r} = K \frac{\varphi(r)}{r}$$

At a temperature T = 293° C, when $\mu = 1.81 \times 10^{-4}$ poise, we have:

$$K = 1.176 \cdot 10^{-11} \text{ cm}^3/\text{sec}$$

This function may be expressed by the well-checked formula of Millikan [11]:

$$\varphi(r) = 1 + \frac{\lambda}{r} (0.864 + 0.29 \cdot e^{-1.25\, r/\lambda})$$

Using these formulas and taking $\lambda = 1 \times 10^{-5}$ cm, D was computed for particles of different sizes. Some typical data are listed in the table. Attention must be given to the fact that the value of D varied within a wide range (three orders of magnitudes) from the finest particles under present consideration ($r = 0.02\ \mu$) to the coarsest ($r = 1.5\ \mu$). It should be noted that we have to limit ourselves to low flow velocities, since we are dealing with a laminar current in the proximity of the cylinder. This requirement is met by extremely small Re numbers and with correspondingly low velocities not exceeding 10 cm/sec. It should be noted that the velocities used in Langmuir's theory do not exceed 3.5 cm/sec. This range of velocities corresponds closely to actual conditions of filtration through fibrous materials. Therefore, it follows generally that for a thin cylinder the product of $\emptyset v_o$ is of small value and does not exceed $\sim 0.02$ cm$^2$/sec., when values of Re attain the maximal limit, in this case 0.1. More accurate results are obtained at Re < 0.1. In spite of the small values of $\emptyset v_o$, the Pekle numbers lie between the limits of the order of several hundred and several hundred thousand (see table); moreover, as d = 2r assumes greater values, the value of Pe increases. Under conditions of the present problem changes in the Pekle numbers are of greater significance since Pe is not only a component of the expression of function U, but also of the basic formula expressing the relative deposition effectiveness [11]. The Reynolds number is of relatively less significance in relation to the magnitude of U in the interval of r values here dealt with: this is indicated by formula (13). The size of U increases slightly as Re diminishes. Generally, as particle sizes increase, the U function increases rapidly, covering a range of magnitudes of three orders in passing from the smallest particle to the largest. Values of U are small at lower velocities; however, increase in r still has the same effect.

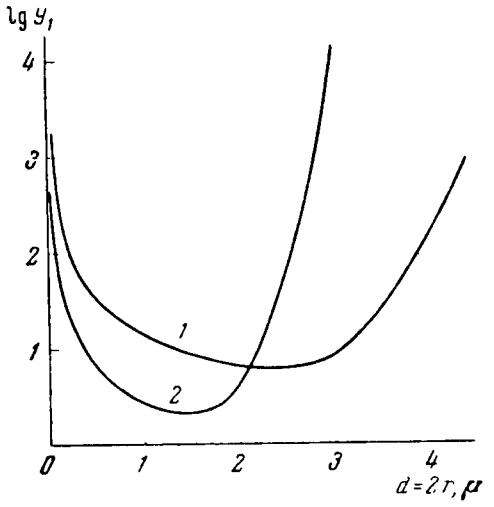
The present analysis of changes in U and V leads to the conclusion that the magnitude of B, the product of two increasing functions of particle radii, ought to increase rapidly in passing from small to large particles. Data in the table show that in the interval of present interest, i.e., of particle diameters ranging from 0.04 to 3.00 μ the value of B increases by more than eight orders of magnitude. This is reflected in considerably greater changes in the Bessel function $I_o(B)$. In view of the minuteness of B for the smaller particles under consideration $I_o(B)$ remains equal to unity for a time; it then increases, slowly at first, then sharply, until it reaches values in the order of several thousands; at this point the following asymptotic formula can be applied:

$$I_o(B) \approx e^B (2\pi B)^{-1/2}$$

Results of calculations are shown in the table. The noted changes in $I_o(B)$ are valid for other velocities and particle diameters. In practically all cases of particles with diameter $d \leq 0.4$ μ it can be assumed that $I_o(B) = 1$, whereas for $d > 2$ μ increase in the values of $I_o(B)$ will increase rapidly.

The characteristic variable, Y, here introduced which represents the relative deposition effectiveness, is expressed as the product of two functions $[Pe]^{-1}$ and $I_o(B)$; the first function decreases with the increase in $d = 2r$ and the second function increases. For small sized particles when $[Pe]^{-1}$ is of high value and $I_o(B)$ is at its minimal value $[I_o(B) = 1]$, their product is comparatively large. As d increases the reciprocal Pekle number diminishes; at the same time $I_o(B)$ increases, though slightly, so that the product (value of) Y is small. With the increase of d, the function $I_o(B)$ eventually increases sharply, and the product increases significantly. It can be concluded, therefore, that function Y has a minimum in the region of medium sized particles. Data in the table illustrate this fluctuation in deposition effectiveness. Thus, the present calculation confirms the existence of particle deposition selectivity on the surface of a cylindrical obstruction, and in a simpler basic form reflects the experimentally established selective aerosol filtration by fibrous materials.

Supplemental studies showed that the position of Y(r) minimum was a function of $v_o$ and of the particle diameter; however, we are not concerned here with an analytical expression of a functional extreme, but limit ourselves to a par-




1 - $v_o$ = 1 cm/sec; 2 - $v_o$ = 5 cm/sec; $\Phi$ = 20 μ; $y_1 = y \cdot 10^5$.

ticular example. Curves in the illustration are plots of calculations for $v_o$ = 1 cm/sec. and for $v_o$ = 5 cm/sec. at $\Phi$ = 20 μ. Calculations were made for r > 0.2 μ at points 0.2 μ apart. A comparison of the two shows that increase in velocity shifts the minimum into the region of smaller size particles and to a drawing together of the arms of the curve, while the minimal effectiveness $Y_{min}$ decreases. Calculations based on other values for cylinder diameter, point to the conclusion that depositional effectiveness was higher for small diameter cylinders than for large ones, and that increase in cylinder diameter shifted the minimum into the region of coarser particles.

The deposition of particles from a gas flow onto a cylinder has been analyzed from the viewpoint of a single process and in the present calculations there was no need to analyze it from the viewpoint of an artificially broken up combination of mechanisms, as is generally done in other similar studies. Ultimately it was found that a functional relationship existed between the deposition effectiveness and the minimum size of particles, which is in agreement with the results of qualitative tests. This functional aspect can be interpreted to a degree in the usual manner, i.e., it can be reasonably assumed that the course of the left arm of the curve was a pure function of the diffusion deposition, whereas the course of the steeply ascending right arm of the curve represented the process of direct interception. The above analysis of the behavior of the defined functions offers the possibility of determining the extent to which the above explanation held true. It appears obvious that as long as the function $I_o(B)$ remained equal to 1, Y(r) was determined solely by the magnitude of Pekle's number, i.e., it was a function of the diffusion coefficient, whereas (variable) criterion β may be considered equal zero, i.e., in this range the ultimate particle size did not affect the depositional prodess ($V \rightarrow 0$). On the other hand, rapid increase in Y beyond the minimum was connected with the predominating role of direct interception when, with the in-

crease in θ the geometric dimensions of the particles begin to manifest their effect even though the value of the diffusion coefficient remained finite.

Thus, unlike the Langmuir theory, our calculations showed that both mechanisms affected the course of the process inseparably; however, pure diffusion deposition can be separated in studies within the range of small particles. Langmuir's calculation method is of more universal application, since it includes the tangential component of velocity $v_\varphi$ with the aid of which the number of deposited particles can be determined at all times and in the presence of any mechanism when the total volume of particles is known. Under such circumstances it becomes necessary to separate and analyze each of the elementary mechanisms theoretically introduced for the purpose of simplification and supplemental assumptions. In this connection it must be admitted that factors which were taken into account, such as diffusion and the geometric particle dimensions were the factors which determined the lower possibility limit of particles deposition onto the cylinder throughout the entire range of practically significant dispersion. Thus, the present method of calculation, based on a minimum number of assumptions appears to have led to a rational explanation of the deposition mechanism, although, admittedly it did not solve completely the entire complex problem of aerosol filtration.

## Conclusions.

1. The present analysis of the static process of aerosol particles deposition onto a cylinder from a flow was made with the aid of convection diffusion differential equation; such analysis indicated that deposition effectiveness was a function of size of particles, cylinder radius (or diameter) and of the linear flow velocity. In instances of particles of finite geometric dimensions the total process can be described as a simultaneous effect of diffusion and of direct interception.

2. Deposition effectiveness as a function of particle radii has its minimum in the instance of any flow in the presence of a small Reynolds number and a moderate r/R ratio; this is in agreement with most experimental data obtained in the study of aerosol filtration.

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## Aerodynamic Investigation of Electrostatic Precipitator C-180 Model.

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(Zaporozhie Coke-Chemical Plant).

Koks i Khimiya, 1958, No. 12, 30-35.

Electrostatic tubular precipitators types C-140 and C-180 are widely used by U.S.S.R. coke-chemical plants for purifying coke gases of tar and oil. Of 68 electrostatic precipitators used by the coke-chemical industry at the beginning of 1958, 46 were type C-140 and 22 type C-180. The sulfur department of the Zaporozhie Coke-Chemical Plant has three electrostatic precipitators type C-180 which are installed in front of scrubbers. The purpose of such installation is to purify the gas from oil drops and from sublimated naphthalene carried

over by the gas as it passed through the benzene scrubbers, to prevent loss in the absorber solution effectiveness, and, consequently, in the sulfur removing operation efficiency. Basically the construction of electrostatic precipitators types C-180 and C-140 is identical. Electrostatic precipitator type C-180 is trade named because it has 180 precipitating electrodes; it is 4600 mm in diameter. Therefore, it is logical to assume that basic defects in construction and gas distribution over the precipitator cross section found in type C-180 will be essentially the same as in precipitator type C-140. With this assumption in mind, studies were made in the plant's laboratory of the aerodynamics of electrostatic precipitator type C-180 in model form. The model was made of plastic material on 1:10 scale. Air flow through the model precipitator was created by a fan which forced through the model over 1000 $m^3$ of air per hour. A full view of the model installation is presented in Fig. 1.

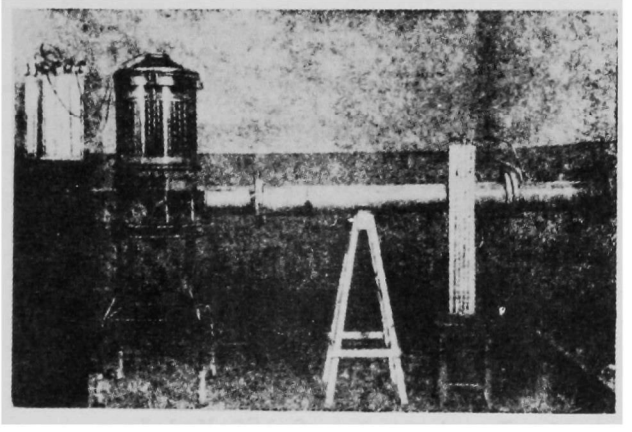


Fig. 1. Model of electrostatic precipitator C-180.

In investigating the aerodynamics of the electrostatic precipitator model a study was made first of the effect of "live" area of the lower perforated distribution screen of the inflow conduit inside the electric precipitator and of the location of the double T-shaped supports on gas flow distribution and on pressure drop reduction. Comparison of results of individual experiments was made by constructing graphs of gas flow velocities over the filter cross section and of the computed coefficients of irregular or unequal distribution [1], which was done as follows: all gas flow velocities determined in the precipitating electrodes were plotted on the ordinate in the order of increasing values; the number of electrodes of corresponding gas flow velocities were plotted along the abscissa. The resulting curve assumed the form of a broken line which depicted the gas flow distribution over the precipitating electrodes. Accordingly, as the distribution tended towards greater regularity the broken line curve tended to become a straight line, and vice versa. This method of plotting produced a true picture of gas flow distribution over the precipitating electrodes and

constituted a convenient comparison of different experimental results. In this way, it was established that the lower distribution screen constituted the basic element the correct design of which might assure even gas flow distribution over the precipitating electrodes; it was also shown that the perforated lower distribution screen originally designed for electrostatic precipitator C-180 had a resistance coefficient of $\zeta = 142$ and a "live" perforation area of 12.8%.

Perforated distribution screen No. 1 was made on the principle of geometric similitude and was tested in the model precipitator in ten experiments. Depending upon the position of the supporting beams the coefficient of unequal distribution ranged between 0.35 and 0.511, indicating that gas flow distribution over the model precipitator cross section was irregular. With prevailing high resistance coefficients the re-distribution of gas flow velocities beyond the perforated distribution screen can be considerable, thereby creating a new distribution irregularity in complete reverse order to the original irregularity of gas velocities distribution effected by the perforated screen. It was concluded, therefore, that perforated distribution screen No. 1 had a resistance coefficient of 142, and could not effect equal distribution of gas flow velocities.

Experiments were then made with distribution screen No. 2 with a "live" or perforated area of 28.0% and a corresponding resistance coefficient of $\zeta = 21.5$. This was the 82nd experiment; it yielded a coefficient of unequal distribution of 0.288 as compared with 0.509 and 0.511 in experiments 70 and 71, correspondingly, in which the previously described perforated distribution screen No. 1 was used. In addition to manifesting a superior distribution of gas flow, perforated distribution screen No. 2 effected a considerable reduction in the pressure drop.

Distribution screen No. 3 had a "live", or perforated area of 35% and a resistance coefficient of $\zeta = 11.8$. This slightly raised the coefficient of unequal distribution, clearly indicating that an increase in the "live" area of the perforated gas distribution screen above 28% lowered the gas flow distribution regularity over the electric precipitator cross section. It was shown in previous studies [2] that an inside angular shaped gas intake conduit distorted the gas distribution with the precipitator and in addition increased its resistance. Leaving the conduit at a high velocity the gas created vor-

texes which enhanced the degree of uneven gas flow distribution already existing in front of the perforated distribution screen.

Determination of gas flow velocities over the precipitating electrodes of the model had shown that due to the prevailing uneven flow distribution no gas flow passed over 13 of the precipitating electrodes, and consequently these electrodes did not participate in the gas purification. Added to this should be another 6 precipitating electrodes through which passed the supports of the broaching frame of the coronary electrodes and gas purifying function of which was nil. This made a total of 19, or 10%, of the precipitating electrodes which were dead in so far as the function of gas purification was concerned. Fig. 2 is a diagramatic presentation of gas flow velocities at all 180 precipitating electrodes based on the results obtained with the experimental precipitator model. Based on an analytical study of the velocity distribution, all gas flow velocities were classed into 5 groups, each designated by a distinguishing mark, as shown in Fig. 2. The marks in the diagram indicate that gas flow velocity distribution over the precipitating electrodes was extremely uneven. Most of the precipitating electrodes over which the gas flow passed at a rate of 10 m/sec. were grouped in the central portion of the precipitating electrodes, the distribution of which followed a more or less vertical diametrical pattern; at the extreme right, also running in vertical direction, were electrodes over which no gas flow was passing and, consequently, did not contribute to the gas purifying efficiency of the electrostatic precipitator. An attempt was then made to determine the cause of the uneven gas flow velocity distribution over the cross section of the electrostatic precipitator model.

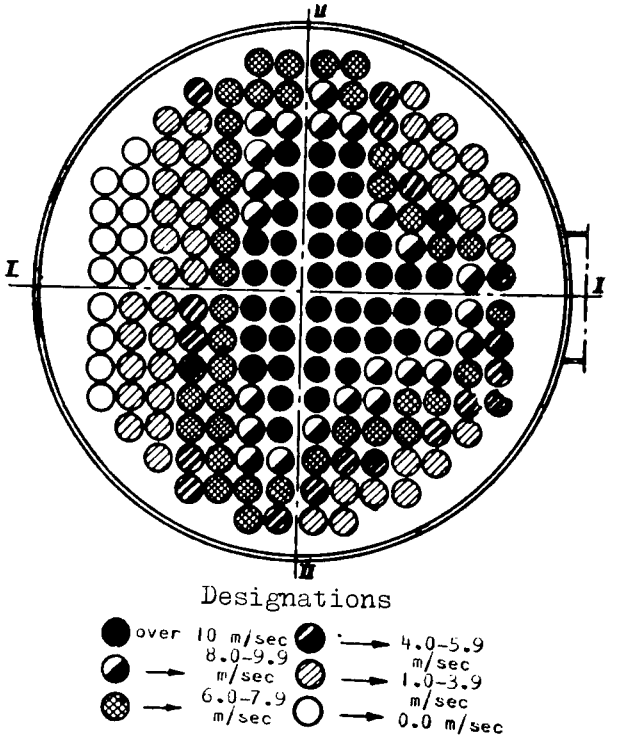



Fig. 2. Diagram of velocities distribution over the electrostatic precipitator cross section.

To accomplish this measurements were made of the dynamic pressures along the section line I-I passing through the axis of the intake conduit, and along section line II-II perpendicular to the direction of I-I, at points marked 1 and 2 below the perforated distribution screen, and at points 3 and 4 above the perforated distribution screen, using a core-type pneumometric tube, as depicted in Fig. 3. Gas flow velocity distribution curves along section II-II, where most of the inactive electrodes were located, are presented in Fig. 3. The graphs show that due to the high resistance and distortion introduced into the gas flow distribution over the precipitator cross section, and also due to the asymmetrical gas delivery by the gas conduit inside the electrostatic precipitator, areas were created at points 3 and 4 above the distribution screen where the gas flow distribution was of negative direction; these are indicated by dash-shaded areas in Fig. 3; gas flow of the opposite direction may also be seen at such points. Inactive precipitating electrodes were also found in these sections. Thus, data related to the gas flow distribution in spaces above and below the perforated distribution screen inside the electrostatic precipitator model corresponded to gas flow velocity measurements obtained at points of outflow from the precipitating electrodes, as shown at point 5 of Fig. 3, and are, therefore, in complete agreement with the theory of equalizing effect of the perforated distribution screen.

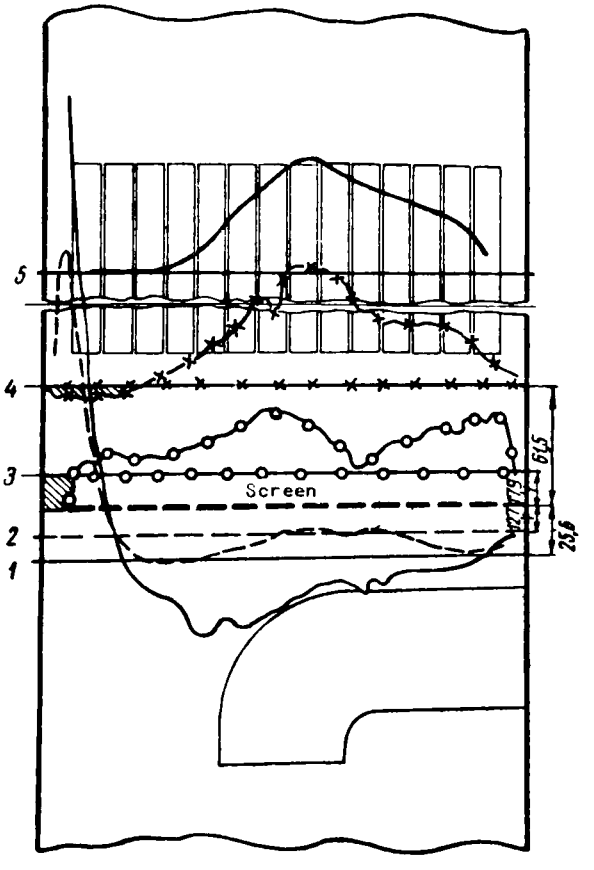



Fig. 3. Dynamic pressure distribution over cross section along II-II above and below the perforated screen.

In experiments Nos. 85 and 86 the inside downward directed section of the gas inflow conduit was removed, using the same perforated distribution tube. Measurements were made of the dynamic pressure at each precipitating electrode and the coefficient of total un-

equal distribution calculated for each experiment. On the basis of the results it was concluded that the removal of the inside downward directed angular part of the gas inflow conduit improved the gas flow distribution along the precipitator cross section considerably, lowered the apparatus resistance and obviated the conditions which were responsible for the formation of vortexes in the space below the distribution screen. Thus, in experiment No. 66, performed with the angular downward directed part of the gas inflow conduit in operation, the coefficient of unequal distribution amounted to 0.350; in experiment No. 85 (the original text has it as No. 35 B.S.L.) to 0.142, and in experiment No. 86 to 0.135. The broken line curves in Fig. 4 depict gas flow distribution in experiment No. 66 with the inside angular portion of the gas inflow conduit intact and gas flow distribution in experiment No. 86 with the inside part of the inflow conduit removed.

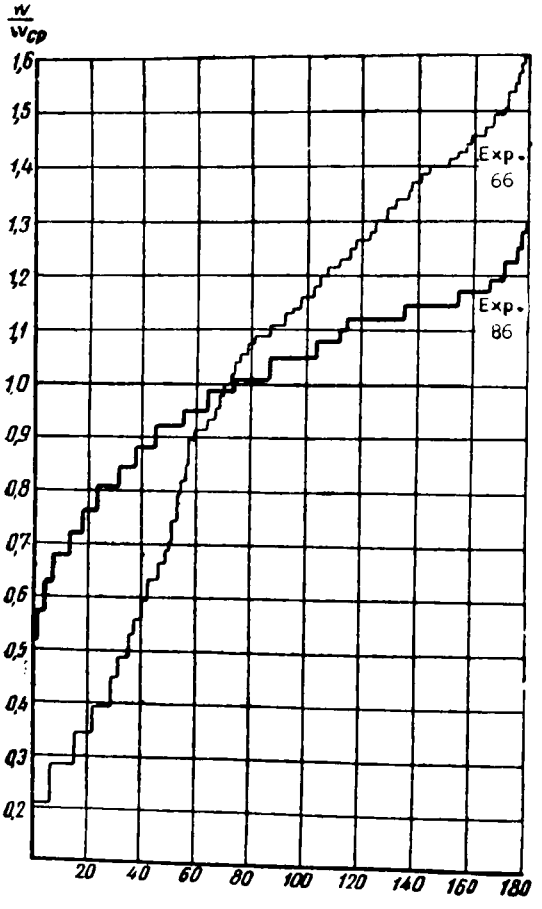



Fig. 4. Curves of velocities distribution over cross section of model electrofilter; experiment No. 66 with inside downward directed gas inflow part, and experiment No. 86 with inside inflow part removed.

The perforated gas flow distributing screens are fastened inside industrial electrostatic precipitators by means of 3 double T-shaped supports placed across the apparatus with the screens superimposed upon them. The supports under the screens form grooves or troughs along which the incoming gas flows. It is natural that such an arrangement should affect the manner of incoming gas spreading underneath the perforated screen, and as a consequence, the course of the gas distribution. The character of such effect was studied experimentally with different arrangements of the double T-shaped supports and with the inside angular downward directed part of the gas inflow conduit removed. The following 3 arrangements of the screen supports were inves-

tigated: 1) the double T-shaped supports were fastened above the perforated screen, which obviated their affecting the manner of gas distribution; 2) the double T-shaped supports were fastened below the distributing screens perpendicular to the axis of the inflowing gas; and 3) the supports were fastened below the gas distributing screens parallel to the axis of the inflowing gas. Measurements were then made of the dynamic pressure at each of the precipitating electrodes using screens types No. 1, No. 2 and No. 3 (previously described). Coefficients of unequal distribution obtained in each of the tests are listed in the table below. Data in the table show that with the use of perforated screens Nos. 2 and 3 best gas flow distribution was obtained when the double T-shaped supports were fastened below the screen in a position perpendicular to the axis of the inflow gas conduit.

| Number of screen | Location of double T-shaped supports | | |
|---|---|---|---|
| | Above the screen | Below the screen | |
| | | Parallel to the axis of gas inflow conduit | Perpendicular to inflow conduit |
| 1 | 0.296 | 0.142 | 0.258 |
| 2 | 0.132 | 0.0817 | 0.0625 |
| 3 | 0.118 | 0.102 | 0.0636 |

The primary purpose of this study was to increase the productive capacity of the electrostatic precipitator without sacrificing its gas purifying efficiency. To that end experimental data obtained with the electrostatic model type C-180 precipitator were used in computing the highest possible productivity rate with the inside part of the gas inflow conduit removed and replacing original screen No. 1 having a perforation area of 12.8% with perforated screen No. 2, tested in experiment No. 91, having a perforation area of 28% of the total screen area. Curves in Fig. 5 depict the distribution of gas flow velocities over the cross section of the model precipitator in experiment No. 67 with the electrostatic filter model type C-180 as originally designed, and in experiment No. 91 with the inside angled section of the inflow conduit removed and perforated screen No. 2 replacing original screen No. 1. Curves were constructed on the assumption that average flow velocity $W'_{av}$ through the precipitating electrode could be brought up to 2 m/sec. without adversely affecting the gas purifying efficiency of the apparatus. This was previously demonstrated by this writer's studies of the aerodynamics of electrostatic precipitator type C-140. In fact, production capacity of the precipitator was enhanced by 48.3%.

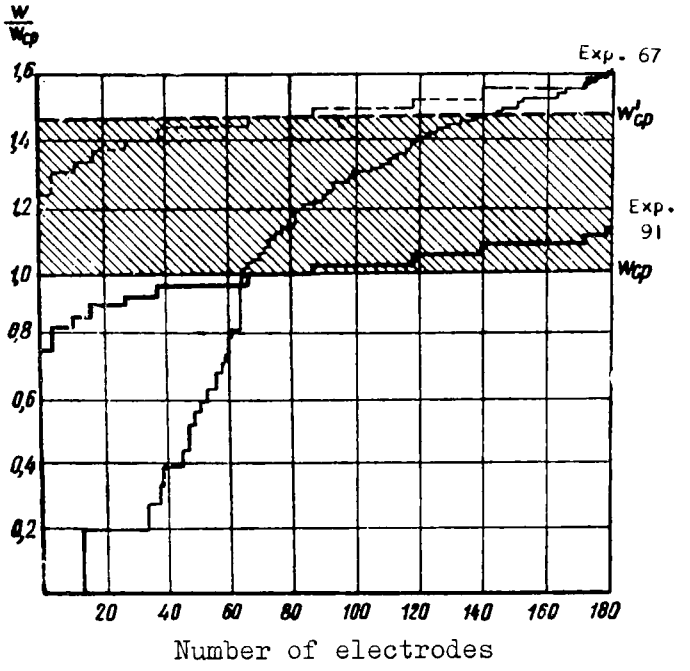
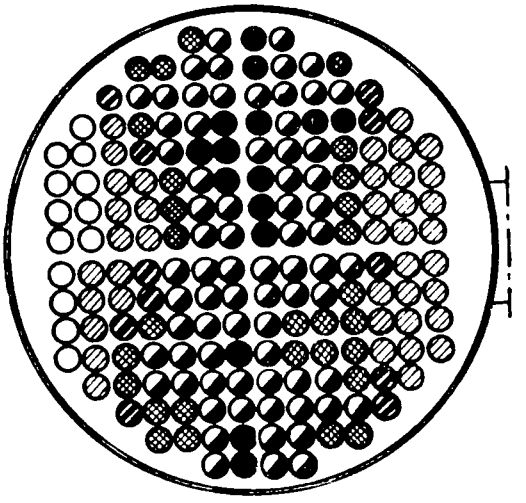


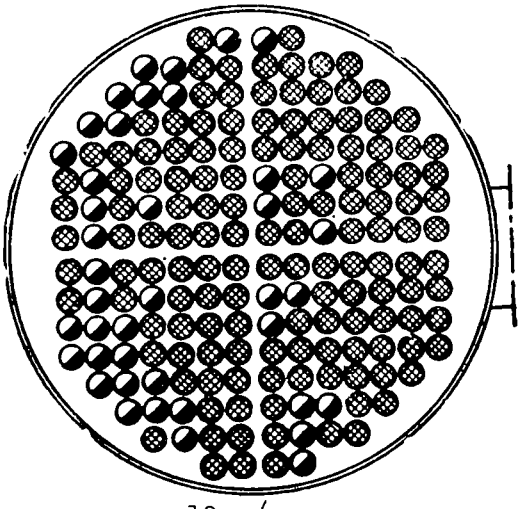

Fig. 5. Curves of velocities distribution over the model cross section. Experiment 67 with original screen (No. 1) and inside downward angled inflow part, and experiment 91 with original screen (No. 1) and inside gas inflow part removed.

The capacity of installed electrostatic precipitators fully accorded with the volume of purified gas under operating conditions in most production plants, and there appeared no need to raise the production capacity of the installations. Under such conditions the opportunity presents itself to reduce the velocity of the gas flow for the purpose of enhancing the degree of gas purification. In planning new installations and expanding activities of existing production departments full use can be made of the experience and data obtained from the study on the increase of electrostatic precipitator production capacity. As was previously mentioned, increase in productivity capacity was attained in experiment No. 91 in which the inside angular downward directed part of the gas inflowing conduit was abolished and perforated distribution screen No. 1 was replaced by screen No. 2 which had a greater percentage of "live" or perforation area; in addition, these changes had also reduced the pressure drop of the entire electrofilter. Thus, as was shown in experiment No. 67 with model electrostatic filter, the resistance, or pressure drop of the entire apparatus, which originally amounted to 125 mm of water column, was reduced to 43 mm after the introduction of the above mentioned changes. Reduction in the dynamic resistance, or pressure drop, thus amounts to 82 mm of water column in the model, which is equivalent to 4 mm of the water column in the actual commercial electrostatic precipitator, on the basis of total dynamic pressure in the industrial electrostatic filter of 16 mm of water column. Two diagrams are presented in Fig. 6 of gas flow velocity distribution over the electric filter cross section with the use of original perforated distribution screen No. 1 as obtained in experiment No. 67, and of

Experiment 67



Experiment 91



● over 10 m/sec. ⊘ 4.0-5.9 m/sec.
◕ 8.0-9.9 m/sec. ⊘ 1.0-3.9 m/sec.
◉ 6.0-7.9 m/sec. ○ 0.0 m/sec.

Fig. 6. Diagram of velocity distribution over the electrostatic precipitator model with original screen (experiment 67), and with new screen and inside projecting inflow part removed (experiment 91).

same velocity obtained in experiment No. 91 after the previously described changes have been introduced. The Zaporozhie Coke-Chemical Plant has three type C-180 electrostatic precipitators installed in front of the sulfur-removing scrubber. The previously described changes have been introduced into one of these filters, as a result of which its pressure drop was reduced and its gas purifying efficiency was increased. Unfortunately, it is not possible to present actual data regarding the reduction in pressure drop and improvement in gas purification efficiency for technical reasons. It is hoped that introduction of the same type of changes in the other 2 electrostatic filters will present the possibility of determining the summary facts in all 3 electric filters.

## Conclusions.

An aerodynamic study was made of the operation of electrostatic precipitator type C-180 on a 1:10 model basis. The purpose of the investigation was to arrive at practical changes which might effect better gas flow distribution over the electrofilter cross section and thereby reduce its pressure drop and enhance its gas purifying efficiency. As a result of such investigation the following 2 changes have been introduced: a) the inside protruding angular

downward directed part of the gas inflow conduit has been abolished; b) the original perforated gas distributing screen No. 1 which had an open area amounting to 18% of the total screen area was replaced by screen No. 2, the open area of which amounted to 28% and in some cases by screen No. 3. Characteristics of screens Nos. 2 and 3 are described below:

| | Screen No. 2 | Screen No. 3 |
|---|---|---|
| Number of perforations | 595 | 680 |
| Diameter of perforations in mm | 100 | 110 |
| Distance between center to center of perforations in mm | 160 | 160 |
| Total live or open area in percent in relation to total screen area | 28.0 | 35.0 |
| Coefficient of resistance | 21.5 | 11.8 |

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## Raising the Efficiency of Electrostatic Precipitators, Type C-140.

P. J. Kuleshov.

(Zaporozhie Coke-Chemical Plant).

Koks i Khimiya, 1956, No. 4, 45-49.

Electrostatic precipitator type C-140 designed by Giprogazoochistka (Government Institute for Designing Gas Purifying Installations) is widely used for purifying coke gas of tars. The designed capacity of the precipitator is 28,000 $nm^3$/hr, whereas the capacity of a single coke oven battery for gas is 22 - 23,000 $nm^3$/hr. [1] Thus, one electrostatic precipitator is required for cleaning gas produced by one coke oven battery. A typical coke-chemical

[1] $nm^3$ - adjusted to normal temperature and pressure.

plant consists of 4 coke oven batteries of 65 coke ovens each; it is usually equipped with 5 electrostatic precipitators: 4 in operation and 1 in reserve. Electrostatic precipitators type C-140 generally operate at high efficiency and attain a 98% coke gas purification if properly utilized. However, if type C-140 electrostatic precipitator is selected without regard to its designed capacity, or if one precipitator is used in serving 2 oven batteries, the efficiency of the installation may fall to 82%. This situation led to the present study of aerodynamic factors controlling the efficient operation of C-140 electrostatic precipitators. Tests made at the Zaporozhie Coke-Chemical Plant in 1952 - 1954 using an experimental model as well as an operating electrostatic precipitator, type C-140, have shown [1] that the flat gas distributing perforated metal screens with 12 perforations placed across the working chamber of the precipitator in front and behind the precipitating electrodes did not assure an equalized distribution of the gas flow across the precipitators: the gas passed in greater volumes through the central tubular electrodes than through those at the periphery. A charge increase in the peripheral tubular electrodes presented the possibility of raising the general productivity of the electrostatic precipitators by approximately 100%.

For the study of the gas flow distribution across the electrostatic precipitators, a model electrostatic precipitator type C-140 was made 1/20 of the original size, in accordance with all usual principles of model making. With this model a study was made of various constructional elements which normally affected the gas distribution over the cross section of electrostatic precipitators, and ways were found for increasing their efficiency. Results of that study were described [2] and incorporated into practice. New distribution screens have been installed in the Zaporozhie Coke-Chemical Plant electrostatic precipitators Nos. 1 and 3, as recommended by the author, which brought about an increase in the precipitators productivity up to 43 - 44 $nm^3/hr$, with a 97% purifying coefficient. Basic deducations arrived at during this study of gas flow distribution were confirmed independently by I. E. Idel'chik [3]. Numerous experiments were performed with individual precipitator sections and corresponding gas flow velocity charts were plotted. This graphic method of presenting gas flow distribution did not indicate the gas volume passed, which should constitute a basic characteristic of an appropriate precipitator construction. It was considered necessary to develop a criterion for the deter-

mination of gas flow distribution over the cross section of a precipitator by a single value. The comparison of individual tests and the complete evaluation of their characteristics were of importance to this study; for this purpose a convenient determinator was developed, namely, the coefficient of uneven gas flow distribution - C.U.D., which characterized the deviation in rate of gas flow from the median.

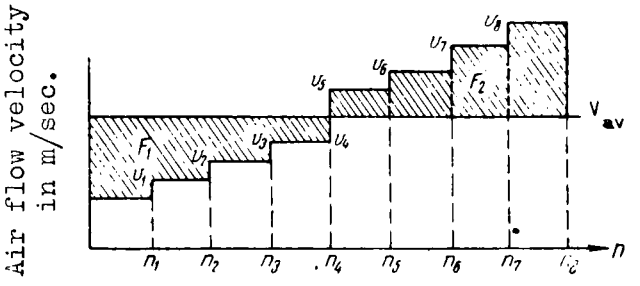


Fig. 1. Curve of air distribution over the precipitating electrodes.

In Fig. 1 the horizontal line represents the median gas flow rate ($v_{av}$) and the stepped-up curve represents actual gas flow rates. The median line and the stepped-up curve form 2 equal areas, the sum of which characterizes the degree of uneven gas rate distribution over the precipitating electrodes in any electrostatic precipitator. This relation, designated here as C.U.D., will tend towards zero with improvement in gas flow distribution.

Mathematically its value can be expressed as:

$$C.U.D. = \frac{F_1 + F_2}{v_{av} \cdot n}$$

By mathematical transformation it can be changed to:

$$C.U.D. = \frac{v_{av}(N_1 - N_2) + \Sigma v_2 - \Sigma v_1}{v_{av} \cdot n}$$

where $v_{av}$ is median velocity of gas flow in m/sec.; $N_1$ is the number of precipitating electrodes where gas flow velocity is below the median; $N_2$ is the number of precipitating electrodes where gas flow velocity exceeded the median; $\Sigma v_2$ is the sum of gas flow velocities above the median; $\Sigma v_1$ is the sum of gas flow velocities below the median; n is the number of precipitating electrodes.

Values of C.U.D. derived from this formula present a complete picture of gas flow velocities distribution across the electrostatic precipitator. This coefficient was used in the study of the effect of screen design and of other construction elements in electrostatic precipitators on the distribution of gas flow, etc. Of all construction details greatly affecting the gas distribution across electrostatic precipitators, the way of gas delivery is the most essential. The present way of gas delivery to electrostatic precipitators

type C-140 create whirling and turbulence in front of the perforated distributing screen and greatly affect gas velocity distribution. These flows and turbulences were recorded visually by a special silk thread screen and by a horizontal pneumametrical manometer tube.

Several ways of gas delivery were studied in an attempt to lessen the effect of gas delivery on gas flow velocity distribution. A lateral gas inflow was tried in connection with a distributing screen which was made previously in connection with central gas inflow resulting in poor gas flow distribution. Results are plotted in Fig. 2.

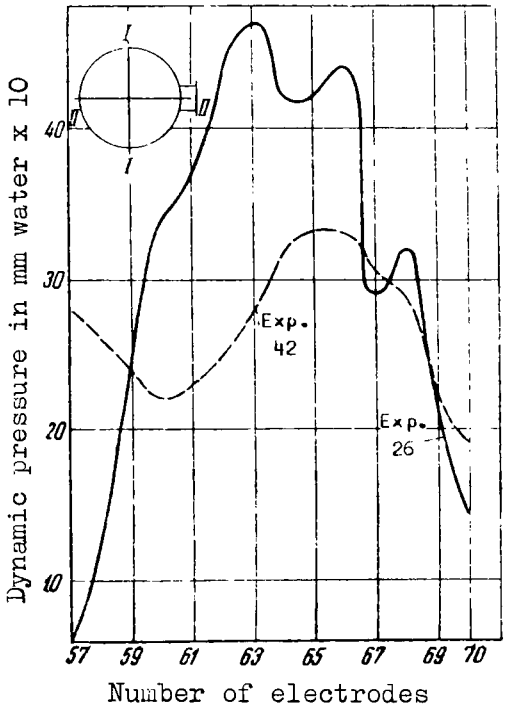


Fig. 2. Curves of dynamic air pressure distribution along I-I section; solid curve with inside gas inflow extension; dash curve with inside inflow extension removed.

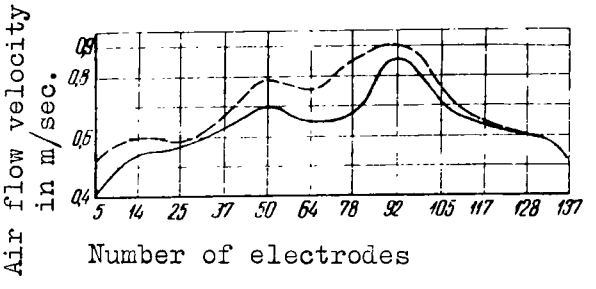


Fig. 3. Curves of velocity changes in the precipitating electrodes along II-II section; solid curves with upper perforated screen; dash curves with upper screen removed.

Curves in Fig. 2 show that distribution of gas flow velocities resulting from lateral gas inflow (Test No. 42) improved as compared with the central gas delivery (Test No. 26). This accorded with the C.U.D. values which were for Test No. 42 - 0.187 and for Test No. 26 - 0.427. Thus, installing a lateral gas delivery and eliminating the inside part of the gas inflow conduit considerably improved the gas distribution across the electrostatic precipitator without additional constructional changes; it also lessened the pressure drop of the electrostatic precipitator.

The perforated screen constituted a basic factor in gas flow distribution across the electrostatic precipitator. Therefore, most of the research was given to the study of an appropriate screen construction. Air flow velocity determinations were made at several electrostatic precipitator cross sections during its work with and without the upper section. Results of these tests,

at cross section II-II, are plotted in Fig. 3. It can be seen that both curves ran a near parallel course, indicating that the upper distributing screen had no effect on gas flow velocities. Therefore, in the Zaporozhie Coke-Chemical Plant all top distributing screens in all electrostatic precipitators have been removed, which reduced the precipitator pressure drop.

A study was made also of several types of distributing screens; with a "live" (perforation) area of geometric similitude and with "live" areas of geometric dissimilitude. Results have shown that distributing screens of the geometric similitude type did not bring about even distribution of gas flow. It has been known that in the presence of turbulence gas flow velocities at the walls of an electrostatic precipitator were considerably lower than in the center. Therefore, distributing screens of geometric similitude "live" design did not assure a uniform distribution of gas flow across the entire cross section of an electrostatic precipitator. More effective distribution of the gas flow can be achieved by the use of a screen with a resistance decreasing concentrically towards its periphery. The latter condition can be achieved either by increasing the number of perforations or their diameters concentrically in direction of the screen periphery. Thus far no one has offered a method for the calculation of such a screen.

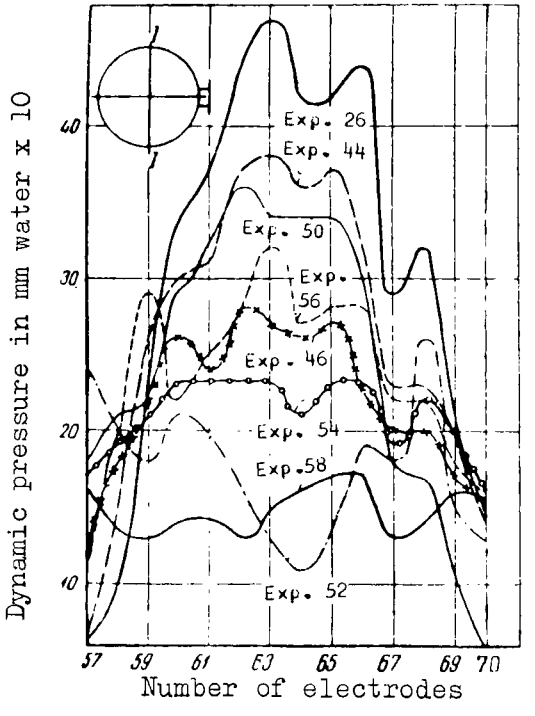


Fig. 4. Curves of dynamic pressure distribution in the precipitating electrodes.

In an attempt to equalize gas flow velocities, a screen was made in which the "live" or open area was in a reverse ratio to the corresponding gas flow velocities in front of the screen. Screens, made on this principle, were tested under regular working conditions and yielded good results. Other attempts were made to increase the gas velocities at the screen periphery by using a screen with a larger "live" or open section and with a ring-shaped slit around its periphery. The "live" section or area of openings of this screen amounted to 32%. Results of such experiments have shown that a screen of this type improved considerably the gas dis-

tribution across the electrostatic precipitator. Fig. 4 contains dynamic pressure distribution curves of the model electrostatic precipitator, which was tested with the usual screens of even, and experimental screens with variable perforation distributions and with a screen having a ring-shaped slit around its periphery. C.U.D. values of corresponding tests are listed in the following table.

Effect of "live" screen area (total perforated area) on coefficient of uneven velocity distribution.

| Experiment No. | Screen No. 4 | "Live" screen area in percent | Screen resistance coefficient | C.U.D. | Screen type |
|---|---|---|---|---|---|
| 26 | 10 | 11.6 | 177.0 | 0.427 | Screen perforations of geometric similitude |
| 44 | 1 | 15.2 | 96.5 | 0.365 | Ditto |
| 50 | 8 | 8.2 | 379.0 | 0.284 | Ditto |
| 49 | 3 | 30.0 | 18.5 | 0.235 | Ditto |
| 46 | 9 | 27.8 | 22.5 | 0.227 | Ditto |
| 52 | 5 | 22.3 | 39.6 | 0.146 | Screen perforations of geometric dissimilitude |
| 54 | 11 | 26.8 | 24.3 | 0.180 | Ditto |
| 56 | 12 | 37.9 | 9.6 | 0.237 | Ditto |
| 58-62 (averages) | 13 | 32.0 | 15.4 | 0.066 | Peripheral ring-shaped slit |

A screen with a ring-shaped peripheral slit brought about best gas distribution; it was easily machined, it lowered the pressure drop of the electrostatic precipitators, it did not require preliminary calculations; it can be recommended for all electrostatic precipitators built with a centrally located inside gas delivery. On the basis of test results obtained with a model, a screen as described just above with a ring-shaped slit at its periphery, was made and tested under actual plant conditions in one of the operating electrostatic precipitators. Data on gas velocities with this screen compared with those obtained with the old type screen were plotted in curve form in Fig. 5.

Course of the curves in Fig. 5 show that with the new type of screen gas distribution velocities across the electrostatic precipitator considerably improved, which permitted to increase its productivity by nearly 100% without lowering its gas purifying efficiency.

A supplemental study was made of the effect of fastening the lower ends of the precipitating electrodes on the productivity of the electrostatic pre-

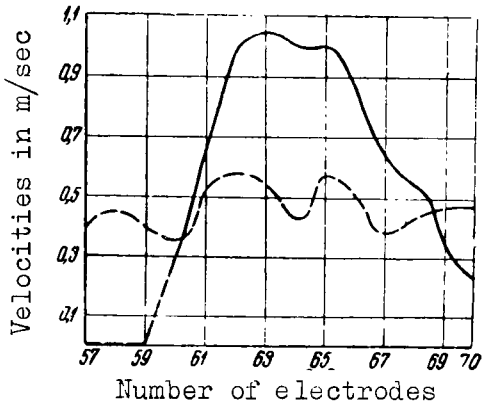


Fig. 5. Curves of air velocity distribution in the precipitating electrodes; solid curve with original (old) screen; dash line with new design distribution screen.

cipitators. It has been known that the manner in which the tubes were fixed at the bottom partition in the precipitators and the thickness of the tube walls determined the mode of the gas entry into the tubes, which had a considerable effect on the resistance coefficient of the tubes [4]. The nearer the gas entrance was to the partition wall, the smoother was the turning action of the gas flow at its entrance into the precipitating tubes and the lesser was the resistance. In the electrostatic precipitator model used in this study the lower ends of the tubular precipitating electrodes were fixed flush with the partition wall. A study was made of the gas flow distribution over its cross section. Fig. 6 shows the effect of the manner in which the tubular electrodes were fastened to the partition wall on the air or gas flow distribution over the cross section of the model electrostatic precipitator. The C.U.D. values also support the significance of the manner in which the tubular electrodes are fastened or suspended in the electrostatic precipitators. For example, in test No. 26, where the tubular electrodes were not fixed to the partition wall, the C.U.D. was equal to 0.427; in test No. 41, where the tubular electrodes were fixed to the partition wall, the C.U.D. was 0.149. The above facts show that fixing of the tubular electrodes to the partition wall significantly affected the gas distribution inside the electrostatic precipitators. This fact should be taken into consideration in the newer designs of the electrostatic precipitators.

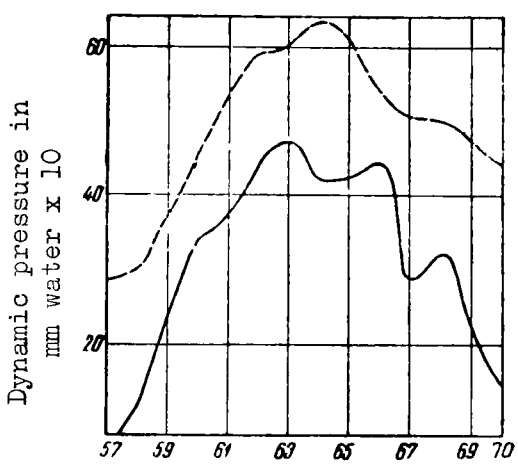


Fig. 6. Curves of air pressure distribution along section I-I; solid curve with electrodes not fixed to end wall; dash line curve with electrodes fixed to end wall.

## Conclusions.

1. The described method of evaluating uneven distribution of gas flow velocities (C.U.D. - coefficient of uneven distribution) permitted to evaluate objectively and with precision the effect of the precipitator design on the gas flow velocities distribution.

2. The upper distributing screen had no effect on the distribution of the gas flow across the electrostatic precipitator, and should be removed.

3. Removal of the gas delivery extension from inside the electrostatic precipitator reduced the pressure drop and improved the gas flow distribution across the electrostatic precipitator.

4. A distribution screen with a variable "live" area (geometric dissimilitude type) and with larger openings at its periphery considerably improved the gas flow distribution.

5. The best gas flow distribution over the electrostatic precipitator cross section was attained with a screen having a large (32%) and even "live" (opening) section over its entire area and a ring-shaped slit at its periphery. The resistance of this screen was low, it was easily machined and its installation is recommended in all industrial electrostatic precipitators [5].

6. The installation of this new type of screen in an industrial electrostatic precipitator resulted in a 100% increase in its productivity without noticeable lowering in its gas purifying efficiency. Such increases in the productivity of the electrostatic precipitators makes possible a 40% saving in equipment investment.

7. Fastening of the precipitating electrodes onto the partition walls considerably improved the gas distribution across the electrostatic precipitator and lowered its hydraulic resistance (pressure drop).

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Construction Defects in Tubular Electrostatic Precipitators (Electrofilters).

P. J. Kuleshov.

(Zaporozhie Coke-Chemical Plant).

Koks i Khimiya, 1958, No. 1, 43-46.

Electric precipitators types C-140 and C-180, used in coke-chemical plants, have many construction defects which lower their efficiency and complicate their use. The following is an analysis of their fundamental defects followed by suggestions for their elimination.

Defects in insulating boxes and insulators. Many plants recently experienced breakdowns of base insulators PO-1 while the electrostatic precipitators were operating. This was accompanied by gas ignition and consequent stoppage of the precipitators' work for long periods of time. A study of the cause of the insulators' breakdown showed that the construction of the corona-electric holders was faulty and could not maintain uninterrupted operation of the electric precipitators. The base insulators broke down due to the fact that their inner surface was in the gas atmosphere of the electric precipitator where the temperature was nearly constant. The outer surface of the insulators was heated by the steam jackets of the insulator boxes. The steam pressure was subject to common fluctuations within the conduits, and there were sporadic steam shutdowns for heating purposes. Under such fluctuations in the surrounding temperature the insulators developed cracks, filled with air and soon broke down. The air inside the insulator boxes gradually formed an explosive mixture resulting in danger of explosion by a short circuit spark at times when current tension overlapped on the surface of the base insulator. Superficial instead of careful investigation of the conditions existing inside the insulator boxes also contributed to this situation.

Gas penetration into the inside of the insulator box also occurred through leaks in its protective lining. The protective lining must be made of a high quality material, such as technical grade glycerin and litharge, which has a sufficient density and good mechanical qualities. It is clear that maintenance of strictly constant temperature is of primary importance in preventing the destruction of the base insulators. Accordingly, it is necessary to place a reducer on the heating system pipeline, so that the steam for heating the insulator box will never be cut off. This will considerably improve the working

conditions of the base insulators. Newly constructed tubular electric precipitators should be provided with an electrical heating system for the insulator boxes and should be equipped with means for regulating their temperature by remote control. At the Zaporozhie, Voroshilov and other coke-chemical plants insulators PO-1 had been replaced by a chain of 4 suspension-type insulators PTs-4.5. This change removed the cause of insulator cracking and the precipitators breakdown. The Government Institute for Desigining Gas Cleaning Installations (Giprogazo-ochistka) recently designed new electrically charged insulator boxes for electric precipitators C-7,2 with a passing through insulator PNV-35 and a chain of insulators P-4.5 or PTs-4.5. To assure a dependable operation of this particular assembly in electric precipitators types C-140 and C-180, it is recommended that the insulator boxes and the supports for the corona-electrodes be changed according to the design worked out by the "Giprogazo-ochistka" as shown in Fig. 1.

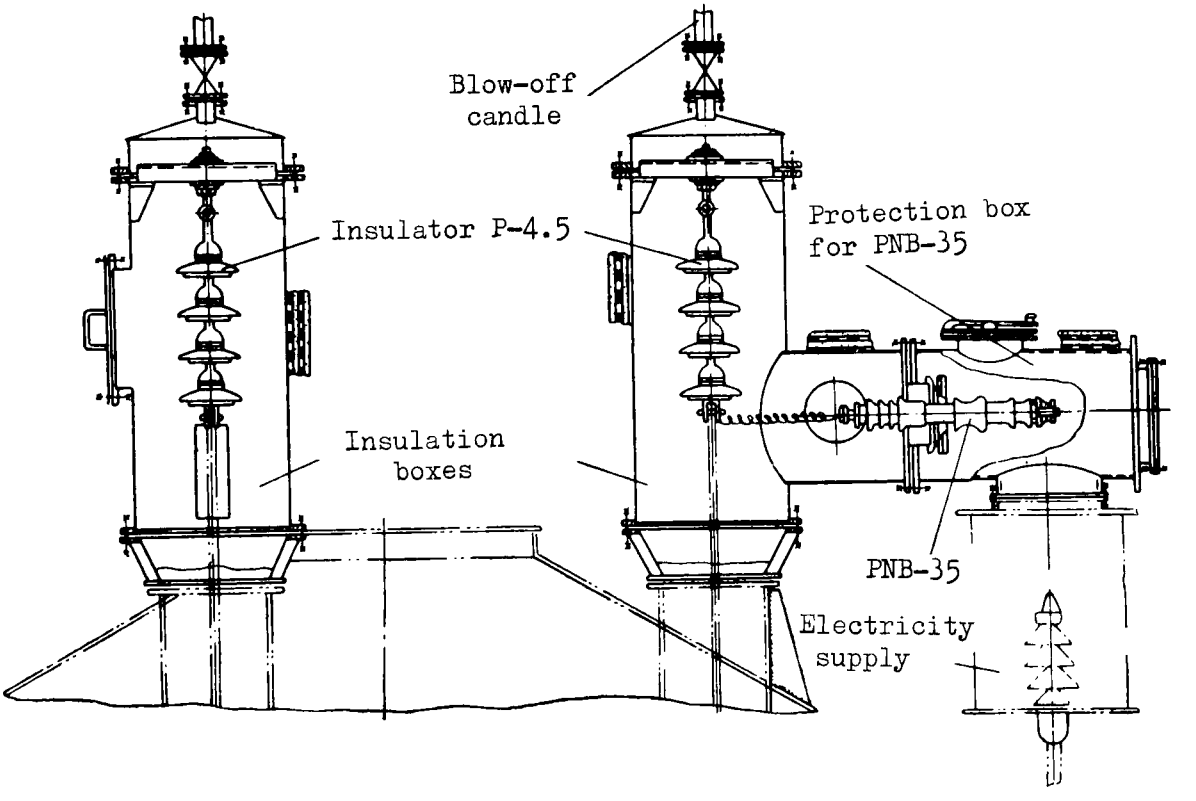


Fig. 1. Rebuilding of insulator boxes.

Corona-electrodes and field tension in electric precipitators. Not enough attention has been paid in the operation of the electric precipitators to the

degree of electric tension delivered to the electrodes. Regardless of the fact that electric precipitators types C-140 and C-180 were designed for 70 KW, most plants operated them at below 50 KW, because of previous experience with defective precipitator construction and installation, when tension exceeding 50 KW, caused spark-overs between electrodes and short circuiting. Feeding lowered electric tension to such electric precipitators served also as a reserve for efficiency improvement. According to the theory of electrostatic precipitation of suspended particles an increased tension enhanced the gas purification efficiency of the precipitator. Therefore, in installing electrostatic precipitators serious attention must be paid to the quality of the precipitating electrodes and to the proper adjustment of the corona-electrodes in order that the potential they have been designed for may be attained. This can be accomplished by using a steel wire of not less than 3.5 - 4 m/m in diameter as the corona-electrodes. Under such conditions corona ignition will occur at a potential higher than in regularly used corona-electrodes of 2 m/m in diameter. Such increase in the diameter of the corona-electrodes will also increase their mechanical stability. This is of importance to precipitator operators, since most breakdowns were due to short circuits caused by torn or burned-out corona-electrodes. The wire used for the corona-electrodes must be of highest quality, without dents or nicks, well annealed and thoroughly straightened out. Extreme electrode strain by weights or by the corona-frame should not be permitted. The weights which keep the electrodes straight shall pull freely over their guides (bearings) in the lower corona-frame and shall have carefully machined long necks for attachment to the corona-electrodes. As a rule, corona-electrodes are made of steel wire; however, in one of the precipitators of the Zaporozhie Plant the corona-electrodes were made of 2 m/m high chrome content nickel-chrome wire. They have been in operation for one year, and are still in good working condition. Corona-electrodes should not be made of low chrome content chrome-aluminum wires because of their rapid deterioration.

Inoperative precipitating electrodes. The most important construction defect in electric precipitators now in use and in those now being designed, is that not all precipitating electrodes are active gas purifiers. For example, 4 precipitating electrodes in electric precipitator type C-140, and 6 electrodes in precipitator type C-180, through which pass the weights supporting

the lower frame of the corona-electrodes, did not function as gas purifiers. Giprogazo-ochistka must take this into consideration and must make changes which would enable all precipitating electrodes of the electric precipitators to operate at full efficiency. Converting the tubes, through which pass the weight supporting the lower frame of the corona-electrodes, into precipitating electrodes would improve considerably the gas purifying operation.

Improved gas distribution in the electric precipitators. Studies made by the Zaporozhie Coke-Chemical Plant, as well as by the Girpogazo-ochistka, brought out construction faults in electric precipitators types C-140 and C-180, which caused uneven distribution of gas flow over the working cross-section of the precipitators and which lowered their efficiency. One of the construction elements that affected the distribution of the gas flow over the entire cross-section of the precipitators was the way gas entered the precipitator. The gas conduit extension inside the precipitator obstructed part of the distributing screen. A conical device installed at the entrance was supposed to equalize the gas flow over the cross-section of the precipitator; instead, it created turbulences and vortexes which aggravated the existing gas distribution uneveness. In studying the aerodynamics of the precipitator, it was found that a lateral delivery of the gas and removal of the gas delivery protruding inside of the precipitator improved the cross flow distribution of the gas. This improvement also lowered the pressure drop of the precipitators. The basic effect on gas distribution throughout the entire cross-section of the precipitator was accomplished by the distributing screen. Precipitators types C-140 and C-180 have 2 identical gas distributing screens - one in front, and another in back of the precipitating electrodes.

Elsewhere (see Koks i Khimiya, No. 4, 1956) it was shown that the upper distributing screen played no part in the gas distribution. On the contrary, by creating an additional point of resistance, this screen made servicing and access to the corona- and precipitating electrodes difficult. Therefore, it is recommended that the upper distributing screen be removed. Existing lower distributing evenly perforated screens in the precipitators did not assure proper and equal gas flow distribution across the precipitator. To remove this deficiency in the Zaporozhie Coke-Chemical Plant different screens were used with more free openings and with an additional circular slit around its edge (see Fig. 2).

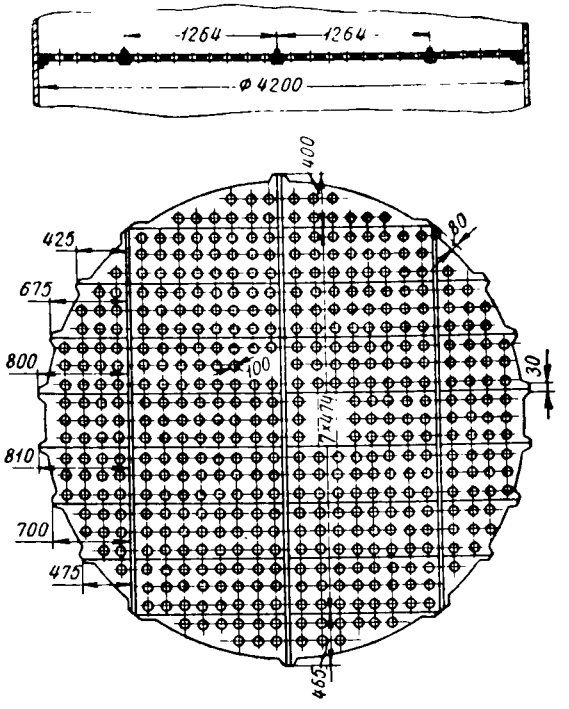


Fig. 2. New type distribution screen for electrostatic precipitator C-140.

The open gas passing area in this type of screen was 32.0% instead of 11.6% as in the old type of screen. The new screen assured an adequately equalized gas stream distribution over the entire transverse section of the precipitator and practically doubled the capacity of the precipitator without lowering its gas purifying efficiency. Moreover, this type of screen aided in the run-off of the tar and reduced the pressure drop of the precipitator. An improvement in the gas flow distribution over the cross-section of the precipitators was achieved also by installing 2 screens instead of one, as in the new C-7,2 precipitator designed by Giprogazo-ochistka. Another serious fault in the construction of the electric precipitators was the single terminal fixation of the precipitating electrodes. The upper ends of the tubular precipitating electrodes were attached to a special screen by means of seams flush with the screen body. The lower ends of these precipitating electrodes were left hanging free. The gas entering the intertubular spaces created a turbulence directly at the entrance to the precipitating electrodes. Tests showed that by fastening the lower ends of the electrodes the gas flow distribution over the enitre cross-section of the electric precipitators improved, accompanied by a lowering in the pressure drop. It must be stated here that Giprogazo-ochistka, in its latest designs of electric precipitators, removed many constructional defects in types C-140 and C-180 electric precipitators. For example, the following improvements have already been incorporated: the upper distributing screen was removed, flow distribution through the entire cross-section of the electric precipitators was improved by removing the projecting inflow conduit from inside the precipitators and installing 2 distributing screens in its place; the construction and operation of the suspended insulators were markedly improved; provision was made for a blow-off valve; the precipitator housing

was heat insulated; many additional changes were incorporated which improved considerably the efficiency of the electric precipitators.

Cut-off slide gates or valves in the electric precipitators. For shutting off the electric precipitators in case of accident, or for regularly planned repairs, the closing of the cut-off slide gates (valves) in the front and in the back of the precipitators has been done usually by hand, which consumed much time and the services of several men working simultaneously. Ignition of gas in the precipitators occurred lately in several plants necessitating their rapid shutting off. None of the plants made extra provision for such an emergency and the shutting-off of the slide gates (valves) was usually delayed. This brought to the forefront the necessity for fast servicing of the shut-off slide gates (valves) at both ends of the electric precipitators by means of an electrically operated remote control. This should expedite the shutting-off and the starting of the electric precipitators. Furthermore, this arrangement should facilitate the control of electric precipitators' operation.

Determination of oxygen content in the gas. The major drawback in exploitation of electric precipitators, which are usually placed in front of gas blowers, is the need for constant control of the gas oxygen content. A considerable vacuum, existing in this part of the gas conduit, is the cause of air sucking into the gas conduit with a formation of an explosive mixture and a consequent danger of ignition of this air and gas mixture inside the electric precipitator. For the detection of such danger the gas in the electric precipitators must be tested regularly every half-hour for oxygen content, using a hand gas analyzer type GKhP-3. Hence, a competent analyst must be always on duty in the section of the electric precipitators. Such arrangement for gas-oxygen control cannot be regarded as satisfactory because: 1) the determination of oxygen concentration in the gas test tube is usually delayed, since it takes 10 - 15 minutes to make just the analysis; 2) it requires full time duty of a special man at the electric precipitator. Instead, the explosive focus should be detected by an automatic gas analyzer at the point of air sucking in; it should be equipped with an automatic signal system adjusted for a maximum permissible oxygen content in the gas.

Gas load of the electric precipitators and their designed production capacity. The efficiency of electric precipitators is closely related to their

output capacity. The latter must be coordinated on a parallel basis with the gas output capacity of the coke ovens. Lacking this, the electric precipitators cannot be used efficiently. For example, the production capacity of electric precipitator type C-140 is 28,000 $m^3$ of normal gas. According to Giprokoks (the Government Institute for Designing Coke Plants), purification of gas received from each coke oven battery of 22,000 - 23,000 $m^3$ of normal gas required the installation of one type C-140 electric precipitator. A discrepancy will also be found upon comparing the gas producing capacity of 4 or 6 coke oven battery plants with the gas cleaning capacity of 2 or 3 electric precipitators of type C-180 used for cleaning coke gas of tar and oil.

It must be mentioned that the throttle valve at gas exits in electric precipitators designed for regulating the volume of gas passing through them were not usable, due to lack in the original design of devices or instructions for maintaining any desired volume of gas flow. This deficiency should be corrected at the earliest possible opportunity.

## Mechanization of the Gas Analyzer ORSAT.

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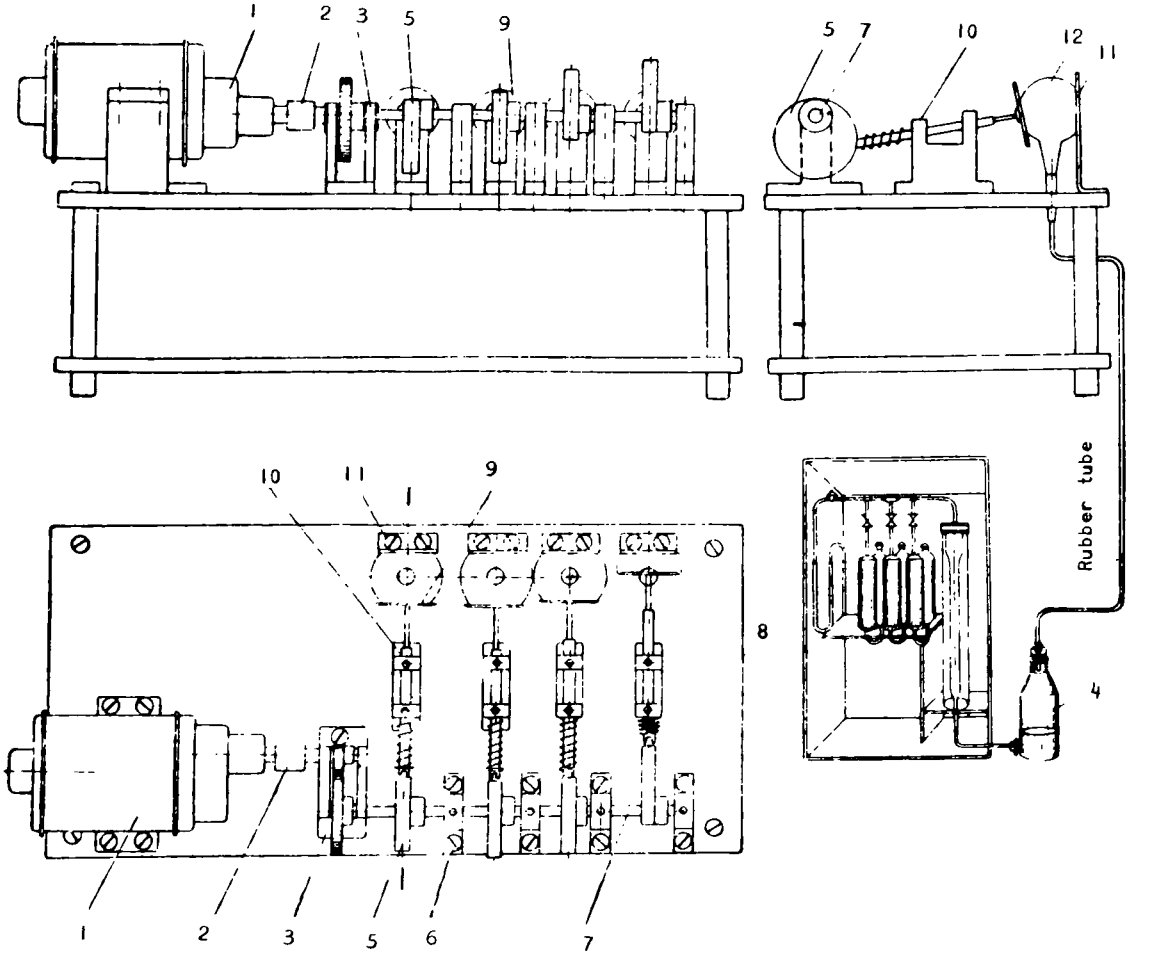
(Zaporozhie Coke-Chemical Plant).

Koks i Khimiya, 1958, No. 4, 53-54.

Control of coke oven heating is based on the analysis of its combustion products (gases) and concentrations of $CO_2$, $O_2$ and CO. The simplest and most frequently used apparatus in such control work is gas analyzer ORSAT. Transfer of the combustion gases from the burette into the absorption tube of gas analyzer ORSAT was usually done by laboratory technicians by manually lowering and raising the water pressure flask. Generally a laboratory technician working with one gas analyzer was able to make up to a maximum of 25 analyses in an 8-hour working day, thus requiring the services of at least 3 or 4 laboratory technicians to check the operation of 6 coke oven batteries. To facilitate the

work for the laboratory technicians and to increase their productivity the Zaporozhie Coke-Chemical Plant developed a method for mechanical transfer of the resulting gases from the burettes into the absorption tubes. This apparatus consists of a water pressure flask and a rubber bulb or balloon which form an assembly unit. Each gas analyzer must be equipped with such an assembly. As shown in the schematic drawing each rubber bulb is operated by a spring type pusher activated by one of several eccentric cams on a common shaft. The cams are set so that at a given time interval only one pusher is brought into action.

The device operates as follows: as shown in the schematic drawing each section of the mechanism consists of a rubber bulb (balloon) connected by a




Plan of mechanized gas analyzer work.
1 - Electric motor; 2 - coupling; 3 - reducer; 4 - water pressure flask; 5 - cam; 6 - shaft bearing; 7 - shaft; 8 - panel; 9 - pusher; 10 - pusher rod director; 11 - vertical stay; 12 - rubber ball.

rubber tube and rubber stopper to a water-filled pressure flask which in turn is connected to the burette of the ORSAT gas analyzer. As the eccentric cam advances the pusher, the latter compresses the rubber bulb forcing its air into the water pressure flask, then forcing the water into the burette, forcing the combustion gases collected in it to pass into the absorbing tubes of the gas analyzer. As the pushers gradually return to their neutral positions the rubber bulbs expand and suck in the air, thereby releasing the pressure within the flask; the replaced water returns from the burette into the pressure flask which in turn creates a partial vacuum in the burette and the gases return from the absorber apparatus into the burette. The mechanism is built to operate 4 rubber bulbs each connected to a separate pressure flask, thus servicing 4 ORSAT analyzers simultaneously, enabling one laboratory technician to attend to 4 gas analyzers and to perform about 90 analyses in an 8-hour shift. Since each gas analyzer has its own balloon, pressure flask and burette, the analyst may, if he wishes, incorporate more apparatuses into operation or he may disconnect some from the chain. Moreover, the independent operation of each unit enables the use of the setup whether all or only part of the units are in operation.

The analysis is performed as follows: the gas sample to be tested is collected manually into a calibrated burette. From the burette 30 ml of the gas is transferred, again manually, into the absorber apparatus after which the apparatus is connected with the rubber balloon. Such a procedure will prevent the sucking in of the absorbing fluid from the absorber apparatus into the burette caused by gas volume decrease as the result of partial gas absorption. The apparatus is attached to the rubber balloon when the latter is at the start of the compression stage. The remaining units are then attached consecutively as described above. After all units have been attached, the first unit is disconnected, the gas is transferred into the calibrated burette and the residual gas volume determined. The volume difference is a measure of the $CO_2$ content. Thirty ml of the gas are then transferred from the measuring burette into the second absorber apparatus for $O_2$ absorption, and the apparatus again placed into operation. An identical procedure is used in determining the CO content.

Results of the tests made with gas analyzer ORSAT manually and by the automatic procedure are listed in the following table.

Results of comparative analyses.

| Percent of absorbed $CO_2$ | | Percent of absorbed $O_2$ | |
|---|---|---|---|
| Mechanized apparatus | Manual apparatus | Mechanized apparatus | Manual apparatus |
| 24.2 | 24.0 | 0.6 | 0.8 |
| 22.6 | 22.4 | 2.2 | 2.4 |
| 8.6 | 8.6 | 4.6 | 4.4 |
| 23.8 | 23.6 | 1.4 | 1.6 |
| 6.8 | 7.0 | 5.2 | 5.4 |
| 23.2 | 23.4 | 1.4 | 1.4 |
| 6.4 | 6.4 | 4.2 | 4.4 |
| 19.4 | 19.2 | 4.8 | 5.0 |
| 24.0 | 24.2 | 1.0 | 1.2 |
| 23.8 | 23.6 | 1.4 | 1.6 |

Data in the table show that differences between the testing procedures were within error limits normal for an apparatus of this type.

Adoption of the mechanical procedure of combustion gas analysis facilitated the work of the laboratory technicians, increased their productivity, and freed one technician for other laboratory work. The apparatus is now in continuous smooth operation.

## A Venturi Apparatus for Ammonia Absorption from Coke Gas Without an Atomizer.

P. A. Semenov, Yu. V. Tumanov and O. S. Chekhov.

(From the Moscow Institute of Chemical Machine Building).

Koks i Khimiya, 1960, No. 8, 34-37.

Present day apparatus used in the chemical industry in connection with mass exchange processes are the most metal consuming and the least efficient. Attempts made by many investigators to enhance the process of mass transmission resulted in the construction of different types of apparatus operated on the direct current principle which sharply enhanced the comparative rate of phase movement and as a consequence, the apparatus efficiency. The Venturi apparatus equipped with an atomizer is a good example of same. All Venturi apparatuses can be divided into 2 groups on the basis of water introduction into the throat. To the first group belong Venturi apparatuses in which the water

is brought to the throat by pressure; to the second group belong apparatuses in which the water is injected into the throat by the gas flow itself (see Fig. 1). A Venturi apparatus without the atomizer feature has many advantages over absorbers in which the liquid is supplied by pressure. Among such advantages the following are the most important: 1) the simplicity and compactness of the construction due to the fact that the absorber and separator are combined into one feature; 2) absence of the sprayer and of the supplemental parts such as delivery pumps, intermediate containers, communications, etc.; 3) the ease with which circulation of the liquid can be attained by the overflow attachment (see Fig. 1); 4) the ease with which a many-stage apparatus can be assembled from the construction parts shown in Fig. 1 without resorting to additional equipment when it is necessary to separate the spray from the water delivery at different stages.

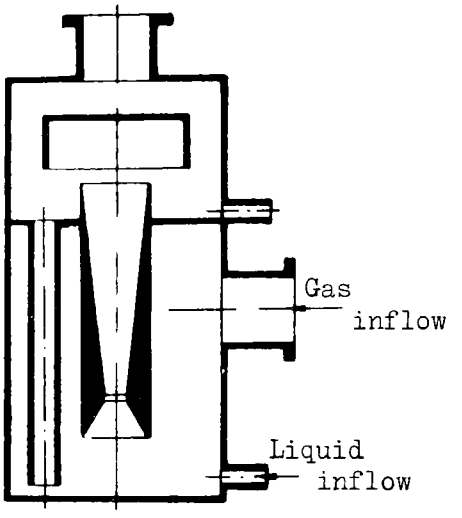



Fig. 1. Basic plan of spray-free Venturi absorber.

On the basis of these advantages it can be recommended that an atomizer-free Venturi be constructed for wide acceptance by many industrial production plants and particularly by those which deal with suspended dust-containing gases or with gas-liquid systems which form sediments in the course of processing [1]. Among mass exchange processes accompanied by sediment formation the most widely used is absorption of ammonia from coke gas by a weak solution of sulfuric acid, which forms crystalline ammonium sulfate separated in the absorption process. Bubblers in use at present in connection with this process are bulky, cumbersome and are characterized by a pressure drop of 500 - 600 mm of water.

It had been suggested that the Venturi absorber equipped with the pressure method of liquid supply into its throat be employed for the intensification of the rate of ammonia absorption from coke gas. Results of experiments performed by these authors along the above-suggested lines indicated that the Venturi absorber possessed a number of advantages over the bubbler. However, the use of the Venturi in its present construction can not be applied to the gas puri-

fication process under consideration because the ammonium sulfate crystals separated from the solution invariably clogged the atomizer and all connections leading from it. On the other hand, methods could be found to eliminate the separation of the ammonium sulfate crystals as suggested by M. D. Kuznetsov and others, by preventing the solution from reaching the point of saturation. The attainment of this necessitated complication of the system because supplementary parts must be added to the installation for the solution evaporation and crystallization. This invariably leads to an increase in the size of the installation which is the complete opposite of the principles of simplicity and compactness characteristic of the Venturi absorber. The same authors suggested that the process of absorption be accomplished in two steps or stages. If this principle is to be followed the installation would be even more complex than the bubbler installation and its dimensions would be still bulkier. In addition, there is no guarantee that danger of the atomizer clogging by foreign and adventitious solid particles would be eliminated. Above considerations led the present authors to conclude that the process of ammonia absorption from coke gas by sulfuric acid could be best accomplished by means of Venturi absorbers minus the atomizers in which the injection liquid was carried by the gas flow itself. Therefore, a study was made of the Venturi apparatus built on such principles. As a first step a study was made of mass transmission in the gaseous phase by the method of water absorption of ammonia from the air-ammonia mixture. Simultaneously with the mass transmission a study was made of the apparatus hydraulic pressure (pressure drop) in relation to the flow rate of the gas through the Venturi throat (w) and rate of spray (L/G). Ammonia concentration changed upon entering the apparatus within the limits of 0.5 - 2.0% by volume. Studies were conducted within velocity limits of air-ammonia mixture in the Venturi tube throat ranging from 30.0 to 72.5 m/sec. and spray changes ranging between 0.3 and 10.0 li/nm$^3$ of the gas. Air consumption was determined by pressure transmission to a normal diaphragm set at a sharp angle. Fluid consumption was recorded by a flowmeter. Ammonia was delivered from a gas pressure tank controlled by a needle valve and a flowmeter. Every experiment was evaluated on the basis of materials used and produced. Three types of Venturi apparatus were investigated in which the conic diffusor angles differed. The throat diameter in each of the Venturi apparatuses measured 20 mm, length of throat 3 mm, and the conic diffusor

angles were correspondingly 8, 17 and 30°. Results of experiments with mass transmission indicated that with value of L/G equal in all cases and rate of gas $w_r$ the productivity coefficient of the apparatus in all three instances was the same, indicating that the conical diffusor angle had no effect on the degree of ammonia absorption as shown by curves in Fig. 2. The dash curve in this figure is a plot of the functional relationship between productivity coefficient and gas flow rate in tests with rate of ammonia absorption by a solution of sulfuric acid. Concentration of sulfuric acid was 6.8%, rate of spray 0.65 li/nm$^3$. A comparison of this curve with a similar curve produced when water instead of sulfuric acid was used under identical conditions of spray rate indicated that in both cases the productivity coefficient had nearly identical values, or to be exact, in case of sulfuric acid it rose by 5% only.

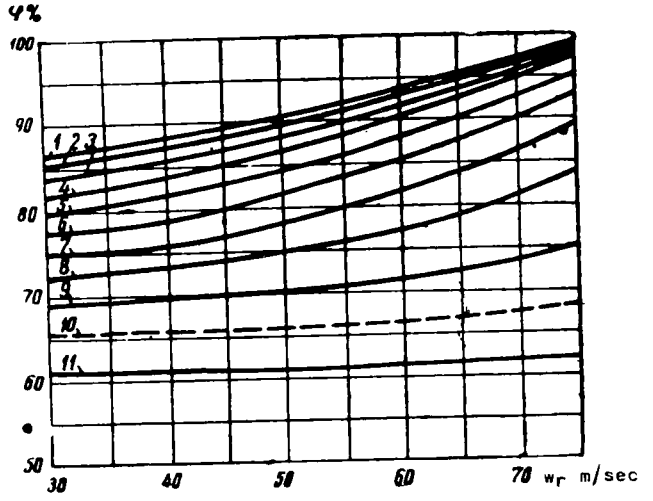



Fig. 2. Functional relation between coefficient of productivity efficiency and gas flow rate inside the apparatus. Solid curves - ammonia absorption by water; dash curve - ammonia absorption by acid.
Spray L/G = li/nm$^3$: 1 - 10; 2 - 9; 3 - 8; 4 - 7; 5 - 6; 6 - 5; 7 - 4; 8 - 3; 9 - 2; 10 and 11 - 0.65.

M. D. Kuznetsov and collaborators [2] studied ammonia absorption from coke gas by an ammonium sulfate solution acidified with 6.0 - 6.5% $H_2SO_4$ and attained a 91 - 99.8% absorption accompanied by low rate of water consumption ranging between 0.35 - 1.1 li/nm$^3$. The solution acidity gradually fell to 4.0 - 4.5%. The original ammonia concentration in the gas was ≈ 10 g/nm$^3$. These authors noted a contradiction in the correspondence between the data and the rate of absorption as recorded by those authors in the report cited.

Thus, a simple check calculation indicated that with a rate of liquid consumption amounting to 0.35 li/nm$^3$ the reported rate of gas absorption ranging between 91 - 92% would be unobtainable even in instances in which the entire acid would enter into the reaction, and that under such conditions maximum degree of gas absorption would range between 79 - 80% and never above.

On the other hand, if the acid concentration were 4.0 - 4.5%, as shown by those authors, then with a rate of liquid consumption equal to 0.35 li/nm$^3$, the rate of absorption should not exceed 34%, at rate of liquid consumption of 0.65 li/nm$^3$ the rate of gas absorption should not exceed 56%, and at the rate of liquid consumption amounting to 1.1 li/nm$^3$ the gas absorption should not exceed 95%. Accordingly, the data on mass transmission obtained with experiments in water absorption of ammonia can be applied with a reasonable degree of accuracy to ammonia absorption with weak solutions of sulfuric acid.

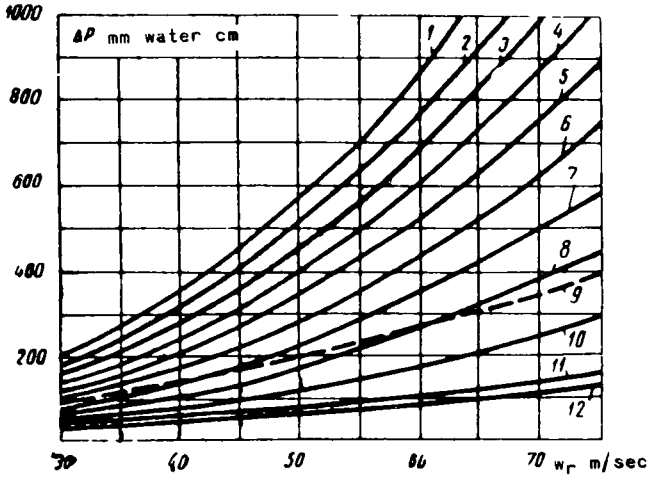



Fig. 3. Functional relation between pressure drop loss and gas flow rate. Solid curves - pressure drop of spray-free absorber; dash curve - absorber pressure drop according to M. D. Kuznetsov.
Spray L/G = li/nm$^3$: 1 - 10; 2 - 9; 3 - 8; 4 - 7; 5 - 6; 6 - 5; 7 - 4; 8 - 3; 9 and 12 - 0.65; 10 - 2; 11 - 1.

Fig. 3 contains curves representing functional relationships between the apparatus pressure drop and the rate of gas passing through a Venturi apparatus having a conic diffusor angle of 8°. Each curve in this graph represents a constant value of L/G. The dash curve represents the functional relationship between the apparatus pressure drop and the rate of gas flow at a constant water spray consumption amounting to 0.65 li/nm$^3$ as shown by the data of M. D. Kuznetsov and others. Curves in the figure indicate that at constant rate of water spray consumption the pressure drop recommended by Kuznetsov and his collaborators is 2 to 3 times as high depending on the particular rate of water spray consumption. It should be noted here that in the experiments here reported determinations were made of the resistance of the Venturi tube and of the separate construction of the apparatus, whereas in the experiments of Kuznetsov and his collaborators the cyclone resistance was not taken into consideration when determining total loss of pressure. Accordingly, the true difference in the results should be even greater. The effect of increase in the conus diffusor angle on the resistance (pressure drop) of the apparatus at gas flow rate of 40.0 m/sec. is shown in Fig. 4. The course of curves in

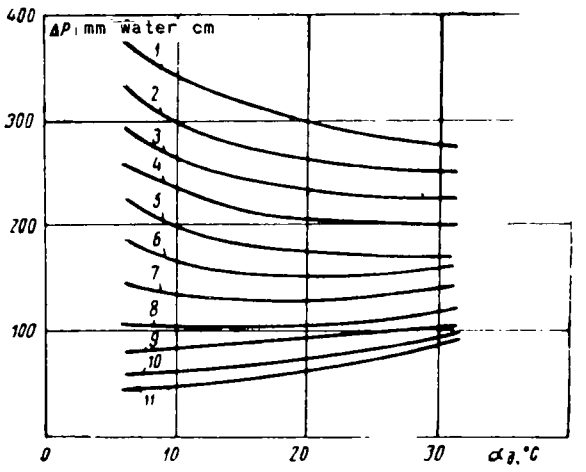



Fig. 4. Effect of diffusor conus angle on the pressure drop of absorber with a Venturi spray tube. Spray L/G = li/nm$^3$: 1 - 10; 2 - 9; 3 - 8; 4 - 7; 5 - 6; 6 - 5; 7 - 4; 8 - 3; 9 - 2; 10 - 1; 11 - 0.5.

that figure shows that with the increase of $\alpha_d$ within the range of low spray resistance slightly increased and dropped slightly within the range of high spray values. Similar results were obtained in studies with different rates of water spray consumption. It should also be noted that with an increase in the volume and velocity of the spray loss of pressure increased considerably with the increase in the in the conus diffusor angle.

The fact that resistance in the atomizer tube falls with the increase in the conus diffusor angle suggests that an angle of $\alpha_d = 30^\circ$ should be used in all types of Venturi absorbers operating at spray density exceeding 3 - 4 li/nm$^3$, since this resulted in a reduced loss in pressure and smaller apparatus dimensions. A comparison of the data obtained on mass exchange and pressure fall in the apparatus leads to the conclusion that ammonia absorption from coke gases should not be conducted at high gas flow rates from the viewpoint of energy consumption since the productivity coefficient of the apparatus increased to an insignificant degree whereas the pressure drop sharply rose. For example, at L/G = 10 li/nm$^3$ and $w_r$ = 40 m/sec., $\varphi$ = 88% and $\Delta p$ = 350 mm of water, with similar L/G and $w_r$ = 60 m/sec., $\varphi$ = 94% and $\Delta p$ = 860 mm of water.

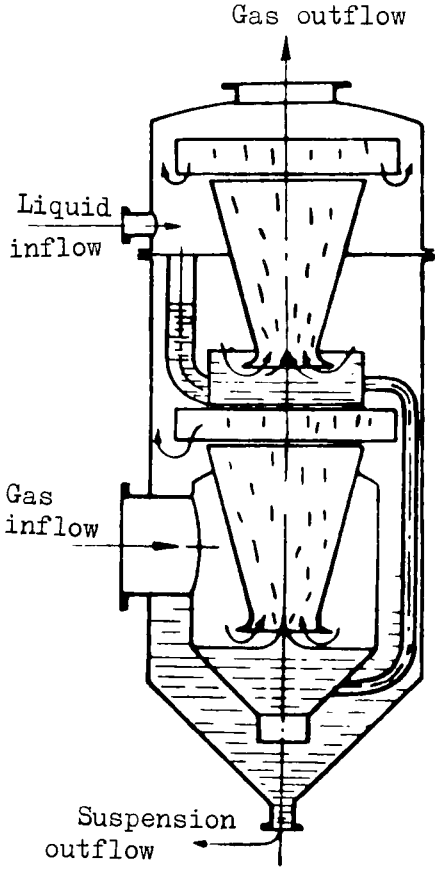



Fig. 5. Construction plan of a two-stage Venturi absorber for sulfuric acid absorption of ammonia from coke gas.

Ammonia absorption from coke gas by sulfuric acid is most advantageous when performed in two stages; at rate of gas flow through the Venturi throat amounting to 40.0 m/sec. and rate of water spray amounting to 6 - 7 li/nm$^3$ of acid per each stage, the productivity coefficient of the entire apparatus would range between 99.0 - 99.5% at total resistance (pressure drop) of 350 - 400 mm of water. A plan of the apparatus construction is presented in Fig. 5. The volume of liquid running over from the upper stage to the lower should equal the volume of fresh mother liquid supplied to the upper stage. The required moistening degree (spray) is attained by repeated circulation of the solution in each stage of the apparatus. Reserve fluid which assures the required degree of spray or moisture is determined experimentally or by preliminary trials. At gas flow rate 40,000 - 45,000 m$^3$/hour an apparatus of the proposed construction should measure as follows: height - 6.0 to 6.5 m; conus diameter - 2.0 to 2.2 m; throat diameter - 0.45 m; and conus diffusor angle - 30°.

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2. М. Д. Кузнецов, Ш. М. Сагаловский и Е. В. Попова. Кокс и Химия, 1959, № 2, 32.

# Nomogram for the Reduction of Actual Coke Gas Volume to Normal at Zero Degrees Centigrade, 760 mm of Mercury and of 4,000 Cal/nm$^3$ of Heat Capacity.

L. S. Blokh.

Koks i Khimiya, 1956, No. 1, 45-46.

Under practical plant conditions it frequently becomes necessary to reduce to actual gas volume as recorded by various types of gas meters to normal volume. In calculating saturated gases at temperatures below the dew point it is also necessary to take humidity into account. In the case of coke gas reduction to normal volume is accomplished according to formula (1):

$$V_{np} = \frac{0.663\ (1 - V_{wv})\ (10330 + p)\ Q}{10^5\ (273 + t)} \qquad (1)$$

in which $V_{wv}$ is the volume of water vapor in 1 m$^3$ of saturated gas at given temperature in m$^3$; p is the gas pressure in mm of water column; t is the gas temperature in C$^o$; Q is the heat capacity of the factual gas in Cal/nm$^3$ of dry gas. The value of $V_{wv}$ is usually found in an appropriate table. After $V_{wv}$ has been found it in still necessary to go through 8 different steps to obtain final results, which is a time-consuming procedure. Hence, the need for a nomogram with the aid of which $V_{np}$ could be determined with practical precision with t, p and Q known without searching for the value of $V_{wv}$ from the table. The nomogram herein presented was checked and found to satisfy all practical requirements. It is made up of equal distribution points and of vertical parallel scales based on formulas having 4 variables. In constructing the nomogram calculation formula (1) was reduced to the following:

$$V_{np} = \tau PQ \cdot 10^{-7}\ m^3 \qquad (2)$$

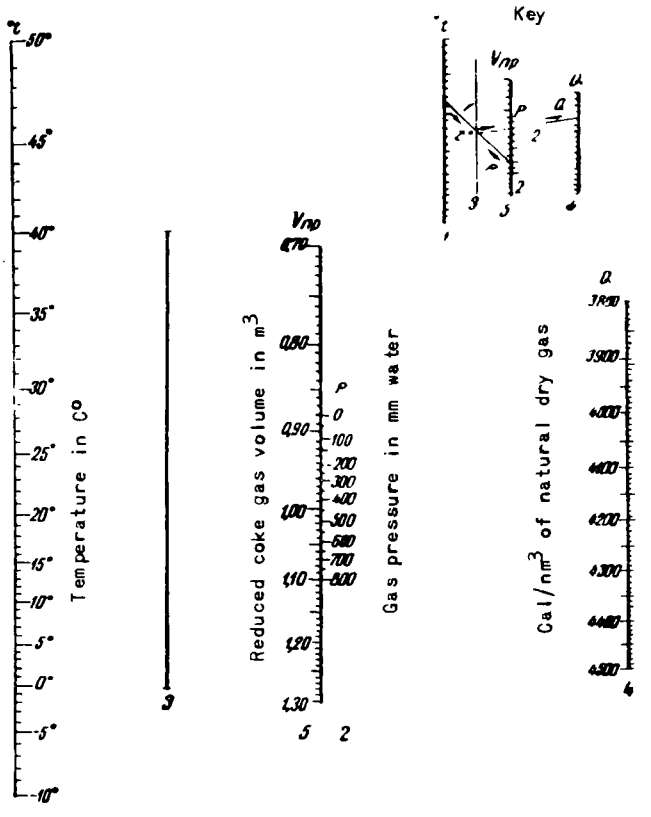
in which

$$\tau = \frac{66.3\ (1 - V_{wv})}{(273 + t)} \qquad (3)$$

and

$$P = 10330 + p \qquad (4)$$

Moduli of logarithmic scales of initial variables are taken at identical values in which case the scale modulus of the unknown variable will be reduced to 1/3. Moduli of logarithmic scales of initial variables have been taken as equal 1 m. Scale 1 was based on formula (3) and graduated for variable t in the range of




Nomogram for reduction of actual coke gas volume to normal.

$-10^{\circ}$ and $+50^{\circ}$; scale 2 was based on formula (4) with variable p in the range of 0 to 800 mm of water column. Logarithmic scale 4 with modulus $\lambda_Q = 1$ m is constructed for values of Q in the range of 3,800 and 4,500 Cal/nm$^3$. Logarithmic scale 5 with modules

$$\lambda_{V_{np}} = \frac{1}{3} \text{ m} = 333.3 \text{ mm}$$

Scale 3 is a blank vertical straight line located halfway between scales 1 and 2. Scale 5 coincides with scale 2 and is located halfway between scales 1 and 4. The key in the upper right hand corner demonstrates the method in which the nomogram is used. For example: assume that a volume of coke gas has to be reduced to normal under the following practical conditions: $t = 30^{\circ}$ C., p = 700 mm of water column; Q = 4,300 Cal/nm$^3$ of dry gas. Using the nomogram join the point which corresponds to 30 on scale 1 with the point indicated as 700 on scale 2 and note where the line intersects blank line 3. This point is then connected with the point corresponding to 4,300 on scale 4; the point of intersection with scale 5 represents the $V_{np}$ value which is equal to 0.997. Symbols in formula (1) are then substituted as indicated below:

$$V_{np} = \frac{0.663\ (1 - 0.0419)\ (10330 + 700) \cdot 4300}{10^5 \cdot (273 + 30)} = 0.994$$

The relative determination error is established as follows: (0.997 - 0.994)/ 0.997 - 0.003 or 0.3%, which is permissible for practical purposes.

Reducing Gas Emission During Coke Oven Charging.

T. P. Varshavsky, R. G. Agapov, F. A. Mustafin and V. A. Permyakov.

(Nizhne-Tagil'sk Coke-Chemical Plant).

Koks i Khimiya, 1956, No. 2, 23-30.

Improper coke oven charging is the chief cause of air pollution with coke gas and coal dust. In the Eastern U.S.S.R. coke plants, coal for coke oven use is crushed and screened, so that 92 - 95% of the particles are not over 3 mm in diameter. Some plants add coal kerosene or coal oil to increase the weight of the coke oven charge. Such a procedure of wetting powdered coal with hydrocarbons in the presence of an original 6% moisture enhances the intensity of air pollution with dust and coal gases and violates working conditions in the vicinity of and over the coke ovens. The All-Union Scientific Chemical Institute (VUKhIN) and the N.-Tagil Coke-Chemical Plant have been conducting an investigation with a view to developing a method for loading coke ovens by steam injectors, which might cut down air pollution to a minimum by reducing coal gas and dust escape from the hatches and risers.

1. Charging crew working conditions above coke ovens. Observation showed that average time of gas and dust escape through hatches amounted to 4 minutes 30 seconds and from stand-pipes to 5 minutes 29 seconds to 6 minutes and 33 seconds. A special diaphragm [1, 2] was used for the determination of the amount of gas escaping from coke ovens. Coke oven charging and operation of the portable diaphragm were as follows: the coal delivery car carried 14.5 tons of powdered coal; as the loaded car was posed over the open hatch, all 3 bunker lids were opened simultaneously and the coal charge run into the oven chamber. Immediately after the coal unloading the delivery car was moved away and the first and second hatches and rising pipe were closed. The risers remained disconnected from the gas collecting main, and the coal charge inside the oven was not levelled. The third hatch remained open, and the portable diaphragm was placed over it and carefully tightened to prevent any gas from escaping, thus forcing all gas coming from the oven to pass into the atmosphere through this diaphragm. This procedure enabled to determine changes in gas pressure created by the portable diaphragm in a group of coke ovens. Amount of gas escaping into the atmosphere during coke oven charging was determined from data obtained on the gas temperature, chemical analysis and moisture.

Experimental data showed that the quantity of gas escaping into the atmosphere from one oven was 66.04 $m^3$. For a coke installation of 4 batteries the monthly loss of gas amounted to 842,000 $m^3$.

In March of 1954 a work time study was made of a single delivery and loading car operation. Moisture content in the coal charge at the time of this study was 5.5%, and the screened coal contained 93.2% of particles up to 3.0 mm in diameter. The coal delivery car remained over the hatch 3 minutes 15 seconds. The reserve, or idling time per delivery car per oven averaged 3 minutes 9 seconds. During October of the same year the work time study was repeated. It was found that the coal delivery car was delayed for 34 seconds. At this time the coal moisture was 6.3% and particles up to 3.0 mm in diameter constituted 91.2%. This indicated that an increase in powdered coal moisture content increased the charging time. Concentration of coal dust in the air in the delivery car operator's cabin was checked next. Air samples were taken at 1.1 - 1.8 m from the cabin floor. This investigation was made according to regulations for determining dust concentration in the air of industrial establishments [3]. Results showed that coal dust concentration in the delivery car operator's cabin at the time of coke oven charging ranged between 218.8 - 383.1 $mg/m^3$, as compared with the maximum allowable limit of 10 $mg/m^3$.

2. Coal loading into coke ovens with one gas collector by steam injection. The existing method of coke oven charging allows insufficient free passage for the gas collected beneath the arched oven ceiling, and there is no provision for its removal from the oven through the stand-pipe. During a new charge the powdered coal is heaped up to the arched oven ceiling (Fig. 1), which causes the gas to escape through the hatches.

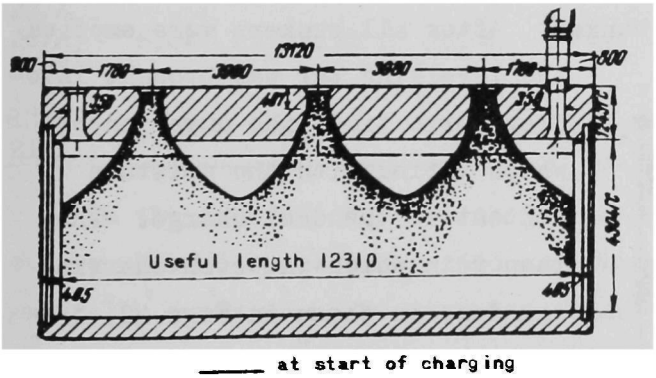



Fig. 1. Old system of charging coke ovens.

The coal accumulation heaping up to the coke oven ceiling acts as an obstructing partition which increases the gas pressure in separated sections inside the coke ovens. Determinations of static air pressure developed during coal charging into the coke oven were made with a U-shaped manometer. Results showed that gas pressure

at the first hatch, before the oven was connected with the gas collecting main, fluctuated from 5 mm to 45 mm, and at the third hatch from 5 mm to 270 mm of water. Maximum pressure at this third hatch was noted during levelling of the coal charge in the oven. The latter measurements were checked with the lids of the first and second hatches down. With the hatches open, gas pressure did not exceed 1 mm of water. The static gas pressure under the arched ceiling of the oven, between the first and second hatches reached 200 mm during the levelling operation, alternately dropping to about 4 - 5 mm, except during the first minute, when it was 20 - 45 mm of water. The static pressure in the riser pipe during coal charging varied from 1.5 to 5.5 mm of water; however, at the start of the charging operation it rose to 18 mm of water. On the basis of the above the following conclusions can be drawn.

1. The main obstruction to gas passage under the arched oven ceiling was caused by the formation of a partition during the coal unloading from the second bunker of the delivery car.

2. The levelling bar acted as an additional obstruction to the gas circulation under the arched oven ceiling.

Static air pressure measurements in the coke oven chambers suggested several ways of coal charging which might reduce the resistance to the gas passage into the riser pipe. The following method for oven charging was developed: the coal charge was started with unloading the first bunker of the delivery car, with the second and third bunkers tightly closed. The coal delivery car was then moved 2 m aside. The attendants covered the first hatch tightly and proceeded to the second bunker in an identical manner. After the second bunker was emptied the attendants removed the lid from the third hatch and discharged the coal from the third bunker. After all bunkers were emptied the levelling bar was brought into play for a time, the duration of which varied with the moisture content in the coal charge. The manner in which the oven charging was done is shown in Figs. 2, 3 and 4.

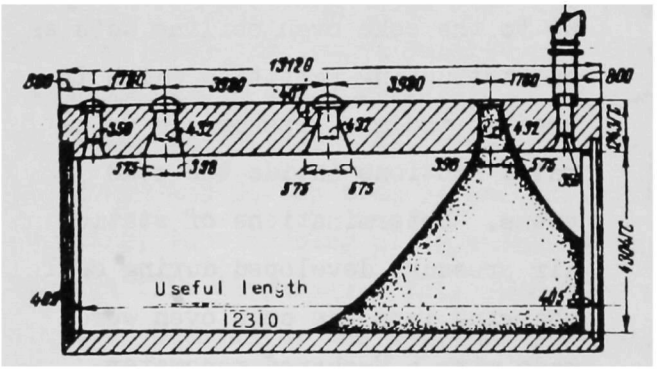



Fig. 2. First step of new coke oven charging system.

Data on charging coke ovens by recommended procedure with coal

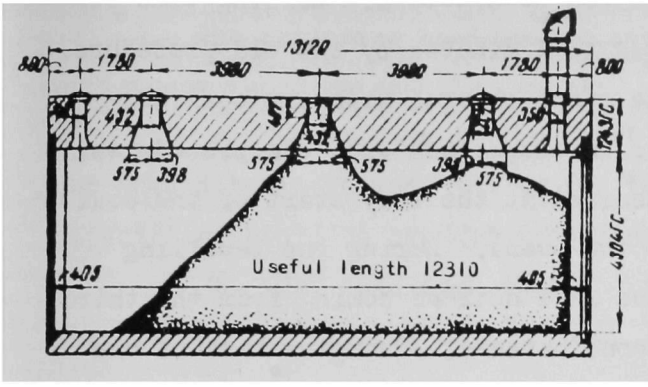



Fig. 3. Second step of new coke oven charging system.

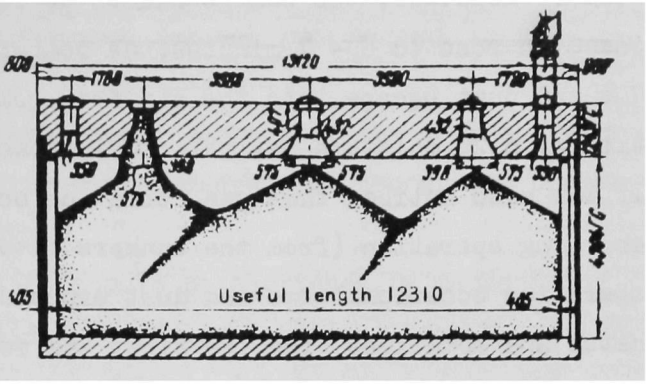



Fig. 4. Third step and levelling stage of new coke oven charging system.

of different moisture content are shown in the following table.

Important factors in charging coke ovens by the new method.

| Dates | Percent of moisture | Percent of 3 - 0 mm particles | Simultaneous (single) charging with dry coal in minutes | Simultaneous (single) charging with wet (oiled) coal in minutes | Charging time of experimental ovens in minutes and seconds | Leveling time after removal of delivery car, in minutes and sec. | Simultaneous (single) starter charging of dry coal in minutes | Notes |
|---|---|---|---|---|---|---|---|---|
| 20/X<br>22/X | 6.2 | 92.0 | 14.45 | 15.41 | 5-21 | 1-00 | 15.1 | Dry charge |
| 26/X<br>29/X | 6.8 | 90.7 | 14.2 | 15.24 | 6-42 | 1-06 | 15.12 | Ditto |
| 29/X<br>31/X | 8.22 | 90.1 | 14.08 | 15.34 | 12-00 | 1-00 | 15.3 | Ditto |
| 22/X<br>26/X<br>31/X | 6.04 | 91.58 | 14.79 | 15.77 | 5-52 | 1-13 | 15.28 | Wet (oiled) charge |
| 18/XI<br>23/XI | 5.86 | 91.0 | 14.9 | 16.27 | 5-56 | 1-03 | 15.28 | Ditto |

In the case of dry coal charge where $W_p$ = 8.2% a non-smoking oven charge can be assured by reducing the coal charge by 1.3 tons. A one coke oven charge generally averaged 12 minutes and occasionally 14 minutes. Accordingly, the new producedure cannot be recommended for coke oven charging with coal containing 8% or more of moisture. Slight gas leakage on top of the coke oven was noted when the ovens were charged by the new procedure with coal containing

6.8% of moisture; the charge had to be reduced by 0.9 tons. Loading time for one oven rose to 6 - 7 minutes, as compared to 4 minutes by the old procedure. Gas and dust escape into the air from coke ovens charged with dry coal containing 6.2% moisture was noticeably lower in comparison with old procedures. It was also noticed that gas formation occurred at the very start of the coal charging operation (from the bunkers into the oven). During the levelling operation occasional gas and dust eruptions were noticed coming from the third hatch and sometimes from the first and second hatches. Charging time of one coke oven took 5 to 6 minutes. Charging coke ovens with wet (oiled) coal of $W_p$ = 6.0% by the new procedure reduced the escape of gas and dust considerably. During coal unloading from the delivery car bunkers and during the coal charge levelling inside the oven, gas escaped through the gap between the telescopic bunker chute and its seat in the hatch, if they had not been properly connected. After the coal delivery car was removed from the top of the oven the third, i.e., last, hatch continued to emit gas until it was closed, but less intensely than usual. Time required for charging one oven chamber was 6 minutes exclusive of the time consumed by the charge levelling operation.

November 23 of the same year a second battery of 23 coke ovens were charged with coal by the new procedure in the course of a second shift. In that time 35 ovens were unloaded and 34 ovens were charged as against the usual output of 56 ovens. The production volume was not fulfilled due to the longer time required for their preparation. However, intensity of air pollution was markedly reduced as compared with results of preceding tests. According to preliminary calculations the gas escaped into the surrounding atmosphere was reduced by about 79%. The average dry coal charge for the plant amounted to 14.9 tons as against 15.28 tons and the average for that shift at the second battery of coke ovens, amounted to 15.45 tons. Time consumed for loading one oven was 6 minutes. The steam injector pressure varied, as in the previous experiments, between 10 and 8 atmospheres. On the basis of results obtained in this study it can be stated that:

1. A new procedure has been developed for charging coke ovens by steam injection which lowered considerably the pollution of air with coke gases and dust. The procedure was tested under actual industrial operating conditions.

2. The drawbacks of this procedure are: a) need to lower the size of the coal charge by 500 kg for coal with 6% moisture, and b) a 2 minute increase in the oven charging time.

3. The following changes are recommended for the improvement in the efficiency in charging coke ovens:

a. Coal loads in the first and second bunkers of the coal delivery car should be increased, and in the third bunker decreased; hence, the bunker capacities should be changed accordingly.

b. The coke oven charging time should be shortened by mechanizing the opening and closing of the hatch lids and of the levelling beam operation.

c. To make more precise fittings between the bunker telescopic chutes and their seats in the hatches.

The new procedure offers the above advantages only when the coal charge moisture is not in excess of 6%.

3. Development of steam injection procedure for charging coke oven equipped with two gas collectors. In 1953 the Nizhne-Tagil Coke-Chemical Plant initiated experiments in the use of steam injection smokeless charging of coke ovens. During the first period of the tests, charging of coke ovens was done according to prevailing ways of operating coke ovens. Coal varying in moisture between 5.5 and 7.5% was tested. Gas and dust concentrations on top of coke ovens decreased only slightly when steam injection was applied to ordinary procedures of coke oven charging. Therefore, a new procedure for coke oven charging was tried equipped with two uprisers. Special features of the new procedure were as follows: steam injection was started as soon as coke ovens were ready for the charge and with both risers closed. Then the oven was charged with coal from the first and third delivery car bunkers with the lid of the second hatch closed. After discharging the coal from the first and third bunkers the coal delivery car was moved aside 3 meters while the attendants locked the lids over the empty bunkers. The coal delivery car was then brought back and the coal from the second bunker discharged into the opened control oven hatch. The levelling bar window was opened as soon as the first and third bunker hatches were locked, and the levelling of the coal charge was started simultaneously with coal charging through the control (second) hatch from the second bunker of the coal delivery car. Coal charge levelling facilitated and speeded up the coal discharge from the second bunker and the coal charge levelling inside the oven. This procedure of coke oven charging was tried during May 1955 with the following types of coal: 8.3% moisture content; screened coal of 93.2% size 3 mm; and single 15.8 ton charge of dry coal.

The proposed procedure yielded a smokeless coke oven charging with steam injection of 8 to 10 atm. pressure. Gas escaping into the air was reduced by 90 - 95%. With an increase in the coal moisture up to 7.5% the efficiency of coal charging by this procedure increased. No gas escaped through the open hatches during coke oven charging except at the end of coal charge levelling inside the oven, when some gas escaped for 5 to 10 seconds from the first hatch. After the levelling bar was withdrawn from the oven the gas escape stopped. With this procedure of coke oven charging battery oven coking time was reduced to 14 hours 50 minutes. Time for loading one oven with coal did not exceed 3 and occasionally, 4 minutes.

This new coke oven charging procedure necessitated the rebuilding of battery ovens Nos. 5 and 7. The two end delivery car bunkers were enlarged to handle the coal charges of not less than 6.5 tons and the capacity of the middle bunker was reduced to not more than 4.5 tons. This reduced considerably the coal loading time as well as the levelling operation. The main characteristics of the new procedure for charging coke ovens can be described briefly as follows:

1. Free passage was created for the gas to enter the riser pipes under the arched coke oven ceiling during the entire coal charging operation.

2. Absolute elimination of outside air sucking into the oven, which made steam injection more effective than with the old coal charging procedure. The Moscow Coke-Chemical Plant adopted the new coal charging procedure developed by the Nizhne-Tagil Coke-Chemical Plant.

It was noted that charging coal into coke ovens by steam injection was accompanied by a tendency on the part of the coal to enter through the risers into the gas collectors. This increased the ash content in the tars up to 40% and clogged the gas mains and valves with heavy coal tar wastes. In addition, the quantity of heavy coal tar wastes increased; these heavy coal tar products can not be removed by clarifying methods, nor do they completely settle out of suspension by gravity. Steam was then forced through the risers for 3 to 5 minutes immediately after each fresh coke oven charge, cutting off the steam injectors at the same time. This completely freed the risers of the heavy coal tar waste clogging. Cleaning gas collecting mains of heavy coal tar wastes can be achieved by running in steam through valves placed equidistantly at the bottom of the gas mains. This method is being tried now at the N. Tagil Coke-Chemical Plant.

The following experiments are now being conducted for the reduction of the ash content in heavy coal tar products:

a. Means are investigated for the removal of formed heavy coal tar wastes by existing facilities, i.e., by improving the operation of existing mechanical separators.

b. A high velocity air current or cyclone is being adopted during the oven charging for the removal of coal dust from the gas before it reached the gas mains.

Results indicated that the above described studies were promising. This will require extensive new experimental studies and specially designed new equipment and apparatus.

## Conclusions.

1. A procedure was developed for charging coke ovens equipped with a single gas collecting main which improved considerably working conditions on top of coke ovens. The procedure is applicable only to coke oven charging with coal of not more than 6% moisture.

The Institute must conduct additional tests with the procedure of coke oven charging where only a single gas collecting outlet was available. Studies must also be conducted for coal delivery car redesigning.

2. A new procedure for charging coke ovens with 2 gas collecting outlets has been recommended and is now in use industrially.

3. Coke oven charging by steam injection caused coal dust to be carried away into the gas collecting mains; therefore, the method of steam injection is not now used in the Eastern U.S.S.R. coke-chemical plants.

4. Results thus far obtained with experiments conducted on cleaning coke gas before it reached the gas collecting mains and the mechanical separators appeared promising.

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Smokeless Coke Oven Charging.

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(Zaporozhie Coke-Chemical Plant).

Koks i Khimiya, 1958, No. 4, 28-30.

The problem of improving sanitary working conditions atop coke ovens during charging and of reducing atmospheric air pollution with coke gas and coal dust has received considerable attention in the U.S.S.R. In July 1956 a conference was called for the discussion of methods used by coke plants to attain smokeless charging of coke ovens. By conference resolution the industry was recommended to adopt the method used by the Moscow Coke-Chemical Plant. The Zaporozhie Coke-Chemical Plant used the steam injection method from the start of its operation in charging coke ovens to sanitize working conditions atop the coke ovens and to lower air pollution with coke gases and coal dust. Adoption of this method created some difficulties. When this method was applied to charging coke ovens with crushed coal containing 91 - 92% of particles up to 3 mm in diameter the amount of ash in the coal tar increased up to 0.22% as against 0.1% with crushed coal of larger size particles, which in turn produced a defective grade of pitch coke. To avoid this, coke oven charging in that plant has been done by the following procedure since 1954: before filling the oven chamber with the coal and before stopping the coal feeding from the delivery car bunkers, all hatches on top of the oven remained open. The oven was connected with the gas collecting main before starting the coal levelling operation, and the steam injection was commenced. By this procedure of coke oven charging the steam injection time was reduced to 70 seconds and the amount of ash in the heavy coal tar waste was reduced. The gas passing through the riser pipes at the start of the charging operation is of low value. It consists of (in percent): $CO_2$ - 2.5; CO - 1.3; $C_mH_n$ - 9.1; $H_2$ - 9.9; $CH_4$ - 11.3; $N_2$ - 65.0 and $O_2$ - 0.9. The 65% nitrogen in the gas indicates that at the beginning of the oven charging air passed through the risers from the oven interior which contained some CO and $CO_2$ formed by the burning coal.

This author was assigned the problem of determining the advantages and disadvantages of steam injection used at the Moscow Coke-Chemical and the Zaporozhie Coke-Chemical Plants to attain smokeless coke oven charging. Under

investigation were coke oven batteries with 2 gas collecting mains. The coal delivery car was equipped with a special mechanism which enabled loading its bunkers with exact volumes of coal. Hatch lids of the coal delivery car bunkers opened and closed automatically in a set order. Each bunker was equipped with an automatic type H7 vibrator. Removing and replacing the hatch lids was done automatically at the exact stops of the coal delivery car. The levelling bar also operated automatically and its stroke amounted to 5.5 meters. Loading openings in the bunkers measured 420 mm in diameter and the hatch openings measured 432 mm in diameter. Coal delivery cars were equipped with telescopic automatically tightening chutes. Tar and heavy tar waste collection was done in mechanical separators which were cleaned before and after each run. Gas pressure and temperature during coke oven charging were checked through openings in the risers at 300 mm above the oven top. A single oven charge of wet (oiled) coal weighed 17 tons.

During this oven charge study 976 coke ovens were tested in the Zaporozhie plant while in full operation. Each oven was charged with 17 tons of coal. The first and second bunkers of the coal delivery car held 5.5 tons of coal each, the third bunker 6 tons. The coal moisture was 8.43% and the ash 7.4%. The coal weighed 0.729 $t/m^3$. Screened sizes of the coal were as follows (in percent): class > 6 mm - 1.6; 6 to 3 mm - 7.3; < 3 mm - 91.1, 44% of the latter measured 0.5 mm and less in diameter. Gas pressures in the riser pipes are shown in the following table.

| Time of gas pressure recording | Pressure in mm of water |
|---|---|
| Open riser pipe during oven charging | -2.2 |
| Closed riser pipe; charge levelling; steam injection: | |
| Steam pressure 5 atm. | -8.4 |
| Steam pressure 6 atm. | -9.0 |
| Levelling operation completed; levelling hatch closed: | |
| Steam pressure 5 atm. | -15.4 |
| Steam pressure 6 atm. | -26.0 |
| No steam injection coke oven connected with gas collector | +11.0 |

At steam pressure of 5 atm. and partial vacuum at the bottom of the risers at 8.4 mm during the charging some of the gas escaped through the open hatches. At steam pressure of 6 atm. and partial vacuum at bottom of the risers 19 mm oven charging proceeded without gas escaping into the atmosphere. Gas escaped into the atmosphere for about 4 - 5 seconds through the control hatch, only before coal loading and before inserting the

levelling bar into the oven chamber after emptying the third bunker. The 480 tons of tar produced during the investigation contained 0.115% of ash. Total ash in the tar amounted to 480 x 0.115/100 = 0.552 tons. The ash entered the tar during the coal charge with the powdered coal; accordingly, coal carried off with the gas during oven charging amounted to 0.552 x 100/7.4 = 7.46 tons. Heavy tars collected during the investigation amounted to 1.8 tons, making the total coal loss equal to 7.46 + 1.8 = 9.26 tons, or 9.26 x 1000/976 = 9.49 kg per single oven, or 9.49/17 = 5.45 kg per single oven charge. During the charging operation the oven was under steam injection for about 170 seconds while the coal was being levelled. Losses from one oven per minute amounted to 0.49 x 60/170 = 3.3 kg per load. As soon as coal levelling was completed and steam injection was discontinued the top layer of small coal particles fused and the discharge of gas and coal dust into the atmosphere stopped.

During the investigation of coke oven loading by the procedure used in the Moscow Coke-Chemical Plant tests were made of the operation of 923 coke ovens. The ovens were charged as follows: first, two end bunkers of the delivery car were emptied and the hatches covered; the middle bunker was then emptied of its coal load. The total coal load amounted to 17 tons. The first and third bunkers in the coal delivery car contained 6.25 tons each, the second (middle) 4.4 tons. When the extreme bunkers were loaded with more coal than specified, trouble was experienced in charging the coal into the oven chambers without the use of the levelling bar. The coal contained 8.55% of moisture and 7.5% of ash. The coal weighed 0.717 t/m$^3$, and was of the following fractional composition: > 6 mm - 1.8%; 6 to 3 mm - 6.8%; < 3 mm - 91.4%, 44% of the latter consisted of particles of 0.5 mm or less in diameter. Injection steam pressure was 6 atm. with a partial vacuum at the bottom of the riser pipe during the levelling operation of 19 mm, and with a closed levelling bar porthole of 26 mm. With the charge completed, the coke oven was connected to the gas collecting main with the riser registering a pressure of 11 mm.

Results of investigations showed that time consumed from the start of coal feeding into the oven to the end of the levelling operation, in accordance with the procedure used in the Moscow Coke-Chemical Plant, equalled 330 seconds; by the procedure of the Zaporozhie Coke-Chemical Plant the time consumed was only 240 seconds. Correspondingly, the time consumed in levelling the coal inside the oven was 320 minutes against 170 minutes. During testing the Moscow Coke-

Chemical Plant procedure 455 tons of tar was produced with a 0.153% ash content. Total ash in the tar weighed 455 x 0.153/100 = 0.696 ton. In other words, with a coal ash content of 7.5% the loss, including gas loss, was equivalent to 0.696 x 100/7.5 = 9.28 tons of coal. Eight tons of heavy tar waste products were produced during the investigation making a total actual charge loss equivalent to 9.28 + 8.0 = 17.28 tons of coal, or a loss of 17.28 x 1000/923 = 18.73 kg of coal per charge, or a loss of 18.73/17 = 1.1 kg of coal per ton. Losses during 320 seconds of steam injection were 18.73 x 60/320 = 3.5 kg/min.

The loss of coal from the coke oven per minute, including loss of gas, was practically identical in both tested procedures, or in actual figures 3.3 kg/min. in the Zaporozhie Coke-Chemical Plant and 3.5 kg/min. in the Moscow Coke-Chemical Plant. It follows that the amount of ash in the tars and in heavy tar wastes extracted by the separators was in direct proportion to the time the ovens were under steam injection during the coal charging operation. There was also a direct proportional relation between the steam injection pressure and the loss in coal dust with the gas. It was noted that at partial vacuum of 8 mm at the bottom of the risers, a complete gas collection was not assured, but the size of the coal particles decreased below 1.5 mm. A drop in partial vacuum at the bottom of the riser to 19 mm assured complete collection of the gas during the coal charging operation with coal particles size increase to 2 mm. With increase in time of oven charging by the Moscow Coke-Chemical Plant procedure there was also a time lag in the work cycle of the coke pusher from the moment of coke unloading to the end of coal loading, amounting to 761 seconds as against 681 seconds, required by the Zaporozhie Coke-Chemical Plant procedure. Additional increase in work intensity of the coke pusher under work conditions existing at the Zaporozhie Coke-Chemical Plant presented the danger of a possible breakdown in the coke delivery.

Tests were also made with the following procedures for charging coke ovens. The total load of coal delivery car was made up as follows: in the first bunker - 6.3 tons, in the second - 4.5 tons, and in the third - 6.2 tons. Charging the oven chamber was done by simultaneously unloading the end bunkers of the delivery car and 22 seconds later emptying the central bunker. With this procedure of coke oven charging all three bunkers contained about 200 kg of residual coal before the levelling bar was set into operation; coal levelling was accomplished by two strokes. Gas was escaping through the

hatches for about 5 - 6 seconds until the levelling bar began to operate. Total time consumed from starting the coal feed from the bunkers to the end of coal levelling amounted to 190 seconds. This third method of oven charging was the most rational of the three methods tested from the point of view of smoke elimination and prevention of coal dust being carried into the gas collecting mains. After the working crew mastered the unloading of the bunkers and levelling of the coal charge inside the oven, the complete loading time was reduced to 170 seconds, and the gas loss in coal equivalent was reduced to a minimum.

## Conclusions.

1. Coal dust carried off by gases during coke oven charging was directly proportional to time of steam injection. Coal dust and ash were carried off by the gas under the following working conditions: if the coal contained 8.5% of moisture; if 91% of the coal particles measured 3 mm or less in diameter and the partial vacuum at the bottom of the riser was 19 mm. Under such conditions 3.5 kg/min. of coal dust were being carried away by the gas.

2. The injection steam pressure must produce a partial vacuum at the bottom of the riser of not less than 19 mm if the coke oven charging is to be attained without any gas escape.

3. The procedure adopted by the Moscow Coke-Chemical Plant for smokeless coke oven charging can be used with coal containing 7% moisture.

4. Coke oven charging in accordance with the procedure of the Moscow Coke-Chemical Plant at the Zaporozhie Coke-Chemical Plant, where the coal moisture content ranged between 8 and 10% had shown that it lengthened the oven loading time, increased the work intensity of the levelling bar, greatly increased the rate of coal dust pick-up by the gases, and increased the ash concentration in the separated tar to 0.153% as against 0.115% by the usual procedure of the coal loading. On the other hand, the efficiency of smoke abatement was considerably higher with the procedure used at the Moscow Coke-Chemical Plant than by the procedure of the Zaporozhie Coke-Chemical Plant.

5. The most promising procedure of coke oven charging was the third which consumed considerably less time than either of the other two methods.

# New Method for Ammonia Absorption from Coke Gas.

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(From the Ural Polytechnic Institute).

Koks i Khimiya, 1960, No. 4, 34-41.

The ammonium sulfate method presently used for ammonia absorption from coke gas has some basic shortcomings:

a) The resulting ammonium sulfate is of low quality as a fertilizer;

b) It requires the use of large quantities of sulfuric acid;

c) The technology of the process lacks adaptability for the production of new substances from the ammonia contained in the coke gas.

In view of the above, it would seem more appropriate to concentrate on obtaining more valuable products than ammonium sulfate. Such products or substances should contain a higher percentage of bound ammonia and should constitute less bulky types of fertilizer manufactured only from coke-chemical raw products. Such substances could be urea, saltpeter, different types of liquid ammonia fertilizers, including liquid ammonia. Of these urea is the most valuable product. It has 46% bound nitrogen and in addition its properties make it one of the most widely used ammonia compounds in the production of plastics, lacquers, plywood glue, foam plastics, etc. [1, 2, 3]. Urea is also used in large quantities in animal husbandry as a cattle protein reinforcer [1, 4]. Net cost of ammonia produced on a large scale with modern equipment is about the same as the net cost of saltpeter which is one of the cheapest produced fertilizers [4]. Coke gas of an 8-battery coke-chemical plant contains ammonia sufficient for the production of 25 - 30 thousand tons of urea annually; this amount compares favorably with the amount of urea synthesized by one of the largest present day urea producing plants [1]. The products enumerated are produced from pure ammonia; therefore, it is essential that the ammonia recovered from coke-chemical gas be obtained in a highly pure state, at the same time keeping the cost of its recovery at a low level.

The present authors studied cycle methods for the recovery of ammonia from coke gases by weak solutions of acid and polybasic acid salts. It was hoped that the use of cycle absorbers might enhance the capacity of the solutions to absorb ammonia, and, what is more, would insure selective ammonia

absorption from coke gas. The chemistry upon which such a process is based can be represented by the following formula:

$$NH_3 + HAn \underset{t_2}{\overset{t_1}{\rightleftarrows}} NH_4An$$

in which HAn represents the acidity and $t_2 > t_1$.

Ammonia separation at higher temperatures is accomplished by increased ammonia salt hydrolysis and by an increased rate of ammonium hydroxide decomposition as per equations below:

$$NH_4An + H_2O \rightleftarrows NH_4OH + HAn$$

$$NH_4OH \rightleftarrows NH_3 + H_2O$$

An analysis of the equation for the purpose of obtaining constants of weak acid salts and weak bases hydrolysis showed that high rate of ammonia catching at 30 - 60° and a favorable recovery rate at 100 - 120° were attainable with an acid having a dissociation constant ranging between $3 \times 10^{-7}$ and $6 \times 10^{-8}$, or with an acid salt at equivalent dissociation constant at any stage of the process. Use of weak acids for ammonia catching by suitable processes has been described previously in the patent literature [5 - 11]. However, in most instances ammonia recovery from coke gas has not been studied. On the other hand, reports of studies on the subject of ammonia recovery from coke gas [5, 6] failed to present adequate information regarding conditions under which recovery has been attained and of the advantages of any of the absorbers used. Results of absorber studies lead to the following conclusions:

1. Borates, phthalates and oxalates could not be used because of their low solubility in water, and, consequently, the degree of ammonia absorption by such solutions did not exceed the degree of ammonia absorption by plain water.

2. Ammonia absorption by double substituted ammonium citrate is reversible. The high solubility of citric acid is conducive to a high degree ammonia absorption (up to 95 g/li). However, this is counterbalanced by the high cost of citric acid.

3. Ammonium acetate in aqueous solution at 50° liberates 50% of its ammonia and becomes converted to the acid salt according to the following formula:

$$CH_3COOH \cdot CH_3COONH_4$$

It appeared at first that the high ammonium acetate solubility in water might offer a rational means for ammonia absorption according to the following equation:

$$CH_3COOH \cdot CH_3COONH_4 + NH_3 \rightleftarrows 2CH_3COONH_4$$

However, a thorough and detailed study of the process showed that by concentrated ammonium acetate solutions it was possible to separate only a small part of the absorbed ammonia at 100 - 120°; in addition, along with the ammonia there were carried over large quantities of acetic acid; and furthermore, solutions of ammonium acetate corroded the equipment, in particular the acidic acetates.

4. Phenol solutions or liquid phenol fractions absorbed ammonia reversibly in quantities of 1 mol. for each 2 oxygroups. Reaction rate between phenol and ammonia was considerably below that of organic acids. Bubbling coke gas through phenol solutions rapidly oxidized the latter. Phenol sulfonic acids could not be used as absorbers of ammonia from coke gas due to the fact that ammonia became permanently bound to the sulfo group and, therefore, could not be recovered; accordingly, the capacity of sulfonic acid solutions to absorb ammonia depended entirely on the number of phenolic hydroxyls in its molecule.

5. Most promising in this respect appeared to be monobasic phosphates; their solutions easily absorbed ammonia and even more easily liberated it in the process of recovery. However, the use of potassium phosphate is not practical due to its low solubility in water. Monosodium phosphate has a higher solubility than any other phosphate; however, its mixed salt $NaNH_4HPO_4$ is also sparingly soluble in water, which renders the use of sodium acid phosphate unfit for the purpose. Best results were obtained with a solution of ammonium acid phosphate, the solubility of which is graphically presented in Fig. 1.

A study was then made of factors controlling rates of absorption and recovery. For this purpose determinations were made of ammonia vapor tension over mono- and dibasic phosphate solutions and their mixtures at different temperatures. Results are listed in Table 1.

Data in the table show that monobasic phosphate solutions could be used under practical conditions for the absorption of ammonia from coke gas at 60°. Recovery of dibasic phosphates of ammonia should be made at 100 - 120°. Complete ammonia recovery from dibasic phosphate solutions was not attainable. Under practical conditions the processed solution will contain 75 - 80% of

the monobasic and 20 - 25% of the dibasic phosphates after recovery. Data on required solution concentrations, spray density and ammonia absorption capacity attainable at different temperatures are presented in Table 2.

Ammonia absorption can also be attained by combining a part of it as tribasic phosphate. However, saturation of the solution to the point of formation of tribasic phosphate raises ammonia absorption only by 7 g/li corresponding to 10% of the tribasic phosphate concentration (solution 7). Further increase in ammonia concentration in the tribasic phosphate solution lowered the absorption coefficient due to the high ammonia vapor tension over the tribasic phosphate solution. In addition, as the tribasic phosphate concentration continued to increase it began to fall out from the solution in crystalline form. Generally, an ammonia absorption rate amounting to 50 - 60 g/li by solutions of monobasic phosphate was attainable at 40 - 50°.

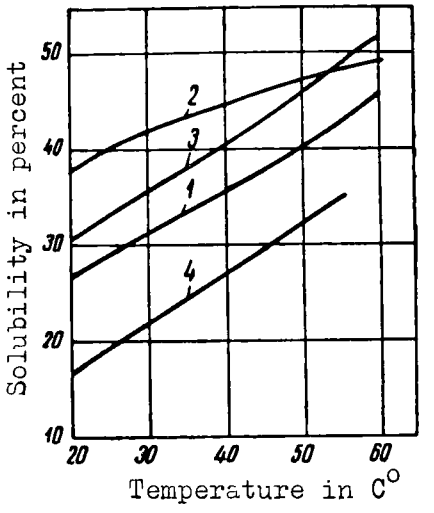


Fig. 1. Solubility of ammonium phosphate. 1 - monobasic; 2 - dibasic; 3 - dibasic solution concentration attainable with ammonia absorption by saturated monobasic solution; 4 - tribasic.

A study was made of pyridine vapor tension over the ammonium phosphate solutions in connection with an investigation of a method described

TABLE 1.

Ammonia vapor tension over surface of $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$ solutions.

| Solution No. | Concentration g/li $NH_4H_2PO_4$ | Concentration g/li $(NH_4)_2HPO_4$ | G/li of ammonia absorbed by $NH_4H_2PO_4$ | Solution pH at 90° | $NH_3$ vapor tension in mm mercury, Temperature in C° 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 | 110 | 120 | Ammonia production capacity in g/li |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 430 | - | - | 3.8 | | - | - | - | - | | | | - | - | |
| 2 | 376 | 62 | 7.9 | 4.4 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.10 | 0.37 | 0.66 | 1.21 | - |
| 3 | 322 | 123 | 15.7 | 3.0 | 0.00 | 0.00 | 0.00 | 0.04 | 0.14 | 0.56 | 0.68 | 1.62 | 3.90 | 7.70 | 3.1 |
| 4 | 215 | 245 | 31.5 | 5.7 | 0.17 | 0.18 | 0.51 | 1.86 | 2.11 | 2.39 | - | 8.46 | 20.00 | | 18.9 |
| 5 | 108 | 367 | 47.0 | 6.6 | 0.33 | 0.49 | 0.77 | 2.36 | 4.41 | 11.60 | | 57.00 | 69.30 | | 33.4 |
| 6 | - | 490 | 63.0 | 7.6 | 3.35 | 6.68 | 12.40 | 23.40 | 52.50 | 81.40 | | 158.00 | 327.00 | | 50.4 |
| 7 | - | 490 | 70.0 | 9.1 | 4.12 | 7.60 | 15.50 | - | | - | - | - | - | | 57.4 |

Notes: 1) Monobasic ammonium phosphate saturated at 40° (430 g/li) was taken as the basis of the investigation. 2) Ammonia productivity capacity was determined on the basis of possible 80% $(NH_4)_2HPO_4$ recovery (ammonia residual - 12.6 g/li).

TABLE 2.

Concentration of monobasic phosphate and degree of ammonia absorption at different temperatures.

| Index | Temperature in C° | | |
|---|---|---|---|
| | 40 | 50 | 55 |
| $NH_4H_2PO_4$ solution concentration in g/li..... | 430 | 490 | 530 |
| Limit of ammonia absorption degree..... | 63 (70) | 72 (79) | 75 (80) |
| G/li of ammonia absorption under working conditions..... | 51 (58) | 57 (64) | 60 (65) |

Note: Data in parenthesis represent degree of ammonia absorption by tribasic phosphate solution.

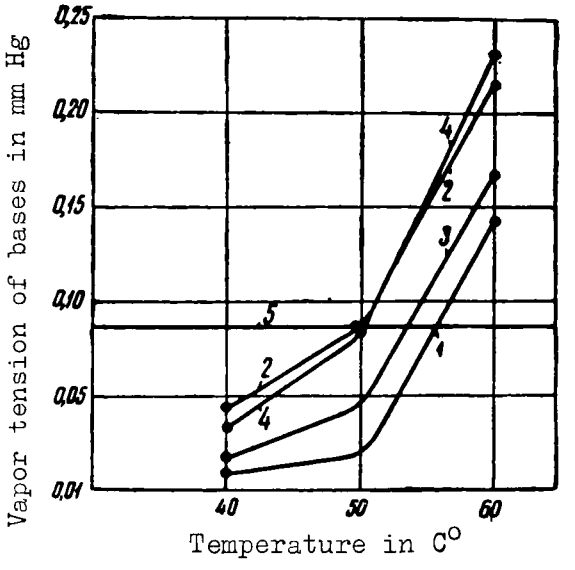


Fig. 2. Vapor tension of pyridine bases over ammonium phosphate solutions.
1 - $NH_4H_2PO_4$ - 430 g/li, pyridine bases 2 g/li; 2 - $NH_4H_2PO_4$ - 430 g/li, pyridine bases 5 g/li; 3 - $(NH_4)_2HPO_4$ - 490 g/li, pyridine bases 0.5 g/li; 4 - $(NH_4)_2HPO_4$ - 490 g/li, pyridine bases - 1.0 g/li.

previously by the present authors [13]. Results are shown in Fig. 2. Results indicate that even under equilibrium conditions pyridine bases were poorly absorbed by ammonium phosphate. Therefore, it is recommended that they be absorbed differentially [12]. A study was then made of the conditions controlling ammonia absorption from coke gases using an installation of 6 - 8 $m^3$/hr capacity in the coke-chemical department of NTMK. Ammonia was absorbed by a disk-type column made of plexiglass. Plates of different type and shapes were used in the test; they were set 150 mm apart. Plan of the apparatus is presented in Fig. 3. Ammonia catching was conducted at 36 - 40°; the solution contained 390 g/li $NH_4H_2PO_4$, and the limit of ammonia absorption capacity was 57 g/li. Results are shown in Table 3.

Data in the table show that ammonia absorption by a solution of monobasic phosphate can be as high as 50 - 60 g/li; this was accompanied by a high degree of absorption selectivity. This was shown by the fact that the absorption of

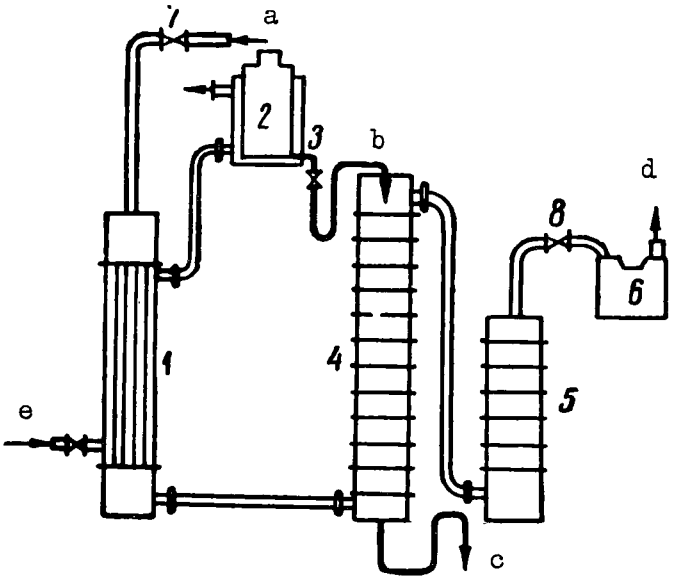


Fig. 3. Plan of experimental setup. 1 - Heat exchanger; 2 - small pressure tank; 3 - waterbath (water jacket); 4 - absorber; 5 - drying column; 6 - flowmeter; 7 - inflow slide valve; 8 - outflow valve; a - direct (inflowing) gas; b - monobasic solution; c - dibasic solution; d - return (outflowing) gas; e - hot water.

pyridine bases ranged between 2 - 5% and volume of acid gases circulating in the solution was negligible. The installation efficiency was high, as shown by the fact that a 5-disk setup brought about practically complete removal of ammonia from the coke gas; this was in good agreement with results of graphic calculation of number of disks required theoretically. No noteworthy changes were observed in the solution absorption capacity. Recovery conditions were investigated using an experimental laboratory installation. Results of experiments conducted at atmospheric pressure

TABLE 3.

Ammonia absorption by monobasic phosphate.

| Exp. No. | Type of disks | No. of disks | Gas consumption in $m^3/hr$ | Spray density in $li/m^3$ | Content in raw gas in $g/nm^3$ | | Content in purified gas in $g/nm^3$ | | Percent of ammonia absorbed | | G/li of ammonia absorbed | | G/li of pyridine bases in solution |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Ammonia | Pyridine bases | Ammonia | Pyridine bases | Ammonia | Pyridine bases | Complete | Practical | |
| 1 | Bell-shaped | 3 | 6 | 0.11 | 6.2 | 0.16 | 0.32 | 0.45 | 94.2 | 2.1 | 53.0 | 42.0 | - |
| 2 | Ditto | 3 | 6 | 0.09 | 6.5 | 0.46 | 0.38 | 0.44 | 93.8 | 4.4 | 67.0 | 56.0 | 0.40 |
| 3 | Ditto | 4 | 6 | 0.10 | 6.5 | - | 0.16 | - | 97.4 | - | 63.0 | 52.0 | - |
| 4 | Ditto | 4 | 6 | 0.09 | 6.4 | - | 0.20 | - | 97.2 | - | 68.0 | 57.0 | 0.45 |
| 5 | Ditto | 4 | 6 | 0.12 | 6.7 | 0.46 | 0.18 | 0.45 | 97.3 | 2.1 | 56.0 | 45.0 | 0.32 |
| 6 | Ditto | 5 | 6 | 0.08 | 4.7 | - | 0.00 | - | 100.0 | - | 61.5 | 51.5 | - |
| 7 | Ditto | 5 | 6 | 0.11 | 6.4 | - | 0.00 | - | 100.0 | - | 58.0 | 47.0 | - |
| 8 | Trough-shaped 4/9 | 4 | 9.5 | 0.10 | 6.5 | - | 0.75 | - | 88.5 | - | 37.5 | 46.5 | - |
| 9 | Ditto 2/5 | 4 | 6 | 0.11 | 6.5 | - | 0.09 | - | 98.9 | - | 58.0 | 47.0 | - |
| 10 | Ditto | 5 | 6 | 0.11 | 6.5 | - | 0.00 | - | 100.0 | - | 59.0 | 48.0 | |

Notes: 1) In establishing complete or theoretical ammonia absorption by a solution, ammonia in the monobasic form was subtracted from total ammonia. 2) In determining ammonia absorbed under working conditions incomplete ammonia recovery was taken into consideration. 3) Lowered ammonia content in the gas was caused by the fact that a part of it became dissolved in the condensate and was deposited in the gas conduit.

or above showed that 75 - 80% of the ammonia bound during monobasic ammonia conversion to dibasic could thus be liberated. Using a desorber having an efficiency equivalent to theoretically computed 8 - 10 disks and changing the reflux number from 0.9 to 3.0 it was possible to liberate ammonia either in the form of 15 - 20% aqueous solution or as 97 - 98% ammonia gas. Plan of the technological model for the absorption of ammonia from coke gas with the aid of monobasic phosphate solution is shown in Fig. 4.

During the investigation viscosity determinations were made of mono- and dibasic phosphate solutions at different temperatures. Results are presented in Fig. 5.

An investigation was made of the corrosion-resistance properties of different materials to mono- and dibasic ammonium phosphate solutions. Results are shown graphically in Fig. 6. Results showed that alloyed steel and nonferrous metals were completely corrosion resistant against the effect of

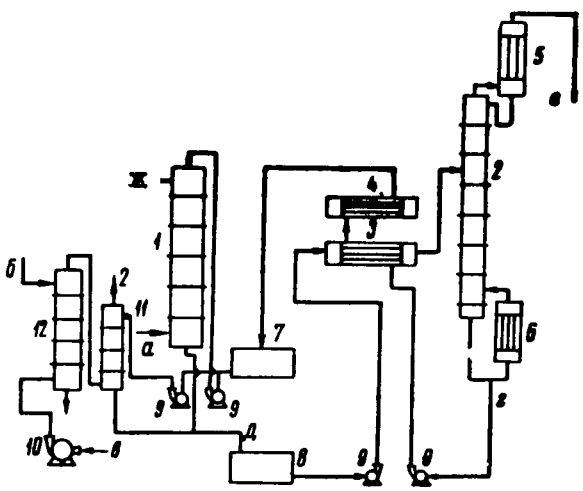

Fig. 4. Technological plan of ammonia catching.
1 - Absorber; 2 - regenerator; 3 - heat exchanger; 4 - cooler; 5 - fractionator; 6 - heater; 7 - monobasic solution collector; 8 - dibasic solution collector; 9 - pumps; 10 - gas blower (exhaust fan); 11 - absorber for ammonia removal from flue gases; 12 - apparatus for ammonia blowing off from tar water; а - coke gas; б - tar water; в - flue gases; г - monobasic solution; д - dibasic solution; е - ammonia or ammonia water; ж - coke gas in catching pyridine bases.

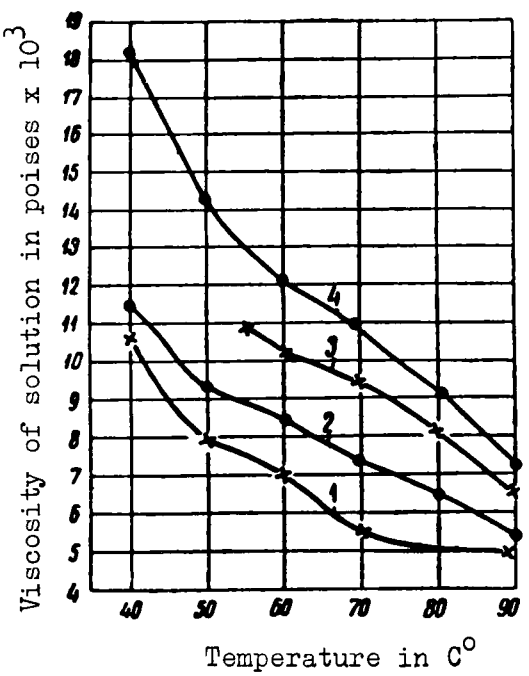


Fig. 5. Viscosity of phosphate solutions.
1 - $NH_4H_2PO_4$ solution, 400 g/li; 2 - $NH_4H_2PO_4$ solution, 490 g/li; 3 - $(NH_4)_2HPO_4$ solution, 490 g/li; 4 - $(NH_4)_2HPO$ solution, 550 g/li.

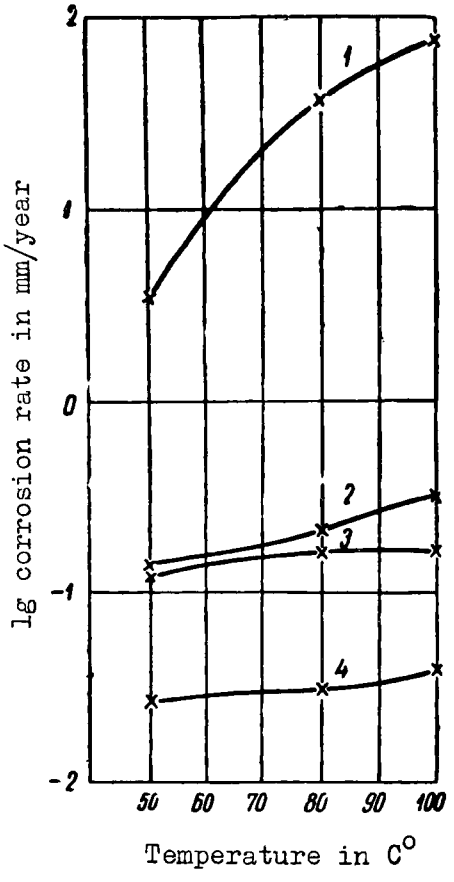


Fig. 6. Corrosion resistance of different materials to $NH_4H_2PO_4$.
1 - Steel St-3; 2 - copper;
3 - steel X-17;
4 - steel X-25.

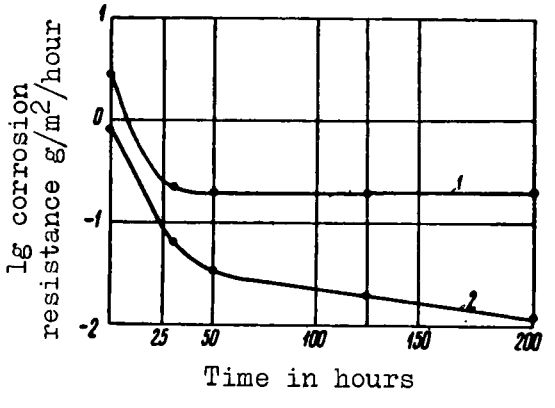


Fig. 7. Effect of inhibitors on corrosion rate at 30°.
1 - Control (no inhibitor); 2 - 0.2% quinoline bases plus 0.2% KSCN.

monobasic ammonium phosphate solutions. Steel St-3 was corrosion susceptible to solutions of monobasic ammonium phosphate, but was completely corrosion resistant to dibasic ammonium phosphate solutions. The corrosion resistant property of steel St-3 to monobasic ammonium phosphate solution was considerably enhanced by the addition to the solution of small quantities of quinoline bases [13], as can be seen from the curves shown in Fig. 7. Hence, absorbers and heat exchangers used in this work can be made of steel St-3.

Ammonia absorption from coke gas can also be accomplished using technical ammophos, which is a mixture of mono- and diammonium phosphates. After a single circulation this mixture will invariably consist of mono-ammonium phosphate.

## Conclusions.

The method herein described possesses the following advantages over other methods:

1. It assures a high degree of ammonia absorption and selectivity for the removal of ammonia from coke gases.

2. Ammonia absorption should be done at ordinary gas temperature (40 - 50°), since this is the temperature range of coke gas delivered by gas blowers; it requires no cooling and no purification from naphthalene.

3. Ammonia absorption can be accomplished by small dimension absorbers of low pressure drop (100 - 120 mm of water).

4. At any given salt concentration in the solution the ammonia absorbing capacity of a solution is independent of ammonia concentration in the gas and of its temperature.

5. The new method increases the choice of derived commercial products to fit the range and nature of different industrial interests, permanent or seasonal. Economic outlays and expected returns should be given serious consideration before the recommended procedure of ammonia catching is installed.

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## Differential Absorption of Ammonia and Pyridine Bases from Coke Gas.


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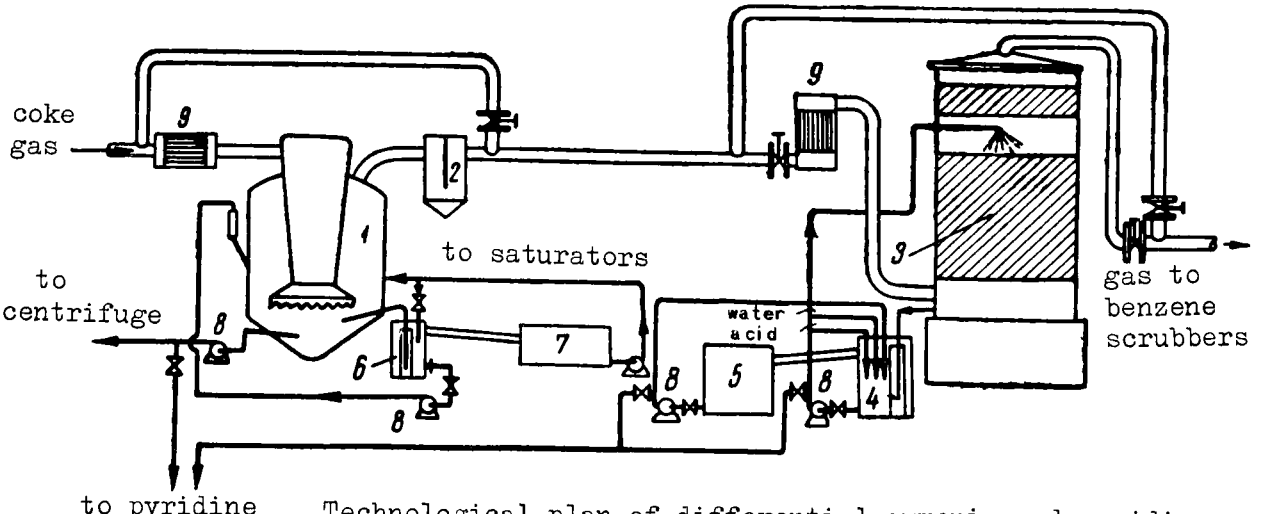
Koks i Khimiya, 1960, No. 6, 32-35.


Light pyridine bases constitute highly valuable basic raw material for the production of many chemical substances. Practical experience in the U.S.S.R. and reports found in foreign literature indicate that coke gas, as a source of naturally occurring pyridine bases, has not been adequately utilized, especially by the method of ammonia saturation. The greater part of

the pyridine bases was allowed to escape with the gas in the process of ammonia saturation. The extent of pyridine bases lost was determined by physico-chemical conditions prevailing in the saturator [1]. With the introduction of new methods of ammonia utilization in the production of phosphates, etc., the simultaneous absorption of ammonia and pyridine bases became non-feasible.

The purpose of this study was to develop a differential method for the absorption of ammonia and pyridine bases from coke gas [1], thereby sharply increasing the recovery of pyridine bases and obviating the shortcomings prevailing in the process of simultaneous absorption of ammonia and pyridine bases. The study was conducted on an industrial scale at the appropriate department of the Chelyabinsk Metallurgical Plant in cooperation with the Department of Fuel and Chemical Technology at the Ural Polytechnic Institute during April - June of 1959 [2].

Plan and method of study. The plant where the study was conducted had an acid scrubber installed in the upper section for the absorption of ammonia from the coke gas at times when the saturator was not in operation. The procedure of the experiments was as follows: coke gas was run into saturator (1) where the ammonia was removed by absorption. From saturator (1) the gas was passed through an acid tank (2) and from there through an acid scrubber (3) for the removal of pyridine bases. While passing through the scrubber the gas was washed by an acidifying solution of pyridine sulfate circulated through the system. Excess of the latter solution was caught in scrubber pan (4) and from




Technological plan of differential ammonia and pyridine base absorption from coke gas.

6 - circulating saturator pan; 7 - common pit; 8 - pumps; 9 - gas preheater.

there ran into collector (5), from which the solution was returned to the circulating system. During the experiments, the number of which was limited, the volume of circulating pyridine sulfate was within the range of 3.5 - 5.0 $m^3$, which obviated any solution excess. The acid scrubber was of the packing filler type and had the following characteristics: diameter 4.5 m, total height 14.49 m, packing ceramic (Raschig) rings measuring 80 x 80 x 8 mm, height of operating packing 4.96 m, and of drying section 0.98 m. Experiments were performed in two steps: in the first step the study was limited to the removal of pyridine bases from the gas after passing the saturator under normal operating conditions. In this case the greater part of pyridine was caught in the saturator and the remaining portion of pyridine bases was removed by absorption in this scrubber. From the saturator this solution was run into the pyridine installation.

In the second stage of the experiment the study covered the course of differential absorption of ammonia and of pyridine bases. In this case the pyridine bases were accumulated to the point of dynamic equilibrium between the bases and the gas in the mother solution. To accomplish this the movement of the mother solution from saturator No. 1 into the pyridine installation was discontinued; this stopped the solution in the circulating saturator from overflowing into the common trough, thereby stopping the interchange or intermixing between the mother solution in saturator No. 1 and the solutions in other saturators. However, due to daily solution deoxidation in saturator No. 1 and a consequent drop in acidity caused by the addition of water, the solution was entirely renewed; simultaneously the concentration of pyridine bases dropped from 21 - 22 g/li to 4 - 5 g/li. It was necessary to check the maximal saturation of the vat of saturator No. 1 with pyridine bases under operating conditions prevailing in the solutions of two other saturators of the pyridine installation; for this reason the saturator was not deoxidized over a period of 5 - 6 working shifts.

Table 1 presents data on the operation of saturator No. 1, and of the oxidizing scrubber and data on the saturation of solutions with pyridine bases and on the concentration of pyridine bases in the gas. Absorption of pyridine bases and their accumulation in the solution occurred at scrubber solution temperatures ranging between 48 - 53°. Results of laboratory studies showed that solution oxidation must be of a concentration which would allow the pres-

TABLE 1.

| Exp. No. | Technological scrubber performance system: Solution temperature in C° | Solution acidity in percent | Pressure drop in mm water | Technological scrubber performance system: Water jacket temperature in C° | Solution acidity in percent | Pyridine bases in solution in g/li: Scrubber | Saturator | Pyridine bases in gas in g/li: Before scrubber | After scrubber | Recovery in percent | Notes |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1st stage: Absorption of pyridine bases with installation in operation. | | | | | | | | | | |
| 1 | 50 | 12.5 | 20 | 53 | - | 60.3 | 8-10 | 0.050 | 0.003 | 94.0 | |
| | 2nd stage: Absorption of pyridine bases with installation not in operation. | | | | | | | | | | |
| 2 | 48 | 8.6 | 15 | 50 | 4.5 | 49.0 | 22.7 | 0.115 | 0.003 | 97.5 | |
| 3 | 50 | 6.5 | 15 | 50 | 6.0 | 76.0 | 18.0 | 0.110 | 0.005 | 95.5 | |
| 4 | 48 | 6.9 | 10 | 50 | 3.8 | 111.1 | 22.0 | 0.360 | 0.009 | 97.5 | |
| 5 | 53 | 7.7 | 10 | 59 | 5.4 | 95.0 | 38.2 | 0.164 | 0.008 | 95.3 | |
| 6 | 52 | 8.5 | 10 | 59 | 2.4 | 100.0 | 32.7 | 0.735 | 0.060 | 92.0 | Scrubber solution in weak circulation |
| 7 | 52 | 8.4 | 10 | 59 | 4.5 | 134.6 | 33.7 | 0.430 | 0.030 | 93.0 | |
| 8 | 50 | 12.0 | 20 | 55 | 4.4 | 47.6 | 14.9 | 0.105 | 0.007 | 93.4 | |
| 9 | 51 | 12.7 | 20 | 58 | 2.6 | 52.3 | 32.2 | 0.420 | 0.030 | 92.8 | Scrubber solution in very weak circulation |
| 10 | 50 | 6.6 | 10 | 52 | 7.2 | 119.9 | 25.7 | 0.105 | 0.010 | 90.5 | |
| 11 | 48 | 7.0 | 20 | 52 | 6.2 | 59.0 | 16.0 | 0.180 | 0.020 | 89.0 | |

ence of acid pyridine sulfate in the solution. Further work showed that an average 30% pyridine sulfate in the presence of a slight amount of ammonium sulfate at 50° had no effect on the rate of absorption of pyridine bases. Maximal saturation of the scrubber solution with pyridine bases amounting to 134.6 g/li was not necessarily the limiting concentration. The maximal concentration of 134.6 g/li was the result of the particular experimental conditions.

Degree of pyridine bases absorption was determined primarily by the mode of operation of the circulating scrubber pump. Comparison of analytical data showed that under conditions of comparable pyridine base saturated solutions and under practically the same pyridine base concentrations in the gas prior to its entrance into the scrubber, loss of pyridine bases with the gas, upon emerging from the scrubber, depended only upon volume of circulating fluid. Where circulation was inadequate scrubber packing became incompletely moistened, allowing the gas to pass through without pyridine base desorption. It should be noted that when solution circulation was near normal, the pump operated below its capacity; this was indicated by the fact that under the conditions of operation it supplied 40 - 45 $m^3$/hr, and in some instances 25 - 30 $m^3$/hr, despite the fact that it was designed to supply 60 $m^3$/hr. However,

even at full capacity operation the pump could not supply the actually required minimal 90 $m^3$/hr. Despite the above discussed impediments, the degree of pyridine bases absorption from the coke gas amounted to 95.5 - 97.7%, and even with a circulation of 30 $m^3$/hr the degree of pyridine bases absorption amounted to 93%.

It was necessary to determine conditions which brought about dynamic equilibrium between the content of pyridine bases in the gas and the mother solution in the saturator. The concentration of pyridine bases in the gas before entering the saturator, where the actual study was performed, ranged between 0.39 - 0.46 g/$nm^3$. Temperature of the saturated vat under normal operating conditions ranged between 50 - 53°. The pyridine installation with regard to the mother solution operated only in connection with the saturator under study, and the concentration of pyridine bases was as low as 8 - 10 g/li. A combined study was made of the following three factors: temperature, oxygen content of the saturator mother solution, and concentration of pyridine bases in the latter. Results showed that equilibrium between concentration of pyridine bases in the saturator mother solution and the gas appeared under the following conditions:

Temperature of the saturator vat in C°..... 55 - 60
Percent of oxygen in the saturator vat..... 3 - 4
Content of pyridine bases in the saturator vat in g/li..... 35 - 40

Under practical operating conditions and vat saturation at 30 - 40 g/li of pyridine bases the degree of saturator vat acidity is of greatest significance for equilibrium attainment due to the fact that it is difficult to create wide range temperature changes. A drop in acidity under such conditions to 2.4%, for example, caused some pyridine bases bound with the mother solution to pass into the gas; this was accompanied by an increase in the content of pyridine bases, in the gas leaving the separator, to 0.735 g/$nm^3$; and vice versa with rise in acidity to 5 - 7% and pyridine bases content in the mother solution to 30 - 40 g/li pyridine base absorption from the gas by the solution in the saturator vat continued. Increasing the saturator mother solution acidity during its deoxidation disturbed the equilibrium, and the pyridine base concentration in the gas, as it emerged from the saturator, became reduced to approximately 0.1 g/$nm^3$. However, in the process of differential absorption of ammonia and pyridine bases beyond all saturators, the deoxidation

process had no effect on the rate of pyridine base absorption; this is due to the fact that with a drop in acidity of the mother solution after its deoxidation to normal value of 3 - 4%, pyridine bases previously absorbed from the gas at a higher acidity again pass into the gaseous form.

Part of the pyridine sulfate solution obtained during the operation of the acid scrubber became neutralized, as it passed through the pyridine installation, by mixing with the saturator mother solution, after a slight amount of it was added to the scrubber solution. Reprocessing solutions saturated with pyridine bases up to 150 - 200 g/li can be obtained in a continuous manner by mixing it with a small amount of saturator mother solution; this can also be done intermittently. In the latter case, as a result of reduced quantity of reprocessed solution and greater saturation with pyridine bases, a solution volume collected over a month can be reprocessed in 3 - 5 days. Reprocessing solutions of pyridine sulfate containing 150 - 200 g/li of bases has many advantages over the present technological procedure; the volume of the neutralizer can be reduced and the ammonia balance can be considerably increased. Thus, in separating of 1 ton of pyridine bases from a solution containing 150 g/li at 7% free acidity, eleven times as much of ammonia is required for the neutralization of the free acid as for the neutralization of the saturator mother solution which contains 10 g/li of bases and 5% free acidity. The remaining free ammonia can be utilized in neutralizing sulfates of heavy pyridine bases in the tar distilling department.

Dissociation constants of low b.p. compounds, such as pyridine and its closest homologues, are of considerably lower magnitude than of high boiling point compounds, and the steam tension is considerably lower; this set of conditions creates a state of selective pyridine base sorption, which constitutes one of the shortcomings of simultaneous ammonia and pyridine trapping. Connected with this is the loss with the gas of most valuable low boiling point pyridine bases. The use of differential absorption should improve the quality of the pyridine bases. The validity of the above considerations was verified by laboratory tests as follows: pyridine bases found in different concentrations in gases emerging from the saturator, from the saturator solutions (derivative bases) and from the acid scrubber, were fractionated. Loss in pyridine bases with ammonium sulfate were slight, amounting to 0.04 - 0.06% in the following instances: in obtaining ammonium sulfate with low content

TABLE 2.

| Experiment number | Nature of experiment | Fractional composition in percent in 100% water-free bases | | | | | |
|---|---|---|---|---|---|---|---|
| | | 100 - 120° pyridine fraction | 122 - 135° α-picolynic fraction | 135 - 151° β and γ picolynic, 2,6 latidynic fraction | Total fraction distilled over up to 151° | 151 - 200° fraction | Above 200° |
| 1 | Pyridine bases absorbed in the saturator bath at average loss of bases with the gas after the saturator 0.15 g/nm$^3$ | 28.8 | 15.8 | 9.4 | 54.0 | 26.6 | 19.4 |
| 2 | Pyridine bases absorbed in the saturator bath at loss of bases with the gas beyond the saturator 0.20 - 0.25 g/nm$^3$ | 23.5 | 14.9 | 8.3 | 46.7 | 23.2 | 30.1 |
| 3 | Pyridine bases absorbed in the acid scrubber from the gas beyond the saturator at average bases content in the gas of 0.10 g/nm$^3$ | 49.4 | 14.4 | 8.1 | 72.9 | 18.6 | 9.5 |

of free sulfuric acid, especially after centrifuging; in reducing the amount of tarry substances and during a thorough removal of the tarry substances. The above described acid scrubber used in checking the differential method of catching ammonia and pyridine bases did not prove the most efficient for the purpose. Preliminary computation showed that pyridine bases absorption from 2 coke batteries could be accomplished by 1 small packed scrubber or by a special type of column ~ 2.5 m in diameter and 2.5 - 3.0 m high. Results also showed that a 100 g/li concentration of pyridine bases in the circulation fluid affected only a slight corrosive effect, not exceeding the one produced by the saturator mother fluid.

The method of differential ammonia and pyridine bases absorption can be employed expediently with the processes currently used in the production of ammonium sulfate in spray-type saturators, especially of the improved type. The use of this differential method in connection with any other procedure of

ammonia absorption is not recommended. In connection with the production of ammonium sulfate the method of differential ammonia and pyridine bases absorption can be used in a modified way by combining the differential and simultaneous trapping of the two substances. In this modified process the scrubber solution and a small amount of the saturator mother solution become neutralized, as a result of which some pyridine bases are trapped in the saturator vat.

## Conclusions.

1. Experiments conducted on an industrial scale showed that differential ammonia and pyridine bases absorption was feasible practically, and that nearly 98% of the substances contained in coke gas could be recovered.

2. A 135 g/li concentration of pyridine bases solution was obtained by this process reducing to 10 - 6% the solution volume carried over into the neutralizer.

3. This process also reduced the volume of ammonia required for the decomposition of the pyridine sulfate bases.

4. The quality of the pyridine bases was also improved due to the absorption of more valuable components, such as pyridines and picolynes.

5. The method of differential separation of ammonia and pyridine bases from coke gas can also be applied to the separation of ammonia with the aid of sulfuric acid, using for the purpose spray-type saturators or in connection with other methods of coke gas component trapping.

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Catalytic Removal of Nitric Oxide and Acetylene from Coke Oven Gas.

M. P. Korsh and F. P. Ivanovskii.

Zhurn. Priklad. Khimii, Vol. 29, No. 10, 1561-1568, 1956.

Coke oven gas contains small amounts of nitric oxide and acetylene, both are dangerous admixtures. Through the interaction between nitric oxide, oxygen and diolefin hydrocarbons, tarry substances are formed which settle in different parts of the fractionating equipment and may cause explosions. The fact that coke oven gas contains nitric oxide and its ability to form nitrogen-containing tars, capable of disintegrating explosively, was established in 1926 - 1928 [1]. The sources of nitric oxide formation in coke oven gas were studied by Shpolyanskii and Filippov [2] and others [3, 4]. Measures have been proposed to prevent or to lessen the formation of nitric oxide and of tarry substances, such as changes in the hydraulic cycle of coking ovens, use of denitrified sulfuric acid for washing coke oven gas, etc. The proposed measures lowered nitric oxide content in coke oven gas. However, the complete removal of nitric oxides appears as the only effective way of combatting the accumulation of potentially explosive tars. Several methods have been proposed for the removal of nitric oxide: by dry absorbents, by liquid absorbents, and by catalytic hydrogenation [5, 9].

The present paper is devoted to a study of the catalytic conversion of nitric oxide at atmospheric pressure with the aid of metallic sulfide catalyzers. Reduction of nitric oxide with simultaneous fixation of the oxygen was studied by these authors [9] at 400 - 500° using a copper-nickel catalyst. Later, the use of an iron catalyst was mentioned in a Russian patent [10]. The metallic catalysts in question were used for the reduction of nitric oxide only in the case of purified gases which contained no sulfur compounds and require high temperatures.

Catalytic removal of nitric oxide from coke oven gas, which always contained sulfur compounds, requires the use of a sulfur resistant catalyst. Tropsch and Kassler [11] studied catalysts resistant to sulfur compounds consisting of molybdenum and tungsten sulfides impregnated into a porous carrier. The investigators in question tested a series of catalysts containing from 1 to 23% of ammonium sulfomolybdate. The results obtained by them could not be utilized, since complete decomposition of nitric oxide required a temperature

of 230°. In tests made by the present authors complete removal of nitric oxide was achieved at 150° with molybdenum sulfide appropriately activated. Catalysts proposed in 1935 [12] consisting of sulfides of iron, nickel, cobalt and copper on a porous carrier proved the most active. With these catalysts it was possible to completely remove the nitric oxides, and simultaneously convert the acetylene at a relatively low temperature (130 - 150°). Best results were obtained with iron and nickel sulfides. The use of cobalt and nickel compounds for the catalytic removal of nitric oxide was later described by Tupholm [13]. According to Shneider [14] iron sulfide, especially in the presence of hydrogen sulfide, proved to be a good catalyst for the removal of traces of hydrocyanic acid. The purpose of the present investigation was to find catalysts suitable for the conversion of nitrogen and acetylene contained in coke oven gas into substances which presented no danger at any stage of coke-chemical processes.

Experimental part. Catalysts and gas mixtures were prepared for study in concentrations corresponding to amounts usually contained in coke oven gas. Special attention was given to freeing the initial gases of oxygen. All tests were made by simultaneously analyzing the initial and final gases for the content of corresponding components in the gas mixture. This method obviated many errors resulting from changes in the gas composition in the course of time, especially since the work was done with such highly unstable and reactive gases as nitric oxide and hydrogen sulfide. For the same reason gaseous mixtures containing nitric oxide and mixtures containing hydrogen sulfide were prepared and stored in separate vessels and mixed only as they entered the contact oven.

A nitrogen-hydrogen mixture was used in the experiments as the carrier gas, to which known amounts of nitric oxide and of hydrogen sulfide were added (Fig. 1). The nitric oxide, measured with capillary (1), was introduced into burette (2), where it was mixed with the nitrogen-hydrogen mixture. Final dilution to the desired concentration was achieved in mixer (3), into which the nitric oxide was forced by mercury. The calculated amounts of nitric oxide in the mixture were verified by check analyses. The hydrogen sulfide mixture was diluted with the nitrogen-hydrogen mixture in large bottle (4) and stored over a layer of vaseline oil. The hydrogen sulfide content of the mixture was checked analytically. The gaseous mixtures thus prepared were directed into contact oven (5). The nitric oxide, passing through mixer (3) passed via flow-

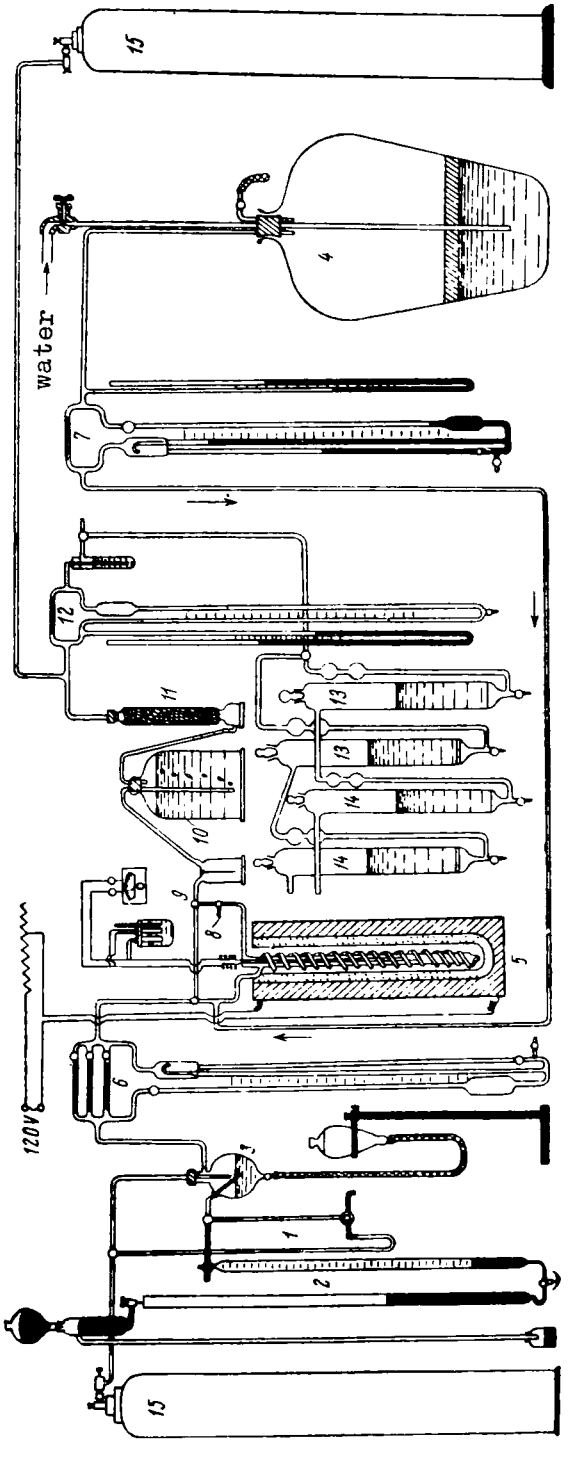


Fig. 1. Plan of installation for catalytic removal of nitrogen oxide and acetylene from coke gas. See text for details.

meter (6), and the mixture containing the hydrogen sulfide via flowmeter (7). After the gas was removed from the contact oven through stopcock (8), it was directed for analysis of the hydrogen sulfide or nitric oxide by closing correspondingly stopcocks (8) and (9). For the determination of nitric oxide the gas, having passed through the alkali scrubber (10), drier (11), and flowmeter (12), entered the analytical apparatus. The latter consisted of a vessel containing potassium permanganate solution (13) (to remove the nitrogen dioxide from the nitric oxide), and an absorption vessel (14), containing Ilosvai reagent to absorb the formed nitrogen dioxide, which was then determined colorimetrically. In many cases, after leaving the contact oven, the gas was diluted with pure nitrogen or nitrogen-hydrogen mixture from flask (15), as an auxiliary step. Sulfides of molybdenum, copper, cobalt, nickel and iron were tested as catalysts in the conversion of nitric oxide and acetylene.

Catalysts were prepared as follows:

a) Sulfomolybdenum catalysts were prepared by mixing a weighed portion of ammonium molybdate dissolved in a small volume of water, with 4 ml of 20% ammonia and heating

the mixture on a waterbath. The solution was then saturated with hydrogen sulfide to obtain ammonium sulfomolybdate. The hydrogen sulfide used for the saturation was first freed of impurities, especially of arsenic compounds, to avoid poisoning the catalyst. The sulfomolybdate thus obtained was applied to porous carriers (pumice, silicagel, aluminum oxide, etc.), which had been thoroughly washed and calcined. The size of the grains was 2 - 2.5 mm. The catalyst was calcined in open air at 250° to decompose the ammonium salts; it was then reduced with hydrogen containing about 30% hydrogen sulfide. Similarly, catalysts were prepared which contained 5, 15.5 and 30% molybdenum disulfide.

b) Catalysts of sulfides of iron, nickel, cobalt and copper were prepared by impregnating porous carriers with solutions of nitrates of corresponding metals. Amounts of nitrates were selected in such a way that after reduction with hydrogen sulfide catalysts contained up to 30% of metal sulfide.

The dry catalyst was calcined in open air at 250° until the nitrate was completely decomposed. The catalyst was then loaded into a reaction tube and with gradual temperature elevation reduced using a nitrogen-hydrogen mixture containing 30% hydrogen sulfide. It was found that the activity of the catalysts depended on the reduction temperature, each having its optimum, which ranged between 200 to 400°. Sulfide catalysts could also be prepared by different methods. Kirkpatrick [15] described a number of reactions by which nickel sulfide catalysts could be prepared.

Tests of sulfide catalysts for conversion of nitric oxide. The catalysts prepared by the above-described method were tested in the apparatus (Fig. 1) in two series: in the first series, the sulfides of copper, cobalt, iron and nickel were investigated for the conversion of nitric oxide. Results of these investigations are listed in the table in which mean values are presented for a number of experiments; they are also presented graphically in Figs. 2 and 3. It can be seen from the table and Fig. 2 that best results were obtained with nickel and iron sulfides. A high degree of conversion was obtained with iron sulfides, with a volume rate of 3000. In Fig. 2 the catalysts are presented conventionally in the form of simple sulfides. Data presented for molybdenum in the table were obtained with a sulfomolybdenum catalyst containing 30% molybdenum disulfide. The effect of molybdenum disulfide concentration on the degree of nitric oxide conversion is shown in Fig. 3.

Nitrogen oxide reduction by metallic sulfides.

| Temperature in C° | Content in original gas: Nitrogen oxide in $cm^3/m^3$ | Content in original gas: Hydrogen sulfide in percent | Content of nitrogen oxide in purified gas in $cm^3/m^3$ | Nitrogen oxide reduction in percent |
|---|---|---|---|---|
| | Copper sulfide, volume rate = 1200. | | | |
| 130 | 4.53 | 0.25 | 1.37 | 69.2 |
| 150 | 2.75 | 0.25 | 0.39 | 86.5 |
| 200 | 2.93 | 0.25 | 0.00 | 100 |
| | Cobalt sulfide, volume rate = 1200. | | | |
| 130 | 3.19 | 0.25 | 0.88 | 71.2 |
| 150 | 2.78 | 0.25 | 0.12 | 95.74 |
| | Nickel sulfide, volume rate = 1200. | | | |
| 80 | 3.44 | 0.25 | 0.53 | 84.8 |
| 120 | 3.14 | 0.25 | 0.20 | 94.7 |
| 150 | 2.80 | 0.25 | 0.04 | 97.1 |
| 200 | 3.10 | 0.25 | 0.00 | 100 |
| | Iron sulfide, volume rate = 3000. | | | |
| 100 | 3.34 | 0.25 | 0.09 | 96.94 |
| 130 | 3.69 | 0.25 | 0.06 | 98.4 |
| 150 | 3.32 | 0.25 | 0.00 | 100 |
| | Molybdenum sulfide, volume rate = 1200. | | | |
| 100 | 4.41 | 0.65 | 1.60 | 64.2 |
| 120 | 3.91 | 0.28 | 0.48 | 88.5 |
| 150 | 4.54 | 0.76 | 0.12 | 97.5 |

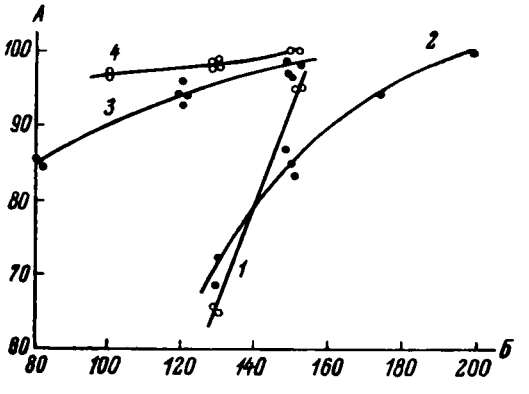


Fig. 2. Effect of different catalyzers on degree of nitrogen oxide reduction.
A - percent of nitrogen oxide reduction; B - temperature in C°.
Catalyzers: 1 - CoS; 2 - CuS; 3 - NiS; 4 - FeS.

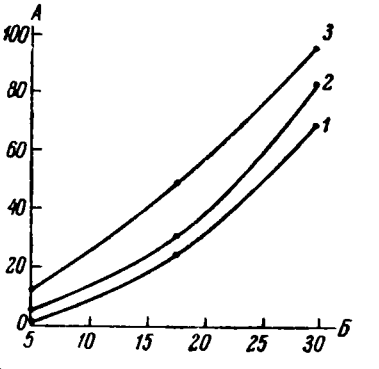


Fig. 3. Effect of molybdenum sulfide content in carrier on degree of nitrogen oxide reduction.
A - nitrogen oxide decomposition in percent; B - percent of molybdenum sulfide.
Temperature in C°: 1 - 100; 2 - 130; 3 - 150.

Tests of sulfide catalysts for conversion of acetylene. In the second series of experiments, the sulfide catalysts were used to convert acetylene. For this purpose the gas was passed over the catalyst as a mixture containing 0.055 to 0.18% acetylene. As the mixture left the catalyst tube, the gas was analyzed for its acetylene content by a colorimetric method, comparing the formed copper-acetylide color with a standard scale of known concentrations. Acetylene was removed from sulfur-containing gases by sulfides of iron, copper, cobalt, molybdenum and nickel. The first three catalysts manifested insufficient activity at 150 - 300° temperature interval. In tests made with sulfides of molybdenum and nickel, total conversion of acetylene at volume rate of 2000 was obtained at 300° for the former and 280° for the latter catalyst. It must be pointed out that in these experiments the acetylene content of the mixture was considerably higher (0.05 - 0.18%) than in the coke oven gas. Therefore, these sulfides can also be used for removing acetylene from coke oven gas.

Discussion of results. The study of catalytic removal of nitric oxide and of acetylene using sulfide catalysts has direct bearing on gas purification in the presence of sulfur compounds. The above tests demonstrated that nitric oxide and acetylene disappeared from the gases as they passed over the catalysts in question. The direction of the general courses of the reaction was studied next. In the presence of hydrogen in the system under consideration, the following reactions must take place:

$$NO + 2.5H_2 = NH_3 + H_2O \quad (1)$$

$$NO + H_2 = 0.5N_2 + H_2O \quad (2)$$

$$NO + H_2S = 0.5N_2 + H_2O + S \quad (3)$$

The probability of any of the reactions taking place is determined by specific free energy changes. Changes in free energy in the above reactions were obtained using thermodynamic data. Without going into details of the calculation method used, negative free energy values were obtained which are shown in Fig. 4; the values indicate that all three reactions are thermodynamically possible. The direction and speed of the reaction are determined by the use of a suitable catalyst. Tropsch and Kassler [11] showed that the basic principle of the method used by them for freeing coke oven gas of nitric oxide with molybdenum sulfide is the catalytic hydrogenation of nitric oxide to ammonia at 230°. No ammonia was produced in experiments performed at 130 - 150° in the presence of iron and nickel sulfide. It was noted that the cold

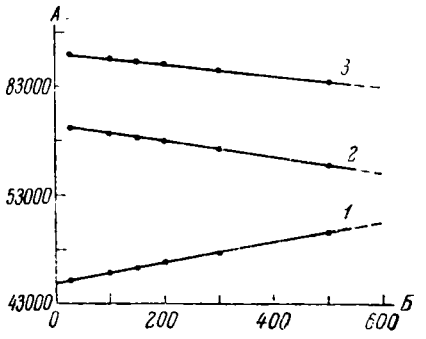


Fig. 4. Effect of temperature on free energy changes. A - Free energy changes $\Delta F$; B - temperature in C°. Reaction 7: $NO + H_2S = 0.5N_2 + H_2O + 1/6\ S_6$; Reaction 2: $NO + H_2 = 0.5N_2 + H_2O$. Reaction 3: $NO + 5/2H_2 = NH_3 + H_2O$.

parts of the reaction and gas outflow pipes became gradually coated with a thin layer of sulfur. A reaction between nitric oxide and hydrogen sulfide apparently had taken place with the deposition of free sulfur.

The removal of acetylene from coke oven gas, together with the catalytic conversion of nitric oxide are of considerable importance. Upon entering a deep cooling apparatus together with coke oven gas acetylene corrodes the copper portions of the apparatus forming explosive copper acetylide. Data found in the literature point to the following possible reaction directions of catalytic conversion of acetylene in gas mixtures: a) decomposition to carbon and hydrogen; b) conversion by water vapor; c) hydrogenation of acetylene to saturated hydrocarbons; and d) polymerization. In the present case, the first two reactions appear less probable, in view of the small water vapor content of the gas, the low temperature and the absence of soot in the products of the reaction and on the catalyst. The probability of the thermodynamic process of acetylene hydrogenation into ethylene according to equation:

$$C_2H_2 + H_2 \rightarrow C_2H_4 \qquad (4)$$

is determined by the free reaction energy changes according to the following equation:

$$\Delta F^\circ = \Delta F_{C_2H_4} - \Delta F^\circ_{C_2H_2}$$

or, in final form:

$$\Delta F^\circ = -36720 + 8.35T \ln T - 0.0022T^2 - 38.6T$$

Below are presented values for free energy of acetylene hydrogenation reactions as derived by the last equation:

| °C | 25 | 100 | 150 | 200 | 300 | 500 |
|---|---|---|---|---|---|---|
| $-\Delta F^\circ$ | 34136 | 32985 | 32050 | 31184 | 28170 | 24939 |

The values indicate possibilities according to which the reaction of hydrogenation of acetylene can proceed. The last one can proceed even at ordinary temperatures. Thus, in the presence of a large excess of hydrogen

in the coke gas and with the use of a suitable catalyst, the reaction of hydrogenation of acetylene appears highly probable. Many reports appeared in the early literature on the hydrogenation of acetylene into ethylene and ethane with the aid of platinum and iron groups as catalysts.

## Conclusions.

1. Active catalysts were found for the complete conversion of nitric oxide and acetylene in gases containing sulfur compounds. Such catalyzers were sulfides of iron, nickel and molybdenum impregnated into a porous carrier.

2. Experiments were conducted with a nitrogen-hydrogen mixture containing nitric oxide and hydrogen sulfide in concentrations close to those found in coke oven gas; complete conversion of nitric oxide was obtained with nickel and iron sulfides at 130 - 150° at a volume rate of 1200 - 3000.

3. Complete removal of acetylene from sulfur-containing gases at an acetylene concentration of 0.05 to 0.18% was achieved at 200 - 280° in the presence of molybdenum and nickel sulfide catalysts at volume rate of 2000.

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# Colorimetric Determination of Lead in Atmospheric Air.

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(From F. F. Erisman Sanitary Research Institute, Moscow).

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In the presence of lead quinalizarin yields a characteristic color which is easily recognized in the presence of 0.005 γ of Pb in 2 ml. In making quantitative lead determinations this author used the following standard comparison scale: test tubes containing 0.05, 0.1, 0.25, 0.5, 1.0, 2.0 and 4.0 γ in 2.0 ml. The developed color ranged from yellow to bluish-rose, with the control tube having a slightly yellowish color. The water used in the preparation of the standard scale must have a pH 6.2 - 6.4. Such water was obtained by double distillation followed by 20 minutes boiling.

Quinalizarin also produced a color in the presence of copper, zinc and iron. Hence, for the determination of lead these interfering metals must be removed. This was accomplished by the method of Golubeva: test solution was treated with 25% ammonia and ammonium chloride, 1 N solution of $Na_2CO_3$ and KCl. The method for removal of interfering metals was checked and found satisfactory.

Samples of air dust were collected by the ash-free filter paper method, aspirating the air at the rate of 2 li/min. After the sample has been collected the filter paper was boiled for 5 minutes in 3% nitric acid; the nitric acid solution was then placed over a boiling waterbath and gradually evaporated to dryness. The dry residue was dissolved in water, placed into a centrifuge tube. Two ml of 25% ammonia solution, 0.2 ml 25% ammonium chloride solution, 0.1 ml 1 N $Na_2CO_3$ solution and 0.1 ml 1 N KCl solution were added. The mixture was brought to a boil and centrifuged; precipitate was washed with ammonia and distilled water, again centrifuged, treated with 10% solution NaOH, again brought to a boil and again centrifuged.

The plumbite solution was neutralized with 3% solution $HNO_3$ to weak acid reaction, placed into a porcelain evaporating dish and evaporated to dryness over a waterbath; the dry residue of lead nitrate was dissolved in 2 ml of water. At this point the eight tube series (including the control) of standard solution was prepared as described above. To all tubes of the standard scale and to the tube containing the test sample add 5 drops of 0.002% of

quinalizerin solution in acetone, allow to rest 2 - 3 minutes and compare colorimetrically.

The method was used in determining lead concentrations in atmospheric air in the proximity of a metallurgical plant, in industrial emissions containing lead, aspirating 50 - 200 ml of the polluted air, depending upon the Pb concentration anticipated. Analytical results showed that the air samples contained lead in the range of 0.05 to 2.75 $\gamma/m^3$.

## Determination of Manganese in Urine.

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Farmakologiya i Toksikologiya, Vol. 18, No. 1, 54-56, 1955.

I. D. Gadaskin showed in 1939 that manganese entered into the composition of normal human and animal tissues and organs in small amounts. Most methods for the determination of manganese in tissues are based on the principle of its oxidation to manganic acid. Lead dioxide, ammonium persulfate, potassium persulfate and potassium periodate are usually used as manganese oxidizers. The polarographic method of manganese determination has also been used to some extent. The most widely employed method for manganese determination is the one in which manganese is oxidized to its semivalent form and determined colorimetrically. This method has been used by Nifontova in 1936 for the determination of manganese in the air. In that method manganese is oxidized by ammonium persulfate in the presence of silver nitrate as a catalyzer. In 1948 Michlin used this method for the determination of manganese in biological substrates. The problem of the present author was to establish the presence of inorganic and organic manganese compounds in rabbit urine. Check tests of the Michlin method made with standard solutions of manganese have always yielded satisfactory results. It was noticed, however, that irregular color

densities were obtained in the preparation of the manganese scale. Experiments indicated that the cause of this was in the improper concentration of different acids. Final results indicated that most satisfactory standard scale was obtained with 15 - 17% sulfuric acid. The use of 20% sulfuric acid was discontinued.

In the experimental tests urine was used to which a solution of manganese salt was added at the rate of 0.04 mg per unit volume; analytical results yielded 0.032 - 0.04 mg, which is equivalent to 70 - 100%.

Treatment of the precipitate with sulfuric acid in a funnel and evaporation of the solution as proposed by Michlin usually consumed much time. To obviate this the following simplification was introduced: the washed precipitate and the filter were placed into a beaker, covered with 15% hot sulfuric acid and left stand for 20 minutes, at the end of which the solution was filtered through an ordinary filter and the manganese determined in the filtrate. The simplified method yielded satisfactory results as indicated in Table 1.

T A B L E 1.

Determination of inorganic manganese compounds in human urine without digestion (mineralization).

| Test No. | Mg of Mn added | Mg of Mn by analysis | Percent of Mn by analysis |
|---|---|---|---|
| 1 | 0.04 | 0.038 | 95 |
| 2 | 0.04 | 0.038 | 95 |
| 3 | 0.04 | 0.038 | 95 |
| 4 | 0.04 | 0.038 | 95 |
| 5 | 0.04 | 0.038 | 95 |

In determining combined manganese 500 ml of the urine were evaporated to dryness over a boiling waterbath. The dry residue was then treated with a combined solution of sulfuric and nitric acids. After the material had become completely digested it was transferred to a porcelain dish and evaporated to dryness. The dry residue was treated with 15% sulfuric acid and filtered; manganese was then determined in the filtrate as described above.

Check tests have indicated that the use of 15% sulfuric acid as a modification to the method yielded satisfactory results. It was noted, however, that in the process of evaporation the solution occasionally developed a yellow color; it was also considered that much time was consumed by the process of sulfuric acid solution evaporation to dryness. Therefore, the sulfuric acid was diluted with water to a 15% concentration and the manganese determined directly.

T A B L E 2.

Determination of manganese with digestion.

| Test No. | Mg of Mn added | Mg of Mn by analysis | Percent of Mn by analysis |
|---|---|---|---|
| 1 | 0.04 | 0.036 | 90 |
| 2 | 0.04 | 0.036 | 90 |
| 3 | 0.04 | 0.04 | 100 |
| 4 | 0.04 | 0.04 | 100 |

It was further demonstrated that the acid concentration affected the determination; it was necessary to dilute the acid to a concentration not exceeding 5 - 6 N. Results obtained by this modification are listed in Table 2. The procedure of the modified method is as follows: add to the urine 500 ml of strong ammonia; 6 - 8 hours later filter the specimen through a Buchner filter; wash 2 or 3 times with hot water. Transfer the filter with the precipitate to a beaker and cover with 15% solution of sulfuric acid. Leave stand for 20 minutes and filter again through filter paper. The filtrate is used for the determination of Mn ions. The standard scale is prepared from a solution of manganese sulfate.

In making quantitative manganese determinations take 500 ml of the urine and evaporate to dryness over a boiling waterbath, first adding 2 - 3 ml of concentrated $H_2SO_4$. Digest the dry residue with a mixture of sulfuric and nitric acids, after digestion has been completed and nitric acid fumes have been eliminated with perhydrol, add water to the flask so calculated that the final acid concentration will amount to 15%. This can be done titrametrically; after this proceed with the manganese determination as described above. The method was tested with urine specimens of rabbits poisoned with manganese chloride over a period of 10 months. Results indicated that manganese was eliminated with the rabbit urine in the form of inorganic and organic compounds. The 24-hour urine specimen was then divided into 2 equal parts, one for the determination of inorganic manganese compounds and the other for the determination of total manganese. Results are shown in Table 3. Tests were also made which indicated that the modified method can be used for the qualitative and quantitative determination of manganese in human and animal tissues and organs.

Conclusions.

1. Inorganic manganese compounds in biological media are determined directly in the filtrate, thereby eliminating unnecessary steps, such as a

TABLE 3.

Determination of manganese in urine of rabbits administered manganese chloride.

| Test No. | Total Mn | Inorganic Mn | Organic Mn | Percent of inorganic Mn |
|---|---|---|---|---|
| 1 | 0.08 | 0.048 | 0.032 | 60 |
| 2 | 0.2 | 0.048 | 0.152 | 24 |
| 3 | 0.2 | 0.04 | 0.16 | 20 |
| 4 | 0.3 | 0.032 | 0.268 | 10.6 |
| 5 | 0.4 | 0.12 | 0.28 | 30 |
| 6 | 0.15 | 0.036 | 0.114 | 24 |
| 7 | 0.08 | 0.012 | 0.068 | 15 |
| 8 | 0.04 | 0.016 | 0.024 | 40 |
| 9 | 0.096 | 0.032 | 0.064 | 34 |
| 10 | 0.12 | 0.02 | 0.1 | 16 |

second processing of the specimen with sulfuric acid followed by its evaporation.

2. In determining total organic and inorganic compounds the urine is wet digested with a mixture of sulfuric and nitric acids and the nitric acid completely driven off, following which the residual sulfuric acid is diluted to 15%, as shown by titrametry, and the manganese ions determined directly in the solution.

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## Rapid Method for the Determination of Carbon Monoxide in the Air of Working Premises.

D. N. Vaskevich, A. I. Bulycheva and P. A. Mel'nikova.

Vodosnozhenie i Sanitarnaya Tekhnika, 1956, No. 1, 12-13.

Improvement in the quality of planned and installed ventilation apparatus in industrial premises requires that they be checked for their efficiency. At present the determination of sanitary-hygienic efficiency of ventilation is considerably impeded by the laborious procedures of chemical air analysis for the content of deleterious vapors and gases. Shortening the time for the determination of deleterious substances may aid considerably in finding the cause of ventilation installation defectiveness and in the early removal of

such causes and, consequently, in raising ventilation efficiency in industrial and working premises.

Carbon monoxide is a most widely occurring industrial poison; it is present in garage exhausts, in foundries, thermic generator, and many other production departments. The importance of timely determination of carbon monoxide concentrations in the air of working premises need not be emphasized. The present method for carbon monoxide determination, as described in GOST 5612-50, is based on the oxidation of carbon monoxide to carbon dioxide by iodine pentoxide. This method is time-consuming, cumbersome, and not always practical. In the course of a working day the laboratorian can perform, at the most, 5 or 6 analyses; the procedure requires a special comparatively complicated set-up and the services of qualified analysts. The official method can not be used for the determination of carbon monoxide concentrations directly at the worker's position. The procedure carried out with the usual type of apparatus requires several days. The method presents considerable difficulties when it becomes necessary to collect and analyze many air samples in a short time. For instance, in making a general inspection of ventilation efficiency in a molding and casting room of a foundry of medium size, it becomes necessary to collect and analyze 30 - 50 air samples in a brief period of time.

The VTsSPS Moscow Institute of Labor Protection developed an indicator method for the determination of low carbon monoxide concentrations in the air of production premises. The method is based on passing the tested air for 3 - 5 minutes through an indicator tube filled with a special white powder (Fig. 1). As the carbon monoxide passes through the tube, the powder acquires a greenish-violet color, the intensity of which is proportional to the carbon monoxide concentration in the air. The intensity of the developed color is then compared with the color of a specially prepared standard series of tubes representing CO concentrations in the range of 0.01 - 0.4 mg/li. The procedure requires 10 minutes and the determination can be made directly on the spot.

Sanitary regulation N 101-54 prescribed that where work was performed continuously 8 hours per day, the carbon monoxide concentration in the air should not exceed 0.03 mg/li; in rooms in which work was performed during 20-minute intervals the

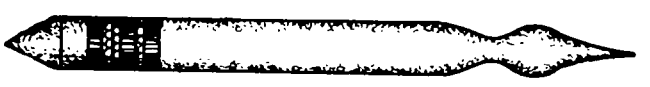

Fig. 1. Indicator tube.

carbon monoxide concentration in the air may be as high as 0.2 mg/li. Tested air in working premises frequently contains pollutants which might interfere with carbon monoxide determinations; in such instances the interfering admixtures may be caught by a special cylinder filter connected to the indicator tube in such a way that the air passes through this filter before entering the indicator tube. The cylinder contains two layers of calcium chloride and activated charcoal. In the process of air passing through the indicator tube acid vapors are given off which corrode the walls of the metallic aspirator. To eliminate this the air is passed through a tube filled with alkali saturated cotton. The indicator tube and the connected filter cylinder are placed into a special housing. This assures the straight line flow of the air through the filters and the tube and simplifies the air sample collection and facilitates the transportation of the setup. The final setup in its casing is shown in Fig. 2. Depending upon the concentration of CO in the air, the latter should be aspirated through the tube in volumes of 1 li or 150 ml. The air is passed through the setup with the aid of a metallic water level aspirator, one tank of which was above a water collecting tank at a definite height. A petcock is arranged between the tanks by means of which it is possible to regulate the outflow of water so that in a period of 3 - 4 minutes either 1 li or 150 ml of air could be aspirated. The general view of the setup is shown in Fig. 3. Here the indicator tube (1) is connected with 2 filters (2 and 3) and through them is connected by means of a rubber tube (4) to aspirator tanks (5) which are attached to a special stand (6). The aspirator

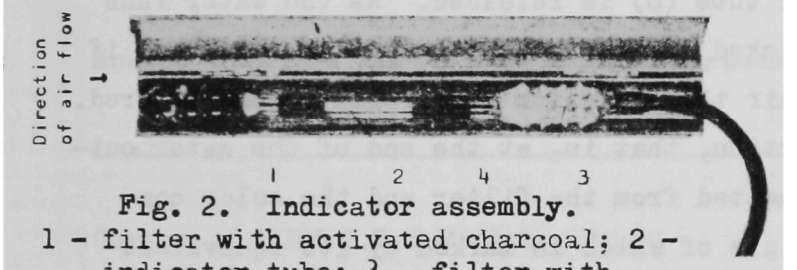

Fig. 2. Indicator assembly. 1 - filter with activated charcoal; 2 - indicator tube; 3 - filter with alkalized cotton; 4 - case.

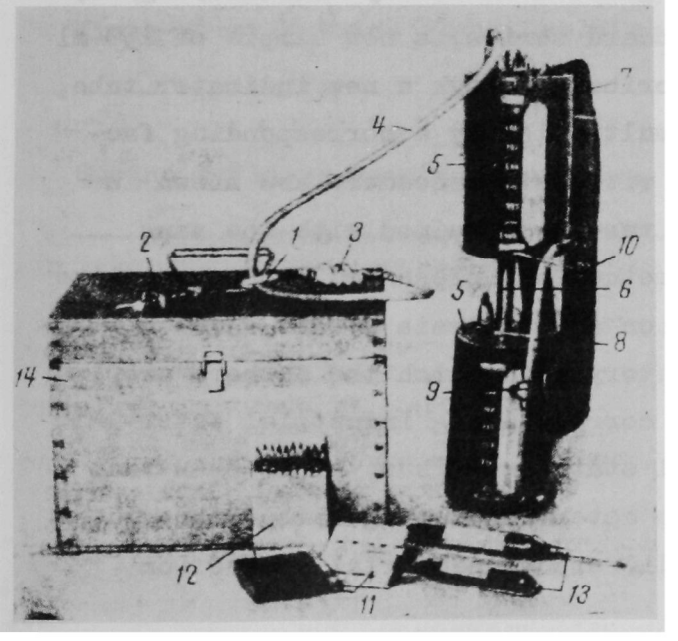

Fig. 3. Device for CO determination. (Details are given in text).

can be carried around by a rubber attachment (7). Aspirator tanks are interconnected by a rubber tube (8) in the middle of which there is inserted a four way stopcock (9). Before sample collecting a Moore pinchcock (10) is placed over rubber tube (8). The apparatus is equipped with a standard set of colors (comparator) (11). There is also a case (12) which contains reserve indicator tubes and ampules (13) with the drying agent and activated charcoal. For storage or transportation purposes the setup is placed into a special box (14).

The sample taking and color comparison are accomplished as follows: the indicator tube is first cut open at both ends by a small file and the end marked by rings is connected to the filter containing the activated charcoal; the other end of the indicator is connected to the second filter containing alkalized cotton. This is then connected to the water aspirator by means of a rubber tube. The setup is then brought to the point of sample collection, and the Moore pinchcock over rubber tube (8) is released. As the water runs out of the upper tank the air is sucked in through the indicator tube, and if carbon monoxide is present in the air the indicator layer will become colored. At the end of the air sample collection, that is, at the end of the water outflow, the indicator tube is disconnected from the filter and the color compared with the standard set, each tube of which is marked by its equivalent carbon monoxide concentration in mg/li. If the color developed in the indicator after aspirating 1 li of air is of greater intensity than 0.09 mg/li, which is the highest equivalent of the standard series, a new sample of 150 ml of air is then aspirated as previously described through a new indicator tube, compared with the standard and the result multiplied by a corresponding factor. Some results obtained by the authors with this procedure are shown in the following table. For control purposes results obtained with the same samples of air by the standard regulation method are presented for comparative purposes. It should be noted that collection and analysis of air samples were not performed by members of the laboratory with which the authors are associated, but by laboratory personnel of corresponding industrial enterprises or of local sanitary-epidemiological stations. Thus, it is seen that the proposed rapid indicator method for the determination of carbon monoxide in the air yielded reliable results under different industrial production conditions.

Comparative data of CO determinations and industrial (practical) conditions.

| Plant and department | Mg/li of CO found | |
|---|---|---|
| | Standard method | New indicator method |
| Vaitovich foundry, casting department | 0.028 | 0.02 |
| | 0.012 | 0.01 |
| | 0.033 | 0.03 |
| | 0.039 | 0.03 |
| | 0.022 | 0.02 |
| Plant "Boretz", casting department | 0.04 | 0.045 |
| | 0.045 | 0.045 |
| | 0.034 | 0.045 |
| | 0.011 | 0.01 |
| | 0.02 | 0.02 |
| Moscow coke gas plant, generator department | 0.02 | 0.01 |
| | 0.11 | 0.12 |
| | 0.02 | 0.02 |
| | 0.01 | 0.01 |
| | 0.04 | 0.045 |
| | 0.006 | 0.01 |
| Garage of MChM U.S.S.R. laboratory | 0.056 | 0.06 |
| | 0.015 | 0.015 |
| | 0.055 | 0.06 |
| | 0.059 | 0.06 |
| Minsk-Kirov Machine Plant, welding department | 0.02 | 0.02 |
| | 0.02 | 0.02 |
| | 0.014 | 0.015 |
| | 0.01 | 0.01 |
| Grodno building materials combine, kiln department | None | None |
| | None | None |
| | 0.028 | 0.015 |
| | 0.018 | 0.015 |

# Comparative Evaluation of Some Methods for the Determination of Beryllium and Its Compounds Applicable to Air Analysis.

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Many methods have been recommended for the determination of small amounts of beryllium in different substances. The methods can be grouped as follows.

1. Colorimetric methods using quinalizarin, naphthazarin, p-nitrobenzeneazoorcin, 1,4-dioxyanthraquinone-2-sulfonic acid, aluminone, alizarin blue BB, thoron, arsenazo, N-resorcinol, berillon II, and other substances. At a given pH each of these reagents changes the color and intensity of its solution in the presence of the beryllium ion; final determination is made by comparison with a standard solution. Minimum determinable amounts of beryllium vary from 0.2 to 2 γ in the volume of solution under study.

2. Fluorescence methods based on the reactions of beryllium ion with morine, 1-amino-4-oxyanthraquinone, 1,4-dioxyanthraquinone, and other substances. Minimum amounts of beryllium that can be determined by these methods range from 0.05 to 1 γ.

3. Spectrographic methods based on measurement of the difference in darkening of the beryllium line and of the element used for comparison: aluminum, thallium, cadmium. The beryllium excitation spectrum is obtained with a carbon arc fed by direct or alternating current of 10 - 16 A, as well as with a condensed spark. The minimum determinable amounts of beryllium, according to literature, range from 0.005 to 1.0 γ. Most of the reagents recommended for colorimetric and fluorescence determination of beryllium are not specific. Such ions as Mg, Ca, Cu, Zn, Al, Fe, Mn, $PO_4$, and others interfere with the determination.

In this connection, it becomes necessary to remove or mask the interfering ingredients. It is suggested, for example, that beryllium be precipitated with phosphates of calcium, iron, aluminum and manganese, with subsequent removal of several cations by electrolysis on a mercury cathode [1], or extraction of the acetylacetonate of beryllium with benzene [2], with subsequent decomposition of the acetylacetonate and re-extraction of the beryllium with 5 N HCl. Trylon B [3, 4], the disodium salt of ethylenediaminotetra-acetic acid, which

forms very stable complexes in alkaline solution with many elements of groups II and III, has found wide use in analytical chemistry of beryllium for the removal of the interfering elements. The beryllium complex is unstable at this pH and is readily decomposed; therefore, it can be determined directly without removal of the admixtures. I. P. Alimarin, I. M. Gibalo, and others made use of the difference in stability of the acetylacetonates and of beryllium complexes and of other metals. Different forms of chromatographic analysis have also been described for the separation of beryllium from mixtures.

The purpose of the present study was to compare several methods for the determination of beryllium in the air. The work was conducted with standard beryllium solutions and also with artificial mixtures containing fixed amounts of calcium, magnesium, iron, aluminum, zinc and manganese. A comparative evaluation was made of the methods for the determination of beryllium with morine, 1-amino-4-oxyanthraquinone, 1,4-dioxyanthraquinone, quinalizerin, thoron, N-resorcinol, arsenazo, and beryllon II. Simultaneously, the tests were made with trylon B in an attempt to counteract cationic interference and to separate the constituents by paper chromatographic partitioning. Results showed that the fluorescence method with morine [1, 5] was the most suited for the purpose. Morine (pentahydroxyflavone) formed with beryllium an intraformational complex having a characteristic yellow-green fluorescence in solutions exposed to ultraviolet radiation. With a beryllium content of 0.02 to 0.8 γ in 5 - 10 ml, the intensity of the beryllium solution glow is proportional to the concentration; with larger amounts of beryllium it is difficult to distinguish any difference in the intensity of the glow.

Optimal pH for this reaction was about 13. Sulfates, chlorides, and nitrates reduced the intensity of the fluorescence. The fluorescence of beryllium solutions was more intense in alkalized distilled water than in solutions of neutralized acids. Minimum determinable amount of beryllium in aqueous solutions was 0.01 γ; in neutralized acid solutions it was 0.05 γ. Depending upon their quantitative levels in the solution under study, a number of elements extinguished the fluorescence of beryllium solutions to a greater or lesser extent. A particularly high degree of extinction was manifested by iron and manganese. It has been established that calcium, magnesium, zinc, manganese, iron and other elements did not interfere with the beryllium determination if trylon B was added to the solution before the addition of alkali.

Trylon B had no marked effect on the intensity of the fluorescence of beryllium solutions.

The fluorescence method for the determination of beryllium with 1-amino-4-oxyanthraquinone and 1,4-dioxyanthraquinone possessed the same sensitivity. Minimum determinable amount of beryllium in alkalinized distilled water was 0.05 γ, in neutralized acid solution, 1 γ. The presence of Ca, Mg, Cu, Zn, Al, Fe, Mn, Si, $PO_4$, and other ions had a greater effect upon the intensity of the solution fluorescence than in the reaction with morine. It was established that the extinguishing action of metal ions was eliminated by adding trylon B to the solution.

In a comparative evaluation of the colorimetric methods based on the reaction of beryllium ion with quinalizerin [6], thoron [7], arsenazo, N-resorcinol [8], and beryllon II [9], best results were obtained with the latter. The reagent was more stable than quinalizerin and gave better contrast transitions of color with changes in the amount of beryllium. The advantage of beryllon II over arsenazo and N-resorcinol rested in the fact that when the reaction occurred under optimal conditions at pH 11 - 13, the effect of many accompanying cations could be eliminated by adding trylon B. When the reaction took place with arsenazo and B-resorcinol, trylon B also formed a complex with beryllium. Upon addition of beryllon II at pH 11 - 13, solutions containing the beryllium ion took on a color ranging from dark blue-violet to light blue. Under such conditions, a control sample free from beryllium assumed a reddish-violet color. Minimum determinable amount of beryllium tested in neutralized acid solution was 0.5 γ.

A standard scale should be prepared ranging from 0.5 to 4 γ at 0.5 γ intervals. Amounts of beryllium greater than 4 γ yielded no distinguishable differences in the intensity of the light blue coloration. It was shown that the simultaneous presence in the solution up to 500 γ of magnesium or calcium, up to 10 γ of iron, or up to 100 γ of aluminum did not interfere with the beryllium determination, provided that trylon B was added to the solution. Supplemental studies were made by the method of ascending partitioning paper chromatography using rapidly and slowly filtering chromatographic paper issued by the Leningrad Paper Factory. The paper was washed with a mixture of acetone and hydrochloric acid. For the development of the chromatogram, a universal indicator was tested, which consisted of an alcoholic solution of 8-oxyquinoline

and an 0.02% morine solution. After it had dried, the chromatogram was kept in ammonia vapor. Under ultraviolet irradiation beryllium spots acquired a greenish-yellow color. The glow intensity and the size of the spots increased with the beryllium concentration. Most complete separation of beryllium from iron, aluminum, calcium, magnesium and manganese was obtained with butyl or isobutyl alcohol saturated with concentrated hydrochloric acid. Fluorescence intensity of spots obtained with 0.01 ml solutions containing 5, 10, 25 or 75 γ of beryllium was readily distinguishable, but the spots were of irregular shapes and tended to diffuse. Results indicated that the method of partitioning paper chromatography, with the above-indicated varieties of paper, and subsequent determination of fluorescence intensity of the spots by comparison with standard spots may be used as a semi-quantitative orientation method.

Subsequent investigations pointed to the promising character of the spectrographic method for the determination of small amounts of beryllium. The work was performed with ISP-22 quartz spectrograph. Spectral excitation was obtained with an alternating current carbon arc (16 A). The 0.015 mm spectrograph slit was illuminated with a three-lens condenser system. The analytical interval between electrodes was 2.5 mm and was kept at this value through the entire period of spectral excitation. Most reproducible results were obtained when beryllium was evaporated from an electrode with an aperture depth of 8 mm and an inside diameter of 1.5 mm; under such circumstances, complete evaporation of the beryllium took place in 2 - 2.5 minutes. A mixture of one part by weight of aluminum sulfate and three parts by weight of spectrally pure powdered carbon was used as the electrode filter. The sensitivity of the method was 0.3 γ of beryllium per test sample.

The following procedure for performing the analysis is recommended:

Collection of air samples and preparation for analysis. If beryllium and its compounds are present in air in the form of an aerosol, the sample is collected at the rate of 8 - 10 li/min. on "blue ribbon" filter paper, fastened in the shape of a cone with a special clamp. The vapor is aspirated at the rate of 2 - 3 li/min. in 2 consecutively joined glass absorbers equipped with a No. 2 porous plate. Distilled water was used for water-soluble compounds and 10% hydrochloric acid for metallic beryllium and for other substances insoluble in water as the absorption solutions for the vapor and as a solvent for beryllium extraction from the filter. The filter paper was transferred to

a glass beaker and treated two or three times with 5 - 10 ml of the solvent. The solution was drawn off by suction after each washing. The wash solutions were combined, and their total volume measured. In calcining beryllium oxide the filter paper was transferred to a crucible, moistened with several drops of concentrated nitric acid, placed in a muffle furnace, and ashed at about 500°. After cooling, 2 ml of concentrated sulfuric acid was added and heated on a sand bath until the precipitate dissolved. The sulfuric acid was driven off and the residue dissolved in 20 ml of 10% hydrochloric acid.

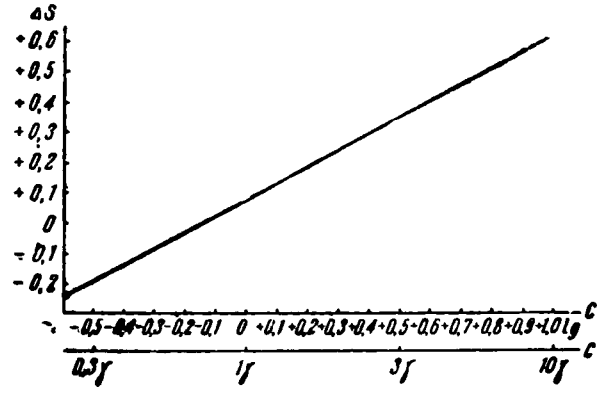
Analysis using morine. Place 1 ml of the test sample in one colorimetric test tube and 5 ml in another. At the same time prepare a standard scale with a beryllium content of 0, 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 γ. Solution volumes in the standard scale and test sample are then brought to 5 ml with 10% hydrochloric acid. Add to each tube 0.5 ml of a 10% solution of trylon B, and neutralize with 10% sodium hydroxide to a weak basic reaction using litmus paper as indicator. Now, add to each tube 0.1 ml of 0.02% alcoholic solution of morine and mix thoroughly. Leave stand for 10 minutes and compare intensity of the yellow-green fluorescence of the sample with that of the standard scale under filtered ultraviolet illumination.

If the test sample does not contain impurities that extinguish the luminescence, trylon B need not be added. If distilled water is used as a solvent, the standard scale is prepared with a beryllium content of 0, 0.01, 0.02, 0.03, 0.04 and 0.05 γ of beryllium. The volume of the solution in the test sample and in the standard scale is brought to 5 ml with distilled water.

Analytical procedure using "beryllon II IREA". Place 1 ml of the sample into one colorimetric tube and 5 ml into another. Simultaneously prepare the standard scale with beryllium content of 0, 0.2, 0.4, 0.8, 1, 2, 3 and 4 γ of beryllium. Raise volume of solutions in the test sample and in the standard scale to 5 ml with 10% hydrochloric acid and add 0.5 ml of a 10% trylon B solution to each tube; neutralize the acid with 20% NaOH solution to the point at which congo (red) paper assumes a violet color, then add an excess of 0.05 ml. Now add 0.5 ml of an 0.02% beryllon II solution to each test sample and standard scale solution, carefully mix; leave rest for 5 minutes and compare with the standard scale, remembering that if the analyzed volume of the test sample contained more than 4 γ beryllium, the differences in the intensity of the light blue coloration would not be discernible.

Chemically pure beryllium sulfate or some other soluble salt can be used in the preparation of the standard solution.

Preparation of the test sample and analysis by the spectrographic method. Place the filter paper into a platinum wire loop and ignite over an agate mortar containing 100 mg of a mixture consisting of three parts spectrally pure carbon dust and one part aluminum sulfate. Add a small amount of alcohol and homogenize thoroughly and evaporate the alcohol with warm air. Prepare standard scales similarly to contain 0, 0.3, 1.0, 3.0 and 10.0 γ of beryllium in 100 mg of charging mixture. Test samples and standard scales thus prepared are loaded into the aperture of the electrode to the tip and photographed on a single photoplate, beginning with the control standard containing no beryllium and through those of higher concentrations, ending with the test samples to be analyzed, by such procedure each standard and test sample are photographed 3 times at slit width of 0.015 mm. The carbon arc is fed by an alternating current of 220W and current intensity of 14 - 16 A. Exposure is 2.5 minutes. The photoplate is developed, fixed, washed, and air dried. The spectrograms are photometered with the MF-2 microphotometer, and determinations made of mean darkening difference ($\Delta S$) of 2348.6 Å beryllium and of 2367.1 Å standard aluminum comparison line. Construct a graph as shown in the figure below plotting logC along the abscissa and $\Delta S$ along the ordinate. The amount of beryllium in the test sample can be determined with this nomogram. The functional relationships between logC and $\Delta S$ within the 0.3 - 10.0 γ range follow the course of a straight line.




Calibrated graph.

In instances when aluminum is present in the air together with beryllium, only spectrally pure carbon dust should be used as the charge. Intensity of the beryllium line darkening is measured with respect to the background.

Conclusions.

1. The most sensitive and promising methods for the determination of beryllium in the air of industrial premises are: the fluorescence method with morine and the colorimetric determination with beryllon II.

2. Use of trylon B as a complex-former eliminated the effect of many interfering elements and made possible the determination of beryllium in the presence of calcium, magnesium, iron, zinc, aluminum, and manganese, without their preliminary separation.

3. The spectrographic method of beryllium determination yielded promising results.

4. The method of paper partitioning chromatography appeared promising as a semi-quantitative method for the determination of beryllium in the presence of calcium, magnesium, iron, manganese and aluminum.

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## Phenol Determination in the Presence of Polyatomic Phenols in the Air During Foundry Casing Pouring.

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Short pouring has become an important attainment of the foundry industry within the last 10 years. Casings used in this process are made of a special mixture consisting of finely ground quartz and heat reactive rosin, mostly phenol-formaldehyde rosin, made with phenol [$C_6H_5OH$], tricresol [$C_6H_4CH_3OH$] and xylenol [$C_6H_3(CH_3)_2OH$]; of late pitch tar has been used as binding material. As a rule, any of these binding materials contained not more than 6% of free phenol, except for cresol rosin which contained 11 - 12% of free

phenol. From the viewpoint of industrial hygiene this is a factor of considerable importance, since in the process of outer casing and core preparation the sand-rosin mixture has to withstand a heat ranging between 240 - 450° and during metal pouring it has to be able to withstand a temperature ranging between 1300 - 1400°.

It has been known that determination of phenol in the air of production premises presented no difficulties, especially when the Milon color reaction or the paranitroaniline diazotizing or sulfanilic acid diazotizing reactions were used. However, the utilization of the above reactions for the determination of phenol in the air as a rule, presents some difficulties under foundry conditions during the process of pouring; this is due to the fact that extraneous color shades came into play which masked the basic character of the color reaction. The cause of such interference is found in the complex composition of heat wood destruction rosin and of other rosins; according to data found in the literature wood rosin contained not only monoatomic but also polyatomic phenols, such as $[C_6H_4(OH)_2.C_6H_3(OH)_3]$. The problem under study concerned the development of conditions which would permit the separation of monoatomic phenol from the above mentioned mixture, so that it could be reliably determined by the colorimetric method. The authors aimed at developing a procedure which would permit the microgram determination of phenol, hydroquinone, pyrocatecin, resorcin and pyrogallol simultaneously present in aqueous solution.

Data found in the literature indicated that action of peroxide on benzene, and in particular of hydrogen peroxide, in the presence of a catalyzer at 45°, resulted in the formation of mono-, di- and triatomic phenols. I. I. Ioffe and E. V. Sokolova showed that the application of concentrated solution of hydrogen peroxide can break down monoatomic phenol without the presence of a catalyzer and without the application of heat, while at the same time having no practical effect on carbolic acid (phenol). The present authors used this as the principle in their studies for the development of conditions required for phenol determination in the air of premises where metal casing pouring was practiced.

Preliminary laboratory studies were conducted as follows: known quantities of phenol, hydroquinone, pyrocatecin, resorcin, and pyrogollol solutions were placed into conical flasks of 50 - 60 ml capacity, the total volume was then

made up to 10 ml; this was followed by the introduction of 2 ml 1 N $NH_4OH$, 0.5 ml of perhydrol (hydrogen peroxide) mixed and left stand for 2 hours at room temperature. Excess of hydrogen peroxide was decomposed by the addition of 0.05 g $MnO_2$.4 (?). The solution was then filtered through cotton. Quantitative determination of phenol was then made according to the diazotization reaction with sulfanilic acid. This reaction possesses a high degree of sensitivity. Molar extinction coefficient determined by these authors with a photocolorimeter FEK-M for the color reaction under consideration was equal to 14,085, whereas for the Milon reaction the extinction coefficient was only 1305. Standard color scale most convenient for use in comparing colors was prepared as follows: final volume was made up to 10 ml with water, and after mixing was left standing for 10 - 15 minutes. See Fig. 1.

Standard color scale for the determination of phenol by the method of combined azo- and diazotizing with sulfanilic acid.

| Colorimetric test tube number | 0 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| Ml of 0.01 mg/li phenol solution | 0 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
| Corresponding to µg of phenol | 0 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Ml of 1 N $NH_4OH$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| Ml of 10% $Na_2CO_3$ solution | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Ml diazotized sulfanilic acid | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |

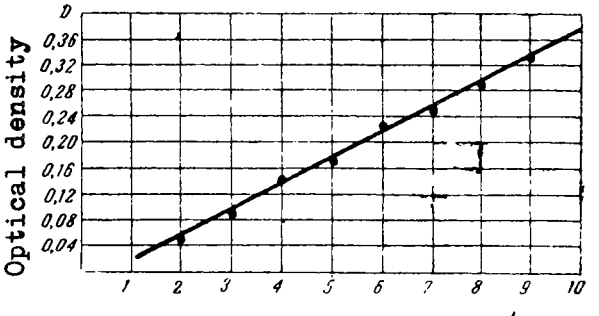


Fig. 1. Photocolorimetric determination of phenol with diazosulfanilic acid.

The following reagents are required for the preparation of the diazo solution: a) solution of 0.0836 g of sulfanilic acid ($H_2NC_6H_4SO_3H.2H_2O$) in 200 ml of water; b) 0.0345 g of sodium nitrite ($NaNO_2$) C.P. in 100 ml of water; c) 0.1 N HCl solution.

The sulfanilic acid is diazotized by placing 10 ml of solution (a), 2.5 ml of solution (b) and 87.5 ml of solution (c) into a 100 ml volumetric flask. The diazo solution will keep for 2 - 3 days at 0 - 5°. Results of quanti-

tative determinations listed in Table 1 illustrate the utility of the standard color scale and the high sensitivity of the determination method.

TABLE 1.

Results of quantitative evaluation of phenol standard color scale by the sulfanilic diazotizing reaction.

| µg of phenol used | µg of phenol determined | | Difference between actual and determined in percent | |
|---|---|---|---|---|
| | By direct visual method | Photocolorimetrically | By direct visual method | Photocolorimetrically |
| 2.0 | 2.0 | 2.0 | 0 | 0 |
| 2.4 | 2.25 | 2.4 | -6.3 | 0 |
| 2.5 | 2.75 | 2.5 | +9.1 | 0 |
| 3.0 | 2.75 | 2.8 | -8.3 | -6.6 |
| 3.5 | 3.5 | 3.6 | 0 | +2.8 |
| 4.5 | 4.5 | 4.55 | 0 | +1.0 |
| 5.5 | 5.5 | 5.5 | 0 | 0 |
| 6.5 | 6.5 | 6.5 | 0 | 0 |
| 7.5 | 7.0 | 7.45 | -6.3 | -0.6 |
| 8.0 | 8.25 | 7.7 | +3.1 | -3.7 |
| 8.5 | 9.0 | 8.5 | -5.9 | 0 |
| 9.0 | 9.0 | 8.9 | 0 | -1.1 |

Note: Photocolorimetric determinations were made in colorimetric cups of 20 mm inside diameter using a green light filter.

Tests were made with aqueous solutions of mixtures of phenol, hydroquinone, pyrocatechin, resorcin and pyrogallol. Results showed that in oxidizing microgram quantities of the above mixture of phenols by the method previously outlined, phenol remained practically unchanged, while hydroquinone, pyrocatechin, resorcin and pyrogallol were completely destroyed by the oxidation. Results of experimental tests are listed in Table 2.

TABLE 2.

| Mg of substance in 10 ml of analyzed fluid | | | | | Determined |
|---|---|---|---|---|---|
| Phenol | Hydroquinone | Pyrocatechin | Resorcine | Pyrogallol | "D" values |
| 7.52 | - | - | - | - | 0.330 |
| 7.52 | 2.2 | 2.2 | - | 2.2 | 0.310 |
| 7.52 | 2.2 | 2.2 | 2.6 | 2.2 | 0.316 |

Higher phenol values than actual began to appear only with a triple excess of polyatomic phenols. Practical determinations were made in the foundry departments of "Stankolit" and in the Moscow brake producing plant in the

TABLE 3.

| Time and place | Phenol found in mg/li of air | |
|---|---|---|
| | "Stankolit" plant | Brake plant |
| Immediately after pouring | 0.019 | 0.037 |
| 3 minutes later | 0.035 | 0.097 |
| 6 minutes later | 0.027 | 0.025 |
| 9 minutes later | 0.057 | 0.003 |
| 12 minutes later | None found | None found |
| 15 minutes later | None found | None found |
| 18 minutes later | None found | None found |
| 21 minutes later | 0.012 | None found |
| 24 minutes later | 0.012 | None found |
| 30 minutes later | 0.012 | None found |

section which employed the method of casting into quartz sand forms held together by PS-1 (peskovaya smola - pitch tar), or shale rosin, or tar binders. Air samples were collected by aspiration at the rate of 0.5 li/min. through two Zaitsev absorbers, each containing 5 ml of water. At the end of sample collection the content of the two absorbers was poured into a ground-to-fit glass stoppered bottle of 50 - 60 ml capacity and oxidized as previously described. After the catalytic decomposition of the excess of hydrogen peroxides with chemically pure pyrolucite ($MnO_2$) the solution was filtered through a compact cotton filter into a 50 ml volumetric flask. The precipitates collected on the filter were washed 3 times with 5 ml of water. The sample was neutralized with 2.2 ml of 1 N solution of HCl, followed by the addition of 5 ml of the diazotizing sulfanilic acid solution, 0.5 ml of 10% solution of $Na_2CO_3$ and 5 ml of 1 N solution of $NH_4OH$; the volumetric flask was then left standing for 15 minutes at 0 - 5°, the volume was made up to the 50 ml mark with water, well mixed and the quantitative phenol determination made as above described, using the previously prepared standard color scale, and the colorimetric comparison made by the visual method. Simultaneously, the standard scale range of 0.02 - 0.12 mg of phenol was processed the same as the sample. See Fig. 2.

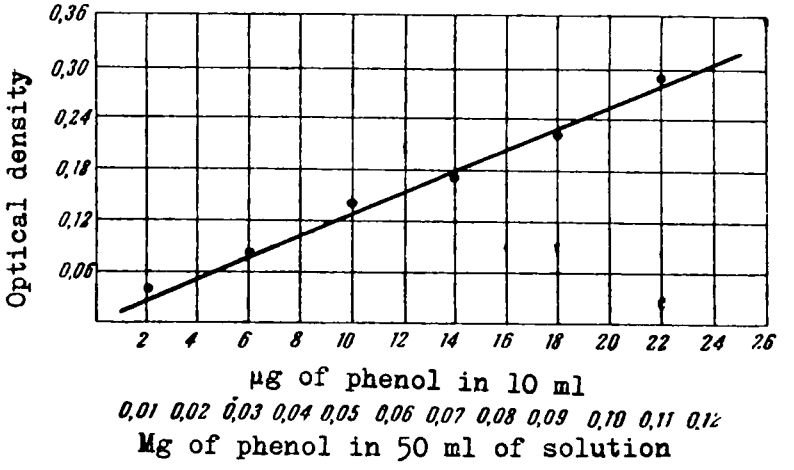


Fig. 2. Photocolorimetric phenol determination by diazosulfanilic acid after separate oxidation.

Following are shown results of phenol determinations in the section of gas emission in the depart-

ment of form casting into the casing prepared from quartz sand and held together by the previously described rosin and pitch binders. Totally different results were obtained by analyzing air samples by the old method, i.e., without the preliminary peroxide decomposition of the polyphenols and the intermediates resulting from heat decomposition of the binders.

For comparative purposes results of same air sample analyses are presented made by the old and new procedures, i.e., with and without preliminary peroxide treatment.

TABLE 4.

| Type of analysis | Exp. No. | Phenol found in mg/li of air | | | | |
|---|---|---|---|---|---|---|
| | | During pouring | 3 minutes later | 6 minutes later | 9 minutes later | 12 minutes later |
| Samples not oxidized | I | 1.6 | - | 1.0 | 0.175 | 0.25 |
| Ditto | II | 1.0 | 1.0 | 1.0 | 0.35 | 0.15 |
| Samples oxidized | I | 0.08 | 0.017 | None found | None found | None found |
| Ditto | II | 0.019 | 0.035 | 0.027 | 0.057 | None found |

As was to have been expected, values obtained by the old method were 20 - 60 times as high as they should have been taking into consideration actual concentration of phenol contained in the binders.

## Conclusions.

A procedure was established for the determination of phenol in the air of foundry department for casting metallic forms using casings prepared from quartz sand held together by binders of different types of rosins and pitch tar, which emitted phenol into the surrounding air simultaneously with polyatomic phenols and other intermediate products of binder materials decomposition by the high heat used in casting. The basic principle of the new procedure is the decomposition of intermediates secondary to phenol by hydrogen peroxide, according to the method of Ioffe and Sokolov. Phenol values in excess of actual began to appear with a triple excess of polyphenols over phenol.

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# Perfecting Direct Gas Sample Taking for the Determination of Benzene Hydrocarbons.

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(From the Yasinovsk Coke-Chemical Plant).

Koks i Khimiya, 1958, No. 1, 52-53.

It frequently becomes necessary to determine the concentration of benzene hydrocarbons in the gas of individual batteries and also in individual coke ovens under practical working conditions. Such determinations have been made by the method of activated charcoal absorption. The system of drawing off and of absorbing the gas for purposes of analysis by the activated charcoal method frequently necessitates interruption of operation due to the fact that the gas diverting pipe and the gas absorption system become clogged with tar and form condensates during sample collection. Therefore, the Yasinovsk Coke-Chemical Plant had introduced some changes into the operation of the gas diverting system and into the absorption apparatus, to eliminate the previously existing difficulties in collecting gas samples. The changes made possible uninterrupted gas sample collecting. The modified apparatus required no constant watching; only once every 3 or 4 hours was the setting of the meter corrected to insure the required rate of gas flow. The plan of the setup is illustrated in Fig. 1.

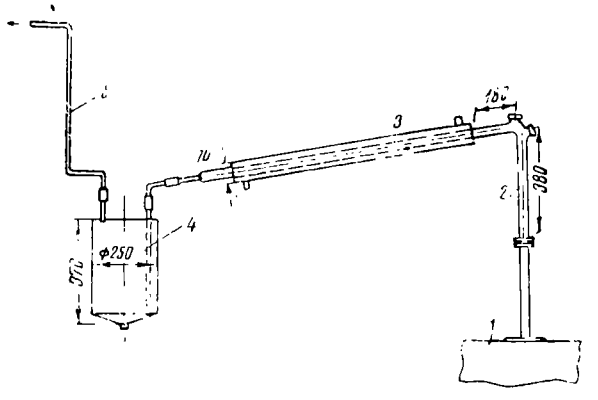


Fig. 1. Plan of the drawing off (suction) installation.

The gas was drawn off from the direct (raw) gas conduit (1) behind the throttle valve, i.e., at the section which maintains an even gas composition of minimal dilution. A vertical pipe (2) 30 mm in diameter and 1200 mm high extended from the gas conduit; a metal (iron) water cooled condenser (3) 1000 mm long and 30 mm inside diameter was attached to the vertical pipe at a descending angle. The tar and condensate ran into the small condenser tank which was equipped with a spigot for the removal of the tar condensate. The consecutive gas cooling in the vertical air cooler (5) and in the water cooler

reduced the concentrations of tar and water vapor in the gas entering the preparation apparatus. The plan of the absorber setup is illustrated in Fig. 2. Gas purification was accomplished in a consecutive order by passing through two glass absorbers (1) containing 30% sulfuric acid solution, an empty safety glass container (2), two glass absorbers (3) filled with cotton, small tanks (4) filled with bog ore, and a control flask (5) filled with copper sulfate to take care of the presence of sulfuric acid before the gas entered the two adapters (6) filled with activated charcoal.

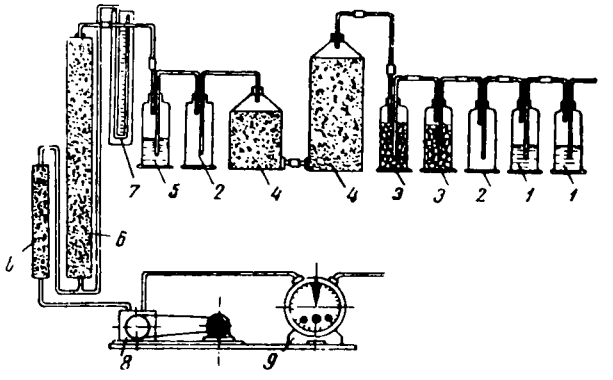


Fig. 2. Plan of the absorber installation.
7 - manometer; 8 - vacuum pump; 9 - gas meter.

The empty safety flask (2) serves as a receiver of any acid which, in its absence, might have been carried over into the cotton on one side and of the copper sulfate into the bog ore on the other side in the event of reverse suction. Insignificant as the described changes may appear, i.e., passing the gas through 30% sulfuric acid solution and then through the absorbent cotton, they nevertheless made possible uninterrupted operation of the setup. This was due to the fact that upon passing through the sulfuric acid solution the gas was deprived of its moisture and of the tar it may have contained, leaving only traces of tar upon the absorbent cotton; and since the gas was deprived of its moisture the possibility of water vapor condensation was eliminated. Equally effective was the purification of the gas from hydrogen sulfide by the bog iron ore.

By the new method gas samples were collected from two batteries over an extended time. The rate of gas flow during gas sample collection varied between 600 - 700 li/hr. The gas drawing off system needed no cleaning throughout the entire period of gas collection and analysis, despite the fact that such an emergency had been anticipated. On the basis of successful operation experienced by the Yasinovsk Coke-Chemical Plant with the new setup, it is recommended that the new method of collecting direct (raw) gas samples for the determination of benzene hydrocarbons be adopted widely by coke-chemical plants.

# An Automatic Gas Analyzer for the Determination of Benzene Hydrocarbons in Coke Gas.

A. T. Bendik and A. E. Eidelman.

(Zaporozhie Coke-Chemical Plant).

With the assistance of M. E. Niemark, M. M. Bragiletskaya, A. S. Musnenko and L. I. Orendarenko.

Koks i Khimiya, 1958, No. 2, 38-40.

The efficiency of benzene scrubbers is judged by the loss of benzene hydrocarbons in the return (purified) gas. Existing chemical tests for the determination of such losses are imperfect because they are time-consuming and lack precision; most important is the fact that the analysis is delayed so that the results refer to a completed shift and, thus, prevent timely information of a current shift in the normal operation of the scrubber. The Zaporozhie Coke-Chemical Plant has been conducting operational check tests of the automatic analyzer type OP-3301 developed by the Leningrad Station, Soviet Union Bureau Designing Apparatuses for Gas Analysis ("G5KB-AGA"). The operational principle of this gas analyzer is based on the utilization of the property of benzene hydrocarbons to absorb wave lengths of 230 to 270 mμ in proportion to their concentration. In the construction of this gas analyzer use was made of the latest photo-electrical and electronic devices.

The basic plan of this gas analyzer, Type OP-3301, is shown in Fig. 1. Coke gas entering this analyzer passes first through an electrostatic precipitator (1) in which the gas is cleared of all dust and vapor impurities; it then passes through chamber (2) where the gas is purified of all components interfering with the analysis, then passes through chamber (3) which regulates the uniformity (in time) of gas delivery into work chamber (4). Next to the latter is the control chamber (5) which is filled with air. Part of the bactericidal

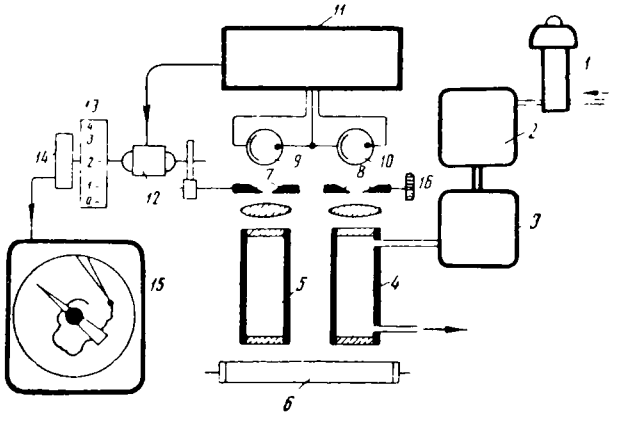


Fig. 1. General plan of the gas analyzer.

ultraviolet lamp (6) light emission is directed into two optical chambers (4) and (5), both equipped with flat quartz windows at their ends, a shutter mechanism of two diaphragms (7) and (8) and two photoelements (9) and (10).

In the absence of benzene hydrocarbons in the tested gas the electrical voltage of 50 cycles frequency at the resistance loads of the photoelements is of equal magnitude but of opposite phases and, therefore, the electrical voltage (tensions) at the entry into electronic system (11) is nil. With the appearance of or increase in the benzene concentration in work chamber (4) the current of the photoelement (10) decreases and as a consequence, tension develops at the entry of the electronic system (11). The electronic system enhances this tension and directs it into a reversible motor (12). The latter begins to rotate, closes the shutter diaphragm (7) and thereby reduces the rate of UV transmission flow and of the current of the photoelement of comparator chamber (5). Rotation of the reversible motor (12) continues until the flow of UV radiation through the work chamber (4) and the comparison chamber (5) become equalized. With the decrease in the concentration of benzene in work chamber (4) the reversible motor (12) starts to rotate in an opposite direction thereby restoring the balanced condition of the optical system. The shaft of the reversible motor carries a graduated disc (13) which indicates the benzene concentration in $g/m^3$ of gas; the shaft also carries a remote slide transmission (14) connected by wires with a secondary automatically recording apparatus (15). There are other auxiliary devices which are parts of the apparatus, the details of which are not here described but which regulate the current supply and work chamber (4) temperatures.

Tests of gas analyzer "GP-3301" under working plant conditions with the cooperation of "UKhIN" and "GSKB-PGA" (now OKBA of analytical apparatus) brought out the need for making many changes and additions in the construction of the apparatus. The most essential factor which insured precision in the work of the gas analyzer was the requisite of a higher chemical gas purification than was originally provided for. It was also necessary to incorporate into the apparatus a supplementary tension stabilizer of the current fed into the booster of the photoelements. The original load resistance of the photoelements of 0.25 vt were replaced by load resistance of 2 vt. The system of distance transmission with the auto-recording millivoltmeter "SG" was replaced by a system having an automatically recording electronic potentiometer

"EPD". These changes and additions insured a dependable 24-hour automatic operation and recording of the analyzer. Check tests showed that determination errors did not exceed 0.5 $g/m^3$.

The apparatus was then tested in analyzing gases purified according to provisions by washing with a 5% potassium permanganate solution mixed in 1:1 with a 15% orthophosphoric acid solution, followed by absorption of the naphthalene by picric acid; it was found that in 2 - 3 hours all gas passage in the cleaning chambers were completely choked by precipitated impurities. Additional absorbers were installed containing 83% sulfuric acid and 80% of alkali. After that the gas purification proceeded satisfactorily; precipitation of solids stopped and the apparatus worked satisfactorily. Results of comparative analyses for the content of benzene hydrocarbons in the gas by the method of absorption by activated charcoal and by the automatic gas analyzer are shown in Table 1.

T A B L E 1.

| $g/m^3$ of benzene hydrocarbons in the gas | | |
|---|---|---|
| As indicated by the automatic gas analyzer | According to the results of activated charcoal absorption | Difference in $g/m^3$ |
| 1.43 | 1.48 | -0.05 |
| 1.25 | 1.14 | +0.11 |
| 1.67 | 1.67 | 0 |
| 1.48 | 1.72 | -0.24 |

Note: Apparatus zero adjusted hourly.

Cleaning of the gases prior to analyzing for benzene by the method of activated charcoal and by the automatic gas analyzer method was done identically. Data in the table show that with careful supervision of the analyzer operation and by a periodic correction of its zero position, the apparatus assured results coinciding with those yielded by the usual test method. Tests were then made with gases purified only by 83% sulfuric acid and 30% NaOH. Results are listed in Table 2.

T A B L E 2.

| $g/m^3$ of benzene hydrocarbons in the gas | | |
|---|---|---|
| As indicated by the automatic gas analyzer | According to the results of activated charcoal absorption | Difference in $g/m^3$ |
| 4.09 | 3.48 | +0.61 |
| 4.00 | 3.64 | +0.36 |
| 2.05 | 2.03 | +0.02 |
| 1.59 | 1.49 | +0.10 |
| 2.56 | 2.51 | +0.05 |
| 2.38 | 2.53 | -0.15 |

Note: Apparatus zero adjusted hourly.

The listed results show the high sensitivity of the apparatus, its ability to dupli-

cate results; results also show importance of proper gas purification before running it into the apparatus and that gas impurities markedly shifted the apparatus zero position. Deviation from the zero point on the apparatus during its continuous work was established by special observations and notes made every 2 hours. It was found that zero mark always shifted in the direction of increase, serving as additional proof of the insufficient gas purification of unsaturated compounds which easily polymerize under the effect of ultraviolet radiation. Further increase in the gas purification by using a greater number of absorbents failed to obviate the necessity of adjusting the apparatus zero point. The fact that shifts in the zero point position basically depended upon the tested gas purity was verified by checking the apparatus on three successive days without gas passage through it. The apparatus performance was normal producing a circle-shaped curve free of any shifts.

There remained the problem of absolute removal from the gas of all compounds which deposited a thin film on the work chamber windows. Formation of the film increased the shift in the analysis results by as much as +0.7 $g/m^3$ per 24 hours. Therefore, it is necessary to be watchful of the condition of the windows in the work chamber and to wash them daily. Incorporation of new physical methods of analysis and of controls, as a rule, calls for a revision of many concepts and definitions. In this instance it concerns benzene losses in the return gases. "Benzene losses" is the term which denotes quantity of hydrocarbons absorbed by activated charcoal from a measured volume of gas after it had been freed of hydrogen sulfide, carbon dioxide, hydrogen cyanide and naphthalene. The talk is generally about "benzene losses", even though it is well known that the hydrocarbons absorbed from the gas by activated charcoal represent a complicated mixture in which benzene proper and its homologues constitute a minor portion.

Concentration of aromatic hydrocarbons in raw benzene of return gas is approximately 50% and varies directly with the extent of the losses. In evaluating the results yielded by the automatic gas analyzer on the concentration of benzene hydrocarbons the fact must be borne in mind that the analyzer records only the content of aromatic hydrocarbons and that "other losses" were held back by the process of chemical purification. Therefore, the amount of benzene losses indicated by the apparatus are considerably lower than the losses arrived at by analysis with activated charcoal. Comparative tests were con-

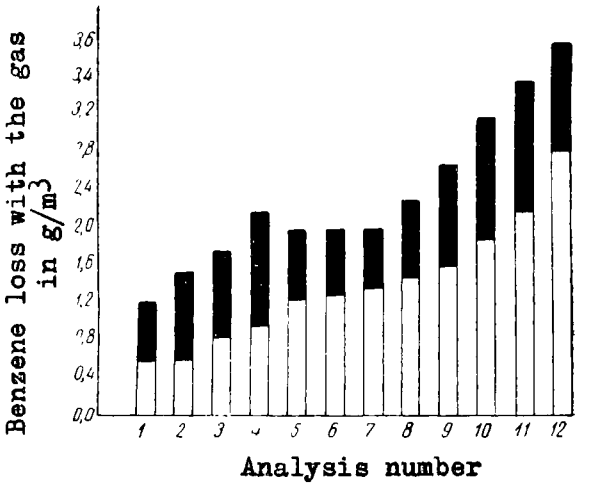


Fig. 2. Results of comparative analyses made by different methods.

ducted to determine extent of loss variations yielded by both methods of analysis. Results are listed in Fig. 2.

Prior to making analysis by the accepted method of absorption by activated charcoal, the gas was freed only of hydrogen sulfide, hydrogen cyanide, carbon dioxide and naphthalene. Results of such analyses are listed in Fig. 2 in the order of increasing benzene content in the gas. The lower section of each column presents data of the automatic gas analyzer, while the total column heights represent losses as determined by the activated charcoal method. The black plots in Fig. 2 show that the activated charcoal absorbed an additional amount of hydrocarbons accounted for as benzene loss. With the introduction of the automatic gas analyzers for plant production control it becomes necessary to revise present ways of evaluating benzene losses in the return coke gases because the automatic analyzer indicated the real content of benzene hydrocarbons.

Results thus far obtained with the automatic gas analyzer in determining the content of benzene hydrocarbons indicated that with further improvements in its construction the apparatus can be made to serve as a finer and more accurate instrument for control of raw benzene absorption from coke gas.

Determination of Simultaneously Present Cyclohexanon and of Cyclohexanonoxime.

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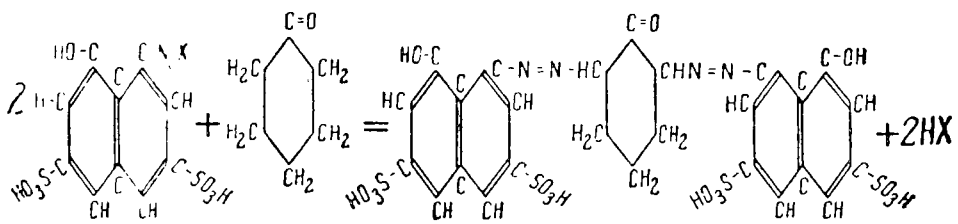
Gigiena i Sanitariya, Vol. 24, No. 12, 71-73, 1959.

This author previously described a method for the determination of cyclohexanon based on its discovered property to form an azo dye with the salt of H-acid diazonium. (See B. S. Levine, Survey of U.S.S.R. Literature on Air Pollution and Related Occupational Diseases, Vol. 1, Department of Commerce, O.T.S. No. 60-21049, pp. 196-201). The salt forming reaction can be presented as follows:



In the course of reaction between the cyclohexanon and the H-acid diazonium salt the cyclohexanonoxime becomes deoximized to a great extent. In the presence of nitrous acid the deoximization of cyclohexanonoxime proceeds at a rapid rate in a quantitative manner. It was found that the addition to the solution containing cyclohexanonoxime of substances which, according to G. Meyer, form double salts in the presence of ketoximes prevented the deoximation of cyclohexanonoxime. Results of the present author's studies showed that rhodenide, tartaric acid and tartrates, sodium sulfite and methanol were also capable of preventing the process of cyclohexanonoxime deoximation. This property of cyclohexanonoxime to become deoximized quantitatively under one set of conditions and to remain completely unaffected under other conditions offers the possibility of utilizing the reaction of the azo dye formation in the determination of cyclohexanon and of cyclohexanonoxime when simultaneously present in the studied medium.

The present author tested this possibility with positive results. Analysis of a mixture of cyclohexanon and cyclohexanonoxime can be made by usual colorimetric methods as well as by the method of colorimetric titration with stand-

ard aqueous solutions of the azo dye. The azo dye needed for the preparation of the standard solution to be used in the analytical colorimetric titration procedure and the technique of the procedure were described by this author previously.

Determination of cyclohexanon in the presence of cyclohexanonoxime.

Reagents required: 1) Diazo solution of H-acid, 0.25% of the monosodium salt of H-acid and 0.1 N solution of sulfuric or hydrochloric acid are mixed just before use in a 1:1 ratio with 1.0% solution of sodium nitrite;

2) 20.0% solution of sodium hydroxide;

3) Standard solution of cyclohexanon containing 50 γ/ml for use in the colorimetric analysis with the aid of a set or by a millimolar solution of the azo dye (0.758 mg/ml) for use in the colorimetric titration method. One ml of the millimolar solution of the azo dye is equivalent to 98 γ of cyclohexanon or 113 γ of cyclohexanonoxime.

The analytical procedure. Place 1 ml of the sample solution into a test tube and add 1 ml of methanol, 0.5 ml of sodium hydroxide solution and 0.5 ml of the H-acid diazo solution and mix well. Leave rest for 2 minutes and dilute to volume of 10 ml with distilled water and make the colorimetric determination. In determining cyclohexanon by the method of colorimetric titration place 1 ml of water into the control tube, add equal amounts of the reagents and dilute with water to the volume of 10 ml. Now add, a drop at a time, the standard solution of the diazo dye to match the color intensity in the tube containing the tested sample. Calculate final cyclohexanon concentration on the basis of the amount of standard dye used in the titration. Results of cyclohexanon determinations by the method described are listed in Table 1.

Determination of cyclohexanonoxime in the presence of cyclohexanon.

Reagents required: 1) 1.0% solution of sodium nitrite;

2) 5.0% by volume of hydrochloric acid;

3) Alkaline mixture prepared by mixing 50% of NaOH and 5.0% solution of sodium sulfate in 1:1 ratio;

4) Solution of diazotized H-acid, prepared as above described;

5) Standard solutions of cyclohexanon or of the azo dye prepared as described above.

TABLE 1.

Results of cyclohexanon determination in the presence of cyclohexanonoxime using the diazonium H-acid colorimetric titration method.

| Taken | | Cyclohexanon found | |
|---|---|---|---|
| Cyclohexanon in γ | Cyclohexanonoxime in mg | γ | % |
| 1 | 0.02 | 1.1 | 110 |
| 3 | 0.05 | 2.8 | 93.3 |
| 5 | 0.10 | 4.9 | 98 |
| 10 | 0.5 | 10.4 | 104 |
| 20 | 2.0 | 19.6 | 98 |
| 22 | 2.5 | 23 | 104.5 |
| 28 | 2.5 | 23.6 | 102.1 |
| 35 | 3.7 | 36 | 102.8 |

Analytical procedure. Place 1 ml of the cyclohexanonoxime containing solution into a test tube and add 0.2 ml of the sodium nitrite solution and 0.2 ml of the hydrochloric acid solution and mix well. Leave rest for 1 minute and add 0.5 ml of the alkaline mixture and 1 ml of diazotized H-acid. Leave rest for 5 minutes, dilute to 10 ml with water and make the colorimetric determination.

In making colorimetric cyclohexanonoxime determination by the method of colorimetric titration place 1 ml of water into a control test tube and add reagents in same quantities as they were added to the sample-containing tube, dilute to 10 ml with water, and add the standard azo dye dilution drop at a time until color intensity in the control tube matches that in the sample containing tube. Calculate final cyclohexanon concentration on the basis of the standard azo dye used, bearing in mind that 7.85 γ of the diazo dye was equivalent to 1.13 γ of cyclohexanonoxime. Results of cyclohexanonoxime determinations in the presence of cyclohexanon by the method of colorimetric titration as above described are listed in Table 2.

In determining cyclohexanonoxime and cyclohexanon in the air use water as the absorber. Aspirate the air through three successive absorber flasks each containing 5 ml of water at the rate of 15 - 20 li/hour to a total volume of 15 - 20 li. Remove 1 ml from each absorber tube for the determination of cyclohexanon and 1 ml from each for the determination of cyclohexanonoxime by the above outlined procedures.

TABLE 2.

Results of cyclohexanonoxime determination in the presence of cyclohexanon using the colorimetric titration method.

| Taken | | Cyclohexanonoxime found | |
|---|---|---|---|
| Cyclohexanonoxime in γ | Cyclohexanon in γ | γ | % |
| 2 | 10 | 1.74 | 87 |
| 3 | 20 | 3.2 | 106.6 |
| 8 | 50 | 7.6 | 94 |
| 10 | 50 | 10 | 100 |
| 15 | 50 | 16 | 106.6 |
| 20 | 100 | 19.6 | 98 |
| 25 | 200 | 26 | 104 |
| 33 | 200 | 34 | 103 |
| 38 | 300 | 37 | 97.4 |
| 40 | 300 | 41 | 102.5 |

## Conclusions.

1. A method is described for the determination of cyclohexanon and cyclohexanonoxime simultaneously present in the medium. Determinations can be made by the usual method of colorimetry or by the method of colorimetric titration with a standard solution of the azo dye.

2. Determination of cyclohexanon or of cyclohexanonoxime by the H-acid diazo salt can be made with aqueous solution samples as well as with air samples.

3. Determination error in small amounts of cyclohexanon did not exceed 10% and of small quantities of cyclohexanonoxime did not exceed 13%.

Editor's remark: Published for purposes of discussion and expression of opinion.

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# Colorimetric Method for the Determination of Ammonia in the Air Using Phenol and Sodium Hypochlorite.

M. I. Poletayev and N. A. Andreyeva.

Gigiena i Sanitariya, Vol. 24, No. 6, 73-74, 1959.

Determination of ammonia in the air of industrial and residential premises has been made largely by the colorimetric method using Nessler's reagent. The sensitivity of this method fully met the needs of sanitary control of the atmosphere. For this reason it has been used widely in sanitary-chemical investigations. However, the chemical reaction on which this method is based is not specific. This method can not be used when the air contains aldehydes such as formaldehyde or acrolein, and hydrogen sulfide. In sanitary-chemical studies situations are frequently encountered in which the air contains aldehydes and hydrogen sulfide simultaneously with ammonia. Therefore, an attempt was made to develop a specific method for the determination of small amounts of ammonia in the air in the presence of aldehydes and/or hydrogen sulfide.

The fact has been known that phenol and sodium hypochlorite yielded a dark blue color in the presence of ammonia salts. The intensity of the developed color depended on the concentration of the ammonium salts in solution. Several variants have been used in the preparation of sodium hypochlorite; likewise, different sorbents were used to absorb ammonia from the air. A combination was finally arrived at for the detection of 0.0003 mg of ammonia in 5 ml of the sample, which is entirely satisfactory for the sanitary evaluation of the atmospheric environment of industrial and residential quarters.

The method. Ammonia is absorbed from the air by passing it through 2 successive Petri absorbers, each containing 10 ml of 0.02 N $H_2SO_4$. Rate of air aspiration should equal 60 li/hour. After aspiration has been completed 5 ml of the absorber solution is taken from each of the absorber tubes and placed into 2 respective colorimetric cups. A set of colorimetric standards is prepared as follows: set up a series of 12 test tubes; prepare a standard solution of $(NH_4)_2SO_4$ containing 0.01 mg of ammonia per ml; place none in the first tube; beginning with the second tube and up, place successively 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 and 1.0 ml of the standard ammonium sulfate solution. The amount of ammonia in the second tube is equivalent to 0.0002 and in the last tube 0.01 mg. Next, the volume in all tubes,

tests and standards, is brought up to 5 ml with 0.02 N sulfuric acid solution. This is followed by the addition of the following: 1.0 ml of 4.0% aqueous phenol solution and 0.5 ml Na-hypochlorite solution prepared as follows: first determine the amount of active chlorine in the hypochloride of lime, which should range between 30 - 35%. To do this dissolve 3.5 g of the lime in a 1000 ml volumetric flask; take 50 ml and place into an Erlenmeyer flask with a ground-to-fit stopper; add 10 - 15 ml of 10% of KI solution and 10 ml of 30% acetic acid; titrate 5 minutes later against the liberated $I_2$ with an 0.1 N solution of sodium thiosulfate ($Na_2S_2O_3$) to the appearance of a faintly yellow color; add a few drops of starch and titrate cautiously drop by drop until the faint yellow color just disappears.

One ml of the 0.1 N thiosulfate solution is equivalent to 0.003546 g of chlorine. Having established the content of active chlorine, take 100 g of the chloride of lime and thoroughly mix for 15 minutes with 170 ml of water; keep on stirring and add 70 g of $Na_2CO_3$ dissolved in 170 ml of water. The mixture will thicken at first and will then liquefy. The supernatant liquid is then separated from the sedimented solid by a suitable method. The clear fluid is diluted with an equal amount of ammonia-free distilled water. Ten minutes after the $Na_2S_2O_3$ solution has been added to the tubes containing the tests and the standard solutions, the blue color intensity in the tubes containing the test solution is compared with the color of the standard tubes. Color in the standard tubes can be relied upon for 24 hours, and the hypochlorite solution will keep for 15 days. The sensitivity of the method should be 0.005 mg in the colorimetric volume used; however, the sensitivity must be checked by control tests and improved if so needed. Aldehydes, such as formaldehyde and acrolein, as well as $H_2S$, in concentrations up to 1 mg per test did not interfere with the ammonia determination. In the presence of amines, such as methylamine, dimethylamine, etc., the method lost its specificity. Results of comparative con-

Ammonia concentration obtained with parallel analyses of water solutions using Nessler's reagent and with phenol and Na-hypochlorite method.

| Nessler method results in mg | Phenol-hypochlorite results in mg | Difference in mg |
|---|---|---|
| 0.241 | 0.238 | 0.003 |
| 0.146 | 0.15 | 0.004 |
| 0.12 | 0.118 | 0.002 |
| 0.113 | 0.112 | 0.001 |
| 0.042 | 0.045 | 0.003 |
| 0.022 | 0.023 | 0.001 |
| 0.018 | 0.023 | 0.005 |
| 0.016 | 0.012 | 0.004 |
| 0.009 | 0.007 | 0.002 |
| 0.006 | 0.008 | 0.002 |

trol tests are presented in the table. Differences between the results of 2 tests did not exceed 0.001 - 0.003 mg. Results of tests made under practical industrial conditions proved the suitability and applicability of the proposed method.

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## Low Temperature Bacteriological Air Investigation.

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Gigiena i Sanitariya, Vol. 24, No. 4, 77-79, 1959.

Winter studies of atmospheric air microflora in Arctic central zones and in the troposphere frequently have to be conducted at low temperatures. Studies of bacterial atmospheric air population at low temperatures are difficult and have been inadequately investigated. Most recent methods of bacteriological air investigation have been based on catching the microorganisms in a fluid medium, such as water, physiological saline, broth, etc., or on meat-peptone agar. Fluid and solid nutrient media freeze rapidly at minus 3 - 5°. In addition the bacterial content of the atmospheric air is usually low in winter, and the process of sample collecting takes a considerably longer time during which the media freezes even at -5°. Canadian investigators S. M. Pady and C. D. Kelly suggested coating the collecting Petri dish bottoms with silico-organic gels of consistency not affected by low temperatures; the air organisms caught by the silico-organic gel are then covered with the agar medium. In 1954 R. B. Mitchell and his co-workers suggested the use of soluble gelatin foam filters.

In investigating atmospheric air microflora at low temperature this author used polysiloxane solutions, the viscose consistency of which did not change within the range of +20 and -60°. Methylethylpolysiloxane solution has a viscosity of 52 centistokes and ethylpolysiloxane solution No. 4 has a viscosity of 45 centistokes. These and polysiloxane, a high-vacuum lubricant trademarked D.S., were used in this study.

Samples were collected by the Pady and Kelly method in Petri dishes coated with the above polysiloxane solutions and lubricant. The Petri dishes with the polysiloxane were sterilized for 2 hours at 180° dry heat. Samples were collected using the Krotov apparatus, and the inoculation was done by pouring nutrient agar into the dishes. At the same time control samples were collected similarly into Petri dishes containing meat-peptone agar. This pouring method was suited to quantitative determinations of microorganisms in certain air volumes, but it had the following shortcomings: a) the under surface of deep bacterial growth excluded the possibility of making differential species studies; b) when inoculation was done by the pouring method, spreaders developed in 40% of the samples, which interefered with accurate quantitative determinations. Best results by the agar pouring method were obtained in Petri dishes coated with the polysiloxane lubricant, which reduced the number of developed spreaders. By the method of polysiloxane lubricant, 73% of air bacteria were caught using the Krotov apparatus as compared with the number of air bacteria developed on beef-peptone agar. Samples of air bacteria collected with liquid polysiloxane could not be counted due to spreader development.

In view of the shortcomings of the pouring method the meat-peptone agar imprint method was tried next, using glass tablets coated with liquid polysiloxane, and later discs made of special glass-lacquer fibers trade-marked LSK-7 coated with liquid polysiloxane; this film lost none of its elasticity within the +200 to -60° temperature range. Glass lacquer LSK-7 films were placed in Petri dishes, the bottoms of which were coated with liquid polysiloxane and sterilized at dry heat. Air samples were collected after which LSK-7 discs were used in making imprints on meat-peptone agar (two imprints from each disc). Usually 1.5 - 2 times as many colonies developed in the first dish as in the second. Counts were made of the total of both imprints. A parallel control determination was made by the Krotov apparatus. Eight series of tests were made at -4.4 to -10°, and 12 at -10 to -21.6°. Each test series

consisted of 12 samples by the imprint method and two control samples by the meat-peptone agar method. The bacterial air content in the control samples ranged between 120 and 1090 bacteria per 1 $m^3$. The bacterial air content obtained by the liquid methylethylpolysiloxane disc imprint method ranged between 118 and 550 bacteria per 1 $m^3$; by the liquid ethylpolysiloxane coating method between 126 and 538 per 1 $m^3$; and by the polysiloxane lubricant coating method between 88 and 405 per 1 $m^3$. Compared with the control bacterial counts on meat-peptone agar, the liquid methylethylpolysiloxane imprint method yielded a count amounting to 67%, the liquid ethylpolysiloxane coating method yielded a 63% count, and the polysiloxane lubricant coating method yielded a 38% count. Prolonged low temperature storage of dishes containing discs coated with liquid polysiloxane had no effect on the physical properties of the LSK-7 material or of the fluid polysiloxane, which proved of value when the preparations had to be stored or transported over long distances without the use of special warming measures.

On the basis of the presented results the following can be recommended: in low temperature quantitative bacteriological studies preference should be given the method of pouring into dishes coated with polysiloxane lubricant. Where quantitative and qualitative determinations of air microflora are to be made at low temperatures, the imprint method should be employed using discs made of LSK-7 material coated with liquid methylethylpolysiloxane or ethylpolysiloxane. The imprint method requires double the nutrient media and dishes due to the double imprint procedure. Final results should represent the sum of both imprint counts.

The above described imprint and pouring methods can be used in studies of air microflora at cold regions or during cold months of the year, depending on the purpose of the investigation, i.e., whether only quantitative or quantitative and qualitative results are sought. It is recommended that the polysiloxane lubricant be used in connection with the pouring method, and fluid methylethylpolysiloxane or ethylpolysiloxane be used in connection with the imprint method.

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Determination of Nitrogen Oxide in Coke Gas.

N. A. Gruzdeva and L. A. Khokhlova with the aid of V. G. Shevchenko.

Koks i Khimiya, 1960, No. 4, 41-48.

Exact determinations of small quantities of oxides of nitrogen [1] is an important part in the control of hydrogen production from coke gas by the process of deep cooling. Microanalytical methods for the determination of oxides of nitrogen in coke gas are based on oxidation of nitrogen oxide in the coke gas by means of appropriate liquid oxidizers. The nitrogen dioxide thus produced is absorbed by water accompanied by formation in equal quantities of nitric and nitrous acids according to the following equations:

$$2NO + O_2 = 2NO_2 \quad (1)$$

$$2NO_2 + H_2O = HNO_3 + HNO_2 \quad (2)$$

According to OST 10233-40 and GOST 8330-57 the method of Shuftan has been used in the U.S.S.R. since 1940 as the standard method for the determination of oxides of nitrogen. The final concentration of nitrogen oxide is determined using the Shuftan correction curve, or Stepanov's nomogram. According to references [2, 3 and 8] the Shuftan method and its correction curve have not become popular in Germany, Czechoslovakia, and France. Instead, the control method for the determination of small quantities of nitrogen oxide based on the principle of permanganate oxidation has found wide application. The basis of the method can be illustrated by the following equation:

$$5NO + 3H_2SO_4 + 2KMnO_4 \rightarrow 5NO_2 + K_2SO_4 + 2MnSO_4 + 3H_2O \quad (3)$$

The present authors studied the precision of the standard method using an analytical setup as shown in Fig. 1. A series of mixtures of nitrogen, nitrogen-hydrogen and coke gas were prepared. Doses were delivered from a 1 ml microburette divided into 0.01 ml and equipped with a three-way stopcock (7), a glass bottle with sealing fluid (13) and a mixer (6). Before an experiment was begun the entire setup was flushed for 1 hour by passing through it pure moisture-free nitrogen or coke gas mixed with oxygen. By raising bottle (13) any desired amount of nitrogen oxide can be forced out of the microburette. Before dose delivery the oxygen supply was cut off, stopcocks P, R and M were closed forcing the nitrogen out through stopcock L. After the oxide of nitrogen was forced into the mixer stopcock L was closed and stopcocks

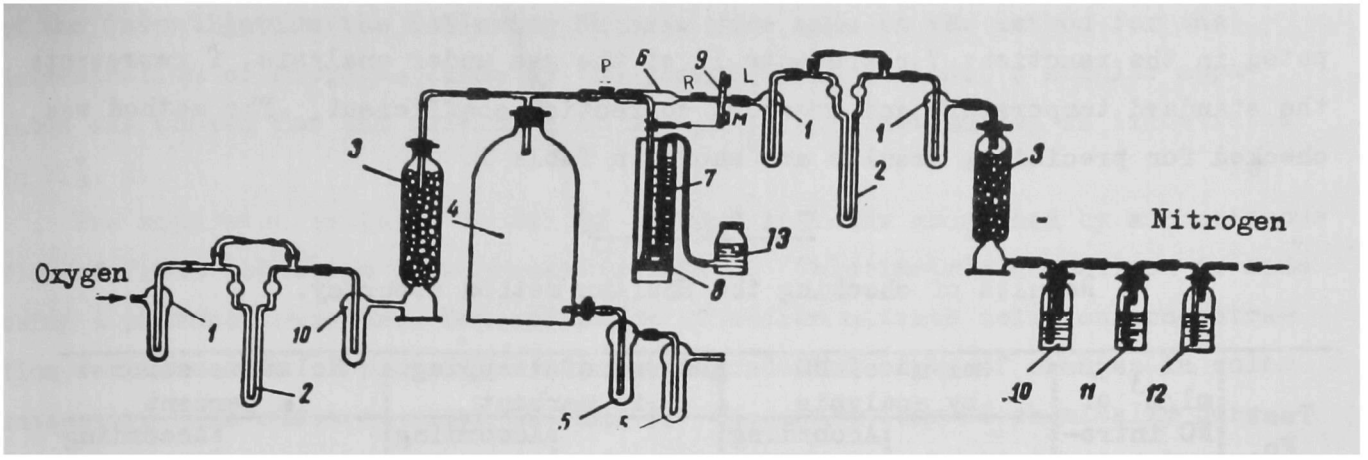


Fig. 1. Setup for the determination of NO in coke gas. 1 - Buffer tube; 2 - flowmeter; 3 - $CaCl_2$ drier; 4 - 10.4 li flask; 5 - absorbers containing metaphenylenediamine solution; 8 - cylindrical water jacket for heat control of burette 7; 9 - four-way outlet tube; 10 - Griss solution glass container for gas purification; 11 - 15% $H_2SO_4$ solution container; 12 - 20% NaOH solution container.

P and R were opened and the gas was directed by opening stopcock M from the capillary opening of the three-way stopcock of the microburette.

Nitrogen oxide was obtained by a reaction of 50% sulfuric acid solution and a mixture of sodium nitrate and potassium iodide in 1:1 proportion [6]. Nitrogen oxide purity was determined by the volume titrametric method improved by the present authors. The principle of the method is as follows: nitrogen oxide is converted to nitrogen dioxide with a 3% hydrogen peroxide solution; the reaction mixture containing nitric and nitrous acids was then titrated with a solution of sodium hydroxide. The concentration of nitrogen oxide was then determined using the Shuftan logarithmic curve (as per GOST) and the result computed by formula (4) was compared with the amount of nitrogen oxide forced into the gas flow. The concentration of nitrogen oxide in the gas was computed using formula (4).

$$NO = \frac{(a + a_1) \cdot 0.01 \cdot 2 \cdot 1000}{V \cdot f} \text{ ml/m}^3 \qquad (4)$$

in which NO represents ml of nitrogen oxide per $m^3$ of the gas, a represents the amount of standard solution in ml the color of which was of the same intensity as the color in the first absorber, $a_1$ represents the amount of standard solution in ml the color intensity of which was the same as in the solution in the second absorber, 0.01 is the quantity of nitrogen oxide in ml equivalent to 1 ml of the standard solution, 2 is the multiplication factor which accounts for the fact that only half of the nitrogen oxide in the gas partici-

pated in the reaction; V represents li of the gas under analysis, f represents the standard temperature and pressure correction coefficient. The method was checked for precision; results are shown in Table 1.

TABLE 1.

Results of checking the Shuftan method accuracy.

| Test No. | $ml/m^3$ of NO introduced | $ml/m^3$ of NO by analysis | | Degree of trapping in percent | | Relative error in percent | |
|---|---|---|---|---|---|---|---|
| | | Computed | According to GOST corrected | Computed | According to GOST corrected | Computed | According to GOST corrected |
| | | Artificial mixture of nitrogen and nitrogen oxide | | | | | |
| 1 | 1.54 | 1.86 | 13.2 | 120.75 | 857 | +20.75 | +757 |
| 2 | 1.73 | 1.35 | 11.5 | 77.61 | 662 | -22.39 | +562 |
| 3 | 1.28 | 1.33 | 11.5 | 103.55 | 898 | +3.55 | +798 |
| 4 | 1.27 | 1.22 | 11.0 | 96.19 | 866 | -3.81 | +766 |
| 5 | 1.16 | 1.30 | 11.4 | 112.00 | 982 | +12.00 | +882 |
| 6 | 5.71 | 5.10 | 22.5 | 89.26 | 394 | -10.74 | +294 |
| | | Artificial mixture of coke gas with nitrogen oxide | | | | | |
| 1 | 2.77 | 3.24 | 19.2 | 117.08 | 696 | +17.08 | +596 |
| 2 | 2.07 | 1.48 | 15.6 | 71.76 | 755 | -28.24 | +655 |
| 3 | 2.12 | 2.00 | 18.0 | 93.84 | 845 | -6.16 | +745 |
| 4 | 0.93 | 0.87 | 12.8 | 93.25 | 1370 | -6.75 | +1270 |
| 5 | 0.79 | 0.82 | 8.6 | 103.66 | 1470 | +3.66 | +1370 |

Data in the table shows that results obtained by the standard method exceeded the actual values by 6 times, whereas the computed results were close to actual concentrations before making the recommended corrections. It is interesting to note that values obtained after adjusting the experimental results with the aid of Stepanov's nomogram [7], as recommended by GOST, deviated from actual values to a still greater degree. Results of the present investigation showed that the precision of the discussed analytical procedure depended upon the complete removal of moisture from the gas. This was verified by the fact that after passing the gas through dried $CaCl_2$ and through a layer of alkaline lumps analytical experimental results were in complete agreement with actual values.

The reliability and precision degree of the permanganate method were checked next using the setup as recommended in GIAP [4 and 5]. The relative error of the permanganate method amounted to an average of ± 17%. As a result

of the investigation the following changes were made in the method for the determination of nitrogen oxide by the permanganate method: a simpler apparatus was chosen for the oxidation of the gas; its construction is illustrated in Fig. 2.

The apparatus cylinder is filled with glass beads moistened by a continuous flow of fresh potassium permanganate solution. Colorimetric comparison is made using a photocolorimeter. Determination of sodium nitrate solution concentration was made with a specially constructed graduated curve of changes in color intensity. The curve is shown in Fig. 3. Concentrations of chemically pure sodium nitrate in Griss solution are plotted along the abscissa and color density (intensity) along the ordinate.

Test solutions obtained after NO absorption from the coke gas are poured into photocolorimetric cups of 20 mm and the color intensity determined photocolorimetrically, using a green light filter. The photocolorimetric reading is then interpreted with the aid of the graduated curve. Data presented in Tables 2 and 3 show that the permanganate method yielded results of the same degree of precision with the VUKhIN

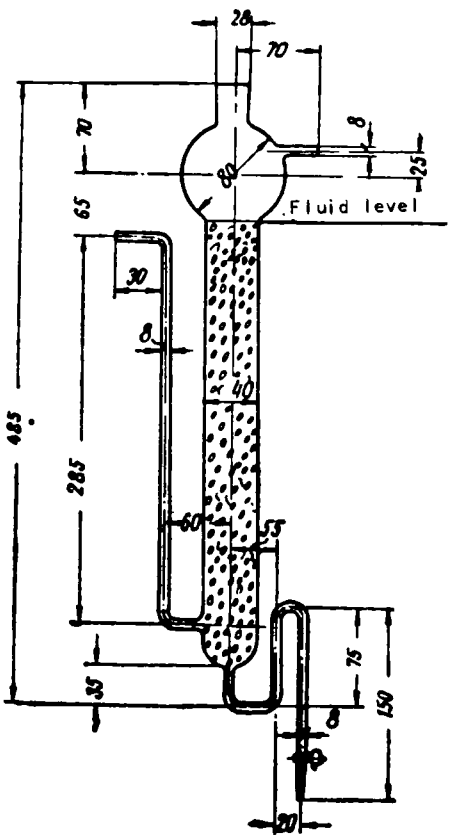


Fig. 2. Nitrogen oxidation apparatus.

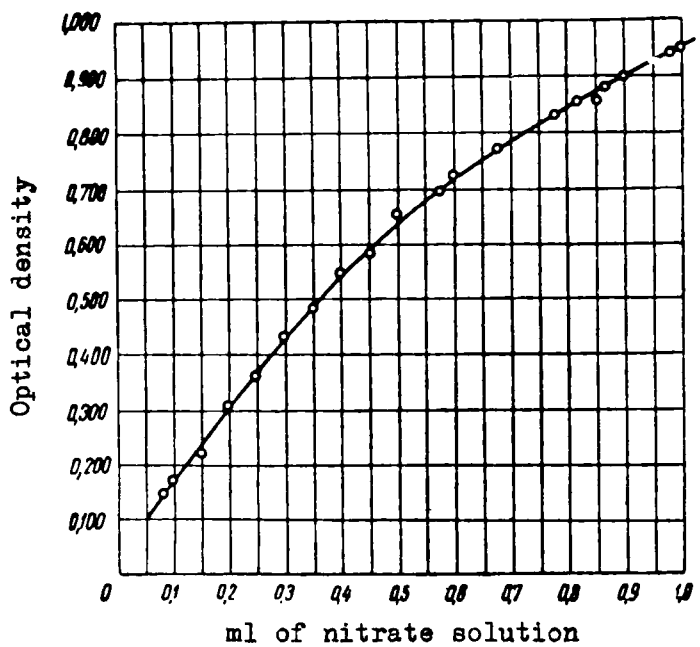


Fig. 3. Graduated curve for the determination of sodium nitrate concentration in working solutions.

T A B L E 2.

Results of checking the accuracy of the permanganate method for the determination of nitrogen in the gas with a recovering oxidizer and nitrogen as the carrier.

| Percent of $O_2$ | $ml/m^3$ of NO introduced | $ml/m^3$ of NO recovered | Percent trapped | Relative error in percent |
|---|---|---|---|---|
| 0.48 | 5.41 | 4.60 | 85.00 | -15 |
| 0.18 | 5.74 | 5.92 | 103.28 | +3.28 |
| 0.89 | 9.35 | 7.26 | 77.63 | -22.4 |
| 0.48 | 5.41 | 5.04 | 93.00 | -7 |
| 0.89 | 4.93 | 5.85 | 118.77 | +18.77 |

oxidizer as with the GIAP oxidizer. Results also indicated that the presence of oxygen and freedom from ammonia and hydrogen sulfide were factors of importance in obtaining reliable results. Parallel tests were made for the comparative evaluation of the Shuftan and permanganate methods. The tests were made at the Kemerov Coke-Chemical Plant using the

T A B L E 3.

Results of checking the accuracy of the permanganate method for the determination of NO in the coke gas with a recovering oxidizer.

| Percent of $O_2$ in coke gas | $ml/m^3$ of NO introduced | Color of original gas, ml of nitrate solution | Color with added NO, ml of nitrate solution | $ml/m^3$ of NO found | Percent of NO derived | Relative error in percent |
|---|---|---|---|---|---|---|
| 0.5 | 2.80 | 0.2 | 1.95 | 2.45 | 80.27 | -19.73 |
| 0.5 | 2.22 | 0.2 | 2.40 | 2.77 | 124.78 | +24.78 |
| 0.5 | 2.74 | 0.3 | 2.20 | 2.38 | 87.15 | -12.85 |
| 0.4 | 5.58 | 0.3 | 4.05 | 4.74 | 85.03 | -14.97 |

T A B L E 4.

Results of comparative analyses of NO determinations in coke gas at the Kemerov Plant as yielded by the permanganate method and by GOST.

| $ml/m^3$ of NO found by GOST | | $ml/m^3$ of NO by permanganate method |
|---|---|---|
| According to Shuftan curve | According to formula (6)* | |
| 5.0 | 0.360 | 0.324 |
| 8.6 | 0.883 | 1.126 |
| 5.9 | 0.445 | 0.567 |
| 5.2 | 0.334 | 0.405 |
| 5.8 | 0.540 | 0.573 |
| 6.8 | 0.510 | 0.557 |

* Probably meant formula (4). B.S.L.

GIAP absorber. Results of parallel tests made under identical conditions are presented in Table 4. Data in Table 4 show that the 2 methods yielded different results. The NO concentration determined by the standard method yielded an average of 6.23 $ml/m^3$ and the permanganate gave an average of 0.58 $ml/m^3$. It should be added that uncorrected results yielded by the

standard method computed with the aid of formula (4) were of the same order of magnitude as the results obtained with the permanganate method.

The procedure for the determination of nitrogen oxide in coke gas by the permanganate method is as follows: the coke gas is passed through a hygroscopic cotton filter (Fig. 4), freed from tar, ammonia, rosin-forming substances, hydrogen sulfide, $CO_2$ and higher oxides of nitrogen. The purified gas is passed into a packed oxidizer (6) at the rate of 24 li/hr where the NO is oxidized into $NO_2$ by an acidified solution of potassium permanganate. The apparatus cylinder is continuously flushed through the experiment with a fresh solution of potassium permanganate coming under pressure from bottle (8). The entire setup must be leak-proof, as shown by an appropriate check. Any well qualified analyst should be intimately familiar with any apparatus testing procedure. The gas to be analyzed is then forced through the apparatus for 15 minutes and the apparatus is connected with oxidizing chamber (7) which is filled with 14 ml Griss reagent. The gas is run in until the solution in the first absorber acquires a color of sufficiently high intensity, which usually takes 15 - 20 minutes. The solutions to be tested are poured into 20 mm colorimetric cups and are evaluated colorimetrically in an appropriate photocolorimeter equipped with a green light filter after which the amount of sodium nitrate is established using a graduated curve shown in Fig. 3. If necessary the examined solution can be diluted to 50% with Griss reagent and the colorimetric results multiplied by 2.

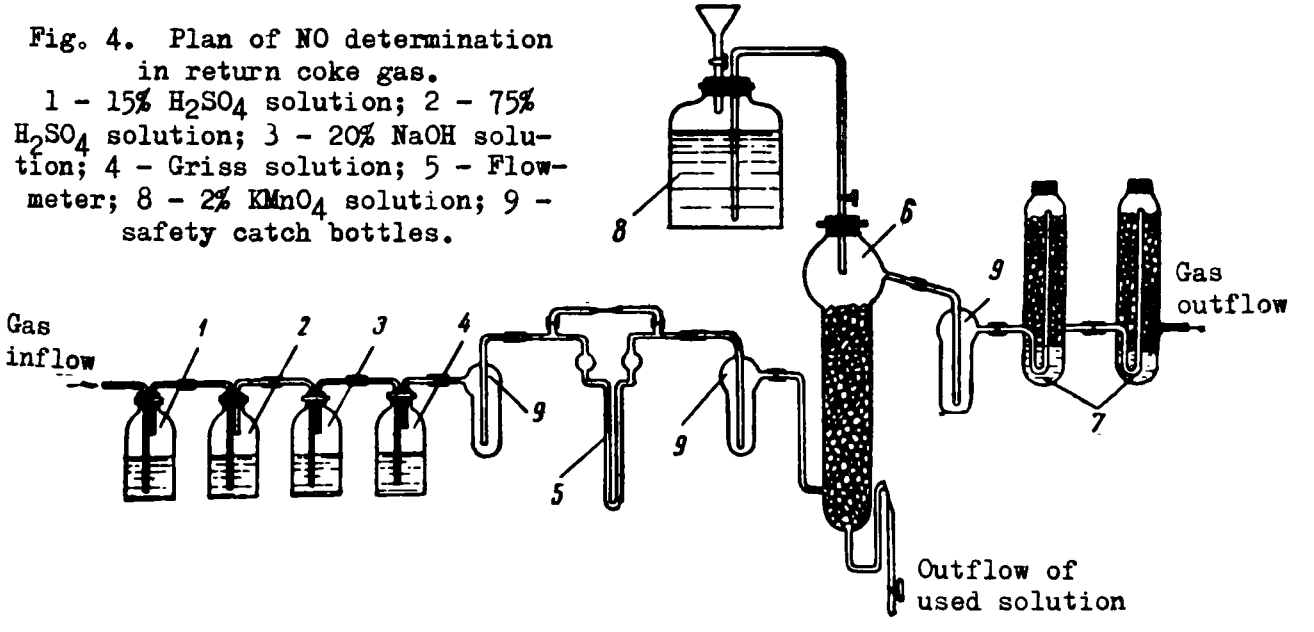


Fig. 4. Plan of NO determination in return coke gas.
1 - 15% $H_2SO_4$ solution; 2 - 75% $H_2SO_4$ solution; 3 - 20% NaOH solution; 4 - Griss solution; 5 - Flowmeter; 8 - 2% $KMnO_4$ solution; 9 - safety catch bottles.

The potassium permanganate solution is prepared by adding 35 ml of 50% $H_2SO_4$ solution to 965 ml of 2% potassium permanganate solution.

The results herein reported show that the permanganate method is simpler and easier to manipulate; however, the standard method has been widely used and is now known to many analysts; therefore, its application in control work in coke-chemical plants may be continued with the following mandatory changes and supplements to GOST 8330-57:

1) The Shuftan curve and Stepanov nomogram corrections should not be used; content of nitrogen oxide in the gas should be computed according to formula (4);

2) Use the more sensitive and more stable Griss reagent for the absorption of nitrogen dioxide;

3) Use 75% $H_2SO_4$ solution for the removal of tar-forming (rosin-forming) substances from the gas.

Technical specifications of GOST 8330-57 in relation to the content of nitrogen oxide in coke gas should be re-evaluated and, if necessary, revised. Coke-chemical plants and manufacturers of nitrogenous fertilizers should accumulate comparative factual information regarding nitrogen oxide content in coke gas prior to and after its purification by the permanganate method and by the method of oxidation with $O_2$, accompanied by changes suggested by VUKhIN.

## Conclusions.

1. Results proved the nonsuitability of the existing standard method of nitrogen oxide determination in coke gas as specified in GOST 8330-57. The method yielded results 6 - 8 times higher than actual NO concentrations in the coke gas. The use of Shuftan curve or Stepanov nomogram corrections only distorted the results and should be deleted from GOST.

2. The use of the permanganate or oxygen gas method for the control determinations of NO concentrations in coke gas, which do not require the use of correction factors, yielded more reliable and more accurate results.

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# Electroencephalographic Determination of Threshold Reflex Effect of Atmospheric Pollutants.

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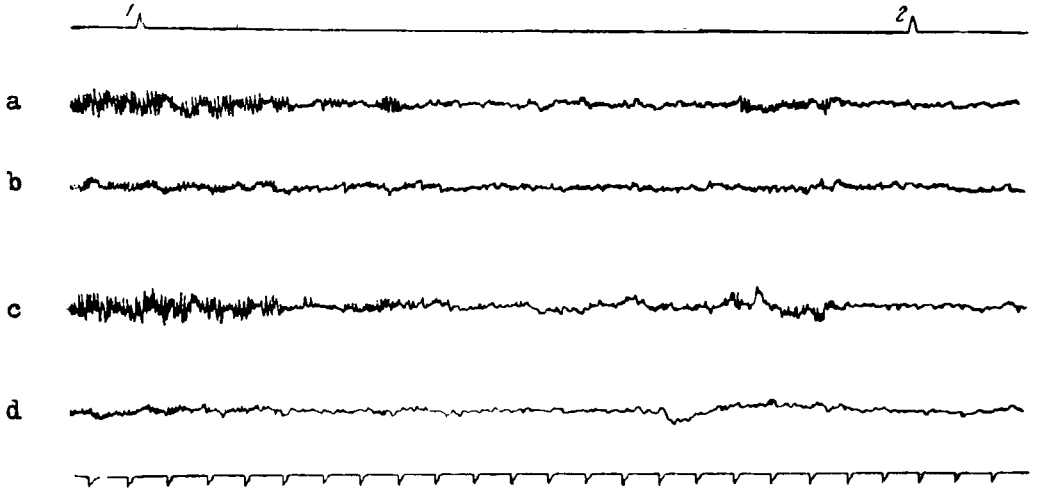
Gigiena i Sanitariya, Vol. 25, No. 1, 57-61, 1960.

Recent scientific studies indicated that determination of allowable limit concentrations of atmospheric air pollutants can be made by the methods of eye adaptation to darkness, optical chronaxy, pneumography and plethysmography. Such studies have been conducted usually by way of establishing minimal concentrations of a pollutant substance in the air which induced a shift in some functional activity of the organism recordable by any of the above-mentioned methods. The mechanism of such determinations is based on the ability of the external factor (air pollutant) to stimulate the central nervous system, which in turn, affected the reaction of one or another functions of the organism, functional changes thus elicited were then recorded objectively and automatically. It must be borne in mind, however, that such mechanism of functional response to external stimulation was the result of a highly complex central activity reacting at different intensities to different chemical stimuli. As a consequence, the sensitivity of the above-described physiological methods differed greatly.

This paper is a report of attempts on the part of the present authors to test the suitability of the electroencephalographic method for the determination of maximal single allowable concentration limits of air pollutants. As the first step tests were made of the effect of odor-emanating substances and other stimulating or irritating substances on reflex responses. Automatic recording of electrical brain activity represents a direct means for the detection of states of stimulation generated in cortical cells by external chemical stimulators. Electric brain activity was recorded by means of a 4-lead amplifying device, 4UN4, and by an ink-recording apparatus ChR-1 in connection with an encephalograph trade named "Al'var". Test persons were selected after medical examination indicated that their olfactory analyzer functioned normally, as shown by the α-rhythm. Test persons were placed into an isolated screen-protected room. A small glass cylinder was firmly fixed

in front of the test person, through which a continuous stream of air was passed at the rate of 30 li/min. At any desired moment the pure air was mixed with a given amount of the tested gas and passed through the cylinder. Desynchronization of central electrical activity or depression in the α-rhythm were used as indexes of the effect induced by the odor-emanating substance under investigation.

Tests were made with $SO_2$ which possessed a clearcut olfactory effect, with $H_2SO_4$ aerosol which usually affected the trigeminal nerve apparatus. Tests were performed by 2 types of modified procedures. The first procedure was based on the effect produced by individual substances under study on the electroencephalogram (EEG). The series of experiments was conducted with $SO_2$ concentrations ranging between 5 - 0.6 mg/m$^3$. Sulfur dioxide gas in 5.0 - 0.9 mg/m$^3$ concentrations elicited a clearcut desynchronization. At concentrations ranging between 5.0 - 3.0 mg/m$^3$ desynchronization usually appeared over the entire period of $SO_2$ administration; at lower $SO_2$ concentrations desynchronization usually lasted between 2 - 6 seconds of a 20-second gas effect test. In some cases desynchronization appeared in the course of $SO_2$ administration and in others immediately upon the introduction of the $SO_2$, as shown in Fig. 1.




Time in seconds

Fig. 1. Electroencephalogram of desynchronization produced by inhalation of 0.9 mg/m$^3$ of $SO_2$.

Upper line: 1 - moment of gas inflow; 2 - gas flow discontinued. a - right hemisphere occipito-sincipital electroencephalogram; b - right hemisphere temporal electroencephalogram; c - left hemisphere occipito-sincipital electroencephalogram; d - left hemisphere temporal electroencephalogram.

TABLE 1.

Presence (+) or absence (-) of desynchronization of α-rhythm upon $SO_2$ inhalation.

| Subject's initials | mg/m³ of $SO_2$ 5-3 | 3-1.6 | 1.5-1 | 0.9 | 0.6 |
|---|---|---|---|---|---|
| N.N. | + | + | + | + | - |
| S.G. | + | + | + | + | - |
| M.L. | + | + | + | + | - |
| G.V. | + | + | + | - | - |
| D.F. | + | + | + | + | - |
| S.N. | ++ | + | + | - | - |

Data showing the effect of 5.0 - 0.6 $mg/m^3$ concentrations of $SO_2$ on the EEG are presented in Table 1. Such data show that 0.9 $mg/m^3$ of $SO_2$ elicited desynchronization in 4 of 6 persons tested. K. A. Bushtueva showed previously that the threshold of $SO_2$ reflex effect on the reflexogenic zone of respiratory organs, as determined by the adaptometric method was also at 0.9 $mg/m^3$ concentration. Therefore, it can be assumed that the electroencephalographic method herein described yielded results approximately analogous to those obtained by the adaptometric method.

The second substance investigated was $H_2SO_4$ aerosol. It was shown that this substance possessed highly irritating properties in the zone of trigeminal innervation. The specific effect of this substance on the central nervous system indicated that concentrations which elicited a feeling of irritation, changes in light sensitivity, and in optical chronaxy coincided with, or actually were, at the 0.6 - 0.85 $mg/m^3$ level. In this connection the question arose whether at the time of the isolated application of $H_2SO_4$ aerosol the cerebral electrical activity had changed in the subthreshold concentration as indicated by verbal accounts or by the above enumerated methods. Studies indicated that the isolated application of $H_2SO_4$ aerosol in subthreshold concentrations elicited no desynchronization recordable by the electroencephalogram. However, desynchronization was noted when threshold concentrations of $H_2SO_4$ aerosol were applied. The effect lasted only 1 - 2 seconds. Desynchronization became manifest at the beginning of $H_2SO_4$ aerosol inhalation, as well as after the inhalation of this substance was discontinued. Data of the tests under discussion are listed in Table 2. Thus, desynchronization of the α-rhythm appeared

TABLE 2.

Presence (+) or absence (-) of desynchronization upon $H_2SO_4$ aerosol inhalation.

| Subject's initials | mg/m³ of $H_2SO_4$ aerosol 0.75-0.6 | 0.5-0.4 |
|---|---|---|
| N.N. | + | - |
| G.V. | + | - |
| L.M. | + | - |
| S.N. | + | - |
| S.G. | + | - |

upon the inhalation of $H_2SO_4$ aerosol concentrations which elicited a feeling of irritation and altered the course of other reflex reactions. In other words, the present modified method of electroencephalography possessed no advantages over methods previously used for the determination of threshold reflex effect produced by air pollutants.

The second modification of the electroencephalographic method for the determination of threshold reflex effect was then tested. It consisted in developing conditioned "electrocortical" reflexes associated with the inhalation of the substances under study. It has been known that a sudden and sharp increase in illumination acted as a conditioned stimulator and elicited desynchronization or α-rhythm depression. By combining the effect of a given stimulator, sound for instance, which alone had no effect on the electroencephalogram, with light, it was possible to create conditions for a temporary association between the two stimulators. Such temporary association manifested itself as desynchronization recorded on the electroencephalogram before responding to any other stimulant which may combine temporarily with the light. Such an association reaction recorded on the electroencephalogram was called "electrocortical" reflex.

In developing conditioned "electrocortical" reflexes, $SO_2$ and $H_2SO_4$ aerosol were chosen as the conditioned stimulators and unbroken light as the unconditioned stimulator. The association of $SO_2$ or of $H_2SO_4$ aerosol with light was tested at intermittent intervals; this was done for the purpose of preventing the development of a time-conditioned reflex. Such a modification of the method offered the possibility of objectively establishing central nervous system stimulation or stimulability to the application of chemical substances in low concentrations, particularly when the stimulation process, due to its low magnitude, did not reflect on the "upper" electroencephalogram during testing of the isolated effect of a chemical stimulant. Thus, the tests described presented a basis for a reply to the question whether or not a chemical stimulator, which by itself had no effect on the electroencephalogram, was able to elicit stimulation of the central nervous system. The method of "electrocortical" conditioned reflexes thus presented the possibility to determine stimulation by chemical agents which, according to the law of temporary association, can or may change the stimulability of cortical cells of the optical and other analyzers.

TABLE 3.

Electrocortical conditioned reflex upon $SO_2$ inhalation.

| Subject's initials | Reflex appearance at mg/m$^3$ of $SO_2$ | | | |
|---|---|---|---|---|
| | 1.5 - 1 | 0.9 | 0.6 | Below 0.6 |
| N.N. | 6 | 12 | - | - |
| S.G. | 5 | 5 | 15 | - |
| M.L. | 6 | 9 | 12 | - |
| G.V. | 9 | 9 | 12 | - |
| D.F. | + | + | 14 | - |

Note: Data in the table show the combination at which conditioned reflex appeared. Dash denotes no appearance of reflex.

$SO_2$ gas effect on the electroencephalogram was studied by this association modification in the concentration range of 1.5 - 0.3 mg/m$^3$. Data of this investigation are shown in Table 3. Data in that table show that in 0.6 mg/m$^3$ concentration $SO_2$ elicited reaction response in 4 of 5 persons tested. The conditioned reaction to $SO_2$ can be developed in 1 day in tests of 6 - 15 associations with light. Desynchronization arose with the lowest latent period of response and was manifest throughout the entire time of $SO_2$ effect. The conditioned reflex changes in the cerebral

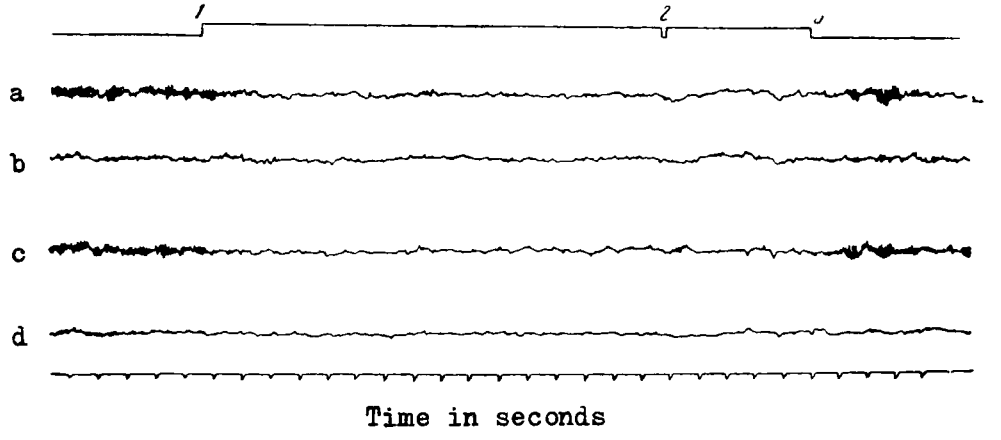



Fig. 2. Conditioned reflex desynchronization on the 8th combination of $SO_2$ effect at 0.6 mg/m$^3$ and uninterrupted light.
Upper line: 1 - moment of gas inflow; 2 - gas flow discontinued. a - right hemisphere occipito-sincipital electroencephalogram; b - right hemisphere temporal electroencephalogram; c - left hemisphere occipito-sincipital electroencephalogram; d - left hemisphere temporal electroencephalogram.

electrical activity are graphically shown in Fig. 2, from which it can be seen that α-rhythm depression occurred at the moment of exposure to $SO_2$ gas in 0.6 mg/m$^3$ concentration, and persisted to the time when it was reinforced with unbroken light, indicating that an "electrocortical" conditioned reflex had been developed. Results of the present investigation indicated that "electrocortical"

conditioned reflex studies constituted a most sensitive method for the determination of threshold reflex activity for odor-emanating substances. Tests made by these authors with substances affecting the trigeminal region, such, for instance, as $H_2SO_4$ aerosol, confirmed the high sensitivity of the method herein described. Thus, as a conditioned stimulator $H_2SO_4$ aerosol was used in 0.4 $mg/m^3$ concentration. The effect of the aerosol alone continued over 10 seconds and another 5 seconds in association with unbroken light. Conditioned electrocortical reflex was usually developed in the course of 19 - 23 $H_2SO_4$ aerosol and light associated effects. Results are presented in Table 4. Investigations here reported point to a high sensitivity of the method of "electrocortical" conditioned reflexes as a procedure for the study of threshold effect of irritating and odor-emanating substances on the reflexogenic zone of respiratory organs. The method is well adapted to the determination of practical maximal single limits of allowable concentrations of atmospheric air and is, accordingly, recommended for that purpose.

T A B L E 4.

Electrocortical conditioned reflex upon $H_2SO_4$ aerosol inhalation.

| Subject's initials | Reflex appearance at $mg/m^3$ of $H_2SO_4$ aerosol | | |
|---|---|---|---|
| | 0.75-0.6 | 0.4 | Below 0.4 |
| N.N. | 8 | 23 | - |
| G.V. | 16 | - | - |
| S.N. | 12 | 21 | - |
| M.L. | 6 | 19 | - |

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# Determination of Benzene, Toluene and Xylene Simultaneously Present in the Air.

E. G. Kachmar.

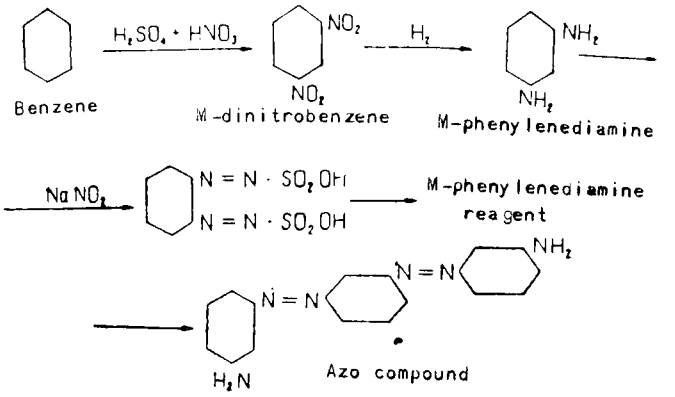
(From the F. F. Erisman Moscow Scientific-Research Institute of Sanitation and Hygiene of the R.S.F.S.R. Ministry of Health).

Gigiena i Sanitariya, Vol. 25, No. 5, 58-62, 1960.

Benzene, toluene and xylene are frequently found in mixed combinations under industrial conditions; more often one of the compounds will contain an admixture of another. Each of these components produce different toxic effects or similar effects of different intensity. Sanitary control of industrial air containing a combination of these pollutants must be based on the differential determination of individual compounds. This cannot be accomplished by the methods described in the literature. In addition, most methods described earlier are not sufficiently sensitive or require the use of special equipment and highly trained laboratory personnel not available to all laboratories.

A method based on the Yanovskii reaction is in current use by sanitation chemists for the determination of benzene and its homologues. This method was first proposed by A. V. Stepanov in 1929, and was later improved and modified by many investigators (M. V. Alekseyeva, 1940; M. K. Borezova, 1940; K. I. Kuz'mina, 1940; B. S. Boykina, 1950; M. S. Bokhovskaya, 1951; S. S. Gitis and I. D. Chapala, 1954). The principle of the method consists in nitrating the benzene (toluene or xylene), extracting the nitro-compounds with ether and determining them colorimetrically in an alkalinized acetone or ether-acetone medium. This method cannot be used when benzene, toluene and xylene are present simultaneously, since the mixture of the different component colors interferes with the qualitative and especially the quantitative determination. The present author undertook to develop methods for the determination of benzene, toluene and xylene present in the air simultaneously and avoiding the use of different solvents if possible. The new methods were based on the formation of azo-compounds.

Benzene was nitrified with a 10% nitration mixture to the dinitro form, which was then reduced with metallic zinc, diazotized in the presence of concentrated hydrochloric acid by a 1% solution of sodium nitrite, and combined with m-phenylenediamine. This author pictures the course of this reaction as follows:




The resulting azo-compound is of a yellow-brown color. The sensitivity of this reaction is 0.005 mg in the volume used for colorimetry. In order to determine benzene by the reaction proposed a standard scale has been prepared of 0.005 to 0.05 mg range in 6 - 8 ml. Standard scale colors were verified photocolorimetrically. A direct correlation was noted between the color intensity and the azo-compound concentration.

For the complete benzene determination under laboratory and industrial conditions, a series of experiments were performed with known amounts of benzene and determined on a parallel basis by the azo-compound formation and the Yanovskii reactions. Results are listed in Tables 1 and 2.

T A B L E 1.

Results of laboratory benzene determinations in mg.

| Benzene introduced | Determined by the Yanovskii reaction | Error | Determined by the azo-compound reaction | Error |
|---|---|---|---|---|
| 0.012 | 0.01 | -0.002 | 0.01 | -0.002 |
| 0.018 | 0.015 | -0.003 | 0.02 | +0.002 |
| 0.024 | 0.022 | -0.002 | 0.02 | 0.004 |
| 0.03 | 0.025 | -0.005 | 0.03 | - |
| 0.04 | 0.04 | - | 0.04 | - |

Data of Tables 1 and 2 show that the results of benzene determinations made by the Yanovskii and by the azo-compound reactions were very close. Control tests showed that the presence of an equal amount of toluene and of an equivalent 60% amount of xylene, did not interfere with the determination, as shown by the data listed in Tables 3 and 4. The toluene determination method was based on the azo-compound formation reaction proposed by M. V. Nifontova (1947) for trinitrotoluene determination. This reaction consisted in the reduction of trinitrotoluene and the combination of the reduced products with diazotized sulfanilic acid. Toluene was nitrified by a hot 10% nitration mixture to the

TABLE 2.

Results of benzene determinations under plant conditions.

| Technological process | Determined by reaction: Yanovskii | Azo-compound | Error |
|---|---|---|---|
| Column color | 0.075 | 0.08 | +0.005 |
| Head color | 0.05 | 0.06 | +0.01 |
| Screen coat | 0.05 | 0.04 | -0.01 |
| Base coat | 0.006 | 0.006 | 0 |

trinitro-compound and reduced with metallic zinc, after which the reduction products were combined with diazotized sulfanilic acid. A yellow azo-compound was obtained. The sensitivity of the reaction was 0.01 mg of toluene in the colorimetric volume. For this determination a standard scale was prepared with a toluene content ranging from 0.01 to 0.05 mg in 6.5 ml. Photocolorimetric checking of this scale showed a direct correlation between color intensity and the azo-compound concentration in solution. Results of parallel tests made under laboratory conditions by the Yanovskii and the proposed method are listed in Table 5.

TABLE 3.

Effect of toluene admixture on benzene determination by the azo-compound reaction, in mg.

| Benzene taken | Toluene added | Benzene determined |
|---|---|---|
| 0.01 | 0.005 | 0.01 |
| 0.02 | 0.01 | 0.02 |
| 0.04 | 0.02 | 0.04 |
| 0.01 | 0.0075 | 0.01 |
| 0.02 | 0.015 | 0.02 |
| 0.04 | 0.03 | 0.04 |
| 0.01 | 0.01 | 0.01 |
| 0.02 | 0.02 | 0.02 |
| 0.04 | 0.04 | 0.04 |

TABLE 4.

Effect of xylene admixture on benzene determination by the azo-compound reaction, in mg.

| Benzene taken | Xylene added | Benzene determined |
|---|---|---|
| 0.01 | 0.005 | 0.01 |
| 0.02 | 0.01 | 0.02 |
| 0.04 | 0.02 | 0.04 |
| 0.01 | 0.006 | 0.01 |
| 0.02 | 0.012 | 0.02 |
| 0.04 | 0.024 | 0.04 |

While similar parallel check tests were made under industrial production conditions, it was found that the toluene used in the plant contained an admixture of xylene, which seriously interfered with the determination of toluene by the Yanovskii reaction, while samples analyzed by the proposed method developed a color identical with the one of the scale, fit for quantitative determination. Additional control tests showed that the presence of an equal concentration of xylene and of half the equivalent volume of benzene did not interfere with the determination. Some results are listed in Tables 6 and 7.

TABLE 5.

Results of laboratory toluene determinations in mg.

| Toluene taken | Determined by the Yanovskii reaction | Error | Determined by the azo-compound reaction | Error |
|---|---|---|---|---|
| 0.016 | 0.02 | +0.004 | 0.02 | -0.004 |
| 0.024 | 0.023 | -0.001 | 0.022 | -0.002 |
| 0.032 | 0.03 | -0.002 | 0.03 | -0.002 |
| 0.04 | 0.04 | - | 0.04 | - |
| 0.05 | 0.05 | - | 0.052 | +0.002 |

In addition to benzene and its homologues air of the industrial production premises contained esters of acetic acid (acetates) and acetone, as components of the solvents, lacquers, etc. A study was made of their effect on the determination of benzene and toluene by the method of the azo-compound reaction. Ethyl and amyl acetates were tested as the most widely and frequently used components. It was found that ethyl and amyl acetates interfered with the determination in amounts above 0.05 mg and acetone in amounts greater than 0.7 mg.

TABLE 6.

Effect of benzene admixture on toluene determination by the azo-compound reaction, in mg.

| Toluene taken | Benzene added | Toluene determined |
|---|---|---|
| 0.01 | 0.005 | 0.01 |
| 0.02 | 0.01 | 0.02 |
| 0.04 | 0.02 | 0.04 |

TABLE 7.

Effect of xylene admixture on toluene determination by the azo-compound reaction, in mg.

| Toluene taken | Xylene added | Toluene determined |
|---|---|---|
| 0.01 | 0.005 | 0.01 |
| 0.02 | 0.01 | 0.02 |
| 0.04 | 0.02 | 0.04 |
| 0.01 | 0.0075 | 0.01 |
| 0.02 | 0.15 | 0.02 |
| 0.04 | 0.03 | 0.04 |

No suitable basis was thus far found for the development of a method for xylene determination in the presence of toluene; for this reason xylene was separated from benzene and toluene. This separation was attained chromatographically. Methods for chromatographic and thermographic analysis of aromatic hydrocarbons were described by I. M. Turkel'taub and L. S. Chemodanova (1957) and Ye. Sh. Gronsberg (1958). Benzene, toluene and xylene were passed through a silicagel column, accompanied by changing the adsorbent temperature as a means of increasing differential adsorption effects. ASK silicagel was used which had been washed with hot water and dried for 4 hours at 150 - 160°. The following studies were made: 1) conditions of benzene,

toluene and xylene adsorption on silicagel; 2) conditions of desorption such as effects of temperature and air volume passed through the silicagel in order to displace the benzene, toluene and xylene.

Experiments were performed as follows: vapors of the three components (benzene, toluene and xylene) were adsorbed in a V-shaped tube filled with silicagel, after which pure air was passed through the tube. The velocity and volume of air forced through varied. The adsorbent temperature was also varied. In heating the adsorbent the tube with the silicagel was placed in a chemotte clay oven of the Reberg type. A constant temperature of the oven was maintained by a type RNSh-55 regulator. A Zaitsev absorber with 2 ml of nitration mixture was placed directly behind the tube to absorb the benzene, toluene and xylene desorbed from the silicagel.

The desorbed hydrocarbons were determined by the Yanovskii reaction and by the proposed methods. Results showed that at 8 - 10° there was little desorption of xylene (6 - 8%). At the same time, benzene was desorbed completely at this temperature when 9 li of air was passed through the silicagel. At 8 - 10°, toluene began to desorb when 10 li of air had been passed through the silicagel, i.e., by passing the 11th li of air. To obtain complete toluene desorption it was necessary to pass another 18 li of air. Desorption of xylene from the silicagel was completed when 10 - 12 li of air had been passed at 80°.

On the basis of the above results the following conditions for the separation of xylene from benzene and toluene are recommended: 1) pass the vapors of benzene, toluene and xylene through a V-shaped tube filled with 4 g of ASK silicagel, which has been processed beforehand at a rate of 10 - 12 li/hr; 2) force through the V-shaped silicagel column air heated to 8 - 10° at the rate of 10 - 12 li/hr; the first 9 li of air will desorb the benzene, then 18 li will desorb the toluene. Then place the tube in a Reberg type oven heated to 80° and pass another 10 - 12 li of air to desorb the xylene. 3) Pass the desorbed hydrocarbon vapors through freshly and consecutively changed Zaitsev absorbers containing 2 ml of nitration mixture; 4) after the separation determine the benzene, toluene and xylene by the Yanovskii reaction or by the proposed new method.

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# Gas-Liquid Radiochromatograph.

M. I. Yanovskii and G. A. Gaznev.

Vestnik Akademii Nauk S.S.S.R., Vol. 30, No. 5, 27-31, 1960.

The use of labeled atoms has become a firmly established procedure in physico-chemical investigations. By introducing into the reaction zone a substance which contained $C^{14}$, for example, and then by determining the composition and the specific activity of the individual reaction products, it was possible to arrive at an understanding of changes which the labeled substance had undergone, this frequently enabled the investigator to obtain a clear picture of the order in which chemical changes or transformations take place. Such a procedure enabled investigators to secure valuable information in a short time regarding such catalytic reactions as, cracking, oxidation of propylene and acrolein, dehydrogenation and dehydration of alcohols, and other reactions. The anticipated wide utilization of labeled atoms in many branches of chemistry was held back by the lack of convenient and efficient methods for the isolation of individual reaction components from the mixture and of rapid and reliable methods for determining their specific radioactivity. Procedures previously used for the analysis of complex hydrocarbons by the $C^{14}$ labeled method consisted of the following steps: isolation of individual components with the use of highly effective refining columns, combusting the isolated compounds to $C^{14}O_2$, converting the latter to $BaC^{14}O_3$, preparing and measuring of targets for specific activity determination. Such an analytical procedure possessed the shortcomings of complexity, difficulty of execution, required highly qualified and specialized scientific personnel and lacked precision.

Attempts were made at the Institute of Physical Chemistry of the Academy of Sciences of the U.S.S.R. to obviate the enumerated shortcomings by combining the method of chromatographic analysis, normally completed in 15 to 30 minutes, with the method of determining specific radioactivity in flow. A combination of the 2 methods made possible to determine the chemical composition and the radioactivity of substances under study, that is, a complete radiochemical analysis was made within the period of time required for the performance of the chromatographic analysis only. This was accomplished by passing the flow coming from the chromatographic column through two detector analyzers, one recording the component concentration in flow and the other the corresponding

specific radioactivity. The ratio between the 2 detector analyzer indexes characterized (determined) the component's specific radioactivity.

Based on this principle the Institute developed, built and tested several types of radiochromatographs which combined the operations of partitioning and identification of the components with the recording of the components' specific radioactivity [1]. Most suitable was the type in which concentration of vapors emerging from the chromatographic column was determined by an ionization detector $Pm^{147}$, and specific radioactivity was determined by a flow counter which recorded gas flow intensification [2]. Such a device is of high sensitivity, simple to operate, yields dependable and stable indexes, and makes possible the determination of radiochemical composition of complex polycomponent mixtures within 20 - 30 minutes. With the procedure and equipment indicated it was possible to make physico-chemical measurements (determinations) under different experimental conditions: follow the course of homo- and heterogeneous reactions at different temperatures, study radiation of the reaction mixture, the mechanism of isotope exchange, etc. The gaseous system of the radiochromatograph is schematically illustrated in Fig. 1. The mixture of gases or liquids to be analyzed is delivered into the upper part of the chromatographic column by a dosing device (10). Before initiating the experiment, the column is flushed with a carrier gas, usually Ar, He, $H_2$, $N_2$, etc., from gas tank B through flow regulator (1). After having been partitioned the mixture components enter the ionization detector (18) and proportional counter (19). The signal from the ionization detector

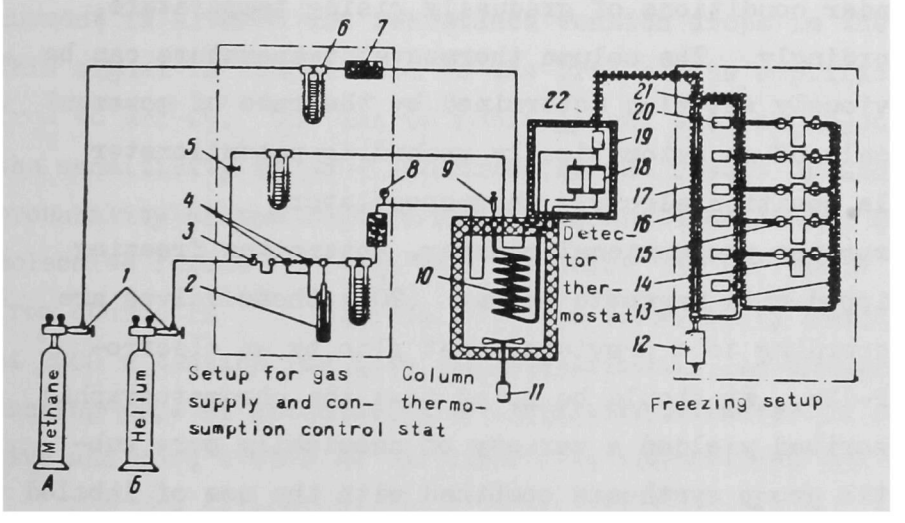


Fig. 1. Plan of gas radiochromatograph.
1 - fine regulator valve; 2 - fluid relay; 3 - reducer PDV-5; 4 - throttle; 5 - clamp; 6 - flowmeter; 7 - drier; 8 - manometer; 9 - injector; 10 - chromatographic column; 11 - fan; 12 - absorber; 13 - collector; 14 - freezing trap; 15 - stopcock of faucet; 16 - collector; 17 - by-pass; 18 - ionizing detectors; 19 - proportional counter; 20 - electromagnetic valve; 21 - three-way stopcock; 22 - safety device.

passing via the electrometric amplifier reaches the poly pointed potentiometer EPP-09; the signal of the proportional counter, passing via a separate channel, reaches the same poly pointed potentiometer by an integrating system of a "Tyul'pan" (tulip) type count recorder. The performance (operation) of the counter in the gas intensification system is adjusted to the gas flow coming from the ionization chamber by the addition of methane from gas tank (A). The radiochromatograph can be adjusted to operate under isothermic conditions or under conditions of previously planned gradual temperature rise. Chromatographic partitioning should be done under isothermic conditions when working with a mixture the components of which have a boiling point difference of a narrow range, such for instance as 20 - 30°. In partitioning a mixture of substances having a wide range of boiling point differences considerable time will be saved by performing the chromatographic partitioning under conditions of a previously determined graduated increase in temperature. Temperatures of chromatographic columns are controlled by an air thermostat for the maintenance of any desired constant temperature; temperatures of the ionization detector and of the proportional flow counter are controlled by a detector thermostat. When partitioning is done under conditions of gradually rising temperature, the thermostats are set accordingly. The column thermostat temperature can be elevated according to a previously set plan determined by the rate of movement of a small vial along the scale of an automatically recording potentiometer EPP-09 equipped with a triple position electric thermoregulator.

The gas flow emerges from the proportional counter, enters the freezing out partitioning system equipped with magnetic valves (20); these valves are switched in automatically according to a previously set plan by an electropneumatic control device KEP-12u. It should be noted that the chromatographic partitioning system here described yielded a variety of chemically pure substances; by means of catalytic group synthesis combined with the use of labeled atoms and subsequent chromatography, as here described, it was possible to isolate pure radioactive divinyl, α- and β-butylene and other hydrocarbons, the purity of which was established by the method of spectroscopic infrared light absorption. All steps of the procedure were directed and operated from an electric control board.

An ionization detector has been described in the literature the basic ingredient of which was $Sr^{90}$. In this case the source of ionizing radiation was

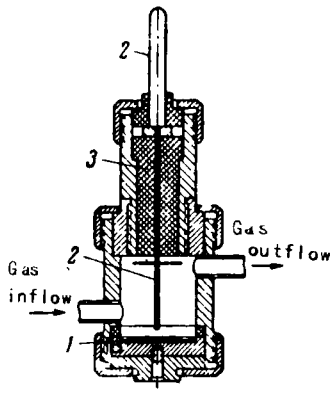


Fig. 2. An ionizing detector compartment. 1 - $Pm^{147}$ ionization source; 2 - collecting electrode; 3 - Teflon heater.

$Pm^{147}$ which was deposited electrolytically in a thin layer of the oxide measuring 2 $cm^2$ and having a specific radioactivity 2.5 mcurie/$cm^2$. The half-life of $Pm^{147}$ is 2.7 years and maximum energy of the β-particles is only 0.22 Mev. With regard to its differential scheme the ionization detector is made up of 2 cylindrical compartments one of which is visible in Fig. 2. Pure carrier gas is run into the comparative compartment, and the gas coming from the chromatographic column flows into the measuring or gaging compartment. The ionization source $Pm^{147}$ is isolated from the working space of the compartment by a terilene film 5 μ thick. Under the influence of the β-particles the gas undergoes ionization in both compartments. The ionization flows are opposite in their direction and, therefore, are mutually compensating when the carrier gas is flushed through the two compartments. As a component enters the measuring compartment the magnitude of the ionization current is altered and resistance tension drops in the order of $1.5 \times 10^9$ ohm. This signal is transmitted to the grid of the amplifier EMU-3 lamp and therefrom to EPP-09. The use of noble gases, such as argon, as carriers enhances the sensitivity by 50 - 100 times as the result of increase in the ionization probability of the organic molecules while colliding with the exciting argon molecules formed in large amounts under the influence of β-radiation coming from source $Pm^{147}$. Maximum detector sensitivity amounts to $1 \times 10^{-6}$% per mv at 2000 v tension fed into the compartment. As compared with the heat conducting type of detector, the ionization detector is considerably more sensitive and more stable at variable flow temperature and velocity.

For the determination of radioactivity of substances in flow coming from the detector use was made of a proportional flow counter (Fig. 3), which insured 100% effective counts and the possibility of working with soft β-emanators, such as tritium, which has a maximal β-spectral energy of 0.0179 Mev. Sensitivity of the proportional counter is 0.001 - 0.0005 mcurie. Use of the proportional counter lowers considerably the amount of radioactive substance necessary for the completion of a kinetic experiment with an adequate degree of precision.

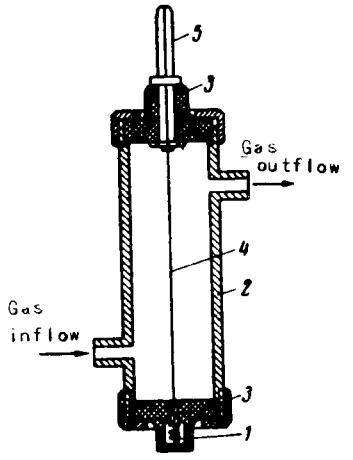


Fig. 3. Proportional flow counter. 1 - spring; 2 - body; 3 - Teflon heater; 4 - thread; 5 - plug.

An example of a typical radiogram of a mixture of radioactive and non-radioactive gases and vapors (Fig. 4) consists of 2 series of curves, curve 1, recorded by the ionization detector and curve 2, recorded by the proportional flow counter. Under conditions of equal and constant time of the detector and the proportional counter, each radioactive peak on curve 1 has a corresponding peak on curve 2. The ratio between the peak area of curve 2 and of curve 1 is in direct proportion to the specific radioactivity of a given component. In the field of kinetics and catalysis the character of the relative change in radioactivity distribution is of great importance. Therefore, there appears to be no need for absolute calibration of the device. However, where such calibration is required or desirable, it can be accomplished by passing through the column a carefully measured dose of a substance having a known specific radioactivity. The described radiochromatograph has been used in the Institute of Physical Chemistry in a series of investigations which proved the utility of radiochromatography and of chromatography in general in studying problems related to kinetics and catalysis. Thus, it was found by the radiochromatographic procedure that butylene formation in the catalytic synthesis of divinyls, according to Lebedev, was attainable by 2 processes - dehydration, formed in the process of butyl alcohol in the presence of a non-coked catalyzer, and by hydrogen redistribution between the coke and divinyl in the presence of a coke catalyzer. Predominance of the second process increases as the quantity of coke increases.

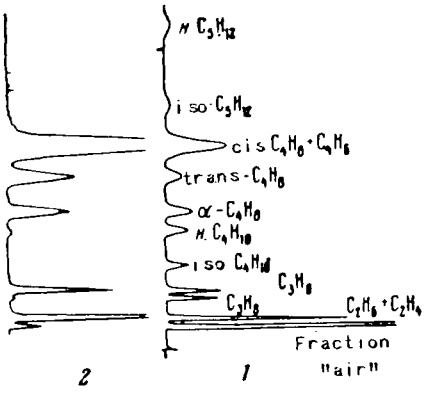


Fig. 4. Typical radiochromatograms of a polycomponent mixture inflow. 1 - concentration; 2 - radioactivity.

By this device and the new chromatographic procedure important information was obtained in the study of isothermic adsorption of individual substances and their mixtures, of catalytic reactions in flow and in the adsorbed layer of the fractional distribution in relation to adsorption temperature, etc. Temperature

curves offer a basis for the calculation of adsorption heat at the surface of catalyzers and adsorbents. It is hoped that the radiographic method here described will make possible the determination of relative adsorption coefficients of individual products in the actual course of a catalytic reaction. This and much more information will undoubtedly be obtained with the aid of this analytical procedure by other investigators.

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## Quantitative Determination of Low 3,4-Benzpyrene Concentrations with Fine Structure Fluorescent Spectrum.

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(Laboratory of Experimental Oncology, Oncological Institute, Academy of Medical Sciences, U.S.S.R.).

Voprosy Onkologii, Vol. 7, No. 7, 42-53, 1961.

In a previous publication [7] this author described a method for the detection of 3,4-benzpyrene in different complex substances and an approximate spectrophotometric method for the determination of 3,4-benzpyrene concentrations [6]. In the first method the products had to be partitioned chromatographically, which increased considerably the reliability and sensitivity of the method as compared with the method described by A. A. Il'ina [9, 10]. The second method was an improvement over the first in that it enabled to make more accurate quantitative determinations of 3,4-benzpyrene. By the use of the 2 methods qualitative studies were made of many substances: an extensive investigation of air pollution [11]; an investigation of 3,4-benzpyrene content

in smoked products processed by different technological procedures [1, 2, 4, 5]; tobacco smoke [8]; etc. However, results of such investigations clearly pointed to the need for the development of a more sensitive method for the determination of 3,4-benzpyrene. Minimal quantity of 3,4-benzpyrene in samples determined by the second method was 10 γ. Securing samples which contained 10 γ of 3,4-benzpyrene with any degree of accuracy proved in some investigations a difficult task, and impossible in other cases. As was shown in a previous publication [11], the aspiration method was successfully applied to the collection of air samples with such low 3,4-benzpyrene concentrations in only a few instances. In another report [3], it was shown that 3,4-benzpyrene determination in the lungs of city dwellers yielded reasonably satisfactory "summary" results of 17 persons; however, it was not feasible to establish the presence of 3,4-benzpyrene in the lungs of individual test subjects, which was the purpose of the investigation. A new method is described in this report which enabled the determination of lower 3,4-benzpyrene concentrations than with any previous tests.

General principles and basis of the method. The above mentioned "approximate" spectrophotometric method was based on the assumption that the light absorption by admixtures present in the benzpyrene fraction was in linear relation to the wave length; a similar assumption formed the basis of R. Cooper's method, used by many investigators abroad. Quantitative 3,4-benzpyrene determinations were made by establishing or measuring the absorption by 3,4-benzpyrene fractions of light of different wave lengths. In the present method fluorescence intensity was used as the index of 3,4-benzpyrene concentration. The possibility of using a fluorometric method for the quantitative determination of 3,4-benzpyrene was indicated in a previous publication [7]. Several circumstances prevented this author from making full use of the fluorometric method at that time: it was difficult to isolate 3,4-benzpyrene in its pure form from the investigated complex products; extensive distortion in the quantitative results due to the presence of other fluorescent admixtures. In the present method the above enumerated difficulties were obviated by combining the principle of spectrofluorometry with the fine structure spectral fluorescence phenomenon recently described by E. V. Shpol'skii and his coworkers [12, 13]. E. V. Shpol'skii and collaborators noted that compound spectra of 3,4-benzpyrene, and other substances, dissolved in normal paraffin

hydrocarbons, such as hexane, n-heptane and n-octane, had changed markedly upon freezing. The comparatively broad bands, observed at room or low temperatures but dissolved in other solvents, broke up upon freezing into a system of narrow bands approximating lines of atomic spectra. These fine lines can be used in simultaneously measuring the relative fluorescence intensity of two or more compounds in solution even when the spectra of such compounds are mutually superimposed under normal conditions. To make such measurement it is only necessary to be able to select one line in each of the compounds which is not in a superimposed position with regard to corresponding lines of the other substances in the solution. When the system of fine lines can be effected, the selection of such a free line presented no difficulties. The method of quantitative 3,4-benzpyrene determination presently described is based on measuring or establishing the comparative intensity of two spectrofluorescent lines: the 3,4-benzpyrene line of $\lambda$ = 4021 Å wave length (see Fig. 1-a) and 1,12-benzoperilene line of $\lambda$ = 4060 Å (see Fig. 1-b); the substances are dissolved in n-hexane and frozen in liquid nitrogen.

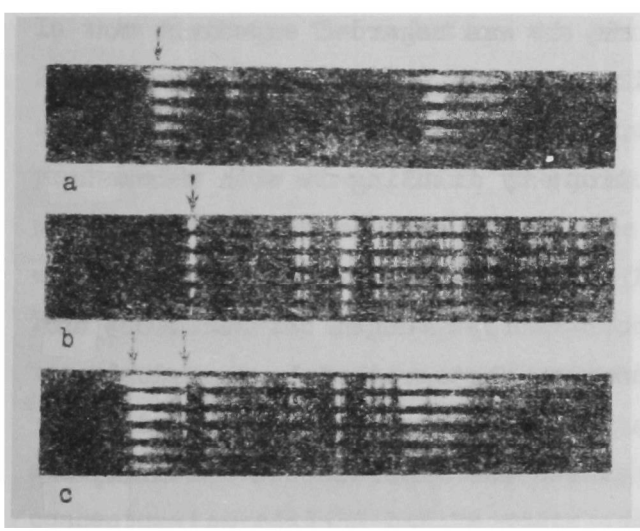


Fig. 1. Fluorescent spectra of hexane solutions of substances frozen with liquid nitrogen taken by means of a gradual clearing agent. a - pure 3,4-benzpyrene; b - pure 1,12-benzoperilene; c - typical picture of a benzpyrene fraction to which 1,12-benzoperilene was added.
Arrows point to two lines the intensities of which are used in determining concentrations.

These lines are so arranged that the slightest illumination of one compound affected the corresponding line of the other compound. At the same time they were arranged in close proximity to one another. As a result the background intensity effected by the fluorescence of the admixtures of structureless spectra differed only slightly at such points. Therefore, it is possible to disregard differences in sensitivity of photographic films at such points. Determination of fluorescence intensity ratios of the two lines was derived by the usual photographic method. As was previously indicated, it was possible to find the relative

intensity of the 2 lines by this method; in other words, it was possible to determine to what extent the intensity of one line exceeded that of the other, and on the basis of such data to establish the concentration correlation of the 2 substances in the solution under study. Determination of the absolute concentration of one of the substances in the solution necessitated a knowledge of the concentration of the other. However, absolute concentrations can be determined even when no quantitative information is available for either of the substances. This can be done by changing the concentration of one of the substances by adding a known quantity of this substance and determining the change in the intensity relationship of the two lines. Data thus obtained can be used for the determination, by a simple calculation, of the original concentration of either compound. Concentration determination based on intensity measurements is naturally possible only when, there existed in the solution, a proportionality between concentration and fluorescent intensity for each of the substances. Consideration was given the fact that the nature of fine spectral structure used in this study had been inadequately defined and its properties insufficiently studied; therefore, it was regarded expedient to establish first whether such proportionality actually existed. This was established as follows: a mixture was prepared of 3,4-benzpyrene and 1,12-benzoperilene to be used as the stock solution; by diluting it with n-hexane, a series of work solutions were prepared. The ratio between 3,4-benzpyrene and 1,12-benzoperilene was the same in all the dilutions, but the concentrations differed, and the 3,4-benzpyrene concentrations ranged between 0.025 and 10 γ/ml. The spectra of all such solutions were photographed by a gradual clarifier and the intensity ratios between the two lines were determined.

Data in Table 1 show that the ratio between the fluorescence intensity of the 2 lines remained constant only in the range of low concentrations. Beginning with 3,4-benzpyrene concentrations of 0.5 - 1.0 γ/ml the value of the ratio diminished as the concentration increased, i.e., the fluorescence intensity of the 3,4-benzpyrene line became weaker as compared with the fluorescence intensity of the 1,12-benzoperilene line. Of importance in this connection was the fact that the rate of fluorescence intensity loss by the 3,4-benzpyrene line with the increase in concentration followed the course of an ascending curve.

The data lead to an important and practical conclusion, namely, that proportionality between fluorescence intensity of the lines and concentration

TABLE 1.

Ratios between intensities of fluorescent spectral line of 3,4-benzpyrene and of 1,12-benzoperilene at constant ratio in their concentrations in relation to degree of solution dilution.

| γ/ml of 3,4-benzpyrene | 10 | 5 | 2.5 | 1 | 0.5 | 0.25 | 0.1 | 0.025 |
|---|---|---|---|---|---|---|---|---|
| At thick solution layer..... | 1.02 | 1.07 | 1.45 | 1.62 | 1.66 | 1.70 | 1.74 | 1.70 |
| At fine solution layer..... | - | - | 1.41 | - | 1.70 | - | - | - |

of substances under study prevailed only in the region of low concentrations, indicating that concentration determination on the basis of fluorescence intensity ratios was possible only in the low concentration region. Data of the basic determination series are presented in Table 1. The determinations were obtained by placing the solutions into tubes 12 - 14 mm in diameter and freezing them so that absorption and light emission occurred in a thick layer. However, this author also made 2 light excitation determinations in fine layers. In this instance the solution was placed in the space between the walls of the 2 tubes one inserted in the other. The thickness of the frozen layer did not exceed 1 mm. Data in Table 1 show that the nature of the results remained practically the same. Thus, the previously discussed concentration effect was not the result of layer thickness. This indicated that in practice it was possible to freeze the solution for analysis in comparatively wide tubes. This presented an advantage, since under such conditions the luminescence intensity was greater than in fine layers.

Final selection of the most suitable concentration range for analysis was made as follows: the functional relation between line intensity ratios and concentration of 1,12-benzoperilene was determined at constant 3,4-benzpyrene concentration; this was done by preparing 2 series of solutions. In the first series of 5 solutions the 3,4-benzpyrene concentration was 0.5 γ/ml, the 1,12-benzoperilene concentrations were varied to give ratios of 3,4-benzpyrene to 1,12-benzoperilene of 1:1, 1:2, 1:5, 1:10 and 1:20. Intensity ratios between the selected lines were determined from the spectrum of each solution. Having established these values, intensity ratios of 3,4-benzpyrene line to intensity of 1,12-benzoperilene line were determined for same concentrations of these substances. Based on proportionality between lines of intensity and substance

concentrations in all 5 tubes identical values for the ratios should have been obtained. Actually, however, the ratio values gradually rose with the increase in 1,12-benzoperilene concentration, pointing to the fact that under given conditions proportionality between line intensities and substance concentrations in solution did not prevail.

In a second series of 10 solutions 3,4-benzpyrene concentration was 0.1 γ/ml and ratio between that and 1,12-benzoperilene concentration ranged between 1:1 and 1:25, at intervals shown in Table 2.

T A B L E 2.

Ratios between 3,4-benzpyrene and 1,12-benzoperilene line intensities at constant 0.1 γ/ml 3,4-benzpyrene concentration and varying 1,12-benzoperilene concentration.

| 3,4-benzpyrene and 1,12-benzoperilene concentration ratios | Logarithms of concentration ratios (log Ibp/Ibl) |
|---|---|
| 1:1 | 0.64 |
| 1:2 | 0.72 |
| 1:3 | 0.72 |
| 1:5 | 0.72 |
| 1:7 | 0.67 |
| 1:10 | 0.70 |
| 1:13 | 0.69 |
| 1:16 | 0.67 |
| 1:20 | 0.72 |
| 1:25 | 0.62 |
| | Average 0.69 |

Data in Table 2 show that line intensity ratio values at same 3,4-benzpyrene concentration were the same in all cases ± allowable error, even though the 1,12-benzoperilene concentration varied. It can be concluded that at 3,4-benzpyrene 0.1 γ/ml and probably at lower concentrations, a proportionality prevailed between intensity of the selected lines and the concentration of the substances in solution. This indicated that analysis should be made with 3,4-benzpyrene concentration not exceeding 0.1 γ/ml.

Another important condition was the following: it appeared that the ratio between fluorescence intensities of 3,4-benzpyrene and 1,12-benzoperilene lines of greatest interest to the analyst depended largely upon another factor, namely, light excitation intensity. Increasing the light excitation intensity enhanced the fluorescence intensity of 3,4-benzpyrene as compared with 1,12-benzoperilene lines. Thus, by considerably reducing the light excitation intensity with a metallic screen, the ratio between the 2 lines was reduced by 60%. Replacing an old lamp by a new one, the light of which was considerably brighter, also changed the line ratios, so that as compared with the results obtained by the old lamp, the concentration of 3,4-benzpyrene increased by 80%. Thus, fluctuations in light excitation intensity substantially distort the re-

sults, unless such fluctuations are properly accounted for. Means were taken or recommended for the elimination, or reduction to a minimum, of errors caused by factors just described, as discussed in the following section.

Technique of analytical procedure and required apparatus and reagents. All preliminary analytical steps, including the isolation of the investigated benzpyrene fraction, were conducted as described elsewhere. Only the actual procedure for the determination of 3,4-benzpyrene concentration was new. For the quantitative determination only n-hexane, liquid nitrogen and photographic films are needed. The following apparatus is required: a setup for photographing spectra of frozen fluorescent solutions and a microphotometer, such, for instance, as MF-2, for the determination of dark lines intensity on the photographic film. Fig. 2 is a schematic drawing of the setup. It consists of ultraviolet light source, for which this author used a quartz lamp SVDSh-250-3 or PRK-4, provided with a special optical device for the concentration of the lamp light upon the test tube containing the frozen solution. The concentration of the light is attained by proper arrangement of transparent quartz prisms, condenser, etc.

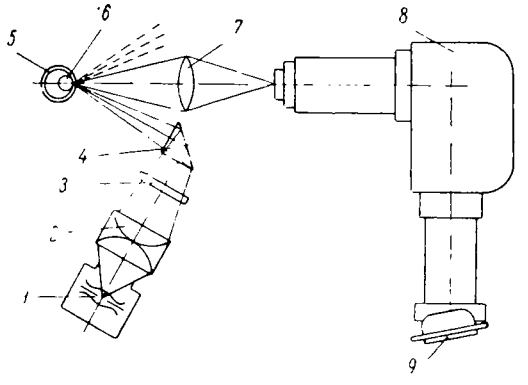


Fig. 2. Plan of spectral setup for the study of fluorescent spectra of frozen solutions. 1 - mercury quartz lamp SVDSh-250 or PRK-4; 2 - quartz condenser; 3 - filter UFS-1 which emits (passes) ultraviolet rays; 4 - quartz prism of complete inside reflection; 5 - quartz or uviolar Dyuarovsk vessel containing liquid nitrogen; 6 - test tube with solution under study; 7 - glass condenser; 8 - spectrograph ISP-51 with gradual clearing agent; 9 - photographic plate.

The following are the analytical steps: the desiccated benzpyrene fraction is dissolved in a known volume of n-hexane; degree of dilution may vary depending upon the quantity of 3,4-benzpyrene contained in the fraction. If it is judged that the 3,4-benzpyrene concentration was low, then it should be dissolved in not more than 10 - 15 ml of the solvent; but the volume must remain fixed. The solution thus prepared is then divided into 2 or 3 even portions or 2 or 3 equivalent portions may be taken from it. To each 3,4-benzpyrene portion 1,12-benzoperilene dissolved in n-hexane is added by a pipette in accurately measured gradually increasing volumes, so that the

first tube, for instance, will contain 1 γ; the 2nd - 2 γ and the third - 3 γ. The dilutions are then poured into test tubes of 10 - 12 mm diameter and the tubes, one after another, frozen in liquid nitrogen in a Dyuarovsk apparatus. The tubes are inserted close to the inner wall of the Dyuarovsk receiver in front of the spectrograph slit. After the solution in the tubes has frozen, the fluorescent spectrum is photographed via the gradual clearing agent. Pictures can be taken with the slits comparatively widely opened. In this instance, using spectrograph ISP-51, pictures were taken with the slit opened to 0.1 mm. Duration of exposure is usually 5 - 10 minutes.

Fractions which are judged to contain higher 3,4-benzpyrene concentrations should be dissolved in larger solvent volumes, and only a portion of that should be used in making the photographic spectrum. For instance, the sample can be dissolved in 10 ml, and only 1 ml used and diluting it to 10 - 15 ml, proceeding further as previously described. Fluorescent spectrographic photographs were similar to those shown in Fig. 1-b. The picture appeared as a series of spectra of different intensity, one below the other. Different degrees of spectral darkening were due to the fact that they were taken at different steps of the gradual clearing agent. Comparing this picture with the ones in Fig. 1-a and 1-b, it can be seen that it consists of 3,4-benzpyrene and 1,12-benzoperilene lines. In the next stage of analysis determinations were made of the ratio intensity of the spectral lines chosen for analysis, that is, 3,4-benzpyrene lines with $\lambda$ = 4021 Å and 1,12-benzoperilene lines with $\lambda$ = 4060 Å. Such determination was made by measuring with microphotometer MF-2 the darkening intensity on the logarithmic scale of these lines in all spectra obtained at different clearing agent steps. After this, curves of darkening intensity are plotted for each line. This is done by the usual method. A curve is constructed by plotting darkening intensities along the ordinate, and degree of light passing through the clarifying agent along the abscissa, using the logarithmic scale on one of the ordinates. Each value of line darkening intensity is indicated by a dot on the graph along the ordinate in terms of its absolute value and along the abscissa in terms of logarithm of light intensity passing through the steps of the clarifying agent by which the spectrum was obtained. By connecting all dots of one line a plot is obtained of its changes in darkening intensity; an analogous curve is plotted for the other line. In Fig. 3 curve I

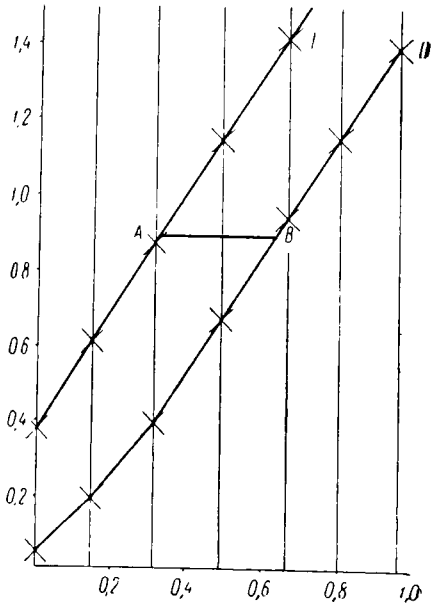


Fig. 3. Typical curves of darkening.
I - darkening curve of 1,12-benzoperilene; II - darkening curve of 3,4-benzpyrene. AB - distance between curves which represent line intensities ratio. Abscissa - logarithms of passing (filtration) through clearing agent; ordinate - logarithm of darkening intensity.

represents darkening intensity of the 1,12-benzoperilene line, and curve II the darkening intensity of the 3,4-benzpyrene line. The horizontal distance between the 2 lines, that is, the distance between two points of equal darkening (section AB in Fig. 3) represents the logarithm of intensity ratio of the 2 lines. The procedure is carried out for each solution. If the dilution of the benzpyrene fraction was appropriately prepared, then the quantity of 3,4-benzpyrene can be established by a simple calculation. For example: assume that 'a' represents the logarithm of intensity ratio between 3,4-benzpyrene and 1,12-benzoperilene lines, then the value of 'a' can be expressed by the following equation:

$$\log \frac{x Ibp}{n Ibl} = a \qquad (1)$$

in which Ibp represents the intensity of 3,4-benzpyrene in a solution containing 1 γ; x is the quantity of 3,4-benzpyrene in γ; Ibl is the intensity of 1,12-benzoperilene line of a solution containing 1 γ; and n is the quantity of 1,12-benxoperilene in γ. Generalization (1) can also be expressed as follows:

$$\log x + \log Ibp - \log n - \log Ibl = a \qquad (2)$$

from which the following generalization can be derived:

$$\log \frac{n}{x} = \log \frac{Ibp}{Ibl} - a \qquad (3)$$

Generalization (3) can be used in calculating 3,4-benzpyrene quantities used in cases in which the original fractions contained no 1,12-benzoperilene. The first part of the equation contains 2 values. As indicated above value 'a' is determined from the curves of darkening. Expression log Ibp/Ibl is the logarithm of ratio of the line intensities of the 2 substances of equal concentrations. As was previously indicated this value is determined under different conditions. At 3,4-benzpyrene 0.1 γ/ml or less and at large interval of

1,12-benzoperilene concentrations this value was constant and equalled approximately 0.69. Therefore, formula (3) can be further simplified as follows:

$$\log \frac{n}{x} = 0.69 - a \qquad (4)$$

Let's now compute the quantity of 3,4-benzpyrene for a case shown in Fig. 3, assuming that the benzpyrene fraction as such contained no 1,12-benzoperilene. In that case value 'a' will be represented by section AB = 0.31; and, since the curve of 1,12-benzoperilene darkening is above the 3,4-benzpyrene curve, its values are negative and, hence, AB = 0.31. According to formula (4) $\log n/x = 0.69 - (-0.31) = 1.0$, and $n/x = 10$. In other words, the quantity of 1,12-benzoperilene in the solution was 10 times as great as the quantity of 3,4-benzpyrene. In the case presented in the graph there was added to the benzpyrene fraction 1 γ of 1,12-benzoperilene; therefore, this fraction would contain $x = n/10 = 1/10 = 0.1$ γ of 3,4-benzpyrene. Results of above computation would, therefore, indicate that the analysis was conducted under properly chosen conditions with regard to ratio of 3,4-benzpyrene and 1,12-benzoperilene concentrations within the previously controlled limits of 1:10 and with 3,4-benzpyrene not exceeding 0.1 γ/ml or 0.1 γ/5 ml of the solution.

Had the conditions of the determination been chosen inappropriately, then the resulting curves of darkening and values of n:x would have indicated that. Assume that $n:x = 0.5$. This would indicate first that the range of concentration ratios was selected unfittingly; and second, if 1 γ of 1,12-benzoperilene had been added to the sample it would then follow that the 3,4-benzpyrene concentration in the solution was high - about 0.4 γ/ml on the basis of total solution volume of 5 ml. Under such conditions it would have been necessary to dilute the fraction 4 times and add another 4 or 5 γ of 1,12-benzoperilene. After having photographed the spectrum of the new solution and having completed all determinations and calculations obtaining the correct values of 3,4-benzpyrene content should present no difficulties.

The above analysis represents a simple case, that is, one in which the benzpyrene fraction contained no 1,12-benzoperilene. However, under practical conditions benzpyrene fractions isolated from many studied products actually contained 1,12-benzoperilene. Even under such conditions it should be possible to make a quantitative determination of 3,4-benzpyrene and of 1,12-benzoperilene without resorting to additional complex procedures of purifying the fraction.

With such possibilities in mind, it was previously recommended that 2 or 3 benzpyrene fraction dilutions be made to which different quantities of 1,12-benzoperilene were to be added. Curves of darkening are then plotted from the spectra of each solution as shown in Fig. 3. Logarithmic ratios between the intensity lines of 3,4-benzpyrene and 1,12-benzoperilene are then found on the plots for each 3,4-benzpyrene solution prepared. Computation of the 3,4-benzpyrene and 1,12-benzoperilene quantities present in the original fraction are then made as follows: three equations are derived from formula (4):

$$\log \frac{n_1}{x} = 0.69 - a_1;\ \log \frac{n_2}{x} = 0.69 - a_2;\ \log \frac{n_3}{x} = 0.69 - a_3$$

Now, assume that the following were obtained as the result of the computations:

$$\frac{n_1}{x} = A_1;\ \frac{n_2}{x} = A_2;\ \frac{n_3}{x} = A_3$$

Assume in addition that the original fraction contained $n_0$ of 1,12-benzoperilene in the sample volume placed into one tube, and that to each tube now containing the same amount of the original solution $n'_1$, $n'_2$ and $n'_3$ of this compound were added correspondingly. The equation can then be presented as:

$$\frac{n_0 + n'_1}{x} = A_1;\ \frac{n_0 + n'_2}{x} = A_2;\ \frac{n_0 + n'_3}{x} = A_3$$

Solving these equations in pairs, that is, 1 and 2, 2 and 3, and 3 and 1, the following 3 expressions are derived for x and $n_0$:

$$x = \frac{n'_2 - n'_1}{A_2 - A_1};\ x = \frac{n'_3 - n'_2}{A_3 - A_2};\ x = \frac{n'_3 - n'_1}{A_3 - A_1} \qquad (5)$$

$$n_0 = \frac{n'_2 - \frac{A_2}{A_1} n'_1}{\frac{A_2}{A_1} - 1};\ n_0 = \frac{n'_3 - \frac{A_3}{A_2} n'_2}{\frac{A_3}{A_2} - 1};\ n_0 = \frac{n'_3 - \frac{A_3}{A_1} n'_1}{\frac{A_3}{A_1} - 1} \qquad (6)$$

Values of the 3 equations under (5) and under (6) are averaged to obtain quantities of 3,4-benzpyrene and 1,12-benzoperilene found in each tube. The averages are used in finding the quantity of 3,4-benzpyrene and 1,12-benzoperilene in the fraction by the usual routine procedure. Generalizations under (5) and (6) are in essence formulas for the calculation of 3,4-benzpyrene and 1,12-benzoperilene amounts. The above outlined calculation procedure is intended for use in analysis employing 3 samples of the fraction under investigation. It is possible to shorten the procedure by using only

2 dilutions, in which case direct single values can be derived for x and $n_0$. Single answers only can be derived from solving single pairs of equations; under such conditions no average values could be derived, and final results may lack the desired precision. Therefore, it would be necessary to repeat the entire procedure should the final results indicate that the selection of analytical conditions was not a fitting one. The above discussion dealt with only one of many possible analytical variants encountered in 3,4-benzpyrene determination. It should be added that a similar procedure of reasoning and calculation can be applied to all varying cases.

It was shown in a preceding paragraph that line intensity ratios varied with the intensity of light excitation. Changes in the intensity of light excitation are accompanied by changes in coefficient 'a' and log Ibp/Ibl which are components of formula (3). Possible errors which may arise in connection with this phenomenon can be avoided by adhering to the following procedure: each time a lamp, as a source of light, is changed, or each time any other type of change is introduced which may affect the intensity of light excitation, such, for instance, as changing a light filter, changing a condenser, changing a Dyuarovsk device, the value of log Ibp/Ibl, which was taken as = 0.69, should be carefully rechecked. In determining the 2 coefficients mentioned and during making practical analyses, it is important to see that the lamp operated under the same current intensity. As a general rule, values of coefficient log Ibp/Ibl should be checked by means of specially prepared solutions of pure compounds even under favorable conditions of analytical determinations. In view of the above, it is essential that solution samples used in checking the coefficients be preserved for future check tests. Should the check test indicate that the coefficient value has shifted, the analysis should be repeated. Results of analysis should not be regarded as final unless and until an appropriate coefficient checking indicated that no noteworthy changes had taken place in the coefficients under consideration. Scrupulous observation of the above instructions will result in securing correct analytical values. It should be noted at this point that fluctuations in the light emanated by the electric bulb introduce no errors of considerable magnitude. Thus, 0.5 amp. fluctuations in the current passing through the lamp, such as 4.5 amp. and 4.0 amp., affected the results only to the extent of 9 - 10%. In the light of the above mentioned cases the

0.69 coefficient used in formula (4) can not and should not be applied in analysis of a newly assembled installation; in such cases new and special supplemental tests should be made.

Procedure for checking the method and a comparison with the approximate spectrophotometric method. The method was checked first by the following procedure: several products were selected which contained no 3,4-benzpyrene. Dilutions were prepared to which known quantities of pure 3,4-benzpyrene and 1,12-benzoperilene were added. Quantitative determinations were then made for 3,4-benzpyrene; the results are listed in Table 3. A comparison of the results obtained with actual amounts added showed that 3,4-benzpyrene could be determined by this method with a high degree of precision; averages of 15 sample analyses showed that the limit of error averaged ± 8%. It is generally conceded that for a photographic method such results are highly satisfactory. The range of error was also comparatively insignificant. In only 3 of 15 analyses did the difference exceed 10%, with 13% being the highest. Data in Table 3 are obtained with 5 3,4-benzpyrene-free fractions. They indicate that none of the products used had any substantial effect on the results.

TABLE 3.

Checking the new method's precision.

| Experiment number | Fraction number | γ of added 1,12-benzo-perilene | γ of added 3,4-benz-pyrene | γ of 3,4-benzpyrene found | Percent deviation |
|---|---|---|---|---|---|
| 1 | 1 | 2 | 0.4 | 0.37 | -8 |
| 2 | 1 | 4 | 0.8 | 0.72 | -10 |
| 3 | 1 | 8 | 0.8 | 0.9 | +12.5 |
| 4 | 2 | 1 | 0.25 | 0.23 | -8 |
| 5 | 2 | 2 | 0.25 | 0.282 | +12.8 |
| 6 | 2 | 3 | 0.25 | 0.269 | +8 |
| 7 | 2 | 2 | 0.5 | 0.45 | -10 |
| 8 | 2 | 3 | 0.5 | 0.5 | 0 |
| 9 | 2 | 6 | 0.5 | 0.54 | +8 |
| 10 | 3 | 2 | 0.5 | 0.5 | 0 |
| 11 | 3 | 5 | 0.5 | 0.46 | -8 |
| 12 | 4 | 2 | 0.5 | 0.50 | 0 |
| 13 | 4 | 5 | 0.5 | 0.56 | +12 |
| 14 | 5 | 2 | 0.5 | 0.51 | +2 |
| 15 | 5 | 5 | 0.5 | 0.46 | -8 |
| Averages..... | | | | | ±8 |

Therefore, it is concluded that foreign substances present in the fractions, and in particular fluorescent substances, had no notable effect on the analytical results.

The next stage was a comparative evaluation of results obtained by the new method herein described and by the old method of "approximate" spectrophotometry. Twenty, thirty or more benzpyrene fractions, derived from different products, were tested by both methods. In evaluating the results the following must be considered: first, all analyzed fractions containing 1,12-benzoperilene should be separated from those free from that compound. This is essential, since the absorption spectrum of 1,12-benzoperilene closely approximates the absorption spectrum of 3,4-benzpyrene. Hence, in analyzing the samples by the old method the 1,12-benzoperilene fraction imparts to 3,4-benzpyrene determinations excessive values. Presence in the fraction of 4.5 γ of 1,12-benzoperilene, as determined by the "approximate" spectrophotometric method, is equivalent to 1 γ of 3,4-benzpyrene. (See note at end of paper). Secondly, the results obtained should be combined into 2 groups: group 1 should contain results of samples which by the "approximate" method yielded comparatively small errors, that is, fractions containing more than 10 γ of 3,4-benzpyrene per sample; and group 2, results of samples which by the "approximate" spectrophotometric method contained less than 10 γ per sample, in which case the accuracy of the old method is not high. The comparative study of the 2 methods led to the following conclusions: in analyzing fractions free from 1,12-benzoperilene containing greater 3,4-benzpyrene concentrations the 2 methods yielded practically coincident values. In the presence of 1,12-benxoperilene the new method yielded lower 3,4-benzpyrene values than did the "approximate" spectrophotometric method, the difference on occasion ranging between 30 - 40%. However, if in using the new procedure the amount of determined 1,12-benzoperilene is computed as 3,4-benzpyrene equivalent and the two values are added, then the old and new procedures will yield close to equal values in most cases. In some instances the summary values may exceed the old values by 10 - 20%, and at most 30%. In samples of low 3,4-benzpyrene concentration the total picture remained generally the same, but the magnitude of differences was somewhat greater, due to the inferior accuracy of the old method analyzing low 3,4-benzpyrene-containing samples. Thus, results indicated that values yielded by the 2 methods were within

reasonable agreement and that results obtained by one method may be regarded as a confirmation of the results obtained by the other method. A comparison of the values yielded by the 2 methods leads to 2 conclusions which give preference to the new procedure.

The preceding discussion clearly indicated that the new method had advantages in analyzing fractions containing 1,12-benzoperilene, a substance which is found in many products. Its separation from 3,4-benzpyrene presents difficulties even in chromatographic partitioning, and complete separation of the two can not always be attained. Admixtures of 1,12-benzoperilene considerably distorted the analytical results yielded by the old method. The presence of 1,12-benzoperilene was no obstacle to the correct analytical determinations by the new method, thereby eliminating the need of thorough partitioning of the 2 substances.

Another even more essential advantage possessed by the new method is its higher sensitivity. By the new method 0.05 - 0.01 γ of 3,4-benzpyrene per sample and in some cases, even lower quantities were determined with reasonable accuracy, whereas the old method was reasonably accurate only in the presence of 10 γ or more of the 3,4-benzpyrene. It has been estimated that the new method was 100 times as sensitive as the "approximate" spectrophotometric method. It is hoped that such increase in sensitivity might prove of value in establishing the presence of this cancerogenic substance. It is also hoped that supplemental studies of the new procedure will make possible its application to analysis of other fluorescent substances.

## Conclusions.

1. Results of a special investigation showed that fine structure spectral fluorescence can be used for qualitative and quantitative determination of 3,4-benzpyrene. Quantitative determination is based on ratio between 3,4-benzpyrene and 1,12-benzoperilene absorption intensity lines. The 1,12-benzoperilene is added specially to the fraction under quantitative study in known quantities.

2. The new method is highly sensitive. By the fine structure spectral fluorescent method determinations can be made comparatively easily of 0.05 - 0.10 γ or less of 3,4-benzpyrene per sample with a high degree of accuracy. Average deviation of 15 control tests was only ± 8%. Deviations exceeding 10% occurred in 3 of the 15 control tests, and none exceeded 13%.

3. The method here described for the determination of 3,4-benzpyrene concentration based on the fine structure spectral fluorescent principle manifested many advantages over previously recommended spectrophotometric procedures. The primary and most basic advantage was in the fact that the new method made possible the determination of minimum 3,4-benzpyrene concentrations 100 times lower than the minimum concentrations required by the previously described methods, retaining the previously mentioned high degree of precision. The second advantage resides in the fact that the presence of slight amounts of 1,12-benzoperilene, the absolute removal of which at times presented great difficulties, did not interfere with the accuracy of 3,4-benzpyrene determination. The presence of 1,12-benzoperilene seriously distorted determination results by previous procedures of this author as well as by any determination procedure based on the principle of light absorption.

4. Principally the presently outlined method can be employed not only in the determination of 3,4-benzpyrene, but equally effectively in the determination of any other substance characterized by fine structure spectral fluorescence. Another advantage is presented by the fact that substances other than 1,12-benzoperilene can be added in making quantitative determinations. It must be borne in mind, however, that in applying this method to the determination of substances other than 3,4-benzpyrene and in using additives other than 1,12-benzoperilene a thorough preliminary study must be made to find the most suitable set of determination conditions.

5. Values yielded by the new analytical procedures were checked on a control basis against values obtained by the previously described "approximate" procedure; results were within the range of statistically satisfactory agreement.

Note: To avoid misunderstanding regarding the old method, it should be borne in mind that 1,12-benzoperilene in the fraction exists only as an admixture to 3,4-benzpyrene and that it can distort the outcome of quantitative determinations; it is for this reason that the old procedure has been referred to as the "approximate" photospectrometric method. On the other hand, the assumption that the fraction contained only 1,12-benzoperilene and no 3,4-benzpyrene and that the old method recorded total 1,12-benzoperilene as 3,4-benzpyrene must be excluded by preliminary qualitative testing of the samples for the presence of 3,4-benzpyrene.

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## Collecting Air Samples for the Determination of Nitrogen Dioxide.

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Accuracy of air sample analysis for content of any particular gas depends on the method of air sample collecting to the same extent as it depends upon the precision of the analytical methods used. Air samples for the analysis of nitrogen dioxide concentration are usually collected by one of three methods: 1) by aspiration of the air through a liquid absorber; 2) by the vacuum method; and 3) by the exchange method. Solutions of NaOH, of sulfanilic acid, of KI and the Griess-Ilosvey reagent have been used as absorbers of nitrogen dioxide. In the exchange method the air is aspirated through a bottle or a gas pipette until the original air in those containers is completely replaced by the air to be tested, which can be accomplished by aspirating through the containers a volume of the air 6 to 10 times the capacity of the bottle or of the gas pipette. The purpose of this study was to make a comparative evaluation of the 3 methods of air sample collection for the determination of nitrogen dioxide concentrations. The experimental procedure was as follows: a known concentration of nitrogen dioxide was prepared inside a glass flask

equipped with a ground-to-fit stopper having two fused-in glass tubes, one extending down to the bottom of the flask, the other protruding only slightly below the lower end of the glass stopper. This served as the source of experimental air containing a known constant concentration of nitrogen dioxide for use in any one of the methods investigated. The gas pipettes or the bottle, as the case may have been, were first thoroughly washed, tested for the presence of oxides of nitrogen and vacuumated (by a water pump). Simultaneously with the collection of a sample by aspiration through liquid absorbers, three samples were collected by the vacuum method. In all tests nitrogen dioxide was determined by the Griess-Ilosvey reagent. Tests were made with air samples containing quantities of nitrogen dioxide in the order of hundredths or thousandths of mg per li. The absorber apparatus was V-shaped and was equipped with a porous filter No. 1. Over 200 tests were made under identical conditions. Results are listed in the table below. The data show that the NaOH solution manifested the lowest absorption of nitrogen dioxide; the solution of sulfanilic acid, which is a constituent of the Griess reagent, was only slightly better. Nitrogen dioxide reacted with sulfanilic acid to form a diazo-compound; however, in the course of air sample aspiration the diazo-compound decomposed because of its high instability. This explains the limited 20% absorption of the nitrogen dioxide. This was verified as follows: air samples were aspirated through the Griess reagent which was accompanied by a rapid diazotization reaction; however the final determination results, though higher than in the case of sulfanilic acid, still amounted to only 45%. The diazo-compounds formed in the Griess reagent reacted with α-naphthylamine to form a dye compound; however, the latter

Summary table of average results of nitrogen dioxide determinations in air samples collected by different methods.

| Collection method | Found in percent |
|---|---|
| Vacuum method | 100 |
| NaOH solution | 17.9 |
| Sulfanilic acid solution | 20 |
| Potassium iodide solution | 43.6 |
| Griess-Ilosvey reagent | 45 |
| Exchange method, slow aspiration rate | 131.5 |
| Exchange method, at the rate of 5 - 6 li/min | 95 - 100 |

reaction proceeded at a rate considerably slower than the first reaction, and much of the diazo-compound decomposed before reacting with the α-naphthylamine. Hence, the lower results. The KI absorber solution absorbed only 43.6% of the nitrogen dioxide.

Results of tests by the exchange method showed that aspiration of the air at the rate of 5 li/min. recorded only 95% of the nitrogen dioxide present in the air sample, and at the rate of 6 li/min. recorded 100%; from this it can be concluded that the rate of air aspiration affected the determination results. On the other hand, when the rate of air aspiration was too low (0.5 - 1.0 li/min.) the final result was 131%. This may be the result of nitrogen dioxide adsorption to the surface of the glass container. Aspirating the air through the gas pipette at the rate of 5 - 6 li/min. yielded analytical results approximating those yielded by the vacuum collection method.

The results presented indicated that nitrogen dioxide was incompletely absorbed by the liquid absorber used and that air samples for the determination of nitrogen dioxide had best be collected by the bottle or gas pipette vacuumation method, or by the exchange method, aspirating the air through the containers at the rate of 5 - 6 li/min.

# Hydrogen Sulfide Oxidation in the Organism.

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Trudy Vsesoyuznoi Konferentsii po Meditsinskoi Radiologii, Eksperimental'naya Meditsinskaya Radiologiya, Medgiz, 1957, 280-283.

Discussions on the mechanism of hydrogen sulfide baths are based on the assumption that upon entering the organism hydrogen sulfide enhanced the number of sulfhydryl bonds accompanied by an increase in the concentrations of glutathione and cysteine. It was also assumed that sulfur accumulated in the organs and that hydrogen sulfide persisted in the circulation for a long time. The purpose of this study was to check the correctness of the above assumptions and to establish, if possible, the course of hydrogen sulfide oxidation in the organism. Studies were conducted by the method of labeled hydrogen sulfide. Four series of investigations were conducted based on different routes of $H_2S$ administration. Tests were made for $H_2S$ concentration in the blood and percent of labeled S incorporated into proteins of different organs.

In the first series six dogs were injected intravenously with $Na_2S$ at the rate of 10 up to 600 γ, with specific activities ranging between 500,000 up to 14 x $10^6$ imp. per kg of body weight. Injection took 10 - 20 minutes. Blood was taken for analysis from the artery and vein opposite the injected side after 1, 3, 5, 7, 8, 9, 10, 11, 13, 15, 20, 30, 45 and 60 minutes. No $H_2S$ was detected in either the venous or arterial blood samples. One hour after the injection of the $Na_2S$ solution the urine contained 11.4% of the injected dose, 60% of which was in the form of inorganic sulfates, 3% in the form of S esters, and the rest in the form of neutral sulfur. No $H_2S$ was found in the urine.

Hydrogen sulfide and products of its oxidation in the organs were investigated as follows: dogs were killed 30 and 60 minutes after the $Na_2S$ injection, the organs removed and tested for specific activity. Results are listed in Table 1. Highest specific activity was found in the kidneys, testicles, lungs, liver, pancreas, and lowest in skeletal muscles.

Experiments of the second series were performed with 26 rats. Animals were injected subcutaneously with a solution of $Na_2S^{35}$ once or daily over 4 - 6 days at the rate of 1 - 8 γ per g of body weight. Specific activity of the injections ranged between 3000 and 6000 imp/min. Simultaneous determinations for the presence of $H_2S$ and intensity of specific activity were made 24 and

TABLE 1.

Specific activity of organs one hour after intravenous injection of $Na_2S^{35}$ equivalent to 6.6 mg of $H_2S^{35}$ of 157 x $10^6$ imp/min.

| Organ | S mg/g of tissue | Imp/min. per g of tissue | Percent of injected activity x $10^{-2}$ | Specific activity x $10^{-2}$ |
|---|---|---|---|---|
| Lungs..... | 1.21 | 24,807 | 1.57 | 13 |
| Kidneys..... | 1.10 | 33,360 | 2.12 | 19 |
| Liver..... | 1.57 | 24,829 | 1.57 | 10 |
| Heart..... | 0.82 | 10,566 | 0.67 | 8 |
| Spleen..... | 1.04 | 13,368 | 0.85 | 8 |
| Pancreas..... | 0.79 | 12,435 | 0.79 | 10 |
| Testicles..... | 0.55 | 13,480 | 0.86 | 16 |
| Skeletal muscles. | 0.93 | 8,819 | 0.56 | 6 |

48 hours after the $Na_2S^{35}$ injection. No $H_2S$ was found in the blood of any rats. Results of studies on the elimination of $S^{35}$ via the urine are listed in Table 2. Data indicate that 24 hours after the $Na_2S^{35}$ subcutaneous injection the urine showed specific activity of high intensity, and that 92 - 99% of the eliminated $S^{35}$ was in the form of inorganic sulfates.

TABLE 2.

Sulfur elimination via urine following subcutaneous administration of $Na_2S^{35}$ equivalent to 220 g of $H_2S^{35}$ of 7.4 x $10^5$ imp/min.

| Days | Ml of urine | Sulfur per 1 ml | | Imp/min/ml | | Percent of total sulfur |
|---|---|---|---|---|---|---|
| | | Total | Inorganic | Total S x $10^{-2}$ | Inorganic S x $10^{-2}$ | |
| 1 | 5.7 | 1.15 | 0.65 | 717 | 702 | 99 |
| 2 | 3.8 | 1.23 | 1.29 | 106 | 98 | 92 |
| 5 | 6.0 | 1.88 | 1.08 | 18 | 10 | 55 |
| 6 | 1.2 | - | 1.65 | - | 10 | - |

Determinations were then made of total and radioactive S in different organs 24 hours and six days after the subcutaneous $Na_2S^{35}$ injection. Data indicate that 24 hours after the injection highest specific activity was found in the liver, lungs, kidneys and spleen; six days after the injection the intensity of specific activity sharply fell in the liver and remained unchanged in the liver and kidneys. Data obtained with rats repeatedly injected with the $Na_2S^{35}$ are also listed in Table 3. The data indicate that following the injection of large $H_2S^{35}$ doses, such as 495 γ on four successive days,

specific activity was registered by all protein fractions of all organs; following the injection of small doses, such as 39 γ on four successive days no specific activity was registered by any of the organ proteins.

TABLE 3.

$S^{35}$ distribution in organs following subcutaneous injection of sodium sulfide.

| Organs | Injected 303.6 γ $H_2S^{35}$ 1.7 x $10^6$ imp/min. | | | | Injected 220 γ $H_2S^{35}$ 7.4 x $10^5$ imp/min. | | | | Injected 495 γ $H_2S^{35}$ 11 x $10^6$ imp/min. | | Injected 37 γ $H_2S^{35}$ 0.39 x $10^6$ imp/min. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mg S per g of tissue | Imp/min/g of tissue | % injected activity x $10^{-2}$ | Specific activity x $10^{-3}$ | Mg S per g of tissue | Imp/min/g of tissue | % injected activity x $10^{-2}$ | Specific activity x $10^{-3}$ | Native imp/min | Protein imp/min | Native imp/min | Protein imp/min |
| Brain | 0.69 | 425 | 2.5 | 36 | 0.79 | 95 | 1.3 | 16 | 34 | 74 | 6 | 0 |
| Lungs | 0.93 | 740 | 4.3 | 46 | 1.18 | 344 | 4.6 | 39 | 67 | 94 | 3 | 0 |
| Kidneys | 1.04 | 720 | 4.2 | 40 | 1.18 | 230 | 3.1 | 26 | 170 | 185 | 3 | 3 |
| Liver | 1.18 | 1100 | 6.5 | 55 | 1.32 | 28 | 0.4 | 3 | 21 | 29 | 1 | 1 |
| Heart | 1.67 | 561 | 3.3 | 20 | 2.00 | 93 | 1.2 | 6 | 28 | 33 | 3 | 0 |
| Spleen | 1.15 | 810 | 4.8 | 41 | 1.24 | 169 | 2.3 | 18 | 101 | 76 | 3 | 0 |
| Muscles | 1.26 | 140 | 0.8 | 6 | 0.98 | - | - | - | 10 | 29 | 1 | 4 |
| | counted 24 hrs. after injection | | | | counted 6 days after injection | | | | 4 days injection | | 5 days injection | |

The third series of experiments was conducted with 23 rats and 2 dogs by inhalation of sublethal $H_2S^{35}$ doses. Inhalation time, including the post-inhalation interval, ranged between 10 minutes and 2 hours. Blood samples were taken during inhalation to check on the presence of $H_2S^{35}$, none of it was detected in any of the blood samples.

Results of blood and organ tests for $S^{35}$ disclosed that following inhalation the specific activity intensity was reduced, especially in the blood and lungs and to a lesser degree in the liver and spleen, while it rose in the kidneys. Results of urine tests made 10 minutes following $H_2S^{35}$ inhalation in the gaseous form indicated that in the course of the first day after inhalation exposure more than 70% of the total S appeared in the urine in the form of inorganic sulfates. The rate of total S elimination *via* the urine in the course of the second day after inhalation exposure fell to considerably lower levels, with the percent of inorganic sulfates increasing. Results thus indicated that the predominant amount of oxidized $H_2S^{35}$ was eliminated *via* the urine in the course of the first two days.

The following was observed in dogs with exposed ureters after 20 minutes $H_2S^{35}$ inhalation: 5 to 10 minutes after beginning inhalation $S^{35}$ appeared in the urine, with maximum $S^{35}$ elimination recorded 2 - 3 hours later; after 8 - 10 hours the rate of $S^{35}$ elimination through the urine had considerably subsided. No $H_2S$ was detected in the urine; 30 minutes following the $H_2S^{35}$ inhalation inorganic sulfates constituted 70 - 90% of the total eliminated S.

Experiments of the fourth series were done with 15 rats kept in baths containing 100 - 200 mg/li of hydrogen sulfide at 36° for 10 minutes. Radioactive $H_2S^{35}$ was added at the rate of 1200 - 1600 γ, the radioactivity of which registered $3 \times 10^7$ to $6 \times 10^7$ imp/min. per 800 ml. Some rats received single treatments and some 4, 5 and 10 treatments. Animals were examined 10 and 30 minutes, and 24, 48 and 72 hours after bath treatment. Results of tests indicated that $H_2S^{35}$ became rapidly oxidized in the organism and that the products of its oxidation appeared in the urine mostly as inorganic sulfates and partly as S-esters. Data listed in Table 4 show that the sum of urine eliminated S compounds constituted 80% of the S contained in the urine. Most of the oxidation products of $H_2S^{35}$ were eliminated through the urine within 24 hours after the bath treatment, as in all cases of hydrogen sulfide administration by the other methods. No $S^{35}$ was found in any organ proteins of rats administered $H_2S^{35}$ by the bath submerging method. Therein lies the difference of $H_2S$ effect on the organism administered by the bath treatment as compared with the injection administration.

T A B L E 4.

Sulfur in urine of rats after hydrogen sulfide bath.

| Rat No. | Hours after bath | Activity | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | Imp/min. g of urine | Imp/min. in total S per ml of urine | Imp/min. in inorganic S per ml of urine | Percent of total sulfur | Imp/min. in S esters per ml of urine | Percent of total sulfur | Percent of neutral sulfur |
| 5 | 24 | 19,430 | 20,610 | 19,814 | 96 | 966 | 4.7 | - |
| 5 | 48 | 1,970 | 2,814 | 2,218 | 79 | 213 | 7.6 | 13.4 |
| 6 | 24 | 6,070 | 6,569 | 3,617 | 55.0 | 306 | 4.6 | 40.4 |
| 6 | 48 | 4,670 | 5,615 | 3,769 | 67.0 | 360 | 6.4 | 26.6 |
| 12 | 24 | 4,220 | 4,239 | 3,554 | 83.8 | 107 | 2.5 | 13.7 |
| 12 | 48 | 690 | 819 | 544 | 66.6 | 24 | 2.9 | 30.5 |

Conclusions.

1. $H_2S$ became rapidly oxidized and eliminated regardless of the method or route of its administration. No $H_2S$ was detected in the blood.

2. Products of $H_2S$ oxidation appeared in the blood, urine, and organs within 5 - 10 minutes after its administration. At that time 50% of the S appearing in the urine was of the inorganic sulfate and sulfur ester type; 30 minutes later the concentration of inorganic sulfates in the urine considerably increased.

3. Most of the products of $H_2S$ oxidation were eliminated by the organism within the first 24 hours. This was true of all methods of $H_2S$ administration.

4. $S^{35}$ appeared in organ proteins only in instances of massive intravenous, subcutaneous and inhalation administration. No $S^{35}$ was detected in the organ proteins following the bath-type of administration.

5. No positive evidence was elicited which might have indicated that S accumulated in the organism as the result of $H_2S$ or $Na_2S$ administration in any of the above described experiments.

## Benzene and Its Homologues as Poisons in Electrical Winding and Insulation Plants.

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The production of winding and insulation materials is an important function in plants of the electrical industry. Workers connected with the production of winding and insulation materials are constantly exposed to the effects of benzene, toluol, and xylol. In this connection, the prevailing significance of sanitary labor conditions has been investigated insufficiently.

The investigation conducted by the present author was directed into two channels: 1) a study of the sanitary-hygienic labor conditions, and 2) a study

of the workers' health. Production of insulation material such as micatape, synthetic tape, micanite, etc. and of different types of winding materials required the use of adhesive substances, coating lacquers, enamels and tars, which have to be mixed with or dissolved in benzene, toluol, xylol, white spirit and ethylol. Application of the lacquers is done by machine, the rollers of which are submerged in a small vat containing the above-mentioned treatment materials. Nevertheless, most steps performed in this industry are accomplished manually using a brush or similar means of application. Part of the treated tape and other materials are placed into special drying ovens; however, much of it is dried in the open air within the working premises. Many other operations, though partly mechanized, are performed manually in the open, so that vapors of the above-mentioned solvents and admixtures saturate the surrounding air. Such pollutants are removed by combined forced and exhaust ventilation systems installed in only part of the working premises. Many of the plants' departments have no ventilation facilities.

Inspection of the plant in 1953, prior to the initiation of this investigation, showed that benzene has been used as the solvent and in many cases also as the diluent, so that it constituted 30 - 85% of the material used in the plant. Benzene was also used in some of the washing operations. In 1953 - 1955 toluol replaced benzene in all except 2 departments, so that toluol instead of benzene constituted 30 - 85% of the solvents used. Toluol, xylol and white spirit were used most frequently in the washing department. Many workers preferred to use xylol. The use of lacquer has been stepped up considerably during the last few years. Thus, silico-organic lacquer, containing up to 85% of toluol, was used in 12 times as many operations in 1955 as in 1952. In the production of clear lacquer glyfuoro-oil lacquer was used mostly; it contained 55% toluol instead of the previously used benzene; the coating lacquers and gray enamel also contained 55% of toluol and xylol. Replacement of benzene by xylol, toluol and white spirit was adopted for the protection of working space air against pollution, without previous investigation or standardization, so that no information existed regarding prevailing concentrations of volatile ingredients in the surrounding air. Studies conducted in 1954 - 1955 showed that concentrations of benzene and its homologues in the air exceeded the limits of allowable concentration, as shown in Table 1.

Data in Table 1 show that in 1954 - 1955, when benzene was still predominantly in use, its concentration in the air exceeded the allowable 0.05

TABLE 1.

Content of benzene and its homologues toluol and xylol.

| Toxic substance | Number of analyses | Limits of concentration fluctuation in mg/li | Average concentration in mg/li | Number of analyses exceeding limits of allowable concentrations |
|---|---|---|---|---|
| Benzene | 170 | 0.002 - 0.5 | 0.15 | 121 (71.1%) |
| Toluol | 110 | 0.01 - 2.5 | 0.32 | 62 (55.9%) |
| Xylol | 256 | 0.03 - 2.0 | 0.17 | 108 (42%) |
| Total | 536 | | | 291 (54.1%) |

mg/li limit in 75% of the tests. Toluol concentration exceeded the official limit in 50% of the tests, and xylol exceeded the limit of 0.1 mg/li in 40% of the tests. The most unpleasant operation with regard to benzene air pollution was the manual brush application of gray enamel to pole coils, placing the micanite into the drying ovens, and application of adhesive micanite. Average toluol concentrations in the air were 2.5 - 4.0 times as high as average benzene concentrations at points where these production functions were performed. Concentrations of xylol in the washing processes ranged between 0.05 - 2.6 mg/li, with an average of 0.41 mg/li. Finishing of coil ends by the brush method and the newly introduced process of insulation removing were not accompanied by xylol evaporation; therefore, no such vapor was found in the air of premises where these and similar operations were performed. Generally, the concentration of benzene and its homologue vapors in the air depended upon their content in the lacquer, the air temperature and the exhaust ventilation operation.

The volume of work in the plant has considerably increased of late without introducing additional health protecting measures. As a consequence, concentrations of benzene and of its replacing homologues, toluol and xylol, were high. Above described labor conditions were the cause of many chronic benzene and its homologues intoxications among workers, symptoms of which were leukopenia, thrombopenia, anemia, nose and gum bleeding, in women excessive menstruation, neurotic syndromes accompanied by vegetative dysfunction on the basis of asthenia, etc. In workers who continued their occupation despite the above symptoms, the gravity of benzene intoxication progressed to a point where they had to be assigned to different jobs. Even then the toxic effects persisted for a long time. Most clear-cut forms of

intoxication arising in a comparatively short work period as 2 years were observed among women working at the preparation of the insulation tape, the lacquer, and those performing the washing function. In studying the general rate of morbidity and loss of work capacity and work days during 1952 - 1954 it was noted that more than 50% of the women workers of the department studied manifested symptoms of a variety of illnesses. This was particularly true of women with long work records. An attempt was made to establish the role played by benzene and its homologues in the so-called "non-occupational morbidity" among women employed in the winding-insulation department. For this purpose a control group was selected from among women workers of the winding-insulation department who showed no signs of intoxication. Rate of "non-occupational morbidity" of this group was investigated on a parallel basis with "non-occupational morbidity" rate among a group of women working in the same department who manifested symptoms of intoxication. Age and work records of the non-toxic controls and the toxic group were nearly the same. Each group consisted of 86 women workers. Results of the investigation are shown in Table 2. Data in Table 2 show that the so-called "non-occupational morbidity" among the women of the toxic group was 1.5 times as high as in the control group. A study of 28 types of "non-occupational" illnesses indicated that 19 occurred in the toxic group at greater frequency than among the women of the control group who had no intoxication symptoms. The greater part of

TABLE 2.

Comparative data on total morbidity among workers suffering of intoxication with benzene and its homologues and among the control group during 1953-1954. (Data represent absolute numbers among 84 workers in each group).

| Group of women | Morbidity indexes of all diseases, occupational intoxication excepted | | | Morbidity indexes of chronic benzene intoxication and of toxic vegetative polyneuritis | | | Total morbidity | | |
|---|---|---|---|---|---|---|---|---|---|
| | Number of sick women | Number of sick instances | Work days lost due to sickness | Number of sick women | Number of sick instances | Work days lost due to sickness | Number of sick women | Number of sick instances | Work days lost due to sickness |
| Women with clear-cut benzene intoxication, or with symptoms suspicious of same | 81 (116.0) | 396 (157.0) | 3,190 (155.0) | 58 | 188 | 3,144 | 88 (118.5) | 584 (232.0) | 6,331 (309.0) |
| Control group | 70 (100.0) | 252 (100.0) | 2,052 (100.0) | - | - | - | 70 (100.0) | 252 (100.0) | 2,052 (100.0) |

Data in parenthesis are in relation to control group assigned the value of 100.

the increased morbidity indexes in the toxic group as compared with the control group were of "non-benzene etiology". Thus, morbidity indexes on days when women of the toxic group felt incapable of working exceeded similar indexes of the control group as shown below:

Grippe..... 4 times as high
Acute catarrh of upper respiratory tract..... 3 times as high
Cardiac muscle disease..... 2.8 times as high
Radiculitis..... 2.7 times as high
Purulent skin diseases..... 2.0 times as high

A considerable number of women with intoxication symptoms were sick up to 18 times in 2 years. Forty women of the toxic group were sick more than 4 times as compared with 17 women of the control group, i.e., 2.4 as many. Thus, results of the investigation indicated that women workers employed in the department under study had typical benzene and its homologues intoxication symptoms and in addition had so-called "non-occupational" diseases of sufficient severity to cause their abstention from work for reasons of work incapacity.

Conclusions.

1. The air of winding and insulation departments of the plant investigated contained benzene and its homologues in concentrations exceeding the allowable limits. In percent of samples investigated the results were as follows: benzene in 71.1%, toluol in 55.9% and xylol in 42%.

2. Most unfavorable operations from the viewpoint of benzene and homologues evaporation were: application of adhesives to micanite on tables manually and their loading into the drying ovens; insulation and lacquering of windings; brush coating of pole coils; and finally, washing and cleaning various finished products.

3. Unsatisfactory labor conditions produced occupational poisoning with aromatic hydrocarbons among the women workers, with symptoms of typical blood picture changes and nervous system disturbances.

4. Continuous and systematic exposure to benzene and its homologues appeared to have created a state of susceptibility on the part of the organism to some common "non-occupational" diseases, as was shown by increase in the morbidity of such diseases in women with toxic symptoms as compared with the control women.

5. Most effective means of health condition improvement are the following: a) replacing toluol and xylol by less toxic solvents; b) hygienic standardization of lacquer, solvent and diluent composition; mechanization to the highest possible degree of now prevailing manual operations, and hermetization of operations which eliminated deleterious vapors.

Installation of effectively operating mechanical ventilation, improvement and insulation of steam pipes, drying chambers and systematic check of compliance with all sanitary-hygienic regulations.

## Hygienic Evaluation of Hydrogenated Coal Gasoline.

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Gigiena Truda i Professional'nye Zabolevaniya, Vol. 1, No. 2, 34-37, 1957.

Gasoline obtained by hydrogenation of Cheremkhovsk coal is a transparent liquid of sp. gr. 0.7288. It begins to boil at 44°, 10% is distilled off at 75° and 90% at 155°; its maximum boiling point is 182°. Its composition includes the following in percent by weight: unsaturated hydrocarbons 0.3; aromatic hydrocarbons 2.2; naphthenes 59.2; and paraffins 38.3; it evaporates 103 times slower than ethyl ether and 10 times slower than "Galosha" petroleum gasoline. The toxic properties of the gasoline were tested on white mice, white rats and rabbits. For purposes of comparison, parallel experiments were performed with "Galosha" petroleum gasoline, the toxicity of which has been studied by N. V. Lazarev, E. N. Levina, Ye. I. Lyublina, I. S. Tsitovich, G. I. Tsobkallo, and others.

Resorptive properties of the gasoline vapor were tested by 2-hour exposure of white mice in a sealed exposure chamber. Each concentration (with intervals of 10 mg/li) was tested on 10 animals. The gasoline vapor concentration in the chamber was produced and maintained as per calculations. In

view of the fact that the volatility of the gasoline obtained by coal hydrogenation was lower than that of gasoline "Galosha", its calculated concentration was checked by chemical analyses.

Results of the experiments showed that hydrogenated coal gasoline had a higher resorptive rate than gasoline "Galosha". Thus, the minimum concentration causing lateral decubitus in white mice was 24.5 mg/li for the hydrogenated coal gasoline, as determined chemically, and 30 mg/li for gasoline "Galosha". Minimum lethal concentration was 21.8 mg/li for the hydrogenated coal gasoline and 60 mg/li for gasoline "Galosha". Absolute lethal concentration was 100 mg/li for gasoline "Galosha"; it could not be determined for hydrogenated coal gasoline since maximum air saturation with vapor of this gasoline amounted to 44.51 mg/li. Maximum number of dead mice at this concentration did not exceed 70%. The resorptive power of the hydrogenated coal gasoline vapor was closer to gasoline "Gudri" obtained by catalytic cracking; according to E. N. Levina's 1952 findings, the narcotic concentration of the latter was 16 mg/li and the lethal concentration 30 mg/li.

The clinical picture of acute poisoning of animals by the vapor of the gasoline under study was different. Animals poisoned with gasoline "Galosha" manifested excitation, and death usually occurred suddenly during the excitation period, accompanied by severe tetanic spasms of the extremities and of the occipital muscles. On the other hand, exposure to hydrogenated coal gasoline rendered animals relatively immobile, they sat quietly and huddled together. Narcosis set in while the animals were in this state. The animals usually died lying in a lateral position, in a few isolated instances death occurred before the state of narcosis set in.

Hydrogenated coal gasoline evaporated more slowly and the concentration of its vapor in the exposure chamber rose gradually, which was reflected in a delayed onset of the toxic condition. For example, animals exposed to the action of gasoline "Galosha" began to show evidence of narcosis within an average of 45 minutes, whereas animals exposed to the hydrogenated coal gasoline began to manifest narcotic effect within 75 minutes. The narcotic effect of gasoline "Galosha" lasted an average of 43.7 minutes, while the narcotic effect of the hydrogenated coal gasoline lasted on the average 87 minutes. Mice exposed to the action of gasoline "Galosha" died on the average after 55 minutes, while animals exposed to the hydrogenated gasoline died on the average after 89 minutes. The slower onset of narcosis,

the more persistent the narcotic state, and the difference in time of death could be explained not only by the slow saturation of the animals' blood with the hydrogenated coal gasoline and its delayed elimination from the organism, but also by the chemical nature of the component parts of this gasoline.

The threshold concentration of gasoline effect on the central nervous system was established in white rats by the conditioned reflex method. Experiments were performed on animals with well-fixed conditioned reflexes to visual and auditory stimuli accompanied by food reinforcement. Chamber gasoline vapor concentrations were first calculated and in the case of the hydrogenated coal gasoline the concentration was checked chemically. Tests with the gasoline were performed with each rat individually 2 - 3 times a week to check their original neuro-pattern. Each test lasted 55 minutes. The effects of individual concentrations were checked 2 - 3 times on the same animals. Nine animals were used in the investigation, and 75 experiments were performed with each of the tested gasolines. Data obtained with the animals preliminarily to the actual testing and data obtained during actual testing prior to exposure to the gasoline were used for control purposes. Results of numerous control experiments showed that the latent period of response ranged between 0.4 and 0.6 seconds, with an average of 0.5 seconds, while reaction time from beginning of the motor reaction to the time of the animal's running to the feed box averaged 0.9 seconds.

Results of the experiments showed that hydrogenated coal gasoline vapor in 0.2 mg/li concentration had no disturbing effect on the conditioned reflexes of the animals. In 0.4 mg/li concentration the gasoline brought about a lengthening of the reaction time, especially at the end of the test period from 0.7 to 1.5 seconds; in 4 of the 60 cases or 6.6% the differential inhibition reflex response to the buzzer sound was disturbed, indicating an impairment in the cerebral cortex function of these animals. An increase in the gasoline concentration to 0.75 mg/li caused a lengthening of the reaction time from 0.7 to 1.1 seconds, and in 8 cases (13.3%) differentiation inhibition was disturbed. A 2.62 mg/li concentration caused impairment of differentiation inhibition in 33 cases (55%). Collapse of positive conditioned reflexes was not observed. The hydrogenated coal gasoline left no after-effects, upon exposure to a concentration of 8 mg/li, the conditioned reflexes returned to normal the following day. Accordingly, the threshold concentration effect on the central nervous system in the animals ranged between 0.4 - 0.75 mg/li.

Experiments with gasoline "Galosha" showed that its threshold concentration ranged between 0.1 - 1.0 mg/li.

One hundred and eight persons participated in the determination of the character and intensity of the odor of the gasoline. Test subjects were mostly healthy persons 18 to 20 years old. In the determination of the odor intensity of the hydrogenated coal gasoline, 27% of the tested persons stated that the gasoline possessed a weak odor, 26% characterized it as moderate, and 47% as strong; 50% of the test subjects identified the odor of the gasoline as such, and 50% as the odor of kerosene. Gasoline "Galosha" was evaluated differently: 5.7% of the subjects evaluated its odor as weak, 59.7% as moderate, and 34.8% as strong. The character of the odor was identified by 92.3% of the test subjects as gasoline and 7.7% as the odor of kerosene. Consequently, the odor of hydrogenated coal gasoline, as compared with that of gasoline "Galosha", was predominantly similar to that of kerosene. It would appear from this that the odor of hydrogenated coal gasoline could not cause any unpleasant odor sensations even under industrial working conditions.

The irritating action of gasoline on intact skin was tested on the tails of white mice and rabbits' ear pinnae. Results of experiments with the tails of white mice (64 animals) showed that hydrogenated coal gasoline caused less pronounced local reactions than did gasoline "Galosha". Thus, 30-minute application of hydrogenated coal gasoline gave rise to an appreciable dilatation of the caudal vessels, which returned to normal within 24 hours except for slight residual exfoliation; gasoline "Galosha" in similar experiments gave rise to marked dilatation of the vessels of the entire tail and in 24 hours to caudal edema and exfoliation. A similar picture of tail inflammation was produced in 100% of the animals after a 60-minute exposure.

Results of experiments with rabbits' ear pinnae showed that 30-minute application of hydrogenated coal gasoline gave rise to a severe inflammatory reaction in the ear in every case. A $1.8^{\circ}$ temperature rise and a 33% swelling appeared at the end of 24 hours. The inside surface of the external ear revealed fissures and small purulent ulcers. Seven days later the size of the external ear began to normalize but alopecia began to develop. Not until the 12th day did the external ear return to its original size, and by the 18th day the fur began to regenerate. With similar exposure, gasoline "Galosha" gave rise to a marked hyperemia of the entire ear lobe and a 15% increase in its size; by the 4th day it returned to normal. No sheeding of fur was noted.

The effect of the gasoline on human skin was tested on 60 males and 15 females 19 to 33 years of age; all had voluntarily expressed their desire to participate in the experiments. Skin tests were made by the so-called "compress" method. Pieces of gauze measuring 10 x 10 mm, folded into 4 layers, were soaked in gasoline and applied to the external aspect of the forearm, covered with wax paper, held in place with a bandage, and left thus for 24 hours. Results showed that hydrogenated coal gasoline produced more marked local effects than gasoline "Galosha". When the hydrogenated coal gasoline tests had been applied to the skin for 24 hours, a positive reaction was observed in 10 of 15 women and in 9 of 60 men; after 48 hours in 14 females and 21 males; and after 72 hours in 12 females and 21 males. The positive reaction appeared in the form of erythemas, edemas, and the presence of vesicular papules. Gasoline "Galosha" produced considerably less pronounced reactions. At the site of application only a slight erythema remained in 5 females and 2 males.

Conclusions.

1. Hydrogenated coal gasoline is of relatively low volatility and of broad fraction composition, with a predominance of naphthene hydrocarbons.

2. In its resportive action hydrogenated coal benzine proved more toxic than gasoline "Galosha" of petroleum origin; its toxicity was similar to the "Gudri" brand of petroleum gasoline.

3. The threshold concentration of hydrogenated coal gasoline gave rise to functional impairment of the central nervous system in white rats similar to that of gasoline "Galosha".

4. The local action of hydrogenated coal gasoline on intact rabbit and human skin was greater than that of gasoline "Galosha".

5. Hydrogenated coal gasoline possessed physico-chemical properties useful to industrial exploitation on par with petroleum gasoline.

6. The adopted maximum permissible concentrations of petroleum gasoline in air of working quarters must also be extended to hydrogenated coal gasoline (N 101-54).

7. Existing sanitary-hygienic regulations applicable to work with petroleum gasoline must extend over work with hydrogenated coal gasoline.

Olfactory and Taste Analyzer Changes in Chronic Carbon Disulfide Intoxication.

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Gigiena Truda i Professional'nye Zabolevaniya, Vol. 1, No. 3, 44-48, 1957.

The toxicity of carbon disulfide as an occupational poison has been known since its introduction into the manufacture of artificial fibers, the rubber industry, and many other industries. A review of the extensive literature on carbon disulfide intoxication indicated that its effect was principally on the nervous system. Lately some investigators attempted to explain the toxic action of carbon disulfide by neuro-vascular changes, with selective blocking of certain zones of the central and peripheral nervous systems. According to U.S.S.R. literature carbon disulfide poisoning presented a clinical picture of mild chronic forms of intoxication, in which functional disturbances of the nervous system predominated. Pathomorphological findings obtained under chronic experimental conditions confirmed the fact that carbon disulfide brought about diffuse changes in the central nervous system.

The purpose of this investigation was to study changes in the olfactory and taste analyzers as indexes of the functional condition of the central nervous system in chronic carbon disulfide poisoning. A thorough study of cortical changes was made through an investigation of the organism's conditioned reflex activity. Reports of such an investigation will be presented at some future time.

The method. The olfactory analyzer was studied by the Elsberg-Levi method, using rosemary, thymol, tar and camphor as olfactory stimuli and 3 to 10 ml as the normal threshold of olfactory sensitivity to all 4 substances. In cases in which the threshold of olfactory senstivity could not be determined, test persons were offered a choice of odor-emanating substances, among which were purely olfactory odors and some which gave rise to trigeminal stimulation. If no odor was perceived from the flask upon active inhalation, it was considered that the subject was anosmic.

Taste sensitivity was determined by the drop stimulation method. In accordance with the topography of the taste zones, drops of different strengths of hydrochloric acid, salt, quinine chloride and refined sugar solutions were placed on the tongue. Normal taste sensitivity was finally recorded as follows: sweet, 0.25 - 1%; sour and salty, 0.13 - 1%; bitter, 0.00025 - 0.003%.

This report deals with data obtained under field conditions in mass surveys of working personnel in 2 plants, and also with a dynamic investigation of patients under treatment or observation of Dr. M. A. Kazakevich in the Institute's clinic for chronic carbon disulfide intoxication. Otorhinolaryngological examinations were made by Dr. L. A. Kozlov. Persons who had inflammation of the nasal accessory sinuses, hypertrophic rhinitis, deviated nasal septi were not included in the statistical evaluation. The 108 workers studied under industrial conditions consisted largely of women spinners from 20 to 30 years of age. Neurological examination revealed that some workers had incipient and pronounced symptoms of chronic carbon disulfide intoxication. A correlative study of results of all examinations indicated that symptoms of chronic carbon disulfide intoxication were accompanied by lowered taste sensitivity to bitter and sweet stimuli and by a lowered olfactory sensitivity to the 4 odor-emanating substances used as stimulating agents.

Curves in Fig. 1 show the condition of the thresholds of olfactory (A) and taste (B) sensitivity in examined healthy workers (I) and persons with chronic $CS_2$ intoxication (II - III). It was noted that among the practically healthy workers there were many with relatively low rosemary odor perception thresholds. Among workers who were under identical industrial conditions but did not have contact with carbon disulfide, the thresholds of olfactory and taste perception were within normal limits. More pronounced changes in the state of the olfactory and taste analyzers were observed among patients under clinical observation for chronic $CS_2$ intoxication. Most of these were women spinners

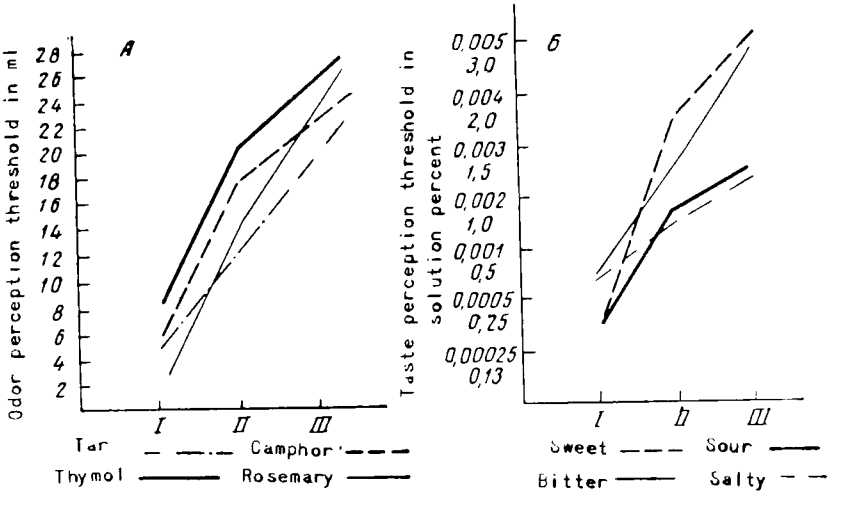


Figure 1.

and washers from 20 to 55 years of age. Fifty-five percent of the patients exhibited olfactory damage in the form of pronounced hyposmia, and 20% in the form of total anosmia. Lowered taste perception was noted with respect to all stimuli used, especially to sweetness (in 50%) and to bitterness (in 30%). (Fig. 1, II).

A comparison of threshold values for olfactory and gustatory perception with the severity of chronic carbon disulfide intoxication disclosed a correlation between the gravity of intoxication and the rise in odor and taste perception threshold. However, no correlation was noted between the change in odor and taste perception acuity and the work duration record.

Dynamic observation of the state of olfactory and taste analyzers in hospital patients was performed in the course of complete clinical and eserine therapy. Despite improvement in the patients' general condition under complex therapy, consisting essentially of intravenous glucose administration, use of vitamins, brewer's yeast, hydrotherapy, no sensitivity restoration was observed in cases of anosmia and hyposmia. Complex treatment effected a lowering of the olfactory and taste sensitivity in patients whose perception thresholds rose only slightly. Best effect was obtained by eserine therapy, which restored the olfactory function in anosmia and completely normalized olfactory sensitivity. A lasting improvement in olfactory sensitivity was noted after 9 - 10 eserine injections. Two to 3 weeks after eserine therapy, and in some cases after 3 and 9 months, olfactory sensitivity was still within normal limits. Parallel studies of taste sensitivity in patients who were under eserine therapy showed the same trend, but restoration of taste sensitivity was less pronounced.

Records were made of the status of olfactory and taste sensitivity in patients receiving single eserine injections in doses of 0.4 - 0.5 ml (1:1000). In contrast to effects of repeated eserine therapy, single eserine injections had no beneficial effect on the manifestations of anosmia. Favorable eserine effect was noted only in hyposmia, and the maximum lowering of the thresholds for all the olfactory stimuli was observed 60 - 70 minutes after eserine injection. However, after 3 - 4 hours the initial threshold perception returned. Determinations of threshold perceptions of taste sensitivity after a single eserine injection revealed no regularity.

To clarify specificity of eserine action in restoring olfactory sensitivity, a study was made of the results of oral administration of caffeine in doses of 0.03 - 0.9 ml, since the latter induced increased excitability of the

cortical cells. Experiments with caffeine were performed before eserine therapy was initiated, with single eserine injection, and in the course of eserine therapy. Like the single eserine injection, caffeine had no effect in anosmia. In the case of hyposmia, caffeine lowered the thresholds of olfactory sensitivity, but by comparison with eserine this lowering was less effective, both as to the degree of threshold lowering and as to the duration of the effect. The greatest lowering was observed after 40 - 50 minutes, and the time of return to initial sensitivity was 1 - 1.5 hours (Fig. 2). Results of caffeine use with a background of eserine therapy, i.e., when the patient took caffeine 5 - 10 minutes after the eserine injection, indicated that this combination brought about a more marked restoration of the olfactory function than did caffeine alone or a single eserine injection. Changes observed in differences of caffeine and eserine effects given as a single dose or as a course of therapy, and changes noted in the course of combined therapy, indicated that eserine apparently played a therapeutic role in the restoration of olfactory sensitivity.

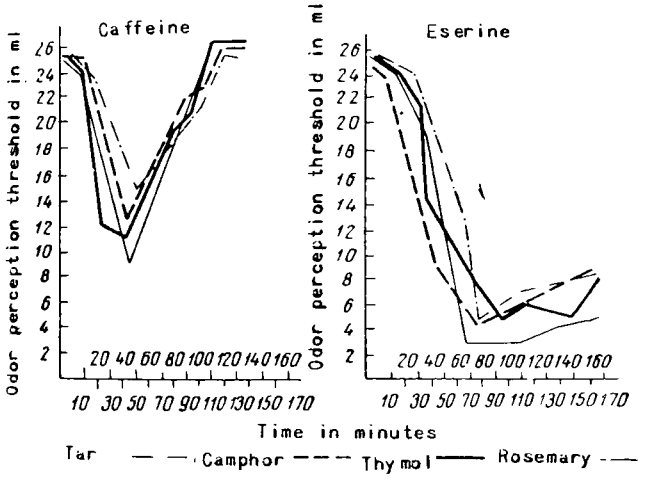


Figure 2.

A review of the literature on the specific anticholinesterase activity of eserine and its stimulating effect on the synaptic apparatus gave rise to the assumption that hyposmia and anosmia resulting from chronic carbon disulfide intoxication were largely connected with the impairment of nerve excitation transmission in the synaptic apparatuses of the olfactory analyzer. The favorable effect of caffeine discovered by this writer apparently was connected with the fact that functional changes which occurred during $CS_2$ poisoning in the cortical part of the analyzer played a part in the lowering of the olfactory analyzer activity. Evidence of the existence of changes in the cortex was obtained through investigations of cortical dynamics by studying the blinking and vascular conditioned reflexes. In agreement with the findings of A. A. Model and L. P. Chepka, results of the present investigation showed that chronic carbon disulfide intoxication was accompanied by changes in cortical activity, which were also reflected as changes in the functional

state of the cortical part of the olfactory and other analyzers. This was in agreement with previous findings of A. A. Model and L. P. Chepka.

## Conclusions.

1. Effect of carbon disulfide vapor on the human organism was accompanied by functional changes in the olfactory and taste analyzers. Changes in the olfactory analzyer appeared in the form of 2 phases: a) a lowering of rosemary odor threshold perception in the absence of clinical symptoms of intoxication; b) a rise in the odor intensity thresholds for all the odor-emanating substances in the clinical study of chronic carbon disulfide intoxication.

Changes in the taste analyzer were noted in chronic carbon disulfide intoxication, which appeared as lowered sensitivity, largely with respect to sweet and bitter stimuli.

2. Anosmia caused by the action of carbon disulfide on the organism was reversible.

3. Restoration of olfactory sensitivity during eserine and caffeine treatment offered a basis for the assumption that the mechanism of olfactory function disturbance was connected with functional changes originating in the synaptic apparatuses of the olfactory analyzer and also in its cortical section.

4. Results of analyzer studies together with clinical findings, may be used as an early diagnosis of chronic carbon disulfide intoxication.

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# Effect of Benzanthrone Poisoning on Liver Function.

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(From the Ukrainian Central Scientific-Research Institute of Labor Hygiene and Occupational Diseases).

Gigiena Truda i Professional'nye Zabolevaniya, Vol. 1, No. 4, 40-46, 1957.

The textile industry has recently presented the chemical industry with a request to increase variety of dyestuffs. This increase referred largely to light and fast vat dyes, among which the benzanthrone derivatives stood out prominently. For this reason benzanthrone production has been rising steadily. Production of benzanthrone, originally regarded as a relatively non-toxic substance, was first started in one of the chemical plants in 1950. It was found soon that benzanthrone possessed strongly toxic properties, giving rise to a peculiar and complex picture of intoxication in workers employed in the dye industry. This led to a study of the occupational toxicological effect of benzanthrone. The work was initiated by the Ukrainian Central Scientific-Research Institute for Labor Hygiene and Occupational Diseases (V. G. Piskunova and co-workers). The clinical picture of occupational benzanthrone intoxication was described with particular reference to symptoms indicative of liver function disturbances.

A combination of methods was used in the study of the liver function, including an investigation of liver detoxification function, its participation in carbohydrate, protein and pigment metabolism, and in the formation of the colloidal-chemical properties of blood. Under investigation were 53 persons diagnosed as having benzanthrone intoxication. The subjects included 43 males and 10 females, among whom there were machine operators and their helpers, mechanics, electricians, workers in the shop laboratory, auxiliary workers, and engineering-technical personnel. On the basis of employment duration the patients were grouped as follows: up to 1 year, 4 persons; 1 to 2 years, 3 persons; up to 3 years, 43 persons; more than 3 years, 3 persons. Clinical symptoms of liver changes, such as enlargement of the liver, tenderness on palpation, intolerance of fatty food, pain in the right hypochondrium, were noted in 29 of the 53 individuals. Persons with benzanthrone intoxication were divided into 3 groups according to V. G. Piskunova:

1. In the first group were placed persons with pronounced clinical pictures of intoxication based on characteristic pigmentation and trophic changes

of the skin, anorexia, emaciation, muscular weakness, enlargement and tenderness of the liver, pain in the right hypochondrium; this group included 21 persons.

2. The second group included persons with symptoms of early intoxication, such as complaints of general weakness, loss of appetite, emaciation, pain in the right hypochondrium, burning of normally exposed skin, especially in sunlight, but without changes in skin coloring; this group consisted of 21 persons.

3. The third group included persons with residual manifestations from previous intoxications; this group consisted of 18 persons. [1]

Factual data obtained in this investigation of benzanthrone poisoning effect on different phases of liver function revealed many pathological deviations from the normal indexes, the frequency with which such shifts occurred and the gravity of the clinical symptomatology. An attempt was also made to establish a correlation between shifts in liver function indexes and the nature of morphologic changes.

In this study the Quick test was regarded as positive when the excretion of hippuric acid, calculated as sodium benzoate, was less than 0.75 g. The following were regarded as pathological blood sugar curves: curves of the "diabetic" type, depressed curves, and curves with an initial hypoglycemic level. A total blood serum protein concentration less than 6.5% was regarded as hypoproteinemia, and an albumin/globulin ratio of less than 1.2 was regarded as pathological. 0.70 - 1.25 g% was set as the limit of normal γ-globulin content of blood serum and 0.35 - 1.0 mg% was taken as the normal limit for bilirubin. The above-indicated values were taken after a study of pertinent data in the literature. Thymol turbidity tests were negative in all 28 cases tested. The cadmium test manifested low sensitivity in this form of pathology. Hence, no further mention will be made of these tests.

Patients were re-examined at intervals of 1 to 11-1/2 months. The entire complex of the liver function tests was performed only on some of the patients. Of those fully tested only 2 cases (patients G-ov and K-ko) were free from indications of liver function pathology; both were in the initial stage of benzanthrone intoxication. In all other cases, functional involvement of the liver manifested itself in one form or another. The number of pathological

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[1] Upon re-examination some of the patients were assigned to different groups which caused them to be mentioned twice.

shifts in liver function values was as high as 5, or 6 in some cases (Sh-va, Ch, Sh-ko and S-ov). Benzanthrone intoxication was accompanied by different disturbances in the functional state of the liver. Results of individual functional tests showed discrepancies in some cases; N. D. Strazhesko insisted that this indicated the need for performing the entire battery of liver function tests on all cases. Nevertheless, it can be said that benzanthrone poisoning was commonly accompanied by a disturbance of the liver function, as shown by the cephalin-cholesterol emulsion test (in 48 of 59 subjects) and protein synthesis function. Disturbances in the latter were of a peculiar character: they appeared in the form of hypoproteinemia (in 50 of 63 subjects), frequently of considerable gravity (below 5.5 g%). In some liver diseases hypoproteinemia was accompanied by lowered albumin/globulin ratio; in benzanthrone intoxication the A/G ratio was below normal in less than 50% of the cases (15 of 32). This fact was apparently related to another characteristic of liver function pathology in benzanthrone intoxication, namely, the tendency toward a lowered concentration of serum γ-globulin. Hyper-γ-globulinemia, usually described in liver diseases, was found in only 14 of 68 determinations. Aside from this, the serum γ-globulin level approached the lower normal limit in 17 patients, and in 26 cases it fell to less than 0.70 g%. Disturbances in the carbohydrate function of the liver were less common and appeared in the form of pathological blood sugar curves ("diabetic" curves, "depressed" curves, initially hypoglycemic curves) in 42 of 74 tests. Disturbances in the detoxifying liver function (hippuric acid synthesis calculated as sodium benzoate) appeared in 30 of 74 tests. Of striking interest was the absence of hyperbilirubinemia in benzanthrone poisoning, although it often accompanied other forms of toxic-chemical liver damage (B. Ya. Agranovich). In 11 of 20 determinations, the bilirubin content was below the control level (0.13 - 0.09 mg%).

The thymol turbidity test was regularly negative, which further differentiated benzanthrone intoxication from other forms of liver poisoning, such as $CCl_4$, trinitrotoluene. The tests failed to discern any correlation between intensity of functional liver impairment and the presence or absence of clinical symptoms indicative of liver pathology. Extensive functional impairment according to certain tests, was noted in cases which showed no clinical symptoms of liver damage, e.g., a reduction of the hippuric acid excretion to 0.35 g in patient V-uk. There were also cases with an inverse relationship.

Generally, the sensitivity of the battery of functional liver tests was considerably higher in benzanthrone intoxication than were clinical observations. Therefore, a correct evaluation of the state of health of persons working with benzanthrone should be made with liver function tests.

Functional liver damage has been encountered so often and with manifestations so serious that it can scarcely be regarded as secondary to the intoxication. It undoubtedly plays a definite role in the pathogenesis of intoxication as such. The nature and extent of shifts in liver functional indexes reflect the stage and gravity of the organism's intoxication. The stage of pronounced intoxication is characterized by a very deep suppression in the liver detoxifying function (in 5 studies the hippuric acid excretion was less than 0.40 g), frequent impairment of the carbohydrate function, and frequent hypoproteinemia. In the initial stage, the cephalin-cholesterol flocculation test was strongly (+++) positive, and this, together with the less common disturbances of the glycemic curve, distinguished this stage from the subsequent stages. In the stage of residual manifestations, lowered hippuric acid excretion was encountered more rarely than in the first 2 stages, and in only one case was the excretion less than 0.60 g; in all other cases, the lowering of the excretion rate was slight.

It must be assumed that changes in the functional state of the liver were among the factors responsible for the cyclic course of the intoxication process. It is possible that the transition from the initial stage to the pronounced stage, the chief manifestation of which was melanin hyperpigmentation of the cutaneous integument, was the result of liver function worsening. As is generally known, functional insufficiency of the liver (estrogen detoxification) was connected with melanin hyperpigmentation observed in hepatic cirrhosis (Whitlock). It is possible that disappearance of pathologic pigmentation was connected with a normalization of liver detoxifying function observed in the stage of residual manifestations. It should be noted that in spite of this normalization, the stage of residual manifestations retained profound disturbances, such as pronounced hypoproteinemia, strongly positive cephalin-cholesterol flocculation test, pathologic glycemic curves. Despite the general improvement of the patient's subjective and objective stages, this condition must be evaluated as a stage in which serious pathology persisted. Thus, re-examination of persons with intoxication in this phase revealed progressive hypoproteinemia. The findings show that in the treatment of patients

in different stages of benzanthrone intoxication it is necessary to apply measures directed to an improvement of liver function. On the clinical side of benzanthrone intoxication, emphasis should be placed on symptoms indicating functional impairment of the vegetative nervous system. In order to clarify the possible connection between these disorders and the above-described disorders of liver function, or the role of innervation disturbances, studies were conducted in which liver functional tests were used against the background of the pharmacological action of drugs on the vegetative nervous system (its parasympathetic region).

TABLE 1.

| Name abbreviated | g of hippuric acid excretion: Control tests | After carbocholine administration | Difference in g |
|---|---|---|---|
| Б-ий | 0.37 | 0.63 | +0.26 |
| В-ук | 0.35 | 0.78 | +0.46 |
| В-ка | 1.10 | 0.90 | -0.20 |
| Г-ко | 0.95 | 1.10 | +0.15 |
| Г-ин | 1.02 | 1.02 | - |
| Г-ов | 0.97 | 1.12 | +0.15 |
| Г-ко | 0.52 | 0.57 | +0.05 |
| Д-ин | 0.61 | 1.11 | +0.50 |
| К-ко | 0.84 | 0.98 | +0.14 |
| К-ий | 0.94 | 1.28 | +0.34 |
| К-ко | 0.73 | 0.93 | +0.20 |
| К-ун | 0.68 | 1.18 | +0.50 |
| Л-ко | 0.68 | 0.76 | +0.08 |
| М-ов | 1.20 | 1.19 | -0.01 |
| М-ая | 0.70 | 1.08 | +0.38 |
| О-ко | 0.95 | 1.25 | +0.30 |
| П-ев | 0.99 | 1.09 | +0.10 |
| Р-ив | 0.98 | 1.17 | +0.19 |
| Р-ой | 0.74 | 0.91 | +0.17 |
| Р-ва | 1.01 | 1.06 | +0.05 |
| С-ва | 0.29 | 0.36 | +0.07 |
| С-ов | 0.74 | 0.82 | +0.08 |
| С-ин | 1.08 | 1.22 | +0.14 |
| С-ов | 0.40 | 0.52 | +0.12 |
| Т-ко | 0.86 | 1.00 | +0.14 |
| Ч-ий | 1.00 | 1.77 | +0.77 |
| Ш-ак | 0.77 | 0.78 | +0.01 |

These studies, made with the background of the action of the vagomimetic drug carbocholine (a single administration of a therapeutic dose, 1 ml of an 0.01% solution subcutaneously) showed that under the influence of excitation of the vagus nerve, hippuric acid synthesis regularly increased, and in 8 cases returned to normal. The most noted increase in hippuric acid synthesis appeared in the initial stage of intoxication (0.30 g, on the average), in the manifest stage of intoxication, 0.15 g, and in intoxication in the stage of residual phenomena, 0.08 g. Administration of carbocholine gave rise to an elevation of the total protein content of the blood serum (Table 2) and albumins just as regularly (in 9 of 10 cases).

TABLE 2.

| Name abbreviated | g% of total serum protein: Control tests | After carbocholine administration | Difference in percent |
|---|---|---|---|
| К-ун | 5.34 | 5.46 | +0.12 |
| К-ко | 5.98 | 5.46 | -0.52 |
| Л-ко | 5.38 | 5.80 | +0.42 |
| О-ко | 5.84 | 6.44 | +0.60 |
| П-ев | 6.60 | 6.80 | +0.20 |
| Р-ив | 6.80 | 6.94 | +0.14 |
| С-ин | 6.26 | 7.54 | +1.28 |
| С-ов | 6.74 | 6.62 | -0.12 |
| С-ов | 6.42 | 6.78 | +0.36 |
| Т-ко | 5.66 | 6.20 | +0.54 |
| Ч-ий | 6.56 | 7.80 | +1.24 |
| Ш-ак | 5.58 | 5.60 | +0.02 |

TABLE 3.

| Name abbreviated | g of hippuric acid excretion: Control tests | After atropine administration | Difference in g |
|---|---|---|---|
| А-ев | 1.07 | 0.65 | -0.42 |
| Б-им | 1.42 | 0.85 | -0.57 |
| Б-ук | 0.98 | 0.70 | -0.28 |
| Г-ко | 0.53 | 0.43 | -0.10 |
| Г-ко | 1.15 | 0.65 | -0.50 |
| Е-ко | 0.70 | 0.75 | +0.05 |
| М-ко | 1.20 | 1.14 | -0.06 |
| М-ая | 0.97 | 0.67 | -0.30 |
| С-ов | 0.77 | 0.49 | -0.28 |
| С-ин | 1.09 | 0.88 | -0.21 |
| Т-ко | 0.58 | 0.49 | -0.09 |
| У-ий | 1.21 | 0.90 | -0.31 |
| Ц-ов | 1.09 | 0.65 | -0.44 |
| Ш-па | 0.94 | 0.77 | -0.17 |

Shifts in blood sugar curves under the influence of carbocholine (23 studies) were insignificant and irregular. Generally, the effect of carbocholine (and consequently that of excitation of the parasympathetic system) on the liver in benzanthrone intoxication may be regarded as favorable. Studies performed in a similar experimental setup with a pharmacologic antagonist of carbocholine, namely, the parasympathetic drug atropine (1 ml of 1:1000 solution subcutaneously) supported this view. As a rule, hippuric acid synthesis decreased against the background of atropine action (Table 3). There was also a regular decrease in the total blood serum protein concentration (Table 4); in 9 cases of 14, albumin concentration also dropped.

The pronounced shifts in the functional indexes of the liver in benzanthrone intoxication under the influence of vegetotropic drugs indicated that the functional liver disorders in this form of pathology were closely associated with disturbances of the regulatory functions of the vegetative nervous system. This

TABLE 4.

| Name abbreviated | g% of total serum protein: Control tests | After atropine administration | Difference in percent |
|---|---|---|---|
| А-ев | 6.00 | 5.64 | -0.36 |
| Б-ин | 5.98 | 5.78 | -0.20 |
| Б-рь | 6.02 | 5.98 | -0.04 |
| В-ук | 7.20 | 5.38 | -1.82 |
| Г-ко | 6.00 | 5.98 | -0.02 |
| Е-ко | 7.10 | 5.38 | -0.72 |
| Г-ко | 6.04 | 5.24 | -0.80 |
| К-ко | 5.44 | 5.68 | +0.24 |
| М-ая | 6.00 | 5.68 | -0.32 |
| С-ов | 5.74 | 5.18 | -0.56 |
| С-ин | 6.08 | 5.80 | -0.28 |
| Т-ко | 5.98 | 5.60 | -0.38 |
| У-ий | 6.42 | 5.80 | -0.62 |
| Ц-ов | 5.78 | 5.36 | -0.42 |
| Ш-па | 5.98 | 5.25 | -0.46 |

indicated that promising results may be obtained from trials of vegetotropic drugs as therapeutic agents in benzanthrone intoxication.

Shifts observed in liver function tests under the influence of vegetotropic pharmacologic agents were directly opposite to those observed in similar studies in epidemic hepatitis by A. L. Myasnikov and co-workers. This difference was apparently connected with the peculiarities of disturbances in the functional state of the vegetative nervous system in various pathological conditions. It is possible that, unlike parenchymatous hepatitis, characterized by hyperfunction of the parasympathetic region of the vegetative nervous system, the tonicity of this region was lowered in benzanthrone intoxication. S. R. Frenkel showed earlier that benzanthrone lowered the tonicity of the sympathetico-adrenal system.

By elevating the tonicity of the parasympathetic region of the vegetative nervous system, it was possible to improve some of the liver function indexes in benzanthrone intoxication, but this cannot serve as a basis for denying the direct action of the toxic principle upon the liver. Benzanthrone can be discovered in the blood by the method of S. R. Frenkel, which can detect 0.2 γ/ml of the toxic agent. Benzanthrone was found in the blood of 14.3% of the cases indicating that it was circulating in the blood in some changed form and that its circulation in unchanged form in the blood was not an essential condition for the development of the intoxication process.

## Conclusions.

1. Benzanthrone intoxication was accompanied by a disturbance of liver function detectable by a combination of liver functional tests.

2. Disturbances of liver function in benzanthrone poisoning were connected to a degree with a functional disorder of the vegetative nervous system.

3. Liver function studies proved of considerable value in diagnosing benzanthrone intoxication and in evaluating the state of health of workers, especially in the stage of residual intoxication.

4. Treatment of benzanthrone intoxication should be aimed at the normalization of liver functions.

5. Benzanthrone was rarely found in the blood of persons with benzanthrone intoxication.

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## Hygienic Characteristics of Tantalaum and Niobium (Rare Metals) Dusts.

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Gigiena Truda i Professional'nye Zabolevaniya, Vol. 1, No. 6, 16-22, 1957.

Present-day technology is associated with widespread use of rare elements, among them tantalum and niobium, highly refractory metals, are readily processed by cold methods, such as rolling, drawing, etc. In their remarkable resistance to corrosion, they are close to the noble metals and in some respects even superior to platinum. Tantalum and niobium are used in the manufacture of vacuum (generator, electron, etc.) tubes and as acid-proof materials. Tantalum is also widely used in plastic surgery as screws, screens, powder, etc. The Directives of the XX Session of the CPSS on the Five-Year-Plan em-

phasize the need for a considerable expansion in the production of tantalum and niobium.

Not much is known of the toxicology of tantalum. In 1955 there were published in the U.S.A. results of investigations on the action of tantalum pentoxide that entered the respiratory organs (Shepards). The author found that intratracheal introduction gave rise to temporary bronchitis, interstitial pneumonia; after a year residual symptoms appeared as focal emphysema and penumonia in the area of the metallic deposits. No fibrosis was observed. This author undertook to investigate conditions prevailing in the manufacture and processing of these metals and with a view to proposing measures for the sanitization of working conditions, to survey the state of workers health in this industry, and to determine experimentally the character and degree of toxic action of tantalum and niobium as a basis for arriving at hygienic standards in the manufacture of these metals. Metallic tantalum and niobium are prepared by the metallurgical powder process, electrolytically or by the reduction of their respective compounds.

This author studied working conditions in plants where tantalum was obtained by reduction of potassium fluorotantalate with the aid of metallic sodium. The metallic powder thus obtained was washed, dried, ground in ball mills, sifted through vibrating screens and pressed into bars at 2.1 ton/$cm^2$. The bars were then fused at temperatures just below the melting point of tantalum (m.p. of tantalum is 2800 - 3000°; bars were fused at 2300°). In this form the tantalum bars had undergone further cold treatment. Tantalum became suspended in the air of working premises in the form of disintegration aerosol. The heat treatment of tantalum was done in vacuum; any vapor created in the process was drawn off and became precipitated on the conduit inner walls. On the other hand, tantalum dust was found in the working premises at points where different operators were stationed. It was found that at the breathing level of workers who cleaned the exhaust conduits tantalum dust concentration ranged from a few milligrams to 70 $mg/m^3$; in the unloading of the ball mills and the sifting of the metallic powder, dust concentration ranged from tenths of a milligram to 120 $mg/m^3$; in weighing the potassium fluorotantalate and loading into the crucible the dust concentration ranged from 15 to 114 $mg/m^3$, or in excess of the maximum permissible concentration for hydrofluoric acid salts as established by N 101-54.

The above indicated operations were all of short duration and were repeated 3 - 4 times during each shift. At intervals between operations and at 2 meters from the operator's position during the operation itself, the dust concentration dropped to 3 - 0 $mg/m^3$. This rapid fall in dustiness can be explained by the high specific gravity of tantalum and by the existence of adequate ventilation at the operator's positions. In addition to tantalum, welders of the tantalum bars may be exposed to the effect of mercury vapor coming from the mercury pumps and the manometers. Women working on all other processes were subjected to the effect of potassium fluorotantalate; the latter is a strong irritant of the upper respiratory tract; the women used hand-made protective respiration masks. The number of workers in this industry was limited; 22 workers, among them 12 welders, were examined medically. All male welders, 26 to 54 years of age, had work records of 3 to 24 years. Chemical operations were performed by women 25 to 56 years of age, with work records of 5 to 25 years. No pathologic changes were found in the welders internal organs. Urine and blood analyses were also normal. However, all welders manifested changes in the vegetative nervous system, probably caused by the mercury vapor; the word probably is here used advisedly, since the mercury vapor concentration in the air of the shop was low. Mercury was found in the urine in 10 of 12 persons examined in amounts of 0.002 to 0.02 mg/li. Chest films of 2 welders and a shop foreman, with work records of 5, 14 and 24 years revealed changes indicative of incipient pneumosclerosis. Neither the female or male welders manifested any changes with respect to the internal organs ascribable to their occupation. X-ray films of female workers revealed no pneumosclerotic changes, despite their many years of work with potassium fluorotantalate (in one case, 24 years). Dental or oral mucosa changes were not indicative of HF effects. Only 2 women workers had chronic hypertrophic rhinitis.

Results of observations under practical production conditions did not permit drawing definite conclusions with regard to the sanitary-hygienic conditions effect on the health of the workers; it became necessary to resort to experimental study on a chronic basis. Accordingly, an experimental study was made of the following: a) the course tantalum followed after it entered the organism through the respiratory and digestive tracts; b) the solubility of some tantalum and niobium compounds in media approximating fluids of the organism; c) the possibility of generalized tantalum action on the organism,

and also the fibrogenic action of tantalum and niobium on lung tissue. The study was conducted by means of labeled radioactive substances.

It has been generally established that the course followed by a substance after it entered the system determined to a considerable extent the degree of its deleterious effect on the organism. The information contained in the literature on the distribution, deposition and elimination of labeled tantalum and niobium from the organism was inadequate. It was known that $Nb^{95}$ had the tendency to accumulate in the skeleton. On the 10th day after administration of a soluble Nb compound, up to 15% of it was deposited in the skeleton. $Nb^{95}$ was also found in the parenchymal organs; 65% of the initially administered $Nb^{95}$ was eliminated with the urine and feces within 20 days of its administration.

Tantalum pentoxide was used in studying the fate of tantalum in the organsim, because it occurred most frequently industrially in that form. $Ta^{182}$ in the pentoxide form was used as the labeled indicator in tracing the dust particles of its compounds. Dust of the active and the inactive part of the mixture employed was highly dispersed (up to 82% of the particles measuring less than 2 mμ). The dust was administered to white rats intratracheally, suspended in physiological saline solution (0.5 ml or 50 mg). Animals were sacrificed variously, after 4 hours to 14 days, and radioactivity determinations were made in sections of the different organs using apparatus "B". It was demonstrated that when tantalum pentoxide was introduced into the lungs, it did not pass from there into other organs, or it did so extremely slowly, remaining unchanged in the lungs almost indefinitely. Tantalum administered orally had not been assimilated by the organism even at the end of 14 days. Approximately 100% of the labeled tantalum pentoxide was eliminated with the feces during the first 4 days, and no tantalum pentoxide was found in the urine.

No sufficiently sensitive test for tantalum was found in the literature; therefore, the solubility of tantalum pentoxide in the gastric fluids, blood serum, and other liquid media with a pH close to that of the physiological media of the organism was studied by the labeled atom method. Two hundred g of active and inactive tantalum pentoxide was placed into flasks containing 100 ml of the solvent; the mixture was filtered and activity determined using the "B" apparatus. Tantalum pentoxide did not dissolve in any of the media, even after 3 months standing. Niobium pentoxide was relatively more soluble

in strong bases than in concentrated acids; it dissolved only in 0.22% of sodium bicarbonate at pH 8.1. After 24 hours 100 ml of the solution contained 0.004 mg from 200 mg of the suspended solid phase, between 10 days and 6 months the level remained at 0.02 mg per 100 ml of sodium bicarbonate. Analyses were performed by the method of Professor I. P. Alimarin. Experimental data obtained on insolubility of tantalum pentoxide and on the slight solubility of niobium pentoxide in biological fluids of the organism in animal experiments and in vitro, were in agreement with the results of chemical investigations of the extremely slight solubility of compounds and the metals themselves in strong acids and bases. The extremely low solubility of the 2 metals and of their compounds in body fluids gave reason to believe that no marked toxic effects might be produced by chronic experiments.

In a way of preliminary orientation this author used effects produced by such related compounds as vanadium as the guide in his experimental work. As the first step, a study was made of the penetrability of tissue barriers and of tissue metabolism in the presence of invading tantalum compounds. For this 18 white rats were kept under identical conditions of general maintenance and nutrition. Six of the rats inhaled a highly dispersed tantalum pentoxide dust in concentration of 130 $mg/m^3$ for 2 hours daily over 6 months. In exactly the same manner, another 6 rats inhaled potassium fluorotantalate dust in 130.2 $mg/m^3$ concentration. The remaining 6 rats served as controls. Inhalations were made in a V. B. Latushkina exposure chamber. Upon completion of the exposures all animals received 7.5 mμ of methionine $S^{35}$ and 10 μcu of $NaHP^{35}O_4$. (Probably a misprint. B.S.L.). Animals were killed 45 minutes, 1.5, 3, 6, 12 and 24 hours after administration of the labeled radioactive compounds. Study preparations were made from blood plasma, liver, kidneys, spleen, brain, muscles, and lungs. Activity of tissues and of extracted proteins was evaluated for each isotope, according to the following indexes: 1) "relative tissue activity"; 2) "relative activity of protein contained in 1 g of tissue", expressed as percent of activity introduced per g of animals weight, and 3) "the relative specific activity of the protein expressed in percent", representing the ratio of the second value to the first. Unlike the first two, the last value reflected degree of labeled compound incorporation into tissue proteins; account was taken of the amount of labeled substance contained in these tissues; on that basis it was possible to determine extent and estimate the rate of methionine and phosphate metabolism in these tissues.

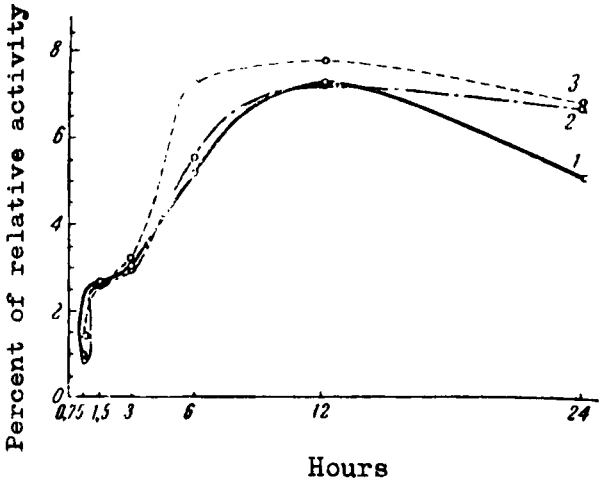


Fig. 1. Changes in the rate of radiophosphorus incorporation into lung proteins following dust inhalation of: 1 - control; 2 - potassium fluorotantalate; 3 - tantalum pentoxide.

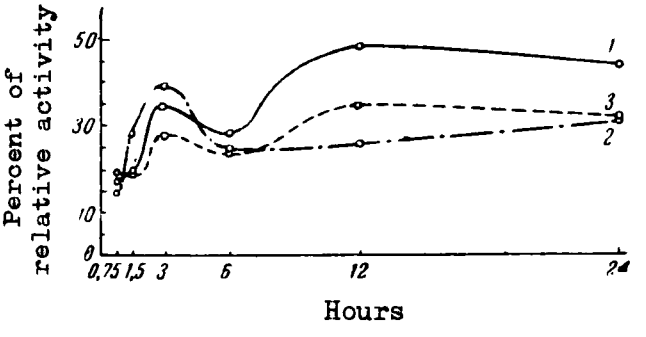


Fig. 2. Changes in the rate of radiophosphorus incorporation into muscle tissue following dust inhalation of: 1 - control; 2 - potassium fluorotantalate; 3 - tantalum pentoxide.

From the data thus obtained and graphically presented in Fig. 1, it might have been concluded that the rate of labeled compounds entry into pulmonary tissues of animals exposed to potassium fluorotantalate dust inhalation, and to a lesser extent, of tantalum pentoxide, was below that of the controls. Actually, the rate of incorporation of these substances into pulmonary tissue proteins was greater than in the controls. These findings indicated a decrease in permeability barriers of the "blood-pulmonary tissue" and some increase in the rate of methionine and phosphate metabolism in the lungs following inhalation of the dust of tantalum compounds under study. Different effects were noted in other organs, as shown in Fig. 2. These findings are in agreement with changes in the general condition of the animals, such as reduced rate of gain in weight in the exposed animals compared with the controls.

Morphological changes in the lungs and other organs were studied in animals exposed to potassium fluorotantalate and to tantalum pentoxide for 4 months, and in animals injected intratracheally with metallic tantalum, its compounds, and niobium pentoxide, once or twice at the rate of 50 mg of dust per dose. Animals were killed after 3, 6 and 9 months. Tissue and section studies were made by Professor P. P. Dvizhkov. Animals treated with potassium fluorotantalate manifested pulmonary tissue changes as diffuse interstitial processes with clearly defined thickening of the interalveolar septi, multiplication of histiocytic elements, and the appearance of collagen fibers (Fig. 3).

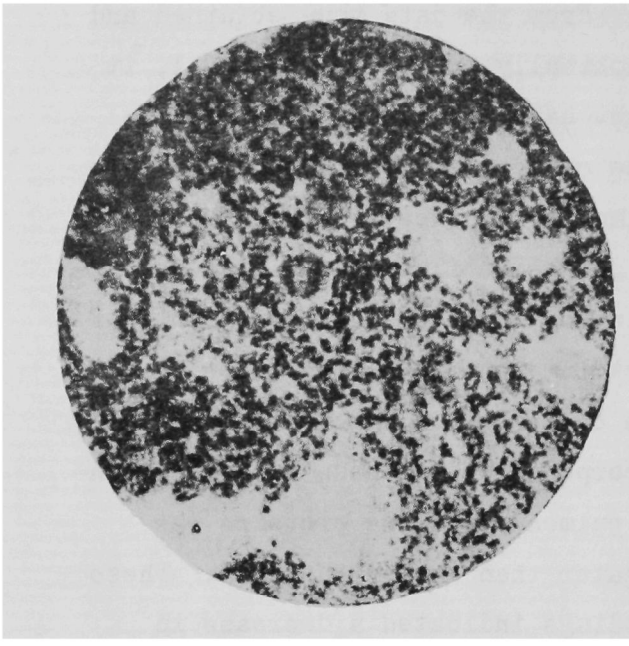

Fig. 3. Four months exposure to potassium fluorotantalate dust inhalation. Lungs: thickening of interalveolar septi; histiocytic element proliferation; thickening of blood vessel walls. Microphoto 80X.

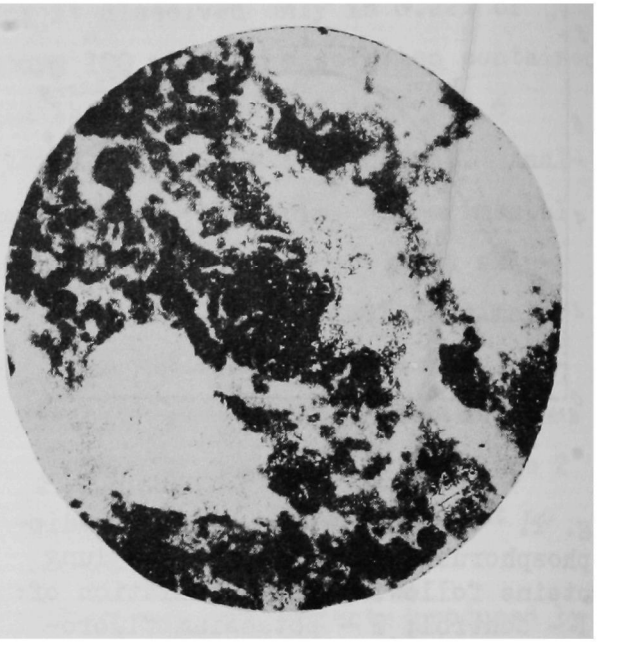

Fig. 4. Nine months of intratracheal administration of tantalum metal dust. Lungs: thickening of interalveolar septi at foci of dust deposition; dust-filled lymphatic vessel. Microphoto 100X.

Tissues of the thymus glands revealed a slight hyperplasia of the reticuloendothelium in the marginal sinuses. Pulmonary tissue reaction in animals exposed to tantalum pentoxide increased with the time elapsed from the moment of dust administration; it remained moderate even after 9 months; thickening of the interalveolar septi, small histiocytic infiltrates, and a slight increase in the number of connective fibers, largely in the places where dust was deposited, made their appearance. No special reaction to the dust was noted in the thymus glands. The reaction of the pumonary tissue to metallic tantalum was similar to but less pronounced than the reaction produced by tantalum pentoxide (Fig. 4). Pulmonary tissues of animals exposed to niobium pentoxide reacted by slight intermediate fibrotic changes in the areas where dust was deposited. No specific changes were found in the internal organs.

## Conclusions.

1. Dusts of tantalum and niobium and of their respective compounds found in the metallurgical powder industry are highly dispersed and insoluble (tantalum) or nearly insoluble (niobium) in liquid media of pH close to that of biological fluids.

2. Tantalum was eliminated almost entirely from the gastro-intestinal tract within the first few days. Its resorption through the intestine had not been noted.

3. The general toxic action of tantalum and niobium compounds was slight, probably due to the extremely low solubility of tantalum compounds.

4. The effects of dusts of niobium and tantalum compounds on pulmonary tissue following inhalation or intratracheal injection varied largely depending on the form of the dust.

Results of some observations pointed to the fact that a fibrotic process might develop in the lungs upon inhalation of dusts of these compounds.

5. Measures related to the elimination of tantalum and niobium compound dusts should be based on the use of dust-abating equipment. Existing sanitary-hygienic standards for fluorine and fluorides may serve as the basis for sanitary-hygienic standards for dusts and vapors of fluorotantalate. Niobium and tantalum and their compounds showed signs of possessing pronounced fibrogenic properties; this should be given serious consideration in establishing appropriate sanitary-hygienic standards for the Nb and Ta metallurgical industries.

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# Pathogenic Properties of Some Dusts Occurring in Ferrous Metallurgy Production Plants.

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Charging blast furnaces pollutes the air of some working areas with dust frequently reaching concentrations of several grams per $m^3$. Most dust-creating in this respect are sinter and coke. Iron ore sinter is a product of fused ore. Sinter usually contains about 50% of iron in the form of ferrous and ferric oxides: calculated on the basis of $Fe_2O_3$ oxides of iron constitute 75 - 80% of the entire material. Content of silicon dioxide mostly ranges between 8 - 10%, occasionally going up as high as 15 - 16%, but the percent of silicon dioxide for any one agglo-plant is fairly constant as a rule. Results of analyses made by this author indicated that free silicon dioxide did not exceed 5%.

Most investigators who studied the effect of dust consisting of oxides of iron alone found that such dust was deposited in the lungs without producing pneumosclerotic changes (S. V. Miller, H. M. Carleton, C. Nasslund, H. E. Harding, and others). Other investigators, such as A. J. McLaughlin, Perry, and others expressed the guarded opinion that iron oxides could elicit pneumoconiotic fibrosis even in the complete absence of silicon dioxide. It has been known that pneumoconiosis, or so-called sidero-silicosis, can be elicited by dust which contained oxides of iron and a varying percent of quartz. With regard to this, reports in the literature indicate that the mild form of coniosis, as distinct from the typical form, may be the result of a comparatively low concentration of $SiO_2$, as well as the result of the assumed protective action of iron oxides. Such opinion was expressed by N. M. Demidenko, P. P. Dvizhkov, E. H. Kettle, C. Nasslund, and others. In the light of such evidence no clear-cut conclusion can be drawn regarding the importance of low silicon dioxide concentrations, especially in the presence of high concentration of iron oxides, in the development of pulmonary processes. Therefore, this author undertook to make a direct study of the problem under consideration. The study included a parallel investigation of the effect of coke dust on the lungs. Coke, used as fuel in the metallurgical industry, is a product

of coal pyrolysis and is composed approximately of 90% elemental carbon and 9 - 11% ash, half of which is silicon dioxide in the form of silicates. According to analyses of the Institute of Labor Hygiene and Occupational Diseases of the Academy of Medical Sciences, U.S.S.R. performed by E. I. Vorontsova, neither coke nor its free dust contained free silicon dioxide. As compared with the importance of the etiology and pathogenesis of anthracosis, coke pneumoconiosis is of mere theoretical interest. N. A. Vigdorchik, E. King, C. V. Harrison, S. C. Ray, M. Landwehr, E. Bruckman, and others are of the opinion that silicon dioxide contained in coal and not the carbon or any other combustible component was the primary etiological factor in the development of anthracosis. In this connection a study of the effect of coke on lungs is regarded by this author of value, since coke contained no free $SiO_2$. On the other hand, many investigators uphold the hypothesis of Hart and Haselette who believe that a connection existed between the aggressiveness of coal dust of different mines and the degree of coal-fixation. The geochemical process of coal fixation is characterized by a gradual increase of free carbon and a reduction in the volatile components. From the viewpoint of this hypothesis coke presents itself as an interesting study subject, since it contains more free carbon and less volatile substances than anthracite, which is the most highly geofixed, and, judged from the frequency of anthracosis, the most aggresive of all mined coals.

This author employed the most widely used bloodless method of intratracheal dust suspension injection into white rats at the rate of 1.0 ml of isotonic solution containing 50 mg of the coke dust. Studies were conducted with 2 types of agglomerates (sinters): Bakal, containing 16.6% of $SiO_2$ of which 5.4% was of the free type, and Magnitogorsk, which contained 8.8% of total and 0.7% free $SiO_2$. Experiments were also conducted with coke of Kuznetsk coal produced by the Chelyabinsk coke department of the metallurgical plant. The coke contained 10.9% of ash, i.e., approximately 5% of total $SiO_2$ and no free $SiO_2$. Animals were sacrificed by rapid decapitation 15, 30, 91, 183, 274, 365 and 548 days after injection of the dust suspension.

Results of the investigation.

Agglomerate (sinter). Fig. 1 represents typical changes produced in the lungs three months after intratracheal injection of Bakal sinter dust. The section shows a considerable amount of brown pigmentation which yielded a re-

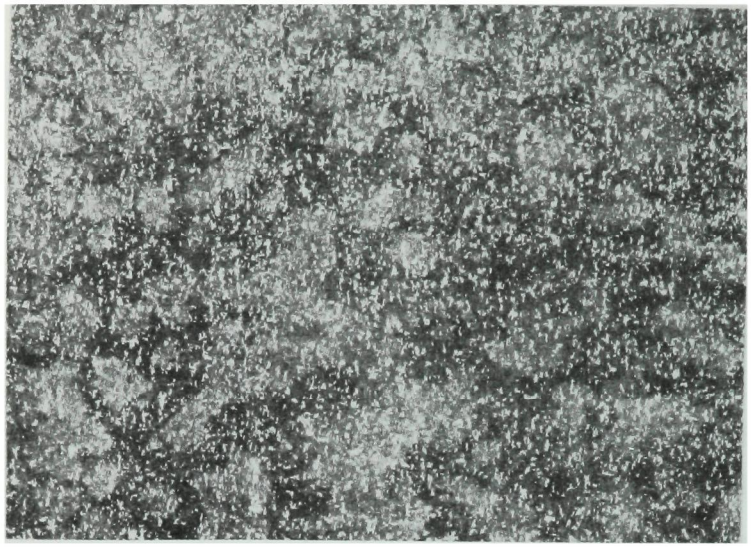

Fig. 1. Diffuse dust distribution of dust in lungs with the formation of dust-cell foci of irregular configuration after 3 months of Bakal agglomerate dust.

action characteristic of iron; the pigmented material was distributed in a diffuse manner in the thickened alveolar septi and partly in the lumens of the alveoli and bronchi; the pigmented material also appeared in the form of characteristically pigmented cellular foci consisting of dust cells and histiocytes. Such a focus was of irregular, poorly delineated shape almost indistinguishable from the surrounding tissue, had none of the characteristic concentric distribution of cellular elements; van Giesen stain failed to show development of collagen fibers either within or around the focus; silver stain brought out a moderate amount of reticular fibers and their hardening. It is thus seen that the focus did not resemble a typical silicotic node; rather it resembled the formations described in experimental "pure" siderosis. The admixture of silicon dioxide to the dust failed to change the histologic picture.

Beginning with the ninth month following the intratracheal injection of Bakal sinter dust the dust cells began to assume a different character. They appeared as foci of miliar and submiliar dimension, located at points of previous alveoli and interstitially. They appeared distinctly unlike the previously observed small foci by having a typically round shape sharply delineated from the surrounding tissue, as shown in Fig. 2. Unlike the small foci of the simple dust cells, these formations appeared as nodes in the sense in which this term is used to denote a characteristic morphologic picture observed in processes of pneumoconiosis. And yet, these small nodes differed substantially from typical silicotic foci by their extremely slow rate of development, having appeared on the ninth month, after which they remained in that stage of development to the end of the first year. The collagen fiber developed generally only as narrow rim around the node; unlike in typical

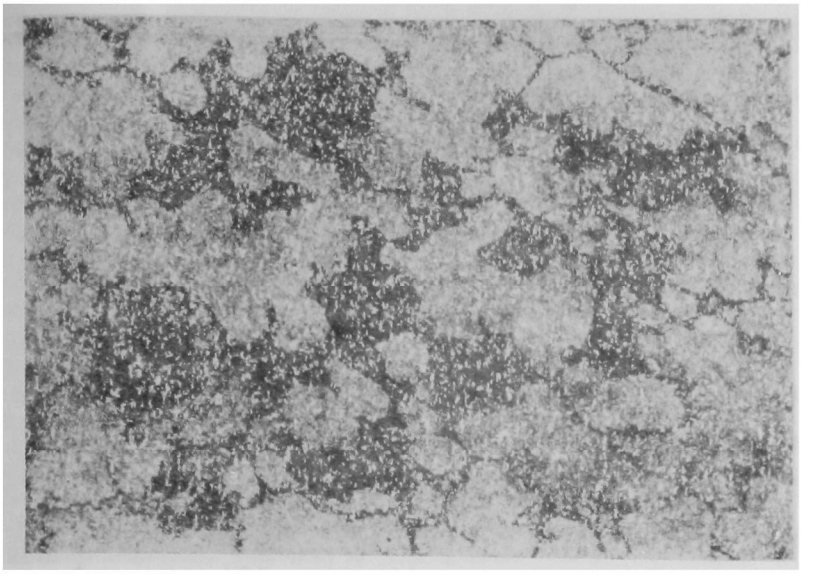

Fig. 2. Lung sections: miliary and submiliary dust cell nodes 12 months after Bakal agglomerate dust administration.

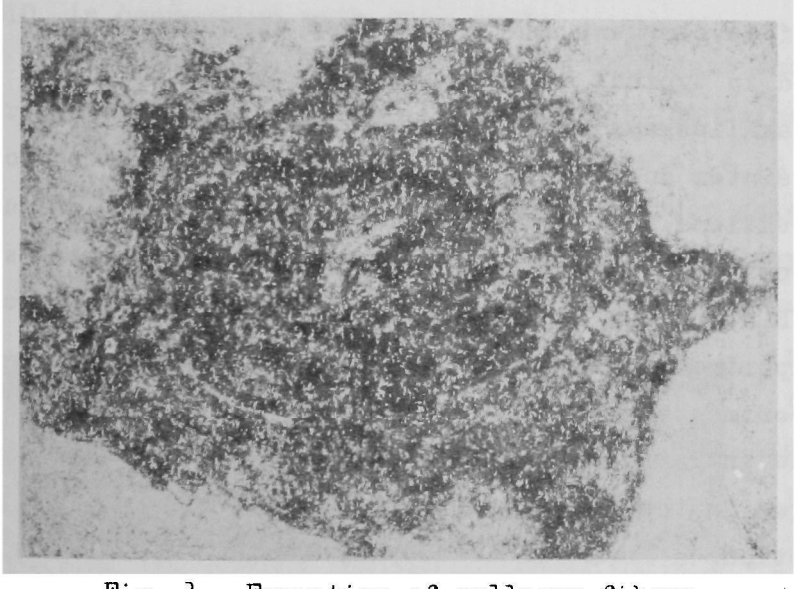

Fig. 3. Formation of collagen fibers peripherally and in the thick of dust cell nodes 18 months after Bakal agglomerate dust administration.

silicosis, no thick retes of argerophilic fibers were observed histologically even 12 months after the dust injection. Nevertheless, sclerosis of the focus (node) developed slowly and gradually, so that after 18 months the development of coarse collagen fibers could be seen within the node as well as around it, as can be seen in Fig. 3.

Development of the type of foci or nodes similar to the ones described above was not observed in the lungs of rats injected intratracheally with Magnitogorsk sinter dust even 18 months from the beginning of the experiments. However, a slight development of connective tissue fibers was observed at points of dust accumulation in the later experimental periods. A comparison of the organism's reactions to the 2 types of injected sinter dust shows that the pneumoconiotic node developed or failed to develop depending upon the $SiO_2$ content in the sinter dust. Therefore, it can be concluded that an increase in the content of free $SiO_2$ to 5% in the presence of 15 - 16% of total $SiO_2$ affected the character of the iron dust effect on the organism. It is possible that in this case an important part was played by the fact that at the 1500° of the sinter formation a part of the quartz may have become converted into

cristobalite and tridymite which, according to some authorities, possessed higher biologically aggressive properties than quartz. The above results present a positive answer to the question posed regarding the significance of different concentrations of $SiO_2$ found in agglomerates (sinters) produced by different plants. This fact, along with any other, must be taken into account in attempting to evaluate the possibilities of pneumoconiosis development at one plant or another.

The present author is of the opinion that even low concentrations of $SiO_2$ found in the Bakalsk agglomerate (sinter) are reason sufficient to regard their effect on the organism not as of the nature of "simple siderosis", but as siderosilicosis. On the other hand, the present writer finds himself at disagreement with those who fail to see basic differences between silicosis and pneumoconiosis elicited by dust having no or only a slight content of $SiO_2$. It should be re-emphasized that the changes herein reported showed a degree of benignness in their slow rate of development and in the fact that they bore no resemblance to changes observed in typical experimental silicosis.

E. I. Makovskaya and E. D. Bakalinskaya in their experiments in 1955 injected rats intratracheally with sinter dust containing 15% of total $SiO_2$; however, they limited their observations to 6 months. They reported finding "isolated nodules and diffuse processes consisting of scar tissue! (exclamation mark is by original author, B.S.L.) and connective tissue". No such phenomena were observed in the experiments here described even in the considerably later stages of the experiments.

Coke. Three months after the intratracheal injection into white rats of coke dust the histologic changes in the lungs presented a less clearly expressed cell proliferation reaction, a less extensive polymorphism of cellular elements than in the sinter dust experiments at the same period of time. Characteristically in this case the dust formed agglomerated conglutinated clumps in spots where dust accumulation was high. These conglutinated masses were not atifarcts, i.e., they did not exist prior to the coke dust injection, but developed in vivo, which was shown by the fact that the phenomenon progressed with time, as can be seen in Fig. 4, and by the fact that whole fields of conglutinated black pigmented material were seen also in the regional bifurcate lymphatic nodes to which the dust is naturally brought by individual coniophages, or into which the free dust may find its way. Recently reports appeared in which special importance was ascribed to the phenomenon of dust

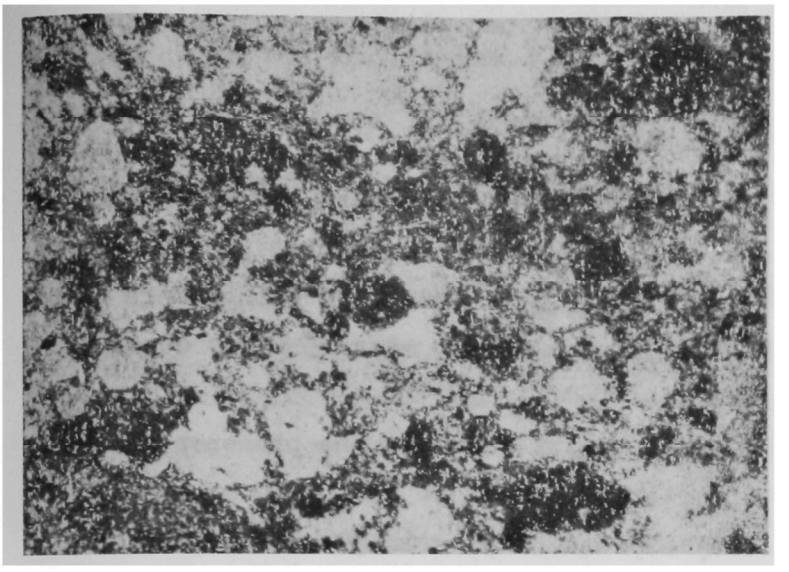

Fig. 4. Lung tissue. Conglutination of coke dust into dust foci 12 months after administration.

conglutination. Landwehr and Bruckman, for instance, express the opinion that the property to conglutinate caused blocking of the lymphatic pulmonary passages, thereby impeding the elimination of quartz dust. King also ascribed considerable significance to this type of blocking of pulmonary lymphatic passages; in his opinion this blocking explained the enhanced fibrogenic effect of $SiO_2$ in connection with coal dust.

Blocking lymphatic passages by coke dust was seen in many histologic preparations. It is true that coke dust contained no $SiO_2$, yet the fact must not be overlooked that prolonged lymphostasis in itself may become an etiological factor in the development of diffuse sclerotic changes in the lungs, as was shown by A. I. Abrikosov and by V. D. Davydovskii. Therefore, it is not surprising that in thickened interalveolar septi, and particularly at points of coke dust accumulation, a slow but unmistakable development of collagen fibers took place, which became particularly pronounced 18 months after the dust injection, as can be seen in Fig. 5. On the basis of such histologic changes the following assumptions are made: a) coke dust can cause the development of pneumoconiosis of anthracosis type following its prolonged inhalation in

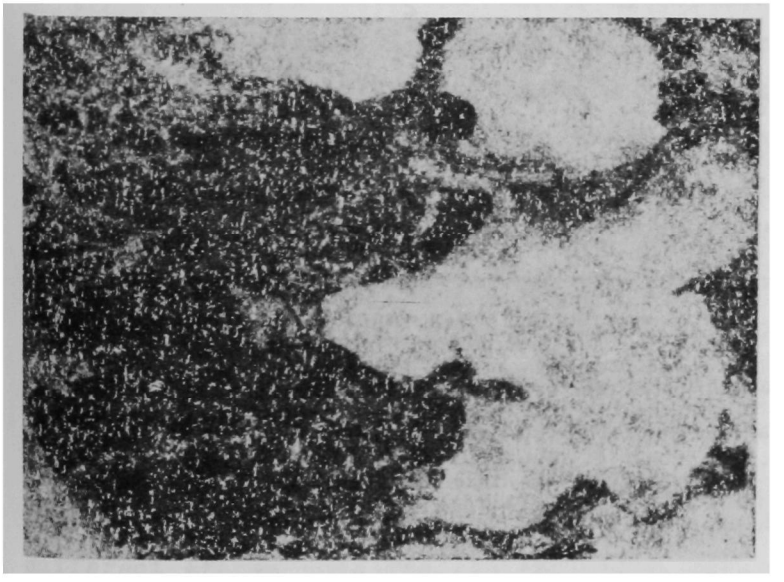

Fig. 5. Lungs. Formation of collagen fibers around the dust foci 18 months after injection of coke dust.

high concentrations; b) coal containing coke dust can elicit pneumoconiosis even in the complete absence of $SiO_2$.

## Conclusions.

1. Two components of modern fuel used in blast furnaces, agglomerate (sinter) and coke, create dust which can elicit true pneumoconiotic pulmonary changes; judged from the results of experiments such pulmonary changes are of a benign character as compared with silicotic pulmonary changes; they develop after a considerably longer exposure time.

2. Coal dust (coke) and agglomerate (sinter) dust in the presence of $SiO_2$ concentrations not exceeding 1%, or in its complete absence, can elicit pulmonary changes in the form of poorly expressed fibrotic processes; it is hypothecated that blocking of pulmonary lymphatic passages by the dust may have a noteworthy auxiliary effect on the development of this type of pathology.

3. The practically negligible concentration of $SiO_2$ in agglomerate (sinter) dust can affect the normal lung tissue reaction imparting to it the characteristics of pneumoconiosis and sidero-silicosis.

4. In evaluating the dangerous aspect for workers in contact with agglomerate (sinter) dust the concentration of the dust, the duration of exposure, etc. should be given due consideration; it should be emphasized, however, that equal consideration should be given the $SiO_2$ concentration in the agglomerate.

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# The Blastomagenic Effect of Polyvinyl Chloride.

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Many writers [5 - 14] presented data pointing to the cancerogenic effects of cellophane and of many plastic materials, including polyvinyl chloride, implanted into rats in the form of films. H. Nothdurft [7 - 9] implanted the following materials into rats intraperitoneally and subcutaneously: polyvinyl chloride, cellulose hydrate, polystyrol in the form of small perforated discs, powder, etc. He also injected silver, gold and platinum plates into mice in a similar manner. Results of his experiments indicated that cancerogenic effects of implanted materials were not the result of any particular chemical structure only, but were connected with the shape and possibly with the condition of tissue hypoxy produced by the disturbed blood circulation.

Contrary to the findings of Nothdurft, B. S. Oppenheimer and his collaborators [13] expressed their opinion regarding the chemical effects of implanted materials on cancerogenesis. Results of experiments conducted by these authors indicated that smooth platelets made from materials of different chemical nature produced different effects. Thus, cellophane AB produced tumors (cancers) in 35.7 - 46.1%, polyvinyl chloride in 38.6%, polyethylene in 12.5% and glass in only 2%. Following the implantation into rats of labeled polymers of polystyrene, polyethylene and polymethylmetacrylate radioactive substances appeared in their urine indicating that the implanted materials were in some way absorbed by the system and may have reacted with the body tissues.

In previous tests performed by this author and his collaborator [4], polyvinyl chloride injected in the shape of cylindrical bodies elicited no cancer tissue growth. The purpose of this investigation was to determine more specifically the cancerogenic effect (properties) of polyvinyl chloride and to establish the possible effect of the shape of implanted material on cancerogenesis. For this purpose 6 series of experiments were performed with polyvinyl chloride of different shapes (see Fig. 1) implanted into white rats. Tests were performed with 139 white rats of both sexes weighing 120 - 150 g which were obtained from the Animal Breeding Institute of the Academy of Medical Sciences of the U.S.S.R. Rats were maintained on the usual diet.

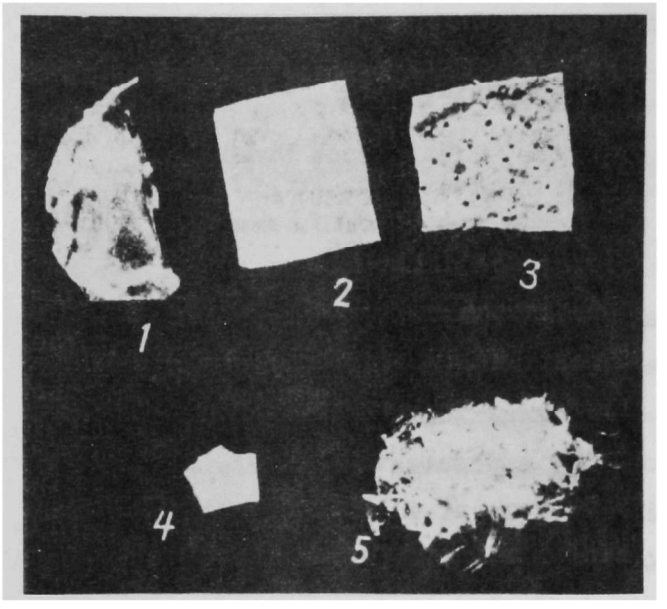


Fig. 1. Different shapes of polyvinyl chloride used in the experimental implantation.
1 - kidney superimposed capsular; 2 - non-perforated platelet; 3 - perforated platelet; 4 - "package-shaped" platelet; 5 - comminuted platelet.

1. Experiments with polyvinyl chloride capsules plated over the kidney. Tests were performed with sheets of polyvinyl chloride such as are used for medical and domestic purposes. The polyvinyl chloride material was first sterilized in 76° alcohol for 4 days or longer. Placing the polyvinyl chloride capsules over the right kidney was accomplished by a modified procedure previously developed for the production of kidney hypertonicity in rats [1] which was also used in previous studies of cancerogenic properties of cellophane [2 - 4]. Tests were made with 37 rats. Sixteen of the rats survived over periods exceeding 7 months; cancers developed in 5 of these, in 4 the malignancies appeared between the 7th and 11.5th months, and in one 19 months after the capsule application.

The (malignant) tumors were of the size of pigeon and in some cases chicken eggs, were nodular and fused with the surrouding organs by mesenteric tissue but never penetrated into the organs. The malignant tissue presented the appearance of fish meat on cross sectioning. The cancer tissue was capsule-shaped and was surrounded by a wall 1 - 3.5 cm thick located around the polyvinyl chloride film-enclosed kidney. The latter was of reduced size, indurated to the feel and showed no differentiation between the cortical and medullary substance upon sectioning. The cancers were connected with the kidney by a thin protusion in 2 cases. The cancer measured 1 x 0.7 cm in one rat and was located within the wall of a thick connective tissue capsule formed around the polyvinyl chloride-enclosed kidney. The capsule showed foci of purulent fusion or liquifaction. Foci of metasteses were found in the mesentery of one rat. Histologic sections were then made of the malignant tissues which were stained with hemotoxyline-eosin. Microscopic examination showed the presence of fibrosarcomas in all cases. Polymorphism, atypical cells, and frequent irregular mitoses were also observed.

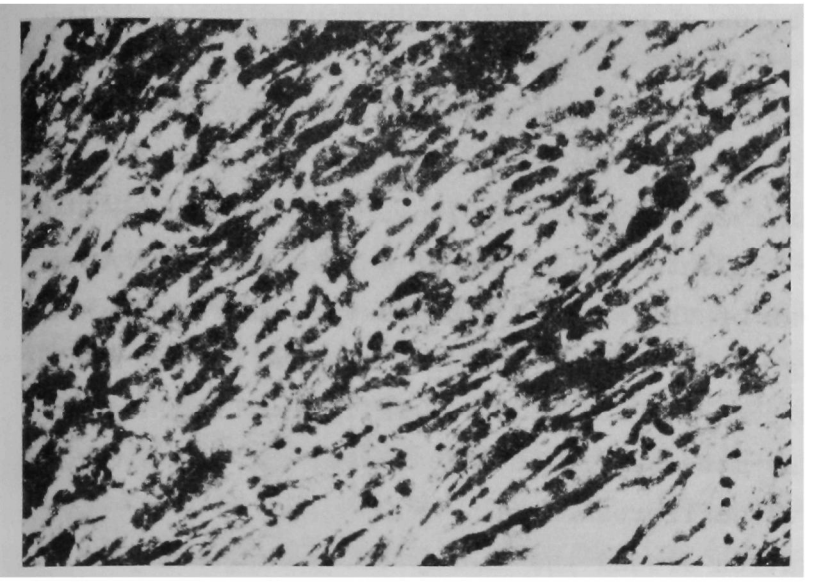

Fig. 2. Micro section of a fibrosarcomatous node. Hemotoxylin-eosin stain 5 x 20.

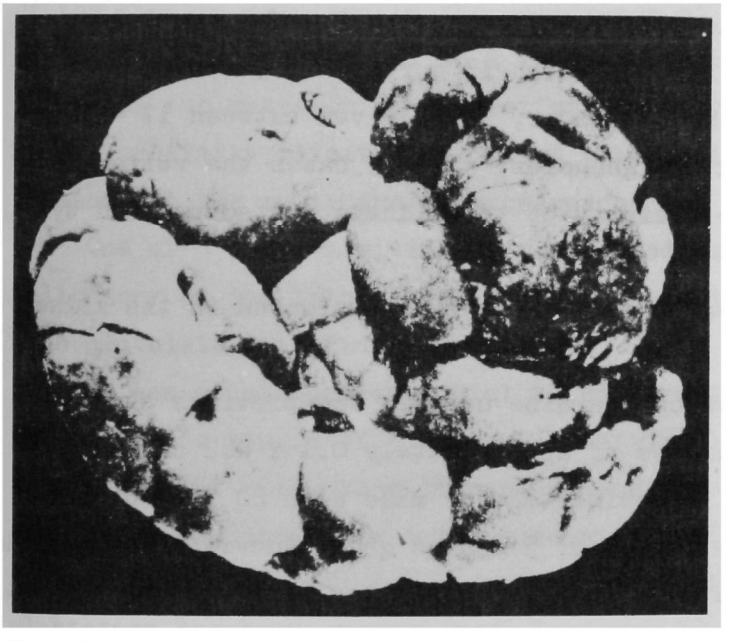

Fig. 3. Sarcoma developed 16.5 months after implantation of a solid polyvinyl chloride platelet close to the right kidney.

2. Experiments with polyvinyl chloride implantation around the kidneys in the form of solid platelets.

Polyvinyl chloride implantations at the right kidney were made with solid platelets 0.1 cm thick and 1.6 x 1.6 cm in area. Seven of the 20 rats thus implanted survived for periods of 11 months and longer. Of 5 animals surviving 16 - 18 months, 2 developed malignancies in the vicinity of the implantation on the 17th month (Fig. 3). One of the malignancies was of the size of a goose egg. As in the case of malignancies developed in the first series, this tumor was indurated, nodular, fused to surrounding tissues as shown in Fig. 3, enclosing in its center the polyvinyl chloride platelet. The second malignancy appeared in the form of a nodule and was 1.5 x 0.5 cm in size; the nodule protruded from the inner surface of the connective tissue capillary wall which became distributed around the implanted polyvinyl chloride platelet. Upon sectioning the nodule looked like fish meat and the capsule cavity was filled with a caseous-purulent fluid. The capsule wall was 1 - 2 mm thick. As in the case of series 1 these malignancies were of the fibrosarcomatous type having characteristic cellular atypism.

3. Experiments with implantation of perforated polyvinyl chloride platelets at the kidney proximity.

The polyvinyl chloride platelets were of the same measurements as in the preceding 2 series and had 35 - 40 needle perforations. Experiments were performed with 15 rats of which 8 survived 12 months or longer. A malignancy developed on the 18th month after implantation in one of 4 rats which survived 17 - 18 months. The malignancy was of the size of a hen's egg, surrounded the polyvinyl platelet and grew through the platelet perforations; no cavity was observed at any point near the polyvinyl platelet. The malignancy was nodular, indurated, fused to the kidney, the mesentery, the intestines, and the liver. Like the others, this malignancy was a fibrosarcoma.

4. Experiments with implantation around the kidney of "package-shaped" polyvinyl chloride.

"Package-shaped" polyvinyl chloride specimens were prepared in the shape of tightly-rolled polyvinyl chloride platelets, measuring 0.4 x 0.6 x 0.2 cm. Experiments were performed with 15 rats of which 13 survived 7.5 months or longer; of these 9 survived 12 months or longer, and 6 lived between 17 - 18 months. None of the rats developed malignancies. In all cases the rolled polyvinyl chloride implanted in the vicinity of the kidneys was surrounded by thin-walled fibrose capsules.

5. Experiments with fragmented polyvinyl chloride implanted in the kidney proximity.

Polyvinyl chloride platelets twice the size used in the previous experiments were cut with scissors into pieces of approximately 0.1 x 0.2 cm and implanted in the kidney proximity. Experiments were made with 20 rats of which 14 remained under observation for a period of 5 months and 4 survived for periods of 11 - 17 months. Autopsy results in all cases showed the formation of compact induration 2 x 1 cm consisting of polyvinyl chloride fragments surrounded by connective tissue. These fragments were fused in spots with the spinal muscles and with the kidneys. Malignant formations had not been observed. The polyvinyl chloride fragments were examined and found to have undergone changes such as the loss of the characteristic gloss, and they acquired a dull milky appearance.

6. Experiments with ground cellophane implanted in the proximity of the kidney.

Cellophane platelets were first cut into small pieces with scissors and then ground in a mortar until the fragments measured 0.05 x 0.01 cm and 0.01 x 0.02 cm. The comminuted cellophane was sterilized as previously described in 76° of alcohol. Amounts of cellophane equivalent to that of the polyvinyl chloride were implanted in these experiments into 32 rats of which 6 survived over periods of 10 - 15 months. Autopsies were performed on all rats; solid lumps measuring 1 - 2 cm were found in all cases at the point of implantation in the proximity of the right kidney. These lumps consisted of cellophane pieces fused by connective tissue. No malignant formations were observed. The nature of the cellophane was changed in a manner similar to the one described for changes in the polyvinyl chloride fragments.

Discussion of results. The results obtained confirmed data presented in the literature regarding the nature of cancerogenic effects produced by polyvinyl chloride [7 - 13]. The superimposition of polyvinyl chloride over one of the kidneys resulted in the appearance of malignancies in 4 of 16 rats which survived 7 - 11 months and in 1 rat which survived 19 months.

Free implantation of non-perforated polyvinyl chloride platelets into the kidney proximity elicited malignant growths in 2 of 5 rats which survived 17 - 18 months. The malignancies appeared on the 17th month of survival.

One of 5 rats surviving over a period exceeding 18 months developed a malignancy on the 18th month after implantation of perforated polyvinyl chloride platelets into kidney proximity.

It was considered essential to confirm the malignant nature of the tumors formed as the result of polyvinyl chloride platelet implantation. Therefore, a specimen of one such malignant tissue was implanted into a normal control rat. This was done by a subcutaneous injection into the control rat of a 25% suspension of the tested malignant tissue. At the moment of writing the transplantation has been carried over 7 generations. Histologically all neoplastic formations proved to be fibrosarcomas. The malignant nature of the neoplasms was confirmed by their properties of transplantation. Metasteses were observed in only one case into the mesentery. The neoplastic localization always occurred at the point of original polyvinyl chloride implantation.

In 5 cases in which polyvinyl chloride capsules were placed over the kidney the malignancies were formed outside the polyvinyl chloride capsules. No neoplastic growth was observed within the kidney location. The new growth was connected to the kidney by means of a thin pedicle in 2 cases. The above data

are not in agreement of Zollinger's affirmation that primary malignant nodes resulting from kidney superimplantation of plastic material formed in the kidney capsule. According to the results of the present authors malignant nodes formed in the connective tissue capsule developing around the point of the plastic implantation, whether the implanted plastic material was in direct contact with the kidney or separate from it. No malignancies developed in any of the animals implanted with either "package-shaped" or powdered polyvinyl chloride even after 10 - 15 months observation; on the other hand, cellophane platelets implanted in the proximity of the kidney or subcutaneously elicited the development of malignant formations in similar time intervals, and, in some instances, in considerably shorter periods of time. This was previously noted and reported on by the present authors elsewhere [2, 4]. Such results appear to indicate that the physical shape or form of the implanted synthetic material was a factor of direct importance or significance, as was previously shown by Nothdurft. These authors implanted polyvinyl chloride in the shape of sticks in previous experiments [4] and found no malignant growth development in any of the animals, which can serve as additional indication of the fact that the shape of implanted synthetic plastic was a factor of considerable significance. Results of the present investigation confirm the above assertion, namely that implantation of the polyvinyl material in the form of a capsule superimposed upon the kidney produced a more intensive blastomagenic reaction that did, so-called, "free" implantation in the kidney proximity. This may be due to the known effect which kidney compression and its isochemization resulting from capsular superimposition had on malignancy genesis. On the other hand, results of the present experiments pointed equally emphatically to the role played by total surface contact between the implanted material and the tissue surrounding it. Nevertheless, it must be admitted that the real significance of the shape of implanted material in relation to malignancy development remains unanswered. Equally unexplained remains the question whether the chemical, physico-chemical, or the purely mechanical factors play the primary role in effecting neoplastic formation, although there exists some evidence indicating that the effect of the implant was in no way the result of intensive mechanical irritation. This was also substantiated by the present results (and results of others) of comminuted and powdered polyvinyl chloride and cellophane implantation, which in the presence of a maximum surface area contact produced

no malignant developments. Further confirmation of the above expressed opinion was presented by results of other experiments reported on by these authors [4]: experimental animals were implanted with glass wool, admittedly a high degree mechanical irritant, and yet no malignancies were produced in any of the animals after 12 months observation. Results of all previous and present studies point to the most probable explanation that blastomagenesis was the result of the complex effect of chemical, physico-chemical and mechanical factors under the conditions of the described experiments, and only future studies may show which of the enumerated factors was of primary significance.

## Conclusions.

1. Implantation of polyvinyl chloride capsules over the kidney, or of polyvinyl chloride perforated or non-perforated platelets in the kidney proximity, but not in direct contact with it, in many instances resulted in sarcoma development. Polyvinyl chloride capsules superimposed over the kidneys, as a rule, elicited malignancy growth in a shorter time than implantation by the other method mentioned above.

2. Some of the experimental results indicated that the shape or form of the synthetic implant was a factor of significance in the malignancy development.

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# Effect of Metallurgical Plants Emissions on Children's Health.

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(From the Ukrainian Institute of Community Hygiene).

Gigiena i Sanitariya, Vol. 24, No. 2, 3-7, 1959.

Ferrous metallurgical plants constitute a potent source of atmospheric air pollution with dust and with a variety of gaseous components. Most intensive air pollution of metallurgical origin comes from blast furnaces, coke-chemical departments, central electric heat and power stations (TsES) and from a variety of metallurgical by-product plants. Results of numerous investigations established highly intensive atmospheric air pollution within a radius of 2 - 3 meters from metallurgical plants by dust, sulfur dioxide, hydrogen sulfide, carbon monoxide and other gaseous air pollutants. The purpose of this investigation was to determine the effect of such air pollutants on the health of inhabitants of two cities which housed within their confines two extensive metallurgical production and processing plants (points 1 and 2); similar investigations were conducted for control purposes in two other cities which had no industrial production or manufacturing plants (points 3 and 4). Simultaneously, a special study was conducted to determine the state of health of children residing at the same 4 points. Such a study was suggested by M. S. Gol'dberg in 1949; the ages of children covered by the investigation ranged between 8 and 14 years. Data on the degree of atmospheric air pollution of each of the 4 inhabited points are listed in Table 1.

T A B L E 1.

| Inhabited section | Concentration in mg/m$^3$ | | | | | |
|---|---|---|---|---|---|---|
| | Dust | | | Sulfur dioxide | | |
| | Maximal | Minimal | Average | Maximal | Minimal | Average |
| 1 | 6 | 0.24 | 1.81 | 0.8 | 0.1 | 0.25 |
| 2 | 4.83 | 0.7 | 2.06 | 0.91 | 0.19 | 0.52 |
| 3 (control) | 0.35 | 0.1 | 0.21 | 0.05 | 0 | 0.05 |
| 4 (control) | 0.37 | 0.14 | 0.25 | 0.27 | 0.01 | 0.05 |

Data in the table show the following: dust concentration in the air at point 2 reached a maximum of 4.83 mg/m$^3$ and at point 1 - 6 mg/m$^3$, both in excess of the maximum permissible concentration. Maximum air dust concentrations at control points 3 and 4 ranged between 0.35 - 0.37 mg/m$^3$ and average con-

centrations between 0.021 and 0.25 mg/$m^3$. It should also be mentioned at this point that the air dust at the industrial points contained 15% of silicon dioxide. According to analyses of M. S. Gol'dberg the ash coming from the electric heat and power station contained 24% of free silicon dioxide, and according to analyses made by N. Ya. Yanysheva 15.8% of free $SiO_2$. Excessive concentrations of sulfur compounds were also found in the air within a 2 - 3 m radius from the ferro-metallurgical plants. Complaints presented by residents at points 1 and 2 in the proximity of the metallurgical plant had reference to unfavorable sanitary-hygienic conditions of every-day living over a radius of 3 m from the ferro-metallurgical plants. Clinical roentgenological studies were made of children living in workers villages located within a 6 m radius belt surrounding the plants; similar studies were made of children living at control point 3 located 20 m from the plants; the socio-economic pattern of residents of the 2 localities were practically identical. Six-hundred and thirty children residing in control point 3 over a period of not less than 3 years were Pirquet and Mantu negative. Three-hundred and fifty-five children residing in villages at points 1 and 4 (control point) were examined similarly. Based on the results of the examinations the children were divided into 4 groups: group I with normal roentgenograms, i.e., with no visible pathologic changes in the chest, lungs, roots and in the pleural folii; group II with changes limited to the roots of the lungs and with symptoms of indurated and petrified glands; group III in addition to hylus and gland induration there were changes in pleura, interlobal and pleural adhesions, tissue changes in the form of exaggerated vascular and connective tissue picture, linear and alveolar fibrosis and foci; group IV with most clearly expressed roentgenological changes in the roots and in the lung tissue characteristic of early stages of coniosis. Results of the roentgenological examinations are listed in Table 2.

T A B L E 2.

| Inhabited section | Groups I + II | | Groups III + IV | | Total |
|---|---|---|---|---|---|
| | Number: | % | Number: | % | |
| 1 | 365 | 68.6 | 167 | 31.4 | 532 |
| 3 (control) | 78 | 81.7 | 20 | 18.3 | 98 |
| 2 | 124 | 73.0 | 46 | 27.0 | 170 |
| 4 (control) | 177 | 95.7 | 8 | 4.3[1] | 185 |

[1] Group III only, none of the children in this category fell into group IV.

For purposes of greater clarity results of children's examinations were divided into 2 groups by combining groups I and II into one group and groups III and IV into another group. A careful study of the roentgenograms showed that children residing in sections

1 and 2, belonging to the combined I and II group constituted correspondingly only 68.6 and 73%, while percentages in the case of children residing in the non-industrial production sections 3 and 4 were correspondingly 81.7 and 95.7%.

On the other hand the percent of children belonging to the combined groups III and IV and who lived in the industrial sections 1 and 2 was correspondingly 31.4 and 27.0%, while children of control point 3 classed as the III-IV combined group constituted only 18.3%; in the case of children residing in control section 4 the percentage of children classed as group III constituted only 4.3% of the total of examined children; no children of control section 4 had to be classed as group IV.

Comparative analysis of the roentgenological results pointed to the fact that school children residing in the areas having polluted atmospheric air, i.e., in the proximity of the ferro-metallurgical plants, showed signs of pulmonary pathology of a more profound type and in greater numbers than did the children residing in control sections 3 and 4, i.e., in localities where the atmospheric air was comparatively free from pollution by the discharges coming from the ferro-metallurgical plants. This is in conformity with M. S. Gol'dberg's findings of 1949-1952 and with the more recent findings of N. Ya. Yanysheva and K. L. Moskovskaya. M. S. Gol'dberg also established a correlation between residence duration in localities with polluted atmospheric air and intensity of pulmonary fibrosis.

No clear-cut correlation of this type could be deduced on the basis of results of the present investigation. This may be due to the fact that the present study covered children who lived within the confines of districts 1, 2, 3 and 4 over periods of not less than 3 years, and that the ferrous metallurgical plants located at points 1 and 2 had been working at full capacity only during the past 4 years, and as a consequence all examined children of the industrial districts 1 and 2 had been exposed to the effects of the atmospheric air pollution over equal periods of time. However, with respect to conditions within the plants this phase of the problem requires further study.

It became important to establish or to exclude the possibility that past infectious diseases among the children might have been responsible for some of the pathological roentgenological findings. Data presented in Table 3 show that frequency of occurrence of infectious diseases among the children of industrial section 2 and the control section 4 was practically the same among all the 4 groups per child, indicating that there was no correlation

TABLE 3.

| Point | Group I | II | III | IV | Average |
|---|---|---|---|---|---|
| 2 | 3.3 | 3.4 | 3 | 3.4 | 3.3 |
| 4 | 3.5 | 3.4 | 3.7 | - | 3.5 |

between the rate of pathologic pulmonary findings and past infectious diseases. Results of special laryngological examination given the children residing in the industrial section 2 and the control section 4 are listed in Table 4.

TABLE 4.

Diseases of the upper respiratory tract in relation to atmospheric air pollution.

| Types of diseases | Point 2 | Point 4 (control) |
|---|---|---|
| Chronic catarrhal rhinitis | 37 | 10 |
| Chronic hypertrophic rhinitis | 13 | 3 |
| Chronic atrophic rhinitis | 3 | 10 |
| Acute rhinitis | 3 | - |
| Chronic rhinopharyngitis | 7 | 7 |
| Chronic catarrhal pharyngitis | 6 | 1 |
| Chronic granular pharyngitis | 10 | - |
| Atrophic pharyngitis | - | 11 |
| Hypertrophic pharyngitis | - | 2 |
| Catarrhal tonsillitis | 33 | 5 |
| Hypertrophic tonsillitis | - | 3 |
| Tonsillar hypertrophy | - | 3 |
| Total of diseases | 112 | 55 |
| Total of examined children | 176 | 185 |
| Average of disease per child | 0.63 | 0.3 |

Data in Table 4 show that diseases of the upper respiratory tract among the examined school children residing in industrial section 2 were twice as numerous as among children residing in control section 4.

Anthropometric measurements showed a general normal physical development of all the tested school children, i.e., of all children residing in the 4 investigated sections or points, although the chest measurements and weight of the children living in industrial sections 1 and 2 were somewhat below the corresponding indexes of the children residing in control sections 3 and 4.

Conclusions.

1. Industrial discharges into the atmospheric air by ferro-metallurgical plants located in close proximity to residential areas may exert an unfavorable effect on health and on the sanitary living conditions of inhabitants over a 3 meter radius belt surrounding the production or processing plant.

2. The approved 1 meter wide sanitary clearance protection zone for metallurgical plants fails to secure the required sanitary conditions of residential areas located immediately beyond the 1 kilometer sanitary protection zone. It follows that the adopted scheme of sanitary clearance or protection zones should

be revised in the direction of appropriate widening to at least 2 kilometers insofar as ferro-metallurgical plants are concerned.

3. The amount of pollutants emitted into the atmospheric air should be reduced by the following means: a) thorough hermetization of technological processes accompanied by the emission of deleterious gases and dust; b) maximum recovery and utilization of industrial by- and waste-products; c) forbid the discharge into atmospheric air of blast furnace and other gases not purified prior to discharge; d) replace presently used hard fuel by gas fuel in all heat and power electric stations; e) electrify intra-plant means of transportation; f) increase the efficiency of the technical utilization of production complexes which emitted deleterious substances into the atmospheric air.

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## Effect of City Air Pollution on the Population's Health.

R. A. Babayants.

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Hygienic literature is replete with data concerning the effect of industrial air pollution on workers health. Many occupational diseases and industrial intoxications caused by dust and gaseous pollutions of the air in production premises have also been known for a long time. Industrial air pollution has reached considerable proportions. Therefore, plants and factories of the U.S.S.R. have been systematically installing modern sanitary-technical equipment for the elimination of dust from the air.

In comparison with industrial air, city air is polluted to a lesser degree and, therefore, its harmful effect on population's health attracted no special attention for a long time, and what is worse, authentic protests of sanitation

specialists and of western European workers against air pollution by industrial discharges during the last century were rejected as the result of investigations of some hygienists. Using primitive methods and tests, the investigating hygienists considered the dust and gas concentrations in the city air as neutral agents of the environment. Reports appeared in the hygienic literature which repudiated the opinions expressed about the harmful effects of city air pollutions. Such tolerant and, indeed, indifferent attitude of physicians towards city air pollution is strangely paradoxical. It is well known that natural atmospheric air containing oxygen "in statu nascendi", ozone admixtures and hydrogen peroxide, as well as negative ions, possessed oxidizing, sterilizing and health restoring properties, and constituted factors of importance in guarding the population's health against many widely spread diseases. It would be logical to consider as credible the opinion expressed regarding the possible harm caused to health by the spread of diseases and the worsening of sanitary living conditions in localities in which the air was polluted with dust and harmful gases.

The first investigation related to air pollution was conducted 50 years ago by the German hygienist Ascher. However, the inadequate number of Ascher's experiments and his statistical interpretations raised numerous justified objections. Ascher's attempt was followed by other authors whose attempts to establish a relation between city population mortality and air pollution failed for lack of scientifically verifiable results. In those days workers were exploited by the rising industrialists and morbidity and mortality rates were largely the results of low level living and work conditions. In comparison with such basic factors other environmental factors, including air pollution, were of comparatively minor significance in relation to rates of morbidity and mortality.

The first attempt to study the effect of community air pollution on the population's health was made in the U.S.S.R. in 1933 by V. P. Tsvetkov, R. A. Tsibul'skii and A. P. Sapozhnikov. X-rays of 19 children living near the Kashirskaya electric power station showed shadows in the lung films. The inadequate number of observations failed to provide a convincing basis for conclusions; but the method of approach to the problem of harmful air pollution effects was a basic one because of its objectivity. M. S. Gol'dberg used this method more extensively 15 years later in his study of the effect of mineral pollutants discharged by the same electric power station, on the health

of school children. After a preliminary examination Gol'dberg selected 285 school children, 8 - 13 years old, who were born and permanently resided in the vicinity of the station. X-ray examinations indicated no changes in the lungs of 41% of the children. Among the remaining 59% changes were seen at roots of the lungs in 24%, at the roots of lungs and in the lungs proper in 18%, and manifest changes in the roots and lung tissue in 17%. In 1939 the Leningrad Medical Institute of Sanitation and Hygiene made a study of the effect on the health of the surrounding population and their living conditions of air pollutants discharged by three large industrial plants. Residents were interrogated as the first step of the investigation. The answers contained complaints of indisposition, headaches, damage to house plants, early mortality of domestic animals, damage to trees in parks and gardens; signs of the latter were visible at a distance of 1000 m from the source of pollution.

The first extensive study of the effect of air pollution on the population's health was conducted on a cooperative basis in 1948 - 1949. The investigation began with a study of clinical histories of patients visiting several polyclinics serving the population of the area where air pollution was 2 - 3 times greater than in the peripheral control zone. The study was conducted simultaneously in three cities nearest to Leningrad: Kolpino, an industrial city, and Zelenogorsk and Pushkin, resort cities with practically identical air pollution. The number of cases studied offered a reliable volume of data which covered 10% of the Leningrad population. In the peripheral control zone the public residences and general living conditions of the population were lagging considerably behind those prevailing in the other air polluted regions. Despite that, the population of the latter areas requested medical

TABLE 1.

Average coefficients of population morbidity of air polluted Leningrad regions compared with those of the control region in 1948 - 1949.

| Disease | Polyclinic Number | | | |
|---|---|---|---|---|
| | 10 | 18 | 17 | 16 |
| Angina | 1.5 | 1.6 | 2.2 | 2.1 |
| Bronchitis | 4.0 | 3.5 | 2.3 | 2.5 |
| Pneumonia | 2.6 | 2.3 | - | 1.8 |
| Pleuritis | 4.5 | 2.5 | - | 3.3 |
| Tuberculosis | 8.1 | 1.4 | - | 1.7 |
| Diseases of the pharynx and tonsils | 4.2 | 2.1 | - | 2.2 |

help in regard to diseases of the lungs, pharynx and tonsils (Table 1) up to 8 times as frequently as did the control section.

A similar ratio was established between Kolpino and Zelenogorsk. A. L. Iorish determined a direct connection between street eye traumas and air aerosol concentration. Thus, when the air in the vicinity of polyclinic No. 9 was highly polluted (612 $g/m^2$ taken as 100%), the number of eye traumas amounted to 248 (also taken as 100%); and in localities with air pollution of 75 and 34%, eye traumas amounted to 70 and 34% correspondingly. Results yielded by the study of clinical histories ran roughly parallel with results of street eye trauma studies. K. Kiyanov used the question method in studying the effect of air pollution caused by emissions from the Syas'sk Cellulose-Paper Combine on the health of the population; his results showed that 25 - 81% of the near-by population complained of headaches, cough, shortness of breath, eye diseases, palpitation of the heart, fatigue, lack of appetite and sweating. Similar complaints coming from the population of the control settlement located at a considerable distance from the Combine, amounted to 6 - 38%, that is 2.5 to 5.0 times less frequently. Similar complaints came from 9% of the children of the control area and from 24 - 59% of the children residing in the vicinity of the industrial plants. Next, medically selected persons were divided into two groups: group 1 included persons exposed to the effect of air pollution; the other group served as a control. Results of this study indicated that changes in the upper respiratory tract, lungs, heart, digestive tract, eyes and oral cavity in the first group ranged between 34 and 56%, while in the control group the highest figure was 28%.

A comparison of population morbidity in the Syas'stroi settlement, the air of which was intensely polluted, and in Novaya Ladoga where the air was pure, indicated that the Syas'stroi population received more medical help than did the population of Novaya Ladoga: diseases of respiratory organs occurred twice as frequently; bronchitis and laryngotracheitis occurred 9 times as frequently; tuberculosis of the respiratory organs occurred 2.5 times as frequently; and other diseases 1.5 - 2.0 times as frequently. In this connection it should be mentioned that home and economic conditions of the Syas'stroi population were of a higher level than of the Novaya Ladoga population.

Results obtained in the study of the effect of air pollution on the health of children compelled special attention. In 1953, K. A. Moskovskaya conducted

a study of the pollution of air surrounding two schools in an industrial area and in a peripheral section with relatively pure air (Leningrad); simultaneously, films were made of the school children's chests. Results showed that suspended aerosol concentration was 3.5 times as high and $SO_2$, 25 times as high in the air of the industrial region. Correspondingly, changes in lungs of school children residing in the industrial zone occurred 5 times as frequently as among the children of the control area.

M. A. Pinigin attempted to coordinate 4-year morbidity data with the effect of the Lesogorskaya Viscose Plant discharges on the health of children. He, too, found increased morbidity among children living close to the plant, as compared with the morbidity of control groups living approximately one km away from the factory. Thus, catarrh of upper respiratory tract occurred twice as frequently, angina 1.5 times as frequently, and bronchitis 1.8 times as frequently, among the children living in the vicinity of the plant as among the control children. This study was followed up in a more thorough manner by Van Tszun-tsyuan. In this instance 4 schools were selected: No. 146, at the edge of the city, where the air was relatively pure; two other schools, Nos. 165 and 173, were located in the central industrial zone of Smol'ninsk at 500 - 1000 m from a group of 15 enterprises which intensely polluted the city air with sulfur dioxide and aerosols. The air was even more intensely polluted near the fourth school, No. 180, situated in the industrial Kalininsk zone, surrounded by many large plants.

The degree of air pollution surrounding these schools was investigated through a full year. Air samples were collected as follows: precipitating aerosols 72; dust 127; sulfur dioxide 132; and classroom air 47 samples. Results of these investigations indicated that the air surrounding the schools in the industrial zones was much more polluted than the air surrounding the school of the control area; with aerosol pollution being 3 times and $SO_2$ pollution 3 - 4 times as intense. Investigation of the effect of air pollution on the children's health included a study of the over-all living conditions of 2500 pupils from the 4 schools. Four-hundred and fifty-one children were selected who were of similar age and who resided in the given section for not less than 5 years, with living space of not less than 5 $m^2$ per member of family, same satisfactory housing conditions, no pulmonary patients in the family, annual vacation spent in the country, monthly income per each member

of the family not below 300 rubles. The state of health of the selected school children was studied from records of systematic examinations made by the school physicians over a period of 5 years and from X-ray films and fluorographic examinations; these were supplemented by examinations at the request of the investigators by the Institute's Department of Otolaryngology and Roentgenoscopy.

Table 2 indicates that morbidity rate among the school children in relation to air pollution was higher and more frequent in the schools located in polluted air areas than in the pure air control area. Average data indicated that grippe occurred 3 times, bronchitis 6 times, angina and catarrh of the upper respiratory tract 7 times, broncho-adenitis and pneumonia 10 times as frequently among the school children of the polluted air areas as among the school children of the control area. At the same time infectious disease morbidity not related to air pollution, such as measles, scarlet fever, diphtheria and rheumatism, was higher in the control zone.

T A B L E 2.

Percent of pulmonary and pharyngeal morbidity among school children in 1958 according to Van Tszun-tsyuan.

| Diseases | School number | | | |
|---|---|---|---|---|
| | 146 | 165 | 173 | 180 |
| Angina | 4 | 33 | 28 | 15 |
| The grippe | 18 | 43 | 33 | 29 |
| Catarrh of upper respiratory tract | 2 | 17 | 10 | 14 |
| Bronchitis | 4 | 10 | 13 | 10 |
| Pneumonia | 1 | 11 | 13 | 8 |
| Broncho-adenitis | 1 | 6 | 6 | 8 |
| Pleuritis | 0 | 2 | 3 | 2 |

T A B L E 3.

Percent of rhinitis among school children in 1958, according to Van Tszun-tsyuan.

| School number | Simple | Hypertonic | Atrophic |
|---|---|---|---|
| 146 (control) | 9 | 2 | 4 |
| 165 | 2 | 3 | 6 |
| 173 | 3 | 6 | 10 |
| 180 | 1 | 7 | 16 |

Results of the otolaryngological examination of school children (Table 3) showed that hypertrophic and atrophic changes of the upper respiratory tract occurred 3 - 4 times as frequently among the school children residing in the polluted air area as among the school children of the control area; the common cold (rhinitis occurred 3 - 4 times as frequently among the children of the control area due to unbalanced conditions of residential heating. X-ray and fluorographic data demonstrated (Fig. 1) that pulmonary changes in the roots and tissues of the lungs occurred approximately four times as frequently among the school children in the polluted air area as among the children of the control area. The effect of city air pollution on

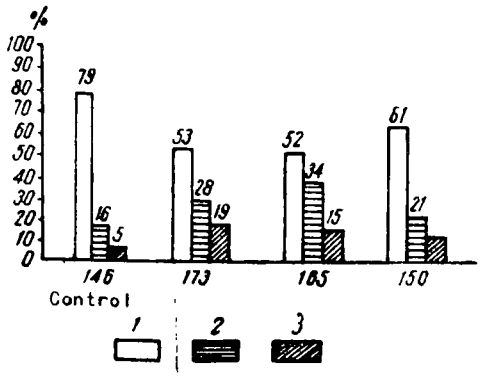


Fig. 1. Pulmonary condition of school children of the schools under study as shown by roentgenoscopy and fluoroscopy in percent in 1958, according to Van Tszun-tsyuan.
1 - Normal; 2 - changes in roots of lungs; 3 - changes in lung roots and tissues.

the population's health was investigated by many U.S.S.R. scientists during the past 5 years. The local Baku investigation conducted by M. M. Efendi-Zade and D. M. Steingrad in 1955 deserves first mention. Results of this investigation disclosed a clear-cut relationship between the occurrence of bronchitis and laryngotracheitis and air pollution with aerosols. D. N. Kalyuzhny's investigations in 1954 - 1955 in the Ukraine yielded similar results. Diseases of the upper respiratory tract in percent of total morbidity ranged between 40 - 71% among people living 500 - 1500 m away from a cement plant; it never exceeded 26% among persons living beyond the 1500 m zone. Results also indicated that complaints of cough, headaches, nausea, worsening of sanitary living conditions, came in considerably greater percentages from persons living within the 0.5 km zone from the plant than from those living 2 km from the plant. In 1958, N. Ya. Yanysheva published the results of her study of population morbidity in an industrial settlement with highly polluted air (up to 15 $mg/m^3$ aerosols). Her data showed that rhinitis, rhinolaryngopharyngitis, tonsillitis and adenitis were found in 60% of the examinees with 18% atrophic forms. These diseases occurred only among 17% of the control persons with no atrophic conditions.

Next of importance in this study was the effect of the particular type of pollution present in the air on the population's health. In this connection particular consideration should be accorded data accumulated on localities the air of which was polluted with sulfur compounds, CO and fluorine. The effect on the organism of city air polluted with carbon monoxide was studied in Leningrad by A. S. Lykova in 1953 and A. F. Sorokina in 1957. In the first investigation 650 air samples were collected at designated points of Leningrad streets and plazas, where the CO pollution was caused by motorized traffic. It was shown elsewhere that the CO concentration in the street air of Leningrad, Moscow, Khar'kov, Chelyabinsk, Saratov, L'vov, Makeevka and Rustavi reached an average of 30, and a maximum of 200 - 360 $mg/m^3$. These concentrations were

considerably below the concentration of this gas in the air of 20 West European and U.S.A. cities, where the CO concentration ranged between 180 - 750 $mg/m^3$ Nevertheless, carbon monoxide concentrations in the air of Leningrad and other U.S.S.R. cities were approaching toxic levels and were considerably higher than the maximum permissible concentrations of CO in the air of sanitary protection zones. Investigation of the effect of these carbon monoxide concentrations on 135 traffic directors, showed that the latter were subject to a very noticeable carbon monoxide intoxication.

Data in Table 4 indicate that specific complaints connected with carbon monoxide intoxication and carboxyhemoglobin in the blood of the examined was as follows: when the CO concentration in places of heavy traffic averaged 25 $mg/m^3$, complaints amounted to 68%, while COHb in the blood averaged 11%; in places with medium traffic, where CO concentration averaged 15 $mg/m^3$, complaints amounted correspondingly to 42%, and COHb averaged 8%; while in places with light traffic, where CO concentration averaged 5.7 $mg/m^3$, complaints amounted

T A B L E 4.

Blood carboxyhemoglobin and complaints of traffic directors in relation to CO air pollution in 1953, according to A. S. Lykova.

| Air sampling points | $mg/m^3$ of CO | | | COHb in percent | | Percent of persons with complaints |
|---|---|---|---|---|---|---|
| | Average | Maximal | Minimal | Average | Maximal | |
| Heavy auto traffic | 25.3 | 128.0 | 4.1 | 10.9 | 22.1 | 68.0 |
| Average auto traffic | 14.9 | 54.0 | 3.2 | 7.9 | 14.2 | 42.0 |
| Light auto traffic | 5.7 | 19.0 | 0.2 | 4.2 | 8.06 | 19.0 |

T A B L E 5.

Average magnitude of sensory, optical and motor chronaxy in σ in traffic directors stationed at highest CO-polluted main highways in relation to work record.

| Work record | Sensory chronaxy | | Optical chronaxy | Motor chronaxy | |
|---|---|---|---|---|---|
| | Forearm flexor | Forearm extensor | | Forearm flexor | Forearm extensor |
| 1-2 | 0.33 | 0.31 | 1.6 | 0.31 | 0.67 |
| 3-8 | 0.36 | 0.52 | 1.65 | 0.38 | 0.76 |
| 10 | 0.45 | 0.65 | 2.40 | 0.50 | 0.93 |
| Control | 0.23 | 0.26 | 1.50 | 0.26 | 0.69 |

to only 19%, and the COHb in the blood averaged 4%. The effect of these concentrations on the entire organism of the traffic directing personnel according to the data of sensory, optical and motor chronaxy, are indicated in Table 5; values of the corre-

sponding indexes rose by 50 - 100%. In 1956 S. F. Sorokina investigated the CO concentration in the air of 160 rooms in 42 gas-equipped apartments by analyzing 800 air samples. Carbon monoxide concentrations in the air of these rooms ranged between 4 - 214 $mg/m^3$ and in the air of the control non-gas-equipped apartments the concentration did not exceed 6.5 $mg/m^3$. Detailed investigation and questioning of 111 housewives living in these apartments showed that 80 complained of carbon monoxide intoxication which was distributed as follows: headaches 41%, dizziness and tinnitus 26%, pain in the heart region 13.5%, nausea and vomiting 11%, and other complaints 8.5%. The COHb concentration in the blood of tenants of gas-equipped apartments reached 27% as compared with 1.8 - 5.5% of the controls.

N. N. Skvortsova made a study of CO concentrations in the air of several areas in the vicinity of 2 metallurgical plants, consisting of 35 investigations with 157 determinations of CO concentrations in the air of near-by dwellings. Average CO concentrations in the air surrounding the plants within a radius of 1200 m ranged between 53 - 113, with 190 $mg/m^3$ as the maximum concentration. The CO concentration within the zone of 500 m radius ranged between 21 - 37 $mg/m^3$ in the air of dwellings, or 3.5 - 6.0 times above the permissible concentration limit for this gas in the sanitary protection zone. Children living near the plants manifested symptoms of erythrocytosis. In 28% of the children the erythrocyte count was as high as 6,000,000. In the 50 and 100 m radius zones no carboxyhemoglobin was found in the blood of 62% of the tested children. In the remaining 38% the COHb concentration in the blood ranged between trace and 24%. Maximum COHb concentration in the controls was 7%.

Effect of small concentrations of sulfur dioxide on the organism was studied experimentally by N. V. Volkova in 1955. She used the chronic exposure method of intoxication and its effect on the conditioned reflex reaction as the indicator. Results listed in Fig. 2 indicated that the latent period of the conditioned motor-nutritional reflex response was delayed considerably by exposure to 20 $mg/m^3$ of $SO_2$; it was still affected but to a lesser degree by exposure to 3 - 7 $mg/m^3$; exposure to 2.5 $mg/m^3$ had practically no effect. Exposure of animals to low concentrations of $SO_2$ markedly affected the animals' respiration.

A. M. Yusupov investigated the effect of air polluted with discharges from the Volkhovo aluminum plant. His results demonstrated that aerosols, $SO_2$

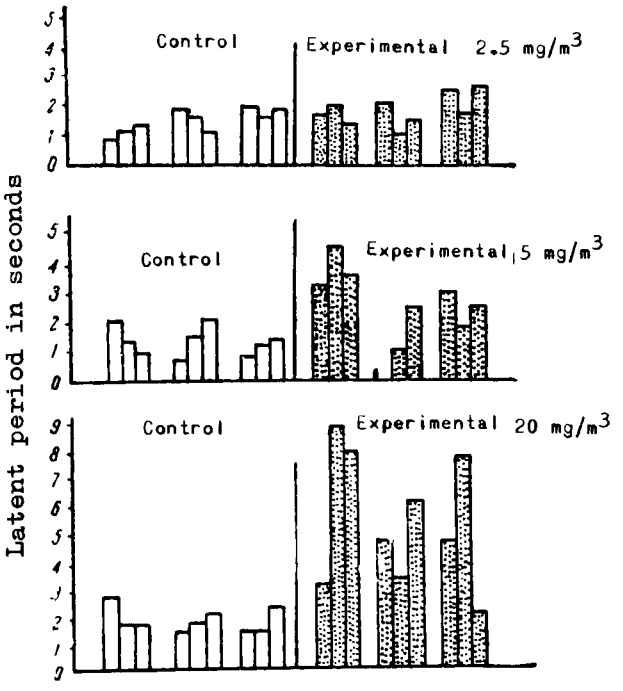


Fig. 2. $SO_2$ effect on conditioned nutrition reflex, according to Volkova, 1953.

and fluorine compounds unfavorably affected the morbidity rate of the Volkhovo population in relation to the previously mentioned specific diseases, even under more favorable general living conditions. Results of observations also showed that frequency of mottled teeth occurrence among the children increased as their residences came closer to the plant. Among 155 examined school children living within the 500 m radius around the plant (Table 6), mottled dental enamel was found in 25%, while among those living 2000 m from the plant mottled dental enamel was seen in only 17 - 18%.

TABLE 6.

Mottled teeth in 155 school children living in the factory region, according to A. M. Yusupova, 1954.

| Meters from plant | mg/m$^3$ of fluorine in the air | Number of children examined | Number of children with mottled teeth |
|---|---|---|---|
| Up to 500 | 0.4 | 34 | 8 |
| Up to 1,000 | 0.2 | 81 | 16 |
| Up to 2,000 | 0.015 | 40 | 6 |

Experimental study of the effect of fluorine polluted air on the living organism was conducted by exposing rats to the air of indoor working premises and to the outdoor air at 125 and 3000 m from the plant. Results showed that fluorine content in animals' bones rose parallel to the increase of fluorine concentration in the air; the same was true of the deterioration of dental enamel and of teeth in general.

Studies extending over the past 40 - 50 years clearly indicated that morbidity due to lung cancer rose considerably. Many scientists hold the opinion that inhalation of polluted air was the cause of cancer. They maintain that city air dust contained cancerogenic substances, such as 3,4-benzpyrene. The latter enter the atmosphere with discharges from factory smokestacks, with exhaust gases from automobiles, with products of incomplete fuel combustion, and

with dust from asphalt and tar-paved roads and streets. L. S. Serebryannikov in his thesis and F. G. Uglov in his recently published monograph presented interesting statistical data which lead to the assumption that increase in lung cancer morbidity and mortality paralleled the increase in pollution of atmospheric air of large cities. Table 7 compiled by F. G. Uglov shows that lung cancer morbidity in the cities has been increasing during the past decades at a steadily rising rate and that it constituted approximately 12% of all cancer types.

TABLE 7.

Lung cancers in relation to all cancers.

| City | Year | Percent | Authors |
|---|---|---|---|
| Moscow..... | 1909 | 2.2 | A. V. Govorov |
| Moscow..... | 1946 | 14.5 | P. P. Dvizhkov |
| Petersburg..... | 1880 - 1909 | 3.04 | A. V. Govorov |
| Leningrad..... | 1932 | 12.24 | N. N. Anichkov, S. S. Veil |
| Rostov-on-Don..... | 1901 - 1920 | 2.54 | S. M. Derizhanov |
| Rostov-on-Don..... | 1921 - 1929 | 16.9 | S. M. Derizhanov |
| Kursk..... | 1927 - 1936 | 11.22 | N. S. Kozlov |
| Kursk..... | 1937 - 1938 | 14.65 | M. V. Mokshina |
| Tbilisi 1/..... | 1923 - 1946 | 12.8 | A. N. Sharashidze |
| Khabarovsk..... | 1938 - 1947 | 12.8 | A. A. Zelenko |
| Petrozavodsk..... | 1950 - 1954 | 11.5 | V. A. Samsonov |

1/ Formerly Tiflis.

Studies of L. S. Serebryannikov and of F. G. Uglov and their conclusions bring into sharp focus the importance of improving the sanitary conditions of the environment, and in this instance, the sanitary condition of the atmospheric and indoor air. Data of the American Cancer Society indicate that during the period of 1930 - 1950 lung cancer in the U.S.A. rose from the last place in 1930 (less than 4 per 100,000 persons) to the first place (20 per 100,000 persons), which is a five-fold rise. In this connection it should be pointed out that during the same 20 years stomach and skin cancers (per 100,000 persons) decreased, cancer of prostate gland and liver increased only slightly, and T.B., the grippe and pneumonia morbidity declined by 50 - 80%. Lung cancer mortality in cities of highly polluted air is greater than in localities having relatively pure air; for example, it is 33 per 100,000 persons in Vienna, 18.4 per 100,000 in Austria's small towns and 10 per 100,000 in that country's resort places.

Evaluating lung cancer mortality in London as 100, lung cancer mortality in localities with higher air pollution will be: 162 for Liverpool, 233 for the Ruhr, while in rural agricultural regions it will be 89.

The steadily increasing use of radioactive substances in practical medicine, in scientific research and in different fields of national economy presents a potential danger of environmental pollution, particularly of the atmospheric air, with these substances. Lowering the standards of specific prophylactic protective sanitation will undoubtedly lead to pollution of the air with dangerous ionizing substances. Results of past experiments indicated that under the influence of ionizing radiation unusual biochemical and biophysical changes take place in many organs, systems, tissues and cells of the organism which inhibit enzyme activity, induce degenerative phenomena, disorganize the immunological mechanism rendering the organism more susceptible to infection; parallel with this the body elimination system will break down so that the organism will become poisoned by the accumulation of tissue and organ decomposition products. As the result of air polluted with radioactive substances, disturbances may originate in the neuro-regulation processes, and the normally regulated functioning of the organism may come to a stop.

The discussion of the effect of air pollution, in particular of outdoor air pollution was limited up to this point to its direct influence on man as an individual. It must be borne in mind, however, that air pollution has many other aspects of equal importance to man: destruction of plant life of economic, decorative and general aesthetic value; corrosion of articles of utility and of art; shortening the life of farm and pet animals; pollution of soil and of water basins. These are only a few of the air pollution phases which create problems requiring immediate and rational solutions.

The above discussed results of air pollution investigations, the effects of sporadically occurring "toxic fogs" or "smogs" and the steadily increasing $SO_2$ concentration in the air leave no doubt that pollution of the atmospheric air of cities is a factor most harmful to the health of the present day city population. Solution of the air pollution problem is the concern of the entire citizenry young and old.

In 1949 the Council of U.S.S.R. Ministers issued a decree entitled "Control Measures Against Atmospheric Air Pollution and Improvement of Sanitary-Hygienic Conditions in Populated Areas". This decree required all enterprises

to purify the waste discharges before their emission into the air via smoke-stacks. Since then thousands of purifying installations were set up for the removal of ashes and dust. According to this decree all sanitary organs of the U.S.S.R. must carry on an incessant fight against all types of air pollution to insure clean air in the populated areas. Health agencies, factory and plant administrators, power station operators and all others concerned must strive towards further practical realization of the complex of preventive sanitation as applied to the elimination of air pollution in accordance with modern hygienic standards.

The complex for the improvement of sanitary air protection should consist of the following: 1) increase the use of smokeless fuel; gasification of residences and public buildings using only pure natural gas and closed combustion systems. Other types of gas, containing large quantities of carbon monoxide, sulfur and other harmful admixtures should be used only in furnaces of factories, plants and electric power stations; 2) changes and improvements in all technological processes of production leading to complete recovery and utilization of waste products; 3) study of effects and determination of maximum permissible concentrations of aerosols and harmful gases in discharged smoke, ventilation exhaust air and other discharges emitted into the atmospheric air; 4) further development of standards of maximum permissible concentrations of harmful air pollutants in sanitary protection zones, when occurring singly or in combination; 5) continuous strict sanitary and technical supervision of all existing and potential sources of air pollution and effecting all sanitary-technical measures for the elimination and liquidation of air pollutions in populated areas.

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Hygienic Properties of Murmansk Ultraviolet Radiation.

N. M. Kaikov.

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The northern regions of the U.S.S.R. are being developed rapidly economically and culturally. There is no longer a desert zone at the polar circle, but a region with a population numbering in the thousands. Therefore, medical and hygienic workers are greatly interested in the living conditions of those who inhabit the polar circle.

The problem of ultraviolet radiation adequacy in the polar regions is a very acute one, in addition to factors of outer atmosphere, which affect men under ordinary conditions such as humidity, temperature, precipitation, wind, etc., there are also specific factors, not encountered in other regions of the U.S.S.R. Such factors as the polar night and the polar day are phenomena of high intensity; they must be dealt with effectively hygienically and medically.

This author's evaluation of the climatic conditions of the north deals only with data related to the number of sun ray hours. Up to recent years there has been no quantitative and qualitative rating of the solar radiation. At 69 - 70° the continuous polar day lasts 55 - 60 days; however, the possibility of using solar radiation during that period is not great, since the sun is low even during mid-day; in the summer many days are foggy, cloudy and windy, and the climatic conditions change sharply. During the polar night, which is just as long as the day, the inhabitants of the polar areas are deprived not only of ultraviolet radiation, but also of natural light.

The author began his observations in 1953 and continued through 1955. The photochemical oxalic acid method, modified by A. N. Boiko and Z. N. Kulichkov was used in the study. In this case the opportunity presented itself to study the effect of ultraviolet rays with a wave length of 435 to 290 megacycles long; that is, practically the entire ultraviolet spectrum which passes through the thick atmosphere of the earth and meets its surface. Observations were carried on around the clock regardless of weather and temperature conditions. The test tube with the solution was heated when necessary.

Data gathered during the 3 years observation are listed in Table 1. Information gathered on climatic conditions around Murmansk during the observation period is shown in the same table.

TABLE 1.

Combined annual observation results of ultraviolet radiation and climatic characteristics.

| Month | Percent of yearly hours of sunshine | | | $mg/cm^2$/month of decomposed oxalic acid | | | Percent of yearly oxalic acid decomposition | | | Erythematous doses per month | | | Maximal height of sun at 69° NL in degrees | Clear days per month | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1953 | 1954 | 1955 | 1953 | 1954 | 1955 | 1953 | 1954 | 1955 | 1953 | 1954 | 1955 | | 1953 | 1954 | 1955 |
| January | 0.15 | | 0.12 | | - | - | | - | - | - | | | 3.2 | 0 | 2 | 0 |
| February | 2.07 | 5.76 | 2.6 | | 81.86 | - | | 2.58 | - | - | 20.5 | | 12.7 | 2 | 6 | 3 |
| March | 8.7 | 10.04 | 13.8 | | 199.34 | - | - | 6.29 | - | | 49.8 | | 24.9 | 0 | 0 | 4 |
| April | 11.6 | 20 | 17.8 | 323.16 | 481.98 | 371.2 | 13.5 | 15.1 | 17.24 | 80.8 | 120.5 | 92.8 | 35.4 | 1 | 1 | 3 |
| May | 14 | 12 | 13.7 | 381.23 | 536.9 | 356.83 | 15.9 | 15.9 | 16.5 | 95.2 | 134.2 | 88.5 | 42.8 | 0 | 1 | 1 |
| June | 26 | 16.1 | 11.7 | 569.3 | 409.05 | 442.05 | 23.8 | 12.9 | 20.3 | 142.5 | 102.2 | 110.5 | 44.3 | 5 | 0 | 0 |
| July | 16.26 | 21.9 | 16.5 | 506.65 | 855.27 | 494.37 | 21.2 | 27.18 | 22.7 | 126.7 | 213.7 | 123.7 | 39.5 | 2 | 5 | 0 |
| August | 9.06 | 8.82 | 15.8 | 339.08 | 411.9 | 319.8 | 14.2 | 13 | 14.7 | 84.7 | 103 | 80 | 29.9 | 2 | 1 | 3 |
| September | 7.8 | 4.08 | 4.9 | 196.31 | 123.65 | 123.26 | 8.2 | 3.9 | 5.66 | 49.2 | 31 | 31 | 18.6 | 1 | 0 | 0 |
| October | 4.29 | 1.3 | 2.86 | 75.82 | 68.31 | 65.11 | 3.2 | 2.15 | 2.9 | 19 | 17 | 16.3 | 7.2 | 3 | 1 | 0 |
| November | 0.07 | - | | - | - | | - | - | | | | - | 0.9 | 0 | 2 | 0 |
| December | - | - | - | - | - | - | - | - | - | - | | - | | 1 | 0 | 0 |

Analysis of the data indicated that the yearly ultraviolet radiation dispersion in Murmansk varied greatly. Of the total ultraviolet rays emitted during the period of February to September, 60% was emitted during May to July, representing 60 - 65% of the total number of annual solar radiation hours. Maximum exposure intensity occurred in 1953 in June, and in 1954 - 1955 in July, coincidental with the maximum number of sunshine hours.

Conversion of the decomposed oxalic acid into equivalents of erythematous doses (amount of ultraviolet rays which decompose 3.7 - 4.1 $mg/cm^2$ of oxalic acid were regarded as equivalent to one erythematous dose) indicated that during the months of maximum illumination the ultraviolet radiation equalled 123 - 213 erythematous doses per month, or 4 erythematous doses per day. It is considered that the least amount of ultraviolet radiation which a man must be exposed to in order to prevent "light starvation" equals 1/8 erythermatous dose. Consequently, the necessary "light starvation" prophylactic effect can be obtained under Murmansk conditions by exposure to less than the total ultraviolet radiation.

Comparing the data here presented with the data of other authors (N. F. Galanin, Sviderskaya, Z. N. Kulichkova, G. S. Yatsula) (Table 2), it appeared that the annual amount of erythematous doses in Murmansk was considerable. The data in Table 2 appear paradoxical. Actually 1954 was more favorable with regard to the amount of ultraviolet radiation in Murmansk than in Leningrad, and very

TABLE 2.

A comparison of Murmansk, Leningrad and Kiev ultraviolet radiation.

| Observation point | Year observed | Total of decomposed oxalic acid | Erythematous doses per year |
|---|---|---|---|
| Murmansk | 1953 | 2391.4 | 598.1 |
| Murmansk | 1954 | 3168.3 | 791.9 |
| Murmansk | 1955 | 2177.6 | 542.8 |
| Leningrad | 1945-1948 and 1953 (average) | 2529 | 646 |
| Kiev | 1952 | 3645 | 911 |

close to that of Kiev. On the basis of the above data one might suppose that during the northerly summer months we would encounter no "light starvation" cases. Actually, this was not so, probably due to the northern summer round-the-clock radiation. Ultraviolet radiation can be utilized in the polar region much the same as in the south during the waking hours.

During the severe polar months precipitation lasts 10 - 20 days each month, the wind velocity reaches 1 - 6 m/sec., average monthly temperature does not go above 13°, cloudiness reaches 4 - 9 balls and there are only 10 - 20 clear days during the whole year; the inhabitants wear closely woven, light colored, impermeable clothing, and practically no ultraviolet rays can reach them according to N. F. Galanin and D. M. Tyukov. As a result of all this, polar region population is experiencing a lack of ultraviolet radiation throughout the year, despite apparently favorable ultraviolet rays conditions during the summer months.

However, "light starvation" can be prevented by properly utilizing what little ultraviolet radiation might be available. During the summer months children should be kept out in the open in all kinds of weather. During the winter months, that is, during the months of December to March, children should be exposed for calculated periods of time to the effect of artificially created ultraviolet rays.

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# Vitamin C in the Organism in Connection with Atmospheric Pollution by Discharges from Synthetic Chloroprene Rubber Manufacture.

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Synthetic chloroprene rubber, widely used in different departments of the domestic economy, is synthesized from acetylene prepared from calcium carbide in plants investigated by this author. Recently acetylene has been obtained from natural gas. Acetylene was converted to monovinylacetylene by dimerization and monovinylacetylene was converted to chloroprene by hydrochloridation and isomerization. The latter was then polymerized and converted into a clear plastic mass of rubber. Many harmful substances are formed at different stages of this manufacturing process which are discharged into the atmospheric air by the ventilation systems and also by the so-called unorganized routes; among such substances are monovinylacetylene, divinylacetylene, tetrameracetylene, chloroprene (2-chlorobutadiene-1,3), dichlorides (dichlorobutene), dimers, and chloroprene polymers, acetylene, and so forth. They find their way into the air as a result of imperfect hermetization of equipment employed in loading and unloading of the raw materials and in the production and processing of the rubber latex, etc. The atmospheric air is also polluted by discharges from out-plant departments, such as the steam boiler room, the manufacture of calcium carbide, chlorine, hydrogen chloride, etc. Such discharges are rich in chlorine, hydrogen chloride, carbide, coal dust, lime dust, soot, carbon monoxide, and $SO_2$. The dust contains compounds of calcium, iron, sulfur, phosphorus, aluminum, arsenic, silicon, etc.

Average single chloroprene concentration in the air was 8.9 mg/m$^3$ 250 m from the plant; 3.3 mg/m$^3$ at 500 m, 6.4 mg/m$^3$ at 1,000 m, and 4.8 mg/m$^3$ at 2,000 m from the plant; average daily concentrations were correspondingly 1.87, 1.94, 1.04, and 0.62 mg/m$^3$ (A. V. Mnatsakanyan, 1955). Prolonged experimental exposure to chloroprene concentrations of 0.3 - 8 mg/li produced a decrease in vitamin C content of the organs, tissues and blood of white rats, guinea pigs, rabbits and dogs. Workers engaged in the manufacture of chloroprene rubber for a long time also manifested a lowered vitamin C content in the organism and particularly in the blood (G. I. Mirzabekyan, V. G. Mkhitaryan, and others).

Functional liver disorders caused by chloroprene intoxication resulted in disturbed ascorbic acid metabolism, as was shown by V. M. Avakyan, Ye. I. Gasparyan, et al., V. Vel'kovich, N. O. Avetisyan, A. M. Troitskaya-Andreyeva, M. K. Khachatryan, and T. A. Asmangulyan, V. G. Ettingen, and others. Chloroprene oxidized vitamin C directly forming unstable peroxides which oxidized many vital compounds (V. G. Mkhitaryan). Therefore, an investigation was made of the population residing in the vicinity of a plant manufacturing chloroprene rubber; the purpose of the investigation was to determine the degree of possible vitamin C deficiency among the human and animal populations, and use it as an index of the unfavorable effects of the plant's discharges on the health of residents and animals.

Domestic cats were taken from dwellings located within 2 km from the plant, brought to the laboratory and sacrificed, immediately dissected, and the organs, especially the liver, spleen, kidneys and heart quickly removed and examined. Specimens were washed free of blood and tested for ascorbic acid content by V. S. Asatian's method. A similar study was made with animals of a control group obtained from a region outside the zone of industrial discharge effects. Ascorbic acid was extracted from the thoroughly ground tissues, using a mixture of equal volumes of 8% metaphosphoric and 16% trichloracetic acid, followed by 3 times repeated extraction with 5% acetic acid. The extract solution was then titrated with a solution of dichlorophenolindophenol. Results are listed in Table 1.

TABLE 1.

Mg% of vitamin C in organs of cats.

| Index | Region | Organs | | | |
|---|---|---|---|---|---|
| | | Spleen | Liver | Kidneys | Heart |
| Averages of 7 cats | Control group | 50.7 | 30.2 | 18.8 | 8.3 |
| Fluctuation limits | Control group | 36.4-60 | 19.8-34.9 | 14-27 | 4.4-11 |
| Averages of 9 cats | Effect of plant discharges | 39.1 | 22.3 | 15 | 7.3 |
| Fluctuation limits | Ditto | 30.6-56.3 | 15.4-28 | 11-18.8 | 6.2-9.1 |
| Average deficiency in percent in relation to control | Ditto | 22.9 | 26.2 | 20 | 12 |

A comparison of averages showed that the ascorbic acid content of all organs under study was considerably lower in animals exposed 1 - 6 years to the air polluted by the chloroprene synthetic rubber discharges. The possibility that vitamin C deficiency might also prevail among those residing in the vicinity of the plant was investigated. For this purpose children of a kindergarten located at 500 m from the plant who lived within a 2 km radius around the plant were examined medically. The control group consisted of children of another kindergarten, located outside the effects of the industrial discharges. Diets in the 2 kindergartens were practically identical as to caloric values and vitamin C content (25 - 45 mg).

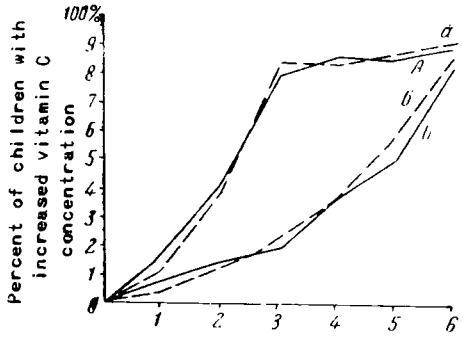
Vitamin C deficiency can be detected in the organism in the following ways: 1) by determining ascorbic acid concentration in the blood; and 2) by the rate of ascorbic acid excretion via the urine after the organism has been saturated with vitamin C. The latter procedure was employed in this investigation, using the method developed by I. I. Matusis and checked by V. V. Yefremov, G. G. Nikogosyan, S. O. Badalyan, and others. In accordance with the procedure, control curves of urinary vitamin C excretion were plotted over periods of 3 - 4 days; the children were then administered 300 mg of ascorbic acid orally and its urinary secretion rate plotted for periods of 4 and 7 hours. Children having no vitamin C deficiency eliminated 14 - 15 mg% of the vitamin with the 2 urinary portions. If ascorbic acid concentration was below this level, the child was administered the same vitamin saturation dose each day, with subsequent analysis of the urine, until the 14 - 15 mg% excretion level was reached. Absence of the 14 - 15 mg% urinary excretion level during the initial testing period was regarded as symptomatic of vitamin C deficiency in the organism. Under observation were 151 children, 48 belonging to the control group. Ascorbic acid content of the urine was determined on 3 successive days before administering the saturation dose and for 6 days following. Determination was made by titration with dichlorophenolindophenol. Results are presented in Table 2.

Data in Table 2, and the curves, show that children of both groups manifested a more or less pronounced vitamin C deficiency in the spring. Vitamin C deficiency was considerably more pronounced in children who lived in close proximity of the synthetic rubber plant. Percentage of children manifesting a rise in the urinary ascorbic acid secretion of 14 - 15 mg% or more after 3

TABLE 2.

Percent of children with increased rate of urinary ascorbic acid elimination of 14 - 15 mg% or higher, following supplemental administration of 300 mg of vitamin C during the spring season.

| Children residing | Children's age in years | Number of children | First day After 4 hours | First day After 7 hours | Third day After 4 hours | Third day After 7 hours | Fifth day After 4 hours | Fifth day After 7 hours | Sixth day After 4 hours | Sixth day After 7 hours |
|---|---|---|---|---|---|---|---|---|---|---|
| Within a 2 km | 4 | 31 | 9.7 | 9.7 | 25.8 | 25.8 | 64.5 | 71 | 96.7 | 96.7 |
| radius around | 5 | 33 | 9 | 6 | 24.2 | 27.3 | 48.5 | 54.5 | 90.9 | 94 |
| the synthetic | 6 | 25 | 8 | 4 | 16 | 16 | 44 | 60 | 80 | 84 |
| rubber plant | 7 | 14 | 0 | 0 | 14.4 | 14.4 | 42.8 | 48.8 | 64.4 | 71.4 |
| Average | | | 6.7 | 4.9 | 20.1 | 20.9 | 49.9 | 58.8 | 83 | 86.5 |
| Control group | 4-7 | 48 | 16.6 | 12.5 | 80.2 | 83.3 | 85.4 | 87.5 | 89.6 | 91.7 |




Days of supplemental intake of 300 mg of vitamin C per day.

Curves of daily increase in urinary vitamin C elimination.
Aa - Children of control group; A - 4 hours after administration; a - 7 hours after administration; Bb - children residing in the plant region; B - 4 hours after administration; b - 7 hours after administration.

days vitamin C administration was only 20.1 - 20.9 among those who lived in the vicinity of the plant and 80.2 - 83.3 among children of the control group. On the fourth day of vitamin C saturation, the percentages of children with urinary vitamin C elimination of 14 - 15 mg% increased to 37.1 - 37.5 and 83.3 - 85.4 respectively; on the fifth day to 49.9 - 58.8 and 85.4 - 87.5; and on the sixth day to 83 - 86.5 and 89.6 - 91.7%. Results indicate that children who lived within a radius of 2 km from the plant and attended the kindergarten located at 500 m from the source of pollution manifested a definite vitamin C deficiency, which was corrected gradually by daily intake of 300 mg of ascorbic acid. Vitamin C deficiency was more pronounced in children 6 - 7 years old than in children 4 - 5 years old. Aside from other causes this can be attributed to the fact that the older children had been exposed to the action of the polluted air for a longer time. In the autumn and summer the same children manifested no symptoms of vitamin C deficiency; this was a normal finding for the Erevan region and was the result of vegetable and fruit availability and also of the fact that the children were sent to camp for 2 months.

As an immediate measure for the correction of the ascorbic acid deficiency among children residing in the vicinity of a chloroprene rubber plant, it is recommended that during the winter-spring months the children's ration be supplemented by 100 mg of vitamin C daily. This is 2 to 2.5 times the amount proposed by G. G. Nikogosyan and S. O. Badalyan as the optimum ascorbic acid intake (40 - 45 mg per day) for children of pre-school age under Erevan conditions.

Volume discharge by the synthetic chloroprene rubber plant into the atmospheric air should be reduced and purifying devices should be installed for the removal of unsaturated chlorinated hydrocarbons from the exhaust gases emitted by the ventilation system.

The 500 m wide sanitary-protection zone provided for in Statue N 101-54 for the synthetic rubber industry must be regarded as insufficient and should be increased to 900 - 1000 m.

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## Effect of Non-Occupational Factors on the Course of Carbon Bisulfide Poisoning.

B. E. Saf'yan.

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Carbon bisulfide is the most important harmful industrial substance discharged into the air by synthetic artificial fiber plants; its concentration in 1956 - 1958 was 2 - 3 times in excess of the permissible maximum. In addition to carbon bisulfide, some plant departments also emit low concentrations of

hydrogen sulfide. Such air pollution becomes aggravated by high humidity, unfavorable temperature conditions, and evaporation of acids and bases. Examination of persons having chronic carbon bisulfide poisoning convinced the present author that the course of intoxication and its outcome depended not only on the presence of so-called unfavorable industrial or occupational factors, but on other factors as well. Practically no references were found in the literature on the significance of non-occupational factors in the development of chronic intoxication by industrial poisons. There was only general mention of such factors, and yet such knowledge is of unquestionable importance not only to investigators, but also to practicing physicians for a better understanding of individual sensitivity and of reasons why intoxications caused by industrial conditions followed different courses of development. In a dissertation by I. D. Makulova, entitled "Dynamic Observations on the Course and Long-Range Sequelae of Several Kinds of Industrial Intoxication", mention was made of the fact that intoxication was aggravated by contact with other toxic substances and by the fact that the patient had dystrophy or physical and mental traumas in the past. Intoxication follows a graver course in women and especially in young women. Delpech expressed the opinion that thin, nervous persons, women and youngsters manifested greatest predisposition to carbon bisulfide poisoning. Zangger showed that alcohol created susceptibility to carbon bisulfide poisoning.

Seventy persons with chronic carbon bisulfide intoxication, or suspected of having same, came under clinical observation in the synthetic fiber plant during 1956 - 1958. Most of them were women (66) 26 to 50 years of age, 31 of whom were 31 years old; 19 had work records of 5 years, the others of more than 5 years. On the basis of the clinical picture and the gravity of the chronic carbon bisulfide intoxication the workers under observation were divided into 2 groups: group 1 included those having pronounced and lasting forms of chronic carbon bisulfide intoxication; to group 2 belonged those having initial forms of chronic carbon bisulfide intoxication and those suspected of having carbon bisulfide poisoning. Each group consisted of 35 individuals of approximately same numbers of men and women of equivalent ages and work records. Most cases were examined and diagnosed by specialists of the Leningrad Institute of Labor Hygiene and Occupational Diseases. Diagnoses were made on a differential basis as follows: vegeto-asthenic syndrome, neurasthenic syndrome with vegetative dysfunction, and toxic encephalopathy. As a rule, these forms were accompanied

by mild manifestations of toxic polyneuritis of the upper limbs. The differential distribution is shown in the following table.

| | Group | |
|---|---|---|
| | I | II |
| Type of intoxication | | |
| Vegeto-asthenic syndrome | 11 | 13 |
| Neurasthenic syndrome with vegetative dysfunction | 10 | 3 |
| Toxic encephalopathy | 10 | - |
| Toxic polyneuritis (beginning form) | 15 | 21 |
| Residual intoxication phenomena | - | 8 |
| Concomitant diseases | | |
| Female diseases | 25 | 4 |
| Diseases of the cardiovascular system | 9 | 6 |
| Chronic gastritis | 6 | - |
| Other diseases | 10 | 2 |

Data in the table show that the first group included the more pronounced forms of intoxication (toxic encephalopathy, neurasthenic syndrome with vegetative dysfunction) and also cases of the graver and persistent vegeto-asthenic syndrome of toxic origin. An examination of residences and of daily living conditions of workers of both groups showed the following: workers lived in 2 sections of a workers' settlement 1.5 - 2.0 km apart. One area, nearest the plant had finer residences equipped with running water, sewers, hot-water heat. However, it was located within a radius of harmful effect of the plant wastes, while the other section had poorer residences, most of which had water cisterns, outdoor privies, and stove heating, but the section was located farther from the plant and was free from the effects of the industrial wastes. Workers of both groups were approximately equally distributed through both sections. The economic status and state of nutrition of the working families under study were satisfactory; all plant workers received the same food rations consisting of bread, meat, butter, milk, vegetables, fruit, sugar and so forth. Most workers had hot meals 2 - 3 times a day; they ate at different and irregular times because of shift work.

A special study was made of workers with unfavorable habits and home and family conditions, such as systematic use of alcohol by the members of the family, frequent conflicts, difficult living conditions, which led to psychic traumas

of the subjects under study, serious infectious diseases, and with mental and psychic traumas recorded in the medical history. Such persons represented 72.7% of the first group and 20.3% of the second. A comparative study of pertinent factors recorded in the medical histories with the frequency and severity of carbon bisulfide poisoning indicated unmistakably that unfavorable home and family conditions constituted a potent primary non-occupational factor which elicited in the workers enhanced susceptibility to carbon bisulfide poisoning as the result of mental and psychic traumatism. This was corroborated by women workers who stated that they were more seriously affected by their husbands' alcoholism, by quarrels between husband and wife, and by conflicts with children, or by serious illness of a member of the family. Experiences of such type generally produce lasting effects with the result that when poisoning sets in each of the unfavorable factors aggravates the condition of the others, so that susceptibility and irritability become enhanced.

Severe psychic traumas in the medical history, especially in combination with infections, were also reflected in the course of the chronic carbon bisulfide intoxications often giving rise to peculiar symptoms of progressing intoxication. Thus, a pronounced neurotic state, such as reactive neurosis, developed in a female worker after a severe psychic trauma caused by the fact that her only daughter nearly drowned; over a period of 3 - 4 years against this background she developed chronic carbon bisulfide intoxication in the form of a manifest neurotic syndrome with hysteroid reactions according to the Institute specialists, who kept the woman under medical surveillance. There were also secondary effects, such as weakening of the organism, lowering of its immunological and mental stability resulting from prolonged contact with carbon bisulfide, all of which made the workers more susceptible to psychic trauma and infection. During the latent period of progressing carbon bisulfide intoxication psychic traumas or infection may also elicit decompensation effects, a "patent" intoxication or relapse. After an influenza attack one worker developed a pronounced and lasting asthenia with vegetative disturbances. The patient, a woman, was referred to the Institute, where it was found that she had symptoms of chronic carbon bisulfide intoxication aggravated by previous influenza infection.

Observation showed that indications of infectious disease in the medical history, independent of psychic traumas, did not necessarily imply an enhanced sensitivity to carbon bisulfide poisoning nor an increase in the intoxication

gravity. As an illustration, one of the female workers manifested a chronic benign intoxication, even though she had malaria in 1939 and typhus and typhoid fever in 1945 - 1947.

Two patients were seen with pronounced and persisting manifestations of chronic carbon bisulfide poisoning who had previously had alimentary dystrophy at the time of the blockade. Three patients were observed who had overindulged in alcohol periodically over many years. In these patients chronic carbon bisulfide intoxication progressed in a serious form with toxic encephalopathy in 2 instances; they were transferred to different work but the symptoms of poisoning persisted for many years. In four of six patients under observations, who had symptoms of cerebral traumas, carbon bisulfide intoxication was severe and protracted. As a rule, the unfavorable vital factors herein described were interconnected, and in their plurality a non-occupational factor played a primary or secondary role.

## Conclusions.

1. Several non-occupational factors such as psychic trauma, unfavorable living conditions, infectious diseases, etc. can elicit the appearance of carbon bisulfide poisoning or they can aggravate the course of chronic carbon bisulfide intoxication.

2. Most frequent among non-occupational factors are unfavorable family or home conditions, and these have manifested the most damaging effects on the workers' health.

3. Non-occupational factors must be considered by physicians called upon to recommend therapeutic procedures, to establish prognosis in persons with chronic carbon bisulfide poisoning, and to prescribe temporary vacation or change to another type of occupation.

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# Ionic State of Air in Living Quarters and Its Hygienic Significance.

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The problem of air ionization in its application in medicine is attracting increasing attention, but the hygienic significance of ionized air has not been studied sufficiently. At present the interest in air ionization as a hygienic factor has grown noticeably with attention focused basically on the physiological significance of the ionic state of indoor air. The so-called electro-hygienic air problem appeared at the end of the last century. I. P. Skvortsov pointed out that a certain degree of atmospheric saturation with electricity was necessary for the organism's normal existence. In his opinion the basic cause of ill effect from bad indoor air was caused by the diminution of electrical properties in the air, and he believed that such a state of air was more harmful than the accumulation of carbonic acid and of other chemical ingredients. I. P. Skvortsov's views were not accepted at that time for lack of supporting experimental evidence. However, his views attracted the attention of Sokolov, Dorno, Iaglou, A. A. Minkh, E. E. Lesgaft, S. P. Speranskii and others, who made special studies, the results of which proved that a lowered air electrical conductivity and a reduction in the number of light ions could be detected in living quarters. During these studies research was also conducted on the effect of individual factors on air ionization in living quarters; the results were compared with the sanitary condition of the indoor air by usually employed methods. Thus, attempts were made to arrive at an evaluation of the physiological significance of the changes produced in air ionization of living quarters and of public buildings. Results obtained and their nature are described below.

The state of indoor air ionization changed considerably under the influence of many factors. To a degree the changes were determined by daily and seasonal fluctuations in atmospheric air ionization; however, under specific conditions, and principally when people were congregated under conditions of bad ventilation, the atmospheric effect became insignificant as compared with the independent movement of a number of light and heavy ions. During the warm season the number of light ions in outdoor air was higher than indoors; the reverse was true in cold weather; this was reflected in the difference in ventilation

effect on the indoor concentration of light ions at different times of the year. The effect of ventilation on the concentration of heavy ions has not been thoroughly followed up; however, it can be assumed that when outdoor air has not been polluted, ventilation lowered the indoor concentration of heavy ions. Basic changes in the ionization state of air in a room crowded with people were affected by life processes which lowered the number of light ions and increased the number of heavy ions. In atmospheric air concentration of light ions was $1000/cm^3$ or more, while in indoor air it frequently dropped to 200 - $100/cm^3$. This drastic drop in ionization occurred in crowded rooms during the first hour; thereafter it decreased at a considerably reduced rate until a constant minimum had been reached (100 - 50 light ions); such irreducible minimum was maintained by the compensating effect of radioactive emanations coming from the building materials. Concentration of heavy ions in indoor air increased to some tens of thousands per $cm^3$, while their concentration in pure air had been estimated in thousands.

Variations in ionic polarity indoors showed no regularity. As a rule, approximately the same low concentration of positive ions had been found in indoor air as in atmospheric air and only in rare cases did the coefficient of unipolarity in indoor air exceed notably that of atmospheric air. Loss in the number of indoor light ions was the result of ion consumption in the process of breathing, contact with the body surface, adsorption to wearing apparel and by settling out with dust particles suspended in the air. The number of large ions increased as the light ions fell out from the air, with settling dust particles or other condensation nuclei, a process which was conducive to the formation of heavy ions; heavy ions also came with exhaled air. The index which expressed numerical changes of heavy and light ions in indoor air can be expressed as N/n. In pure atmospheric air the ratio of heavy to light ions is only 50:1; in indoor air this ratio is considerably higher. This relationship between concentrations of heavy and light ions in the air can, therefore, be used as a criterion in judging the sanitary-hygienic purity of air. The degree of heavy ion predominance over the light ions offers itself as a sensitive, reliable and constant "electrical" index of good air.

Results of hygienic tests established that a definite connection existed between ionization of indoor air and its hygienic state; it strengthened the assumption that changes in the ionic state of indoor air affected man's organism. Special attention was paid to fluctuations in light ion concentrations,

since it was thought that the electric interchange between the organism and the atmosphere was effected via the light atmospheric ions. Dorno (1927) called attention to this interchange. Recently, Winsor and Beckett (1958) proved experimentally that the human body was the absorber of atmospheric ions. Hutchinson, Spolverini, Beckett and others linked the reduction in number of light ions with the loss by air of its refreshing quality, its lowered physiological and chemical activity, which, in their opinion, was the cause of unfavorable effects of bad indoor air. The question of changes in the number of heavy ions had been treated differently: Wait was of the opinion that increase in the number of heavy ions was the cause of feeling of "heaviness" sensed in a crowded room, while Birman and Loeb attached to it no physiological significance.

The assumptions that fluctuations in the degree of indoor air ionization was of sanitary-hygienic significance has been refuted by such investigators as D. I. Kagan and V. N. Kovalenko, Loeb, Kunow, Bodien, Liese, and others. D. I. Kagan pointed out that changes in the number of light ions not exceeding 100 - 200/$cm^3$ exerted no special physiological action, and that changes in degree and type of atmospheric air fluctuated within considerably wider limits, to which the human organism has fully adapted itself biologically. This opinion is supported by the fact that highly ionized air employed in medical practice did not essentially affect the organism of healthy people (Harrington, L. L. Vasil'ev and others). At the Vienna Conference of the Association on Resortology and Climatology in 1939 it was agreed that natural air ionization should be regarded only as a factor of purely theoretical significance.

Thus, the question of the hygienic significance of indoor air ionization becomes a debatable subject which required further physiological studies to obtain information as to whether changes taking place in the absolute numbers and in the ratios between different ions in indoor air had any effect on the organism of man and animals. At the present time it is possible to refer only to single attempts in this direction. For example, Japanese authors under the leadership of S. Kimoura (1933 - 1939) claimed that, despite former concepts, maintenance of animals in a de-ionized atmosphere was not endangering their life; this has been subsequently confirmed, by Kornblush, and in the U.S.A. by Nedzel (1955). At the same time other Japanese scientists obtained results which indicated that prolonged keeping of animals in artificially de-ionized air arrested their growth, decreased the concentration of inorganic blood phosphorus and accelerated the development of experimental rickets. The studies indicated that

people living in rooms from which light ions have been removed developed symptoms of indisposition, headache, perspiration, etc., even though all other air conditions remained undisturbed. The above indicated symptoms largely disappeared when 500 - 2000/$cm^3$ negative ions were introduced into the room air. Experiments conducted by D. A. Lapitsky with animals supported the concept that the introduction of artificial negative aero-ionization into closed spaces prolonged the stay of persons in a room having a limited supply of oxygen.

The data presented cannot be regarded as adequate for the solution of this controversial subject. The data should be broadened and confirmed by more advanced experimental and analytical procedures. If such research should produce scientific evidence of the physiological significance of ionization of indoor air, then the next step will be to establish optimum concentrations of light ions necessary to artificially introduce into hospitals, schools, offices, etc. The creation of an artificial ionic indoor air atmosphere may prove intrinsically beneficial whether or not natural reduction in their concentration may be deleterious. Increased concentrations of light ions at a given predominance of ionic polarity can be beneficial to the general state of health of normal persons, stimulating their activity and enhancing their mental and physical efficiency. Despite the above conjectures, the expediency of creating a constantly increased level of air ionization in rooms has been doubted. Kornblush (1959) showed that the periodic effect of ionized air was more beneficial to health than its continuous effect. Beckett (1959) stated that a condition of physical comfort did not indicate that all factors of the surrounding atmosphere had to be maintained at a specific level; periodical effects, in particular of such a dynamic factor as electrical properties of air can act as intensive physical stimuli.

At the present state of air ionization research attention should be focused on the question of supplemental indoor air ionization, and investigations in the field of developing means for freeing indoor air from heavy ions (Wait) can be postponed. However, the problem of enriching air with light ions must be investigated not only from the purely physical, but also from the chemical point of view. The process of ion formation is closely connected with the chemical composition of the atmosphere in which ionization takes place. It was observed that indoor air contained different concentrations of ionized molecules of oxygen, nitrogen, carbonic acid, etc. According to E. A. Chernyavskii, Pontani, and others, this fact is of substantial physiological significance. In all probability this may be true, but, according to results obtained by L. L. Vasil'ev,

ions of dissimilar chemical composition which carried identical electric charges acted on the functional indexes generally in like manner. This subject calls for greater precision, even though it is difficult to solve it owing to the insufficient knowledge concerning the relationship between the atom and the electron, which varied for different gases present in the atmosphere. There are reasons for the assumption that persistent negative ions represent to a greater degree molecules of oxygen and water vapor (P. N. Tversky). This fact deserves attention, since it bears closely on the possible favorable effect of negative ions.

Many phases of this problem must be solved before the application of artificial air ionization into practical life can be recommended. However, there is a trend in that direction, especially on the part of sanitary engineers whose opinions are based on a priori physiological assumptions and faulty primitive notions that, in the process of conditioning and ventilation exchange, air was losing the greater part of its light ions (Currier, 1928). Subsequent studies by Yaglu and other American hygienists established that the assumed diffusion and adsorption of ions upon metallic surfaces did not exceed 30% of their original concentration and that such loss was fully compensated by air warming. Air condensation lowered the degree of ionization, air washing and filtration removed the light ions of mobility exceeding 0.9 cm/sec. and increased the concentration of heavy negative ions at the expense of the total air electric effect. Tests made by P. F. Afanasyeva in one of the Moscow cinema theaters, which had an air-conditioning system, showed that the number of light ions in the air of the theater decreased by 30 - 45% one half hour after the air-conditioning system began to operate; after an hour the loss in air ions amounted to only 5%, and ultimately the original concentration of light ions was restored almost completely.

For the past 30 years, artificial air ionization has been applied experimentally in schools, hospitals, and other public buildings in America and other foreign countries; but such experimental application has remained limited, and individual American scientists have expressed themselves categorically against the incorporation of aero-ionization into air-conditioners (Loeb, Harrington). Despite the fact that the question of the significance of air ionization was first raised in the U.S.A., unanimity of opinion on that subject is lacking in that country. Murphy (1954) regards light ions as a necessary quality in the state of air and believes that only artificial production of negative ions

could create a sufficient density of ions in conditioned air. Specialists in the field of air-conditioning, such as Hutchinson, Beckett, and others, manifest a positive interest in the question of artificial aero-ionization as a matter of principle, but stress the fact that knowledge of its aspects was of an empirical character and the basic scientific-physiological principles for the application of aero-ionization were still lacking (1954 - 1959).

American scientists were paying considerable attention also to purely physical aspects of this question. Serious studies were in progress with a view to working out methods for the generation of ions which might assure uniform air ionization throughout an entire residence or building, which would be safe to operate and easy to service and be free from any danger to the occupants. Production of light ions by high tension current has been rejected in the U.S.A., using instead radioactive sources and thermo-ionizers, based on the utilization of thermo-electronic emission from red hot metals (Beckett, Hicks, Skilling). Successful studies in this field are now conducted in the U.S.S.R. (Ya. Yu. Reinet, P. K. Pryuller, E. A. Chernyavskii, and others).

Attention should again be directed to the new points of view which recently appeared concerning the physiological significance of continuous and brief periodic actions of aero-ions. Such views are of practical significance: if brief periods of inhalation of artificially ionized air should prove more effective, the installation of uninterruptedly working aero-ionization equipment in rooms and in ventilation systems would be superfluous. It should be mentioned here that M. P. Davidov and T. A. Trambitskaya favored periodic air ionization in hospital wards by radioactive ionizers. Study of sportsmen during periods of intensive training conducted by M. A. Vytchikov and A. A. Minkh indicated that daily brief periodic effects of light air had advantages over continous ion effect and, therefore, should be preferred.

Artificial ionization of indoor air appears to be of some physiological significance; in addition attention should be directed to the need for freeing air of dust and microorganisms (O. N. Nitchkevich and N. G. Ivanchenko, E. Yu. Zuikova, A. I. Franch, A. L. Chizhevsky). In this respect the direct bactericidal action of aero-ions comes into play. E. A. Chernyavskii observed a decrease of bacteriological infections in cotton plants exposed to the effect of artificial aero-ionization. L. M. Dobrolet established the cidal effect of negative ionization on microflora of skin wounds. Krueger and co-authors experimented with staphylococci suspended in droplets of water and found that high

concentrations of positive and negative ions accelerated the destruction of microbes by acting directly on the cells and increased the rate of the droplets evaporation. According to Pollard's data, negative ions decreased the toxic effects of air bacteria and viruses.

It can be stated in conclusion that the question of the type of air present in living quarters and in public buildings is of vital interest and of practical significance. This assertion can not be refuted despite the fact that many aspects of this problem are still in a debatable stage. On the other hand, reasons are still lacking for ascribing to air ionization any universal sanitary-hygienic qualities. It can be stated merely that air ionization is one of many factors in atmospheric air the action of which manifests itself in its interplay and interrelation with other physical and chemical factors prevailing in the air. Therefore, the question of the physiological significance of air ionization in living quarters must be solved as an aspect of the general problem of air hygiene and should not be treated abstractedly as "aero-ionization for aero-ionization's sake". Overestimation of the significance of the air ionization factor may perhaps be tolerated in popular scientific magazines; in practical sanitation and hygiene it can lead to unnecessary costs and efforts and may discredit the true degree of the hygienic significance of the electrical properties of air.

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Sanitization of Gumbrin Clay Processing.

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Subbentonite and bentonite clays, trade named gumbrin and askonite, found in the Caucasus possess high adsorption properties and are widely employed in purifying and clarifying crude oil products and mineral oils. Gumbrin thus used is first dried and ground. Transportation, drying and grinding of gumbrin is accompanied by intense dust elimination. The sanitary-hygienic labor conditions during gumbrin processing at the Baku Crude Oil Refining Plant basically reflected the technology and equipment involved. Gumbrin is obtained in the vicinity of village Gumbrin (hence its name) and is delivered to the Baku plant in open railroad gondolas. Gumbrin is unloaded from the gondolas and stored in a special building from which it is loaded into hand wheelbarrows and dumped onto conveyors, which in turn, deliver the material onto other means of conveyance which bring them to the grinding and drying departments. In the drying department the gumbrin clay is loaded into a drying drum heated by flue gas. As gumbrin passes through the drying drum, rotating at an angle, it is automatically delivered into a bucket elevator which delivers it to an upper located conveyor which, in turn, delivers it to the mill bunkers and from there, by means of rotating dosers, it is delivered into the grinder. A disk equipped with a cutting blade similar to one used in plows delivers the clay into rollers equipped with a retaining ring. The rollers force the clay into the ring and grind it to a powder. Simultaneously, hot air is drawn into the mill from a furnace heated to 480°. The dried and powdered clay and the hot air enter an upper located separator in which larger particles are removed and returned to the grinder. The powdered sifted clay is delivered by air vacuum suction into cyclones where it is precipitated and by means of special valves is then delivered into collecting bunkers. It can be seen from this brief description that the process of gumbrin grinding lacked appropriate hermetization and necessary mechanization. As a result, the air of the production premises contained gumbrin dust concentrations exceeding by far the allowable limit of dust concentration in working premises. Air pollution with gumbrin dust also extended into the atmospheric air.

TABLE 1.

Chemical composition of gumbrin after calcining at 800°, in percent.

| Grind | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO |
|---|---|---|---|---|
| Kutansk | 70.02 | 15.05 | 1.68 | 7 |
| Local | 71.8 | 17.8 | 2.52 | 4.67 |

The basic part of gumbrin, an alumosilicate, consists of silicon dioxide which causes silicosis even in its combined form. (See Table 1). Medical examinations were made of 48 workers employed as gumbrin grinders; 10 of these manifested symptoms of silicosis, stages I and II, and 3 had symptoms of silico-tuberculosis, while 2 showed signs of pre-silicosis. Twelve of the workers affected with silicosis had long time work records. Gumbrin dust concentrations sharply exceeded the limits of allowable concentration mostly because of inadequate hermetization of the technological processes; concentrations varied with the time of the year. During the cold months of the year, when gumbrin contained more moisture, gumbrin dust concentrations in the air were considerably lower (see Table 2). How-

TABLE 2.

Gumbrin dust concentrations in the air of working premises, in $mg/m^3$.

| Place and conditions of sample taking | Concentration fluctuations | Gumbrin dust concentrations | | |
|---|---|---|---|---|
| | | February-March | April-May | June-July |
| | | Working space air temperature | | |
| | | 9-11° | 17-20° | 26-31° |
| Silo section | Average | 105 | 206.6 | 507 |
| | Maximal | 199 | 286.6 | 668.4 |
| | Minimal | 42.6 | 130 | 320 |
| Including: | | | | |
| Mixer building | Average | 136.5 | 269.8 | 356.2 |
| | Maximal | 199 | 286.6 | 386 |
| | Minimal | 126 | 252 | 320 |
| Moving the bulldozer | Average | 49.3 | 143.3 | 657.9[1] |
| | Maximal | 54.2 | 160.6 | 668.4 |
| | Minimal | 42.6 | 130 | 646 |
| Mill section | Average | 43.9 | 138.7 | 598.2[2] |
| | Maximal | 52 | 152.7 | 684 |
| | Minimal | 33.6 | 126 | 506 |
| Including: | | | | |
| At bucket elevator | Average | 49.4 | 146.2 | - |
| | Maximal | 52 | 152.4 | - |
| | Minimal | 46.4 | 138.4 | - |
| At slanted mill platform | Average | 39.7 | 131.2 | - |
| | Maximal | 44.6 | 136.4 | - |
| | Minimal | 33.6 | 126 | - |

1/ During throwing down ground gumbrin.
2/ Near the Fuller pump.

ever, increasing the moisture content of gumbrin prior to grinding it proved impractical, due to the fact that raising the gumbrin moisture content lowered sharply its technological properties and reduced its effectiveness in the purification of the mineral oil. Therefore, it was suggested that the dust suspended in the air of the grinding rooms be removed by dry type dust catchers in order to eliminate the possibility of the gumbrin dust finding its way into the atmospheric air and into workers' premises.

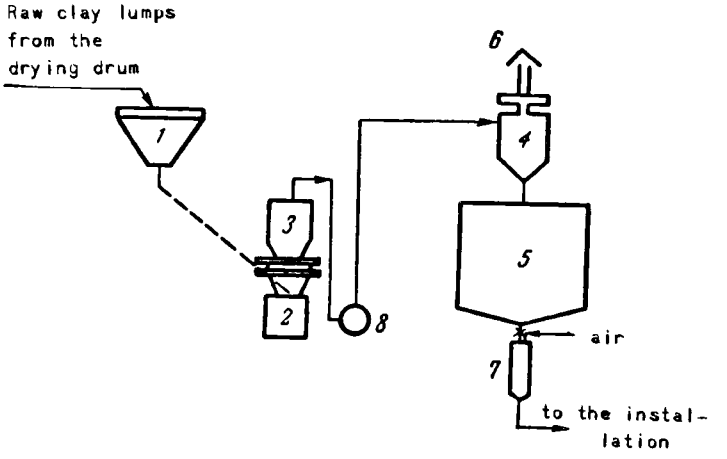


Fig. 1. Plan of mill operation without dust catchers.
1 - Bunker; 2 - mill; 3 - mill separator; 4 - cyclone; 5 - silo; 6 - cupola vent; 7 - doser; 8 - ventilation (fan).

The Baku Crude Oil Processing Plant has been operating on such a basis. Prior to the installation of dust catchers, the raw clay lumps were delivered from the drying drums via the bunkers into the mills or grinders together with hot air coming from the air heating ovens, into the mill or grinder, and from there via the mill separator into the ventilator which delivered it into a cyclone and therefrom into a collecting pit or silo. A part of the steam formed in this process, the hot air with suspended gumbrin dust, were discharged into the atmosphere, polluting same. The clay was removed from the collecting or storage silo as needed with the aid of a pneumatic dose feeder into the appropriate section of lubricating oil purification. The cupola vent shown in Fig. 2 was stopped up and vapors, hot air and clay dust found their way into the ventilator and therefrom into the dust catcher in which the dust was directed downward by a special partition system finally falling upon a layer of lubricating oil which was automatically maintained at a constant level. The air purified in the dust catchers was then discharged into the atmosphere. The dust-saturated oil was removed at definite time intervals and replaced by fresh oil. From the doser the clay was directed into the final installation.

Preliminary data obtained in checking the improved procedure indicated a high degree of atmospheric air purification and a dust concentration not exceeding the allowable sanitary limits. Nevertheless, in such sections as the storeroom and the pit or silo and in the loading and unloading room, high gumbrin

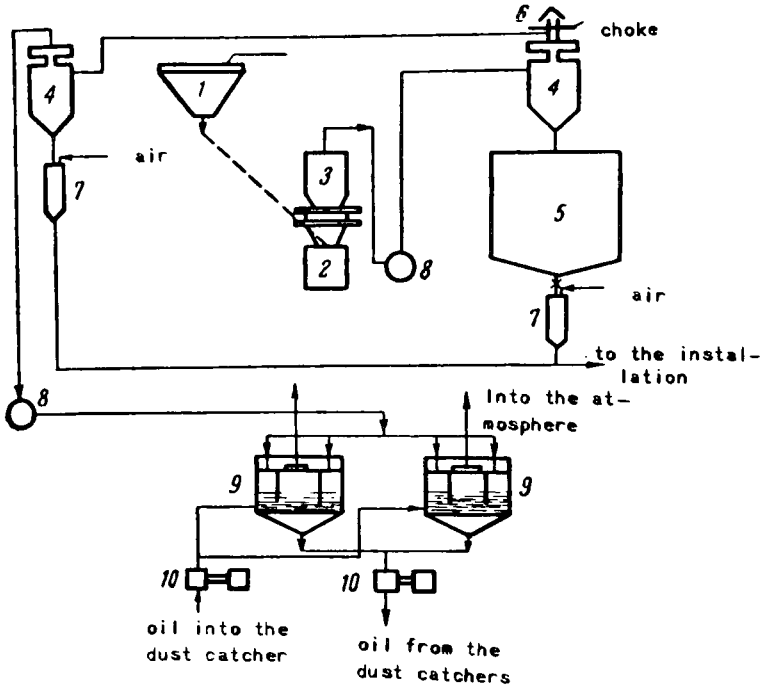


Fig. 2. Plan of clay grinder operation after dust catcher installation.
1 - Bunker for raw clay; 2 - mill or grinder; 3 - mill separator; 4 - cyclone; 5 - silo; 6 - cupola vent; 7 - doser; 8 - fan (ventilator); 9 - dust catcher; 10 - pump.

dust concentrations in the air persisted presenting a danger source for the development of silicosis among the workers employed at such points. New appropriate purification means must be adopted to improve the labor conditions; loading and unloading should be done mechanically and under hermetical conditions; the same is true of the milling processes.

Conclusions.

1. Gumbrin clay grinding was accompanied by intense pollution of the air of working premises.

2. Cases of pneumoconiosis have been uncovered among workers assigned to the gumbrin milling department.

3. Workers employed at processing and application of gumbrin clay in crude oil refining plants should be medically examined prior to their assignment and at definite time intervals in the course of their employment.

4. Steps in gumbrin processing, its transportation, loading and reloading, drying and grinding should be mechanized as much as possible and all means applied to secure hermetization which should reduce if not completely eliminate, gumbrin dust in the surrounding air.

Hand Lead Contamination of Workers in Contact with Ethyl Lead Gasoline.

I. I. Brekhman, V. A. Matyukhin and N. K. Fruentov.

Gigiena i Sanitariya, Vol. 25, No. 7, 97-98, 1960.

A study was made of lead quantity found on the hands of automobile drivers, workers in automobile garages, auto repair shops, etc. This was done as follows: at mid-day and at the end of the work day washings were obtained from the workers' hands, from steering wheels and from other automobile surfaces. The washing was done with gasoline B-70 which was previously tested and found to contain no tetraethyl lead. The method used for the determination of small amounts of lead in the washings was based on the decomposition of tetraethyl lead by a hot alcoholic iodine solution followed by a nephelometric determination of total lead by the potassium bichromate method. (Since no differential organic and inorganic lead determinations were made in the washings the total results may appear slightly exaggerated. Editor's Note).

Results of 300 tested washings are presented in the table below in percentages of the total number of tests. The data show that 3.6% of automobile drivers and 4% of auto station, auto repair shop and other similar workers' hands were free from tetraethyl lead; no such free cases were found among 50 workers engaged in the aviation industry. The average tetraethyl lead found on the hands of automobile drivers amounted to 0.125 mg and on the hands of workers in automobile garages and automobile repair shops amounted to 0.115 mg, while on the hands of the technical workers in the aviation industry the amount of lead found was 0.249 mg. Such high hand contamination of the technical aviation personnel

Mg of lead in hand washings of different specialists in percent of total number investigated.

| Content of tetraethyl lead | Automobile drivers | Workers in garages, repair shops, filling stations, and the like | Technical aviation personnel |
|---|---|---|---|
| 0.5 - 0.41 | 1.2 | - | - |
| 0.4 - 0.31 | 1.2 | - | 17.5 |
| 0.3 - 0.21 | 14 | - | 65 |
| 0.2 - 0.11 | 33 | 54 | 11.5 |
| 0.1 - 0.01 | 47 | 42 | 5 |
| 0 | 3.6 | 4 | - |

with tetraethyl lead is easily explained by the fact that aviation gasoline contained 2 - 3 times as much ethyl fluid as did automobile gasoline.

It was also shown that a considerable amount of tetraethyl lead was deposited on the steering wheels. In 89% of the cases it ranged between 0.1 - 0.2 mg and in 11% it amounted to 0.3 mg or more. About the same amount of tetraethyl lead was found on the automobile handles and hand operated transmission parts and on the outside of the automobile. Tetraethyl lead was also found on many objects in the airplane cabins, in amounts of 0.4 - 0.5 mg. Similar results were obtained with washings of servicing personnel which contained up to 0.3 mg of the tetraethyl lead. Of particular interest was the fact that auto traffic directing and other personnel not having direct contact with tetraethyl lead also showed the presence of tetraethyl lead in their hand washings, to a considerable extent. Washings of the hands of other workers connected with different types of automotive and aviation driving, piloting, servicing, etc. functions contained tetraethyl lead in quantities ranging between 0.1 - 0.5 mg. Results indicated that despite existing instructions regarding personal hygiene, contamination of hands and possibly other parts of the body of above enumerated personnel has not been eliminated or reduced. Chronic intoxication with tetraethyl lead, therefore, appears as a possibility. This can only be eliminated by strict observation of personal hygiene as outlined in sanitary-hygienic instructions, by a thorough consistent and persistent cleaning of contaminated machine parts and surfaces with kerosene, soap and water, etc. to the point of almost complete elimination of tetraethyl lead. It may be desirable to instruct auto drivers, airplane pilots and other workers connected with functions immediately related to the operation of automobiles and airplanes to carry with them jugs containing kerosene or soap and water and towels so that they can wash their hands free of tetraethyl lead at every possible opportunity.

Duration of Carbon Monoxide Excretion from the Body.

L. A. Tiunov, T. I. Sokolova and V. P. Paribok.

Farmakol. i Toksikol., Vol. 20, No. 4, 76-78, 1957.

Data presented in literature on the rate of carbon monoxide excretion from the body are contradictory. According to Roughton and Root half of the carbon monoxide is excreted within 20 minutes after it has been inhaled; according to Pace, Strajman and Walker (cited by Lilienthal, 1950) the CO elimination period is between 34 - 84 minutes. Data in the literature indicate that after prolonged inhalation of low carbon monoxide concentrations under industrial conditions it remained in the body for a long time (Kohn-Abrest, 1948). It is possible that carbon monoxide reacting with tissue enzymes (N. S. Pravdin) may linger not only in the blood, but also in the tissues. In this study, using the labeled atoms method, these authors investigated the rate of carbon monoxide excretion from the blood and the possibility of its being retained by the tissues.

Methods used. Use was made of $C^{14}$ in the form of carbonate. $C^{14}$ was obtained according to the method of Bernstein and Taylor (1947); carbon dioxide, $C^{14}O_2$ was obtained from barium carbonate and converted to $C^{14}O$ in a zinc reducing column heated to 400 - 500°. Experiments were conducted on cats in an exposure room of 90 liters capacity. Soda lime absorbed the exhaled $CO_2$ and the partial vacuum created as the result of absorbed $CO_2$ was automatically replaced by oxygen, thus retaining a constant atmospheric pressure. This enabled the authors to expose the animals to any carbon monoxide concentration desired for many hours under conditions free from excessive $CO_2$. The concentration of $C^{14}O$ was determined with the aid of TM-20 radiation end-counter, fed via a high voltage cable by a "B" type installation.

Blood containing $C^{14}O$ was injected intravenously into the animals in some tests. Samples of the cats' blood were taken from the marginal ear vein at one hour intervals after exposure was completed. Blood activity was determined by the end-counter as mentioned above. Count precision equalled 0.25. After the $C^{14}O$ had been completely eliminated from the blood, the animals were killed, the brain, liver, heart and muscles were removed, finely cut up with scissors and ground in a mortar with dry ice and acetone. The homogenized tissues were spread in even layers and 2 $cm^2$ portions placed into foil cups, using an end-type radiation counter and the specific activity of the samples was determined.

## TABLE 1.

Time of $C^{14}O$ elimination from the blood of experimental animals after different type and duration of CO administration.

| Test No. | Means of CO administration | Duration of inhalation exposure | mg/li of CO at end of exposure | Time of CO elimination from the blood in min. 50% | 90% |
|---|---|---|---|---|---|
| 1 | Intravenous | | | 15 | 148 |
| 2 | Intravenous | | | 14.5 | 159 |
| 3 | Intravenous | | | 22 | 77 |
| 4 | Inhalation chamber | 395 minutes | 0.0029 | 105 | 232 |
| 5 | Inhalation chamber | 350 minutes | 0.063 | 30 | 98.5 |
| 6 | Inhalation chamber | 366 minutes | 0.078 | 124 | 219 |
| 7 | Inhalation chamber | 23.5 hours | 0.070 | 93 | 287 |
| 8 | Inhalation chamber | 24 hours | 0.147 | 182 | 351 |
| 9 | Inhalation chamber | 47 hours | 0.058 | 141 | 410 |
| 10 | Inhalation chamber | 49 hours | 0.024 | 55 | 180 |
| 11 | Inhalation chamber | 49 hours | 0.07 | 40 | 193 |

## TABLE 2.

$C^{14}O$ content in organs.

| Test No. | CO concentration in chamber and duration of exposure | Imp/min. in blood prior to exposure | Organs | Imp/min. in organs |
|---|---|---|---|---|
| 1 | 0.024 mg/li 48 hours | None | Brain | 1 |
| | | | Heart | 8 |
| | | | Liver | 9 |
| | | | Tissue | 1 |
| 2 | 0.07 mg/li 48 hours | 1 | Brain | 1 |
| | | | Heart | 2 |
| | | | Liver | 3 |
| | | | Tissue | 2 |
| 3 | 0.147 mg/li 24 hours | 1 | Brain | 8 |
| | | | Heart | 7 |
| | | | Liver | 4 |
| | | | Tissue | 7 |
| 4 | 0.063 mg/li 6 hours | 4 | Brain | 8 |
| | | | Heart | 4 |
| | | | Liver | 6 |
| | | | Tissue | 5 |
| 5 | 0.078 mg/li 6 hours | 3 | Brain | 1 |
| | | | Heart | 2 |
| | | | Liver | 5 |
| | | | Tissue | 1 |
| 6 | Intravenous injection of $C^{14}O$-saturated blood | 4 | Brain | 3 |
| | | | Heart | 4 |
| | | | Liver | 2 |
| | | | Tissue | - |

Results of the research. Table 1 shows the rate of $C^{14}O$ excretion from the blood. For purposes of comparison the time at which 50% and 90% of $C^{14}O$ were excreted is shown in the table. Rate of $C^{14}O$ excretion from the blood varied with each animal in each of the experiments. At no time was the 90% $C^{14}O$ elimination delayed byond 410 minutes, or 7 hours at the most, so that the organism was almost completely free of $C^{14}O$, even in animals exposed to the gas for 49 hours. Results of the experiments show the rate of $C^{14}O$ excretion from the blood not from the entire organism. To determine whether some carbon monoxide was retained by the tissues, $C^{14}O$ determinations were made in the organs after the carbon

monoxide had been excreted from the blood completely (Table 2). Results in Table 2 indicate that carbon monoxide or any $C^{14}$-containing product of its conversion in the body was retained in the organs in extremely small amounts, practically traces. If allowance is made for the fact that residual blood in the tissues may contain more significant amounts of $C^{14}O$ at the time of tissue examination than did the peripheral blood, then the content of $C^{14}$ in the tissues must be considered as near zero.

## Experimental Study of Working Conditions and Atmospheric Air Pollution with Ethylmercuric Chloride During Treatment of Cereal Grains in the Omsk Oblast.

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(From the Regional Sanitary-Epidemiological Station and the Department of Labor Hygiene of the Medical Institute).

Gigiena Truda i Professional'nye Zabolevaniya, Vol. 2, No. 5, 20-24, 1958.

Granosan has been used for the disinfection of cereal grains from spores and microorganisms. Granosan, NIUIF-2, is a 2% mixture of ethylmercuric chloride, EMC, ($C_2H_5HgCl$) and talc. According to L. I. Medved, N. S. Pravdin, S. N. Kremneva, and others, EMC is more toxic than vapors of mercury and of mercuric chloride, and according to L. I. Medved, and I. M. Trakhtenberg, and others, it is also cumulative. E. A. Drigichina, A. K. Karimova, E. I. Yaroslavskii, and others described cases of acute and chronic poisoning with EMC in which the predominant symptom was disturbance of the central nervous system. L. I. Medved and others made a hygienic evaluation of working conditions on farms of the Ukraine and Belorusiya using granosan. The present author made a similar study in the Omsk oblast, where climatic conditions and other local characteristics were different from those prevailing in the Ukraine or in Belorusiya. The study was conducted during May in 1956 and 1957 in the Tavrichesk and Kalachinsk regions in three kolkhozes, where the seed or grain treatment was done manually by shovel mixing and by machine PU-1 in an apparatus PSP-0.5. The EMC was used at the rate of 100 g per C of seeds or grain; mixing

was done with shovels in the open air. Machine PU-1 has a grain bunker equipped with a worm gear for the delivery of the grain and a special slit and a sliding control shutter; there is also a small bunker for dry grain treatment by means of a special mixer, which also serves as the granosan deliverer, the rate of which is controlled by a sliding shutter as in the case of the grain delivery; the machine is also equipped with a small tank and a special arrangement for wet treatment of grain. In the dry treatment the seeds and the granosan are delivered into a special mixing compartment by means of a worm gear conveyor. The machine is brought into operation by mechanically engaging a special driving gear. Apparatus PSP-0.5 consists of a metallic drum; 50 g of the grain and a desired dose of the granosan are placed into the drum which is then rotated for 5 minutes, and the treated grain is removed from the apparatus.

Fifty-seven air samples were collected for the determination of EMC in the dust, and another 57 air samples for the determination of EMC vapor; 102 wash water samples were collected from the hands of the working personnel, their clothes, protecting respirators and of surrounding objects; records were kept of the duration of work. EMC determinations were made by the method recommended by the Kiev Institute of Labor Hygiene and Occupational Diseases, which is based on the colorimetric estimation of a resulting precipitate of $CuIHgI_2$. Analytical results of air samples taken at the workers' breathing level are listed in Table 1.

Lowest concentration of EMC was found in the air at the point of grain treatment by machine PU-1 manually operated; concentrations of EMC in air samples collected during operation of apparatus PSP-0.5 were, on the average, five times as great as in the case of machine PU-1 hand operated; the mechanically operated machine PU-1 produced a dust concentration 14 times as intense, and the shovel mixing process produced an EMC air concentration 41 times as intense. Among the air samples collected at the manually operated machine PU-1 only one had a concentration exceeding the allowable limit in a 1.4 ratio. GOST specifies no limit for allowable concentration of EMC in air of working zones, but there is one for Hg; therefore, results here dealt with are with reference to limits of Hg concentration. It should be noted at this point that in dealing with organic mercury compounds, such as ethylmercuric chloride, a concentration of 0.00001 mg/li in the air at the level of workers' breathing should not be regarded as the permissible limit, as was indicated by I. M. Trakhtenberg in Gigiena i Sanitariya, 1950, No. 6, p. 17.

TABLE 1.

Mg/li of ethylmercuric chloride in the air at breathing level during seed or grain treatment of different methods.

| Treatment method | mg/li of ethylmercuric chloride in the air | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Vapor | | | Dust | | | Total | | |
| | Minimal | Maximal | Average | Minimal | Maximal | Average | Minimal | Maximal | Average |
| Manual, in the barn | 0.000 018 | 0.001 188 | 0.000 411 | 0.000 066 | 0.000 48 | 0.000 182 | 0.000 084 | 0.001 668 | 0.000 58 |
| PSP-0.5, in the barn | 0.000 053 | 0.000 079 | 0.000 066 | 0.000 004 | 0.000 005 | 0.000 005 | 0.000 058 | 0.000 083 | 0.000 071 |
| PU-1, manual rotating, in the open air | 0 | 0.000 022 | 0.000 009 | 0.000 003 | 0.000 007 | 0.000 05 | 0.000 003 | 0.000 025 | 0.000 014 |
| PU-1, mechanically rotating, in the open air | 0.000 02 | 0.000 055 | 0.000 04 | 0.000 055 | 0.000 22 | 0.000 153 | 0.000 075 | 0.000 275 | 0.000 193 |

During one hour collection of an air sample, cereal seed was treated and discharged onto an open platform over a period of six minutes; another six minutes was required for shoveling the treated seed into bags, and an additional 12 minutes for weighing and transporting the filled bags. In another instance it took 15 minutes to treat the seed and pour it into the bags, and 9 minutes to empty the machine onto the open platform. The concentration of EMC in the air amounted to 0.0000007 mg/li. In another instance, in which the air dust concentration was only 0.000003 mg/li, the air sample was negative for EMC vapor. In the latter case the entire process of machine grain treatment took 18 minutes and the treated grain was emptied into bags tightly attached to the discharge opening. Such an arrangement could not be secured in the case of the manual grain treatment, which has now been abolished by special sanitary regulation. Machine PU-1, operated by mechanical gear meshing, discharged the treated grain with considerable force, so that at the point where the grain was discharged directly onto the open ground, the air became permeated with a heavy concentration of EMC dust. Where the grain was mechanically filled into bags, the process was so rapid

that before the workers were able to remove the bag, the grain overflowed onto the ground. Attaching a hose of heavy but soft material directly and tightly to the discharge opening of the machine reduced considerably the air pollution with the dust and vapor of EMC. Grain treatment by means of apparatus PSP-0.5 created considerably less dust, but created considerably higher EMC vapor concentrations. This was due to the fact that the treated grain was discharged onto an open surface of considerable area which was accompanied by the vaporization of the EMC; and since the treatment was conducted inside a closed barn, the EMC vapor concentration tended to accumulate. Another important observation indicated that in the treatment of grain with EMC by machine, it was important to insure smooth and uninterrupted operation.

The next step in this investigation dealt with the determination of EMC air pollution concentrations in relation to distance from the point of grain treatment. The study was conducted in the vicinity of grain treatment barns located along a straight line; air samples were collected on the lee side of the barns. Results are presented in Tables 2 and 3. Data in the tables show that EMC was present in all air samples collected at all the distances indicated, up to 200 meters; the same was true of tests made on wash waters from objects at same distances from the points of grain granosan treatment up to

T A B L E 2.

Ethylmercuric chloride in the air at x distance from point of treatment by manual rotating machine PU-1.

| Meters from machine | mg/li ethylmercuric chloride in the air | Ratio of ethylmercuric chloride in the air of working point at indicated distance | Air temperature | Percent of relative humidity | Air current velocity in m/sec |
|---|---|---|---|---|---|
| 1 | 0.000 019 | 1:1.4 | 20 - 21 | 53 - 74 | 0.8 - 1.2 |
| 5 | 0.000 01 | 1:0.8 | 25 - 26 | 53 | 0.9 - 1.8 |
| 10 | 0.000 004 | 1:0.4 | 27 - 28 | 22 | 0.9 - 1.8 |
| 25 | 0.000 009 | 1:0.7 | 27 - 28 | 18 - 22 | 1.6 - 4.1 |
| 50 | 0.000 022 | 1:1.2 | 27 | 21 | 3.9 - 5.5 |
| 100 | 0.000 005 | 1:0.3 | 24 | 26 | 2.7 |

T A B L E 3.

Ethylmercuric chloride concentration in the air at x distance from the storage barn.

| Meters from the barn | mg/li of ethylmercuric chloride in the air |
|---|---|
| 10 | 0.000 024 |
| 30 | 0.000 02 |
| 60 | 0.000 02 |
| 100 | 0.000 02 |
| 150 | 0.000 027 |
| 200 | 0.000 026 |

200 meters which is the regulation width of the sanitary clearance zone for plants engaged in the treatment of seeds with disinfecting poisonous chemicals. Results of analyses are listed in Table 4. Wind velocity had a determining effect on the spread of air pollution with EMC over the treatment-surrounding territory, as is shown in Table 2. At wind velocity of 0.8 - 1.8 m/sec, the concentration of EMC in the air rapidly diminished as the distance from the points of treatment increased; however, beyond a certain high velocity the relation between EMC air concentration and distance from the source of origin became less evident. At wind velocity up to 5.5 m/sec and at a distance of 50 m from the source of origin (PU-1 machine) the EMC air concentration rose to 0.000022 mg/li. Data listed in Table 3 were obtained under weather conditions characteristic of the month of May changes in Western Siberia, with prevailing sharp turns to low temperatures accompanied by northern winds. In such instances the EMC concentration in the air at 200 m from the source was twice as high as the limit of its allowable concentration. The data thus show that the prescribed 200 m sanitary protection zone may be inadequate for granosan treatment plants under weather conditions prevailing in the steppe and forest belt of Omsk oblast.

T A B L E 4.

Ethylmercuric chloride in washings from surfaces of environmental objects per 100 $cm^2$.

| Washings from - | Number of washings | Average of ethylmercuric chloride |
|---|---|---|
| Inside treatment barns | 10 | 0.000 5 |
| Outside surface of barn walls | 6 | 0.000 24 |
| At distance of: | | |
| up to 50 m | 17 | 0.000 18 |
| up to 150 m | 11 | 0.000 16 |
| up to 200 m | 2 | 0.000 1 |

Concentration of EMC in air samples taken 152 m from the point of grain treatment with granosan by means of PSP-0.5 apparatus ranged between 0.000008 and 0.00002 mg/li. Samples of air collected at the kolkhoz yard surrounded by different buildings 1 m from the barn housing the operating apparatus showed a concentration of EMC of 0.000008 mg/li, while the air sample collected at the center of the yard had an EMC concentration of 0.00002 mg/li. On the basis of such findings it seems logical to recommend that seed treatment with granosan be done at a point where natural ventilation was most favorable.

Temperature is another factor of importance. Observations made during the present investigation showed that at +4 to +6° the air contained twice as high a granosan dust as EMC vapor concentration. As temperature rose, rate of EMC

vaporization became enhanced so that at 28° the concentration of EMC vapor became the predominant air pollutant. The results justify recommending that grain treatment with granosan be done preferably, if not exclusively, at time when low temperature prevailed, that is during the early morning or late evening hours of the month of April.

V. A. Russkikh and A. Ya. Tubina found that EMC remained suspended in the air for a long time and that EMC settled upon different objects became easily redispersed with air currents; therefore, it appears rational to suggest that during the seasons of grain or seed treatment with granosan, when the poison is constantly present in the air, and especially during the working hours of the day, workers should be forbidden to be exposed to the effects of EMC for more than 4 hours.

A study was also made of the effectiveness of protective devices. Samples of wash water from 7 semi-mask type of respirators KB-2 were analyzed. The outer surface of the respirator masks showed a deposit of 0.0003 mg of EMC and the inside surface 0.00005 mg of the chemical, indicating that this type of protecting respirator failed to adequately perform the protective function for which it had been designed; in other words, the cotton and gauze padding proved ineffective. L. I. Medved showed that gauze and cotton combined pads placed over the nose and mouth had only a slight protective effect, and analyses made by the present author indicated that an area of 100 cm of a gauze-cotton mask contained 0.002 mg/li of EMC on either side of the mask. V. A. Russkikh and A. Ya. Tubina recommended that mercury vapor absorber "AS" be used to protect the workers' respiratory organs; this absorber operated over 7 days without letting through any of the poisonous vapor. It is here recommended that kolkhozes and sovkhozes be supplied with adequate numbers of "AS" mercury vapor absorbers. Observations made by the present author clearly indicated that the use of rubber gloves during grain or seed treatment with granosan should be made mandatory, since tested samples of hand wash-water from women who worked with bare hands, showed the presence of 0.00035 to 0.0006 mg of EMC.

Supplemental tests showed that a 100 $cm^2$ area of the coverall had deposited upon it 0.0007 - 0.0002 mg of EMC. Therefore, it is imperative that the working clothes should not be carried out or worn outside the granosan treatment premises.

As previously indicated, most, if not all, workers engaged in the process of grain or seed treatment with granosan were women. They were asked questions pertaining to their occupation in relation to health. Most of the women complained of loss of appetite, sweet taste in the mouth, and 3 of the women workers

complained of persistently frequent nose bleeding. One month after the grain treatment with granosan was concluded, 8 of the women workers were again questioned concerning their health. Of the 8 only 2 presented no complaints of affected health. The remaining 6, while still in condition to work, complained of head-aches, especially of frontal head-aches, loss of or reduced appetite, insomnia, and 2 women complained of somnolence. On woman experienced vomiting spells at the end of the fourth work day, which recurred at some intervals over a period of 3 days. It could be assumed that all complaints and episodes may have been the result of light poisoning with EMC.

Conclusions.

1. Process hermetization and complete elimination of EMC dust or vapor discharge into the air should bring about a decided sanitary-hygienic improvement in the process of grain and seed treatment with granosan. The manual method of treatment, forbidden by sanitary regulations, should be abolished totally. Machine PU-1 and apparatus PSP-0.5 may be used, provided they were in good operating condition and are intelligently exploited.

2. Air analyses showed that with increase in wind velocity during open air grain treatment with granosan EMC dust and vapor concentrations frequently were in excess of the recommended limit of allowable concentration at distances as great as 200 m from the point of treatment. This is particularly true in instances of improper machine operation. Therefore, it is recommended that the presently adopted sanitary clearance zones be widened for the Omsk oblast in accordance with its local meteorological characteristics.

3. Grain treatment with granosan should be carried out in the open at low temperatures, preferably in the early morning or late evening hours.

4. It is essential that all sanitary-hygienic regulations applicable to this type of work be observed strictly and faithfully. Workers should be limited to a four hour work day.

5. Protective respirators of the gauze-cotton semi-mask type without mercury vapor absorbers proved ineffective for the protection of the workers' organs of respiration against the deleterious effect of EMC dust, and especially vapor.

6. Practice of personal hygiene in accordance with regulations prescribed for workers employed in the treatment of grains and seeds with granosan or other disinfecting poisons must be strictly and scrupulously enforced for the effective protection of the workers' health.

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## Carbon Monoxide in Typical Auto-Tractor Machine Shops.

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Gigiena i Sanitariya, Vol. 24, No. 5, 80-82, 1959.

Carbon monoxide is formed in auto-tractor machine shops by agricultural machines coming in for repairs, by tractors being checked, and particularly during electric welding and other processes of machine repairing. Project MTM No. 1662 developed by the agricultural trust in 1954 provided that tractors and other machines coming in for check-up or repairs should be brought in by so-called universal stands to reduce the concentration of carbon monoxide in the air of the machine shops by cutting down on the amount of exhaust gases. This author inspected tractor machine shops of the Vinits region and found that the precautionary measures provided for in Project MTM No. 1662 had not been taken advantage of and that practically all machines were coming in and going out on their own power. The reason for that was, in the first place, the insufficient number of universal moving stands in the MTM, and, second, the poorly designed and unstable moving stands which presented some danger to the machines being moved in and to the workers.

This author studied the pollution of motor transport station air with carbon monoxide, using the microtitrimetric method. Samples were taken at the level of workers' breathing. Two hundred air samples were analyzed. Results are listed in the following table. Data in the table show that carbon monoxide

Carbon monoxide concentration in the air of MTS repair shops, built according to Project No. 1662.

| Section or department | Conditions and place of air sample collecting | Number of analyses | Limits of CO concentration fluctuation in air in mg/li | Remarks |
|---|---|---|---|---|
| Disassembly and washroom | Heating the caustic solution in vats in machine washing section | 4 | 0.03-0.05 | Outside gates were widely opened periodically |
| Ditto | Heating the caustic solution at different points on the premises | 6 | 0.02-0.03 | Ditto |
| Testing station | So-called cold motor burnishing near moving stand | 16 | 0.058-0.072 | |
| Ditto | Ditto, near second stand | 4 | 0.02-0.045 | Samples were taken with fan in operation |
| Ditto | So-called hot motor burnishing near the stand | 6 | 0.023-0.257 | Ditto |
| Ditto | After so-called hot motor burnishing near the second stand | 4 | 0.09-0.1 | Ditto |
| Copper casting | Bushing casting, preliminary heating of bearings on the forge, smelting of bearing alloys - position of smelter | 26 | 0.045-0.2 | Ventilation was in operation only periodically |
| Mechanical welding | During operation of one forge - position of smith | 36 | 0.028-0.168 | Ventilator in continuous operation, door leading to street open occasionally |
| Ditto | During operation - at the position of electric welder | 26 | 0.02-0.23 | |
| Assembly in central part of shop | During tractor rolling into shop - at different points of the central track | 13 | 0.02-0.15 | Outside gate wide open |
| Smith and mechanical shop | Starting tractor motor in assembly division for a period of 2-3 min. at different points of assembly section | 6 | 0.02-0.05 | |
| Repair and testing of liquid fuel apparatus | After regulating of fuel atomizer - at different points of the premises | 13 | 0.03-0.095 | |

concentration at the level of workers' breathing in most instances exceeded considerably the limit of allowable carbon monoxide concentration in the air of working premises. Lowest carbon monoxide concentrations were found in the disassembly and cleaning sections and in the mechanical machine shops; during testing and "cold burnishing" of the motors, vapors of heavy hydrocarbons and of carbon monoxide were discharged into the air of the testing station, so that even with the exhuast fan in operation the concentration of these pollutants exceeded the allowable concentration by 2.0 to 11.5 times. Particularly high concentrations of carbon monoxide were created in the air of the testing station when the motors were tested under heavy loads or so-called "hot burnishing". Such concentrations of carbon monoxide were 6 to 9 times as high as the allowable limits at the point of testing and 3 times as high 2 m away. A few hours after the "hot burnishing" of the motors the carbon monoxide concentration in the air of the test room was still in the neighborhood of 0.82 mg/li with the exhaust fans in operation. The cause of air pollution with carbon monoxide in the premises of the test station, especially during the so-called "hot motor burnishing" was due to the fact that the connections between the outdoor-leading exhaust pipes and those of the tested motors were leaking and, therefore, did not serve the purpose originally designed for, namely, the direct exhaust of the gases into the atmospheric air. The low efficiency of the ventilation installed in the motor tractor shops (MTM) was clearly indicated by high carbon monoxide concentrations in the air of the copper casting and general welding sections, where the pollution concentration was twice as high as the limit of allowable concentration, with the exhaust fan in operation. In the copper casting department of the Strizhev Motor Tractor Station (MTS), the operation of the electric fan created a vibration and noise of high intensity (up to 82 - 86 db.); this was due to the technically faulty installation of the fan and caused the workers to switch the fan off and carry on their work under conditions of air highly polluted with carbon monoxide, which rose to 0.2 mg/li. The exhaust fan installed in the mechanical welding department which, according to the provisions made in the typical plans, was supposed to take adequate care of the air of the working space, housing a double forge and an electric welding installation, proved inadequate and was not able to insure the complete removal of gaseous products from the working premises housing only one forge and an electro-welding installation, as can be seen from the data shown in the table. The exhaust hood over the position of the electric welder was installed above 2.5 m; this was too high

a position and the dust and gaseous products formed during electric welding passed into the exhaust hood only partially. The greater part of them remained at the point of origin and became disseminated by the prevailing air currents over the entire section. When welded materials were covered with dirty crude oil residuals the CO concentration in the air at the level of workers' breathing rose to 0.218 - 0.30 mg/li. Thus, it can be seen that the location of these two work operations, not technologically related to one another, in one and the same room, served no good purpose since it increased through summation the deleterious aspects of air which affected the mechanic (smith) and the electric welder. The CO concentration of the air at the workers' breathing level reached 0.15 mg/li in the assembly department occupying the central part of the shop during the tractors incoming, as can be seen from the data in the table; such a concentration exceeded the limit of allowable CO concentration in the air of working premises 5 times. Thus, workers in the tractor repair shops, built according to the new plan No. 1662, were subjected to the continuous effects of high concentrations of carbon monoxide. In the course of the above investigation workers frequently complained of headaches, heavy feeling in the head, which are characteristic complaints in chronic carbon monoxide poisoning.

Conclusions.

1. The air of premises housing motor tractor shops built according to plan No. 1662 contained carbon monoxide concentrations during the working period which exceeded the hygienically allowable concentration limits and which usually led to chronic CO intoxication.

2. The presence of high carbon monoxide concentrations in the air of such typical tractor repair shops indicated the following: a) the need for more favorable technological solution of bringing tractors and other agricultural machinery into the repair shop; b) the fan, installed according to the provision of project No. 1662, worked in the motor test station, in the copper casting and in the machine welding departments at low efficiency, calling for imperative changes in the original ventilation provisions.

3. Formation of high carbon monoxide concentrations in the air during so-called "hot burnishing" inside the testing station premises resulted primarily from the careless way in which the motor exhaust pipes were connected to the outdoor-leading pipes; this inadequacy should be resolved immediately.

4. Housing of the smith and the electric welding functions in one room is considered inappropriate, since the two functions are of completely independent

nature, and when operating in the same room caused accentuated air pollution.

5. Rate of artificial ventilation in the mechanical welding shop should be considerably enhanced and, in addition, the exhaust hood over the work table of the electric welder should be lowered to enable the dust and gaseous products formed during electric welding to be caught and carried off by the exhaust air.

6. Mechanical ventilation should be installed in the room housing liquid fuel testing apparatus, and provision should be made for the removal of low dispersed particles of crude oil distillation products from the point of their formation.

City Street Air Pollution by Autotransport Using Ethylated Gasoline.

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Gigiena i Sanitariya, Vol. 25, No. 4, 15-18, 1960.

In connection with the growing autotransport, hygienists are faced with the serious problem of safeguarding the air of populated areas against pollution by exhaust gas, in particular from pollution caused by burning ethylated gasoline. During ethylated gasoline combustion part of the lead compounds remain within the engine and part are discharged into the air. According to data of foreign investigators (Preis, Hirschler and their collaborators), an automobile burning ethylated gasoline discharged 70 - 80% lead into the air. Increase in speed proportionately increased the rate of lead discharge. Tests made at the F. F. Erisman Moscow Scientific-Research Institute of Sanitation and Hygiene of the U.S.S.R. Ministry of Health established that an idling GAZ-51 motor vehicle discharged into the air 0.3 g of lead for each kg of combusted ethylated gasoline, 0.87 g of lead per same amount of combusted gasoline when running at the rate of 15 km/hour, and 0.9 g of lead when running at the rate of 40 km/hour. According to Witt's 1957 report the air in the U.S.A. urban streets contained up to 30 - 40 $\gamma/m^3$ lead compounds. Jacklin reported that the yearly lead discharged by the autotransport in Switzerland amounted to 165,000 kg. Preis presented the following data regarding the lead content in the streets of Zurich.

T A B L E 1.

Pollution of Zurich region in 1948 - 1955.

| Sample collecting point | Number of auto machines per hour | $\gamma/m^3$ of lead |
|---|---|---|
| City center | 240 | 0.8 |
| City center | 350 | 1.3 |
| At city outskirts | 650 | 0.9 |
| At city outskirts | 800 | 1.7 |

According to Jacklin's 1956 data, the lead content in the air of Basel was 4.8 - 7 $\gamma/m^3$. A search of the U.S.S.R. literature indicated that M. K. Nagibchenko's 1958 report was the only one on the subject under consideration. The present paper is a report of a study on air pollution by non-organic lead compounds coming from autotransport operating on ethylated gasoline. Air samples were collected by the aspiration method, using a motor vehicle engine GAZ-51 and a setup shown in Fig. 1. The motor vehicle was installed at any desired point of a street or courtyard. A metal elbow (1) was attached to the suction opening of the carburetor and a rubber hose (2) 1.5 m long was connected to the free end of the elbow; a rubber tube (3) 8 - 10 mm in diameter was connected to the free end of the hose and the joint made leakproof with adhesive tape. If four or more samples were to be collected at the same time, a three-way metal pipe (4) was attached to the open end of the hose to connect it with three rubber tubes. Special holding devices (5) and adapters (6) containing special filters were attached to the rubber tubes; the filters consisted of analytical filter paper FPP-15 or absorbent cotton dipped in nitric acid, washed with hot water, and dried. Filter paper FPP-15 proved best for the purpose. The rate of aspiration in either case was 20 - 25 li/min. and was regulated by a flowmeter (7). It was possible to collect 4 - 6 samples at one time. Samples were collected at pedestrian's breathing level.

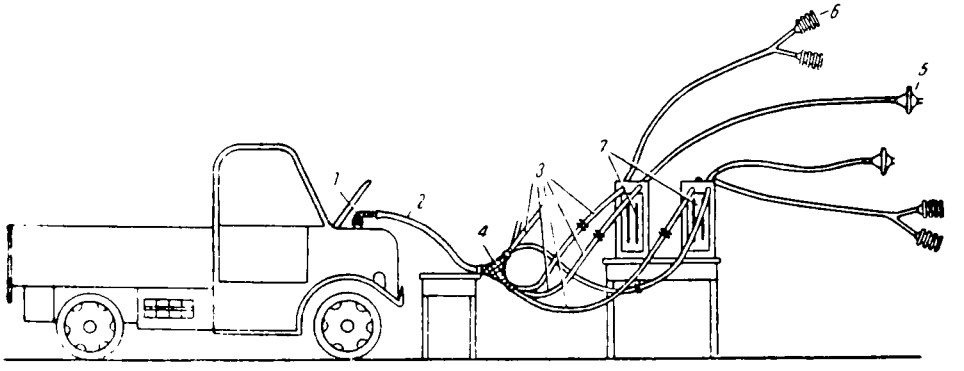


Fig. 1. Setup for air sample collection.

The described method was used for collecting air samples on sidewalks among pedestrians during heavy traffic. No industrial establishments were located in the immediate vicinity where the air samples were collected. Tests were made during the spring and summer seasons. Only winter samples were collected in Perm in 1957. Lead determinations were made on the basis of 24-hour averages; but air samples were collected 4 times a day between 0 and 3 o'clock, 6 and 9 o'clock, 12 and 15 o'clock and 15 and 21 o'clock. 14.4 - 18 $m^3$ of air was aspirated for each air sample. Lead determinations were made by the potassium chromate method. Filtered samples were treated with sulfuric acid converting the lead to lead sulfate; filters were then ashed at 500 - 550°; the lead sulfate dissolved in 3% solution of ammonium acetate followed by treatment with potassium chromate, and the lead ion determined accordingly.

Air was tested in Tula, Chelyabinsk, Perm, Kuibyshev and Gor'kii. Studies in Tula were conducted by members of the F. F. Erisman Moscow Scientific-Research Institute of Sanitation and Hygiene in cooperation with Tula's District Sanitary-Epidemiological Station. In other cities the work was conducted by local municipal sanitary-epidemiological stations. Final interpretation of results was made at the F. F. Erisman Moscow Institute. Samples totalled 157. Results of analyses are presented in Table 2.

TABLE 2.

Average daily lead concentrations in city air in $\gamma/m^3$.

| City | 1957 | | | 1958 | | |
|---|---|---|---|---|---|---|
| | Number of air samples | Concentration | | Number of air samples | Concentration | |
| | | Maximal | Average | | Maximal | Average |
| Tula | 19 | 6.94 | 1.40 | 55 | 0.50 | 0.24 |
| Chelyabinsk | 20 | 15.00 | 3.86 | - | - | - |
| Kuibyshev | 20 | 0.62 | 0.36 | 20 | 1.00 | 0.68 |
| Perm | 10 | 3.10 | 1.90 | 10 | Below the method's sensitivity | |
| Gor'kii | - | - | - | 3 | 0.08 | 0.03 |

Results indicated that in 1957 the air was heavily polluted with lead. Decreases in street air lead pollution noted in some of the cities in 1958 was due to the reduced amount of lead added to the gasoline at the time. In 1958 non-ethylated gasoline only was used in Perm, hence the absence of lead pollution in the street air. In 1958 both ethylated and non-ethylated gasoline was used in Tula. Data in Table 2 show that heaviest concentrations of lead were found in

the air of Chelyabinsk streets. Average 24-hour lead concentrations in the air of all cities except Kuibyshev during 1957 exceeded the 0.7 $\gamma/m^3$ limit of allowable atmospheric air concentration for community air. Lead concentration in the air of city streets varied throughout the day. The lead concentration was higher during the day than during the night. Fig. 2 shows that increase in lead air pollution ran parallel to the increase in motorized traffic. Jacklin (1956) was of the opinion that city dwellers were being subjected to lead poisoning.

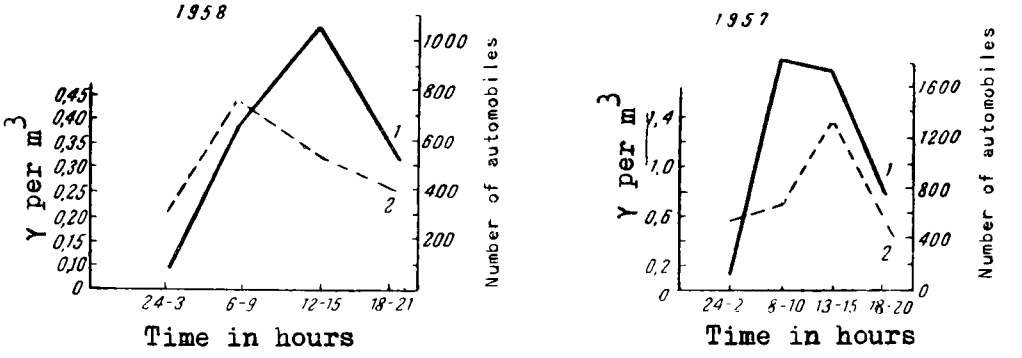


Fig. 2. Lead concentration in atmospheric air in relation to automotive traffic intensity.
1 - Number of automobiles; 2 - lead concentration

Members of the F. F. Erisman Moscow Scientific-Research Institute of Hygiene and Sanitation conducted supplemental polyclinical and hematological studies on street traffic directing personnel of Tula posted at points of heaviest motor traffic. The study covered 41 traffic directors posted within the city and 44 outside the city limits. The entire traffic directing personnel consisted of males close to 40 years old; all appeared to be in good physical and nutritional condition; all had work records of over 6 years; all were subjected to rigid medical examination in 1957 - 1958. Some manifested deviations in the nervous system (vegetative dysfunction), in the cardiovascular system (dystrophic and hypertonic or hypotonic). Blood pictures showed the presence of reticulocytes and erythrocytes with basophylic granules; basophylic erythrocytes with granules were also found in traffic directors of Chelyabinsk. Deviations from the normal functioning of individual organs were found less frequently among men stationed at city outskirts than among those in the city proper. Two traffic men were examined while in the hospital; lead poisoning was discovered in one, despite the fact that he had never been in contact with lead.

Conclusions.

1. The air tested in city streets was heavily polluted with lead exhausted by the autotransport; the deleterious effect of the lead was demonstrated.

2. It was recommended that the use of ethyl lead gasoline be discontinued.

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## A Study of Automotive Exhaust Gases.

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Fuel undergoes many physical, thermodynamic and chemical changes in the internal combustion engine. Incomplete combustion of liquid fuel in the automobile engines results in the formation of toxic compounds, which are discharged into the surrounding atmosphere with the exhaust fumes. The composition of automotive exhaust gases depends upon the technical condition of the engine, the manner in which it is used, and on many other factors. The composition of exhaust gases has been studied by many investigators, but certainty and finality in this respect are still lacking.

The present authors undertook to determine the organic substances in the atmospheric air in the immediate proximity of automobile exhaust gases on the street sidewalks during heavy automobile traffic. Quantitative determinations were made of formaldehyde, acrolein, ketones, unsaturated and aromatic hydrocarbons, and also of the total amounts of carbon and carbon monoxide. Hydrocarbons and carbon monoxide were determined using a gas analyzer in which the organic substances were combusted on a platinum spiral to carbonic acid; the latter was absorbed by

barium hydroxide and titrated with acid. Formaldehyde was determined by the sensitive and specific method of chromotropic acid. Acrolein was determined colorimetrically by the color reaction with tryptophan. Unsaturated hydrocarbons were determined by the bromination method and calculated on the pentose basis. Aromatic hydrocarbons were determined by the Yanovskii reaction, and the results calculated as benzene. Ketones were determined by two nephelometric methods: with demidon (demeton? B.S.L.) and by the iodoform method and the results expressed as acetone. Samples were collected by the vacuum method into special pipettes of 0.5 - 1 li capacity at a distance of 0.5 m from the exhaust pipes of small "Volga", ZIL-110 and "Pobeda" types of automobiles burning high octane gasoline; GAZ-51 trucks burning low octane gasoline, and ZIL busses burning Diesel oil. Results of more than 100 analyses are listed in Table 1.

T A B L E 1.

Total organic carbon and CO in $g/m^3$ in automachine exhaust.

| Index | Type of automachine | | | |
|---|---|---|---|---|
| | "Volga" | ZIL-110 | "Pobeda" | Autobus ZIL |
| Total organic carbon | 15.4 - 20.1 | 9 - 20.4 | 3.3 - 21.2 | 0.2 - 1.4 |
| Amount of CO | 2.2 - 4.5 | 1.1 - 3.2 | 1.1 - 5.0 | 0.13 - 0.34 |

Table 1 shows that exhaust gases contained considerable concentrations of carbon monoxide and of total carbon. Of considerable interest is the fact that engines burning Diesel fuel produced gases which contained lower concentrations of carbon monoxide and less total carbon. Formaldehyde, acrolein, ketones, unsaturated and aromatic hydrocarbons were determined in 40 air samples each. Some of the results are listed in Table 2.

A study of the data in Table 2 shows that automotive exhaust fumes polluted atmospheric air with formaldehyde, acrolein, ketones, unsaturated and aromatic hydrocarbons. Formaldehyde was present in proximity of almost all engines studied; its concentration reached 2 $mg/m^3$. Acrolein in concentrations up to 20 $mg/m^3$ was found only near the exhaust pipe of GAZ-51 truck, which was burning low-grade gasoline. No ketones were found in the exhaust gases of light "Volga" and "Pobeda" automobiles which were burning high-grade fuel. Ketones were found in concentrations of 6 - 20 $mg/m^3$ in the exhaust gases coming from engines of GAZ-51 truck and ZIL bus, which were burning low-grade gasoline or Diesel fuel. Unsaturated hydrocarbons were found in the exhausts of all auto-

TABLE 2.

Organic substances in the air 0.5 m from the automobile exhaust in $mg/m^3$.

| Automobile make | Formaldehyde | Acrolein | Ketone (acetone) | Unsaturated hydrocarbons (pentene) | Aromatic hydrocarbons (benzene) | Fuel type |
|---|---|---|---|---|---|---|
| "Volga" | 0.08 | None found | None found | 20 | 5 | High octane gasoline |
| | None found | None found | None found | None found | 4 | |
| | None found | None found | None found | 30 | 10 | |
| | 0.24 | None found | None found | 40 | 16 | |
| | 0.68 | None found | None found | 40 | None found | |
| | None found | None found | None found | 40 | 26 | |
| "Pobeda" | 0.04 | None found | None found | 5 | 16 | High octane gasoline |
| | 0.06 | None found | None found | 12 | 20 | |
| | 0.12 | None found | None found | 26 | 24 | |
| | 0.24 | None found | None found | 68 | 32 | |
| | 0.32 | None found | None found | 200 | 60 | |
| | 0.4 | None found | None found | 470 | 30 | |
| GAZ-51 | None found | 4 | 2 | 20 | 8 | Low octane gasoline |
| | 0.1 | 12 | 6 | 50 | 24 | |
| | None found | 16 | 8 | 90 | 32 | |
| | None found | None found | 10 | 100 | 40 | |
| | 0.04 | 20 | 12 | 120 | 80 | |
| | None found | None found | 13 | 130 | 120 | |
| Autobus ZIL | 0.16 | None found | 8 | 5 | None found | Diesel fuel |
| | 0.2 | None found | 14 | 50 | None found | |
| | 0.4 | None found | 16 | 60 | None found | |
| | 2.0 | None found | 18 | 80 | None found | |
| | 2.0 | None found | 20 | 140 | None found | |

motive vehicles, while aromatic hydrocarbons were present only in the exhausts of machines burning gasoline.

Air samples were collected on sidewalks at pedestrian breathing levels during heavy automobile traffic; while vehicles were in motion and while they stopped for traffic light changes on avenues, and in narrow side streets which had no traffic lights. The above mentioned substances were present in 31.3% of the tested air samples. Some of the results are shown in Table 3.

Data listed in Tables 1, 2 and 3 show that incomplete fuel combustion in motor vehicles was a potent source of atmospheric air pollution with organic compounds injurious to the population's health. Automotive exhaust gases should be rendered harmless by oxidative catalytic complete combustion of automotive fuels. In this respect use can be made of palladium, hopcalite, oxides of man-

TABLE 3.

Harmful substances in street air in $mg/m^3$.

| Street | Carbon monoxide | Formal-dehyde | Acrolein | Ketone | Unsaturated hydro-carbons | Aromatic hydro-carbons |
|---|---|---|---|---|---|---|
| Wide | 4 | 10.0 | None found | 0.2 | 16 | None found |
| | 22 | 10.0 | None found | 1.0 | 20 | None found |
| | 25 | None found | None found | None found | None found | None found |
| | 70 | None found | None found | None found | None found | None found |
| | 80 | 0.6 | None found | 2.0 | 30 | None found |
| | 80 | 10.0 | None found | 2.0 | 160 | None found |
| Narrow | 14 | 0.04 | 0.001 | 0.10 | None found | None found |
| | 30 | 0.016 | 0.002 | 0.10 | Trace | None found |
| | 47 | 0.12 | 0.004 | 0.16 | None found | Trace |
| | 50 | 0.2 | 0.004 | 0.80 | None found | Trace |
| | 50 | 0.6 | None found | None found | None found | Trace |
| | 50 | 0.8 | None found | None found | None found | Trace |

ganese, vanadium, cobalt, iron, chromium, or mixtures of same. The best catalyst, platinum, was recommended by Gudry in 1950 and used in France as a "combustion completer", called by the author "oksicat" (short for oxy-catalyzer). The active principle of "oksicat" is a combination of platinum and aluminum, which converts atmospheric oxygen into the monatomic form, which accelerates the oxidative process. One of the favorable aspects of this catalyst is its ability to react at 250°.

In collaboration with the Scientific-Research Institute of Automotive Motor Designing the present authors tested the "Moskvich-407" engine to which Gudry's combustion device was attached in the place of the muffler. At the time of the test determinations were made for concentrations of oxygen, carbon dioxide, carbon monoxide and the above enumerated organic substances. Air samples were collected near vehicles with motor running at different speeds, carrying loads of different weight. Samples were collected by the aspiration method with and without the catalytic oxidizing device. Results of the tests are listed in Table 4.

Data in Table 4 show that without the Gudry device the exhaust gases contained 1 - 8% of carbon monoxide, which was reduced to 0.5% when the Gudry device was attached; the organic compounds underwent complete combustion.

TABLE 4.

Analysis of exhaust gases of automobile "Moskvich-407" with and without catalytic oxidation.

| r.p.m. | Running | Power in l.s. | Fuel consumption in kg/hr | Gas consumption in $m^3$/hr | No catalytic oxidation | | | | | | With catalytic oxidizer | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Percent of CO | Formaldehyde | Acrolein | Acetone | Pentene | Benzene | Percent of CO | Formaldehyde, acrolein, acetone, pentene, benzene, in mg/$m^3$ |
| | | | | | | In mg/$m^3$ | | | | | | |
| 580 | Idling | - | 0.7 | 6.0 | 5.5 | 1.0 | 100 | None found | 250 | 90 | 0.5 | None found |
| 1,430 | 7.5 | - | 4.3 | 34.8 | 7.8 | None found | 80 | Ditto | - | 8 | - | Ditto |
| 1,420 | - | 12.5 | 2.9 | 39.8 | 1.1 | Ditto | 400 | Ditto | - | 30 | None found | Ditto |
| 2,620 | - | 5.1 | 2.9 | 38.0 | 2.2 | 3.0 | - | Ditto | 35 | 100 | Ditto | Ditto |
| 1,400 | - | 7.0 | 2.0 | 28.3 | 1.8 | 1.0 | 60 | Ditto | - | 50 | 0.25 | Ditto |
| 1,400 | - | 3.1 | 1.7 | 20.0 | 2.6 | 0.5 | 30 | Ditto | 20 | 20 | None found | Ditto |
| 2,600 | - | 14.6 | 4.1 | 55.5 | 1.3 | 0.2 | 90 | Ditto | 8 | 40 | Ditto | Ditto |
| 2,600 | - | 10.4 | 3.5 | 50.0 | 2.3 | 0.2 | 90 | Ditto | 7 | 30 | Ditto | Ditto |

Conclusions.

1. Air of cities with heavy automotive traffic is contaminated by exhaust gases containing considerable amounts of toxic compounds.

2. Vehicles burning Diesel fuel discharged considerably larger amounts of formaldehyde into the air than vehicles burning gasoline.

3. Acrolein and acetone were found in the exhaust fumes of vehicles burning low-grade fuel.

4. High concentrations of aromatic hydrocarbons were found in exhaust fumes of vehicles burning gasoline.

5. Unsaturated hydrocarbons were found in samples collected near all motor vehicles.

6. Supplementary catalytic combustion of exhaust gases can be effective in abating atmospheric air pollution by automotive exhaust gases.

7. Data listed in the tables point to the need for systematic sanitary inspection of automobiles and examination of city air for concentrations of carbon monoxide and such organic substances as formaldehyde, acrolein, saturated and unsaturated hydrocarbons and other substances.

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## Effect of Superphosphate Production Discharges on Children's Health.

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Gigiena i Sanitariya, Vol. 25, No. 5, 89-96, 1960.

Parallel with a study of the effect of superphosphate production discharges on the health of the population this author, in cooperation with physicians of local children's institutions, carried out a thorough and systematic medical examination of the children residing within the region of a large superphosphate producing plant in the winter of 1953 - 1954. Medical examinations included general examinations with emphasis on chest X-rays and results of tuberculin tests. The study covered 2,053 individuals of whom 1,375 were children residing in the superphosphate plant district and 678 control children. The factory district consisted of 2 settlements: the southern, located at 0.5 - 1.7 km south of the plant; and the western, located 0.5 - 3 km west of it. The settlements' atmospheric air was intensely polluted by the harmful components of discharges coming from the superphosphate plant (Z. Ya. Lindberg). Air samples collected in the inhabited zone 500 m from the plant yielded the following analytical results in terms of limits of allowable concentrations in community air: fluorine compounds 16.2 times as high; sulfur dioxide 9.5 times as high; $H_2SO_4$ aerosol 27.9 times as high; and oxides of nitrogen 33.9 times as high. The analytical

results were as follows at 3000 m from the plant: concentration of fluorine compounds 3.3 times as high as the limit of allowable concentration; sulfur dioxide 1.7 times as high; $H_2SO_4$ aerosol 3 times as high; and oxides of nitrogen 3.2 times as high. Such intense air pollution was the result of inefficient exhaust pipes (18 - 34 m) of the plant.

The control district was located more than 10 km from the superphosphate plant and had no industrial establishments on its territory. In this district no harmful substances were detected in the atmospheric air. The character of buildings, the population's social-economic status were approximately on the same levels as in the factory district. Medical examination of children from the factory district disclosed that a high percentage had enlarged lymphatic glands and a catarrhal condition of the upper respiratory passages, the frequency of which could be ascribed to the irritating effect of the plant discharges. (Table 1). Distribution according to ages is shown in Table 2.

T A B L E 1.

Catarrh frequency of upper respiratory tract and lymphatic gland enlargement as compared with the control region.

| Settlement | Total | Number examined | | |
|---|---|---|---|---|
| | | With catarrh of upper respiratory tract | With enlarged lymphatic glands | |
| | | In percent | | |
| Southern village | 318 | 1,740 | 164 | |
| Western | 1,058 | 1,040 | 249 | |
| Control region | 662 | 100 | 100 | |

Frequency of catarrhal conditions of upper respiratory passages in children of the factory district in relation to residence duration is shown in Table 3. This table contains no data on the control district since the frequency of catarrhal conditions in the upper respiratory passages had no relation to residence duration.

T A B L E 2.

Catarrh frequency of upper respiratory tract according to age groups.

| Settlement | Number examined | | | Percent of frequency in relation to the control region | | |
|---|---|---|---|---|---|---|
| | Upper age of creche nursery | Preschool age | School age | Upper age of creche nursery | Preschool age | School age |
| Southern village | - | 46 | 272 | - | 1,563 | 2,052 |
| Western village | 33 | 58 | 967 | 222 | 621 | 1,318 |
| Control region | 61 | 60 | 541 | 100 | 100 | 100 |

TABLE 3.

Catarrh frequency of upper respiratory tract in relation to length of residence in the plant region.

| Residence duration | Number examined | | Percent frequency in relation to children of less than 3 years residence | |
|---|---|---|---|---|
| | Southern village | Western village | Southern village | Western village |
| Up to 3 years | 92 | 216 | 100 | 100 |
| Longer than 3 years | 225 | 809 | 122 | 199 |

Data in Table 3 show that frequency of catarrhal conditions of the upper respiratory passages in children living in the southern settlement was 17.4 times as high and in the western settlement 10.4 times as high as in children living in the control district; the frequency increased noticeably with children's age and length of residence in the factory district. Children living in the settlements of the factory district showed an increasing frequency of lymphatic gland enlargement, especially of the neck. A wider occurrence of some pathological conditions in children living in the factory district can be regarded as the result of the harmful effect of the plant's discharges on the child's organism. X-ray examinations were made of most of the children included in the study plan. Children living in the southern settlement were examined in the district's tuberculo-preventive clinic by an X-ray of the chest, and those living in the western settlement were examined fluoroscopically on the spot by the physicians of the same clinic. Children of the control district were given X-ray examinations of the chest in the district's polyclinic. Medical specialists of the tuberculo-preventive clinic regarded the fluoroscopic examination diagnostically on par with that of chest X-ray examination. Changes detected in the lungs were grouped as of tubercular and of non-tubercular origin; at the recommendation of the specialists the non-tubercular changes were classed as broncho-

TABLE 4.

Results of roentgenologic examinations of children of all ages.

| Settlement | Number examined | Percent frequency of pulmonary changes in relation to the control region | |
|---|---|---|---|
| | | Of non-tubercular origin | Of tubercular origin |
| Southern village | 300 | 663 | 376 |
| Western village | 985 | 1,212 | 268 |
| Control region | 618 | 100 | 100 |

adenites and as changes at the roots of the lungs. Results of examinations are listed in Table 4. Frequency of lung changes of tubercular origin ran parallel to the length of residence in the factory district, as shown in Table 5.

TABLE 5.

Frequency of pulmonary changes of tubercular origin.

| Residence duration | Number examined | | Percent frequency in relation to children of less than 3 years residence | |
|---|---|---|---|---|
| | Southern village | Western village | Southern village | Western village |
| Up to 3 years | 79 | 164 | 100 | 100 |
| Longer than 3 years | 221 | 788 | 238 | 318 |

According to the X-ray findings pulmonary changes of a presumably tubercular origin were noted among children of all groups in the following ratios in relation to positive changes seen among the children of the control group: 3.76 times as many among the children living in southern village and 2.68 as many in the western village; correspondingly pulmonary changes of non-tubercular origin were numerically 6.63 and 12.12 times as many. In this connection it should be noted that in terms of absolute numbers, cases with pulmonary changes of tubercular origin predominated. All children were also given the Pirquet tuberculin skin test. Children reacting negatively to the Pirquet test were given a supplemental intradermal Mantu test, and children reacting to either of the tests were regarded as tuberculin positive. Results of the tests are listed in Table 6.

TABLE 6.

Tubercular infection among children of all ages.

| Settlement | Number | Percent frequency in relation to control region |
|---|---|---|
| Southern village | 300 | 185 |
| Western village | 1,002 | 168 |
| Control region | 616 | 100 |

Data indicating the effect of residence duration on frequency of tubercular infection are listed in Table 7. Data in Table 7 show that the number of children from the factory district who had been infected with tuberculosis was in the southern settlement 1.85 times and in the western settlement 1.63 times as high as in the control district, and it increased with the length of the residence in the air polluted district.

TABLE 7.

Tubercular infection among children in relation to residence duration in the plant region.

| Residence duration | Number examined | | Percent of infection in relation to children of less than 3 years residence | |
|---|---|---|---|---|
| | Southern village | Western village | Southern village | Western village |
| Up to 3 years | 85 | 183 | 100 | 100 |
| Longer than 3 years | 215 | 786 | 314 | 573 |

Analysis of the results of medical examinations, including the X-ray and tuberculin tests of children residing in the 2 villages of the industrial district and of those residing in the control district brought out a clear-cut relationship between the frequency of pathological conditions and the intensity of atmospheric air pollution with harmful substances.

Results of this study were used by bodies of the Sanitary Inspection in their presentation of a request for the imperative intensification of the fight against atmospheric air pollution by discharges from the superphosphate plant. As the result of such a request the following corrective measures had been instituted: an additional electrostatic sulfuric acid precipitator had been installed, the device for the recovery and utilization of fluorine compounds had been rebuilt, new equipment was installed for the recovery and utilization of oxides of nitrogen, and a 100 m vapor and fumes exhaust pipe had been erected for the wider dispersion of the plant's exhaust gases.

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# Two Cases of Acute Carbon Monoxide Poisoning.

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(From the Stalinsk Medical Institute and Stalinsk Municipal Sanitary-Epidemiological Station).

Gigiena i Sanitariya, Vol. 25, No. 8, 63-63, 1960.

Sanitary inspectors of gas-equipped buildings frequently encounter cases of gas seeping into living quarters as a result of improper exhaust conduits or due to defects in the gas mains. The two cases of gas poisoning here described occurred in living quarters which used coke gas for domestic purposes; the coke gas contained 4.5% of carbon monoxide.

In the first instance a family of 5 were affected who lived on the second floor of a gas-equipped house; all were hospitalized as a result of symptoms of acute poisoning, such as loss of consciousness, convulsions, rigidity of the nape of the neck, vomiting, etc. Tests for possible food poisoning were all negative. A few hours after the application of appropriate therapeutic means patients were discharged from the hospital in a favorable condition. Results of air analysis in the apartment showed the presence of carbon monoxide concentrations ranging between 0.09 - 0.25 mg/li. Higher concentrations were found at the grate of sub-floor ventilation. Air samples were collected in different apartments located on the first floor directly beneath this particular apartment. Results showed that the outlet for the combusted gas was damaged and partly clogged, as a result of which products of gas combustion penetrated into the upper floor apartment.

Instance number two. Seventeen persons were brought to the hospital with symptoms of acute gas poisoning. All patients lived on the first floor of a gas-equipped house. Analyses of air samples collected in different apartments of the first floor showed the presence of carbon monoxide in concentrations ranging between 0.15 - 0.5 mg/li, and as high as 0.25 mg/li in basement samples. Careful inspection disclosed that 2 gas mains were passing underground 6 m away from the house, both of medium pressure. A leak developed in one of the conduits and the escaping gas found its way into the house through the foundation into the basement and from the basement to the apartments on the first floor.

# Carboxyhemoglobin in the Blood of Persons Directing City Traffic. [1]

A. A. Vasil'eva and M. D. Manita.

(Moscow City Sanitary Epidemiological Station).

Gigiena i Sanitariya, Vol. 25, No. 12, 77-80, 1960.

Z. G. Vol'fson, A. S. Lykova, V. Z. Martynyuk, Z. V. Babayan, and others, previously reported that carboxyhemoglobin concentration in the blood of persons directing city street traffic was higher than in the blood of control persons. The following is a preliminary report of a study conducted by the present authors on the carboxyhemoglobin content in the blood of persons directing street traffic in the city of Moscow. The authors employed a spectrophotometric method based on the property of different hemoglobin forms to absorb light rays in different spectral regions. For the particular purpose at hand COHb in the blood was determined by a V. V. Popov modified procedure; Popov employed an automatically recording spectrophotometer SF-2M. The principle of the modification is as follows: use was made of the difference in light absorption by COHb and reduced hemoglobin, PHb, in the 534 mμ wavelength spectral region. In this region the difference in light absorption by COHb and PHb is at its maximum, and follows the law of Bear. At this wavelength reading magnitudes characterize the degree of blood saturation with CO. At wavelength 563 mμ there appeared no difference between light absorption by COHb and PHb; the quantity of hemoglobin is determined at this point and converted to COHb with the aid of a special formula. (Authors fail to present the formula. B.S.L.).

The procedure proposed by Popov was used in this study in a somewhat different way. Instead of diluting the blood 1:75 in 0.005 ml of N NaOH, [2] the present authors used a 1:100 dilution of the blood, and for the following reasons: the optical density scale on spectrophotometer SF-4, which was at the authors' disposal, was graduated up to 2. Optical densities of 1:75 blood dilutions were close to the limiting 2 calibration point of the instrument, and readings at such points were not accurate to the degree desired. Therefore, the present authors used the blood in a 1:100 dilution; this raised the degree of reading accuracy to the maximal level, because the values fell within the cen-

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[1] The original title translated literally would read: "Concerning the Problem of Carboxycarbon Content in the Blood of Street Traffic Directors". B.S.L.

[2] This is an obvious error: it should have been "with 0.005 N NaOH". B.S.L.

tral part of the reading scale. In mass analyses of blood for COHb concentrations, 0.1 ml of blood was taken by finger puncture, prepared for the spectrometric reading, and the optical density determined accordingly.

The technic is as follows: with the aid of a blood micro-pipette take 0.1 ml of finger blood; the pipette should be first moistened with 5% solution of Na-citrate; blow the blood out into a 10 ml volumetric flask; rinse the pipette several times with 0.005 N solution of NaOH and blow out into the volumetric flask; now bring the volume up to the 10 ml mark with the 0.005 N NaOH; mix and pour the entire solution into a test tube with a ground-to-fit glass stopper; the tube volume should be such that the diluted blood will be in contact with the glass stopper. Bring the tube with its content to the laboratory and begin the spectrophotometric determination not later than 1.5 - 2.0 hours after the blood specimen has been obtained. Remove 5 ml of the clear diluted blood into a tube and add 1 mg of Na-digitonine as the reducing agent. Make spectrophotometric determinations for optical density of the diluted blood in spectral regions of 534 and 563 mμ. Use formula and convert to COHb in the blood. Determination time should not exceed 5 minutes.

For comparison purposes blood of street traffic directors was studied on a parallel basis with the blood of suitably selected control persons residing in Moscow, none of whom were engaged in city traffic directing at any time. However, one of the control persons was a chauffeur, and his COHb concentration was 8.0%. On days when COHb was determined in the blood of city traffic directing personnel, the time was set close to 9:00 a.m. when traffic was at its highest, and when the CO concentration in the air ranged between 15 - 16 $mg/m^3$. Seventy-six blood specimens were tested for COHb concentration covering two shifts of traffic directing personnel numbering 16; 50 blood specimens were collected and analyzed in the summer and 26 blood specimens in the winter of 1959; blood specimens were taken at 7:00 o'clock, before duty performance and at 17 o'clock at end of tour of duty. Test subjects ranged between 31 and 47 years of age; 4 of 16 did not smoke; 10 lived in gas-equipped residences and 6 in non-gas-equipped residences. Results are presented in Table 1.

Results listed in Table 1 show that COHb concentration in the blood prior to assuming tour of duty ranged between 7 - 30.2%; at the conclusion of the work day the blood COHb concentration rose by 50 - 100% in 23 of 39 persons; in 8 persons morning and evening COHb blood concentrations were nearly identical; in another 8 persons the morning values were higher than the evening values. The

TABLE 1.

Results in percent of COHb determinations in the blood of city street traffic directing personnel.

| Smoker | Summer | | | | Fall | |
|---|---|---|---|---|---|---|
| | First investigation | | Second investigation | | | |
| | Before tour of duty | After tour of duty | Before tour of duty | After tour of duty | Before tour of duty | After tour of duty |
| Yes | 12.0 | 17.0 | Not tested | Not tested | Not tested | Not tested |
| Yes | 20.0 | 23.0 | Not tested | Not tested | 17.6 | 16.0 |
| Yes | 18.0 | 20.0 | 12.5 | 25.0 | 11.5 | 28.0 |
| Yes | 29.0 | 26.0 | 11.6 | 30.0 | 18.0 | 25.5 |
| No | 18.6 | 12.0 | 17.0 | 25.0 | 14.8 | 23.3 |
| No | 16.2 | 12.0 | 9.4 | Not tested | 23.0 | 24.0 |
| No | 30.2 | 11.0 | 12.7 | 19.0 | 7.0 | 30.2 |
| Yes | - | - | 19.5 | 23.0 | 9.8 | 22.8 |
| Yes | 16.4 | 28.4 | 15.5 | 12.4 | Not tested | Not tested |
| Yes | - | 40.0 | 9.0 | 19.0 | 20.0 | 20.0 |
| Yes | 25.6 | 14.4 | Not tested | Not tested | 22.4 | 32.0 |
| Yes | 12.5 | 17.0 | 12.0 | 34.5 | 13.0 | 18.0 |
| No | 20.9 | 21.6 | 17.2 | 20.6 | 17.3 | 16.0 |
| Yes | 14.0 | 20.0 | 18.4 | 17.5 | 18.0 | 16.0 |
| Yes | 24.4 | 25.1 | Not tested | Not tested | Not tested | Not tested |
| Yes | 22.0 | 15.0 | 14.0 | 35.0 | 11.5 | 12.0 |

reason for the above seemingly paradoxical results has not been determined. No differences were observed in the COHb blood concentration among workers residing in gas-equipped and those residing in non-gas-equipped homes. Results of the study of Moscow residing controls compared with those of the traffic directing personnel are listed in Table 2.

Results in Table 2 show the following: blood samples of 28 controls were free from COHb, which included 25 of 44 tested in the summer and 3 of 58 tested in the fall; 34 of 102 had a blood COHb concentration ranging between 0.0 - 6.0%, and 37 between 7.0 - 12.0%, and in only 3 cases did it range between 13.0 - 18.0%. Thus, data in Table 2 show that COHb concentration in the blood of city street traffic directing personnel in the summer and in the fall was at higher levels than in the blood of Moscow residing control persons. This is in agreement with the results obtained by Z. V. Babayan in a similar study made in Leningrad. No differences were noted between the blood COHb concentration of smokers and non-smokers in any of the groups studied.

Information obtained from the polyclinic of the Ministry of Internal Affairs concerning morbidity of the studied city street traffic directing personnel for

TABLE 2.

Data from comparative parallel determinations of blood COHb content in the fall of 1959 in Moscow residing control persons and in city street traffic directing personnel.

| Percent of COHb | Summer | | | | Fall | | | |
|---|---|---|---|---|---|---|---|---|
| | Moscow controls | | Traffic directors | | Moscow controls | | Traffic directors | |
| | Males | Females | Before tour of duty | After tour of duty | Males | Females | Before tour of duty | After tour of duty |
| 0.0 | 1 | 24 | - | - | - | 3 | - | - |
| 0.0 - 3.0 | 2 | 3 | - | - | - | 3 | - | - |
| 4.0 - 6.0 | 3 | 3 | - | - | 7 | 13 | - | - |
| 7.0 - 9.0 | 3 | - | 1 | - | 8 | 5 | 1 | - |
| 10.0 - 12.0 | 3 | - | 3 | 4 | 4 | 14 | 3 | 1 |
| 13.0 - 15.0 | 1 | - | 5 | 2 | - | 1 | 2 | - |
| 16.0 - 18.0 | 1 | - | 7 | 3 | - | - | 4 | 4 |
| 19.0 - 21.0 | - | - | 4 | 5 | - | - | 1 | 1 |
| 22.0 - 24.0 | - | - | 2 | 3 | - | - | 2 | 3 |
| 25.0 - 27.0 | - | - | 1 | 4 | - | - | - | 1 |
| 28.0 - 30.0 | - | - | 2 | 2 | - | - | - | 2 |
| 30.0 | - | - | - | 2 | - | - | - | 1 |
| Totals | 14 | 30 | 25 | 25 | 19 | 39 | 13 | 13 |

1959 showed the following: 44 visited the polyclinic; of these 23 complained of headaches; one visited the clinic 5 times, 3 four times each, and 1 came twice. In reply to questions many of the traffic directing personnel complained of vertigo toward the end of the day. The above is a report on a preliminary study; it is being continued by the Moscow City Sanitary-Epidemiological Station.

## Conclusions.

1. Sixteen Moscow city street traffic directing workers were examined for COHb blood concentration as described in the text. Results of analyses of 76 blood specimens showed a higher level of COHb blood content than in appropriately selected controls.

2. COHb blood concentration among the Moscow residing controls ranged between 0.0 - 6.0% in the summer and 0.0 - 12.0% in the fall; COHb concentration in the blood of Moscow traffic directing personnel ranged between 12.0 - 40.0%.

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# Effect of Poisoning with Some Phospho-Organic Insecticides.

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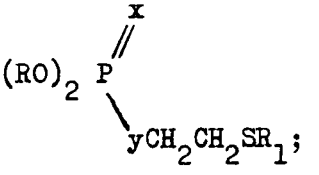
(From the Kiev Scientific-Research Institute of Labor Hygiene and Occupational Diseases).

Arkhiv. Patologii, Vol. 22, No. 9, 44-49, 1961.

Among chemical poisons used to control insects harmful to farm crops, an increasingly great importance should be ascribed to the phospho-organic insecticides (POI), and in particular to mercaptofos (sistoks) and substances of the M group (M-74, M-81, M-82). These insecticides are similar in their chemical structure, physico-chemical properties, and in the character of their biological action. The general formulas for these compounds are:



mercaptofos (thione isomer) - R = $C_2H_5$, X = S, y = O, $R_1$ = $C_2H_5$;

mercaptofos (thiole isomer) - R = $C_2H_5$; x = O, y = S, $R_1$ = $C_2H_5$;

M-74 (disiston) - R = $C_2H_5$, x = y = S, $R_1$ = $C_2H_5$;

M-81 (ekatin) - R = $CH_3$, x = y = S, $R_1$ = $C_2H_5$;

M-82 - R = $CH_3$, x = y = S, $R_1$ = $CH_3$.

The enumerated insecticides are liquids of low volatility with unpleasant odors, relatively insoluble in water and readily soluble in organic solvents (M. I. Kabachnik, et al, 1956; N. N. Mel'nikov, et al., 1958); they are used in the form of emulsions. Studies of the toxicity of mercaptofos (Wirth, 1953; Diehamann and Rakoczy, 1955; Yu. S. Kagan, 1956, 1957; and others) and of the compounds of group M (Yu. S. Kagan, 1956, 1957; G. L. Taranovich, 1956; K. S. Shadurskii and co-authors, 1957) showed their high toxicity to animals and their ability to penetrate into different organs not only when introduced internally but also when coming in contact with intact skin or mucosa, and also to bring about an intoxication characterized by the stimulation of the choline-reactive systems of the organism. There have been descriptions of serious and fatal mercaptofos poisonings in human beings (Kaiser, 1953; Naeve, 1957; Maresch, 1957; Metcaef, 1957) and of changes in cholinesterase activity as the result of agri-

cultural use of this insecticide (Yu. S. Kagan, 1956, 1957; V. A. Kryuchkova, 1957; M. Ye. Machabeli, 1957; and others). Literature contains only scanty data regarding morphologic changes in cases of poisoning with these insecticides and particularly regarding the connection between these changes and the clinical aspects of the intoxication and the biochemical shifts. Thus, Naeve performed an autopsy on a man who died of mercaptofos poisoning and found hemorrhages in the gastric and duodenal mucosae and also parenchymal dystrophy of the liver. The present authors obtained data (1957) regarding the morphological changes in the cerebrum in experimental animals poisoned with mercaptofos. There are no data in the literature related to the morphological changes in animals poisoned with insecticides M-74, M-81 and M-82.

This paper presents findings in the clinical course of poisoning by mercaptofos and its analogues and the blood cholinesterase and pseudocholinesterase activity paralleled by morphological changes noted in animals treated with POI by various routes, such as oral administration, cutaneous administration, inhalation, and intravenous injection. The effects of a single and repeated toxic doses of the insecticides in different concentrations were investigated.

Methods of investigation. The toxic preparations were injected into white rats, mice and cats in the form of emulsions prepared by mixing the substances with OP-7 (polyethylene glycol esters) and then diluting with water to 0.1 - 1.0%. The test preparations were administered intragastrically; cutaneously to a shaved portion of the skin of the rabbit's back, and by inhalation in a special chamber. Changes in the animals' behavior, in their weight and in the cholinesterase and pseudocholinesterase activity of the blood served as indexes of poisoning. All dead animals (280) were autopsied, and the organs of 189 (58 cats, 30 rabbits, 28 mice and 73 rats) examined histologically. The organs studied were the cerebrum, the heart, the liver, the lungs, the spleen, the thyroid and pancreas, the adrenals, and the testes. Celloidin sections were stained with hematoxylin-eosin, van Gieson, sudan III, and silver nitrate impregnation according to Foote. The brain sections were stained with toluidine blue and also by the Beletskii-Shtern method. Following the organic phosphorus insecticide administration, the time of intoxication picture appearance, its severity, and the survival time of the animals, differed with each poison, the dose, the route of entry into the organism, and the animal species.

Two hundred and sixty mice were administered single toxic and lethal doses of the POI compounds. The $LD_{50}$ doses for mice were as follows: 8 mg/kg for mer-

captofos; 4.8 mg/kg for M-74; 37 mg/kg for M-82, and 23 mg/kg for M-82. During the first 10 minutes to 2 hours the animals were somewhat lifeless, depending on the dose and the compound used, then they developed dyspnea, twitching of individual muscles and fibrillation of the muscles of the entire body, salivation, and tremor. Some mice exhibited ataxia and tension of the caudal muscles. As a rule, a brief spasmodic period ensued before the animal died. All such manifestations appeared considerably more rapidly with mercaptofos and M-74 poisoning (death within the first few hours) than with M-81 and M-82 poisoning (death within 10 days). The intoxication picture in 158 rats ($LD_{50}$ for mercaptofos - 3.5 mg/kg; for M-74 - 3.4 mg/kg; for M-81 - 74 mg/kg; and for M-82 - 75 mg/kg) did not differ greatly from the one described above. Rats exhitibed a more pronounced tremor and at times clonic spasms. The rats exuded a characteristic reddish secretion from the lacrimal glands, which was connected with the production of the pigment protoporphyrin (Burgen, 1951).

Nine of 18 cats receiving fatal doses (mercaptofos - 3 mg/kg; M-74 - 3 mg/kg; M-81 - 20 mg/kg) showed a degree of depression and decreased activity; after 30 - 60 minutes the animals became excitable and aggressive and flung themselves about the cage. Motor excitation symptoms were more pronounced with mercaptofos intoxication and less with the compounds of the M group. Voluminous salivation appeared next; it progressively rose in intensity to the stage of continuous flow from the mouth. Rasping respiration developed, dyspnea increased followed by the appearance of fibrillar twitches of the muscles, tremor in the paws, and periodic attacks of clonic spasms. The animal's condition gradually worsened, respiration became weaker, involuntary defecation and urination appeared, and coma set in. The cats died in a state of increasing respiratory weakness. In 12 of the poisoned rabbits no pronounced symptoms of motor excitation were noted; instead a state of depression prevailed. There was considerable salivation, muscular fibrillation, and bradycardia. Pupils of most animals were somewhat constricted, in other animals the pupils remained dilated.

The POI compounds were then applied to rabbits cutaneously (lethal dose of mercaptofos, 10 - 20 mg/kg; M-74, 3 - 5 mg/kg; M-81 and M-82, 50 - 150 mg/kg). Symptoms similar to the ones previously described appeared slowly in 36 rabbits. Mercaptofos or M-74 applied cutaneously caused the animals death during the first day of the experiment; M-81 or M-82 similar applied killed the animals on the 2nd - 3rd day.

Rats and cats were exposed once for 4 hours to POI vapors, the lethal concentrations of which were 0.015 - 0.02 mg/li for mercaptofos, 0.01 - 0.014 mg/li for M-74, and 0.02 - 0.025 mg/li for M-81 and M-82. Most animals died after several hours or on the 2nd - 3rd day after exposure. During exposure the animals exhibited pronounced pupilary contraction, salivation, muscular fibrillation and tremor. Cutaneous administration of POI compounds to cats produced less severe effects than did oral administration.

In chronic experiments in which various routes of POI administration were employed the animals exhibited no signs of poisoning for 5 - 6 days to 6 months, depending on the dose; salivation, muscular fibrillation, and other signs characteristic of the previously described single administration of toxic doses of the poisons appeared during 2 or 3 days, and at times only on the day of death. Repeated administration of POI lowered the intensity of the convulsive component. Blood cholinesterase and pseudocholinesterase activity was reduced by more than 50% in all the animals administered toxic doses of POI,; this symptom appeared before the other signs of intoxication during the period of progressive intoxication, blood cholinesterase activity was reduced to 20 - 10% or it was completely depressed. Regardless of the route of POI administration autopsies of animals that died within 1 hour to 15 days of a single exposure to a lethal dose revealed different degrees of venous plethora of the internal organs and of the cerebrum. Many animals exhibited microfocal and even macrofocal pulmonary hemorrhages. Examination of the cerebrum and internal organs one hour after administration of the poison revealed extensive vascular dilatation, distension of the smaller vessels and laceration of individual cells of the endothelium and looseness and edema of the walls. Most pronounced changes in the vessels were noted when the animals were poisoned with M-74. The cerebral cortex, caudate nucleus, and optic thalamus exhibited dystrophic changes in the individual nerve cells during the early days of the intoxication, manifested as swelling, eccentric position of the nuclei, pulverization of the Nisel bodies, and partial, rarely total chromatolysis. In rare instances and particularly in the cerebral cortex and subcortical nuclei, individual nerve cells were seen in a state of karyolysis and karyocytolysis after 15 days of exposure to the POI. Hearts of all the animals showed changes in the form of turbid swelling of the muscle fibers, accompanied by clearly manifested venous engorgement and occasional microfocal hemorrhages (in 30 of 75 animals). Intermediate microfocal infiltrates composed of lymphoid cells and histiocytes were seen less frequently.

In addition to engorgement, the liver exhibited a turbid distension of the cells, and the nuclei of many cells had undergone pyknosis. An enlargement of the Nisel spaces occasionally was noted, which resulted from the accumulation of a liquid and which stained a pale color by eosin. Widely scattered foci of tissue necrosis were seen in 2 animals which died 15 days after POI administration. Kidneys revealed dilated lumens of the convoluted tubules; in each case, the lumen was filled with small lumps of eosinophilic protein masses interspersed with individual epithelial cells. The epithelium of the canaliculi was distended; the cells were poorly outlined and the nuclei of many cells had undergone lysis. The lumens of the glomerular capsule were free or contained eosin-stained liquid. Many nuclei of the cubic epithelium which lined the straight canaliculi had undergone pyknosis. Stroma capillaries were dilated and showed signs of stasis. Pulmonary vessels of the septi were markedly dilated, and many exhibited stasis and hermorrhages extending into the perivascular tissue. Scattered focal hermorrhages were observed containing varying amounts of hemosiderin. Fifteen animals exhibited focal inflammatory changes. The argyrophilic fibers in the myocardium, liver, kidneys and lungs were thickened or fused; this change was noted during the day following the mercaptofos administration. The spleen revealed venous engorgement and medullar hyperplasia; cells of the testicular germinal epithelium and of the adrenal cortex manifested dystrophic phenomena; in 10 animals, the cortical and medullary substance of the adrenals revealed hemorrhages.

Autopsies of 82 animals, dead after repeated administration of mercaptofos, (the deaths occurred after 2 weeks to 6 months), revealed distension of the myocardium, of the renal canalicular epithelium, and of the hepatic tissue, in addition to very pronounced engorgement; fatty dystrophy of the liver was noted early in cats. Numerous hemorrhagic foci were visible in the lungs; 12 of 82 animals developed small airless grayish-red foci. Microscopic examination of brains of all animals revealed engorgement of the membranes and tissue of the brain; walls of many small vessels were loose and edematous; their endothelium was distended; the nuclei of the endothelium were enlarged and markedly hyperchromic. Proliferation of the endothelium and adventitial cells were seen in the animals dead after 3 - 6 months.

Swelling and ectopia of the nucleus and total chromatolysis were observed in most nerve cells of the cerebral cortex; in addition, groups of nerve cells in a state of karyolysis, karyocytolysis, and cirrhosis were seen frequently.

Similar changes were seen in the subcortical nuclei, but they were much less pronounced. Nerve cells of the caudate nucleus were shrunken and stained in a diffuse manner. Similar changes were observed in the nerve cells of the medulla oblongata and in the ganglionic layer of the cerebellum. Many of the nerve cells had undergone total chromatolysis, karyolysis, or karyocytolysis. In addition, the ganglionic layer of the cerebellum revealed prolapse foci situated at different distances, and groups of cells in a state of cirrhosis, accompanied by nuclear pyknosis and protoplasmic hyperchromatosis; the latter was stained intensely by toluidine blue. The myocardia of all autopsied animals revealed engorgement, focal hemorrhages, and distention of the muscle fibers. In 28 of 82 animals, micro- and macrofocal accumulations of histiocytes and lymphoid cells were observed among the muscle fibers (Fig. 1). These changes were accompanied by fatty infiltration of the myocardium in some of the animals.

Fig. 1. Lymphoid type and histiocyte cells infiltration in cat's cardiac muscles. Exposure to mercaptofos vapors. Died after 6 months. Hematoxylene-eosin stain x 400.

Liver of all animals revealed distention and inflammatory changes; intertrabecular spaces and interlobular connective tissue showed serous exudate accumulation or infiltration composed of lymphoid and histiocyte cells. Fatty dystrophy with necroses of individual groups of cells was seen in 35 of 82 animals, vacuolar dystrophy in 18 of the animals.

Kidney changes appeared as engorgement phenomena and as granular and vacuolar cellular dystrophy of the convoluted tubules epithelium. Lumens of the capsules of many hyperemic glomeruli in 26 animals revealed a serous fluid with a large number of epithelial cells lining the inside surface of the external capsular leaf. The following changes were seen in the lungs: engorgement of the capillaries, stasis with intravascular breakdown of erythrocytes, plasmorrhagia, and hermorrhagic foci with large amounts of hemosiderin. Argyrophilic fibers in the myocardium, liver, kidneys and lungs were thickened and acquired a lilac tinge upon silver impregnation. The lungs of animals revealed intraalveolar fibrillar development (Fig. 2). The spleen was engorged, its pulp was hyperplasic, and there were signs of hemosiderosis.

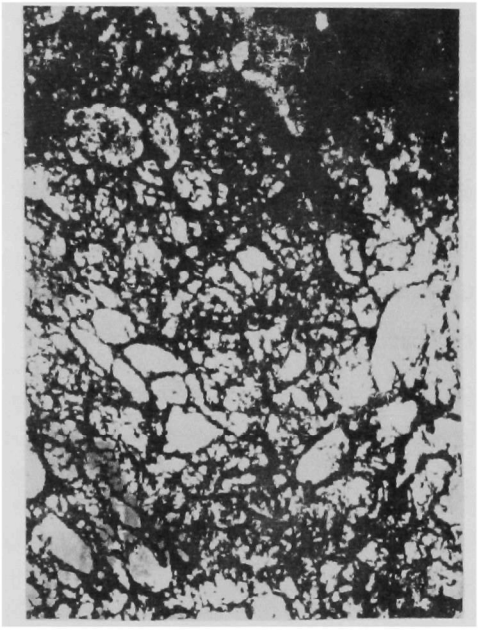


Fig. 2. Thickening and interalveolar development of argyrophilic fibers in cat's lungs. Exposure to mercaptofos. Died after 6 months. Silver nitrate impregnation x 200.

Cells of the germinal epithelium of the testicular canaliculi revealed dystrophic changes, the adrenal cortex cells had a lowered lipid content, and the thyroid gland contained less colloid.

Conclusions.

1. Administration of organic phosphorus insecticides (mercaptofos, M-74, M-81, M-82) to mice, rats, cats and rabbits by several routes in toxic and lethal doses brought about marked vascular disturbances and extensive dystrophic and focal necrobiotic changes in the brain and internal organs.

2. Intoxication with POI compounds first gave rise to vascular disturbances, dystrophic changes in the nerve cells of the brain, particularly the cortex and subcortical nuclei, and also condensation and liquefaction of the basic argyrophilic substances. These were followed by the development of dystrophic granular, vacuolar, fatty, and less often, inflammatory and necrobiotic changes, with lethal doses, in the liver, kidneys, myocardium and glands of internal secretion.

3. Morphological changes discovered in the experimental animals were not specific for the action of organic phosphorus insecticides and were apparently dependent not only on changes in the acetylcholine metabolism but also on disturbances in other aspects of metabolism and on hypoxia, which is especially characteristic of the administration of toxic and lethal POI doses.

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Modern Approach to Air Dustiness in Workshops.

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Normalization of environmental conditions is the task of hygiene. During recent years scientific research institutions and institutions dealing with practical problems of health protection, labor unions and different industries, gathered new data on the effect of harmful air pollutants; this led ot a revision of limits of existing maximum permissible air pollutant concentrations and to an extension of the list of standardized harmful air admixtures.

In accordance with sanitary standards for industrial enterprise planning (N 101-54), industrial dusts were divided into "toxic" and "non-toxic"; a considerable number of different dust types was included into the "non-toxic" group for which only 2 concentration limits were recommended: up to 2 and 10 $mg/m^3$. Included in the non-toxic group was also a considerable number of dust types containing quartz, asbestos and different metallic dust combinations.

The standardization principle recently became the subject of considerable discussion. Thus, at the symposium on pneumoconiosis, conducted in Moscow in May 1957, the question was raised about basing pollution standardization not on hygienically arrived at concentration levels, but on concentrations technically attainable industrially (P. N. Torskii, Z. G. Linkin). Similar opinions were voiced at the meetings of the Commission on Silicosis Control at the Academy of Sciences, U.S.S.R. Such opinions met with sharp opposition from hygienists and a majority of engineers and technicians. The development of U.S.S.R. technique and technology has been progressing so rapidly that elimination of dust in industrial processes presented no great difficulty. Work on silicosis control in the mining industry indicated that mining engineers were able to solve complex technical problems of dust control in the mines; in a number of mines in Krivorozh'e, the Ural, Uzbekistan, etc., air dustiness was reduced to 2 $mg/m^3$, and in some cases to 1 $mg/m^3$. The system of dust elimination in the mines was developed sufficiently well for a variety of work conditions, and the problem was only one of consistent application of measures developed and of a systematic control of their effective operation. There are also definite systems for the elimination of dust formation in coal concentration (enrichment) plants, in drying-grinding shops, in foundries, and in building material plants. Therefore, there is no need to be guided by levels of outdated technology accompanied by

considerable dust formation. Planning organizations, technicians and builders of different industry branches should be urged to create new dust-free technological processes. Scientifically proven sanitary norms must urge engineering departments to devise more perfect industrial technological sanitizing installations.

Lately the question has also been raised regarding the appropriateness of standardizing air dustiness by the gravimetric method. At the Jubilee Session of the Institute of Hygiene and Occupational Diseases, A.M.S., U.S.S.R., in 1953, participants of the Committee on Silicosis Control again raised the question of changing to the particle count method widely used abroad. In this connection studies related to the hygienic importance of mass versus number of polydispersed dust particles and fractions of different degrees of dispersion conducted experimentally demonstrated conclusively the preeminent significance of the dust mass effect. Experimental data coincided to a considerable degree with the information gathered on lowered morbidity in pneumoconiosis which ran parallel to the mass of suspended dust. Previous data on lower morbidity rate in silicosis among sandblast operators also ran parallel to gravimetric dust concentration; analogous results were obtained by A. S. Plakhin in foundries; investigations of labor conditions and silicosis morbidity in the mining industry yielded similar results. Attempts to compare air dust counts with rate of morbidity among workers showed no clear connection between the two, as might have been expected theoretically. Data presented by foreign authors and exchange of experience with them indicated that the count method was used mainly because it was simpler and not necessarily most reliable.

It appeared that in conducting scientific research in the field of air dust pollution by the gravimetric method use was made of dry and liquid filters, electric precipitators, etc. No legislation exists in foreign countries controlling maximum permissible dust concentrations in the air, and such recommendations proposed by individual counties or states of the U.S.A. up to the present had no legal status. At first these recommendations were made in gravimetric terms (Lehman, Mavrogordato); later they were expressed in terms of number of particles per 1 $cm^3$. However, recently the hygienic importance of dust mass has been recognized in foreign countries. Thus, at the 1956 U.S.A. Convention, physicians specializing in industrial sanitation recommended that in addition to the count method the gravimetric method should be used in connection with certain types of dust, mainly of toxic nature. In 1957 the International Labor Organization

(ILO) recommended that dust concentration be expressed in gravimetric terms. The importance of the gravimetric method of determining air dust concentration for hygienic purposes has been established.

Next in importance is the principle on which to base the determination of the limits of allowable dust concentration. This, indeed, constitutes a complex and difficult problem. Unfortunately, so far no clear and incontestable data have been presented establishing safe threshold of aerosol inhalation, because methods for the study of the effect on man of harmful substances still lack the required precision. Data obtained regarding the state of health of those working in the presence of certain concentrations of different active aerosols could not be used as criteria in this study, since the disease effected far advanced injuries beyond the initial forms of the effect on the organism. For toxic air-suspended aerosols, created in industries newly introduced into the national economy, limits of allowable concentrations must be arrived at experimentally as early as possible without waiting for the development of symptoms of occupational diseases. However, such experimental data must be regarded as tentative, subject to revision on the basis of results of future clinical observations and supplemental experiments.

Thus far it was not possible to verify the necessity of establishing separate norms for maximum single and mean work day concentrations, due to the fact that in the majority of aerosols existing research methods enable the determination only of average concentrations for a more or less prolonged time period. However, despite these limitations, extensive data were accumulated during recent years on the study of the effect of different types of industrial aerosols. Based on the summary and evaluation of new data obtained from work of institutes, university departments and practicing physicians a list was prepared of maximum permissible concentrations; it was presented at the 1957 Symposium on the Problem of Pneumoconiosis, and published later in the journal "Labor Hygiene and Occupational Diseases" (1957, No. 4). The list presented concentrations of 34 individual aerosols. It was discussed at the Symposium, at the meeting of Labor Hygiene Section of the Scientific Society of Hygienists, and at the meeting of the Committee on Hygiene of the Scientific Medical Council of the Ministry of Health, U.S.S.R. Together with a list of maximum permissible concentrations of vapors and gases the list of dust concentrations was sent to all institutes of hygiene and labor protection and planning, to all technological chemical institutes, and to the National Committee on Chemistry of the Council of Ministers of the

U.S.S.R. More exact definitions were suggested and additions to a number of concentration values of toxic aerosols were introduced in the course of discussion; these were taken into consideration and discussed at the meeting of the Committee on Hygiene of the Scientific Medical Council at the Ministry of Health, U.S.S.R., as a result of which the following list was prepared.

Dust and other aerosols in $mg/m^3$.

a) Mineral and organic dust

| | | |
|---|---|---|
| 1. | Dust containing over 70% free $SiO_2$ in its crystalline modifications (quartz, crystabalite, tridymite) | 1 |
| 2. | Dust containing over 10% and up to 70% free $SiO_2$ | 2 |
| 3. | Asbestos dust and mixed dust containing over 10% of asbestos | 2 |
| 4. | Dust of glass and mineral wool | 3 |
| 5. | Dust of other silicates (talcum, olivine, etc.), containing under 10% of free $SiO_2$ | 4 |
| 6. | Dust of baryte, apatite, phosphorite, cement (containing under 10% $SiO_2$) | 5 |
| 7. | Dust of artificial abrasives (corundum, carborundum) | 5 |
| 8. | Dust of cement, clays, minerals and their mixtures containing no free $SiO_2$ | 6 |
| 9. | Coal and coal-rock dust, containing over 10% free $SiO_2$ | 2 |
| 10. | Coal dust containing under 10% free $SiO_2$ | 4 |
| 11. | Coal dust containing no free $SiO_2$ | 10 |
| 12. | Tobacco and tea dust | 3 |
| 13. | Dust of vegetable and animal origin (cotton, flax, flour, grain, wood, down, etc.), containing 10% and more free $SiO_2$. | 2 |
| 14. | Dust of vegetable and animal origin containing under 10% of free $SiO_2$ | 4 |
| 15. | Dust of pressed powders (phenolic aldehyde and amino-plastics) | 6 |
| 16. | Organic and other non-toxic dust | 10 |
| 17. | Hexachlorane | 0.1 |
| 18. | Hexachlorbenzene | 0.9 |
| 19. | Hexachlorcyclohexane ($\gamma$-isomer) | 0.05 |
| 20. | Heptachlor | 0.01 (?) |
| 21. | Dinitrothiocyanogenbenzene | 2 |
| 22. | Octamethyl (octamethyltetramidopyrophosphoric acid) | 0.2 |
| 23. | Pentachlornitrobenzene | 0.5 |

| | | |
|---|---|---|
| 24. | Compound 125 (dinitrofluorocresol type) | 3 |
| 25. | Thiophos (thiophosphate) | 0.05 |
| 26. | Chlorindin (pyrimethamine) | 0.1 |
| 27. | Chlorten | 0.2 |
| 28. | Ethylmercuric phosphate | 0.005 |
| 29. | Ethylmercuric chloride | 0.005 |
| b) Aerosols of metals, metalloids and their compounds | | |
| 30. | Aluminum, aluminum oxide, aluminum alloys | 2 |
| 31. | Beryllium | 0.002 |
| 32. | Vanadium and its compounds: | |
| | a) Smoke of vanadium pentoxide | 0.1 |
| | b) Dust of vanadium pentoxide | 0.5 |
| | c) Ferrovanadium | 1 |
| 33. | Tungsten, tungsten carbide | 6 |
| 34. | Ferric oxide with admixture of fluorine or manganese compounds | 4 |
| 35. | Cadmium oxide | 0.1 |
| 36. | Cobalt (cobalt oxide) | 0.5 |
| 37. | Manganese | 0.3 |
| 38. | Molybdenum (soluble compounds) | 4 |
| 39. | Molybdenum (non-soluble compounds) | 8 |
| 40. | Arseneous acid anhydride and arseneous oxide | 0.3 |
| 41. | Nickel, nickelic oxide | 0.5 |
| 42. | Lead and its non-organic compounds | 0.01 |
| 43. | Selenium amorphic | 2 |
| 44. | Mercuric chloride | 1 |
| 45. | Tantalum | 10 |
| 46. | Tellurium | 0.01 |
| 47. | Titanium | 10 |
| 48. | Thorium | 0.05 |
| 49. | Trichlorophenolate of copper | 0.1 |
| 50. | Uranium (soluble compounds) | 0.15 |
| 51. | Uranium (non-soluble compounds) | 0.75 |
| 52. | Chromic anhydride, chromates, bichromates (as $Cr_2O_3$) | 0.1 |
| 53. | Zinc oxide | 5 |
| 54. | Zirconium | 5 |
| 55. | Alkaline aerosols (as caustic soda) | 0.5 |

Note: Departures from the above values can be made with the permission of the State Sanitary Inspection where workers remain on production premises a short time only.

This project [1] has certain shortcomings as pointed out during the discussion. However, arriving at more precise values or adding new substances would require considerable time; the Committee on Hygiene concluded to approve the list of values as presented, believing that additions could be introduced upon future revision of the list within the next 3 - 4 years.

Taking into consideration the importance of hygienic norms and the need for a comprehensive development of research work, attention should be given first to the development of methods for the study of aerosols and their properties and of the effect of aerosols on the organism. It is also necessary to equip the laboratories with facilities for micro-gravimetric analysis for the performance of rapid and precise study of air dustiness.

During recent years the importance of degree of dust dispersion has been receiving wider recognition. Experimental research conducted by this author earlier (1952 - 1955) enabled him to discern a slight biological activity of dust particles up to 2 μ in diameter only in the presence of certain total mass values. Experimental research conducted at the Institute of Labor Hygiene and Occupational Diseases, Academy of Medical Sciences, U.S.S.R. in 1957 - 1958 (T. A. Kochetkova, T. T. Lubova and E. V. Khukhrina) indicated that small quartz particles numbering millions produced no pronounced experimental silicosis if the total mass was small. At the same time, a greater mass of such highly dispersed dust could produce a sharp reaction with symptoms of acute emphysema, etc. The importance of high dispersion aerosols was also demonstrated in the Sverdlovsk Institute of Labor Hygiene (V. T. Velichkovskii and others) in studies of aerosol condensation.

Results of the above studies emphasize the need for more rigid limits for the density in the air of dust particles less than 2 μ in diameter. However, when speaking of dust dispersion degree, the hygienists should have in mind not microscopic determination of dispersion degree. The microscopic method yields a "dust formula" only according to the number of particles without regard to

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[1] At present this project has been approved by the Chief State Sanitary Inspection as a regulation on maximum permissible concentrations. Editor.

mass. Nevertheless, determination of dust dispersion according to particle diameter fractions must be used when conducting hygienic research. This should be made mandatory because the methods are well developed theoretically and practically (N. A. Figurovskii, N. N. Tsyurupe) and can be used even with very small samples (2 - 3 mg) of dust.

The need is urgent for the development of methods for the determination of dust properties and their chemical composition. Most industrial aerosols are of complex composition; in addition new unstudied chemical compounds might permeate into the organism which might considerably complicate the final effect. Thus, it was shown that the presence of small admixtures of fluorine compounds in phosphorite dust affected mineral metabolism, reduced the rate of calcification of tuberculosis nuclei, thereby increasing T.B. morbidity. Complete analysis of the chemical and mineralogical composition of aerosols should be made by latest research methods, with emphasis on spectrography, X-ray, electronography, etc. Study of biological activity of a number of aerosols presents considerable difficulties in the choice of research methods.

In the majority of cases suggested levels of maximum permissible concentrations were arrived at on the basis of data obtained from a study of workers' morbidity paralleled by experimental data. However, it is known that many occupational diseases caused by aerosol inhalation may persist for years without manifesting clear symptoms and may be diagnosed only after the worker has left his occupation, as, for example "late" silicosis. Some diseases, such as chronic bronchitis and emphysema in textile women workers, are still not classed as occupational diseases, even though the effect of the textile dust is of importance in the etiology. There is no doubt that the diseases of respiratory organs caused by the effect of dust of some metal oxides may persist, diagnosed as non-occupational diseases. Most early disease forms are difficult to diagnose. As a rule, it is difficult to establish the effect of the general state of morbidity on the organism's reactivity to low dust concentrations which cause no clearly expressed symptoms of occupational disease, but may have a so-called diffused general effect on the organism.

Animal experiments are conducted to define more accurately the character of a disease, peculiarities of its course and dates of its origin. Micro-pathology of pulmonary tissue and of lymph node and weight change records are used as indicators in studying the effect of different aerosols. In some cases conditioned reflexes, gas metabolism, condition of individual organs and systems, such as the

functions of respiration, blood circulation, etc. are studied specifically. A single intratracheal introduction to white rats of 50 mg of dust suspension in physiological solution, followed by examinations of pulmonary and lymph node preparations at different intervals is used extensively, and has become an almost standard procedure. This method permits making a comparative evaluation of biological activity of some dust varieties, containing silicon dioxide (dust of various ores, silicates, abrasives, etc.). However, it should be pointed out, that the use of a single intratracheal injection of dust suspension is not always expedient, particularly in studying dusts of weak biological activity. Large dust doses have a marked mechanical, sometimes acute effect, unlike the chronic effect of dust on humans. Studies should not be limited to morphological changes characteristic of diseases in their later stages. It is necessary to develop physiological, biochemical and immunological investigation procedures. These investigations should aid in disclosing early symptoms of aerosol effect and serve as more positive bases for the determination of new maximum permissible concentration levels.

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# Present-Day Status and Future Problems in Sanitary Protection of Community Atmospheric Air in the U.S.S.R.

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In fulfillment of the resolutions adopted at the XXI Conference of the K.P.S.S. (Communist Party of the Soviet Union) means are now being instituted for the gasification of cities and workers' villages, for the electrification of railway transportation, etc. For the past ten years large scale sanitization means have been introduced throughout the land, and the functions of the state sanitary control organizations have been broadened and their authority reinforced. Such organizations are now keeping careful watch over the protection of atmospheric air purity, development of scientific research in that field, determination of appropriate limits of allowable air pollutant concentrations, and methods and devices for the purification of industrial discharges before their emission into the atmospheric air. In this connection particular attention has been given to sources of air pollution and their effect on the health of workers, children, and general population. Among organizations participating in such work are research institutes of hygiene, sanitation, clinical medicine and regional sanitary-epidemiological stations, etc. Morbidity studies among populations related to industrial atmospheric air pollution are now being conducted in 40 cities and workers' villages. Results of correlated statistical studies clearly point to the etiological connection between certain types of morbidity and industrial and other atmospheric air pollution. Morbidity studies must constitute a mandatory part of any investigative and corrective system of atmospheric air protection. Such studies should be participated in by local and regional hospitals and clinics and the results should be verified and analyzed by appropriate statistical analysis. Such a method of morbidity study has proved its value in health investigations conducted in heavily industrially and otherwise heavily air polluted areas.

For instance, a study was made of general morbidity, types of diseases of a population residing in a region where the aluminum chloride department of a metallurgical plant emitted into the air pollutants containing components deleterious to human and animal health. A medical survey of the population and a

statistical investigation of clinical histories kept in the files of the regional clinic indicated that the population morbidity was considerably higher when the plant was operating; this was particularly true of conjunctivitis, acute inflammatory processes of the upper respiratory tract, tracheobronchitis, bronchitis, etc. Results of such investigations place in the hands of appropriate authorities scientific data on the basis of which requirements can be formulated for the correction of the local unsanitary conditions by plant management and regional sanitary authorities. During the last ten years atmospheric air has been investigated for the content of cancerogenic hydrocarbons of the 3,4-benzpyrene type caused by industrial discharges and automotive vehicles exhaust gases. The presence in the air of such substances and the rise in cancer morbidity among urban residents gave rise to a number of urgent sanitary hygienic problems.

The urgency of the fight against cancer was first discussed in June of 1956 at the All-Union Conference of Hygienists, Epidemiologists, Microbiologists and Infectionists. In December of the same year the All-Union Conference was held on problems related to cancerogenic substances prevailing in the surrounding environment; the discussion was centered mostly on means to be used in the fight against cancer. It was mentioned that U.S.S.R., as well as foreign investigators, as a result of their studies, felt that there existed a connection between the presence of cancerogenic substances in industrially polluted air and the increase in frequency of cancer occurrence among urban populations. As a result of such findings the State Sanitary Inspection of the U.S.S.R. organized a committee in March of 1957 which was endowed with the responsibility to investigate the presence of cancerogenic substances in the external environment and to study means of combatting same. The committee was assigned the task of coordinating such work by engaging the planned cooperation of pertinent scientific educational institutions, industrial research laboratories, etc. It is to be regretted that even as of this date, many authorities and scientists fail to recognize the importance of this hygienic problem. It is suggested that immediate priority be given the following studies: a broad investigation of cancer morbidity among inhabitants of industrial cities and towns; a parallel study of the degree of air pollution of such localities with 3,4-benzpyrene and other cancerogenic substances; a determination of sources at which cancerogenic air pollutants originated, such as industrial enterprises, autotransport, etc.; development of cancer preventing means and methods.

The problem of sanitary protection of atmospheric air against pollution in the U.S.S.R. is closely bound with some economic problems of national importance Lack of means for the proper purification of certain industrial emissions before they are thrown into the atmospheric air results in tremendous losses of certain valuable substances in the form of waste products. For example, it has been estimated that the cement industry lost 16 - 20% of its production with the emission gases; it should be added that the lost cement consists mostly of the most finely ground and, therefore, most valuable part of the cement. Air pollution and great national economic losses are also caused by the fact that many of the gas purifying dust catching installations are inefficiently operated, as, for instance, in the Riga Superphosphate Plant, "Maardu" Chemical Combine, Sterlitamask Soda-Cement Combine, Slavseda and Donsoda combines, the Volkhovsk Aluminum Plant, etc. The inspection office of the Technical Supervision over the Operation and Correct Utilization of Gas Purifying Installations inspected 2000 gas purifying installations in 540 enterprises of different industrial branches. On the basis of the inspection results and taking into consideration that there existed 2000 enterprises which had gas purifying installations, an estimate was made of the technical condition of the gas purifying installations and of the grand total of valuable materials lost due to inefficient operation of gas purifying equipment. Greatest offenders in this respect were the cement, the nonferrous metallurgical, and the chemical industries, the Sverdlovsk, Kemerov, Gor'kii, Stalin, Krasnoyarsk and several other sovnarkhozes (Soviet communal enterprises). Organizations of the State Sanitary Supervision and research sanitary-hygienic institutes have been devoting much of their efforts to the control of means and methods used in the sanitary-protection of atmospheric air. In this connection they have urged that future scientific investigations in the field of air pollution abatement and prevention be regarded as one of the practical and basic means of attaining and maintaining air purity. They also urged that greater emphasis be placed on the determination of limits of allowable concentrations of air pollutants, on the development of more sensitive and more specific means for the qualitative and quantitative determination of poisonous substances in the air, on the broader application of toxicological and pharmacological studies of all types of air pollutants, on the effect of atmospheric air pollutants on health of populations and general living conditions, including the effect on animal and plant life, and on monuments and other esthetic and decorative objects; particular stress is laid on broader and more inclusive

checking and evaluating and re-evaluating the effectiveness of existing and of proposed means for the protection of atmospheric and indoor air.

As of this day limits of allowable air pollutant concentrations have been established for over 30 toxic substances; this attainment has substantially improved the sanitary condition of community air in previously badly polluted localities, but also accumulated a vast store of practical and theoretical experience which can now be applied with ever greater expediency to the improvement of indoor and outdoor air sanitation in the future. Proposed limits of allowable air concentrations are presented to the Office of the State Sanitary Inspection where they are discussed and finally incorporated as mandatory regulations into the National Sanitary Code, which means that all Union production industries, their branches and plants must comply with such regulations.

As new types of finished products are being manufactured, such as organosynthetic products, new air pollutant and new toxic waste products develop which necessitate new sanitary, toxicological and general pharmacological investigations, new determinations of limits of allowable concentrations, and new equipment and installations for their removal from the final discharge gases or ventilation air. Then, there is the problem of determining limits of allowable concentration of toxic substances when two or more such pollutants are present in the air; in such cases either synergism or antagonism come into play, or possibly both, to some extent. The solution of air pollution problems of this type presents many difficulties and calls for the cooperation of the physical chemist, pharmacologist-toxicologist, chemical analyst and sanitary hygienist. There are also air pollution problems which baffle the physician-sanitary-hygienist (industrial physician in the U.S.A. B.S.L.). One such problem is presented by oxides of nitrogen as air pollutants. Previous studies indicated that between 5 - 10 tons of oxides of nitrogen had been discharged daily by a given industrial plant and that population complaints were frequent, persistent and serious; despite that laboratory studies failed to find actual pathologic conditions which might indicate any need for extreme and stringent demands for a lowered nitrogen oxides concentration in the air. This may be due to imperfection of the methods used in determining the limit of allowable nitrogen oxides concentration in community and indoor air. Consideration must also be given the fact that oxides of nitrogen, as a rule, occur simultaneously with sulfuric anhydride ($SO_3$) and sulfuric acid aerosol.

Data obtained for limits of allowable community air pollutants can and should be used in efforts to determine the degree of purification industrial waste gases must undergo before they are discharged into the atmospheric air. Computation formulas should be derived which the sanitary personnel of any pertinent establishment could use for the practical determination of degree of gas purity at any phase of industrial production, or at any time or rate (intensity) of production. Studies must be intensified also along the lines of air pollution with radioactive substances; unfortunately this phase of air pollution has received insufficient attention on the part of air pollution scientists. (To my knowledge this is not true; such studies have been conducted mostly by classified agencies and to some degree by general scientists, but the results have been designated as classified. B.S.L.).

Increase in state sanitary control over the purity of community atmospheric air development of the science of hygiene in this field stimulated a rise of work in developing technical means for the purification of industrial emissions into the atmospheric air. Thus, in 1949 thirteen research projects related to the purification of industrial emissions discharged into the atmospheric air were studied in 5 institutes; in 1950 - 1951 projects of such character were under study in 66 institutes affiliated with such industries as the non-ferrous metallurgical, machine building, construction material processing, chemical and similar industries. Despite that, progress along the development of methods for the purification of discharge gases from oxides of nitrogen and hydrogen sulfide in plants producing artificial fibers (meaning the synthetic products industries, B.S.L.) has been far from satisfactory. From the viewpoint of production the supply fell lamentably short of the demand and from the viewpoint of information seeking, scientific institutions failed to provide timely, numerically sufficient and at times scientifically or practically adequate replies to inquiries. As of this date 75% of the inquiries still remain unanswered. Scientific research institutes have developed many methods (including equipment, installations and procedures) for the purification of discharge gases from oxides of nitrogen, hydrogen sulfide and carbon bisulfide in plants producing artificial fibers, for the purification of gases of blast furnaces and boiler operated plants of 500 - 1900 tons of steam per hour capacity, for the purification of metallurgical industry gases emitted by new processes, and for gas purification in a variety of other industries. However, the problem of complete automation of gas purifying installations remains unsolved.

New methods of industry management opened up possibilities for governmental sanitary agencies to inspect and control conditions, means and facilities in the protection of atmospheric air against industrial pollution. Such inspection, supervisory and corrective experience has been growing in depth and extent. Accumulation of such experience over the past 10 - 15 years is now being applied by the All-State and other national and regional planning organizations in the preparation of plans for the construction of new and rebuilding old industrial production plants. It is now possible to incorporate into new construction plans provisions for sanitary-hygienic purifying installations, ventilation facilities and other types of sanitizing equipment. This in essence is the principle of prophylaxis, and upon such a principle all scientific research pertaining to sanitation and hygiene, especially in the realm of air pollution prevention, should be organized and conducted. This should also be the guiding principle of sanitary inspectors, supervisors and similar authoritative personnel, whether All-Union or regional. The industrial sanitary-hygienic physician should consult statistical morbidity data wherever available on a current basis, so that upon the suspicion of unfavorable trends, preventive means and measures could be instituted at the earliest possible moment; wherever such statistical information is not available the physician should by his own effort secure same. Such a procedure is the very core of preventive industrial medicine, hygiene and sanitation.

With the above viewpoint as the basic principle, the Office of the State Sanitary Inspection of the U.S.S.R. cooperated with the U.S.S.R. Gosplan (State planning) in preparing plans for future development and realization of the Seven-Year-Plan. This viewpoint also constituted the basic guiding principle of work conducted by State Sanitary Inspection bodies of the R.S.F.S.R. (Russian Socialist Federated Soviet Republic, which was the original nucleus of the present U.S.S.R., and the entity of which had been retained for reasons of political and economic dominance, B.S.L.), the Ukrainian, Kazakh, Lithuanian, and other Socialist Soviet Republics, which participated in the preparation of state plans of various Soviet republics, and which developed means for the abatement of atmospheric air pollution. As a result, air dust intensity has been reduced and atmospheric air pollution has been notably abated in the cities of Moscow, Saratove, Gor'kii, Baku, Kashir and other industrial cities.

Future developments in the line of sanitary protection of atmospheric air depend to a large extent upon the organizational intensification of the work of

supervising and inspection governmental bodies, and incorporation and intensification of regional sanitary-epidemiological station activities in the field of atmospheric air pollution control. The time is now ripe for a revision of the methodological specifications for the study of community air pollution. Now is the time to end the old controversy which began in 1938, namely, what method should be preferred, the aspiration or the sedimentation. All data on limits of allowable community and indoor air pollutants have been obtained by the aspiration method and expressed in terms of weight units per unit of air volume; for this reason alone, if for no other, the aspiration method of air sample collecting should become the standard official one.

The resolutions adopted at the XXI Congress of the K.P.S.S. (Communist Party of the Soviet Union) regarding "The Key Figures for the Development of the U.S.S.R. National Economy for the Period of 1959 - 1965" provided for further expansion of atmospheric air protection based on the expectation that progress will be made in the technology of different types of industrial production, technical and technological means of gas emission purification, general industrial automation, high specialization and cooperation among different national industries. New types of production, manufacture and processing which came into being as a result of experimental research and semi-practical tests have brought with them heretofore unknown sanitary-hygienic problems which required immediate solution from the viewpoint of atmospheric air pollution with new types of toxic raw materials and waste products. In this way research scientists, sanitarians and industrial physicians have been faced with urgent and challenging demands which, it is hoped, they will be able to meet within a reasonably short time.

Improvement in production technology obviating the emission of deleterious substances into the atmosphere coupled with a rational solution of sanitary protection of atmospheric air should effect large scale economies in that, on the one hand, many valuable raw and by-products now discharged into the air will be conserved, and, on the other hand, initial production gases contain immeasurably less of a waste product load, so that the cost of their purification will fall to lower figures. Once such a state of sanitation in atmospheric air will have been attained, it will be possible to turn the present sanitary clearance zones into special types of residential areas. In this connection it should be borne in mind that many production plants and combines are not surrounded by any type of sanitary clearance zones, and that residents in the proximity of such plants and combines are frequently exposed to the harmful effect of the industrial

discharges. Improvement in production and processing technologies, by lessening the amount of gas or ventilation air contained pollutants, will reduce the extent of community air pollution to the limits of allowable concentrations, and in some instances even below such limits.

During the May 1958 Plenum of the Central Committee of the Communist Party of the Soviet Union it has been resolved that greatest emphasis should be placed on the development of the chemical industry. The first impetus of this will be felt in the production of polymer materials, the use of raw materials and semi-processed products applicable to such production. A search will be instituted for cheaper and more easily available usable raw materials, such as crude oil gases (natural gas), gases eliminated during crude oil processing, products of the coke-chemical industry, gases from the turf and shale industries, waste products created by the lignine plant processing and agricultural by- and waste products. The manufacture of artificial and synthetic fibers, plastic masses, synthetic resins, synthetic rubber, synthetic alcohols, and the like is accompanied by the creation or emission of substances possessing toxic properties. At practically every stage of such materials production large quantities of gases, vapors and dust are eliminated which are being thrown into the atmospheric air via the ventilation systems. In this connection the following will be among the problems which will urgently require solutions during the next "semiletka" (seven-year economic progress plan): a study of new technological processes on an experimental semi-industrial scale; the effect of complex mixtures of new pollutants discharged into the atmosphere by the modern type of production and manufacturing plants on the health of populations and on general living conditions; expanding and extending scientific research for the determination of limits of allowable concentrations of the new pollutants; determination of widths of sanitary clearance zones surrounding the new types of production plants and combines; determination of smokestack heights; etc. All such problems should be given earliest possible priority in the course of the current "semiletka" (seven-year economic plan).

Sanitary-hygienic studies and development of sanitary-hygienic standards should not only be in step with progress made in general industry, they should in fact, run a few steps ahead of industrial developments, and, so to speak, anticipate the sanitary-hygienic needs of the steadily progressing industrial developments. The fact is that all necessary conditions for such action on the part of the research investigators are in existence, most basic among which are

experimental semi-industrial installations of a great variety. It is noted with regret that sanitary-epidemiological stations have participated in such advanced scientific industrial studies only to a slight degree, despite the recognition that only through the participation of such stations on the broadest possible scale can such scientific studies attain the wide application essential to success under the anticipated "semiletka" conditions. The public health ministries of the individual Soviet republics should endeavor without delay to expand the activities and responsibilities of the regional sanitary-epidemiological stations, enlarge their laboratories, equip them with all necessary modern apparatus (and library facilities) and staff them with well-trained competent technicians and technologists.

In connection with what has been stated and outlined above the following initial steps should be instituted without delay:

a) Speed up the development and production of means, methods and installations for the purification of gases and other industrial emissions so as to meet the rising demand for such equipment by the newly constructed industrial production plants as a step toward preventing the air from becoming polluted at the very outset;

b) Improve the efficiency in the utilization of gas and air purifying installations by instituting a strict inspection and supervision system of the condition of installations, and the duty performance by the operating personnel;

c) Effort should be unsparingly exerted in the direction of increasing the tempo of scientific research and of the practical utilization of results attained. No effort should be spared to keep scientific research several steps in advance of actual industrial developments.

State sanitary inspection organizations on their part should concentrate their time and activities on problems related to the location of new and reconstruction and possibly relocation of old industrial production and manufacturing enterprises; they must increase strict enforcement of existing sanitary-hygienic regulations prescribed by the sanitary code adopted for the purpose of liquidating community air pollution; they must cooperate with sanitary authorities of individual republics, regions and sovnarkhozes (soviet peoples economic bodies) in planning means for the protection of atmospheric air, and see that such plans were in accord with the state sanitary code for the protection of atmospheric air; they should keep careful records of their experiences in the realm of air pollution abatement, so that such records may be of use and value in plan-

ning sanitary means of air protection at some future time. In order that different educational institutions may effectively cooperate in the work of preventing community air pollution by the newly arising types of production, manufacture and processing, the Office of the State Sanitary Inspector of the U.S.S.R. should help such institutions to acquire an adequate amount of modern apparatus and equipment needed for air pollution research in any specific phase of study.

Proposals for methods and procedures, as well as for development of equipment, apparatus and installations connected with air protection against pollution, should be approved by the special Committee on Air Sanitation mentioned in one of the preceeding paragraphs.

## Sanitary Protection of Atmospheric Air in Poland.

Ya. Yust.

Gigiena i Sanitariya, Vol. 25, No. 1, 84-85, 1960.

Problems related to the sanitary protection of atmospheric air have been insufficiently investigated in Poland, and means for the protection of air pollution are still in the stage of organization. Supervision over the sanitary protection of atmospheric air has been under the jurisdiction of the Office of the Chief Sanitary Inspector, Ministry of Public Health, and controlling agencies were assigned to sanitary-epidemiological stations. Actual systematic inspection and investigation has not been undertaken as of the present, except in response to local complaints presented by a village or a city section where air pollution became intolerable, and in instances where choice had to be made for the location of a new village. In such cases the method of Owens (see U.S.S.R. Literature Survey, Vol. 3, Department of Commerce, O.T.S. No. 60-21475) has been used in connection with the sedimentation method, including $SO_2$ and occasionally F determinations. No regulation requiring determination of limits of allowable air pollutant concentrations and no methods to eliminate air pollution are in existence in Poland at present. The Polish Ministry of Public Health is now

considering the formulation of such a sanitary regulation. In view of the fact that Polish authorities had no experience with methods for the determination of effective combat against air pollution, they centered their attention on the appropriate localization of newly arising industrial enterprises. New plants, and some old ones, are being equipped with dust-catching installations, but gas purifying installations are still rare. Only few sanitary scientific investigations have been conducted in the field of atmospheric air. Studies in the field of finding connection between the state of the population's health and air pollution are still in the initial developmental stages in Poland. The Polish Ministry of Public Health receives reports from different sections of the country where metallurgical industrial plants prevail; such reports indicate that the state of health of children living in close proximity to metallurgical plants has been worsening steadily. The Institute of Motherhood and Childhood regards air pollution as the primary, if not the only important factor in such deterioration of children's health.

The problem of automotive exhaust gas on the organism has received attention prior to the last war, and it was natural that no exhaust gas concentrations deleterious to human health should have been found in the air at that time. The Presidium of Academy of Sciences appointed a special Commission whose responsibility it was to organize studies of atmospheric air pollution and means for combatting same. This work has been conducted by medical organizations and institutes in cooperation with the Central Institute of Labor Protection, the Department of Heat Technique of the Mining Academy, the Institute of Non-Ferrous Metals, etc. Consultation connected with problems of the sanitary protection of atmospheric air has been assigned to different planning organizations and to institutes associated with certain branches of different industries. Significant systematic studies of atmospheric air pollution are now being conducted at only two points, namely, at the Katovits region and in Warsaw. Such studies are conducted at the Katovits region by the Geographic Institute of Yagellonsk University in Krakow in cooperation with the State Hydro-Meteorological Institute which has been investigating the climatologic characteristics of the Gorno-Silezsk industrial region known by the initials as GPO (a mining district), and by the Department of Climatology of Vrotslavsk University in cooperation with the Laboratory of Climatology of the Geographic Institute, Polish Academy of Science; studies are centered on the determination of atmospheric air dust pollution and intensity of solar radiation in the territory of GPO. The Institute of Labor

Medicine in Rokitnits has been studying GPO atmospheric air pollution with $SO_2$. In addition the Regional Sanitary-Epidemiological Station of Katovits city has initiated a general sanitary-epidemiological investigation. Studies made thus far by the method of Owens indicated that maximal dust intensity in some regions was 4,000 particulates per ml, with an average of 2,853 particulates per ml during the months of January and June. Results of sedimentation tests made of the GPO air were as follows: maxima ranging between 12.0 - 17.7 $t/km^2/24$ hrs., and averages of approximately 11 $t/km^2/24$ hrs.; however, in some regions only 1.5 $t/km^2/24$ hrs. were found. $SO_2$ concentration in the air of GPO ranged between 0.025 - 1.206 $mg/m^3$, rising on occasion to 5.45 $mg/m^3$. Intensity of solar radiation in regions of highest air dust concentration was reduced by 30 - 37%.

Warsaw air has been investigated by the Department of Community Hygiene of the State Institute of Hygiene. The purpose of such investigation has been the determination of boiler-operated heat and power electric stations discharges on the sanitary condition of the city's atmospheric air. In June of 1957 a seminar was conducted at the State Institute of Hygiene located in Warsaw in which sanitarians and other pertinent workers participated; the purpose of the seminar was to convery information and stimulate attempts to place the work of atmospheric air pollution protection on a broader basis.

The problem of sanitary atmospheric air protection should be approached the same as any other important social problem from the viewpoint of health and national economy. In this connection attention is called to the following urgent sanitary-hygienic problems related to the protection of air pollution:

a) Data should be obtained to show the extent of loss to national economy caused by inappropriate fuel combustion, discharge into the atmospheric air of valuable raw products and similar phases;

b) Determine the mechanism of deleterious effect of air pollution in any given territory in relation to predominating meteorological conditions;

c) Establish limits of allowable concentrations of deleterious substances in atmospheric air;

d) Institute appropriate and mandatory regulations for the control of newly constructed villages and different industrial production plants;

e) Exert pressure in the direction of purifying equipment installation in newly erected industrial production plants. Sanitary-epidemiological authorities should insist that provision be made for purifying dust and gas equipment in the preliminary and final plans made for such plants;

f) Institute systematic check of the sanitary condition of atmospheric air using a standardized procedure;

g) Initiate systematic investigation of the deleterious air pollution effect on human health, and develop means for its elimination which would simultaneously and automatically protect the air against pollution.

Third All-Union Conference on Methods for Air Dust Pollution Studies.

P. N. Torskii.

Gigiena i Sanitariya, Vol. 25, No. 2, 95-96, 1960.

On May 19 - 21, 1959, a Conference was held in the Institute of Labor Hygiene and Occupational Diseases of the U.S.S.R. Academy of Medical Sciences on research methods for air dust pollution; the Conference was organized by the Silicosis Prevention Commission of the U.S.S.R. Academy of Sciences. Ninety specialists of the engineering and sanitary-hygienic profession attended the Conference, at which 20 reports were presented.

E. V. Khukhrina talked about "Methods for the Study of Air Dust Pollution in Relation to New Data on the Hygienic Significance of Pollutants Concentrations". She enumerated the following basic requisites:

a) Dust control must be aimed to determine the dust mass which affected the organism and to establish weight indexes for its concentration in the air;

b) Collection of air samples must be conducted to enable the simultaneous determination of average and highest concentrations even in cases where their effect was of short duration;

c) The picture of fractional particulate dispersion should take into account differential gravimetric values;

d) Parallel with the above, studies should be made of the physico-chemical properties of dust, its electrical characteristics and biological effects.

The Conferees manifested considerable interest in the presentation of A. I. Frank of the Institute for Labor Hygiene and Occupational Diseases, A.M.N., U.S.S.R., who recommended that in making gravimetric dust determinations filter

cloth trade-marked FPP-15 be used. Experiments confirmed that this cloth possessed many advantages: low pressure drop and high filtration efficiency, high dust retention capacity, non-hygroscopicity; light weight which was of value in weighing small quantities of dust with a high degree of accuracy. Prof. Ya. B. Reznik of the Odessa Institute of Medicine in his report entitled, "Determination of Air Dust by the Use of Membrane Filters", demonstrated that it was possible to introduce the membrane filter into the study of air dust under practical conditions.

Parallel with reports presented on improvements made in existing devices, such as the VDK ultramicroscope, the field meter for ultramicroscopy in aerosols, designed by the Leningrad Institute of Labor Hygiene and Occupational Diseases, (LIGTPZ), G. Y. Vlasenko and G. S. Berezhyk described new devices which were in the process of completion and final testing in their application in mines. The following devices were mentioned as examples:

A device for the visual determination of low coal dust concentrations in mines, IMP-1, developed by the Makeev Institute of Scientific Research (MakNII) and the Institute of Hypercoalautomatization and presented by V. T. Malikov (MakNII); a solar-reflectoscopic device for the determination of settled coal dust thickness (POTOP-3), developed by MakNII and reported on by M. D. Krivitskii; an electrostatic precipitator designed by the Mining Institute of the Kazakh S.S.R. Academy of Sciences and reported on by M. I. Volokhov.

Many devices required constructional improvement and adaptation for use under coal mine conditions; among such were: an acoustical dust gauge, developed by the Central Laboratory of Scientific Research Gostekhnadzor R.S.F.S.R. and reported on by S. S. Anisimov; an automatic dust collector for detecting air dust by the gravimetric method, developed by the Mining and Metallurgical Institute of the Armenian Sovnarkhoz and reported on by A. N. Zhamkochyan; a device for the rapid collection of dust samples, essential to the determination of degree of dust dispersion (electrostatic dust precipitator), developed by the Khar'kov Institute of Labor Hygiene and Occupational Diseases, based on the utilization of charges in dust particles and reported on by A. I. Kosenko; a device for the determination of concentrations and electrical charges of dust by the ultramicroscopic method, developed by the Khar'kov Institute of Labor Hygiene and Occupational Diseases and reported on by A. I, Kosenko. Mention should be made of the portable micro-projection camera AN, U.S.S.R.

reported on by V. I. Uskov, a description of which was published earlier. V. V. Kudryashev, in his report entitled, "Concerning Indirect Methods of Dust Control", analyzed causes of errors made in utilizing visual methods in aerosol studies in mines. P. N. Torskii, in his report entitled, "Concerning Methods and Apparatus Employed in Dust Control in Czechoslovakia", cited facts collected during a trip to Czechoslovakia by a group of Soviet specialists to study and exchange experiences in the fight against mine dust. A. I. Frank of the Institute of Labor Hygiene and Occupational Diseases, A.M.N., U.S.S.R. in his reported entitled, "Determination of the Composition of Dispersed Dust by Microgravity Sedimentation Analysis", proposed the utilization of sensitive quartz spirals for micro-weighing in connection with the analytical computation method developed by N. N. Tsyurup. The report by N. I. Smetanin of the Tashkent Institute of Medicine entitled, "Device for the Determination of Dust Dispersion Based on Fractional Weight", called for the use of a device found of little practical value. V. V. Skobunov presented a report entitled, "Concerning the Method of Gas Dust Control in the Mining Shafts"; he based his method on a theoretical assumption regarding gas and dust distribution by ventilation currents.

The Conference noted that since the 1953 (Second) Conference on Dust Control Methods, considerable progress has been made in the development and construction of new dust determining devices and in the study of new types of filtering materials. However, during these years only one device, the AER, of the many demonstrated at the Conference in 1953, had received wide practical application. Very little attention has been paid to the study of physico-chemical characteristics of dust, which delayed considerably the development and acceptances of the new dust measuring apparatus.

Reports were discussed at considerable length after which the Conference resolved to pursue the following essential aims:

1. To direct attention of practical workers in dust creating occupations and in sanitary-epidemiological institutions engaged in designing and making dust-measuring apparatus and in developing methods for dust control, to the importance of solving these problems in accordance with the specifications formulated by E. V. Khukhrina in her report.

2. To apply greater effort to the development of rapid methods for the determination of dust intensity and to the development of methods and apparatus for remote and automatic dust intensity determinations.

3. To institute systems of comparative evaluation of the practicability and efficiency of the following: a) cloth filters FPP-15; b) membrane filters; c) device for the determination of small coal dust concentrations (MakNII); d) radiation-reflecting device for measuring the thickness of settled coal dust (POTOP-3, MakNII); e) portable counter for ultramicroscopic aerosol measuring (LIGTPZ); f) ultramicroscope VDK; g) photoelectrocolorimeter IGD AN, U.S.S.R.; h) automatic dust catcher of the Armenian Sovnarkhoz; i) device for the determination of dust concentration designed by the Khar'kov Institute of Labor Hygiene and Occupational Diseases; j) electrostatic precipitator IGD AN of the Kazakh S.S.R.; k) electroconimeter EK-4 IGD AN of the Kazakh S.S.R.

4. To create a special committee headed by E. V. Khukhrina who would be responsible for the realization of the above objectives during the first quarter of 1960. Headquarters of the Committee shall be in the Institute of Labor Hygiene and Occupational Diseases of the U.S.S.R. Academy of Medical Sciences.

5. To expedite the development of the newly proposed methods for weighing dust samples collected by filters made of FPP-15, proposed by the Institute of Labor Hygiene and Occupational Diseases, and by membrane filters as proposed by the Odessa Institute of Medicine, with a view to applying such methods to the micrograviметric and dispersometric methods of dust determinations. Hopes were expressed for the possible use of material FPP-15 under practical conditions.

6. To note with interest the initiative of institutes which volunteered to undertake the development of rapid methods for the determination of air dust intensity and of equipment required for the purpose; to recommend that the above mentioned equipment and apparatus be modified, so as to increase their sensitivity and precision, and to establish the effects of humidity and aerosols which develop during the work with spray devices on the composition of dispersed dust.

7. To regard as imperative, in evaluating hygienic working conditions and the effectiveness of sanitary-technical measures, the adherence to the recommendations stipulated in the "Provisional Directives for Methods in Collecting Air Dust Samples", by the Committee on Fight Against Silicosis affiliated with the Academy of Sciences, U.S.S.R.

Third All-Union Conference on Sanitary Protection of Atmospheric Air.

L. F. Glebova and S. I. Murovannaya.

Gigiena i Sanitariya, Vol. 25, No. 1, 107-109, 1960.

The Third All-Union Conference on problems of the sanitary protection of atmospheric air was held in Kiev, May 26 - 30, 1959. It was called by the A. N. Sysin Institute of General and Community Hygiene, A.M.N., U.S.S.R., by the Ukrainian Institute of General Hygiene of the Ukrainian S.S.R. Ministry of Health, and by the Committee on the Sanitary Protection of Atmospheric Air of the U.S.S.R., representing the State Sanitary Inspectorate. Approximately 250 delegates attended the Conference, representing 14 Union republics, workers of institutes of scientific research and sanitary hygiene, professors of hygiene in medical institutes, workers of sanitary-epidemiological stations, of technical planning and scientific research institutes, of factories, sovnarkhozes, of the Ukrainian S.S.R. Gosplan, and of many other organizations.

The Conference was opened by Prof. N. N. Litvinov, Director of the A. N. Sysin Institute of General and Community Hygiene, A.M.N., U.S.S.R. Sixty-two reports were presented covering the most important questions of the day. Lively discussions by 400 participants of the Conference followed the presentations of the reports. A report on "The Present Condition of Atmospheric Air in Cities", was presented by Yu. D. Lebedev, Deputy Chief of the State Sanitary Inspectorate of the U.S.S.R. The report consisted of a critical analysis of work accomplished and outlined concretely the needs of future scientific research, the problems of practical and effective measures required for the protection of atmospheric air raised by the vast growth of production in existing industrial establishments and by development of new industrial areas in the U.S.S.R.

Prof. D. N. Kalyuzhnii, Director of the Ukrainian Scientific-Research Institute of Community Hygiene, summarized the principal results attained in the field of atmospheric air hygiene in the Ukraine and outlined the next perspective for scientific research in that field. Prof. V. A. Ryazanov, Chairman of the Committee on Sanitary Protection of Atmospheric Air, affiliated with the State Sanitary Inspectorate of the U.S.S.R., reported on future plans for scientific research into the protection of atmospheric air from newly created industrial emissions. He stated that the most important present problem concerned

the universal broadening of research in hygienic standardization of atmospheric pollutants as individual ingredients and as co-existing factors. The high tempo development of industry, and especially of the synthetic chemical industry, necessitated an intensified rate of endeavor in this field. M. S. Gol'dberg and L. F. Glebova, Candidates for Medical Sciences, presented a report entitled, "The Hygienic Reason for Sanitary-Protective Zones Between Industrial Enterprises and Residential Areas", and suggested a plan for a new sanitary classification of industries and of sanitary-protective zones, based on an analysis of research materials collected during a study of atmospheric air pollution in cities and workers' settlements in areas allocated to industrial production, manufacturing and processing.

M. F. Skatchko, Manager of trust "Gazoochistka" (Gas purification) reported on the present state of purification of industrial discharges which polluted the atmospheric air. He noted that a considerable amount of work had been conducted through the years 1955 - 1958, along the lines of planning, assembling and technical assistance, in the field of gas purification. Since 1959, 66 departments of institutes have been working on 199 assigned projects in the field of gas purification; the Institute "Giprogazoochistka" (Gas hyperpurification) has developed many gas purification projects for dust-catching devices. However, the techniques of gas purification and dust collecting were still far behind the growing demands of industry. Prof. A. I. Pakhomychev and his collaborators, E. A. Sarkisyansk and I. K. Atyakina, reported on the results of their study on the organism's reaction to the effects of small concentrations of toxic substances. Many reports were devoted to the problems of determining limits of allowable concentrations of toxic substances in atmospheric air. Chao Chen-li and B. A. Gofmekler of the Department of Municipal Hygiene of the Central Institute of Post-Graduate Medicine reported on their experimental findings in the determination of limits of allowable concentrations of methanol and acetates in atmospheric air; A. V. Mnatsakanyan, Senior Scientific Associate of the Armenian Institute of Epidemiology and Hygiene reported on concentrations of chloroprene; R. S. Gildenskjold, Scientific Associate of the F. F. Erisman Moscow Scientific-Research Institute of Sanitation and Hygiene reported on concentrations of carbon bisulfide; V. N. Kurnosov, Scientific Associate at the A. N. Sysin Institute of General and Community Hygiene, A.M.N., U.S.S.R., reported on concentrations of mercury. Considerable interest was

roused by the reports of K. A. Bushtueva entitled, "New Data on the Combined Action of Sulfuric Acid Aerosol and of Sulfur Dioxide Gas"; of M. I. Gusev entitled, "Effect of Small Lead Concentrations in the Air on the Organism of Man and Animals"; of A. A. Shmakov entitled, "Powder Dust of Snake Weed and of Asbestos as Pathogenic Factors in City Air"; of M. K. Khachatryan entitled, "Vitamin C in the Organism in Relation to Atmospheric Air Pollution by the Emissions from Synthetic Rubber Manufacture"; of A. S. Lykova entitlted, "Concerning the Toxic Effect of Oxides of Nitrogen". These reports stressed the pathohistological, biochemical and physiological methods of research for the determination of the harmful effect of low concentrations of toxic substances in chronic experiments.

Considerable time was devoted to the question of the hygienic evaluation of atmospheric air pollution in cities and industrial centers by discharges coming from leading branches of the national industry. More than 20 reports were devoted to this problem in relation to non-ferrous metallurgical plants (Prof. I. S. Koryakin and co-workers, N. R. Pakhotina, A. V. Mnatsakanyan and M. I. Nikosyan, and others); in relation to ferrous metallurgy (V. F. Dokuchaeva and N. N. Skvortsova); in relation to the chemical industry (Z. Ya. Lindberg, N. P. Gordynya, A. M. Ibragimov and A. N. Melkumyan, and others); in relation to the building material industry (M. V. Kryzhanovskaya and T. K. Ignatyeva, S. A. Davydov and collaborators, and others); in relation to cellulose-cotton combines (K. K. Kiyamov, E. Chapkevichene and V. Songailo); and many others. New data on atmospheric air pollution by fumes from solvents were presented by N. F. Izmerov.

A special session was devoted to the question of atmospheric air pollution with cancerogenic substances (reports by V. S. Serebrennikov, L. M. Shabad, Ya. M. Grushko, P. P. Dikun, N. N. Volkov and T. K. Mosolnikov, and others). The reporters and discussants stressed the need for intensifying research to determine the nature and sources of atmospheric cancerogenic pollutants, the need for prophylactic measures and for attracting clinical oncologists to cooperate in the efforts to solve this problem.

Mention should be made of reports dealing with problems of atmospheric air pollution with exhaust gases from automotive vehicles and problems dealing with measures for its prevention (F. I. Dubrovskaya, M. V. Alekseyeva, V. A. Khrustaleva, I. V. Datsenko, D. P. Partsef, M. D. Garbarenko). Studies of

atmospheric air in city main streets disclosed the presence of 3,4-benzpyrene, high concentrations of carbon monoxide, oxides of nitrogen and in the presence of automotive vehicles using ethylated gasoline, high lead concentrations. Two reports were devoted to results of experimental sanitary control of atmospheric air in cities by Zh. L. Gabinova of Moscow and Z. Ya. Rudchik of Stalin District, Donbass. New devices and methods for research in atmospheric air pollution were described in reports by L. F. Kachor, E. V. Rychter and Ya. G. Kiskho. The reports were accompanied by work demonstrations of the apparatus.

All reports stimulated animated discussions. Hygienists and physiologists (Prof. Babayants, Prof. Ya. M. Grushko, Prof. I. S. Kandror, Prof. L. M. Shabad, Prof. L. I. Los, M. S. Sokolovskii, and others), engineers, representatives of planning and economic bodies - all participated actively in the discussion.

At the closing session of the Conference a far-reaching resolution was passed, which outlined the need for intensification of the fight for clean atmospheric air in cities by improving the technology of production, of means for gas purification and dust collection and by general improvement in the domestic production technology and economy. The Conference resolved to recommend that the U.S.S.R. Ministry of Health submit to the Government a special report on the present state of atmospheric air pollution in cities and industrial centers in relation to diseases among city populations, accompanied by suggestions of basic relief measures to be instituted without delay in the fight against atmospheric air pollution. The Conference recognized that in determining limits of allowable concentrations of atmospheric air pollutants and in establishing sanitary protection zones, additional experimental studies were required, first to find a basis for limits of allowable concentrations for each of the toxic substances emitted by industrial enterprises manufacturing raw materials, intermediate products, materials used in the preparation of plastics, synthetic resins and fibers, rubber, etc., and to find a formula or method for the determination of limits of allowable concentrations of harmful pollutants simultaneously occurring in the air. The Conference emphasized the urgent need for extending experimental methods for the study of effect of cancerogenic air pollutants on animals and the need for determining the connection between frequency of cancer occurrence among a population and the presence in the surrounding air of different concentrations of 3,4-benzpyrene (benzo-phenanthrene) or of other cancerogenic substances.

Resolutions were passed to intensify the fight against automotive vehicles exhaust gases.

The Conferees recognized and emphasized the following pressing needs: 1) to organize a systematic serialized production of gas-purifying and dust-collecting apparatuses by specialized plants in quantities adequate to meet the domestic requirements; 2) to make research studies in development of apparatuses for the automatic control of gas concentrations emitted into the atmosphere by industrial plants before and after purification a part of scientific institutes' regular program; 3) to form an inspection body within the trust "Gazoochistka" whose duty it shall be to supervise the operation of gas-dust-collecting installations and the personnel in control of instruments for the determination of the coefficient of effective operation of gas-cinders-dust collecting installations; 4) to organize the affiliates of the Scientific-Research Institute for Industrial and Sanitary Purification of Gases (NIIOGAZ) in Siberia which covers enterprises of the Ural Mountains, of Kazakhstan and of Central Asia, in the Ukraine, which included the Transcaucasion Republics; 5) to create in one of the country's higher technical institutes a center for the training of specialists in the field of gas purification, dust collection and waste products recovery.

To intensify the control over the sanitary protection of atmospheric air, the Conference requested that the U.S.S.R. Ministry of Health undertake the following: 1) create responsible positions in air protection for sanitary physicians in sanitary-epidemiological stations of districts planning to erect new industrial production enterprises; 2) organize, beginning with the F. F. Erisman Moscow Central Institute of Post-Graduate Medicine, courses for training chemists for laboratories of sanitary-epidemiological stations which conduct research in atmospheric pollutions; 3) improve facilities in sanitary-epidemiological stations, in institutes of hygiene and in departments of laboratory equipment and apparatus development for research in atmospheric air pollution and its effect on the organism.

The Committee for Sanitary Control of Atmospheric Air of the U.S.S.R., affiliated with the State Sanitary Inspection, was delegated to organize at the A. N. Sysin Institute for General and Community Hygiene a permanent exhibition of equipment and instruments for the study of atmospheric air pollution, displaying foreign and domestic models of installations, equipment and technological procedures.

The Conference appealed to hygienists and technicians at large to cooperate in every way possible to make its resolutions a reality in the field of general air pollution abatement and prevention.

## Some Problems Connected with Sanitary Conditions in Cement Producing Plants.

A. M. Belevitskii.

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The rapid growth of cement manufacture anticipated by the Seven-Year-Plan of U.S.S.R. national economy planners presents authorities of the cement industry with a number of responsibilities from the viewpoint of workers' health; foremost among such responsibilities is the one associated with the demand to improve sanitary conditions in cement plants. In cement production workers deal with masses of raw and semi-processed materials, and with final products, all of which eliminate high dust concentrations. An average capacity cement plant has a daily turnover of 100 tons of materials to be treated by different mechanical processes; some of the materials have to be transported over long distances or be replaced from upper to lower positions, etc. Such conditions create dense concentrations of highly dispersed dust of rapid motility and penetrability into all sections of the cement plant.

Cement is produced by two different processes: the wet, and the dry processes. In the case of the former the raw materials to be treated go through most stages of production as wet masses, or in the form of a slurry which is dust-free. In the second method the raw materials go through completely dry, or almost completely dry, treatment processes. In the case of the wet method dust appearance begins with the calcining stage. In the second case dust appears at the first stage of the work. In the production of cement by the wet process, as can be judged from the above statement, the problem of dust creation is not completely obviated. In the production of cement by the dry method the problem of dust creation not only exists but is of such gravity

that it overshadows all other existing sanitary problems, and no satisfactory solution has been either found or proposed thus far.

The dry method for the production of cement requires no consumption of fuel for slurry drying and from this viewpoint it is a highly economical one. It can be easily understood, therefore, why foreign countries, and in particular Germany, have used mostly the dry process of cement production. A similar tendency has been noted of late in the U.S.S.R. It is fitting, therefore, that before the dry process becomes widely accepted in the U.S.S.R., methods should be found for the elimination of cement dust from the air of production premises. It should be noted in this connection that much work has been done in the U.S.S.R. in that direction of late, chiefly by adopting electrostatic precipitators built by the Moscow and Leningrad Institutes of "Giprogazoochistka" (Gas Purification). These installations have not solved the problem of dust elimination completely, since they have no bearing on the reduction of dust concentration prevailing at points of servicing personnel employment. This is due to the fact that directors and administrators of cement producing plants have paid no attention to problems related to the sanitary condition of different departments of cement producing plants. Furthermore, even high authorities responsible for development of newly planned industrial, in this case cement producing plants, failed to make provision for the sanitization of the plants' individual departments. As an example of the above, mention can be made of the Krivoi Rog dry cement producing plant, which was built according to a plan proposed by the "Yuzhgiprotsement" Institute and which was set into operation as recently as the latter part of 1955. All intradepartmental suction installations of this plant proved deficient or entirely inoperative, while dust creation resulting particularly from interdepartmental material transportation reached unheard of high concentrations. Data obtained by the Krivoi Rog Municipal Sanitary Inspection Office indicated that at many work positions dust concentration exceeded the allowable limits by thousands of percent. Due to such deficiency in sanitary safety provisions the plant had to be closed for the reconstruction of the dust catchers and of the general ventilation system. The corrective measures cost the government more than 500 million rubles. In addition, the unfavorable working conditions resulted in a rapid turnover of the workers, which lowered the productivity and efficiency of the work. In the long run the plant fell behind its assignment.

It must be admitted in this connection that past experience had indicated that the problem of dust elimination, especially in such industries as cement production presents many difficulties. On the other hand, the same experience also showed that the solution of the problem required no new special discoveries; it was only necessary to apply the present engineering knowledge and experience to the problem in a common-sense way. An unfortunate and harmful misconception has become rooted in the minds of industrial directors and plant administrators: they believe that dust abatement means consisted of the installation of exhaust equipment of sufficient force and capacity to remove or precipitate the dust completely, regardless of the amount generated at certain production points. The causes which generate the dust failed to interest them, and all their efforts have been exerted in the direction of improving the exhaust and aspiration ventilation systems. This is an inexcusable error, since factory experience has indicated that most effective means for dust elimination or abatement must begin not with the installation of dust catchers, but with the elimination of sources of dust generation as such. Where this can be successfully accomplished dust-catching installations and exhaust ventilation can be kept ready for operation in emergency cases. In the case of cement plants the selection and construction of dust removing installations should be based not only on the specific characteristics of the production functions since the nature of cement production does not lend itself to easy hermetization. It is also necessary to take into consideration the steps of raw materials delivery to various points and of the intertransportation of the final product, steps which are accompanied by intense air dust generation. The Krivoi Rog Cement Plant can be taken as an example of careless attitude on the part of pertinent authorities to such problems of sanitation and hygiene as dust abatement and dust elimination. In that plant all dust-emanating raw, semi-processed and processed products are conveyed from point to point by open belt conveyor systems, the total length of which exceeds 1 km; the conveyor system as such requires numerous transfers of the material from one conveyor belt to another. After the conveyors have been in operation for a time the dust in the conveyor passages was so heavy that one had to pass through them by "feeling" his way blindly. Such were the conditions the personnel servicing the conveyors had to work under. Subsequently, the plant had introduced certain corrective measures: about 40% of the conveyors were dismantled without any

loss in productivity; the remainder of the conveyor system was reorganized in a way which reduced the intensity of dust generation. However, even a basic reconstruction of the aspiration and exhaust systems did not prove adequate for the catching, precipitation and removal of the tons of dust generated at practically every meter length of the conveyor system.

General plant experience indicated that, wherever possible, use should be made not of mechanical but of pneumatic conveyor systems which had the advantages of complete hermetization and required no special means of efficient maintenance. The pneumatic conveyor system is more certain and more convenient in every respect. It can be easily incorporated into any type of plant premises, it is simple in construction and utilization and requires no extensive initial financial outlay.

Among objections frequently raised against the installation of pneumatic conveyor systems is the fact that its operation consumes a considerable amount of electric energy and that it frequently wears out as a result of destructive properties of certain abrasive components used in the cement industry. It is true that planners of pneumatic conveyor systems have not had sufficient experience to be able to design compact and economical conveyor systems which, incidentally, is the main reason for high electric energy consumption by such systems. However, it should be known by now that the above difficulties have been resolved. In 1955 - 1956 Engineer Yu. N. Mikol'skii, in cooperation with the present writer, developed a revised pneumatic conveyor system, now in operation at the Krivoi Rog Cement Plant (Tsement, 1956, No. 4), the operation of which consumed less than half of the electric energy previously consumed, and considerably reduced the number of servicing personnel. Another cause of high energy consumption by the pneumatic conveyor system was found in the lack of required construction specifics. As a rule the operation of pneumatic helical pumps used in cement plants has found no application as basic equipment. This is the cause of excess power consumption and of complicated and cumbersome conveyor systems. The production of pneumatic conveyor system equipment and parts should be put on a broad scale without delay.

The wear and tear of the pneumatic conveyor main channels is not a technical problem but rather one of organization. The Belgorod Cement Plant changed the construction of individual parts of the pneumo-conduits in 1954 and applied a special protective lining at points of highest wear. The application of such

simple means reduced the wear of the main conveyor lines to less than 10%. This resulted in an annual economy of 194,000 rubles. However, the primary advantage was not so much the economic savings as the fact that wear of main conduits was practically stopped, thereby obviating work stoppages for repair and at the same time considerably improving sanitary working conditions. There is a woeful lack of information or knowledge bearing on the problem of abatement or elimination of dust emitted by basic and auxiliary technological equipment inside of many departments especially in the hearth departments. In this case the leading role must be played not by dust aspirators or mechanics, but by technologists whose primary responsibility shall be to so organize the process of dust conveyance so that the existence of negative pressure be insured at all zones or sections of the furnace aggregate under all conditions of its operation. In the case of the usual rotating kilns this problem can be resolved comparatively easily. The problem becomes more complex in connection with furnaces equipped with conveyor calcinators, so frequently used in the dry system of cement production. For example, when the calcinators of the Krivoi Rog Cement Plant were put into operation, it appeared during the first few days that their actual method of operation differed sharply from the one provided by the plan, as was shown by the fact that furnace gases and dust were being emitted systematically from the furnaces into the department premises. Supplementary dust installations were being installed one after another, and even then only a slight amount of the dust and gases were removed from the working premises. Experience indicated that the operation of furnaces with conveyor type of calcinators largely depended upon gas permeability through the calcinating screen, and this in turn was connected with the quality of raw material granules loaded into the furnace. Studies indicated that it was necessary to secure better knowledge of the raw material granulation, specifically to secure highly stable and heat-resistant granules from raw materials of any composition. B. A. Petrov of the Leningrad Giprotsement Institute tried to investigate new original methods of consolidating the granules. Such investigation progressed slowly, and the results thus far obtained in the laboratory experiments have thrown no light on the situation under practical conditions.

Aspiration or exhaust ventilation systems in operation in different departments of the cement plant up to the present failed to satisfy the management in many respects and are very often being reconstructed and rearranged

in the process of actual utilization. As a result such exhaust ventilation systems frequently become complicated, cumbersome, regulated with difficulty, and in relation to the original purpose operated highly inefficiently. Under such conditions cases have been seen in which the resulting complicated and cumbersome exhaust ventilation system itself became a source of dust distribution within the working premises. It is the opinion of the present writer that the time has come when new types of inside exhaust systems should be devised specifically for cement plants. It should be noted in this connection that in the case of cement plants, specifications for each department should be different, since the type of materials used and many other circumstances or conditions differ with each department. This means that a careful study should be made of the suitability of scrubber type for any particular production department. The same is true of dry dust catchers. Existing scientific research laboratories dealing with problems of dust sanitization of the cement industry have not been able to cope with the magnitude of the problem, and have not been in a position to satisfy the rising demand for installations and equipment. For instance, the exhaust ventilation and aspiration laboratory of the Leningrad Giprotsement Institute, which by the way is the largest research institute taking care of the sanitary-hygienic needs of the cement industry, has a staff of not more than 15 or so workers, and it occupies several small rooms. The Institute has no semi-industrial facilities, on the one hand, while, on the other hand, it is not able to test the effectiveness of certain designed equipment under factory conditions, due to the fact that its scientific and technical personnel which, as previously indicated counts only 15, have considerable difficulty in coping with the accumulated demands for general information and installations.

Under the present conditions it appears most appropriate to enlarge the facilities and services of the existing laboratory, basically reorganize the methods of approach to problems and their execution, or else to create one single central laboratory dealing with the problem of dust abatement and elimination as applied to all industries. Organization of a central laboratory, had such action been agreed upon by all concerned, would enable the investigators to conduct intensive and extensive research along the lines of perfecting existing and designing new dust-catching equipment and installations. It is recognized that in the total problem of dust elimination the cement industry

might appear as a minor factor. Nevertheless, a factor it is, and in addition, some basic principles of the problem it creates and which call for urgent solution are different from problems of the same general nature in other industries.

Then, there is the problem of electrostatic gas purification which in principle is intended for the liquidation of dust discharged into the atmospheric air. In this connection it can be stated that dust elimination from the air of indoor premises cannot be completely solved by electrostatic precipitators. The problem must also be approached from the viewpoint of protection of exhaust or aspiration equipment and installations against the effect of abrasive dusts, of developing high quality U.S.S.R. filtering cloth for use in bag filters, improvement in the hermetization of transport and conveyor conduits, etc. Such problems are at present given little attention, while others are entirely neglected. By creating a central dust elimination laboratory these problems might receive greater attention. (Note by B.S.L. - It is frankly recognized that this paper contains nothing of intrinsic value insofar as specific scientific and practical information is concerned. However, it does clearly indicate how short the U.S.S.R. is of reaching the desired sanitary-hygienic goals, how poorly some of their so-called research and applied institutes are, and how inadequate are some of the equipment, installations, and materials used in gas purification and dust catching and abatement. The last paragraph herein translated is not the end of the original paper; however, enough has been said to present a reasonably clear idea of certain industrial sanitary-hygienic situations in the U.S.S.R. And since the remainder of this paper was judged to be repetitive of inadequacies and shortcomings and of proposals for improvement, the translation was stopped).



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