EPA-670/2-73-098
December 1973

Environmental Protection Technology Series

Odors Emitted From Raw And Digested Sewage Sludge

Office of Research and Development
U.S. Environmental Protection Agency
Washington, D.C. 20460

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, Environmental Protection Agency have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

EPA-670/2-73-098
December 1973

ODORS EMITTED FROM RAW AND DIGESTED SEWAGE SLUDGE

by

Bernard A. Rains
Mario J. DePrimo
I. L. Groseclose

Grant No. WPRD 23-01-68
Project No. 11010 EZQ
Program Element 1BB033

Project Officer

Dr. William Garner
Region VII
U.S. Environmental Protection Agency
Kansas City, Missouri 64108
816/374-5736

Prepared for

OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D. C. 20460

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 - Price $1.15

EPA Review Notice

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

Odors emitted during thickening of raw and secondary sludge have been responsible for adverse criticism at many sewage treatment plants. This study was undertaken to identify typical odor causing substances and evaluate selected conventional methods for controlling or eliminating these substances. A styrofoam dome covering a sludge thickener was utilized to control atmospheric conditions and concentrate odors.

Field collected vapor samples were analyzed using gas chromatography techniques. Analyses using both polar and nonpolar column material indicated that the major odor causing compounds were mercaptans and amines. Other compounds which were minor contributors to odor were aldehydes, alcohols, and organic acids.

Odor control methods selected for study included air dilution, activated carbon adsorption, and chlorine oxidation. Air dilution using cyclic operation of an exhaust fan was found to be an effective means of odor control when outside atmospheric conditions were conducive to odor dissipation. Passing vapors through activated carbon filters was not completely effective in odor control since a detectible residual odor remained. A 1.5 mg/l solution of chlorine was effective in removing all odors from vapor samples bubbled through the solution.

This report was submitted in fulfillment of Project Number 11010 EZQ, Grant Number WPRD 23-01-68, by the Metropolitan St. Louis Sewer District under the partial sponsorship of the Environmental Protection Agency.

CONTENTS

	PAGE
Conclusions	1
Summary and Recommendation	3
Synopsis	3
Future Work	4
Introduction	5
General Statement	5
Objective and Scope of Study	5
Odor Causing Substances	6
Description of Field Equipment and Procedures	9
Sludge Thickener and Dome	9
Gas Sampling Procedure	9
Odor Threshold Sampling and Evaluation	16
Odor Treatment Techniques	17
Inorganic Gas Determinations	20
Description of Laboratory Equipment and Procedures	24
Gas Chromatograph Column Selection	24
Selected Column Evaluation Using Standards	24
Chromatogram Comparison Procedure	29
Column Temperature Effects	29
Infrared Analyses	35
Results of Odor Identification Study	37
Relative Retention Time Determinations	37
Odor-Retention Time Comparisons	46
Compound Concentration Evaluation	50
Threshold Evaluation and Odor Treatment Results	54
General Statement	54
Selection of Odor Panel	54
Treatment by Air Dilution	54
Carbon Adsorption of Odors	57
Chlorine Treatment of Odors	59
Acknowledgements	63
References	65
Appendix	67

LIST OF FIGURES

No.		Page
1.	PLACEMENT OF FABRICATED DOME ON THE THICKENER WALL.	10
2.	THICKENER WITH DOME INSTALLATION COMPLETE.	11
3.	SCHEMATIC FLOW DIAGRAM OF COLDWATER CREEK TREATMENT PLANT.	12
4.	SCHEMATIC FLOW DIAGRAM OF THE GAS SAMPLING EQUIPMENT.	14
5.	STAINLESS STEEL CONDENSATION TRAP USED IN INSULATED DEWAR FLASK.	15
6.	GAS SAMPLING TRAIN.	15
7.	THRESHOLD ODOR TESTING APPARATUS.	18
8.	ADSORPTION COLUMN AND SAMPLING APPARATUS FOR ACTIVATED CARBON ODOR TREATMENT EVALUATION.	18
9.	SCHEMATIC FLOW DIAGRAM FOR ACTIVATED CARBON TREATMENT EVALUATION.	19
10.	CROSS SECTION OF LAB APPARATUS USED FOR CHLORINE TREATMENT EVALUATION.	21
11.	SCHEMATIC FLOW DIAGRAM OF THE AMMONIA ABSORPTION EQUIPMENT.	23
12.	CHROMATOGRAPHIC SEPARATIONS OF A DOME-GAS GRAB AND CONDENSATE SAMPLE FROM THE SAME DAY.	30
13.	CHROMATOGRAPHIC SEPARATIONS OF DOME-GAS CONDENSATE SAMPLES ON CARBOWAX 20M AT VARIOUS TEMPERATURES.	32
14.	CHROMATOGRAPHIC SEPARATIONS OF DOME-GAS CONDENSATE SAMPLES ON SE-30 AT VARIOUS TEMPERATURES.	33
15.	CHROMATOGRAPHIC SEPARATIONS OF DOME-GAS CONDENSATE SAMPLES ON PORAPAK Q AT VARIOUS TEMPERATURES.	36

LIST OF FIGURES

No.		Page
16.	RELATIVE RETENTION TIME OF DOME COMPOUNDS ON CARBOWAX 20M AT 55°C AND 5 X 10^{-12} AMP.	41
17.	RELATIVE RETENTION TIME OF DOME COMPOUNDS ON SE-30 AT 90°C and 5 X 10^{-12} AMP.	41
18.	RELATIVE RETENTION TIME OF VARIOUS STANDARDS ON CARBOWAX 20M AT 55°C.	44
19.	RELATIVE RETENTION TIME OF VARIOUS STANDARDS ON SE-30 AT 90°C.	45

LIST OF TABLES

No.		Page
1.	Retention Time of Selected Standards Using Various Columns.	26
2.	Peak Elutions (Minutes) Observed for Bag And Condensate Samples Using Designated Columns And Temperatures.	28
3.	Relative Retention Times of Dome Compounds on Carbowax 20M at 55°C.	38
4.	Relative Retention Times of Dome Compounds on SE-30 at 90°C.	39&40
5.	Comparison of Relative Retention Times of Standards and Condensate Peaks.	42
6.	Retention Time of Organic Acids and Dome Compounds on Carbowax 20M.	48
7.	Odor Thresholds of Several Organic Compounds. (17,18)	49
8.	Comparison of Odor Types with Operational Measurements.	51
9.	Maximum and Minimum Concentrations Recorded for Identified Odor Compounds.	52
10.	Sensitivity of Personnel to Triangle Test.	55
11.	Threshold Levels and Air Dilution Requirements for Dome Atmosphere.	58
12.	Carbon Adsorption of Dome Odors.	60
13.	Typical Chlorine Treatment Results For Dome Odor Removal.	62

CONCLUSIONS

1) The compounds identified in the vapors emitted from the sludge thickener were: ethyl, propyl, tert-butyl, tert-amyl, amyl mercaptans; diallylsulfide, isopropanol, propanol, butanol; acetaldehyde, propionaldehyde; ethylamine, butylamine, hexylamine, diisopropylamine, dibutylamine, diisobutylamine, triethylamine; acetic, propionic, and isobutyric acids; ammonia; hydrogen sulfide; and methane.

2) The discernible odors, which were a function of the type and amount of waste present in the thickener, could be typified as being either rancid, fecal, cabbage-like, skunk-like, or sour.

3) A correlation between the blanket depth, peaks eluted on the gas chromatograph, and the various odor types was found to exist.

4) Propyl mercaptan (cabbage-like odor) and ethylamine (rancid) were the only compounds identified in the dome that were present in concentrations above their threshold levels.

5) The inorganic gases, hydrogen sulfide and ammonia, and the organic gas, methane, were present in the dome atmosphere but could not be quantitated.

6) Threshold odor levels varied depending upon quantity of sludge being thickened.

7) Odor control by air dilution of the dome atmosphere can be accomplished by operation of an exhaust system during optimum atmospheric conditions.

8) Carbon adsorption removes offensive type odors from vapors emitted during sludge thickening but some discernible odors are not affected.

9) Oxidation of sludge thickener odors by scrubbing with a water solution containing 1.5 mg/l of residual chlorine is effective in reducing the odors below detectible limits.

SUMMARY AND RECOMMENDATIONS

SYNOPSIS

Vaporous compounds emitted from a sludge thickener were identified using gas chromatography as mercaptans, alcohols, amines, organic acids, and aldehydes. Samples were collected in the field by pumping quantities of the atmosphere within a styrofoam dome covering a sludge thickener through a sampling tube to a condensate trap supported in a Dry Ice-alcohol bath. The relative retention times of the sample components and laboratory standards, as determined by gas chromatography from eluted peaks on a Carbowax 20M and an SE-30 column, were compared. Flame-ionization was used as the detector system.

The quantity of odorous compounds emitted by the sludge thickening process was found to be a function of the quantity of waste sludge present. A correlation between the blanket depth, peaks eluted on the gas chromatograph, and the various odor types was found to exist. The discernible odors could be typified as being either rancid, fecal, cabbage-like, skunk-like, or sour. The cabbage-like odor was noted on days when a large concentration of propyl mercaptan was present. A pungent, rancid odor was detected when a large amount of ethylamine was present. The other noticeable odors could not be correlated with any one identified compound. Methane, hydrogen sulfide, and ammonia were qualitatively identified by gas chromatography and/or wet test methods. Their concentrations, however, were below the detectible limits of Orstat or Tutweiler gas analyzers. The dome vapors were not concentrated sufficiently to yield absorption information except for water and carbon dioxide bands on an infrared spectrophotometer using a 10-meter cell.

An odor panel was selected to determine the threshold level which could be utilized as a base-line value for evaluating treatment of the odors within the dome atmosphere. It was found that the threshold levels varied from day to day complicating efficiency evaluations using air dissipation as an odor control technique . Cyclic operation of the exhaust system was considered to be an effective odor control method during optimum atmospheric conditions.

Activated carbon adsorbed most of the detectible odors from the dome, however, some of the odor causing organic compounds were not removed by the carbon. Samples of the gas taken after passage through a carbon filter had a slight, detectible odor resembling lard.

The treatment method that was found to be the most efficient as far as complete removal of the odor was chlorine oxidation. It was found that bubbling the dome vapors through a chlorinated water solution containing 1.5 mg/l of residual chlorine could effectively remove all obnoxious odors present.

FUTURE WORK

Because of the numerous compounds that were eluted during the study by the gas chromatograph and not identified, further investigation is needed. Selected absorbents could be used to collect a particular class of organic compound considered, based on previous results, to be present. Such collected compounds could be released under controlled laboratory conditions and identified by using a gas chromatograph equipped with a column particularly suited for separation of that class of compound. Temperature programming and other detector systems could be utilized effectively. Research on the threshold levels of the compounds should be made to determine their effect individually and together on olfactory perception.

Treatment methods using chlorinated water or effluent as a scrubber solution should be evaluated on a large scale. Laboratory evaluation of the chlorine oxidation products would also be necessary.

Further studies concerning the effects of climatic changes and type of waste being treated upon odor formation and its control are advisable.

INTRODUCTION

General Statement

Numerous complaints from the residential community surrounding the Metropolitan St. Louis Sewer District's Coldwater Creek Sewage Treatment Plant were part of the initiating force that led to a study of odors emitted by the sludge thickening process at the plant. This process was considered the major source of objectionable odors due to its retention of actively decomposing organic sludge from primary and secondary treatment units.

A dome constructed of styrofoam and an exhaust system were installed on the thickener to control the emission of odorous gases from the surface of the decomposing sludge as well as concentrate vapors for purposes of identification. Initial study indicated that it was not feasible to catalog the odor emissions from the thickener before dome installation, because there was no means of segregating effects of odors from industrial and agricultural sources in the surrounding region. Covering the thickener prior to research presented a more controlled environment for odor studies without the influence of climatic changes, wind current, and interferences from other adjacent odor sources within the plant such as grit and primary basins. Elimination of the odors was the ultimate goal of the study and a controlled atmosphere above the thickener provided a convenient means of confining the odors for any treatment considered necessary.

This report presents in total all data collected, analyses performed, and conclusions formulated as a result of the study.

Objective and Scope of Study

The primary objective of the study was to utilize instrumentation and gas concentration techniques to identify and evaluate quantitatively the odors emitted from the sludge thickener. Guided by the identification and concentration results, selected treatment methods were conducted to determine their effectiveness in odor reduction and control.

The project proceeded in five phases which were as follows:

1) Construction of dome and installation of exhaust system.

2) Startup of thickener unit and stabilization of operation.

3) Sampling and identification of odor components.

4) Determination of odor thresholds.

5) Evaluation of odor reduction by air dilution, activated carbon adsorption and chlorine oxidation.

Observations relative to thickener operation and dome atmospheric conditions were recorded for daily and bi-weekly grab and condensate samples collected through a period covering spring and late summer months. Data were obtained by gas chromatography utilizing the several columns which gave best recovery and separation of peaks and by infrared spectrophotometry. Wet chemistry methods were used to determine the non-organic dome atmosphere constituents. The effect of sampling time, moisture removal, cold trap configuration, and condensation time were evaluated in order to optimize and standardize sampling conditions.

Odor Causing Substances

Odors emitted from decomposing organic wastes can be highly disagreeable. The odor causing compounds are bacterial breakdown products of fats and nitrogen and/or sulfur-containing organics such as proteins (1). Odors are not caused entirely by inorganic gases such as NH_3 and H_2S, but rather a wide assortment of volatile organic compounds.(2) (3) In his studies of odors emitted from various locations in a sewage treatment plant, Glaser (1) was able to absorb specific volatile gases and correlate their formulation with sewage influent characteristics and time of day. He measured sulfides by first passing the gas through a cadmium sulfate-sodium hydroxide absorption solution, and then adding this solution to a mixture of ferric chloride and p-aminodimethylaniline to form methylene blue. In a similar

manner he determined the presence of mercaptans by first absorbing the gas in a solution of mercuric nitrate and nitric acid and then developing color in the solution with N, N-dimethyl-p-phenylenediamine and Reissner solution. The presence of aldehydes was determined by forming an aldehyde complex with sodium bisulfite and then later titrating the complex with iodine. Of the compounds he found the most odorous and obnoxious were the mercaptans and sulfides.

Miner and Hazen [4] indicated that the odor in a swine building could not be attributable only to ammonia and further work revealed the presence of three amines in addition to the ammonia. These compounds were identified using gas chromatography as methylamine, ethylamine, and triethylamine.

Burnett [2] concluded from his work on poultry wastes that the odors emitted therefrom contained acetic, propionic, isobutyric, n-butyric, isovaleric, and n-valeric acids. These compounds all have sour type odors with the most disagreeable being isobutyric, n-butyric, isovaleric, and n-valeric acids. The heterocyclic compounds, indole and skatole, were also found to be present in the liquid portion of the waste. Both these compounds have extremely obnoxious odors even in dilute concentrations and they both tend to persist for long periods on clothing and other fabrics. Other odorous compounds detected by gas chromatography were methyl mercaptan, ethyl mercaptan, methyl sulfide, diacetyl, n-propyl mercaptan, acetoin, n-butyl mercaptan, and methyl disulfide. He did not study the amines, but he did state that when his extracts were made alkaline the strong characteristic fish type odor of amines was emitted.

Such research leads to speculation concerning the components causing odors at a domestic wastewater treatment plant. Complex mixtures of volatile organics could certainly create some of the odors noticeable at such plants.

Yet to be studied are the synergistic effects of malodors. We are aware that a variety of essences are carefully compounded to produce the pleasant odor of perfumes. It is highly probable that individual compounds that have unpleasant odors also enhance and modify the pure odors of each other. Such interaction of odorous materials makes

it quite difficult to identify specific odor causing compounds and the causative source. The development of methods to control odor emissions may be more effective once such relationships are understood.

DESCRIPTION OF FIELD EQUIPMENT AND PROCEDURES

Sludge Thickener and Dome

A dome was constructed from styrofoam by the Dow Chemical Company and positioned as shown in Figures 1 and 2 on the 65-ft. diameter sludge thickener at the Coldwater Creek Plant. The air space which is bounded by the dome's inner surface, the liquid level and the effluent channel has a volume of 31,370 cu. ft. The air exhaust and duct system installed by a local contractor has a capacity of 16,600 cu. ft./min., which theoretically allows a complete air exchange of the dome every two minutes.

Different operating depths of sludge in the thickener were evaluated to determine effects on the subsequent digestion of the sludge. Residence time in the thickener is thus directly related to sludge blanket depth. The liquid surface to sludge depth chosen as the most effective operating level was six (6) feet. That is, the distance measured from the water surface to the sludge interface was maintained at about six feet. The depth of sludge then at the center of the tank was about ten feet due to the conical bottom. One sludge pump operated continuously and another pump was put in service between the noon to midnight hours. This second pump would be turned off when the sludge level in the thickener dropped below nine (9) feet. For further sludge thickener operational details refer to Appendix A of this report.

Dilution water from the final clarifier is piped into the dome each day from 8:00 a.m. until 4:00 p.m. as indicated in Figure 3 which presents the operational flow pattern for the Coldwater Creek Plant. This maintenance procedure to freshen the contents of the thickener is maintained unless primary sludge has to be bypassed directly into the digesters during periods of high solids loadings.

Gas Sampling Procedure

Vapor samples were collected from the dome atmosphere by filling a Hamilton 1-liter gas-tight syringe at the center of the dome and injecting it through a septum into a 1-1/3 liter Saran bag. Water and air temperatures were recorded at the same location as well as the interior relative humidity.

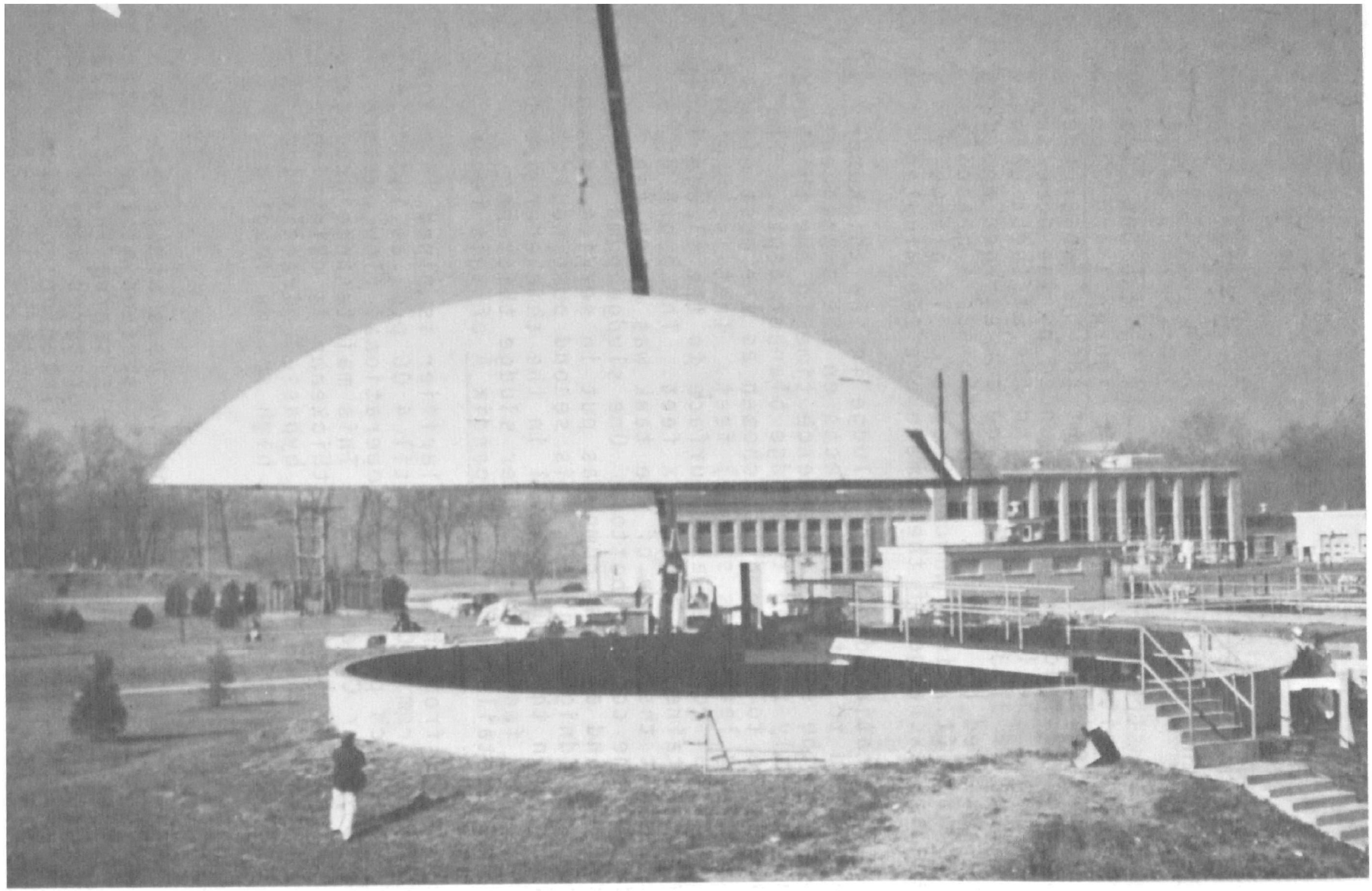


FIGURE 1. Placement of fabricated dome on the thickener wall.

FIGURE 2. Thickener with dome installation complete. Note exhaust motor and effluent duct to left and sampling compartment to right of entrance.

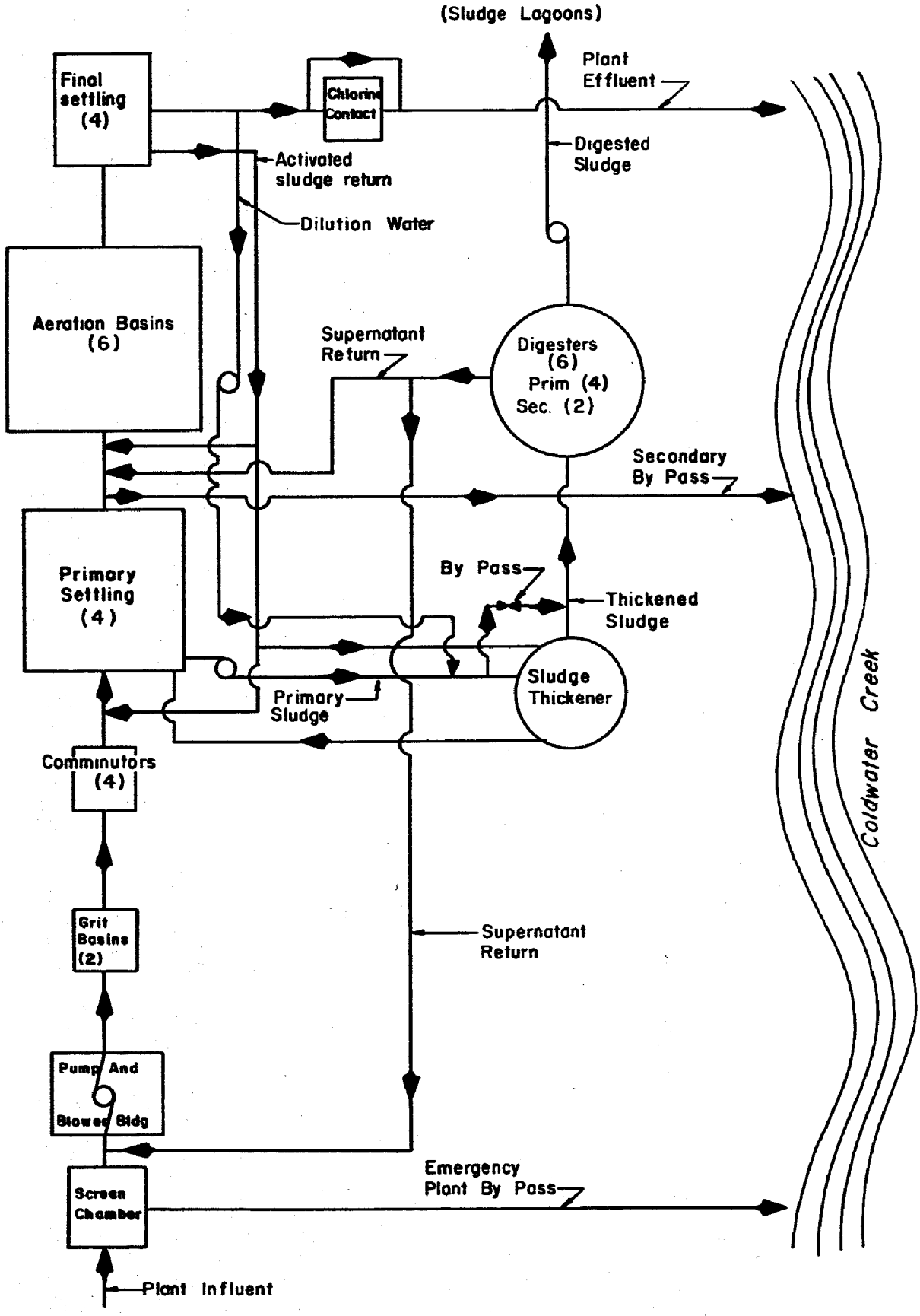


FIGURE 3. Schematic flow diagram of Coldwater Creek Treatment Plant.

Concentration of vapors was accomplished by using a polyethylene tube that extended from the center of the dome to the sampling train shown in Figure 4. The train consisted of two insulated glass wells equipped with a thermometer to measure the gas temperature before and after passage through the condensation trap, a gas flow meter to record the volume of gas that passed through the sampling line, and a carbonvane pump with a 2 cu. ft./min. pumping rate. Plastic quick disconnects were used to join the polyethylene tube sections, and Swagelok fittings were used to join the metal and polyethylene tubes.

In order to prevent damage to the gas meter from the cold gas, a 20-ft. coil of aluminum tubing was installed in the line to bring the influent gas back to ambient temperature prior to entering the flow meter. The condensation trap shown in Figure 5 is a 5-ft. x 1/4-in. o.d. coiled stainless steel tube that was fitted with Whitney valves. The coiled configuration of the trap gave the vapors an extended contact time in the cold bath.

Initially a 1-inch glass fiber filter was placed inside of the dome at the head of the sampling tube but its use was discontinued for two reasons: 1) the dome was devoid of large quantities of atmospheric particulate matter and it was therefore not necessary to filter the vapors and 2) the filter tended to adsorb and restrict the free flow of the vapors.

The sampling train with condensation trap as shown in Figure 6 was purged for 5 min. to dislodge the stale gases and condition the apparatus for the next sample. The trap valves were closed and the trap placed in the dry ice-alcohol bath for several moments to cool the stainless steel coils prior to the sampling run. The temperature of the ice bath was maintained at minus 78°C during each run. Sampling was terminated when the flow through the coil was reduced as noted by a temperature rise of the exit thermometer. This occurred after 15 to 20 minutes into the run. The trap was then disconnected from the vacuum line, sealed, and the pump shut off. During the 15-20 minute sampling time normally 20-40 cu. ft. of vapor passed through the sampling train. The quantity of sample collected was highly dependent upon the relative humidity and concentration of odorants inside the dome. While the sample was condensing, the temperature and relative humidity in the interior of the

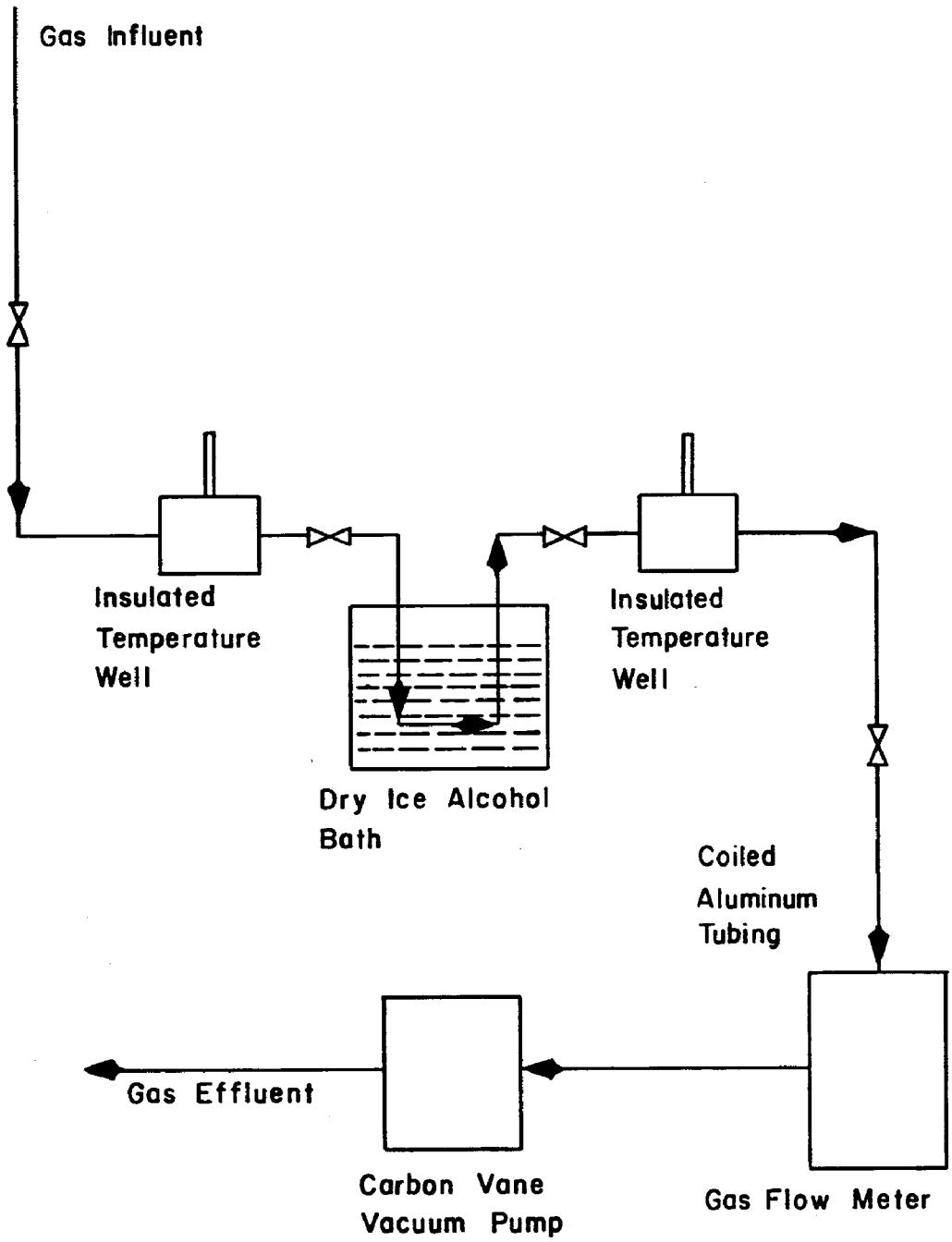


FIGURE 4. Schematic flow diagram of the gas sampling equipment.

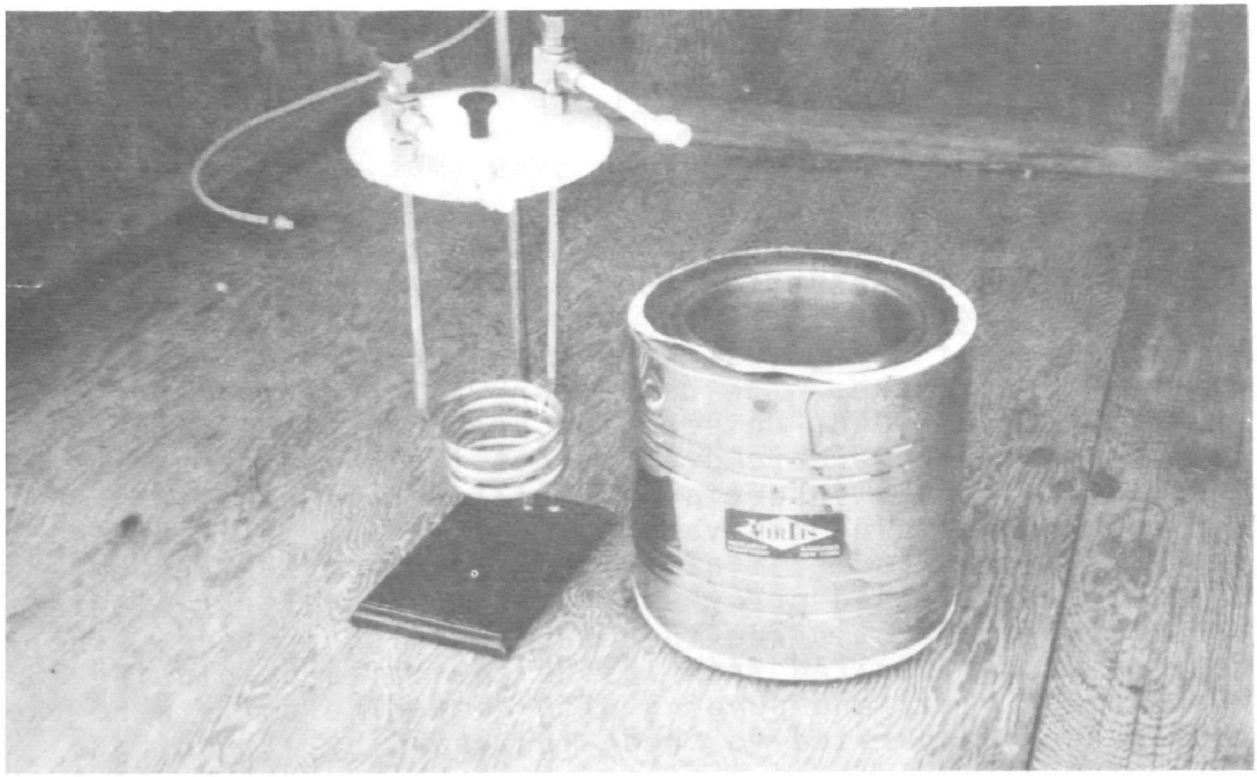


FIGURE 5. Stainless steel condensation trap used in insulated Dewar flask.

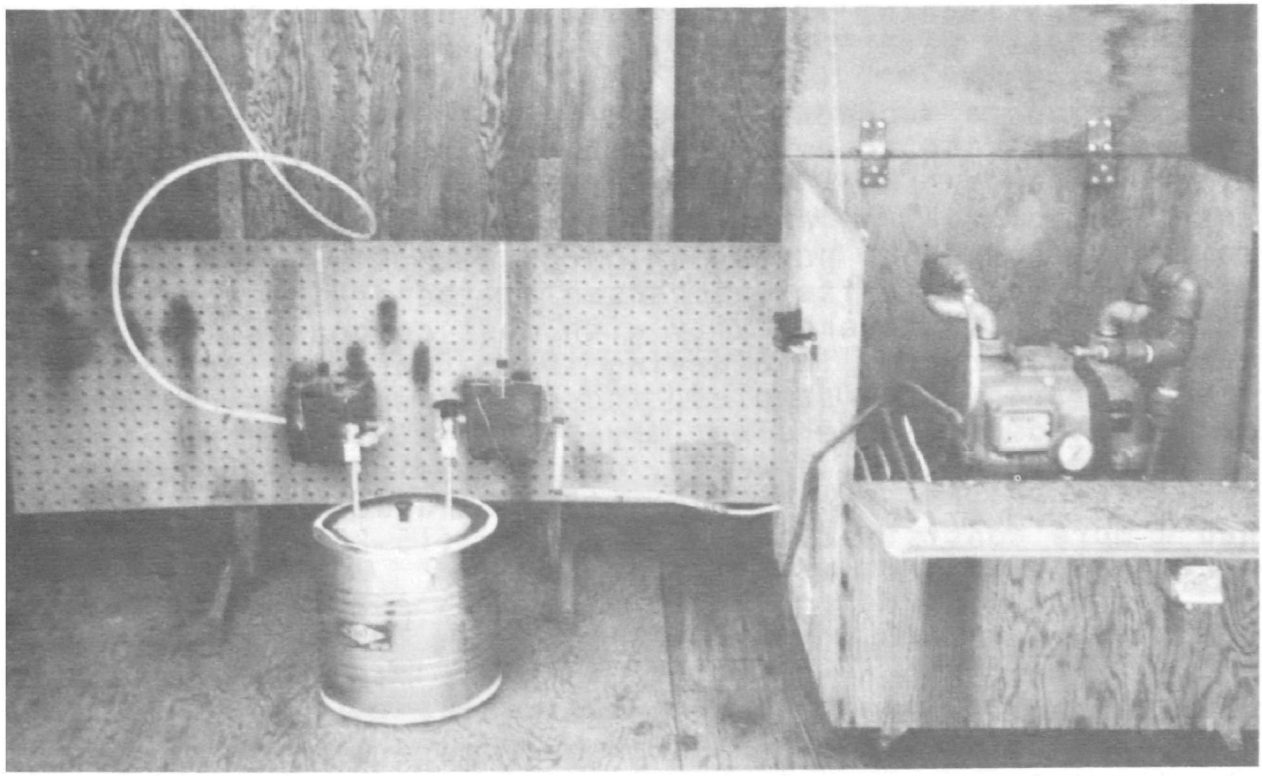


FIGURE 6. Gas sampling train. Gas enters tubing at left and flows through insulated thermometer wells and condensation trap. Flow meter and vacuum pump are on right.

dome were recorded as well as the temperature of the entrance and exit thermometer wells in the sampling train. The sample was transported to the laboratory and warmed slightly using hot water for 15 minutes to facilitate vaporization of the gases. The sample coil was then cooled to room temperature. The condenser was connected to a mercury manometer for determining pressure within the coil. Samples of vapor were removed by putting a rubber septum on the gas condenser, inserting a Hamilton 5-ml gas-tight syringe, and opening the valve. The syringe was flushed several times prior to final withdrawal from the septum. The trap was cleaned prior to another run by first blowing air through the coils and then washing with acetone. The acetone was evaporated from inside the coils by placing them in hot water and purging with air. The coils were then cooled and pressurized to check for leaks by attaching a laboratory air line and sealing while under pressure. A soap solution was applied to detect the presence of any leaks around connections. If no leak was found, the system was left pressurized until the collection of the next sample. During the cleaning process there was from 3.5 to 4.0 ml of condensate water removed from the trap.

A comparison of condensate peaks eluted on a gas chromatograph was made to determine the trapping efficiency of: 1) a vapor sample with water removed prior to entry into the coiled trap and 2) a vapor sample without water removed. Anhydrous potassium carbonate with a few pieces of indicating Drierite was chosen as the drying agent because of its nonreactivity with most compounds.[5] The material was placed in a drying tube ahead (upstream) of the cold trap. The samples, those that were desiccated as well as those that were not dryed, had similar chromatograms. The collection time, however, of the desiccated samples was inconsistent from run to run while the undesiccated samples had a more consistent collection time (15-20 min.) prior to a rise in effluent gas temperature.

Odor Threshold Sampling and Evaluation

Odor threshold levels were determined by following the procedure of ASTM-19.[6] Saran bags were used to collect the vapor samples as shown in Figure 7. Fresh samples were collected daily as indicated previously at the center of the dome by using a Hamilton 1-liter gas-tight syringe and injecting into a Saran bag. The temperature and relative

humidity inside the dome were recorded. All syringes (gas transfer and odor panel) were cleaned in odor free soap, rinsed thoroughly with distilled water, and allowed to dry. Syringes were considered dirty when panel members detected a residual greasy odor inside the syringe even after successive purging with odor free air.

Successive dilutions of the gas sample being evaluated were given to the individual panel members until the threshold odor level was reached. For example, if a panelist required a 0.001 dilution, a master syringe was used to make a 0.01 dilution of the gas and then 10 ml of this was transferred to the panelist's syringe which was then filled with odor free air to the required volume for final dilution. Odor free dilution air was obtained by passing compressed air through a carbon filter equipped with a teflon tube into a collection bottle where syringes could be inserted.

Odor Treatment Techniques

Treatment of odors by air dispersion or simple dilution was evaluated by collecting samples of the dome atmosphere and preparing several dilutions in the laboratory using odor free air. The dilutions were prepared by injecting known volumes of dome atmosphere and odor free air into Saran bags using the techniques described earlier for threshold odor evaluations. These diluted samples were then compared by the odor panel to determine odor intensity.

A system developed to filter out odor constituents using activated carbon as shown in Figure 8. The apparatus consisted of a glass tube that had a quick disconnect on one end connected to the main line of the sampling train. The other end was attached to a 250 ml glass sampling bulb that contained a rubber septum where a syringe could be inserted and treated gas samples removed at selected time intervals. The sampling bulb was hooked to the flow meter and vacuum pump of the main sampling line as shown schematically in Figure 9. A 10-gram sample of 4 to 10 mesh activated carbon was packed into the glass tube and glass wool was used to hold the charcoal firmly inside the tube. [7]

Initially, a sample of untreated gas was collected from inside the dome for an odor threshold level determination using the method described previously for odor sampling.

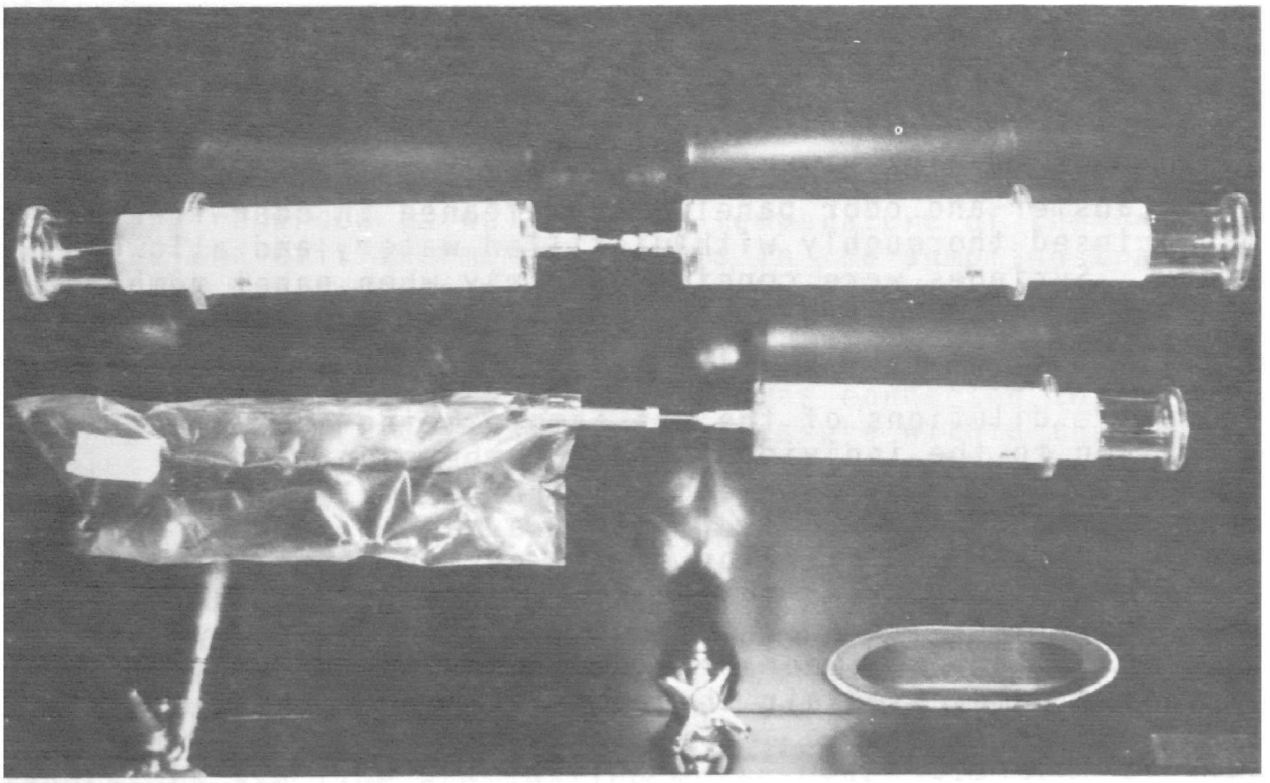


FIGURE 7. Threshold odor testing apparatus with Saran sample bag above and transfer syringes with special adaptor for odor dilution below.

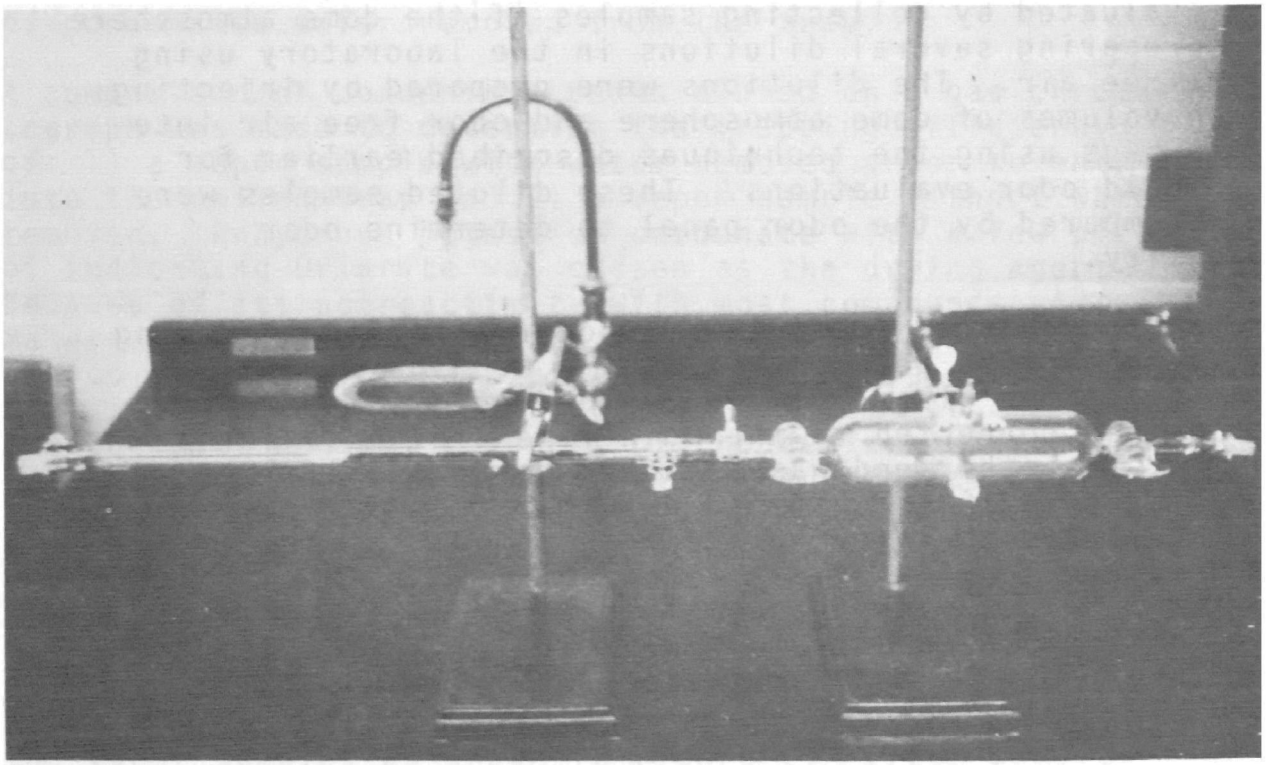


FIGURE 8. Adsorption column and sampling apparatus for activated carbon odor treatment evaluation.

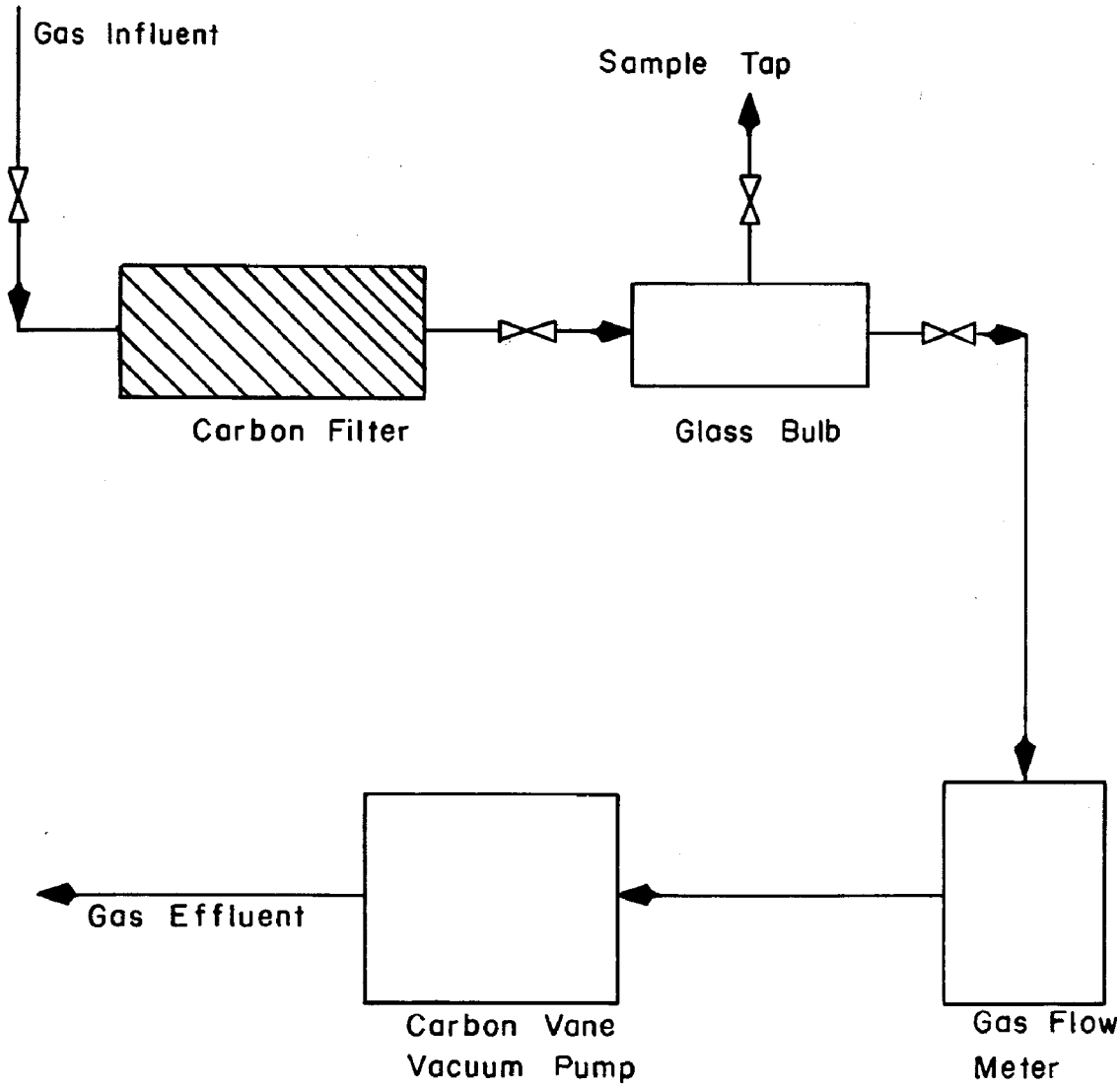


FIGURE 9. Schematic flow diagram for activated carbon treatment evaluation.

The pump was then started and gas allowed to flow through the activated carbon and sampling bulb. At 5 minute intervals (about 10 cu. ft. gas volume) the pump was stopped and a sample of treated gas was collected by inserting the 1-liter syringe into the septum of the sampling bulb and withdrawing a 1-liter sample. The sample was then transferred to a 1-1/3 liter Saran bag. The total volume of gas that had passed through the filter was also recorded and the pumping was continued. A 100ml sample was also withdrawn from the sampling bulb and tested immediately for presence of odor in the treated gas. If odor was noted, the sampling run was terminated since it was considered the carbon had become saturated.

The bag samples for the sampling run were brought back to the laboratory and odor panel members were given successive dilutions from each bag collected following the procedure for odor threshold sampling. At the first sign of an odor breakthrough a threshold odor was determined on that sample. This threshold odor was then compared with the odor threshold from the sample taken at the start of the run from inside the dome.

To determine the effectiveness of chlorine on oxidation of odor components, samples of dome gas were bubbled through distilled water containing a known concentration of chlorine. Figure 10 shows the apparatus used during the chlorine evaluation. Two cylindrical containers were filled with a fixed volume of chlorinated water. A septum in the bottom of the inverted cylinder was used as the port to withdraw a treated sample. The threshold of this treated gas was determined and compared with the threshold level of the untreated gas using odor free air as the diluting component. Both treated and untreated samples were originally collected at the center of the dome.

Inorganic Gas Determinations

Since inorganic gases such as H_2S, O_2, CO_2, N_2, NH_3 and CO cannot be detected by flame-ionization gas chromatography, it was necessary to use Orstat and Tutweiler gas analyzers and other techniques to attempt to identify and quantitate these gases. The Orstat analyzer also detects the organic illuminants, methane and other combustible hydrocarbons and is sensitive down to the

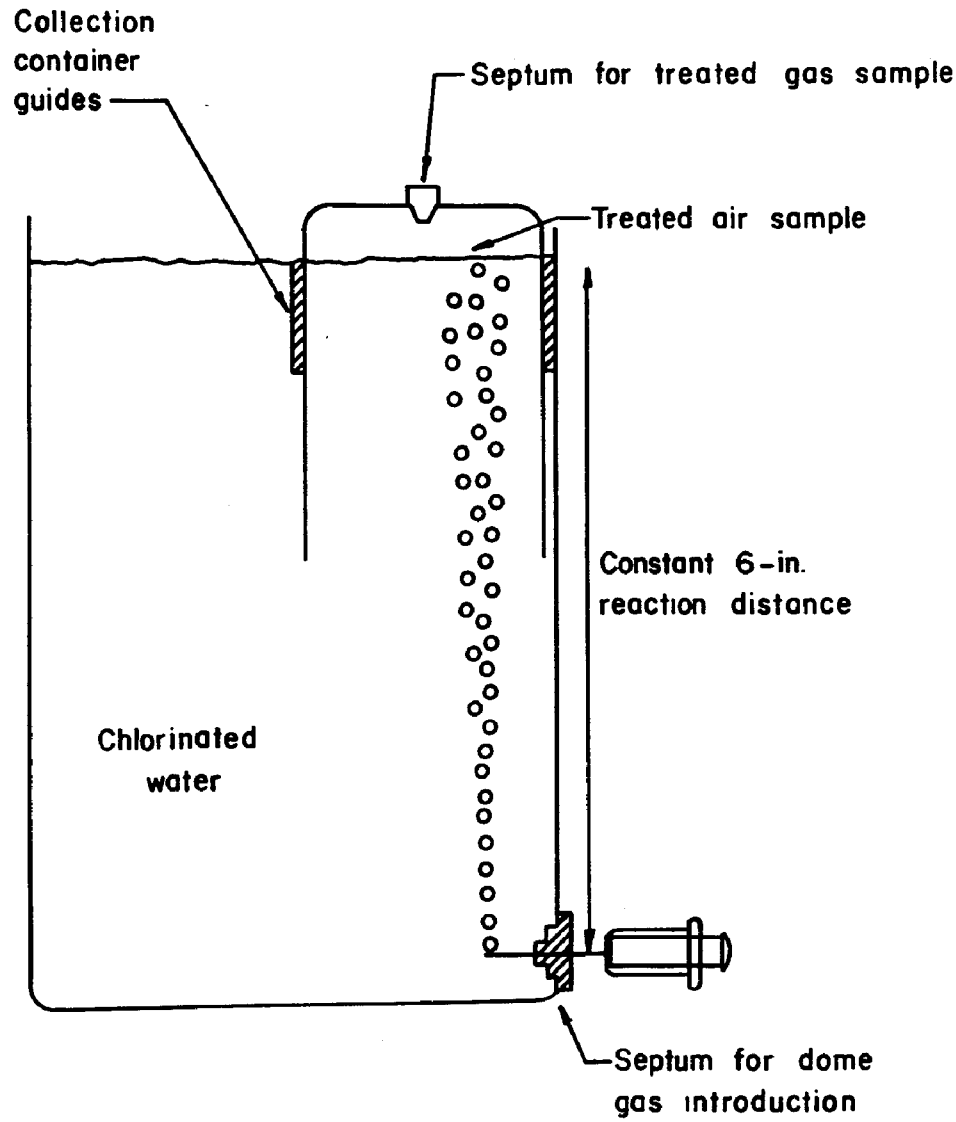


FIGURE 10. Cross section of lab apparatus used for chlorine treatment evaluation.

0.8% level for CO_2, O_2, N_2, CO and methane. Samples were collected in the same manner as other grab samples and brought back to the laboratory for inorganic gas evaluation. Each sample was injected into the two gas analyzers by means of water displacement until a specific volume of gas had entered the collection chamber. Each specific analysis was conducted according to standard procedures.

Initially, qualitative tests for the presence of H_2S and NH_3 were made according to the method of Day, Hansen and Anderson.[8] An open vial of hydrochloric acid inside the dome noticeably fumed white vapors which indicated the presence of NH_3 and/or amines. The darkening of moist lead acetate paper placed inside the dome showed the presence of H_2S gas, which was also indicated by the metal sulfide reaction of copper wire used to fasten the sampling line inside of the dome.

Ammonia was determined by the apparatus shown in Figure 11.[4] An aerator pump placed inside the dome forced vapor first through a 2% boric acid absorption solution and then through a flow meter. After 24 to 48 hours of operation, the pump was disconnected from the absorption bottle and the volume of gas that passed through the solution during that time interval was recorded. The bottle was then sealed and returned to the laboratory. Nessler's reagent was used to determine the concentration of ammonia present in the solution.[9] Dome vapors were allowed to percolate through the absorption solution for a minimum of one day to a maximum of three days. Even after the three day time interval, there was no development of color in the solution upon the addition of the Nessler's reagent. There was, however, a clouding of the solution which indicated that aldehydes and/or amines had been absorbed. Because of the lack of sensitivity of the methods utilized for quantitative analysis of inorganic odor causing gases present within the dome, more effort in this area was considered unjustified. The inorganic odorous gases such as H_2S and NH_3 obviously were not major contributors to odors emitted by the thickening sludge.

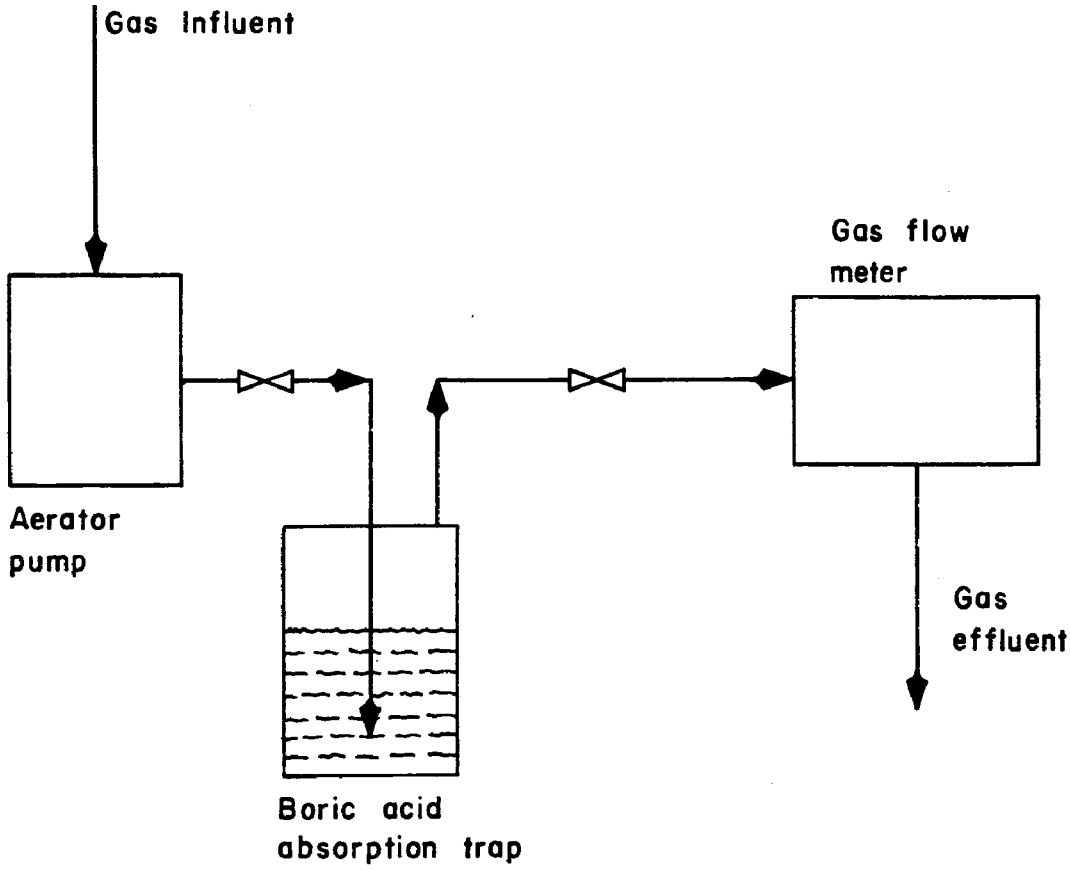


FIGURE II. Schematic flow diagram of the ammonia absorption equipment.

DESCRIPTION OF LABORATORY EQUIPMENT AND PROCEDURES

Gas Chromatograph Column Selection

A Beckman GC-4 gas chromatograph, equipped with a dual-flame ionization detector, was the major instrument used in the laboratory for analysis of dome gas samples.

A 10-ft. x 0.125-in. o.d. stainless steel column with 10% SE-30 on 100 to 120 mesh Chromosorb G was the column chosen to identify indole, skatole, amines, and sulfur compounds that might be present in the dome atmosphere. (2,4,10,11) For the analysis of organic acids a 10-ft. x 0.125-in. o.d. stainless steel column packed with 18% Carbowax 20M + 2% H_3PO_4 on 60 to 80 mesh C-22 Firebrick was selected.(2,12) The alcohols and carbonyls if present could be detected by using a 5-ft. x 0.125-in. o.d., stainless steel, 100 to 120 mesh, Porapak Q, P, or QS column although the other columns could also be used in identification of these and sulfur compounds.(2,13) All columns were purchased with the above specifications from the Beckman Company.

The Carbowax column was conditioned according to the procedure of Andrews, Thomas, and Pearson(12) at a helium flow rate of 25 ml/min and a column temperature of 185°C for 4 hours. A conditioning solution of 0.05 M propionic and acetic acids was prepared of which 10-µl samples were injected at ten minute intervals for 2 hours into the column using a Hamilton syringe. The SE-30 column was conditioned at 250°C overnight without any helium flow. Further conditioning was necessary at a column temperature of 230°C and a helium flow rate of 40 ml/min for 2 hours.(14) The individual Porapak columns were conditioned at a column temperature of 230°C and a helium flow rate of 50 ml/min for 4 hours.(15)

Selected Column Evaluation Using Standards

To determine whether compounds that might be present in the dome environment would separate and elute on selected columns, a series of liquid and vaporous standards were prepared for injection into the columns. A column comparison of such standards would also enable determination of the optimum temperatures at which the columns would give maximum separation without excessive elution time. The following standard compounds were injected at various temperatures on the selected columns: acetone, propionic

and butyric acids, diethylsulfide, butyl- and ethyl-amines, isopropanol, and diacetyl.

The sample size used for the liquids was between 0.1 and 1-μl. The procedure followed was to increase the injected sample size until peak elution was noted. The lowest sample size was then injected to ascertain whether this quantity gave a detectable response. The different size sample injections were selected to condition the column so no adsorption of these types of compounds whether from standards or dome samples would take place on the column. All standard injections were made with a Hamilton 1-μl sampling syringe.

The compounds used for the column evaluation and for the comparison of standard retention times with dome components were purchased as kits from the Polyscience Company. The SE-30 column eluted symmetrical peaks for amines, ketones, alcohols, and sulfur compounds without any tailing. However, organic acids tailed on this column. There was tailing of the organic acids on the Porapak P and QS columns at three column oven temperatures. Other materials were eluted in a short time. Both the Carbowax 20M and Porapak Q columns eluted the standard compounds at the selected oven temperatures except for amines which were held up on the Carbowax 20M column. The elution time of the standards on the various columns at selected temperatures are shown in Table 1.

After column response and retention time of the individual standards were determined, a mixture of isopropanol, acetone, diacetyl, butylamine, and propionic acid was prepared by injecting a 1-μl sample of each of these standards into a 125-ml glass container fitted with a rubber septum. The bottle was placed in water at 65°C to hasten the vaporization of the volatile materials. A portion (1-ml) of the vaporized mixture was then withdrawn and injected into the column with a Hamilton 5-ml gas-tight syringe. The mixture for the Carbowax 20M column did not contain the amine nor the diketone but contained instead butyric acid. The mixture for the SE-30 column did not contain the propionic acid. The purpose of injecting the standard mixture was to determine whether the columns would separate these compounds in mixed vapor form.

The SE-30 column separated the mixture at a temperature of 97°C. The mixture of acetone, isopropanol, and propionic and butyric acids was separated on the Carbowax

TABLE 1

RETENTION TIME OF SELECTED STANDARDS USING VARIOUS COLUMNS

Column	Temp (°C)	Acetone (min)	Propionic Acid (min)	Butyric Acid (min)	Diethyl-sulfide (min)	Isopro-panol (min)	Butyl-amine (min)	Diacetyl (min)	Ethyl-amine (min)
Carbowax 20M	124	.4	1.2	1.5	---	---	NR	---	NR
"	90	---	5.6	8.8	---	---	---	---	---
"	70	1.2	16.9	30.1	1.57	2.4	---	---	---
Porapak QS	166	2.8	9.0	T	---	2.9	9.8	---	---
"	150	3.6	14.4	---	16.0	4.6	15.1	8.8	---
"	143	---	14.8	---	---	4.7	---	9.9	---
Porapak P	170	2.0	---	T	---	2.1	---	---	---
"	166	2.3	7.2	---	8.7	2.1	6.2	4.4	1.8
"	152	3.1	9.6	---	---	2.7	9.8	6.6	---
Porapak Q	170	4.2	17.5	41.0	8.6	4.2	8.8	8.9	1.6
"	148	6.7	40.5	---	---	7.7	14.2	16.1	2.4
SE-30	97	1.9	T	T	4.2	4.2	1.8	3.5	---

Notes: NR = no response from the compound.
T = tailing of the component.

20M column at an oven temperature of 70°C. At temperatures of 166°C and 150°C the Porapak P column would not separate the mixture into separate components and it only eluted two peaks in both cases. The mixture on the Porapak QS column at a temperature of 150°C tailed considerably and could not be separated. The Porapak Q column did not resolve the acetone, isopropanol, butylamine, and diacetyl at 170°C, but the mixture was totally resolved at a column temperature of 148°C. Tailing was the major cause of poor separation on the columns that would not resolve the mixture. Helium flows were maintained at 30 ml/min.

While the column evaluation with selected standards was being conducted, periodic injections of dome grab and condensate samples were made. Oven temperatures used were those that gave the best separation of the standards. The average peak retention times recorded for 5 ml vapor sample injections are presented in Table 2. Observations made from these results were: 1) that the Carbowax and SE-30 columns separated the many peaks of the condensate sample at a much lower oven temperature than the Porapak columns and 2) that the bag (grab) sample did not have a sufficient concentration of organic vapors for detection upon elution from the Carbowax and SE-30 columns. The Porapak columns did not resolve the condensate sample at either a high or low oven temperature. This suggests that the components were either being held on the columns or that the compounds were all eluting at the same time from the column. Further experimentation with these columns at different oven temperatures did not remedy the situation. All aforementioned preliminary work was conducted at a helium flow rate of 30 ml/min.

The decision was made to utilize the Carbowax 20M and SE-30 columns primarily with Porapak Q as a backup for detailed chromatographic identification since good standard separation was achieved by this column. The volume of dome vapor sample selected for injection into the gas chromatograph throughout the study was 5 ml. The temperatures of the SE-30 and Carbowax 20M columns chosen were 90°C and 55°C, respectively. Other column oven temperatures were necessary, however, for Carbowax 20M (75° and 90°C) and SE-30 (110° and 130°C) for the acid and the indole analyses.

TABLE 2

PEAK ELUTIONS (MINUTES) OBSERVED FOR BAG AND CONDENSATE SAMPLES USING DESIGNATED COLUMNS AND TEMPERATURES

SE-30 @97°C (Bag)	SE-30 @97°C (Condensate)	Carbowax 20M@ 70°C (Bag)	Carbowax 20M@ 70°C (Condensate)	Porapak QS @143°C (Bag)	Porapak QS @143°C (Condensate)	Porapak P @152°C (Bag)	Porapak P @152°C (Condensate)	Porapak Q @148°C (Bag)	Porapak Q @148°C (Condensate)
.8	.8	.7	.8	.2	.4	.1	.2	.2	.4
1.3	1.1	.9	1.0	.7	.8	.6	.6	.6	.7
1.9	1.2	1.1	1.1	7.7	2.4	1.2	1.3	1.1	1.3
2.6	1.2	2.9	1.3	16.6	3.9		2.6	2.3	2.4
8.4	1.5	6.2	1.9	24.8	15.9		7.8	4.8	3.8
	1.6	14.1	2.1						7.6
	2.6		2.6						25.5
	8.4		2.8						
	3.6		3.6						
	4.2		3.9						
	6.3		4.4						
	7.8		4.8						
	10.0		5.2						
	10.9		5.8						
	11.5		6.4						
	13.3		7.5						
	14.2		8.4						
	16.0		9.3						
	16.9		10.4						
	17.8		11.1						
	19.1		12.6						
	20.1		13.5						
	21.2		14.4						
	22.4		15.7						
	23.5		16.3						
	24.6		17.1						
	26.7		17.7						
	29.3		18.7						
	31.4		19.8						
	34.8		21.1						
	38.6		22.0						
	40.8		24.0						
			25.6						
			26.9						
			29.4						
			32.0						
			33.8						
			36.9						
			40.1						

Chromatogram Comparison Procedure

Sampling by the bag method as previously mentioned failed to concentrate the dome components in sufficient quantity for detector response. The chromatograms reproduced in Figure 12 show the elution of a number of peaks from a condensate sample while that of a grab sample collected the same day does not elute peaks even at a relatively low attenuation. The initial peak on both the grab and condensate chromatograms on the Carbowax 20M and SE-30 columns at 55°C and 90°C is due to the presence of methane inside of the dome. The retention time (0.7 minutes) of this peak and that of a methane gas standard were similar on both columns. The retention time of methane was subtracted from each of the retention times of the various eluted peaks to compute the adjusted retention time for each component. Methane was injected with the standards to also compute their adjusted retention times.

The major portion of the chromatographic evaluation of the dome vapors was performed with condensate samples whose chromatograms were compared to standards run on the same day as the sample was collected. It was noted that a standard of diallylsulfide injected on the Carbowax 20M column and a standard of diisobutylamine injected on the SE-30 column consistently eluted at the same time as peaks that were distinguishable and well separated on chromatograms of dome samples injected on both columns. These peaks were therefore used as internal standards on the dome sample chromatograms, and a sample of either diallylsulfide or diisobutylamine was injected as an internal standard with each known compound. These internal standards were not utilized with the condensate samples because of the risk of addition of extraneous peaks from impurities and possible masking of the large number of peaks eluted from the condensate.

Column Temperature Effects

A column temperature was selected for each column which would enable the complete resolution of the condensate peaks without excessively long retention times. Condensate samples were injected into the chromatographic columns at several column oven temperatures, and printouts of the corresponding peak separations were compared. Carbowax 20M at an oven temperature of 55°C proved to be the column packing that gave maximum separation of the

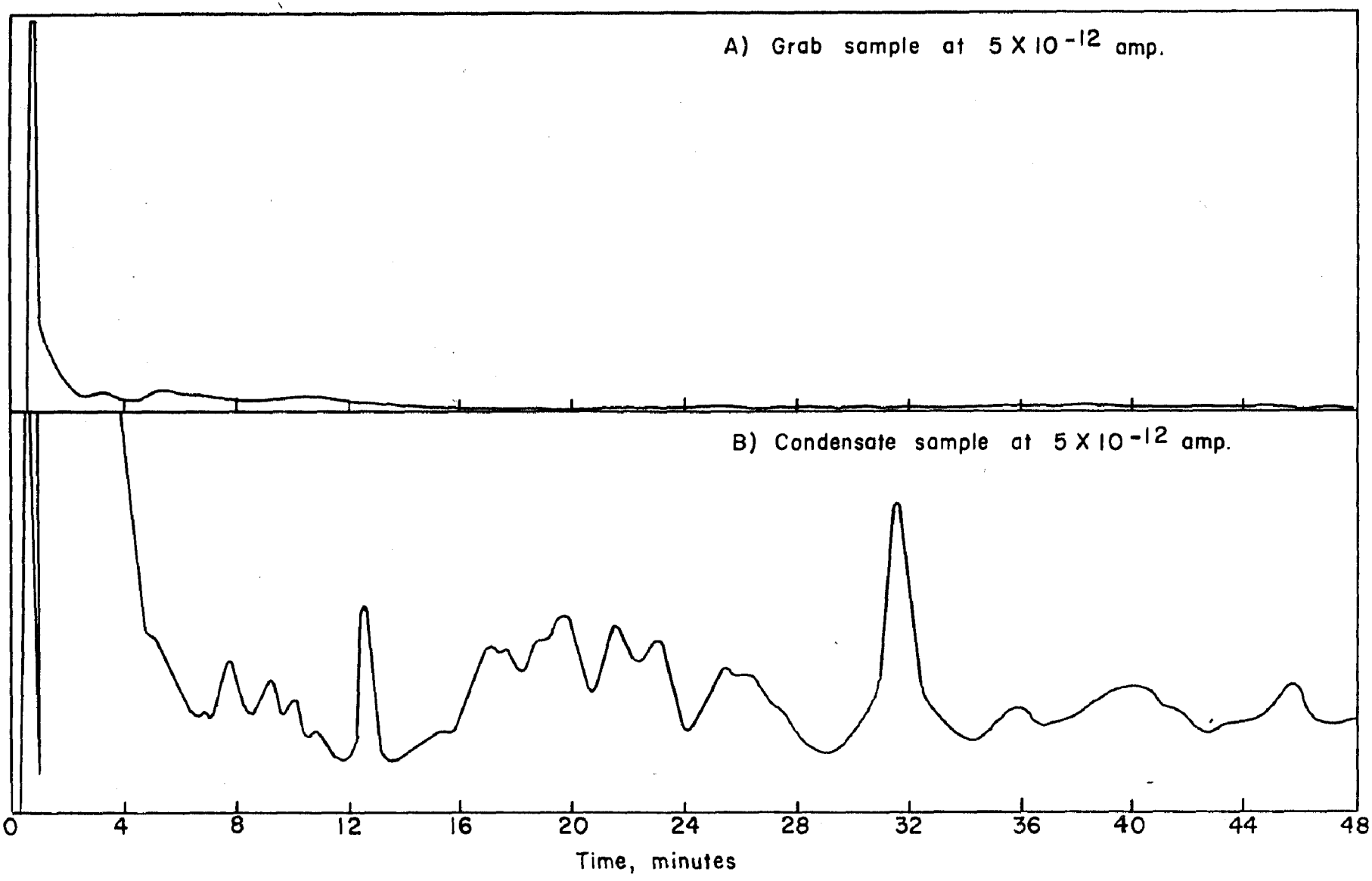


FIGURE 12. Chromatographic separations of a dome-gas grab and condensate sample from the same day. Conditions: 10-ft X 1/8-in stainless steel column, 18% Carbowax 20M + 2% H_3PO_4 on 20- to 50-mesh C-22 Firebrick at 57°C with 5.0-ml volume samples.

condensate sample into its individual peaks. The column oven temperatures and the resulting chromatograms shown in Figure 13 were used initially during the Carbowax 20M column evaluation. Temperatures below that of 55°C failed to yield well defined elution peaks. As indicated in Figure 13 (A) the peaks were resolved and had a symmetrical shape, however, sufficient separation between the peaks was not achieved. Figure 13 (B) and (C) show the effects of a twenty degree increase of the column temperature on peak elution and separation. The peaks tended to merge together at 75°C and 90°C and eluted within a very short retention time.

Vaporized standards were also injected on the column at these various oven temperatures in order to determine the effect of temperature on peak elution and geometry of these reference compounds. Indications were that the optimum oven temperature was 55°C for comparison of the reference compounds with the components of the dome condensate mixture.

The organic acid standards presented a special problem. At the lowest oven temperature, they tended to tail and have excessively long retention times. Many of these organic acid standards and some condensate materials (14 in number) had retention times greater than the 48 minute limit of Figure 13 (A). This fact along with the excessive retention times of the acids at the low oven temperature made it necessary to utilize the higher oven temperatures when comparing condensate compounds with organic acid reference compounds on the Carbowax 20M column. The returning and stabilization of the recorder zero to baseline after elution of the condensate peaks shown in Figure 13 (B) and (C) indicated that all the major components in the dome vapor had been eluted within the selected time interval. At the higher oven temperature there was no further elution of new peaks that might have been held on the column.

Peaks were not eluted from the SE-30 column at the 55°C temperature utilized for evaluation of the Carbowax 20M Column. Figure 14 (A) shows the results of an injection of a condensate sample on the SE-30 column at the oven temperature of 55°C. The retention of most condensate compounds at the low oven temperature made it impossible to operate the gas chromatograph as a dual-flame ionization system with the Carbowax 20M column hooked to

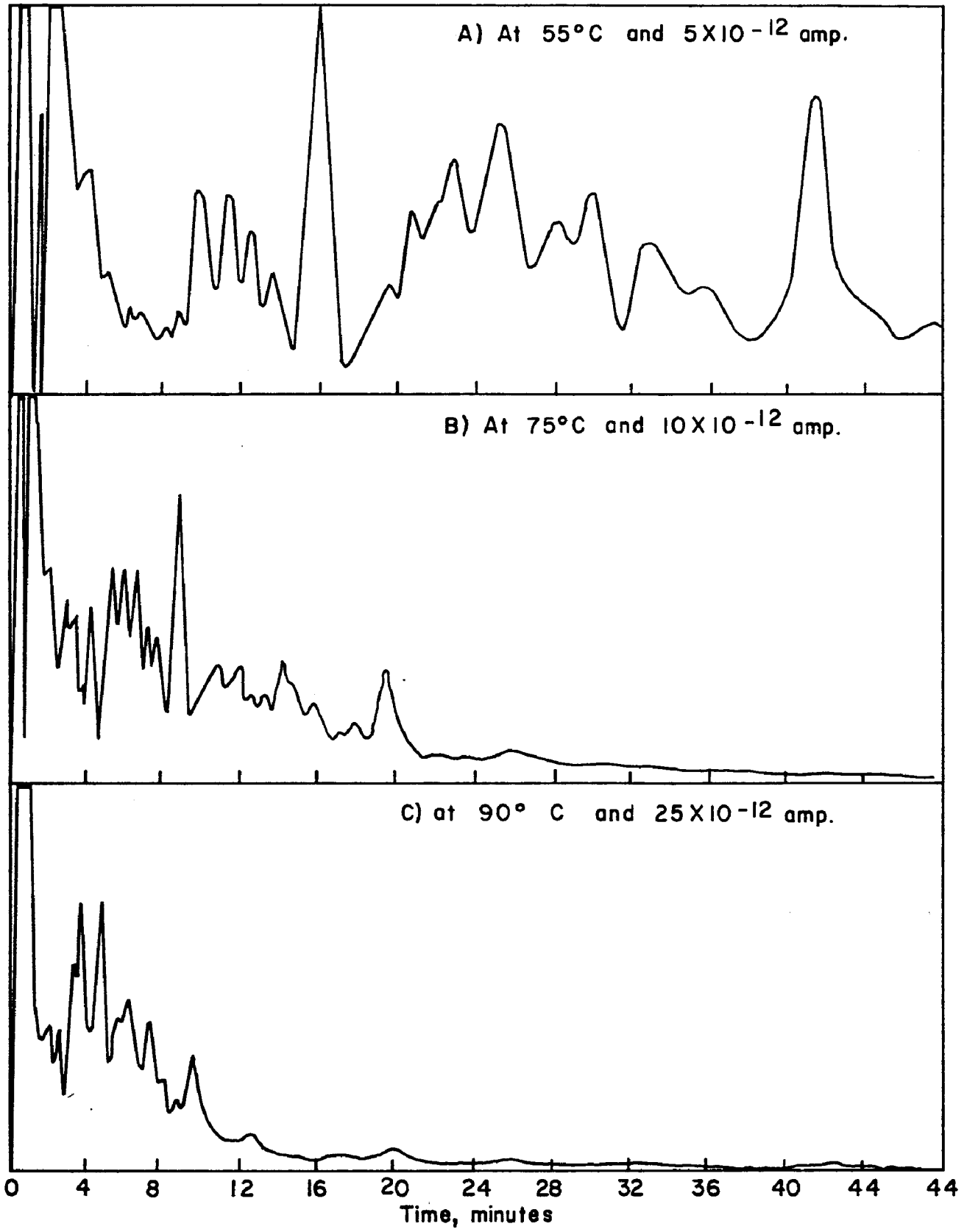


FIGURE 13. Chromatographic separations of dome-gas condensate samples on Carbowax 20M at various temperatures. Conditions: 10-ft. X 1/8-in. stainless steel column, 18% Carbowax 20M + 2% H_3PO_4 on 30- to 50-mesh C-22 Firebrick with 5.0-ml. sample volumes.

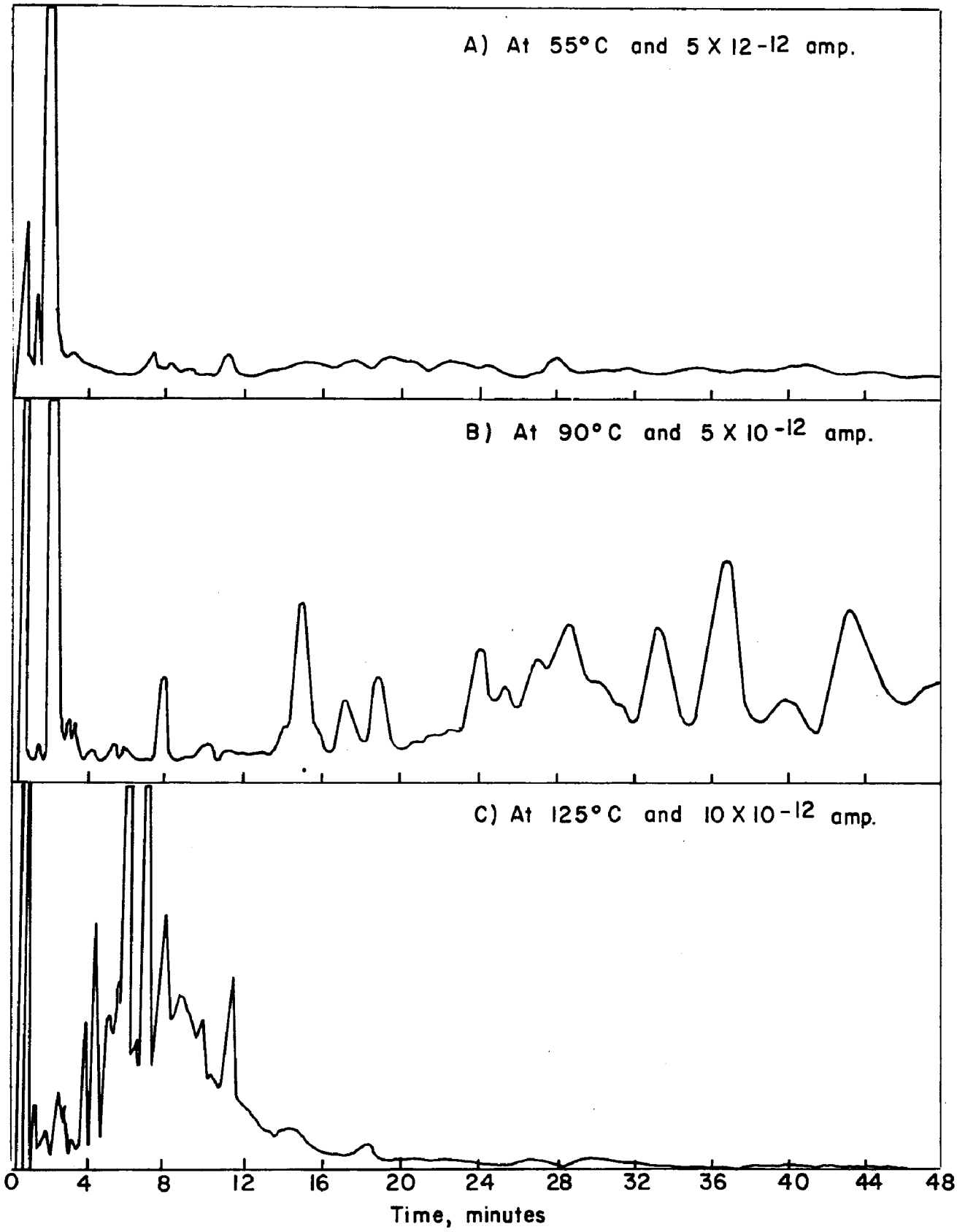


FIGURE 14. Chromatographic separations of dome - gas condensate samples on SE - 30 at various temperatures. Conditions: 10 - ft X 1/8 - in stainless steel column, 10% SE - 30 on 100 - to 120 - mesh Chromosorb G with 5.0 - ml sample volumes.

one detector and the SE-30 column hooked to the other detector. An injection of a specific condensate sample could not be made on both liquid columns in one day, however, since there was insufficient time during the day to change the oven temperature and rerun the sample. It was therefore decided to analyze the condensate mixture on the SE-30 column after several days of evaluating samples on the Carbowax 20M column. The oven temperature of 55°C utilized initially with the SE-30 column was near the minimum temperature limit of the substrate material.[16] This temperature probably did not make the material fluid enough on the support phase to permit an adequate separation and diffusion of the dome materials through it. A further temperature increase to 90°C (Figure 14 (B)) caused elution of the components of the condensate sample as shown by the resolution and symmetrical peaks. A further increase of the oven temperature (Figure 14 (C)) produced merged peaks at a reduced retention time. The temperature of 125°C however, did present a stable baseline which indicated that there were no additional materials retained on the column.

The standards also failed to elute with reasonable retention times from the SE-30 column at a temperature of 55°C. The temperature of 125°C also ran the standards together, so their retention times could not be determined. The relative retention times of the standard reference compounds and condensate samples were compared on both the Carbowax 20M and SE-30 columns at the optimum separation temperature of 55°C and 90°C, respectively. A column helium flow rate of 30 ml/min was used throughout the study with a hydrogen flow rate of 30 ml/min and an air flow rate of 300 ml/min.

Porapak Q when used presented a special problem because of the nature of the column material. The column packing is not a liquid substrate coated on a solid support as is the Carbowax 20M and SE-30 columns. The media is actually a solid material that is able to separate organic materials because of the special properties and structure of the porous polymer beads used as packing material. Such column material necessitates the injection of organic mixtures at higher temperatures than are generally used with liquid columns in order to elute the organic components within a reasonable time.

Since the Porapak Q column was able to separate a mixture of standard reference compounds as mentioned in a previous section, condensate samples were injected at various oven temperatures to determine the effects of temperature upon peak separation and elution. As shown in Figure 15 (C) the lower oven temperature of 60°C did not elute any peaks from the condensate sample injections as did the Carbowax 20M column at this temperature. The column temperature was therefore increased. As is indicated in Figure 15 (B) and (C) more peaks were eluted at the higher temperatures, but the column performance never did match that of the Carbowax 20M and SE-30 columns. The Porapak Q at the higher temperatures was either retaining the compounds or failing to resolve the individual components into their respective peaks by allowing elution of many of the peaks at one time. The oven temperature could not be increased above 200°C because the pressure drop became too great across the column and the pressure regulator at its maximum capacity could not maintain a column helium flow rate of 30 ml/min. Due to the high oven temperature necessary to elute peaks using Porapak Q column material and the poor separation of these peaks at such temperatures, the column was not used in subsequent evaluation of the dome condensate compounds.

Infrared Analyses

A Beckman IR-10 spectrophotometer and a Beckman 10-meter gas cell were also used for odor component identification. The 10-meter gas cell was used to analyze the vapors collected by both grab and condensate sampling methods. Both condensate and bag samples were scanned using the cell's 10-meter pathlength. Attenuation was necessary at times to adjust printout of some minimal absorption bands detected. Results obtained were not encouraging and more detailed infrared analysis was considered impractical.

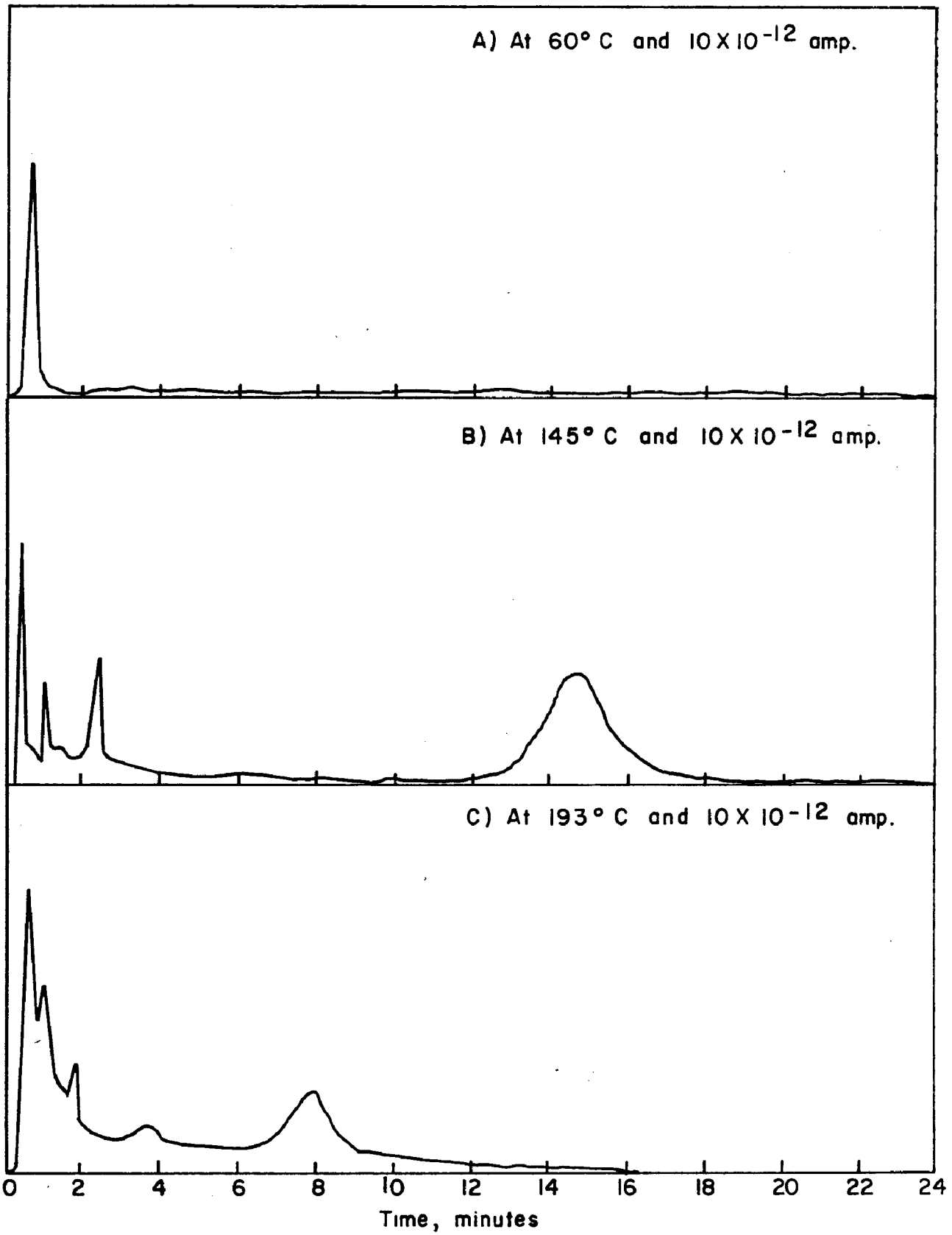


FIGURE 15. Chromatographic separations of dome - gas condensate samples on Porapak Q at various temperatures. Conditions: 5-ft. X 1/8-in. stainless steel column, 100 - to 120 - mesh packing and 5.0 - ml samples.

RESULTS OF ODOR IDENTIFICATION STUDY

Relative Retention Time Determinations

A total of 25 condensate samples were collected between the months of April through July, 1971. Fourteen condensate samples were run on the Carbowax 20M column and 11 were run on the SE-30 column utilizing the procedures described previously. Tables 3 and 4 present relative retention times of those peaks separated on the Carbowax 20M and the SE-30 columns for all sampling days. Certain peaks were always present in the condensate sample while others appeared only occasionally. Typical separations on the Carbowax 20M and SE-30 columns of some of the numbered peaks in Tables 3 and 4 are shown in Figures 16 and 17. These chromatograms represent those condensate samples that were run at the optimum separation temperature on both columns, i.e., 55°C on Carbowax 20M and 90°C on SE-30. Peak number 12 on Figure 16 and peak number 23 on Figure 17 had retention times similar to the laboratory standards of diallylsulfide and diisobutylamine, respectively. Since these peaks were always easily distinguishable and well separated on the daily chromatograms from the condensate samples, as stated previously, they were made the reference compounds in the condensate mixture for the basis of relative retention time calculations.

From the reproductions of the chromatograms (Figures 16 and 17) it is noted that some peak numbers present in Tables 3 and 4 are absent. These missing peaks appeared only on certain sampling occasions as trace components or they were not well resolved on most sampling days.

When the relative retention times of standards that were eluted on both columns were compared with the relative retention times of the condensate peaks under similar chromatographic conditions, a number of the standard and condensate peaks eluted at the same time.

The relative retention times of both the standards and numbered condensate peaks are compared in Table 5. The compounds whose retention times on both columns matched with laboratory standards are as follows:

TABLE 3

RELATIVE RETENTION TIMES OF DOME COMPOUNDS ON CARBOWAX 20M AT 55°C

Month Day	PEAK NUMBER DESIGNATION																										
	1	2	3	4	5	6	7	8	9	10	11	12*	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
4-6	.03	.06	.11	.26	.31		.52			.78	.86	1.00	1.15		1.45				2.06		2.31	2.59	2.78			3.18	3.85
4-7		.06	.10	.26	.32	.41	.52		.70	.76	.84	1.00	1.11	1.20	1.42	1.77	1.88	1.99	2.06		2.28	2.52	2.72	2.96	3.11	3.30	3.75
4-8		.06	.11		.32	.42	.53		.68	.77	.85	1.00	1.10	1.19	1.41	1.75	1.86		2.03		2.24	2.51	2.69	2.90	3.05	3.23	3.68
4-13	.03	.08	.12	.27	.32					.76	.82	1.00	1.12	1.23	1.41			1.96			2.21	2.50	2.70		3.12		3.71
4-15	.03	.07	.12	.26	.31	.42	.53			.75	.84	1.00	1.10	1.19	1.40	1.72	1.88	1.94		2.18	2.26	2.48	2.68		3.04	3.18	3.78
4-16	.03	.07	.12		.31	.43	.54			.76	.85	1.00	1.11	1.19	1.41	1.74	1.86	1.94		2.17	2.24	2.48	2.65	2.90		3.16	3.70
4-19		.07	.12		.31	.41	.52		.69	.74	.84	1.00	1.10	1.18	1.40		1.84	1.94	2.02	2.17	2.24	2.48	2.68	2.93		3.22	3.68
4-20		.08					.51		.70	.74	.84	1.00	1.10	1.19	1.41	1.72	1.84	1.97	2.06	2.14	2.30	2.52	2.74	2.84	3.00	3.28	3.81
4-21		.07				.41				.74	.84	1.00	1.10	1.18	1.40	1.74	1.87	1.94	2.01		2.24	2.46	2.65	2.89		3.17	3.65
4-27		.08						.60		.75	.87	1.00	1.12	1.22	1.43	1.77	1.90	1.98	2.06		2.28	2.52	2.72	2.95	3.10	3.23	3.72
4-30	.03	.08	.10			.42	.53	.59	.70	.76	.84	1.00	1.11	1.20	1.41	1.76	1.86	1.95	2.02	2.17	2.25	2.48	2.67	2.95		3.19	3.68
5-4		.07	.11	.26	.30	.46	.53			.74	.83	1.00	1.09	1.17	1.39	1.72	1.89	1.98		2.10	2.20	2.40					3.68
5-5		.08	.10		.31	.42	.50		.71	.75	.84	1.00	1.10	1.20	1.41	1.75	1.85	1.93	2.02	2.12	2.24	2.46	2.67	2.94			3.67
5-12		.06	.10		.30	.41	.52	.57	.70	.76	.85	1.00	1.10	1.20	1.42	1.78	1.89	2.00	2.08		2.30	2.57	2.78		3.02	3.28	3.82
AVE.	.03	.07	.11	.26	.31	.42	.52	.58	.69	.75	.84	1.00	1.10	1.19	1.41	1.74	1.87	1.96	2.04	2.15	2.26	2.50	2.70	2.92	3.06	3.22	3.73

* Peak No. 12 (Diallylsulfide) internal standard.

TABLE 4

RELATIVE RETENTION TIMES OF DOME COMPOUNDS ON SE-30 AT 90°C

Month Day	PEAK NUMBER DESIGNATION																			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
5-14	.04	.06		.08		.16	.19	.25	.32		.35	.41	.46	.50	.54	.61	.64	.68	.73	.79
5-18	.03	.05		.09	.11	.16	.18	.24	.32				.46	.50		.58		.67		.79
5-19		.05		.09		.15	.19	.24	.32				.45	.49				.67	.72	
5-20		.05		.09		.16	.19	.25	.31	.34			.46	.50		.60			.73	
5-25	.04	.05		.09		.16	.19	.25	.32		.36		.46	.50		.60		.68	.74	
5-26	.04	.05		.08		.16	.19	.25	.31	.33	.35		.46	.50		.61	.64	.68	.74	
6-1	.03	.05		.09	.11	.16	.19	.25		.33				.50		.60		.68	.74	
6-2	.04	.05		.09		.16	.18	.25		.33		.38	.45	.50		.60		.67	.74	
6-4	.03	.05		.09		.16	.18	.26		.33	.35			.50		.61		.68	.73	
6-8	.04		.07			.15	.19	.26	.30	.33			.45	.50		.61		.68		.78
6-16	.03	.05	.07	.09		.15	.19	.25	.32		.35			.50		.60		.68		.79
AVE.	.04	.05	.07	.09	.11	.16	.19	.25	.31	.33	.35	.39	.46	.50	.54	.60	.64	.68	.73	.79

Table IV (Cont'd on next page).

TABLE 4 (continued)

RELATIVE RETENTION TIMES OF DOME COMPOUNDS ON SE-30 AT 90°C

Month Day	PEAK NUMBER DESIGNATION																			
	21	22	23*	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
5-14	.84	.95	1.00	1.06	1.17	1.28	1.40	1.47	1.52	1.64	1.73	1.85	1.97	2.08	2.16	2.28	2.54	2.75	2.97	3.32
5-18		.94	1.00	1.06	1.17	1.28		1.47	1.52	1.63	1.74	1.86	1.98	2.09		2.28	2.53	2.80	2.99	3.32
5-19			1.00		1.16	1.27				1.62										
5-20	.84	.96	1.00	1.06	1.17	1.28	1.39		1.52	1.63	1.73	1.88	1.98	2.08		2.28	2.53		2.98	3.32
5-25	.86	.95	1.00	1.05	1.16	1.28		1.48	1.58	1.64	1.73	1.86	1.98	2.08		2.28	2.53	2.76	2.98	3.32
5-26	.85	.94	1.00	1.06	1.17	1.28	1.40	1.46	1.54	1.65	1.74	1.85	1.98	2.08		2.29	2.54	2.76	2.99	3.34
6-1		.94	1.00		1.18	1.30				1.66	1.75	1.86	1.99			2.30	2.55		3.01	
6-2	.84	.95	1.00	1.05	1.17	1.28	1.40	1.47	1.53	1.64	1.74	1.86	1.98	2.08		2.29	2.54	2.76	3.00	3.34
6-4	.84	.94	1.00	1.04	1.17	1.28	1.36	1.46		1.63	1.73	1.85	1.98		2.16	2.27	2.52		3.09	3.31
6-8		.94	1.00	1.06	1.17	1.28	1.37	1.46	1.53	1.65	1.74	1.85	1.98		2.16	2.29	2.55	2.74	2.99	3.34
6-16	.85	.94	1.00	1.06	1.17	1.28	1.40		1.53	1.64	1.74	1.87	1.98	2.08		2.29	2.54	2.78	3.07	3.34
AVE.	.84	.94	1.00	1.05	1.17	1.28	1.39	1.47	1.53	1.64	1.74	1.86	1.98	2.08	2.16	2.28	2.54	2.76	3.01	3.33

* Peak No. 23 (Diisobutylamine) internal standard.

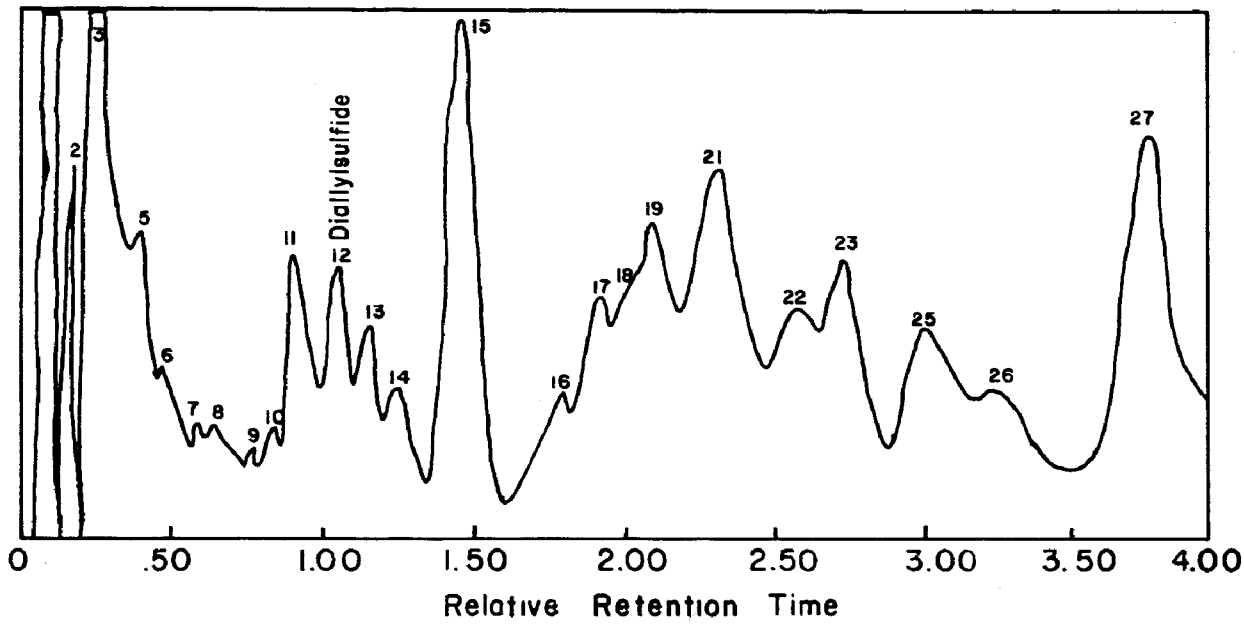


FIGURE 16. Relative retention time of dome compounds on Carbowax 20M at 55° C and 5×10^{-12} amp.

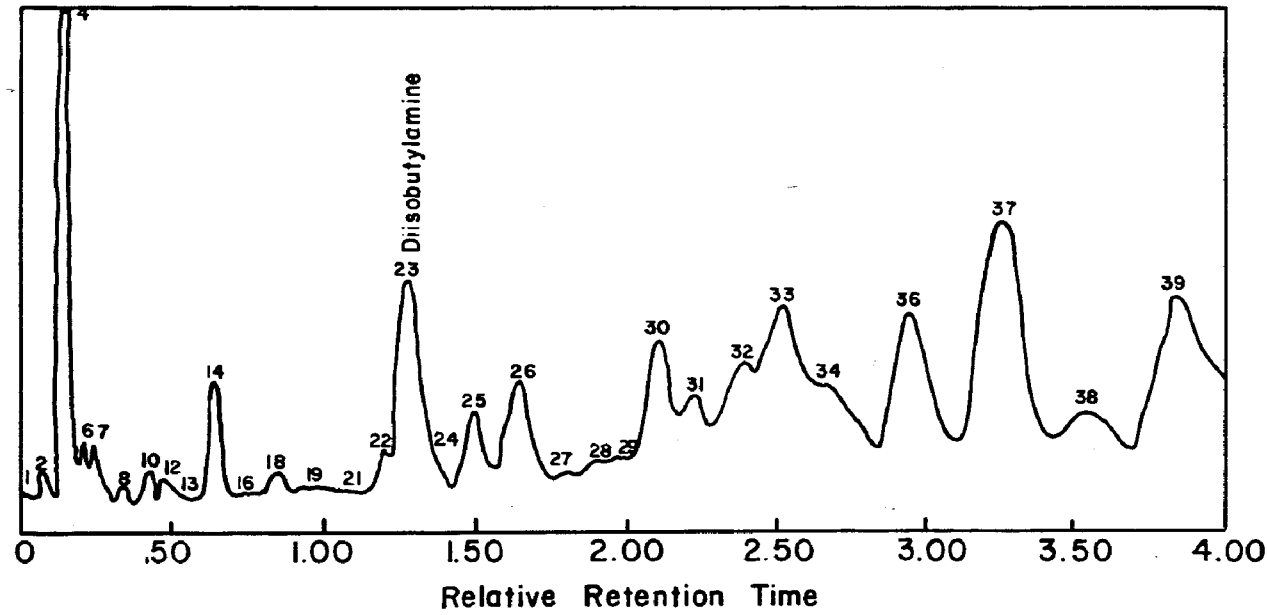


FIGURE 17. Relative retention time of dome compounds on SE - 30 at 90° C and 5×10^{-12} amp.

TABLE 5

COMPARISON OF RELATIVE RETENTION TIMES OF STANDARDS AND CONDENSATE PEAKS

COMPOUND	COLUMN	OVEN TEMP. °C	RELATIVE RETENTION TIME (STANDARD)	DOME PEAK NO.	RELATIVE RETENTION TIME (CONDENSATE)
Ethyl mercaptan	C-20M(3)	55	.03	1	.03
	SE-30	90	.08	4	.09
Propyl mercaptan	C-20M	55	.08	2	.07
	SE-30	90	.16	6	.15
tert-Butyl mercaptan	C-20M	55	.10	3	.11
	SE-30	90	.15	6	.15
sec-Butyl mercaptan	C-20M	55	.14		
	SE-30	90	.24	8	.25
Isobutyl mercaptan	C-20M	55	.16		
	SE-30	90	.26	8	.25
Butyl mercaptan	C-20M	55	.21		
	SE-30	90	.33	10	.33
tert-Amyl mercaptan	C-20M	55	.26	4	.26
	SE-30	90	.36	11	.35
sec-Isoamyl mercaptan	C-20M	55	.37		
	SE-30	90	.46	13	.45
Amyl mercaptan	C-20M	55	.54	7	.52
	SE-30	90	.68	18	.68
Hexyl mercaptan	C-20M	55	1.47		
	SE-30	90	T(4)		
Heptyl mercaptan	C-20M	55	2.97		
	SE-30	90	T		
Diethyl sulfide	C-20M	55	.17		
	SE-30	90	.31	9	.31
Di-n-propyl sulfide	C-20M	55	1.12	13	1.10
	SE-30	90	1.12		
Di-n-butyl sulfide	C-20M	55	2.46	22	2.49
	SE-30	90	T		
Diallyl sulfide (1)	C-20M	55	1.00	12	1.00
	SE-30	90	T		
Methyl disulfide	C-20M	55	.22		
	SE-30	90	.41	12	.39
Isopropanol	C-20M	55	.52	7	.52
	SE-30	90	.07	3	.07
Propanol	C-20M	55	.87	11	.84
	SE-30	90	.15	6	.15
Butanol	C-20M	55	2.16	20	2.15
	SE-30	90	.31	9	.31
Isopentanol	C-20M	55	4.37		
	SE-30	90	.45	13	.45
Acetaldehyde	C-20M	55	.04	1	.03
	SE-30	90	.06	2	.05
Propionaldehyde	C-20M	55	.06	2	.07
	SE-30	90	.12	5	.11
Butyraldehyde	C-20M	55	.14		
	SE-30	90	.16	6	.15
Valeraldehyde	C-20M	55	.38		
	SE-30	90	.33	10	.33
Acetone	C-20M	55	.01		
	SE-30	90	.12	5	.11
Diacetyl	C-20M	55	.14		
	SE-30	90	.15	6	.15
Acetic acid	C-20M	55	3.22	26	3.22
Propionic acid	C-20M	55	4.20		
Ethylamine	SE-30	90	.09	4	.09
Propylamine	SE-30	90	.23		
Butylamine	SE-30	90	.39	12	.39
Hexylamine	SE-30	90	1.28	26	1.28
Diethylamine	SE-30	90	.13		
Dipropylamine	SE-30	90	.48		
Diisopropylamine	SE-30	90	.24	8	.25
Dibutylamine	SE-30	90	1.88	32	1.86
Diisobutylamine (2)	SE-30	90	1.00	23	1.00
Triethylamine	SE-30	90	.31	9	.31
Tripropylamine	SE-30	90	1.57		

NOTES:

(1) Diallylsulfide-internal standard
(2) Diisobutylamine-internal standard
(3) (C-20M) signifies Carbowax 20M
(4) T=tailing of the component

1. ethyl mercaptan
2. propyl mercaptan
3. tert-butyl mercaptan
4. tert-amyl mercaptan
5. amyl mercaptan
6. isopropanol
7. propanol
8. butanol
9. acetaldehyde
10. propionaldehyde

The compounds that were identified as being present in the dome atmosphere by using the Carbowax 20M column alone were the following:

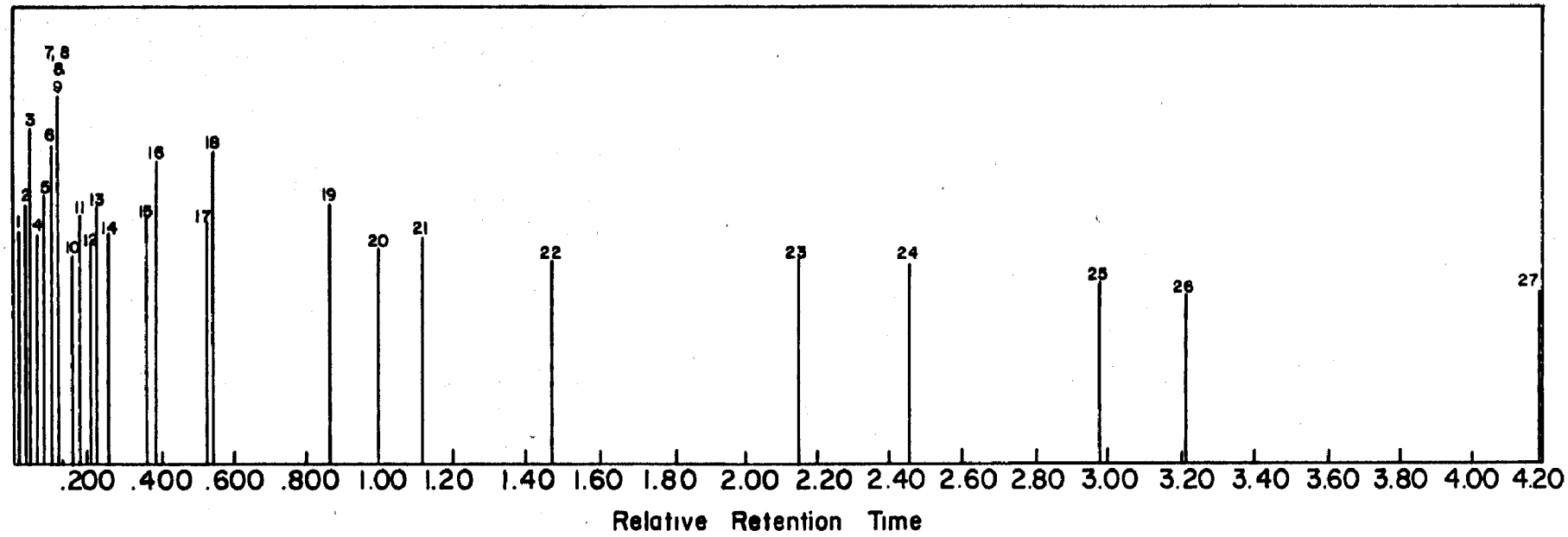
1. diallylsulfide
2. acetic acid

The following amines were identified in the dome atmosphere using the SE-30 column:

1. ethylamine
2. butylamine
3. hexylamine
4. diisopropylamine
5. dibutylamine
6. diisobutylamine
7. triethylamine

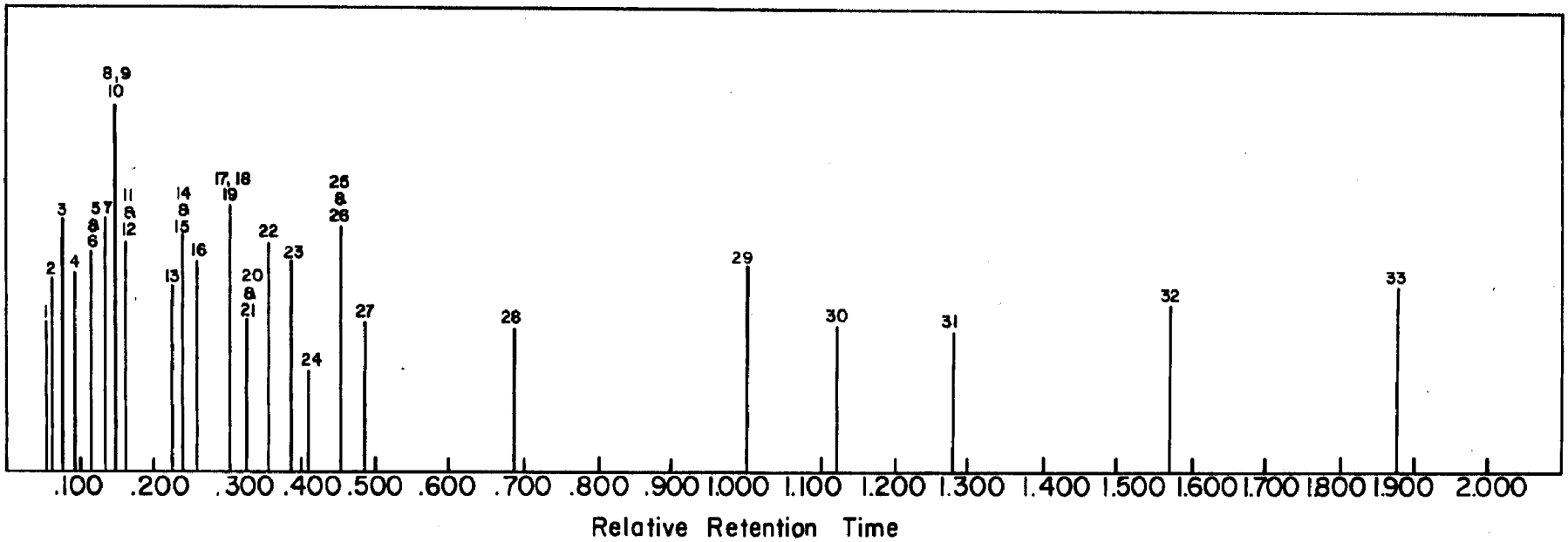
The mercaptans (ethyl, propyl, tert-butyl, tert-amyl, amyl) and diallylsulfide all have strong, offensive odors which were particularly noticeable as being present inside the dome on certain sampling days. The alcohols (isopropanol, propanol, and butanol) and the aldehydes (acetaldehyde and propionaldehyde) were judged unimportant as far as major odor contributors, however, they might have a synergistic effect on the composite odor in the dome atmosphere. The acetic acid standard and a comparative condensate peak had large relative retention times at 55°C and further analysis for specific organic acids was considered necessary. The amines would contribute a very pungent odor to the dome atmosphere, but most amines do not have as low a threshold odor level as the sulfur compounds (17). Amines therefore must be present in large amounts before a distinct amine odor can be detected in the presence of sulfur compounds.

The relative retention times of the standards on the Carbowax 20M and the SE-30 columns are shown diagramatically in Figures 18 and 19. It is noted from these figures that most of the standards eluted rapidly on both columns



KEY:		RRT			RRT			RRT
1.	Acetone	.01	10.	Isobutyl mercaptan	.16	19.	Propanol	.87
2.	Ethyl mercaptan	.03	11.	Diethyl sulfide	.17	20.	Diallyl sulfide	1.00
3.	Acetaldehyde	.04	12.	Butyl mercaptan	.21	21.	Di-n-propyl sulfide	1.12
4.	Propionaldehyde	.06	13.	Methyl disulfide	.22	22	Hexyl mercaptan	1.47
5.	Propyl mercaptan	.08	14.	tert-Amyl mercaptan	.26	23	Butanol	2.16
6.	tert-Butyl mercaptan	.10	15.	sec'-Isoamyl mercaptan	.37	24	Di-n-butyl sulfide	2.46
7.	sec-Butyl mercaptan	.14	16.	Valeraldehyde	.38	25	Heptyl mercaptan	2.97
8.	Diacetyl	14	17.	Isopropanol	.52	26	Acetic acid	3.22
9.	Butyraldehyde	.14	18.	Amyl mercaptan	.54	27.	Propionic acid	4.20

FIGURE 18. Relative retention time of various standards on Carbowax 20M at 55°C.



KEY:		RRT			RRT			RRT
1.	Acetaldehyde	.06	13.	Propylamine	.23	25.	Isopentanol	.45
2.	Isopropanol	.07	14.	Diisopropylamine	.24	26.	sec - Isoamyl mercaptan	.46
3.	Ethyl mercaptan	.08	15.	sec - Butyl mercaptan	.24	27.	Dipropylamine	.48
4.	Ethylamine	.09	16.	Isobutyl mercaptan	.26	28.	Amyl mercaptan	.68
5.	Acetone	.12	17.	Butanol	.31	29.	Diisobutylamine	1.00
6.	Propionaldehyde	.12	18.	Diethyl sulfide	.31	30.	Di - n - propyl sulfide	1.12
7.	Diethylamine	.13	19.	Triethylamine	.31	31.	Hexylamine	1.28
8.	tert - Butyl mercaptan	.15	20.	Valeraldehyde	.33	32.	Tripropylamine	1.57
9.	Diacetyl	.15	21.	Butyl mercaptan	.33	33	Dibutylamine	1.88
10.	Propanol	.15	22.	tert - Amyl mercaptan	.36			
11	Propyl mercaptan	.16	23.	Butylamine	.39			
12.	Butyraldehyde	.16	24.	Methyl disulfide	.41			

FIGURE 19. Relative retention time of various standards on SE - 30 at 90° C.

with the exception of the acids on Carbowax 20M and the amines on SE-30. The acids at the 55°C temperature on the Carbowax 20M column did not give a symmetrical peak but tended to tail with a resultant inconsistent retention time. It was therefore necessary to reinject these standards at a higher temperature on the Carbowax 20M column in order to obtain consistent retention times and sharp peaks. For comparison, dome condensate samples were also run at the higher temperature. The amines on the SE-30 column and especially the diamines and triamines tended to elute much later from the column at the 90°C temperature. However, the peaks were symmetrical and did not tail. It is interesting to note that a major portion of the peaks in the dome atmosphere elute much later than many of the low boiling vaporized standards that were used for comparison. This suggests that the dome compounds that were not identified are probably rather high boiling materials that have large vapor pressures, and possibly complex materials such as sulfur or nitrogen compounds with nonsimilar alkyl groups attached to the sulfur or nitrogen atom. Further investigation would be necessary to confirm this premise.

Confirmation could be obtained by first finding the amount of sulfurous or nitrogenous compounds present in a fixed gas volume, and then selectively absorbing these materials by specific functional group reactions. These absorbed materials could later be analyzed chromatographically by using a column that is known to effectively separate a mixture of such compounds. Temperature programming would probably be warranted to separate such a wide assortment of materials with different boiling points. Detection systems specific for these type of compounds would also be of great assistance.

Since the organic acids tailed considerably on the Carbowax 20M column at a low temperature, and since the standard peaks of acetic and propionic acids eluted much later than comparative dome compounds, condensate samples and standard organic acids were injected at higher temperatures into the Carbowax 20M column. A chromatogram was developed as presented previously in Figure 13 for the comparison of these retention times.

Odor-Retention Time Comparisons

Samples were collected from the dome on days that a very

noticeable sour-acid odor was detected in the atmosphere. Portions of these samples were injected into the Carbowax 20M column with a helium flow rate of 30 ml/min. A comparison of the retention times of organic acids and peaks from dome samples is presented in Table 6. Acetic, propionic, and isobutyric acids (as identified in the dome mixture from Table 6) all have very disagreeable odors that were especially noticeable on certain days inside the dome. The pH of the waste liquid inside the sludge thickener was always between 5.8 and 6.9 during the study. This pH range would enable the acids to be in a nonionized form and therefore volatilization of the acids into the atmosphere would be highly possible.

The water that was collected as condensate in the collection trap had a very distinct sickening-sweet odor which was not detected inside the dome. This odor smelled much like that of the skatole standard used in the laboratory. The odor became more intense upon heating the material. Standard solutions of skatole and its homolog, indole, were prepared by dissolving 25 mg of the material in 5 mg of isopropanol. One-microliter portions of the skatole and indole solutions were injected into the SE-30 column at oven temperatures of 110°C and 130°C. The isopropanol eluted from the column as expected. There was no elution however of the skatole or indole in a half-hour period. Comparison of retention times with the dome materials could not be made. This indicates that there was either adsorption or large retention times of the indole and skatole on the SE-30 column.

The threshold odor level in air for mercaptans, sulfides, and amines has been measured in the very low parts per billion range.(17) Aldehydes and alcohols have a level that is in the parts per million range, while the organic acids represent a wide range of threshold concentrations. (17) Threshold values of several odorous compounds with their characteristic odors are listed in Table 7. (17, 18)

It is noted from Table 7 that molecules with the same functional group all exhibit the same characteristic odor. The sulfur containing organics are detected in very minute quantities and have a very unpleasant odor. The alcohols are detected only in much greater concentrations and elicit a pleasant odor. The alcohol response would probably be less offensive to humans and therefore quantities which were present in excess of threshold would not be disagreeable. In the case of the sulfur compounds anything above

TABLE 6

RETENTION TIME OF ORGANIC ACIDS AND

DOME COMPOUNDS ON CARBOWAX 20M

COMPOUND	Temp. (°C)	Retention time of standards (min)	Retention time of dome compounds (min)
Acetic	75	8.23	8.70
Propionic	75	10.88	10.70
	90	6.45	6.20
Isobutyric	75	12.95	12.40
	90	7.30	7.20
Butyric	75	18.40	
	90	10.00	9.50
Isovaleric	75	27.50	
	90	13.70	
Valeric	75	37.90	
	90	18.70	18.60

TABLE 7

ODOR THRESHOLDS OF SEVERAL ORGANIC COMPOUNDS (17,18)

CHEMICAL	Odor threshold (ppm)	Characteristic odor
Formaldehyde	1.0	Straw-like
Acetaldehyde	.066	Green sweet
Acetic acid	1.0	Sour
Butyric acid	.001	Sour
Methylamine	.021	Fishy
Dimethylamine	.047	Fishy
Trimethylamine	.0002	Fishy
Methanol	100.0	Sweet
Ethanol	10.0	Sweet
Hydrogen sulfide	.00047	Rotten Eggs
Ammonia	46.8	Pungent
Diallyl sulfide	.00014	Garlic
Dimethyl sulfide	.0037	Decayed vegetables
Diethyl sulfide	.0028	Garlic-like
Dipropyl sulfide	.011	Foul
Dibutyl sulfide	.015	Unpleasant
Methyl mercaptan	.0021	Decayed cabbage
Ethyl mercaptan	.00026	Decayed cabbage
Propyl mercaptan	.0016	Unpleasant
Butyl mercaptan	.0010	Unpleasant
t-Butyl mercaptan	.00008	Unpleasant

threshold would be highly offensive. The odorous organic compounds such as the amines, acids, and aldehydes have increasing obnoxious odors as the molecular weights increase up to a certain weight. Further increase beyond this weight results in decreasing odor perception.[1] Characteristic odor types inside the dome were recorded by laboratory personnel on sampling days. These odors can be classified into fecal, rancid, cabbage-like, sour, and skunk-like. Table 8 lists the odor types for the sampling days along with the temperatures of the wastewater and dome atmosphere, relative humidity inside the dome, wastewater pH, and blanket depth in the sludge thickener.

The water and atmospheric temperatures are seasonally dependent and they increased slightly as the weather became warmer. The odor types observed appear to be dependent on the depth of the sludge in the thickener. The fecal and rancid odors are typical of low sludge levels (greater blanket depth) with the cabbage-like and sour odors associated with a high sludge level. The skunk-like odor appears to be a transition odor between high and low levels of sludge in the thickener.

On the days that a descriptive odor was noted inside the dome, there was a noticeable increase in concentration or appearance of certain peaks on the chromatogram of that day's condensate sample. Peak numbers shown on Figures 16 and 17 are compared with identified dome compounds in Table 9. Peak number 2 on the Carbowax 20M column (see Figure 16 and Table 9) was more concentrated when the cabbage odor was noticed (propyl mercaptan). Peak number 3 was higher when the sour odor prevailed (tert-Butyl mercaptan). On the days when rancid and fecal odors were prevalent no significant change in any peaks on the chromatograms was observed. On the SE-30 column,(see Figure 17 and Table 9), peak number 4 was more concentrated for the rancid and fecal odor days (ethylamine). Peak number 2 on the SE-30 column appeared on both the sour and skunk odor days (acetaldehyde).

Compound Concentration Evaluation

The quantitation of identified materials from the dome was accomplished by comparing under similar conditions the peak heights of the compounds from the dome chromatogram and the peak heights of vaporous standards that were injected into the gas chromatograph. Standards were prepared by first injecting with a Hamilton syringe a 1-μl liquid

TABLE 8

COMPARISON OF ODOR TYPES WITH OPERATIONAL MEASUREMENTS

Month Day	Temp. (°C) Water	Atmosphere	Relative humidity	Characteristic odor-type	pH	Blanket depth(ft)
4-6	56	48	86	fecal	6.1	8.5
4-7	56	55	66	fecal	6.1	8.5
4-8	58	61	51	fecal	6.0	8.5
4-13	60	55	82	rancid	6.1	8.5
4-15	62	63	60	fecal	6.1	8.0
4-16	60	66	55	fecal	6.1	8.0
4-19	62	69	57	fecal	6.2	7.5
4-20	64	71	54	cabbage-like	5.8	7.5
4-21	62	64	75	cabbage-like	6.0	7.5
4-27	62	63	74	cabbage-like	6.1	5.5
4-30	63	60	69	cabbage-like	6.0	5.5
5-4	62	63	57	cabbage-like	6.3	6.0
5-5	64	64	80	cabbage-like	6.0	5.2
5-7	64	65	90	cabbage-like	6.0	2.2
5-10	64	69	90	sour	5.9	1.0
5-12	64	56	71	sour	---	6.0
5-14	64	65	67	rancid	6.1	5.2
5-18	66	70	65	fecal	5.9	9.0
5-19	66	67	64	rancid	6.0	8.5
5-20	66	67	68	rancid	6.0	8.2
5-25	62	62	70	rancid	6.8	8.5
5-26	62	62	84	rancid	6.8	8.5
6-1	66	69	72	fecal	6.9	8.5
6-2	66	73	67	rancid	6.6	9.0
6-4	68	74	79	skunk-like	6.0	7.5
6-8	68	72	86	skunk-like	6.2	7.2
6-16	64	72	86	sour	5.9	3.2
6-21	64	75	71	sour	6.0	3.0
6-25	64	80	76	sour	---	5.5
6-29	64	79	69	sour	6.1	5.5
7-14	64	74	91	sour	6.0	5.5

TABLE 9

MAXIMUM AND MINIMUM CONCENTRATIONS RECORDED FOR IDENTIFIED ODOR COMPOUNDS

COMPOUND	Dome Maximum ($x10^{-4}$ ppm)	Dome Minimum ($x10^{-4}$ ppm)	Column	Dome Peak No.*
Acetaldehyde	78	1.6	SE-30	2
Isopropanol	1.4	.26	SE-30	3
Propanol	20	4	C-20M	11
Butanol	82	2.4	C-20M	20
Ethylamine	270	1.5	SE-30	4
Butylamine	.0014	.0005	SE-30	12
Diisopropylamine	.066	.0035	SE-30	8
Diisobutylamine	.99	.07	SE-30	23
Dibutylamine	.14	.016	SE-30	32
Triethylamine	.21	.08	SE-30	9
Diallylsulfide	48	.09	C-20M	12
Ethyl mercaptan	.38	.16	C-20M	1
Propyl mercaptan	26000	.05	C-20M	2
tert-Butyl mercaptan	5.1	.023	C-20M	3
tert-Amyl mercaptan	.58	.23	SE-30	11
Amyl mercaptan	.14	.023	SE-30	18

* refer to Figures 16 and 17

sample into a 125-ml sampling bottle capped with a septum containing cap. This bottle was then placed in warm water to volatilize the material completely. A specific volume of the sample as a vapor was withdrawn with a 1-ml Hamilton gas-tight syringe and the vapor was injected into the column. Gaseous volumes were chosen such that the comparison of the standard and the dome peak were both recorded at the same attenuation. Further dilution of the standard vapor was necessary in some cases to keep the peak from going offscale.

The experimentally determined maximum and minimum concentrations of some odorants in the dome atmosphere are presented in Table 9. Comparing these values with threshold values for some of the compounds as presented previously in Table 7 reveals that many of the compounds are below their threshold levels except for the mercaptans and ethylamine. Propyl mercaptan and ethylamine appeared to be the only identified compounds present in concentrations above their threshold levels.

Those compounds with concentrations below the threshold level listed for compounds with a similar functional group, although not major odor contributors, may have a synergistic effect on odor perception. Obviously, no one compound detected on a given day can be considered totally responsible for the perceived odor.

THRESHOLD EVALUATION AND ODOR TREATMENT RESULTS

General Statement

This section presents the results from various tests conducted to evaluate treatment methods for dome odor control. These tests included: (1) dilution of the odors with air, (2) adsorption of odors by activated carbon, and (3) oxidation of odor compounds with chlorine. The effectiveness of each method was determined through a threshold odor evaluation by a selected group of individuals.

Selection of Odor Panel

Laboratory personnel assigned to the Industrial Waste Division of MSD and working at the Bissell Point Sewage Treatment Plant were asked to serve on the odor panel. Eight people were initially screened, with four of these chosen for the panel. Selection of the four panel members was based on results of the screening tests with those individuals having the most sensitive sense of smell used for detailed odor detection. The most sensitive individuals were used so that efficiency evaluations of odor treatment methods would be stringent.

The panel members were screened utilizing the "triangle test".[19] This test allowed each person to evaluate three odor flasks for similarity of odors. Two flasks contained one per cent vanillin solution in benzyl benzoate while the third contained a one per cent methyl salicylate solution in benzyl benzoate. Starting with these one per cent solutions, personnel were asked to determine the control odor (i.e., methyl salicylate) in increasingly dilute solutions from a random arrangement of the flasks.

At low concentrations vanillin and methyl salicylate smelled similar and only the most sensitive individuals were able to distinguish the control odor as indicated in Table 10. The plus mark indicates that the individual had chosen the control odor correctly from a set of three flasks while a zero shows no response. Personnel with reference numbers 1, 2, 4 and 8 were chosen to serve on the panel.

Treatment by Air Dilution

The simplest form of treatment is the dilution of an odor to a level where it is undetectable, that is, below the

TABLE 10

SENSITIVITY OF PERSONNEL TO TRIANGLE TEST

Standard Odorants (% w/w)	1	2	3	4	5	6	7	8
1	+	+	+	+	+	+	+	+
0.1	+	+	+	+	0	+	+	+
0.05	+	+	+	+	0	+	+	+
0.01	+	+	0	+	0	0	0	+
0.0025	+	0	0	0	0	0	0	+
0.000125	0	0	0	0	0	0	0	+

Key: + = odor difference detected

0 = no difference detected

threshold level. The threshold level is defined according to ASTM[6] as the amount of dilution required to make the odors barely perceptible to 50 per cent of the population. During the study since very sensitive individuals were used on the odor panel this percentage would be reduced considerably and is therefore referred to as "odor threshold for 50% of the panel members."

Grab samples collected at the center of the dome around 9:30 a.m. in the morning were given a threshold level evaluation by 2:00 p.m. the same day. Odor samples collected from the dome each morning were diluted with various volumes of odor free air in the laboratory prior to panel evaluation.

Table 11 presents the results from the threshold level determination on individual samples taken during the months of June and July, 1971. Each threshold level is given as a per cent concentration on a volume per volume basis. The threshold value that would be detected by 50 per cent of the panel members shown in Table 11 was determined by finding a midpoint between the value of maximum per cent odor concentration perceptible to all panel members and the minimum per cent odor concentration perceptible to none of the panel members on each sampling day. For example, on June 21st the maximum detectable concentration by all panel members was 0.3 per cent since at a concentration just below this level, Panel Member "A" could not sense the odor. However, Panel Member "C" could detect the odor at 0.05 per cent concentration, but not at the next dilution which was 0.04 per cent. The threshold level for 50 per cent of the panel members was therefore calculated to be:

$$\frac{0.3 + 0.04}{2} = 0.17$$

In order to give meaning to the concentration of daily odors inside the dome, the odor concentration was defined in terms of a predetermined threshold level. ASTM[6] defines this level as the number of cubic feet that one cubic foot of odorant will occupy when it is diluted to the odor threshold. The formula for calculating odor concentration is:

$$C = \frac{V}{Vs} \quad [1]$$ where, C is the odor

concentration in odor units/cu. ft., Vs is the volume in milliters of original sample that is contained in the most dilute sample in which odor was detected, and V is the volume of the syringe used. In this study the syringe volume was 100 ml.

An odor unit is defined as one cubic foot of air at the odor threshold. The odor concentration (C) on June 21st was therefore calculated to be:

$$C = \frac{100}{0.17} = 588 \text{ odor units/cu. ft.}$$

Table 11 lists these odor concentrations as determined from panel results. From the definition of odor concentration, these values in Table 11 represent the number of cubic feet (or any other conveniently measurable unit) by which one cubic foot of dome air must be diluted in order to produce the threshold level concentration. In the example one cubic foot of dome air would have to be diluted with 588 cubic feet of odor free air to reduce the odor below detectible levels. The sludge thickener dome at the Coldwater Creek Plant has a volume of 31,370 cu. ft. Therefore, the amount of air needed to dilute the entire dome atmosphere to the threshold level is found by multiplying the odor concentration by the dome volume. Further investigation of the meterological effects in and around the treatment plant which was beyond the scope of the study is necessary before a procedure involving outside air dilution can be adequately adopted.

Carbon Adsorption of Odors

Another method investigated for treatment of dome odors was adsorption using activated carbon. The use of activated carbon can be economical if regeneration is feasible. It is a good adsorbant for most organic compounds and its efficiency is not affected by moisture.[21,22] The procedure for carbon treatment evaluations has been described previously.

Table 12 lists the results for one week of concentrated sampling and adsorption testing during the month of July. The threshold values before and after treatment are compared with the quantity of carbon used to treat a specific

TABLE 11

THRESHOLD LEVELS AND AIR DILUTION REQUIREMENTS FOR DOME ATMOSPHERE

MONTH DAY	Odor threshold level for each panel member A	B	C	D	Odor threshold for 50% of the panel members	Odor Concentration (odor units/cu ft)(1)	Air volume needed to reach threshold (cu ft)
6-21	.3	.2	.05	.1	.17	588	18,446,000
6-22	.4	.05	.2	.3	.22	454	14,242,000
6-23	.08	.07	.04	.01	.04	2500	78,425,000
6-24	.3	.2	.2	.5	.30	332	10,415,000
6-25	.01	.09	.01	.08	.05	2000	62,740,000
6-28	.1	.3	.3	.3	.20	500	15,685,000
6-29	.1	.05	.03	.1	.06	1666	52,262,000
6-30	.3	.3	.3	.03	.16	625	19,606,000
7-1	.05	.05	.1	.2	.12	833	26,131,000
7-14	.2	.2	.03	.03	.11	909	28,515,000
7-15	.3	.1	.1	.1	.54	185	5,803,000
7-16	.04	.1	.04	ND(2)	.06	1666	52,262,000
7-19	.2	.6	.2	ND	.35	286	8,971,820
7-20	.3	.4	.4	ND	.30	333	10,446,000

NOTES: (1) Average odor concentration 873
(2) ND signifies not detected

volume of air from the dome. The efficiency of activated carbon treatment was calculated using the following formula[7]

$$\% \text{ Efficiency} = \frac{\text{conc. of entering gas} - \text{conc. of effl. gas}}{\text{conc. of entering gas}} \times 100$$

At the breakthrough point (the time at which odors were first noticed in the discharge from the filter), the efficiency of the activated carbon treatment was calculated for the study period, efficiencies for carbon adsorption were between 97% and 99%.

The efficiency of the process depends greatly on the type of organics being adsorbed. Some organics were observed to pass through the filter without being adsorbed. A typical odor that did not appear to be adsorbed by the carbon was similar to the odor of lard. Even though most dome odors were adsorbed by the carbon, the odor panel noticed the greasy lard-type odor in samples taken from the filter discharge even before the breakthrough point was reached. This odor was totally dissimilar to the characteristic odors present inside the dome.

Panel members were instructed to compare a sample of diluted and untreated dome gas with samples of filter discharge to determine the breakthrough time. An evaluation was not made of the increase in odor intensity after the breakthrough point. The carbon filter could probably have been operated for a longer time until the odors emitted reached a level of around 200 odor units which was determined by previous studies as the point where the odors became objectionable.

The quantity of dome atmosphere that can be treated with a known weight of carbon is represented in Table 12. These values represent the amount of carbon needed for a 98% efficient treatment of odors. The average is 0.102 gram of carbon per cu. ft. of dome air.

Chlorine Treatment of Odors

A number of laboratory techniques were investigated to evaluate treatment of odors with chlorine. In the first method studied a chlorine scrubber solution was attached to the carbon adsorption system, with the carbon filter removed, and connected to the sampling train at the dome.

TABLE 12

CARBON* ADSORPTION OF DOME ODORS

Month Day	Before treatment odor units/ cu ft	After treatment odor units/ cu ft	Efficiency	Weight of carbon (grams)	Gas volume (cu ft)	Carbon/gas volume grams/cu ft
7-1	835	10	99	10.5	109	.096
7-2	760	10	99	10.6	100	.106
7-6	910	25	97	9.6	80	.120
7-7	715	15	98	10.3	130	.079
7-8	835	15	98	10.0	90	.111
					Average	.102

* Activated carbon used was 4-to 10-mesh as manufactured by the Cliff-Dow Chemical Company.

However, as the dome gas was bubbled through the solution most of the chlorine was lost by volatilization rather than chemical oxidation of the odorous compounds. An identical solution was similarly stripped of chlorine when odor free air was passed through it using the same flow conditions as that of the dome gas.

The second method studied utilized treatment of the odors by injecting air diluted chlorine gas into a Saran bag containing a known concentration of dome gas. It was very difficult to determine accurately the amount of chlorine injected into the sample bag and therefore the method was not used for treatment evaluation.

The method selected for chlorine treatment evaluation has been described earlier (see Figure 10). The results from this method are presented in Table 13. The most significant point made during these chlorine evaluations was that water alone is an effective reducer for most of the odors. There was a 10 to 100 fold reduction in odor by merely bubbling the dome gas through water. The optimum chlorine concentration for treatment of dome odors was found to be 1.5 mg/l. At this concentration in the chlorine solution, all odors were effectively removed. This was proven when the odor panel members could detect a very faint dome odor in a bag sample that was passed through the chlorine solution. At concentrations greater than the 1.5 mg/l level only the odor of chlorine was detected.

The combination of water and chlorine appears to provide effective treatment of the odors. On a practical scale the dome atmosphere can be bubbled through a large scrubber tank which has a chlorine concentration maintained at 1.5 mg/l. If post chlorination is practiced, as it is at the Coldwater Creek Plant, odorous gases could possibly be bubbled through the final effluent at the discharge of the chlorine contact basin (see Figure 3). The residual chlorine concentration in the effluent must be controlled to insure adequate odor reductions.

TABLE 13

TYPICAL CHLORINE TREATMENT RESULTS FOR DOME ODOR REMOVAL

Chlorine Concentration (mg/l)	Initial Odor Concentration (odor units/ cu ft)	Final Odor Concentration (odor units/ cu ft)	Odor Type
1.15	2000	25	Dome-like
1.50	"	1	Very faint odor
2.20	"	2-10	Chlorine
H_2O blank	"	33	Dome-like

ACKNOWLEDGEMENTS

Appreciation is expressed to the Environmental Protection Agency (EPA) for the financial assistance which in part allowed this study to be undertaken. Recognition is made also to Mr. Otmar O. Olson and Dr. William Garner of the EPA for their guidance during implementation of the study and review of project results.

Special thanks is given to Mr. Thomas Wydrzynski for analytical assistance provided during laboratory evaluations and to Mr. Stan Lamb whose drawings appear throughout this report.

REFERENCES

1. Glaser, J. R., "Air Pollution From Sewage Treatment", Ph.D. thesis, University of Texas, Austin, Texas, (1969).

2. Burnett, W. E., "Air Pollution From Animal Wastes Determination of Malodors by Gas Chromatographic and Organoleptic Techniques", Environ. Sci. Technol., 3, No. 8, p. 744 (August, 1969).

3. Lebeda, D. L., Day, D.L., Hayakavva, I., "Air Pollutants in Swine Buildings with Fluid Waste Handling", Paper presented at the National Meeting of the American Society of Agricultural Engineers, New Orleans, Louisiana, (December 8, 1964).

4. Miner, J. R., Hazen,T.E., "Ammonia and Amines: Components of Swine-Building Odor", Trans. Am. Soc. Agr. Engrs.,12, p. 772 (1969)

5. Farrington, P.S., Pecsok, R. L., Meeker, R. L., Olson, T. J., "Detection of Trace Constituents by Gas Chromatography Analysis of Polluted Atmosphere", Anal. Chem., 31, No. 9, p. 1512 (September, 1959).

6. "Measurement of Odors in Atmospheres (Dilution Method)", ASTM Designation: D1391-57 (1957).

7. Jacobs, M. B., "The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents", Interscience, New York p. 96, (1949).

8. Day, D. L., Hansen, E. L., Anderson, S., "Gases and Odors in Confinement Swine Buildings", Trans. Am. Soc. Agr. Engrs., 8, p. 118, (1965).

9. American Public Health Association, Standard Methods for the Examination of Water and Wastewater, p. 226, Thirteenth Edition, New York, APHA, (1971).

10. Dedio, W., Zalik, S., "Gas Chromatography of Indole Auxins", Anal. Biochem., 16, p. 36 (1966).

11. Bednas, M. E, Russell, D.S., "Determination of Natural Gas Leakage via Gas Chromatography of Drill Core Samples", Journal of Gas Chromatography, 5, p. 592 (November, 1967).

12. Andrews, J. F., Thomas, J. F., Pearson, E. A., "Determination of Volatile Acids by Gas Chromatography", Water and Sewage Works, 4, (1964).

13. Mahadevan, V., Stenroos, L., "Quantitative Analysis of Volatile Fatty Acids in Aqueous Solution by Gas Chromatography", Anal. Chem., 39, No. 13, p. 1652 (November, 1967).

14. McNair, H.M., Bonelli, E. J., Basic Gas Chromatography, Consolidated Printers, Berkeley, p. 67 (1969).

15. Thompson, B., "GC Column Conditioning", Technical Bulletin 801A, Beckman.

16. "Chromatography/Lipids", Catalog 1970, Supelco, p. 7.

17. Leonardos, G., Kendall, D., Barnard, N., "Odor Threshold Determinations of 53 Odorant Chemicals", Journal of the Air Pollution Control Association, 19, No. 2, p. 91 (February, 1969).

18. Stern, A.C., Air Pollution, Academic Press, New York, p. 509, (1962).

19. Benforado, D.M., Rotella, W.J., Horton, D. L., "Development of an Odor Panel for Evaluation of Odor Control Equipment", Journal of the Air Pollution Control Association, 19, No. 2, p. 101 (February, 1969).

20. Daniels, F., Alberty, R.A., Physical Chemistry, John Wily and Sons, New York, p. 327, (1966).

21. Turk, A., "Industrial Odor Control and Its Problems", Chem. Eng., 76, No. 24, p. 70 (November, 1969).

22. Yocom, J.E., Duffee, R.A., "Controlling Industrial Odors". Chem. Eng., 77, No. 13, p. 160 (June, 1970).

23. Culp, G., Slechta, A., "Plant Scale Reactivation and Reuse of Carbon in Wastewater Reclamation", Water and Sewage Works, 113, No. 11, p. 425 (November, 1966).

APPENDIX A

Sludge Thickener Operational Instructions for the Coldwater Creek Plant

The operation of the sludge thickener during the project is summarized by the following:

1. "Depth of Blanket" (D.O.B.) shall be interpreted to mean the measured distance from the water surface of the thickener down to the point that the blanket-finder light goes out. This reading will provide the basis for routine operations which are very slow moving trends in most cases.

2. The No. 1 thickened sludge pump shall be operated as the "lead" pump, twenty-four hours per day for normal service, and No. 3 thickened sludge pump shall be operated from twelve noon until twelve midnight each day unless a blanket depth reading below 9 ft. is indicated at which time this pump shall be shut down. Until the first D.O.B. reading of 8 ft. is recorded, this second level pump is to remain off. If the first 8 ft. D.O.B. reading falls into the normal twelve noon to twelve midnight operating period for No. 3 thickened sludge pump, it shall be turned on to complete the pump schedule and definitely be turned on the following day.

3. The dilution water pump shall be operated each day from 8 a.m. until 4 p.m. (approximately) unless special orders are issued cancelling this operation for the day due to weather conditions, or other reasons.

4. Thickener bypassing, thereby pumping raw sludge directly to the primary digesters, requires special considerations and interpretations. Whenever the indicated raw sludge density reading doubles from the normal trend and establishes that trend for one (1) hour, the raw sludge shall be bypassed directly to the digesters. During the intervening bypass period only No. 3 thickened sludge pump shall be used until the first thickened sludge sample indicates dilute (watery) sludge or the raw sludge flow is returned to the thickener when a drop in density to 150 per cent of the original normal rate is noted. This method of control is necessary to allow for drifting sludge density meter trends.

5. If dilute sludge is noted in a sample of thickened sludge while raw sludge is being routed direct to the primary digesters for an extended period, the following actions shall be taken.

   A. The thickener sweep mechanism is to be shut off.

   B. The thickened sludge pump (No. 3) is to be shut off.

   C. The daily dilution water pumping schedule is to be maintained.

   D. Once daily on the 4 p.m. to 12 a.m. shift the thickener drain valve shall be opened for 2-3 min.

   Steps C and D shall be completed daily until the thickener is restored to normal service. When switching raw sludge feedback to the thickener, the normal pumping schedule with thickened sludge pumps is to be resumed.

6. The key to overall control will be the D.O.B. reading. The lowest D.O.B. trends occur Sunday, Monday, and Tuesday with much higher levels of D.O.B. occurring toward the latter part of the week which is in part due to a heavier waste activated sludge disposal program.

*U.S. GOVERNMENT PRINTING OFFICE:1974 546-316/257 1-3

SELECTED WATER RESOURCES ABSTRACTS

INPUT TRANSACTION FORM

1. Report No.

2. Accession No.

W

4. Title

Odors Emitted from Raw and Digested Sewage Sludge

5. Report Date

6.

8. Performing Organization Report No.

7. Author(s)

Bernard A. Rains, Mario J. DePrimo & I. L. Groseclose

10. Project No.

11010EZQ

9. Organization

Metropolitan St. Louis Sewer District
10 East Grand Avenue
St. Louis, Missouri 63147

11. Contract/Grant No.

Grant WPD 23-01-68

13. Type of Report and Period Covered

12. Sponsoring Organization **Environmental Protection Agency**

15. Supplementary Notes

Program Element 1BB033 EPA-670/2-73-098
ROAP 21-ASD

16. Abstract

Odors emitted during thickening of raw and secondary sludge have been responsible for adverse criticism at many sewage treatment plants . This study was undertaken to identify typical odor causing substances and evaluate selected conventional methods for controlling or eliminating these substances. A styrofoam dome covering a sludge thickener was utilized to control atmospheric conditions and concentrate odors.

Field collected vapor samples were analyzed using gas chromatography techniques. Analyses using both polar and nonpolar column material indicated that the major odor causing compounds were mercaptans and amines. Other compounds which were minor contributors to odor were aldehydes, alcohols, and organic acids.

Odor control methods selected for study included air dilution, activated carbon adsorption, and chlorine oxidation. Air dilution using cyclic operation of an exhaust fan was found to be an effective means of odor control when outside atmospheric conditions were conducive to odor dissipation. Passing vapors through activated carbon filters was not completely effective in odor control since a detectible residual odor remained. A 1.5 mg/l solution of chlorine was effective in removing all odors from vapor samples bubbled through the solution.

17a. Descriptors

odor
odor abatement
sewage
sludge
sludge treatment

17b. Identifiers

odor control
malodors

17c. COWRR Field & Group 05D

18. Availability

From EPA

19. Security Class. (Report)

20. Security Class. (Page)

21. No. of Pages

22. Price

Send To:

WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

Abstractor Bernard A. Rains

Institution Metropolitan St. Louis Sewer District