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DOT/OPSO-75/08

STUDY OF THE PROPERTIES OF THE NUMEROUS ODORANTS AND ASSESSMENT OF THEIR EFFECTIVENESS IN VARIOUS ENVIRONMENTAL CONDITIONS TO ALERT PEOPLE TO THE PRESENCE OF NATURAL GAS

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FINAL REPORT

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I. Summary

The Institute of Gas Technology, under contract from the Office of Pipeline Safety Operations of the Department of Transportation, has conducted a study to provide present state-of-the-art information on the odorization of natural gas. The input data for the study came from three sources: A literature survey of past and present gas industry odorization practices, a questionnaire (Appendix A) submitted to those responsible for the gas industry's odorization programs, and a series of personal interviews with pertinent employees of individual gas companies and odorant suppliers.

The 112 companies who responded to the questionnaire send out nearly 10.5 trillion CF of natural gas per year and purchase more than 6 million pounds of odorant. Most believe that the gas industry's odorization practices are effective in protecting property and life and in promoting gas as a safe fuel. They consider the present odorants to be effective overall in warning of inside leaks, but they recognize the need for an improved odorant that will not be removed on passage through soil.

More companies prefer tertiary butyl mercaptan blends than any of the other commercial odorants available, primarily because of their stability. Thiophane is a distant second choice.

Positive-displacement chemical-pump odorizers are used by 73 companies and are the most highly regarded of all the five types of odorant-addition equipment, Absorption-bypass odorizers are nearly as popular (71 companies), despite some problems with trying to maintain a set addition rate over the designed flow rate and over summer-winter temperature changes. Meter-driven pump odorizers present more maintenance problems than the others; for that reason, they are used by fewer companies (51).

Ninety-three companies check odor levels with odorometers and 43 use other instruments. Sixteen companies report the use of gas chromatographs for odorant concentration testing; two companies use chromatographs with sulfur-specific detectors.

Titrators are most often used to monitor odorant concentration continuously. Room tests and chemical tests are used less frequently.

When odor fading is observed it usually occurs in a specific part of the system, and supplemental odorieation is sometimes required. The few instances of odorant-caused corrosion nearly always involve copper. A few companies do collect pipeline liquids containing odorant, but disposal is seldom a problem.

Few companies question the effectiveness of today's odorants, except for the problem with soil adsorption. Odorant-addition equipment is usually considered quite reliable; however, improvements are needed to increase the constancy of odorant addition. Also needed are a) better odorizers for small, low-flow systems and b) odor-monitoring equipment that would provide high performance at low cost.

Odor-monitoring equipment and procedures are still in need of improvement; they should be studied and redesigned to make better use of available technology.

Gas industry odor technologists consider current Federal regulations "fair" and "workable" and feel "they can be lived with." The concept of a performance standard is attractive. However, those charged with the responsibility for gas industry odorieation programs recommend that further regulation be considered carefully in terms of its real contribution to safety.

11. Introduction

A. Program Objective

The objectives of the work herein reported were to collect, analyze, and evaluate data on the current state-of-the-art of odorization technology. The Office of Pipeline Safety Operations, U. S. Department of Transportation, authorized the Institute of Gas Technology (IGT) to conduct this study because some reports and investigations of accidents and some published papers have pointed out deficiencies in current odorization practices. Government and industry need to evaluate these practices and to develop a means of improving the performance of odorants and odorization equipment.

B. Data Acquisition

Factual data for the report were compiled from three sources: a comprehensive literature search in IGT's Technical Information Services Center, an in-depth survey of gas industry personnel conducted by questionnaire and by telephone contact, and a series of personal interviews with staff members of individual gas companies and odorant suppliers.

The literature search utilized the Institute's Microfilmed Abstract System for Technical Information Retrieval (MASTIR). This high-speed, key-word document retrieval system searches its file of indexed abstracts, which come from many sources including research reports, unpublished papers and reports, articles published in journals, society proceedings, bibliographies, patents and patent information, books, codes, and specifications. The file is continually updated by contributions from IGT's research publications and abstracts from the Center's Gas Abstracts, a monthly publication that surveys some 225 domestic and foreign scientific, engineering, and trade journals; transactions and proceedings; bulletins of technical and scientific societies; and publications of government agencies.

In addition to MASTIR, the facilities of the IGT library were used. It contains the world's largest collection of textbooks and reports on gas engineering and technology. Also available' was the world-famous John Crerar Library's collection of over 1.1 million technical journals, books, and documents.

The questionnaire was submitted to 122 gas transmission and distribution companies, and the survey included a representative number of municipal

Companies. Replies were received from 112 respondents. The questionnaire was designed to elicit information concerning industry experience with odorants, odorization and monitoring equipment, and procedures. Respondents were given the opportunity to offer personal opinions in each of the areas under investigation and to describe specific problems they have encountered, the frequency of these problems, and the methods used or being used to solve them.

Personal interviews had the same objective. However, the personal, informal approach elicited some comments and opinions that may not have been included when answering the questionnaire, which gas company personnel were asked to sign, Valuable information was given by odorant suppliers, for whom the questionnaire was not entirely relevant.

The 112 companies replying to the questionnaire have an annual sendout of 10,468,019 X 10^6 cubic feet of gas. Purchasing 6,296,108 pounds of odorant, they operate 5,689 conventional odorizers and 10,689 farm tap and individual odorizers.

Of the 112 companies replying, 4 do no odorization whatever, 31 companies supplementally odorize gas that has naturally occurring odor, 13 supplement a supplier's odorized gas with their own odorant, and 88 companies odorize gas that has no odor, naturally occurring or added.

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III. Historv of Odorization in the United States

Although odorization of natural gas was suggested as early as 1885 as a means of detecting leaks,[1] the first commercial procedure for odorizing city gases was not introduced until 1905 with the use of Pintsch gas condensates to odorize water gas.[2] Subsequently, the Bureau of Mines in 1920 studied twenty-four stenches for detecting leakage of blue water gas and natural gas.[3] Except ethyl mercaptan, all were found to be unsuitable as practical odorants. In 1931 the Bureau of Mines in cooperation with the American Gas Association (A. G. A.) published Monograph No. 4,[4] an investigation of warning agents for fuel gases. Odor or irritating properties were measured for 57 substances of 89 evaluated.

Several explosions occurred in Los Angeles, California, in 1927 shortly after straight natural gas was substituted for mixed gas. Speculation that these incidents might have been prevented had the gas possessed a characteristic odor prompted the three companies operating in the Los Angeles basin to investigate gas odorization. Discarding ethyl mercaptan because of its high cost and nauseating odor, they requested Standard Oil Co. of California to investigate the possibility of supplying a light oil possessing a concentrated "refinery odor." The resulting "Calodorant" was first used for large-scale odorization in Los Angeles in 1929.[5] Leak complaints increased tremendously. Calodorant was a complex mixture of sulfur compounds – mostly sulfides, but not hydrogen sulfide.

Also during 1929 the Union Gas and Electric Company conducted a 10-day test with ethyl mercaptan in Middletown, Ohio; 720 leaks were discovered.

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1. Hilt, L., "Chronology of the Natural Gas Industry," Amer. Gas J. 172, 29-36 (1950) May.

2. Senatoroff, N. K., "Odorization Practices," A. G. A. Proc. – 1950, PC-50-20.

3. Katz, S. H. and Allison, V. C., "Stenches for Detecting Leakage of Blue Water Gas and Natural Gas," Tech. Paper 267. Washington, D. C.: Bureau of Mines, U.S. Department of the Interior, 1920.

4. Fieldner, A. C. et al., "Warning Agents for Fuel Gases," Monograph 4. Washington, D. C.: Bureau of Mines, U. S. Department of the Interior, May 1931.

5. Cox, R. O., "Developments in Natural Gas Odorization," Gas Age 94, 69-71, 107-8, 110 (1944) October 5.

Calodorant was injected into the distribution systems of the Community Natural Gas Co. in both Brownwood and Cisco, Texas, in 1929. Numerous leaks were detected.

Odorization was begun in New Orleans in September 1930. At about the same time the Public Service Co. of Colorado began to odorize the gas distributed in Denver and other cities. Calodorant was the odorizing agent in both instances.

In 1937 a Texas law was passed requiring the odorisation of all gas used for domestic fuel purposes within the state. Subsequently, Louisiana enacted legislation requiring the odorization of domeatic gas.

The Sharples Solvents Corp. developed a more concentrated odorant than Calodorant, called Pentalarm,[6] composed principally of amyl mercaptan. It possessed a good gas-like odor and high odorizing value and was available in any desired quantity. Pentalarm 86 and Calodorant No. 3 enjoyed wide usage through the early 1940's.[6]

Captan, an odorant formulated from the sulfides of paper mill operations and the mercaptans and phenols occurring as by-products of gasoline manufacture, was introduced in 1942. Shortly thereafter, Natural Gas Odorizing, Inc., offered other Captan odorants based on the branch chain mercaptans: isopropyl, tertiary butyl and secondary butyl.

When Pennwalt Chemical Co. acquired Sharples Chemical Co. in the early 1950's, Pentalarm 86 was dropped in favor of the Spotleak line, which was similar to the Captan line.

For a number of years in the 1950's the American Gas Association sponsored research on odorants at Arthur D. Little, Inc.[7-10] Screening of more

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6. Gill, C. E., "History and Purpose of Gas Odorization." Paper presented at IGT Odorization Short Course, Chicago, June 1965.

7. Deininger, N. and McKinley, R. W., "Investigation of Newodorants for Natural Gas," Interim Rep. No: 1, A. G. A. Gas Prod. Res. Rep. Arlington, Va., May 1953.

8. Kendall, D. A. and McKinley, R. W., "Development of Unique Odorants for Natural Gas," A. G. A. Gas Prod, Res. Rep. Arlington, Va., May 1953.

9. McKinley, R. W, and Larratt, A. E., "Study of Commercial Odorants for Natural Gas," A. G.A. Gas Prod. Res. Rep. Arlington, Va., May 1954.

10. McKinley, R. W. and McDowell, I. T., "Development of New Odorants for Natural Gas," and "Effect of Gas Odorant Adjuncts on the Odor Profiles of Natural Gas Odorants," A. G. A. Gas Prod. Res. Rep. Arlington, Va., August 1955.

than 300 materials failed to lead to an ideal odorant, but the program stimulated manufacturers to develop several improved odorants.

The early 1960's saw the increased popularity of mercaptan sulfide blends as improved odorants.[11-13] Advantages claimed for these mixtures are – reduction of tendency to fade, greater stability, and increased odor intensity.

Further developments in odorants will come, no doubt, out of the search for an odorant that has better soil penetration properties and in odorants for liquefied natural gas (LNG) and substitute natural gas (SNG). These latter innovations will probably not differ greatly from today's commercially available odorants.

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11. Gieruszczak, T. E., "Merits of Mercaptan-Sulfide Blends as Odorants," A.G.A. Oper. Sect. Proc. – 1964, 64-P-166.

12. Olsen, A. W., "Merits of Sulfide-Mercaptan Blends as Odorants," A. G. A. Oper. Sect. Proc. – 19.64, 64-P-169.

13. Olund, S. A., "Merits of Sulfide-Mercaptan Blends as Odorants," A. G. A. Oper. Sect. Proc. – 1964, 64-P-171.

IV. Gas Odorants in Current Use

A. Chemical and Physical Properties of Odorants

A number of physical and chemical properties of the low-molecular-weight organo-sulfur compounds are pertinent to their use as gas odorants. In recent years these have been discussed by Baum,[14] Nevers,[15] Fitzgerald,[16] Roberson,[17] and Blair.[18] Cencer, in 1967, presented a report on gas odorants and their properties to the A. G. A. Distribution Conference. (See Appendix B.)

More than a dozen properties are given in commercial odorant spe-cifications, but only a few are of practical significance in odorization technology. Some are important to odorant effectiveness, whereas others relate to odorant handling.

The specific gravity of an odorant is the ratio of the mass of a given volume of odorant to the mass of the same volume of water, both at a temperature of 60°F. Practically, it is easy to measure and can be used to distinguish several types of odorants.

The weight of odorant in pounds per gallon at 60°F is specified by suppliers for all commercial odorants. Because the weight per gallon can vary considerably over the temperature range normally encountered, temperature corrections must be made when measuring odorant consumption by reading a liquid-level gage at stated intervals. Otherwise inventory records can show a substantial error.

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14. Baum, E. O., "The Merits and Chemistry of Basic Odorants," in "Proceedings of the Twenty-Fourth Annual Appalachian Gas Measurement Short Course - 1964," Tech. Bull. No. 73, 499-500. Morgantown: West Virginia Univ., February 1964.

15. Nevers, A. D., "The Chemistry of Commercial Gas Odorants." Paper presented at IGT Odorization Short Course, Chicago, June 1965.

16. Fitzgerald, W. J., "Physical Properties of Odorants," ibid.

17. Roberson, S. T., "Chemical and Physical Properties of Odorants." Paper presented at IGT Odorization Symposium, Chicago, March 1971.

18. Blair, B. C., "Odorization of LPG and Natural Gas. Odorant Characteristics and Properties," in Proceedings of the Forty-Ninth International School of Hydrocarbon Measurement, 114-16. Norman: Univ. of Oklahoma, 1974.

The average molecular weight of an odorant, the sum of the weight percent of each component multiplied by its molecular weight, gives an indication of the composition of the odorant and is primarily useful to the analytical chemist.

When needle-valve-controlled drip-type odorizers were common, the viscosity – resistance to movement within a liquid – of odorants was of some importance. Although these odorizers are little used now, viscosity is still important where liquid meters are used to measure odorant flow through a line. Viscosity changes with temperature, and some types of flow meters are sensitive to viscosity changes.

Reid vapor pressure is the equilibrium vapor pressure at 100°F. These values are of little importance in actual odorization practice, but may indicate the degree of nuisance problems that can be caused when opening odorant drums or tanks in hot locations. The vapor pressure of some odorants drops sharply with temperature, and this behavior is sometimes responsible for reports that a drum of odorant has lost its smell. These observations are usually made during extremely cold weather, when the odorant emission is much less than in mild or hot weather, because of the low vapor pressure at low temperature.

The boiling range of an odorant is described by the distillation data, which are best presented as a curve showing temperature plotted against percent evaporated. The flatness of the curve for a given odorant is an indication of the suitability of that odorant for use in evaporation bypass odorizers. In general, blends with a spread of 40°F or less are suitable for this application. A high end point temperature can be an indication of unwanted "heavy ends" in the odorant. "Heavy ends" cause spillage odors to linger and prolong the nuisance.

In tables of physical properties of commercial odorants, volatility is given as the pounds of odorant vapor at saturation (in equilibrium with liquid odorant) in one million standard cubic feet of gas at 0°F and 1000 psi pressure. Large discrepancies exist in the data among odorants having similar chemical compositions, because in some cases the values were calculated from the vapor pressure of the odorant and in other cases were determined experimentally. Although these values for commercial odorants show that many times more than a sufficient amount of odorant to provide adequate warning can be put into a million cubic feet of gas, they do not assure that all the odorant added will remain in the gas, because they do not take into consideration the effects of pipe walls, dust, moisture, condensates, and differences in gas composition. Volatility data are more useful in comparing the probable degree of adsorptive loss in the pipeline of one odorant versus another,

Cloud point, which **is** an indication of the moisture content of an odorant, is the temperature at which a haze appears in an odorant as it is cooled. This haze forms as the odorant becomes supersaturated with water and the water droplets separate, giving the odorant a cloudy appearance. A low cloud point is desirable to avoid equipment failure caused when these droplets freeze and plug needle valves, orifices, etc. Tertiary butyl mercaptan and thiophane in particular must be thoroughly dried by the manufacturer to give low cloud points to odorants based on these compounds.

The temperature at which an odorant changes from the liquid state to the solid state is its freezing point. This is significant only with regard to tertiary butyl mercaptan, because it is the only odorant compound with a freezing point **(t 32%)** above —100%. Other mercaptans and sulfides are blended with TBM to provide antifreeze properties while maintaining the desired odor intensity.

Flash point is an indication of the flammability of an odorant. Its practical significance is related to storage and handling. All gas odorants have flash points higher than gasoline and lower than kerosene. Fire hazards can be minimized by exercising the same caution used in handling gasoline.

Although numerical values for water solubility of odorants are listed in the trade literature, they are not relevant to odorant absorption by water in contact with odorized gas. The partial pressure of the odorant, not the saturation level in water, limits odorant absorption from the gas. Solubilities of odorants in water are usually negligible, and the slight differences among the various odorants are of no practical significance.

When used at the rate of one pound per million cubic feet, the sulfur contribution of most odorants is approximately one-quarter grain per hundred cubic feet, much lower than the sulfur content of any competitive fuel. Under usual conditions, odorants are not **a** factor in pipeline corrosion.

The sulfur content of odorants is listed in tables of odorant properties as percent by weight., Its practical significance is two-fold: **1)** the sulfur content indicates the approximate molecular weight of the mercaptans and sulfides that make up the oodorant, and 2) the injection rate in pounds of odorant per million cubic feet of gas can be calculated conveniently from the results of gas analyses that commonly determine sulfur content as weight per unit volume.

In general, the chemistry of odorants is the chemistry of the low-molecular-weight organo-sulfur Compounds, particularly the lower molecular-weight mercaptans, the thioethers (alkyl sulfides), and the cyclic sulfide tetrahydro-thiophene (THT, or thiophane). A relatively few mercaptan and sulfide reactions relate to the performance of the commercial odorants.

Mercaptans are by far the most reactive class of odorant compounds. Of major importance is the oxidation of mercaptans to disulfides as typified by the reaction –

$$3Fe_2O_3 + 2CH_3CH_2SH \rightarrow CH_3CH_2\text{-}S\text{-}S\text{-}CH_2CH_3 + 2Fe_3O_4 + H_2O$$

This reaction is known to occur under the conditions prevailing in new pipelines, and results in the common phenomenon of odor fading. The resulting disulfides have practically no odor relative to the original mercaptans. The rate and extent of mercaptan oxidation is strongly affected by the quantities of mill scale, rust, and pipeline dust that frequently exist in pipelines.

The location of side chains on the carbon atom linked to the mercaptan radical decreases the activity of the mercaptan radical. Thus, tertiary butyl mercaptan is the most resistant to oxidation, followed by the secondary mercaptans such as isopropyl and secondary butyl mercaptans. Primary mercaptans are oxidized more easily than the others. If tertiary butyl mercaptan is arbitrarily assigned a relative reactivity of 1, the relative reactivities of some other compounds are as shown in the following table.[19]

Compound	Relative Reactivity
Tertiary Butyl Mercaptan	1.00 (Reference)
Isopropyl Mercaptan	1.36
Secondary Butyl Mercaptan	2.0
Normal Butyl Mercaptan	91.0
Normal Propyl Mercaptan	98.3
Normal Amyl Mercaptan	123
Ethyl Mercaptan	227
Methyl Mercaptan	1820
Hydrogen Sulfide	5000+

19. Natural Gas Odorizing, Inc., Organization Manual. Houston, n. d.

With strong oxidizing agents such as hypochlorite, permanganate, and peroxide, the oxidation can be carried through sulfenic and sulfinic acids to the sulfonic acids. Because the sulfonic acids are practically odorless when compared to mercaptans, strong oxidants are used to neutralize spilled mercaptan and to deodorize tanks and drums.

Another important chemical property of mercaptans to be considered is their reactivity with metals. Odorants in natural gas are frequently blamed for a variety of problems resulting from sulfide deposits found in tubing and fittings. However, corrosion by direct mercaptan attack at the temperatures and concentrations existing in odorized gas is improbable. Hydrogen sulfide is far more reactive than mercaptans and can surge through natural gas pipelines during periods of improper scrubber operation.

Concentrated liquid mercaptans are potentially more reactive with metals. For this reason copper and copper alloys should be avoided in odorant handling and storage.

The alkyl sulfides and the cyclic sulfide are highly resistant to oxidation and are far more stable chemically than the mercaptans. In addition, the cyclic sulfide is thermally more stable than sulfides or mercaptans.

B. Olfactory Characteristics

Although the chemical and physical properties of odorants are of considerable practical importance, olfactory characteristics are fundamental in the use of these sulfur compounds to give warning through the sense of smell of the presence of natural gas. An effective natural gas odorant should have a unique odor, an odor that the public will immediately associate with natural gas. All the commercial odorants in current use are considered to have a "gassy" odor, some more so than others; and in this survey 109 of 110 industry respondents indicated that the odorants in their gas are totally satisfactory in "effectiveness in warning of presence of gas" (question V-G).

The strength of response for a given concentration of an odorant should be sufficient to arrest attention and give warning when gas containing 1 lb/million SCF is present at a gas-in-air concentration of less than 1%. At usual odorization rates of 0.25 to 1.0 lb/million SCF, the concentration of odorant in the gas is 1 to 4 ppm by volume. A 1% gas-in-air concentration would result then in an odorant concentration of 10 to 40 ppb. Because the thresholds (the concentration at which the odor is first detected) for odorant compounds are about one part per billion or less, a more than adequate safety factor seems evident.

That currently used commercial odorants are adequate in strength or intensity is amply demonstrated by 107 "satisfactory" replies from 109 companies to the section of question V-G that deals with odorant effectiveness in regard to strength.

Gas industry odor technologists use the term "impact" to describe ". . . the initial sensory impression received by the observer.. . ." Impact includes such factors as intensity, feeling factors (sensory responses, other than olfactory, occurring in the mouth, nose, and eyes), and odor character. It is generally agreed that mercaptans produce a greater impact than sulfides. However, just as the intensity of mercaptan-sulfide blends may be greater than that of either compound alone (synergism), greater impact may also result from blending mercaptans and sulfides.

When the sensitivity of observers to an odorant is unaffected during repeated exposure, the odorant is described as having "persistence." This is in contrast to an odorant that fatigues or causes diminished sensitivity after repeated exposure. Of 110 replying companies, 103 rated the odorants in their gas "satisfactory" as to persistence; seven checked "needs improvement."

Those in the gas industry responsible for odorization are well satisfied with the olfactory characteristics of today's odorants. In answer to those questions relating to olfactory properties, we received 319 replies of "satisfactory" and 10 of "needs improvement."

C. Commercial Odorants

Most gas odorants today are about the same chemically as they were in the early to middle 1960's. However, the mercaptans and sulfides are made synthetically and almost any pure compound is available as well as any combination of mixtures. Because the number of pure compounds involved is far less than the innumerable quantities of mixtures used as natural gas odorants, it is appropriate to discuss each compound separately.

More tertiary butyl mercaptan (TBM) is used in making commercial gas odorants than any other single component. In this present survey 70 companies of 98 companies odorizing gas used an odorant containing TBM as the major component. It has a low odor threshold, a "gassy" odor, and is the most resistant to oxidation of all the mercaptans. Because of its high freezing point (32° F), TBM has to be blended with one or more other compounds to prevent freezing when being used as an odorant. A very popular odorant is a mixture of 75% to 80% TBM and 20% to 25% other mercaptans or dimethyl sulfide.

Second in importance as a component of odorant mixtures is isopropyl mercaptan (IPM). It is made from hydrogen sulfide and propylene, and the commercial product always contains some normal propyl mercaptan. It is popular in odorizing gas that has some natural odor. Although not as resistant to oxidation as TBM, it is sufficiently stable for use in normal applications as a gas odorant.

Normal propyl mercaptan is more easily oxidized than the branched chain mercaptans and is not a major component in gas odorants. However, it is present in low concentrations in odorants that contain isopropyl mercaptan because it is a by-product from the manufacture of IPM and is difficult and expensive to remove. Even in small amounts it does contribute to the overall character of odorant blends, giving "body" to the odorant. Normal propyl mercaptan has a stong odor and presents problems in handling because it is difficult to mask.

Secondary butyl mercaptan was prevalent in mercaptan mixtures recovered as refinery by-products. It is now made synthetically and is blended in odorants used for gas that contains some natural odor and in odorants for small wick odorizers. Its high boiling point and low vapor pressure prevent over-odorization in hot summer weather. This mercaptan is less resistant to oxidation than TBM, but this is generally not a problem in its use as a gas odorant. Because it is difficult to mask, it can be used to boost low odor levels caused by temporary masking conditions in a pipeline.

The cyclic sulfide, thiophane (tetra hydrothiophene, or THT), was most often used in concentrated form. It is no longer highly popular, but is sometimes used as a supplemental odorant. Methanol and hexane are sometimes used as diluents, and THT-mercaptan and THT-sulfide blends are available.

It has a "gassy" odor but low impact. It is difficult to over-odorize with THT because, above a certain concentration, odor intensity increases very little if at all. Although liquefied petroleum (LP) gas is not covered in this report, THT is sometimes the odorant chosen for LP gas odorization.

The sulfides, particularly dimethyl sulfide (DMS), are widely used as blend materials, most frequently with TBM. Originally a by-product of the wood-pulp industry, DMS has been used extensively in mercaptan-sulfide blends. Pure DMS has an odor associated with the wood-pulp industry, but when it is mixed with TBM, the odor of the blend is a typical "gassy" odor. Dimethyl sulfide does not oxidize in pipelines, and the use of a mercaptan-sulfide blend assures that some odor will remain if the mercaptan is lost through oxidation. Mercaptan-sulfide blends, however, have less impact than straight mercaptan mixtures. Blends of DMS-mercaptan range in concentration from 10% DMS to 90% DMS. Although weaker than straight mercaptan odors, these blends can be detected under normal conditions at gas-in-air concentrations below 1%.

Diethyl sulfide has seen limited use recently in this country, but is the major component (72% by weight) of the odorant that British Gas has adopted for national use. With the exception of a lower vapor pressure, its chemical and physical properties do not differ markedly from those of dimethyl sulfide.

Methyl ethyl sulfide has replaced dimethyl sulfide in a few commercial blends. Because its boiling point is close to that of TBM, very narrow boiling-range mixtures can be blended that may be useful in vaporization-type odorizers. Its odor intensity is somewhat less than that of DMS, but it should present no problems in mercaptan-sulfide blends.

V. Odorization Practices in the Gas Industry

A. Criteria for Selection of an Odorant

1. Odorization Program Goals

In 1930 Holtz[20] reported, "The gas utilities operating in the Los Angeles Basin united in investigating the feasibility of odorizing the natural gas so as to enable easy detection of small leaks." Twenty years later, Powell[21] gave these reasons for adding odorant to natural gas: "...for the main purpose of giving a warning of the presence of gas leaking from unlit appliances or piping connections into a dwelling before an explosive concentration of the gas can accumulate. Secondarily, the discovery of the location of leaks is aided if the escaping gas has an odor."

According to Loper (1956),[22] "Odorization is performed for the sole purpose of giving to the gas an odor which will be readily detected when a gas leak is present." His company based its odorization policy on the premise that "... gas must have an odor that is readily detected when a gas leak is present, but at the same time the gas should not have an excessive odor that will result in an undue volume of reported 'nuisance' leaks."

Cofield[23] in 1966 stated that his (large transmission) company odorizes for two reasons: "The first is to fulfill our tariff provisions.. .. Secondarily, we must fulfill the requirements of certain states' regulatory bodies.. .."

In the same year, Kyhos[24] gave as the principal reasons why odorization of gas is necessary, "...safety and regulatory requirements which, of course, leads us back to safety – public welfare, the safety of the consumer." While

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20. Holtz, L., "Odorization of Natural Gas," Proc. Pac. Coast Gas Assn. 21, 303-13 (1930).

21. Powell, J. S., "Selection of an Odorant for Natural Gas Odorization," Proc. Pac. Coast Gas Assn. 41, 134-38 (1950).

22. Loper, B. H., "Odorization From the Customers Service Department Viewpoint," A. G. A. Proc. – 1956, CEP-56-12.

23. Cofield, W. W., "Criteria to Consider When Setting Specifications for Odorants," A. G. A. Oper. Sect. Proc. – 1966, 66-P-494.

24. Kyhos, B., "Odorization for Distribution Systems," Gas Age 133, 31-33 (1966) August.

serving on a panel on odorization in 1970, Calaway et al.[25] had this to say, "The fact that all gas distributors use three to ten times as much odorant as that required by law indicates that safety and leak detection are foremost in the minds of gas industry personnel." Lehman[26] in 1971 concluded, "...our goal in an odorization program is to accomplish maximum safety at minimum cost." He goes on to say, "It would be desirable to have an odorant that would be unnoticed when the quantity of gas escaping is insignificant, but gives ample warning of a potential hazard."

The literature excerpts quoted above are representative of numerous expressions of two themes manifesting odorization goals and recurring frequently throughout the 45-year history of natural gas odorization: "leak detection" and "safety." Concommitant with the goal of safety is the desire for an odorization technology that will minimize leak complaints caused by insignificant leaks not presenting a hazard. A third theme, "regulatory requirements," appears with increasing frequency in more recent papers.

Although our questionnaire did not inquire about goals of odorization programs, we would conclude, based on past history and on comments made during personal interviews and in private communications, that gas industry odorization programs are designed to achieve these goals – 1) to provide for the safety and protection of property, consumers, and the general public; 2) to facilitate leak detection; and 3) to meet state and federal regulations and national codes.

2. Characteristics of an Ideal Odorant

As early as 1930 Holtz[27] set forth the "general characteristics that a desirable odorant should possess." He listed this summary of "necessary qualities":

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25. Calaway, M.E., Smith, C. D. and Woolfall, G. E., "Odorization (Panel)," in Proceedings of the Forty-Fifth Southwestern Gas Measurement Short Course, 183-88. Norman: Univ. of Oklahoma, 1970.

26. Lehman, E. A., "Selection of an Odorant." Paper presented at IGT Odorization Symposium, Chicago, March-April 1971.

27. Holtz, L., op. cit.

1. Harmless and neither toxic nor nauseating.
2. A penetrating odor similar to the artificial gas smell.
3. Noncorrosive.
4. Insoluble in water.
5. Odor must be retained by gas and not absorbed by mains or meters.
6. Burn completely without harmful or odorous products of combustion.
7. Must not set up chemical reactions.
8. Must be cheap and readily available.

In 1941 Parker[28] added "non-fatiguing to the sense of smell."

Powell[29] in 1950 suggested for this ideal, "It should have a characteristic odor so that the odor of the odorized gas would not be confused with other odors common in dwellings." Johnson[30] in the same year described the odor of ideally odorized gas as "unpleasant, distinctive, similar to that of manufactured gas. . . ." Both Powell and Johnson advocated effective soil penetration as a characteristic of the ideal odorant. Covell[31] considered a gassy odor less important than "...that the odor not be absorbed by the soil in case of leakage." According to Whitehead,[32] an odorant that would "approach optimum customer safety at minimum expense. . . would be one having an early threshold value and increasing in odor intensity to one of 'moderate to strong' at a gas-to-air ratio of 0.5 percent." This odorant intensity should not increase at higher injection rates. Such an odorant, in Whitehead's opinion, "would provide the flexibility needed to assure a balance between soil penetration and odorant stability against fading. . ."

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28. Parker, R. W., "Survey of Odorizing Practice in Gas Transmission," Petrol. Eng. 12, No. 10, 14, 114, 116, 119, 120 (1941).

29. Powell, op. cit.

30. Johnson, E. E., "New Developments in Odorants," A. G. A. Proc. – 1950, PC-50-21.

31. Johnson, E. E., ibid.

32. Whitehead, A. L., "Experiences With Major Changes in Odorization Practices," A. G. A. Oper. Sect. Proc. – 1970, 70-D-32.

With the exceptions of soil adsorption problems and infrequent fading because of mercaptan oxidation, today's commercially available odorants meet the major criteria proposed for an ideal odorant. No one odorant or blend of odorants, however, is best for all systems at all times. A recent tabulation of commercial gas odorants (Appendix C) lists 55 natural gas odorants from three suppliers.[33] Because competition dictates that they all supply comparable products, this total really represents 15 to 20 distinct odorants. That such a variety of odorants exists to serve the gas industry's needs substantiates Henderson's contention voiced in 1952,[34] that the often heard "prayer for an ideal odorant" would go unanswered. "One would get the impression," he wrote," that a material could possibly be produced which would be ideal for any and all companies to use regardless of the local circumstances and conditions surrounding the distribution and utilization of gas. This is a completely fallacious theory." In corroboration of Henderson's views, some companies today use as many as three or four different odorant formulations to cope with a variety of local conditions and the unique characteristics of individual transmission and distribution systems.

B. Industry Practice – Odorant Selection and Odorization Rates

1. Gas With Naturally Occurring Odor

Thirty-six companies reported that their gas has naturally occurring odor (question 11-A). For 20 companies the odor was of a sulfur type; for 4, nonsulfur (e.g., hydrocarbon); and for 13, a combination of sulfur and nonsulfur (Figure V-1). (One company reported two situations.)

The minimum percent of gas in air just detectable reported by 8 companies was <0.1%; by 18, between 0.11% and 0.50%; by 4, between 0.51% and 0.99%; and by 1 company, 1%.

Thirty-one companies suppplement the naturally occurring odor, 28 continuously and 5 intermittently. Two companies supplement both continuously and intermittently in different parts of their systems.

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33. Heath Consultants Inc., Commercial Gas Odorants and Relative Odor Contribution. Stoughton, Mass., 1973.

34. Henderson. E. L.. "Odorization of Gas." A. G.A. Proc. -- 1952, DS-52-1.

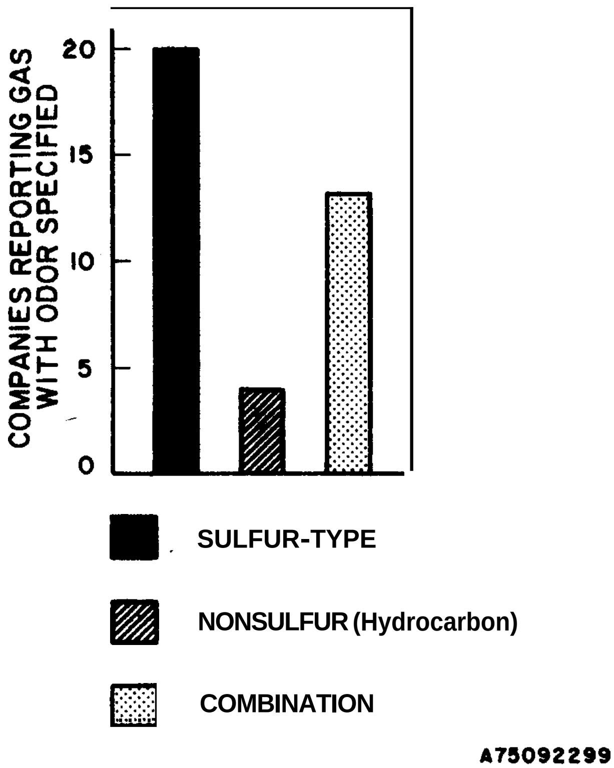

Figure V-1. KINDS OF NATURALLY OCCURRJNG ODORS

Straight mercaptan odorants are used most frequently (14 companies) for supplemental odorization of gas with a naturally occurring smell. Tertiary butyl mercaptan is the major component of the straight mercaptan formulations used by 11 companies. Mercaptan-sulfide blends, next in popularity, are used by 11 companies. Of the 11 companies, 9 use TBM-sulfide blends. Although thiophane is used by eight companies to supplement naturally occurring odor, two of the eight use a dilute thiophane formulation.

Those companies using straight mercaptans to supplement naturally occurring odor do so at rates from 0.25 lb/million SCF to 1 lb/million SCF. The rates mentioned most frequently were in the range 0.25 to 0.50 lb/million SCF.

Mercaptan-sulfide blends were added in quantities from 0.1 to 1.4 lh/ million SCF. A rate of 0.75 lb/million SCF was reported by six companies. Introduced amounts ≤0. 5 lb/million SCF were reported by three companies. Two companies reported rates between 1.0 and 1.4 lb/million SCF.

Of the six companies that reported using thiophane (concentrated) to supplementally odorize gas having a naturally occurring smell, four add 0.75 lb/ million SCF, one adds 1.29 lb/million SCF, and one adds 1. 5 to 2.0 lb/million SCF. The two companies using dilute thiophane introduce 0. 3 lb/million SCF and 1.47 lb/million SCF, respectively,

Twenty-six companies replied to the question (11-A, 6), "What final odor level is achieved (supplemental and naturally occurring)?" (See Table V-1.)

Table V-1. FINAL ODOR LEVEL, NATURALLY OCCURRING PLUS SUPPLEMENTAL

Final Odor Level, lb/10⁶ SCF	Number of Companies Providing Utility Gas With This Final Odor Level
0.25-0.49	2
0.50-0.74	6
0.75 -0.99	9
1.00+	5
Final Odor Level, % gas in air	
<0. 1	1
0.1-0.25	2
<1	1
No answer	5

Fifteen companies, or 58 percent of those replying to the question, reported final odor levels from 0.5 to 0.99 lb/million SCF, five (19%) reported 1.0 lb/million SCF or more, and two companies (8%) reported <0.5 lb/million SCF. Four companies reported equivalent % gas-in-air detection limits, three (12%) with <0.25% gas in air and one (4%) with <1% gas in air.

2. Gas With No Naturally Occurring Odor, to Which Odorant Is Added

Of the 112 companies replying to the questionnaire, 98 companies add odorant to gas with no naturally occurring smell (question II-B). Seven companies use two different odorants, and three companies use three different odorants. Straight mercaptan blends are most popular; these are added by 52 companies. (See Table V-2.) Forty-five of these companies introduce TBM-base mercaptan blend-s; two others add blends of isopropyl and other mercaptans; another six reported mercaptan blends without further designation. (One company employs two different mercaptan-base odorants.)

Tertiary butyl mercaptan-sulfide blends constitute the next most popular class of compounds used to odorize gas with no natural smell. Twenty-one companies prefer TBM-DMS blends, and four prefer TBM-MES blends.

Table V-2. ODORANT SELECTION FOR GAS WITH NO NATURALLY OCCURRING ODOR

Odorant Type	Number of Companies Providing Utility Gas With This Odorant
TBM-other mercaptan	45
TBM-sulfide	25
Isopropyl-other mercaptan	2
Isopropyl-other mercaptan-sulfide	7
"Mercaptan"	6
Thiophane	19
Sulfide (major component)-mercaptan	6
Ethyl mercaptan	1

The cyclic sulfide thiophane is used by 18 companies. It is added without dilution by 11 companies and with dilution by 8. (One company adds both concentrated and dilute thiophane.) In four instances the diluent is TBM; four companies did not identify the diluent.

Seven companies odorize with an isopropyl mercaptan containing lesser amounts of other mercaptans and sulfides,

Sulfide-mercaptan odorants are used by five companies. Dimethyl sulfide is the major component in three formulations, methyl ethyl sulfide in two and diethyl sulfide in one. (One company uses two different MES blends.) One DMS blend contains isopropyl mercaptan, and the other two contain TBM. One DES blend contains TBM; the other two contain TBM and secondary butyl mercaptan, respectively.

One company adds ethyl mercaptan to propane-air mixtures used for peak-shaving.

Odorization rates for TBM-mercaptan blends range from 0.25 to 1.5 lb/million SCF. Seventeen companies reported quantities ≤ 0.5 lb/million SCF. Fourteen companies reported introducing between 0.51 and 0.75 lb/million SCF. Eleven companies add odorant at rates of 0.76 to 1.0 lb/million SCF, and three add 1.0 to 1.5 lb/million SCF.

TBM-sulfide blends are added in amounts ranging from 0.2 to 1.0 lb/million SCF. Seven companies add ≤ 0.5 lb/million SCF; nine add 0.51 to 0.75 lb/million SCF, and nine add 0.76 to 1.0 lb/million SCF.

Of 11 companies that odorize with concentrated thiophane at rates of 0.23 to 2.0 lb/million SCF, seven add ≤ 0.5 lb/million SCF, three add 0.51 to 0.75 lb/million SCF, and one adds 1.6 to 2.0 lb/million SCF. Thiophane-TBM blends are added at a rate ≤0.5 lb/million SCF by two companies and in quantities of 0.6 lb/million SCF and 0.75 lb/million SCF by two others. Four companies add other dilute thiophane odorants at rates of 1.0 to 2.0 lb/million SCF.

Isopropyl mercaptan is the major component in the odorant blends used by nine companies. Two of these blends contain only mercaptans, but six contain approximately 10% DMS and one contains 10% DES. The straight mercaptan blends are added in quantities of 0.15 lb/million SCF and 0.6 lb/million SCF. Four of the sulfide-containipg blends are added at a rate of 0.5 lb/million SCF, and three at 0.75 lb/million SCF.

Six companies. add odorants described only as "mercaptan" at rates of 0.1 to 1.0 lb/million SCF. Three add 0.75 lb of odorant/million SCF of gas, two add 1.0 lb, and one adds 0.1 lb.

Another six companies odorize with sulfide (major component)-mercaptan formulations at rates of 0.6 to 2.5 lb/million SCF: three at approximately 0.75, two at approximately 1.0, and one at 2.0 to 2.5 lb/million SCF.

The odorization rate for ethyl mercaptan that one company adds to propane-air mixtures used for peakshaving is 0.5 to 1.5 lb/million SCF (average, 0.55).

Table V-3 summarizes the odorant selection and odorization rate data for gas with no natural smell, to which odorant is added. (See Table V-3.)

Table V-3. ODORANT SELECTION AND ODORIZATION RATE
(Number of Companies Odorizing at Selected Intervals)

	Odorant Addition Rate, lb/10^6 SCF					
	≤0.5	0.51-0.75	0.76-1.0	1.1-1.5	1.6-2.0	2.1-2.5
TBM-mercaptan	17	14	11	3	--	--
TBM-sulfide	7	9	9	--	--	--
THT (concentrated)	7	3	--	--	1	--
THT-TBM	2	2	--	--	--	--
THT-diluent	--	--	1	2	1	--
IPM-mercaptan	1	1	--	--	--	--
"Mercaptan"	1	3	1	1	--	--
IPM-mercaptan-sulfide	4	3	--	--	--	--
Sulfide-mercaptan	--	2	2	1	--	1
Ethyl mercaptan	--	1	--	--	--	--

Question II-B, 1(c) asks, "What minimum percent of gas in air is normally detected as a just-recognizable gas odor?" The detection limits reported range from < 0.002% [sic] to 1% gas in air. Of the values reported, 52% were ≤ 0.25% and 74% were ≤ 0.50%. (See Table V-4.)

Thirty-three companies reported that they obtain odorized gas from a supplier (question II-B, 2). Five companies receive gases blended with two different odorants, and one buys gases infused with three different odorants. Suppliers add TBM-mercaptan odorants to gas delivered to twenty companies [question II-B, 3(a)]. Eight companies receive gas containing an isopropyl mercaptan odorant, and four receive gas containing a TBM-sulfide odorant.

Table V-4. DETECTION LIMITS FOR GAS WITH NO NATURALLY OCCURRING ODOR TO WHICH ODORANT HAS BEEN ADDED

Ranges of Detection Limits, %	Number of Companies Providing Utility Gas With Detection Limits in This Range*
so. 1	28
0.11-0.25	23
0.30-0.50	22
0.70-1.0	16
<1%	2
Unknown	7

* Fourteen companies do not add odorant.

* * *

The gas supplied to **two** companies is odorized with thiophane. One company receives gas odorized with "mercaptan." Five companies do not know what odorant is in the gas supplied to them.

Those gases odorized with TBM-mercaptan blends contain odorant at levels from 0.38 to 1.5 lb/million SCF [question II-B, 3(b)]. Thirteen companies receive gas with S0. 5 lb of odorant/million SCF *of* gas. Four receive gas odorized at a level of 0.51 to 0.75 lb/million SCF, and one at 1.5 lb/million SCF. Two companies do not know the odorant level of the gas they receive.

Isopropyl mercaptan-other mercaptan odorants at levels between 0.25 and 0.5 lb/million SCF are present in the gas supplied to six companies. Two companies receive gas with 0.6 lb/million SCF of this odorant.

Four companies receive gas odorized with TBM-sulfide blends. One odorant level is 0. 34 lb/million SCF; the other three are approximately 0.75 lb/million SCF.

Thiophane (concentrated) at a level of 0.4 lb/million SCF is in the gas supplied to one company; a dilute thiopane (60%) concentration of 0 to 1 lb/million SCF is used in the gas supplied to another.

One company receives gas containing 0. 35 lb/million **SCF** of "mercaptan."

Of the five companies that did not identify the odorant in the gas they receive, four could not report the odorant level; one reported a level of 0.5 lb/million SCF.

Detection limits ["minimum percent of gas in air normally detected as a just-recognizable gas odor" — question II-B, 3 (c)] reported for odorized gas received from a supplier were in the range 0.1% to 1%. Forty-five percent of the values reported for 40 gases were in the range 0.04% to 0.3% gas in air; 70% were in the range 0.04% to 0.5%. Eleven of 20 values reported for gases with TBM-mercaptan odorants and three of four values for gases with TBM-sulfide blends were ≤0.3%. Five of eight values for gases containing isopropyl mercaptan odorants were greater than 0.4%. One company receiving gas odorized with thiophane (concentrated) reported a minimum detection limit of 0.45%; another receiving gas odorized with dilute thiophane reported a minimum detection limit of 0.1% gas in air. The one company receiving gas odorized with "mercaptan" also reported a minimum detection limit of 0.1%. Of five companies receiving gas with unidentified odorant, four reported detection limits of ≤0.5% gas in air.

Fourteen companies supplement a supplier's odorized gas with their own odorant (question II-B, 4). The total odorant content of the gas supplied to customers was from 0.5 to 1.0 lb/million SCF for eight companies, from 1.1 to 1.5 for four, and from 1 to 2 for one. One company did not report the odorant content of the gas supplied to its customers.

C. Odorant Injection

1. Equipment Types and Characteristics

Equipment for introducing odorant into a gas stream falls into two broad classifications: evaporation- or absorption-type odorizers (including wick odorizers) and liquid-injection odorizers. Papers by Buczek,[35] Detert,[36] Lincoln,[37] and Trader[38] provide a thorough review and summary of the operating characteristics of the two types of odorizers.

35. Buczek, F, L., "Operation and Maintenance of Gas Odorizing Equipment," in "Proceedings of the Twenty-Fifth Annual Appalachian Gas Measurement Short Course – 1965," Tech. Bull. No. 77, 237-57. Morgantown: West Virginia Univ., February 1966.

36. Detert, F. L., "Evaporation Odorizers." Paper presented at the IGT Odorization Symposium, Chicago, March 1971.

37. Lincoln, J. E., "Liquid Injection Odorizer Installations," ibid.

38. Trader, R. L., "Selection of Odorizer Instrumentation," in "Proceedings of the 32nd Annual Appalachian Gas Measurement Course – 1972," Eng. Exp. Sta. Bull. No. 108, 213-19. Morgantown: West Virginia Univ., 1973.

Evaporation odorizers mix odorant vapor with gas in a bypass stream and then return the mixture to the pipeline. The largest number of odorizers in use today are of this type, but the largest volume of gas is odorized with liquid-injection odorizers. Evaporation-type odorizers are generally lower in cost. They are used most successfully when low volumes of gas (<10 million SCF/day) are to be odorized and when the gas contains essentially no water or liquid hydrocarbons.

To minimize temperature variations that can cause changes in odorant vapor pressure resulting in fluctuations in odorant addition rate, odorant supply tanks for these systems are often located underground. The odorant used with these odorizers should have a narrow distillation range to prevent enrichment of higher boiling components in the tank, resulting in variations of odor level.

Evaporation-type bypass odorizers are extremely simple because of the absence of moving parts. Despite this simplicity, ideal operation is usually precluded because of the effects of temperature changes, the presence of condensate in the gas, and a poor choice of odorant.

Wick-type odorizers are used to odorize gas furnished to an individual customer, e. g., a farm tap off a transmission line or a rural system serving only a few customers. Overodorization is a problem at low gas flow rates.

The two most common types of commercially available injection odorizers are the meter-driven pump-type odorizer and the positive-displacement chemical-feed pump. The meter-driven pump-type odorizer utilizes a pressure differential at the full gas stream pressure – produced by an orifice or a partially closed valve – to drive a small domestic meter located in the odorizer compartment. The meter is connected through a chain-and-sprocket drive to a scoop that dips liquid odorant from a bowl and transfers it into a tube connected to the gas stream. The odorant then evaporates and mixes with the gas stream. The rotational velocity of the meter varies directly with the main gas flow rate, so that proportional addition of odorant is achieved. The entire mechanism is encased and operates at line pressure.

Meter-driven pumps operate over a wide range of odorant injection rates; however, because of meter wear at high flow rates, their use is generally restricted to stations with throughputs of <100 million SCF/day.

Positive-displacement chemical-feed pumps are gaining in popularity, particularly in systems with very high volume gas flows. Diaphragm pumps are preferred over piston displacement pumps because of fewer problems with leakage of gas odorant around the packing and the stuffing box.

A large number of pump installations are set up for automatically controlled proportioning of odorant addition. However, extensive auxiliary instrumentation is required to vary the rate of odorant addition with changes in gas flow. Two types of odorant-injection control are used. The first uses an orifice and transducers to convert the static and differential pressures to signals that serve as inputs to a pneumatic-flow computer. Further conditioning of the signal results in an output to a valve positioner, which adjusts the stroke of the pump to inject odorant in proportion to the flow. A second method of injection control uses an electrochemical titrator to monitor the odorant level of the gas downstream of the injection and to feed back the result to a controller that adjusts the odorant-injection rate.

Drip-type odorizers represent the third class of liquid-injection odorizers. They are used primarily for very small to moderate flow rates and are often preferred to provide temporary supplemental odorization of new lines.

Table V-5 summarizes the replies to the first part of question 111-A, which asks users to identify the kinds of odorizers they operate.

Table V-5. TYPES OF ODORIZERS IN USE

Odorizer Type	Number of Companies Operating This Type of Odorizer
Wick	30
Absorption-Type Bypass	71*
Drip	5
Meter-Driven Pump	51†
Pos-Displ Pump	73‡

* Five companies operate two types of absorption-type bypass odorizers.

† One company operates two types of meter-driven pump-type odorizers.

‡ Six companies operate two types of positive-displacement pump-type odorizers, and one operates three types.

2. Maintenance and Operating Experiences

Evaporation-type odorizers are adversely affected by variations in odorant temperature, by odorant blends with broad distillation ranges, and by condensable hydrocarbons in the gas. Temperature fluctuations can be minimized by burying the odorant tank underground, and careful selection of odorant minimizes accumulations of heavy ends. Knock-out traps are recommended where significant concentrations of condensable hydrocarbons are encountered. Oxidation and deterioration of the odorant can be a factor if a very high temperature has to be maintained to ensure adequate vaporization. Adjustment of the restriction in the main line for correct pressure differential is frequently a trial-and-error procedure that can require days and weeks to find the correct adjustment.[39]

Wick-type odorizers require periodic draining of accumulated heavy ends; another source of trouble arises from the deposition of dust from the inlet gas on the wicks.[40]

Bubble-type odorizers present the same problems as other bypass odorizers. Odorant concentrations change with pipeline pressures and ambient temperatures, and partial fractionation of odorants may also occur. Frequent adjustments are required; even then this type of odorizer can over- or underodorize the gas stream.[41]

Drip-type odorizers are susceptible to plugging of the odorant needle valve or liquid orifice used to control the liquid-odorant flow. Poor control of liquid flow also results from ambient-temperature fluctuations, changes in pipeline pressure, and changes in the liquid level in tanks in gravity-fed installations.

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39. Lee, H. L., "Design and Operation of Odorization Installations," in "Proceedings of the Twenty-Second Annual Appalachian Gas Measurement Short Course - 1962," Tech'. Bull. No. 67, 300-09. Morgantown: West Virginia Univ., February 1963.

40. Covell, P. L., "Experience in Odorization Shows Need for Standardized Procedures," Amer. Gas J. 171, 27-29 (1949) December.

41. Reynolds, L., "Methods of Odorization," in "Proceedings of the Twenty-Ninth Annual Appalachian Gas Measurement Short Course - 1969," Eng. Exp. Sta. Bull., 389-91. Morgantown: West Virginia Univ., 1970.

The major problem encountered with meter-driven pump-type odorizers is frequent servicing to replace worn parts, particularly where large gas loads (exceeding 20 million SCF/day) are odorized. Hydrate formation has caused sticking or blocking of the odorant float valve. When the valve is blocked open, all of the odorant drains out of the storage tank, In earlier designs the odorant drained into the system. Later designs incorporate a safety overflow tank equal in volume to the storage tank.[42]

These odorizers should be serviced every *6* months, and the meter should be removed and rebuilt at 18 to 24-month intervals as part of a preventive maintenance program.

Positive-displacement pumps of the piston type require frequent changes of lubricating oil, which becomes contaminated with odorant. Some users have observed rapid wear and short plunger life because it is sometimes necessary to tighten the packing gland excessively to prevent odorant leakage to the atmosphere. A complete overhaul may be necessary as frequently as every 2 years in order to renew the plunger and packing.

Diaphragm-type positive-displacement pumps are not subject to the contamination and leakage problems of piston pumps. They are generally used with automatic control of injection rate. Vapor lock can be a problem, and provision is often made to provide a constant head of liquid odorant to the intake of the pump in order to avoid vapor lock.

Newby and Wilby[43] described the experience of the Southern California Gas Co. with integrating direct-liquid-injection odorizers. These units, in which an integrating orifice meter is used to inject liquid odorant at a rate proportional to gas flow, are very accurate over a wide range of gas flow rates. Mechanically they are extremely reliable. Their operation is not affected by temperatures, nor by the presence of water or other contaminants in the gas. Adjustment of odorant addition rate is positive and can be made quickly and easily. One man, using simple tools, can easily inspect, remove, and replace all components.

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12. Lee, H. L., op. cit.

43. Newby, A. B. and Wilby, F. V., "An Improved Odorieing Integrator," Proc. Pac. Coast Gas Assn. 48, 112-16 (1957).

An automated odorizer described by Vlasek[44] uses a pneumatically driven pump to inject odorant into gas. The pump consists of an enclosed Bourdon tube whose free end is coupled with a reciprocating pneumatic motor. Seven of these pumps operated for 2 years with no trouble whatever. The only difficulty experienced was presented by the seal on the shaft. A change in seal material corrected the problem.

In question 111-A users of odorant-addition equipment were asked to evaluate their odorizers in terms of operating and maintenance characteristics. There is good correlation between these evaluations and the experiences reported in the literature by users of each type of odorizer. For example, positive-displacement chemical pumps, which have been reported to be virtually trouble-free and extremely accurate, are used by 73 companies and were rated "satisfactory" or "outstanding" in all respects by 54 companies (74%). (See Table V-6.)

Meter-driven pump-type odorizers, another class of liquid-injection odorizers, are used by 51 companies. One company operates two types. Only 28 companies (55%) consider this type of odorizer "satisfactory" or "outstanding" in all categories. This reflects maintenance difficulties and problems in maintaining constant rates of odorant addition (Table V-7).

The third type of liquid-injection odorizer, the drip odorizer, is used by only five companies represented in the survey. (See Table V-8.) The limited data from this small sample should be interpreted with caution. However, the only problem they appear to present relates to maintaining constant odorant-addition rates. No "unreliable" or "outstanding" ratings were reported.

Ratings assigned to absorption-type bypass odorizers are indicative of users' problems with fractionation of odorant, checking for satisfactory operation, and maintaining set addition rates (Table V-9). Despite these shortcomings they make up, based on the results of our survey, the second most popular odorizer class. However, only 24 of 71 companies (34%) considered them "satisfactory" or "outstanding" in all five categories.

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44. Vlasek, H. C., "Design of an Automated Odorizer," A.G.A. Oper. Sect. Proc. - 1968, 68-D-71.

Table V-6. EVALUATION OF POSITIVE-DISPLACEMENT PUMP-TYPE ODORIZERS
(Number of Respondents* Assigning Each Rating)

Rating	Operating or Maintenance Characteristics† A	B	C	D	E
Outstanding	29	10	27	20	33
Satisfactory	45	62	48	46	47
Needs improvement	5	8	6	9	0
Unreliable	2	1	0	3	0
No reply	--	--	--	3	1

* Seventy-three companies operate this type of odorizer; six report two models; one company reports three models.

† A Ability to maintain a set addition rate over the designed 'range of gas flow rates.

B Ease of maintenance.

C Ease of checking for,satisfactory operation.

D Operation at set odorant-addition rates over summer-winter temperature changes.

E Freedom from odorant composition changes such as selective evaporation of lighter components.

Table V-7. EVALUATION OF METER-DRIVEN PUMP-TYPE ODORIZERS
(Number of Respondents" Assigning Each Rating)

Rating	Operating or Maintenance Characteristics† A	B	C	D	E
Outstanding	11	4	6	7	11
Satisfactory	36	31	42	35	38
Needs improvement	4	16	3	8	0
Unreliable	0	1	1	2	0
No rely	1	--	--	--	3

* Fifty-one companies operate this type of odorizer; two companies operate two models.

† A Ability to maintain a set addition rate over the designed range of gas flow rates.

B Ease of maintenance.

C Ease of checking for satisfactory operation.

D Operation at set odorant-addition rates over summer-winter temperature changes.

E Freedom from odorant composition changes such as selective evaporration of lighter components.

Table V-8. EVALUATION OF DRIP-TYPE ODORIZEKS
(Number of Respondents" Assigning Each Rating)

Rating	Operating or Maintenance Characteristics†				
	A	B	C	D	E
Outstanding	0	0	0	0	0
Satisfactory	3	5	5	3	4
Needs improvement	2	0	0	2	1
Unreliable	0	0	0	0	0

* Five Companies.

† A Ability to maintain a set addition rate over the designed range of gas flow rates.

B Ease of maintenance.

C Ease of checking for satisfactory operation.

D Operation at set odorant-addition rates over summer-winter temperature changes.

E Freedom from odorant composition changes such as selective evaporation of lighter components.

Table V-9. EVALUATION OF ABSORPTION-TYPE BYPASS ODORIZERS
(Number of Respondents* Assigning Each Rating)

Rating	Operating or Maintenance Characteristics†				
	A	B	C	D	E
Outstanding	0	13	3	1	3
Satisfactory	43	52	44	38	45
Needs improvement	29	11	24	31	22
Unreliable	4	0	5	6	4
No reply	--	--	--	--	2

* Seventy-one companies use these odorizers; five use two models.

† A Ability to maintain a set addition rate over the designed range of gas flow rates.

B Ease of maintenance.

C Ease of checking for satisfactory operation.

D Operation at set'odorant-addition rates over summer-winter temperature changes.

E Freedom from odorant composition changes such as selective evaporation of lighter components.

Nearly 11,000 wick-type odorizers are used by **30** companies for farm taps, rural services, individual customers, and company domestic use. Ten thousand are in continuous use (one company operates 5400), and 800 others are used for supplemental odorization **[question** III-B, **(2)** and (3)]. **Wick** odorizers are easy to maintain, but they present problems in checking for satisfactory operation. Half the companies using them indicate a need for improvement in ability to maintain set addition rates. (See Table V-10.)

Other odorizers in use total 5556 fixed (107 companies) and 133 supplemental types (24 companies). (See question III-C.)

3. Supplemental Odorization

Supplemental odorizers (question III-B) are used by 31 companies either to odorize or to boost odor level in specific areas of a system. They are used twice as frequently on a femporsry basis (25 companies) as on a year-round, continuous basis (12 companies). Temporary supplemental odorization is used most frequently to condition new pipe (17 companies). Other reasons reported are - to boost odor level (4), to odorize regasified LNG (3), to odorize gas withdrawn from storage (1), and to meet emergencies (2).

More than half of those companies that use supplemental odorizers on a continuous basis did not report a reason (7). Others reported that they use supplemental odorizers to counteract fading (1), to boost odor level (1), to supplement naturally occurring odor (1), and to add odorant to regasified LNG (2).

D. Odor-Level Monitoring Practices

1. Odor-Level Tests by Company Personnel

Olfactory tests by company personnel are probably the earliest and still most widely practiced method of monitoring the odor level in natural gas. Ninety-three companies of 112 in our sample monitor odorization levels with odorometers (question IV-B). These devices supply gas-air mixtures to an outlet for "sniffing" and allow the operator to measure the gas/air ratio that produces a detectable gas odor.

Two types of odorometers are in wide use by transmission and distribution companies. Both types maintain a constant air flow and control the gas flow with a needle valve. One type measures the gas concentration by means

Table V-10. EVALUATION OF WICK ODORIZERS
(Number of Respondents* Assigning Each Rating)

Rating	Operating or Maintenance Characteristics† A	B	C	D	E
Outstanding	0	3	0	0	0
Satisfactory	14	22	15	15	19
Needs improvement	12	4	10	9	6
Unreliable	4	1	5	6	4
No reply	--	--	--	--	1

* Thirty companies use these odorizers.

† A Ability to maintain a set addition rate over the designed range of gas flow rates.

B Ease of maintenance.

C Ease of checking for satisfactory operation.

D Operation at set odorant-addition rates over summer-winter temperature changes.

E Freedom from odorant composition changes such as selective evaporation of lighter components.

of a flowmeter; the other, by means of a combustible gas detector. Table V-11 is a summary of the data reported for question IV-C. The first type is preferred by 71% of the companies making odorometer measurements.

Table V-11. COMPANY PREFERENCE FOR TWO TYPES OF ODOROMETER

Odorometer Type	Number of Companies Using This Type †
Gas/air measurement by flowmeter	66
Gas/air measurement by combustible gas indicator	10
Miscellaneous *	2
Unspecified	22

* "Self-built gas/air dilution odorometer," and "large, precision, wide range employing a reference gas (lab use).

† Ninety-three companies use odorometer; seven companies use both types.

Buczek[45] has described a preferred method for conducting odorometer tests.

Variations in the sensitivities of human noses and in the sensitivity of an individual nose from day to day are reflected in the repeatability (same operator) and reproducibility (different operators) data reported in answer to question IV-D. Seventy-six companies answered this question, and 47 (62%) reported "good" for both the same and different operators. At one end of the scale 4 companies reported "excellent"-"excellent" and one reported "poor"-"poor." Seventy-five companies (99%) reported "good" or "excellent" for repeat tests by the same operator. For repeat tests by different operators, 63 companies (83%) reported "excellent" or "good"; 9 (12%) reported "poor."

Quantitative 'numbers indicating repeatability and reproducibility were reported by 31 companies. Twenty,-five (81%) reported repeatability (same operator) of better than 0. 5%. Twenty-three (74%) reported reproducibility (different operators) of 0.5%.

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45. Buczek, F. L., "Procedure for Determination of Fuel Gas With Air Dilution Apparatus," A.G.A. Oper. Sect. Proc. - 1966, 66-P-472.

"Sniff" tests (e.g., by extinguishing a pilot and noting the odor of the unburned gas) are sometimes performed daily at fixed locations throughout a distribution system. Some companies use a combination of fixed locations and random sampling, e.g., in customer homes - often with the customer as witness. Such tests include a written notation of adequacy, which is kept as part of the permanent odorixation records.

Room tests are convenient when the odor level is to be checked by a number of people simultaneously. These are usually conducted for more important purposes than routine control, such as official or policy matters and research studies. There are two types of room tests: "walk-in" and "simulated leak." In the "walk-in" test, the desired quantity of gas is injected into a closed room; the observers enter and note the intensity and character of the odor. In the latter test, gas is admitted into a closed room with the observers already present in the room.

Room tests are required of those companies operating in the State of Texas, but are used by other companies as well. In reply to question IV-I, 13 companies reported that they conduct room tests.

Olfactory tests - odorometer tests, "sniff tests", and room tests - are performed by 100 companies (question IV-G) as frequently as 3 times a day (two companies) and as infrequently as once a year (one company). The number of locations checked varies from 1 to 150 (checked by one company annually). Twenty-six companies make daily tests, 1 at 60 locations; 26 make weekly tests, 1 at 60 locations. Five companies make tests every 2 weeks at 7 to 40 locations. Monthly checks are made by 28 companies at 1 to 70 locations. Three companies test quarterly at 50, 56, and 95 points. Semiannual tests are made by five companies.

Sixteen companies report "all service calls include an odor check." One company makes "sniff tests" on all leak-complaint calls and another on all "set" and "turn-on" calls.

2. Customer Leak-Comdlaint Calls

Calls to the gas company by customers reporting what they believe to be the odor of leaking gas have been widely used as a method of monitoring odor level of the gas. However, the' change in call rate from the normally observed number provides a better indication of odorization problems in a distribution system.

Geographic distribution of leak-complaint calls is frequently used as an indicator of odorant fading in the system. Once a normal pattern of leak complaints (with reference to both volume and distribution) has been established, changes in the distribution of leak complaints can point out areas where fading (or over-odorization) has occurred.

Classification of leak calls can significantly improve any odor-level monitoring program based on leak complaints. Whitehead,[46] Lehman,[47] and Loper[48] have developed systems for classifying leak complaints. Whitehead concluded, "The optimum between customer safety and odorization economy then becomes that combination of odor and stability which will maintain that odorant intensity which would give a steady maximum ratio level of medium and small leaks found for a minimum ratio of total odor calls received."

Lehman classified complaint calls as "leak, burner odor, foreign odor, and no odor found." Actual leaks were found in 52% of the calls. Sixty-five percent of all leaks were less than one-half the amount that would escape from an unlit range-top pilot. Based on several quite conservative assumptions, he was able to demonstrate that to be hazardous an inside leak would have to leak at a rate of 24 CF/hr. This is more than the capacity of two unlighted range-top burners. In his investigation, however, only 2% of all leaks were greater than 2.0 CF/hr.

Loper found that 70% of leak complaints were, in fact, actual leaks, 20% were no leaks, and 10% were described as resulting from foreign odors.

In our survey, 42 companies replied to question IV-A, 1 (d) having to do with "nuisance" calls (not caused by leaks requiring corrective action). Two companies reported less than 1%, and one company reported 95%. The replies of 25 companies were in the range 25% to 50%.

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46. Whitehead, A. L., "Development of an Optimum Odorization Program." Paper presented at the IGT Odorization Symposium, Chicago, March 1971.

47. Lehman, E. A., "Investigation of Odor Complaints," ibid.

48. Loper, B. H., op. cit.

In 1964 Denham[49] reported the results of a survey that established an acceptable range of one to eight leak calls per 1000 customers per week averaged over summer and winter. His small sample (20 companies) may not be entirely representative, but an interesting comparison can be made with the data in Table V-12. The range of values reported question8 IV-A, 1(a), (b), (c) as average was 0,8 to 8 for winter and 0. 5 to 8 for summer. "Unacceptably high" values ranged from 1.6 to 10 for winter and 1.0 to 10 for summer. "Unacceptably low" values ranged from 0.22 to 7 for winter and 0.15 to 5 for summer.

Table V-12. AVERAGES OF DATA REPORTED* IN REPLY TO QUESTION IV-A, 1

Rate Level	Calls per Week per 1000 Meters: Winter	Summer
Rate experienced as an average	2.4	1.8
Rate considered unacceptably high	4.6	3.0
Rate considered unacceptably low	1.3	1.1

* Forty-five companies reported.

Recently, several companies have sought to increase the effectiveness of their odorization programs and to promote greater safety by educating the public to recognize the smell of odorized natural gas.[50-52] These companies distributed specially designed bill inserts (containing samples of encapsulated odorant) that instructed the customer to scratch the encapsulated area, sniff it, and learn to recognize the smell of odorized gas. Such promotions have been quite successful and fill a need not often recognized: many people, especially young people, are not familiar with the odor of leaking natural gas because

49. Denham, J. P., "Summary of Questionaire on Method for Odor Level Determinations," A.G.A. Oper. Sect. Proc. – 1964, 64-P-145

50. Mitchell, R. D., "Odorization Encapsulation Education," A. G. A. Oper. Sect. Proc. – 1970, 70-D-12.

51. Trittschuh, J. O., "Encapsulated Mercaptan Used to Educate Customers," ibid., 70-D-10.

52. Niederer, E., "Safe-T-Sniff Bill Inserts," ibid., 70-D-5.

there are currently fewer gas leaks than there were in past years. This happens because appliances have been improved, and a new technology and new safety measures have been introduced.

3. Odorant Concentration Measurement

a. Continuous Monitoring Instruments

Continuous monitoring of odorant concentration is most often done with electrochemical titrators that indicate the concentrations of oxidizable sulfur compounds present as a function of current flow during the titration. Differentiation between different classes of sulfur compounds – H_2S, mercaptans, sulfides, and residual sulfur compounds – can be made using selective absorbers to remove compounds by functional group class.

Seventeen companies reported that they use titrators to continuously monitor odorant concentration (question IV-H). Eleven companies monitor only one or two points in the system; three monitor five, six, and seven points; two companies monitor three points; and one monitors four. Some points monitored represent areas with as few as 100 customers; other have as many as 200,000.

b. Periodic Testing Methods

Several methods, other than odorometer tests, are used by the 43 companies that replied positively to question IV-E. Thirty-two companies prefer titrators; 16 prefer chromatographs. Fourteen companies use special-purpose gas chromatographs, and two use general-purpose instruments with sulfur-selective detectors. Miscellaneous instruments reported (question IV-F, 3) included: MSA universal tester (2), mercaptan tube, microcoulometer, and "room test" (?).

E. Operating and Maintenance Practices

1. Avoiding Nuisance Odors

At least three factors must be considered in all attempts to avoid nuisance odors: proper design of odorizer installations, care and attention when filling odoriaers and disposing of odorant drums, and good housekeeping practices.

The most prevalent nuisance odor problems occurring around odorizer installations result from two types of odorant-handling problems: escaping odorant vapors and liquid odorant spills. Vapor-escape problems can best be handled with masking agents that can cover the downwind odors. Spill areas can be deodorized with scented detergents, which are effective on the spill itself but do not mask odors at some distance from the spill.

Oxidizing agents may be used to convert the odorant compounds to less odoriferous compounds. Potassium permanganate can be used to oxidize sulfides, cyclic sulfides, or mercaptans; hypochlorite bleaches can be used with mercaptans. However, dry concentrated oxidizing agents, such as potassium permanganate or hypochlorite, should not be used directly on odorant because of the danger of spontaneous combustion.

The vapor pressure of the spilled odorant and thus the degree of downwind contamination may be reduced by covering the area of the spill with kerosene or some other low-vapor-pressure hydrocarbon.[53] Odorant spilled on the ground is best treated by turning over the earth, covering it with bleach, and then spraying with kerosene. An alternative way, if no gas hazard is present, is to turn over the earth, mix it with kerosene, spread the dirt out again, and ignite the mixture.[54] Coryell[55] successfully eliminated malodors by spraying a fogging solution into the atmosphere at the point where odorant was spilled. The fogging solution consisted of 1% of a masking agent dissolved in kerosene.

A concentrated solution of calcium hypochlorite dissolved in water has been used to destroy the residual odor in an empty odorant drum. It works by oxidizing the mercaptans.[56] Household bleach, generally 5% sodium hypochlorite, may

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53. Plunkett, G. R., "Modern Odorant Handling Techniques," in Proceedings of the Forty-Eighth Southwestern Gas Measurement Short Course, -21. Norman: Univ. of Oklahoma, 1973.

54. Woolfall, G. E., "Accidental Overodorization, Spills, Drum Cleaning and Vapor Control." Paper presented at the IGT Odorization Symposium Chicago, March 1971.

55. Coryell, R. I., "Odorization Technique in New York City," Gas 33, 45-49 (1957) November.

56. Harvey, I. W., "Handling Odorants," Gas 45, 70-72, 76, 78, 80 (1969) May.

also be used for both treating spills and deodorizing drums; however, because it is more dilute, larger quantities are required.

Deodorization of odorieed vent gas may be accomplished by burning it in a vapor-proof lamp equipped with a wick that dips into a mixture of kerosene and a masking agent.[57]

The various fittings and connections are a common source of nuisance odors around odorization installations. Wherever possible, all permanent connections should be welded and hydrostatically tested. However, a simple screw joint properly installed with pipe dope or Teflon tape will make a satisfactory seal.[58]

Activated charcoal may be used directly on odorant spills, to treat odorant drums, and in air filters installed in permanent odorizer buildings to remove odorant leaks from the interior atmospheres of the buildings. The spent carbon in the filters may be disposed of by burning or by regenerating it with steam.[59]

The questionnaire contained no specific question relating to nuisance odors. However, one of the 112 companies responding did mention nuisance odors relating primarily to the atmospheric release of odorant as a result of blowdown and hydrostatic testing.

2. Disposal of Pipeline Liquids

Very little of signficance has appeared in the literature concerning the disposal of pipeline liquids containing odorant. Although 29 companies reported having these liquids (question V-I), none indicated a real problem in disposing of them. Table V-13 is a list of the ways in which gas companies dispose of these liquids.

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57. Woolfall, G. E., op. cit.

58. Ormston, R. H., "Instrumentation, Installation and Operation of Various Odorization Equipment," in "Proceedings of the 16th Annual Appalachian Gas Measurement Short Course - 1956," Eng. Exp. Sta. Bull., 390-402. Morgantown: West Virginia Univ., 1957.

59. Dunkley, W. A., "New Gas Odorizer Buildings in Memphis," Gas Age 106, 13-15, 58, 60 (1950) September.

Table V-13. METHODS OF DISPOSING OF PIPELINE LIQUIDS CONTAINING ODORANT

Methods of Disposal	Number of Companies Using This Method
Collect and flare (sometimes mixed with other fuels)	10
Sell to refineries, processors, or waste disposal agencies	12
Bury	2
Blow-off	2
Inject into wells	2
Evaporate	1
Return to system	2

3. Corrosions From Odorants

Metals used in gas distribution systems that may be corroded by odorants include copper, iron, and aluminum. Corrosion by liquid odorants may result from the odorant compounds themselves or from impurities in commercial-grade odorants (such as tertiary butyl chloride used in the manufacture of tertiary butyl mercaptan). In the presence of water, tertiary butyl chloride forms hydrochloric acid, which is very corrosive to aluminum.[60] Corrosion of copper appears to result from attack by hydrogen sulfide and by polysulfides, which are formed by oxidation of mercaptans. During an investigation of the internal corrosion of copper tubing in natural gas distribution systems, Clark[61] found that the corrosion consisted of cuprous sulfide and that the formation is initiated by polysulfides. The corrosion takes the form of thin plates of chalcocite and digenite that appear within 5 to 6 years after the service is installed. Particles of these compounds were carried along in the gas stream with sufficiently high velocity to deposit in pilots and orifices, causing blockage.

60. Wilby, F. V., "Relation of Odorants to Corrosion." Paper presented at the IGT Odorization Symposium, Chicago, March 1971.

61. Clark, J. C., "Experience in Internal Corrosion in Copper Services," ibid.

As long ago as 1939, Kruger[62] reported a study of the corrosion rates of several metals attacked by odorized natural gas. He stated that'black iron experiences the greatest corrosion; nickel-chromium stainless steel, the least. Silicon-bronze; 85-15 brass; commercial grades of copper, lead, and zinc; monel metal; chromium steel; aluminum; and aluminum-magnesium alloy had an intermediate amount of corrosion, Of these, silicon-bronze showed the greatest corrosion; the aluminum-magnesium alloy showed the least.

Propyl, butyl, and amyl mercaptans corrode copper significantly in the presence of water; methyl mercaptan does not. Wilby[63] lists these and several other reactions that take place, under a variety of conditions, between copper, steel, and aluminum and several classes of sulfur compounds: hydrogen sulfide, mercaptans, polysulfides, and sulfur dioxide.

Kruger reported-an experiment with gaseous-phase mercaptans contacting copper in which he determined that at ambient temperatures copper is not attacked by mercaptans in the gas phase. At high temperature (800°F) mercaptans corrode copper actively to produce a gray or black surface. The high-temperature oxidation of copper is accelerated by gases such as hydrogen sulfide, hydrogen chloride, sulfur dioxide, and ammonia. These gases promote oxidation even at room temperature.

It is apparent that conditions favoring odorant compound reactions with metals seldom exist in gas industry practice, because only nine companies reported corrosion that they attribute to the odorant in their gas (questions V-H and I). Every one of these companies had copper corrosion problems. One also experienced pitting of iron by concentrated odorant. (See Table V-14.)

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62. Kruger, R. E.', "Organic Sulfur Committee Report of Corrosion Survey," A.G.A. Proc. - 1939, 517-58.

63. Wilby, F. V., op. cit.

Table V-14. CORROSION PROBLEMS CAUSED BY ODORANTS IN NATURAL GAS

Problem	Number of Companies That Have This Problem
Flaking of copper lines	6
Corrosion of appliance tubing by naturally occurring odorants	2
Corrosion of pipe or fittings by H_2S or sulfide odorant	1
Pitting of iron by concentrated odorant	1

VI. Odor Retention in Utility Piping Systems

A. Chemical Stability of Odorants

Chemical reactions of odorants, particularly mercaptans, are sometimes responsible for the odor fading observed in utility piping systems. Andreen and Kroencke[64] studied the oxidation of mercaptans to disulfide in a bench-scale flow reactor packed with rusted-steel spheres and under conditions that were chosen to simulate those that exist in a typical distribution company. They found that the oxidation of mercaptans is an "...unsteady reaction characterized by an initial period of high reaction." The rate of reaction then decreases rapidly and levels off, approaching zero.

This investigation of the kinetics of the oxidation of mercaptan on simulated pipeline surfaces was continued by Johnson.[65] He concluded that a) physical adsorption of mercaptans on pipeline surfaces cannot account for a significant fraction of the amounts of various odorants that disappeared in pipelines and b) odorant alteration is caused by chemical transformation of one odorant species to form other species with lesser or greater odor levels. He determined that the oxidation of mercaptans occurs at low temperatures on a mixture of hydrous iron oxides to form disulfides and that the rate of oxidation decreases as the molecular weight of the mercaptan increases.

Miller et al.[66] suggest that other types of chemical reactions of odorant compounds, such as reactions between mercaptans and metallic iron or copper, decomposition of mercaptans to olefins, and oxidation of thiophane are improbable in normal distribution lines.

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64. Andreen, B. H. and Kroencke, R. L., "Stability of Mercaptans Under Gas Distribution System Conditions," A. G.A. 0-per. Sect., Proc. - 1964, 64-P-136.

65. Johnson, J. L., "Kinetics of Odor Fading." Paper presented at the A. G.A. Basic Research Symposium, Chicago, March 1967.

66. Miller, S. A., Kaeplin, J. A. and Viswanath, D. S., Survey of the Chemistry of Odorant Compounds (A. G. A. Catalog No. OR/ 53). New Pork (Arlington, Va.): American Gas Association, 1961.

B. Phvsical Loss of Odorants

The physical loss of odorants in pipelines results from a) adsorption on pipeline walls and on deposits such as rust and from b) absorption caused by the odorant's solubility in such things as natural gasoline, alcohol, sealants and fogging oil. Olsen[67] noted the effect of fogging oil on odor loss and reported that when fogging rates are greater than 1 gal/million CF, the loss of odor is in direct proportion to the fogging rate. He also reported on a series of tests on the scrubbing effects of various other liquids. All the oils and alcohols tested scrubbed a considerable amount of odor from the gas. Thus, the use of alcohol to prevent freeze-up in pipelines may cause a loss of odor intensity if the alcohol is sprayed into the gas stream at too high a rate. Coryell[68] has described a loss of odorant in an old gas main apparently caused by large quantities of iron oxide deposits. Supplemental odorization was required to restore and maintain the odor level in the main.

Thirty-six companies in our survey reported that .they experience odor fading in parts of their systems other than new piping (question V-A). However, they did not indicate whether the fading was caused by the physical loss of the odorant or through chemical reactions.

C. Odorant Retention Under Special Conditions

1. New Piping

Gas companies commonly experience odor fading in new gas mains; it often necessitates supplemental or spot odorization to condition these new mains. Coryell[69] has suggested two mixtures for use in conditioning new pipe: One is a low-vapor-pressure oil containing a rust inhibitor; another is a mixture of kerosene (80%), mercaptans (10%), and sulfide (10%).

Wicht and Deutsch[70] recommended coating the internal surfaces of new mains with epoxy resin to minimize odor fading. They also used a mixture of motor oil or used transformer oil and odorant to condition new mains.

67. Olsen, A. W., "Masking of Odorants," A.G.A. Oper. Sect., Proc. - 1960, CEP-60-18.

68. Coryell, R. L.', "Supplemental Odorization Practices." Paper presented at the IGT Odorization Symposium, Chicago, March 1971.

69. Coryell, ibid.

70. Wicht, A. H. and Deutsch, I., "Factors Affecting Stability of Odorants in Gas, "A.G.A. Oper. Sect., Proc. - 1959, CEP-59-2.

2. Gas Passage Through Soil

Adsorption of odorant by soil is a major problem in odorization technology. Indeed, removal of odorant during passage through soil was probably a contributing cause to several accidents that prompted *the* Office of Pipeline Safety to initiate this study.

The most thorough study of the adsorption of odorant by soil conducted to date was carried out at the Institute of Gas Technology.[71] The results of this study showed that, when typical odorant compounds are used at normal concentration levels, the effects of odorant properties are relatively minor compared with the effects of variables usually encountered in the field.

The most important factors determining the extent and rate of odorant adsorption were found to be the type of soil, the moisture content of the gas and soil, and the odorant space velocity. The effects of these variables greatly outweigh differences due to odorant compound type, the gas or air equilibration of the soil, fogging oil, the oxygen content'of the gas, and the iron oxide content of the soil. Sandy or organic soils are essentially nonadsorptive; dry clay soils tend to retain large quantities of odorant.

Cable[72] reported that the removal of odorant passing through cinders may have been caused by oxidation by the iron oxide present, but that, with other types of soils, physical adsorption was the primary mechanism. Olsen,[73] reporting on tests conducted to determine whether the odorants in natural gas would be removed by the types of surface soils in Rhode Island, stated that even clay, which filters out the greatest amount of odorant, left sufficient odor to meet the odorant requirements of the State of Rhode Island.

The need for improved odorants with better soil-penetrating properties was listed by 30 companies in our survey as the area of odorization technology most in need of research (question VI-D).

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71. Tarman, P. B. and Linden, H. L., "Soil Adsorption of Odorant Compounds," IGT Res. Bull. No. 34. Chicago: Institute of Gas Technology, 1964.

72. Cable, R. C., "A Pilot Plant Study of Gas Odorant Adsorption by Various Soils," M.S. Thesis, Texas College of Arts and Industries, Kingsville, May 1952.

73. Olsen, A. W., op. cit.

VII. Research in Odorization Technology

A. Odorant Selection Criteria

Since Holtz[74] first set forth the characteristics of an ideal odorant, few have been able to add significantly to his list. His criteria have been restated by a number of workers in the field, they have been paraphrased and expounded upon; but they have seldom been improved upon.

Holtz, however, did not foresee the need for an odorant that would not be adsorbed by soil. (He did note that the odor must not be absorbed by mains or meters.) The increasing recognition in recent years that the ideal— and certainly the practical – odorant should readily penetrate soil has been a major development. Now that the need for such an odorant has been recognized, intensive effort must be exerted to meet that need.

Another significant development has been the concept advanced by Lehman[75] and by Whitehead[76] that the ideal odorant should have a maximum as well as a minimum odor level. Such an odorant would prevent overodorization and would minimize "false" leak calls, which are a major cost in most odorization programs.

B. Response of the Human Nose to Natural Gas Odorants

Several recent studies have measured the intensity of gas odorants as a function of concentration. Nevers and Oister '' measured the odor intensity as a function of concentration for TBM, dimethyl sulfide, and thiophane. With TBM, the relation was an approximate correlation to the Weber-Fechner law, which states that the magnitude of stimulus must be increased geometrically if the magnitude of a sensation is to be increased arithmetically. This can be put in the form of an equation:

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74. Holtz, L., op. cit.

75. Lehman, E. A., op. cit.

76. Whitehead, A. L., "Development of an Optimum Odorization Program," op. cit.

77. Nevers, A. D. and Oister, W. H., "Problems in the Critical Comparison of Odor Intensities," A.G.A. Oper. Sect. Proc. - 1965, 65-P-126.

$$(\text{sensation intensity}) = C \log (\text{stimulus intensity})$$

Over a more limited concentration range, thiophane and DMS also fit this law, but with a different slope. At low concentrations, the odor intensity of a mixture of TBM and DMS is approximately the sum of the odors of the two individual compounds, but at higher concentrations, a synergistic effect may occur, with the blend being more intense than either of the two compounds alone.

McClure[78] made a study of the sensitivity of the human nose to mercaptans and thiophane. His results revealed that a 150% change in concentration is necessary to definitely establish a change in odor level. He also found that, for an equal change in odorant concentration, mercaptans affect the odor level to a greater degree than does cyclic sulfide.

In his evaluation of nine commercial odorants, Dotterweich[79] used five levels of odorant intensity to describe the intensity of odorized gas in a room (1% gas in air) as a function of the concentration of odorant in the gas. (The odorants were not identified.) He concluded that any of the concentrated odorants should give a perceptible odor at a concentration of 1% gas-in-air when the odorant concentration is 0. 5 lb/million SCF.

In another study, Wilby[80] measured the thresholds of 18 mercaptans, sulfides, disulfides, and trisulfides, and some mixtures of two or more of these compounds. He found that the odors of all compounds tested were additive. There were no synergistic or anergistic effects noted. This was particulary true with compounds having like functional groups, i. e., mercaptans mixed with mercaptans or sulfides with sulfides, Deininger and McKinley[81] recommended, in the conclusions to their investigation of new odorants, that the so-called "booster" odorants that greatly reinforce inherent odors be further investigated.

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78. McClure, J. S., "Odorant Concentration as Compared to Odor Intensity," A.G.A. Oper. Sect. Proc. - 1960, CEP-60-10.

79. Dotterweich, F. H., "Natural Gas Odorants," Gas Age 105, 23-24, 51-52, 54 (1950) June.

80. Wilby, F. V., "Variation in Recognition Odor Threshold of a Panel," J. Air Pollut. Contr. Assn. 19, 96-100 (1969) February.

til. Deininger, N. and McKinley, R. W., op. cit.

Ripperger[82] measured the "odor strength" of tetrahydrothiophene, dimethyl sulfide, and mercaptan mixtures using the so-called "K" values. "K", a measure of odorant intensity, is the amount of odorant that one must add to 1 cu m of air to get to odor step "2." He distinguished five odor steps.

Kniebes et al.[83] measured the barely perceptible odor threshold for several common odorant compounds. These tests were performed in an odor-test room supplied with temperature- and humidity-controlled charcoal-filtered air into which odorants were added at subthreshold and higher levels. The relative intensities of several compounds and some mixtures were measured at levels high enough above background to permit easy recognition. There was evidence of some synergism in mixtures containing normal butyl mercaptan and dimethyl sulfide, or methyl ethyl sulfide or diethyl sulfide. The above were in mixtures with normal butyl mercaptan. When dimethyl sulfide was measured in a mixture with tertiary butyl mercaptan or tetrahydrothiophene, the synergistic effect could not be confirmed because the differences were within experimental error.

A measure of the number of odor levels is indicated by the "just noticeable difference" value. The JND value is the smallest difference in concentration that can be detected by the nose as a difference in intensity. The general definition of JND is that this difference be detectable 50% of the time. Kniebes et al.[83] measured the "just noticeable difference" values for several sulfur compounds; in each case, the JND value was found to be approximately 30%. Leonardos[84] cites a JND for a limited number of odorants of 60%. Nevers,[85] in agreement with McClure,[86] found values of approximately 150%, but the definition of JND used by these authors was detection of an intensity change by all observers 100% of the time.

82. Ripperger, W., "Compositions, Properties, and Chemical Stability of Odorants," Gas und Wasserfach 108, 933-36 (1967) August 18 (German text).

$3. Kniebes, D. V., Chisholm, J. A. and Stubbs, R. C., "Relative Odor Intensities of Sulfur Compounds Near Their Threshold Concentrations." Paper presented at the American Society of Heating, Refrigerating and Air-conditioning Engineers Symposium on Odors and Odorants: The Engineering View, Chicago, January 27-30, 1969.

84. Leonardos, G., Kendall, D. and Barnard, N., "Odor Threshold Determinations of 53 Odorant Chemicals," J. Air Pollut. Contr. Assn. 19, 91-95 (1969) February.

85. Nevers, A. D., op. cit.

86. McClure, J. S., op. cit.

Another characteristic of odorants is their persistence or resistance to olfactory fatigue. Dravnieks,[87] in describing the mechanism of fatigue or adaptation to an odor, states that it may occur either through fatiguing of the senses or through adaptative processes in the neural network. Recovery of sensitivity depends on the intensity of the stimulus and may take from minutes to hours.

Amoore,[88] discussing the problem of specific anosmia in relation to gas odorization, says that about one person in 100 cannot smell normal butyl mercaptan; in addition, anosmias to dimethyl disulfide and tertiary butyl mercaptan have been observed with frequencies possibly as high as several percent of the people tested.

According to our survey, 14 companies have been or are engaged in research relating to human response to gas odorants (questions VI-C).

C. Odor Test Methods

1. Subjective Methods - "Sniff Tests"

Several psychophysical methods for making olfactory measurements have been described by Wilby[89]:

- Single stimulus - Subject makes judgement such as "strong" or "weak."
- Paired comparison - Two stimuli are presented simultaneously, and the subject indicates that one has more or less of a given attribute.
- Triangle method - Three stimuli are presented; two are alike, one different. The subject is asked to choose which is different.
- Rating scale - A modification of the "single stimulus" method; the subject gives the stimulus a numerical rating.

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87. Dravnieks, A., "Properties of Olfactory Systems." Paper presented at the IGT Odorization Symposium, Chicago, March 1971.

88. Amoore, J. E., "Odor Blindness as a Problem in Odorization," A.G.A. Oper. Sect. Proc. - 1968, 68-D-73.

83. Wilby, F. V., "The Odor Comparator - An Improved Instrument for Quantitative Odor Measurement," A.G.A. Oper. Sect. Proc. - 1964, 64-P-225.

- Method of limits - Successively increasing intensities are presented until the subject can detect the odor. Also called the "threshold method."

Wilby finds the threshold method the most practical measure of odor strength because it is the direct function of the concentration of odorous molecules in the air and directly relates to the size of the gas leak that a customer is likely to detect. It is also the easiest to measure and the most reproducible. He suggests that odor measurements should be compared with an odor standard to minimize variations among individuals and day-to-day variations of one individual.

In a discussion of the relative advantages of the threshold method and other techniques of odor measurement, Durfee[90] proposed a nine-point subjective rating scale for odor intensity; he points out the advantages of being able to defatigue the subject's nose by having him breathe purified air between tests.

Design requirements for the study of the threshold of odor perception within a large population of human subjects were discussed by Sullivan, Adams, and Young[91] in a paper that describes a mobile laboratory built into a bus. A dynamic odor generation system provides a range of concentrations within the exposure chambers from ppm values to at least 1 ppb. Each subject provides comprehensive information concerning many variables: age, sex, smoking habits, respiratory abnormalities, and occupation. Data are analyzed for possible significant influence upon the response to odor levels.

Union Carbide[92] developed an "odor fountain" to measure odor levels and reported them in terms of an "odor index," a dimensionless term obtained by dividing the vapor pressure of the test compound by its threshold. This technique has been helpful in pinpointing potential environmental pollution control problems.

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90. Durfee, R. A., "Appraisal of Odor-Measurement Technique," J. Air Pollut. Contr. Assn. 18, 472-74 (1968) July.

91. Sullivan, D. C., Adams, D. F. and Young, F. A., "Design of an 'Odor Perception and Objectionability Threshold' Test Facility," in Atmospheric Environment, Vol. 2, 121-33. United Kingdom: Pergamon Press, 1968.

92. "Putting the Nose to the Test," Chem. Week 112, 35-36 (1973) March 14.

An investigation of fatiguing – loss of sensitivity to an odorant on long exposure to a constant concentration – was carried out by Cain.[93] He determined that with 1-propanol perceived magnitude decayed quite rapidly at first, but, within minutes, approached a steady state at 36% of the initial perceived magnitude. With eugenol as the odorant, the steady-state value was slightly above 40% of the initially perceived magnitude.

Iso-valeric acid, methyl salicylate, and pyridine were selected by Kerka and Humphreys[94] for a study conducted on the effects of temperature and humidity on odor perception, They concluded that an increase in humidity at a constant temperature tends to lower the intensity level of an odor and that the extent of the effect of humidity upon odor perception is not the same for all of the odorants studied. An increase in temperature at a constant humidity appears to lower the perceived odor level slightly, but more data are needed to confirm this phenomenon.

The "profile method" of odor evaluation is based on the abilities of experienced observers who a're capable of studying, recognizing, and describing odors. In discussing this approach, Sullivan[95] points out that the fatigue effect suggests that gas odorants might be made up of special blends that delay or prevent adaptation.

Field tests for adequate odorization are frequently carried out with a portable air-dilution apparatus that provides a gas-air mixture of known concentration at a "sniffing port" for evaluation by an observer. New developments and improvements have been made in these instruments in the last 25 years. In 1955, Nevers[96] described an apparatus of this type. A cam-driven synchronous motor was used to drive a hypodermic syringe to inject

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93. Cain, W. S., "Perception of Odor Intensity and the Time-Course of Olfactory Adaptation," ASHRAE Trans. 80, Part I, 53-75 (1974).

94. Kerka, W. F. and Humphreys, C. M., "Temperature and Humidity Effect on Odor Perception," Heat., Piping Air Cond. J. 28, 129-36 (1956).

95. Sullivan, F., "Sensory Evaluation of Odor Problems," A. G.A. Oper. Sect. Proc. – 1969, 69-D-36.

96. Nevers, A. D., "How Odorants Are Evaluated by Use of New Apparatus," Amer. Gas J. 182, 20-23 (1955) February.

an odorant into a gas stream at concentrations of 0.5 to 1.0 lb/million SCF. The injection rate was accurate and reproducible, and the degree of dilution could be changed instantly by the adjustment of one valve. This apparatus was one of the best that had been developed up to that time.

White's instrument (1951)[97] was novel in one respect: A single stream of gas flowing from a main supplied all the power. Other odorometers developed during that period required not only the gas, the odor of which was to be measured, but also auxiliary equipment – an air compressor or blower with an electric motor to supply air for dilution.

At the same conference at which White discussed his apparatus, Wilby[98] described a portable odorometer made of aluminum. Glass and/or stainless steel, which are probably the best materials for odor-free construction, would not be as suitable for *a* portable instrument.

In 1954, Cascioli and Coryell[99] described a battery-powered odorometer that later became commercially available, and Gilkinson,[100] in 1960, reported a portable, lightweight battery-operated odorometer for general field use.

One company responding to the questionnaire reported that it had been involved in the development of a new odorometer (question V-C). Twenty-four companies cited the need for more efficient and economical ways of measuring odor level (question V-D).

2. Objective Methods – Measurement of Odorant Concentration in Gas

The research carried out in past years on the objective measurement of odorant concentration in gas has been confined to two instrumental techniques: electrochemical titrations and gas chromatography. Titrations are

97. White, C. E., "New Instrument Designed to Disclose Odor Concentration Levels in Gas," Proc. Pac. Coast Gas Assn. 42, 100-03 (1951).

98. Wilby, F. V., "Portable Odorometer and Method for Measuring the Odor Level of Odorized Gas," Proc. Pac. Coast Gas Assn. 42, 104-08 (1951).

99. Cascioli, A. F. and Coryell, R. L., "New Odorometer Shows Good Results," Gas Age 113, 9, 10, 52 (1954) January 28.

100. Gilkinson, R. W., "Rocheter Gas Develops a Portable, Lightweight Battery-Operated Odorometer," Gas 36, 67-69 (1960) December.

used for both continuous on-stream monitoring and for field work; chromatographs are used for periodic testing in the field.

One of the earliest reports on electrolytic titrators described a successful application to the problem of gas odorants evaluation in the field and to that of odorant dosage control.[101] The authors used the data from these typical applications to show the practical features of the titrator and interpreted the data in the light of such operational characteristics as reliability, maintenance requirements, and accuracy of data. Some years later, Mason[102] reported IGT's experience with the Titrilog. He encountered variations in sensitivity from one compound to another, from one instrument to another, and from time to time on the same instrument.

Austin,[103] in 1965, described a new model with a sensitivity of better than 0.1 ppm of hydrogen sulfide.

Many users of the early Titrilog encountered maintenance problems because of the sensitive circuitry and complicated sampling system. The discovery of a practical coulometric bromine-sensing electrode and the development of transistor electronics led to the introduction of a new, wide range electrolytic titrator designed to meet the specific requirements for continuous monitoring.[104]

Andreen et al.[105] made a comparison of four instruments used to analyze for trace levels of sulfur compounds in gas, Two of the four instruments were

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101. Austin, R. R., Percy, L. E. and Escher, E. E., "The Automatic Recording Titrator and Its Application to the Continuous Measurement of the Concentration of Organic Sulfur Compounds in Gas Streams," A.G.A. Proc. – 1949, 505-15.

102. Mason, D. M., "The Titrilog: Its Application to Odorization Problems," Amer. Gas J. 184, 18-20 (1957) August.

103. Austin, R. R., "A New Recording Electrolytic Titrator," A. G.A. Oper. Sect. Proc. – 1965, 65-P-121.

104. Austin, R. R. and Robison, J. R., "Determination of Hydrogen Sulfide and Total Sulfur by Titration Methods," in Proceedings of the Forty-Seventh Annual Southwestern Gas Measurement Short Course, 262-69. Norman: Univ. of Oklahoma, 1972.

105. Andreen, B. H., Kniebes, D. V. and Tarman, P. B., "Instrumental Methods of Analysis for Odorant Compounds in Natural Gas," IGT Tech. Rep. No. 7 for Project P-39. Chicago: Institute of Gas Technology, July 1963.

titrators, one was a mercaptan analyzer, and one was a gas chromatograph. The titrators and the mercaptan analyzer gave reasonably accurate results when properly calibrated. The gas chromatograph (developed at IGT) could measure odorant compounds in concentrations as low as 0.001 gr S/100 CF. A fully portable gas chromatograph with somewhat lower sensitivity was developed for use in the field.

Both chemical and instrumental methods of sulfur compound analysis were evaluated by Wilby.[106] Of the chemical methods he examined, none were suitable for the analysis of mercaptans in natural gas, The methylene blue method was best for hydrogen sulfide. In the absence of oyxgen and/or carbon dioxide, the titrators were satisfactory for continuously recording sulfur concentrations at levels of 0.3 gr S/100 CF.

Gas chromatography of gas odorants was first described by Spencer et al.[107] in 1958. They reported an accuracy of 5% of the amount present. (The samples were liquid odorant not odorized gas.)

In 1962, Andreen and Kniebes[108] described a procedure that could be used for the gas chromatographic analysis of sulfur compounds in natural gas. An argon ionization detector provided the required sensitivity, and 12 C_2-C_4 mercaptans and sulfides were separated on several combinations of three columns which were switched in and out of the carrier-gas stream during an analysis.

Later, in 1965, Wilby[109] was able to achieve a higher sensitivity with a procedure that includes a low-temperature concentration of a large gas sample, temperature programing, and a microcoulometric detector.

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106. Wilby, F. V., "Comparison of Methods of Analysis for Sulfur in Natural Gas," A.G.A. Oper. Sect. Proc. - 1966, 66-P-241.

107. Spencer, C. F., Baumann, F. and Johnson, J. F., "Gas Odorants Analysis by Gas Chromatography," Anal. Chem. 30, 1473-74 (1958) September.

108. Andreen, B. H. and Kniebes, D. V., "Determination of Sulfur Compounds in Natural Gas by Gas Chromatography," A. G.A. Oper. Sect. Proc. - 1962, CEP-62-13.

109. Wilby, F. V., "Determination of Sulfur Compounds in Natural Gas by Gas Liquid Chromatography Using Low-Temperature Sample Concentrations, Temperature Programming and Microcoulometric Detector (A Panel)," A.G.A. Oper. Sect. Proc. - 1965, 65-P-136.

Further gains in sensitivity were achieved by Gibbons and Goode,[110] who used a flame photometric sulfur-selective detector to analyze 2 to 10 ppm of natural gas odorant at a repeatability of better than 0.25 ppm. Goode[111] later drastically lowered the detection limits with an improved flame photometric detector and a sample concentration step.

Kniebes et al.[112,113] have reported the development of the Odotron, a special-purpose gas chromatograph equipped with a flame photometric detector. The Odotron is designed to respond only to those compounds that contribute odor to natural gas. It gives a direct readout of odor intensity. In 1972 Kutzleb described a commercial model based on this IGT instrument.[114]

The automated gas chromatographic measurement of ambient concentrations of sulfur dioxide, hydrogen sulfide, methyl mercaptan, and dimethyl sulfide was described by Stevens et al.[115] Detection limits were as low as 0.002 ppm.

Stubbs[116] investigated the response of the flame photometric detector. His results show that its response varies with the square of the sulfur concentration in the flame and is independent of the type of sulfur compound.

In reply to question VI-C, six companies reported that they were involved in research to develop analytical methods to measure odorant concentrations in gas. There were 40 general replies to question VI-D expressing the need for research on more effective and more economical equipment.

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110. Gibbons, P. A. and Goode, K. A., "Sulfur Selective Detector in Natural Gas Chromatography," Gas J. 336, 27-29 (1968) October 9.

111. Goode, K. A., "Gas Chromatographic Determination of Sulfur Compounds in North Sea Natural Gas by Flame Photometric Detector," J. Petrol. Inst. 56, 33-41 (1970) January.

112. Kniebes, D. V., Chisholm, J. A. and Stubbs, R. C., "An Instrument for Direct Measurement of Odor Level in Natural Gas," A.G.A. Oper. Sect. Proc. - 1969, 69-D-69.

113. Kniebes, D. V., Chisholm, J. A. and Stubbs, R. C. (assigned to Institute of Gas Technology), "Method for Measuring Odor Level in Natural Gas," U.S. Patent 3,686,930 (1972) August 29.

114. Kutzleb, R. E., "The Odotron," in "Proceedings of the 32nd Annual Appalachian Gas Measurement Course - 1972," Eng. Exp. Sta. Bull. No. 108, 207-212. Morgantown: West Virginia Univ., March 1973.

115. Stevens, R. K, et al., "Gas Chromatography of Reactive Sulfur Gases in Air at the Parts-per-Billion Level," Anal. Chem. 43, 827-31 (1971) June.

116. Stubbs, R. C., "Response of the Flame Photometric Detector to Sulfur Compounds." Paper presented at the IGT Odorization Symposium, Chicago, March 1971.

VIII. Discussion

A. Effectiveness of Industrv Odorization Practices

1. Odorants in Use

Results of this survey indicate that present-day natural gas odorants have a high degree of acceptance among gas industry personnel responsible for odorization programs. In particular the olfactory characteristics of commercial gas odorants are generally regarded as excellent. They possess the requisite "gassy" odor and are adequate in strength. Because of their persistence, fatiguing is minimized and sensitivity of observers is not diminished upon continued exposure, These characteristics combine to promote effectiveness in warning of the presence of gas.

Respondents did not rate odorants so highly in regard to resistance to fading ("satisfactory" - 91; "needs improvement" - 17). This probably reflects experience with straight mercaptan odorants in which isopropyl mercaptan is the major component, because TBM-base mercaptan blends and TBM-sulfide blends are known to be relatively stable.

Much less agreement is expressed regarding odorants' resistance to being lost upon soil contact. More than half of those replying consider this to be one odorant characteristic that needs improvement.

On the question of overall "effectiveness of odorants used" (question VI-A), opinion is nearly equally divided between "fully satisfactory" and "satisfactory, but needs improvement." No one, however, rates today's odorants as "unsatisfactory" in this regard.

2. Odorant Injection Equipment

Liquid-injection chemical-pump odorizers are the most highly regarded of all types of injection equipment. Results of our survey indicate that they are also the most popular odorizers. Users rate them nearly perfect in freedom from compositional changes, considering them very easy to maintain and to check for satisfactory operation. They do an excellent job of maintaining a set addition rate within the designed range of gas flow rates.

The characteristic for which these pumps received the lowest rating was the ability to maintain set odorant addition rates despite summer-winter temperature changes. Even in this regard, however, chemical pumps ranked as highly as any other type of odorant injection equipment. Fluctuations in odorant addition rate are caused by variations in odorant specific volume with temperature. This is also a problem with other types of odorizers. Chemical-pump liquid-injection odorizers are typically installed at large-volume gas purchase points ($>$ 100 million SCF/day). Better rate control can be maintained with integrators or titrators as ancillary equipment.

About half of the companies odorizing gas use meter-driven liquid-injection pumps and rate them almost as highly as chemical pumps. Meter-driven injection odorizers are well able to maintain set addition rates over the designed gas-flow range. They are considerably more difficult to maintain than other injection equipment, but checking for satisfactory operation is quite easy. They are about equal to chemical-pump odorizers in their ability to maintain set addition rates throughout the range of summer-winter temperature changes. In the opinion of almost all users, motor-driven injection pumps are free from difficulty over odorant composition changes. Corrosion is a problem because of the aluminum meter case, and meter wear at high flow rates limits this equipment to throughputs of less than 100 million SCF/day.

Evaporation-type odorizers were reported in use nearly as often as chemical pumps. Their outstanding characteristic is ease of maintenance. About half of the users rated these odorizers unreliable or in need of improvement regarding operation at a set rate throughout the extremes of summer and winter temperatures. Approximately forty percent of users found them unreliable and in need of improvement regarding constant addition over the designed range of gas flow rates, ease of checking for satisfactory operation, and freedom from odorant composition changes.

Wick-type odorizers have only two things to. recommend them: low cost and ease of maintenance. Half the users considered them unreliable or in need of improvement in other operational characteristics.

Only five companies reported the use of drip-type odorizers. No one considered them unreliable in any respect; however, they are not completely satisfactory in maintaining constant addition rates over wide ranges of flows and summer-winter temperatures.

3. Odor Monitoring Procedures

The most widely used odor-monitoring procedure involves field testing at specified locations with an odorometer. It gives a direct measure of odor level, but is subject to the vagaries of the individual human nose. When carried out in the proper manner, this procedure gives a reliable indication of whether or not gas is adequately odorized.

Room tests are a very accurate means of determining the odor level of a particular gas. However, the facilities, time, and personnel involved make this method expensive. Since the facilities are not generally portable, this kind of test, which measures only one point of a system, may not adequately represent the entire system.

Another type of olfactory test is being carried out with increasing frequency. Many companies adhere to the practice of having service personnel conduct "sniff" tests whenever a meter is set, repairs are made, or leak checks are made. This procedure provides a much better checkout of the entire system than would otherwise be practical.

Odor calls, service requests from customers detecting gas odors, are used by forty percent of the respondents to the questionnaire to monitor odor level. However, the call rate is too sensitive to factors other than odor level— e.g., weather changes, seasons, extraneous environmental odors – to be a good measure of odor level. (Up to 50% of leak calls may be caused by foreignodors – solvents, kerosene, gasoline – or by pilot outages or leaks so small that they do not require corrective action.) Leak calls can pinpoint problem areas, but adjusting odor injection rates on the basis of call rates is not an effective means of achieving an adequate odor level.

Electrochemical titrators and gas chromatographs provide objective determinations of odor level if the precise correlation of intensity with concentration for the individual compounds in an odorant blend is available. One commercially available, special-purpose gas chromatograph is designed to correlate concentrations of selected odorant compounds with olfactory response data for the average nose and to read out directly in odor level.

In assessing the overall adequacy of the gas industry's odorization technology, those responding to the questionnaire ranked "odor monitoring equipment" as most in need of improvement, followed secondly by "odor monito'ring procedures."

B. Current Trends

1. Problem Areas

a. Existing Problems

A consideration of the gas industry's experience in odorization technology as expressed in the literature, in responses to the questionnaire, and in personal contacts leads to the recognition of a number of problems involving odorants, odorant injection equipment, and odor monitoring procedures. Odorant fading has been a problem historically; but the industry's experience in recent years with TBM and with sulfides has produced a trend away from isopropyl mercaptan odorants, which are most susceptible to this phenomenon because of oxidation. The industry also recognizes that the condition of pipe walls is an important factor in fading caused by adsorption and is taking steps wherever possible to clean up pipelines in order to alleviate this problem.

Adsorption of odorants by soil continues to be a major problem. A number of instances have been recorded recently of extensive property damage, severe personal injury, and deaths in fires and explosions caused by natural gas leaks that went undetected because the gas had lost its odor while passing through soil. Research in this area should be accelerated. However, the probability of developing an odorant with adequate soil penetration properties is not very high given the nature of the adsorption process and certain practical requirements of the odorant.

Currently used odorants, because they consist of sulfur compounds, are deleterious to certain industrial processes; e. g., they poison catalysts. Although the odorants can be removed, removal is inconvenient and costly. Non-sulfur odorants would be a welcome alternative.

The major problem with odorant injection equipment centers around the inability to maintain a constant injection rate throughout a wide range of gas flows. Also there is a particular need for an odorizer that will supply odorant uniformly to small low-flow systems of less than 100 customers. Another problem is one of cost; industry wants, in essence, generally better and more economical injection equipment.

Minor problems cited include corrosion of fittings; leaks around valves, pumps, etc., giving rise to nuisance odors during maintenance; gas condensate buildup in bypass odorizers; and plugging of orifices and valves by condensate and hydrocarbon hydrates.

Problems with odor monitoring procedures are specific to the method used. Because odorometer testa are subject to individual variations in sensitivity of the human nose, ambient odors can cause inaccuracies in the determination of odor level of the gas. Leak complaint call rates, although useful, do not correlate directly with the odor level in gas because of the influence of other extraneous factors. Instrumental methods – e. g., titrators and gas chromatographs – require expensive, complex equipment and highly trained personnel to operate it and interpret the results.

b. Future Problems

Future problems may be encountered in the odorization of hydrogen and low-Btu utility gas, and substitute natural gas produced from coal, oil, and shale. Hydrogen, because of its lower explosive limit, may have to be odorized at higher concentration levels. This may require modification of some types of odorant injection equipment or development of new types of odorizers. However, odorants for hydrogen and for substitute gases will probably be comprised of blends of the individual odorant compounds used today. An additional problem may occur in the odorization of hydrogen because of the possibility of fractionation of hydrogen-odorant mixtures. When these mixtures effuse through orifices or small leaks, hydrogen can leak preferentially because of its low molecular weight, resulting in low odorant concentration in the hydrogen gas. A similar fractionation problem may be encountered when liquefied natural gas is revaporized.

2. Federal Regulations – Industry Opinions

Industry leaders and industry odorization technologists are in general agreement in the opinion that the present regulations are fair, workable, and generally effective in promoting safety. They also oppose any additional requirements that would place an unnecessary and severe burden on the industry to conform to regulations that would not result in a greater measure of protection to property and human life.

IX. Recommendations

A. Odorization Practices

Regarding odorization practices of the industry we recommend, upon consideration of the survey results, that -

- Those companies using isopropyl mercaptan-base odorants switch to TBM-mercaptan or TBM-sulfide blends,
- Distribution companies initiate studies, the results of which will allow them to set maximum odor levels for their own individual systems in order to minimize nuisance calls, which are detrimental to an effective odorization program.
- Each company strive to make more effective use of present odor monitoring procedures and available odor monitoring instruments.
- Educational efforts to train the public to recognize and report gas odors be intensified and extended. We particularly urge the adoption of programs involving the distribution of encapsulated odorant as bill inserts.

B. Federal Regulations

By means of the survey, industry has indicated a general acceptance of present Federal regulations. The performance concept is deemed reasonable and workable. It is recommended that current regulations be maintained and that any further regulation be considered carefully in terms of its real contribution to safety.

C. Fields for Research

High priority should be given by government, industry, and odorant suppliers to research efforts for developing an odorant blend that will have better soil penetration characteristics. However, the shotgun approach must be avoided. The problem is a formidable one, and only a concentrated, well-defined program limited in focus would have an acceptable probability of success. Many practical considerations dictate that primary emphasis be placed on mixtures of the currently used mercaptans and sulfides.

The gas industry should apprise odorant-injection equipment manufacturers of the problems with their current products regarding constancy of odor addition rate and cooperate with them in research efforts to develop generally improved, lower cost odorizers.

In the area of odor monitoring equipment, there is a great need for research by individual companies and the industry as a whole to develop means for more effective use of those instrumental methods that give an objective measure of odor level. This requires further research on the correlation between odorant concentration and olfactory response, particularly synergistic effects. The industry should make known to instrument manufacturers the great need for lower cost instruments that measure odorant concentration and correlate concentration with olfactory response to give an objective measure of odor level.