EXECUTIVE SUMMARY

ARB Contract A4-046-33

THE PERCEPTION OF HYDROGEN SULFIDE ODOR IN RELATION TO SETTING AN AMBIENT STANDARD

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Prepared for California Air Resources Board

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Hydrogen sulfide gas is an air pollutant which can arise from sewage treatment, geothermal development and oil refining, to name a few sources. Although hydrogen sulfide is poisonous at higher concentrations, with an industrial permissible exposure limit of 10 parts per million (ppm) in the air, it was to minimize annoyance to the general public, from its unpleasant, rotten-egg odor, that the Board set an ambient air quality standard of 0.03 ppm (averaged over one hour) in 1969.

As part of a periodic review process in 1984, the Staff requested a summary of current scientific knowledge about the odor of hydrogen sulfide: its detectability, its intensity, and the degree of annoyance it can cause.

The most straightforward of these three properties to measure, and the one that has received the most attention in the literature, is the detectability, usually expressed as the lowest concentration of the gas in air, that the average person can detect. Twenty-six publications have addressed this concept, using a variety of room-test and instrumental air-dilution methods. The geometric mean (or the median) of all the determinations comes out at 0.008 ppm. There is rather poor consistency among the results. Nevertheless, the odds are 2 to 1 that the true threshold lies between 0.005 and 0.012 ppm. This is, of course, considerably lower than the ambient standard of 0.03 ppm, which indicates that well over half of the people would be able to detect hydrogen sulfide odor at the ambient standard level.

One of the sources of uncertainty in the threshold measurement is that people vary a great deal among themselves as regards their sensitivity to this and other odors. The standard deviation, a statistical measure of this variation, is a factor of 4-fold. This means that, in a random group of say 100 healthy people, only 68% would have individual odor thresholds between 0.002 ppm and 0.032 ppm hydrogen sulfide. The most sensitive of the group would likely be 250 times more acute than the least. A consequence of this variability is that, to prevent anybody at all from detecting the odor of hydrogen sulfide, it would require a quite unrealistic tightening of the ambient standard, to 0.001 ppm or less; this would demand virtually unattainable, and generally uneconomic, engineering controls. At the present ambient standard of 0.03 ppm hydrogen sulfide, it may be estimated that 83% of people could detect the odor.

In line with the properties of the other senses, the sense of smell operates on a logarithmic scale. That is, the perceived intensity of the odor sensation depends upon the logarithm of the concentration of the stimulus chemical in the air. From field work on hydrogen sulfide pollution, it has been found that the intensity of the odor increases only about 20% for each doubling of the gas concentration. Accordingly, lowering the concentration of hydrogen sulfide by means of a stricter ambient standard would have a disappointingly small effect in reducing the intensity of the odor.

There has been less attention in the literature to what is probably the most important aspect of hydrogen sulfide odor: the amount of annoyance it causes. The most informative study was by Winneke and Kastka in West Germany in 1977, with the same objective as here, the development of odor control regulations. They researched other unpleasant odors (an insulation factory and a tar oil plant) but the principles are probably the same for hydrogen sulfide. They measured the odor concentration (dilution-to-threshold ratio) at increasing distances from the pollution sources, and compared the data with the results of a comprehensive questionnaire given to residents in the same locality. The questions elicited to what extent the people were annoyed by the odors, with particular attention to the unpleasant sensations from the odor itself, the interference it caused with social life, and the degree to which physiological symptoms of headache or nausea were associated with the odor.

From a consideration of this and related research by other authors, it may be concluded that, as a provisional rule, an unpleasant odor is at or above the threshold of annoyance for half the people, when its concentration reaches 5 times the average threshold of detection. When this multiplier is applied to the odor detection threshold of hydrogen sulfide, it indicates that the threshold of odor annoyance for this compound is about 0.040 ppm. Assuming the same standard deviation as for odor detection, it may be estimated that, at the present ambient standard of 0.03 ppm hydrogen sulfide, about 40% of people exposed would experience annoyance from the odor.

For the future, whereas it would be desirable to reduce the frequency of odor annoyance, by decreasing the ambient air standard for hydrogen sulfide, the anticipated benefits tend to be modest, and the engineering expense to maintain compliance would escalate rapidly. Further research would perhaps be more effectively directed to evaluating pollution odors as such, rather than measuring individual chemicals. Most sources of potential annoyance have multiple chemical ingredients, and hydrogen sulfide is often not the major offender.

FINAL REPORT

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Abstract

This is a review of the scientific literature relating to the odor of hydrogen sulfide. There have been 26 published reports on the detection threshold concentration, of which the median is 0.008 parts per million, by volume, of hydrogen sulfide. Among a group of 100 healthy, normal observers, there is likely to be a 250-fold range of odor sensitivities. The perceived intensity of the odor sensation increases by a factor of 1.2 for each doubling of the hydrogen sulfide concentration. Evaluations of odor recognizability, unpleasantness and annoyance, have been reported in five publications. Factors responsible for annoyance can be categorized as the unpleasant odor sensation itself, its effects on social life, and the instigation of headache or nausea. As a provisional rule, it appears that when an unpleasant odor reaches about 5 times its detection threshold concentration, then this is the median threshold for odor annoyance. The present ambient air quality standard for California is 0.03 ppm for hydrogen sulfide, averaged over one hour. At this concentration, it may be estimated that 83% of people are able to detect the odor, and 40% will experience odor annoyance.

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Disclaimer

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Summary and Conclusions

Hydrogen sulfide is a gas which smells like rotten eggs. Appreciable amounts of it may escape into the atmosphere from such sources as sewage treatment plants, geothermal operations or petroleum refineries. When this happens, it may cause annoyance to neighboring residents or businesses, and give rise to odor complaints to regulatory Agencies.

The present ambient air quality standard for hydrogen sulfide, adopted by the California Air Resources Board in 1969, is a concentration of 0.03 parts per million, ppm (30 ppb, or parts per billion), averaged over a period of one hour, which is not to be equalled or exceeded. Among the several factors which the Board wished to consider, when the standard came up for review in 1984, were the current status of scientific knowledge on the odor detectability threshold for hydrogen sulfide, and any information on the threshold for annoyance caused by this odor.

The Contractor was asked to review the technical literature on these topics, and prepare a summary report of the principal factors that are involved.

The odor threshold of hydrogen sulfide is defined as the lowest concentration of the gas in the air that can be detected by the average healthy person. There have been 26 reported scientific studies on this question, but there are many possible sources of error in such measurements, which show a rather unsatisfactory range of variation. The median (actually a geometric mean) of all 26 reported thresholds comes out at 8.0 ppb hydrogen sulfide, with 2:1 odds that the true threshold lies between 5 and 12 ppb. Part of the uncertainty arises from the very wide variation of individual olfactory sensitivities among normal, healthy people. The standard deviation is a factor of 4-fold, which means that 16% of people ahve thresholds below 2 ppb, and 16% above 32 ppb. This factor alone makes it virtually impossible to select an achievable standard that would satisfy everybody.

There are many factors which modify the responsiveness of the sense of smell, generally by reducing the sensitivity. These include age, smoking habit, head-cold or allergy, inattention or distracted attention, and odor fatigue. To be able to recognize and identify an odor generally requires about 3 times higher concentration than is needed just to detect it. The perceived intensity of odor sensation increases by a factor of 1.2 for each doubling of the concentration of hydrogen sulfide.

Several approaches have been described for assessing the degree of annoyance caused by unpleasant odors. These include both laboratory work to find the threshold concentration at which an odor is considered unpleasant, and field work to measure the odor units (multiples of the threshold concentration) at various distances down-wind from the source. In the extensive work reported by Winneke and Kastka from West Germany, a detailed questionnaire was also used to assess the degree of annoyance caused by the odors. They considered three categories of annoyance: the odor sensation itself, the effects it had on social and daily life, and any disturbing physiological responses such as headache or nausea.

Six published studies were found which relate to the recognizability, unpleasantness and annoyance associated with a variety of unpleasant odors (petrochemicals, Kraft mill stack gases, and odor pollution from an insulation factory and a tar oil plant). The Contractor has derived from these data an averaged value for the ratio between odor annoyance threshold and odor detection threshold, each based on the 50% response level. Provisionally, it is concluded that, for an unpleasant odor, the threshold of annoyance is at approximately 5 times the threshold of detection. If this rule is applied to hydrogen sulfide, the median threshold of odor annoyance would be expected to be at 40 ppb.

A Table is provided which indicates, for selected levels of hydrogen sulfide between 200 and 0.5 ppb, the best scientific estimates of odor intensity, odor detectability, and odor annoyance. Some representative values are listed in the following abbreviated Table (with concentrations of hydrogen sulfide quoted in ppm, for comparison with the California standard):

Hydrogen sulfide concentration (ppm)	Persons able to detect odor (%)	Persons annoyed by odor (%)
0.04	88	50
0.03[a]	83	40
0.025	80	37
0.02	74	31
0.008	50	11

[a] The current California ambient standard

This Table demonstrates that even a substantial downward revision of the ambient standard for hydrogen sulfide, which could be very expensive for industrial engineers to achieve, would not eliminate odor annoyance among the population. The problem therefore evolves into a matter of balancing the cost/benefit ratio, while maintaining a tolerable limit on annoyance.

Recommendations

In the Contractor's opinon, any further technical research to be sponsored by the Board on odor detection and odor annoyance should be broadened to evaluate odor pollution by source, rather than by one (e. g. hydrogen sulfide) or a few named chemicals. This is because the majority of pollution sources generate complex mixtures of odorous chemicals, that would be impossibly tedious to evaluate by the classical procedure of chemically separating the individual compounds and determining their thresholds.

For regulatory purposes, a good starting point would be the measurement of the odor units (dilution to threshold ratio) in air samples taken at the factory fence. If the odor value is over 5 units, there is the potential for odor annoyance to occur. Further evaluation of the air samples should include an estimate of odor intensity (by comparison with calibrated standards). The techniques of threshold and intensity measurements are well worked out in the literature. A further evaluation, of actual odor annoyance, would be highly desirable, but probably needs more research to select an agreed method.

Odor pollution appraisals should be conducted by trained panels of disinterested observers, having average smell sensitivity (individually or as a group). Such panels could work on bag samples in the base laboratory, or be dispatched with a mobile laboratory to wherever an odor pollution problem is reported. They would test the air at various distances from the suspected source.

Considering that the first intimation of an odor problem received by regulatory Agencies is usually a telephoned or written complaint, it would be desirable to develop some sort of calibration of the relationship between odor complaint and odor threshold or odor annoyance. This might be achieved by studying Air Pollution Control District records.

BODY OF REPORT

A. Introduction: The Olfactory System

The sense of smell is one of our five senses, that provide vital information about the environment. It is a chemical sense, responding to minute traces of chemical vapors, in the form of volatile molecules that evaporate from the source material and are carried by air currents. When these molecules are sniffed into the upper part of the nasal cavity, they can excite specialized nerve cells, that convey electrical impulses to the olfactory bulb of the brain, and generate a sensation of odor. The strength of the smell, and whether it is pleasant, neutral or repulsive, depends upon the concentration and chemical identity of the stimulus molecules, and the specific affinities of our nervous receptors.

Hydrogen sulfide vapors occur naturally in various situations which are significant for the survival of the species. At its weakest intensity, the odor can be appetizing, as in a fresh boiled egg, or even a Limburger cheese. A little stronger, and the odor becomes disgusting, and may even be nauseating (Yant, 1930), as in a bad egg, or other spoiled protein food. Here the sense of smell is providing a valuable warning, because, even though this small amount of hydrogen sulfide is not poisonous, it may be associated with pathogenic or putrefactive bacteria that do generate harmful toxins. Much higher concentrations of hydrogen sulfide, dangerous in their own right, can develop in decomposing waste (sewer-gas), in caves and mines (stink-damp), and near volcanic activity. These may be among the evolutionary reasons why human olfaction is especially sensitive to hydrogen sulfide, and why there is an instinctive revulsion from its odor.

Elusive as these phenomena may seem, they have been subjected over the years to a great deal of scientific evaluation. The following review is intended to provide appropriate basic information on the sense of smell, with particular reference to hydrogen sulfide, that should be taken into consideration in selecting a rational standard for this chemical in air quality management.

B. Methods for Determining Odor Thresholds

1. Concept of odor threshold. Most people would find that air containing 100 ppb hydrogen sulfide is obviously odorous. (Concentrations in this Review are expressed in ppb, v/v, that is, parts per billion, by volume, of hydrogen sulfide gas in air, where one billion = 10^9.) On the other hand, few people could detect any odor in 0.1 ppb hydrogen sulfide. This opening statement raises at least three difficult scientific problems. It is not easy to prepare and/or analyze samples of air containing such low, yet precise, concentrations of hydrogen sulfide (Lindvall, 1970). There is continuing debate as to the exact definition of the olfactory threshold (Engen, 1971), that is, the lowest concentration of hydrogen sulfide that can just be detected as odorous. Different people are far from equal in their ability to smell various chemicals (Amoore, 1968). Fortunately hydrogen sulfide has been the subject of at least 26 published determinations of its odor threshold, according to a recent systematic review (Amoore and Hautala, 1983). The authors, their methods and principal results are listed in Table I. For details, the reader may refer to the original papers cited in the References.

2. Static tests. The room test is simple in principle. A tightly sealed room of known volume is fitted with a fan to circulate the air. By means of a gas syringe or similar device, a measured volume of hydrogen sulfide gas is discharged into the room and dispersed by the fan. The resultant dilution is calculated, assuming perfect mixing. People then enter the room, and record on questionnaires whether or not they can smell anything. The room is then opened and thoroughly aired out; then the test is repeated with other concentrations of hydrogen sulfide. Difficulties include loss of hydrogen sulfide on opening the door to enter the room, and adsorption of the odorant to the walls of the room, or to the clothing of the test subjects. Four of the authors in Table I used this method. Variations on the static method use serial dilutions in smaller tubes, bottles or flasks, which avoids some problems, but may introduce others, such as a higher surface-to-volume ratio, and hence greater possibility for adsorption.

3. Dynamic tests. The majority of modern tests on the threshold of hydrogen sulfide have used specially-designed instruments, which can be classed as dynamic olfactometers. A continuous main-stream of odorless (or deodorized) air is passed through the instrument at a measured rate by a fan, pump or pressure cylinder, and delivered to the test subject via a hood, mask or nose cone. A fractional side-stream of hydrogen sulfide is bled into the main-stream of air

Table I. Published reports on group average odor detection thresholds for hydrogen sulfide (ppb, v/v in air).

Author, Year	Method	Threshold (ppb)
Valentin, 1848	Serial dilutions in tubes	1400
Kulka, 1911	Room test	17
Henderson, 1922	Analysis of effluent air-stream	< 0.72
Henning, 1924	Serial dilutions in bottles	0.072
Katz, 1930	Dynamic olfactometer	130
Fair, 1933	Serial dilutions in water	28
Thomas, 1943	Air dilution	25
Loginova, 1957	Dynamic olfactometer	29
Fen-Djuy, 1959	Dynamic olfactometer	14
Sanders, 1961	Dynamic olfactometer	45
Baikov, 1963	Dynamic olfactometer	14
Cederlöf, 1966	Dynamic olfactometer	7.2
Young, 1966	Multiple dynamic olfactometer	5.8[a]
Sakuma, 1967	Room test	5.0
Adams, 1968	Multiple dynamic olfactometer	4.6[a]
Basmadzhieva, 1968	Dynamic olfactometer	8.6
Kendall, 1968	Room test	0.47
Leonardos, 1969	Room test	4.7
Wilby, 1969	Dynamic olfactometer	4.5
Lindvall, 1970	Dynamic olfactometer	0.43
Randebrock, 1971	Dynamic olfactometer	8.7
Stephens, 1971	Air dilution	48
Winkler, 1975	Dynamic olfactometer	2.1
Williams, 1977	Dynamic olfactometer	190
Thiele, 1979	Dynamic olfactometer	1.1
Winneke, 1979	Dynamic olfactometer	1.9

(continued)

(Table I, continued)

Total number of reports = 26

Geometric mean = 8.05 ppb
Standard deviation = x/÷ 8.2
Standard error = x/÷ 1.51

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[a] Programming errors in the original computations have recently been corrected; for untrained observers, and adjusted to age 40, these values should be lowered to 1.9 ppb (Dr. Francis Young and Mr. Bruce Weir, personal communications). This would change the geometric mean to 7.45 ppb.

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at a precisely controlled rate, and thoroughly mixed by a venturi or other turbulence before it reaches the nose of the subject, who has to indicate whether or not an odor is detected. Different concentrations of hydrogen sulfide are delivered to the subject, with appropriate intervals for re-equilibrating the instrument and resting the subject's nose. Sixteen of the authors in Table I used one form or another of dynamic olfactometer. The methods for achieving the dilution and conducting the test vary widely, and indeed there is as yet no generally agreed "standard method" for olfactometry. The dynamic methods reduce the problem of odorant adsorption, but it is necessary to check the flow-rates accurately, and two or more stages of air dilution, with associated possibilities for error, may be needed to reach the threshold of an odorant as powerful as hydrogen sulfide. In some of the best-controlled experiments, the intermediate dilution of hydrogen sulfide has been monitored continuously by a coulometric analyzer (Adams et al., 1968), and the final dilution ratio has been confirmed by use of radioactive H_2S^{35} and a scintillation counter (Lindvall, 1970).

4. Criteria for threshold. Most of the authors in Table I have reported what may be termed "operational thresholds", as defined in their own descriptions of methods. The subject takes a sniff, from the test room or the olfactometer, and states whether or not he or she perceives an odor. If the odor is moderate, the subject should have no doubt. When it is weak, peoples'

Others are more liberal, and tend to report an odor even when nothing has been added to the air sample. To some extent, these opposing psychological characteristics tend to compensate, if the data are averaged for a reasonably large group of subjects, say 10 or 15 or more. Such averaging is generally applied anyway, for another reason -- that people range quite widely in their individual thresholds.

The operational odor threshold is commonly defined as that concentration of hydrogen sulfide at which just 50% of the subjects in a group report the perception of an odor, and 50% do not detect any odor. It may be determined by graphical interpolation from the observed frequencies of odor detection at various hydrogen sulfide concentrations (preferably using log/probit graph paper; Amoore and Hautala, 1983; Lindvall, 1970). Alternatively, the individual detection threshold for each member of the group may be determined, then their geometric mean calculated (convert to logarithms, find their arithmetic mean, and take the anti-logarithm). The use of logarithms is recommended, because the relationship between odor-intensity sensation and odorant concentration is exponential (Lindvall, 1970; Amoore, 1982). In practice, if the individual odor detection thresholds among a large group of people are plotted as a function of the logarithm of the odorant concentration, then the frequency of occurrence of various threshold sensitivities usually exhibits a normal or Gaussian distribution (bell-shaped curve). In any case, the odor detection threshold of hydrogen sulfide is a statistical average, representing the olfactory sensitivity of an imaginary "average man".

C. Hydrogen Sulfide Thresholds in the Literature

In Table I, the 26 literature threshold values have been placed in chronological order, and all converted, if necessary, to concentrations expressed in ppb. An immediately disturbing feature of this compilation is wide range of values reported. Valentin's (1848) threshold is 20,000 times higher than Henning's (1924). Since then, the experimental techniques have evidently improved somewhat, and the range of values reported in the other 24 papers does not exceed a 500-fold variation. Considering that all these measurements were made by experienced scientists and published in refereed Journals or respected textbooks, all should perhaps be given equal consideration, at least in the first statistical analysis (Amoore and Hautala, 1983). Making an assumption, that the mean thresholds determined by different experimenters are also logarithmically distributed, the geometric mean (numerically equal to the median) of all 26 detection thresholds is 8.05 ppb, as indicated at the foot of Table I. The standard deviation among these measurements is a factor of x/÷ 8.2. That is, aproximately 68% of all the thresholds fall in the range between one-eighth of the mean (1 ppb) and eight times the mean (66 ppb). The standard error of the mean, taking into account all 26 observations, is a factor of x/÷ 1.51. Hence, there is an approximate probability of 2/3 (68%) that the true detection threshold for hydrogen sulfide lies between 8.05 ÷ 1.51 = 5.3 ppb, and 8.05 x 1.51 = 12.2 ppb.

This statistical treatment makes the uncertain assumptions that any experimental errors inherent in the 26 reports are logarithmically distributed with median 1.0, that each experimenter estimated the mean detection limit of the same population, using hydrogen sulfide of the same purity, and again that the individual detection limits are logarithmically distributed in this population. Equal weight is given to each report, even though these vary widely in their internal statistical confidence. Valentin (1848) and Henning (1924) seem to have used just one subject, whereas Adams et al. (1968) tested more than 4000 subjects. Large numbers of subjects, however, can produce a more precise result, but not necessarily more accurate. Using only 4 observers, Leonardos et al. (1969) demonstrated that hydrogen sulfide from a commercial cylinder had an odor threshold one-tenth of that generated in the laboratory from sodium sulfide. Lindvall (1970) noted a three-fold variation of odor intensity between different cylinders of technical-grade hydrogen sulfide from the same manufacturer. Both authors recognized that small proportions of unidentified but highly odorous impurities were probably responsible for these differences. Very few of the published reports (Table I) have expressed concern with the purity of the hydrogen sulfide they used. In retrospect, by re-reading the experimental methods, a committee of experts might be justified in assigning weightings to each report, giving expression to the probable precision and accuracy of the procedures described.

For the purposes of this Review, the geometric mean hydrogen sulfide detection threshold of 8 ppb will be adopted as a point of reference, to which other sensitivity factors can be applied. It is the most broadly-based estimate presently available, but it will always be open to revision, as critical re-assessments or improved experimental re-investigations are published.

D. Normal Distribution of Olfactory Sensitivities in the Population

A convenient scale of odorant concentrations for measuring the detection thresholds of individual subjects is the binary step scale. In this, each test concentration step is one-half of the preceding step. This is a logarithmic scale, on base 2. When a large group of subjects have their individual thresholds measured to a given compound on this scale, the results typically follow a normal or Gaussian distribution (Amoore, 1968; Adams et al., 1968). The standard deviation of this distribution is approximately the same for all odorants so far tested, averaging very close to ±2.0 binary steps, or a factor of 4 (Amoore et al., 1977). Accordingly, 68% of persons tested should have individual thresholds within the range of one-quarter of the median, and four times the median.

On the assumption that this generalization also applies to hydrogen sulfide odor, Table II was drawn up, to show the expected distribution of individual thresholds around the adopted median of 8 ppb. The Table shows the standard deviations, factors, and ppb ranges for both above-average and below-average thresholds. Approximately 68% of people should have thresholds between 2 ppb and 32 ppb. Towards the extremes, the two least sensitive persons in a group of 100 people are likely to have individual thresholds more than 250 times higher than the two most sensitive in the group. Subjects in good health can normally reproduce their individual threshold measurements within ± 1 binary step, or a factor of 2 (Amoore, 1970). Hence the variation of olfactory threshold in the population is substantial and stable, and should be considered in setting an air quality standard.

E. Factors Influencing the Perception of Odor

In the course of measuring olfactory thresholds for research purposes, observations have been made of numerous factors which may affect the sensitivity of an individual's nose. These are assembled in Table III. The findings are expressed as factors (multipliers), and also applied to the adopted normal geometric mean threshold of 8.0 ppb for hydrogen sulfide. Most of these observations were made with odorous chemicals other than hydrogen sulfide, so it does not necessarily follow that the same factor applies.

Table II. Expected distribution of individual detection thresholds for hydrogen sulfide odor

Deviation	Thresholds range		Frequency
	(factor)	(ppb)	(percent)
> 2 x S.D. low	< 0.0625	< 0.5	2
1 - 2 x S.D. low	0.0625 - 0.25	0.5 - 2.0	14
0 - 1 x S.D. low	0.25 - 1	2.0 - 8.0	34
0 (Mean)	1	8.0	-
0 - 1 x S.D. high	1 - 4	8.0 - 32	34
1 - 2 x S.D. high	4 - 16	32 - 128	14
> 2 x S.D. high	> 16	> 128	2

Table III. Conditions expected to influence the olfactory detection threshold for hydrogen sulfide

Class of persons[a]	Factor	Threshold (ppb)
Average 40 yr. man	1	8.0
Average woman	0.8	6.4
18 yr. person	0.5	4.0
62 yr. person	2	16
Moderate smoker	1.1	8.8
Smoking during test	4	32
Chewing during test	4	32
Head cold	4	32
Nasal allergy	4	32
Un-trained	1.4	11
Un-directed test	4	32
Mis-directed test	26	210
Sleeping during test	20,000	(160,000)[b]
Odor <u>recognition</u> threshold	3	24

[a] Understood to be average 40 yr. persons, unless indicated

[b] Theoretical; concentrations of H_2S above 100,000 ppb (100 ppm) quickly <u>abolish</u> the sense of smell; 1,000,000 ppb (1000 ppm) is rapidly fatal (NIOSH, 1977).

1. Gender; age. All other considerations being equal (age, health, etc.), men and women have almost equal olfactory sensitivities (Venstrom and Amoore, 1968; Lindvall, 1970). It has usually been found that increasing age, at least over 20 years old, is associated with decreasing sensitivity (Kimbrell and Furchtgott, 1963). Thus the olfactory threshold has been reported to increase by a factor of 2 for each 22 years of aging above 20 (Venstrom and Amoore, 1968). In Table III the expected thresholds are given for an average 40-year old person (or for a group of people averaging 40 years and similar in other respects). There is no noticeable trend of sensitivity between young adults and children down to 5 years, the youngest at which a reliable odor threshold test can usually be conducted (Whissell-Buechy and Amoore, 1973).

2. Smoking; eating; nasal distress. Moderate tobacco-users have been found to have virtually the same smell senstivity as non-smokers of the same age (Venstrom and Amoore, 1968; Lindvall, 1970). This is true, however, only if they have not smoked for at least 10 minutes before test. Thresholds increase by a factor of about 4 if the subject is smoking, chewing flavored gum or candy, or sipping a soft drink during or immediately before the test (Amoore et. al., 1968). The wearing of perfume has little effect on the subject using it, as long as the test odor is different in character from the perfume, but it tends to affect other subjects in the vicinity. A head cold or a nasal allergy also increases the threshold about 4-fold, provided that it is still possible to breathe through the nose.

3. Training and motivation. An important group of factors is the motivation of the subjects taking the smell test. All the thresholds so far mentioned are "directed test" thresholds, in which the subject is attentive, working under laboratory conditions, and doing his or her best to detect an odor. Usually the subjects have had considerable training and practice in smell testing, before the actual test runs are made. Nevertheless, as Young and Adams (1966) showed in experiments with hydrogen sulfide odor, completely un-trained subjects could enter the test facility and achieve an average threshold concentration that was only 1.4 times higher than that for the trained subjects.

Much larger effects were recorded by Whisman et al. (1977), in which they tested whether un-trained naive subjects would notice the warning odor (ethyl mercaptan or thiophane) from bottled gas in a room they were entering. In the "undirected test", after leaving the room, they were questioned for their impressions, with no emphasis being placed on odor. In the "misdirected test", their attention while in the room was deliberately distracted by asking each to read some print in a dim light, and to judge the temperature. (Each subject was used for only one test.) When Whisman's original data were re-calculated on log/probit coordinates as described by Amoore and Hautala (1983) the undirected conditions resulted in a four-fold raised threshold of detection. The misdirected scenario caused a 26-times increased threshold.

Thus the threshold of perception of even these unpleasant odors is strongly influenced by the degree of attentiveness or distraction of the subject. In the extreme case of a soundly-sleeping person, it takes about 20,000 times the directed threshold concentration (of a non-irritating odorant) to awaken the subject (Fieldner et al., 1931, re-calculated by Amoore and Hautala, 1983). Another factor is that of odor recognition, as opposed to detection. Hellman and Small (1974) presented data for 101 compounds, from which it may be calculated that recognition of the specific character or quality of an odor requires about 3 times higher concentration than that for mere detection as something different from plain air. All of these factors must have an influence on the noticeability of hydrogen sulfide as an air pollutant. Measurements made specifically on hydrogen sulfide, if available and well established, should take precedence over the generalized factors assembled in Table III.

F. Supplemental Considerations

1. "Smell-blindness" and "super-smellers". There are comparatively rare individuals in the population whose sensitivities to odors depart even further from the norm. About 1 person in 500 has no sense of smell at all (Patterson and Lauder, 1948) which can happen for a variety of medical or occupational reasons (Sherman et al., 1979). More common, perhaps a few percent, are people who have a normal sense of smell in other respects, but cannot perceive certain sulfurous odors (Amoore, 1968). At the other extreme, some individuals, either naturally or due to some pathology, can achieve thresholds less than one-thousandth of normal (Sherman et al., 1979).

2. Intensity of odor sensation. As the concentration of an odorant increases above the threshold,

the intensity of the odor sensation increases, but not in a simple proportion. Accoding to Stevens (1960), the perceived intensity I follows a power (exponential) function of the odorant concentration C:

$$I = kC^n$$

In logarithmic terms:

$$\log I = n \log C + \log k$$

Thus the logarithm of the intensity depends upon the logarithm of the concentration. Standardized values for the exponent n have been assembled by Patte et al. (1975), who derived the laboratory value $n = 0.51$ for hydrogen sulfide. Under field conditions, with less-trained observers, the exponent n averaged 0.26 in Lindvall's (1974) experiments with hydrogen sulfide. According to his measurements, the perceived odor intensity increases only by a factor of 1.2 for each doubling of the hydrogen sulfide concentration.

3. Odor fatigue. With continuing exposure to an odor, the sensation gradually decreases, and may even disappear (see review by Engen, 1971). This is more correctly known as adaptation. Unlike adaptation to sound, the smell sensation cannot be recaptured by renewed attentiveness. Ekman et al. (1967) measured the changes of perceived intensity of hydrogen sulfide odor at concentrations of 700, 900, 2,600 and 6,400 ppb. Most subjects experienced an exponential decrease of intensity, that dropped to a steady level within 2 - 5 minutes, and did not change appreciably up to 15 minutes. One of 8 subjects indicated virtually complete loss of odor sensation, and another a substantial loss. The other six showed relatively moderate (approximately 50%) decreases of perceived intensity, yet this corresponds with an apparent reduction of hydrogen sulfide concentration by 74 - 93%, depending upon which value of the exponent n is applicable.

On restoration to breathing pure air, with intermittent smell testing, the sensitivity recovered asymptotically and almost completely in about 4 minutes. The average results were nearly the same at all four concentrations of hydrogen sulfide tested. Even with much longer exposures, recovery seems to be quite rapid. Tests have been made on Kraft pulp-mill workers exposed daily to the odors of hydrogen sulfide, mercaptans, thio-ethers, etc. (NCASI, 1971). When tested right after coming off a 6 - 8 hour work shift, after a short time in the odor-free laboratory, they exhibited the same odor detection threshold for the Kraft odor as non-mill workers.

4. Mixtures of odorants. In most practical situations, not just a single compound, but a mixture of odorants is responsible. Some rules that may be helpful in evaluating mixtures have been reviewed by Amoore (1982). The detection threshold of a mixture can be quite accurately predicted by comparing the thresholds and concentrations of the components. The relative contribution of each compound may be estimated from its concentration C divided by its threshold C_t (Guadagni et al., 1966). This ratio gives the number of "odor units" U developed by that compound:

$$U = C/C_t$$

Guadagni and his collaborators showed that:

$$U_m = U_1 + U_2 + U_3 + \ldots$$

where U_m represents the total odor units of a mixture, made up from the odor-unit contributions of all the separate components. This has become known as the "rule of additivity".

When matched to a standard supra-threshold odor intensity, the two components of a binary mixture contribute apporoximately additively to the total odor intensity (Köster, 1969). The mathematics for predicting the odor intensity of multi-component mixtures has not yet been perfected, but an empirical vector summation method developed by Berglund et al. (1973) is quite effective.

5. Enhancement; counteraction; suppression. Certain added vapors can cause quite unpredictable alterations of smell sensation. The perceived odor strength of hydrogen sulfide has been reported to be increased by the simultaneous presence of 600 ppb nitric oxide in the air, which by itself is imperceptible (Lindvall, 1977). The addition of a small amount of a second, pleasant odor (lavender oil) may be able to reduce the apparent intensity of a stronger, unpleasant odor such as pyridine (Cain and Drexler, 1974). Even if the overall intensity is not reduced, the noticeability of the unpleasant component may be reduced. This effect is known as "masking", and is efficiently used in many commercial odor-counteracting products.

Another type of odor suppression has been described by Schleppnik (1978). The vapor of

4-cyclohexyl-4-methyl-2-pentanone, even below its own olfactory threshold, specifically inhibits the perception of those unpleasant odors that are due to the ionizable molecules of mercaptans, amines and carboxylic acids. Hydrogen sulfide belongs to this class. The perception of most neutral molecules, and hence many pleasant odors, is unaffected. The product, now available commercially (Veilex™; Non-Scents™), acts directly on the sense of smell, and the effect is reversed promptly when exposure to the inhibitor ceases.

6. Other sources of confusion. It should be remembered that when hydrogen sulfide occurs as an industrial or municipal by-product, it seldom occurs alone. Fugitive vapors from pulp mills, refineries or sewage plants, may contain hydrogen sulfide, but it is likely to be accompanied by other compounds which can change the character of the odor and may have even lower detection thresholds. Such compounds as trimethylamine and alkyl mercaptans can be smelled at concentrations so low (less than 1 ppb) that they cannot be monitored by any direct-reading instrument, but have to be pre-concentrated by a trap-and-purge technique.

In and around a home, the air is sometimes unpleasantly odorous, for reasons unrelated to industry. Kitchen, bathroom, baby and pet odors often contain hydrogen sulfide. Barbecuing, garden fertilizers, pesticide sprays and cesspools can release hydrogen sulfide and other odors in the same chemical family (thiols). Manure accumulations in cattle, pig and horse farming make their contribution, and the skunk and other mustelidae can discharge extremely malodorous sulfur compounds when alarmed. Without careful sniffing and recollection, it is not always easy to identify these natural odors, and distinguish them from industrial sources.

G. Relationships between Detection and Annoyance Thresholds

"It should be recognized that the activation of the sense of smell does not necessarily cause annoyance or unpleasantness to an individual. The intensity, quality, frequency and duration are important factors that can contribute to annoyance" (Prokop, 1974). This section will examine some contributions that have been made to the difficult task of evaluating odor annoyance.

1. Measuring the unpleasantness of odors. Adams, Young and Luhr (1968) measured and

reported the detection thresholds for hydrogen sulfide by thousands of untrained subjects (visitors to a mobile laboratory at County fairs). At the same time, they asked the subjects to check whether the odor was pleasant or unpleasant; but these hedonic data were never published. Recently Dr. Francis Young has made the original data set available on magnetic tape to the Air Resources Board and to Systems Applications Inc., where Mr. Bruce Weir has run a statistical analysis. The average threshold concentration at which hydrogen sulfide was considered unpleasant was only 1.6 times the average concentration at which it could just be detected.

The same research group also conducted a similar study with Kraft pulp mill stack gases, which typically contain predominant concentrations of hydrogen sulfide (NCASI, 1971). These test subjects also were untrained in odor assessment, but they were mostly employees in the offices or plant at the pulp mills. Possibly as a consequence of their familiarity with the Kraft odor at or near their workplace, the average threshold for an "unpleasant" designation was considerably higher than the threshold for odor detection; approximately 6 times higher when the data for all 75 panelists are averaged.

The threshold for an "unpleasant" characterization is regarded as an "objectionability threshold" by Adams <u>et al</u>. (1968) and in the NCASI (1971) report. Admittedly they do show that, at a concentration equal to or only very slightly above the detection level, untrained observers can decide whether an odor is pleasant or unpleasant in character. This does not necessarily mean it is objectionable. In fact, Winkler (1975) argued that it would be unreasonable to set an industrial odor emission limit any lower than the <u>recognition</u> threshold of the substance. In the experiments he described with hydrogen sulfide, the recognition threshold was ten times higher than the detection threshold.

If an odor is regarded as unpleasant, then the degree of unpleasantness is closely related to the intensity of the odor. Dravnieks (1977) has measured the relative unpleasantness of many industrial odors by a magnitude estimation procedure, setting "moderately unpleasant" at a scale value of 100. The intensities of the odors were evaluated on the "butanol scale" (Moskowitz <u>et al</u>., 1974). This is a reference series of concentrations of 1-butanol vapor, delivered by a portable dynamic olfactometer, that can be used for comparative purposes when assessing the intensity of the odor under consideration. The new reference scale gives more consistent results in inter-Laboratory comparisons than the older 0 - 5 category-scaling method ("none - very faint - faint - moderate - strong - very strong"; Katz and Talbert, 1930). Dravnieks' (1977) graph exhibits an approximately linear relationship between the relative unpleasantness of various industrial odors, and their intensities on the butanol scale (log ppm).

2. Field evaluation of odor pollution. The full characterization of an odor pollution problem from a single industrial source has many aspects, and is very laborious. As an example, we may take the work of Lindvall (1970, 1974, 1977) and his collaborators on Kraft mill emissions in Sweden. Finding the typical composition of the sulfurous effluent gases, and the concentrations and odor thresholds of these compounds, is just the start of the problem. At various points down-wind of the plant, the concentrations of the odorants should be measured. Nevertheless, the odor may be due in part to chemicals that have not been identified in the effluent or, if identified, may not have had their individual odor detection thresholds measured. Therefore it is advisable to determine the overall odor threshold at the sampling point. This is done by taking a sample of the air, and diluting it with pure (odorless) air until the odor threshold is just attained. The ratio of the number of volumes of the diluted sample, to the volume of the poluted air taken, gives the number of "odor units" in the polluted air (Lindvall, 1977; Guadagni et al., 1966).

The testing is done either by taking bag samples of the polluted air to the laboratory, or by bringing a mobile laboratory to the field. Such measurements depend upon the sensitivity of the panelists, who should be chosen to represent, either individually or collectively, an "average man". The odor unit values obtained, which are simply multiples of the average detection threshold, may be compared with the factors listed in Table III, to obtain a rough idea of the likely perceptibility of the odor by various classes of observers. Bearing in mind that odorants can differ quite markedly in the slopes of their intensity functions (Patte et al., 1975), the perceived odor strength should be estimated by observers at various points downwind, preferably using reference standards of intensity, consisting of sniff-bottles containing standard solutions of odorants (Lindvall, 1974). The use of reference standard odors decreases the problem of individual variability in olfactory sensitivity between different observers.

Detailed surveying of the odor pollution plume by means of stationary observers, or observers traveling in cars along roads lying approximately cross-wind, is necessary for a two-dimensional and temporal understanding of the odor distribution (Lindvall, 1970). If the industrial plant has several suspected sources of pollution, an innocuous and odorless marker gas (e. g. sulfur hexafluoride) can be injected into one of the stacks, and measured by laboratory analysis of the air samples. The results often reveal a surprising lack of homogeneity in the odor plume, especially at short distances from the plant (Lindvall, 1974). Due to topographical or micrometereological causes, these findings can explain apparently contradictory population reports in the neighborhood of a pollution source.

A somewhat different approach is taken by Sullivan and Leonardos (1974). They use a small group of highly trained odor chemists for field work. The chemists first become familiarized with the subject plant, and with the possibly different-smelling processes that may be in operation. In the field, the chemists then try to relate any odors they detect to the particular sections of the plant where they originate. They also evaluate the perceived intensity of odor in the field according to a 0 - 3 category scale ("threshold - slight - moderate - strong") that is based on the Flavor Profile Method (Caul, 1957). If possible, odors are also sampled at the source by drawing 500 liters of polluted air through a Chromsorb® 102 trap, then eluting with pentane, diluting with nonane, and delivering at a known dilution with pure air to the subject in a test chamber. In this way the dilution-to-threshold ratio (odor units) of the source gas can be calculated. For several odors associated with a coffee factory, the authors provide equivalencies between odor units and category ratings; for example, 64 units of spent-grounds odor rated 2 on the category scale. This system is especially valuable where more than one industrial or other sources may be involved in the overall pollution, and it is desirable to determine the relative contributions of each.

3. Quantitative assessment of annoyance reactions. "In most cases, however, it is not possible to establish a quantitative objective measure of acceptability or the degree of annoyance by chemical or sensory methods of analysis. Public reactions of subjective annoyance can probably best be evaluated by sociological inquiry methods" (Lindvall, 1970). The chemical and physiological groundwork described in the earlier sections of this Review is a necessary prerequisite to the evaluation of annoyance reactions caused by odors. A major difficulty in any kind of attitude survey is that the inquiry itself may polarize the viewpoints of the individual respondents, and indeed of the whole

subject population, once it is known that an investigation is in progress.

Flesh (1974) endeavored to avoid such a bias, by designing a questionnaire that masked the true purpose of the inquiry, and by comparing the results obtained in a community having odor problems with an odor-free community that was otherwise matched geographically and socioeconomically. The interviews were conducted in person or by telephone with a randomly selected sample of residents in each area. From the number of responses to key questions, the proportion of residents who are bothered by odors can be determined, and also the likely sources of the odor complaints can be identified.

A statistical approach was used to determine if an odor problem exists in a given community, i.e. if for the test area the proportion of residents interviewed that were bothered by odors was significantly greater (95% confidence level) than the proportion of residents bothered by odors in the control area. If the value of the normal deviate, z, exceeded 1.65, a community odor problem was considered to exist. The results were converted to an "odor index", on a scale with maximum 10. Results are given for approximately 30 interviews in each of 24 communities in 4 air-pollution control Agencies; odor problems were found to exist in 14 communities (Flesh, 1974). Replicate surveys in four communities demonstrated an adequate self-consistency in the results. Methods are also described for searching for an economic impact of odors on property values in residential areas, but significant effects are not anticipated, except in the extreme case that more than half of those interviewed in test areas claim to be bothered very much by odors.

The questionnaire developed by Winneke and Kastka (1977) deals openly and in depth with the perception and effects of environmental odors. It clearly depends upon conscientious answering by the respondents, but additional controls are provided by the use of relatively odor-free comparison areas, and by correlating the subjective responses with dilution-to-threshold measurements of the odors in the locality. Their work was intended to help with the development of odor control legislation in the Federal Republic of Germany. The questionnaire contains 40 possible odor-annoyance reactions, for each of which the respondent has to give a self-assessment. For example: "How often does it happen that odors induce headache with you?" The subject's answer is on a seven-point scale from 0 = "never" to 6 = "permanently ". The questionnaire was tested in Duesseldorf, with a known odor-problem area close to a soap and detergent plant, and two otherwise comparable odor-free areas near a glass works and a steel mill. From a random sample of 1000 inhabitants drawn from the census files, 700 were interviewed in person.

The complete set of data obtained in response to the questionnaire were submitted to a computerized statistical analysis. The first step was a principal components analysis, intended to reveal any inherent associations (item clusters) among the 40 selected odor-annoyance reactions. It yielded six components with eigenvalues larger than 1.0, that is, potentially significant. The second step was a Varimax rotation of these component factors, to find out how much of the original odor-annoyance scale data could be correlated with these factors. More than 50% of the total variance in the raw data could be accounted for by just the first three component factors.

Winneke and Kastka (1977) reviewed the odor-annoyance reactions that make up each component factor, and concluded that they could be categorized in the following manner:

1. Generalized annoyance based on sensory (odor) experience
2. Social-emotional annoyance reaction (affecting daily life)
3. Somatic-vegetative (autonomic nervous system) annoyance

Smaller follow-up studies on subsamples of the original samples, in odorous and odor-free areas, confirmed that there is a markedly stable attitude toward ambient odors, amenable to scientific study.

This system of odor-annoyance assessment has been tested by Winneke and Kastka (1977) in two more cities: an insulation plant in Cologne emitting phenolic compounds, and a tar-oil plant in Duisburg emitting hydrocarbons and sulfur compounds. Measurements were made at various distances form the plants, and recorded in three Figures, from which it is possible to read off some comparable representative data (Table IV). The insulation plant behaved as a point-source, and the degree of pollution on the lee side, measured in odor units by a mobile laboratory, decreased quite steeply at increasing distance from the plant out to 1600 meters. They measured both the median (50%) and extreme (95%) values of the polllution. From these values it can be figured that, aproximately 5% of the time, the odor units exceeded 7-times the median value. This implies that certain chemical measures of average pollution, obtained by cumulative air sampling over an interval

Table IV. Odor pollution and odor annoyance near industrial plants in the Ruhr.

Estimated data, interpolated from Figures 3, 1 and 2 of Winneke and Kastka (1977).

Source	Distance from plant (meters)	Pollution Odor units[a]		Odor-induced disturbances		Degrees of annoyance by odors		
		50%	95%	Headache	Nausea	Sensory	Social	Somatic
Insulation plant (phenolics)	100	13	110	92	70	5.2	4.0	3.5
	400	5	16	58	45	3.4	2.0	1.1
	1600	-	-	26	4	0.0	0.8	0.0
Tar-oil plant (hydrocarbons & sulfur cpds.)	10	15	110	65	44	4.2	2.8	1.8
	400	40	450	74	64	4.5	2.8	2.4
	1400	20	100	70	56	3.9	2.8	1.9

[a] Odor concentrations that were <u>not</u> exceeded 50% or 95% of the time, respectively.

of a half-hour or more, may not reflect the minute-by-minute variations of intensity that can give rise to odor annoyance (Lindvall, 1974).

From Table IV it can be seen that among inhabitants 100 meters outside the insulation plant, where the median pollution was 13 odor units (13 times average odor-detection threshold), over 90% of those interviewed has at least occasional headaches that they attributed to odors from the plant. Occasional odor-induced nausea was the assertion of 70% of those people. With increasing distance from the plant, out to 1600 meters, the odor pollution and somatic complaints dropped off to insignificance. Winneke and Kastka (1977) also combined the various single items in the questionaire to give annoyance scores (degrees of annoyance) for the three main dimensions of sensory, social and somatic annoyance. The results for the insulation plant at Cologne are shown at the right side of Table IV (after subtracting background-annoyance values obtained from odor-free areas in Duesseldorf). The decrease with distance is now more clear-cut and amenable to statistical treatment. -

The tar-oil plant at Duisburg (lower half of Table IV) performs as an area-source, with no decrease of odor pollution even out to 1400 meters down wind from the plant. In fact, probably because of some topographic effect, there was noticeable <u>increase</u> of odor-units at the 400 meter distance. The incidence of headache and nausea continued at a high level right out to 1400 meters, with indeed slight increases in these parameters at 400 meters. The combined degrees of annoyance (right side of Table IV) reflected the same trends. The good correlation observed, for both factories, between odor pollution units and odor annoyance reactions, lends increased confidence to this multi-dimensional approach. Winneke and Kastka (1977) put forward the hypothesis that the social-emotional and somatic aspects of odor annoyance are actually indicative of more severe degrees of disturbance than are the sensory or stimulus-centered odor experiences.

4. <u>Estimating the annoyance/detection ratio</u>. This Review has not located any published research explicitly directed to the level of annoyance caused by hydrogen sulfide pollution. Nevertheless, scattered through the literature there have been some observations that certainly provide some indication of the likely magnitude of the effect. Considering that the odor detection threshold concentration, both for pure substances and mixtures, is an accessible and relatively well understood

measurement, this may be a useful point of reference for assessing any incremental odor stimulus that is capable of causing annoyance, particularly for unpleasant odors.

Five References address this problem in various ways (Table V). As mentioned earlier, Winkler (1975) found that the odor recognition threshold of hydrogen sulfide is approximatley 10 times its detection threshold. He argued that unless an odor was recognizable, it could not very well be categorized as objectionable. Hence the recognition threshold might serve as a lower limit for an emission standard. Among the petrochemicals examined by Hellman and Small (1974) there were 34 that were described as unpleasant in hedonic tone. The average ratio between recognition and detection threshold for these compounds is 3.1.

Another approach we have seen is that of Adams and co-workers (1968) who showed that un-trained observers could, on average, characterize the odor of hydrogen sulfide as unpleasant, at only 1.6 times its odor detection threshold concentration. In later work (NCASI, 1971) on the more complex effluent gases from Kraft pulp mills, they found that workers employed in, or persons economically associated with, the mill plant or offices did not consider the Kraft odor unpleasant until it reached an average of 6 times the mean detection threshold. This level of tolerance, by workers accustomed to the odor, might be interpreted as an upper limit for an acceptable ambient level.

The most thorough work on this topic, with a multi-faceted questionnaire and analysis of responses, has been conducted by Winneke and Kastka (1977) among people living near factories which are sources of odor pollution. Using their criteria of occasional odor-induced headache or nausea in about 50% of the exposed population, it appears that from 5 to 15 odor units of pollution are capable of causing annoyance (see Table IV). There may of course be a moderate level of tolerance, or odor fatigue, among residents in an industrial city. Winneke and Kastka (1977) also developed more comprehensive averaged values for degrees of annoyance based on larger sets of sensory, emotional and physiological responses, that seem to run in parallel with the headache and nausea evaluations.

As a first attempt at quantifying the annoyance/detection ratio for unpleasant odors, it seems appropriate to give equal weight to all six of these estimates. The geometric mean for the ratio, at the foot of Table V, is 5.3 odor units. This implies that when an unpleasant odor reaches an average

Table V. Tentative basis for estimating the ratio of annoyance threshold to detection threshold for unpleasant odors.

Odorous substance	People tested	Judgment criterion	Ratio (odor units)	Source of data (Author, year)
Hydrogen sulfide	Laboratory panel	Odor recognition	10	Winkler, 1975
34 Unpleasant petrochemicals	Laboratory panel	Odor recognition	3.1	Hellman, 1974
Hydrogen sulfide	County fair visitors	Judged unpleasant	1.6	Adams, 1968
Kraft stack gases	Paper mill workers	Judged unpleasant	6	NCASI, 1971
Phenolics	Factory neighbors	Occasional headache, nausea	5	Winneke, 1977
Hydrocarbons & sulfur compounds	Factory neighbors	Occasional headache, nausea	15	Winneke, 1977

Geometric mean = 5.3 odor units

Standard deviation = x/+ 2.2

concentration only about 5 times its detection threshold for the individual observer, it will very likely be recognized (so long as his attention is not distracted), it will be judged unpleasant, and it will cause undesirable emotional, social and physiological reactions among approximately 50% of people thus inadvertently exposed.

H. Discussion: Considerations for a Hydrogen Sulfide Standard

1. Industrial exposure limits for hydrogen sulfide. The current State of California hydrogen sulfide ambient air quality standard is set at 0.03 ppm (30 ppb) over a one-hour averaging period. This may be contrasted with the California permissible exposure limit (PEL) for industrial safety, which is 10 ppm (10,000 ppb) for hydrogen sulfide, or 333 times higher. The California PEL is the same as the Federal standard, which in turn was derived from the Threshold Limit Value (TLV) recommended by the American Conference of Governmental Industrial Hygienists (ACGIH). The TLV is based on the best available industrial health data (ACGIH, 1977), and is the time-weighted average concentration for a normal 8-hour work day and 40-hour work week, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

It seems most unlikely that there could be any direct pathological or physiological damage caused to the body by 30 ppb hydrogen sulfide, even with continuous 24-hour daily exposure. Rather, the California ambient standard is basically intended to minimize odor annoyance and psychosomatic symptoms, such as those described by Winneke and Kastka (1977). In order to eliminate completely such reactions from the population, it would be necessary to set the ambient standard so low that nobody could perceive the odor of hydrogen sulfide. This is the philosophy pursued in the Soviet Union (Novikov, 1957; Malyarova, 1967), where the recommended maximum industrial exposure standard (for odorous chemicals) is routinely set at, or slightly below, the lowest concentration detectable by the most sensitive member of the odor panel (usually 12 - 15 subjects). The Russian Committee on Atmospheric Pollutants then sets the average level for community (24-hour) exposure at one-third of the maximum allowable industrial exposure.

Using the median threshold and geometric standard deviation assumed in Table II, the mean detection threshold of the most sensitive individual among 15 subjects is 0.94 ppb hydrogen sulfide (John K. Moore, California ARB, personal communication). A logical weakness in such a definition is that it does not provide a stable concentration limit. Statistically, the more people that are tested in a normal distribution, the lower will be the threshold of the most sensitive observer. In support of the extreme Russian policy, their scientists have demonstrated several other neurological reflexes (ophthalmologic and encephalographic) in response to odorants, occurring at the same, or even lower, concentrations than the odor threshold (Bushtueva, 1962; Malyarova, 1967).

2. Inconsistency of hydrogen sulfide as odor indicator. Setting a limit on hydrogen sulfide emissions from Kraft mill soda recovery furnaces has been tried in Sweden as a method for odor control in the environment (Lindvall, 1977). He instructed observers in a mobile laboratory at the stack-base to compare the effluent gases with known dilutions of hydrogen sulfide. Their task was to adjust the concentration of hydrogen sulfide in the laboratory air-stream, until it matched the intensity of the odor from the stack gases, which were tested at several dilutions with air. Depending upon the source of the stack emissions, and their dilution, there were discrepancies of 1000-fold to 100,000-fold in hydrogen sulfide concentration, between equal-intensity dilutions of the stack gases and of the laboratory hydrogen sulfide, even though the predominant sulfur compound in the effluent is hydrogen sulfide. Lindvall (1977) further showed that the correlations between odor intensity and hydrogen sulfide concentration at different mills could have very different slopes.

A clear implication in Lindvall's data is that pulp mill emissions can contain odorants, presumably sulfur compounds, whose odor thresholds are at least 1000 times lower than that of hydrogen sulfide. Similar results are contained in the NCASI (1971) report, where the odor threshold for Kraft stack gases at two mills was 0.02 - 0.03 ppb on the basis of total reduced sulfur (TRS; i.e. all divalent sulfur compounds combined). This is 320 times lower than the odor threshold of 8.0 ppb for hydrogen sulfide adopted in this Review. Similar wide discrepancies, between the odor threshold of the emissions and their hydrogen sulfide content, are to be expected for other fugitive reduced-sulfur mixtures, such as may be encountered in connection with petroleum refineries and sour-gas wells.

Despite the relative convenience, precision and objectivity of ambient hydrogen sulfide measurements, it becomes apparent that they can be reliable as a basis for odor pollution control only in certain narrowly-defined situations, such as:

1. Where hydrogen sulfide is the sole, or at least the predominant and lowest-threshold, odorous species in the effluent.
2. Where the chemical mixture in the effluent is constant, and the hydrogen sulfide concentration has been previously demonstrated to be a consistent indicator of the overall odor threshold of the mixture.

For example, situation No. 1 might apply to geothermal steam, but the necessary conditions should be proved experimentally. Situation No. 2 could apply to certain refinery or pulp mill processes, but the correlation would have to be established initially, and then re-evaluated whenever there is a change of feedstock or processs conditions. An ambient air quality standard based on hydrogen sulfide concentration would have to be made applicable and equitable to all industries where fugitive emissions contain any hydrogen sulfide.

3. Detectability, intensity and annoyance of hydrogen sulfide levels. In deliberating the pros and cons of revising the ambient hydrogen sulfide standard, presently 30 ppb in California, it may be informative to consider a tabulation that sets out the predicted changes in detectability, intensity and annoyance of the odor, that would likely be associated with various hydrogen sulfide levels (Table VI). The calculations have been based on the currently most probable values of the mean detection threshold, the standard deviation of the threshold, the exponent of the odor intensity equation, and the ratio between annoyance and detection thresholds. (Revised calculations can be made if different values are later accepted for these properties.) The first two columns of Table VI provide data similar to the last two columns of Table II, but re-evaluated for round-number hydrogen sulfide levels and cumulative detection frequencies, which may be more convenient for purposes of standard-setting. At the current standard of 30 ppb, approximately 83% of people would be expected to be capable of detecting the odor. The perceived intensity at the threshold of 8.0 ppb is put arbitrarily at a value of 1.00. On this scale, the intensity at 30 ppb hydrogen sulfide would be only 1.41. The fourth column of Table VI expresses the hydrogen sulfide concentrations in odor units, or multiples of the odor threshold. The odor-unit scale tends to exagggerate the influence of odorant concentration.

The concepts developed in Section G-4 above, regarding the threshold of annoyance, permit the addition of a final column to Table VI for illustrative purposes. The percentages there entered are

Table VI. Predicted effects of ambient hydrogen sulfide level on frequency of odor detection, intensity of odor sensation, and incidence of annoyance by odor.

Hydrogen sulfide (ppb)	Persons able to detect odor[a] (%)	Perceived odor intensity[b] (ratio)	Odor units[c] (median)	Persons annoyed by odor[d] (%)
200	99[e]	2.31	25	88
100	96[e]	1.93	12	75
50	91	1.61	6.2	56
40	88	1.52	5.0	50
35	87	1.47	4.4	47
30	83	1.41	3.7	40
25	80	1.34	3.1	37
20	74	1.27	2.5	31
15	69	1.18	1.9	22
10	56	1.06	1.2	17
8	50	1.00	1.00	11
6	42	0.93	0.75	8
4	30	0.83	0.50	5
2	14	0.70	0.25	2
1	6	0.58	0.12	1
0.5	2	0.49	0.06	

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[a] Based on adopted mean detection threshold of 8.0 ppb and S.D. ± 2.0 binary steps.

[b] For those who can detect the odor. Based on Lindvall's (1974) value for the intensity exponent, $n = 0.26$.

[c] Hydrogen sulfide level divided by mean detection threshold (8.0 ppb).

[d] Based on assumption that mean annoyance threshold is 5 x mean detection threshold, and S.D. ± 2.0 binary steps.

[e] Theoretical for a normal distribution. These percentages may be reduced by the occurrence of selective smell-blindness.

calculated on the assumptions that the median threshold for odor annoyance occurs at 5 times the median threshold concentration of odor detection, and that the standard deviation of individual thresholds for odor annoyance is the same (± 2 binary steps of concentration) as it is for the individual thresholds of odor detection. Accordingly, the expected point for 50% of the population to experience odor annoyance is at 40 ppb hydrogen sulfide. At the current California ambient air quality standard for hydrogen sulfide of 0.03 ppm (30 ppb), about 40% of people would be expected to feel odor annoyance.

Due to the inherent mathematical properties of the sense of smell, successive reductions in hydrogen sulfide level, which may be progressively more difficult and expensive to achieve by engineering improvements, can only produce less than proportionate, and rather un-rewarding, reductions in odor detectability, intensity and annoyance. The cost/benefit ratio will therefore escalate rapidly if the ambient standard is decreased.

It may be desired to estimate the changes that could be produced in the detectability, intensity and annoyance of hydrogen sulfide odor, due to the presence of one or other of the conditions listed in Table III. As a conjecture and approximation, it may be justifiable to multiply all the column of hydrogen sulfide levels in Table VI by the appropriate factor selected from Table III. This, in effect, displaces the log/probit curve to the right (usually). There may, however, also be a substantial change of slope, as was observed with the mis-directed test (Amoore and Hautala, 1983).

In applying an ambient air quality standard to a particular industrial operation, the aggregate odor background from all other sources in the area should be considered. Even total suppression of sulfurous emissions from one industry may not significantly reduce the odor problem in a community, unless all other man-made sources of odor in the neighborhood are equally effectively controlled. Also, any natural and irreducible background odor should be taken into account, such as hot springs, fumaroles, marsh-gas, skunks, stink-horns, etc. Just as our surroundings are seldom silent, yet we tolerate some noise, our environment is not always odorless, and we may be unreasonable to expect it to be so.

4. <u>Regulations for ambient odors in other States</u>. A review on the status of odor control

regulations was published by Prokop (1974). The diversity of types of standard, specified levels, methods of evaluation and measures for control, reflects the acknowledged difficulty in writing effective legislation for ambient odors. Among the 50 States, 35 have some form of odor regulation. Thirty-two of them include an odor nuisance standard, but probably insufficiently explicit to be implemented without Courtroom proceedings. Eight States specify a maximum permitted ambient odor level. This is usually expressed as a limit on the total number of odor units in the polluted air (i. e. the dilution-to-threshold ratio, Section G-2) with or without a specified method of measurement.

Only one State (Connecticut) specifies ambient ppm limits, for 58 odorous pollutant compounds. These limits were based on the odor recognition (not detection) threshold, defined as the minimum concentration at which all four (not the usual 50%) of the trained subjects made correct identifications or close descriptions (Leonardos et al., 1969). As of 1974, no State had adopted any odor intensity-matching or perceived odor intensity measurement. None had any clearly-defined evaluation of odor unpleasantness, objectionability or annoyance.

It would be helpful to know if any State or Country (West Germany?) has in the meantime developed regulations based on intensity and/or annoyance factors; and, if so, how successful they have been in controlling ambient air quality.

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