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Air Pollution Aspects of Odorous Substances. A Literature Survey

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AIR POLLUTION ASPECTS OF ODOROUS SUBSTANCES
A LITERATURE SURVEY

by

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ABSTRACT

A state-of-the-art literature survey relative to air pollution aspects of odorous substances is presented. Background information is provided on the nature and characteristics of odorous substances, odor perception and odor classification. Major sources, and the odors emitted from each source, are identified. The effects of odors are discussed and the legislative aspects of odor control have also received consideration. Methods for qualitative and quantitative measurement of odors and odorants have been discussed in some detail. Finally, odor abatement methods and best practicable control technology are reviewed.

RÉSUMÉ

Le présent rapport qui reflète l'état actuel des connaissances dans le domaine comporte une étude bibliographique de la pollution par les substances nauséabondes. Des renseignements de base sont donnés sur la nature et les caractéristiques de ces substances, sur la perception olfactive et sur la classification des odeurs. On identifie les sources les plus importantes d'émission et la nature des odeurs particulières qu'elles dégagent. L'effet des odeurs est étudié et les notions juridiques de la lutte contre les odeurs sont aussi abordées. Des méthodes d'olfactométrie, quantitatives et qualitatives, sont traitées. Enfin, les méthodes utilisées pour la réduction des dégagements ainsi que les meilleures techniques praticables font aussi l'objet d'un examen.

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1 INTRODUCTION

This report is intended as an introduction and guide to existing scientific, technical, and other literature dealing with the air pollution aspects of odors. Key references only have been cited, but the contents of this literature review were extracted from a much larger selection.

As public concern for the improvement of air quality grows, the sensory aspects of air pollution are becoming increasingly important. Odors represent one of the harshest sensory insults associated with air pollution and are emitted from a large variety of sources. As a result, objectionable odors are directly responsible for a major share of public complaints regarding air pollution. For a long time the visible or sensory aspects of air pollution — smoke, odors, and haze — have served the concerned citizen as indicators to the severity of air pollution in a community. Yet, odors have in the past received considerably less attention from regulatory agencies than other types of air pollutants. This situation is largely the result of two major factors. First, most odors constitute a public nuisance rather than a health hazard. Second, there is a lack of reliable, objective methods for odor measurement.

Odor abatement can usually be achieved through the implementation of existing control technology such as oxidation, scrubbing, or adsorption systems. Nevertheless, effective odor control can be highly elusive. The development of new technology for preventing or controlling odorous emissions has progressed slowly because of inadequate information about the nature, causes, and quantities of odorous emissions and the large number of odor sources. Needed most, however, are better methods for odor measurement and evaluation. Their absence imposes serious constraints on the evaluation of the effectiveness of different types of odor control systems and makes enforcement of odor control legislation very difficult.

2 BACKGROUND INFORMATION

2.1 The Nature of Odorous Substances

The sensation of smell results from nasal inspiration of specific chemical compounds which are said to possess an odor. Most gases and vapors that are not normal constituents of air are odorous in certain concentration ranges. To a first approximation, the main factor determining the odorous properties of a molecule is its molecular structure (stereochemistry). However, no rigorous relationship has been discovered between the odor of a molecule and its molecular structure. Empirical observations involving the human olfactory organ, the nose, combined with modern chemical analysis are still the only dependable criteria for correlating the odorous properties of a molecule with its physico-chemical characteristics.

2.2 Perception of Odors

2.2.1 The Olfactory Sense. Surprisingly little is known about the sense of smell despite its important influence on our daily lives and voluminous research literature on the subject. No satisfactory general theory exists to explain how the nose and the brain detect, identify, and recognize an odor. Physiologically, the nose is a culminating organ giving the sense of smell a directional faculty. Location of a source of odor by a trained observer (olfactory triangulation) is possible within an angle of acceptance of only 7-10 degrees (1). This is a remarkable feat considering the small distance separating the nostrils (about 20 mm). Olfaction increases from an early age up to about fifteen years and declines after 45 years of age. In between, i.e., for some thirty years, a normal person enjoys these powers to the full. At 78 years, about one third of the population are anosmatic, but at 26 years of age only 5% are anosmatic (2).

2.2.2 Theories of Olfaction. Since 1870, more than 30 theories have been advanced to explain olfaction. An excellent summary of the theories proposed up to 1967 has been presented by Moncrieff (3). The advent of the 1960's brought a quickening interest in basic odor research. During the last 15 years the number of research workers involved, the volume of papers published, and the frequency of national and international conferences have all increased rapidly. However, there still seems to be no concentrated interdisciplinary attack on the main problem areas. For the purpose of discussion, the numerous theories of olfaction can be grouped into wave theories and contact theories (4).

2.2.2.1 *Wave Theories*. These theories are based on the premise that olfaction can occur at a distance from the odorous substance and hence the molecules are assumed to emit radiation which reaches the olfactory receptors. Because it has now been established that contact of the odorant molecules with the olfactory receptors is definitely required, the "no-contact" or wave theories may be rejected.

2.2.2.2 *Contact Theories*. The theories in this group assume contact of odorant molecules with the olfactory receptors. There are two sub-groups: one assumes chemical interaction and the other physical interaction of odorant molecules with olfactory receptors. Since 1950, the major contact theories proposed have recognized that the odor of a molecule cannot be directly related to its functional groups (chemical interaction) but must be related to the molecule as a whole. Currently, the four most popular theories based on odor as a "whole-molecule" property are: the Dyson-Wright Vibration Theory, the Moncrieff-Amoore Stereochemical Theory, the Beets "Profile Functional Group" Theory, and the Davies Adsorption Theory. Roderick (4) and more recently Hopton and Laughlin (5) have described the salient features of each theory. However, none of the theories mentioned can explain fully either how an odor is perceived or those properties of an odorant molecule that determine its characteristic odor. In summary, although most investigators would agree that the effects of molecular size and shape play an important role in determining odor, no one has yet been able to find a general and direct correlation.

2.3 Sensory Characteristics

Sensations produced by the presence of one or more odorants in inhaled air exhibit four dimensions: detectability, intensity, quality, and acceptability (6). In the context of air pollution the most significant factor in odor evaluation is its hedonic characteristic (acceptability).

2.3.1 Detectability and Threshold Properties. To be sensed, different odorants require different minimum concentrations. Thus, for each odorant there exists a liminal quantitative value below which no conscious sensation of odor will be caused. This value is known as the olfactory detection threshold and is derived from observations under laboratory conditions. The olfactory detection threshold reflects the ability of a test subject to distinguish between odorous air and air containing no odor. This should be contrasted with the recognition threshold – the ability of the subject to recognize the character or identity of the odor. Generally, recognition requires a substantially higher odorant concentration than detection.

Customarily, threshold concentrations are expressed in milligrams of the odorant per cubic metre of air (mg/m^3) or in parts per million (ppm). Olfactory threshold data reported in the literature often differ by as much as one or even two orders of magnitude, and these values should be considered as qualitative indicators only and should be interpreted merely to mean that one substance can be smelled at a concentration so many times higher or lower than another. An illuminating discussion of factors affecting experimentally determined threshold concentrations was presented at the Second International Clean Air Congress by Cleary (7). Tabulations of olfactory thresholds for many common odorants are available (8, 9).

Laboratory measurements of odor thresholds involving the human nose are based on dilution of an odorous gas or vapor in purified air. The detection threshold of an odorant can be expressed as the number of dilutions required to reach an odorless mixture. Because odor threshold data reported in the scientific literature have usually been produced by using a number of test subjects – an odor panel – the published data are usually averaged values. The concept of "effective dosage" (ED) is very useful under these circumstances. ED_{50}, for example, is used to specify the odorant concentration at which 50% of the panelists can perceive the odor. Similarly, but less frequently, the symbols ED_0 or ED_{100} are used to denote threshold values at which 0% and 100%, respectively, of the panelists can smell the odor.

A practical method for determining the olfactory threshold is with an instrument called an olfactometer. The olfactometer allows preparation of a known dilution of an odorous substance in air and presentation of the odorous air to the nose. The concentration of odorant is varied until the subject can only just detect the odor. Normally, the detection of an odor in air indicates that the odorous substance is present at a concentration greater than 10^{-8} of its saturation vapor pressure.

2.3.2 Relationship between Odor Intensity and Odorant Concentration. Odor intensity can be mathematically related to the concentration of an odorant in air, but is dependent upon the chemistry of the odorous molecules in a complex fashion. Many studies have shown that, for the sense of smell (as for the other human senses) a power law applies (10):

EQUATION [1] Stevens' Law or the Psychophysical Power Law

$$I = k(C)^n \quad \text{or} \quad \log I = \log k + n \log (C)$$

Where I is the intensity of sensation
C is the concentration of the odorant
k and n are coefficients

The values of the exponent, n, are always less than unity and for most odorants n is in the range 0.2 to 0.8, with the value depending on the odorant and varying to some degree with the observer (11).

What implications does the psychophysical power law have for odorous air pollution and its control? First, any reduction in the intensity of the odor sensation can be achieved only through a much larger reduction in the odorant concentration. Second, because malodorous emissions from stationary as well as mobile sources usually contain more than one odorant, the degree of effectiveness of abatement measures which are implemented to control the existing problem can vary considerably for different odorants, especially if the values of the exponent n are very different for the odorants involved.

The situation often becomes very complicated because the net resultant intensity of a mixture of odorants can be generated in one of four possible ways (4):

(a) Independent effects: the components act independently and no odor is perceived until the threshold concentration of at least one component is reached;

(b) Additive effects: the intensity of sensation for the mixture is the sum of the intensities associated with the individual odorants;

(c) Subtractive effects: the components counteract one another;

(d) Synergistic effects: the mixture will have an enhancement of intensity in excess of simple addition.

There is no physical (objective) scale for measuring the intensity of odors, however, several sensory (subjective) scales exist. Experience has shown that odor intensity ratings are greatly facilitated by odor intensity reference scales (11). The simplest of these is category scaling where a numerical or word scale is used to record the intensity of the sensation. Typically, four to seven categories are used. More categories, especially beyond 10, do not seem to resolve the intensities better because the scatter in judgement increases. Another method relies on direct comparison of odor intensities of the same odorant at different concentrations.

In many situations it is not necessary to have an absolute measure of intensity. Under such circumstances the intensity of a perceived odor is not expressed in terms of concentration units of the odorant, but in terms of an odor intensity index (OII). An OII value represents the number of times a substance must be diluted by a factor of 2 to reach the threshold concentration. Thus, for example, when a substance has to be diluted to 1/32nd of its concentration to reach its threshold, the odor intensity index equals five ($32 = 2^5$).

2.3.3 Odor Quality. The "average human nose" has a remarkable ability to distinguish slight differences in the quality of two odors that are of the same intensity. Because the total range, or gamut, of odorous substances is enormous, a systematic classification of odor qualities is important. The quality as well as the intensity of an odor may change with the concentration of the odorant as illustrated by the classic example of the jasmine odor of skatole when present in air at low concentrations and its fecal odor at high concentrations. Studies of odor quality rely traditionally upon two distinct types of psychological scaling: profile rating and proximity analysis.

2.3.4 Acceptability. The acceptability of an odor is strongly dependent upon the context within which it is experienced. Thus, an odor which is "out of place" or "does not belong" is much less acceptable than the same odor when it is perceived within the expected context.

Dravnieks (11) has described a procedure for determining the degree of acceptability of an odor (its hedonic rating). Panelists categorize the pleasantness of an odor on a 7-point scale ranging from -3 (most unpleasant) through 0 (neutral) to +3 (most pleasant).

In the context of air pollution, scales for acceptability of common odors normally do not extend over the entire range of pleasantness/unpleasantness because in most cases concern is with odors of differing degrees of unacceptability. Most odors that are byproducts of industrial operations or of the bacterial or thermal decomposition of organic matter are objectionable to the vast majority of people. Even odors that are normally considered pleasant, like bakery or coffee-roasting exhausts, become unpleasant to people who are exposed to them over a prolonged period of time.

The evaluation or appreciation of odors, as opposed to their mere sensation, involves man's higher mental faculties and differs with race, nationality, sex, environment, social level, and age (2). An odor may be offensive to one person, but not to another. Much will depend on the concentration of the odor, association of ideas, novelty of the experience and other factors which are all imponderable. This, together with the fact that no instruments have yet been devised which can measure an odor as one measures sound or radiation, emphasizes the difficulty of obtaining reproducible results.

2.4 Odor Classification

It is thought that man can appreciate and distinguish about 4000 different odors, but unfortunately, it has not been possible to reduce these into a basic set of fundamental odors. Attempts to assign odor qualities into a manageable number of odor classes have been made by Linnaeus (1756), Zwaardemaker (1895), Henning (1915), Crocker and Henderson (1927), and Amoore (1962) among others (12). So far, no one has succeeded in producing a generally acceptable ordering of odor characteristics based on chemical structures or physical properties despite the undoubted chemical nature of the stimulus.

At present an odor can only be characterized in terms of similarity to other odors or by association with other sensory attributes. In a typical semantic procedure for odor classification, the panelists establish to what extent (usually on a 5-9 point scale) the odor X is described by each of the sensory terms in a list consisting of selected sensory descriptors. An alternative method is the reference odor procedure. It has the advantage of avoiding difficulties with personal meanings of terms. For instance, with a set of 7-10 reference odorants, the panelists rate the extent to which the odor X is similar to each of these.

2.5 Physico-Chemical Characteristics of Odorants

Certain relationships between the olfactory properties of a substance and its physico-chemical parameters have been discovered. From the nature of the olfactory system it is obvious that, to be smelled at all, a material must have certain physico-chemical properties. In the first place, it must be volatile. The second requirement for an odorous substance is that it should be soluble in water, even if only to a very slight extent. If it is completely insoluble, it will be barred from reaching the olfactory nerve endings by the watery film that covers their surfaces. Another common property of odorous materials is solubility in lipids (fatty substances). This characteristic enables them to penetrate to the nerve endings through the lipid layer that forms part of the surface membrane of every cell.

With the exception of iodoform (molecular weight = 394) all known odorous compounds have molecular weights falling within the range of 17 (NH_3 = 17) to about 300. The lack of odor of high molecular weight compounds is thought to result mainly from their lack of volatility, although this can not be the only factor (13). Beyond these common properties the characteristics of odorous materials have been vague and confusing.

3 ODOR SOURCES, ODORANTS EMITTED, AND SOURCE RANKING

3.1 Odor Sources

Odorous emissions arise from a large number of sources. Sources of odor can be broadly classified into confined sources and unconfined sources.

3.1.1 Confined Sources. Odor sources may be confined to a specific point of emission such as a vent, stack, or exhaust duct. Under these conditions the location, composition, concentration, and volumetric discharge of the source can be specified. Such definite characterization facilitates the establishment of relationships between the odor source and odor measurements made in the community. In general, an odor source may be said to be confined when its rate of discharge to the atmosphere can be measured, and when the atmospheric discharge is amenable to representative sampling and to physical or chemical treatment for purposes of odor abatement. For meteorological diffusion calculations the location where the odor is discharged into the atmosphere is assumed to be a point in space (14).

3.1.2 Unconfined Sources. An unconfined source does not readily lend itself to quantitative characterization or to control by physical or chemical means. Some examples are: garbage dumps, settling lagoons, drainage ditches, outdoor chemical storage areas, and soil contaminated by spillage of odorous matter. For unconfined sources of odor, emission characteristics (both discharge rate and composition) are highly variable. As a result, characterization of such sources is apt to be difficult and unreliable (15). For the purpose of meteorological diffusion calculations, an unconfined odor source is often represented by an imaginary emission point. Such an assignment may be made on the basis that, if all the odor from the unconfined area were being discharged from the "emission point", the dispersion pattern would just include the unconfined source.

3.1.3 Odor Source Inventories. An inventory of odor sources may be used to establish the nature and potential seriousness of known or suspected odor sources, to predict the scope of odor control procedures needed for abatement, to relate odor sources to effects in the community, or to establish regulatory or enforcement policies (16). Unfortunately, there is no standard method for compiling odor source inventories. A few of the methods that have been used are: a) gaseous emission rates and threshold data; b) odor types based on qualitative description or generating processes; c) community complaints; and d) social and economic effects.

3.1.4 Description of the Source. Adequate description of both fixed and mobile odorant sources requires attention to detail possibly ignored in the investigation of other kinds of air pollution because odor nuisances and adverse reactions can result from very brief exposure times and very low concentrations (trace level impurities). Moreover, there may be strong mediation of receptor response to the odor stimulus by attitudes developed or modified by other factors (17).

In general, source and emission characterizations which are useful in relating the dose to the response, would provide more valuable information than simple listings of odorant emissions from various sources. Properly applied, such descriptions could provide guidance in evaluating the usefulness of existing data, in acquiring new data, in designing models of transport phenomena, and in evaluating characteristics and abatement strategies.

When the chief public officials responsible for air pollution control in 67 major United States cities were surveyed in 1955, it was found that 78% of the air pollution agencies received complaints specifically identifying odors as the cause, and 68% responded that the public interest in air pollution was increasing because of odor pollution incidents (18). A list of those sources of objectionable odors in the ambient air most frequently reported by municipal air pollution control bureaus in the United States was compiled by Kerka and Kaiser in 1958 (19).

By reviewing the scientific and technical literature published over the past fifteen years, Hopton and Laughlin (5) of The Ontario Research Foundation established an inventory of the odor sources generally considered to be of major importance in an industrialized environment. The primary odor-producing industries, along with representative processes are listed in Table 1 together with common chemical classes of odorants usually associated with these sources. In addition, for many processes, the specific odorants determined in the emissions are also identified.

TABLE 1 INVENTORY OF ODOROUS EMISSIONS (5)

Industry	Processes	Odorant Classes	Individual Odorants
Agriculture	Poultry	Mercaptans, sulfides, amines, indoles, alcohols, aldehydes, ketones, esters	Hydrogen sulfide, dimethyl sulfide, methyl, ethyl, propyl and butyl mercaptans; indole, skatole, diacetyl, acetone
	Swine		Hydrogen sulfice, ammonia, methyl and ethyl amine, triethylamine, methanol to pentanol, methanal to hexanal, octanal, decanal
	Dairy cattle		Hydrogen sulfide, dimethyl sulfide, diethyl sulfide, methyl mercaptan, ammonia, ethylamine, trimethylamine, propyl and butyl acetate
	Beef cattle		Idole, skatole, methanol, ethanol, isopropanol methanol, ethanal, methyl, propyl, and butyl acetates; ethyl formate
Chemical processing	Chemical milling	Oxygenated organics Chlorinated organics	–
	Detergents and soaps	Acids, alcohols, and oils	–
	Paint manufacturing	Acids, alcohols, aldehydes, ketones	–
	Pesticide manufacturing	Chlorinated phenyls	–
	Resin kettles	Alcohols, acids, aldehydes, phenols, amines, glycols, esters, chlorinated organics	Vinyl chloride, phthalic anhydride, maleic acid, fumaric acid, styrene, vinyl acetate, di-isocyanate
	Rubber compounding	Alkyl amines, organic acids, aldehydes, plasticizers	–
	Varnish cookers	Acids, aldehydes, ketones, phenols, terpenes, mercaptans, substituted furans	Clycerine, acrolein, allylsulfide, butyl mercaptan, thiophene

TABLE 1 INVENTORY OF ODOROUS EMISSIONS (5)

Industry	Processes	Odorant Classes	Individual Odorants
Combustion	Municipal, Pathological, Wood } Waste incinerators	Acids, aldehydes, hydrocarbons, ammonia, sulfur oxides, nitrogen oxides	–
	Oil burners	Aldehydes, acids, hydrocarbons, sulfur oxides, nitrogen oxides	–
Food and allied industries	Coffee roasting	Acids, aldehydes, hydrocarbons, phenols, mercaptans, sulfides	–
	Deep fat frying	Oils	–
	Feather processing	Fats, fatty acids, mercaptans, and sulfides	–
	Fermentation	Alcohols, aldehydes, acids, tannins	–
	Fish processing	Amines, aldehydes, acids, diamines	Trimethylamine
	Grain drying	Acids, aldehydes, hydrocarbons	–
	Rendering plants	Acids, alcohols, aldehydes, amines, fats, fatty acids, mercaptans, sulfides phenols	Ammonia, hydrogen sulfide, ethylamine, diethylamine, trimethylamine, dimethyl sulfide, butyric acid, butylamine, propylene sulfide, valeraldehyde, amyl alcohol and others
	Smoke houses	Acids, aldehydes, ketones, phenols	–
Metallurgical	Coke ovens	Aromatic and aliphatic hydrocarbons, aldehydes and sulfides	Hydrogen sulfide
	Core ovens	Acids, aldehydes, hydrocarbons, phenols pitch	–
	Cupolas	Acids, aldehydes, hydrocarbons	–
Pulp and paper	Kraft Mills: Digestors, Evaporators, Recovery furnaces	Mercaptans, sulfides, alcohols, terpenes camphors	Methanol, acetone, di-pinene, hydrogen sulfide; methyl, ethyl, propyl, butyl mercaptans; dimethyl and diethyl sulfide; dimethyl and diethyl disulfide; methyl allyl sulfide; diallyl sulfide

TABLE 1 INVENTORY OF ODOROUS EMISSIONS (5)

Industry	Processes	Odorant Classes	Individual Odorants
Refineries	Catalyst regenerators Cracking units Sulfur recovery units Flares	Acids, aldehydes, amines, phenols, mercaptans, sulfides, hydrocarbons, hydrogen sulfide, ammonia	—
Sewage treatment		Mercaptans, sulfides, amines, indoles	Methylmercaptan, dimethyl sulfide, indole, skatole, hydrogen sulfide
Surface coating	Spray booths Baking ovens	Alcohols, aldehydes, ketones, aromatic and aliphatic hydrocarbons, ethers, esters, acids	—
	Vinyl cloth production	Plasticizers, chlorinated hydrocarbons, aldehydes, ketones, hydrocarbons	—
Transportation	Gasoline engines	Hydrocarbons, aldehydes, and nitrogen oxides	—
	Diesel engines	Naphathalenes, indans, tetralins, cycloparaffins, aldehydes, alcohols, phenols, thiophenes, indenes, and many others	Tetralin, methyl tetralin, dimethyl tetralin, trimethyl tetralin, methylinden, benzothiophene, thiophene, phenol, acrolein, formaldehyde, and many others
	Aircraft engines	Similar to diesel engines	—
Miscellaneous	Asphalt roofing manufacturers	Aliphatic and aromatic hydrocarbon and aldehydes	—
	Debonding of brakeshoes, wire and drum reclamation	Acids, aldehydes, hydrocarbons nitrogen oxides	—
	Dry cleaning	Hydrocarbons, alcohols, aldehydes and chlorinated organics	e.g. Perchloroethylene
	Glues and gelatins	Acids and amines	Ammonia, methylamine, dimethylamine, formic to heptanoic acids, 3-methyl butyric acid, 4-methyl pentanoic acid
	Mineral wool production	Phenols, aldehydes, sulfur oxides	—
	Solvent degreasing	Chlorinated organics	Trichloroethylene and perchloroethylene

3.1.5 Industrial. Odorants are produced as unwanted by-products in many industrial processes (20). For example, odorous substances are known to be emitted during normal operations in the petroleum industry (refineries and natural gas plants), petrochemical plant complexes, chemical plants, coke oven installations, Kraft process pulp and paper mills, chemical processing industries, dye manufacture, viscose rayon manufacture, sulfur production and manufacture of sulfur-containing chemicals, iron and metal smelters, cement plants, fertilizer plants, food processing plants, rendering plants, and tanneries.

3.1.5.1 *Petroleum Industry.* The main sources of odor pollution in refineries are untreated gas stream leaks, vapors from crude oils and raw distillates, and fumes from process and condensate sewers (21). Typical refinery processing systems that produce malodorous emissions are cracking units, catalytic reforming units, and sulfur recovery units. The cracking process tends to convert the sulfur containing crude oil into hydrogen sulfide in the heavier materials and mercaptans in the gasoline fractions (22).

3.1.5.2 *Petrochemical Plant Complexes.* Malodorous gases are produced in petrochemical plants during cracking and other desulfurization reactions.

3.1.5.3 *Chemical Industry.* Odorous compounds are produced in many chemical operations. In general, they are formed when nitrogen or sulfur compounds are associated with organic materials at high temperatures. In many operations the end products have highly offensive odors (e.g. carbon disulfide, pyridine, and thiophene). Known odor-generating operations in the chemical industry are the manufacture of sulfur-containing dyes, the production of viscose rayon, neoprene, ethyl and methyl parathions (pesticides), organic thiophosphates, ammonia, aldehydes, and many other organic chemicals. Inorganic processes which produce odorous compounds include the manufacture of barium chloride (from barium sulfide), phosphorus, pigments, lithopone, and sodium sulfide. Hydrogen sulfide is emitted during the manufacture of stove clay and glass (23).

3.1.5.4 *Coke Oven Plants.* Malodorants are produced in significant quantities in coking operations. The effluent gas from coke ovens contains about 5,000 to 13,000 $\mu g/m^3$ of hydrogen sulfide (or about 6.7 lb/ton of coal charged). Odorous emissions can occur throughout the complete coking cycle from coke oven charging to hydrogen sulfide removal (24).

3.1.5.5 *Pulp and Paper Mills.* The production of malodors is an undesirable side effect that has long been associated with the Kraft pulping process. Hydrogen sulfide, mercaptans, organic sulfides, and organic disulfides are produced and released into the atmosphere at a number of locations in Kraft pulp mills. According to Sableski (25) investigations at the

University of California have shown that 80% of the total gaseous sulfur appears as hydrogen sulfide and methyl mercaptan. Emission of these substances is responsible for the characteristic "rotten cabbage" or "rotten eggs" odor in the vicinity of Kraft paper mills. Major sources of odorous emissions from Kraft mills listed in order of decreasing contribution to atmospheric pollution are: the recovery furnace, evaporators, digestors, lime kiln, oxidation tower, and dissolving tank (26).

3.1.5.6 *Iron-Steel Industries and Foundries.* Malodorants are given off in many metallurgical processes. As an example, typical hydrogen sulfide exhaust emissions from foundries range from 4 to 100 pounds per 500 tons of castings produced per day (27).

3.1.5.7 *Miscellaneous Production Sources.* There are many other sources of odors which may cause complaints (20). Some of these include the paint industry, varnish kettle cookers, wire reclamation, electroplating, cement production and breweries. Among the more important non-industrial sources of odor are garbage dumps, sewage works, agricultural operations, motor vehicles, and, occasionally, gases of natural origin (sulfur springs, decaying vegetation, etc.) (28).

3.1.6 Food and Agricultural Related Sources

3.1.6.1 *Food Processing.* Even odors from food processing evoke frequent complaints. Food processing includes operations such as slaughtering, smoking, drying, cooking, baking, frying, boiling, dehydrating, hydrogenating, fermenting, distilling, curing, ripening, roasting, broiling, barbecuing, canning, freezing, enriching, and packaging.

3.1.6.2 *Livestock Slaughtering.* Slaughtering operations have traditionally been associated with odorous air contaminants, though many odorants are due to by-product operations rather than to slaughtering and meat dressing itself (20). Odors can arise from slaughter houses, stockyards, and from the storage of blood, intestines, hides, and paunch manure (partially digested food found in animal entrails) before or during shipping or further processing.

3.1.6.3 *Edible Meat Processing.* Odors are also emitted from edible meat processing. However, compared to odorous emissions from inedible rendering processes, they are relatively minor (23).

3.1.6.4 *Inedible Rendering of Animal Matter.* Most animal matter reduction systems can be classified as dry-rendering, air-drying, or wet-rendering. Odors arise mainly from the raw materials (especially during the grinding operation), cookers, dryers, percolators, and presses. Many factors may significantly influence the offensiveness and quantity of odors produced

(20). In general, rendering plants produce a variety of odorous emissions depending on the types of raw material and process equipment used. Although both batch and continuous rendering processes are in use, the latter are becoming more popular for economic reasons, especially for new installations. Modern continuous rendering plants generally emit less odor than established installations because they feature enclosed material handling systems (29). Studies were conducted by the Fats and Proteins Research Foundation Incorporated in 1967 and 1972 to identify the compounds responsible for rendering odors (30, 31).

3.1.6.5 *Fish Processing.* In the fishing industry, odors are unavoidable because of the composition of fish. Objectionable odors can usually be expected in fishing wharfs, canneries, and reduction plants. Heavy odor emissions resulting in nuisance complaints can often be traced to poor sanitation. Trimethyl amine is the principal compound associated with fish odors (23). Reduction of inedible waste from fish to fish meal is carried out in about the same manner as for the animal rendering process. This reduction process is capable of producing large quantities of odorants (32).

3.1.6.6 *Other Food Processing Industries.* The origin, nature, and extent of odorous emissions from other food manufacturing operations such as coffee-roasting, production of spices and condiments, as well as fruit and vegetable processing have been discussed by Faith (33).

Significant air pollution problems are associated with the confinement of large numbers of animals such as cattle, hogs, poultry and sheep as a direct result of the animal wastes. Odors from animal wastes are especially annoying near feed lots, or where field-spreading of unstabilized waste from confinement housing is permitted adjacent to residential or recreational areas. Animal production on farms also produces odor problems, of course, but the number of people affected is relatively small. About 45 odorous compounds have been identified so far in the gaseous emissions resulting from animal waste degradation processes (34).

3.1.7 Sewage and Waste-Water Treatment

3.1.7.1 *Sewage Treatment.* Complaints of objectionable odors frequently come from the immediate vicinity of sewage treatment plants, especially during the summer months when the daytime temperatures are high and there is little or no air movement (20). In most cases these odor problems are experienced only in areas immediately adjacent to sewage treatment plants or open manholes. Malodorous gases are produced biologically in sewers and treatment plants through breakdown and hydrolysis of proteinaceous materials (like cystine and methionine) and by reduction of sulfates. A survey of odors emitted most frequently at some 300 sewage treatment plants in the United States shows that methyl mercaptans, methyl sulfides, and amines are major odorants, followed by indoles and skatoles, as well as hydrogen sulfide (35). Factors that influence odorant generation in sewers include temperature, content, age, and pH value of sewage; flow velocity; and ventilation of the sewer.

3.1.7.2 *Waste-Water Treatment.* Odor-causing substances in waste-water may be broadly classified as either inorganic gases or organic vapors. The inorganic gases usually arise as a result of biological activity in the waste-water collection and treatment system. Likewise, the organic vapors often arise from biological activity but may result from direct additions of waste chemicals from industry (36). The major malodorous inorganic gases resulting from biological activity include hydrogen sulfide (H_2S) and ammonia (NH_3). The principal odors of an organic nature arise from the anaerobic decomposition of compounds containing nitrogen and sulfur. These offenders include mercaptans, indoles, skatoles, and various other nitrogen and sulfur-bearing organics. Other compounds, including organic acids, aldehydes, and ketones, may be significant.

3.1.8 Stationary Combustion/Solid Waste Disposal Sources. Odorants are released when wood, coal, oil, or gas are burned. The quantity of odorant will depend upon the amount of sulfur in the fuel and the efficiency of the combustion process. In an efficient combustion system the hydrocarbons, sulfur, and nitrogen compounds will be oxidized to carbon dioxide, water, sulfur oxides, and nitrogen oxides. However, if the combustion is incomplete, malodorants such as hydrogen sulfide and aldehydes are formed (37).

3.1.9 Mobile Sources. Gasoline vapors and automobile exhaust frequently generate odor complaints. In general, gasoline engine exhaust odorants are not as offensive as diesel exhaust odors.

3.1.9.1 *Diesel Engines.* Exhaust gases emitted by diesel engines are characterized by odors that are offensive in varying degrees to many members of the general public. The increasing use of diesel-powered vehicles (trucks, buses, etc.) in urban environments has resulted in a widespread public awareness of the diesel odor problem (38). While smoke from diesel engines has in the past received the bulk of regulatory attention around the world, the offensive odor of diesel exhaust has probably drawn more criticism from the general public. Although the two are commonly associated, this generalized association is misleading. Discernible odor almost always accompanies any visible smoke, but virtually clear exhaust may also carry highly offensive odors.

Odor is undoubtedly the prime sensory attribute of diesel exhaust under the normal circumstances of human exposure. As a result a large number of investigations have been conducted to identify the odorous components in diesel engine exhausts (39). Exhaust constituents and odors have frequently been related to aldehyde concentration in diesel exhaust because aldehydes have a characteristic odor and cause sensory irritation at exceedingly low concentrations. It has been discovered that the quality of odor may change with different fuels, engines, load, rpm, and other factors (40). There is considerable evidence that the most pronounced and objectionable odors and the highest aldehyde concentrations in diesel exhausts occur at conditions of "no-load idle" and deceleration, or acceleration after idle (20).

Another factor that influences the odor production characteristics of diesel engines is the mechanical condition of the engine. So far, attempts to associate factors in engine design with the odor problem have not provided a reliable technical basis for judgements. Combustion quenching, poor air utilization, and partial oxidation of unburned fuel in the exhaust system are suspect as contributing to generation of odorants. Because the quantity or quality of objectionable odor cannot be reliably associated with any one or any combination of fuel factors, fuel specifications cannot be used as an approach to odor abatement.

3.1.9.2 *Aircraft Odors.* Lozano et al. have reported odor concentrations for various types of jet aircraft (41). These authors point out that the odor concentration is highest for fan jet engines at idle, and this concentration (1000 odor units per standard cubic foot) is approximately 3 times higher than for diesel engine exhaust at idle.

3.1.10 Natural sources. In nature, odors are produced primarily from the decomposition of proteinaceous materials (vegetable and animal) by bacterial action (42). They develop principally in stagnant and insufficiently aerated water. Odor from these sources are variously described as fishy, aromatic, grassy, and septic. Dimethyl sulfide and methyl mercaptan, either together or separately, have been found among the volatile constituents of certain green, brown, and red algae. Robinson and Robbins have estimated the annual world wide production of some odorants (43). They found that forest fires, brush fires, and open field burning contribute significant amounts of odorants to the ambient air.

3.1.11 Miscellaneous Other Sources. In addition to those specifically mentioned, many other sources of odors are known. For example, odors are associated with production and use of fertilizers, insecticides, paint solvents, and other solvents, wastes from domestic animals and household pets, and the composting of organic matter.

3.2 Odor Classification and Ranking

As part of the national survey of the odor problem in the United States, which was conducted by Copley International Corporation, 85 air pollution control agencies were asked to indicate the major criteria used for defining odor pollution problems in terms of the type of odor, its seriousness, its areal extent and its frequency (44). The results obtained were as follows:

Number of agencies	Major criteria
16	Nuisance complaints received/number of people affected
10	Determine if detrimental to health and welfare
6	Definition of malodor/definition of source
5	Subjective judgements by agency personnel
4	Scentometer
2	Defined in local air pollution codes and regulations
2	Scientific instrumentation
40	No answer (no criteria)

The most common chemical types of odorants are compounds (both organic and inorganic) that contain nitrogen, sulfur, oxygen, or one of the halogens in their molecular configuration. Ranking of odorant classes on the basis of increasing average odor threshold results in the following order (5):

(1) Sulfides and mercaptans (Sulfur-containing compounds)

(2) Amines and N-heterocyclics (Nitrogen-containing compounds)

(3) Aldehydes, ketones and acids (Oxygen-containing compounds)

(4) Esters, alcohols, and chlorinated compounds (Oxygen- or chlorine-containing compounds)

(5) Hydrocarbons (Compounds containing carbon and hydrogen only)

Through classification of the many different odorants emitted from the various sources previously described, Hopton and Laughlin (5) produced a ranking of industries and processes with respect to odor pollution problems as shown in Table 2. From this Table it may be seen, for instance, that the emissions from varnish cookers, coffee roasting, feather processing, coke ovens, pulp and paper processes and certain refinery processes have odorants in the same categories and hence similar approaches (e.g., to odor control) are indicated.

The usefulness and validity of this approach is vindicated by the impressive correlation achieved in ranking odor sources on the basis of average thresholds of odorant

TABLE 2 RANKING OF INDUSTRIES AND PROCESSES WITH RESPECT TO ODOR POLLUTION PROBLEMS

Ranking	*Based on public complaints received by government agencies/officials	**Based on the average thresholds of odorant classes found in emissions
Group 1	Rendering plants	Rendering plants
	Agriculture - feedlots	Agriculture - feedlots
	Sewage treatment plants	Refineries
	Refineries	
	Pulp and paper	
Group 2	Surface coating	Pulp and paper
	Municipal incinerators	Sewage treatment plants
	Resin kettles and varnish cookers	Coke ovens
	Cupolas and core ovens	Varnish cookers
	Transportation - diesel exhaust	Coffee roasting
Group 3	Chemical processing industries such as paints, detergents, soaps, etc.	Resin
		Rubber compounding
	Food and allied industries such as coffee roasting, fermentation, grain drying, etc.	Fermentation
		Fish processing
Group 4		Cupolas
		Core ovens
		Paint baking
		Grain drying

* Taken from published data for local areas in the U.S.

** Assuming emissions containing more than one odorant type to have odor intensities in the order: sulfides and mercaptans $>$ amines $>$ aldehydes, ketones, acids $>$ alcohols, hydrocarbons and chlorinated solvents

classes found in emissions as compared to the ranking based on the number of complaints by the public to government air pollution control officials and agencies.

To arrive at a preliminary estimate of the odor potential of industrial operations in a given community, Copley International Corporation in co-operation with Engineering-Science Incorporated employed the concept of an "aggregate odor characteristic coefficient" (representing the combined effects of a specific source, including the quality, intensity, acceptability, and pervasiveness of the odorous emissions) and combined it with a measure of the odorant production activity for that industry. In that study, the common industrial odorants were assigned a quartile ranking (from 1 - 4) on the basis of increasing odor strength as measured by concentrations required to produce threshold perceptions.

3.3 Areal Extent of Odors

Refineries, chemical plants and Kraft process pulp and paper mills have been found to be the most significant sources of odor emissions from the viewpoint of areal extent (44). The average area affected by odorous emissions from refineries has been reported to be 10 square miles, and that from chemical facilities in excess of 5 square miles. Odors have been definitely detected 8 miles away from Kraft paper mills and have even been reported by some observers at a distance of 40 miles (7).

The least significant sources, in terms of areal extent of odor impact, are rendering plants, paint and varnish operations, and tanning facilities. There is a correlation between the size of the facility and category of source, and the areal extent of odor impact. For example, refinery and chemical facilities are generally large complexes with a significant number of stacks and confined odor sources, whereas rendering plants and other facilities generating a small areal impact are usually relatively small installations with unconfined odor sources.

3.4 The Canadian Situation

There is a paucity of published data with respect to potential or existing sources of odorous air pollutants in Canada. Yet it seems reasonable to assume that the odor sources responsible for eliciting an annoyance reaction from the Canadian public would not be very different from those encountered in the United States. However, the seriousness of existing or potential odor problems and the relative importance of various contributing emission sources would be expected to vary in different communities and could possibly be quite different in various parts of Canada. The existing situation is, of course, highly dependent on the nature of the major odor source or sources in the locality under consideration. Odor surveys have been conducted in Calgary and Edmonton for the Alberta Department of the Environment.

4 EFFECTS OF ODORS

4.1 Human Reactions and Responses to Environmental Odors

The following types of adverse human reactions to odors in the ambient air are known or suspected on the basis of either laboratory or field studies (17):

(1) Disease states, including causation or agravation; and

(2) Annoyance reactions, including action taken to abate perceived annoyance.

Variations in human response to odor exposure are caused by demographic variables (such as sex, age, marital status, income, and occupation) and differences in individual or collective attitudes towards a pollution source, resulting either in tolerance towards the odor or anxiety concerning the effects on health and property. In a community setting, annoyance at odor exposure is reported more frequently by persons with a propensity towards neurosis, sensitivity to aircraft-noise, and displeasure with other aspects of community life. On the other hand, persons who fail to detect or be annoyed by odor could have deficiencies related to clinical conditions such as upper respiratory infections. The contribution of these "extraneous" factors is probably least when the dose is very strong, or so weak as to produce no reaction at all in the average person, but their effect must be taken into account in any study of dose-response relationships (6).

4.1.1 Social Aspects. Offensive odors provoke people to complain about the quality of the air environment because malodors are one of the first obvious manifestations of air pollution. With an increased standard of living in the industrialized nations of the world, the annoyance reaction resulting from exposure to malodorous air pollutants has assumed increasing importance. This trend can be expected to continue and will probably even accelerate through the 1970's. In the Province of Ontario, for example, it has been estimated that over 80% of complaints from the public to provincial air pollution control officials are a direct result of odor pollution. Malodors can ruin personal and community pride, interfere with human relations and activities in various ways, discourage capital improvements or investments in a community, decrease socio-economic status, hurt a community's reputation, and can seriously interfere with normal enjoyment of life or property.

In the United States and in Sweden a considerable amount of the research into the effects of odorous air pollution has been directed towards measurement and evaluation of dose-response relationships through the use of sensory, chemical, and sociological methods of analysis (6, 17). Unfortunately, the data now available from long-term community studies do not show clearly to what extent an adverse reaction within the population would change if the exposure were halved or doubled, for instance. Moreover, epidemiological data refer to particular situations only. Because of the potential influence of factors unrelated to the actual odorant dose, sociological studies may yield data which do not remain valid over extended periods of time. Community attitudes towards the source of emission seem to be particularly important in this respect. Attitudes towards environmental protection and adverse effects resulting from the presence of environmental contaminants may change considerably with the foreseeable future and as a result odor exposures considered acceptable today could become unacceptable.

4.1.2 Physiological Manifestations. It has been shown that offensive odors are capable of producing nausea, vomiting, and headache. Moreover, they can result in loss of appetite, impair nutrition, curtail water intake, disturb sleep, upset the stomach, hamper proper breathing, and offend the senses (17, 20, 45, 46, 47). At elevated concentrations an annoying odor may become a nasal irritant, but not all odors cause irritation at high concentration.

4.1.3 Pathogenic Effects of Odor Pollution. The influence of odors on the health and comfort of human beings is difficult to prove. (17). In this connection it is of interest to note that, according to the constitution of the World Health Organization (WHO), "Health is a state of complete physical, mental and social well-being and not merely the absence of disease or infirmity" (48). Odors per se are usually not the cause of organic disease. However, an odor or odorant may incite an allergic response. Thus, the presence of an odor may precipitate attacks of asthma or may aggravate other allergic conditions. In many cases, it is difficult to determine whether an allergic patient was affected by an odor or the odorant substance itself.

Some highly toxic substances, such as hydrogen sulfide, are associated with offensive odors, but the dangerous properties of these substances do not derive from the odor itself. In fact, odor is often valuable in serving as a warning of the presence of an injurious gas. Generally, odor bears no relationship to toxicity and some highly poisonous gases are odorless or have a rather pleasant odor (e.g. hydrogen cyanide, whose odor resembles that of almonds). There are some odorous substances that represent a potential health hazard, especially under conditions of occupational exposure. Their danger lies not in their odor or in their toxicity alone, but in the fact that the maximum acceptable concentration (MAC) in each case is less than the olfactory threshold, so that even the nose, which is normally a very sensitive odor detector, cannot warn of their presence. Some of these substances, along with the pertinent numerical data, have been listed in Table 3 (1).

For these odorous substances an instrumental detection and warning system is of paramount importance. Organoleptic assessment is hopelessly inadequate. In general, if the ratio "olfactory threshold/MAC" is less than unity, the smell will be perceived by the nose before the pathogenic concentration is reached. For a ratio of unity the slightest impairment in olfactory function will raise the threshold value above the MAC level. Ratios greater than unity indicate danger when relying on the nose instead of an instrumental detector. The cases where threshold/MAC < 1 and threshold/MAC > 1 are clear cut. There is no danger in the first case, but immediate danger in the latter instance. Only when the ratio equals, or approaches, unity is there hidden danger. Ozone is an example. A number of years ago when its maximum acceptable level was set at 1 ppm, Russian publications strongly suggested a reduction to 0.5

TABLE 3 SOME VAPORS WHOSE MAXIMUM ACCEPTABLE CONCENTRATION (MAC) VALUES ARE LOWER THAN THEIR OLFACTORY THRESHOLD VALUES (OT_v)

Substance	Olfactory Threshold Value (mg/m^3)	MAC (mg/m^3)	Ratio OT_v/MAC
Acrolein	35	0.25	1400
Camphor	100	2	50
Dioxane	620	360	1.7
Hydrogen selenide	10	0.2	50
Methanol	7800	260	30
Methyl formate	5000	250	20
Methylene glycol	190	80	2.4
Ozone (original values)	0.2	0.2	1
Ozone (latest proposal)	0.2	0.05	4
Petrol, light	3300	200	16.5
Sulfur dioxide	79	13	6.1
Trichloroethylene	1350	520	2.6

ppm and as a result the American Conference of Governmental Industrial Hygienists standardized it at 0.1 ppm. German hygienists now accept only one-half that value, viz., 0.05 mg/m^3.

When the question of odorous air contaminants and their relevant effect on health was discussed at the Karolinska Institute Symposium on Environmental Health, held in Stockholm in June 1970, Goldsmith (6) emphasized that: "The present position of odor as a public health problem relates to three major factors. First, the largest proportion of public complaints about air pollution are complaints in fact about odor exposures in very many locations. Second, many of the most fundamental industrial processes upon which technical development depends are associated with the risk of producing community odor. This includes pulp and paper plants, petroleum refineries and chemical factories, solid wastes recovery systems, motor vehicles (particularly diesel vehicles), and many more. Third, the measurement of odor has posed some very serious obstacles to the study of the relationship between exposure and its effects".

4.2 Economic Aspects

Because malodors can ruin personal and community pride, interfere with human relations, discourage capital investment, lower socio-economic status, and damage a community's reputation, the economics of a community may be closely related to, and adversely affected by, an odor pollution problem (20). People have a natural tendency to avoid communities and localities with obvious odor problems.

Economic theory suggests that property values are usually reflective of neighborhood, occupant, and property characteristics. To the extent that they are considered objectionable by both buyers and sellers of property, their presence is negatively incorporated into the value of developed and undeveloped real estate. The results of studies by Ridker and Henning (49, 50) and Flesh (6) tend to support these premises. The resulting decline in market and rental property values, tax revenues, pay rolls, and sales can be disastrous to a community.

Air pollution in the form of malodors has been cited as the reason for certain lawsuits, petitions, picket-lines, riots, and even forceful closure of industrial plants (51). On the other hand, odorous industries may be an economic advantage to a community because they provide job opportunities both in the industry itself and in business which services the industry and its employees. In general, socio-economic aspects of odorous air pollution are difficult to assess.

5 LEGISLATIVE ASPECTS

5.1 Existing Regulations

Odors constitute one of the most complex and often one of the most objectionable of all air pollution problems. Yet, although some regulatory agencies have enacted laws prohibiting the type of air pollution that interferes with the reasonable enjoyment of life and property, very few specific odor pollution standards or regulations have been established in the industrialized nations. When concentrations of air pollutants (e.g., sulfur dioxide, ozone, nitrogen oxides, etc.) can be directly related to amounts of property damage and/or ill health, emission standards may be established and enforced. However, in the case of substances causing an objectionable or annoying odor such relationships are generally non-existent. Consequently, odor emission standards, when they have been established, are usually based on the number of complaints received and they are often inadequately backed by nuisance laws (44).

Hemeon (52) has advanced compelling arguments why he considers that the sensory offenses associated with air pollution should receive much higher priority in governmental policy than has been accorded them in the past.

Existing odor control regulations consist of a variety of partially successful measures including (53):

(1) nuisance type restrictions based on ambient air detection of odors;

(2) process restrictions for certain known odor producing sources; and

(3) control equipment requirements for specific source operations.

The three categories of regulations either specify techniques that are likely to reduce odorous emissions or declare that such emissions must not cause objectionable conditions. Most odor regulations are directed at elimination or reduction of odors in the ambient air. Human response to ambient odor must be the ultimate criterion of acceptable odorous emissions.

5.2 Doctrine of Nuisance

The most frequently used regulatory approach relating to odor abatement is through existing or proposed nuisance ordinances (54). Public nuisance is a term applied to a miscellaneous group of conditions that cause inconvenience, discomfort, annoyance, damage, or harm to the general public (55). In many countries such conditions are prohibited and are punishable by criminal sanctions. Generally, the public authorities may also proceed by injunction to prevent the continuation of a nuisance.

Many of the early air pollution laws attempted to deal with the problem by classifying certain discharges into the atmosphere as nuisances and consequently subject to abatement. However, this approach was gradually discarded as cumbersome and unreliable, as well as inadequate to deal with the modern array of pollutants, because it does not overcome the problem of identifying sources of air pollution. Moreover, it makes inadequate provision for the employment of preventive measures or for the use of engineering knowledge and techniques to control known or suspected sources of air pollutants. For the control of odorous emissions, however, public nuisance laws still remain a major regulatory instrument.

Evaluation of an alleged odor nuisance must take a number of factors into account (56). The most important of these are: odor intensity, odor quality, odor duration, odor frequency, time of day or week. Equal weight should not, however, be given to each individual factor. It should be possible to combine all of the relevant factors by a method of proportional weighting to arrive at a quantitative estimation of the overall magnitude of the odor nuisance as a basis for control. In fact, First (56) has proposed just such a system that provides a numerical method for arriving at an objective judgement of the degree of nuisance associated with a particular set of conditions involving the factors listed above.

Leonardos (54) has presented an excellent critical review of odor control regulations in existence in the United States. At the present time, there are no federal regulations in the United States for the control of odor, and odorants have been classified as "non-criteria pollutants" by the Environmental Protection Agency (57). In the absence of United States federal regulations on odorous air pollution, the development of odor control regulations has been left to state and local air pollution control agencies. Hence, a variety of odor control regulations and approaches have been formulated. In reviewing the existing regulations, Leonardos found that their rationale was based largely on five papers that appeared in the literature during the last 15 years. These regulatory approaches have been summarized in Table 4. A number of states have incorporated more than one approach into their regulations.

5.3 Regulations and Development

Effective control of odorous air pollution requires the support of legislation under which the desired degree of control can be achieved, of technical support whereby control of odorants and their emission sources can be undertaken, of a control organization to ensure that the existing regulations are implemented, and of surveillance activities to ascertain actual conditions and to check the effectiveness of the control measures that have been installed. The following discussion deals solely with the first of these requirements – the nature and

TABLE 4 UNITED STATES ODOR CONTROL REGULATIONS (MAJOR REGULATORY APPROACHES)

Regulatory approach	*Proposed by*	*Adopted by*
Scentometer (Ambient odor limits)	Huey, et al., 1960	Colorado, District of Columbia Illinois, Kentucky, Missouri, Nevada, Wyoming
Source control	Mills, et al., 1963	Connecticut, Idaho, Illinois, Maryland, Minnesota, Montana, North Carolina, Oregon, Pennsylvania, Vermont, Wyoming
Objectionability criteria	U.S. Public Health Service, 1966	Connecticut, Nevada, South Dakota, Vermont, West Virginia, Wisconsin
Threshold concentrations	Leonardos, et al., 1969 (but not recommended for air quality criteria and standards)	Connecticut
Instruments - based (Analytical measurements at source or in ambient air)	Feldstein, et al., 1973	Bay Area Air Pollution Control District (California)

scope of the legal framework that needs to be established.

According to Hemeon (52) the basic requirements for an effective, fair, and practicable odor regulation are the following:

(a) an ambient air standard for malodors which can be measured and which relates to the welfare of people;

(b) a standard that can be administered objectively employing simple techniques;

(c) odor emission standards that are compatible with ambient air standards; and

(d) the availability of reliable measurement methods.

Based on these criteria, Hemeon proposed an exemplary odor control regulation. Other suggestions for model odor control regulations have also been put forth (7, 29, 56).

Air quality criteria are of paramount importance as a prelude to the adoption of air quality standards. Establishment of air quality criteria for odors would be extremely useful to all regulatory agencies. Work towards such criteria is under way in a number of countries (6).

5.4 Scientific Basis for Performance Standards

A firm scientific basis for establishing performance standards requires that each odor problem is clearly defined in terms of degree of annoyance produced, the size of the population exposed, the frequency and duration of the events, the extent and nature of odorous emissions, and the cost-benefit relationship of odor control (17). To establish regulations on a firm scientific basis, one must have available a substantial amount of information on the specific quantities of odorants and the types of odorant chemicals involved, as well as knowledge of how much reduction in concentration is required to eliminate annoyance. Even though it is not possible to establish performance standards at present for the whole range of odorous emissions that produce significant annoyance reactions, specific controls could be established for some of the most important, objectionable, and persistent odorants. For instance, the United States Environmental Protection Agency has been considering the development of standards of performance for new rendering plants in compliance with the United States Clean Air Act of 1970 (29).

In summary, because the major problem involved in the development of viable odor control regulations revolves around the issue of how odorous air pollution is measured, one of the primary requirements for the effective control of odor should be sound measurement techniques. Also, for the solution of existing community odor problems it is of utmost importance that the regulations formulated or adopted specify what levels of odorants are acceptable as well as how such levels should be determined, especially at ambient air concentrations. Unfortunately, many of the existing methods upon which current regulations rely give only partial answers, at best, while at worst, these may seriously underestimate the extent of an odor problem (54).

5.5 Enforcement Procedures

Although odors are a very common cause of air pollution complaints, few regulations have been directed towards abatement of specific odor sources. Perhaps the main reason has been the lack of generally acceptable methods for quantifying the obnoxiousness of a given odor. Intensity may be measured at least semi-quantitatively, but annoyance is a highly subjective concept. In the past, most control authorities have resorted to nuisance laws to abate odors. Unfortunately, nuisance regulations are notoriously ineffective except in obviously intolerable situations. More recently there have been attempts to state both emission and air quality standards in terms of allowable dilutions (odor units). Perhaps the most effective rules are those that are directed towards specific emissions and/or emission sources. So far the lack of objective measurement methods coupled with the lack of specificity in most existing odor control regulations have made enforcement difficult at all administrative and judicial levels (56, 57).

5.6 The Canadian Situation

In Canada, the primary responsibility for air pollution control within the federal jurisdiction is vested in the Minister of the Environment and is delineated in the Clean Air Act which was officialy proclaimed on November 1, 1971. The Clean Air Act recognizes an odor as an air contaminant that, if emitted into the ambient air, creates or contributes to the creation of air pollution. It defines air pollution as "a condition of the ambient air, arising wholly or partly from the presence therein of one or more air contaminants, that endangers the health, safety, or welfare of persons, that interferes with normal enjoyment of life or property, that endangers the health of animal life or that causes damage to plant life or to property".

As a result of the constitutional division of powers and responsibilities between the federal government and the provincial governments of Canada, the federal government does not possess a constitutional responsibility for controlling adverse effects of air pollution on property or the welfare of persons. This responsibility is a provincial jurisdiction. However, the federal government does share with the provinces the authority to pass legislation for the protection of public health. Thus, under the Clean Air Act, National Emission Standard Regulations have been formulated for air pollutants constituting a significant danger to health.

For air pollutants that do not represent a significant danger to public health, (on the basis of the best information currently available), National Emission Guidelines are proposed. These guidelines are not regulations and as such are not enforceable by the federal government.

Because it is generally accepted that the majority of odorous substances do not represent a health hazard, but should rather be viewed in terms of their nuisance potential, odors fall into the second category of air pollutants. Thus, if in the future environmental requirements are formulated for controlling odors, these requirements would be announced through National Emission Guidelines.

The federal government is now compiling background information on available control technology to contain odorous emissions from the meat and fish processing industries in Canada, because odors from both these industries have caused a significant number of complaints from the general public. Once compiled, the background information can be used to identify best practicable control technology for odor abatement from these two industries and a "code of good practice" can then be formulated. Such a code can be used to provide guidance to the provinces in controlling odors from the meat and fish processing industries and as a basis for developing provincial regulations pertaining to odorous emissions.

6 MEASUREMENT METHODS

From a relatively crude beginning during the latter part of the 19th century, odor measurement techniques developed slowly until the 1930's and somewhat more rapidly thereafter until the 1950's. In 1955, Matheson (58) provided an excellent bibliography and review of the development of odor measurement devices and procedures. Since then a significant number of publications devoted to this topic have appeared (6, 59, 60).

For the purpose of discussion, most odor measurement methods can be conveniently grouped into two major categories: organoleptic or sensory methods and analytical (both instrumental and chemical) methods. Some approaches to odor measurement rely upon more than one of these techniques at a time. Sensory methods of odor measurement are subjective techniques which rely on the human olfactory system. Sensitive noses can detect odors in quantities impossible to determine with commercially available instrumentation or chemical methods. Only the human nose can "measure" the four sensory attributes of odor mentioned previously (intensity, quality, detectability, and acceptability).

Numerous chemical and instrumental techniques exist for the measurement of odorous substances, but many of these suffer from a lack of sensitivity and are only useful within a limited range of odorant concentrations. The utility of these methods has, in the past, been rather limited because odorous atmospheres usually contain complex mixtures of odorants at extremely low concentrations. In contrast, the human olfactory organ is able to detect literally thousands of different odors over a very broad range of concentrations. Most odor measurements that are carried out, either in the field or in a laboratory, are designed to provide information regarding the threshold characteristics of the odorous substance as well as its nature and concentration. Considerable research has been done on methods for the determination of odor threshold values and characterization of odorous substances (61).

6.1 Sampling Considerations

Three principal types of sampling procedures are commonly employed:

(a) dilution sampling (results in reduction of odorant concentration);

(b) concentration sampling (results in enhancement of odorant concentration); and

(c) sampling with no change in concentration.

Dilution procedures for sampling odor sources like stacks or oven exhausts, for example, are often employed to reduce concentrations and temperatures to levels suitable for human exposure without permitting condensation of the odorant material. On the other hand, a dilute odorant may have to be concentrated before it can be adequately characterized by chemical or instrumental methods of analysis. Comparative examinations, e.g., of infrared spectra or gas-chromatograms then become much more informative. The most widely used methods of sample concentrations are freeze-out trapping and adsorptive sampling (usually with activated carbon or silica gel) (14). Proper sampling procedures are of major importance in the accurate determination of odorant concentrations and sample characteristics. Turk and Mehlman (62) have pointed out some of the potential problems associated with sampling of odorous air mixtures.

When analytical equipment of high sensitivity is to be used to analyze the odor samples, it is sometimes possible to take a "grab" sample directly into an evacuated bottle or plastic bag without any attempt to concentrate the sample. Plastic bags have been used successfully for the short term storage (18 to 70 h) of a range of organic vapors. However, the concentrations of water-soluble gases decrease due to concomitant moisture.

Low-temperature condensation has two distinct advantages as a sample collection method. First, the concentrated odorous material is immediately available for further separation or analysis. Second, condensation is the most reliable method for preserving the odorants without chemical reaction. The main disadvantages of collection by condensation are that the equipment is somewhat cumbersome and that large quantities of water are condensed.

6.2 Sensory Methods

Because a viable physical or chemical odor detector has not yet been developed, methods of odor detection, measurement and comparison must, of necessity, rely on the sense of smell as the ultimate criterion. However, the response of the human olfactory system does not permit an absolute measurement of odor and, therefore, only relative odor characteristics can be established. In studies of odorous sources of air pollution, several samples of air must normally be compared for odor intensity, odor threshold, odor quality and odor acceptability (hedonic rating).

It is important to relate any program of sensory odor measurement to realistic analytical objectives. Odor intensities and thresholds cannot be well understood unless one realizes that odor intensity is not the same as odorant concentration. Odor intensity is a judgement of how strong an odor is in terms of a sensation experienced by the observer. Odor intensity is related to odorant concentration by the psychophysical power law. It is the intensity of an odor that is measured by sensory methods.

Odor intensity measurements involving organoleptic procedures usually involve three basic operations each of which contribute some degree of inaccuracy to the final result.

(a) Sampling - care must be taken that the sample is truly representative of the conditions being assessed.

(b) Dilution - the odor sample is serially diluted with odor-free air to the desired odorant concentration level.

(c) Determination of Threshold Dilution - the diluted samples are sniffed to determine the odor threshold value. The use of a pre-screened number of judges — an odor panel — improves reproducibility and accuracy of the last step.

6.2.1 Vapor Dilution Technique. Vapor dilution is the most commonly used form of sensory analysis. The normal procedure entails the sampling of an odorified atmosphere at a sampling station (in ambient air, at an odor source, or any other desired location), adjustment of odorant concentration in the sample by dilution or concentration, and presentation of the adjusted sample to a single observer or panel of observers for evaluation of the threshold odor concentration. Vapor dilution techniques can be classified into static, continuous, or volatilization methods, depending upon the manner in which the sample is presented to the observer (63).

Some of the odor presentation devices that have been developed on the basis of the vapor dilution technique are listed below (20).

(1) Static Method

Checkovich - Turner osmometer
Barail osmometer
Elsberg - Levy olfactometer
Fair - Wells osmoscope

(2) Continuous Method

Allison-Katz odorimeter
Zwaardemaker olfactometer
Proctor & Gamble osmo
Scentometer
Nader odor evaluation apparatus

(3) Volatilization Technique

Flask dilution method
Enclosed sniff-blotter technique

Of these devices the scentometer deserves special mention. This particular instrument was developed by Norman A. Huey and his colleagues in the late 1950's and was subjected to considerable evaluation before its commercial introduction (64). The fundamental purpose of the scentometer was to provide a ready tool for the measurement of ambient odor intensity by air pollution inspectors as a means of documenting odor problems. It combines the sampling and measurement functions into a single, utilitarian unit that is portable, inexpensive, and requires only one person for its operation. However, this last feature may become a disadvantage when it is desirable to have the opinion of an odor panel rather than a single observer. The scentometer has found its most useful application under the following set of conditions:

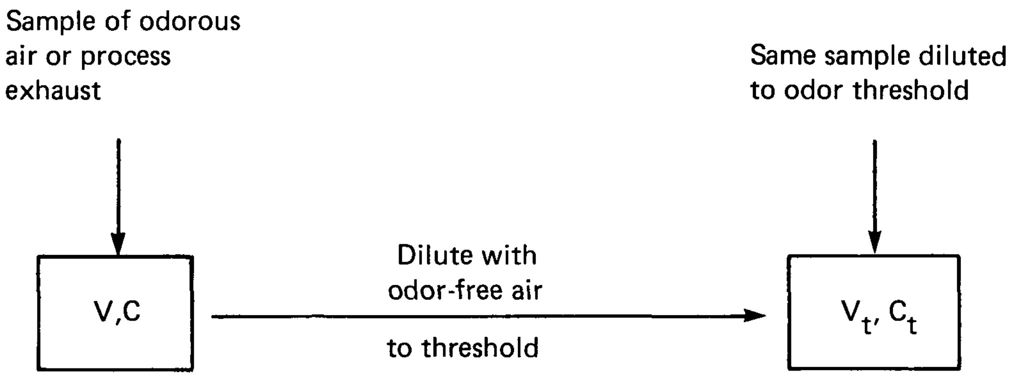
(a) day-to-day evaluation of odor sources, with the instant readout providing an opportunity for rapid feedback to effect abatement enforcement;

(b) general odor problem identification; and

(c) in those special circumstances where legal liability or compliance questions require explicit documentation of an odor emission.

A schematic diagram of the methodology, terminology, and scope of characterizing odors by the dilution-to-threshold technique is shown in Figure 1. In this method the threshold data are obtained by diluting a given sample of odorous air until the odor can no longer be detected. The dilution ratio thus obtained is referred to as the "threshold odor number" or the "number of odor units per unit volume" where an odor unit

Principle:



m = mass of odorant
V = volume of sample
C = concentration of odorant

m = (no change)
V_t = volume at threshold
C_t = threshold concentration

$C = m/V \qquad C_t = m/V_t$

$$\frac{C}{C_t} = \frac{V_t}{V} = \begin{cases} \text{Odor dilution ratio} \\ \text{Threshold odor number} \\ \text{Odor pervasiveness,} \\ \text{Odor units per cu. ft (ASTM} \\ \quad \text{definition, V in cu. ft).} \end{cases}$$

Containers used:

Syringes
Plastic bags
Steel bombs (using partial pressure ratios, $V_t/V = P/P_t$)
Flow systems (using flow rates, $V_t/V = Q_t/Q$, where Q is flow rate)

Odor free diluent:

Usually ambient air purified through activated carbon.

FIGURE 1 ODOR MEASUREMENT BY THE DILUTION-TO-THRESHOLD TECHNIQUE (65) is taken to be 1 unit volume of air in which the odor is at the threshold level. The odor threshold so determined is expressed in subjective units such as "thresholds", "odor units" or "dilutions". Frequently, a median response or ED_{50} threshold is used. This is the dilution at which 50% of the test subjects will report the presence of an odor sensation.

It is important to point out some of the inherent assumptions of this approach (65). These are:

(a) the mass of odorant is constant (this ignores the effect of adsorption on container walls at very low concentrations;

(b) the odorant is a gas or vapor (this ignores the possible effect of aerosols or condensation nuclei); and

(c) the odor threshold concentration is an intrinsic property of the odorant (this ignores the variability of response among human observers).

The experimental results of measurements using the dilution-to-threshold technique theoretically provide a basis for estimating:

(a) the degree of dilution required to deodorize a given odorous emission;

(b) the proportion of odorant that must be removed from a sample of air to eliminate the odor; and

(c) the volume of air that can be contaminated (or odorized) by a given volume of the odorous sample.

It should be noted, however, that such data do not constitute a basis for estimating:

(a) the odor intensity of the sample at concentrations above threshold, i.e., at supra-threshold levels;

(b) the quality of the odor; and

(c) the objectionability or acceptability of the odor, i.e., its hedonic character.

6.2.2 Supra-Threshold Measurements. Sensory supra-threshold measurements rely heavily on the direct application of subjective rating scales. Such measurements require the use of odor panels and detailed statistical analyses of the resultant subjective data. Accordingly, these techniques have been confined primarily to laboratory investigations.

A sensory technique of odor measurement that has been applied with some measure of success involves the use of odor reference standards (66, 67). Such standards may be used as comparisons either for odor intensity values, for different qualities of odor, or for both. The sensory characterization of both odor quality and intensity is called a quality-intensity profile.

A series of prepared odorant concentrations is referred to as a "sniff kit". Sniff kits are especially useful for determining odor intensity or objectionability for odors that are too complex for any meaningful physico-chemical analysis. The kit in effect contains odor reference standards for the odor source in question. An example of this approach is the set of reference standards developed for sensory evaluation of diesel exhaust odor (68).

Sensory techniques can be classified broadly into field-oriented or laboratory-oriented methods. Field-oriented sensory techniques can be utilized either directly (obviating the need for sampling), or in conjunction with an intermediate sampling step. Direct field-oriented sensory measurements are used commonly in evaluating ambient odor situations. However, for source evaluation direct sensory measurements are frequently not possible because of extremes of temperature, or because relatively high concentrations of noxious components make the source intolerable for human exposure. Under such circumstances a sampling step is required. It is generally implicit that a sampling step is required in conjunction with laboratory oriented sensory techniques.

6.2.3 Laboratory Studies. A number of studies by various laboratories on sensory analysis of single odorants have been useful in defining minimal detection levels as well as supra-threshold response of the human nose to a variety of odorous materials (69). Because the total human response to odor involves odor intensity, quality and hedonic aspects, as well as the interactions of all three factors, the situation is very complex and progress slow. Further research is required to develop viable models for application to the ambient air environment.

6.2.4 Field Studies. A considerable amount of empirical data has been gathered during sensory odor measurements conducted in the field, both at the source as well as in the ambient air (17).

6.2.5 Odor Panels. Sensory testing is concerned with measuring physical properties by psychological techniques. To increase the reliability and precision of odor measurements, sensory evaluations are usually made by a number of human odor judges, who, taken as a group, represent an odor panel.

6.2.5.1 *Selection of Panelists.* Selection and training of subjects who are to be judges on an odor panel is of great importance, because substantial variations occur from one person to another with respect to the sensory response elicited by a given olfactory stimulus. Age, sex, smoking habits, prior experience, learned responses, and extraneous stimuli, among other factors, all influence an individual's perception of odor (70). To evaluate the hedonic tone or frequency of an odor experience in the environment the panelists should be demographically representative of the entire population.

Because of the variation in human judgement with respect to all the major characteristics of an odor, sensory evaluations of environmental odors should involve an odor panel comprising five or more persons. Dravnieks (11) has suggested that, whenever possible, the number of panelists per panel should exceed seven so that some simple statistical tests can be applied to the results.

Three main types of tests for selection of odor judges appear to have gained wide acceptance (71).

(a) Triangle Test: Three test samples are presented consecutively. Two are identical, the third is different. The candidate is requested to identify the different or "odd" sample.

(b) Intensity Rating Test: A series of dilutions of an odorant in an odorless medium is prepared and one sample is removed from the series. The candidate is asked to place it in the series according to its odor intensity.

(c) Multicomponent Odor Identification Test: This test presents three mixtures to the candidate. These mixtures contain, in sequence, 2, 3, and 4 odors out of a possible total of 8 known standards. The candidate is told how many components to look for.

Rossano (14) has presented a discussion of criteria for the selection of human judges for odor measurements as well as recommendations for experimental conditions under which sensory tests should be conducted.

6.2.5.2 *Testing Procedures.* In general, sensory odor measurements involve at least three basic operations: sampling, dilution, and evaluation. Each of these steps contributes some degree of inaccuracy to the final result.

For odor measurements employing odor panels it is essential that presentation of the odor be conducted in a controlled and standardized manner to ensure that the entire panel is exposed to a common stimulus. Sample preparation must also be carefully controlled so that interfering contaminants are not introduced. The ASTM Manual on Sensory Testing Methods (72) lists the most common test forms employed in sensory (psychometric) methods.

A definitive measurement of an environmental odor must be based on determination of the threshold concentration (if not known) and determination of the type, quality, and intensity of the odor. Considerable research has been conducted on ways of reliably measuring threshold values of odorous substances and characterizing their supra-liminal intensity (73).

6.2.5.3 *Sample Presentation and Measurement.* Both static and dynamic dilution methods are used to present samples of odorous air to panel members. Most of the techniques employed to quantify odorous emissions involve vapor dilution to a previously defined threshold-sensing value. The most commonly used method is based upon the ASTM procedure D1391-57, as modified by Mills and his co-workers of the Los Angeles Air Pollution Control District (59). It is also the only method currently recognized by the United States Environmental Protection Agency.

Numerous problems exist with this technique, particularly for dilution in the vicinity of the threshold level. Recommendations for improvements in this procedure and comparative evaluations between the ASTM syringe-dilution technique and various other sensory odor measurement methods are currently under review by a Task Force of the ASTM Committee (E-18) on Sensory Evaluation of Materials and Products.

Extensive research and development work in the area of characterization of atmospheric odors has been performed by Turk and co-workers (62). Because no universally accepted system of odor quality descriptors of primary odors has so far been developed to describe the large variety of odorants encountered in polluted atmospheres, Turk devised an empirical approach that does not entail any assumptions concerning primary odor types. The key to this approach is the use of chemically-based odor quality reference standards.

6.2.5.4 *Interpretation of Results.* The actual values obtained for odor thresholds depend on the type of test procedure, panelist selection and screening criteria, detectability criteria etc., and can be defined only within the context of these parameters. Thus, an experimentally determined value for the detection threshold of a specific odorant is not a physical constant, such as boiling point, for instance, which can be established with a high degree of accuracy.

For an odorous air sample collected from a specified emission source the odor threshold is obtained as a dilution number, with a high number representing a low odor threshold. This dilution number may also be considered as the number of odor units contained in each unit volume of gaseous emission, where an odor unit is defined as 1 unit volume of contaminated air having an odor which can just be detected by 50% of an odor panel. The product of the volume rate of emission of an odorous substance multiplied by the number of odor units in the exhaust stream gives a measure of the emission rate of odorants (odor units per minute) and can be used in much the same way as emission rates of other air pollutants (e.g., kg or lb/min of particulate matter or of gases such as SO_2 or nitrogen oxides).

It should be remembered that there are factors other than odor intensity that must be taken into account in the assessment of an odor problem. Some of the more important of these factors are:

(a) the quality or hedonic character of the odor;

(b) the change in odor intensity as a function of odorant concentration;

(c) the type and extent of interaction with other odorants which may be present;

(d) the duration and frequency of odor episodes; and

(e) the time of day as well as the day of the week during which an objectionable situation exists.

6.3 Physico-Chemical Methods

6.3.1 Instrumental Methods. With respect to a considerable number of odorants the human nose is still more sensitive than currently available detecting devices, but there are odorous substances which can be readily detected by instrumental methods at concentrations at or below the olfactory threshold. Because many odorants evoke an odor sensation at concentrations below 1 ppb (vol), instrumental measurements usually require very specialized techniques. One of the primary requirements in the application of instrumental methods to the measurement of odorants in ambient air is very high analytical sensitivity.

Probably the most useful and popular instrumental technique for subjective-objective odor correlation measurements is gas chromatography. This powerful analytical tool has been an important instrument in supplementing the capabilities of the human nose in odor detection, identification and analysis (74, 75). With commercially available detectors such as flame ionization, helium ionization, flame photometric and coulometric detectors, for example, gas chromatography may be used for both source and ambient air analysis.

Depending upon the concentrations of the odorants present in a given air sample, other instrumental techniques (such as spectrophotometric methods in the infrared, ultraviolet, or visible portions of the electromagnetic spectrum; conductometric, coulometric, amperometric, or other electrochemical methods; and various chromatographic or spectrometric methods) may or may not be applicable to the analytical determination of odorants. In many cases the combination of gas chromatography with mass spectrometry yields sufficient analytical data for positive identification (as well as quantification of odorant species) because almost every chemical substance has unique mass spectrum. After separation by gas chromatography the individual odorous components of the original sample are fed directly into the mass spectrometer arranged in tandem with the gas chromatograph.

Alternatively, instrumental analytical techniques which yield data on total concentrations of selected compounds (or classes of compounds) may also provide a good correlation with odor intensity and quality. Examples of such methods include measurement of total reduced sulfur gases (TRS) from Kraft pulp mill operations and total hydrocarbons or oxygenates from combustion sources. Also, for some emission sources other species such as CO, NO, and CO_2 which in themselves possess no odor, have been correlated with odor intensity and used as indicators of the completeness of combustion processes. However, the precise nature of the association and the conditions under which such correlations are applicable are still being debated.

Hall and Salvesen have prepared, under contract to the United States Environmental Protection Agency, a state-of-the-art literature review regarding instrumentation available to measure specific odorants in emissions from stationary sources of air pollution (76). Odor sources considered were: Kraft pulping operations, petroleum refining/petrochemical operations and animal rendering plants. One of the objectives of this review was to examine the possibility of substituting a quantitative approach based on the measurement of odorants for the subjective measurement of odors. The authors concluded that instrumental measurement of odorants rather than sensory measurement of odors is a valid approach only in situations where prior agreement exists on what odorants are primarily responsible for the odor problem.

An analytical approach which has shown itself to be of tremendous diagnostic value in odor measurement and identification relies on a combination of sensory and instrumental methods. A gas chromatograph is equipped with a "sniffing port" in parallel with a conventional detector. The sniffing port permits subjective evaluation of the odor characteristics of the various odorants in a contaminated air sample. The gas chromatogram produced may then be annotated with various odor descriptors for specific peaks and the resultant record is called an "odorogram". In this way the major components responsible for the observed odor of a sample can, in principle, be located in the gas chromatogram and once they are identified their amounts can be quantitatively determined from the response of the chromatograph detector. The major odorants may be identified, if required, by various analytical procedures such as spectrophotometric methods, wet chemical analysis, or mass spectrometry, for instance.

6.3.2 Wet Chemical Analysis. Odorants, like other air pollutants, are also amenable to classical chemical analysis. In many cases, however, such an analysis is difficult and time consuming especially when the odor is a complex mixture of many odorants at low concentrations. Another short-coming of chemical methods is based on the fact that odorants belonging to the same homologous series but differing in molecular weight, usually exhibit distinctively different odor characteristics. As a result, analysis by chemical functional groups has little practical value in odor analysis unless only one species of a particular chemical class is the principal odorant. For these reasons wet chemical analysis generally cannot provide the type of information necessary for effective odor control programs.

6.3.3 Objective Odor Measurement. The previous discussions raise the question: "Can odors be measured objectively"? The answer to this question depends upon the possibility of correlating odor thresholds, intensities, and odor qualities to physico-chemical parameters which can be measured without the use of the human nose. Present knowledge of the psychological, physiological and chemical aspects of olfactory phenomena is inadequate. A rationale upon which to base physico-chemical measurements of odor per se does not exist. Those objective methods that now exist measure odorant, not odor. As such they complement sensory methods by offering an objective measure of the causative agents of a highly subjective phenomenon (6).

7 ODOR ABATEMENT

Odor abatement has been discussed in some detail in a number of reviews (77, 78) and books (2, 79). The primary goal of the application of odor control technology is the achievement of a situation representing no objectionable odor to the receptor public. A wide variety of control techniques are applicable to odorants, corresponding to the wide variety of odorants themselves (14). The abatement methods employed depend largely on the odor producing process, the odorant(s) and other substances in the waste gas stream. As with other forms of air pollution, control of odors at the source is the most effective means of abatement.

To a first approximation, all odor abatement approaches can be placed in one of three basic categories: 1) elimination of the source of odor; 2) elimination of odor perception; and 3) efforts to reduce odor. Odor abatement techniques and systems rely primarily on the traditional approaches for controlling gaseous air pollutants. More specifically, most odors can be either eliminated or reduced by:

(a) process changes or product modifications,

(b) oxidation methods,

(c) absorption (liquid scrubbing),

(d) adsorption,

(e) condensation,

(f) odor modification, and

(g) dispersion and dilution.

Sometimes a combination of two or more of these methods is required for an effective solution of an existing odor problem. In the past, chemical oxidation and masking (odor modification) have been the most widely employed odor abatement methods (80).

The cost of installing and operating odor control equipment can often be offset by economic benefits derived from the application of control methods. For example, odorous compounds are frequently controlled by incineration and the heat generated (e.g., by the recovery furnace in Kraft pulp mills, rendering plant incinerators and sewage gas burners) can be used to advantage in a variety of ways. The recovery of valuable by-products can also result in improved economy for a process.

Byrd and Phelps (73) have presented a method of arriving at the most economic approach to effective odor control. Other authors (81, 82, 83) have also offered advice intended to aid the selection of an economical yet effective odor control method for a given process or a given set of conditions. Nevertheless, achievement of an effective odor control system is difficult. Most odors are caused by very small concentrations of odorants. It is unlikely, therefore, that the exact composition and concentration of the odorous materials will be known. Because the exact chemistry of the odorous compound usually will not be known, selection of the most suitable equipment must often be based upon past experience with the same system or inference from similar systems.

7.1 Process Changes and Product Modifications

These abatement methods are too often overlooked, yet they should be among the first considered. Chemical processes are so diverse that it is difficult to suggest specific remedies. Quite often, however, re-use or recycling of emissions, substitution of odorless solvents or reactants for odorous ones, better equipment maintenance and adjustment of process temperatures residence times, or other conditions can significantly reduce or completely eliminate odor production. Sometimes even slight process changes minimize odor generation and are more effective and more economical than existing control equipment.

7.2 Oxidation Methods

When these methods are employed careful attention to design features is necessary to achieve complete oxidation. With many organic odorants the degree of oxidation of the molecule is directly related to the objectionability and pervasiveness of the odor. This can be seen from the following examples.

Substance	Odor Description	Odor Threshold Value (ppb)
Butyl alcohol	Mild odor	10 000
Butyraldehyde	Bad odor	70
Butyric acid	Very bad odor (smell of rancid butter)	1

It is quite instructive to note the decrease in odor threshold values in this series as the degree of oxidation increases. This change of odor threshold by a factor of 10^4 illustrates the importance of complete oxidation to eliminate an odor. Partial oxidation may actually increase the seriousness of an odor problem. In this particular example, unless 99.99% conversion of the alcohol to CO_2 and H_2O is achieved, the odor emitted from the oxidation system would be worse than that of the original emission.

Oxidation methods can be conveniently discussed in terms of two major categories: incineration and chemical oxidation.

7.2.1 Incineration of Odors. Complete combustion is generally accepted as the most reliable way to deodorize malodorous gases. Many odorous gases or vapors are organic compounds containing the chemical elements C, H and O and, therefore, are capable of being incinerated completely to odorless products (carbon dioxide and water). Because of rising fuel costs, incineration may not be the most economical method. However, the economics of this technique are enhanced if the odorous materials provide a significant fuel source. Incineration can be economically competitive with other odor control methods for high concentrations of odors in low volumes of air.

For complete combustion of odors four conditions are essential:

(a) there must be sufficient oxygen;

(b) the gases must be thoroughly mixed;

(c) the temperature must be high enough; and

(d) sufficient time must be allowed for the oxidation to reach completion.

Three categories of incineration methods for odor abatement are flame incineration, thermal incineration, and catalytic incineration.

7.2.1.1 *Flame incineration.* Flame incineration or direct combustion is used when the odorous emissions contain a high concentration of combustible material. It is the least costly form of incineration because the contaminant is used as the fuel. A typical example is a "flare" in the petroleum industry. Flame incineration is most effective when used in a combustion chamber under carefully controlled conditions. Auxiliary fuel (e.g., natural gas or oil) is usually not required but may need to be added to maintain temperature above the lower flammable limit of the odorous substances. Operating temperatures are often over 2500°F.

7.2.1.2 *Thermal incineration.* Thermal incineration takes place in a gas or oil-fired combustion chamber where the odorous gases are heated to their combustion temperature and thoroughly mixed for a sufficient time to ensure that the oxidation reaction goes to completion.

Whereas a direct flame brings about incineration by free radical mechanisms at 2500°F and higher, thermal incineration of most odorants begins at temperatures as low as 900 to 1000°F. Normally, operating temperatures range from 1000 to 1600°F depending on the odor to be eliminated and the design of the combustion chamber. Residence time and turbulence for maximum flame contact and temperature are important in thermal incineration. Flame detention times are usually 0.3 sec. or longer. Typical examples of thermal incineration are afterburners designed to eliminate odors from incomplete combustion processes. Heat recovery is usually employed to minimize fuel costs. When this is the case, thermal incineration can be considerably more economical than flame incineration. In some instances it is possible to re-circulate odorous air streams into boiler furnaces or other combustion devices as secondary (or "make-up") air and thus destroy the odor without the use of additional fuel (23).

Thermal incineration has been applied to a number of odor-producing processes, including: coffee roasting, animal rendering, rubber and resin curing, varnish cooking, paint baking, asphalt blowing, phthalic anhydride production, foundry core ovens, wirecoating ovens, printing presses, deep fat frying and fish scrap digesters (84).

7.2.1.3 *Catalytic incineration.* Catalytic incineration enables odorous compounds to be oxidized at even lower temperatures, usually around 850°F. Typical operating temperatures for catalytic combustion range from 600 to 1000°F. Noble metals such as platinum and palladium are most often used as catalysts for the oxidation of odors. Basic design requirements are the same for catalytic and thermal systems. They must provide thorough mixing of combustibles with air, enough heat input to raise the temperature of the gas stream to the required level, even temperature and flow distribution, and a sufficient residence time of the odorous gases to accomplish complete incineration. Application of catalytic incineration assumes the absence of catalyst poisoning agents, activity suppressants or fouling agents in the exhaust stream (85). An advantage of catalytic combustion is the lower operating temperature and thus lower fuel consumption as compared to the other incineration methods. Catalytic combustion is often used to destroy odors from diesel exhausts, nitric acid, plant tail gases, paint solvents, chemical manufacture, food processing, coating ovens and coke oven emissions.

7.2.2 Chemical Oxidation. Chemical oxidation often can be the most effective, economical and reliable method for the treatment of odorous air. The oxidant can be a gas (e.g., ozone), a liquid solution (e.g., an aqueous solution of sodium hypochlorite), or a solid (e.g., pellets of potassium permanganate adsorbed on activated alumina). Other chemical oxidants that are commonly used to control odors are chlorine and chlorine dioxide. The exhaust from fish meal driers, for example, is often mixed with 20 ppm of chlorine solution and then absorbed by sea water in a scrubber (86). Because chemical oxidizing agents do not always achieve complete oxidation of odorous substances (especially at low odorant concentrations), it is important to assess each agent strictly in terms of the odor abatement it accomplishes.

Ozonation can be an effective method of odor control if the odorant is an organic substance. The ozone dosage required for effective odor control will vary depending upon retention time, temperature and humidity (81). A mistake frequently committed with ozone oxidation is that insufficient contact time is allowed and not enough attention is paid to other design parameters of the ozonation system. The use of ozone as an oxidant is impractical in occupied spaces because ozone concentrations required for effective action would be far too toxic to be tolerable to humans (14). Ozone treatment has been used, however, to deodorize exhaust gases in stacks where no human exposure is involved. Ozone has been used successfully for the treatment of sewage digestion odors in Japan (29). If it is properly engineered, ozonation may be extremely effective, but there is also the extremely serious problem of the introduction of dangerous pollutant (O_3) into the atmosphere.

Sodium or potassium permanganate are used for odor control by direct treatment of unconfined odor sources (for example, by direct application of the solution to the ground in cattle feed years), by scrubbing with aqueous permanganate solutions or by the use of granular beds of adsorbent impregnated with permanganate. The oxidizing effectiveness of permanganate depends on the pH of the medium and increases in the following order: neutral $<$ alkaline $<$ acidic. Alkaline media are used predominantly, because acidic permanganate is very corrosive. Potassium permanganate solutions have been shown to possess significant deodorizing potential for sulfur compounds, amines, phenols, unsaturated compounds such as styrene and acrolein, and many other odorants (87).

7.3 Absorption (Liquid Scrubbing)

Absorption or scrubbing can be used as an odor abatement method, when odorous gases are soluble or emulsifiable in a liquid or react chemically in solution. Odors may be absorbed by physical or chemical means, using water, oil, or other liquids or solutions in scrubbers. Common types of scrubbers are the spray tower, impingement scrubber, packed tower, marble bed and venturi scrubber. Water is most often used as a scrubber liquid and acids, bases or oxidizing agents are added if required. Success in odor removal by scrubbing depends largely upon identifying the odorants and finding a scrubber liquid that reacts rapidly and completely with these substances. Odor removal by wet scrubbing is a function of the residence time of the odorous air in the scrubber, the available contact area, the solubility of the odorant in the scrubber liquid, and the concentration of the odor in the inlet gas stream (29).

Examples of potential scrubbing reagents are $KMnO_4$, $NaOCl$, $NaHSO_3$, lime water, Cl_2, ClO_2, H_2SO_4, HCl, $NaOH$, Na_2CO_3, ethylene glycol, and certain amines. Potassium permanganate solutions are highly efficient in oxidizing odor and are especially well suited for oxidizing sulfur compounds. It has been reported (29) that the most effective reagents for amines, mercaptans, and aldehydes are, respectively, hydrochloric (or sulfuric) acid, sodium (or calcium) hydroxide, and sodium (or calcium) bisulfite.

As a rule, no single scrubbing reagent can effectively remove all the odorants in an emission from a typical odor source. Even if a suitable universally effective scrubbing agent could be found, the odor would merely be concentrated in the liquid phase and thus become a potential water pollution problem. Because of the cost of most oxidizing agents, oxidative scrubbing is usually employed only with odorous emissions containing low concentrations of oxidizable odorants.

Absorption has been used as an odor abatement method in rendering plants, asphalt plants, fish processing plants, and soap manufacturing.

7.4 Adsorption

Odorous gases and vapors are adsorbed on surface-active materials to widely differing extents under comparable conditions and tables of retentivity data can be found in the literature (46, 88). The control of atmospheric odors by adsorption is for all practical purposes limited to the use of activated carbon or charcoal as the sorbent because its efficiency is not reduced in the presence of moisture. Adsorption with activated carbons can be an effective and economical odor control method for emissions with low concentrations of odorous compounds (89).

Although activated carbon has a high affinity for some odors, it is selective. It is usually effective only below 125°F. The gas stream must be cleaned of any particulate matter before being fed to the adsorber. Activated carbon will serve to remove odors until the carbon is saturated, at which time it must be reactivated. Adsorbent beds must be carefully designed and continuously monitored to avoid displacement and breakthrough of some odorants caused by the presence of more strongly adsorbed materials. Unfortunately carbon is also a catalyst for decomposition and oxidative reactions of organic matter, and the hot carbon in a freshly reactivated solvent recovery bed may actually produce nuisance odors if it is not cooled sufficiently before being returned to its adsorption function.

Problems with adsorption as an odor abatement method include batch to batch variation in adsorptive capacity. Low capacity or short retentivity for some odorants, and without regeneration, relatively short adsorbent life. Nevertheless, adsorption with activated charcoal filters can be an effective and economical method of collecting and concentrating highly diluted odorous pollutants.

Activated coconut-shell charcoal is reported to exhibit a high adsorptive capacity for fumes of acetic acid, alcohols, benzene, toluene, carbon tetrachloride, disinfectants, gasoline, mercaptans, ozone, phenol, pyridine, turpentine, and other fumes. It is not satisfactory for acetaldehyde, amines, ammonia, and formaldehyde, among other substances (89).

7.5 Condensation

Condensation is used primarily when steam is present in an odorous exhaust. It is not effective for what are called non-condensable or "hard-core" odors. Honda has tabulated temperatures of condensation for various malodorous substances (90). When it is applied to odorous steam vapors, it is one of the cheapest methods of reducing odor. Condensation should be considered if solvent or vapor recovery is desired. It is a particularly useful abatement method in situations involving toxic or flammable odorants.

Condensation is often used as a preliminary stage to reduce the load of other abatement procedures, especially absorption and adsorption, because better efficiencies are attained with these procedures at low temperatures, and relatively high odorant concentrations. Condensation can be achieved by refrigerant coils and condensors. Condensors are divided into two basic categories: surface and contact. In the surface type, coolant does not make contact with the vapors or condensate. Their disadvantage is that they are usually more expensive and require more maintenance than the contact type. In contact condensors the coolant, vapors and condensate are intimately mixed. Types of contact condensors include spray, jet and barometric condensors. Disadvantages of the contact type condensors are their large coolant requirements and the fact that the coolant (usually water) can be used only once, due to odor and water pollution problems.

7.6 Odor Modification

The sensory quality of an odor may be modified by the addition of other odorous substances under conditions that do not involve chemical changes. There are two odor modification methods: counteraction (or neutralization) and masking (or reodorization). Masking does not alter the composition of the original odor but only obscures its original quality whereas counteraction relies on achieving a reduction in the intensity of the original odor through the addition of a counteractant which may in itself be an odorant.

In both methods, initial equipment costs and operating costs are comparatively low. Odor modification is used in competition with chemical oxidation, adsorption, or scrubbing systems and for unconfined odor sources such as lagoons, settling ponds and garbage dumps, to which other abatement systems cannot readily be applied. The relative effectiveness of odor modification as compared with the physical/chemical abatement systems previously discussed is very difficult to evaluate.

Advantages of odor modification methods are minimum capital investment for equipment, ease of application and immediate availability for known nuisances. The most serious disadvantage is the danger of covering up a toxic gas so recognition is impossible. Not all odors can be masked. In particular strong acids, even in trace amounts, will defy masking agents because the agents commonly used decompose under acid conditions. Odor modifying agents need to be selected or formulated by experienced personnel. Materials used are usually chosen from industrially available high intensity odorants. Alcohols, aldehydes, and esters are classes of compounds that are frequently present in chemicals used for odor counteraction and masking.

Odor modification is considered to be unethical by many people in the field of odor control, because no attempt is made to reduce the amount of odorous substances. Because odor modification does not eliminate the odorous compound it is not applicable to irritable or toxic odorants. To some individuals the masking agent may even be more objectionable than the original odor. Also, dilution and dispersion can result in the original odor again becoming dominant (91). The usefulness of odor counteractants is possibly even more questionable than that of masking agents. While there appears to be some basis for odor counteraction, sound scientific data are lacking.

7.7 Dispersion and Dilution

In the past, dispersion and dilution were the primary methods employed by many industries for reducing complaints resulting from annoying odors. Today, these techniques are regarded unfavorably and are generally unsatisfactory for the current level of attack on odor pollution problems. Dilution or dispersion of an odor, through an elevated source such as a stack, will obviously result in odor-free air as the odorant concentration is reduced below the olfactory threshold level. However, unfavourable meteorological conditions or the presence of particulate matter to which odorants may adhere, make these techniques highly unreliable. Turk (66) has given a number of reasons why dispersion and dilution are ineffective methods for odor abatement. Whenever practical, odors should be eliminated at or near the source.

7.8 Other Abatement Methods

A number of other methods for odor abatement, which have been applied with varying degrees of success, are described in the literature. Some of these are irradiation of odors (2), containment (90), particulate removal (20), biological control (92), and source elimination (82).

7.9 Evaluation of the Effectiveness of Abatement Methods

The low olfactory thresholds of many common odorants and the difficulty inherent in the selection of reliable methods for odor control make it necessary to assess the effectiveness of any odor abatement method that may be implemented (17, 93). Evaluations of the effectiveness of odor control systems have relied upon community odor surveys, sensory measurement by odor panels or trained observers, physico-chemical measurements at the source and/or in ambient air, and ancillary methods such as use of tracer gases and dispersion calculations, for example.

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