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**The chemistry
of industrial toxicology**

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2nd edition

industrial toxicology

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Preface

to the second edition

Since the first edition of this book was published, the number of substances which potentially menace the health of the industrial worker has materially increased. These substances include some inorganic materials and many organic compounds, especially pesticides. Very likely the most important, and certainly the best publicized, have been the radioactive isotopes.

During the past few years the control of the commoner hazards has improved to such an extent that occupational illness is now rarely encountered in this country from substances such as benzene and carbon disulfide. Moreover, industrial hygiene has developed rapidly in many countries outside the U.S.A., and the findings in these countries have confirmed broadly the earlier experience of America and Western Europe with the familiar industrial poisons.

Standards of permissible concentrations of toxic substances have found increasing acceptance and become increasingly severe. Also, many new analytical methods have been developed over the past decade, with particular emphasis on the analysis of body fluids.

In the second edition an attempt has been made to include the more important of these new developments in the field of industrial toxicology.

HERVEY B. ELKINS

December, 1958

Preface

to the first edition

Although the literature of industrial toxicology contains many papers dealing adequately with the chemistry of various industrial poisons, nearly all books on the subject are written primarily from the medical point of view.

Although the vital role played by the physician in controlling occupational disease is duly recognized, it is not amiss to point out that the most important single step in the prevention of many occupational illnesses is control of fumes or dust. Measurement of the effectiveness of such control, in the long run a medical problem, can best be made initially by chemical methods. Furthermore, responsibility for the protection of workers rests primarily with industry; and those most intimately acquainted with the industrial processes and materials involved are industry's own chemists and engineers.

In this book an attempt is made to treat industrial poisons primarily from the point of view of the chemist and engineer. This means that the harmful substances themselves will be emphasized, and the industrial processes in which they are used, rather than the symptomatology and pathology of their effects on the human being. Some mention of the nature of the injuries caused is essential; but emphasis is placed on the probable seriousness of such effects, rather than on their complete physiological characterization.

It is hoped that this volume will provide a convenient source of information on the basic properties of the common industrial poisons;

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PREFACE TO THE FIRST EDITION

that it will stimulate the interest of the industrial chemist in problems of occupational illnesses of toxic origin; and that it will encourage employers to utilize the knowledge and training of their chemists and chemical engineers in protecting their workers from harmful substances to which they are exposed.

HERVEY B. ELKINS

January 3, 1950

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I.

Fundamentals

INTRODUCTION

Poisons have long been of interest to mankind. Primitive man encountered toxic substances in plants, insects, and reptiles. In time he learned to prepare poisonous brews of organic origin. As the arts of mining and metallurgy were developed, inorganic poisons such as compounds of arsenic and mercury became known. The effects of toxic gases, such as carbon dioxide, found in caves and wells, and carbon monoxide and sulfur dioxide, from fire, were no doubt known long before the existence of gases was discovered.

With the development of the science of chemistry dozens of new elements, hundreds of inorganic substances, and thousands of organic compounds were discovered and studied. The effects of many of these substances when ingested or inhaled by animals, and even by man, were investigated. Medical science, in quest of new drugs, has sponsored the largest part of these investigations. Most effective medicines are somewhat toxic, and the importance of knowing the limiting safe dosage and physiological effects of substances which are to be swallowed by or injected into sick persons is obvious. The use of such toxic materials as mercury compounds and morphine in the treatment of disease is based on a thorough knowledge of their toxicology.

The need for control of insect pests, which consume vast quantities of foodstuffs and spread many infectious diseases, has resulted in further study of the properties of toxic compounds. Insecticides and fumigants, which can be effective without greatly endangering human

lives, have been developed; but the need for new and improved agents and methods is still great. Some of these materials, such as the pyrethrum extracts, are relatively non-toxic to man; but others, such as many of the organic phosphates, are very poisonous to humans.

The occurrence of poison gases in warfare has been highly sporadic, the most important being in World War I. Their employment at that time, and the ever-present possibility of later use, have stimulated further exhaustive researches on toxic materials.

Thus far we have considered poisons which have been deliberately used for their effects upon some form of life. There is another host of substances which are employed for other purposes entirely but which may constitute an incidental poisoning hazard. Thus lead water pipes, cadmium-plated ice trays, and arsenic-pigmented wall-paper have all been responsible for numerous poisonings. Accidental poisonings from carbon monoxide gas occur almost daily; and children have contracted lead poisoning by sucking lead-painted toys.

Industrial toxicology deals with still another phase of poisoning—that suffered by workers in the course of their employment in mining, manufacturing, and mercantile establishments. Although the fundamental principles of toxicology apply whenever poisonous substances are absorbed, in practice there is a great difference in emphasis between the study of industrial poisons and the study of war gases, or general public health hazards.

Thus drugs are usually taken through the mouth or by injection into the blood stream, the dosage is carefully controlled, and medical supervision is close. Most industrial poisonings, except for dermatoses, result from inhalation of the toxic agent, medical supervision, if any, is at best remote, and dosage is determined with difficulty. War gases are often inhaled, but they are intended to give immediate effects, whereas most industrial poisonings are typically gradual in their development.

In spite of the long history of mercurial drugs, the maximum safe dosage of mercury vapor was not known until determined by the United States Public Health Service and the Connecticut Department of Health in a study of felt-hat plant workers. The limiting safe concentration of lead dust was similarly determined by investigations of storage-battery workers and bears little relationship to allowable lead concentrations in drinking water. In spite of the hundreds of soldiers exposed to chlorine gas in World War I, the effects of long-continued inhalation of small concentrations of chlorine are still unknown.

In short, industrial toxicology has properly been developed to a large extent independently of other branches of toxicology. Although

its medical aspects are obviously of great importance, the chemical and industrial phases are equally significant. This book seeks to outline those aspects of industrial toxicology which are the primary concern of the chemist, engineer, and factory manager.

AVENUES OF ABSORPTION

Systemic industrial poisonings usually result from inhalation of the toxic agent. This fact is fairly obvious as far as gases, like carbon monoxide, and dusts which attack the respiratory system, such as silica, are concerned. With volatile liquids there is a possibility of absorption through the skin, and occasionally this is important. As a rule, however, skin absorption is secondary to absorption by inhalation when systemic effects are considered. Local injury to the skin, due to direct contact with a liquid or solid, is, of course, common.

With solid substances, inhalation and ingestion are the most important avenues of intake. Industrially, inhalation is again the most important, and toxic solids are most dangerous when dispersed in the air as dusts or smokes. This fact is frequently not recognized in the trades affected. Evidence of the major importance of inhalation as a source of metal poisoning is conclusive, however.

Ingestion of toxic substances along with food, in workrooms where the housekeeping is not good, or where workers are careless about washing, no doubt occurs to some extent. As a general rule, however, there is also a considerable dust inhalation where such conditions exist.

The classical cases of industrial poisoning via ingestion were those of radium dial painters, who absorbed radium mainly from the practice of using their mouths to point the brushes wet with radium-bearing paint.¹ Another group involved shinglers, who contracted lead poisoning from lead-coated nails, owing to their habit of holding extra nails in their mouths.² These, of course, are isolated instances of exceptional practices. In the majority of situations the toxic dust carried into the body is suspended in the air breathed by the worker.

Absorption through the skin is still less common with solids but may occur with certain liquids, especially those of low volatility. Phenol, cresol, nitrobenzene, aniline, lead tetraethyl, and many of the organic phosphate insecticides, such as parathion and TEPP, are liquids that present an equal or greater hazard through skin absorption than through inhalation. Other liquids and vapors, however, have been shown to pass through the skin to such a degree that gas masks or respirators do not give complete protection against high con-

centrations. Hydrogen cyanide, for instance, passes through the unbroken skin if enough is present in the air. Animals have been poisoned experimentally through the skin by certain of the chlorinated hydrocarbons. This fact should be borne in mind where very high concentrations of vapors or gases are present and individual respiratory protection is provided.

ELEMENTS OF RESPIRATION

An excellent discussion of respiratory processes is given in Henderson and Haggard's *Noxious Gases*.³ Only a few fundamental principles will be outlined in this volume.

The respiratory system is divided into two main parts: the upper respiratory tract, consisting of the nose and throat; and the lower respiratory tract, or lungs. The nose, throat, bronchi, and bronchioles are essentially air passages leading to the alveoli, the minute cell structure of the lungs. In the alveoli the gases in the lungs are separated from blood capillaries by very thin walls, and, since the total surface is very great (90 square meters), diffusion of the lung gases into the blood stream is rapid. Ordinarily the blood receives oxygen and gives up carbon dioxide, which is discharged to the air upon exhalation.

If the air inhaled contains other gases or vapors, they ordinarily reach the blood in a similar fashion. However, if the gas is water-soluble, much of it may be deposited on the moist walls of the throat, bronchioles, and other passages of the upper respiratory system, and very little may enter the alveoli. Nevertheless, it finds its way into the blood stream, although less rapidly than via the alveoli. Since the latter cells are the most sensitive portion of the respiratory system, a corrosive gas may vary greatly in its effects, depending on where it is absorbed. Thus the water solubility of a gas or vapor, especially one whose action is primarily irritation, is an important property from the toxicological standpoint.

With a dust, smoke, or mist, the particle size may determine whether it is absorbed mainly in the upper or lower respiratory tract. As a general rule, the smaller the particle size, the greater the proportion which reaches the alveoli of the lungs, and the faster and more severe the action.

Rate of Breathing

Unless voluntarily controlled, the rate of respiration is determined primarily by the concentration of carbon dioxide in the blood, and

secondarily by the blood-oxygen concentration. Since both values are affected by the rate of oxygen consumption, it follows that physical exertion, which creates an immediate demand for oxygen, stimulates breathing. The degree of this effect is very great, as shown in Table 1 (from *Noxious Gases*).³

TABLE 1
RATE OF BREATHING FOR AN AVERAGE MAN

<i>Activity</i>	<i>Air Inhaled</i> (l/min)
Resting in bed	6
Sitting	7
Standing	8
Walking—2 miles per hour	14
Walking—4 miles per hour	28
Slow run	48
Maximum exertion	65–100

Thus the volume of air breathed per minute varies nearly fourfold when one changes from a light sedentary occupation to moderately severe exertion (walking 4 miles per hour). The rate of inhalation of any toxic impurity in the air increases by the same ratio. It is apparent that this factor must be considered in interpreting data regarding the effects of toxic fumes in the air.

CIRCULATION

The blood, which has approached equilibrium with the lung gases, passes through the arteries and eventually deposits its load of oxygen in the body tissues, at the same time picking up carbon dioxide resulting from the combustion of carbohydrates. If the blood contains dissolved gases or other substances not normally present, these also are deposited to some extent in appropriate tissues, according to the fundamental laws of physical chemistry.

The rate of circulation is increased by physical effort, although to a somewhat lesser extent than is respiration.

RATE OF ABSORPTION

1. Non-Reactive Gases and Vapors

Gases and vapors which do not react immediately with the body fluids or tissues to form non-volatile compounds are progressively

dissolved in the blood until equilibrium is reached. With a gas that is relatively insoluble in blood and body tissues, such as helium, equilibrium is approached rapidly. With highly soluble vapors, like methanol, equilibrium is approached very slowly, and in practice it is probably never even approximately attained. Thus any immediately apparent toxic effects, such as narcosis, result more rapidly from a gas of low solubility in blood and tissue than from one that is readily soluble.

2. Reactive Gases and Vapors

If the gas reacts irreversibly in the body to form a non-volatile product, equilibrium is not reached, and the amount of gas absorbed is proportional to the total amount inhaled.

3. Dusts and Smokes

Similarly, all the dust of a non-volatile compound which is trapped by the respiratory system is retained. Not all the particulate matter retained by the respiratory passages is absorbed directly into the blood stream, however. According to some estimates more than half is deposited in the upper respiratory passages and subsequently swallowed. If the particles which reach the lungs are insoluble, many of them may be eliminated from the lungs, raised by ciliary action, and finally swallowed.⁴

ELIMINATION

Removal of waste matter from the body takes place mainly through the respiratory tract, the intestinal tract, and the bladder and urinary tract. Toxic substances are eliminated through these same channels. Gases, such as carbon monoxide and radon, are removed mainly through the lungs.

Vapors of lower volatility, especially water-soluble compounds such as methanol, may be eliminated mainly through the urine. Other vapors, such as those of benzene and toluene, are converted to non-volatile oxidation products, which in turn are excreted in the urine.

Many metals, such as lead, manganese, and radium, are excreted chiefly through the intestines in the feces. Relatively large proportions of certain metals, however, notably mercury, uranium, and arsenic, are found in the urine.

Reactive compounds of elements commonly found in the body in large amounts, like hydrochloric acid or hydrogen sulfide, may be

neutralized or destroyed, and the resulting products enter into regular metabolic processes.

Ingested material usually passes directly into the intestines from the stomach and is often eliminated without being taken into the blood stream. For this reason many substances, e.g., lead compounds, are more toxic when inhaled than when ingested.

Minor avenues of elimination of toxic compounds include perspiration, hair, and nails.

The excretion of most toxic organic compounds, and of gases, is usually a matter of hours, or at most of days. Many of the poisonous elements, however, can be stored for long periods of time in the body. Metals with chemical properties similar to those of calcium (radium, lead, and plutonium, for example) may be deposited in the bones. Mercury is also stored in various parts of the body for long periods. Fluorine, too, is stored in the bones. If further absorption of the toxic element is discontinued, excretion of the stored portion is begun and continues until it is virtually eliminated from the system.

Conversely, if there is a long continued intake of some toxic element, excretion may increase until it balances absorption. This is a condition frequently found in chronic poisoning.

HARMFUL EFFECTS

The pathological changes induced by toxic materials will not be discussed in detail in this volume, since such a discussion belongs properly to the medical consideration of toxicology. Some appreciation of the organs and processes injured by various poisons is desirable, however, even in a purely chemical approach.

There are three types of acute effect which may result from the inhalation of any toxic fume, but particularly from gases and vapors. These are asphyxiation, irritation of respiratory organs, and narcosis. In addition there are other responses which may be acute but are more typically chronic. These include damage to blood, nervous system, liver, kidneys, bones, etc. Many of these effects are exerted independently of one another, but sometimes one predominates, often to the virtual exclusion of all others.

Asphyxiation

Oxygen is necessary to sustain life, and, as we have already seen, an increased amount is needed if work is being done. Table 2 indicates the result of reduction in the oxygen content of the air.³

TABLE 2

EFFECT OF REDUCED OXYGEN

<i>Partial Pressure of Oxygen (mm mercury)</i>	<i>Oxygen in Atmosphere at Sea Level (%)</i>	<i>Response</i>
120-160	16-21	No notable effect
90-120	12-16	Increased respiration, slight diminution of coordination
76- 90	10-12	Loss of ability to think clearly
45- 76	6-10	Loss of consciousness, death

Asphyxiation may be brought about by mechanical obstructions, by reduction of air pressure, by dilution of air with another gas until the concentration of oxygen is reduced by reduction of the oxygen content of the air, or by chemical action which prevents access of oxygen to, or inhibits use of oxygen by, the tissues.

The simple asphyxiants, gases which act only by diluting the air, include most of the inert gases, also hydrogen, methane, ethylene, nitrogen, and carbon dioxide. In order to reduce the oxygen content to a fatal degree, a vapor concentration of about 50 per cent must be attained. This is possible only with a gas or a very volatile liquid; and in such concentrations the direct effects of most gases are in themselves fatal.

Chemical asphyxiants are relatively few in number. They include carbon monoxide, the cyanides, and possibly hydrogen sulfide.

Asphyxiation may also result from the inhalation of irritant gases, which injure the respiratory system so that it is no longer able to convey oxygen from the air to the blood stream.

Irritation

Direct irritation of the respiratory tract, the eyes, and the skin is frequently produced by toxic materials, characteristically by strong acids, alkalies, and oxidizing agents. Some degree of irritation is also caused by many solvent vapors.

The most pronounced irritation is produced by substances readily soluble in water, such as ammonia and hydrochloric acid. Such gases, however, affect mainly the upper respiratory passages. Injury to these organs is less serious than damage to the lungs, which is likely to occur when gases with similar chemical properties but only slightly soluble in water are inhaled.

The influence of water solubility, which in general parallels solubility in body fluids, is shown in Table 3.

TABLE 3
WATER SOLUBILITY AND TOXICITY OF CORROSIVE GASES

Gas	Hydrolysis Product	Solubility in Water at 0° C	Toxicity, Concentration Dangerous in 1 Hour ¹
		(moles/l)	(ppm)
Ammonia	Weak base	53	3000
Hydrogen chloride	Strong acid	23	1000
Sulfur dioxide	Weak acid	3.6	500
Chlorine	Strong acid	0.2	50
Phosgene	Strong acid	Very slight	25

The soluble gases, hydrogen chloride and ammonia, act mainly on the nose and throat, being absorbed by the moist linings of those passages. Sulfur dioxide, chlorine, and phosgene, being less soluble in water, pass through the upper respiratory tract to a greater extent and damage the lungs. The identity of the tissues affected, rather than the chemical reaction causing the damage, is largely responsible for the wide difference in toxicity.

It is probable that differences in physical rather than chemical properties are responsible for other anomalies noted in the toxicities of related compounds.

Another important feature of the irritant gases and vapors is that the soluble ones are more immediately irritating in low concentrations and therefore act as warning agents. No one can unconsciously inhale more than a single breath of air containing a lethal concentration of ammonia, for example. Fatal inhalation of such gases occurs only when the victim is trapped and unable to escape, whereas with less soluble gases the immediate effects of breathing a dangerous amount may be almost unnoticeable.

In addition to corrosive substances that owe their irritant properties to their chemical activity, there are some relatively inert substances, especially organic compounds, that have a pronounced irritating action upon the respiratory system. The reason for this is not clear; but, as a rule, with chemically similar compounds the less volatile are the more irritant. The lachrymators, which are as a group highly irritant, are in general moderately reactive esters of low volatility.

Narcosis

The symptoms of narcosis, or anesthesia, include impairment of mental facilities, muscular incoordination, lightheadedness, and laughing jags. If exposure is continued, the ability of the mind to function

clearly decreases until unconsciousness occurs. Death eventually results, usually from respiratory failure.

Narcosis is caused by the direct action of the toxic substance on the nervous system. Apparently all organic solvents and many solids that are soluble in fats are capable of producing some degree of anesthesia. The greater the fat solubility, in comparison with the water solubility, the more potent the narcotic properties of the compound. Thus the alcohols are weak anesthetics, and the hydrocarbons and chlorohydrocarbons are relatively strong.

This relationship is the basis of the Meyer-Overton theory of narcosis: that the narcotics act on the lipoids in the membranes of nerve cells, and alter their permeability and electrical polarization.

In the past, toxicity has, on occasion, been mistakenly identified with anesthetic power. Thus trichloroethylene is a more powerful anesthetic than carbon tetrachloride, and animal experiments with these vapors in high concentrations led to the conclusion that trichloroethylene was the more toxic of the two. Actually carbon tetrachloride is also a powerful liver and kidney poison, and in low concentrations this effect is more important than anesthesia. The result is that contrary to the earlier interpretation carbon tetrachloride is in reality the more hazardous of the two compounds.

Many symptoms of asphyxiation and anesthesia are quite similar. This is apparently due to the fact that in both conditions the primary effect is to impair the functioning of the brain—in asphyxiation by denying it sufficient oxygen, and in anesthesia by direct action.

Damage to Nervous System

Asphyxiation and anesthesia, if not carried to a fatal conclusion, are usually transitory. In other words, there are no permanent ill effects. Severe carbon monoxide poisoning, however, sometimes does result in permanent damage to the nervous system.⁵ Injury to the nervous system resulting from long-continued absorption of a toxic agent is apparently not related to either asphyxiant or anesthetic properties, however. Thus, of the solvents, methanol, one of the weakest anesthetics, is one of the worst offenders in producing permanent damage to the nervous system. The optic nerve is damaged in typical methanol poisoning. Other alcohols and many ethers, carbon disulfide, and some of the halogenated hydrocarbons are also reported to have a cumulative effect upon the nervous system.

Of the elements, chronic mercury and manganese poisonings usually involve the nervous system.

Liver and Kidney Damage

Injury to the liver and kidneys is noted from a majority of the substances discussed in this book. Fatal industrial poisonings involving these organs have been reported from carbon tetrachloride, tetrachloroethane, hexachloronaphthalene, trinitrotoluene, and dioxane. Many other organic vapors have been shown to cause liver and kidney injury in animal experiments. Certain of the heavy metals, especially uranium, are primarily kidney poisons.

Blood Changes

Many toxic substances cause blood changes, either transitory or permanent. Benzene is one of the worst of this class. Its primary effect is apparently on the bone marrow, where blood cells are formed. Arsine and lead have been found to produce blood changes. The nitro compounds, such as TNT, also act upon the blood. Organic phosphates destroy the enzyme, cholinesterase, which is present in red blood cells.

Bone Damage

Under some conditions, usually involving long exposure to relatively low concentrations, certain agents cause serious injury to bone structure. Fluorine, which is deposited in the bones, is one such poison. Chronic poisoning from yellow phosphorus usually involves necrosis of the jaw bone. Cancers frequently develop in bones in which radium is deposited. No doubt plutonium, strontium⁹⁰, and other radioactive bone-seekers will have a similar effect. However, non-radioactive heavy metals apparently do not injure bone structure materially, even though many such metals are deposited in the bones.

Cancers

Skin cancer is caused by long-continued contact with certain constituents of coal tar and shale oil. Beta-naphthylamine and some related amines cause bladder tumors when inhaled over long periods. Radioactive substances also produce tumors, cancer of the lung being attributed to the inhalation of radon, and bone tumors to radium stored in the bones.

Undoubtedly, prolonged absorption of artificially radioactive elements will produce cancers under suitable conditions. Radioactive

elements are of a higher order of toxicity than elements that owe their harmful effects solely to chemical reaction.

Other Effects

Damage to other organs predominates with a few substances. For instance, direct injury to the heart is reportedly caused by barium compounds. Strong acids damage the teeth. Hydrogen sulfide causes conjunctivitis, an eye affliction quite different from the lachrymation caused by many irritant vapors.

Ability to cause sterility is often popularly attributed to new and unknown substances or conditions of environment. In some cases the reproductive organs of animals have been damaged by heavy dosages of toxic materials.⁶ To the author's knowledge, however, industrial use of toxic substances rarely if ever causes sterility in workers unless the exposure is great enough to cause other more typical symptoms.

2.

Evaluation of hazards

The hazardous conditions produced by certain industrial processes are well and accurately known. Usually, however, there is a need for more precise methods of determining whether or not a hazard exists. In a chemical investigation of the potential dangers from toxic substances there are several steps.

PRELIMINARY INFORMATION

A preliminary estimation of the condition can be made on the basis of relatively meager data. The following points should be considered:

1. Toxicity of substances handled or present.
2. Physical properties of such substances.
3. Possibilities of absorption by workers.
4. Quantities involved.
5. Continuity of exposure.
6. Complaints or evidence of injury.

Frequently, harmful effects, other than skin irritation, occur only if the air is contaminated with the toxic material. No process involving poisonous substances can be considered safe until all possible sources of serious atmospheric contamination have been eliminated.

Gases, unless confined in a completely enclosed system, automatically escape and diffuse throughout the workroom air. Leaks

in illuminating gas systems may produce a dangerous concentration of carbon monoxide. Methyl chloride poisoning has resulted from leaky mechanical refrigeration. Harmful concentrations of gases are more often released from chemical reactions, however. Thus carbon monoxide is produced in many combustion processes, nitrogen dioxide by various reactions of nitric acid, and arsine from the action of nascent hydrogen on arsenic compounds. Under such conditions the toxic gas is not ordinarily included in any list of substances employed in the plant processes, and its presence must be either deduced from the operations carried out or detected by suitable tests.

When volatile liquids are used at room temperature, harmful vapor concentrations are theoretically possible if the vapor pressure of the liquid exceeds the maximum safe vapor concentration. This condition occurs with virtually all liquids boiling below approximately 170° C and with many of substantially lower volatility. As a general rule, however, a harmful condition does not exist unless the vapor concentration at saturation exceeds the maximum allowable value by a factor of 20 or more. An atmosphere saturated with benzene vapor, for example, contains about 10% by volume, or 4000 times the maximum allowable concentration of 0.0025%. With the less toxic and less volatile toluene the corresponding ratio is 200, with tetrachloroethylene 200, and with mercury 190. Liquids boiling above 150° C do not usually present a vapor hazard unless they are highly toxic or unless their evaporation is hastened by heat. If a spray or mist is produced, of course, the volatility of the liquid assumes a position of minor importance.

Only a few solid substances (e.g., *p*-dichlorobenzene) are sufficiently volatile to produce a vapor hazard when handled cold. Others, such as the chloronaphthalenes, are commonly safe at room temperature but become dangerous when heated. Certain of the metals, like cadmium and zinc, vaporize readily at temperatures slightly above their melting points. Their vapors condense in the air, however, and are inhaled as a smoke of finely divided solid particles, and not as a vapor. The great majority of the toxic metals, including lead, do not volatilize appreciably much below a red heat. Nevertheless, a dust hazard may result from handling a dry powder or from grinding, cutting, pulverizing, and similar operations.

If conditions are favorable for contamination of the atmosphere by a toxic material, the quantity of gas, vapor, dust, or smoke being dispersed should be ascertained. As a rule a benzene hazard, for example, is improbable if less than a quart daily is consumed in a relatively small area. With more toxic substances (i.e., maximum

allowable concentration below 25 ppm) smaller amounts will produce a harmful concentration of vapor, and vice versa.

Frequently much of the preliminary information can be obtained without even seeing the process in question. It is best, however, to make an actual inspection of the operation, in order to verify any statements of existing conditions, to secure additional data, some of which have invariably been overlooked, and to obtain a firsthand picture of the situation.

When the inspection is made by an outsider, such as a government or insurance company representative, it serves a twofold purpose. The first is to observe the operation itself; the second is to confirm the preliminary report received, ordinarily based on statements of company representatives. Although few employers deliberately falsify facts, their opinions on matters concerning the health of their workers are often unavoidably subject to prejudice. Similarly the statements of employees on details of their work are, for the most part, accurate, but they are prone to magnify ills attributable to their jobs. Frequently when a process involving dust or fume is being examined, the employer comments that conditions are much worse than usual, whereas workers state that the visitor selected a poor time to observe the operation because the fumes are not nearly so thick as on most days.

Some idea of the degree of atmospheric contamination may be obtained by direct observation. Thus most gases and vapors are detectable by odor. Absence of a harmful concentration of trichloroethylene or ammonia, for example, can be assumed if the odors of these substances cannot be detected. With some volatile compounds, however, the sense of smell cannot be relied upon to pick up a dangerous concentration. Carbon monoxide, of course, is virtually odorless. With carbon tetrachloride and benzene the odor threshold for most people approximates the maximum allowable concentration, so that any detection by odor perception is indicative of a probable hazard. Hydrogen sulfide, on the other hand, can be detected in concentrations so far below the harmful level that objectionable odors may be present in the absence of even a borderline hazard.

Dusts and smokes can be seen when present in high concentrations. Harmful concentrations of smokes of low toxicity, such as zinc oxide, are readily visible under favorable conditions. Concentrations of dust of the order of 1 mg per cubic meter of air, which are well above the safe limit for many metals (such as cadmium and lead), are not easily seen. Smokes, which have a very small particle size, show up more readily than the coarser dusts.

It should be emphasized that estimates of atmospheric contamination based on sensory perception are reliable only when made by highly trained observers who have had wide experience in evaluating such impurities.

THE ENGINEERING APPROACH

If the data available include the amount of gas or vapor released to the workroom air, it may be possible to calculate the approximate concentrations which probably exist. Suppose, for example, an operation requires 1 qt of carbon tetrachloride per hour, all of which evaporates into the air of the room. A quart (about 3 lb) of carbon tetrachloride forms approximately 8 cu ft of vapor. If the room is ventilated at a rate of 80,000 cu ft per hour, the average concentration of carbon tetrachloride vapor in the room should be 100 ppm (0.01%).

Only under ideal conditions does this method of calculation yield highly accurate results. One reason for this is that workers are often exposed to local concentrations of the gas or vapor which may differ widely from the average room concentration. Unfortunately this method has often been improperly applied. Thus in one instance the toluene exposures of a number of workers were calculated from monthly records of consumption of solvent and the capacities of the fans ventilating the rooms where the work was done. The results obtained were of questionable value. In another situation the maximum concentration of benzene vapor was calculated from the amount of vapor evaporated per day and the volume of the room, with zero ventilation assumed for the room. According to the calculation, these workers were exposed to over 4500 ppm of benzene vapor.

In determining the amount of ventilation needed for a given process, calculations similar to the above have been very helpful. The results should be checked by direct tests, however, if a potentially serious hazard is involved.

Whenever processes are controlled by local exhaust ventilation, engineering tests of air velocities often tell whether or not the control is adequate. Sometimes, where the process is more or less standard, data on the performance and capacity of the exhaust system are more valuable than air tests, unless the latter cover a much wider range of conditions than is usually practicable. The granite industry furnishes a good example of such processes, where the requirements for control by local exhaust of certain dusty operations have been worked out with a high degree of precision.⁷

CHEMICAL TESTS

The most precise method of evaluating the worker's environment, from the standpoint of its effect on his health, is a chemical analysis of the workroom air. This does not mean a complete analysis for all components, since the oxygen, nitrogen, and carbon dioxide contents are usually within normal limits. But the quantity of harmful impurity, be it dust, smoke, mist, vapor, or gas, is the important factor whenever the main source of possible hazard is respiratory tract absorption.

Air analysis has many advantages over other methods of estimating exposure. It is the only method that actually tests the environment. It determines which are the important sources of contamination and whether or not ventilating systems are effective. A minimum of cooperation from the employee is required.

Although special apparatus is necessary, the technique of determining most atmospheric impurities is not particularly difficult since few interfering substances are usually present. Direct-reading indicators are available to determine numerous gases and vapors. These are very convenient and most useful for ferreting out sources of contamination. Most such devices are not too satisfactory for sampling over long periods of time, however. For determining the average concentration an absorbing unit that removes the impurity as the air is drawn through is commonly employed. Sometimes grab samples of the air are taken in suitable flasks or bottles for analysis in the laboratory.

As a general rule the most important value is the average concentration of impurity to which the worker is exposed over a complete job cycle. This often involves not only a long sampling period, but also an easily portable sampling device which can be moved about with the worker, at least in a limited area. Only when the source of contamination is not directly affected by the worker's activities can the sampling device be set up on a table in the middle of the room and allowed to operate without supervision.

It is desirable to obtain at least one set of check samples. Not only are checks a good practice in any sampling procedure, but, when tests are made in a factory, conditions are likely to be abnormal during the first hour or so. After the novelty of the test situation has worn off, the workers usually resume their normal tempo, and more representative data are obtainable.

A recommended practice is to take three sets of samples—one representing the operator's exposure, one of the general air, and one

near the probable source of contamination. This is a good procedure, but it must not be forgotten that the concentration of dust or fume actually breathed by the workers is of paramount importance.

In lieu of direct analysis of the air, various indirect methods may be employed. The most common of these is analysis of filters of respirators which have been worn by workers on the process in question. This gives a measure of the impurity which would have been inhaled if the respirator had not been worn, minus what, if any, passed through or around the respirator. It is a useful check, but it can be employed only for a limited group of toxic elements.

Sampling devices actuated by the breathing of a worker have been successful in a few cases, but they require more cooperation from the individual worker than usually can be expected.

Concentrations of vapors and gases are ordinarily expressed as parts per million by volume, or as percentage by volume. Smokes, dusts, and mists, however, are computed as milligrams per cubic meter, or 10 cubic meters, of air. The maximum concentration of dusts or smokes encountered seldom exceeds 100 mg per cubic meter of air. This corresponds to less than 50 ppm of a vapor or gas in the molecular weight range of 50 to 150, in which most industrial vapors and gases fall.

Although air analyses are much more precise than indirect methods of estimating atmospheric concentrations of poisons, they are often not ideal measures of the existing degree of hazard. It is frequently very difficult to obtain a representative sample, especially since most processes change more or less from day to day, and conditions vary, owing to weather changes, even if the process remains the same.

The exposure of the worker depends not only on the concentration of fume in the air but also on his rate of breathing. We have already seen that this can vary several fold, depending chiefly on the degree of exertion of the individual and undoubtedly on other factors as well. Air analysis, of course, tells nothing of absorption through the skin or of ingestion of toxic substances. Finally, when personal protective devices such as respirators and gas masks are worn, the exposure of the worker cannot be determined from the concentration of fume or dust in the air.

BIOCHEMICAL TESTS

The concentration of toxic agent in body tissues or excreta often gives a more accurate measure of the worker's exposure than can be obtained by any tests on his environment. Determinations of this sort are considered here as biochemical tests.

It has been shown that inhaled fumes may be destroyed in the respiratory tract or dissolved in the blood and carried through the body and made available to the tissues. The further fate of these fumes depends on their physical and chemical properties. Volatile and unreactive substances are eliminated as they entered, via the lungs; less volatile substances are excreted in the urine, feces, or perspiration, or in some cases deposited in the hair and nails. Storage for long periods in the bones or other tissues is not uncommon with the toxic elements, but it does not often occur with organic compounds.

The presence of toxic material in the blood, urine, or breath does not necessarily imply poisoning. Analysis of the excreta of apparently healthy workers for toxic ingredients is primarily for the purpose of detecting excessive exposure to the poison and is not intended otherwise. On the other hand, if an individual shows symptoms of lead poisoning, for example, presence of an abnormally high lead concentration in the urine confirms the diagnosis by proving an exposure to lead. Analysis of urine or blood for volatile poisons in suspected chronic poisoning cases, however, is often futile since the poison is usually eliminated rapidly. Thus the urine sulfate test, extremely valuable as an index of benzene exposure, has often been mistakenly applied to patients with benzene poisoning long after their contact with benzene has ceased.

Expired Air

Analysis of expired air may help to detect recent exposure to carbon monoxide and has been employed as a test for alcoholic intoxication. It is most successful, however, in the measurement of radium exposure. Radium disintegrates at a constant rate, giving off the radioactive gas radon. The radon given off by radium deposited in the bones finds its way into the blood, whence it is carried to the lungs and exhaled. Determination of the radioactivity of the expired air gives a measure of the quantity of radium stored in the body, which is an index of past exposure to radium.⁸

Blood Analysis

Examination of blood for carboxyhemoglobin is a common method of determining recent carbon monoxide exposure. The lead content of blood is preferred by some authorities to other indices of lead exposure, especially in suspected cases of active plumbism. The bromide content of blood has been shown to rise after inhalation of sublethal amounts of methyl bromide.⁹

Most analyses for toxic substances require several grams of blood, however, and samples of this size are not often taken except under direct medical supervision. When other methods of evaluation are available, they are therefore usually preferred to analysis of blood samples.

Urine Analysis

Analysis of urine for toxic elements, compounds, or reaction products is the most widely applicable of the biochemical tests. The author prefers urine analysis to other tests in the evaluation of lead, mercury, fluoride, arsenic, and uranium exposures. It is useful for determining absorption of selenium, tellurium, toluene, methanol, trichloroethylene, trinitrotoluene, and benzene, as well as plutonium, tritium, strontium⁹⁰ and many other radioisotopes. More work needs to be done on the excretion of these compounds and of cadmium. Analysis of urine for numerous other toxic compounds or their degradation products has been suggested, but most of such tests are still in the experimental stage.

The metals, as a rule, are excreted rather slowly, over a relatively long period of time, especially when they have been absorbed in small quantities daily for several weeks or months. Samples can be collected after a lapse of several days following the last exposure without great loss in the content of mercury or lead, and probably of other toxic elements. If there has been a single short exposure, however, elimination falls off rapidly. Thus the urinary excretion of mercury, at a fairly high level immediately after a tooth is filled, commonly diminishes to a trace after a few days.¹⁰

With many organic compounds the presence of the toxic agent is transient. Benzene and toluene are converted into non-volatile compounds which are largely found in the urine but are eliminated rather rapidly. The urines of persons with substantial benzene exposure have been found normal 16 hours after the end of exposure, and a change toward normal (increase in sulfate ratio) has been noted 4 hours after exposure ceased. The urine sulfate test for benzene absorption is, therefore, reliable only if the urine specimen is obtained during, or within a few hours after, exposure. Other organic substances, such as methanol and trichloroethylene, are excreted more slowly, and a few, such as DDT, are stored in the body for considerable periods of time.

Contamination is a problem in securing urine specimens for certain tests, such as lead content. The author has found the extreme pre-

cautions recommended by some authorities unnecessary in the majority of cases, however.

The variations in the amounts of toxic elements in the urine of different individuals with the same exposure, and of the same individuals at different times, have led to several proposals for alternate methods of calculating results. One suggestion, made for lead but presumably applicable to other elements, is to determine the hourly excretion by obtaining the time required for secretion of the urine sample analyzed.¹¹ A more convenient method is to make a correction for specific gravity. Thus, if the normal specific gravity is 1.024 and the specimen in question has a gravity of 1.012, the corrected lead (or other toxic substance) content is obtained by multiplying the measured value by $0.024/0.012$, or 2. Urinary lead values corrected in this manner have been more consistent than uncorrected values.¹²

Fecal Analysis

Many of the toxic metals, notably lead, radium, and manganese, are excreted primarily in the feces. The difficulties of analysis, as well as of obtaining samples, discourage the average investigator from this test. Analysis of feces for toxic substances is confined largely to clinical and experimental studies.

Analysis of Hair and Nails

Arsenic is deposited in the hair and nails, and analyses of these materials are useful in determining a past arsenic exposure.

PHYSIOLOGICAL METHODS

The methods of evaluating hazards so far considered have been primarily physical or chemical; that is, they have consisted of directly determining or calculating the quantity of toxic agent being absorbed or excreted. There usually is a definite relationship between rate of absorption and rate of excretion, and the same result is achieved by either method.

A further type of test consists of determining not the *amount* of toxic material but the *degree* of its effects on the persons exposed. Although some such tests can be interpreted by a layman, the majority can be dealt with intelligently only by a physician.

Determination of lead in urine is primarily a chemical problem.

In fact, only a well-equipped and well-staffed chemistry laboratory can carry out such a test properly. Interpretation of the results is comparatively simple. The body cannot transmute other elements into lead; therefore an abnormally high content of urinary lead means an abnormal absorption of lead. If a group of lead workers all show highly leaded urines, it is reasonable to assume that they are acquiring the lead on their jobs. It does not mean, however, at least to the chemist, that these individuals have lead poisoning. Very likely the majority of them are perfectly healthy. In fact it would be abnormal if, after large amounts of lead were absorbed, it failed to show up in their urines.

The effects of toxic substances on the body tissues are another matter altogether, however. Such effects may be very simple and obvious—for example, the irritation of the nose or throat caused by gases like ammonia or hydrogen chloride, or by solvent vapors such as butanol and amyl acetate. Again, they may be more subtle and delayed, like the headaches resulting from continued carbon monoxide exposure. They may consist of dizziness and lack of coordination, as from inhalation of high concentrations of gasoline vapor. Nausea, such as is caused by carbon tetrachloride, may be the predominating effect.

These are all subjective symptoms, indicating an early stage of poisoning. In certain cases, as with irritation caused by certain gases and vapors, especially lachrymation, some degree of immunity is apparently established.

If the exposure is continued, other effects may develop. The nausea caused by carbon tetrachloride vapor may be followed by serious liver damage. Continued inhalation of various irritating substances may cause ulceration of the nasal passages. Repeated low-grade narcosis by some solvents may result in damage to the nervous system.

With other toxic agents the warning symptoms come too late. Long-continued exposure to benzene frequently produces no symptoms until the prognosis is unfavorable. Lead and mercury poisoning, when detected, may be so far advanced that complete recovery is doubtful. The same is true, to an even greater degree, with silicosis.

Physiological Tests

There are, however, tests to detect early stages of poisoning before clinical symptoms ordinarily appear. Thus chest x-rays often detect silicosis long before it becomes disabling. Blood changes caused by

benzene poisoning are detectable before subjective symptoms are in evidence. Blood changes also occur in early stages of TNT poisoning. A reduction in the cholinesterase activity of the blood is a reliable indication of organic phosphate poisoning. A rise in the coproporphyrin content of the urine ordinarily precedes other signs of lead poisoning. Tests for tremor may disclose chronic mercurialism before it becomes obvious.

It is apparent that such tests should be carried out under medical supervision and interpreted by a competent physician. It must be further emphasized that all these tests depend on measuring damage already done to the body tissues. Such injury may, of course, be trivial, but often it is not; and the chemical or biochemical test, which can determine the hazard before injury is done, is preferable from the worker's standpoint.

The physiological tests are most valuable where no suitable biochemical tests are available. They also tend to differentiate between susceptible and resistant individuals.

SIGNIFICANCE OF TESTS

When the amount of toxic substance has been determined by suitable means, it is necessary to know whether a harmful condition exists. Ordinarily the concentration of poisonous agent found is compared with the maximum allowable concentration—a concentration judged to be without serious effects even for long-continued exposure. A concentration below the maximum allowable level is considered satisfactory, and a higher concentration is unsatisfactory for other than brief periods.

In the discussion of harmful substances in Chapter 3 through 10, suitable methods of evaluation are listed. In general, chemical or biochemical tests are preferred, and physiological tests are recommended as a second choice, if at all. This does not mean that medical examinations, including such tests, are undesirable for workers exposed to the agent in question. On the contrary, the author believes that all workers exposed to injurious substances should periodically undergo complete medical examinations. These are primarily to detect any possible ill effects of the environment upon the worker, however, and to note any changes in the worker that would make him more susceptible to an unfavorable environment. These examinations should not replace tests of the environment itself, for which purpose the evaluation tests are recommended.

Frequently the tests or calculations indicate a hazardous condition, but no adverse effects upon the health of workers are apparent. It is often possible for a group of persons to be exposed without injury to dosages of toxic materials above the maximum allowable value, for these limits are sufficiently low to protect the more susceptible section of the population as well as the more resistant and the average individual.

Often, however, the absence of evidence of harmful action is misleading, and the workers suffer from non-spectacular and usually minor ailments which are caused or aggravated in part by their working environment. In other workers there is a long latent period during which no symptoms appear, followed eventually by illness, incapacitation, and sometimes death. The author has seen enough serious cases of poisoning develop in groups of apparently healthy employees to put his trust in measurements of fume concentrations rather than lay opinions of the physical condition of the workers.

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