

ANALYTICAL STUDIES OF THE ENVIRONMENT

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ABSTRACT

Analytical studies of the environment have dealt primarily with toxic materials that may affect the health of man. Studies may also be made to evaluate nuisance effects and economic factors associated with corrosion, staining and damage to plant and animal life. It is important to note that many so-called pollutants are also essential trace elements. Analytical studies of the environment, therefore, should provide a broad background of knowledge for a true evaluation of the nature of the environment and changes that are taking place.

A brief review of toxic and carcinogenic materials reveals that there are many hazards to man that are present in the environment. Analytical methods for studying water quality and ambient atmospheres are of critical importance. The analytical problems are very complex and there is great need for a concerted effort to develop suitable analytical procedures and to collect reliable analytical data. It may surprise many to learn that although waters have been analysed for many centuries, no one has yet truly determined the nature and amount of all inorganic species in natural waters, let alone the various organic species that must be present. The study of air pollution is similarly deficient in methodology.

A review of the current status of analytical chemistry as applied to air and water pollution studies is made. Some important deficiencies in our present knowledge are pointed out.

An evaluation of the environment implies both qualitative and quantitative appraisals of toxic and carcinogenic compounds that may be present in foods and food additives, waters and the atmosphere. With the present concern about water and air pollution it is often overlooked that the nature and distribution of various nutrients and essential trace elements is also a matter of great importance. It is not possible in this short discussion to consider all of the aspects of the environment, nor is it possible to even list all of the species present in the environment that are important and, therefore, of analytical interest. Only the analytical aspects of water and air quality studies will be considered. In the case of water, the study of the oceans and seas will be omitted, as will the grossly polluted water such as trade waste and sewage. Likewise, in discussing air quality, the discussion will be limited to the ambient atmosphere and only brief mention will be made of grossly polluted air such as that represented by stack emissions.

There are many reasons for analysing waters and air to determine the nature and extent of pollutant species that may be present. Disregarding such considerations as nuisance effects, aesthetic considerations, and

economic factors associated with corrosion, staining, and damage to plant and animal life, it is sufficient to evaluate environmental quality in terms of potential or actual hazards to human life. It is well known that there are a wide variety of toxic materials in the environment to which humans are exposed¹. Acute toxins such as hydrogen cyanide, hydrogen sulphide, hydrogen selenide, acrolein, fluorine, formaldehyde, and ozone are familiar to all chemists. Many semi-acute, cumulative and additive toxins are also known to most chemists. The special category of hazards designated as carcinogens may justify special attention². Polycyclic aromatic hydrocarbons and other carcinogenic substances in cigarette smoke and in the ambient atmosphere have attracted the attention of chemists for a number of years. Benzo(a)pyrene is a carcinogen that is often mentioned not only in the scientific literature but in the public press. Unfortunately, many chemists fail to recognize the potential hazard of aromatic amines and nitroso compounds. Also, they often overlook the fact that some arsenic, chromium, and nickel compounds are known to be carcinogenic to man and some compounds of beryllium, cadmium, cobalt, lead, and selenium have been indicted as possible carcinogens because of their known carcinogenicity to animals.

The question of toxicity and/or carcinogenicity is a complicated one and a review of methods used in establishing appropriate standards is beyond the scope of this discussion. It is not even practical to review the philosophies that apply to different experimental approaches for establishing the nature and extent of hazards, such as carcinogenicity, as they apply to man. It can be mentioned, however, that the entry route of chemical hazards is of great importance. Hazardous materials may enter the body through skin contact, ingestion, or inhalation.

Skin contact may be an important entry site for chlorinated hydrocarbons, many of the pesticides, and certain natural toxins such as urishiol, the toxic principle of poison ivy, poison oak, and sumac. Ingestion is universally recognized as a major means by which poisons enter the body. It should not be overlooked, however, that many ingested toxins are inactivated by digestion and other natural processes. For example, it is apparent that ingested benzo(a)pyrene presents little or no hazards while the same compound rubbed on the skin induces skin cancers.

Inhalation of toxins presents a special hazard. It is often overlooked that man breathes about fifteen cubic metres of air every day of his life, and this represents a total mass of material of the order of fifteen kilogrammes. One part per million of toxin in the air that is breathed, therefore, represents a far greater insult than the same concentration of the toxin that may be present in the water that is drunk, or the food that is eaten, for that day. Furthermore, the inhaled toxin may have a far more dramatic effect than the ingested toxin because of the more direct transfer of the material into the blood stream.

In view of the preceding comments it must be pointed out that not only bad effects are associated with contaminants of the environment. From a philosophical standpoint, it is really debatable whether many so-called contaminants are actually such, or whether they might better be designated as natural constituents of the environment. With world-wide attention focused on mercury, it is inconceivable that this metal has only recently been introduced by dastardly industries that operate with complete dis-

regard for man's welfare. Almost certainly mercury has been in the soils and, therefore, in the waters and atmosphere of the earth since the beginning of time. The same thing can be said about sulphur dioxide, hydrogen sulphide, selenium dioxide, ammonia, and countless other so-called pollutants that are now attracting universal attention. It must be recorded also before going into specific analytical problems that are involved, that metals such as manganese, zinc, copper, and chromium, to mention a few, are essential trace elements. The question really arises as to how much of the respective materials is present and how and in what form the materials are introduced in the physiological system.

The analytical chemist has now reached a point of respectability and responsibility that places him in a unique position in our modern society. The more sensitive the methods he develops, the more certain segments of our society worry about 'pollutants' and their effect on the ecology. Unfortunately, there are not enough analytical chemists in the world today to develop the necessary analytical methods required at this moment, let alone to perform the countless analyses that must be made before a true evaluation can be derived regarding our environment, the changes that are taking place, and the true significance of what happened in the past, what is taking place now and what is likely to occur in the future.

WATER ANALYSES

The sampling of waters and the preservation of water samples

It is obvious to any analytical chemist that proper sampling is a most important part of the total process of water analysis. Unfortunately, the analytical chemist seldom has the opportunity or time to collect the samples and he can only give guidance to those that do. He must recognize the instability of the sampled water and do his best to correct or prevent changes in the sample composition that occur between the time of sampling and the time of analysis. It is interesting to note that historically water analysis has been subdivided into a number of classifications, including bacteriological examinations, sanitary chemical analyses, boiler water analyses, complete mineral analyses, etc. The progress of the field of water analysis can be deduced from *Standard Methods of Water Analysis*, which was prepared jointly by committees of the American Public Health Association, American Waterworks Association and the Water Pollution Control Federation in collaboration with a committee of the American Chemical Society. This reference was first copyrighted in 1917. The sixth edition appeared in 1925 and contained 119 pages. The latest edition (13th) appeared in 1971 and contains 845 pages. Early editions understandably presented wet chemical methods (no pun intended) while later editions introduced more and more sophisticated determinations employing a wide variety of instruments.

The classical analyses for mineral content of waters involved primarily the determinations of total solids, loss on ignition, dissolved oxygen, biochemical oxygen demand, hardness, colour, turbidity, and, for treated waters, free chlorine. The mineral content was determined and the cations that were included were limited primarily to calcium, magnesium, and the so-called R_2O_3 group (iron, aluminium, and manganese). Occasionally

the alkali metals were determined, but usually they were simply calculated after determining the total number of equivalents of anions, subtracting the total number of equivalents of other cations and allotting the difference to alkali metals. The anions that were determined were the chlorides, sulphates, nitrates, and alkalinity (bicarbonate and hydroxide). Occasionally, sulphide, fluoride, phosphate, and silica were also determined.

Present analyses of water include, in addition to those determinations mentioned above, the determination of various heavy metals such as mercury, lead, cadmium, copper, chromium, zinc, nickel and cobalt. Special determinations are sometimes made for silver, vanadium, osmium, rhenium, germanium, indium, zirconium, tungsten, molybdenum, scandium, selenium, arsenic, uranium, and beryllium. It is now quite common to measure radioactivity and to include the determination of pesticides, detergents, and various organic material such as phenols.

From the extensive list of determinations just enumerated, one might be led to believe that we know all that there is to be known about waters and the only need is to do more analyses and collect more data. This is far from the truth.

There are some acute future needs in the field of water analysis. Admittedly, we need better methods for all of the determinations being performed now. The fact that seems to be universally overlooked is that no one has ever truly analysed a water sample. We must now come up with some methods for detecting and determining species present. A moments reflection convinces one that we have only scratched the surface or muddied the water! Any thinking chemist realizes that the determination of iron in water is important, but what about the fluoride and the phosphate that are present? Assuming that fluoride and phosphate are determined, what about oxalate, formate, tartrate, and citrate? Obviously, oxalates, citrates, tartrates, formates, and other organic acids and their salts are present. It is inconceivable that iron exists as Fe^{3+} when various complexing ligands are also present in the same aqueous system. The various species of iron must be important from the physiological standpoint, and, therefore, they should be determined. Iron citrate, for example, must certainly be discharged into the Gulf of Mexico through Tampa Bay and other discharge points where drainage from the citrus belt of Florida carried among other things both iron and citrate. The 'Red Tide' that is a scourge in the Gulf of Mexico and the lovely Florida beaches might very well be attributed to the bloom that results when iron is made nutritionally available to the organism. Extending this thinking to other trace metals such as copper, vanadium, zinc, and mercury must prompt the analytical chemist to new efforts in unexplored fields (waters?). Along more obvious lines, the analytical chemist must develop more and better automated analytical methods. Devices such as ion-selective electrodes hold great promise and many variations and improvements can be hoped for in the future.

AIR ANALYSES

Sampling and preservation of samples

The problems of obtaining representative samples of water and insuring

a minimum of change between the time of sampling and the time of analysis have already been mentioned. In the case of air samples the problem of sampling is infinitely more difficult. It is obvious from simply observing a plume of smoke and noting how it twists, weaves and sometimes even changes direction completely that obtaining representative air samples is a most difficult problem. Less obvious probably is the problem associated with changes that take place during the sampling operations. Because the atmosphere is such a dilute system, many pollutants can coexist in the ambient atmosphere without reaction, but cannot normally survive when concentrated during sample collection. An example of the problem is the well-known case of sulphur dioxide which is considered to be one of the most common and most important of the air pollutants. The concentration of sulphur dioxide in the air is so small that the pollutant must be concentrated before determinations can be made. The collection of sulphur dioxide was often done in early studies by simply bubbling measured volumes of the air through a trapping solution such as sodium hydroxide. During the sampling process, the trapped sulphur dioxide was contacted intimately with other pollutants and was thus subjected to possible attack. Obviously, the sampled air contained oxygen and this naturally led to some air oxidation of the sulphur dioxide. The oxidative process was often enhanced by the presence of catalytically active pollutants such as particulates containing iron and copper. The sampling problem for sulphur dioxide was solved in 1956 by the introduction of the so-called West-Gaeke method for determining sulphur dioxide which employed tetrachloromercurate(II) as the trapping medium³. The sulphur dioxide reacts with the tetrachloromercurate(II) to produce the very stable complex dichlorosulphitomercurate(II). The stabilized species resists air oxidation as well as the effect of most other coexisting pollutants. Only relatively large amounts of oxides of nitrogen or ozone present problems and the problems that do occur can readily be obviated. The analytical finish of the method depends on a colour development involving the use of formaldehyde and acid-bleached *p*-rosaniline hydrochloride.

The sampling problem can also be illustrated in the case of fluorides. The fluorides are among the most important air pollutants, especially in regard to their effect on vegetation, where as little as two or three parts per billion of HF may seriously damage or kill certain valuable plants. In collecting and concentrating fluorides for subsequent analysis it is always to be expected that calcium, lead, manganese, iron, and aluminium salts will also be collected. It is obvious to the chemist that solutions containing salts of these metals will tend to react with fluoride to form complexes or other species that may tend to invalidate final fluoride measurements.

One of the most overlooked sampling problems is that of the airborne particulates⁴. It has been the custom to use the so-called hi-volume samplers which pull tremendous volumes of air at high velocities through filters. The filters may be made of filter paper, glass fibres, or a variety of organic mats. Although the filter medium is usually quite efficient in removing and isolating the particulate materials, there are other problems that have been almost universally overlooked. Some pollutants, such as selenium dioxide, have sufficient vapour pressure that they volatilize almost as rapidly as they

are collected. Another problem that is becoming more widely recognized is that of the contamination of the filters and the extremely difficult associated problem of establishing corrective blanks for many of the elements of interest. A final sampling problem that must be mentioned is that of sulphuric acid aerosol, which is probably a universal pollutant of great significance because of its corrosiveness and its effect on health. There is probably no way known at this time for collecting sulphuric acid aerosol without having it react in part with other pollutants. During the sampling period while sulphuric acid is being collected, sulphur dioxide present in the airborne samples will also be trapped, at least in part, and converted at least partially to sulphur dioxide and alternately sulphuric acid.

After discussing the problem of sampling air pollutants, it is necessary to at least mention the applications which require the determination of individual pollutant species. There are at least five major categories requiring analytical studies. Stack sampling and analysis is a special and complicated problem relating, of course, to point sources of pollutants and is obviously important in regulatory efforts in the control and ultimate abatement of atmospheric pollution. The sampling of gaseous and particulate species from rapidly moving air streams in tall stacks, often operated at high temperatures and involving both laminar and turbulent air flow, is obviously a major operation. Large masses of sample can be obtained readily to minimize some of the analytical problems, but the sampling process is one that is time consuming and difficult.

A second type of application involves what might be called 'effect measurement'. Classic examples of this type of study are the use of corrosion coupons and sulphation plates, or lead peroxide candles. The corrosion coupons obviously provide a means for determining the relative corrosiveness at different locations of the atmosphere on test materials such as aluminium, copper, stainless steel, galvanized iron, etc. The sulphation plates or lead peroxide candles serve in a similar manner for establishing the relative exposure to sulphur dioxide in the ambient atmospheres. The lead peroxide candle does not provide true quantitative values on concentration of sulphur dioxide, but instead provides information on the relative amounts of sulphur dioxide present in respective locations. Sulphur dioxide, to which the candle is exposed, is converted to give fixed sulphates which are ultimately removed to the laboratory and precipitated as barium sulphate for final quantification.

Ambient air sampling and analysis is presently the principal method used for the study and control of air pollution problems. Sampling is accomplished by a wide variety of procedures and devices. Grab samples may be taken by means of hand-operated pumps or portable units operated off automobile batteries. Mobile laboratories are often used for both sampling and on-the-spot analyses. In many cases, sampling stations are located in semi-portable sheds or in parked trailers. After collection, the samples are usually examined to determine the nature and amount of individual gaseous pollutants. Air borne particulates are usually collected and the dust burden determined in terms of some dust-stain index and/or total mass per cubic metre.

As more effort and money is expended in evaluating air quality, there is a rapid trend towards the use of monitoring stations that are highly automated

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and, in many cases, designed for feeding out data into central laboratories for data processing. Continuous monitoring equipment involves a great outlay for initial investment, but tends to reduce the average cost for data when the investment in equipment and personnel is averaged out over a period of years. Continuous monitoring systems reduce the demand for highly specialized manpower and often provide more reliable data than that obtained by individual effort on the part of technicians who may have only limited scientific training and experience. There is a serious philosophical deficiency, however, in the case of continuous monitors because many administrators naively assume that a sulphur dioxide monitor, for example, measures only sulphur dioxide and that the results are beyond question or criticism. Reams of data are accepted as convincing evidence; this may be analogous to lies that are repeated so often that they become accepted as truth.

The analytical needs may be summarized ultimately as falling into two major categories. Reference methods are needed that will establish with the utmost reliability the true values of individual pollutant species that are present in the atmosphere under study. Utility methods are also needed that will provide general information that is reasonably reliable and can be obtained with modest investments in equipment and manpower. Utility methods are particularly important for field studies for use in developing countries and for use by small organizations having limited resources.

The scope of the analytical problems involved in the analysis of air for the detection and determination of polluting species can be appreciated by noting that the pollutants include both inorganic and organic materials. They may be gases, liquids or solids and the concentrations of interest are at the parts per billion or low parts per million level. Determinations must apply to microgramme–nanogramme amounts of material and studies may be made on a single particle of an airborne particulate, or may involve the evaluation of collected airborne particulates where concentrations of particles may run to 40 million particles per cubic metre or even greater.

The evaluation of air quality is sometimes made by subjective studies. This is particularly true in the study of odour problems or in evaluating the impact of eye irritants that sometimes offend large populations or broad-urban areas.

Objective evaluation of air quality may involve physical or chemical studies, or both. Among the physical techniques, photography, microscopy, spectroscopy, gravimetry and densitometry are commonly applied. Chemical analyses are performed using titrimetry, colorimetry, and spectrophotometry. Special techniques that are widely used include gas chromatography, neutron activation, and ring-oven techniques.

In conclusion, it should be noted that the analytical chemist has a great responsibility and an immediate challenge in determining the quality of our environment, the changes that are taking place and in the ultimate effort that is obviously required for environmental improvement.

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