

## *SAMPLING, ANALYSIS AND INSTRUMENTATION IN THE FIELD OF AIR POLLUTION*

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### I. INTRODUCTION

The subject of air pollution has been dealt with repeatedly in the past, from various points of view. However, one has the feeling that in the different meetings the discussions have centred on the more general aspects or on very specialized factors, while rightly stressing the general importance of the problem from the chemical and physical, health, epidemiological, agricultural and zootechnical angles. Such discussions have dealt with the sources of pollution and methods of control and inspection, while the responsibility for pollution has been laid on the ignorance and the lack of interest of town dwellers, the absence of specific legislation and the ineffectiveness of the existing legislation. Finally, some given aspect of a special field has perhaps been dealt with in detail—for example, some specific sampling and analytical technique for one, two or more components of air pollution.

The impression left is one of the initial chaos attendant on all human endeavours, leading to the conviction—at least in the purely technical field with which we are concerned here—that it is necessary to standardize methods and means, as regards sampling and analysis at any rate. Such standardization will yield as clear a picture as possible of the data useful as a basis for general plans for the solution of a problem of such fundamental importance as air pollution.

It is possible to use sampling methods A or B (recommended as the best by different authors) to sample the same impurity X, with considerable differences in efficiency. Moreover, methods C and D (also arbitrarily chosen by investigators as being the best ones) may be used for analysis of the samples, with different limits as regards accuracy, sensitivity and selectivity and, furthermore, with results also affected by the skill, objectivity

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and working conditions of the operator. While this state of affairs continues, any trustworthy and definitive comparison of results will remain impossible—that is, it will be impossible to deal with a variety of conditions and circumstances in a uniform manner, except within the range of tolerance covering the straying of the results from the true figures which arises from the various causes indicated above.

For this reason, in the conviction that it is essential to overcome the obstacle of the “ subjective ” nature of the results, which arises from the disparity of methods and the personal equations of the various workers or experimenters, the author is putting forward in this report, not a definite plan for immediate standardization at this stage, but a preliminary contribution towards selection, from the available material, of those methods which seem most suitable for narrowing the range of “ tolerance ” already mentioned. It should be pointed out, however, that there are two negative aspects with regard to such a selection: (a) the result will, in turn, doubtless show traces of the personal views of those making the selection; and (b) the reason why the use of instrumental means in the field of analytical research connected with the problem of air pollution has not yet become general, but has so far been reserved only for the best-equipped research institutes, is essentially a financial one, this question of finance probably being in most cases the main reason for the indifference with which the problem of air pollution is regarded in many countries.

Although the first point may appear relevant, the second—at least as far as we are concerned here—can be regarded as negligible, since we are not considering the drawing-up of a budget of any kind but are only trying to determine the most objective and efficient technical and scientific methods for sampling and analysis. In saying this, we do not wish to disregard the value of the research work carried out by various investigators so far, nor do we forget the future work which will still be necessary. Instrumentation is, in fact, nothing more than the application of new means to old and tried methods, an application which, apart from the benefits it has already shown, will lead to a streamlining of the work as regards both space and time and make it possible to extend the field of application of the methods themselves to situations which could not be investigated by ordinary means.

## II. SAMPLING

### General

The sampling methods used for the study of air pollution can be classified under three different headings:

- (1) Sampling of impurities of every nature, ranging from particulate matter to gases;
- (2) Sampling under various environmental conditions, ranging from samples taken from conduits or chimneys to samples taken in the open air;

(3) Sampling methods varying according to the time factor, ranging from intermittent to continuous sampling.

The major difficulties encountered in each of these categories of sampling generally relate to: (a) the problem of collecting samples which are genuinely representative of the condition of the mass of air under study; (b) the problem of avoiding the introduction of errors arising from the methods used for the separation of the various components of pollution, which is necessary for the analysis of each of these components; (c) the problem of preventing any change in the concentration of particulate matter, in suspension as a result of the sampling operations.

### **Preliminary Considerations and Stages of Sampling : Principles Governing the Avoidance of Sources of Error**

Before putting forward a tentative systematic enumeration of sampling devices, we shall discuss a few points of a general nature relating to the principles to be followed to ensure correct sampling, as free as possible from direct or indirect causes of error and capable of giving directly all the necessary information, or making possible its subsequent acquisition.

#### **Statistical studies**

Statistical studies are of the utmost importance to establish the basic data (e.g., the size and frequency of sampling) necessary to the drawing-up of a good plan of research. By their use it is also possible to extract the maximum amount of information from the results, thus enhancing the completeness and accuracy of the research. Statistical studies naturally solve such problems in terms of probability—that is, by definition they do not give absolute results but only indicate the percentage probability that a given series of data will be accurate within certain limits.

#### **Size of the samples**

The samples should naturally be big enough to make analysis possible. Consequently the persons carrying out the sampling and the analysts should always agree beforehand to make a joint study of the types of sampling devices, the methods of sampling and the size of the samples necessary and adequate for the type of analysis to be carried out.

#### **Changes in the sample during and after sampling**

This is one of the fundamental causes of error. In fact, many substances which, when present in low concentrations, can co-exist without reacting with one another and consequently without undergoing any appreciable change, may when sampling has been continued long enough to bring about

a high concentration—for example, in order to provide the analyst with an adequate amount of material for analysis—react with the formation of other substances which were perhaps not present either in the waste gases or in the atmosphere. Particulate matter, moreover, may agglomerate or break up, so that the sample collected may show statistical and dimensional properties completely different from what they are in reality. These possibilities should always be borne in mind by the investigator so that he can try to avoid such serious sources of error.

### **Continuous and intermittent sampling**

Automatic, continuous or intermittent recording apparatus is becoming more and more widely used in atmospheric analysis because of the outstanding advantages it offers. Apart from leading to a saving in time and staff, such apparatus is sometimes sufficiently sensitive to detect minute concentrations of impurities that generally escape the notice of even the most experienced workers using the normal analytical means. In some cases, recent research has shown that it is precisely these minute traces of impurities which are the cause of the most unpleasant aspects of air pollution, ranging from damage to plant life to physiological effects in man, such as irritation of the eyes. Many of these continuous recording machines combine the operations of sampling and analysis, so that any differentiation between the two operations for purposes of classification becomes pointless.

### **Sampling of volatile constituents**

The major difficulties involved in the sampling of volatile components of air pollution relate to the efficacy of the methods used, the concentrations which it is necessary to attain, and the subsequent separation of other components in order to analyse the volatile substances. In such cases, the only useful advice of a general nature which can be given is to carry out sampling with large volumes of air so as to have the maximum quantity of the substance available for analysis and to eliminate, as far as possible, the need for subsequent concentration.

### **Sampling of particulate constituents**

It has already been seen how the possible agglomeration or breaking up of particulate matter may lead to errors of evaluation. In order to eliminate these sources of error the sampling should be carried out under conditions which are as isokinetic as possible, above all when the particles are very small.

This signifies that sampling should be performed in such a way that, as far as possible, the gas stream carrying along the particulate matter should undergo no disturbance or change of speed on entering the collecting device.

It is almost impossible, however, to ensure perfectly isokinetic conditions, since the final container will always represent a disturbing factor. Thus sampling takes place practically always under more or less anisokinetic conditions, which may lead to inevitable errors in the determination of both the quantity and the dimensions of the suspended matter. In order to reduce anisokinetic conditions to a minimum, the gas stream should be sampled as far as possible in the same direction and at the same speed as the stream itself, but at least never counter-current.

Furthermore, to avoid reducing the efficiency of sampling, deposits and condensation should not be allowed to form on the walls of the sampling vessel; the collecting surface should therefore be as close as possible to the source of the gas stream. Obviously, a 100 per cent yield of the total pollutant content is not possible, but a fair approximation can be achieved by carrying out selective sampling in relation to the size of the particles.

### **Sampling of waste gas**

Numerous difficulties encountered in this type of sampling arise from the particularly variable characteristics of waste gas—namely, very high temperatures, lack of uniformity in the composition of the gas flow, and differences in speed due to disturbances of all kinds. For all these reasons it is impossible, in the present state of our knowledge, to lay down any general rules, and it is necessary to adopt those methods which are best suited to the special conditions which it is felt will occur in the particular case concerned.

The only general directive which can be given is that the gas stream should be sampled at several points and the largest possible number of samples taken, or that average samples should be taken after a careful study of the conditions of the gas flow, so as to determine as far as possible the variables of the flow and whether these are cyclic or periodic in nature.

### **Sampling in the open air**

In the case of sampling in the open air the main difficulties arise from: (a) the high dilution of the pollutants dispersed in the air to be sampled; (b) the consequent need to collect large samples (without, however, unduly prolonging the sampling time); and (c) the difficulty of sampling under isokinetic conditions, in particular because of the frequently rapid changes in the direction of the wind.

Here, more than in any other case, continuous recording instruments are valuable. Several of them should be placed simultaneously at various points in the area under examination. Synchronous meteorological measurements, again continuously recorded, should also be available for each instrument so as to supply the essential information for identifying at any moment the characteristics of the source of pollution with respect to the wind speed

and direction and other basic meteorological data. It is in fact wind and atmospheric stability factors which play the major part in bringing about special conditions of dilution or concentration of pollutants in the air.

Various mathematical formulae have been introduced for defining the theoretical concentrations, detectable at ground level, of gaseous or particulate effluents coming from individual sources (point sources, linear sources, etc.). Such formulae may be of great value, particularly for converting results actually obtained under given meteorological conditions to those which should be obtained under different conditions.

Furthermore, a study of the topographic and orographic features of the area is necessary for the integration of all sampling data, since such features have a considerable influence on the variability of meteorological factors and the limitation of the volumes of air affected by the discharge of pollutants.

### **Methods for following the movement of air masses**

In some cases it may be necessary to analyse the movement of air masses in order to determine the speed of diffusion and the distance at which polluting substances discharged into the air from one or more sources can be detected. In such cases, use may be made of fluorescent substances (zinc and cadmium sulfides, zinc sulfate, etc.), which are discharged into the air by means of a special fog or smoke generator and which are then looked for in samples collected at various distances and at different times in the area under study.

## **Instruments for Sampling Waste Gases and for Atmospheric Sampling**

### **Devices for general use**

Almost all sampling apparatus requires aspirating and measuring instruments, in addition to the collecting device. Almost all, but not all, since occasionally the sample is collected by the displacement of gas or liquid or by the filling of containers which have first been evacuated and which have a known volume. In such cases—nearly all of which are of instantaneous sampling—a measuring device may be unnecessary and the aspirating apparatus can be omitted, provided that the gas to be sampled is under sufficient pressure to displace the liquid or gas filling the collecting vessel. Instantaneous sampling is usually undertaken only in special cases, when it is required to determine the conditions at a given moment, and is employed primarily for sampling waste gases in the immediate neighbourhood of the outlet of conduits or pipes—that is, when sufficient pressure is available for displacement of the contents of the collecting vessels.

However, sampling is generally not instantaneous but more or less prolonged and, as has been said, calls for aspirating and measuring devices as

well as, in the case of the direct sampling of a gas stream, probes—that is, sampling devices which can reach any point in the cross-section of a conduit which has been selected for sampling.

### *Probes*

Probes for sampling gas free of particulate matter are generally simpler than those used for gas streams containing solids or liquids in suspension. Such probes are nothing more than tubes suitable for penetrating into the gas stream, and should be constructed of materials which do not react with the substances to be sampled. Since it is not uncommon to encounter special temperature conditions or corrosive matter, probes should be made of stainless steel, or—better still—of glass or quartz.

The length of the probes should be such that they can penetrate to any point of the gas stream to be sampled, since the latter may not be uniform as regards flow, speed or composition. The internal diameter of the probe should be such that it conveys the sample to the receiving vessel at the speed considered most suitable for the particular case. At the same time, the diameter should not be too small, so that the probe does not readily become choked when particulate matter is present and also so as to facilitate cleaning, which should be undertaken as often as possible.

To ensure the isokinetic sampling conditions to which reference has been made, the opening of the probe should face the gas stream to be sampled, and the diameter of the opening should be such that sampling can take place without changing the speed of the effluent.

### *Meters*

Since the precision and accuracy of an analysis largely depend on an exact knowledge of the volume of gas sampled, such devices must be extremely accurate. Meters for the measurement of dry gas are used for preference. They are fitted with manometers and thermometers which indicate, at the point of measurement, the pressure and temperature of the gas stream sampled, so that the volume of gas read off can be converted to standard temperature and pressure, or its weight determined.

### *Suction devices*

No special directions can be given in this connexion, since any suction device may be used which has adequate volumetric capacity under the necessary conditions of reduced pressure. Vacuum pumps driven by electric motors are the most common apparatus used. If there is any danger that the gas to be sampled will ignite, the pumps may be fitted with special anti-combustion motors or, if only very low power is required, they may be worked by hand. Otherwise the gas can be absorbed by using jet pumps

employing water or steam, or special pumps driven by a gas motor actuated by liquid carbon dioxide.

### **Devices for sampling gases and vapours**

#### *Absorbers*

A gas can be sampled by means of suitable absorption reagents provided it dissolves with sufficient rapidity in these reagents. For this purpose use is made of U-tube absorbers of the type laid down for the determination of sulfur by the American Society for Testing Materials. These absorbers are filled with a certain measured amount of reagent and fitted with a porous glass partition, so that the air or gas led into them passes through the reagent solution in the form of very fine bubbles, thus ensuring intimate contact. Sampling by means of such absorbers is usually carried out at an average rate of about 100-150 litres per hour of gas stream. The absorbers may be arranged in series of two or more elements containing the same reagent solution to ensure more-complete absorption of the impurity in question, or in series of two or more elements containing two or more different reagent solutions so as to absorb different pollutants successively from the same volume of gas or air sampled.

Several years' experience in the Institute of Sanitary Engineering in Milan has shown that units of the type described above can also be usefully fitted up in parallel series. Ten or more units can be used in this way for the simultaneous sampling of several pollutants. The arrangement which at present seems most advisable (according to experience in the Institute) is the installation of parallel pairs of absorbers (mounted in series) corresponding to the number of polluting substances which it is desired to detect.

This arrangement achieves the completeness of absorption considered necessary, and at the same time makes possible the simultaneous sampling of any desired number of pollutants.

By selecting the most suitable absorbent solutions at present available, the gaseous components listed below can be determined under the conditions mentioned in concentrations as low as 0.1 p.p.m. by volume:

- oxides of sulfur
- oxides of nitrogen
- ammonia
- hydrogen sulfide
- hydrochloric acid
- hydrofluoric acid
- hydrocyanic acid

Even lower concentrations can be determined by prolonging the sampling time or decreasing, where applicable, the speed of the gas flow through the absorbers.

When the polluting substances collected are present in minute traces and the sensitivity of the analytical method to be employed is very close to the limit of quantity of pollutant which can be collected by absorption, it is possible to improve the degree of absorption by using a more complicated arrangement. A much smaller quantity of reagent is injected as a fine spray into a small bulb, into which the sample of gas containing the contaminant to be absorbed is rapidly and simultaneously injected from another storage vessel by means of an alternate "emptying" and "refilling" cycle. In this way intimate contact is brought about between the reagent and the contaminating substance in the sample, a minute quantity of the component to be determined being concentrated in a very small volume of reagent liquid.

This particular type of sampling by absorption may be employed for the determination of ozone, hydrocarbons or organic solvents and, with suitable auxiliary refrigeration equipment, the samples thus obtained can be used for infra-red and ultraviolet spectrographic analysis.

### *Adsorbers*

The collection of samples by means of adsorption involves considerable difficulty, not so much as regards the apparatus but as regards the need for preliminary investigation to determine what adsorbing medium will give the best results, both quantitatively and qualitatively.

This type of sampling is used especially for ozone and the light hydrocarbons. Adsorption is brought about by aspirating the air or gas to be sampled through adsorption columns containing silica gel, activated charcoal or any other suitable agent. After adsorption, the different pollutants can be extracted from the column in various ways: (a) if the adsorption on silica gel has been carried out at the temperature of liquid air (procedure used to detect down to two or three parts per hundred million by volume of ozone), the sample can be extracted by raising the temperature to  $-120^{\circ}\text{C}$ ; (b) the same procedure of raising the temperature serves to separate various fractions of light hydrocarbons from the adsorption column, by taking advantage of the different boiling points of these fractions; or (c) a jet of inert gas passing through the adsorption column can act as an eluent and behave in the same way as an elution solvent in liquid chromatography.

### *Condensers*

In this procedure the gas stream sampled is cooled in suitable containers, thus bringing about the condensation of the volatile substances present. As in the case of the absorption devices previously described, these so-called condensation traps can be arranged in parallel pairs and in series at decreasing temperatures. By using various coolants—for example, ice, dry ice, liquid nitrogen, or liquid air—the components can be separated

by fractional condensation. However, the quantitative assay of the various pollutants in the sample may be hampered by the formation of crystals, which may first deposit and then volatilize on the less cold parts of the apparatus. This drawback can, however, be reduced to a minimum by dividing off the cooling chamber with suitable porous glass partitions.

Such devices are used in particular for the sampling of odoriferous substances.

#### *Collectors under reduced pressure*

For some substances, such as nitric acid and aldehydes, having a high molecular weight, absorption in aqueous solutions is sometimes incomplete. In such cases it is preferable to use bottles of known volume for collecting under a pressure reduced to 200 mm Hg or even less. The absorbent solution chosen is first introduced into the bottle and the pressure is then reduced. Next, the sample is admitted until the internal and external pressures are equal, and the container is shaken continuously so as to ensure maximum absorption.

This method is used especially in the construction of automatic analysers for the oxides of nitrogen. Such analyses range in sensitivity from 0.005 to 5 p.p.m. by volume, and employ a colorimetric reagent, the colour produced being measured photo-electrically.

#### *Samplers for mass spectrometric analysis*

Sampling for mass spectrometric analysis can be carried out in various ways, either by compressing the gas sample in a pressure flask so as to concentrate a large quantity of gas in a small volume, or by filling evacuated containers. The sampling technique employed should first be agreed upon with the analyst in charge of the mass spectrometer, since it has a considerable influence on the results obtained.

#### *Plastic containers*

Special polyethylene bags, strengthened with at least five layers of plastic material and sealed while hot, are much used for collecting and transporting large volumes of air. These bags have the advantage that they can be used for the successive analyses of small fractions of the sample taken. Moreover, polyethylene is inert with respect to very many substances, among which are sulfur dioxide and formaldehyde. On the other hand, plastic bags are not suitable for collecting and storing aerosol suspensions, because of the possible generation of electrostatic charges as a result of which the aerosols tend to move towards and condense on the walls.

## Devices for sampling particulate matter

### *Sedimentation methods*

Sedimentation is a very suitable method for sampling suspensions of pollen, but not dust suspensions, because the particles may clump together or become dispersed over the walls of the sampling device, making it difficult to collect them quantitatively. The sedimentation rate of the smallest particles contained in aerial suspensions may also be considerably lower than that of the larger particles, so that the latter tend to predominate on the sampling slides.

The apparatus for sampling by means of sedimentation consists of a glass surface, measuring about 3 cm × 10 cm, arranged horizontally in a protecting metal frame. The latter consists of two metal discs, about 20 cm in diameter, arranged horizontally and roughly 10 cm apart. The slide is placed in a holder about 3 cm above the lower metal disc. The whole apparatus is mounted on a rod, provided with a support, about 90 cm high, and placed on top of a high building.

The slide becomes coloured and the pollen granules are identified and counted under the microscope, the results being reported as "number of granules per cm<sup>2</sup> of slide collected in twenty-four hours". The method is simple and economical, but not suitable for quantitative assay of the pollen content of a given volume of air. Particles of homogeneous smoke can, however, be measured by observing their sedimentation rate in a special sedimentation chamber by means of the Tyndall effect produced by a beam of light. In this way it is possible to measure sedimentation rates ranging from 4 cm to 160 cm per hour, corresponding respectively to matter with a density of 1 g/ml and matter with a density of 2 g/ml, such as sulfur.

Sedimentation jars, which are very simple and economical, can also be used for gravimetric determination of the matter deposited in a given period of time, but they give results which are only very approximate and are hardly reliable.

### *Visual and photometric methods*

These are devices for direct observation of the state of dispersion of the particles in the air or in a waste gas, thus eliminating errors arising from the clumping together or breaking up of the particles which may occur when other means are used for collecting them.

The Ringelmann cards are an example of a visual method. They consist of a series of five cards numbered from 1 to 5, divided up into squares formed by black lines on a white ground, the ratio between the areas of the squares on the different cards being 20, 40, 60, 80, and 100 per cent. These cards are placed at the eye-level of the observer, at a distance of about one and a half metres and as near as possible to the source of the smoke. The

observer compares the density of the smoke with the intensity of the grey spots which the various Ringelmann cards produce, and describes a source which is practically clear (non-opaque) as No. 0 and a smoke which is 100 per cent black as No. 5. The observations are repeated at intervals of 15-30 seconds and the readings are then related to the theoretical value of the density as determined for Ringelmann card No. 1—that is, a smoke with a 20 per cent density—by means of the formula:

$$\frac{\text{Total of the different numbers of the Ringelmann cards} \times 20}{\text{Number of observations}} = \text{Percentage density of the smoke}$$

This very simple method clearly gives only very approximate results, which may also be completely arbitrary at times, varying according to the position of the observer with respect to the source.

More accurate is the slit ultramicroscope, where the slit is in the form of narrow cell through which is passed the sample at a rate slow enough to ensure that the time of passage is sufficient for purposes of observation. It is usually possible to make about 60 observations per minute and thus obtain a satisfactory statistical average; it is also possible to count particles with diameters of less than 0.1  $\mu$ .

Another very sensitive device is a transverse dispersion Tyndallometer. Here the flow of the sample is observed by means of transverse illumination which shows up the particles so that they can be rapidly counted. This can be done directly by an experienced operator or, still better, by electronic counting and automatic recording apparatus. With such apparatus it is possible to count particles of about 0.6  $\mu$  in diameter at a speed of 1-1000 units per minute.

Smaller particles can also be observed by using suitable photographic equipment which takes a picture of the sample every two seconds, registering the condensation droplets formed around the particles and thus enabling a subsequent count to be made.

### *Impingers*

This type of sampling consists in the interception of aerosol particles by placing obstacles in the path of the gas stream. When a gas stream is forced to go round an obstacle, the particles in it tend—because of their inertia—to diverge from the direction of the stream and collect on the surface of the obstacle. Of course, since the inertia of a particle is proportional to its mass, the smaller the particles the greater will be their tendency to follow the direction of the gas stream in its flow round the obstacle. The efficiency of this type of sampling is given by the ratio between the number of particles intercepted by the apparatus and the number which would have been intercepted if none of them had been deflected in any way. For maximum efficiency, this method should therefore be reserved for rather large particles, using small samples and a high rate of flow.

There are many types of device employing this principle, ranging from simple microscope slides exposed to gas streams or suspended in the air at right angles to the direction of the wind, to cascade impactors. The latter consist of a series of slides arranged at right angles to one another and it is possible to "select" the particles by gradually reducing the diameter of the opening of the tubes directing the gas stream from one slide to another, at an average rate of flow of approximately 17 m per minute.

Using cascade impactors it is possible to trap particles of submicronic size with the arrangement in series just described, but conveying the gas stream to the last slide at a very high velocity, equal to the speed of sound.

A special arrangement for continuous sampling employs a jet of gas which is made to impinge on a series of slides mounted radially around the circumference of a cylindrical wheel placed in a vacuum chamber, so as to cause the assembly of slides to rotate. More complex apparatus employs a microscope in conjunction with the simple impinger and sometimes also a camera for taking periodic pictures of the slides. In place of the slides tubes containing solvents or inert liquids can be used, in the former case for chemical analysis of the solution obtained, and in the latter for microscopic examination of the particles dispersed in the liquid.

### *Filtration methods*

Many factors are involved in the filtration of aerosols through porous media. The use of filters should aim essentially at enabling subsequent examination of the particulate matter to take place, but—apart from gravimetric measurements—such examination is often not easy, because of the difficulty of separating the matter filtered out from the filtration device.

One way of overcoming this drawback is to use soluble filtering media—for example, sugar or salicylic acid crystals—dissolving them in water and separating the particles retained by filtering the solution. However, it is essential to make sure that filtering media of this type (generally used in several layers) do not react with the particulate matter. Other filters used with good results include certain filter papers (ash-free), asbestos fibre or glass wool.

Recently, molecular filters, consisting of special plastic substances with very fine pores, have been introduced. These have the advantages of offering a minimum of resistance to the gas stream and also—when they are transparent—of being suitable for direct examination of the particle size, by determining the intensity of the light transmitted when the filters are moistened with oil having a suitable refractive index.

Such filters can also retain extremely small particles which would pass through practically any other filtering medium. Furthermore, they are soluble in acetone, making possible the practically complete recovery of the particulate matter in the laboratory and its subsequent analysis by other

means, as required. Their sole disadvantage is that they lose their favourable properties when exposed to high-temperature gas streams.

#### *Cyclone-type sampling*

These devices are very suitable for sampling light ashes and dusts and can attain an efficiency of nearly 100 per cent. They have the following advantages: (a) simplicity of construction; (b) they can be made from materials resisting high temperatures; (c) they can be made to any size; and (d) the samples collected can be rapidly recovered.

The principle employed is to bring about a cyclonic or vortex movement of the gas or air to be sampled in a cylindrical container, so that the suspended matter is separated by centrifugal force.

#### *Thermal precipitation methods*

This method of sampling is based on the principle that hot surfaces repel particles suspended in the air, and that the particles thus repelled collect on cold surfaces. An airstream is made to cross the space round a heated filament situated between plates, with the result that the particles repelled by the hot filament settle on the plate. If the collecting plates are covered with colloidal matter, they can be directly examined under the electron microscope. The addition of an agitating device to the collecting plates helps to ensure a more uniform distribution of the particles which have been in suspension. The efficiency of such samplers is so high that it is not possible with any other sampling device to trap any particles which may have escaped.

#### *Electrostatic precipitation methods*

The principle employed here consists in submitting the gas stream to be sampled to the action of suitable electric fields so as to encourage the deposition of the particles in suspension on electrodes between which a high potential difference is maintained. In this case too, the efficiency may reach almost 100 per cent, but the samples obtained serve only for gravimetric analysis, since the particles are collected in a state of agglomeration which may be very pronounced.

Such devices are not suitable for sampling in the presence of explosive gases.

### III. ANALYSIS

#### **General**

The atmosphere contains such an enormous number of substances, in concentrations which vary so greatly over the course of time, that continuous determination of its exact composition may be regarded as a problem which

will remain very difficult to solve. The analyses which are made more or less daily concern only certain impurities known or suspected to be present in the air, and these represent only a small proportion of the total number of foreign substances dispersed in the atmosphere.

At the present time, there are not always analytical techniques available for dealing with the special forms and low concentrations of many atmospheric pollutants, but nevertheless even today it is possible to gain much useful information concerning a substantial number of pollutants by using analytical methods developed for other purposes.

It is the task of the analyst to obtain as much data as possible on the nature of the pollutants at the point selected for sampling. In some cases it may suffice to know the concentration of certain radicals or functional groups present in the sample. In other cases, however, apart from a knowledge of the chemical composition of the pollutants found, it may also be useful to know their physical nature, and consequently the sample should be collected in the form most suitable for the subsequent analytical investigation.

Since the aim of analysis in the special field of air pollution is to obtain information which can give an over-all picture, even if only an incomplete one, of the whole problem it is evident that certain requirements should be satisfied as regards concordance between the sampling and analytical techniques. These requirements are as follows:

(1) the efficiency of the sampling device used should be known as accurately as possible;

(2) the sampling device chosen should cause the minimum of change in the composition of the various substances to be detected;

(3) the apparatus should be sufficiently clean and the reagents sufficiently pure to give blank determinations which are lower than the lowest suspected concentrations of the substances sampled;

(4) the sampling method should supply the analyst with a quantity of pollutants within the quantitative limits called for by the sensitivity of the analytical technique to be used;

(5) the methods employed for the determinations should be as sensitive as possible and their repeatability should be satisfactory.

Other special difficulties are connected with the choice of analytical method, when there is not sufficient information on the conditions under which the compound to be examined may occur, since every analytical technique has its limitations, of which the most important are those relating to the concentration of the compound to be detected and the presence of interfering substances.

For all these reasons, a preliminary reconnaissance is advisable, using various analytical methods, such as microscopic methods, analytical methods based on the absorption of infra-red and ultraviolet light, emission spectrographic methods, X-ray diffraction and polarography—all of which

unfortunately require, in addition to a specialized and skilled technical staff, special, high-precision equipment. On the other hand, the importance of the problem of air pollution is such as to warrant special consideration and the confrontation of all difficulties, no matter of what type they may be.

The very large variety of methods which have been applied, or which have possible application, to the analysis of atmospheric samples can be divided into three basic groups—namely, chemical methods, instrumental methods, and biological methods.

Since the second category is the one with which we are most concerned here, this report will deal only in general with the first and third groups, devoting more space to the field of analytical instrumentation as applied to atmospheric investigation. Of course, it will not be possible to describe in detail any particular instrument, for in view of the large range of instruments of all types on the market this would call for a separate examination of each example followed by a comparative study, which would require a special treatment beyond the limits of the present paper.

## Analytical Methods

### Chemical methods

In general, quantitative methods of chemical analysis can be subdivided into: gravimetric methods; volumetric methods (acidimetric and alkali-metric methods, oxidation and reduction methods, precipitation methods); colorimetric methods; nephelometric and turbidimetric methods; and chromatographic methods.

#### *Gravimetric methods*

Gravimetric methods of analysis are based on the principle of isolating the substance to be assayed in the form of one of its compounds which shows the maximum insolubility under the test conditions and has a known chemical composition. The weight of the compound is then determined and from this the quantity of the substance concerned can be calculated. Sometimes, however, the substances to be determined are already suitable for direct weighing so that in this case the assay involves only the direct determination of their weight. Gravimetric methods comprise the most simple analytical techniques, and can be used for:

(1) The determination of a gas (sensitivity approximately 1 mg). The methods may be applied to substances adsorbed on silica gel, activated charcoal or other adsorbents, by weighing the quantity of precipitate obtained with given reagents (as in the case of sulfur dioxide, which can be determined by weighing the sulfate precipitated as barium sulfate). Very large samples are usually required.

(2) The determination of dusts and soot collected in sedimentation jars following long sampling periods (of the order of 30 days for example) (sensitivity approximately 1 mg).

(3) The determination of particulate matter dispersed in the air (sensitivity 0.1 mg), sampled by collection on filter paper, by means of the impinger or electrostatic precipitators. Here too, rather large samples are necessary and the use of the micro-analytical balance may be required.

### *Volumetric methods*

In volumetric analysis, the components are not weighed but determined by means of reagents of known concentrations. As has been mentioned, these methods include:

(1) Alkalimetric and acidimetric methods for the determination of bases and acids, using solutions of an acid or a base, respectively, in the presence of indicators which undergo a colour change according to the alkalinity or acidity of the medium. (Substances used as indicators are electrolytes, generally weak acids or bases and in the undissociated state—that is, when they are electrically neutral—their colour should differ from that of their ions.)

(2) Oxidation and reduction methods which are based on the oxidation or reduction of the compound to be analysed by means of a standardized substance, the quantity of oxygen given up or consumed being measured according to the colour change developed in the reaction, in the presence or absence of an indicator.

(3) Precipitation methods (suitable in particular for assaying the halogens) in which use is made of silver nitrate solutions of known strength which precipitate the halogen in the form of silver halides.

Acidimetric and alkalimetric methods can be used for the volumetric determination of acid and basic substances and are very sensitive, being able to detect less than 0.01 p.p.m. by volume of the gas stream sampled. They call for large samples. Examples of these methods are the determination of sulfurous anhydride, oxidized to sulfuric acid, and of ammonia, by means of direct titration with standard solutions of sodium hydroxide and sulfuric acid respectively.

Other gases can be determined with a sensitivity exceeding 0.01 p.p.m. by volume, by means of iodometry (oxidation and reduction), particularly in atmospheres of known composition, using samples obtained by absorption, as in the case of sulfuric anhydride, chlorine, aldehydes and oxidizing agents. For the last mentioned, this is perhaps the most sensitive and advisable method.

Finally, the halogen acids in particular (hydrochloric acid, hydrofluoric acid, hydriodic acid) and their salts can be assayed by precipitation, but the reaction is not sufficiently sensitive to be of wide application.

### *Colorimetric methods*

Colorimetric methods are on the whole the most satisfactory type of determination among the various analytical procedures known today. A very large number of elements, radicals and organic compounds form coloured complexes with special reagents, and such colorimetric reactions are sometimes sufficiently sensitive to detect even the most minute traces of the compounds which are being sought. Naturally they call for the use of suitable and more or less sensitive apparatus for determining the intensity of the coloration produced, such as visual, filter or other types of photometer, photo-electric apparatus using photo-cells or photo-tubes, indicators or recorders. This might therefore seem to be more a branch of instrumental analysis, but since the colorimetric techniques have entered into very extensive use they can now be considered as simple chemical methods. This is all the more true in that they involve only the instrumental measurement of actual and specific chemical reactions, and sometimes also normal titrations with special indicators. They can be used for the analysis of gas and particulate matter, sometimes with a sensitivity of less than 1  $\mu\text{g}$ , but occasionally they require large samples and difficult separation and concentration techniques for the compounds to be examined.

The colorimetric tests include some of the best assay methods, particularly in the analysis of metallic vapours or dusts, formaldehyde, oxides of nitrogen, ammonia, chlorine, hydrogen sulfide, fluorine, carbon monoxide, carbon dioxide, as well as many other organic and inorganic compounds. Sulfurous anhydride, for example, can be assayed with a sensitivity of 0.001 mg, by measuring the violet colour produced by the reaction of benzidine sulfate with N-1-naphthyl-ethylenediamine hydrochloride.

### *Nephelometric and turbidimetric methods*

Nephelometric and turbidimetric methods involve procedures in which the precipitates, obtained by means of specific reactions, are quantitatively assayed by optical measurement of light passing through the corresponding suspensions. They are suitable for the determination of gas and particulate matter, do not require specially large air samples and find their best application in the determination of sulfurous anhydride (by means of precipitation as barium sulfate and estimation of the turbidity produced by the precipitate with a sensitivity of 0.005 p.p.m. by volume) and of chlorine (which is precipitated as silver chloride, likewise with a sensitivity of 0.005 p.p.m. by volume).

### *Chromatographic methods*

Chromatographic methods make possible the separation and identification of many substances by means of adsorption on adsorption columns, or

on specially sensitized paper, followed by the elution of the various compounds adsorbed with selective solvents. In this way, the components of complex mixtures can be separated without undergoing any chemical change. Traces of inorganic ions can be detected by such methods with extreme accuracy and with considerable saving in time and material as compared with other methods.

The sensitivity of such methods is very high (sometimes less than 1  $\mu\text{g}$ ) and furthermore they are suitable for any kind of substance. They are particularly useful, however, for metals and volatile organic compounds. Their application to air analysis is still in the initial stages although they are already being extensively used in special cases—for example, the determination of benzpyrene in urban atmospheres.

### **Instrumental methods**

In order to ensure analytical specificity, selectivity and sensitivity, methods are required which are based on clearly defined physical principles, as well as apparatus designed for the exact application of such principles.

In general, instrumental analysis is the application to analytical chemistry of special physical and physico-chemical methods. Such methods are finding an ever increasing application because of the extreme rapidity with which they enable certain types of analysis to be carried out (otherwise too long and complex if the ordinary methods are used) and because of their efficiency in cases where the classical methods generally give unsatisfactory results. In principle, however, it is not possible to make a fundamental distinction in classification between instrumental and non-instrumental methods. Even the simplest of the chemical methods—namely, gravimetric determination—also calls for the use of an instrument—the balance—which, although its employment is of a routine and elementary nature, nevertheless remains an instrument. Furthermore, as we have seen, colorimetric, nephelometric and turbidimetric determinations also require the use of sensitive instruments for assessment of the intensity of the colour or turbidity (produced by given reactions), by measurement of the light absorption caused by the particles suspended in a liquid (turbidimetry) or measurement of the intensity of the light dispersed by a suspension of particles in a liquid medium (nephelometry).

Determinations of pH and salinity are sometimes necessary in the analysis of air, using samples obtained by absorption of the gas phase under study in the simplest of absorbing media—namely, water—so as to determine, for example, the concentration of certain acid or alkali mists or the amount of salts, such as sodium chloride, in suspension. Potentiometric titration is used, for instance, in the analysis of atmosphere containing sulfides or mercaptans, and in this method the indicator is replaced by the electromotive force developed between a reference electrode and a measuring electrode.

Both these methods form part of a group constituting that branch of analytical chemistry which is known today as "electro-analytical chemistry".

This latter makes use of the phenomena which occur in an electrochemical cell (that is, a cell consisting of two metal electrodes—of the same or different metals—immersed in the same or two different electrolytes and connected to apparatus suitable for the exchange of electric energy with the cell). According to the particular case, the behaviour of the cell is determined by measuring the various electrical quantities involved, namely:

(1) the amount of electricity flowing in the circuit of the electrochemical cell (coulombometric method);

(2) potential difference in the electrochemical cell (potentiometric and potentiometric titration methods);

(3) current flowing in the electrochemical cell circuit (amperometric and amperometric titration methods);

(4) current-potential difference (voltametric methods, which include the polarographic methods);

(5) resistance, or better its converse, conductance, of the electrochemical cell (conductometric and conductometric titration methods);

(6) dielectric constant (high frequency methods);

(7) other methods (electrogravimetric, electrolytic separation methods, etc.).

In view of the fact that optical determination methods, in colorimetric, nephelometric and turbidimetric analysis, as well as the electrochemical methods, are in constant and routine use as auxiliaries to the normal methods of chemical analysis, we shall describe in this chapter only those instrumental methods (and the fundamental information they provide) whose complexity is such that they still represent special means of research, not yet in routine use, but whose application to the field of air pollution can bring about significant advances in our knowledge and in the solution of the problem itself. These methods are the following: emission spectrometric methods; absorption spectrometric methods (spectrophotometry) in the ultraviolet and infra-red regions; X-ray diffraction methods; mass spectrometric methods; polarographic methods (polarography); methods employing microscopy; refractometric methods; combustion or thermal conductivity methods; other instrumental methods (radioactivity, sound absorption).

We shall deal in a separate section with automatic (recording) apparatus for sampling and analysis.

### *Emission spectrometric methods*

The general definition of spectrometric methods includes all techniques based on the phenomena of emission or absorption (and possibly the related fluorescent re-emission) of electromagnetic radiation in the visible, infra-red and ultraviolet regions of the spectrum. For obvious reasons, we shall not

deal with spectroscopy—although this is first in chronological order—and shall limit ourselves to spectrometry and in particular to spectrometric emission methods. The fundamental principle upon which such analytical methods are based is that any element, when in an excited state, has its own special emission spectrum, so that emission spectrometry is widely used to determine the composition of mixtures or compounds and is indispensable in the exploratory examination of particulate matter.

Emission spectrometry can be applied to the analysis of more than 70 of the known elements. The alkaline and alkaline-earth elements can be detected with the highest attainable sensitivity—namely, down to 0.1 p.p.m. by weight of the quantity of substance examined—while some 40 - 50 other elements can be detected with a lower degree of sensitivity, ranging from 10 to 1 p.p.m. by weight. This analytical technique, by now well established, requires high precision apparatus for its application. Such apparatus consists of: (a) a source of radiation; (b) a means of splitting up the radiation, which may be either a prism or a grating; and (c) a receptor, which can be either a photographic plate, as in the case of the older spectrographic equipment, or a series of photo-tubes, as in the more modern spectrometric apparatus.

Spectrometric analysis (quantitative) involves the spectroscopic characterization (qualitative) of the elements, based on identification of the characteristic lines in their emission spectrum. Such identification can be made by means of a comparator microscope for measurement of the distance between the lines themselves, while quantitative determination is based on the consideration that the energy emitted for a given spectral line of an element is proportional to the number of excited atoms and consequently to the concentration of the element in the sample.

In air analysis, spectrometric emission methods are applied mainly in research work, especially for the identification of the elements present in particulate matter. The method is particularly indicated for beryllium, sodium, potassium, calcium, lead, cadmium and antimony.

#### *Absorption spectrometric methods (spectrophotometry)*

Spectrophotometry, based on the absorption of a certain range of electromagnetic radiation in the visible, ultraviolet and infra-red regions of the spectrum, is one of the most important of all instrumental methods of analysis and is consequently of potential value for the analysis of impurities in the atmosphere. Absorption in the visible spectrum is the basic principle of the methods of measurement applied in colorimetric and turbidimetric analysis, which, as has been seen, can be applied to the analysis of both gaseous and particulate matter. These methods are frequently sufficiently specific, although it is sometimes necessary to isolate and concentrate the compound to be examined so as to avoid interference by other compounds.

The absorption varies with the wave-length of the incident radiation, so that measurements should be carried out either with monochromatic light or with light having a limited spectrum, which can be produced by using special light filters. The wave-length of the beam emerging from the source of radiation is suitably adjusted in this way and then passes through a layer of the substances to be examined, while the intensity of the non-absorbed radiation is determined with a suitable detecting apparatus.

In the visible region of the spectrum, the concentration of a coloured substance analysed spectrophotometrically can be derived from the Lambert-Beer relationship, according to which light absorption is proportional to concentration, when the layers analysed are of equal thickness. However, spectrophotometric methods can also be applied to the analysis of colourless substances by studying absorption in the ultraviolet region of the spectrum, but this method is not satisfactory for the analysis of compounds present only in traces.

The difficulties in practical application to atmospheric analysis are thus inadequate sensitivity and the interference arising from the presence of numerous other substances in the atmosphere. Nevertheless, good results can be obtained in the analysis of impurities in industrial atmospheres and in gaseous effluents when the determination is carried out directly on the gas stream or when suitable sampling devices are employed after the gas has been washed. In general, such methods are suitable for organic substances, in particular benzene and aromatic compounds. Infra-red spectrometry is more successful, on the other hand, since it can be applied to either solid, liquid or gaseous substances.

So far, most of these applications have been restricted to the field of research, but it is to be hoped that these techniques will have wider practical application, in view of the following advantages:

(1) all the molecules of a substance in the solid, liquid or gaseous state, as well as in solution, have a characteristic infra-red spectrum;

(2) a single spectrogram can serve to identify at one and the same time: the radicals, the elements with which they are substituted and their position in the molecule;

(3) the spectrum shows both the nature and the quantity of the substance being analysed;

(4) this gives an indication of the degree of purity of the sample prepared;

(5) the techniques used are very simple;

(6) only relatively small samples are required.

However, it should also be borne in mind that:

(1) the sharpness of the spectrum decreases with increasing molecular weight;

(2) in the present state of this technique, we have not sufficient knowledge to classify all the possible absorption bands, so that in many cases pure, standardized reference samples are necessary;

- (3) traces of impurity show up only if their absorption is high;
- (4) dilute solutions are difficult to analyse unless the substances present are strongly absorbent.

Samples for infra-red spectrophotometric analysis often call for considerable preliminary chemical manipulation and, with few exceptions, natural, untreated gas samples are not very suitable. The impurities must often be concentrated or isolated by means of absorption or cooling, or a combination of both, and in this way exceptionally high sensitivity can be attained, as in the case of ethylene, which can be detected in concentrations as low as three parts per thousand million of air by volume.

Other substances present in the atmosphere to which this type of analysis can be applied are: (a) mixtures of esters, aldehydes or alkalis, sampled by adsorption on charcoal, followed by condensation using an ice-salt cooling mixture or dry ice, and subsequent extraction with carbon tetrachloride; (b) chlorinated hydrocarbons, sampled by fractional condensation—benzene and hydrocarbons; and (c) carbon dioxide, carbon monoxide, hydrocyanic acid, water vapour, ozone.

Still in the field of spectrophotometric analysis, it is possible to make use of a phenomenon shown by certain substances—namely, the re-emission of the light energy absorbed in the form of a fluorescence, whose intensity is measured. By means of this measurement of fluorescence it is possible to analyse trace amounts of certain kinds of atmospheric components, but it is sometimes necessary to eliminate interfering substances so as to ensure the specificity of the determination.

The sensitivity obtained with this method is often less than 1  $\mu\text{g}$ . To date, it has been used for the detection of beryllium, antimony and hydrofluoric acid.

#### *X-ray diffraction methods*

These are suitable for the qualitative and quantitative analyses of crystalline substances, such as certain mineral dusts which can be present as a suspension in the atmosphere. However, X-ray diffraction methods should be considered rather as analytical procedures ancillary to other forms of analysis, such as emission spectrography or the methods of analytical chemistry. It is of particular interest that the samples used for such analyses can be recovered and used for other determinations employing other techniques.

X-ray diffraction methods also form part of the spectrometric methods, but while the latter involve measurements ranging from a wave-length of 40  $\mu$  (extreme limit of the infra-red) to 0.2  $\mu$  (extreme limit of the ultraviolet) X-ray diffraction measurements involve wave-lengths of the order of 0.0001  $\mu$ . The sensitivity of such methods thus arises from the great penetrating power of X-rays, also as regards solid bodies which are opaque to any other form of radiation.

It is known in fact from mineralogy that crystals can serve as diffraction gratings in the study of X-rays and that each crystal has its own particular diffraction pattern, so that it is possible to identify unknown substances by comparing their diffraction patterns with those of known substances. Quantitative determinations are sometimes possible, based on measurement of the intensity of the diffraction lines after having photographed them on a film. Nevertheless, these methods are mainly of qualitative interest since their quantitative sensitivity does not exceed one per cent of the substance examined. Moreover, they require very large samples and considerable practical experience on the part of the investigator. They are employed principally for the detection of quartz crystals in the air.

#### *Mass spectrometric methods*

Mass spectrometry is based on the principle that if a gas is ionized by means of electric discharges, and if the collimated beam of positive ions produced is subjected to the simultaneous action of an electric field and a magnetic field at right-angles to each other, then the ions are deflected from their initial straight-line direction of propagation and become distributed along a curve, the deflection being proportional to the mass of the ions. The result is a mass spectrum, and the apparatus which records it on a photographic plate bears the name of "mass spectrograph", while a "mass spectrometer" is an apparatus in which the radii of curvature of the paths of the various ions can be altered by changing the speed of the ions or the intensity of the magnetic field. In this way the nature and the quantity of the various kinds of ion can be determined by measuring the current flowing in a collecting circuit when the radius of the paths is changed.

Mass spectrometry has recently aroused some interest in connexion with the atmospheric pollution caused by petroleum refining, because of its rapidity and satisfactory sensitivity at the concentrations of waste gas involved. Naturally, this method calls for a wide knowledge of mass spectra in order to make comparisons and identifications. The samples need not be very large, but it is essential to isolate and concentrate the fractions to be examined and to convert these into gaseous form.

The method can be used for the identification of toxic gases with a sensitivity of 100 p.p.m. by volume with samples of only 50 ml of air. The sensitivity can be considerably increased by using samples concentrated by cooling, and in this way a sensitivity of 0.001 p.p.m. by volume can be reached in the case of certain compounds. The method is useful in particular for hydrocarbons and compounds of hydrocarbons with chlorine, nitrogen and oxygen.

#### *Polarographic methods*

Among the electrochemical methods of analysis listed at the beginning of this chapter must also be mentioned one making use of the chemical

phenomena which occur in an electrochemical cell, and based on interpretation of the ratio between current and potential difference. This method is generally referred to as voltametry or polarography, in the particular case where a dropping mercury electrode is used. In the polarograph, the voltage applied to the cell is regulated by means of a potentiometer and the current which passes through the cell is read on a galvanometer. These methods are applicable to the determination of any substance which can be reduced or oxidized, so that they can be used to identify a large number of organic and inorganic compounds.

To obtain the maximum sensitivity and specificity, various chemical treatments are necessary in order to isolate and concentrate the sample, although the simultaneous determination of several compounds is sometimes possible. Substances such as the following can be analysed polarographically: antimony, arsenic, benzene, bismuth, cadmium, chromium, cobalt, copper, formaldehyde, lead, manganese, nickel, oxides of nitrogen, thallium, tin, titanium, vanadium, and zinc.

Furthermore, it is possible to distinguish between a certain number of aldehydes and ketones (formaldehyde, acetaldehyde, butylaldehyde, crotonaldehyde, acetone, methylisobutylketone, cyclohexanone) in semi-carbamide solution. A sensitivity of 0.1  $\mu\text{g}$  of aldehyde per ml of solution can be attained.

#### *Methods using microscopy*

The use of microscopy in air pollution research is limited to the examination of particulate substances of all types for counting the particles themselves, measurement of their size, and optical observation of their surfaces. In this way the following can be examined: tarry matter, small drops of oil or water, crystals such as quartz and ammonium sulfate, nitrates, sulfates, halides, and ammonium carbonates.

Microscopy is sometimes combined with chemical procedures for the preparation of precipitation samples and their crystallization. According to the type of apparatus used, particles with diameters as small as 0.2  $\mu$  can be detected, and with the use of the electron microscope, which extends sensitivity to as low as 50  $\text{\AA} = 0.005 \mu$ , it is possible to study even smaller particles present in the atmosphere. While the non-electron microscope gives quantitative results only as regards the number and size of the particles, the electron microscope, although requiring a difficult and special preparatory technique, can yield an absolute analysis of particulate matter, since such apparatus can also be used for X-ray diffraction measurements with very small amounts of substance.

#### *Refractometric methods*

These are based on the use of the refractometer for determining the refractive index of the substance under study. The technique is of limited

application in air analysis, because of its lack of specificity and sensitivity. It can be used solely under conditions in which only one or two known vapours or gases are to be determined whose refractive indices are sufficiently different from that of air to permit a certain degree of accuracy at the lower concentrations.

Refractometric methods can be used for the analysis of emanations from waste gas pipes and in areas very close to the source of pollution. In this way, variations in the refractivity of the air due to an unknown proportion of vapour or gas present in it can be determined and, on comparing these values with the unit of change in refractivity—that is, the change caused by the presence of 1% of vapour or gas in the air at 25° C and 760 mm Hg (using standardized samples for the various substances)—the percentage present of the substance concerned can be determined.

#### *Thermal conductivity methods : combustion*

Since the measurement of the thermal conductivity of gases and vapours cannot serve to identify the gas, but is only a method for evaluating the concentration of known substances, procedures based on such measurements do not have a very wide application. They give only an over-all index of the thermal conductivity of a gas mixture and consequently can only be applied to those cases where the conductivity can be measured before and after eliminating a particular constituent, so that the latter can be determined from the difference.

In certain cases, however, it is possible to use a combustion apparatus known as an explosimeter, which gives the concentration of vapour or gas as a percentage with respect to the minimum explosion limit. In this method, a filament is electrically heated in special apparatus to a temperature at which the gas or vapour becomes oxidized and burns at the surface of the filament. In other cases, chemicals are used to bring about catalytic oxidation of the gas. The energy developed during oxidation (combustion) is then measured with a thermocouple. This is the method most used for determining carbon monoxide, but even in this case there is the difficulty of dilution.

Such methods are consequently of little value for work on air pollution and, as had been said, are limited to the industrial analysis of gaseous effluents.

#### *Other instrumental methods*

*Radioactivity.* Analytical methods based on the measurement of radioactivity have also been used in atmospheric analysis to detect substances and impurities present as traces. There are two basic methods for the measurement of radioactivity, deriving from the dilution and activation techniques, respectively.

In the first case—that of dilution—the element to be detected is diluted with one of its radioactive isotopes and the specific activity of the diluted substance is subsequently measured with a detector. This method calls for the isolation of a measurable amount of substance and is considerably upset by impurities and by samples which are not well selected. As regards air pollution, it is used practically only to measure the efficiency of smoke filters.

The second method—activation—is perhaps the most sensitive of all known analytical methods. It consists in the artificial transformation of the substances under examination into their radioisotopes and subsequent measurement of the quantity of disintegration product. This method is not subject to interference, because of the invariability and specificity of the half-life periods of the radioisotopes. However, as always in complex analytical methods using instruments, the greatest difficulties are those involved in the sampling, manipulation and preparation of the samples, apart from the problem of obtaining technical personnel with sufficient experience in this field of analysis and research.

*Sound absorption.* This method of analysis is used for measuring particle size. It is based on the fact that particles subjected to the influence of a sound field of a particular frequency are affected by those vibrations whose amplitude is related to their size. The instrument used for this purpose consists of a sound generator which can be adjusted to the desired frequency, a thin observation cell, towards which the sound is directed and into which the sample is introduced, combined with a lighting system and a means of observation or photographic recording. The photograms obtained show the paths corresponding to the vibratory movements of the particles, and by measuring them the particle sizes can be determined. However, very dilute samples are necessary, since only a few particles should be present in the cell if clear and interpretable photograms are to be obtained.

### *Conclusions*

From the preceding it can be seen how the same substance can be determined by a variety of methods. It is the task of the analyst to make a critical comparison of the various possible methods which can be applied. Some procedures are very suitable for routine work and not practicable for research work, and vice versa. No precise rules can be laid down for the choice of the method and means of analysis, except that those procedures should be selected which give the best “accuracy”, and highest “sensitivity”, the highest “selectivity” and the best “precision”, without forgetting that rapidity of analysis is also an important factor.

The “accuracy” is the sum total of the errors—absolute or relative—which can influence the results of an analysis. It should not be confused with “precision”, which represents the repeatability of the experimental

results. "Sensitivity" expresses, as an absolute quantity, the minimum amount of substance which can be analysed, or the minimum analysable concentration in a solution or in any other medium of dispersion. The "selectivity" of a method is shown by enumerating those substances which interfere with it.<sup>1</sup>

It is difficult to find a combination of all these properties in their highest degree in one and the same method. However, it is probable that by combining a wide range of techniques optimum results can be obtained. In the field of air pollution, nevertheless, there is always the inherent difficulty of sampling, as already discussed.

### Continuous recording instrumental methods

Under certain circumstances, calling for repeated analyses in order to determine the behaviour of a source of pollution and study its effects with respect to time, automatic, continuous recording apparatus are of value. These instruments combine the functions of sampling and analysis in the same apparatus. Although such apparatus is not usually extremely accurate, nevertheless it furnishes graphs which can be of great value in directing the research worker towards more-specific tests employing discontinuous sampling and analysis, under the conditions indicated as the most interesting ones.

Apparatus of this type is constructed on the basis of the chemical, electrochemical, optical and other principles already enumerated. It can be applied for research both on gaseous substances and on particulate matter.

In this field, most attention has certainly been directed to sulfurous anhydride among gaseous impurities, since it is the most widespread and the one which perhaps has given rise to most incidents and disputes. One of the most widely used automatic analysers for the determination of sulfurous anhydride is the Thomas autometer, which measures the electrical conductivity of the sulfuric acid solution produced by the oxidation of sulfurous anhydride following absorption in slightly acidified water containing hydrogen peroxide.

There are two versions of this apparatus, an accumulating and an instantaneous model. The accumulating types record conductivity continuously for absorption periods of 30 minutes, while the instantaneous types record the concentrations at two-minute intervals. Both types can be combined into a third or "mixed" type, in which the concentrations are determined at intervals of two minutes, as well as the average concentra-

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<sup>1</sup> It should be explained in this connexion that both in the foregoing and in the following pages, as can easily be seen, the figures for sensitivity are expressed sometimes by weight and sometimes by volume. In the first case this means, as previously mentioned, the minimum quantity of substance, as an absolute value, which can be analysed, while in the second case it means the minimum concentration of substance which can be detected in a gaseous mixture, whether waste gas or the atmosphere. Thus the expression "parts per million" indicates the number of cubic centimetres of substance under examination per cubic metre of gaseous mixture, under normal conditions of temperature and pressure—i. e., 0° C and 760 mm Hg.

tions over 30-minute intervals. Since, however, many gases or aerosols yield an electrolyte in solution, such apparatus measures the total pollution and not only that specifically due to sulfurous anhydride, although the total is expressed in terms of the latter.

Another apparatus, the titrilog, also measures sulfurous anhydride down to a concentration of 0.02 p.p.m. by volume, by means of oxidation of the gas stream in an electrolytic cell in the presence of bromine. Again, this apparatus is sensitive not to sulfurous anhydride alone but also to many other gases which can be oxidized, such as hydrogen sulfide, mercaptans and unsaturated hydrocarbons. On replacing the bromine by a starch-iodide solution and titrating the oxidizable substances photometrically, better selectivity is possible, since iodine is less reactive than bromine with such substances. Even in this case, however, it is not possible to eliminate all interference, at least as regards hydrogen sulfide.

With suitable modifications, however, such apparatus can be used in a more selective manner, so that the titrilog can also give values for hydrogen sulfide and the mercaptans and the autometer can detect any substance which gives an electrolyte in water, either directly or after combustion. Thus, the autometer can be used to determine hydrogen sulfide with a sensitivity of 0.01 p.p.m. by volume, following the production of sulfurous anhydride by combustion of the hydrogen sulfide on a platinum filament electrically heated to 550° C. The same apparatus, with lower selectivity and sensitivity, however, can also be used for measuring the amount of hydrofluoric acid present in the air.

For the latter compound another analysing apparatus has been developed with a sensitivity of 0.1 parts per thousand million by volume of hydrofluoric acid, which records the quantity of hydrofluoric acid by measuring the fluorescence which the latter produces with certain magnesium salts. Other equipment can give the concentration of hydrogen sulfide by measuring the variations in the intensity of light transmitted through plugs impregnated with lead acetate during the passage of a gas stream containing hydrogen sulfide. It is possible in this way to cover concentrations ranging from 0.1 to 500 p.p.m. by volume.

Recording analysers are also applied for the analysis of oxidants (ozone, oxides of nitrogen, chlorine). Such apparatus measures electrometrically or photometrically the amount of iodine liberated from solutions of potassium iodide by the oxidants.

An automatic instrument, the microsensor, can detect and measure many kinds of gaseous impurity in amounts as low as 0.1  $\mu\text{g}/\text{l}$ . It consists of a colorometric comparator which measures the colour changes produced on paper sensitized with special reagents. It is intermittent in action, with cycles varying according to the speed of reaction of the substances to be detected with the sensitizing reagents. In general, these cycles do not exceed 10 seconds in length.

Particulate matter can also be dealt with by recording apparatus. In these instruments, the intensity of light dispersed in the atmosphere owing to the presence of particles is measured and the visibility recorded directly. It is possible to relate these measurements of opacity to the particle concentration and size, following suitable calibration of the apparatus. The same principle—namely, measurement of the intensity of the light dispersed in the atmosphere owing to the presence of particles—is also made use of in apparatus counting the number of particles present, although the sensitivity of such measurements is rather low. The electrostatic principle is also applied to the continuous counting of particles, by measuring the impulses produced by the particles settling on the metallic filament which acts as precipitator. Instruments of this type are sensitive to particles  $2.5 \mu$  or more in diameter.

A modification of the autometer already mentioned makes it possible to record the quantity of sulfuric acid present in the air in the form of aerosol. This apparatus is provided with an electrostatic precipitator consisting of a rotating stainless steel disc which collects the sulfuric acid droplets and is washed by a continuous stream of water. In this way, a solution is formed whose conductivity is measured electrolytically. Naturally, this apparatus also measures any other acid mist and can be specific only if placed near a known source.

Another example of a sampler and analyser is a monitor for atmospheric radioactivity, in which the aerosol is deposited electrostatically on the sampling device, connected to a continuous recording radiation counter.

### **Instrumental methods for the control of radioactivity**

Among the causes of air pollution, those arising from radioactivity are becoming increasingly important, both because of the growing number of industries employing radioisotopes and because of the development of nuclear plants (both for power and for research), with the consequent production of fissile materials, decontamination of waste matter, etc.

Ionizing radiation causing pollution can vary very widely in type—that is, electromagnetic and corpuscular radiation, comprising alpha rays, beta rays, gamma rays, X-rays, proton beams, electron beams, slow neutrons and fast neutrons. Exposure to such radiations may cause considerable harm to living tissue, so that it is becoming increasingly necessary to employ suitable detectors in order to afford some protection against the possibility of harm of this kind. The problem is so important, and the reliability of the indications given by these detectors is such that occasionally, particularly in the case of measuring instruments installed near sources of pollution, they are fitted with alarm signals which are set off whenever the radiation level exceeds—in the zone under control—the danger limit which has been established for the various forms of radiation. The problem is rendered part-

icularly complex by the uncertainty of the definitions of the measuring units (both fundamental and derived) used for radiation and of the basic concepts related thereto. The physical nature and intensity of the radiation also present other difficulties, as does our still very slight knowledge of the results of the interaction between radiation and matter and its effects on the living cell and tissues.

Among measuring instruments in this field (including pocket control and safety detectors for plant personnel) the following may be listed: ionizing chambers; Geiger-Müller counters and proportional counters; scintillation detectors; photographic detectors; chemico-colorimetric indicators; and colorimetric measuring instruments.

## **Biological methods**

### *Effects on plants and animals*

It is often possible to identify a pollutant and a source of pollution by analysis of vegetation and of the body fluids of animals bred in the infected area. In certain cases, the tissues and organs of dead animals are very useful for the identification of toxic substances and the interpretation of the analytical results obtained. When, in fact, the concentration of a pollutant remains below the toxic level, there is no way in which its effect on plants and animals can be directly observed. However, when these limits are exceeded, harm is visibly caused to plant and animal life, according to the chemical nature of the pollutant, the time of exposure and climatic conditions. Sometimes the effects caused can be so specific as to serve as a sufficiently sensitive means of determining the nature of the contaminant. Complications may be introduced, however, owing to the concomitant effects of a variety of substances.

Biological studies of the effects on plant and animal life suitably exposed to the polluted atmosphere can be useful as regards both gases and particulate matter. Many tests are extremely sensitive and specific: beryllium can be detected in amounts as low as  $0.0003 \mu\text{g}$  and lead in as little as  $0.01 \mu\text{g}$ . Such tests may require very large samples, however, and often call in addition for the isolation and concentration of the components.

### *Sensory tests*

Finally a certain number of substances can be detected because of their organoleptic properties; odour, lacrimation and irritant effects on the respiration can be important factors, making it possible to assess the extent of pollution. In such cases, nevertheless, quantitative evaluation is seriously limited by the many subjective and physiological influences to which perception is exposed. The sensitivity of such methods is consequently very limited and they should be reserved in particular for qualitative research or reconnaissance, and be entrusted to specially "sensitive" personnel, trained

for the recognition of given substances on the basis of their organoleptic properties.

#### IV. CONCLUSIONS

As mentioned in the introduction, this report represents a preliminary contribution towards a selection from among the available material of whatever may seem most suitable for attaining a more limited range of tolerance. This is necessary in view of the infinite variety of special conditions and circumstances applying to the use of sampling and analytical apparatus and methods in the field of air pollution. In this paper, an attempt has therefore been made to select sampling methods and to give a critical review of analytical procedures in use at the present time, or potentially suitable for use, in the various laboratories of countries interested in the problem of air pollution.

However, as was foreseen and as has been mentioned, considerable difficulties were encountered from the outset in the classification, selection and interpretation of sampling and analytical methods and techniques. These difficulties are of some importance as regards the problem of ensuring that the presentation is universally understandable. From the outset they have arisen from a lack of uniformity among the various authors in describing their work—a lack of uniformity which is not limited moreover to nomenclature, but also extends to the presentation and interpretation of the data. For this reason it would seem advisable to conclude this report by giving a few suggestions, with the aim of eliminating, as far as possible, all uncertainty in the presentation, reading and interpretation of future contributions in this field. If these suggestions were followed it would be possible, without an effort out of proportion to the results, to ensure the highest degree of uniformity attainable in this field.<sup>1</sup>

(1) Definition of the terms and expressions used (and creation of any which may be necessary) seems essential in order to establish a glossary of terms relating to air pollution. This glossary, which could subsequently be converted into a multi-lingual international dictionary, would give a definite and authoritative interpretation of all words or expressions, and any circumlocutions which today may be necessary to indicate special circumstances and cases could be translated into precise and logical terms having an absolute, international significance. In this way it would be possible, in time, to create a technical and scientific language applying specifically to the huge field of air pollution and eliminating all words and expressions which—although idiomatically correct in the various languages—are not scientifically “precise”, this adjective being derived here from the noun “precision”

<sup>1</sup> It should be pointed out that standardization in the field of air pollution is being promoted by the Commission on Toxicology and Industrial Hygiene of the International Union of Pure and Applied Chemistry, and that the American Society for Testing Materials Committee D-22 has developed a programme for standard air sampling methods.

as used in chemical analyses, when it expresses the repeatability of experimental results.

(2) After having studied the large volume of work carried out in the fields of sampling and analysis as related to air pollution, and after having briefly explained the principles and the nature of the information supplied by a selection of the various methods and techniques employed, it appears urgently necessary to attempt to standardize the latter, so as to avoid any doubt or uncertainty in the comparison of experimental results from different sources.

The American Public Health Association, the American Water Works Association and the Federation of Sewage and Industrial Wastes Association have compiled a selection of standardized methods for the examination of water, sewage, industrial wastes, etc. This outstanding publication,<sup>1</sup> which has now reached its tenth edition, is still so young that it continues to include (and can hardly avoid doing so in future) methods indicated as under test—that is, methods which have not yet been sufficiently tried out and tested to be put forward as standard.

The proposal which we wish to make, therefore, is that of drawing up as soon as possible an initial list of sampling and analytical methods which might be termed “for guidance”. The various workers could, in the course of time, contribute the experience, controls and tests necessary to transform this list of methods “for guidance” into standard methods which, in addition to giving experimental details, would also state their efficiency, accuracy, precision and selectivity, with respect both to sampling and to analytical techniques.

It must be recognized, however, that such a task would involve considerable difficulties, because of the widely divergent conditions and circumstances under which the qualitative and quantitative examination of polluted atmosphere and of the open air may have to take place. These conditions and circumstances also exist in other fields, such as that of water supply, but on a much smaller scale, both numerically and quantitatively, so that it is easier to classify, prevent or overcome them. The initial work suggested as a basis should not be postponed because of this, however, since it could well be a source of improvements and developments in our knowledge of this particular field to an extent which might seem incredible at the present time.

(3) The presentation of analytical results should be made “uniform”, for in this field one is really confronted with a kind of babel, quite apart from differences between units of measurement, whether decimal or otherwise. Side by side with “grams per litre” and similar expressions, we find “percentage by weight” and “percentage by volume”, “parts per

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<sup>1</sup> *Standard methods for the examination of water, sewage and industrial wastes*, 10th ed., 1955, Baltimore, Waverly Press.

million by weight" and "parts per million by volume", as well as other mixed expressions. In addition to results converted to "0° C and 760 mm Hg", there are others expressed at "25° C and 760 mm Hg", as well as still other intermediate forms. Finally, sensitivity of the various methods, as well as being expressed in absolute figures, is expressed in relative values, and so on.

Results are expressed in so many and such diverse ways that usually the conversion of any considerable number of them, from one form to another, for purposes of comparison, becomes an arduous task, sometimes economically impracticable for reasons of time. Again, it should not be forgotten that there are many papers in which the data are reported without any reference to the units of measurement employed. All this shows how necessary, if not indispensable, is the standardization of the way in which results are expressed. Tables for the conversion of one form of presentation into another are not sufficient; it is also necessary for the standardized methods suggested above to employ definite and constant units of measurement. This would lead to an enormous saving of time and greater clarity in the results, as well as to an accurate technical and scientific picture of the possibilities and limitations of present and future research in the field of air pollution.

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