

ANALYTICAL METHODS FOR THE STUDY OF AIR POLLUTION

PHILIP W. WEST

*Environmental Sciences Institute, Coates Chemical Laboratories, Louisiana
State University, Baton Rouge, Louisiana 70803, U.S.A.*

ABSTRACT

Air pollution studies require a great variety of techniques. The analytical methods used should have great sensitivity and reliability and they must be applicable to organic as well as inorganic substances; they must apply to the study of gases, liquids (mists), and solids (airborne particulates); and they should be suitable for spot checking in the field and for continuous sampling and monitoring. Recent developments have contributed significantly in providing the necessary analytical chemical tools. Particularly important are the developments of gas chromatographic procedures, atomic absorption spectroscopy, new spectrophotometric and fluorimetric methods, and ring oven procedures. New reagents are being introduced that provide sensitive and selective reactions and ion-selective electrodes hold great promise.

INTRODUCTION

Pliny the Elder is said to have died due to volcanic fumes and protests were registered during the reign of Edward I (1272–1307) over pollution caused by the use of 'Sea' coal. During the reign of Edward II a citizen was punished by torture for filling the air with 'pestilential odour' resulting from his use of coal. During the following 500 years various observations of pollution and consequent attempts to regulate the use of coal are recorded, and in 1819 the British Parliament appointed a committee to study the possibility of smoke abatement. Parliament was concerned with the odours and health hazards of polluted air and apparently was also alarmed by the attack on buildings and works of art caused by the action of sulphurous and sulphuric acids that were produced from burning of high-sulphur coal.

The need for studying air pollution becomes apparent when it is recognized that in 1952, 4000 people in London died from 'air pollution' but no single pollutant could be cited as the lethal agent. Likewise, the 1948 episode in Donora, Pennsylvania, in which almost half of the population was made ill and many deaths occurred, has never been adequately explained in terms of specific pollutants. In both the London and Donora disasters, sulphur dioxide was found to be present. Likewise, in 1962, sulphur dioxide was found to exceed normal levels in London, Rotterdam, Hamburg, and the Eastern section of the United States and in each of the areas offended, there was a noticeable increase in death rate. Nevertheless, in each instance where sulphur dioxide might

possibly be associated with increased mortality rates, the levels measured were well below those considered to be lethal or even significantly hazardous. A great challenge in air pollution research at this time is the need for specifically identifying and determining the various pollutants that may be hazardous to health, or which may adversely affect corrosion rates or lead to such other economic losses as damage to crops. The magnitude of the problem is best appreciated when it is realized that the concentration of pollutants falls in the parts-per-million to parts-per-billion ranges and the absolute amount of a given pollutant may only be a few micrograms, nanograms, or even picograms per cubic meter. Furthermore, pollutants may be organic or inorganic materials and they may exist as solids, liquids (mists) or gases. It is obvious that the interest and the talents of the world's best analytical chemists should be captured to identify significant pollutants and to monitor and help control their levels in the ambient atmosphere.

The magnitude of the problem of defining what is significant is not always appreciated by the scientific community. Effects of air pollution may not be apparent except through statistical evaluations after months or years of exposure. Certain species may not be significant themselves but their metabolites may be of critical importance. Conversely, a given substance may exhibit harmful properties only when present in relatively high concentrations and yet be dastardly in certain mixtures because of synergistic effects. Too often, even analytical chemists think in terms of Al^{3+} , Cl^- , F^- and SO_2 but overlook the combined species such as $[\text{AlF}_6]^{3-}$, or do not study the amount of sulphur dioxide or hydrogen chloride that may be adsorbed on particulate surfaces such as alumina, sodium chloride or soot.

Before discussing analytical chemistry, let us consider the impact of air pollution and its true significance. First, we all have a vital interest in the problem—we may each have shortened (or lengthened) lives, depending on what is present (or absent) in the air where we live. Air pollution incidents such as those that have been recorded in London and Donora have had dramatic effects. Likewise, accidental emissions of large quantities of pollutants such as chlorine, phosgene, or hydrogen sulphide have resulted in loss of life in many instances—too many instances to record. But, what about the more insidious effects? Chronic respiratory illness, cardiovascular defects, cumulative toxins and carcinogens are all problems that must be considered.

Certain mundane topics should also be introduced. Corrosion costs millions of dollars a year in the United States alone. The soiling of fabrics by air pollutants likewise costs millions and the costs become astronomical when items such as pollution's contributions to light bills, traffic delays and damage to crops and other vegetation are included. Finally, aesthetic values should be appraised and few persons would deny that there are subtle losses caused by gloomy, smoky skies and grimy, bleak buildings.

ANALYTICAL APPROACHES

The analytical approaches employed in the study and control of air pollution are rapidly attaining a degree of sophistication that would have been impossible to achieve even one decade ago. The relatively crude and inefficient gravimetric and titrimetric methods once used have been replaced by sensitive,

reliable and rapid procedures such as those based on chromatography, infrared spectroscopy, fluorometry, spectrophotometry, atomic absorption spectroscopy and ring oven techniques. In spite of the progress that has been made, there is still much to be done. Fortunately, the fundamental principles are well established and most of the effort remaining can be directed toward their applications for air pollution study. In addition to the techniques mentioned above, developments and applications in the fields of the electron microprobe, x-ray fluorescence, ion-selective electrodes, thin-layer chromatography, specific reactions, dispersion staining and neutron activation will contribute significantly.

The needs for analytical advances fall in three general areas; critical or definitive studies, field tests and monitoring methods. The definitive studies of air pollution require analytical approaches that are the ultimate in reliability and sensitivity. Critical or referee determinations must provide exact data for research, standards for reference analytical comparisons and legally acceptable information for presentation in cases involving litigation. Field methods are required for emergency use and for surveys and similar investigations, where qualitative information and immediate quantitative approximations are required. Finally, there is great need for continuous and automatic measurements that can provide basic background data on pollutant levels, variations in concentrations, and interrelationships existing between significant species in complex mixtures of pollutants.

Among the common gaseous pollutants, sulphur dioxide, hydrogen sulphide, oxides of nitrogen, hydrogen fluoride, chlorine, hydrogen chloride, hydrogen cyanide, ammonia, carbon monoxide, ozone and hydrocarbons (and their derivatives) are of most general concern. Particulate pollutants are of interest in terms of the total dustfall, sootfall or stain index. The identification and determination of individual species is becoming critically important and it is no longer acceptable to report only simple values of mass or particle counts. For example, both organic and inorganic carcinogens should be measured. In the latter group asbestos, arsenic, beryllium, chromium and nickel have been indicted as carcinogenic to man; and lead, selenium, titanium, cadmium, cobalt, mercury, silver and zinc have been demonstrated to be carcinogenic in animal studies.

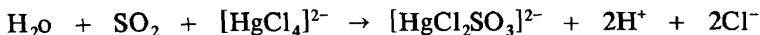
Much could be said about the determination of other gaseous pollutants, but here only brief comments on analytical methods for the more important pollutants can be offered.

Sulphur dioxide as a pollutant

Sulphur dioxide may be considered to be the most important air pollutant, because it is the most universally distributed and is associated with high corrosion rates, plant damage and general toxic effects. The determination of low concentrations of sulphur dioxide has long been a challenge. One problem associated with its determination, for example, has been that of sampling. Various trapping systems have been employed, such as the use of caustic solutions in bubbler devices, whereby rather large volumes of air are sampled and the sulphur dioxide is absorbed and fixed as the corresponding sulphite. This approach has suffered somewhat from lack of efficiency but even more, it

has suffered because of reactions that take place during sampling. The most obvious problem in this case is the atmospheric oxidation which converts part of the sulphur dioxide to the trioxide and thus prevents any exact determination of absolute amounts of either species. In addition to the problem of sampling sulphur dioxide, the determination itself has, until quite recently, been far from ideal. The usual procedure has been to acidify the collected sample and titrate the sulphur dioxide with standard iodine. Obviously such a method suffers from interferences from other reducing agents, such as sulphides, and lacks sensitivity. Other methods have been used such as trapping in hydrogen peroxide with subsequent titration of the sulphuric acid produced. Again the method is neither specific nor sensitive and the procedure is tedious.

In 1956 the so-called West-Gaeke procedure was published¹ which has become the definitive method for determinations of sulphur dioxide. The method is essentially specific, it is sensitive and reliable, and it is rapid and direct. The important innovation introduced by this method was the extraordinary efficiency of the sampling and stabilizing of the sulphur dioxide. Through the use of a trapping solution of tetrachloromercurate(II), the sulphur dioxide is efficiently isolated by the following reaction:



The dichlorosulphitomercurate(II) formed is remarkably stable and prevents the oxidation of the sulphur dioxide to the trioxide during the sampling and normal storage period. The analytical finish is by a spectrophotometric procedure based on the colour developed with acid-bleached *p*-rosaniline hydrochloride in the presence of formaldehyde. There are no interferences except from excessive amounts of oxides of nitrogen or from large amounts of certain metal salts. Any interference that may be anticipated can be obviated by very simple steps^{2,3}.

Field methods for determining sulphur dioxide are not generally satisfactory, so that it is best to use the West-Gaeke method, which can be done in a mobile laboratory or which can be employed by field sampling with subsequent determinations in a regular laboratory because the collected samples are stable for at least a week.

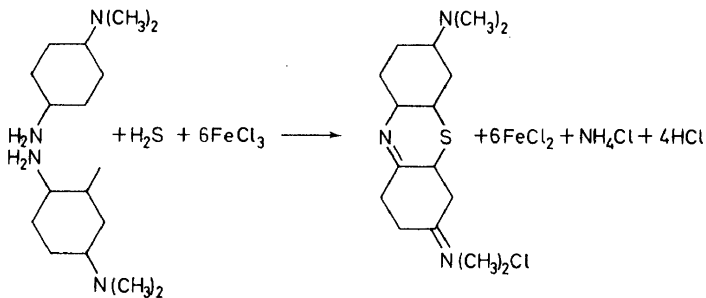
The monitoring of sulphur dioxide can be done by recording analyzers which may operate on any one of a number of principles. One approach utilizes the hydrogen peroxide scrubber to convert sulphur dioxide to sulphur trioxide and the resulting sulphuric acid is then measured conductimetrically. Because conductance is a general property of soluble electrolytes, some error is likely when this approach is used, although corrections can be made automatically that will balance out much of the background conductance caused by diverse electrolytes present in the air being monitored. Sulphur dioxide monitors have also been designed which utilize coulometry for measurement. Coulometry has been applied to bromimetric response to sulphur dioxide passing through an anodic detector having electrogenerated bromine. As bromine is reduced, an equivalent amount is replaced by electrogeneration from reserve bromides and the current flow is measured as a faradaic function of the sulphur dioxide present in the sample stream. Oxidizing or reducing agents must be absent or must be removed. The West-Gaeke method has been used in a number of ways in monitoring systems. The tetrachloromercurate(II) scrubbing and stabilizing

solution has been employed as a primary step in a coulometric instrument and the method has been utilized in its entirety in a spectrophotometric monitoring unit. A Technicon unit has also been adapted for utilization of the basic reactions of this procedure.

Much more could be presented in summarizing the development of methods for determining sulphur dioxide. Better perspectives result, however, when other pollutants are also discussed. As inferred previously, sulphur dioxide by itself probably cannot be indicted for deaths caused in the air pollution disasters that have dramatized the hazards of pollution. Instead, concern is noted over any and all pollutants and the true appraisal of the problem requires detailed knowledge of the nature of the ambient atmospheres and duration and intensity of each specific exposure.

Determination of hydrogen sulphide

For studies of hydrogen sulphide, the synthesis of methylene blue,



provides the basis for its determination in the parts per billion range as required for most surveys of community atmospheres⁴. The sulphide is trapped in an alkaline zinc or cadmium solution and the colour is developed and measured spectrophotometrically. The procedure is essentially specific. Field determinations are generally restricted to higher concentrations, 0.1 ppm or more, where odour nuisances are important. Detector tubes are satisfactory for the field studies and are readily available from commercial sources. The detector tubes usually contain support granules of gels impregnated with silver cyanide. Paper tapes impregnated with lead acetate are widely used for continuous monitoring with sequential tape samplers. Studies now in progress show the ion-selective sulphide electrode to be remarkably sensitive and reliable, and these electrodes should find wide use in field studies and in monitoring equipment.

Determination of nitrogen oxides

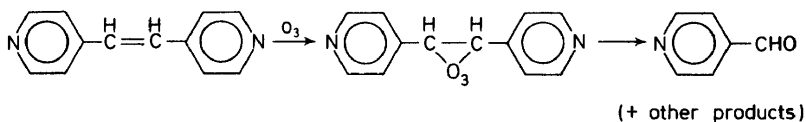
Oxides of nitrogen are important pollutants because of their physiological effects and corrosiveness, and because of their role in photochemical reactions to produce smogs. Nitrogen dioxide is the usual species measured, although total nitrogen oxides are sometimes obtained by oxidation of the various

species with hydrogen peroxide, after they have been trapped in alkaline solution. The Saltzman method, which is a modification of the familiar Griess-Ilosvay reaction employing sulphanilic acid for diazotization and *N*-(1-naphthyl)-ethylenediamine dihydrochloride for coupling, provides a very sensitive and reliable procedure for the determination of nitrogen dioxide⁵. The total oxides of nitrogen have not been as convenient to measure, their determination being dependent on the phenoldisulphonic acid method for nitrates which involves evaporation and other time-consuming steps; moreover, the method is subject to interference from chlorides and is relatively insensitive. The recent introduction of the chromotropic acid procedure⁶ has aided greatly in the solution of this problem, because it provides a sensitive, direct and reliable method for determining nitrates.

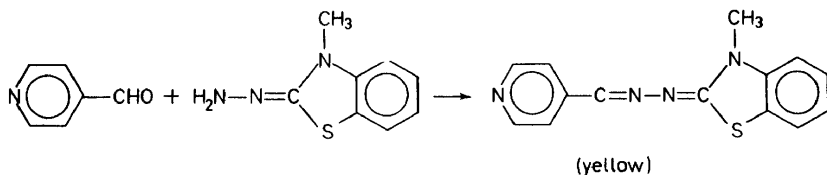
Determination of ozone

Ozone is a common pollutant which is an irritant accused of producing pulmonary fibrosis. It is also involved in photochemical reactions. There is a great need for a sensitive and reliable method for determining ozone. The standard procedures in present use are really oxidant determinations employing neutral or alkaline potassium iodide. Ozone and other oxidants oxidize iodide to iodine which is subsequently measured colorimetrically. Ozone, hydrogen peroxide, organic peroxides, chlorine and other oxidants all react to liberate iodine, so that the method is in no way specific. To make matters worse, dusts and certain reducing agents, which may coexist in the air, interfere and there is some interference from nitrogen dioxide.

A most significant contribution to the analytical chemistry of ozone has been made by Bravo and Lodge⁷ who employed the specificity of the ozonolysis reaction as the basis for determining ozone in air. They used 4,4'-dimethoxystilbene as the reagent; the resulting ozonide reaction product cleaves to form anisaldehyde which can then be determined by means of a very sensitive colorimetric reaction. This approach has been modified by Hauser and Bradley⁸ who proposed the use of 1,2-di(4-pyridyl)ethylene as the reagent. The pyridine-4-aldehyde produced by the ozonolysis:

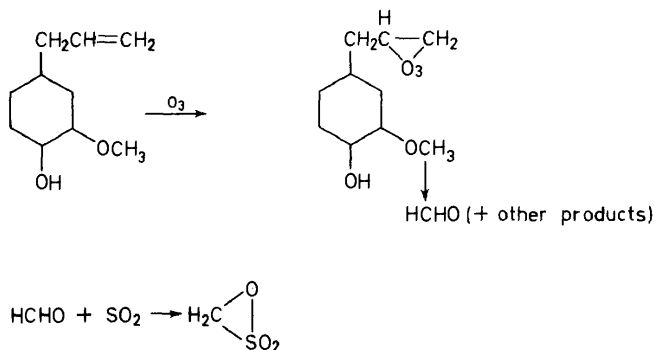


is then determined by a simple spectrophotometric method:



More recently, West, Lodge and Sachdev⁹ have studied the ozonolysis approach for determining atmospheric ozone, in an attempt to eliminate the

necessity of using hazardous reagents and with the goal of developing a rapid, stoichiometric and specific method. Because formaldehyde can be determined very readily by reversing the West-Gaeke method for sulphur dioxide, which has already been automated, a reagent was sought that would cleave to yield formaldehyde quantitatively. Eugenol was found to fit all requirements and the reaction steps, which are summarized below, provide a rapid, reliable and specific basis for determinations of ozone; the final product is determined



spectrophotometrically by means of *p*-rosaniline hydrochloride. This method of attacking the analytical problems of air pollution may serve as a guide, since a unique property of a pollutant has been exploited to provide the basis for a specific and sensitive measurement.

Determination of hydrogen fluoride

Hydrogen fluoride and soluble fluoride particulates present serious pollution problems, especially because of the serious damage that they may cause to vegetation. Exposure to as little as one part per billion of hydrogen fluoride may damage some plants, and concentrations of fluoride ion of $1 \mu\text{g}/\text{m}^3$ may harm a variety of plants, including gladiolas, apricots, prunes and peaches. Earlier methods for determining fluoride were directed mainly at high pollution levels and required tedious distillations and titrimetric procedures. With the general occurrence of low, but significant, amounts of fluoride, it is fortunate that two developments have now made it possible to make measurements at levels well below those previously considered possible. In 1959, Belcher, Leonard and West introduced alizarin complexan (alizarin fluoride blue) as a reagent for fluoride¹⁰. The Belcher reagent has been adapted for use in air pollution studies and provides an essentially specific, sensitive and reliable approach for fluoride determinations. Another important innovation has been the introduction of the ion-selective fluoride electrode. The single crystal, lanthanum fluoride electrode has proved to be sensitive and reliable and should soon find use in fluoride monitoring equipment.

The complexity of air pollution studies imposes requirements beyond the simple availability of a good reagent, sensor or instrument. For example, in the case of fluoride determinations it is not practical to measure the fluoride concentration in the ambient atmosphere itself but instead, a sample must be

collected by scrubbing a suitable volume of the atmosphere under study so as to trap the fluoride and establish it in some suitable aqueous system. Although fluoride can coexist in air with other common pollutants such as lead(II), calcium, manganese(II), iron(II and III) and aluminium, the sampling process introduces complications because of the incompatibility of such mixtures in aqueous solution. Many investigators have overlooked such problems or have chosen to ignore them. The isolation of fluorides from such possible interferences is normally a laborious and time-consuming process. However, a convenient procedure has recently been introduced which does permit the sampling and isolation of fluoride in a single step¹¹. The sample is collected by passing it through a pre-scrubber containing hot (70°) sulphuric acid which traps potential interfering species but permits hydrogen fluoride to pass through. The hydrogen fluoride is subsequently trapped in a second scrubber containing distilled water and the fluoride is then determined through the use of lanthanum alizarin complexan.

Determination of other pollutants

Because this cannot be a complete treatise, important pollutants such as chlorine, ammonia, hydrogen cyanides and carbon monoxide will be omitted from discussion. Likewise, organic gases will not be discussed, other than to mention that long-path infrared equipment has played an important role in the identification of a number of pollutants, and non-dispersive infrared equipment has been used for the monitoring of the total hydrocarbon burden. Infrared spectroscopy has also been used, of course, for studies of organic pollutants collected and concentrated from air by means of freeze-out techniques. Mass spectrometry has also been used to study pollutants, either concentrated by freeze-out or obtained by chromatographic concentration and separation. Gas chromatography has provided great assistance in the study of organic pollutants, and has been of the utmost importance in research, field studies and monitoring programmes.

The analysis of inorganic particulate pollutants has become increasingly important. Emission spectroscopy has furnished the most information to date, particularly for routine monitoring programmes such as that conducted by the U.S. Public Health Service. More recently, atomic absorption spectroscopy has been introduced for critical evaluations of metal concentrations. Atomic absorption methods have great advantages of selectivity and sensitivity while at the same time they are relatively uncomplicated and quite low in cost. Particulate samples can be collected by high-volume samplers, the particulates put into solution and the respective metals determined by relatively straightforward spectroscopy. Studies just completed show that there is considerable advantage in modifying this approach by introducing a dithizone extraction step to concentrate and stabilize the metals before their atomization and determination by atomic absorption spectroscopy^{12, 13}. The dithizone extraction is performed with ethyl propionate as the solvent; this proves to be extremely effective in enhancing the spectroscopic sensitivity, and at the same time it provides a convenient separation, free from hazards that might be encountered with other solvents. Through the use of mixed ligands, the extraction of metals into ethyl propionate can be extended to include most of the metals that are of greatest current concern.

ANALYTICAL METHODS FOR THE STUDY OF AIR POLLUTION

A provisional priority list of inorganic carcinogens has been proposed which includes arsenic, asbestos, beryllium, cadmium, chromium, cobalt, lead, nickel, selenium, silver and zinc. With the exception of arsenic, asbestos, chromium and selenium, all these species may be concentrated and stabilized through complexation with a dithizone-oxine-acetylacetone mixture followed by extraction into ethyl propionate, and then determined by atomic absorption spectroscopy¹⁴. Although the total exposure from all environmental sources must, of course, be considered ultimately, only the contributions due to air pollution are considered here. *Table 1* summarizes the present knowledge of inorganic carcinogens with respect to their known concentrations in United States atmospheres, and the applicability of atomic absorption spectroscopy to their determination.

Table 1. Atomic absorption spectroscopy of some inorganic carcinogens

<i>Metal</i>	<i>Concentration</i> [†] , $\mu\text{g}/\text{m}^3$		<i>Sensitivity</i> , $\mu\text{g}/\text{ml}$ (with 10 \times concn by extraction)	<i>Range for linear calibration graphs</i> $\mu\text{g}/\text{ml}$
	Ambient atmosphere	Industrial atmosphere		
Beryllium	1.4 max. 0.02 av.	variable	0.002	0.0-0.10
Cadmium	0.17 max.	variable	0.001	0.0-0.10
Cobalt		variable	0.004	0.0-0.20
Lead	6.3 max. 0.6 av.	variable	0.005	0.0-0.60
Nickel	0.83 max. 0.03 av.	variable	0.004	0.0-0.30
Silver	—	variable	0.002	0.0-0.3
Zinc	8.4 max. 0.01 av.	variable	0.001	0.0-0.10

[†] From Air Quality Data, National Air Sampling Networks, U.S. Department of Health, Education and Welfare, Public Health Service, Division of Air Pollution.

Of special interest are current investigations of the use of atomic absorption spectroscopy for continuous monitoring of important metals. Special spectrometers are being introduced for monitoring stations in New York City and Wayne County (Detroit), Michigan. In addition, an atomic absorption spectrophotometer has been developed for the direct monitoring of samples for silver content; the sensitivity is so good that as little as 3 μg of silver per cubic metre of air can be determined¹⁵. Of even greater importance is the development of lead monitoring equipment¹⁶ which readily measures directly the lead content of the ambient atmosphere.

Applications of the microscope

Some mention must be made of microscopical studies of airborne particulates. The microscope has been invaluable for obtaining particle counts, and in the hands of a competent microscopist it has often provided definitive information regarding the nature and possible sources of particulate pollutants. Identification of individual dust particles can often be made by simply noting the general appearance or crystal morphology. Polarized light microscopy has

often been useful in making more exact identification studies but the technique does have limitations; the two principal deficiencies are the special skill required and the need, usually, of relatively large particles so that sufficient optical data can be obtained for positive identification.

The recent introduction of dispersion staining for the identification of pollutant particles offers a compromise approach. This is an identification technique based on the refractive index characteristics of the particle being studied, compared to the refractive index dispersion of a selected liquid mounting medium. Annular stops in the back focal plane of a microscope are used to produce coloured particle boundaries. One stop (annular) shows a colour with wavelengths comparable to those at which the medium and particle match in refractive index. The second stop (central) shows the complementary colours of those shown by the annular stop, which represent wavelengths that are highly refracted by the particle. The dispersion staining colours can be systematically applied for identifying many isotropic and anisotropic compounds¹⁷. An extremely important reference covering this and other microscopical methods has been published by McCrone and his associates¹⁸.

Applications of the ring oven

A versatile technique for the identification and determination of airborne particulates involves the use of the ring oven. This technique was first described by Weisz¹⁹ and adapted to air pollution studies by West, Weisz, Gaeke and Lyles²⁰. The methods offer great promise for studies of particulate pollutants because they are rapid, convenient, sensitive and reliable. The equipment is very inexpensive, and the necessary technique can be acquired in a few hours. Ring oven studies can be used in the field and they are especially useful for the evaluation of dust stains collected on sequential tape samples²¹.

CONCLUSION

In spite of the great progress made during the past decade, methods for the analytical study of air pollution are still in great need of improvement. There is a real danger that too much confidence is being placed in faulty data obtained through use of antiquated methods by naïve investigators. There is an increasing problem caused by misplaced faith in black boxes that are advertised and sold as x, y, or z-analyzers. Highly trained analytical chemists realize that most black boxes are not specific in measuring the amount of a given species, but instead measure some general property associated with, but not limited to, the substance in question. The faith that many engineers, physicians, and scientists have in analytical methods and analytical gadgets is almost flattering; let us hope that thoroughly dependable instruments and procedures that have true selectivity or specificity can soon be provided so that this confidence will be justified.

To conclude this discussion let it be recorded that air is our most precious resource. The water we drink can be treated, altered or substituted; we can even avoid drinking water, as such, for extended periods of time. Likewise, foods are processed and modified according to our likes and needs; we can

live for days and even weeks without food. Air, however, is almost a fixed asset. There is only so much available. When we pollute it we must live in our own filth. We cannot avoid using it and we must all breathe the same quality of air, even if some might be able to afford a better product if it were available on an individual basis.

Society demands the establishing of air quality standards. These are now being developed and appropriate analytical techniques must be provided to enable the attainment of these standards through proper monitoring and control procedures. The responsibility of providing the critical analytical methods clearly rests with the specialists in analytical chemistry.

Acknowledgement

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