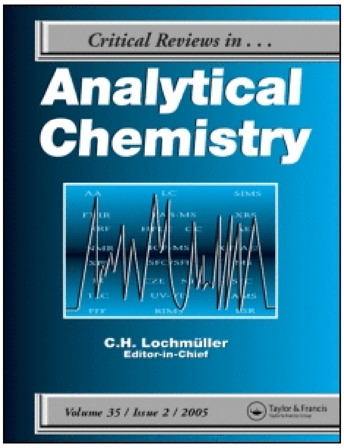

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RECENT ADVANCES IN AIR POLLUTION ANALYSIS

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I. INTRODUCTION

Atmospheric pollution has been with us for a very long time. The progress of urbanization and industrialization has entailed the exposure of ever more individuals to substantially polluted ambient air close to the source. Even those living in remote rural areas are often subject to exposure to transported pollution carried over hundreds or even thousands of kilometers in contaminated air masses.

Despite this long history of human exposure and the extensive implementation of air pollution control technology for more than a century, it is only over the past 20 years that attention has focused upon devising sensitive, specific techniques for the analysis of pollutants in ambient air. This, together with ever more sophisticated health-effects studies, has led governments to recommend and implement strict air quality standards, reliant upon comprehensive monitoring programs.

Since the science of air pollutant analysis is a rather recent one, a state-of-the-art review of the subject is akin to a review of recent advances, and such a treatment is attempted here. Emphasis is given to tried techniques of known practical application for field measurements. When appropriate, recent developments — not yet fully tested — will be described where they appear to offer a genuine improvement over presently available methodology and have a potential for use in the field.

The most important aspect of improved analytical methodology is the great advance in specificity which has been achieved in recent years. Many of the techniques in use 20 years ago suffered from major interferences and have been shown subsequently to yield unreliable results in ambient monitoring. Nowadays, in the case of most pollutants of ambient air, at least one technique without significant interferences is available to the analyst. Hand in hand with these advances in specificity have gone improvements in calibration techniques. In most of the older analytical methods, concentrations of a pollutant gas were inferred from the assumed stoichiometry of the analytical reaction. In some instances, particularly the analyses of nitrogen dioxide and ozone, the assumed stoichiometry has now been shown not to be realized in practice, and in some reactions variable nonintegral stoichiometric relationships have been demonstrated. Such advances have been made possible by developments such as the permeation tube which permits generation of a standard gas mixture of accurately known composition. Since for an analytical method the calibration is an essential component of the experimental procedure, in this review appropriate calibration methods are described for each pollutant rather than discussing advances in calibration methodology in a separate section.

The second most important advance in analytical methodology is the great improvement in sensitivity and response time over recent years. This has often arisen from the replacement of wet chemical methods of limited sensitivity, involving prolonged sampling times, by continuous physical sensors of extremely high sensitivity and rapid response. This improvement has allowed the study of lower pollutant concentrations than previously, and has enabled definition of the rapid temporal variations in concentration undergone by many ambient air pollutants. Such variations may be important in defining the health hazards and environmental damage associated with a particular pollutant. In many instances, long-term average measurements of concentration give an incomplete picture of the pollution at that location and fast response sensors are to be preferred.

In the area of particulate pollutant analysis, major developments have occurred in sampling methods, particularly in respect of size fractionation. In this context, it has recently become clear that interaction of some gaseous pollutants, particularly SO_2, oxides of nitrogen, or nitric acid vapor, with filter media can give rise to the formation of spurious contaminants. Hence SO_2 is converted to SO_4^{2-} when sampling through glass fiber media: giving entirely unreliable SO_4^{2-} analyses. Attention has also focused recently upon the identification of specific chemical compounds in atmospheric particles, rather than individual elements or ions. Such "speciation studies" will be reviewed.

Nowadays it is necessary to have concern for pollution of the stratosphere, as well as the troposphere. In this review, however, comment will be restricted to techniques of analysis of tropospheric air. It should also be noted that methods for the analysis of outside ambient air, rather than those used in the workplace or for measurements in the industrial stack, will be the subject of discussion.

II. GASEOUS POLLUTANTS

A. Sulfur Compounds

1. Sulfur Dioxide

A technique which merits mention if only for its longevity is the hydrogen peroxide method. Air is bubbled through one volume H_2O_2, in which SO_2 is converted to sulfuric acid:

$$SO_2 + H_2O_2 \rightarrow H_2SO_4$$

In the simplest form used in Britain by the National Survey of Smoke and Sulfur Dioxide[1] and by air monitoring networks in several other countries, the hydrogen peroxide is used at an initial pH of 4.5 to avoid interference from atmospheric CO_2 and is titrated back to this pH using sodium borate, upon termination of air sampling. The method has the advantage of cheapness, and is useful in indicating long-term pollution trends. Serious interferences detract from its value, however. Ammonia gives a stoichiometric negative interference, while HCl interferes in a positive sense. Additionally, evaporation of water during the 24-hr sampling period causes an alteration of pH and an overestimation of SO_2 concentrations.

Techniques have been developed based upon manual or continuous[2] conductimetric analysis of H_2SO_4 formed in hydrogen peroxide, but both are subject to interferences from a range of pollutants which enhance the conductivity of the solution. Perhaps the best approach is the analysis of sulfate formed from SO_2 collected in hydrogen peroxide. Use of this sampling technique in conjunction with ion chromatographic analysis of sulfate has shown a collection efficiency of 100% for SO_2 concentrations in the range of 24 to 1300 $\mu g/m^{-3}$ with a 24-hr sampling period.[3]

The U.S. Environmental Protection Agency (USEPA) reference method for SO_2 is based upon the West-Gaeke method and involves the collection of SO_2 as disulfitomercurate (II) in potassium tetrachloromercurate (II) solution:[4]

$$[HgCl_4]^{2-} + 2SO_2 + 2H_2O \rightarrow [Hg(SO_3)_2]^{2-} + 4Cl^- + 4H^+$$

The collected SO_2 is analyzed colorimetrically after addition of acidic pararosaniline and formaldehyde leading to formation of pararosaniline methyl sulfonic acid. The colored solution is reported to follow Beer's law over the range of 0.8 to 27 μg SO_2 in 25 mℓ of solution. The lower limit of detection is 25 μg/m^{-3} (0.01 ppm)* in a 30-ℓ air sample.[5] The method has been refined to overcome interference from oxides of nitrogen, by addition of sulfamic acid; ozone by time delay; and heavy metals by EDTA-disodium salt and phosphoric acid.[5] This method is still very widely used in air sampling networks, commonly with a 24-hr sampling period.

An extremely convenient means of SO_2 collection involves the use of impregnated filters. These may be impregnated with 0.5 *N* KOH;[6] 25% K_2CO_3 in a 10% glycerol/water (humifactant) medium[7] or tetrachloromercurate.[8] After addition of the impregnating reagent to a cellulose filter, excess reagent is removed and the filter dried under an infrared lamp. Collection efficiency is very high at face velocities up to 70 or 90 cm/sec^{-1} for K_2CO_3/glycerol and KOH, respectively[7,6] and relative humidities from 30 to 100%. The collected sulfite is subsequently leached from the filter and oxidized to sulfate prior to analysis in this form. To avoid interference from atmospheric particulate sulfates, these are removed from the air stream by filtration prior to passage of the air through the impregnated filter. Johnson and Atkins[9] reported that unexposed filters impregnated with K_2CO_3/glycerol/water gave a blank analysis of <1.1 μg SO_2 per filter, and that SO_2 in a 0.5 m^3 sample, obtained in about 10 min, could be determined to 2 to 3 μg/m^{-3}. Impregnated filter papers may conveniently be used in conjunction with automatic tape samplers[10] allowing good temporal resolution of concentration data from unattended monitoring stations.

Electrochemical methods can provide continuous sensitive analysis of SO_2 in air. Commercially available coulometric instruments depend upon the reduction of free iodine or bromine by SO_2:

$$SO_2 + I_2\,(Br_2) + 2H_2O \rightarrow SO_4^{2-} + 2I^-\,(2Br^-) + 2H^+ \qquad (1)$$

Air entering the instrument passes initially through a silver wire scrubber which eliminates interferences from H_2S, O_3, and Cl_2, but allows passage of some NO_2 which gives an interference of <5% on a mol/mol basis and mercaptans which give 100% interference.[10] The air stream then enters an aqueous solution of KBr, Br_2, and H_2SO_4. Reduction of Br_2 occurs according to reaction (Equation 1). By means of two electrodes in the cell, the Br_2 concentration is converted to redox potential which is compared continuously with a reference potential. A drop in the Br_2 concentration causes passage of current through the cell via two other electrodes which causes oxidation of bromide to bromine until the original Br_2 level is restored. The current passed relates directly to the mass of SO_2 introduced into the cell. Response times of 30 sec (90% rise) with a detection limit of 5 μg/m^{-3} are possible in instruments which incorporate auto-zero and calibration and are designed for 3 months unattended operation.

An alternative electrochemical method has been described by Lindqvist[11] and is based upon the anodic oxidation of SO_2 in a galvanic cell. Sample air is passed through a porous anode against a head of electrolyte on the other side, and a differential measurement technique with a cell with two anodes and one cathode is used. The lower detection limit is about 3 μg/m^{-3} and the response time (90% rise) is 66 sec at a concentration of 42 μg/m^{-3} and 16 sec for 150 to 750 μg/m^{-3}. Generally good agreement with measurements using other established methods was found.[11]

Possibly the most frequently used continuous technique of SO_2 analysis is based upon the flame photometric detector. Gaseous sulfur compounds are burned in a reducing hydrogen/

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* In air pollution terminology, 1 ppm is a volume mixing ratio of 10^{-6}; 1 ppb is 10^{-9}; and 1 ppt is 10^{-12}.

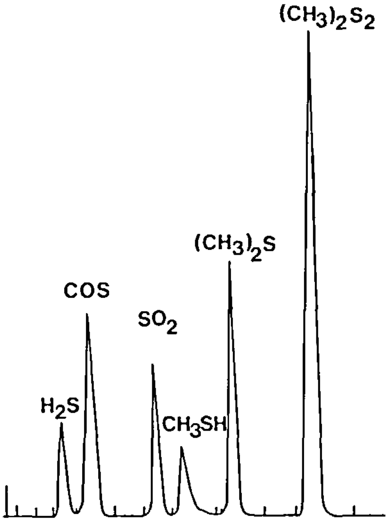


FIGURE 1. Typical chromatogram of volatile sulfur compounds,[16] obtained on an acetone-washed Porapak QS column (R = CH_3) now sold as Supelpak-S.

air flame and the emission of the S_2 species at 394 nm is measured[12] using an optical filter and a photomultiplier tube. In most urban atmospheres, the reading of the flame photometric analyzer is an excellent measure of the SO_2 concentration.[13] In other environments, however, such as in the vicinity of a Kraft mill, interferences from other sulfur compounds are important. The major interferent, H_2S, may be eliminated by use of a silver wool scrubber[14] and other scrubbers of undefined composition are available commercially which remove all reduced sulfur compounds.

The use of gas chromatographic separation of volatile sulfur compounds prior to flame photometric analysis was first proposed by Stevens and co-workers.[15] This gave separation of H_2S, SO_2, CH_3SH, and $(CH_3)_2S$, but not of H_2S and COS in a 10-mℓ air sample. Using a teflon® column packed with acetone-washed Porapak QS, de Souza and co-workers[16] were able to separate H_2S, COS, SO_2, CH_3SH, $(CH_3)_2S$, and $(CH_3)_2S_2$. Using an electrically switched gas sampling valve, the system may be automated and allows analysis of the individual gaseous sulfur compounds with a detection limit of 5 to 10 ppb (Figure 1).

When used as a continuous analyzer, the normal flame photometric sulfur detector has a detection limit of 0.5 ppb with a response time (90% rise) of about 25 sec. A very much faster response detector has recently been described[17] having a response time of 80 msec. It is shown in Figure 2. One problem inherent in very fast response analysis of SO_2 is that sample lines, even when constructed of teflon®, appear to adsorb SO_2, especially at higher relative humidities, causing an extended response time.[18]

Another method available commercially uses gas phase fluorescence of SO_2 excited by pulsed light of wavelength 214 nm.[19,20] The technique is very sensitive (0.5 ppb detection limit), but the more sensitive instrument is of rather slow response time, with a 90% rise time of 2 min. Interference due to quenching of excited SO_2 by other molecules is a possible problem.[21]

The preferred means of calibration of SO_2 uses a permeation tube. This consists of an FEP-teflon® tube containing liquid SO_2.[22] When maintained at a constant temperature, SO_2 permeates through the wall of the tube at a constant rate which may be determined gravimetrically. Hence the permeation tube is suspended in a constant temperature oven through which a constant, measured flow of clean air is passed, thus generating a standard atmosphere of precisely known composition.

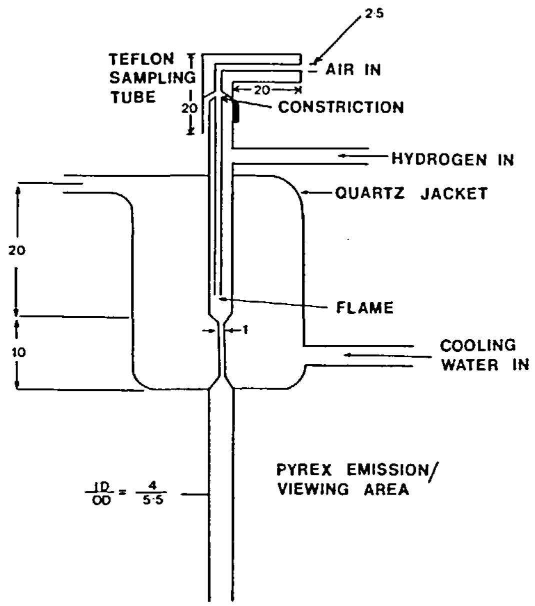
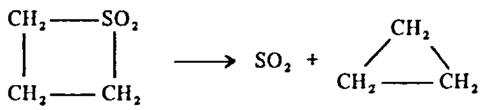


FIGURE 2. Burner design in fast response analyzer for sulfur dioxide.[17] Approximate dimensions are in millimeters.

An interesting alternative calibration technique which appears never to have been exploited widely is based upon thermal decomposition of trimethylene sulfone.[23] This compound is maintained at constant temperature and volatilized into a controlled gas stream. The resultant gas stream is passed through a heated tube causing pyrolysis of the sulfone in reactions such as



The SO_2 concentration is dependent upon the vapor pressure of the sulfone, from which it may be calculated. Alternatively, gas chromatographic analysis of the hydrocarbon product may be used as a measure of SO_2 formation.

2. *Other Gaseous Sulfur Compounds*

Recently, some interest has focused upon other gaseous sulfur compounds (H_2S, CH_3SH, $(CH_3)_2S$, $(CH_3)_2S_2$, CS_2, COS) because of their role in the global sulfur cycle. Gas chromatographic analysis with flame photometric detection, as described above, is suitable for analysis at the ppb level.[15,16] If greater sensitivity is required, preconcentration must be carried out prior to gas chromatography. Braman et al.[24] describe the use of gold-coated glass beads to preconcentrate H_2S, giving an ultimate detection limit of 0.1 ppt for a 100ℓ sample, although some interferences were found. Using cryogenic trapping with liquid nitrogen, Sandalls and Penkett[25] were able to analyze COS, CS_2, H_2S, SO_2, and $(CH_3)_2S$ at concentrations down to 0.02 ppb.

B. Nitrogen Compounds

1. *Nitric Oxide and Nitrogen Dioxide*

Other than close to a major source of nitric oxide, the predominant compound in ambient air is normally nitrogen dioxide due to rapid atmospheric oxidation of NO by ambient ozone.

The older, wet chemical procedures of analysis are based upon trapping of NO_2 as nitrite which is used in a diazotization reaction and determined subsequently as an azo dye.

Until quite recently, the U.S. reference method for NO_2 in ambient air was a modification of the method of Jacobs and Hochheiser,[26] in which nitrogen dioxide is collected in a bubbler containing 0.1 *M* sodium hydroxide solution. The resultant nitrite is used to diazotize sulfanilamide (4-aminobenzene sulfonamide) and coupled with N – (1-naphthyl)ethylenediamine [N – (naphthalene-1 ethane-1,2-diamine)] in an acid medium, leading to formation of an azo dye which is determined spectrophotometrically at 540 nm. The method is calibrated with standard nitrite solutions and a collection efficiency of 35% was assumed, with results corrected accordingly.[27] When calibration with NO_2 generated dynamically from permeation tubes was attempted, however, collection efficiencies from 15 to 70% were found, dependent upon the NO_2 concentration, and an interference from NO was also revealed subsequently.[27]

The nonstoichiometric nature of the NO_2 to nitrite conversion has also led to doubts over other analytical procedures. In the once-common Saltzman procedure, NO_2 is collected in a fritted bubbler containing an aqueous mixture of sulfanilic acid (4-aminobenzene sulfonic acid), N – (1-naphthyl) ethylenediamine dihydrochloride, and acetic acid.[28] The technique is normally calibrated using solutions of nitrite, despite the report of Saltzman[28] that the stoichiometry is variable in the range of 0.48 to 0.72 mol of nitrite per mol of NO_2, and that different designs of bubblers vary substantially in their efficiency with respect to NO_2 sampling. Stoichiometry factors for continuous NO_2 analyzers based on the Saltzman reaction have been found to be in the range of 0.7 to 0.9.[29] A negative interference by ozone has been demonstrated by Baumgardner et al.[30] in the continuous analyzer, but Adema[31] questions the existence of this interference for manual sampling. Dependent upon the sample bottle and reagent purity, either zero, positive, or negative interferences were observed in the manual Saltzman method.[31]

Modifications to the Jacobs-Hochheiser procedure have been proposed. Axelrod et al.[32] suggested the determination of nitrite by fluorometric analysis with 5-aminofluorescein. This method increased analytical sensitivity substantially, allowing measurement of NO_2 levels as low as 0.01 ppb. These authors, however, explicitly ignored the problem of variable stoichiometry and collection efficiency. The latter parameters may be improved by addition of 0.1% sodium arsenite to aqueous sodium hydroxide absorbing solution. This is intended to increase the rate of conversion of NO_2 to nitrite and gives a constant high collection efficient of 82%.[33] Nitric oxide and carbon dioxide are positive and negative interferents, respectively, but cause an insignificant effect at normal urban pollutant levels.[33] In a collaborative test, it was concluded that this method will produce accurate, precise measurements of ambient NO_2 concentrations,[34] and indeed the method has been adopted by a number of air monitoring networks. The lower detection limit is reported as 8 $\mu g/m^{-3}$.

An alternative sampling medium for NO_2 is triethanolamine in aqueous solution.[35] Gold[36] suggests reactions as follows:

$$2\ NO_2 \rightleftharpoons N_2O_4$$

$$N_2O_4 + (HOC_2H_5)_3N \rightarrow (HOC_2H_5)_3\overset{+}{N}NO(NO_3^-)$$

$$(HOC_2H_5)_3\overset{+}{M}NO(NO_3^-) + H_2O \rightarrow (HOC_2H_5)_3\overset{+}{N}H(NO_3^-) + HNO_2$$

The predicted NO_2^-:NO_2 stoichiometry of 0.5 was found in practice only at concentrations above 10 ppm NO_2 and was somewhat variable at lower concentrations,[36] rendering the method of rather limited value.

Mulik and co-workers[37] adopted an empirical approach in attempting to find an improved NO_2 sampling reagent. They recommended an absorbing solution containing triethanolamine, guaiacol (*o*-methoxyphenol), and sodium metabisulphite, with analysis of collected nitrite

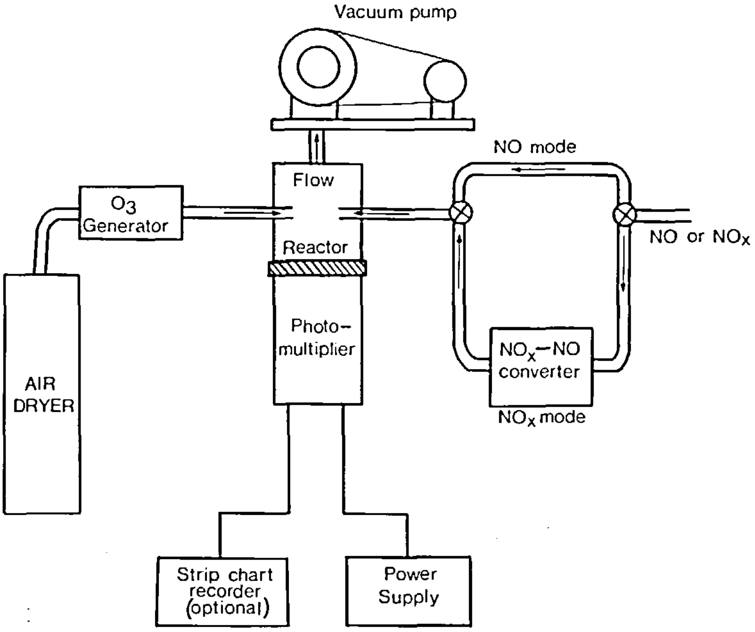


FIGURE 3. Chemiluminescent analyzer for NO and NO_x.

as an azo dye using sulfanilamide and ANSA (8-anilino-1-naphthalenesulfonic acid). A 93% collection efficiency was found in the range of 20 to 750 $\mu g/m^{-3}$ NO_2 without apparent interferences.[37] An independent testing of this method also showed high collection efficiency, but with considerable scatter.[38] The method is particularly convenient for 24-hr sampling, when analysis may be delayed.

Copper shot may be used as an absorbent for NO_2 at ambient levels. Heating in a hydrogen carrier stream causes desorption of collected NO_2, which may be catalytically converted to ammonia.[39]

If wet chemical analysis of NO is required, then analysis of NO_x (i.e., NO + NO_2) is carried out by prior oxidation of NO in the air sample to NO_2. This was at one time most commonly carried out using acidic potassium permanganate, but the oxidation process is by no means quantitative, with an efficiency of 70% being typical.[40] More recently, the use of chromium trioxide coated on firebrick or molecular sieve[41] has become common. This reportedly gives an oxidation efficiency of 100%,[41] allowing determination of NO concentrations by difference.

The technique used by most air monitoring networks for oxides of nitrogen analysis is based upon the chemiluminescent reaction of nitric oxide from ambient air with ozone produced by an ozonator within the instrument:

$$NO + O_3 \rightarrow NO_2^* + O_2$$
$$NO_2^* \rightarrow NO_2 + h\nu$$

The electronically excited NO_2 emits light in the 600- to 3000-nm region with a maximum intensity near 1200 nm.[42] In the presence of excess ozone, the light emission intensity varies linearly with the concentration of nitric oxide from 1 ppb to 10^4 ppm.[42] The apparatus is shown in Figure 3, and may have a response time (90% rise) as low as 2 sec. There are no known interferences in the chemiluminescent analysis of NO. Commercial analyzers also measure NO_2 by prior conversion to NO (and hence determination of NO_x) in a heated carbon, stainless steel, or molybdenum converter. Some instruments cycle between an NO

Table 1

RESPONSE OF TWO COMMERCIAL CHEMILUMINESCENT NO-NO_2-NO_x ANALYZERS TO NITROGEN-CONTAINING COMPOUNDS IN NO_2 AND NO_x MODES[43]

Compound	Converter[a]	Response[b] (%)	Standard deviation (%)	Linear correlation coefficient	Range of concentration tested (ppb)
Peroxyacetyl nitrate	M	92	1.0	1.00	0—410
Nitric oxide[c]	M	102	1.0	1.00	0—140
Peroxyacetyl nitrate	C	98	3.0	1.00	0—500
Nitric oxide[c]	C	100	1.0	1.00	0—145
Ethyl nitrate	M	103	6.0	0.99	0—355
Ethyl nitrite	M	92	1.0	1.00	0—66
Nitroethane[d]	M	6	0.4	0.96	0—340
Nitroethane[e]	M	7	0.3	1.00	0—240
n-Propyl nitrate	C	92[f]	—	—	—

[a] M, molybdenum; C, carbon.
[b] Least-squares analysis over indicated range of concentration.
[c] Measured in the NO_x mode with no NO_2 in the same stream — i.e., NO = NO_x.
[d] Air diluent.
[e] N_2 diluent.
[f] Determined for a single concentration.

mode, in which ambient air passes direct to the reaction chamber, and an NO_x mode involving prior passage of the air through the converter, as in Figure 3. The disadvantage of this arrangement is that as only NO or NO_x is measured at any one time, NO_2 measurements are inevitably rather imprecise, especially if rapid temporal variations in NO or NO_2 are occurring. This problem is largely overcome in later instrument designs involving two reaction chambers, one run continuously in the NO mode, and the other measuring NO_x. The chemiluminescent reactions are monitored either by two photomultiplier tubes, or by alternate exposure of a single photomultiplier tube to the light from each reaction chamber. By such an arrangement, near real-time NO_2 measurement is possible.

In an important paper, Winer et al.[43] report an examination of the interferences in the chemiluminescent analysis of nitrogen dioxide caused by reduction of other nitrogenous air pollutants to NO in the converter. Both carbon and molybdenum converters were found to cause a near-quantitative positive interference from peroxyacetyl nitrate (PAN), ethyl and propyl nitrates, and ethyl nitrite, while nitroethane gave a much smaller positive interference. The degree of interference relates linearly to concentration, the results being shown in Table 1. This interference is probably of little significance in most ambient air monitoring applications, but may be important in some instances, especially those related to laboratory studies of chemical reaction of atmospheric significance where, e.g., PAN/NO_2 ratios higher than those in ambient air may be created. Some halocarbons also interfere,[44] but this is unlikely to be of significance in ambient air monitoring.

A comparative study of instrumental methods for NO_2 analysis has been reported.[45] Chemiluminescent analyzers were found to have advantages over coulometric or colorimetric analyzers in terms of response time and required maintenance. The use of polyethylene sample lines is to be avoided,[18] while short teflon® sample lines are free from interference.[18]

Calibration of NO/NO_x analyzers is not an entirely straightforward matter. Cylinders of dilute NO calibration gas are readily available and serve to calibrate the NO mode of a chemiluminescent analyzer. Standard atmospheres of NO_2 are less readily available, but may be generated using permeation tubes. Problems can arise from diffusion of water vapor into NO_2 permeation tubes (affecting gravimetric calibrations) unless the tube is always kept in

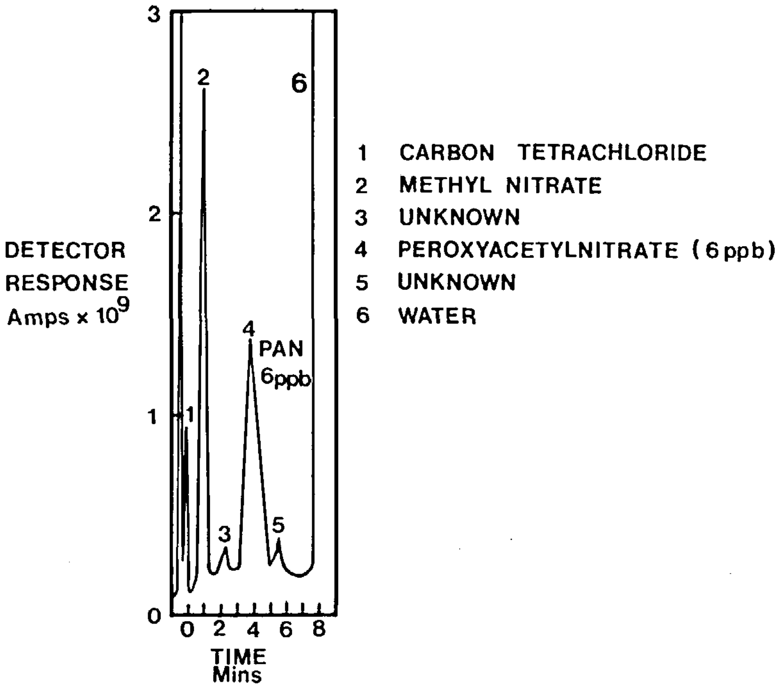


FIGURE 4. Chromatogram from the determination of PAN in ambient air.[10]

a dry environment. A better solution is the use of gas phase titration, in which a standard atmosphere of NO is oxidized quantitatively to NO_2 by excess ozone, generating a known NO_2 atmosphere.[46] Any NO_2 impurity in the NO cylinder will cause an interference, and must be determined by an independent method such as the TGS method.[46] Gas phase titration equipment is commercially available and may be used also for calibration of ozone analyzers.

2. *Nitrous Oxide*

Until recently this was a compound of little interest to the atmospheric scientist due to its very low chemical reactivity in the troposphere. Concern over its possible effect upon concentrations of stratospheric ozone has stimulated some interest of late.

Bock and Schutz[47] report the preconcentration of nitrous oxide from ambient air upon molecular sieve type 5A, from which it may be desorbed at 250 to 300°C into a gas chromatograph where it is separated on a molecular sieve type 5A column and detected by a thermal conductivity detector. LaHue and co-workers,[48] however, report that N_2O is thermally unstable at 250 to 300°C and recommend desorption from the molecular sieve trap by water vapor-saturated helium, with subsequent collection on silica gel in a dry ice/isopropanol bath. Heating of the silica gel is used to transfer the N_2O to the gas chromatograph.[48] A silica gel column and helium ionization detector have also been recommended for gas chromatographic analysis of nitrous oxide.[49]

3. *Peroxyacyl Nitrates*

The most important of these compounds, peroxyacetylnitrate (PAN), is analyzed by gas chromatography using electron capture detection according to the method of Darley and co-workers[50] modified by the Intersociety Committee.[51] Air from a 2-mℓ stainless-steel sample loop is swept onto a teflon® G.C. column containing 5% Carbowax E400 on 100/120 mesh HMDS-treated Chromosorb W. Other electron capturing constituents of the air are also detected, giving a chromatogram such as that shown in Figure 4.[10]

The system is calibrated using a standard atmosphere of PAN, produced in the laboratory by photolysis of ethyl nitrite in pure oxygen.[51] The PAN so formed is assayed by infrared absorption measurement[52] prior to dilution and injection into the gas chromatograph.[10] The method is sensitive to less than 1 ppb of PAN and has no known interferences. The response of the electron capture detector to PAN is linear at the lower concentrations typical of the atmosphere, but shows nonlinearity as concentrations approach 1 ppm.[10]

Holdren and Rasmussen[53] have described an effect of water vapor upon the gas chromatographic analysis of PAN in which sensitivity is decreased substantially at low relative humidities. When these observations were tested by Lonneman[54] at the U.S. Environmental Protection Agency, no such effect was found and these authors concluded that it was an artefact of the equipment used by the former authors.[53] Holdren and Rasmussen,[55] however, reported other observations of this phenomenon, and later Watanabe and Stephens,[56] in reviewing the situation, concluded that PAN losses occurred only in dry acid-washed flasks, probably due to adsorption on active sites. The use of moist air as a calibration medium was recommended.[56]

In smog chamber studies, Pitts and co-workers[57] have used a high resolution Fourier multiplex infrared spectrometer to identify various secondary pollutants, including PAN. This technique has also found application in the analysis of ambient air.

4. Nitrous Acid and Nitric Acid

Both of these substances are of considerable importance as secondary pollutants, but present considerable analytical problems. Few ambient air analyses have been reported.

Nash[58] has reported analyses of HNO_2 in ambient air made by sampling through bubblers in series containing first 0.1 *N* alkali and then 0.004 *M* guaiacol (*o*-methoxyphenol). The former reagent collects HNO_2 quantitatively and a small portion (about 10%) of the more abundant pollutant NO_2. The latter bubbler collects all NO_2 converting 73% to nitrite.[58] Analysis of the nitrite in each bubbler using Saltzman's reagent and the application of a correction for the NO_2 converted to nitrite in the first bubbler allows estimation of the nitrous acid concentration.[58] Interferences from other pollutants which might yield nitrite upon alkaline hydrolysis require investigation.

A variety of techniques has been reported for the analysis of HNO_3. Measurements are complicated by the fact that particulate ammonium nitrate is in equilibrium with gaseous NH_3 and HNO_3, and removal of either gaseous constituent from the air will displace the equilibrium. This question is discussed further in the context of analysis of particulate nitrates *(vide infra).*

Nitric acid vapor may be separated from particulate nitrate by passage through an inert filter (quartz or teflon®). Absorption of HNO_3 in water or dilute alkali generates nitrate, but this cannot be discriminated from nitrate formed together with nitrite when NO_2 is dissolved in water. Hence some more selective form of HNO_3 collector is required, and Okita et al.[59] used a cellulose filter impregnated with sodium chloride, which collects HNO_3 selectively by the reaction:

$$NaCl + HNO_3 \rightarrow NaNO_3 + HCl$$

The collected nitrate is then determined via wet chemical means. This system was tested extensively by Forrest and co-workers[60] who found HNO_3 collection efficiencies of approximately 95% for NaCl-impregnated filters placed downstream from a pretreated quartz particulate filter. Interference due to nitrate formation from NO_2 on the NaCl filter was nil, but some NO_2 and HNO_3 formed nitrate on the quartz filter, especially at higher relative humidities.[60] Other interferences arise from decomposition of nitrates on the quartz filter in contact with sulfuric acid aerosol, releasing gaseous HNO_3 and also from partial volatilization of NH_4NO_3 from the quartz filter *(vide infra)* during prolonged air sampling, which is then collected as HNO_3 on the impregnated filter.[60]

Continuous measurements of gaseous HNO_3 with a ppb detection limit may be made by a chemiluminescent technique. A dual reaction chamber NO-NO_x monitor is modified by fitting a molybdenum converter to the inlet of both reaction chambers, hence placing both chambers in an NO_x mode.[61] One inlet is then preceded by a nylon filter which removes gaseous HNO_3, but allows passage of all other contributors to the NO_x signal. The difference between the signals from the two channels is then representative of the HNO_3 concentration. It should be noted that Winer et al.[43] tested the response of a commercial chemiluminescent NO-NO_x analyzer to HNO_3 and found an ill-defined response function indicative of reaction of HNO_3 with sample lines and instrument components. Hence any development of a system such as that reported by Joseph and Spicer[61] would require considerable verification in terms of sensitivity to HNO_3 and linearity of response.

Both HNO_2 and HNO_3 have been identified by Fourier transform IR in smog chamber studies,[57] and Hanst et al.[62] claim a detection limit of 10 ppb for HNO_3 in ambient air using a long path infrared absorption system.

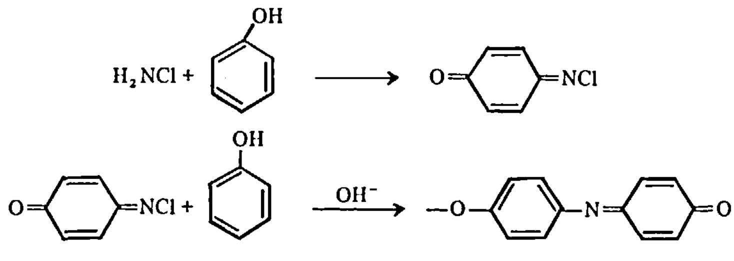
Shaw and co-workers[62a] report a "denuder difference" technique for artifact-free determination of nitric acid vapor. Two parallel filter assemblies are used: in one a nylon filter collects both gaseous HNO_3 and particulate nitrate; in the other a similar filter is preceded by a diffusion denuder coated internally with strong base which removes the acidic gaseous HNO_3, but passes aerosol nitrate. The difference in nitrate levels of the two filters is a measure of the atmospheric concentration of HNO_3. This technique is one of several tested in an interlaboratory intercomparison of methods for HNO_3 analysis.[62b]

5. *Ammonia*

The majority of measurements of gaseous ammonia in air are made by wet chemical techniques, involving prior trapping of ammonia from a sample of air. A dilute acid collecting solution has been widely used, but Okita and Kanamori[63] have shown the collection efficiency of such solutions over lengthy sampling periods to be rather low. Consequently most workers now use impregnated filter papers for ammonia sampling. Shendrikar and Lodge[64] developed an impregnated filter paper based upon a Whatman No. 1 or No. 41 paper soaked in 3% ethanolic oxalic acid solution and vacuum dried. This was found to give quantitative collection of ammonia from ambient air.[64] Eggleton and Atkins[65] report an impregnated filter paper prepared from a Whatman No. 41 paper impregnated with potassium bisulfate which has a collection efficiency in excess of 95% for linear face velocities up to 70 cm/sec^{-1} and relative humidities of 30 to 100%. In our own experience with these latter filters, the only problem to arise has been due to saturation of the filter impregnant with ammonia during 24-hr sampling of abnormally high ambient ammonia levels (up to 100 $\mu g/m^{-3}$) close to a fertilizer works.[66]

The collected ammonia is leached into aqueous solution, often using ultrasonic agitation. It may then be analyzed by a ring oven technique[64,67] involving reaction with *o*-phthalicdicarboxylaldehyde reagent. Most workers, however, chose to analyze ammonia by the indophenol blue reaction, involving formation of a chloramine by reaction of ammonia and hypochlorite, with subsequent formation of a blue dye by reaction of the chloramine with phenol. According to Patton and Crouch,[68] the reaction sequence is as follows

$$NH_3 + OCl^- \longrightarrow H_2NCl + OH^-$$



In practice, the modification due to Weatherburn,[69] involving catalysis of the reaction by sodium nitroprusside, is very commonly used for ambient air analysis. The sensitivity of the method is typically 0.02 mg/ℓ$^{-1}$ NH_4^+ in aqueous solution.

Other wet techniques for the analysis of NH_4^+ include ion chromatography and the NH_3 ion-selective electrode.[70] The electrode method has been reported for analysis of ammonia in waste waters and seawater,[71] showing a Nernstian response over the range of 0.02 to 2.0 mg/ℓ$^{-1}$ (NH_4-N). Detailed evaluation of potential interferences relevant to air pollution studies is, however, necessary.

Two continuous instrumental techniques of ammonia analysis have been reported. Both involve oxidation of NH_3 to NO in type 316 stainless-steel tubing at >800°C:

$$4NH_3 + 5O_2 \xrightarrow[Fe_2O_3/CrO_3]{\Delta} 4NO + 6H_2O$$

In the method described by Sigsby et al.,[72] a subtractive method is used with a chemiluminescent NO analyzer. The instrument is run with a permanently fitted converter and is cycled between analysis of ($NO + NO_2 + NH_3$) and analysis of ($NO + NO_2$), the latter mode involving removal of ammonia from the inlet by absorption in a tube containing acidic $Cr_2O_7^{2-}$ on 30 to 40-mesh firebrick, according to the reaction:

$$2NH_3 + Cr_2O_7^{2-} + 2H^+ \rightarrow (NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$$

This system was designed for analysis of vehicle exhaust gases,[72] but use of a more sensitive chemiluminescent analyzer would allow analysis of ambient air concentrations if the ammonia scrubber were shown to be of adequate efficiency. Indeed it is reported that by use of a phosphoric acid prescrubber, ambient NH_3 concentrations in the range of 0.001 to 0.01 ppm have been measured.[73]

In a system involving the same NH_3 to NO converter, ammonia may be determined subtractively using two instrumental modes: an ($NO + NO_2$) mode with a conventional low temperature NO_2 to NO converter, and an ($NO + NO_2 + NH_3$) mode using the high temperature oxidative converter.[74] No ammonia scrubber is required. This method is effective for concentrations of $NH_3 > 5$ ppb with a response time of 2 sec. As such, it would not be suitable for measurement of background ambient ammonia concentrations which would require greater sensitivity.

Good temporal resolution of atmospheric ammonia concentrations may be obtained using any of three recently reported techniques. The first involves removal of ammonia from air using a simplified Venturi scrubber.[74a] Analysis of the trapped ammonia is by derivatization with *o*-phthalaldehyde in the presence of a thiol in pH 10.4, aqueous borate buffer to form an intensely fluorescent 1-alkylthioisoindole product. It is reported that reproducible measurements of <0.1 ppb ambient ammonia with less than 2 min time resolution may be obtained.[74a]

Ammonia may be collected from air and separated from particulate ammonium salts by passage of air through a pyrex® glass tube of internal diameter 0.3 cm, coated with citric acid.[74b] The higher diffusivity of gaseous ammonia in relation to the ammonium particulates causes a high removal efficiency for the former at the walls of the tube with little collection of the particulate material. Automation of the collection system, with analysis of collected ammonia by Nesslers reagent, allows determination of normal ambient air levels of ammonia with averaging periods down to 30 min.[74b]

An alternative method involves collection of ammonia on Chromosorb T.[74c] Desorption by flushing with air at 100°C and detection of ammonia by a chemiluminescent or optoacoustic analyzer allow measurement of ambient concentrations in the range of 0.5 to 22 ppb with sampling times of 40 min or less.

An important limitation applies to the analysis of ammonia in ambient air. Prior separation of particulate NH_4^+ is necessary to avoid interference, and this is readily achieved by a prefilter, although acid materials collected on the filter may cause loss of ammonia in the collector. Secondly, as a consequence of its high vapor pressure, particulate NH_4NO_3 collected on the filter paper may subsequently volatilize into the air stream and be analyzed as ammonia. These questions will be dealt with in detail in a later section.

C. Oxidants

1. Ozone

There is no specific wet chemical method available for analysis of ozone in air. The methods used are based upon the work of Saltzman and Gilbert[75] and rely upon the capacity of ozone to oxidize potassium iodide. Unfortunately peroxyacylnitrates, hydrogen peroxide, and to a limited extent nitrogen dioxide also oxidize KI, and the results from the method are described in terms of a concentration of "oxidant".[76]

The potassium iodide method has two major variants. In the more common technique 1 or 2% neutral-buffered KI is used as an absorbing reagent and the iodine released is determined spectrophotometrically.[76] In the other method, 2% unbuffered KI is the reagent, and a visual end-point titration is used for calibration.[77] The overall reaction is assumed to be as below, with an I_2/O_3 stoichiometry of 1:1:

$$O_3 + 2H^+ + 2I^- \rightarrow I_2 + H_2O + O_2$$
$$I_2 + KI \rightarrow KI_3$$

Boyd and co-workers,[78] however, compared the KI method with an independent measure of ozone concentration (UV absorption at 254 nm) and found a stoichiometry for I_2/O_3 of 1.5. The stoichiometry was pH dependent and a complex reaction mechanism was proposed.[78] This work stimulated a considerable volume of research. Parry and Hern[79] showed that oxidation of iodide to iodate was thermodynamically feasible and could be catalyzed by a glass frit, a finding which was supported by the work of Flamm and Anderson.[80] Subsequently, Flamm[81] found that ozone analysis with 1% neutral-buffered KI gave results 15 to 30% larger than those obtained by UV absorption if an I_2/O_3 stoichiometry of 1.0 was assumed. A second product of the O_3-KI reaction which slowly liberates additional iodine was tentatively identified as H_2O_2. Flamm[81] also developed an alternative reagent consisting of 1% KI/0.1 *M* H_3BO_4 which gave consistent agreement with UV photometry in the range of 0.1 to 3.5 ppm ozone.

Pitts and co-workers[77] used comparison with IR spectroscopic measurements to evaluate the stoichiometry of the 2% neutral-buffered KI method, finding a dependence upon relative humidity:

at 3% R.H. $[O_3]_{KI} = 1.14\,[O_3]_{IR} + 0.013$

at 18% R.H. $[O_3]_{KI} = 1.12\,[O_3]_{IR} + 0.001$

and at 50% R.H. $[O_3]_{KI} = 1.23\,[O_3]_{IR} + 0.001$

The humidity dependence was not explained. These workers found an excellent agreement between ozone analyses by UV and IR photometry. In a further paper, Pitts et al.[82] report that the ratio of ozone measured by the 2% *buffered* KI method to ozone measured by the 2% *unbuffered* KI procedure is ~1.4. Hence neither method gives results which are reliable in relation to the photometric procedures.

The question of positive interferences in the KI method has already been mentioned. There is, however, also a quantitative negative interference due to SO_2 reduction of iodine.

This is eliminated by prior passage of the air stream through an absorber of chromium trioxide impregnated paper.[83] This absorber has the effect of oxidizing NO to NO_2, hence in some circumstances causing a positive interference as NO_2 oxidizes KI with about 10% efficiency relative to an equimolar concentration of ozone.[76]

Several continuous instrumental analyzers, some still available commercially, have been based upon the ozone-potassium iodide reaction. These include a continuous colorimetric monitor[84] and an ion-selective electrode monitor in which an iodide-specific ion electrode is used to measure the loss of iodide ions from solution.[85] Alternatively, continuous electrochemical methods may be used employing either an amperometric[86] or a galvanic cell.[87] Perhaps the most sophisticated electrochemical devise is based upon differential galvanic measurement.[88] An aqueous electrolyte containing buffered NaBr and NaI is contained in a recirculating galvanic cell containing two platinum cathodes and one anode. The air sample is split into two streams which pass through separate branches of the cell, and one gas stream is scrubbed of reducing agents and the other of reducing agents plus ozone before entering the cell. Hence the differential galvanic current is directly related to the concentration of ozone and interferences are very slight.[88]

Despite the considerable sophistication of some such analyzers, they are still hampered by rather slow response times, generally of the order of minutes, and by uncertainties over the stoichiometry of the ozone-iodide reaction. Since the liberation of iodine is now known to have both a rapid and a slow component, such instruments are unlikely to give reliable temporal resolution of ozone concentrations. Even if calibrated against the manual neutral-buffered KI, other drawbacks such as the apparent humidity dependence of the ozone-KI reaction severely limit the value of the data obtained. Indeed, substantial deviations between the results of instrumental electrochemical oxidant analyzers and measurements based upon other instrumental techniques have been demonstrated,[89-91] although these may be due in part to differences in instrumental response times.[91]

In view of the problems with the KI method, it is not surprising that the report by Negerbradt et al.[92] that the chemiluminescent ozone-ethene reaction could be used for continuous monitoring of atmospheric ozone was followed rapidly by commercial production of analyzers based upon this measurement principle. Ambient air and ethene from a cylinder enter a reaction vessel at atmospheric pressure through concentric tubes facing a photomultiplier tube. Light emission is centered on 435 nm and the method may be used for ozone concentrations in the range of 0.001 to 100 ppm, over which the response is linear. Typical instrumental response times (90% rise) are of the order of 2 sec. The light emission is thought to be due principally to formation of electronically excited formaldehyde, HCHO ($^1A_2$), and α-dicarbonyl compounds:[93]

$$C_2H_4 + O_3 \rightarrow \text{ozonide} \rightarrow CH_2O^*$$
$$CH_2O^* \rightarrow CH_2O + h\nu$$

Because of their simplicity, reliability, and stability, chemiluminescent analyzers have been very widely used for ambient air ozone analysis. The only major problem has been that of calibration. Steady concentrations of ozone may be generated using a Pen-Ray UV lamp with a stabilized power supply, but there is no simple means of determining the concentration of the standard atmosphere. Initially the neutral-buffered KI method was adopted, and all measurements were related to this technique. However, as doubts developed over the stoichiometry and reliability of this method, other more satisfactory methods of ozone source calibration were investigated.

The major candidates for ozone calibration techniques were UV photometry at 253.7 nm and gas phase titration of nitric oxide (described above in relation to oxides of nitrogen analyzers). De More and Patapoff[94] described a single-beam UV photometer with 5-m path

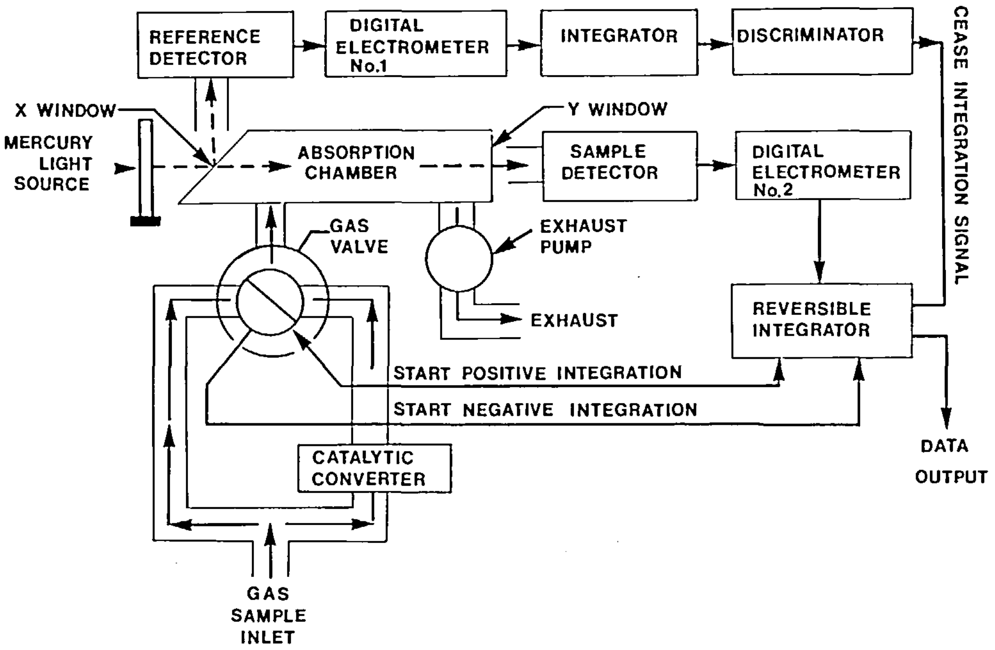


FIGURE 5. Schematic diagram of a UV absorption analyzer for ozone (Dasibi model 1003-AH).

length, while Bass et al.[95] constructed a double-beam instrument of 3-m path length with a precision of better than 10% at a 0.05 ppm ozone concentration. Muldoon and Majahad[96] have discussed the construction of an ozone calibration system based on gas phase titration, while Stedman recommends a flow-independent gas phase titration procedure.[97] In a comparison of ozone calibration techniques, Paur[98] reported that gas phase titration and UV photometry agree within 2.5% in the 150- to 700-ppb O_3 range, and deviate by only 3% from the borate-KI procedure. De More and Patapoff[94] also found good agreement between gas phase titration and UV photometry, but recommended the latter method for routine use as the former is more susceptible to experimental error.

An interesting variant on existing chemiluminescent methods has been reported by Eastman and Stedman.[99] In order to produce a very fast response analyzer suitable for ozone flux measurement by eddy correlation, a chemiluminescent oxide of nitrogen analyzer was reversed to mix ambient air in one stream with a stream of nitric oxide from a cylinder. A response time of less than 0.2 sec was achieved.[99]

The UV photometric technique forms the basis of commercially available ambient air ozone analyzers. In a single-cell instrument air is alternately drawn through the cell direct, and through a catalytic converter which decomposes ozone without causing loss of other atmospheric constituents (Figure 5). This is necessary in ambient air analysis to allow elimination of interference due to other UV-absorbing atmospheric components (e.g., aromatic hydrocarbons, mercury vapor) as the difference between the absorbance readings in the two operational modes is due only to ozone. The instrument is sensitive to 0.001 ppm ozone and has a digital display updated at intervals of 12 or 24 sec. The 90% rise time of 18 sec is slower than for chemiluminescent analyzers, but the instrument has the advantage of being a primary standard, not requiring supplementary calibration equipment.

The only reported interference is due to UV-absorbing organic molecules.[99a] The response is a transient one, lasting several measurement cycles. The only serious drawback of such an interference arises in plume studies where an interferent is traverse at high speed.[99a]

2. *Hydrogen Peroxide*

Although not an air pollutant of major concern, there has been some recent interest in this compound from the viewpoint of establishing its concentration in photochemical smog, and due to its possible importance in the atmospheric oxidation of sulfur dioxide.

Bufalini and co-workers[100] have applied the method of Cohen and Purcell[101] to the analysis of H_2O_2 in air at Hoboken, N.J. under moderate smog conditions. The analytical procedure involves collection of H_2O_2 in an impinger, followed by reaction with Ti(IV) and 8-quinolinol to give a colored complex believed to be peroxidized titanium 8-hydroxyquinolate.[101] Bufalini et al.[100] report that O_3, NO_2, NO, and alkenes do not interfere and SO_2 at 20 ppm gives only a 0.7% interference.

Kok and co-workers[102] developed a chemiluminescent procedure for analysis of H_2O_2 in air based upon reaction with luminol in the presence of a Cu(II) catalyst. Using a 15- to 20-min air sample collected in a midget impinger, a detection limit of 0.4 ppb H_2O_2 in air was found, and in a continuous system the limit was 1 ppb. These concentrations are well below those measured by Kok et al.[103] using this technique, as well as that of Cohen and Purcell[101] and a new method. The latter method involved bubbling air through an aqueous solution of titanium tetrachloride/hydrochloric acid and measuring the absorbance of the colored complex resulting from reaction with H_2O_2 at 410 nm. The agreement between the three methods was not very good, but all gave the same order of concentration in the Southern Californian atmosphere (10 to 30 ppb).[103] The luminol chemiluminescence method has also been used to measure levels of H_2O_2 in rainwater samples.[104]

D. Carbon Compounds

1. *Total Hydrocarbons and Reactive Hydrocarbons*

The nondispersive infrared technique[105] has now been almost entirely superseded for ambient air measurements. Its value is limited severely by the rather low overall sensitivity (detection limit about 1 ppm as hexane) and the substantial variability in response to different hydrocarbons. Interferences from high concentrations of CO, CO_2, water vapor, and oxygenates may also be important. Improvements in instrument design, such as the incorporation of a narrow band-pass filter to give wavelength sensitivity and a thermistor bolometer detector have given enhancements in sensitivity and selectivity,[42] but this is still not a technique to be recommended for ambient air analysis of hydrocarbons.

The flame ionization analyzer using a conventional flame ionization detector[106] is the usual technique employed for total hydrocarbon analysis. This is sensitive to as little as 0.01 ppm (as methane) with a response time (90% rise) of 5 sec. The response is a function of the rate of introduction of carbon atoms to the flame, and calibration is with methane. The only important interferences are oxy- and halogenated hydrocarbons which cause a less than stoichiometric response.

The high natural background concentration of methane (about 1.4 ppm) dominates the response of the total hydrocarbon analyzer, other than in situations of substantial pollution. This can only be eliminated by independent measurement of methane levels, as in the sequential methane, CO, and total hydrocarbon analyzer described later, or by removal of nonmethane hydrocarbons (NMHC) from the inlet air stream of a total hydrocarbon analyzer on a cyclic basis. This may be carried out cryogenically[107] since at 77 K, the temperature of liquid nitrogen, 95% of NMHC may be condensed without effect on methane.

One of the major reasons for interest in hydrocarbon concentrations is the importance of reactive hydrocarbons in photochemical smog formation. Since individual hydrocarbons vary greatly in their atmospheric reactivity, and hence their potential to promote smog formation, if an assessment of the reactivity of a particular atmosphere is required analysis of specific hydrocarbons is normally necessary. An alternative technique is suggested by Krieger et al.[108] who report a reactive hydrocarbon monitor based upon measurement of the chemiluminescence at 306.4 nm from the reaction of oxygen atoms with reactive hydrocarbons. The light intensity caused by individual hydrocarbons was found to correlate well with their known reactivity in atmospheric photochemistry. An ultimate sensitivity of 6 ppb ethene equivalent was reported with a linear response to at least 1000 ppm.[108]

In a related technique, Quickert et al.[109] replaced the ethene supply of a chemiluminescent ozone monitor with a supply of ozone from an electric discharge. Thus the chemiluminescent reaction of hydrocarbons with ozone was utilized, and the instrument was found to respond only to alkenes. The highest sensitivity was to ethene, for which a detection limit of 3 ppb was reported.[109] Since the instrument responds also to higher alkenes, but with lesser sensitivity, it is difficult to envisage application of this method, other than in an atmosphere where one alkene is highly predominant.

2. *Specific Hydrocarbons*

There is a vast range of hydrocarbons, both in terms of chemical type and molecular weight, which occur in ambient air. No single technique is suitable for analysis of all hydrocarbons, and a method will be selected dependent upon the range of volatilities which is of prime interest. The analytical methods used are all based upon gas chromatographic separation, but a range of sampling methods is available. In general, a method will be suitable either for the C_2-C_5 range of compounds, or for the less volatile C_6-C_{20} hydrocarbons.

Sampling of C_2-C_5 hydrocarbons normally involves collection of air (perhaps 1 ℓ) in an inert bag of aluminized polyester film,[110] Saranex,[111] or FEP-teflon®.[112] As ambient ozone will react with alkenes in the bag and hence deplete their concentration, the air is drawn into the bag through an ozone scrubber consisting of a tube packed with potassium permanganate.[113] Hydrocarbon concentrations are then stable over a period of days. If concentrations of hydrocarbons in the air are high, direct injection of an aliquot of air (1 mℓ, normally) into the gas chromatograph may be used. For ppb-level sensitivity, however, preconcentration is necessary and a sample of air (50 to 200 mℓ) is passed through a freeze-out loop containing glass beads and cooled in liquid oxygen.[114] Diversion of the carrier gas through the freeze-out loop, together with gentle warming, cause elution of the hydrocarbons into the gas chromatograph, where the optimum separation is normally achieved by programming upwards from initial subambient temperatures.[114] Freeze-out of water vapor from the air sample may cause problems both by blockage of the loop, and by interference with the analysis itself.[114] This problem can be overcome by passage of air through a potassium carbonate drying tube prior to entry into the freeze-out loop.[115] A variant on the cryogenic sample concentration technique is reported by De Greef et al.[116] who used a short (10 cm) column of Porapak S at −95°C (liquid nitrogen/acetone) to preconcentrate ethene from large volumes of air. Elution at 100°C and gas chromatographic separation from other hydrocarbons allowed analysis of ethene at concentrations in the 0.01- to 0.1-ppb range.[116] A very similar sampling technique has also been applied to the analysis of other low molecular weight compounds.[117]

Knoeppel et al.[117a] report efficient collection of C_2-C_5 hydrocarbons on carbon molecular sieve. A stainless-steel column containing 1 g of carbon molecular sieve may be used to sample up to 60 ℓ of air before breakthrough of C_2 hydrocarbons. Using subsequent thermal elution and gas chromatographic separation on an alumina column, good sensitivity was obtained.[117a] Stephens and Hellrich[117b] introduced ambient air from a 4.4-mℓ sample loop onto a Porapak N column held at 64°C. Elution of C_1-C_2 hydrocarbons occurs within 3 min and these pass separately to a flame ionization detector. C_3+ hydrocarbons are then backflushed as a single slug directly to the detector, providing separate measurements of CH_4, C_2H_6, C_2H_4, C_2H_2, and then all other nonmethane hydrocarbons (C_3+). Minimum detectable concentrations for C_1-C_2 compounds are 1 to 2 $\mu g/m^{-3}$ and 100 to 200 $\mu g/m^{-3}$ for C_3+ compounds.[117b]

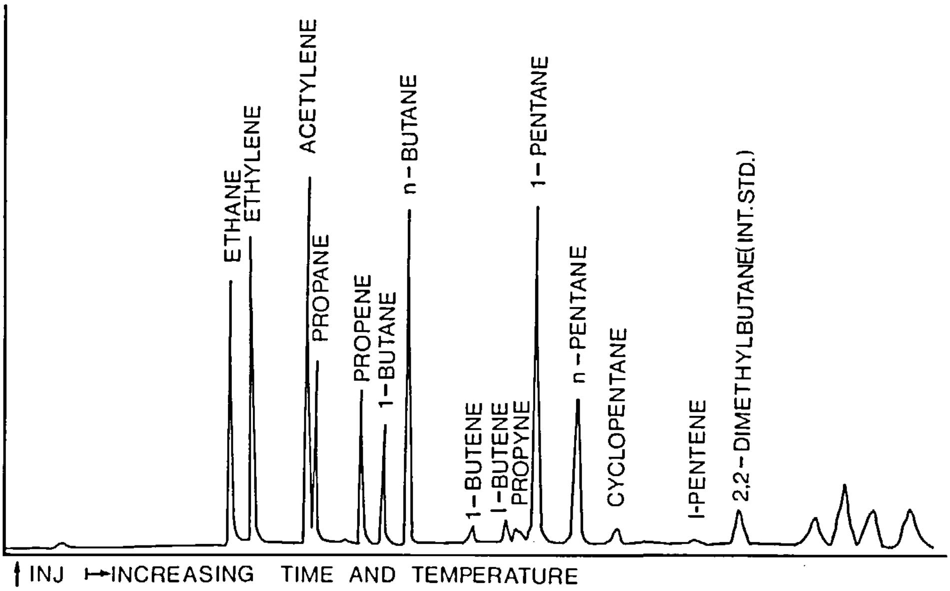


FIGURE 6. Typical chromatogram from the analysis of atmospheric hydrocarbons.[114]

The analysis of hydrocarbons of low molecular weight at low ambient concentrations involves a rather demanding chromatographic separation. The use of chemically bonded stationary phases such as Durapak *n*-octane-Porasil C[114] or Durapak OPN-Porasil C[118] has provided the low column bleed and high resolution necessary for this analysis. Calibration is by preparation of hydrocarbon mixtures at ambient concentration levels by dilution of more concentrated mixtures.[110] A typical chromatogram is shown in Figure 6.

Preconcentration of higher molecular weight (C_6 to C_{20}) volatile hydrocarbons has been carried out using a carbon adsorbent[119,120] or a porous polymer.[121,122] A review of the considerations in selecting such a procedure has been given by Melcher et al.[123]

Hydrocarbons are adsorbed very strongly on activated carbon[119] or graphitized carbon black.[120] Normally an air sample volume is selected such that the breakthrough of the most volatile compounds of interest is just avoided. The collected hydrocarbons may then be extracted using a solvent such as carbon disulfide,[119] or may be thermally desorbed at 400°C directly into the gas chromatograph.[120] An interesting variant on the charcoal method is described by Twibell and Home.[124] Ferromagnetic wires are coated with a thin layer of highly active charcoal and suspended in a polluted atmosphere for 1 to 2 hr. They are then inductively heated in the Curie point pyrolysis system of a gas chromatograph causing elution of the collected hydrocarbons. The mass of each hydrocarbon collected by the charcoal is related to the atmospheric concentration and compounds such as benzene and toluene may be determined at levels down to <1 ppb.[124]

Adsorption tubes containing support-bonded chromatographic phases, such as the silicones $(C_{18}H_{37}SiO_{3/2})_n$, on various types of Chromosorb have been developed for sampling organic pollutants from the air.[125] Porous polymer adsorbents have also been used widely, with Tenax GC[121,126] and Chromosorb 102[122] proving the most satisfactory. Such adsorbents may be used in two distinct ways. Either the volume of air sampled is restricted such that no breakthrough of the compounds of interest occurs, or sampling is continued far beyond initial breakthrough and an equilibrium concentration of each hydrocarbon is retained on the adsorbent.[127]

The collected compounds are eluted from the porous polymer at an elevated temperature into an inert gas stream. Since elution is a rather slow process, the hydrocarbons must be condensed in a cooled tube, and then subsequently flash vaporized into the gas chromatograph.[121,122] Dravnieks et al.[122] have described a system suitable for this procedure. Recent work has indicated that oxygenated decomposition products of Tenax GC may be formed during air sampling, by the influence of UV light if a glass adsorption tube is used, or of ozone.[128] These decomposition products, such as phenol, benzaldehyde, and acetophenone, may interfere in the subsequent gas chromatographic analysis.

Greatly improved resolution of hydrocarbons by gas chromatography has been made possible by the introduction of capillary columns. Considerable success has resulted from the use of a 600 ft × 0.02 in. nickel with emulphor ON 870 column,[126] a 200 ft × 0.02 in. OV-101 SCOT column,[129] and a 120 m × 0.32 mm Ucon HB 5100 column.[119]

Identification of individual compounds eluted from the gas chromatograph may prove problematic. Flame ionization detection is normally used and this may be supplemented by the normal techniques of standard addition and selective subtraction.[130] The rather recent introduction of the GC-MS technique, especially when coupled to a computer data system, has allowed identification of individual compounds from their mass spectra.[130] For example, Grob and Grob report the identification of 108 different compounds by this technique in two samples of urban air,[119] and Raymond and Guichon identified over 70 peaks.[120]

While the greatest interest has been focused on anthropogenic hydrocarbons, natural compounds may be of importance in air chemistry. Stevens and co-workers[130a] report measurements of biogenic isoprene and α-pinene in air in the Great Smokey Mountains.

Calibration of the gas chromatograph for the analysis of hydrocarbons is often carried out only by direct injections of liquid standards, either into the adsorption tube, or directly into the chromatograph itself. The diffusion cell technique for establishing dynamic standard atmospheres of volatile liquids[131,132] is much neglected and can provide an invaluable check upon calibrations performed by other methods.

3. *Oxygenates*

Oxygenated hydrocarbons are important products of atmospheric photochemical reactions, but have received rather little attention from the analytical viewpoint. There are relatively specific wet chemical methods for the analysis of acrolein and formaldehyde, while gas chromatography is required if a wider range of compounds is to be analyzed.

Acrolein may be determined at concentrations down to 0.01 ppm in a 50-ℓ air sample by reaction with 4-hexylresorcinol in an ethanol-trichloroacetic acid medium in the presence of mercuric chloride.[133] A blue-colored product is determined spectrophotometrically at 605 nm. Acrolein may also be collected using activated molecular sieve type 13X. After desorption into distilled water, determination by gas chromatography allows measurement of acrolein in air at sub-ppm levels.[134]

Formaldehyde may be collected in distilled water and analyzed by reaction with a chromotropic acid-sulfuric acid solution where a purple monocationic chromogen with an absorption maximum at 580 nm is formed.[135] The method is sensitive to 0.1 ppm formaldehyde in a 25-ℓ air sample, but may be used for determination of lower concentrations by extension of the sampling period.[135]

An alternative wet chemical method used for the determination of total volatile water-soluble aldehydes utilizes the collection of aldehydes in a 0.05% aqueous 3-methyl-2-benzothiazolone hydrazone hydrochloride (MBTH) solution.[136] The resulting azine is then oxidized by a ferric chloride-sulfamic acid solution to form a blue cationic dye determined spectrophotometrically at 628 nm.[136] The method is sensitive to 0.03 ppm of aldehyde (as formaldehyde) in a 25-ℓ air sample. The MBTH reagent will form colored products by reaction with a wide range of compounds, but in practice may be considered specific to water-soluble aldehydes when analyzing ambient air. Sensitivity has been found to decrease as the aldehyde chain length increases.[136]

Acetaldehyde and propionaldehyde, as well as some ketones and higher molecular weight aldehydes, may be collected in 1% sodium bisulfite solution and analyzed by gas chromatography from injection of a 4-μℓ aliquot of the solution.[137] Using a flame ionization detector, detection limits are 0.02 ppm for acetaldehyde and 0.03 ppm for propionaldehyde and the butyraldehydes in a 120-ℓ air sample collected over 1 hr, and may be reduced proportionately with longer sampling intervals.[137]

Hoshika[138] reports a method for collection of acetaldehyde on 25% tris (2-cyanoethoxy) propane on Shimalite support maintained in liquid oxygen. Elution at 100°C and gas chromatographic analysis allows analysis of ppb concentrations.[138] Five percent tris(2-cyanoethoxy)propane on Carbopack B may be used to separate the nine lower aliphatic carbonyl compounds[39] and might well find application in analysis of atmospheric samples.

4. Carbon Monoxide

Many wet chemical methods have been proposed over the years for analysis of CO at urban ambient levels. The only one listed by the APHA is dependent upon reaction of CO with an alkaline solution of the silver salt of *p*-sulfaminobenzoic acid to form a colloidal suspension of silver.[140] The method is used to analyze grab samples of air and covers the range 0 to 400 ppm CO if the absorbance is measured at 425 nm, and 400 to 1800 ppm at the 600 nm wavelength.

The infrared absorption by CO may be used for physical determination. Using a 10-m path length, measurement of absorbance at 4.67 μm will provide accurate measurements of concentrations in excess of 10 ppm.[141] Nondispersive infrared analysis is recommended for continuous analysis of CO in ambient air.[142] Interferences from water vapor and CO_2 may be overcome by drying the air sample and by use of a cell of CO_2 in line with the sample cell, respectively. A detection limit of 0.5 ppm with a response time (90% rise) of 5 sec is possible in commercially available instruments.[143]

Another type of commercially produced continuous CO analyzer uses an electrochemical cell.[144,145] The sensor consists of a sensing electrode, a counter electrode, a reference electrode, a housing containing sulfuric acid, and two face plates.[145] The sensing electrode is a teflon®-bonded diffusion electrode catalyzed with platinum at which CO is oxidized:

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$$

Current flows to the counter electrode where the reaction is

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

The cell is sensitive to other gaseous reducing agents, but selectivity is enhanced by use of a prefilter which removes the most important interferences.[145] The response time (90% rise) is 25 sec and the instrument is sensitive to concentrations down to 1 ppm.[143]

Carbon monoxide may be reduced with hydrogen over a nickel catalyst to form methane which is detected by flame ionization detection.[146] This forms the basis of the most sensitive type of instrumental CO analyzer which is produced commercially to analyze CO, methane, and total hydrocarbons on a cyclic basis.[147] The instrument is shown in schematic form in Figure 7. Hydrogen carrier gas flushes a small air sample from a sample loop through a stripper column (Cl) packed with an adsorbent porous polymer for sufficient time to allow passage of methane and carbon monoxide, but not the heavier compounds which are subsequently removed by backflushing. Passage of the methane and carbon monoxide through a chromatographic column containing molecular sieves (C3) causes separation of these compounds which are passed to the flame ionization detector via a catalytic methanator. Modification of the instrument allows passage of C_2 hydrocarbons through the stripper column

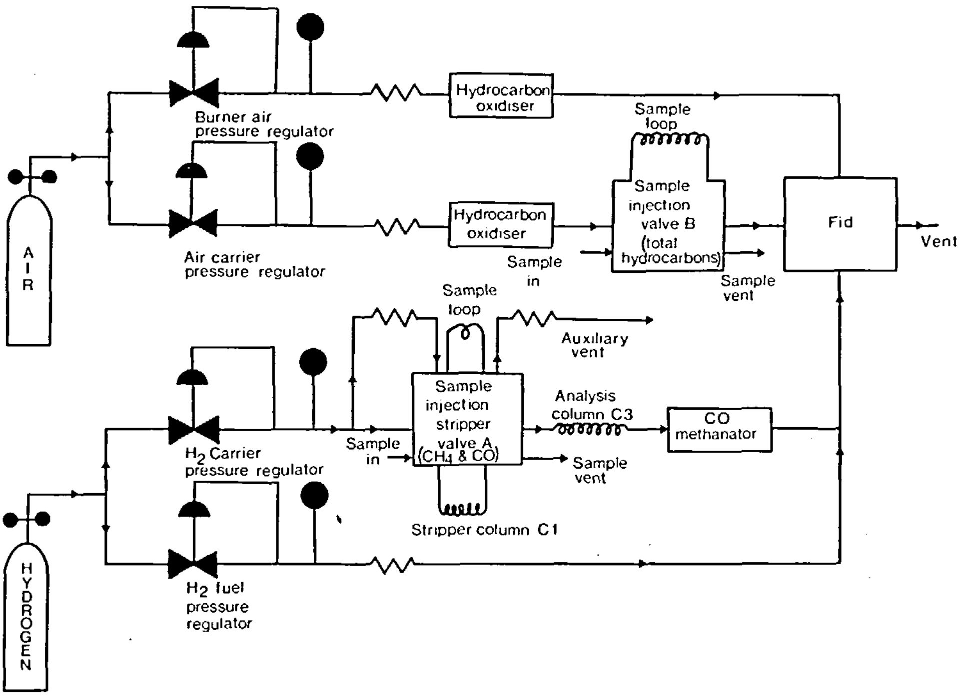


FIGURE 7. Schematic diagram of a gas chromatographic analyzer for carbon monoxide, methane, and total hydrocarbons.

and these are separated on a second column containing porous polymer and passed directly to the detector. Total hydrocarbons are determined by passage of a 10-mℓ air sample directly to the flame ionization detector via valve B. The carrier gas is air, purified by catalytic oxidation of impurities and this, rather than more conventional carrier gases, eliminates problems resulting from radical changes in flame characteristics upon introduction of the polluted air sample into the detector.[147] The instrument is sensitive to 10 ppb CO, but since it operates on a cyclic basis, has the serious disadvantage of not providing continuous measurements.[143] Rather, grab samples are analyzed periodically, with a minimum time interval typically of 10 min.

E. Halogen Compounds

1. Halocarbons

This is an area which has attracted considerable interest over recent years as a result of the discovery that halocarbons generated in the troposphere can diffuse into the stratosphere where they may cause depletion of stratospheric ozone. The highly inert chlorofluorocarbons (freons) are also used in atmospheric science as an indicator of anthropogenic pollution within a air mass. Hanst[148] has reviewed the sources and importance of the major halocarbon compounds.

The earlier work on halocarbons used gas chromatographic separation with ^{63}Ni electron capture detection and was typically capable of detection limits of 1 ppt (10^{-12}) and 10 ppt for fluorocarbon-11 (CCl_3F) and fluorocarbon-12 (CCl_2F_2), respectively.[149,150] The use of a freeze-out system allows analysis of 500-mℓ air samples with an improvement of detection limits to the ppt level for a range of compounds.[151] Using gas chromatography with mass spectrometric detection and computer identification, Pellizari et al. detected 21 halogenated hydrocarbons in ambient air including vinyl chloride, trichlorethylene, various chlorofluorocarbons, alkyl chlorides, chlorinated aromatics, bromoform, and chloroform.[152] Air was

Table 2
HALOCARBONS SOUGHT IN THE ATMOSPHERE OF THE RURAL NORTHWEST[a]

Halocarbon	Retention time (min)	Masses monitored	Concentration (ppt)
Dichlorodifluoromethane	4.0[b]	85, 87, 101	230 ± 10
Fluorotrichloromethane	6.0[b]	101, 103	125 ± 8
Methyl chloride	5.6[b]	47, 49, 50, 52	530 ± 30
Dichloromethane	3.0[c]	49, 51, 84, 86	<5
Chloroform	7.4[d]	83, 85	20 ± 10
Carbon tetrachloride[e]	4.0[c]		120 ± 15
Ethyl chloride		64	<5
1,1- and 1,2-dichloroethane		63, 98	<5
1,1,2-Trichloroethane		97, 99	<5
1,1,1-Trichloroethane	6.7[d]	97, 99	100 ± 15
1-Chloroethylene		62, 64	<5
cis, trans, and 1,1-dichloroethylene		61, 96	<5
Trichloroethylene		93, 128	<5
Tetrachloroethylene	7.7[d]	164, 166	20 ± 10
Methyl bromide		94	<5
Methyl iodide		142	<5

[a] Measurements made in rural Pullman, Washington from December 1974 to February 1975.

[b] 20 ft × 1/16 in. stainless-steel Durapak n-octane/Porasil C(100 to 200 mesh) column; 10 cm^3/min^{-1}.

[c] 50-ft SCOT OV-101 column; 10 cm^3/min^{-1}.

[d] 20 ft × 1/16 in. stainless-steel Durapak Carbowax 400/Porasil F (Low K'); 6 cm^3/min^{-1}.

[e] Measured by electron capture gas chromatography.

From Grimsrud, E. P. and Rasmussen, R. A., *Atmos. Environ.*, 9, 1014, 1975. With permission.

sampled through Tenax G.C. adsorbent, with subsequent thermal desorption.[152] Grimsrud and Rasmussen[153,154] also used gas chromatography-mass spectrometry, claiming an improved detection limit of about 5 ppt for individual compounds relative to the electron capture detector when analyzing a 20-mℓ air sample. Quantitative analyses were obtained for 19 separate compounds, shown in Table 2.

An alternative infrared technique has been reported for the analysis of fluorocarbon-11, fluorocarbon-12, and carbon tetrachloride at concentrations down to 10 ppt.[115] Air is liquefied in a cryocondenser system, from which N_2 and O_2 are boiled off. The residual compounds are allowed to warm to room temperature, whence they are drawn into a 120-m infrared gas cell via a CO_2 filter consisting of caustic soda pellets. A range of compounds may be identified quantitatively from their infrared absorption spectra.[15]

Polychlorinated aromatic compounds may exist in air both as vapor and in association with atmospheric particles. Hence any sampling methodology should aim to collect both physical forms. Polychlorinated biphenyls (PCB) have been sampled by means of a glass fiber filter backed with a tube of 1/4-in. ceramic saddles coated with OV-17 silicone oil.[156] Subsequent extraction with hexane and analysis by gas chromatography with electron capture detection allowed measurement of PCB concentrations in the 0.05 to 5 ng/m^{-3} range, calibrated by comparison with a standard of commercial Aroclor 1254.[156] Polychlorinated naphthalenes may be collected with a glass fiber filter followed by two precleaned polyurethane plugs in tandem.[157] The collection substrates are extracted triply with toluene at 25°C, and analysis by gas chromatography with mass spectrometer/computer identification allows quantification of individual isomers at concentrations down to 0.3 ng/m^{-3}.[157]

2. *Hydrogen Halides*

This subject area has received rather little attention. Analysis of HF is normally carried out by trapping in a basic medium, after preseparation of particulate fluorides using an inert (e.g., teflon®) membrane filter. Analysis of collected fluoride is best performed using a specific ion electrode.[158]

Hydrogen chloride may be collected from moist air using a 1-m pyrex glass tube coated internally with $NaNO_3$. Air is passed at 100 mℓ/min^{-1}, and collected chloride is analyzed by microcoulometry.[159] Using short sampling intervals (<100 sec), the technique has been shown to be applicable to the analysis of ppm levels of HCl. Extension of the sampling interval may allow analysis of HCl at lower levels, but this point would require confirmation, especially with regard to collection efficiencies. An alternative technique applicable at the ppb level[160] uses a KOH/triethanolamine impregnated filter following a polystyrene filter to remove particulates. Flow rates of approximately 1 m^3/min^{-1} are used, and collected chloride is determined by constant current coulometry, which is sensitive to about 400 μg HCl equivalent.[160]

F. Metal Vapors and Alkyls

1. *Mercury*

Elemental mercury vapor can exist in air in appreciable concentrations and many methods have been devised for its analysis. Only recently, however, has it been realized that mercury can also exist in ambient air in a considerable range of physicochemical forms. These forms include elemental vapor, vapor-phase alkyl mercury (e.g., CH_3HgCl), and dialkyl mercury [e.g., $(CH_3)_2Hg$], as well as inorganic mercury salts which may be in either particulate or gaseous form (especially $HgCl_2$).

Direct atomic absorption measurement at 253.7 nm is adequate for determination of elemental mercury vapor at concentrations down to 5 μg/m^{-3}. For the lower levels more typical of ambient air, a preconcentration is required. Thus mercury vapor may be collected from ambient air by amalgamation on silver wool[161] or silver gauze.[162,163] Subsequent release by thermal deamalgamation and elution into an ultraviolet spectrophotometer allows determination of the mercury without interference from organic air pollutants,[163] or from dimethylmercury, sulfur dioxide, hydrogen sulfide, or nitrogen dioxide at normal ambient levels.[161] For 24-hr sampling periods, ambient mercury levels from 15 ng/m^{-3} to 10 μg/m^{-3} may be determined using silver wool collection,[161] or from 5 ng/m^{-3} to 100 μg/m^{-3} using sampling times of 2 hr or less and a silver gauze collector.[162,163] While use of a prefilter during air sampling will prevent interference from particulate forms of mercury, it is not clear to what extent vapor-phase inorganic mercury or monomethylmercury is collected by silver wool and hence reduces the specificity of this technique.

Acknowledging the problems of specificity, Scaringelli et al.[164] developed a technique for collection of all forms of mercury by adsorption on charcoal backed by a fiber filter to ensure trapping of both gaseous and particulate forms. Subsequent heating of the sampler with nitrogen elution frees the collected compounds which are pyrolyzed to form elemental mercury, and collected on silver wool. Thermal deamalgamation from the silver wool allows atomic absorption measurement of total mercury.[164] Alternatively, using purified activated charcoal, direct analysis of the charcoal by neutron activation may be used to determine total mercury concentrations down to 0.5 ng/m^{-3}.[165] In a related method, a porous graphite tube plated with gold was shown to be an efficient collector of particulate and elemental mercury. Subsequent insertion of the tube in the heated graphite atomizer of an atomic absorption instrument allows determination of the collected mercury.[166]

More detailed information upon mercury speciation is provided by the method of Trujillo and Campbell.[167] Particulate mercury is collected by a prefilter, which is followed by a tube containing in sequence Carbosieve B (45/60 mesh) and silvered Chromosorb P. The Car-

SPECIFIC ABSORPTION TUBES FOR MERCURY IN AIR[169]

Tube order no.	Composition	Function
1	Glass wool filter, preheated to blank	Removes some particulate; passes other mercury forms
2	Chromosorb-W, 4—60 mesh, 3% SE-30	Removes $HgCl_2$ particulate which passes the filter; passes CH_3HgCl, $(CH_3)_2Hg$, elemental Hg
3	Chromosorb-W, 45—60 mesh treated with 0.05 *M* NaOH	Removes CH_3HgCl; passes elemental Hg, $(CH_3)_2$ Hg
4a	Silvered glass beads	Removes elemental Hg; passes $(CH_3)_2Hg$
4b	Gold-coated glass beads	Removes $(CH_3)_2Hg$

bosieve B was shown to give quantitative collection of CH_3HgCl, C_2H_5HgCl, $(CH_3)_2Hg$, and $(C_6H_5)_2Hg$ over a 24-hr sampling period, but to retain elemental Hg vapor only slightly. Hence the latter is collected by the silvered Chromosorb P. Thermal desorption of the collected mercury allowed analysis of the mercury in the range of 0.3 ng to 2.5 μg, with a precision of ±5% at the lower concentration.[167] Thus separate analyses of particulate Hg, organic Hg, and elemental Hg are obtainable.

Two systems enable a more complete discrimination of mercury species in ambient air. Henriques et al.[168] separated particulate mercury with a Millipore prefilter. A gold filter, coated with a gold-silicon alloy, collected elemental mercury vapor, a scrubber containing acid permanganate solution trapped methylmercury, and other readily oxidized mercury compounds, and last in the train, a pure gold filter collected dimethylmercury and other gold-soluble mercury compounds.[168] Analysis was by vapor atomic absorption. Braman and Johnson[169] describe a sophisticated technique suitable for determination of several forms of mercury at levels down to 0.1 to 1 ng m^{-3}. The various collectors used are shown in Table 3. High collection efficiencies were found. Mercury was eluted from the adsorption tubes by heating and passage of helium carrier gas, and passage through a d.c. discharge chamber caused excitation of Hg, and the resultant emission at 257.3 nm was measured[169,170] (Figure 8). The detection limit of the analytical procedure was about 0.01 ng.

Scheide and co-workers[171] have produced a valuable account of the calibration of mercury analyzers. Continuous analyzers are calibrated via a continuous generation of mercury vapor, while methods requiring a period of sample collection may also be calibrated from such a source, or by injection of a known volume from a static standard atmosphere of known concentration.[171] Details of instrumental design are included.

2. *Lead Alkyls*

A minor portion of lead in urban air is in the form of vapor-phase lead alkyls. It appears that while lead is relatively stable in dialkyl, trialkyl, and tetraalkyl forms, the only forms of any real significance in air are inorganic lead and tetraalkyllead.[172,173] The latter may take the form of tetramethyllead (TML), tetraethyllead (TEL), or the three mixed methylethyl derivatives [$CH_3(C_2H_5)_3Pb$; $(CH_3)_2(C_2H_5)_2Pb$; $(CH_3)_3C_2H_5Pb$].

Total tetraalkyllead may be determined by collection in iodine monochloride and subsequent analysis by extraction into methylisobutyl ketone as the ammonium pyrrolidinecarbodithioate[174] or dithizone[175] complex and atomic absorption determination. This method, however, is sensitive to all lead in the solution and relies upon both a highly efficient separation of particulate inorganic lead by prefiltration of the air stream, and a low lead blank. Such requirements are not always met and results by this method may be open to considerable doubt.[172] An elegant modification to this method utilizes the fact that te-

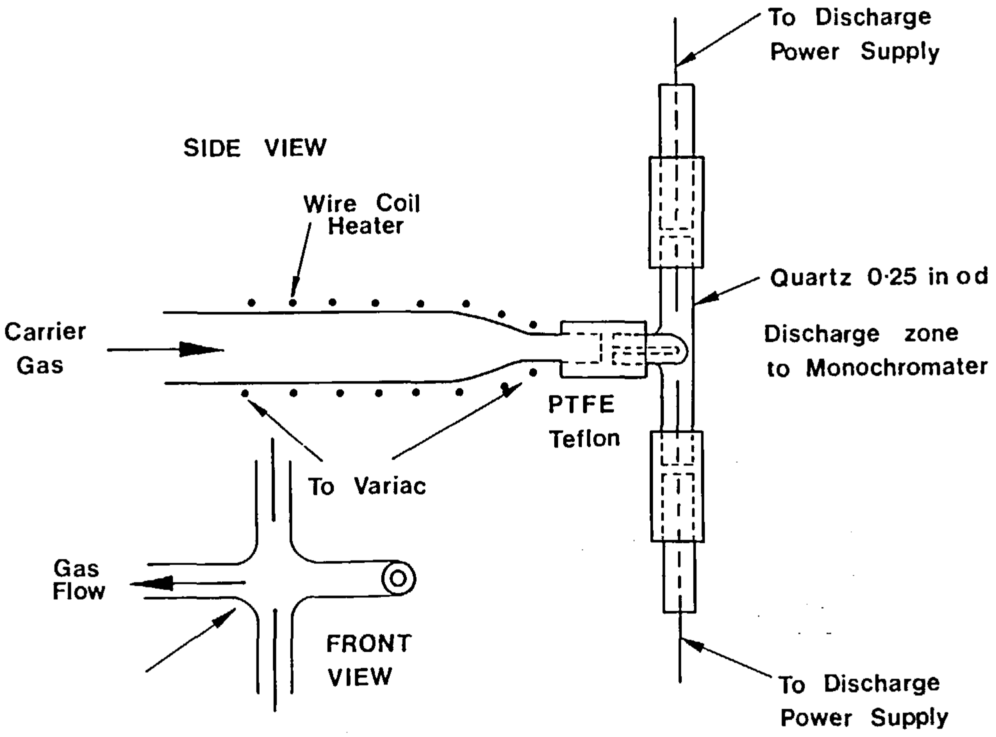


FIGURE 8. Schematic diagram of detector system for analysis of mercury in air.[169]

traalkyllead collected in iodine monochloride is converted quantitatively to dialkyllead.[176] After addition of EDTA to complex inorganic lead, the dialkyllead is extracted with dithizone in CCl_4, from which it may be back-extracted into a dilute HNO_3/H_2O_2 solution and determined by flameless atomic absorption.[176] The method as originally proposed by Hancock and Slater[176] was designed for a 1-hr sampling period, with a detection limit of 0.04 μg (Pb)/m^{-3}. Further development of the method has enabled its use for sampling periods of 6 hr,[177] or 24 and 48 hr, the latter providing a detection limit of 0.25 ng (Pb)/m^{-3}, sufficient for determination of tetraalkyllead in maritime air.[178]

The separate determination of individual tetraalkyllead compounds in air requires preconcentration and gas chromatographic separation. Preconcentration may be upon gas chromatographic packing material at −78°C,[179] or upon glass beads at −130°C.[180] Subsequent rapid desorption into a flame atomic absorption instrument was used by Harrison et al.[179] for analysis of total tetraalkyllead in air at concentrations down to 0.01 μg (Pb)/m^{-3} in a 30-min air sample. Analysis may, however, be by gas chromatography-mass spectrometry,[181] although Radziuk et al.[182] found that the characteristic lead isotope ratio could not be found in ions with m/e values corresponding to alkyllead fragments. They concluded that considerable interferences arise from other high molecular weight compounds in ambient air, and reported this technique as being unsatisfactory. An alternative and specific method of detection subsequent to gas chromatographic separation is provied by flameless atomic absorption,[180] or by a microwave plasma using the 405.78-nm lead emission line.[183] The detection limits of these techniques are shown in Table 4 and the gas chromatographic/AAS separation in Figure 9.

III. PARTICULATE POLLUTANTS

A. Physical Parameters

This subject area is in itself worthy of a review article. Comments made here, however,

Table 4
METHODS FOR DETERMINATION OF TETRAALKYLLEAD IN AIR

Method	Approximate detection limit[a] (as Pb)
Activated carbon/AAS	5 μg[b]
Iodine monochloride/flameless AAS	2 ng
Adsorption tube	
Flame AAS	0.2 ng
GC — flameless AAS	0.04 ng
GC — microwave plasma	0.006 ng

[a] Detection limits refer to TML.
[b] Limited by lead blank in activated carbon.

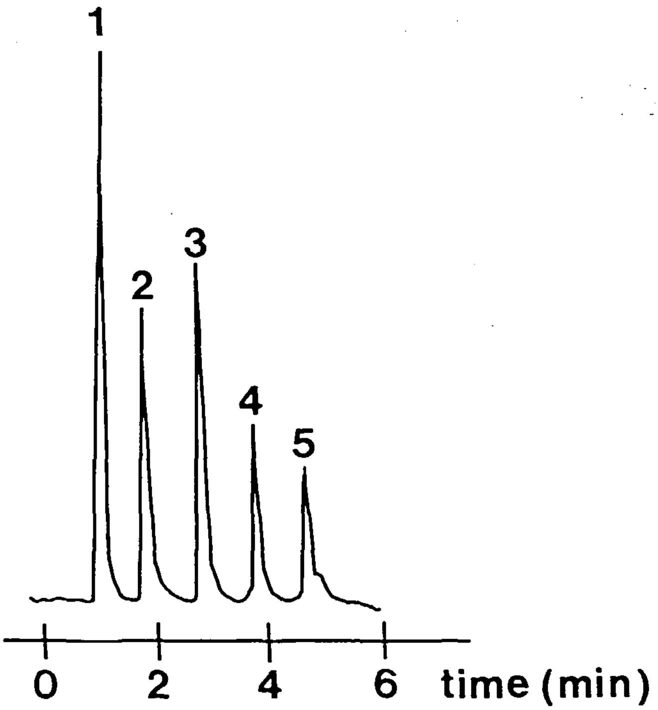


FIGURE 9. Typical gas chromatographic separation of tetraalkyllead compounds, with detection by atomic absorption. 1, tetramethyllead; 2, trimethylethyllead; 3, dimethyldiethyllead; 4, methyltriethyllead; 5, tetraethyllead.[180]

will be restricted to subjects likely to be of direct relevance to those whose prime aim lies with the chemical, rather than physical, characterization of atmospheric particulates.

1. Total Suspended Particulate Measurement

Three methods are used primarily: gravimetric (Hi-Vol sampler), smoke stain, and integrating nephelometer. The gravimetric measurement,[184] although labor intensive, is widely accepted as the true reference standard.

The smoke stain method relies upon measurement of the soiling of a filter paper by atmospheric particles to indicate the airborne particulate loading. In Europe, smoke stain is assessed by measurement of reflectance[185] and in the U.S., transmittance is determined.[186] The method has the advantage of being automatable by use of tape samplers. The transmittance measurement is converted to a "soiling index" in units of coefficient of haze (COH) per linear foot, or meter.[186] The reflectance measurement, however, is reported in terms of a concentration of "standard smoke".[185] While 30 years ago the measurement of "standard smoke" may have related closely to the concentration of total suspended particulates determined gravimetrically, nowadays this not the case. Recent work at Warren Spring Laboratories, England has shown a close correlation between "standard smoke" and organic carbon, but not total suspended particulates.[187]

The integrating nephelometer measures light scattering from suspended particles.[188,189] It has the great advantage of giving rapid response continuous measurements and is commercially available. The disadvantage lies in the fact that the instrument measures the scattering coefficient of the air, which is a function not only of suspended particulate concentration, but also of particle size and morphology. Hence uncertainties arise in interpretation of the measurements in terms of concentrations of atmospheric particles.

Kretzschmar[190] has compared the three major techniques: smoke stain reflectance, gravimetric measurement, and integrating nephelometer. Unfortunately, however, cellulose filters, rather than the more usual glass fiber, were used and the known inefficiency of the former may have led to an underestimation of concentrations measured gravimetrically The results of the three methods were nonetheless found to correlate significantly. The concentrations measured by smoke stain reflectance had a mean value, however, which was less than one half of those from the other methods [$\bar{x}$ (gravimetric) = 122 μg/m^{-3}; $\bar{x}$ (nephelometric) = 132 μg/m^{-3}; $\bar{x}$ (smoke stain) = 55 μg/m^{-3}]. The author concluded that the 24 hr-average results obtained from the nephelometer were in fairly good agreement with those derived gravimetrically.[190] Dalager,[191] in a similar study, compared measurements by smoke stain reflectance, smoke stain transmittance, β-radiation attenuation, and gravimetric measurement using Whatman No. 41 cellulose filters. All four techniques were found to give very different results. The two optical methods (smoke stain reflectance and transmittance) did provide a good correlation and the gravimetric and β-attenuation methods showed a fair correlation, but the optical methods correlated very poorly with the other techniques. A significant finding was that the regression equations derived were not of a universal nature since changes in aerosol composition affect measurements other than those made gravimetrically.[191]

Recent years have seen an increasing awareness of the size selectivity of aerosol samplers, in particular its dependence upon inlet design. Wind tunnel experiments have shown that the standard Hi-Vol sampler at a wind speed of 4.6 ms^{-1} and an 8% level of turbulence has only 55% efficiency for sampling 15-μm particles when the wind is at 45° to the ridge of the roof.[192] The variation of efficiency with particle diameter is shown in Table 5. This problem has led to the production of size-selective inlets[193] designed generally to give a sharp cut-off at 15-μm particle diameter, since particles of $>$15 μm are assumed to be of little significance in the context of health effects.

2. *Methods of Particle Size Discrimination*

A number of highly elegant techniques are available for purely physical characterization of particle size distributions; no chemical information whatever is generated. Review of such methodology is outside the scope of this article and the interested reader is referred to the recent reviews by Liu[194] and Pui and Liu.[195] The air pollution chemist requires instrumentation capable of providing a physical separation and collection of particles on a size basis in sufficient quantity to allow subsequent chemical analysis.

Table 5
SAMPLING EFFICIENCY OF HI-VOL SAMPLER AT 15 ft/sec^{-} [192]

Sampler orientation	Particle diameter (μm) 5	15	30	50
0°	97%	35%	18%	7%
45°	100%	55%	41%	34%

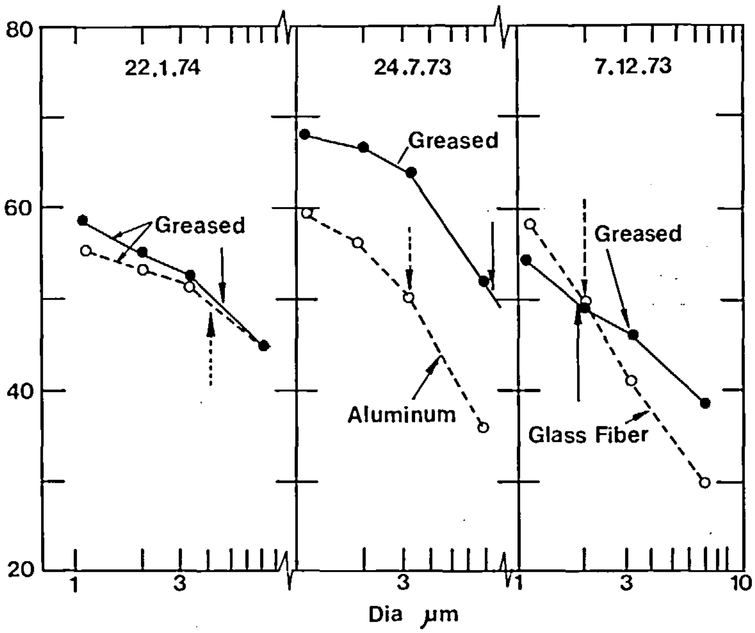


FIGURE 10. .Cumulative size distributions determined by impaction on various substrates.[197] The vertical arrows represent the location of the mass median diameter for each size distribution.

The most widely used instrument in this context has been the cascade impactor, available in a variety of forms employing flow rates in the low volume (5 to 30 ℓ/min^{-1}) or high volume (600 ℓ/min^{-1}) range. The lowest 50% cut-off stage before the back-up filter has in most cases been at about 0.4 μm. Recently, however, cascade impactors have been marketed giving 50% cut-off stages down to 0.08 μm.[196] The very high velocities required to impact particles of these aerodynamic sizes, however, necessitate the use of very fine jets and hence only rather low flow rates (3 ℓ/min^{-1}) are possible giving a rather small sample for chemical analysis.

Dzubay and co-workers[197] have compared the use of dry and greased collection surfaces in a high volume cascade impactor, finding substantial errors due to particle bounce when dry collectors are used as is normal when subsequent chemical analysis is to be performed. Consequently, distorted size distributions result (Figure 10). This discovery led to the development of the virtual impactor and its incorporation in a dichotomous sampler.[198] In the dichotomous sampler (Figure 11), a flow of 7 ℓ/min^{-1} is directed at an inlet leading to a filter through which only 1 ℓ/min^{-1} of air is drawn. Larger particles enter the inlet (virtual impaction) and are collected on the filter. The smaller particles follow the remaining 6 ℓ/min^{-1} air stream and are collected on a separate filter.[198] These samplers have been adopted

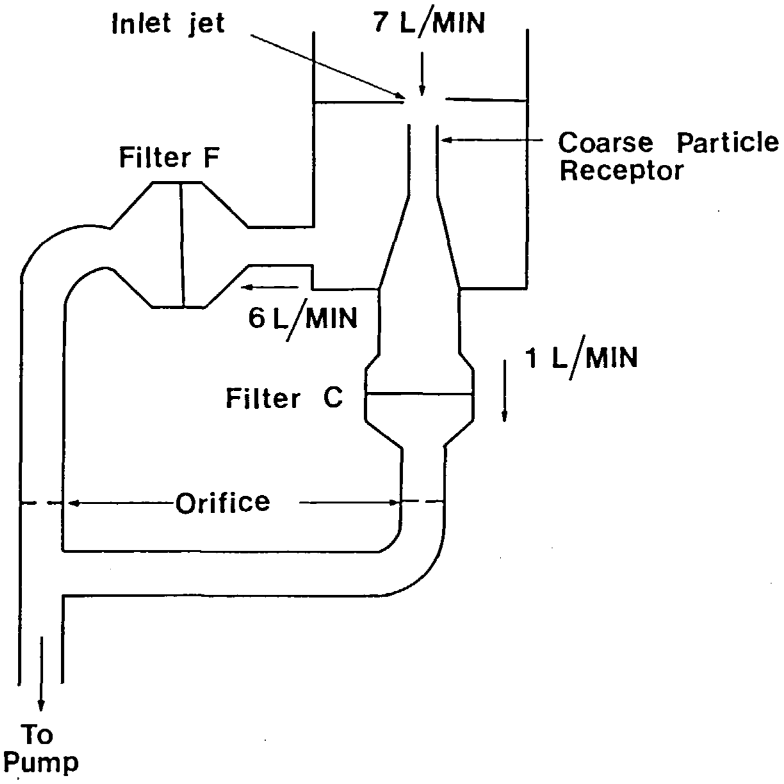


FIGURE 11. Schematic view of a dichotomous sampler that contains a single-stage virtual impactor.[198] More recent designs operate at a total flow of 16.7 ℓ/min^{-1}, and 10% of flow to the coarse filter.

by the USEPA for use in air monitoring networks and are available commercially using a flow of 16.7 ℓ/min^{-1} with 10% of the flow to the coarse filter and the balance through the fine filter. The flow rates are generally selected so as to divide particles into a 0 to 2.5-μm (respirable) fraction and a 2.5- to 15-μm fraction. The sampler has the benefit of avoidance of errors due to particle bounce, but in its present form can only give very limited information upon size distributions.

Some air pollutants such as lead and sulfate have been found to exist primarily as particles of <0.3 μm and cascade impactors are of limited use for particle fractionation. In this size range, the diffusion battery, which separates particles on the basis of their diffusive rather than inertial properties, is useful. There are a number of forms of diffusion battery, the best known consisting of a sequence of collimated holes[199] or mesh screens.[200] The former type was used by Marlow and Tanner[201] for the fractionation of sulfates, but had the disadvantage that no preseparation of large particles was carried out which meant that errors could arise from impaction of large particles in the early stages of the battery.[201] An improved system reported by Harrison and Pio[202] (Figure 12) uses a high volume impactor, which acts as a preseparator and fractionator for large particles, in combination with the commercially available screen type diffusion battery.[202] This has enabled the generation of detailed information upon the size distribution of sulfate, nitrate, ammonium, and hydrogen ions in 24-hr air samples,[202] and could be used for a far wider range of air contaminants.

3. *Filter Efficiency*

Until recent years it has been common to assume that all air filters are of uniform and high efficiency. The development of theoretical models of filtration, and of instruments for

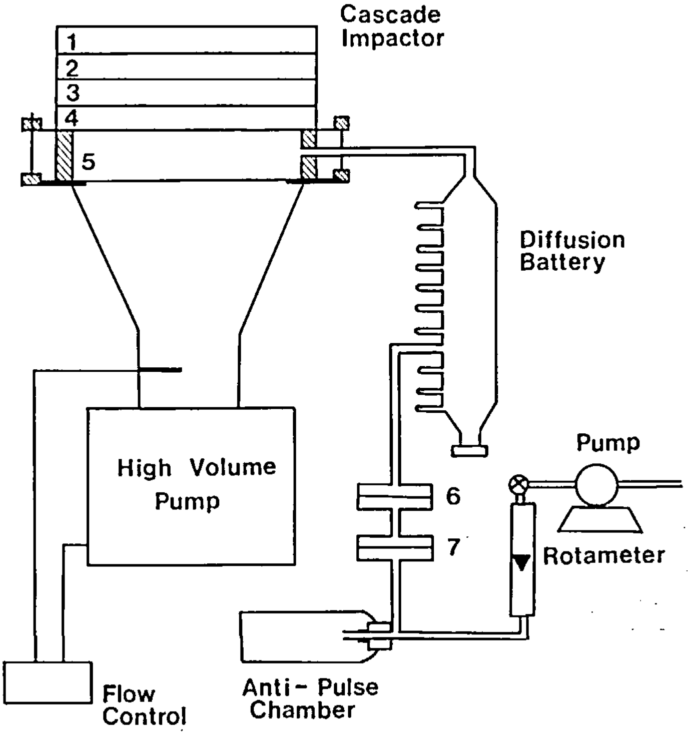


FIGURE 12. Schematic diagram of an aerosol sampler combining a high volume impactor with a diffusion battery. 1 to 4, impactor stages; 5, impactor back-up filter; 6, teflon® filter; and 7, ammonia impregnated filter.[202]

the generation of monodisperse aerosols and the measurement of filter penetration, have led to a realization that some filters may in fact be of very low efficiency.

The mechanism of air filtration is complex and the efficiency of a filter is a function of particle size (see Figure 13). High filtration efficiency is typically seen for very small particle sizes, for which Brownian diffusion provides an efficient mode of collection, and for very large particles where direct interception and inertial impaction are operative. In some instances electrostatic attraction may also be of importance. Spurny has developed a theoretical approach to the prediction of the efficiency of membrane[203] (e.g., Millipore and Nuclepore[204]) filters, which has related well to measurements of efficiency made with monodisperse aerosols of differing sizes.[205-207]

In general, membrane and Nuclepore filters are found to be of very high efficiency, although Skogerboe et al. have produced experimental evidence of considerable inefficiency of membrane filters under conditions of very low loading.[208] Megaw,[209] however, questioned these findings, ascribing the low efficiencies to the experimental methodology used. Biles and Ellison[210] have demonstrated efficiencies as low as 15% for cellulose fiber filters such as Whatman No. 1, No. 4, and No. 541 for sampling lead and black smoke in urban air. Efficiency increased considerably with filter loading, consistent with the results of Skogerboe et al. for membrane filters.[208] Other workers have reported low efficiencies for cellulose fiber filters, particularly Whatman No. 41.[205,211,212] John and Reischl,[211] using a condensation nucleus counter also reported significant penetration of Nuclepore 0.8-μm pore size filters by particles in ambient air. Membrane, glass fiber, and PTFE filters were all found to be of extremely high efficiency in these tests.[211] Confirmation of the high efficiency of glass fiber is given by Spurny et al.[205] who found 99.9% efficiency at 0.03-μm particle diameter and 99.0% at 0.3-μm diameter. Their work does, however, show that face velocity may

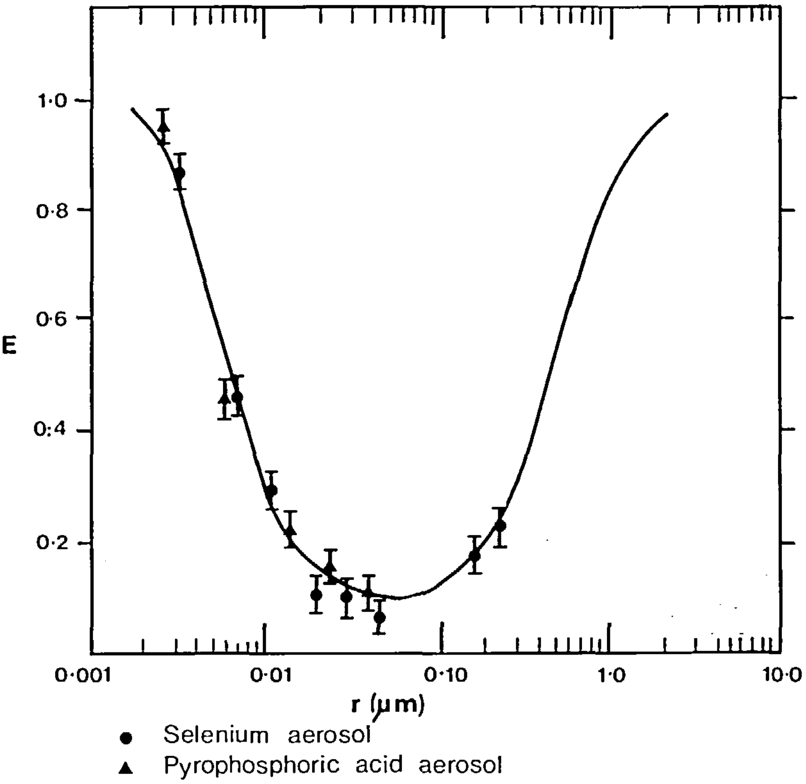


FIGURE 13. Theoretical curve and experimental determination (points) of the efficiency (E) of a 5-μm pore diameter Nuclepore filter at a 5 cm/sec^{-1} face velocity as a function of particle radius (r).[204]

have an important bearing upon filter efficiency, and Cohen[213] found discrepancies between measurements of particle concentrations using Hi-Vol samplers with glass fiber filters at different air flow rates. A difference of 1% was found between Hi-Vols operated at 50 and 60 CFM, but when operated at 40 and 60 CFM, a 3.8% difference was found. Cohen[213] ascribed the discrepancy to reduced filter efficiency at the higher rate of flow, but did not consider whether the inlet efficiency of the sampler for large particles might be reduced at a higher flow rate. Recent data on filter efficiencies are reported by Liu et al.[213a]

B. Particulate Sulfate, Nitrate, Ammonium, and Hydrogen Ion

Excluding sulfate in marine aerosol, it is usual to find an approximate ion balance of $[SO_4^{2-} + NO_3^-]$ (equiv) and $[NH_4^+ + H^+]$ (equiv) in other types of ambient air. The latter ions are the predominant counter ions for both sulfate and nitrate in air. The major part of atmospheric sulfate and nitrate arises from oxidation of SO_2 and NO_x in air; the initial product is the acid, and the ammonium salts are formed subsequently by reaction with gaseous ammonia. From the analytical viewpoint these atmospheric components are best considered together.

1. *Sampling Interferences*

It is only rather recently that the problem of sampling interferences has arisen in the case of these substances. It is appropriate first to discuss the question of filter artifacts: sulfate and nitrate generated on the filter surface itself.

Glass fiber filters are basic, and Pierson and co-workers[214] have found considerable artifact sulfate to be formed on glass fiber filters by interaction with gaseous SO_2. In contrast, PTFE

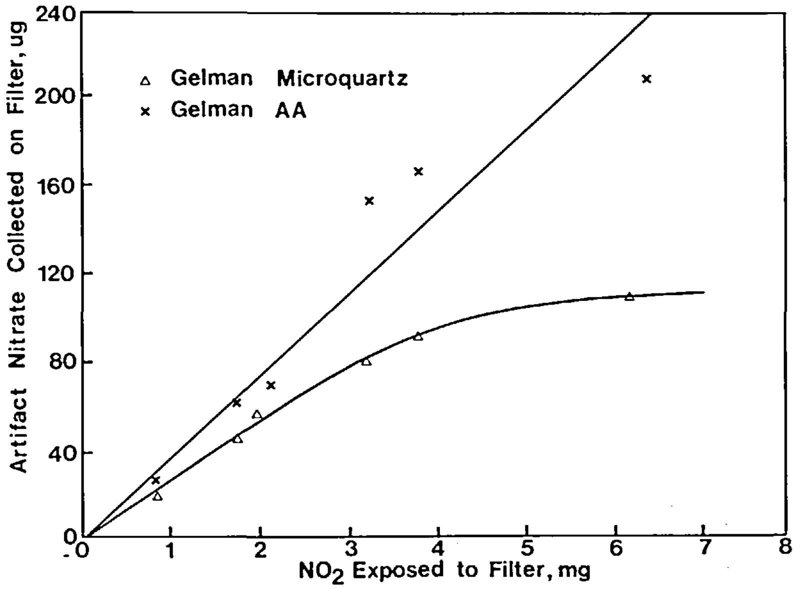


FIGURE 14. Artifact nitrate as a function of filter NO_2 exposure.[220]

membrane and pH-neutral quartz filters gave little or no artifact sulfate. Coutant[215] examined the effect of environmental variables upon artifact sulfate formation. The important variables were found to be relative humidity, temperature, and SO_2 concentration, and filter characteristics such as alkalinity and blank sulfate content. It appears from these studies[214,215] that there is a limit to the capacity of a filter for artifact formation, and hence once that limit is reached, the greater the air sample volume the smaller the error in estimation of the atmospheric sulfate concentration.

Another sampling problem with sulfates can arise from neutralization of sulfuric acid aerosol on a basic filter surface. Klockow et al.[216] found Nuclepore and Mitex (PTFE) filters to be the least reactive in this regard. Barton and McAdie[217] have suggested that prewashing of glass fiber filters with hot H_2SO_4 and thorough rinsing is a suitable pretreatment to avoid H_2SO_4 neutralization. If both H_2SO_4 neutralization and sulfate artifact formation are to be avoided, however, the use of either PTFE or quartz fiber filters is recommended. The latter type of filter has been widely used by Tanner et al.[218] who use a prewashing with hot concentrated H_3PO_4 to ensure neutrality prior to air filtration.

Artifact formation can be a very major interference in nitrate sampling. Appel et al.[219] found that measured mean particulate nitrate values at Californian sites differed by as much as a factor of 2.4 depending on filter medium and sampling rate. A glass fiber (pH = 9) Hi-Vol filter collected on average approximately 10 $\mu g/m^{-3}$ artifact nitrate compared to 8.5 $\mu g/m^{-3}$ true particulate nitrate. Fluoropore (PTFE) filter media were found to be the only media which gave reliable nitrate collection. The source of artifact nitrate was concluded to be gaseous HNO_3, rather than NO_2, which was collected significantly only at high ozone concentrations.[219] Spicer and Schumacher[220] have similarly studied interferences in nitrate sampling. They report interferences from both NO_2 and gaseous nitric acid, with a saturation effect. Figures 14 and 15 show the reported artifact nitrate as a function of NO_2 and HNO_3 exposure for two filter types.[220] In a later study Appel et al.[221] confirm that clean PTFE prefilters permit passage of >98% of HNO_3, but found that atmospheric particulate matter on the PTFE filter could retain HNO_3.

Another confusing interference affects nitrate and ammonium measurements. Recent work in two laboratories[222,223] has shown that ammonium nitrate in air is in equilibrium with gaseous nitric acid and ammonia:

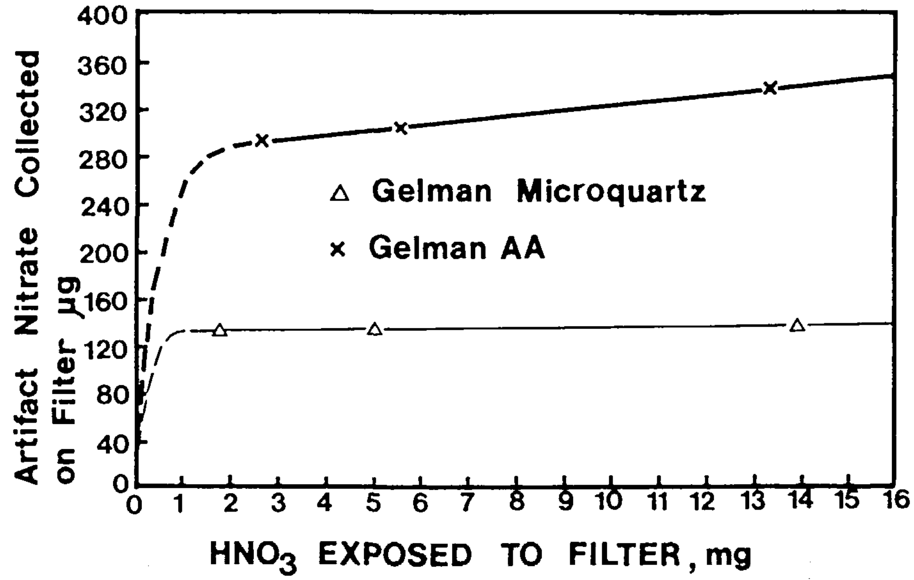


FIGURE 15. Artifact nitrate as a function of filter HNO_3 exposure.[220].

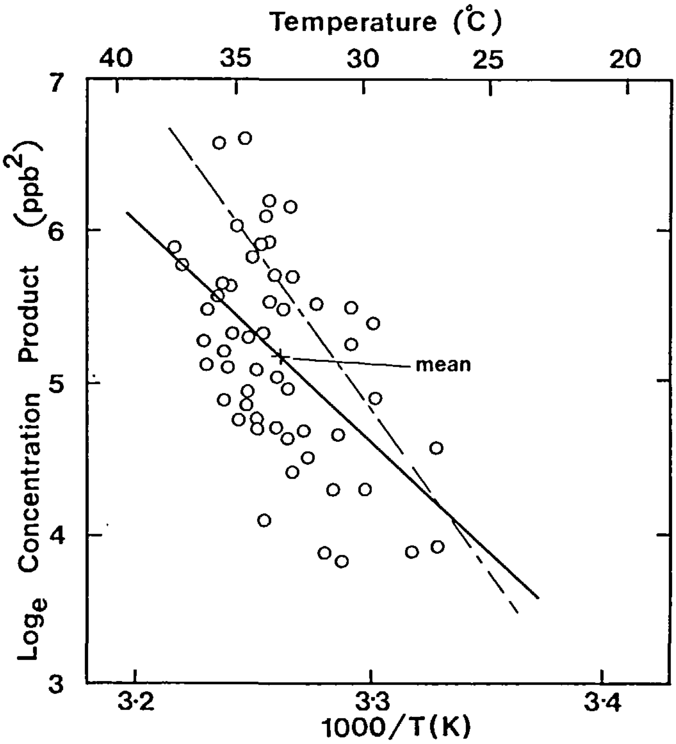


FIGURE 16. Logarithm of the NH_3-HNO_3 concentration product (ppb^2) vs. the reciprocal ambient temperature (K). (——) Regression line for ambient air data points. (— - —) Regression line calculated from thermodynamic data.[222]

$$NH_4NO_3\ (s) \rightleftharpoons NH_3\ (g) + HNO_3\ (g)$$

Indeed Doyle et al.[222] cite simultaneous atmospheric measurements of HNO_3 and NH_3 in support of this contention. The equilibrium is temperature dependent and the concentrations of the components of the equilibrium can be predicted from Figure 16. One consequence of this equilibrium is that ammonium nitrate collected on a filter may volatilize after collection, if stored under conditions of lower gaseous pollutant concentration[224] and may also volatilize from a prefilter during air sampling if the concentrations of gaseous HNO_3 and NH_3 diminish. This can cause a negative error in NH_4NO_3 measurements and a positive error in HNO_3 and NH_3 measurements made on a collector used after the filter.[221]

A problem of a very different nature arises in sulfate analysis. Scott and Cattell[225] have demonstrated the stability of ammonium sulfate with respect to ammonia loss. When sampling sulfuric acid aerosol, however, reaction of collected H_2SO_4 with gaseous ammonia is reported to cause a severe sampling interference,[216] giving a positive interference for NH_4^+ and a negative interference for H^+. The approach to this problem has been to use an ammonia denuder. The internal walls of a small bore glass tube are coated with an acidic reagent, either phosphoric acid[226] or oxalic acid,[227] and air, without prefiltration, is drawn through the tube. The tube dimensions are such that gaseous ammonia is totally removed from the air stream by diffusion to the tube walls, while particulate pollutants due to their lower diffusivity are not significantly deposited. This technique may be used for analysis of gaseous ammonia without interference from particulate ammonium[227] or for sampling acid sulfates[221,227] subsequent to the diffusion denuder which removes the ammonia interference. Our own work has confirmed the effectiveness of the ammonia denuder, but reveals problems when both nitrate and sulfate analyses are required. Sampling in parallel using two systems, one with an ammonia denuder and one without, shows that while the ammonia denuder system shows higher levels of H^+ collection, the measured concentrations of NO_3^- are diminished apparently due to dissociation of NH_4NO_3 during passage through the ammonia denuder, due to the displacement of the equilibrium conditions of this compound.[228] Consequently, extreme care must be exercised in selection of a sampling system for analysis of SO_4^{2-}, NO_3^-, NH_4^+, or H^+ dependent upon the precise objectives of the work in hand.

2. *Analysis of Sulfate*

Once sampling is completed, an analysis for total sulfate may be required. If more detailed information upon sulfate speciation is wanted, a technique from the later section will be appropriate.

Sulfate has never been an easy ion to determine, although recent developments allow a far more precise analysis than was previously available. Wet chemical methods in common use include the methylthymol blue method,[229] the barium chloranilate method,[230,231] and the thoron method,[232] all of which have been available for a considerable number of years. Colovos et al. have reported a technique for linearizing the calibration curve in determination of sulfate by the methylthymol blue (MTB) method. This involves an alteration in the barium to MTB ratio. Sensitivities of 0.5 $\mu g/m\ell^{-1}$ in a range of 10 $\mu g/m\ell^{-1}$ were obtainable.[229] A sensitive technique reported recently involves reaction of sulfate with a barium-nitrosulfonazo III [2,7-bis (4-nitro-2-sulfophenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid] chelate complex which releases free azo chelating dye.[233] The extent of the reaction is determined spectrophotometrically as a decreased absorbance due to breakdown of the barium-dye chelate.

$$\text{Ba-dye chelate} + SO_4^{2-} \rightarrow BaSO_4 + \text{dye}^{2-}$$

The working range of the method is 1 to 12.5 $\mu g/m\ell^{-1}$ with a coefficient of variation of 3% in the range of 6 to 12.5 $\mu g/m\ell^{-1}$ and 13% over 1 to 4.5 $\mu g/m\ell^{-1}$. The only serious interference is due to Ca^{2+} which can be removed by ion-exchange pretreatment of the sample.[233]

The development of ion-exchange chromatographic analysis[234] has revolutionized the analysis of anions. The application of this technique to the analysis of sulfate in ambient

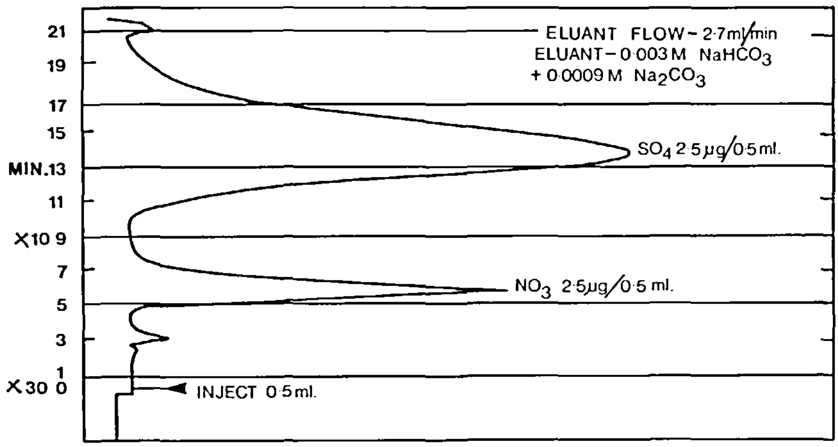


FIGURE 17. Ion chromatographic analysis of sulfate and nitrate in an ambient aerosol sample.[235]

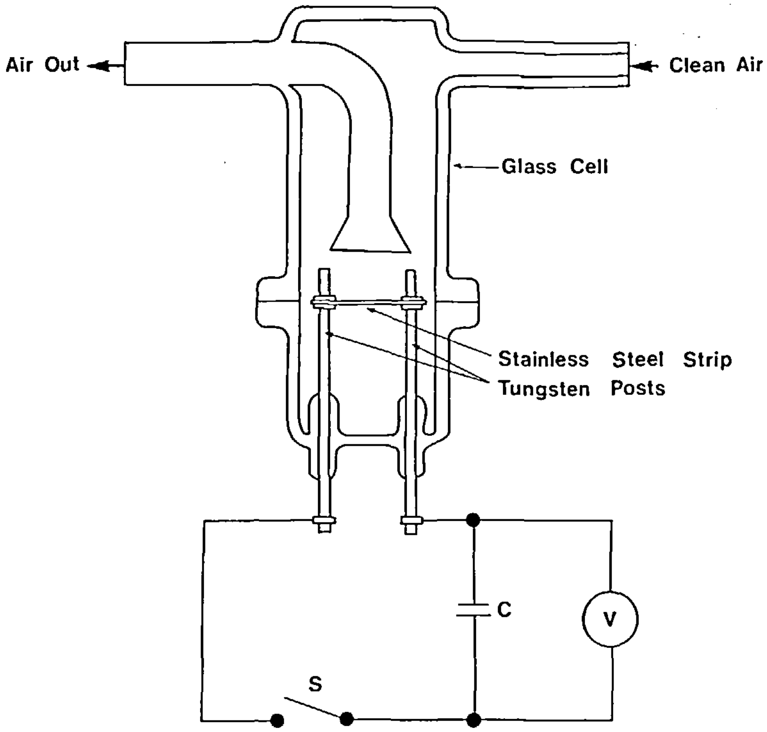


FIGURE 18. Aerosol vaporization apparatus for determination of atmospheric sulfates.[236]

aerosols is described by Mulik et al.[235] The detection limit of the technique is reported as 0.1 $\mu g/m\ell^{-1}$ with a relative standard deviation of 3% at the 5 $\mu g/m\ell^{-1}$ level.[235] A typical chromatogram is shown in Figure 17.

Two groups have reported use of a physical technique for the analysis of airborne sulfate.[236,237] The apparatus is shown in Figure 18. Sulfates are vaporized by electrical heating of a sample placed on the stainless-steel strip. The vapor is swept from the cell by a stream of clean air and the sulfur content is quantified by a flame photometric sulfur analyzer. The method responds to all sulfur compounds which evaporate or decompose below about 1200°C and has a lower limit of detection of 1 ng sulfur.[236] One drawback of the method is that sulfate collected on air filters must be extracted into water, which requires preconcentration before analysis, as only 5 μℓ of extract may be used for flash vaporization.[236] Husar et al.[237] have developed sampling techniques designed to minimize this problem and to optimize overall sensitivity. Results were, however, on average 23% lower than obtained on the same samples by X-ray fluorescence (XRF) analysis.[237]

Dzubay and Stevens have used XRF to analyze sulfate collected by a dichotomous sampler.[198] This technique has the advantage of analyzing a wide range of elements in the same sample. The detection limit was reported as approximately 5 μg/cm^{-2} on an air filter surface.[198] The method is of course sensitive to all particulate sulfur, but comparison with other techniques shows that to a good approximation all such sulfur may be assumed to be in the form of sulfate. Stevens et al.[228] compared energy-dispersive XRF analysis with ion chromatographic analysis of coarse (>3.5 μm) air particulates. A linear regression analysis revealed:

$$SO_4^{2-}\ (IC) = -0.30\ \mu g/m^{-3} + 0.92\ SO_4^{2-}\ (EDXRF)$$

and showed a correlation coefficient of 0.905. For fine (<3.5 μm) particulates, however:

$$SO_4^{2-}\ (IC) = 0.04\ \mu g/m^{-3} + 0.98\ SO_4^{2-}\ (EDXRF)$$

with a correlation coefficient of 0.997. Hence an excellent agreement is seen for the smaller particles, while for the large particles, representing a much lower sulfate concentration, there is apparently some unexplained form of systematic discrepancy. In this work, Stevens et al.[226] determined particulate sulfite by ion chromatography after ultrasonic extraction into 5×10^{-5} N perchloric acid at 0°C (to inhibit oxidation to SO_4^{2-}). In all samples sulfite represented less than 2% of total sulfur.

X-ray fluorescence analysis has also been compared with three wet chemical procedures:[238] the methylthymol blue method, the barium chloranilate method, and a modification of the method of Brosset et al.[239] which involves removal of cationic interferences by ion exchange, reaction with excess barium to precipitate $BaSO_4$, and subsequent reaction of excess barium with thorin to form a colloidal complex which is determined spectrophotometrically. The three wet chemical techniques showed agreement within 16% for all filter media tested, and XRF gave closely comparable results.[238]

3. *Analysis of Nitrate*

The Intersociety Committee recommends analysis of nitrate either by the 2,4-xylenol method[240] or the brucine method.[241] The former method has been widely used, although Appel et al.[242] report a serious interference in the analysis of atmospheric particulates. Negative errors of up to a factor of three were reported in the presence of vehicle-related aerosols. The magnitude of the error correlated with the lead concentration, but the latter pollutant was apparently not the interfering agent.[242] The other commonly used wet chemical procedure for nitrate involves reduction to nitrite with hydrazine sulfate in alkaline solution[243] or with a copper-cadmium reduction column. The nitrite is then determined by a diazotization reaction in a modification of the Saltzman procedure.[28,243] In the unlikely event of nitrite being present in a sample, this would interfere, but can be allowed for by separate analysis of an aliquot of sample without the reduction step. Appel et al.[242] also employed this procedure and concluded that it was free of interferences under the air sampling conditions used.

Ion chromatography is now coming widely into use for analysis of nitrate in air samples. The limit of detection is reported to be 0.1 μg/mℓ$^{-1}$ with a relative standard deviation of 1% at the 5 μg/mℓ$^{-1}$ level.[235]

4. *Analysis of Ammonium*

The catalyzed indophenol blue method[69] is commonly used for analysis of ammonium leached into water from air samples. The sensitivity of the method is approximately 0.02 $\mu g/m\ell^{-1}$ with a linear range up to at least 5 $\mu g/m\ell^{-1}$.

Ion chromatography may also be used for analysis of NH_4^+. Concentrations as low as 0.09 $\mu g/m\ell^{-1}$ may be determined[70] with a high precision (relative standard deviation 2.9%). Neither aliphatic amines nor alkali metal ions interfere and good agreement with other methods is reported.[70]

Eagan and Dubois[244] describe the use of ion-selective electrodes for the analysis of NH_4^+ in air particulates. Both the Orion NH_3 electrode and the Beckman NH_4^+ electrode were tested using aqueous extracts from Hi-Vol samples. Both electrodes were capable of operation over the range of 0.1 to 10 $\mu g\ m\ell^{-1}$ NH_4^+ in solution, corresponding to 0.03 to 30 $\mu g/m^{-3}$ in a 2000-m^3 air sample.[244] Results were of acceptable accuracy and precision and compared well with analyses by the indophenol blue method.

5. *Analysis of Acidity and Speciation of Sulfates*

Two assumptions regarding sulfate speciation and acidity measurement are generally accepted. First, the only strong acid present in ambient air in particulate form is sulfuric acid: hence measurements of H^+ in aerosols, should correspond closely to H_2SO_4 concentrations. Second, in most ambient aerosols, the major sulfates present are $(NH_4)_2SO_4$, NH_4HSO_4, and H_2SO_4. Other sulfates are present, but generally at very much lower concentrations. There will inevitably be exceptions, such as in maritime air where Na_2SO_4 may be a major component.

The most straightforward approach to the analysis of airborne acidity is the titration of aqueous extracts of atmospheric particles. A Gran titration plot[245] is used and development of the technique has been due primarily to Brosset.[246,247] Although some information upon sulfate speciation may be inferred from the slope of the Gran plot,[246] chemical interactions within the aqueous titration medium and the presence of other, weak acids severely limit this aspect of the analysis.

The major alternative approach to sulfate speciation and acidity determination is based upon the methods devised by Leahy et al.[248] These involve selective extraction of H_2SO_4 using benzaldehyde; NH_4HSO_4 using isopropanol; and $(NH_4)_2SO_4$ using water. This has the advantage of avoiding addition of water, hence preventing chemical interactions between species prior to extraction. A pyrolytic method, based upon selective volatilization of sulfates, was also tested by these workers[248] and found to be considerably less selective. The selective extraction techniques have been applied widely by Tanner and co-workers.[201,218] Recoveries of H_2SO_4 and NH_4HSO_4 from different filter media by benzaldehyde are shown in Table 6 and were derived using ^{35}S-labeled H_2SO_4. Comparison of the benzaldehyde extraction and Gran titration techniques revealed considerable divergences, attributed to the presence of large amounts of weak acid affecting the titration, which the authors did not attempt to identify.[218] A further comparison of the benzaldehyde extraction and Gran titration techniques is reported by Appel and co-workers.[249] These authors concluded that in the presence of atmospheric particulate matter on a filter, H_2SO_4 aerosol recovery was $\leq 30\%$ by benzaldehyde extraction, but usually $>60\%$ by strong acid titration using acid-washed quartz fiber or teflon® filters.[249] The benzaldehyde technique has been criticized by Eatough et al.[250] who applied it to the analysis of smelter flue dusts. Their results indicated that bivalent metal bisulfate salts and some sulfite salts could also be extracted. Additionally, if benzoic acid is present as an impurity in the benzaldehyde, bivalent metal sulfate salts may also be extracted.[251]

West and co-workers[251,252] have developed a technique by which H_2SO_4 may be converted to a relatively inert substance on an impregnated filter and determined in that form. A glass

Table 6
BENZALDEHYDE EXTRACTION OF H_2SO_4 AND NH_4HSO_4 FROM FILTERS[218]

Sample	Amount (μg)	No. of determinations	Filter material	Recovery (%)	Method
H_2SO_4	10	2	Quartz	75	^{35}S
	20—40	2	Mitex 5 μm	71	^{35}S
	30	1	Fluoropore 0.2 μm	90	^{35}S
	20—40	4	Quartz	78	^{35}S
	70—80	4	Quartz	86	SO_4^{a}
	100	5	Any of the above	94 ± 8	^{35}S
NH_4HSO_4	10—70	3	Fluoropore 0.2 μm	1.2	^{35}S
	34	2	Fluoropore or quartz	111[b]	^{35}S

[a] Soluble sulfate determined by turbidimetry.
[b] Extraction by methanol.

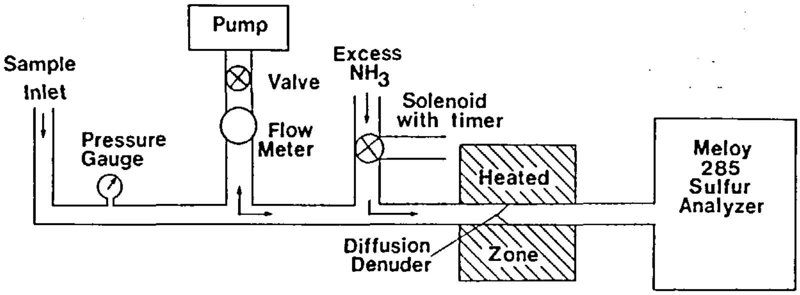


FIGURE 19. Continuous analyzer for measurement of aerosol sulfur and sulfuric acid in ambient air.[256]

fiber filter is impregnated with 2-perimidinylammonium bromide which reacts with H_2SO_4 to form perimidinylammonium sulfate. This may be pyrolyzed to form stoichiometric amounts of SO_2 which are analyzed. Reaction of the collected acid with basic materials on the filter surface is inhibited.[251,252] More recently, these authors have developed a technique of colorimetric analysis of the organic sulfate after reaction with HNO_3 to form 2-amino,4,6,9-trinitroperimidine. The sensitivity of the method is 0.1 μg H_2SO_4 and the working range is 0.2 to 50 μg H_2SO_4.[253]

In a method devised by Huygen,[254] sulfuric acid collected on a filter is reacted *in situ* with diethylamine and the amount of diethylamine absorbed is determined photometrically by conversion to the copper-dithiocarbamate complex. The detection limit is 0.2 $\mu g/m^{-3}$ and the reproducibility is about 10%. Other acidic particles may interfere to the extent of about 20% and ammonium sulfate may also cause a small interference.[254] A further development of the Huygen method is reported by Dzubay et al.[255] In this case ^{14}C-labeled trimethylamine is used and the β-ray activity of the filter is determined, with calibration by comparison with known laboratory-generated H_2SO_4 samples. Comparison of this method with the Gran titration procedure using ambient aerosol samples showed reasonable concurrence.[255] The relative response to H_2SO_4 and NH_4HSO_4 was not investigated.

Tanner et al.[256] have described an ambient aerosol sulfur monitor using continuous flame photometric detection. Sulfur dioxide is removed from the air stream by a diffusion denuder coated internally with sodium carbonate (Figure 19). The response of the flame photometric analyzer is then due to aerosol sulfur compounds. The denuder is heated and may be made to selectively remove H_2SO_4, but to pass $(NH_4)_2SO_4$ and NH_4HSO_4. If ammonia is then added to the air stream on a cyclic basis, H_2SO_4 may be determined by difference.[256] Baseline fluctuations due to changes in atmospheric pressure and humidity necessitate additional components in the analytical system[257] and it appears that the ultimate complexity is such that this is an instrument unlikely to find routine use.

Certain of the above techniques are best calibrated using a sulfuric acid aerosol generator. The considerations in design of such a generator and the experience with a system involving combination of vapor-phase SO_3 and water vapor to form H_2SO_4 in the submicrometer size range are described by Chang and Turkington.[258] An alternative design is provided by Tanner et al.[256]

C. Particulate Metals

Improved techniques for metal analysis have stemmed naturally from the greatly improved instrumentation which has become available in recent years. It is not the function of this review to chart the progress of instrument design, but rather to report the application of presently available instrumentation to the analysis of metallic air pollutants.

Particular metals are sampled from the air most commonly using high efficiency filters. Analysis of such filters may be carried out by techniques involving no prior extraction of the metals (e.g., X-ray fluorescence, neutron activation), or those involving prior extraction and dissolution of metal (e.g., atomic absorption, anodic stripping voltammetry).

1. X-Ray Emission Analysis

X-ray fluorescence (XRF) is a widely used nondestructive technique of analysis of airborne particles. Methods suitable for analysis of a wide range of elements by both wavelength and energy-dispersive methods have been reported.[259,260] Birks[261] has shown that sensitivity and detection limits in XRF analysis may be predicted theoretically, and that such predictions may be used to indicate the optimum instrumental parameters for the element and sample.

The type of air filter used may have an important influence upon XRF analyses. O'Connor et al.[262] showed that substantial penetration of particles occurs into the body of cellulose filters, and that a consequent correction of XRF data for absorption of radiation by the filter medium is necessary. In this aspect, glass fiber filters are superior to cellulose.[262] One means of overcoming problems due to absorption corrections is to fold air filters with the loaded side inwards.[263] This enhances sensitivity and makes absorption corrections simpler and more accurate. The technique was proven for both Whatman cellulose and Nuclepore filters.[263]

One major problem in X-ray analysis is the preparation of suitable thin film standards. The many methods available for preparing standards have been reviewed by Breiter et al.[264] Pradzynski and Rhodes[265] report the development of two types of standard: for water-soluble trace elements, solutions were deposited on glass fiber filters and dried, and for nonvolatile trace elements, solutions were prepared from 10-μm quartz powder spiked with compounds of the element and deposited from air suspension.[265] An interesting new technique involves mixing a solution of different elements and a radioactive tracer (^{24}Na) with the water-soluble polymer methylcellulose.[266] Thin film standards are produced by spreading an even film of the mixture on a glass plate and allowing it to dry, the concentrations of the trace elements being determined from the tracer activity. Excellent precision and accuracy were reported.[266]

The use of particle (proton)-induced X-ray emission (PIXE) for the quantitative analysis of airborne particles has been reported.[267] In a comparative study of PIXE and energy-dispersive XRF of air particulates, Ahlberg and Adams[268] report that using the criterion of equal number of counts in the spectra, PIXE gives about 3 times lower detection limit for air filters and 30 times lower for a cascade impactor sample.

2. Instrumental Neutron Activation Analysis (INAA)

This is now well established as a technique for the analysis of airborne particles.[269,270]

INAA has been applied to the analysis of 2500-m^3 air samples collected using 20 × 25 cm glass fiber filters in the U.S. National Air Sampling Network.[271] Including arsenic, 26 elements were determined and 13 of the 26 were above the detection limit in over 20% of the samples analyzed.[271] An NBS urban air particulate reference standard has been analyzed by INAA with the quantitative determination of 32 elements.[272]

3. *Anodic Stripping Voltammetry (ASV)*

The high sensitivity of ASV analysis for Pb, Cd, Cu, and Zn in particular has led to its use for the analysis of metals in extracts of air particulate samples. Both Sturrock et al.[273] and MacLeod and Lee[274] have analyzed samples collected on a cellulose filter tape sampler using voltammetric techniques. The high sensitivity obtained enabled the discrimination of diurnal variations in metal concentrations. Samples collected on Nuclepore filters have been similarly analyzed.[275]

With a view to further enhancing sensitivity, Ryan and Siemer developed a voltammetric cell of volume only 0.1 to 0.3 mℓ in order to study concentrations of Pb, Cu, and Cd which had been collected on a porous graphite filter.[276]

4. *Atomic Absorption Spectrophotometry (AAS)*

This is the preferred technique for many workers, due to the relatively inexpensive equipment, high sensitivity, and applicability to a wide range of elements.

Pretreatment of the air filter sample involves ashing and/or extraction. Recommended procedures vary enormously and each sample must be judged on its merits. While strong oxidizing acids may be required for many samples,[277] other workers have recommended the use of dilute acid solutions with ultrasonic treatment[278] for extraction of lead and cadmium from unashed filter samples. In the case of aluminium, hydrofluoric acid treatment is essential to ensure decomposition of silicate matrices.[279] A comparison of wet ashing with both high and low temperature ashing methods has been reported by Kometani.[280] Even low temperature ashing causes loss of arsenic in marine air particulates.[281] Recoveries of 41 to 86% were found, measured against analysis by INAA.

Flameless atomic absorption is generally preferred over flame methods due to the considerably greater sensitivity. Interferences do occur, but the use of matrix modification techniques and/or standard additions will generally overcome such problems. Addition of magnesium has been reported as a valuable matrix modification in the analysis of As in marine air particulates.[282] Suitable methods for low volume air sampling and flameless AAS analysis have been reported for the metals Cd, Cu, Fe, Pb, and Zn,[277] Al, Ca, Cd, Co, Cr, Fe, Mg, Mn, Ni, Pb, and Zn,[283] and for Cd, Pb, and Mn in size-fractionated aerosols.[284] Automation of AAS analysis with electrothermal atomization for the determination of lead in atmospheric particles has been described by Pickford and Rossi.[285] A useful comparison of wet ashing and AAS analytical methods for Pb and Cd in air particulates showed good precision and accuracy even with several variations in technique.[286]

In an attempt to reduce blanks and enhance analytical sensitivity, several workers have developed methods based upon direct use of a graphite cup, or of a graphite tube containing a small membrane filter, as an air sampler for direct insertion into an AAS instrument. Thus Siemer et al.[287] report use of direct filtration through porous graphite as a means of sampling beryllium in air. Measurements made in the range of 2 to 20 $\mu g/m^{-3}$ in an air sample volume of 50 mℓ showed an analytical precision of 15%. In the method devised by Noller and Bloom,[288] a small Millipore filter disc is inserted in a modified graphite cup for use as an air sampler. While these methods may indeed give a very high sensitivity, the inconvenience and expense of using graphite cups as air samplers, and the time delays involved in their insertion in the AAS instrument, have led to few workers adopting these methods for routine use.

Cold vapor atomic absorption may be used for the analysis of particulate mercury in air. Dumarey et al.[289] recommend the use of quartz fiber filters for air sampling. After sampling, the mercury is released by pyrolysis and collected on a gold-coated sand absorber prior to thermal desorption into the cold vapor AAS. Kermoshchuk and Warner[290] report a technique involving the addition of 5% potassium permanganate and concentrated HF to an air filter in a sealed polyethylene bottle. When dissolution of the sample and filter is complete, the resultant dissolved mercury is reduced to vapor and analyzed by the usual cold vapor AAS procedure.[290] Mercury recoveries in excess of 90% were found.

5. *Other Methods*

Optical emission spectrometry, although rather little used, is applicable to the analysis of air particulates. Instrumental conditions and sensitivities for 24 elements are reported by Scott et al.[291] Spectroscopic graphite electrodes may be used as filters for airborne particles, with subsequent direct analysis by emission spectrometry giving very high sensitivity.[292]

Mass spectrometry, using a spark source, has been reported for the analysis of nanogram quantities of 28 elements in air particulates collected on a nitrocellulose filter pad.[293] Silver was used as an internal standard, and an air sample of 10.8 m^3 was collected over 9.5 hr. By impinging air particulates on a heated Fe ribbon and analysis of the ion current with a small magnetic sector mass spectrometer,[294] it is possible to continuously analyze for Li, Na, K, Rb, Cs, Sr, U, Pb, Cr, and Cu in air at concentrations in favorable cases down to 10^{-13} g/m^{-3}. This technique shows promise for further development.

A comparison of AAS with X-ray photoelectron spectroscopy (XPS) revealed the drawbacks of the latter technique for the nondestructive analysis of air filters.[295] XPS is sensitive only to the surface layer of the sample and led to the discernment of three types of sample inhomogeneity: localization heterogeneity, thickness heterogeneity, and heterogeneity of particle composition.[295] The finding that air filter samples are not of identical composition across the whole filter surface has consequences for other analytical methods, such as XRF if the whole exposed filter surface is not scanned by the X-ray beam.

D. Particle-Associated Organic Compounds

1. *Polynuclear Aromatic Hydrocarbons (PAH) and Derivatives*

Some lower molecular weight PAHs are of substantial vapor pressure and hence exist in vapor and particle-associated forms simultaneously.[296] Sampling of particle-associated material is usually by Hi-Vol, or high volume impaction methods with glass fiber substrates for filters or impaction surfaces. In most studies, subsequent extraction of PAH has used a Soxhlet, with a variety of solvents including dichloromethane,[297,298] benzene,[299] and cyclohexane.[300] Golden and Sawicki[301] report improved extraction efficiencies by extraction at room temperature with ultrasonic treatment and addition of glass powder to absorb polar coextractives. The ultrasonic technique is also substantially faster, taking only about 40 min, as against 6 to 8 hr typical for Soxhlet extraction.

It is also possible to remove PAH from glass fiber filters by thermal desorption at 300°C under nitrogen.[302] The desorbed PAHs are collected on a precolumn, from which they are desorbed rapidly into a gas chromatograph. Good sensitivity is achievable since the sample is not diluted with solvent, but no preseparation of interfering compounds is possible.

One common means of PAH separation is thin layer chromatography (TLC). By careful selection of stationary phase and solvents, and the use of two dimensions, good separations of common PAH may be achieved. After removal of individual fluorescing spots from the plate, PAH may be extracted into a solvent and determined individually by fluorescence measurement.[303,304] PAHs separated by TLC may also be characterized by mass spectrometry, if required.[305]

A sequence of gel filtration, column adsorption chromatography, and charge transfer complexation with 2,4,7-trinitro-9-fluorenone yields PAH fractions sufficiently pure for UV/

visible and mass spectrometric investigation.[306] Alternatively, thin layer chromatography involving a preliminary group separation on alumina, with subsequent two-dimensional TLC on aluminium oxide/40% acetylated cellulose with fluorescence detection, is a useful technique.[307] Paper chromatography[308] is also reported to give adequate separation of PAHs in airborne particulates.

Excellent gas chromatographic separations of PAHs extracted from airborne particulates may be obtained by use of glass capillary columns. If prior separation of PAHs from interfering compounds is not carried out, then a detector more selective than the FID is required. Hence Burchfield et al.[302] report use of an electron capture detector and a gas phase spectrophotofluorometric detector. Mulik and co-workers[309] have described a gas phase fluorescent detector which may be used to completely resolve benzo(a)pyrene from other fluorescent PAHs which when used as a gas chromatographic detector allows measurement of B(a)P levels as low as 20 pg m^{-3} in a 24 hr Hi-Vol sample.

Bartle and co-workers[310] used a solvent partition procedure to separate PAH from interfering aliphatic hydrocarbons prior to GLC analysis with FID detection. Preseparation of PAH has also been carried out using Sephadex LH20[298] and silica adsorption chromatography. Commonly used GLC columns for PAH analysis are SE52[297] and Dexsil 300 GC.[311] Janini et al.[312] report some greatly improved separations of PAH by use of a packed column with nematic N,N′-bis(p-methoxybenzylidene)-α,α′-bi-p-toluidine stationary phase.

The use of GC-MS can be valuable in the examination of unknown PAH mixtures in environmental samples. This is now a popular technique and the methodology involved has been described by Lao et al.[313,314] Mass spectrometry was also found to be valuable in the identification of methyl-substituted PAH in petroleum pitch volatiles.[311] After identification of major compounds by MS, a GC-UV technique was adopted for quantitative use.[311]

In very recent years, high performance liquid chromatography (HPLC) has come much into favor as an analytical tool for determining PAHs. On-line UV and fluorescence detection[299,300] are both possible, the latter technique having advantages in the presence of possible UV-absorbing interferences in the matrix. Using a reverse-phase ODS Zorbax column and fluorescence detection,[300] a 10-ng detection limit was reported for B(a)P. With improved fluorescence detector design, Das and Thomas[315] report that using a deuterium light source and an excitation wavelength < 300 nm, picogram detection limits are attainable.

When a separation technique such as HPLC fails to give complete separation of isomers, further detailed information upon the components of a mixture may be obtained by use of the Shpol'skii effect. At very low temperatures in specific solvents, PAHs exhibit quasilinear fluorescence spectra and hence by scanning the spectrum, lines due to a number of constituents of a mixture may be separately identified. This has been used with UV excitation to identify methylated forms of pyrene,[316] or with X-ray excitation for a range of compounds.[317]

Nitro derivatives of some PAH in air particulates have been separated by thin layer chromatography and characterized by fluorescence quenching.[318]

2. *Other Organic Compounds*

Cautreels and Van Cauwenberghe[319] have reported a comprehensive scheme for the detection of organic compounds in airborne particulates. Samples collected on glass fiber filters are extracted into benzene and separated into neutral, acid, and basic fractions each of which is analyzed quantitatively by GC-MS. The neutral fraction contains PAHs, saturated aliphatic hydrocarbons, and polar-oxygenated compounds; the acid fraction, fatty acids and aromatic carboxylic acids; and the basic fraction, nitrogen-containing analogs of PAH.

GS-MS analyses have also been used to analyze a wide range of aliphatic and aromatic hydrocabons isolated from Hi-Vol samples by Soxhlet extraction with methanol.[320] Grosjean and co-workers[321] utilized methane chemical ionization mass spectrometry in conjunction with gas chromatography to identify C_3-C_{10} aliphatic dicarboxylic acids in air.

Table 7
QUANTITATIVE X-RAY ANALYSIS OF SUSPENDED PARTICULATE AT PROVO OREM SITES

	Lindon		Geneva			BYA	BYU	
Component	**HV-1**	**HV-2B**	**GF-20**	**GF-22**	**TF-8**	**GF-16**	**GF-21A**	**GF-48A**
Biotite	0.3	0.7	—	—	—	—	—	—
Muscovite	10.1	6.9	—	—	—	—	6.3	8.1
Gypsum	0.7	—	1.2	0.7	—	—	7.4	6.0
Kaolinite	1.1	—	7.4	—	—	—	3.3	1.2
Quartz	16.1	9.6	21.7	10.4	13.7	15.3	18.4	12.5
Calcite	10.3	11.6	18.0	8.0	16.5	13.2	10.3	7.0
Plagioclase	1.4	—	8.3	—	—	—	—	—
Dolomite	2.2	1.3	—	2.9	6.3	—	4.8	—
Slag glass	4.7	3.0	2.7	16.5	—	—	—	—
Hematite	3.5	3.2	4.4	7.6	4.7	—	7.1	2.7
Magnetite	2.6	1.3	0.4	4.9	0.8	—	—	—
Carbonaceous fly ash	16.8	5.4	21.5	11.5	25.5	25.3	42.5	27.6
Siliceous fly ash	31.1	57.1	14.5	37.5	32.5	46.2	0	34.9

Note: All concentrations are percentages by weight.

From Davis, B. L., *Atmos. Environ.*, 15, 613, 1981. With permission.

E. Physicochemical Speciation of Inorganic Compounds in Atmospheric Aerosols

In recent years it has become clear that simple elemental or ionic analysis of airborne particles does not provide adequate information from which to assess the toxicity or environmental mobility of a pollutant. More detailed information upon chemical composition and bonding is required and this is known as the physicochemical speciation of the pollutant. Thus, e.g., the solubility, environmental mobility, and availability of lead sulfide are slight, until oxidative conversion to lead sulfate occurs. Ingested lead sulfide is also absorbed from the human gastrointestinal system into the bloodstream far less readily than more water-soluble forms of lead, such as lead chloride.

Techniques for physicochemical characterization of airborne particles are at a fairly early stage of development.[322] Nonetheless, some do yield valuable information and these will be described.

1. X-Ray Powder Diffraction (XRD)

XRD is a powerful technique which can unequivocally identify specific chemical compounds of crystalline form within a mixture such as in airborne particles. It is sufficiently sensitive to identify components making up as little as approximately 1% of a mixture, but is entirely insensitive to compounds present in a noncrystalline form.

Davis and Cho[323] and Davis[324] have described a quantitative technique capable of identifying specific substances on a Hi-Vol filter. This involves addition of a thin layer of a reference material to the filter surface prior to XRD analysis. In a later paper, Davis[325] reports the identification of a range of mineral materials, shown in Table 7.

In our own experience, natural mineral components of the aerosol, such as α-quartz and calcite, which have strong diffraction patterns can often obscure the diffraction lines due to the pollutant substances of interest. As a consequence, Biggins and Harrison,[326] in studying the automotive lead compounds in urban air, took a particle size fraction ≤2.1 μm by impaction, hence eliminating a large proportion of the natural mineral material which is of

Table 8
RESULTS OF X-RAY DIFFRACTION ANALYSES OF ROADSIDE AIR

Size range (µm)	Lancaster Town Hall		Shap, M6 Motorway	
	November 20—22, 1978	December 1—4, 1978	September 19—21, 1978	October 17—19, 1978
⩾7.0	NaCl Na_2SO_4 α-SiO_2 $CaCO_3$	NaCl α-SiO_2 $CaCo_3$ $CaSO_4 \cdot 2H_2O$ PbBrCl		
3.3—7.0	NaCl Na_2SO_4 α-SiO_2 $CaCO_3$ $CaSO_4 \cdot 2H_2O$	$CaCO_3$ $CaSO_4 \cdot 2H_2O$ PbBrCl	α-SiO_2 $CaCO_3$ $CaSO_4 \cdot 2H_2O$	
2.0—3.3	NaCl Na_2SO_4	NaCl $(NH_4)_2SO_4 \cdot PbSO_4$	$CaCO_3$ $CaSO_4 \cdot 2H_2O$ α-$2PbBrCl \cdot NH_4Cl$ PbBrCl (m)	
2.0—1.1	NaCl $CaCO_3$ PbBrCl	$(NH_4)_2SO_4$ $(NH_4)_2SO_4 \cdot PbSO_4$ PbBrCl (t)	$CaCO_3$ $CaSO_4 \cdot 2H_2O$	$CaCO_3$ $CaSO_4 \cdot 2H_2O$ (*)
⩽1.1	NaCl α-SiO_2 $(NH_4)_2SO_4$ $(NH_4)_2SO_4 \cdot PbSO_4$ PbBrCl	$CaSO_4 \cdot 2H_2O$ $(NH_4)_2SO_4$ $(NH_4)_2SO_4 \cdot PbSO_4$ $(NH_4)_2SO_4 \cdot 2CaSO_4$	Na_2SO_4 (t) α-SiO_2 $CaSO_4 \cdot 2H_2O$ (t) $(NH_4)_2SO_4 \cdot PbSO_4$	$CaCO_3$ $CaSO_4 \cdot 2H_2O$ $(NH_4)_2SO_4 \cdot PbSO_4$ (*)

Note: m, minor phase; t, phase present at trace level; *, major component unidentified.

From Biggins, P. D. E. and Harrison, R. M., *Atmos. Environ.*, 13, 1213, 1979. With permission.

larger dimensions. Similarly, O'Connor and Jaklevic[327] used a dichotomous sampler for this purpose. In subsequent work, Biggins and Harrison[328] carried out a fuller size fractionation by Hi-Vol Andersen impactor and subjected each size fraction to separate XRD examination. The results appear in Table 8. These workers have also reported the identification of a range of sulfate compounds in the atmosphere, mostly by XRD techniques.[329] An alternative means of particle fractionation is the use of a density gradient, as reported by Fukasawa et al.[330] who identified a number of minerals in urban air using this technique.

The use of a Guinier camera can give enhanced sensitivity in XRD analysis of airborne particles.[326] Nonetheless, most workers use diffractometers, and O'Connor and Jaklevic[331] have investigated the optimum instrumental settings and filter substrates for examination of airborne particles by XRD. PTFE and polycarbonate filter substrates were considered superior to cellulose ester in view of their lower mass/area ratios which result in lower background levels. These workers have also shown that for ammonium sulfate, an abundant atmospheric component, line broadening in XRD due to small crystallite sizes is unlikely to be a problem with atmospheric samples.[332]

2. *Electron Microscope/Microprobe Techniques*

These methods, unlike XRD, are used to investigate the chemical composition of individual particles, or of a small area of a sample, rather than looking at bulk composition. Thus, in general, only small, possibly statistically insignificant, numbers of particles are examined, but this may yield valuable information nonetheless upon source and particle characteristics.

A range of techniques is available, which vary according to their spatial resolution and quantification capabilities. All use an electron beam as primary energy source, and rely upon

Table 9
RELATIVE AMOUNTS OF IMPORTANT PARTICLES ON EACH IMPACTOR STAGE FOR THE UIA SITE (%)

	Stage			
Particle	**5**[a]	**4**	**3**	**2**
Water-soluble sulfates[b]	78	89	16	5
$CaSO_4 \cdot 2H_2O$	2	1	10	19
Fly ash (Al-Si type)	7	4	41	37
Fe-oxide spheres	10	3	23	13
NaCl	0	0	2	8
SiO_2	2	1	1	1
Other particles	1	2	7	17
Total	100	100	100	100

[a] "Mean projected particle diameters" are for stage 5, 0.57 μm; stage 4, 1.1 μm; stage 3, 2.2 μm; and stage 2, 4.9 μm.

[b] Includes $(NH_4)_2SO_4$, Na_2SO_4, and K_2SO_4.

From Bloch, P., Adams, F., Van Landuyt, J., and Van Goethem, L., *Proc. Eur. Symp. Phys.-Chem. Behav. Atmos. Pollut.*, 307, 1979. With permission.

the energy-dispersive analysis of secondary X-rays as a tool of chemical analysis. Most commonly, a scanning electron microscope has been used. Thus Butler et al.[333] examined individual particles rich in lead and halogens; titanium; vanadium and sulfur; and zinc. They report that particles down to 0.5 to 1 μm diameter could be focused and analyzed with a detection limit of 0.9% by weight for transition elements. Analyses were semiquantitative. Yakowitz et al.[334] report an improved method using electron microscopy and microanalysis (EMMA) with the ability of examining particles as small as 0.05 μm, with a semiquantitative X-ray analysis facility and the very useful capability for selected area diffraction analysis.

Bloch and co-workers[335] have used transmission electron microscopy with energy-dispersive X-ray emission analysis to obtain chemical composition, and selected area electron diffraction to determine the crystalline structure of individual particles (if crystalline). Aerosol samples were collected directly on a Formvar foil attached to a 200-mesh transmission electron microscope grid which could be incorporated directly in the microscope. The results from examination of ambient aerosol samples are summarized in Table 9, and represent one of the best available sets of data using this type of method.

Lead compounds in vehicle exhaust and in ambient air have been examined with an electron microprobe by Ter Haar and Bayard.[336] Fresh exhast was reported to contain $PbBr_2$, PbBrCl, Pb(OH)Br, $(PbO)_2PbBr_2$, and $(PbO)_2PbBrCl$ and 10% of intermediate halides, but after 18 hr, approximately 75% of Br had been lost along with 30 to 40% of the Cl. The major products appeared to be lead carbonates, oxides, and oxycarbonates (or basic carbonate). This very detailed work was criticized subsequently by Heidel and Desborough[337] who claimed that such detailed identification of compounds is not possible with the sensitivity available with the electron microprobe, the method of calibration, and the assumptions that have to be made. Specific criticisms were that solid particles were assumed whereas they may be porous or fluffy, only a 0.2-μm spot on each particle is analyzed which is assumed homogeneous, relocation of individual particles of only 0.2 μm is not believed to be feasible, and many particles are smaller. Additionally, the lead content of some of the compounds differs by only 0.2%, while Heidel and Desborough[337] determined that errors limit the discrimination level to 10.8% so that, for instance, $(PbO)_2PbCl_2$ and PbBrCl are barely distinguishable from $PbCl_2$, which in turn is indistinguishable from Pb(OH)Cl and $(PbO)_2PbBrCl$.

Thus it appears that even the microprobe is unable to define many compounds with certainty. In all of these techniques, elements of atomic number <11 are not analyzable and this factor together with the semiquantitative nature of the other elemental analyses makes unequivocal characterization near impossible, as supporting electron diffraction data are available on few instruments only. The major benefit of electron microscope methods is that an evaluation of particle size and morphology is possible, simultaneous with chemical composition information.

3. *Miscellaneous Techniques*

Techniques for speciation of atmospheric sulfates have been described in an earlier section. These all give rather indirect evidence of speciation, dependent upon assumptions over the range of sulfates present in air, and the nature of atmospheric strong acids.

Photoelectron spectroscopy (ESCA) may be used to characterize the composition of the surface layer (approximately 2.5 nm) of atmospheric particles. It can also provide limited information upon the valence state of an element. For example, in an ESCA examination of smelter flue dusts, Eatough et al.[338] reported finding sulfur as S(+6) (i.e., sulfate), S(+4) (sulfite), S(O) (elemental sulfur), and S(−2) (sulfide).

Laser-excited Raman spectroscopy has been shown capable of providing limited data upon speciation in atmospheric aerosol samples. Thus Etz and Rosasco[339] identified calcium sulfate (anhydrite) by this technique and Rosen and Novakov[340] reported the presence of elemental carbon in a crystal form similar to that of activated carbon.

X-ray absorption spectroscopy, using a synchrotron radiation source, may be used to discriminate between different compounds of zinc, iron, and copper in atmospheric samples.[341] Scanning the K X-ray absorption edge gives an absorption spectrum characteristic of a given compound, allowing identification of $ZnSO_4$. $(NH_4)_2SO_4$, ZnO, and $ZnSO_4$ in atmospheric samples.

Indirect information on physicochemical species may be provided by very detailed ion balance studies on aerosols. Using this technique, Harrison and Pio[342] identified NaCl, $MgCl_2$, $(NH_4)_2SO_4$, H_2SO_4, NH_4NO_3, and NH_4Cl in airborne particles collected at Lancaster, England.

F. Remote Sensing Techniques

This is an area in which tremendous advances have been made in the past decade. However, despite the availability of sophisticated instrumentation for a number of pollutants, the use of remote sensing techniques has been severely limited by the very considerable capital cost of equipment.

The correlation spectrometer[343] is probably the most well-established remote sensing technique. It is most commonly used with a natural sunlight source for the analysis of nitrogen dioxide and sulfur dioxide. The concentration units are ppm-meter as an integration over the full path length occurs and no spatial resolution of concentration within the light path is possible. The detection limit for SO_2 using a Xenon light source is reported to be 5 ppb over a 1-km path.[344] The most common application of the correlation spectrometer has been in the study of plumes from tall stacks,[345] for which this technique provides an excellent means of tracing the transport and dispersion of a plume, when the instrumentation is incorporated within a mobile laboratory. In a comparative study of eight correlation spectrometers, a good intercomparison of readings was found after alignment and calibrations had been optimized.[346]

While correlation spectrometers normally operate in the UV/visible wavelength range, long-path infrared absorption spectroscopy can also be used to analyze a wide range of pollutants in air. Hirschfeld[347] has examined theoretically the most effective operational system and recommends a two-station remote device with an array of distal retroreflectors employing a correlation Fourier transform spectrometer as receiver. Pitts' group at Riverside have presented measurements of many important minor smog products at ppb levels in air determined with a Fourier transform infrared spectrometer.[348]

The use of tunable lasers[349,350] allows long-path absorption measurements of a range of gaseous pollutants such as NO, NO_2, SO_2, CO, and O_3. Hinkley and Ku[349] report a tunable semiconductor diode laser system for monitoring CO, H_2O, and NO over long outdoor paths. Futher developments in lasers will assist in the development of instrumentation,[350] while perturbation spectroscopy, using electric or magnetic fields to perturb molecular energy levels and tune a near coincidence into exact coincidence with the laser, is also subject to investigation.[351] Work is also proceeding on an optoacoustic detector for laser monitoring of ammonia in ambient air.[352]

In long-path laser absorption methods, a detector is used to monitor absorption of specific wavelengths in the light path. In Lidar techniques, however, the back-scattered radiation from a laser is monitored, allowing spatial resolution of pollutant concentration data, since in a pulsed system the time taken for receipt of back scatter is a function of the distance of travel. There are three types of light scattering process: Mie scatter due to aerosol particles; Rayleigh scatter due to gas molecules; and Raman scatter due to both. Probably the most promising experimental technique is differential lidar.[353] Back-scattered radiation is subject to attenuation at wavelengths absorbed by pollutants. Hence by monitoring back-scatter intensity at two close wavelengths, one strongly absorbed and one unabsorbed by a pollutant, the concentration of that pollutant may be inferred, as well as its spatial distribution. Careful choice of wavelengths is necessary to avoid spectral interferences. In one study, useful information on sulfur dioxide concentrations was obtained up to a range of about 2 km.[353]

Raman back-scatter is highly characteristic of the scattering molecule, and De Long[354] has examined the theoretical possibility of monitoring a wide range of pollutants by this technique. An experimental system was sensitive only to rather high pollutant levels, in the range of 40 to 700 ppm, although it was thought possible to improve those limits markedly.[354] Some progress towards a laser-Raman monitoring system for ambient sulfate aerosols has been made.[355]

Clearly there is great potential in remote sensing techniques, but considerable development work remains to be done before reliable and versatile instrumentation for routine use becomes available.

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