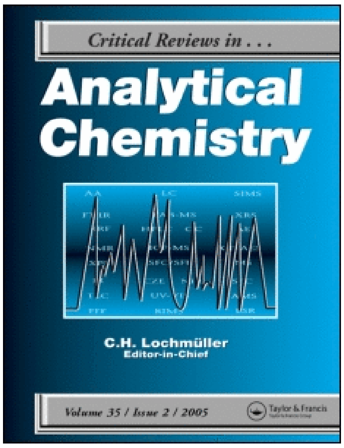

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MEASUREMENT OF ATMOSPHERIC POLLUTANTS RELEVANT TO DRY ACID DEPOSITION

Ivo Allegrini and Franco De Santis

I. INTRODUCTION

The transfer of acid gases and particles from the atmosphere to the earth's surface, where they exert adverse environmental effects, is called acid deposition. Relevant removal processes occur during dry weather conditions, during the formation of clouds or by scavenging of falling rain or other hydrometeors. The first removal process is called acid dry deposition while the last two, known as rainout and washout, respectively, are lumped together into the phenomenon of acid wet deposition.

Estimates of acid wet deposition may be obtained from the mass, diameter and number, and composition of hydrometers. These methods are relatively well established and they are mainly concerned with the representativeness of the sample collected (e.g., with wet collector design, sampling operation, storage of the sample). In spite of these issues wet deposition methods have long been used in many networks even at continental scale. In those instances, fairly good data sets have been obtained.

The methods for estimating dry deposition are much more in a development stage. In general, while sampling procedure for monitoring wet deposition are practically already susceptible of (or very close to) standardization, there is no accepted way of quantitatively monitoring for dry deposition of acid pollutants. Indeed, the primary mechanism for dry acid deposition is the turbulent transport and sedimentation which bring gases and particles to the laminar boundary layer close to the surface. The pollutant is then chemically or physically captured on the surface by processes of diffusion, convection, or inertial impaction. Thus, the measurement of dry deposition is actually the measurement of the flux of acidity carrying pollutants through a given surface. Surrogate surfaces such as dustfall buckets, spheres, Teflon plates, Petri dishes, glass microslides, and other plates have been used over the years. However, problems related to the aerodynamic microstructures of such surfaces and their chemical and biological properties prevent a reliable use of quantitative data.

The most common (and useful) way for the parametrization of dry deposition is the use of an inferential technique based on the concept of deposition velocity. The deposition velocity of a given species multiplied by its concentration over a given surface yields the flux of acid pollutant which is deposited on the surface.

Flux estimates rely on measurements of the atmospheric concentration of selected acid species and on the evaluation of meteorological and surface properties which affect the deposition velocities. Methods for the measurement of the deposition velocities are well known.[1] In the eddy correlation technique, the flux of pollutant through an horizontal plane is measured by integrating the instantaneous product of the vertical component of the wind velocity vector and the concentration. In the gradient method the flux is measured through the vertical turbulent diffusion coefficient and the vertical concentration gradient of the species of interest. Some values for the dry deposition velocity are given in Table 1. They range from very low values for particles in the range 0.1 to 1 μm, to large values reported with reactive acids such as HNO_3. For the latter the deposition velocity depends exclusively on transport because the surface resistance is near zero for virtually any surface.

Methods for the measurement of the dry deposition velocity and fluxes are in general cumbersome and absolutely useless or impractical for the routine monitoring of the dry deposition. Nevertheless, the spatial and temporal distribution of the pollutants responsible for acid deposition represents critical aspects in understanding the basic pathways of removal as well as the mechanisms of formation, transport and interaction of atmospheric pollutants in the atmosphere, thus a practical approach to the problem of dry deposition would be the application of the so-called Concentration Monitoring Approach, according to which measurements of selected chemical compounds (mainly sulfur and nitrogen containing species) are carried out in a variety of locations in order to estimate their potential impact on dry deposition.

Typically, the species of interest for acid deposition are present in the atmosphere at parts per billion (ppb) concentra-

Table 1
Dry Deposition Velocities for Atmospheric Pollutants[111]

Species	Range	Mean value
SO_2	0.1—2.0	0.8
NO_2	0.01—1	0.4
NH_3	±2*	1.0
HNO_3	1—20	<5
HCL	1—20	<5
Acid particles	0.01—1	0.1
Alkaline particles	0.1—5	>0.1

Note: Negative velocity means that ammonia is also released by surfaces.

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tion levels, as it is shown in Table 2 for the most important compounds. Their determination is, therefore, a challenging analytical task. Over the past several years it has been recognized that early measurements have been fraught with a number of errors due to interference or as a result of complex physical and chemical phenomena which occur during sampling. The development of techniques for measuring the concentration of such species has been the focus of substantial research effort which enhanced our ability to provide reliable measurements of them.

The main approaches for the measurement of acid compounds consist of instrumental methods, usually spectrophotometric, which are able to give directly and in real time the concentration of the species of interest and of enrichment methods which provide concentration data integrated over the sampling period.

The search for new and improved methods has led to investigations into the suitability of a variety of analytical techniques ranging from highly sophisticated physical methods, implemented in some existing research instruments, to simple methods susceptible to be applied without intervention of particularly skilled technicians in the field. It is important that such methods be reliable in operation, convenient to use and very accurate. Over the last few years a number of methods have been evaluated in intercomparison field studies, in most cases leading to improvement in either selectivity or reliability. As a result, most currently available methods and instrumentation now meet the above requirements of sensitivity, reliability, and suitability and air chemists might apply them with reasonable confidence levels providing that they know very well limitations and applicability ranges of the adopted methods. Since air chemistry might be very different, methods and procedures developed in particular instances to solve specific problems could not be useful in a different situation and, unless an absolute measurement method is used, serious errors might arise using the same technique in a different environment.

Table 2
Typical Concentrations (ppb) of Chemical Species Related to Acid Deposition

	Species	Concentration
Gas phase	SO_2	0.2—30
	NO_2	0.2—30
	HNO_3	0.1—20
	HNO_2	0.2—10
	HCl	0.05—10
	NH_3	0.1—20
	PAN	0.05—5
Particles	Sulfates	0.2—40
	Nitrates	0.1—10
	Strong acidity	0.02—10

In addition, compounds relevant to dry acid deposition show, according to the measurement location, concentration ranges over two orders of magnitudes, and ratios with potential interferents ranging from very low to very large figures. Thus, a selected analytical method which is very suitable in the vicinity of the emission might not be suitable for remote locations and vice versa. Since many measurements relevant to acid deposition are carried out in remote or very remote locations, emphasis will be given to such environmental situations.

Knowledge of the limitations and advantages of the different methods is a key element in assessing a strategy for the evaluation of dry acid deposition. This review has been prepared with the following aims:

1. To assess the state of the art of the analytical methods used for relevant compounds in either gas phase and particulate matter
2. To provide a basis for comparison of the methods by means of a proper discussion on possible interferences in order to properly design intercomparison campaigns
3. To aid in the selection of procedures which appear promising for development into methods suitable for field application and for network deployment
4. To stimulate research and development on analytical methods which appear to fulfill the basic requirements for a monitoring activity

Following the format adopted in the biannual reviews published by Analytical Chemistry, the subject matter has been divided in different sections. Since some of the analytical procedures surveyed may be applied to different compounds, we decided to describe in length such methods in the section dealing with the more important (or representative) species.

II. NITROGEN COMPOUNDS

A. Nitrogen Oxides

Nitrogen oxides (NO and NO_2, collectively referred to as NO_x) play a central role in different topics of the atmospheric chemistry such as acid deposition, stratospheric ozone depletion, and photochemical smog formation. They are primarily emitted as NO from combustion processes such as internal combustion engines, boilers, incinerators, etc.

Nitrogen oxides quickly react in the atmosphere following complex mechanisms and processes which involve light and reactive compounds such as hydrocarbons, ozone and radicals to generate a number of reactive species often referred to as NO_y.

Among the instrumental methods proposed for the determination of NO and NO_2, chemiluminescence based techniques have gained much consensus. The principle of operation is based upon the reaction of ozone with nitric oxide:

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

$$NO_2^* \rightarrow NO_2 + h\gamma$$

The excited NO_2 molecule emits radiation of wavelength longer than 600 nm (600 to 3000 nm with a maximum near 1200 nm) which is amplified by a photomultiplier tube. A linear response from about 4 ppb NO to 100 ppm NO has been found. NO_2, CO_2, CO, C_2H_4, NH_3, SO_2, and H_2O in commonly encountered concentrations in polluted air do not interfere in the measurement.[2] Chemiluminescence represents an approach to achievement of very low limits of detection. In principle, a measurable signal can be obtained from each analyte molecule and background can be reduced to very low levels because no light is used. Side reaction producing non emitting products and quenching of the chemiluminescence reduce the response but a proper choice of instrumental parameters allows the achievement of high sensitivity levels.

Since the first development of a chemiluminescence analyzer and the first paper on homogeneous chemiluminescence measurement of NO with ozone, many analyzers have been described in the literature and commercial versions are available. Many papers have been published to report modifications of commercial analyzers for obtaining greater sensitivity. A study on the factors defining the sensitivity and its optimization, has been done by Mehrabzadeh.[3] A negative interference to the chemiluminescence reaction occurs in the presence of liquid water droplets or aerosols. Excess water and particles (e.g., in engine emissions measurements) must be removed from the gas entering the reaction chamber.[4]

NO_2 and other nitrogen containing species can be measured by using this method providing that they are first converted to NO. NO_2 is thermally converted to NO over molybdenum at 200°C (or chemically over $FeSO_4$) and is determined by a subtractive technique in the NO_2 channel. Other nitrogen containing substances may also be converted to NO by the molybdenum converter and therefore the chemiluminescence analyzer is not specific for NO_2. A study on the response of the NO_x analyzer to nitrogen containing compounds showed that a positive interference for NO_2 is observed with nitric acid,[5,6] methyl and ethyl nitrate,[7] peroxyacetylnitrate (but not with peroxybenzoylnitrate), nitrogen pentoxide, certain nitroaromatics, and some chlorine containing compounds.[6] Also organosulfur compounds show a small positive interference in the NO_2 mode (indicating that they are in part removed by the catalytic converter).

The cited studies suggest that this method could be not fully suitable for continuous field monitoring when the concentrations of NO_2 are expected to be low and at levels comparable to those of the interfering species. A study has been conducted to investigate the loss of sensitivity observed as a consequence of continuous operation of NO_x chemiluminescence monitors. It has been found that this decrease is caused by a deposit of NH_4NO_3, contained in particulate phase, on the glass filter which separates the reaction chamber from the multiplier.[8]

The most promising instrumental method for NO_2 is based on the measurement of the chemiluminescence produced when NO_2 is sampled over a surface wetted with a luminol solution. It is well known that the chemiluminescence reaction of luminol with oxidizing agents such as H_2O_2, Cl_2, or ClO_4^-, is the basis for a possible analytical technique for these species. This reaction requires a metal ion catalyst such as Cu^{2+} or Cr^{3+}. The reaction of luminol with NO_2, however, requires no metal ion catalyst and, on the contrary, the chemiluminescence emission is decreased in the presence of metal ions.[9] It is interesting to note that the chemiluminescence is produced by the reaction of molecular NO_2 and not through the reaction with nitrite (or nitrate) ions. Unlike the conventional chemiluminescence NO_x analyzers this method measures NO_2 directly without prior conversion to NO. No interference has been found for H_2O_2, NO, HNO_3, NH_3, CO, SO_2. However, the response for O_3 is about 0.2% and the interference for PAN and HONO has not been clearly stated yet. The response of the instrument is less than 1 s and its sensitivity reaches 5 pptv.[10] Field operation and intercomparison would be helpful to define the operative performances of this instrument which appears to be the best candidate for the monitoring of nitrogen dioxide in remote sites.

Other spectroscopic techniques which have been specifically applied to the measurements of nitrogen oxides include tunable diode laser absorption spectrometry (TDLAS), long path Fourier transform IR spectrometry (FTIR), and differential optical absorption spectroscopy (DOAS). Although they provide useful methods, major points of these techniques are the unequivocal identification of the analyte coupled to a high level of sensitivity (fractions of ppb) and a relatively short response time. Nevertheless, they are still rather expensive and cumbersome for routine monitoring. For a detailed discussion of the instrumental features of these techniques the reader is referred to the articles by Schiff et al. (for TDLAS),[11] Tuazon et al. (for FTIR),[12] and Perner (for DOAS).[13]

The relative importance of nitrogen dioxide in the definition of processes leading to atmospheric acidity and photochemical pollution, stimulated research and development also addressed to accumulation methods. A very suitable accumulation procedure makes use of an alkaline guaiacol coated annular denuder. NO_2 reacts with guaiacolate ion and is converted to nitrite ion which is successively analyzed in the extract, after leaching the denuder with water, by ion chromatography.[14] A cylindrical denuder coated with MnO_2 has also been used.[15] Other accumulation procedures based on the use of triethanolamine impregnated molecular sieves as solid sorbent and subsequent ion chromatography of nitrite ion are best suited for personal monitoring because of their limited sensitivity.[16] Florisil coated with diphenylamine (DPA) has also been proposed. NO_2 reacts with DPA to form 4-nitro, 2-nitro, and N-nitroso DPA derivatives analyzed by high performance liquid chromatography with UV detector.[17]

Although many of these methods might be suitable for the measurement of trace amounts of nitrogen dioxide, they are limited by interferent reactions which take place with HONO and with the possible oxidation of nitrite ion during the sampling step. Therefore, limitations and possible interferents must be taken into account if any accumulation method is employed in the field.

B. Nitric Acid

Nitric acid is a very important metabolite of the chemical processes responsible for acid deposition and photochemical pollution. It is usually formed in gas phase through the homogeneous reaction:

$$NO_2 + OH^{\bullet} \rightarrow HNO_3$$

which accounts for most of nitric acid present in the atmosphere. Since the above reaction involves OH radicals, it proceeds to a large extent during photochemical episodes where a noticeably large amount of radicals are available. Nitric acid might be directly deposited through dry deposition processes to the surfaces or might be adsorbed in cloud droplets and then transferred to the surface.

Nitric acid may react with ammonia giving rise to the formation of ammonium nitrate aerosols which might play an important role in visibility degradation. Unfortunately, nitric acid and ammonia in gas phase are in thermodynamic equilibrium with ammonium nitrate in particulate matter, thus many analytical methods, in principle adequate for nitric acid, might change the said equilibrium with resulting positive or negative artifacts which should be taken into account in the selection of any proposed method.

Tunable diode laser absorption spectrometry (TDLAS), fully described in the ammonia chapter, provides some attractive features for real time tropospheric measurements of nitric acid since the detection limit is 0.35 ppb.[11] Such a low figure makes this technique preferable to the long-path FTIR method which is characterized by a detection limit of 4 ppb, unsuitable for most ambient concentrations.[12] However, much work remains to be done in the sampling procedure as air filtration and reactions on the cell walls might give rise to artifacts which could affect the measurement. In addition, cost and complexity do not allow an extensive application in routine field monitoring, even though such a drawback might be counterbalanced by the "multiparametric" capability of the diode laser.

A chemiluminescence differential method has been developed by Joseph and Spicer.[5] In this method the sample stream is split so that a fraction passes through a nylon filter to remove HNO_3 before passing through the molybdenum catalyst converter. In another channel NO_x plus HNO_3 is measured; therefore the difference between the channel outputs corresponds to the net concentration of nitric acid. A similar approach making use of heated pyrex beads to reduce HNO_3 to NO_2 and of granular $FeSO_4$ to reduce NO_2 to NO has been employed by Kelly.[18] The interference of HONO on these methods based on the removal of HNO_3 from the sample has been first shown by Sanhueza et al.[19] who found that HONO was quantitatively adsorbed by nylon cartridges at the operating conditions.

Differential methods, making use of two measuring channels, such as those described, could be used for the measurement of nitric acid providing that the amount of "no-HNO_3-channel" output is much less than the HNO_3 channel; otherwise the relative errors in the determination of the net amount of nitric acid might be very large. Unfortunately, that is not the case in the monitoring of the atmosphere in remote locations.

Much monitoring work for nitric acid (and for nitrate in the particulate matter) has been done by resorting to the double filter pack technique which consists of two filters stacked in line, the first used for the removal of particulate nitrates such as ammonium nitrate, and the second of nylon[20] or impregnated with NaCl[21] or tetrabutyl ammonium hydroxide,[22] for the collection of nitric acid. After sampling, nitric acid can be determined by extraction of the filter and analysis for nitrate using spectrophotometry or ion chromatography. Filter pack methods have been chosen as sampling devices for a number of acidity monitoring networks, for example EMEP in Europe, APIOS in U.S., APN in Canada. These methods have been scrutinized for artifact formation and a variety of possible interactions have been demonstrated to occur.

Positive artifacts may result on the prefilter from the volatilization of ammonium nitrate[20] as well as by the reaction of strong acids with the particulate nitrate to form gaseous nitric acid which is collected downstream on the second filter.[23] In addition, the collection medium may interact with NO_2, especially under high relative humidity conditions and in the presence of relatively high ozone levels, to form nitric acid.[20,21,24] Collection of HONO on nylon filters, yielding nitrite ions, has been observed in laboratory and field experiments. During photochemical episodes nitrite is oxidized to nitrate with efficiency up to 100%.[25] Quartz and glass filters have been used to collect particulate nitrate until it was demonstrated that significant amounts of NO_2 and HNO_3 could be adsorbed by the filters.[26] The use of a Teflon prefilter limits the extension of this artifact but it does not preclude the possibility of a reaction on the material already collected. In general it could be said that the use of a prefilter for the separation of the particulate matter results in a completely unpredictable behavior and, in many cases, does not allow the collection of tiny amounts of reactive gases. Therefore, the use of the filter pack should be limited only to the measurement of the total nitrates (gas phase and particulate matter) and only when negligible interferences in the measurement are expected.

The most suitable approach to the accumulation method which provides the separation between nitrates in gas phase and in particulate matter is the use of a diffusion tube. In its basic design a diffusion tube consists of a cylindrical glass tube (60 to 90 cm long, with an internal diameter of 4 mm) whose inside wall is coated with a suitable reactive substance (Figure 1). Gaseous nitric acid molecules diffuse to the tube wall which acts as a sink while nitrate and other particles, which are characterized by a much lower diffusion coefficient, proceed unaffected through the tube, and are recovered on a back-up filter. The capability of the diffusion tube to selectively remove the gas phase from an incoming air stream is such that the term "denuder" has been developed for this device. After sampling, the gas molecules adsorbed on the wall and the particulate matter collected on the filter might be extracted with water and analyzed according to classic analytical methods, for instance ion chromatography.

The quantitative performances of a denuder can be derived by means of the working equation which relates the collection efficiency (1 − Cz/Co) for a given species which is quantitatively uptaken by the denuder wall of a denuder having length L:

$$Cz/Co = 0.819 \exp(-14.62\ DL/4F) \qquad (1)$$

which is known as the Gormley-Kennedy equation, with D the diffusion coefficient of the species and F the flow rate through the tube.[27]

The concept of diffusion sampling for HNO_3 has been implemented in several methods either based upon the analysis of the reactive layer (e.g., Na_2CO_3,[28] NaF,[29] or nylon[30]) extracted with water or with an alkaline solution after sampling, or by using the diffusion tube as a denuder for the removal of nitric acid from the sample stream. The latter application has been employed in the so-called DDM method (denuder difference method) depicted in Figure 2. It consists in the sampling of air by using two nylon filters one of which is preceded by a MgO or Na_2CO_3 coated denuder so that the difference in the amount of nitrate ion found on both filters is the measure of gaseous nitric acid.[31]

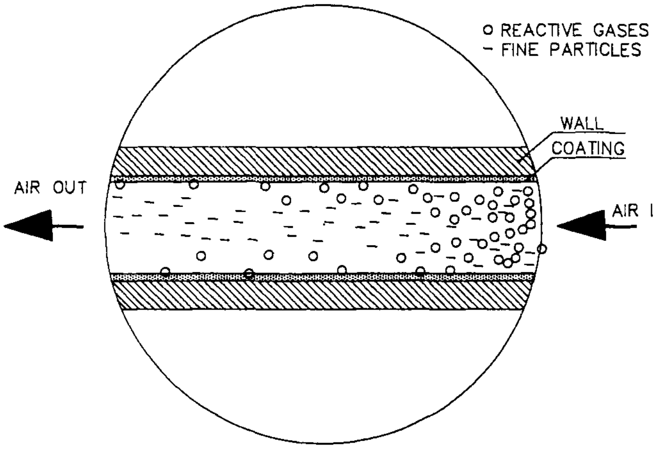

FIGURE 1. Diffusion channel (denuder) where selective separation of gases from particles is obtained.

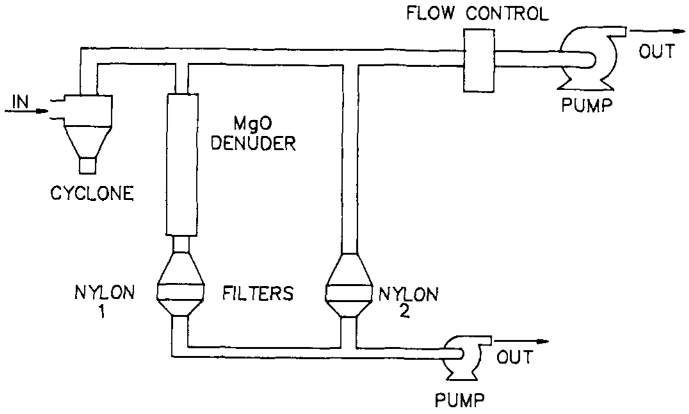

FIGURE 2. Basic scheme of the denuder difference method for the measurement of nitric acid.

The denuder difference method is still a differential method so that is is not suitable if the ratio of the particulate nitrate to nitric acid is much larger than one.

The main drawback of the aforementioned application of cylindrical diffusion tubes is that they reach a large absorption efficiency only at low flow rates. As a consequence long sampling times are required to collect sufficient analyte. Higher flow rates have been obtained by using a parallel multiple assembly.[32] This approach is impractical if the content of the exposed tubes has to be analyzed. Another flaw of the conventional open tube design is that, owing to their length, the coupling of differently coated diffusion tubes in the simultaneous sampling of several reactive species is rather cumbersome.

A new design for the diffusion tube which is superior in several aspects to the open tube design has been developed.[33] The denuder is made by using two coaxial cylinders so that air is passed through the annular space which is coated with a specific gas absorbing substance. Since the collection efficiency of an annular denuder depends on the tube length and on the inner and outer tube diameters, a larger operating flow rate (up to 20 l/min) is achievable in comparison to the open tube design. Indeed, it could be shown that for an annular denuder, Equation 1 changes into a similar relationship:

$$Cz/Co = 0.82 \exp(-22.53\ DL/4F)(d_1 + d_2)/(d_1 - d_2) \qquad (2)$$

where d_1 and d_2 are the inside and outside diameters of the annulus, respectively.[33] Thus, selecting the proper values for d_1 and d_2 it can be shown that an annular diffusion tube of a given length can operate at flow rates many times (typically 30) larger in comparison to a tubular one or that it can reach the same efficiency in 1/30 of the length. Na_2CO_3 coated annular denuders have been employed for the determination of several species of interest for the acid deposition such as HNO_3, HONO, HCl, SO_2, and others.[34]

A field performance evaluation of carbonate coated denuders revealed that in some particular conditions (essentially during photochemical episodes) the determination of nitric acid was affected by an artifact due to the oxidation of nitrite to nitrate. This study resulted in the adoption of a sodium chloride coated denuder for sampling HNO_3.[35] A train consisting of a sodium chloride and a sodium carbonate denuder set in series has been proposed for the simultaneous collection of HNO_3, HONO, and SO_2[36] and is shown in Figure 3 which also shows typical ion-chromatograms which are obtained by the water extracts of the denuders.

Sampling of nitric acid has been performed by using a very short nylon denuder which collects only a constant fraction of HNO_3 under transition flow conditions ($2100 > Re < 3500$) in a device which has been called "transition flow reactor". A filter is placed downstream of the denuder to collect particulate nitrate and, eventually, other reactive gases by using a train of filters coated with different materials.[37] Since the concentration of HNO_3 is inferred from the collection efficiency on the nylon strip, a strict control of the flow rate is necessary. Interferences of NO_2 and HNO_2 on nylon denuders which results in large errors in the measurement of nitric acid have been demonstrated in laboratory and field conditions.[25,38]

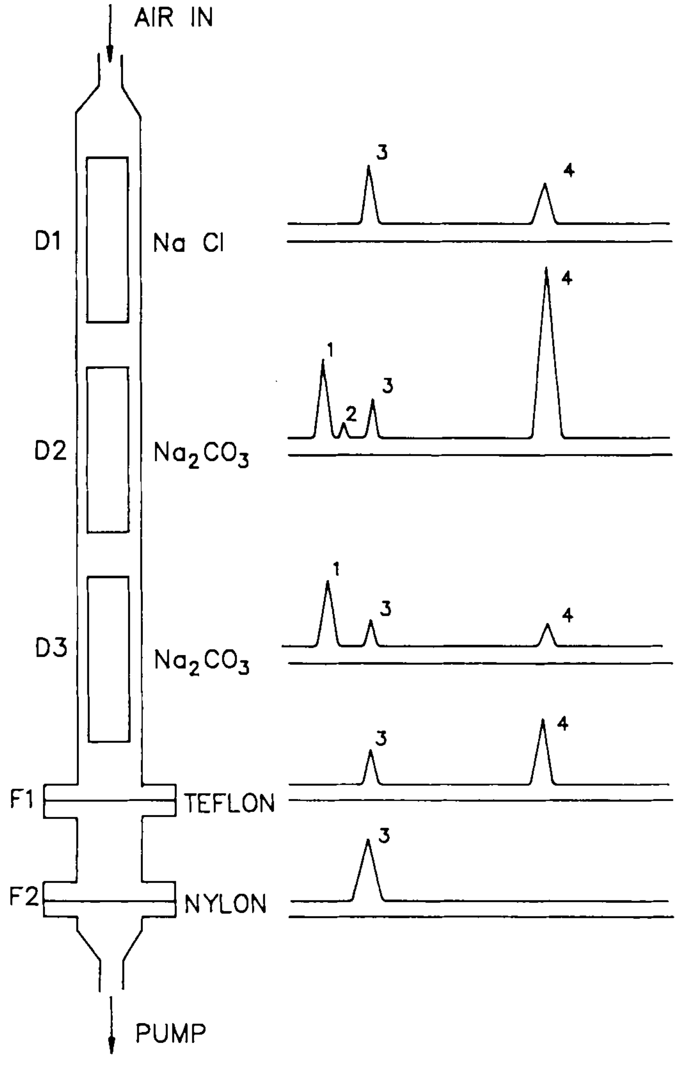

FIGURE 3. Typical sampling train for the measurement of acidic components in the atmosphere with ion chromatograms of the water extracts with relevant anions: (1) nitrites, (2) methylsulfates, (3) nitrates, (4) sulfates.

Automatic techniques based on the use of denuders have also been developed. A rotating annular denuder (see chapter on peroxides) has been employed for the direct collection of reactive gases, including HNO_3, on proper aliquots of absorbing solutions which are periodically collected on vials used in automated samplers for Ion Chromatography. This technique allows a time resolution as low as 15 min and a sufficiently large sensitivity for ambient concentrations.[39]

HNO_3 has also been collected on tungstic acid and thermally released, after sampling, as NO_2 which is measured by means of a chemiluminescence detector with a detection limit as low as 0.07 ppb for 40 min collection and analysis cycle.[40] Possible interferences by NO_2, HCN, PAN, and n-propyl nitrate, have been tested and found to be significant under typical condition of a moderately polluted area.[41] Another technique adaptable to automation makes use of a diffusion tube coated with $Al_2(SO_4)_3$. The HNO_3 collected is thermally converted to NO_x and analyzed by gas chromatography/photoionization detection[42] or by means of chemiluminescence.[43] However, also in this case, artifacts due to absorption of nitrous acid and nitrogen dioxide might impair the measurement of nitric acid at very low concentration levels. The obvious advantage of the automatic techniques resides in the relatively short time response which can be well down to a few minutes. This feature is of particular interest for the measurement of the dry deposition velocities by means of the gradient method.

C. Nitrous Acid

The importance of nitrous acid in the acid deposition processes has been recognized very recently. The mechanisms of formation of HONO have been identified with the thermal reaction between NO_2 and water:

$$2NO_2 + H_2O \rightarrow HONO + HNO_3$$

which takes place on surfaces. Thus the formation of HONO removes NO_2 from the atmosphere, competing with that of HNO_3. However, nitrous acid is rapidly photolyzed by sunlight and, in addition, the boundary layer over day is generally very high, thus the daylight concentration of HONO is very small. This behavior is completely opposite to that of nitric acid which peaks in the early afternoon and drops to zero overnight. The photodissociation of HNO_2 yields OH radicals which may trigger the reactions leading to the formation of photochemical pollution.

Long-path (0.5 to 2.5 km) UV differential optical absorption spectroscopy (DOAS) has been employed for the measurement of ambient nitrous acid.[44] The method is based on the measurement of the absorbance on a distinct absorption peak of the species of interest and the absorbance at a wavelength on the side of the peak. Figure 4 shows the schematic diagram of a DOAS spectrometer. Light emitted by a suitable source, traverses an air parcel at distances of some kilometers and is collected on a spectrograph. The conventional exit slit is replaced by a mask which allows the detector to measure selected portions of the spectrum according to the species which has to be measured. The differential technique allows observation regardless of atmospheric turbulences and the presence of absorbing interfering substances. Although not yet extensively used for routine monitoring purposes, it provides a means for a direct measure of HNO_2 because it combines high sensitivity and selectivity. This technique also allows the measurement of formaldehyde, nitrogen dioxide, sulfur dioxide, and ozone. With a time resolution of 20 min a detection limit of 50 ppt HNO_2, 300 ppt HCHO, 300 ppt NO_2, 40 ppt SO_2, and 5 ppb ozone is obtained for pathlength of 10 to 15 km.

Denuder based techniques for HNO_2 have also been developed. The use of the denuders in such a case is not intended for the separation of gas phase and particulate matter, but to "modulate" the absorption in order to reduce or to correct for the possible interference coming from NO_2 and PAN. Sodium carbonate coated cylindrical[45] and annular denuders[34,36,46] on which nitrous acid is very efficiently collected have been used. After sampling the denuders are leached with water and the nitrite concentrations determined. NO_2 and PAN are partly uptaken on the denuder surface giving interferent nitrite and a small amount of nitrate. As a result, the measurement of the nitrite content of the leached solution does not ensure a correct measurement of HNO_2. The contribution of these interfering species to the measurement of HNO_2 is taken into account by using two denuders in series. The rationale for this disposition lies in the fact that the operating conditions may be chosen in order to ensure a complete collection for HNO_2 and a rather low collection efficiencies for the interferent species. In such a situation the amount of interferent collected in the first denuder is equal to that collected in the second one which can be used to correct the data obtained from the first denuder. In other words, the first denuder contains nitrite due to HNO_2 and the interferents, while the second denuders will only contain nitrite due to interferents; thus the difference between the nitrite content in the first and second denuder yields the net amount of nitrous acid.

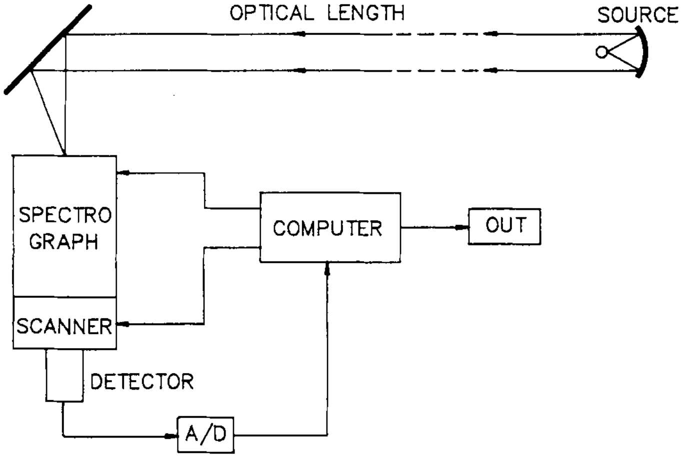

FIGURE 4. The principle of the differential optical absorption spectrometer (DOAS) which is able to measure many pollutants over an extended pathlength.

Such technique is very general and should be applied anytime an interferent might cause problems in the determination of a given species. By taking advantage of the different reactivities of a selected coating with respect to the analytes and the interferences, it becomes possible to define a way for the correction. Figure 5 shows a general example of the principle applied to the measurement of the species A which is present in atmosphere with the species B. Let us suppose that, after sampling and extraction of the denuders, both species give rise to the same analyte Q and that the collection efficiency of the denuder is large for the species A and very small for the species B. The mass distribution function of the common analyte Q along the denuder length z is such that the species having a large collection efficiency (A) is entirely distributed on the first part of the denuder ($L > z > 0$), while the species with a low collection efficiency (B) will be almost evenly distributed along the tube length.

This correction technique is very general and does not necessarily apply to the evaluation of HONO only. For instance, if a very accurate measurement of nitric acid is to be performed, the small deposition of particle containing nitrate on the denuder walls must be taken into account. Even though the diffusion coefficient for particles is extremely low, compared to that of the species in gas phase, there is a chance to collect particles which interfere with the measurement of gaseous nitric acid. This is, of course, particularly true if the ratio of particulate nitrate to gaseous nitric acid is very large. The use of two diffusion tubes coated with NaCl will allow the correction for the interference of particulate matter.[36] However, the correction is often very low so that, in most instances, one denuder is enough to provide good analytical results.

In a subsequent investigation the stability of the nitrite collected on the denuder has been studied and its conversion in the presence of atmospheric oxidants to nitrate observed.[35] Since, as shown in the previous section, a sodium carbonate diffusion tube also collects nitric acid, it is impossible to estimate the amount of nitrate due to oxidation in comparison to the nitrate due to nitric acid. By running two sodium carbonate denuders in series after a sodium chloride denuder, which removes nitric acid, the amount of nitrate found on the second and third denuders is due only to the oxidation of the nitrite and thus a correction can be applied for the measurement of nitrous acid. Such a procedure has been shown to provide accuracy and precision better than 5% regardless of atmos-

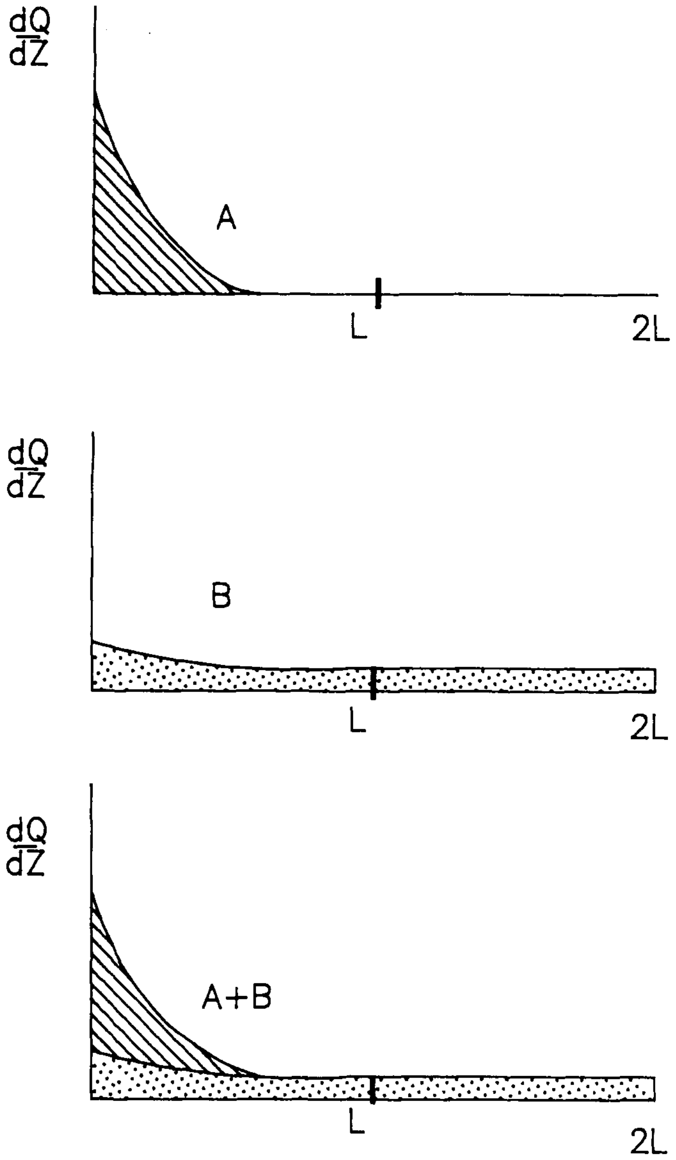

FIGURE 5. Differential method applied to two denuders in series for the evaluation of a given species (A) and an interferent (B) which gives rise to the same analyte (Q) and mass distribution functions.

pheric conditions which might alter the response of the analytical methods.

III. SULFUR COMPOUNDS

A. Sulfur Dioxide

Sulfur dioxide is probably the most important compound in the definition of the acidic properties of the atmosphere. It is emitted in large quantities by the combustion of fossil fuels (coal and oil) and is oxidized in homogeneous and heterogeneous phases into sulfuric acid and sulfates. SO_2 oxidation in droplets is almost certainly the most important aspect of multiphase atmospheric chemistry, while the reaction with $OH^{\bullet}$ radicals is the major removal mechanism in the gas phase. A certain amount of SO_2 is naturally emitted by volcanos and related geothermal activity. The effects on human health and on the environment have been well evidenced with the results that investigations on sulfur dioxide and its methabolytes are relatively complete. In addition, since the presence of sulfur dioxide in the atmosphere is a clear sign of pollution generated by stationary combustion sources, air quality standards have been issued in all industrialized countries. The need for extensive monitoring networks promoted research and development of many instruments and devices intended for the measurement in polluted areas.

Instruments employing flame photometry and pulsed fluorescence methods have extensively been used for the determination of sulfur dioxide. In the flame photometry detector the sample is burned in a hydrogen rich flame. A chemiluminescent reaction occurs and light emitted in the visible and ultraviolet is measured. The method is not specific since any sulfur containing species will interfere.[47] Higher specificity and sensitivities are obtained by the pulsed fluorescence method[48] since the only interferencs are the aromatic hydrocarbons which can be eliminated in the sampling stream by using a catalyst tube placed in line. Such methods gained much consensus for monitoring purposes, but they are completely inadequate for the evaluation of sulfur dioxide in relatively remote locations where the observed concentrations could be as small as a few parts per billions.

A rapid and sensitive method for the determination of SO_2, based on the enhancement of the chemiluminescence reaction of luminol with NO_2 in alkaline solution has been proposed. The enhanced chemiluminescence signal is proportional to the concentration of SO_2. Negligible interference from ambient concentrations of CO, propylene, ethylene, N_2O, NO, NO_2, and NH_3 has been found. The interference of CO_2 and O_3 has been removed by buffering the luminol solution and by using a precolumn packed with ferrous sulfate coated glass beads. A 95% response is obtained within 2 min; however the detection limit is still not below about 3 ppb. When H_2S and ethyl mercaptan are present strong interferences are observed. Their removal by using Ag wool scrubbers has been proposed.[49]

Adequate sensitivities seem to be achieved by DOAS (differential optical absorption spectrometry) which can be applied to the measurement of sulfur dioxide because of the strong absorption bands located at 215 nm and at 300 nm. Field measurements demonstrate the reliability of the method which is, however, limited to the solution of specific scientific problems. Indeed, DOAS is an instrumental method which has limited possibilities in being deployed on the field in unattended remote monitoring locations. The method shows its power when used to determine the concentration of SO_2 integrated over a pathlength as large as kilometers as a part of specific scientific problems addressed to the understanding of the physical and chemical processes of the transport and transformation of sulfur dioxide. A monitoring network for the dry acid deposition, on the contrary, requires several monitoring locations employing methods simple to operate, possibly inexpensive and readily manageable as far as quality control and quality assurance procedures are concerned.

A sensitive, selective, and relatively fast response method for sulfur dioxide at low concentration is based on mercury (I) ion disproportionation in solution promoted by SO_2. The sample air is bubbled through a mercury (I) solution contained in a thermostated cell. The mercury vapor released by the reaction is swept from the solution and determined by absorption at 254 nm. Lower detectable limit is claimed to be about 0.2 ppb.[50] Alternatively, a gold coated piezoelectric crystal has been used to measure the elemental mercury by monitoring the change in the oscillation frequency of the crystal due to the formation of a mercury amalgam. H_2S and CS_2 promote the disproportionation reaction and should be removed from the gaseous stream by bubbling the sample through a silver nitrate solution.[51] The instrument based on mercury reaction seems to be the best candidate for the continuous monitoring of SO_2 in relatively remote locations with a sufficient degree of accuracy and precisions. Many research institutions are nowadays evaluating the instrument for a possible extensive field deployment.

Accumulation methods are very popular for the routine monitoring of SO_2. They employ either impregnated filters or diffusion denuder tubes. A typical sampling train consists of a Teflon filter for the collection of particles, followed by an impregnated alkali filter for the collection of SO_2 (filter pack). After sampling, the filters are leached with water and analyzed by ion chromatography as regard their sulfate contents. The influence of SO_2 concentration, temperature, and humidity on the collection efficiencies has been extensively investigated. It has been shown that the efficiency falls sharply for relative humidities less than 30%.[52]

A more versatile triple filter pack employing a front Teflon filter, an intermediate nylon filter for the collection of HNO_3 and a Whatman filter impregnated with an aqueous solution of 10% glycerin and 25% potassium carbonate has been employed to collect simultaneously particulate matter, nitric acid, and SO_2.[53] A study has been performed to assess the importance of a negative bias due to retention of SO_2 on nylon filters.[54] The results suggest that nylon filters are highly variable in their ability to collect SO_2. In particular, a commercially available batch produced before 1984 presented only a slight interference (less than 4% at operative conditions) whereas, after that time, as a consequence of a change in the fabrication process, a batch of nylon filter, used for the same experiment, reached retention efficiencies as high as 70%. The study also shows that since some organic sulfur compounds as dimethyl and methyl hydrogensulfate are retained by nylon, it is uncertain how much of artifact sulfate is due to SO_2 as opposed to other sulfur compounds. Additional artifacts on using the filter pack technique might arise from irreversible absorption on the front filter as it was discussed for nitric acid. However, the problem of irreversible adsorption of SO_2 on the front filters is very reduced in comparison to those experienced for HNO_3; thus the use of a filter pack for the accumulation monitoring of sulfur dioxide exhibits enough reliability if the said limitations are properly taken into account.

Several papers based on the use of diffusion techniques have been devoted to the collection of SO_2 using cylindrical denuders coated with a mixture of tetrachloromercurate and malein buffer[55] and with sodium carbonate and glycerin. The former coating has been adopted before the extensive use of the ion chromatography with the suppressor column which allowed an easy evaluation of anions in the water extracts of the latter coating. As discussed before, the use of annular denuders for the measurement of SO_2 provides detection limits (as low as 1 and 0.05 $\mu g/m^3$ for 1 and 24 h sampling periods, respectively) low enough for most applications because fairly large collection efficiencies could be achieved even at relatively large operating flow rates. In addition, operating capacity and reproducibility make the method particularly suitable for the extensive routine monitoring of sulfur dioxide.[36]

When using the annular denuders for the evaluation of sulfur dioxide, it is a good practice to extensively use the differential method. Indeed, many sulfur compounds, as said before, might be collected on the carbonate wall giving rise to sulfate which erroneously simulate the presence of SO_2. The extent of such interference depends upon many parameters, but it has been experienced that on placing two annular denuders in series coated with Na_2CO_3, extracting the denuders with water and analyzing the sulfate content of the tubes, the amount of analyte found in the second denuder is never negligible and, if the concentration of SO_2 is low (less than 2 ppb), the interference might be extremely large.

Sulfur dioxide, as said before, is an ubiquitous pollutant whose transformation rate is relatively low. This means that in a given location, its concentration might reach highly variable levels according to the dynamic characteristics of the air masses passing on the sampling location. The vicinity of an urban settlement or of an industrialized area increases the range of concentration expected in a given location. Therefore, if a reliable measurement of SO_2 through an accumulation method must be performed, it is necessary to plan the sampling step in order to not exceed the breakthrough volume of air. This means that the sampling time should be the result of a compromise between large sensitivity (large volume of sampled air) and sufficient capacity.

This concept has been largely overlooked and, as a consequence, many data sets could be affected by negative errors due to the breakthrough of SO_2 in the sampling train. The practical definition of capacity may be given in terms of total amount of analyte which is collected over a certain substrate at an efficiency which should not be below a given value.

Again, the use of two denuders in series will allow the use of the second as a quality assurance tool to detect any breakthrough from the first one.

B. Dimethyl and Monomethyl Sulfates

The reaction of SO_2 with organic compounds in the atmosphere and the oxidation of reduced sulfur compounds, eventually results in the formation of dimethylsulfate which is removed from the atmosphere by hydrolysis to monomethyl sulfuric acid and sulfuric acid. The characterization of these compounds is a very important step in order to understand the cycle of naturally emitted sulfur compounds. Analytical techniques making use of denuders, filters, and sorbent systems for the collection of dimethylsulfate and monomethyl sulfuric acid in aerosols and in the gas phase have been described.[56,57]

Dimethyl sulfate has been identified both in the particulate matter and in the gas phase. The analysis has been performed indirectly by ion chromatography, either after hydrolysis to mono methylsulfonic acid and sulfuric acid or by exposure of a fraction of the collected sample to NH_3 gas to convert dimethylsulfate to monomethylsulfate and methylamine. An automated sorbent bed-gas chromatograph system has been employed for the real time monitoring of gas phase dimethylsulfate. Dimethylsulfate is quantitatively collected by XAD resin at room temperature, thermally desorbed, and analyzed by using a sulfur specific FPD detector. Monomethylsulfuric acid in gas phase has been collected by using a carbonate coated annular denuder and the monomethylsulfate anion determined by IC in the denuder extract.

Figure 3 shows a typical ion chromatogram of denuder extracts as obtained by a typical train consisting of a NaCl denuder for the collection of HNO_3, and two Na_2CO_3 coated denuders in series which are used for the collection of acidic compounds. The chromatogram of the first denuder shows a NO_3^- signal due to the uptake of HNO_3 plus a small signal due to a small absorption of SO_2. The second denuder shows peaks corresponding to NO_2^- coming from HNO_2, to NO_3^- coming from the incomplete oxidation of NO_2^-, to monomethylsulfate ion from methylsulfuric acid, and to SO_4^{2-} corresponding to SO_2. The third denuder extract is characterized by the presence of traces of NO_2^- and NO_3^- due to the uptake of NO_2 and PAN, and a significant amount of SO_4^{2-} which must be attributed partly to sulfates in particulate matter and partly to poorly reactive sulfur-containing species which hydrolyze to sulfate in the denuder extract. As a conclusion, a proper use of a denuder train allows the analysis of many important compounds for the acid deposition issue including the metabolites of naturally emitted sulfur compounds.

C. Sulfur Reduced Compounds

Other sulfur compounds of interest for acid deposition include H_2S, CH_3SH, $(CH_3)_2S$, COS, and $(CH_3)_2S_2$, which are generally defined with the term "reduced sulfur". Those compounds are usually emitted by natural processes either in soil or marine environments. As it was discussed before, they might play an important role in the atmospheric acidification in remote locations where emissions by anthropogenic activities are very limited since they react with oxidizing agents yielding a series of compounds ending with sulfuric acid and sulfates. In addition, it has been shown that, at least on a global scale, biogenic and anthropogenic emissions of sulfur compounds are thought to be very similar; thus the contribution of anthropogenic activities to the global acidification can be estimated only through a better understanding of the natural sulfur cycle.[58]

The methods for the measurement of reduced sulfur can be either coulometric detection or thermal oxidation to SO_2 and then detection by pulsed fluorescence. SO_2, which is normally present at much higher concentration levels, is removed from the sample by using a proper scrubber. Two commercial analyzers, based on these principles, have been compared in a side-by-side field study. Interferents as COS and terpenes have been evaluated. At typical monitoring situations normally encountered in the field they do not affect the measurements.[59]

Direct analysis of organosulfur compounds is usually critical due to their low concentrations. Among the preconcentration techniques, chemisorption onto gold foil,[60] and cryogenic trapping[61,62] are used. The most suitable preconcentration method involves sorption on solid sorbents and subsequent thermal desorption and gas chromatographic analysis employing a flame photomeric detector which is specific to sulfur-containing compounds. Chromosorb 102, XAD2, XAD4, XAD7, and Tenax have been tested for their breakthrough volume and suitability according to this procedure and XAD4 has been shown to be the best porous polymer for preconcentration of these species from the atmosphere.[63]

IV. OTHER ACID COMPOUNDS

A. Peroxides

Many peroxides are formed in the atmosphere through photochemical processes, resulting in tiny concentrations of hydrogen peroxide and peroxyacetylnitrate (PAN) which have been shown to damage many plants and trees. Interest in the determination of H_2O_2 stems also from the fact that this species may be considered a source of hydroxyl radicals in the gas phase and a primary oxidant for SO_2 in liquid phase.

The collection of gaseous H_2O_2 in water traps followed by its determination using wet methods has been strongly questioned. A positive artifact by ozone and a negative artifact by SO_2 have been demonstrated.[64] A continuous gas phase sampling technique using scrubber coil in combination with a fluorometric analysis has been described. This method makes use of peroxidase enzyme to catalyze the dimerization of hydroxyphenylacetic acid in presence of hydroperoxydes. In order to distinguish H_2O_2 from organic peroxides, catalase is added to destroy H_2O_2 prior to the peroxidase reaction in a second channel. The interference of pollutants at atmospheric concentration has been investigated and found to be negligible at levels of about 2 ppb of H_2O_2.[65] Sampling of H_2O_2, using impingers or diffusion scrubbers, after removal of O_3 by gas-phase reaction with nitric oxide has been proposed.[66]

The determination of H_2O_2 by using an unique application of the denuder technique has been reported by Slanina.[39] The authors used water to coat an annular denuder, counteracting the evaporation by rotating the tube during sampling so that a layer of water is always present in the annulus to wet the active surfaces of the denuders (Figure 6). In the operating automatic mode, water is pumped at a flow rate such that a volume of solution can be extracted from the outlet and collected in vials suitable for analysis according to the species of interest. For the determination of H_2O_2, it is necessary to eliminate interferences due to ozone and to reactions with sulfite ion formed by the absorption of SO_2. The detection limit for the rotating annular denuder is about 0.01 $\mu g/m^3$. Generation of H_2O_2 by ozone can also be prevented by adding a stream of NO to the air sample. As said before, the rotating denuder is also suitable for other gases of interest for the acid deposition problem.

An annular denuder coated with titanium (IV) oxalate-sulfuric acid has been recently employed to collect H_2O_2. The reactive layer is extracted with a solution of xylenol orange and the absorbance of the complex formed with titanium measured by spectrophotometry. The interference of O_3 is taken into account by using a differential method, i.e., two denuders in series as outlined before in the section dealing with nitrous acid. A detection limit of about 0.03 ppb is reached for 1 h sampling.[67]

Gas chromatography coupled to electron capture detection (ECD) has been widely applied for measuring ppb concentrations of PAN, peroxypropionylnitrate (PPN), and methylnitrate (CH_3ONO_2) in ambient air samples. As it is well known these are secondary pollutants formed in the atmosphere during photochemical smog episodes as result of chemical reactions involving NO_2 and naturally and anthropogenic emitted reactive hydrocarbons. Many observations confirm that fairly large amounts of PAN are detected in the atmosphere when high levels of ozone and free acidity are developed as the results of photochemical reactions. Although it is unlikely that PAN and related compounds may contribute to atmospheric acidity, there are many reasons to promote the monitoring of these pollutants. First, in polluted areas PAN and related compounds act as sinks for NO_2 contributing to the control of HNO_2 and HNO_3 formed during photochemical pollution. In addition, since the lifetime of PAN is fairly large, such compound can be hydrolyzed in remote regions contributing to the transport of potential acid compounds.

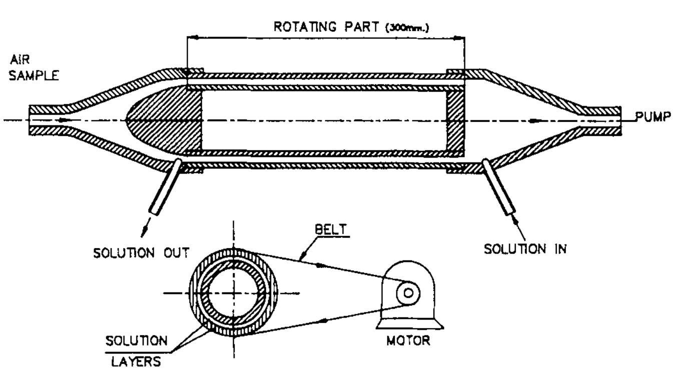

FIGURE 6. A wet annular denuder which is continuously coated with a layer of water.

The gas chromatographic technique employs a Chromosorb WHP + 10% Carbowax column kept at a temperature of 35 to 40°C. By choosing proper operating conditions of the ECD it is possible to obtain a minimum detectable level for PAN of 0.13 ppb in less than 15 min.[68]

Cryotrapping has been used for PAN. Samples are stored at liquid nitrogen temperature and later determined by GC-ECD.[69] A proper modification, designed for aircraft sampling has been developed by Meyrahn.[70] The thermal instability of PAN and the nonlinearity of ECD detectors give rise to a number of difficulties in calibration procedures. A method for the calibration of PAN that uses a chemiluminescence NO_x analyzer, suitable for field use, has been described.[71]

B. Aldehydes and Organic Acids

The major anthropogenic source of aldehydes in the atmosphere is the combustion of fossil fuels, while the photochemical oxidation of hydrocarbons leads to the formation of aldeydes and other carbonyl compounds as intermediates.[72] This probably provides the main natural sources of these compounds. Aldehydes react in the atmosphere giving rise to several compounds which includes PAN and radicals. Especially photochemical smog episodes cause the destruction of HCHO leading to an enhancement of HO_x radicals so that the mixing ratios of the two most abundant aldehydes might be interpreted as an indirect measurement of atmospheric reactivity. In addition, HCHO and CH_3CHO have been found in precipitations and can react to form carboxylic acids which are present in large quantities in precipitants where they might account for more than 60% of the total acidity in rain.[73] Very recently, carboxylic acids have been also evidenced in relatively remote areas.[74]

Most of the available methods have been developed for determining formaldehyde gas, including those specifically addressed for the measurement in indoor air or in occupational settings. However, they may not be suitable for the relatively much lower concentrations predominant in ambient air.

FTIR[12] and differential absorption in the near ultraviolet[13] have been used for the measurement of aldehydes *in situ*. With suitable optical paths, the detection threshold is of the order of a few ppb for formaldehyde. Wet analytical procedures such as the chromotropic acid method or the sodium hydrogen sulfite method have also been applied but their interest in field applications is very limited.

The only widely adopted procedures are based on the reaction with 2,4-dinitrophenylhydrazine (DNPH) followed by the analysis of the hydrazones by HPLC.[75-77] DNPH coated substrates packed in sorption cartridges have also been used[78] and recently a new technique based on nebulization/reflux principles for the collection of HCHO has been proposed.[79] Quantitative analysis of HCHO at 0.1 ppb is feasible with a resolution time of 20 min. The analysis is performed by using HPLC with UV photometric detection. HCHO has been collected on annular denuders coated with bisulfite-triethanolamine. After sampling the sorbent layer was extracted and analyzed by the chromotropic acid method.[80] Denuders have also been used for the measurement of HCHO and CH_3CHO in atmosphere. They are quantitatively collected at flow rates of about 1 l/min on annular denuders coated with DNPH, obtaining collection efficiencies larger than 95%. The method has been found very useful for field application.[81]

Carboxilic acids, as said before, have been evidenced in samples intended for the analysis of other acidic compounds. For instance, an alkaly impregnated filter extracted with water shows noticeable amounts of acetic and formic anions. However, the straightforward assignation to the presence of the corresponding carboxilic acid might be misleading. In other words, the said anions might be the result of the artifacts which take place on the surface of any absorption materials. Even in this case, the possibility offered by diffusion denuders open many possibilities in understanding such processes and in providing suitable methods for the measurement of organic acids because the same experimental set-up used for other compounds (SO_2, HNO_2, etc.) may be envisaged.

C. Haloacids

Haloacids pose heavy problems only in the vicinity of selected industrial plants where noticeable amounts of HCl and HF are emitted. In remote locations, halocarbons should not contribute significantly to the total acid deposition. However, some measurement of HCl might shed some light on the heterogeneous reactions between NaCl particles with sulfur containing gas molecules which result in the formation of HCl.

The most suitable methods for the measurement of haloacids are based on the use of filter packs and diffusion denuders. As said before, filter packs might experience positive and negative artifacts; therefore denuders should be preferred. A sensitive technique which combines collection of HCl at ppt levels by means of silica gel denuders and derivazation with 7-oxabicyclo-(4,1,0) heptane after thermal desorption has been described. The epoxide and HCl react in the injector of a chromatograph and HCl is converted into 2-chlorocyclohexanol which is determined by a Hall electrolytic conductivity detector.[82]

An annular denuder coated with alkali has been employed for the collection of HCl and HF. Since the latter might be displaced by SO_2, care must be paid to the total operative capacity of the denuders when they are used in a polluted site. The diffusion tubes are extracted with water and analyzed as regards their ionic content by means of ion chromatography or ion selective electrodes. The sensitivity of the method for the measurement of trace concentrations of HCl is often impaired by laboratory and field blanks;[83] thus strict quality assurance procedures must be implemented for reliable measurements.

D. Ammonia

Ammonia is a very important compound in the definition of the atmospheric acidity because it is the species which is able to buffer, to a certain extent, the acidity carried out by gases and particles. A substantial part of the acids of the atmosphere generated by the oxidation of SO_2 and NO_x is neutralized by ammonia. The final product of the neutralization reactions is the formation of ammonium salts in particulate matter, generally ammonium sulfate and bisulfate and ammonium nitrate. The major source of ammonia is to be identified into bacterial activity which takes place in the soil. Thus, the emission rate is a complex function of the type of soil, temperature, season, etc. Locations experiencing extensive animal settlements are those with the higher emissions.

Ammonia, as well as nitric acid, is in equilibrium with ammonium nitrate in particular matter which causes many of the artifacts encountered during the sampling. Since the equilibrium constant is dependent upon temperature and relative humidity, the atmospheric concentrations of ammonia might range from fractions to tens of $\mu g/m_3$. The importance of such compounds is such that many efforts have been placed in order to achieve accurate and sensitive measurement methods.

FTIR with a 900-m pathlength has been used to measure ammonia in gas phase at a concentration level of 10 ppb.[84] Another instrumental *in situ* technique is based on *o*-phthalaldehyde fluorescence derivatization[85] with a detection limit of 0.2 ppb and with a time resolution of about 2 min. The use of a dual catalyst chemiluminescence technique has been proposed. The procedure is based on the use of a high temperature catalytic converter which oxidizes ammonia to nitrogen oxide and a low temperature catalyst which converts NO_x to NO. Passing a fraction of the sample air stream through the high temperature converter (stainless steel operated at 700°C) yields total NO_x plus NH_3 while the other portion is passed through the low temperature converter to yield only total NO_x. The NH_3 concentration is obtained by the difference between the two outputs.[86,87]

Probably, the best candidate for a reliable instrumental measurement of ammonia is the use of the tunable diode laser spectrometry (TDLAS). Almost all molecules of interest for the acid deposition, absorb IR radiations in the region useful for diode laser application (2 to 15 μm). The very high spectral resolution of tunable diode lasers permit the selection of a single roto-vibration line which makes interferences from other gases very unlikely.

The operating scheme of a TDLAS instrument is outlined in Figure 7. It consists of several diode lasers to cover a relatively wide range of emitting frequencies which are mounted on the same cryostat. In order to get the desired sensitivity and detection limits, a long absorption path can be obtained by using a multipass white cell. The diode laser output frequency is scanned by changing the current flowing through the diode and, since the absorption line can be scanned in a fraction of a second, the measurement response time is limited only by the residence time of the sampled gas in the white cell. This is usually just a few seconds which makes the system very attractive for the measurement of the dry deposition. The cell is kept at a pressure of about 25 mmHg in order to reduce the pressure broadening of the absorption line and this results in an increased sensitivity and reduced interferences from other gases. The spectrometer is operated in frequency modulated mode under control by means of a computer.[11]

As said before, the TDLAS technique can be adapted to the measurement of many gases of interest for the acid deposition issue, NH_3, HNO_3, H_2O_2, and HCHO being the most promising for extensive monitoring application. It is quite surprisingly the observation that TDLAS and related techniques have been developed a long time ago and only recently a certain number of reports (e.g., Grisar et al.)[88] clearly demonstrate the possibilities open by such analytical method. The spectrometers to be used in TDLAS have been developed in order to be easily mounted on vans or on aircraft without many major problems. The only drawback of the technique is related to its extractive nature. In other words, in order to perform the analysis, air must be filtered and drawn through a system at reduced pressure. This might alter the thermodynamic equilibrium of many gaseous compounds yielding erroneous results. Secondary surface reactions and irreversible adsorption might also take place in the white cell, contributing to a reduction of the system reliability. Those aspects should be the subject of intensive investigation in order to prove the applicability of TDLAS for the measurement of the dry deposition components. Sensitivities for most species of interest for the dry acid deposition is down to tenths of parts per billions.

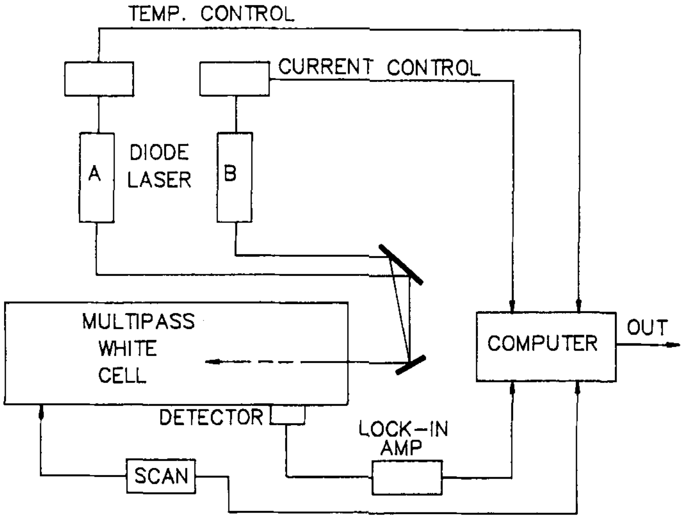

FIGURE 7. Schematic diagram of a tunable diode laser spectrometer which allows the measurement of several compounds relevant to the acid deposition issue.

Among accumulation methods, ammonia has been measured by preconcentration on Chromosorb T and subsequent analysis, after thermal desorption, by chemiluminescence,[89] or by using a double filter pack composed by teflon and oxalic acid impregnated filters. However, the preconcentration of NH_3 by using these integrative techniques is complicated by the interference from ammonium containing particulate matter. Artifacts may arise from interactions between gas and particulate matter, or can be released by ammonium salts when they react on the filters with alkaline particles. In addition, ammonium nitrate easily vaporizes from filters. These effects are sources of serious errors which might impair a correct measurement of ammonia in gas phase and ammonium on particulate matter even using spectroscopic techniques, as said before, as the sample should be drawn in the measurement cell at low pressure and after a filtration to remove particulate matter (see Allegrini et al. and references therein).[91]

Enrichment procedures based on the use of acid coated diffusion tubes followed by filters overcome the problems related to the artifacts described earlier. Methods based on the use of oxalic acid as coating material for cylindrical[90] and annular denuders[91] have been described. However, oxalic acid is not very suitable for the simultaneous measurement of ammonium in particulate matter since it readily volatilizes from the denuder walls increasing the total acidity found on the backup filter. In such cases, the use of citric or phosphoric acid is to be preferred. After sampling, the denuders and the filter are extracted with water and analyzed as to their ammoniun ion content by colorimetry or ion chromatography.

A sampling train which has been shown to provide a correct measurement of ammonia in gas phase and ammonium on particulate matter makes use of an annular denuder coated with oxalic acid which removes ammonia in gas phase, and of a teflon filter in line for the collection of ammonium salts. Since the filter is exposed to air which does not contain ammonia, ammonium nitrate dissociates into gaseous ammonia which is collected on a back-up denuder or on a back-up impregnated filter. Thus the ammonium ion found in the first denuder gives ammonia in the gas phase, while ammonium in particulate matter is given by the sum of ammonium remaining on the filter and that found on the back-up denuder. Dissociation of ammonium nitrate during the transit time on the denuders has been shown to proceed at a negligible extent. The use of high efficiency annular denuders allows measurements with a relatively low integration time (less than 1 h).[91]

V. PARTICULATE MATTER

Accurate measurements of suspended particulate matter are of great importance in the acidification of the atmosphere as particulate phase contains most of the metabolites from primary emitted pollutants. The deposition velocities of suspended particulate matter have been measured to be very low and this consideration must be properly taken into account in order to assess the environmental impact of particles. However, it has been shown that acidic particles are of great importance for the health effects since while acidic gases are removed in the upper respiratory tracts, particles might penetrate lungs giving rise to pathologies which probably are responsible for the health effects in moderately or heavily polluted locations.

The evaluation of suspended particles from a physical standpoint limits the measurement to the size distribution and the total mass per unit volume. On the other hand, methods for chemical analysis must be critically reviewed as well as the procedures for the sampling and for the evaluation of the relevant species. Again, the possibility of positive and negative artifacts could severely limit the applicability of a suggested technique in field applications.

Analysis of particulate matter is usually performed by sampling on a proper filter medium which is leached with a proper solution and analyzed according to classic methods, such as ion chromatography. However, physical and chemical representativeness must be assured in order to obtain meaningful results. The sampling flow rate and the inlet should be such that a well defined size distribution is transferred on the filter medium. Inertial effects on the sampling line due to wind and sampling streamlines might change the sampling efficiency for a given size range giving rise to errors. Chemical representativeness might be impaired due to reaction of particles collected on the filters with species contained in the sampled air. A typical example is the reaction of particles with HNO_3 or with SO_2, which results in an overestimation of SO_4^{2-} and NO_3^- content. Evaporation of NH_4NO_3, as said before, causes errors in the measurement of ammonium and nitrate content.

In order to define the size distribution of collected particles, a proper sampling head followed by a size classifier should be used. Unfortunately an unbiased definition of particulate matter has not yet been stated, therefore any measurement reflects the size distribution of the particles which have been effectively collected. This is dependent upon the sampling flow rate and the geometry of the sampler, calling the scientific community to an effort to define the meaning of the term "particulate matter". Since the species of interest for the acid deposition problem are accumulated in the low size region, several sampling trains employ size classifiers, as cyclones, for the separation of larger particles.

Gas-particles interactions can be avoided only by using denuders. Since classic tubular denuders are not able to withstand large flow rates, annular denuders should be used. A sampling train which could be effectively used to remove gaseous components for a representative collection of particulate matter consists of one annular denuder coated with Na_2CO_3 which removes acid gases followed by a second denuder coated with citric acid which is effective for gaseous ammonia. Air is drawn into a Teflon cyclone having a cut size of 2.5 μm at 15 l/min which removes large particles and into a filter pack. The front (Teflon) filter is used for the collection of particles, the second filter (nylon) collects evaporated nitrates, and the third (acid impregnated) removes evaporated ammonia. After sampling, the filters are leached and analyzed by ion chromatography or spectrophotometry as to their ionic content.[91]

An attractive method for the measurement of ions collected on filters has been described by McClenny et al.[92] The method is based on the analysis of FTIR spectra of filters used for the collection of particles. It is suitable for sulfate and ammonium ions at sensitivity levels comparable to those obtained by ion chromatography. The method offers the significant advantages of a nondestructive technique, no sample preparation, and rapid analysis; thus it might be considered among the best candidates for routine analysis of field collected samples.

Instrumental measurement of the chemical content of particulate matter is a very stimulating research field since classic chemical methods are time consuming and require adequate expensive manpower. The very first instrumental monitoring of particles has been the sulfur specific flame photometric detector (FPD). When the air is sampled through the hydrogen rich flame of FPD, a signal from sulfur containing gases and aerosols is obtained. If the two contributions are separated before the detector, a reliable measurement is obtained. A modulation can be achieved by means of a pulsed electrostatic precipitator which alternatively allows particle free and ambient air passing through the detector. A synchronous detection allows the measurement of sulfur in gas phase and sulfates in particulate matter (sulfuric acid and ammonium sulfates). However, the nature of this method is differential; thus unreliable results might be obtained if the concentration of sulfur containing particles is much less than that of the gaseous phase.

Since most sulfur in gas phase is present as SO_2 and H_2S, a separation between gases and particles might also be achieved by means of a specific denuder. The flow rate through the FPD is so low that a short cylindrical denuder, coated with PbO_2 might be used.[93] Proper design of a modified FPD detector allows detection limits as low as few parts per billions.

Direct instrumental measurement of some species relevant to acid deposition may also be performed by means of the thermodenuder. This is a thermoanalytical technique used for the determination of many compounds, including H_2SO_4. The air is drawn first in a denuder which removes species in gas phase which might interfere with the determination of particulate matter. The air stream is then allowed to pass through a heated denuder where the species of interest dissociates into molecules which are collected on the walls. After sampling, the walls can be analyzed as to their content or the walls thermally desorbed and the evolved gases measured by means of instrumental methods.

The advantage of such technique resides in the fact that the choice of proper coating and thermodynamic conditions might modulate the species which are collected. This technique allows the measurement of sulfuric acid, nitric acid, hydrochloric acid, ammonia, and the corresponding ammonium salts.[94] An automatic system based on the use of a rameic oxide surface for the determination of H_2SO_4 down to 0.1 μg/m^3 with a resolution time of 5 min has been described. After sampling the tube is heated at 800°C and the evolved SO_2 measured by means of a FPD.[95]

VI. RADICALS

Radicals are highly reactive species which play a central role in controlling photochemical processes. Since they are present at very low concentration levels, their determination must be achieved by means of highly sophisticated techniques which are reported into this review for completeness. The most important radical present into the troposphere is $OH^{\cdot}$. It is mainly formed as the result of UV photolysis of ozone and reacts with many species to generate secondary pollutants. The homogeneous oxidation of SO_2 and NO_2 into sulfuric and nitric acid, respectively, has been discussed before.

Laser induced fluorescence (LIF) has been used for tropospheric aircraft[96] and ground[97] measurements. LIF techniques are highly sensitive and selective since $OH^{\cdot}$ concentration of 2.5×10^5 molecules/cm$_3$ has been detected. Possible interferents to this method are the laser induced dissociation of O_3[98] and the self-generation of OH.[99] Long path absorption spectroscopy by using a laser radiation at 308 nm has been successfully used for the measurement of tropospheric $OH^{\cdot}$ levels. This method is less sensitive to the previous one and the development of the original instrumentation has resulted in a better sensitivity of the order of 3×10^6 molecules/cm^3. Absorption by other atmospheric species and self generation of $OH^{\cdot}$ are considered potential problems.[100]

A chemical method based on the reaction of radical species with ^{14}CO and on the measurement of $^{14}CO_2$ has been proposed by Campbell.[101] A technique based on the chain reaction of peroxy and oxyradicals with NO and CO has been suggested. The NO_2 produced is measured by luminol chemiluminescence. The substitution of CO with nitrogen allows the correction for the interfering species. This technique is characterized by a lower detection limit of 1 ppt in ambient air.[102] An alternate chemical method has been used by forming an adduct with a spin-trapping agent which is then determined by electron spin resonance (EPR) and gas chromatography-mass spectrometry.[103] The claimed limit of detection is 2×10^5 OH molecules/cm^3.

Nitrate radicals ($NO_3^{\cdot}$) have been measured by rapid scanning differential optical absorption (DOAS). Absorption bands with optical density as low as 10^{-4} have been recognized. Detection limits for nitrate radicals range from 1 ppt to several ppt depending on the pathlength and the concentration of particulate matter.[104]

VII. FIELD INTERCOMPARISONS

Since there are many available analytical methods for the analysis of compounds relevant to the acid deposition issue in the past few years several field intercomparisons have been organized. The aims of such activities can be summarized as follows:

1. To compare "standard methods" with those developed in laboratory in order to check sensitivity, accuracy, and suitability for the use in field conditions
2. To explore the possibility of retrofitting sampling stations with advanced instrumentation and/or analytical methods

Although the results of these exercises are far to be conclusive, the information which can be derived have been very useful to establish the relative performances of the different methods used during the intercomparisons.

A great deal of attention has been paid to the measurement of nitric acid in gas phase and nitrate in particulate matter due to the complex chemistry of atmospheric nitrogen containing compounds. These are responsible for many possible artifacts which might impair the measurement of such important species. Intercomparisons specifically designed for nitric acid have been reported by Spicer et al.,[105] Anlauf et al.,[53] Mulawa and Cadle.[106] Most of the efforts have been spent for the characterization of the filter pack method since it would be the simplest and cheapest to implement for routine nitric acid measurements. Data show that filter pack frequently gives positive artifacts due to the losses of ammonium nitrate from the prefilter. The extent of such bias is strongly dependent upon sampling conditions and the relative concentrations of nitric acid to particulate nitrate. The filter pack might be suitable for the measurement of the sum of nitrates in gas phase and in particulate matter; however, its ability in discriminating between the two forms is very poor and far to be demonstrated in several environmental conditions.

A number of very interesting intercomparison exercises have been performed in California in September 1985 and 1986, the results of which have been recently published.[107] Problems related to inlets for particle classification which might retain a substantial amount of nitric acid have been found. In addition, denuder based methods gained more consensus for the measurement of most acid compounds in gas phase and in particulate matter.

From a recent intercomparison carried out at Research Triangle Park, North Carolina (U.S.),[108] it can be concluded that the transition flow reactor yields excess nitric acid, while the annular denuder method suffers from biases due to the oxidation of HNO_2 to NO_3^-, which, as said before, might be completely eliminated by using a NaCl coated denuder. The findings, although favoring the denuder method, still do not permit a complete endorsement for field deployment without further development and field testing.

The European Community, within the action COST 611 on "Physico-Chemical Behavior of Atmospheric Pollutants" organized an intercomparison campaign on the use of denuder in Schauinsland (FRG).[109] The results show that there is sufficient agreement on the measurement of particulate matter, while noticeable differences have been observed for most compounds in gas phase. On the basis of these findings, a second experiment in artificially polluted atmospheres by HCl and HNO_3 has been carried out at Essen (FRG), in December 1986. In this exercise, it has been shown that all filter methods failed in selectivity, experiencing losses relative to denuder based methods. The latter yield a good performance giving results which are in good agreement between themselves and the Laser-based method. Results from thermodenuders did not show the same precision.

In an intercomparison campaign, coordinated by EMEP (Cooperative program for monitoring and evaluation of the long range transmission of air pollutants in Europe)[110] particular attention has been paid to the measurement of SO_2 in gas phase and sulfates in particulate matter according to the EMEP standard procedures. The results show that there are not negligible differences between the methods, even though most participants made use of the same analytical procedures. Differences in the results for particulate matter have to be attributed to the sampling efficiencies when different samplers are used. As far as particulate matter is concerned, a standardization of the sampling procedures is strongly recommended.

Problems encountered with the intercomparison exercises which have been so far performed are related to the design of the experiment. Owing to the complexity of the artifacts which might arise from many analytical methods intended for the evaluation of the dry acid deposition, it seems that a trivial comparison between different methods does not provide many information regarding to reliability of the methods. Therefore, the design of any intercomparison experiment should be addressed to the understanding of the reasons why a certain set of data is inconsistent. This philosophy has been applied to a large intercomparison exercise which has been organized by European Community Commission in the early fall 1988 near Rome, Italy, and addressed to nitric acid and particulate nitrate.

VIII. CONCLUSIONS

A great effort should be made to determine with enough sensitivity and accuracy the relevant species which are present in the atmosphere at very low levels. It should be stressed that a complete knowledge of the processes governing the transformation and deposition of the said compounds could be achieved only if a complete set of experimental data are obtained on the area under investigation. This limits the use of automatic instruments which are not able to provide multiparametric response, thus the development of relatively simple, field operated multiparametric equipments for the evaluation of atmospheric acidity is urgently needed. A list of criteria parameters to rate individual analytical methods for the species involved in acid deposition is given in Table 3. Ratings are given in five classes ranging from A to E in descending rank according to the specified criteria as given at the bottom of the table. The list and ratings are not exhaustive even though they well reflect the state of the art of acid deposition measurements.

Reports on measurement of atmospheric acidity from components in gas phase and in particulate matter, show that several data sets are inconsistent. This is mainly due to the scarce attention which has been, at least so far, paid to quality control and quality assurance. This also limits the international compatibility, availability and usefulness of environmental information in this field in particular and the progress in protecting the environment in general. Activities for improvement and harmonization of techniques and practices of measurement of the parameters relevant to the acid deposition issue should be encouraged at national and international levels.

Table 3
Measurement Methods-Reference Table

Pollutant	Analytical method	I	II	III	IV	V	VI	VII
SO_2	Filter pack	A	A	B-D	A	A	D	A
	Denuders	B	B	D	A	A	E	A
	Thermodenuders	B	A	B	E	C	B	C
	Flame photom. detec.	E	C	B	D	C	A	A
	Molecular UV fluor.	A	B	B	D	B	A	A
	Annular denuder met.	A	A	C	B	A	E	B
HNO_3	Denuder difference	A	A-D	D	C	B	D	A
	Filter pack	E	A	C	A	A	D	A
	Annular denuder met.	A	A	C	B	A	E	B
	Transition flow reac.	A	A	C	C	C	C	C
	Nylon denuder	A	A	D	A	A	B	B
	Fourier tran. spectr.	A	E	B	E	E	B	D
	Diode laser absorption	A	C	B	E	E	B	D
	Tungstic acid denuder	C	A	B	D	D	B	C
HNO_2	Denuders	D	A	D	A	A	D	B
	Annular denuder met.	B	A	C	B	A	D	B
	Diff. absorp. spectrum	A	C	B	E	E	C	C
NH_3	Denuders	A	A	D	A	A	B	A
	Annular denuder met.	A	A	C	B	A	B	B
	Filter pack	C	A	C	A	A	A	A
	Diode laser absorption	A	B	B	E	E	B	D
NO_2	Gas phase chemilumin	D	B	A	D	A	A	A
	Luminol chemilumin	B	A	A	C	A	A	B
	Denuders (guaiacol)-ADM	A	A	C	B	A	D	A
	Filter pack (TEA)	D	A	D	A	A	D	A
	Diff. absorp. spectrum	A	A	A	E	E	C	B
HCl, HF, $(CH_3)HSO_4$ org. acids	Filter pack	D	A	D	A	A	D	B
	Annular denuder met.	A	A	D	B	A	D	B
	Denuders	B	A	D	A	A	D	B
H_2O_2	Annular denuder	B	A	D	B	A	D	C
	Enzyme-catal. fluor.	B	A	B	C	C	B	D
	Chemiluminescence	C	D	B	C	C	B	D
Aldeydes	Absorption traps	A	A	C	C	B	D	C
	Annular denuder	B	A	D	B	A	D	C
Hydrocarb	Absorption traps	A	A	C	C	B	D	C
PAN	Electron capture det.	A	B	B	C	A	B	C
SO_4^{2-}	Filters	C	A	D	A	A	D	A
	Ann. denuder + filter	A	A	D	B	A	D	B
	Flame phot. + denuder	C	C	B	C	A	B	A
H_2SO_4 $(NH_4)_2SO_4$	Thermodenuders	A	A	B	E	C	B	B
NO_3^-	Filters	E	A	D	A	A	D	A
	Ann. den. + filter pack	A	A	D	B	A	D	B
	Denuder difference	A	A	D	B	B	D	A
$(NH_4)NO_3$	Thermodenuders	A	A	B	E	C	B	C
NH_4^+	Filter pack	E	A	D	A	A	D	A
	Denuders + filter pack	A	A	D	B	A	D	B
$OH^\cdot$	Laser long path abs.	B	B	B	E	E	C	C
NO_3^-	Diff. absorp. spectr.	A	B	B	E	E	C	C

Key Entries:

I - specificity (A = highly specific to E = not specific); II - sensitivity (A = highly sensitive to E = not sensitive); III - time resolution (A = seconds to E = several hours); IV - cost of equipment (A = low cost to E = very expensive); V - field monitoring (A = very suitable to E = not suitable); VI - manpower requirement (A = low to E = large); VII - development stage (A = fully developed to E = lab. prototype).

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