



Project Summary

Sampling and Analytical Methods Development for Dry Deposition Monitoring

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The U.S. Environmental Protection Agency (EPA) plans to implement a dry deposition monitoring network. The constituents of interest are HNO_3 , NO_2 , SO_2 , NH_3 , NH_4^+ , NO_3^- , SO_4^{2-} , H^+ (acidity), and O_3 . The objective of this research was to identify the most promising sampling and analysis methods for network deployment in relation to these constituents.

A phased approach consisting of literature reviews, laboratory studies, and field evaluations was employed. Literature reviews were used to identify those methods that appeared promising for direct application or for development into methods suitable for field application. The identified methods were tested and refined in laboratory studies. In those cases where the methods remained potentially acceptable after laboratory investigation, field evaluations were performed.

A field study was then conducted in the Research Triangle Park, North Carolina, between August and December of 1986 in which selected airborne gaseous and particulate acidifying species were measured using different types of samplers, and the differences observed under field sampling conditions were evaluated. The bulk of the full report presents and compares results collected in the 1986 study using the Annular Denuder System (ADS) with those collected using the Transition Flow Reactor (TFR). Comparisons were also made with results from the Filter Pack (FP), Tunable Diode Laser Absorption Spectrometer (TDLAS) methods and methods of other investigators. The overall goal was to use the results of

the field evaluation along with other information gathered during this project to assess the current status of available sampling and analysis methods and identify method strengths and weaknesses that must be considered prior to their field deployment.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The phenomenon of acid deposition has received increasing attention in recent years. Acid deposition is the transfer of acidic substances in the earth's surface by wet or dry deposition. Dry deposition includes all processes by which airborne contaminants are removed from the atmosphere at the earth's surface, excluding those processes directly aided by precipitation. Dry deposition contributes substantially to the acidic deposition burden, at times accounting for more than 50 percent of the total. Efforts to monitor dry deposition and to investigate its behavior will provide insight into its role in the larger problem of acidic deposition.

The U.S. Environmental Protection Agency (EPA) plans to implement a dry deposition monitoring network. The constituents of interest and the sampling and analysis methods to be used, however, require definition. Many of the airborne chemicals that are thought to be important contributors to ecosystem acidification are given in Table 1, along with their nominal concentrations.

Table 1. Contributors to Ecosystem Acidification

	Constituent	Concentration ($\mu\text{g}/\text{m}^3$)
HNO_3	Nitric Acid	0.1 - 10
HNO_2	Nitrous Acid	0.1 - 2
NO_2	Nitrogen Dioxide (an acidifying precursor)	0.2 - 30
SO_2	Sulfur Dioxide (an acidifying precursor)	0.1 - 20
NH_3	Ammonia	0.1 - 30
NH_4^+	Ammonium (particulate)	0.05 - 5
NO_3^-	Nitrates (particulate)	0.1 - 5
SO_4^{2-}	Sulfates (particulate; may be H_2SO_4 , NH_4HSO_4 , or $(\text{NH}_4)_2\text{SO}_4$)	0.2 - 20
H^+ and Acidity	Strong Hydrogen Ion (particulate)	0.01 - 10
O_3	Ozone (an oxidant)	2 - 200
H_2O_2	Hydrogen Peroxide (an oxidant)	0.1 - 5
RCOOH	Organic Acids	0.1 - 10
PAN	Peroxyacetyl Nitrate (an oxidant)	0.05 - 50
HCHO	Formaldehyde	0.1 - 50

The objective of the current research was to investigate sampling and analysis methods for several of the constituents in the above list. Emphasis has been placed on the first nine species, excluding nitrous acid. The overall goal was to identify the most promising methods for network deployment. The following four factors must be considered in selecting sampling and analysis methodologies.

Species to be Measured

The species identified above were selected as having the highest priority for monitoring. This listing should change with increased understanding of the important species and processes that influence ecosystem acidification.

Time Resolution

Although the time resolution has not been firmly defined, the needs of large-scale air quality models will heavily influence these requirements. Currently, time resolution ranging from 6 hours to 1 week is anticipated to be sufficient to satisfy program needs. As a result, integrated sampling over the required time scale can be employed. This eliminates the requirement for complex and capital intensive continuous instrumentation in many cases.

Quality of Measurements

Accuracy and precision define the quality of measurements. Reasonable accuracy and precision goals for monitoring activities are ± 10 to 20 percent. It is expected that these will differ and depend on the reactivity/importance of the species under consideration. Several factors influence the quality of the measurements: collection and recovery efficiency, sensitivity, species concentration, selectivity, and susceptibility to contamination.

Collection and recovery efficiencies above 80 percent are desirable. Sensitivity, species concentration, and sampling rate are interrelated. Since monitoring sites are generally expected to be located in relatively remote locations, species concentrations are expected to be quite low (i.e., ppb to ppt levels). The sensitivity of the analytical finish will determine the minimum amount of the species of interest that must be sampled. The method must be selective. Ideally, it would be free of physical influences such as humidity and temperature effects. In addition, it should be free of chemical interferences. Susceptibility to contamination should be identified and minimized.

Method Complexity

The recommended methods are expected to be used by competent, but not necessarily highly skilled, field technicians. The analytical finish is expected to be performed in a well-equipped laboratory, using established, well-developed, but not prototype or research, equipment. Thus, the methods must be simple to use in the field and should require minimal manipulation of the sample, both in the field and in the laboratory.

Background

Two broad types of methods are available for sampling dry deposition constituents: chemical-specific methods and multiple-constituent systems. Due to the number of species to be monitored, this development program emphasized multiple-constituent systems. Descriptions of these latter systems are presented here along with information summarizing literature findings and experimental results obtained through October 1986.

Multiple Constituent Systems

Currently, there are three multiple-constituent sampling systems that have been reported for collecting acidifying constituents from ambient air. They are the Filter Pack (FP), the Transition Flow Reactor (TFR), and the Annular Denuder System (ADS). For each system, the species sampled for subsequent analysis are given in Table 2.

Table 2. Summary of Multiple Constituent Sampling Systems and Species Sampled

Species	System		
	FP	TFR	ADS
HNO_3		X	X
HNO_2			X
NO_2		X	
SO_2	X	X	X
NH_3		X	X
NH_4^+	X	X	X
NO_3^-		X	X
$\text{HNO}_3^+ \text{NO}_3^-$	X	(X)	(X)
SO_4^{2-}	X	X	X
H^+ /Acidity	X	X	X

FP

The Filter Pack approach is employed in networks operated by Environment Canada and the Ontario Ministry of the Environment. The system consists of a three-stage filter pack sampling at approximately 20 Lpm. An open-face 2 μm pore size Teflon filter is the first element, followed by a 1 μm pore size nylon filter, followed by an impregnated (K_2CO_3 and glycerin) Whatman-41 filter. The filter size is approximately 47 mm in diameter. Since open-face filters are used, sampling is not size selective. The extract from the Teflon filter is analyzed for IC for SO_4^{2-} and NO_3^- , by IC in one network and by colorimetry in the other for NH_4^+ , and by colorimetric titration for acidity. The nylon filter is extracted in 0.003 NaOH and analyzed by IC for NO_3^- and SO_4^{2-} . The impregnated Whatman-41 filters are analyzed for SO_4^{2-} by IC which is added to that recovered from the nylon filter and reported as SO_2 .

The FP has the following limitations:

- As a result of potential positive and negative biases in HNO_3 and particulate NO_3^- sampling, the sampler does not provide HNO_3 concentration data. The sum of the NO_3^- from the Teflon and nylon filters represents Total Inorganic Nitrate (TIN).
- The presence of acidic particles on the Teflon filter offers the potential for neutralization and change in speciation of acidic sulfates when NH_3 is present in sampled air.
- The system does not permit the determination of gaseous NH_3 . As a result, it also offers the potential for high bias of particulate NH_4^+ estimates derived from Teflon filter extracts.
- The potential biases in nitrate sampling, coupled with the potential neutralization of acidity by gaseous NH_3 , make interpretation of H^+ /acidity data from the Teflon filter extract difficult.
- The system does not permit the determination of HNO_2 . However, if HNO_2 is transmitted by the Teflon filter, then it should be retained on the nylon and K_2CO_3 -coated filters.
- Sulfate collected on the nylon and impregnated Whatman-41 filters must be summed to infer SO_2 con-

centration, since nylon can collect SO_2 as SO_4^{2-} .

- Since the approach does not employ size selective sampling, distinction of the distribution of chemical constituents between coarse and fine particles is not possible.

The advantages of FP are simplicity, low cost of deployment, and high sensitivity. The FP approach has been used in different configurations for network sampling in Canada since the late 1970's. Thus, of the systems considered, the FP has the largest historical database.

TFR

As the name suggests, the TFR incorporates Transition Flow Reactors and filter collection media. As shown in Figure 1, the TFR system is comprised of modules arranged in series to collect various constituents of interest. The first module is a Teflon cyclone having a D_{50} ($p = 1.0$) of 1.8 μm at 33.2 SLPM and of 2.5 μm at 17.3 SLPM. The second and third modules are two TFR for determination of HNO_3 and NH_3 , followed by a filter pack containing a 2- μm pore size Teflon filter, a 1- μm pore size nylon filter, and an oxalic acid impregnated glass fiber filter. The first TFR uses a nylon strip as a partial denuder to remove a constant fraction (i.e., 8.5%) of gaseous HNO_3 under transition flow conditions. The second TFR uses a Nafion strip as a partial denuder to remove a constant fraction (i.e., 17%) of gaseous NH_3 . The subsequent Teflon and nylon filters collect particulate sulfate (PS), particulate nitrate (PN), and HNO_3 vapor. PS is determined from the analysis of sulfate from the Teflon filter. The total gaseous HNO_3 is determined from the analysis of nitrate from the nylon strip, and the PN is then determined algebraically, using the nitrate found on the Teflon and nylon filters. The total gaseous NH_3 is determined similarly, using the analysis of ammonium from the Nafion strip, and the particulate ammonium is found algebraically, using the ammonium found on the Teflon and oxalic acid coated filters.

Downstream of the filter pack, the flow splits with 14.3 Lpm to a mass flow controller and pump, while 1.8 Lpm passes through two TEA-coated glass fiber filters for collecting SO_2 and NO_2 . This low volume stream then passes to a mass flow controller and pump. A third flow stream at a nominal rate of 1.0 Lpm is drawn from the base of the stagnation

zone of the cyclone to prevent particle accumulation in the event of heavy particle loading.

The TFR has the following limitations:

- The system does not permit the determination of HNO_2 .
- Nitrates collected in the cyclone and not removed during sampling may volatilize to give artificially high values of gaseous nitric acid.
- HNO_2 may be collected to some extent on the nylon filter, while the remainder is likely to be collected on the TEA-coated filters, acting as a positive bias.
- The collection of PAN and TEA may provide bias for NO_2 determinations.
- Sulfur dioxide is likely to be collected on currently available nylon filter materials. If this retention of SO_2 is significant, SO_2 determinations using results from the TEA-coated filters will require adjustment.
- The potential for deposition and partial retention of acidic and basic gases and particles on the Teflon filter makes interpretation of acidity determinations difficult and may prevent unambiguous inference of atmospheric particulate constituents.

The TFR advantages include: it can be used for sampling dry deposition constituents for periods of 1 to 7 days; it is modular, easy to install and ship; sample analysis is by existing, accepted methods (i.e., IC and colorimetry); and it is reasonably simple to operate.

ADS

The ADS collects gas samples with annular denuders and particulate matter on filter collection media. As shown in Figure 2, the ADS is comprised of modules arranged in series to collect various constituents of interest. The first module is a Teflon cyclone similar to that employed by the TFR. The second and third modules are two annular denuders for collection of HNO_3 , HNO_2 , and SO_2 , followed by a third annular denuder for collection of NH_3 . The fifth element is a filter pack containing a Teflon and a nylon filter.

The nominal sampling rate is 15 Lpm. Ambient air is passed under laminar flow conditions through the annular space

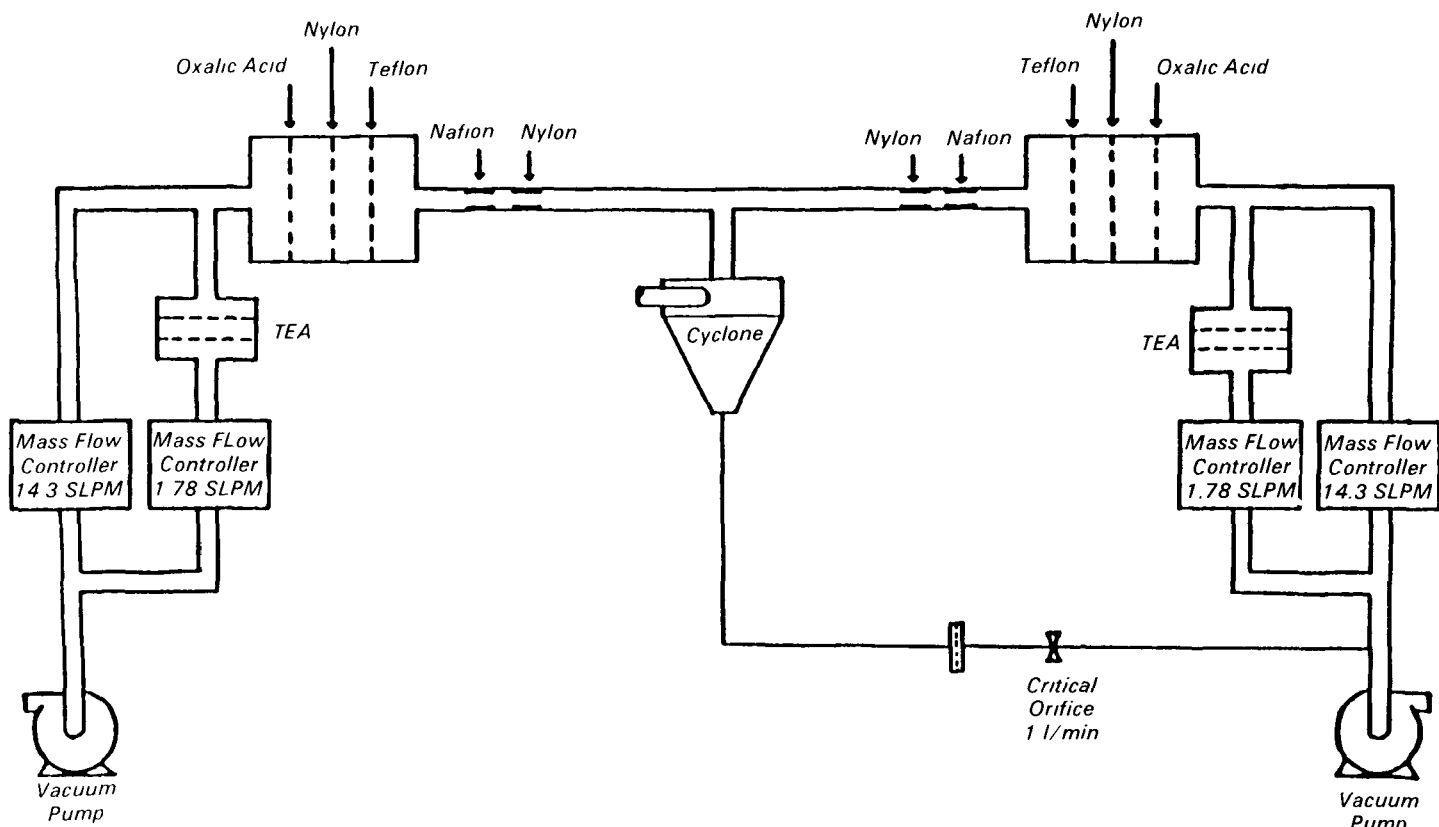


Figure 1. Transition flow reactor sampling system.

between two concentric tubes. The outside of the inner tube and the inside of the outer tube are coated with a specific gas-absorbing solution. For the first two denuders, this coating contains Na_2CO_3 , for the third denuder, the NH_3 -absorbing coating contains citric acid. The annular design permits a reduction in denuder tube length and an increase in flow rates over the conventional open-tube denuder design. The third denuder is followed by a Teflon filter to collect PS, nonvolatilized nitrates, and particulate ammonium, while the nylon filter collects HNO_3 that is passed due to volatilization from the Teflon filter. A third filter may be added downstream of the nylon filter to collect any volatilized ammonium.

HNO_3 and SO_2 are determined from the differences between IC analyses of NO_3^- and SO_4^{2-} in the aqueous extracts of the first and second denuders. Analysis of the second denuder extract confirms the near quantitative collection of these species and permits a quality control check.

HNO_2 is deposited nearly quantitatively on the first denuder. Deposition of PAN and NO_2 ranged from 1 to 3 percent. Since deposition of these two species is very small on the first denuder, the deposition should be approximately the same on the second denuder. The recovery of HNO_2 , PAN, and NO_2 as NO_2^- on the first two denuders, and the low deposition of the latter two species, permits the determination of HNO_2 by using the difference in NO_2^- between the first two denuders. Extract analysis can be performed by either IC or colorimetry.

NH_3 and NH_4^+ are determined from colorimetric NH_4^+ analysis of the aqueous extract of the citric acid-coated third denuder and Teflon filter, respectively. PS and nonvolatilized nitrates are determined by IC analysis of SO_4^{2-} NO_3^- in the aqueous extract of the Teflon filter. Nitrate analysis of the 0.003 N NaOH extract of the nylon filter permits determination of volatilized nitrates. Fine PN is determined by summing the nonvolatilized and volatilized nitrates.

The ADS has several limitations:

- The system does not currently permit the determination of NO_2 .
- Care must be taken at high humidities to prevent dissolution and loss of capacity of Na_2CO_3 denuder coatings, and data must be inspected at low humidities to ensure good collection efficiencies.
- The collected HNO_2 may undergo *in situ* oxidation to nitrate on the first denuder, giving rise to artificially high values for HNO_3 and low values for HNO_2 .
- Nitrates collected in the cyclone and not removed during sampling may volatilize to give artificially high values of gaseous nitric acid.
- The loss of HNO_3 by volatilization from the Teflon filter makes interpretation of the acidity determinations difficult.

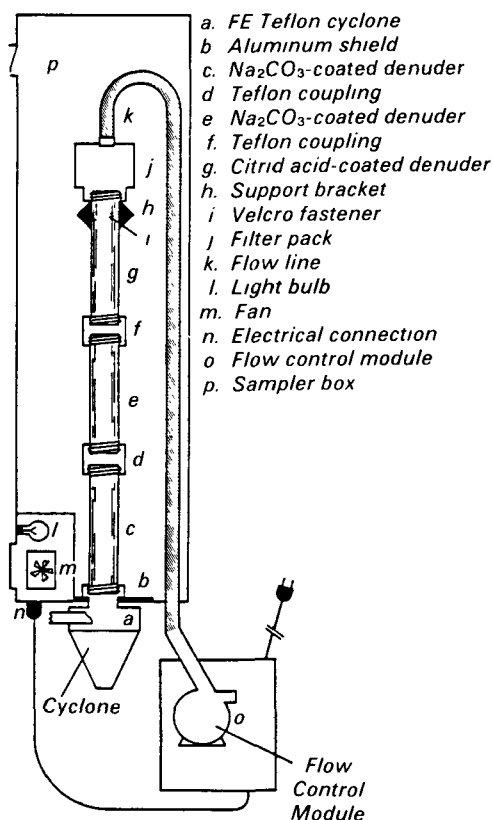


Figure 2. Annular denuder sampling system.

f. In the absence of an NH₃ collection medium such as a coated filter downstream of the nylon filter, a portion of the volatilized particulate NH₄⁺ may be lost.

The ADS has advantages. It can be used for sampling dry deposition constituents for periods of hours to 7 days; it is modular, easy to install and ship; sample analysis is by existing, accepted methods (i.e., IC and colorimetry); and it is reasonably simple to operate.

Conclusions and Recommendations

The chemical-specific sampling and analysis methodologies for many chemical constituents of importance in ecosystem acidification have been reviewed and evaluated. Their status is summarized in Table 5 of the full report.

Recommended methods are given for four species: HNO₃, NO₃⁻, SO₄²⁻, and O₃. The bulk of the methods are designated as favored, i.e., the method, at its current state of development, holds promise for

providing unambiguous concentration data for the species of interest and for achieving routine implementation in an air monitoring network. Two (i.e., RCOOH and HCHO) are in the research mode, and no assessment can be made at this time. For some species, well-established methodologies may exist (e.g., FTIR and TDLAS), but their resource and/or manpower requirements prevent them from consideration in network application.

The selection of a multiple constituent sampling system is not clear. The FP can provide estimates of concentrations of total inorganic nitrate, total particulate sulfate, and SO₂ and biased estimates of particulate NH₄⁺ and acidity at a relatively low potential cost. The TFR and ADS offer estimates of a larger number of constituents but at a larger potential cost. The ADS can provide concentration estimates of HNO₂, but not NO₂; whereas the TFR can provide NO₂, but not HNO₂. Although successful field trials have been reported for the TFR, successful deployment for measuring HNO₃ and fine particulate NO₃⁻ was not realized by RTI in the field study described in the report. As a result, the TFR cannot be endorsed for HNO₃ or fine particulate NO₃⁻ measurements at this time. From an operational perspective, the ADS is marginally preferable to the TFR. Thus, while the available evidence does not provide overwhelming support for the selection of either the TFR or the ADS for deployment in an air monitoring network, on balance the ADS does appear to have a slight advantage over the TFR. Additional development and field tests are recommended to provide the comparisons necessary to assess the merits of two sampling systems more clearly. It is also recommended that data quality objectives (DQO's) be clearly established for the species of interest. This will permit selection of a sampling system that is optimized to meet user needs.

The full report has focused on the analysis and discussion of results of a methods comparison study conducted in the fall of 1986 by RTI and others at the EPA dry deposition site at Research Triangle Park, North Carolina. This study consists of 13 daily samples; weekly data were also collected with the ADS. The term TFR normally refers to the TFR system operated daily by RTI throughout the study; TFR(EPA) refers to the TFR operated by EPA/ASRL on 5 of the 13 study days.

Selected conclusions and findings drawn from this study are given below.

- Detection limits for the ADS and TFR are generally less than 0.15 ppb, except for NH₃ with the ADS at 0.4 ppb and for SO₂, NO₂, and NH₃ with the TFR at 0.4, 0.5, and 1.6 ppb.
- Both ADS and TFR showed good precision for the measured species except fine particulate NO₃⁻. In general, paired daily samples had median CVs of less than 20 percent.
- Quality control checks indicate ambient TFR HNO₃⁻ and fine particulate NO₃⁻ results to be suspect. In 24 of 26 cases, TFR Fine NO₃⁻ results were negative. This invalidated TFR Fine NO₃⁻ results and prevented their use in subsequent analyses. Results of the current study do not permit the endorsement of the TFR for the determination of HNO₃ or Fine NO₃⁻.
- Statistical comparisons of ADS and TFR results show no difference for Total NO₃⁻, particulate NO₃⁻ on Teflon filters, Total SO₄²⁻, and NH₃; the ADS estimate to exceed that of the TFR for Fine SO₄²⁻, SO₂, and H⁺; and the TFR estimate to exceed that of the ADS for HNO₃, Total NH₃+NH₄⁺, and Fine NH₄⁺.
- Total NO₃⁻ as measured by the ADS, TFR, and FP are in good agreement. Total SO₄²⁻ as measured by the ADS, TFR, and FP are also in good agreement.
- Nitric acid spiking experiments indicate that appreciable amounts of HNO₃ may be retained by Teflon cyclones, and that HNO₃ transmission approaches 100 percent for some types of Teflon after a brief conditioning period.
- A substantial difference in particle collection efficiency by the ADS and TFR cyclones resulted from sampling at different flow rates. This is most apparent for particulate nitrates where the cyclone catch accounted for 59 percent of the total in the ADS and 85 percent in the TFR.
- Denuding the sampled atmosphere of all the gaseous HNO₃ and NH₃ in the ADS caused substantial volatilization of collected fine particulate nitrates: 52 percent for daily samples and 93 percent for weekly samples. This and the difference in cyclone efficiencies prevent meaningful direct comparison

of nitrates on the Teflon filter for the ADS and TFR.

- Nitric acid, as measured by the ADS, FP, and TFR(FP), a nonstandard interpretation of TFR data, are in good agreement with those of the TDLAS (i.e., the differences between the TDLAS results and those of each of the three listed measures are not significant at the 95 percent confidence level). Two sets of TFR results were collected by independent operators (RTI and EPA). Differences between TDLAS results and one of the TFR results are significant. The daily TFR results are consistently much higher than those of the TDLAS. The five daily TFR(EPA) measures of HNO_3 are also consistently higher but are in better agreement with TDLAS results.
- Nitrogen dioxide as measured by the TFR and TDLAS are highly correlated, although differences between the two sets of results are statistically significant.
- Both nitrate and ammonium are volatilized from the ADS Teflon filter. A nylon filter is employed downstream to collect volatilized nitrate. The ADS, as operated with no provision to collect volatilized NH_4^+ , undersamples particulate NH_4^+ . It is recommended that a citric acid-coated filter be incorporated in the ADS to collect volatilized ammonium.
- Total particulate NH_4^+ as measured by TFR and FP are in good agreement and exceed measurements with the ADS.
- H^+ concentrations measured with the ADS exceed those with the TFR because undenuded NH_3 in the air sample reaching the TFR Teflon filter neutralizes a portion of the H^+ collected on the Teflon filter with that sampler.
- SO_2 concentrations measured with the ADS exceed those measured with the TFR by approximately 30%. Laboratory tests suggest that the TFR results require a correction for reduced SO_4^{2-} recovery efficiency (i.e., 80 percent) under humid conditions.
- Field studies have demonstrated that the ADS can be successfully deployed for sampling periods of 4, 6, 10, 12,

and 22 hours, and up to 7 days. The results are subject to a potential high bias for HNO_3 (from HONO oxidation) and potential low biases from inlet losses, oxidation of HONO and NH_4^+ volatilization (if a citric acid-coated filter is not added). Field studies have demonstrated that the TFR can be successfully deployed for sampling periods of 22 hours and 7 days. The results are subject to a low potential bias for SO_2 (if SO_2 collected on the nylon filter and a recovery efficiency correction are ignored). TFR results may be unreliable for HNO_3 and Fine NO_3^- . These findings, although favoring the ADS, do not permit the complete endorsement of either the ADS or the TFR for field deployment without further development and field testing.

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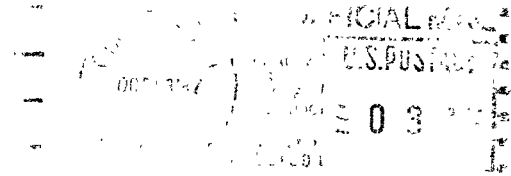
The complete report, entitled "Sampling and Analytical Methods Development for Dry Deposition Monitoring," (Order No. PB 87-233 318; Cost: \$24.95, subject to change) will be available only from:

*National Technical Information Service
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