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ANALYTICAL TECHNIQUES FOR AMBIENT SULFATE AEROSOLS

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by

S. A. Johnson, D. G. Graczyk, R. Kumar,
and P. T. Cunningham

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Chemical Engineering Division

June 1981

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ANALYTICAL TECHNIQUES FOR AMBIENT SULFATE AEROSOLS

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S. A. Johnson, D. G. Graczyk, R. Kumar,
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ABSTRACT

This report describes work done to further develop the infrared spectroscopic analytical method for the analysis of atmospheric aerosol particles, as well as some exploratory work on a new procedure for determining proton acidity in aerosol samples.

Earlier work had led to the successful use of infrared (IR) spectrophotometry for the analysis of nitrate, ammonium, and neutral and acidic sulfates in aerosol samples collected by an impactor on a Mylar-film substrate. In this work, a filter-extraction method was developed to prepare filter-collected aerosol samples for IR analysis. A study was made comparing the IR analytical results on filter-collected samples with impactor-collected samples. Also, the infrared analytical technique was compared in field studies with light-scattering techniques for aerosol analysis.

A highly sensitive instrument for aerosol analysis using attenuated total internal reflection (ATR) infrared spectroscopy was designed, built, and tested. This instrument provides a measurement sensitivity much greater (by a factor of 6 for SO_4^{2-}) than that obtainable using the KBr-pellet method. This instrument collects size- and time-resolved samples and is potentially capable of providing automated, near real-time aerosol analysis.

Finally, this report describes some exploratory work on a novel approach to the determination of proton acidity in filter- or impactor-collected aerosol samples. In this technique, the acidic sample is reacted with an excess of a tagged, vapor-phase base. The unreacted base is flushed off and the amount of the tag retained by the sample is a direct measure of the proton acidity of the sample. In this work, the base was tagged with Ge, which can be conveniently determined by the X-ray fluorescence technique.

I. INTRODUCTION

We have developed a method for the chemical characterization and analysis of airborne particulate material as a function of particle size and time. Our technique, which is based on the infrared (IR) spectroscopic analysis of particulate samples, has been used to show that there are, indeed, significant variations in the chemistry of airborne particulate with size and that, within a specific size range, the chemistry does change with time.[1,2] Of particular significance has been the identification of ammonium sulfate as the predominant constituent of submicrometer particles and the observation that the degree of acidity of this sulfate is highly variable with time. This work has been directed toward further development of the infrared spectroscopic method, as well as other techniques for the detailed characterization and analysis of atmospheric neutral and acidic sulfates.

The infrared characterization of airborne particulate material has been developed to the point where quantitative determination of neutral sulfate is possible for samples containing from one to several hundred micrograms of this ion. Systematic variations of absorption-band position and intensity in the spectra of some sulfate samples are associated with the degree of acidity of the sample. This infrared method permits analysis of sulfate in samples that have been collected on Mylar film using an inertial impactor.

This report describes the work conducted in three distinct, but interrelated, program areas. The first was a laboratory effort to develop a procedure whereby samples collected on filters may also be analyzed using the previously developed infrared spectrophotometric method. The second element was participation in two field studies for the comparison of various sampling and analytical methods for the determination of ambient sulfates. Finally, this report describes development work on a new instrument and a new procedure for the measurement of atmospheric sulfates with increased sensitivity.

II. FILTER-EXTRACTION METHOD FOR SULFATE ANALYSIS

Airborne particulate matter is commonly collected by a variety of filtration and impaction methods, each having its advantages and disadvantages. At ANL, samples for infrared analysis are collected with a Lundgren impactor.[1,2] The design of the impactor facilitates sample handling and supplies the necessary time- and size-resolution. The particles are classified into four size ranges during collection, while a controlled rate of movement of the collecting substrate past the impaction nozzles provides the time-resolution needed. The use of the impaction principle, however, limits the sample to those particles larger than ∿0.3-μm-dia. To extend the capability of the infrared spectroscopic method to particles smaller than 0.3-μm-dia, a method was needed to recover the sulfate from the impactor after-filter.

Previous procedures for analyzing sulfate *via* filter-extraction recovery resulted in neutralization of the acid sulfate. A new procedure, using concepts like those of Citron and Underwood,[3] has been investigated wherein sulfate can be quantitatively recovered from filter-collected samples while apparently maintaining the acidity of the sample. The new procedure and the sulfate standardization are described below.

A. Filter Handling and Extraction

The procedure starts with the extraction of the water-soluble material from the filter by ultrasonic agitation of the filter in 10-20 mL of distilled, CO_2-free water. After several minutes of ultrasonic agitation in a freeze-drying flask, the filter is removed and saved for a second extraction if desired. In preliminary tests the second extract of the filters was found to be free of sulfate and one extraction was determined to be sufficient. A weighed amount of potassium bromide is added to the extract in the flask, and the solution is immediately frozen by partially immersing the flask in liquid nitrogen. The water is removed by freeze-drying, which takes 4-8 h. The dry sample is removed from the flask and pressed into a pellet for subsequent infrared spectroscopic examination. Samples of ammonium acid sulfate aerosol, produced using a flow reactor to simulate ambient conditions, were collected on Fluoropore filters (Teflon, Type FALP-3700, Millipore Corporation) and extracted using this freeze-drying procedure with good results. In preliminary tests, the acidity of the sulfate was maintained throughout the procedure without any apparent neutralization or reaction with the KBr. Some material is lost during transfer from the freeze-drying flask; therefore, the KBr is weighed again to account for these losses. Care must be taken in handling and storage of the filters to prevent neutralization prior to the extraction. The possibility exists that neutralization could take place during the collection process. This has not been a problem with impacted samples but may be with filter samples since the collected particles have greater exposure to the gas stream. An ammonia denuder in the incoming gas stream may be one method to alleviate this, should it prove to be a problem.

However, subsequent work using reagent-grade ammonium bisulfate to prepare the standards showed that the freeze-drying process for the filter extract may not always maintain the acidity of the original sample. Depending upon the freeze-drying conditions (*e.g.*, temperature of the sample and time for drying), the loss of NH_3 and H^+, along with water from the freeze-drying matrix, may alter the acidity of the dried sample. This problem has not been completely resolved for samples of acidic ammonium sulfates, but this aqueous extraction/freeze-drying procedure does give acceptable results for neutral ammonium sulfate samples.

B. Sulfate Standardization

Quantification for sulfate was accomplished by preparing standard solutions containing 43.10 mg/L and 65.44 mg/L of "ultra-pure" 99.99% ammonium sulfate (Research Organic/Inorganic Chemical Corp., Sun Valley, CA). Aliquots were pipetted into the freeze-drying flasks, and the procedure described above for filter samples was followed for the standards. The results for these standards are presented in Fig. 1, which is a Beer's law plot of the absorbance for the 1400-cm^{-1} NH_4^+ band and the 1110-cm^{-1} and 620-cm^{-1} SO_4^{2-} bands. The lines represent a least-squares fit of the data. As can be seen, straight-line relationships are achieved over the range of sample weights. The correlation coefficients and the values of the absolute absorbance for the three bands are:

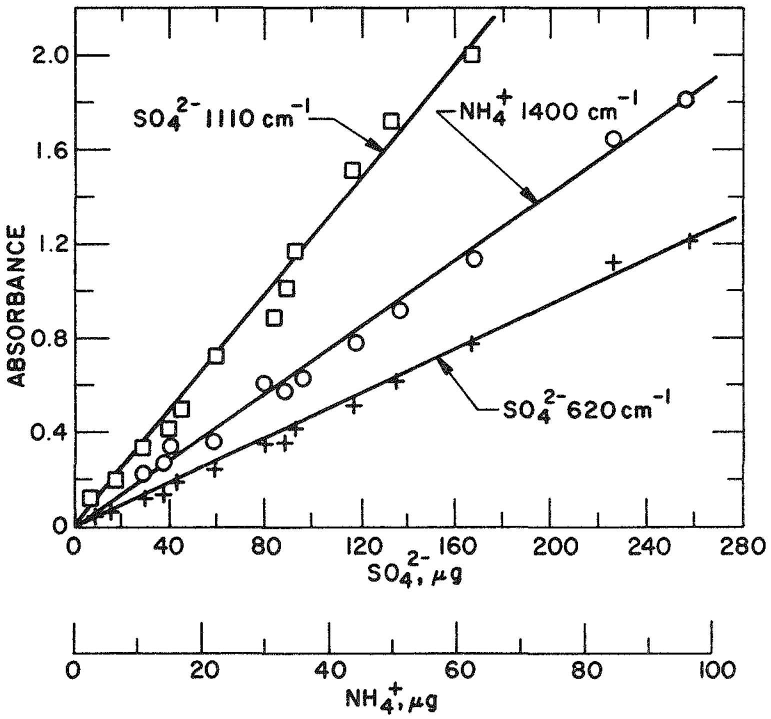

Fig. 1. Beer's Law Plot for Ammonium Sulfate Standards Prepared by Freeze-Drying

SO_4^{2-}, 620-cm^{-1} band

Absolute Absorbance = 4.67 × 10^{-3} × µg SO_4^{2-}

Correlation Coefficient = 0.999

SO_4^{2-}, 1110-cm^{-1} band

Absolute Absorbance = 12.17 × 10^{-3} × µg SO_4^{2-}

Correlation Coefficient = 0.997

NH_4^+, 1400-cm^{-1} band

Absolute Absorbance = 1.86 × 10^{-2} × µg NH_4^+

Correlation Coefficient = 0.999

The 620-cm^{-1} band is recommended for analytical use since it is relatively free from interference in ambient samples and since it does not have sloping-baseline problems commonly found in spectra from cloudy KBr pellets.

III. RESULTS OF FIELD STUDIES

In order to compare the results from our procedure of impactor collection and infrared spectroscopic analysis with the results obtained by other sampling and analytical techniques, we participated in two separate field studies where samples were collected simultaneously by several different techniques for *in situ* or subsequent analysis by the respective investigators.

A. Comparison of Sampling Techniques

During August and September of 1975, a field comparison study was conducted in the St. Louis region in coordination with the Environmental Protection Agency (EPA). The sampling phase of the study entailed the simultaneous collection of airborne particulate matter by ANL, the EPA, and other participants, at both a rural and an urban site. Only the samples obtained by ANL and the EPA are discussed here. The ANL samples were collected using Lundgren impactors with a time resolution of 2 h, while the EPA samples* were collected on 37-mm-dia Fluoropore (Teflon) filters using a dichotomous sampler with a time resolution of 24 h. The results on the samples from Stage IV of the Lundgren impactor (size range 0.3 to 1.0-μm aerodynamic diameter) and the coarse (>3.5-μm-dia) and the fine (<3.5-μm-dia) size fractions from the dichotomous sampler have been compared.

Table 1 presents the sulfate-analysis results for the EPA filters prepared by the freeze-drying procedure and then analyzed by infrared spectroscopy as described in II-A and II-B above. The sample weights were determined gravimetrically by the EPA. The values for loading of the air are calculated from these weights and the sampling air flow rates. The sulfate values are presented in three ways: total weight of sulfate per filter (μg), percent of the mass collected that is sulfate (%), and loading of the sulfate in the air ($\mu g/m^3$). In all but three of the coarse-particle samples, either the sulfate values were close to our limit of detection by IR, or the infrared spectra had interfering bands; therefore, no values for sulfate are listed for most of the coarse-particle samples. Table 2 gives the sampling and analytical data on the samples collected by ANL on Stage-IV of the Lundgren impactor in 2-h collection periods. (Stage IV collects particles from 0.3 μm to 1.0 μm aerodynamic diameter.)

Figures 2 and 3 are plots of the results for sulfate from the Stage-IV impactor samples and the dichotomous fine filter samples for the period Aug. 28 to Sept. 4, 1975. In Fig. 2, the amount of sulfate is plotted as weight percent of the total sample. The points indicate the values for the 2-h impactor samples and the bars indicate the values for the 24-h EPA filter samples. Figure 3 presents the same data plotted as $\mu g\ SO_4^{2-}/m^3$ air. As can be seen in the % SO_4^{2-} plot, Fig. 2, the values for the filter samples are somewhat higher but generally in the same range as those for the impactor samples; when sulfate is plotted as $\mu g/m^3$, Fig. 3, the filter values are substantially higher than the impactor values. These trends are consistent with the current understanding of the size distribution and chemical

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*The thirty EPA samples were supplied to us by T. Dzubay, EPA.

Table 1. Sulfate Found on EPA Filter Samples

Collection Date	Particle Size	EPA Filter Number	Sample Mass, μg	Sample Loading in Air, $\mu g/m^3$	Sulfate Analysis		
					Wt/Filter, μg	Percent of Mass, %	Sulfate Loading in Air, $\mu g/m^3$
				Urban			
Sun., Aug. 24	Fine	207	300	15.5	20.6	6.9	1.1
	Coarse	5207	300	15.5	–	–	–
Mon., Aug. 25	Fine	208	270	13.7	31.7	11.7	1.6
	Coarse	5208	400	20.2	–	–	–
Tues., Aug. 26	Fine	209	580	33.3	75.8	13.1	4.4
	Coarse	–	–	–	–	–	–
Thur., Aug. 28	Fine	211	770	39.5	210.5	27.3	10.8
	Coarse	5211	450	23.1	7.5	1.7	–
Fri., Aug. 29	Fine	212[a]	170	26.4	33.2	19.5	5.2
	Coarse	–	–	–	–	–	–
Sat., Aug. 30	Fine	213	430	21.7	166.0	38.6	8.4
	Coarse	5213	200	10.1	–	–	–
Sun., Aug. 31	Fine	214	540	27.9	209.2	38.7	10.8
	Coarse	5214	310	16.0	–	–	–
Wed., Sept. 3	Fine	217	510	26.5	82.0	16.1	4.3
	Coarse	5217	740	38.5	–	–	–

(contd)

Table 1. (contd)

Collection Date	Particle Size	EPA Filter Number	Sample Mass, µg	Sample Loading in Air, µg/m^3	Sulfate Analysis		
					Wt/Filter, µg	Percent of Mass, %	Sulfate Loading in Air, µg/m^3
				Rural			
Sun., Aug. 24	Fine	807	290	15.3	47.5	16.4	2.5
	Coarse	5807	280	14.8	–	–	–
Mon., Aug. 25	Fine	808	180	9.2	19.5	10.8	1.0
	Coarse	5808	200	10.2	6.6	3.3	–
Tues., Aug. 26	Fine	809	350	17.6	92.9	26.5	4.7
	Coarse	–	–	–	–	–	–
Sat., Aug. 30	Fine	813	400	20.4	138.1	34.5	7.0
	Coarse	5813	250	12.8	5.2	2.1	–
Sun., Aug. 31	Fine	814	510	27.4	159.5	31.3	8.6
	Coarse	5814	280	15.1	–	–	–
Wed., Sept. 3	Fine	817	640	31.5	142.8	22.3	7.0
	Coarse	5817	550	27.1	–	–	–
Sat., Sept. 6	Fine	820	430	22.1	122.7	28.5	6.3
	Coarse	5820	–	–	–	–	–

[a] 8-h sample.

Table 2. Results of Analysis of Stage-IV Lundgren Impactor Samples Collected by ANL during the Comparison Study

Sample Identification	Collection Date	Sample Start Time	Samp. Time, min	Air Flow Rate, m^3/min	Samp. Wt., µg	SO_4^{2-}, µg	NH_4^+, µg	NO_3^-, µg	Acidity[a]
Urban									
I-72-IV- 1	8/28/75	1400	120	0.101	140	29.63	10.72	0.0	0.0
I-72-IV- 2	8/28/75	1600	120	0.101	86	28.41	9.11	0.0	0.0
I-72-IV- 3	8/28/75	1800	120	0.101	132	31.80	9.79	0.0	0.0
I-72-IV- 4	8/28/75	2000	120	0.101	206	144.70	40.04	2.03	0.0
I-72-IV- 5	8/28/75	2200	120	0.101	214	43.72	13.28	0.0	0.0
I-72-IV- 7	8/29/75	0200	120	0.101	108	30.16	11.16	0.0	0.0
I-72-IV- 8	8/29/75	0400	120	0.101	198	68.06	20.72	0.0	0.0
I-72-IV- 9	8/29/75	0600	120	0.101	394	151.20	37.04	0.0	0.0
I-72-IV-10	8/29/75	0800	120	0.101	228	76.22	28.18	0.0	0.0
I-73-IV- 1	8/29/75	1000	120	0.104	48	15.16	4.84	0.0	0.0
I-73-IV- 2	8/29/75	1200	120	0.104	84	21.18	6.89	0.0	0.0
I-73-IV- 3	8/29/75	1400	120	0.104	62	14.35	4.76	0.0	0.0
I-73-IV- 4	8/29/75	1600	120	0.104	56	11.37	3.65	0.0	0.0
I-73-IV- 5	8/29/75	1800	120	0.104	24	5.05	2.22	0.0	0.0
I-73-IV- 6	8/29/75	2000	120	0.104	34	10.84	3.88	0.0	0.0
I-73-IV- 7	8/29/75	2200	120	0.104	38	10.32	3.92	0.0	0.0
I-73-IV- 8	8/30/75	0000	120	0.104	48	8.37	2.51	0.0	0.0
I-73-IV- 9	8/30/75	0200	120	0.104	32	11.78	3.46	0.0	0.0
I-73-IV-10	8/30/75	0400	120	0.104	26	6.68	2.36	0.0	0.0
I-73-IV-11	8/30/75	0600	120	0.104	40	11.07	4.19	0.0	0.0
I-73-IV-12	8/30/75	0800	120	0.104	66	32.73	10.93	0.0	0.0
I-73-IV-13	8/30/75	1000	120	0.104	80	27.31	8.89	0.0	0.0
I-73-IV-14	8/30/75	1200	120	0.104	74	39.75	12.98	0.0	0.0
I-73-IV-15	8/30/75	1400	120	0.104	90	45.87	14.04	0.0	0.0
I-73-IV-16	8/30/75	1600	120	0.104	152	95.54	31.23	0.0	0.0
I-73-IV-17	8/30/75	1800	120	0.104	172	107.84	33.02	0.0	0.0
I-73-IV-18	8/30/75	2000	120	0.104	162	84.70	28.58	0.0	0.0
I-73-IV-19	8/30/75	2200	120	0.104	186	74.67	25.55	0.0	0.0
I-73-IV-20	8/31/75	0000	120	0.104	128	45.88	17.66	0.0	0.0
I-73-IV-21	8/31/75	0200	120	0.104	116	55.05	18.44	0.0	0.0
I-73-IV-22	8/31/75	0400	120	0.104	96	40.01	14.50	0.0	0.0
I-73-IV-23	8/31/75	0600	120	0.104	182	76.95	26.06	0.0	0.0
I-73-IV-24	8/31/75	0800	120	0.104	150	39.16	24.81	0.0	0.23
I-73-IV-25	8/31/75	1000	120	0.104	100	40.94	19.28	0.0	0.0
I-73-IV-26	8/31/75	1200	120	0.104	118	40.83	17.49	0.0	0.13
I-73-IV-27	8/31/75	1400	120	0.104	64	23.43	8.01	0.0	0.0
I-73-IV-28	8/31/75	1600	120	0.104	116	43.48	16.49	0.0	0.0
I-73-IV-29	8/31/75	1800	120	0.104	220	88.31	31.30	0.0	0.0
I-73-IV-30	8/31/75	2000	120	0.104	154	78.08	29.12	0.0	0.0
I-73-IV-31	8/31/75	2200	120	0.104	146	61.58	26.19	0.0	0.0
I-73-IV-32	9/ 1/75	0000	120	0.104	164	88.36	30.82	0.0	0.0
I-73-IV-33	9/ 1/75	0200	120	0.104	116	36.86	12.33	0.0	0.0
I-73-IV-34	9/ 1/75	0400	120	0.104	70	20.44	7.70	0.0	0.06
I-73-IV-35	9/ 1/75	0600	120	0.104	284	80.90	33.12	0.0	0.0
I-73-IV-36	9/ 1/75	0800	135	0.104	116	52.45	17.29	0.0	0.0
I-74-IV-25	9/ 3/75	1030	120	0.099	60	21.46	8.87	0.0	0.0
I-74-IV-26	9/ 3/75	1230	120	0.099	62	21.40	8.05	0.0	0.0

(contd)

Table 2. (contd)

Sample Identification	Collection Date	Sample Start Time	Samp. Time, min	Air Flow Rate, m^3/min	Samp. Wt., μg	SO_4^{2-}, μg	NH_4^+, μg	NO_3^-, μg	Acidity[a]
I-74-IV-27	9/ 3/75	1430	120	0.099	86	26.16	9.09	0.0	0.0
I-74-IV-28	9/ 3/75	1630	120	0.099	100	30.35	11.20	0.0	0.0
I-74-IV-29	9/ 3/75	1830	120	0.099	160	61.27	20.21	0.0	0.0
I-74-IV-30	9/ 3/75	2030	120	0.099	106	30.26	9.23	0.0	0.0
I-74-IV-31	9/ 3/75	2230	120	0.099	118	28.75	10.09	0.0	0.0
I-74-IV-32	9/ 4/75	0030	120	0.099	114	14.56	4.68	0.0	0.0
I-74-IV-33	9/ 4/75	0230	120	0.099	72	17.12	6.36	0.0	0.0
I-74-IV-34	9/ 4/75	0430	120	0.099	94	18.82	6.16	2.58	0.0
I-74-IV-35	9/ 4/75	0630	120	0.099	82	9.43	3.36	1.52	0.13
I-74-IV-36	9/ 4/75	0830	135	0.099	42	9.60	3.85	0.0	0.0
				Rural					
I-75-IV-12	8/30/75	1200	120	0.104	70	26.92	9.52	0.0	0.0
I-75-IV-13	8/30/75	1400	120	0.104	98	51.73	18.72	0.0	0.0
I-75-IV-14	8/30/75	1600	120	0.104	111	61.36	19.11	0.0	0.0
I-75-IV-15	8/30/75	1800	120	0.104	125	72.98	22.75	0.0	0.0
I-75-IV-16	8/30/75	2000	120	0.104	128	59.82	20.70	0.0	0.0
I-75-IV-17	8/30/75	2200	120	0.104	107	35.76	8.15	0.0	0.0
I-75-IV-18	8/31/75	0000	120	0.104	75	29.78	9.99	0.0	0.0
I-75-IV-19	8/31/75	0200	120	0.104	85	37.20	12.66	0.0	0.0
I-75-IV-20	8/31/75	0400	120	0.104	111	45.96	16.42	0.0	0.0
I-75-IV-21	8/31/75	0600	120	0.104	121	71.58	24.83	0.0	0.0
I-75-IV-22	8/31/75	0800	120	0.104	114	41.49	14.80	0.0	0.0
I-75-IV-23	8/31/75	1000	120	0.104	116	31.45	11.90	0.0	0.0
I-75-IV-24	8/31/75	1200	120	0.104	152	41.52	20.29	0.0	0.16
I-75-IV-25	8/31/75	1400	120	0.104	128	49.20	18.96	0.0	0.0
I-75-IV-26	8/31/75	1600	120	0.104	94	31.94	12.74	0.0	0.0
I-75-IV-27	8/31/75	1800	120	0.104	139	63.15	23.31	0.0	0.0
I-75-IV-28	8/31/75	2000	120	0.104	117	52.28	18.94	0.0	0.0
I-75-IV-29	8/31/75	2200	120	0.104	118	35.76	12.55	0.0	0.0
I-75-IV-30	9/ 1/75	0000	120	0.104	100	41.99	17.89	0.0	0.0
I-75-IV-31	9/ 1/75	0200	120	0.104	94	30.11	12.56	0.0	0.0
I-75-IV-32	9/ 1/75	0400	120	0.104	108	44.02	16.95	0.0	0.0
I-75-IV-33	9/ 1/75	0600	120	0.104	185	86.05	31.43	0.0	0.0
I-75-IV-34	9/ 1/75	0800	120	0.104	214	85.05	34.15	0.0	0.0
I-75-IV-35	9/ 1/75	1000	120	0.104	224	97.83	41.66	0.0	0.0
I-75-IV-36	9/ 1/75	1200	110	0.104	86	53.06	21.32	0.0	0.0
I-76-IV-24	9/ 3/75	1200	120	0.101	62	16.38	7.53	0.0	0.0
I-76-IV-25	9/ 3/75	1400	120	0.101	68	30.81	13.23	0.0	0.0
I-76-IV-26	9/ 3/75	1600	120	0.101	62	14.37	5.13	0.0	0.0
I-76-IV-27	9/ 3/75	1800	120	0.101	54	15.65	6.93	0.0	0.0
I-76-IV-28	9/ 3/75	2000	120	0.101	78	19.82	7.74	0.0	0.0
I-76-IV-29	9/ 3/75	2200	120	0.101	118	29.97	10.94	0.0	0.0
I-76-IV-30	9/ 4/75	0000	120	0.101	95	29.11	12.22	0.0	0.0
I-76-IV-31	9/ 4/75	0200	120	0.101	64	21.62	9.21	0.0	0.0
I-76-IV-32	9/ 4/75	0400	120	0.101	61	20.51	9.05	0.0	0.0
I-76-IV-33	9/ 4/75	0600	120	0.101	54	17.50	7.80	0.0	0.0
I-76-IV-34	9/ 4/75	0800	120	0.101	44	16.38	7.67	0.0	0.0
I-76-IV-35	9/ 4/75	1000	120	0.101	26	9.28	4.23	0.0	0.12
I-76-IV-36	9/ 4/75	1200	120	0.101	36	12.73	5.30	0.0	0.0

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[a] Acidity is expressed as the molar ratio of H^+ to SO_4^{2-}.

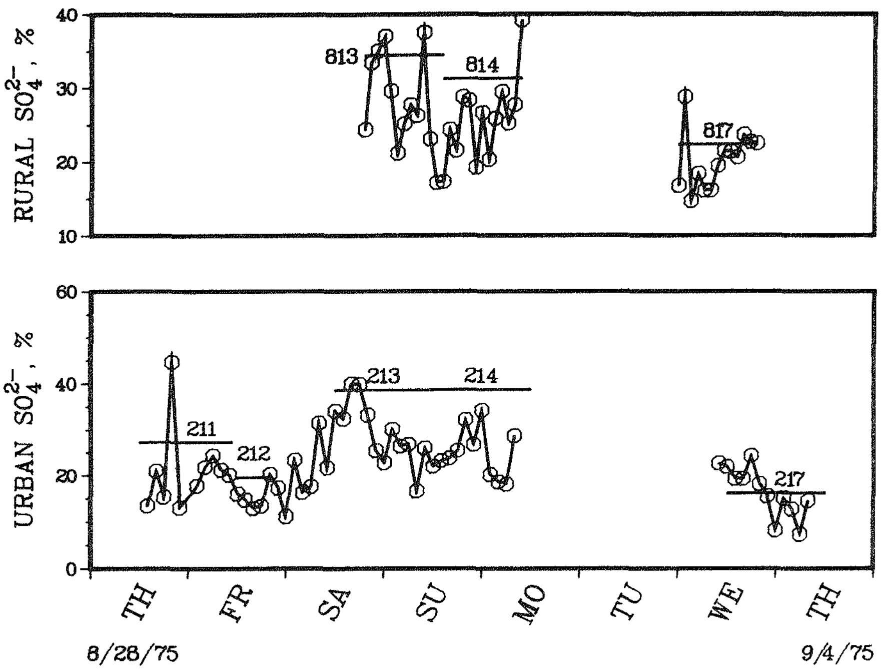


Fig. 2. Comparison of Results from Infrared Analysis of EPA Fine Filter Samples (numbered bars) and ANL Stage-IV Lundgren Impactor Samples (circles), Plotted as % SO_4^{2-} of the Total Sample Weight.

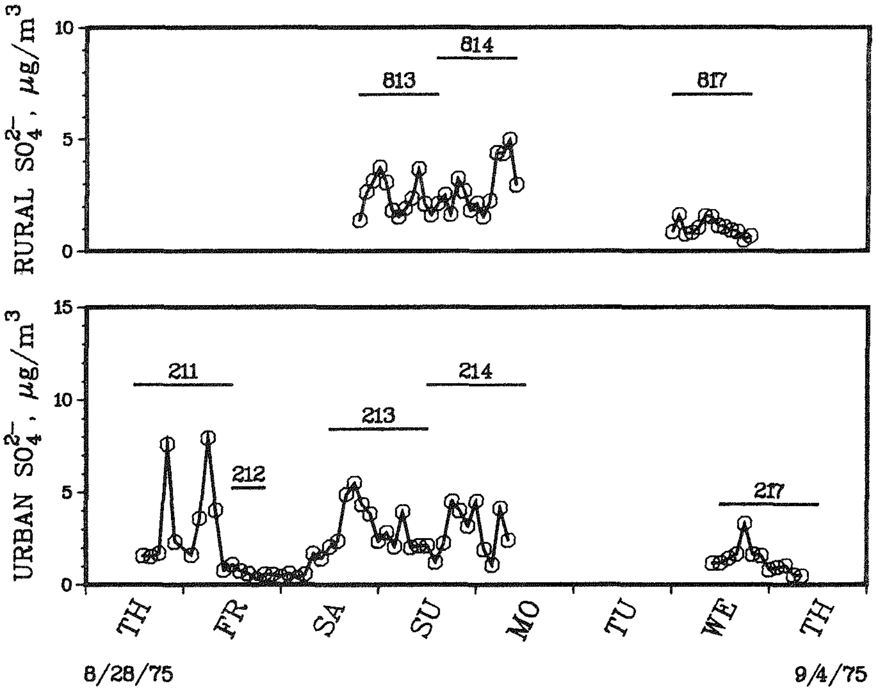


Fig. 3. Comparison of Results from Infrared Analysis of EPA Fine Filter Samples (numbered bars) and ANL Stage-IV Lundgren Impactor Samples (circles), Plotted as µg SO_4^{2-}/m^3 Air.

character of atmospheric particles; *i.e.*, they are attributed to the fact that the fine filter of the dichotomous sampler collects all particles below 3.5 μm in aerodynamic diameter while Stage IV of the impactor collects only a narrow size fraction between about 0.3 and 1.0 μm. Figure 2 then implies that the impactor-collected samples are approximately representative of the % SO_4^{2-} to be found in the fine particles. However, since the filter collects all the material in the entire range, when plotted as μg SO_4^{2-}/m^3, Fig. 3, the filter values are significantly higher than the impactor values, indicating that a substantial mass fraction, perhaps two-thirds judging from Fig. 3, of the SO_4^{2-} passes Stage IV of the impactor and would be found on the after-filter. It must also be pointed out that collection losses are probably greater in the impactor than in the dichotomous filter device, and this would also result in lower values for the impactor samples than for the filter samples when plotted as μg SO_4^{2-}/m^3.

In our analysis of samples from Stage II and Stage III (nominal particle sizes collected by these two stages are 3.0 to 10.0 μm and 1.0 to 3.0 μm, respectively) of the Lundgren impactor, we examine the upper portion of the range collected by the fine filters. The Stage-II and -III samples have very little, if any, sulfate, which indicates that the balance of sulfate found on the filters must be accounted for in the particles small enough to pass the fourth stage of the impactor and be collected on the after-filter. This demonstrates the need for the analysis of time-resolved after-filters. The development of the filter-extraction procedure now affords us this capability.

Also of note in the comparison study is the significant variation of sulfate with time as revealed by the impactor samples collected every two hours. These variations are greatly damped in the 24-h filter samples. This points out the need for time resolution as well as size resolution in atmospheric sampling if the chemistry of airborne particulate matter is to be fully understood.

The results shown in Figs. 2 and 3 also point out the need for a finer time resolution for atmospheric sampling than the 24 hours used with the dichotomous sampler. In addition to the sulfate-ion concentration fluctuating significantly during a 24-hour period, the sulfate acidity also undergoes changes that may not be detected in an aggregated 24-hour sample. For instance, Table 2 shows infrequent occurrence of acidity in impactor-collected samples, but no acidity was detected in any of the filter-collected samples. Examination of the infrared spectra of impactor samples showed significant acidity in three contiguous samples, I-73-IV-24, I-73-IV-25, and I-73-IV-26, covering a 6-hour period from 0800 to 1400 on Aug. 31, while neither of the EPA samples 213 or 214 covering the same time period showed any acidity. It should be noted that the computer analysis of the infrared spectral data did not identify sample I-73-IV-25 to be acidic (hence the acidity value of 0 in Table 2) due to an as yet unexplained shift in the absorption-band frequencies. However, visual examination of the IR absorption spectrum confirms that the sample was significantly acidic. The absence of acidity in the filter-collected samples is most likely due to their having been neutralized by basic materials collected on the filters during the balance of the 24-hour sampling periods. Thus, a fine time resolution of atmospheric aerosol sampling reveals variations in the aerosol chemistry and mass concentrations that are masked when only aggregated samples are collected over 24-hour periods.

B. Measurement of Sulfate Acidity at Tyson, MO

The infrared method developed at ANL was used in a two-week field study of the occurrence of acidic sulfates at Tyson, MO. Two other research teams also participated in this study, using light-scattering techniques developed at the University of Washington,[4] Seattle and at Washington University,[5] St. Louis.

Time- and size-resolved samples were collected continuously using the Lundgren impactor for the two-week period at Tyson from September 12-26, 1975, with concurrent aerosol analysis by the light-scattering techniques. The results of the samples collected on Stage IV of the impactor are tabulated in Table 3. (As in previous field experiments, samples collected on Stages II and III had very little sulfate and little or no acidity). The data in Table 3 indicate strong acidic sulfate episodes on September 16 and 17, which were also observed by both of the light-scattering techniques. The sulfate values shown in Table 3 are for the neutral sulfate fraction only and are not directly comparable to total sulfate in the case of samples with appreciable acidity.

Table 3. Analysis of Stage-IV Lundgren Impactor Samples Collected by ANL at Tyson, MO

Sample Identification	Collection Date	Sample Start Time	Samp. Time, min	Air Flow Rate, m^3/min	Samp. Wt., μg	SO_4^{2-}, μg	NH_4^+, μg	NO_3^-, μg	Acidity[a]
I-77-IV- 1+2	9/12/75	1000	240	0.103	2	1.21	0.96	0.0	0.0
I-77-IV- 3+4	9/12/75	1400	240	0.103	18	0.0	0.73	0.0	0.0
I-77-IV- 5+6	9/12/75	1800	240	0.103	90	0.86	0.32	0.0	0.0
I-77-IV- 5+6	9/12/75	1800	240	0.103	90	0.91	0.20	0.0	0.0
I-77-IV- 7+8	9/12/75	2200	240	0.103	34	0.0	0.0	0.0	0.0
I-77-IV- 9+10	9/13/75	0200	240	0.103	22	0.0	0.86	0.0	0.0
I-77-IV-11+12	9/13/75	0600	240	0.103	18	1.19	1.08	0.0	0.0
I-77-IV-13+14	9/13/75	1000	240	0.103	12	0.0	0.0	0.0	0.0
I-77-IV-15+16	9/13/75	1400	240	0.103	8	0.0	0.0	0.0	0.0
I-77-IV-17+18	9/13/75	1800	240	0.103	8	0.0	0.34	0.0	0.0
I-77-IV-19+20	9/13/75	2200	240	0.103	48	2.94	2.26	0.0	0.0
I-77-IV-21+22	9/14/75	0200	240	0.103	46	0.0	0.0	0.0	0.0
I-77-IV-23+24	9/14/75	0600	240	0.103	48	5.26	3.19	0.0	0.0
I-77-IV-25+26	9/14/75	1000	240	0.103	34	4.57	2.30	0.0	0.0
I-77-IV-27+28	9/14/75	1400	240	0.103	14	2.77	1.51	0.0	0.0
I-77-IV-29+30	9/14/75	1800	240	0.103	34	8.53	3.59	0.0	0.0
I-77-IV-31+32	9/14/75	2200	240	0.103	38	4.69	2.58	0.0	0.0
I-77-IV-33+34	9/15/75	0200	240	0.103	54	11.64	5.00	0.0	0.0
I-77-IV-35+36	9/15/75	0600	236	0.103	78	19.20	8.12	0.0	0.0

(contd)

Table 3. (contd)

Sample Identification	Collection Date	Sample Start Time	Samp. Time, min	Air Flow Rate, m^3/min	Samp. Wt., μg	SO_4^2 , μg	NH_4^+, μg	NO_3^-, μg	Acidity[a]
I-78-IV- 1	9/15/75	1003	120	0.103	44	3.58	1.80	0.0	0.0
I-78-IV- 2	9/15/75	1203	120	0.103	32	4.15	2.14	0.0	0.0
I-78-IV- 3	9/15/75	1403	120	0.103	42	7.68	3.96	0.0	0.0
I-78-IV- 4	9/15/75	1603	120	0.103	54	7.59	4.12	0.0	0.0
I-78-IV- 5	9/15/75	1803	120	0.103	72	10.43	5.29	0.0	0.0
I-78-IV- 6	9/15/75	2003	120	0.103	80	8.95	4.31	0.0	0.0
I-78-IV- 7	9/15/75	2203	120	0.103	80	12.33	6.38	0.0	0.0
I-78-IV- 8	9/16/75	0003	120	0.103	88	14.43	8.03	0.0	0.0
I-78-IV- 9	9/16/75	0203	120	0.103	172	6.92	5.65	0.0	0.20
I-78-IV- 10	9/16/75	0403	120	0.103	136	0.0	4.76	0.0	0.50
I-78-IV- 11	9/16/75	0603	120	0.103	104	8.43	11.86	0.0	0.50
I-78-IV- 12	9/16/75	0803	120	0.103	100	6.47	8.29	0.0	0.50
I-78-IV- 13	9/16/75	1003	120	0.103	226	0.0	20.97	0.0	1.00
I-78-IV- 14	9/16/75	1203	120	0.103	246	0.0	15.58	0.0	1.00
I-78-IV- 15	9/16/75	1403	120	0.103	138	15.82	18.07	0.0	0.33
I-78-IV- 16	9/16/75	1603	120	0.103	76	8.32	6.12	0.0	0.20
I-78-IV- 17	9/16/75	1803	120	0.103	82	13.98	7.98	0.0	0.0
I-78-IV- 18	9/16/75	2003	120	0.103	86	14.19	8.66	0.0	0.0
I-78-IV- 19	9/16/75	2203	120	0.103	100	13.42	8.37	0.0	0.0
I-78-IV- 20	9/17/75	0003	120	0.103	108	12.12	6.74	0.0	0.0
I-78-IV- 21	9/17/75	0203	120	0.103	160	9.16	8.21	0.0	0.30
I-78-IV- 22	9/17/75	0403	120	0.103	156	12.19	11.49	0.0	0.30
I-78-IV- 23	9/17/75	0603	120	0.103	220	21.80	21.14	0.0	0.26
I-78-IV- 24	9/17/75	0803	120	0.103	158	22.91	17.43	0.0	0.18
I-78-IV- 25	9/17/75	1003	120	0.103	184	21.53	17.94	0.0	0.16
I-78-IV- 26	9/17/75	1203	120	0.103	124	24.37	15.11	0.0	0.10
I-78-IV- 27	9/17/75	1403	120	0.103	264	21.82	19.98	0.0	0.29
I-78-IV- 28	9/17/75	1603	120	0.103	84	16.26	8.43	0.0	0.0
I-78-IV- 29	9/17/75	1803	120	0.103	83	4.79	1.89	0.0	0.0
I-78-IV- 30	9/17/75	2003	120	0.103	120	4.81	1.98	0.0	0.0
I-78-IV- 31	9/17/75	2203	120	0.103	94	8.53	3.81	0.0	0.0
I-78-IV- 32	9/18/75	0003	120	0.103	62	10.22	4.42	0.0	0.0
I-78-IV- 33	9/18/75	0203	120	0.103	58	4.33	1.38	0.0	0.0
I-78-IV- 34	9/18/75	0403	120	0.103	60	9.64	4.34	0.0	0.0
I-78-IV- 35	9/18/75	0603	120	0.103	50	7.89	3.51	0.0	0.0
I-78-IV- 36	9/18/75	0803	108	0.103	80	8.97	3.81	0.0	0.0
I-79-IV- 1	9/18/75	1003	120	0.102	350	21.67	12.77	0.0	0.0
I-79-IV- 2+3	9/18/75	1203	240	0.102	138	16.68	11.92	0.0	0.0
I-79-IV- 4	9/18/75	1603	120	0.102	60	10.17	6.30	0.0	0.0
I-79-IV- 5	9/18/75	1803	120	0.102	116	19.79	11.99	0.0	0.0
I-79-IV- 6	9/18/75	2003	120	0.102	88	10.93	6.67	0.0	0.0
I-79-IV- 7	9/18/75	2203	120	0.102	222	2.15	1.92	0.0	0.28
I-79-IV- 8	9/19/75	0003	120	0.102	80	1.94	1.27	0.0	0.0
I-79-IV- 9+10	9/19/75	0203	240	0.102	32	0.0	0.75	0.0	0.0
I-79-IV- 9+10	9/19/75	0203	240	0.102	32	1.99	0.76	0.0	0.0
I-79-IV-11+12	9/19/75	0603	240	0.102	40	3.20	0.78	0.0	0.0
I-79-IV-13+14	9/19/75	1003	240	0.102	70	5.49	2.30	0.0	0.0
I-79-IV-15+16	9/19/75	1403	240	0.102	38	4.24	2.26	0.0	0.0
I-79-IV-17+18	9/19/75	1803	240	0.102	98	7.00	3.43	0.0	0.0
I-79-IV- 19	9/19/75	2203	120	0.102	44	1.47	1.08	0.0	0.0
I-79-IV-20+21	9/20/75	0003	240	0.102	36	4.38	2.63	0.0	0.0

(contd)

Table 3. (contd)

Sample Identification	Collection Date	Sample Start Time	Samp. Time, min	Air Flow Rate, m^3/min	Samp. Wt., µg	SO_4^{2-}, µg	NH_4^+, µg	NO_3^-, µg	Acidity[a]
I-79-IV-22+23	9/20/75	0403	240	0.102	58	3.50	1.87	0.0	0.0
I-79-IV-24+25	9/20/75	0803	240	0.102	30	2.99	0.75	0.0	0.0
I-79-IV-26+27	9/20/75	1203	240	0.102	42	11.52	5.87	0.0	0.0
I-79-IV-28+29	9/20/75	1603	240	0.102	22	3.95	2.54	0.0	0.0
I-79-IV-30+31	9/20/75	2003	240	0.102	34	4.65	2.50	0.0	0.0
I-79-IV-32+33	9/21/75	0003	240	0.102	36	0.0	20.96	0.0	1.00
I-79-IV-34+35	9/21/75	0403	240	0.102	36	0.0	9.60	0.0	1.00
I-79-IV- 36	9/21/75	0803	109	0.102	26	2.83	4.07	0.0	0.47
I-80-IV- 1+2	9/21/75	1004	240	0.106	36	22.42	10.43	0.0	0.0
I-80-IV- 3+4	9/21/75	1404	240	0.106	56	22.35	12.95	0.0	0.0
I-80-IV- 5+6	9/21/75	1804	240	0.106	138	17.24	11.54	0.0	0.0
I-80-IV- 7	9/21/75	2204	120	0.106	60	16.70	9.82	0.0	0.0
I-80-IV- 8	9/22/75	0004	120	0.106	0	13.65	8.52	0.0	0.0
I-80-IV- 9	9/22/75	0204	120	0.106	48	11.39	7.40	0.0	0.0
I-80-IV- 10	9/22/75	0404	120	0.106	32	5.41	3.54	0.0	0.0
I-80-IV- 11	9/22/75	0604	120	0.106	136	0.0	5.10	0.0	0.0
I-80-IV- 12	9/22/75	0804	120	0.106	66	15.23	9.03	0.0	0.0
I-80-IV-13+14	9/22/75	1004	240	0.106	61	11.72	6.93	0.0	0.0
I-80-IV-15+16	9/22/75	1404	240	0.106	64	17.68	9.84	0.0	0.0
I-80-IV-17+18	9/22/75	1804	240	0.106	88	27.53	14.84	0.0	0.0
I-80-IV-19+20	9/22/75	2204	240	0.106	92	21.81	11.38	0.0	0.0
I-80-IV- 21	9/23/75	0204	120	0.106	72	24.66	12.83	0.0	0.0
I-80-IV- 22	9/23/75	0404	120	0.106	64	27.18	13.98	0.0	0.0
I-80-IV- 23	9/23/75	0604	120	0.106	76	21.35	10.86	0.0	0.0
I-80-IV-24+25	9/23/75	0804	240	0.106	62	17.30	10.63	0.0	0.0
I-80-IV-26+27	9/23/75	1204	240	0.106	30	7.14	4.47	0.0	0.0
I-80-IV-28+29	9/23/75	1604	240	0.106	58	18.41	10.41	0.0	0.0
I-80-IV-30+31	9/23/75	2004	240	0.106	76	15.80	9.57	0.0	0.0
I-80-IV- 32	9/24/75	0004	120	0.106	86	23.40	12.87	0.0	0.0
I-80-IV- 33	9/24/75	0204	120	0.106	94	18.16	10.26	0.0	0.0
I-80-IV- 34	9/24/75	0404	120	0.106	86	25.52	13.55	0.0	0.0
I-80-IV- 35	9/24/75	0604	120	0.106	86	16.69	10.22	2.15	0.0
I-80-IV- 36	9/24/75	0804	109	0.106	52	12.08	7.22	0.0	0.0
I-81-IV- 5+6	9/24/75	1813	240	0.105	12	4.97	2.97	0.0	0.0
I-81-IV- 7+8	9/24/75	2213	240	0.105	28	7.71	4.34	0.0	0.0
I-81-IV- 9+10	9/25/75	0213	240	0.105	58	12.37	7.02	0.0	0.0
I-81-IV-11+12	9/25/75	0613	240	0.105	58	17.05	9.74	0.0	0.0
I-81-IV-13+14	9/25/75	1013	240	0.105	48	19.06	10.51	0.0	0.0
I-81-IV-15+16	9/25/75	1413	240	0.105	58	17.10	8.50	0.0	0.0
I-81-IV-17+18	9/25/75	1813	240	0.105	32	9.91	6.01	0.0	0.0
I-81-IV-19+20	9/25/75	2213	240	0.105	68	10.95	6.07	2.32	0.0
I-81-IV-21+22	9/26/75	0213	240	0.105	0	10.49	6.58	1.99	0.0
I-81-IV- 23	9/26/75	0613	120	0.105	66	0.0	4.73	2.70	0.0
I-81-IV-24+25	9/26/75	0813	165	0.105	40	0.0	3.49	2.14	0.0

[a] Acidity is expressed as the molar ratio of H^+ to SO_4^{2-}.

IV. DEVELOPMENT OF A NEW INSTRUMENT AND PROCEDURE

A. The ATR-Impactor Device

A new approach for aerosol sampling and analysis, which combines the principle of impaction with attenuated total internal reflection (ATR) infrared spectroscopy,[6] has been developed. Such a device, called an ATR-impactor, could provide much greater sensitivity than the KBr-pellet technique described above, while minimizing manual sample handling; it also has the potential for fully automatic operation. A prototype unit has been designed and fabricated, and the initial laboratory and field tests have been completed. The design of the instrument and some of the initial results are presented in this section.

1. Background

The KBr-pellet method has proven quite useful and continues to be employed on a routine basis in ongoing, large-scale studies of the chemistry of airborne particulate matter. However, as the scope of the studies has changed from single-site, short-term experiments to multisite, long-term programs which generate large numbers of samples, the need for an improved method for ambient aerosol sampling and analysis has become apparent.

Several aspects of the present KBr-pellet method need improvement. First, sample preparation is time-consuming and tedious. The nature of the preparation procedure has defied attempts at mechanization and/or automation. With large-scale programs, the sample preparation makes an analysis of all of the samples prohibitively expensive. Another area where improvement is desirable is the time resolution of the sample, which is, of course, dependent on the analytical sensitivity. Also, in the present KBr-pellet method, the possibility exists of altering the sample during collection and/or in the subsequent handling and time delay before analysis. For these reasons, an instrument is needed that would minimize sample handling, provide greater sensitivity, and approach real-time analysis. The ATR-impactor fulfills these needs.

2. Design

The ATR-impactor combines the use of an impactor for sample collection with ATR spectroscopy for sample analysis. A detailed discussion of the principles of ATR has been presented by Harrick.[6] Briefly, ATR spectroscopy is based on the attenuation of infrared (IR) radiation as it is internally reflected at the outer surfaces of a suitable infrared-transparent medium. The medium is in the form of an internal reflection element (IRE), which has surfaces at appropriate angles so that the light may enter, reflect internally several times, and then exit to the detector. Light which has entered and is being transmitted through an IRE is attenuated by IR-absorbing substances which are within about one-half wavelength of, but external to, the surface of the IRE. Using the ATR principle, infrared absorption spectra of substances can be obtained by simply placing them in intimate contact with an IRE, as if the light had passed through the substances in the conventional way. The ATR spectrum closely resembles the absorption spectrum obtained by passing the light beam directly through the sample. By appropriately arranging the geometry of an IRE, multiple reflections can be achieved, each being comparable to a separate pass through the sample, resulting in greatly enhanced sensitivity.

It is possible to use the ATR principle for sensitive, real-time analysis of atmospheric aerosol by impacting particles directly onto an IRE arranged in an infrared spectrophotometer for combined sampling and analysis. This would be feasible only if the spectrophotometer or some other detection device can be operated in the field. Such a device would eliminate sample handling and preparation, while providing enhanced sensitivity and real-time analysis. However, in the prototype instrument that we have built, the spectrometer is not included in the sample-collection device. The sample is collected by impaction onto an IRE, which is subsequently transferred to the spectrometer without any additional sample preparation.

The currently used IREs are polished plates of KRS-5, which is 42 mol % thallium bromide and 58 mol % thallium iodide. KRS-5 is attractive for ATR work due to its high refractive index (2.38 at 2000 cm^{-1}) and its wide range of transmission (5000-250 cm^{-1}) in the infrared region. However, KRS-5 is fairly soft, is toxic due to its thallium content, and must therefore be handled with care. Other materials, such as germanium and zinc selenide, are available and have also been used in the unit.

The prototype unit, shown schematically in Fig. 4, consists of four impactor stages; the first three are from a cascade centripeter--a commercially available virtual impactor (BGI, Inc., Waltham, Massachusetts). The centripeter stages have nominal 50% cut points of 14-, 4-, and 1.2-μm aerodynamic diameter, and are used to remove the larger particles which are not analyzed. The fourth stage has a nominal 50% cut-point value of 0.5 μm and thus collects the accumulation-mode size fraction of the sampled ambient aerosol. As shown in Fig. 4, the air flow is split after it passes the third stage of the centripeter and is then drawn through two separate nozzles so that the particles are deposited on the two opposite sides of the IREs or ATR plates. Time resolution is provided in the fourth stage by moving the IREs past the nozzles at a controlled rate. This is shown more clearly in Fig. 5, which shows detailed front and side views of the air nozzles and IREs in the ATR-impactor.

The fourth stage of the ATR-impactor was designed according to the procedure of Marple and Willeke.[7] For an air flow rate of 30 L/min, which is the nominal operating air flow for a single centripeter, the specifications for the fourth stage nozzle are as follows: slit width, 0.203 ± 0.025 mm; slit length, 20.0 ± 0.13 mm; slit throat depth, $0.203\,^{+0.13}_{-0.00}$ mm; and slit-to-plate distance, 0.305 ± 0.05 mm. The collection surfaces are formed by the IRE, which is 25-mm wide × 5-mm long × 2-mm thick. The ends of the IRE are beveled at an angle of 45°, as shown in the top view in Fig. 5. A second set of nozzles was constructed with slit widths of 0.406 ± 0.025 mm, for use with the higher flow rates needed for airborne plume studies. With these nozzles, the flow rate was increased to a nominal value of 60 L/min. Two centripeters mounted in parallel on a special head-end adapter were used to accommodate this higher flow rate. Flow-limiting critical orifices were inserted between the impactor and the pump to control the flow. A differential pressure gauge was permanently mounted across the critical orifice to monitor the pressure drop across the orifice.

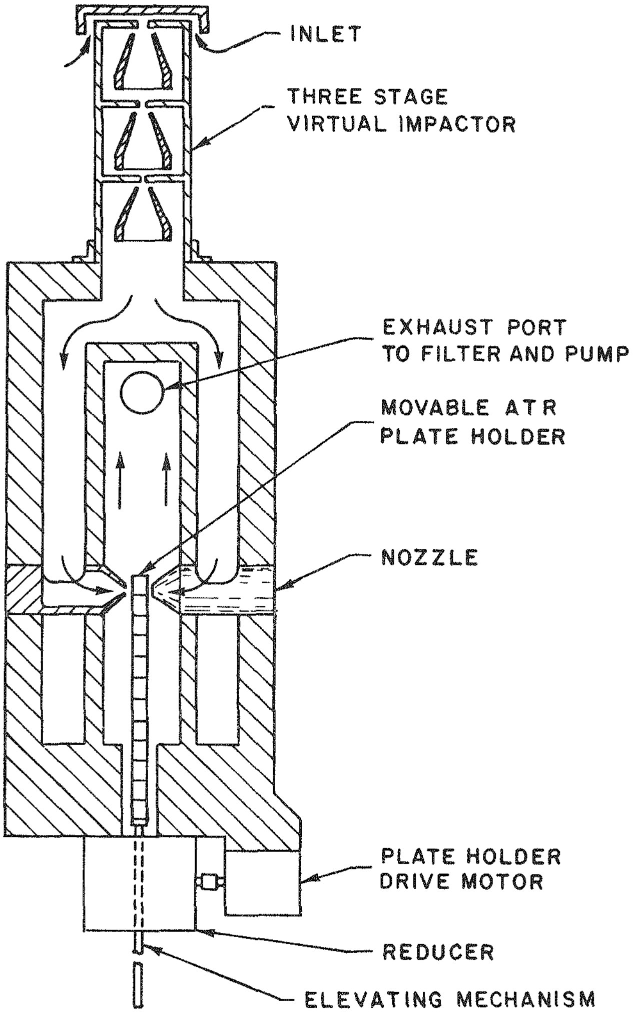


Fig. 4. Schematic Diagram of the ATR-Impactor

In the present design, the ATR-impactor system is not fully automated. The IREs with the collected samples are removed from the impactor for analysis on a Digilab Model FTS-14 Fourier-transform infrared (FTIR) spectrophotometer. A 4X variable-angle beam condenser, Model 4XTBC-VA (Harrick Scientific Corp., Ossing, New York) is used on the IR spectrophotometer to accommodate the IREs. In the prototype unit, up to 20 individual IRE plates are held side by side in a holder. During collection, the holder is driven at a constant speed, thereby moving the series of IREs between the two nozzles and collecting an even deposit of particles on the opposite surfaces. During analysis, an individual spectrum is obtained from each IRE to provide the time resolution. Collection times can be varied by changing the drive speed.

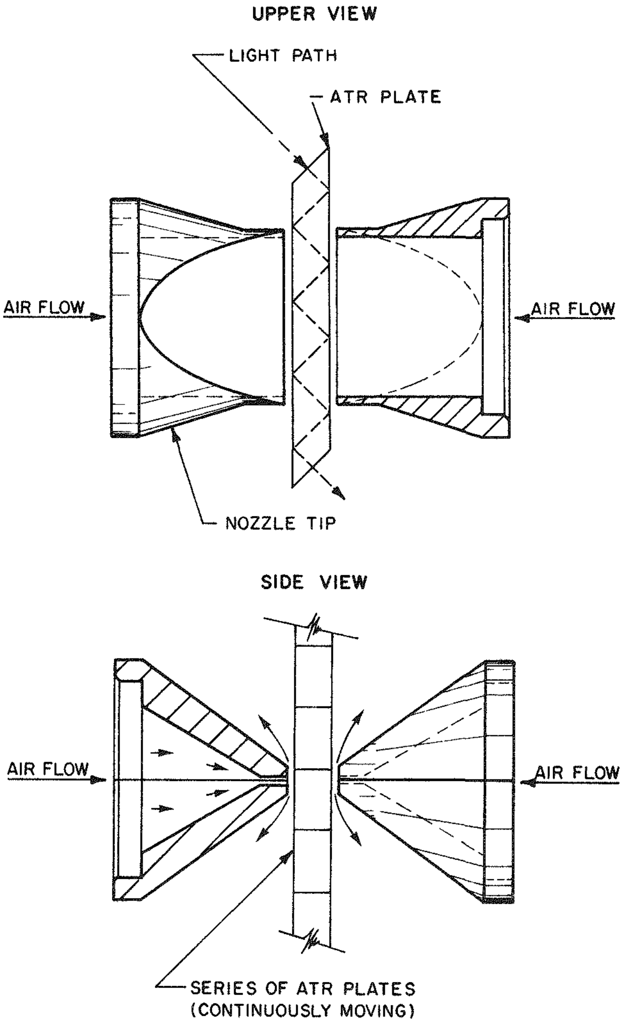


Fig. 5.

Detail of Nozzles and ATR Plates

It is anticipated that future ATR-impactor units could have built-in infrared light sources and detectors, tuned to the appropriate wavelengths of light. In this way, specific species could be detected as they are collected, thereby supplying near real-time detection. If necessary, a stream of inert gas could be passed over the ATR plates and samples immediately after collection to limit their exposure to any reactive ambient gases.

3. Results and Discussion

a. Initial Field Trials

In the first field trials of the ATR-impactor using the 30-L/min air flow nozzles, a comparison was made between the ATR method and our standard KBr method. Figure 6 presents infrared spectra of ambient samples collected simultaneously and analyzed using the two methods. As expected, for the submicrometer-sized ambient particulate matter, the spectra reveal the presence of ammonium sulfate and nitrate. To make the spectra directly comparable, the absorbance scale has been adjusted to account for differences in the air sampling rate. The ATR spectrum was from a sample

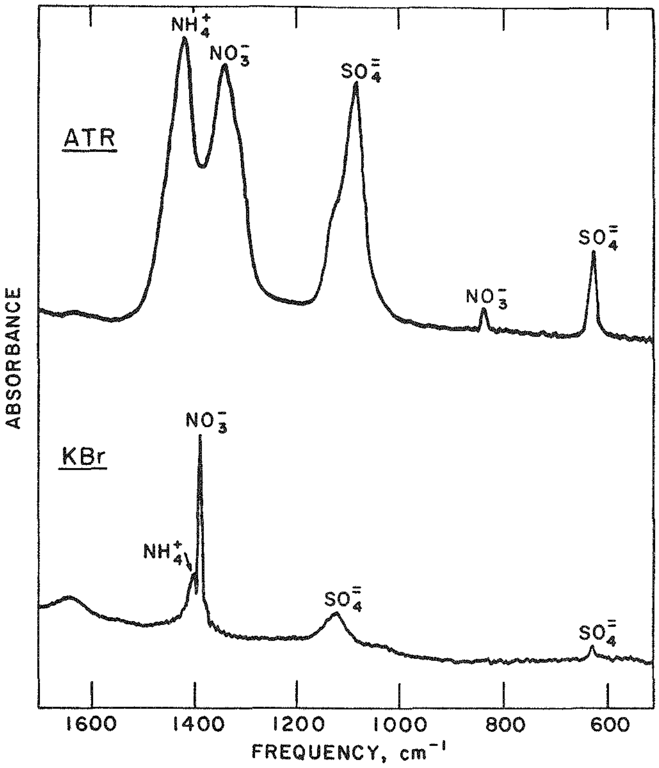


Fig. 6. Infrared Spectra of Ambient Aerosol Samples Collected Simultaneously to Illustrate the Greater Sensitivity of the ATR Method *vs.* the KBr-Pellet Method

collected for 55 min at a flow rate of 30 L/min. Based on our established calibration curves for the KBr method using the 620-cm^{-1} sulfate band, there were ∿10 μg of sulfate on the IRE. The absorbance for the 620-cm^{-1} band in the ATR spectrum is 0.14 absorbance units. As can be seen in Fig. 6, the absorbance at 620 cm^{-1}, based on peak height, is at least six times greater in the ATR spectrum compared to the KBr spectrum which represents the same amount of sulfate. Similarly, the 1110-cm^{-1} sulfate band, the 1400-cm^{-1} ammonium band, and the 840-cm^{-1} nitrate band are comparably enhanced in the ATR spectrum.

A different situation exists for the 1384-cm^{-1} nitrate band and warrants further explanation. It has recently been found that this very sharp and strong band at 1384 cm^{-1} is due to a matrix effect of the KBr on the nitrate and not to a chemisorbed or surface nitrate species as previously believed. The matrix effect causes the nitrate to appear as a free ion. Because of its strength, the 1384-cm^{-1} band is a very sensitive indicator of the nitrate content of samples prepared in KBr pellets. In the ATR spectrum, this nitrate band is much broader and occurs at 1337 cm^{-1} since the matrix effect is absent on the IRE. Thus, for this nitrate band, the ATR method is only slightly more sensitive than the KBr method. The 840-cm^{-1} nitrate band is seen in the ATR spectrum but is too weak to be detected in the KBr spectrum since the matrix does not enhance this nitrate absorbance mode.

It should be mentioned that the bands are shifted by varying degrees in the two types of spectra. Only small shifts are seen for most bands, except, as explained above, for the 1384-cm^{-1} nitrate and the 1110-cm^{-1} sulfate bands which are both noticeably shifted. Laboratory studies of known materials have verified the identity of these shifted bands. The shoulder at 1120 cm^{-1} in the ATR spectrum has not been identified, but, as will be seen, it may be related to the nitrate bands.

In Fig. 7, two ATR spectra of the same ambient sample are shown. The lower spectrum, labeled fresh, was obtained within ten minutes after collection. Additional spectra were obtained from the sample within 24 hours following collection and no changes were detected. However, the top spectrum, labeled aged, was obtained after six-months storage and, as can be seen, several changes had occurred. The nitrate bands at 1337 cm^{-1} and 830 cm^{-1} had disappeared, the 1415-cm^{-1} ammonium band had diminished, and the 1120-cm^{-1} shoulder was barely detectable. Since the two sulfate bands at 1080 cm^{-1} and 615 cm^{-1} remained unchanged, this indicated that the ammonium nitrate in the sample was volatile enough to be completely removed during the storage period. The sample had been stored on the KRS-5 IRE in air in a closed plastic Petri dish. Unfortunately, no other spectra were obtained during the storage period.

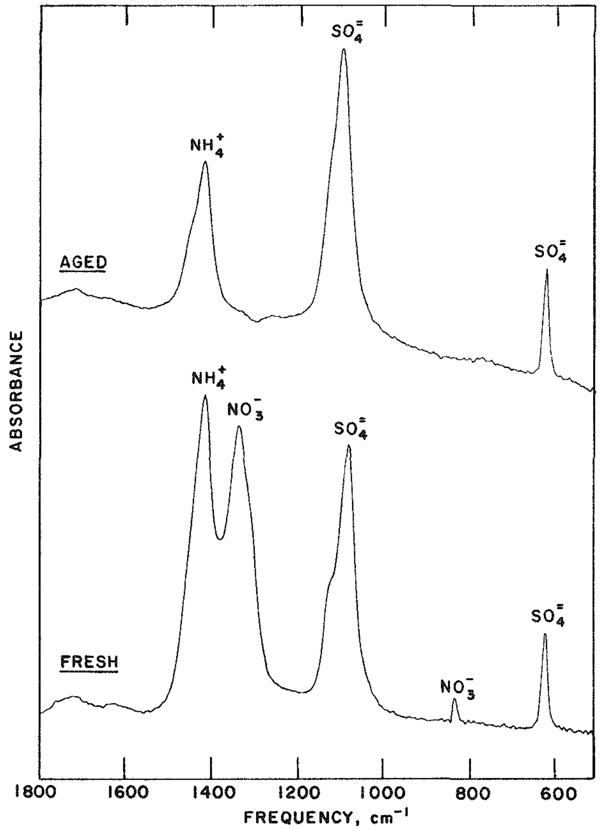


Fig. 7.

Infrared Spectra of an Ambient Aerosol Sample Immediately after Collection (fresh) and after Six-Months Storage (aged)

One of the objectives in the design of the ATR-impactor was to supply time resolution short enough to enable the study of the changing aerosol chemistry of a power-plant plume. In preparation for the airborne-plume studies, ground-based tests were conducted at ANL using the dual centripeter inlet and a 75 L/min air flow rate. Samples were collected with 12-min, 4-min, and 1-min time resolution. The spectra of all of these samples revealed the presence of neutral ammonium sulfate. Figure 8 presents the spectra from the 4-min and the 1-min samples. As is evident, even in the 1-min sample the ammonium sulfate absorptions are easily detectable. It is estimated from a sample collected with another impactor and analyzed in the routine manner using a KBr pellet that the 1-min sample contained ∿0.5 μg of sulfate.

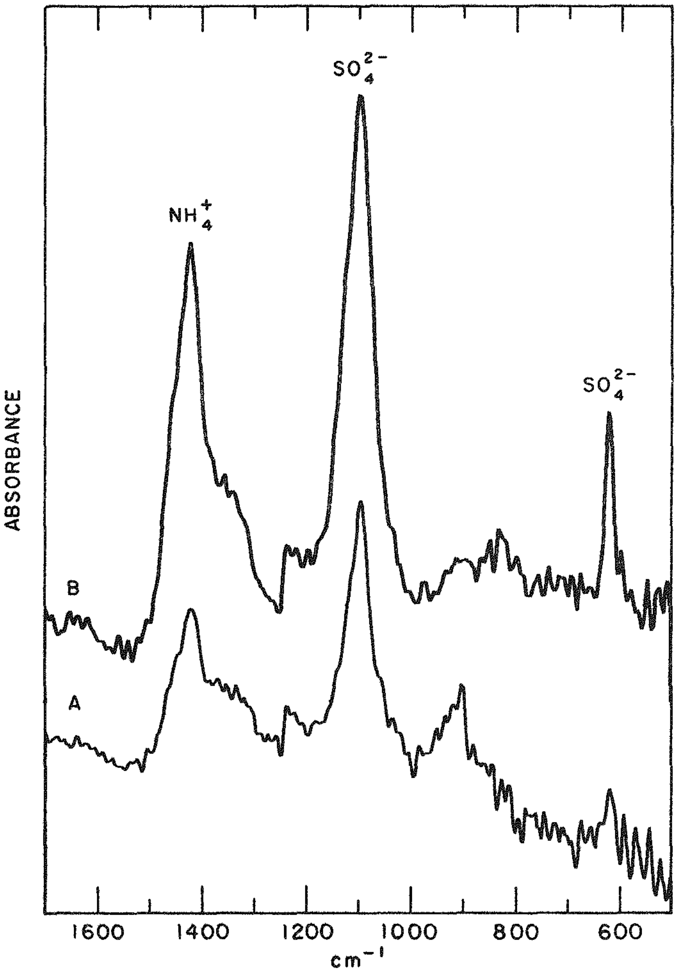
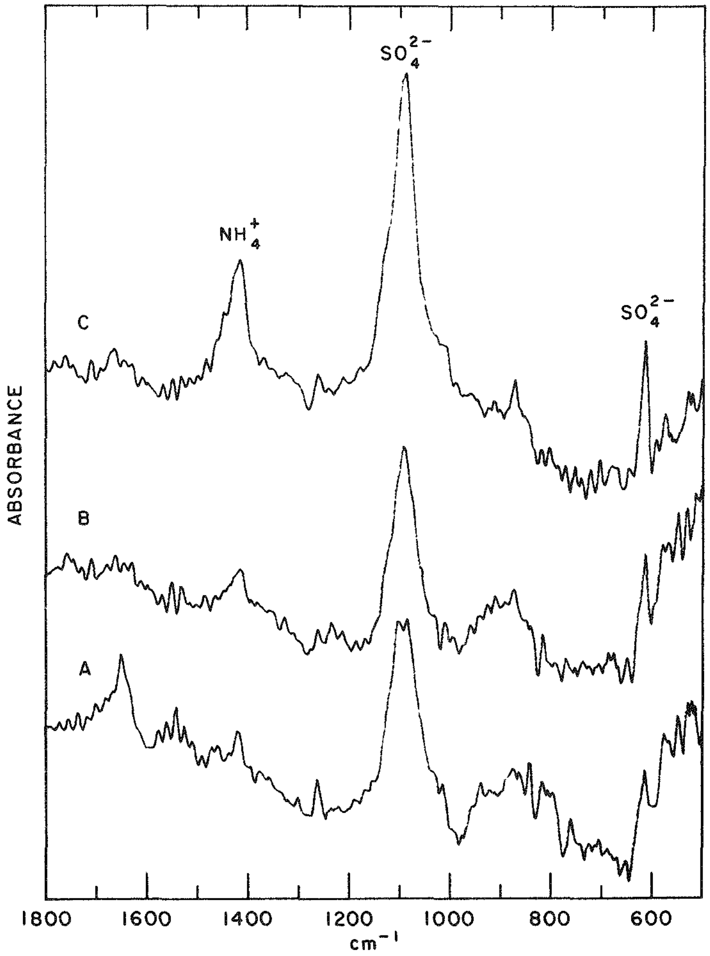


Fig. 8. Infrared Spectra of Submicrometer Ambient Aerosol Collected with ATR-Impactor. A: 1 minute collection at 75 L/min. B: 4 minute collection at 75 L/min.

b. Airborne-Plume Studies

During the week of April 14-18, 1980, the ATR-impactor underwent airborne trials in a plume from a power plant near Centralia, WA. The trials were conducted using the Battelle Pacific Northwest Laboratory (PNL) DC-3 aircraft which is fully instrumented for airborne pollutant studies. Our main objective for these trials was to demonstrate the feasibility of using the ATR-impactor for studies of plume chemistry and to determine what problems might arise. A constant flow rate of 64 L/min was established using a calibrated critical orifice and a rotary vane vacuum pump (Model 0740, Gast Corp., Benton Harbor, Michigan) outfitted with a 28VDC motor. To facilitate the quick changes needed to accommodate the varying collection conditions during the flights, the unit was equipped with a reversible, variable-speed control unit (Model IM100, Minarik Electric Co., Los Angeles, CA) for driving the internal reflection elements. This arrangement worked very well.

Figure 9 presents three of the ATR spectra from samples collected during the flights. As can be seen in Fig. 9, sulfate can be



A: SINGLE TRAVERSE, 6 MILES FROM STACK.
B: SINGLE TRAVERSE, 20 MILES FROM STACK.
C: THREE CONSECUTIVE TRAVERSES, 20 MILES FROM STACK.

Fig. 9.

Infrared Spectra of Power-Plant Plume Samples Collected with ATR-Impactor easily detected even in a single traverse of the plume with a collection time of 101 seconds. It was estimated that the total plume particle loading for this sampling was about 10 $\mu g/m^3$, which would correspond to a fairly typical loading of only sulfate for summertime ambient air in the Midwest.

c. General Observations

Some general observations have been made during the initial work with the ATR-impactor. Microscopic examination of the sample on the IRE revealed that for a one-hour collection period, where $\sim$10 μg of sulfate was collected, less than 25% of the surface of the IRE was actually covered with the particulate matter. With this small amount of coverage, each individual particle has open area between it and the nearest neighbor. This is important in minimizing interactions between collected particles. Spectra obtained from ambient samples with 15-min time resolution (15-min per IRE) showed that the coverage of the IRE surface was below 10%. For a 1-min sampling, the coverage would be even less. The limit of detection is estimated to be well below 0.5 μg of sulfate per sample.

In addition to the field tests of the ATR-impactor, some laboratory work has also been done. This involved the collection and analysis of aerosols generated from known materials, mainly for the purposes of IR absorption band verification.

4. Summary

The ATR-impactor has successfully completed initial laboratory and field tests and has shown that it offers several important advantages for the spectroscopic chemical characterization of ambient and plume aerosol. It has been shown that the infrared bands of the collected material are at least six times more intense than the bands obtained by the conventional KBr-pellet technique. For sulfate, the limit of detection is thus less than 0.5 μg. This is sufficient for 1-min time resolution on the analysis of typical ambient concentrations of sulfate using the prototype unit with a flow rate of 64 L/min. Time resolution of this order is desirable for plume studies, as well as for detailed studies which may lead to a better understanding of the dynamics of atmospheric chemistry.

Another advantage lies in the virtual elimination of the time-consuming sample handling and preparation procedures. This enables the incorporation of spectral measurement devices directly into the sampling unit, thereby providing for analysis as the sample is being collected.

B. X-Ray Fluorescence Method for the Determination of Proton Acidity in Aerosol Sulfates

This new method is being developed with the objective of measuring the proton acidity of atmospheric aerosol samples directly on the collection substrate by means of an acid-specific reagent of suitable characteristics. The important properties of such a proton-acceptor reagent include volatility, selectivity, stability, and detectability. The possibility of using a proton acceptor containing a heavy-element tag that could be detected by X-ray fluorescence spectroscopy (XRF) was investigated because of the potential for good selectivity and sensitivity provided by the XRF technique. In addition, such a method would be well suited for automated analyses and facile introduction into existing monitoring programs.

In the proposed method, the atmospheric aerosol sample would be exposed to a vapor-phase, tagged, proton acceptor until any acidity in the sample is completely neutralized. The excess reagent would be removed by flushing with an inert gas, leaving behind a nonvolatile tagged neutralization product. The amount of the tag element would then be measured by the XRF technique, and the acidity of the aerosol sample would thus be determined.

1. Reagent Selection

The characteristics which the reagent of choice should exhibit are:

(a) Volatility: The proton acceptor should be volatile so that reaction with the sample could be carried out in the gas phase to prevent undesired reactions or losses resulting from solvent effects. In addition, excess reagent could be removed by gentle heating under an inert gas flow. It is assumed that the product of the reaction would be a nonvolatile compound which would become immobilized on the sample collection substrate.

(b) Selectivity: The reagent of choice should be specific for the strong acid components in the sample, such as H_2SO_4 and HSO_4^-, and should not react with such weak acids as water vapor or ammonium ion, which are expected to be present in the sample.

(c) Stability: The reagent of choice should be resistant to decomposition by air oxidation or high temperatures.

(d) Detectability: The reagent of choice must contain a functional group which may be determined quantitatively at levels corresponding to sample acid concentrations by means of a selective, sensitive method. Possible groups which have been suggested include radioactive "tags" such as tritium or carbon-14, fluorescent organic functional groups, and heavy-element tags suitable for determination by X-ray fluorescence. X-ray fluorescence is already used for routine elemental analysis of filter samples and possesses outstanding selectivity and sensitivity characteristics. Acidity measurements by this method could thus be readily introduced into existing monitoring programs.

Examination of possible candidates for the proton-acceptor reagent led to the choice of an organo-germanium compound containing an amino group on one of the organic side chains. Gas-phase titrations of acid aerosols and particulate matter using ammonia have been described, and a method for sulfuric acid using diethyl amine has been used to determine total sulfate acidity.[8] Organo-germanium compounds show excellent stability, and the sensitivity of the XRF technique for the determination of germanium is exceptional.

Because of the above considerations, as well as ease of reagent synthesis, trimethyl-3-aminopropyl-germane [$(CH_3)_3Ge\text{-}(CH_2)_3\text{-}NH_2$], TAPG, was selected as the reagent for investigating the feasibility of this technique.

2. Discussion of Experimental Procedures

a. Impactor Samples

A flanged glass neutralization chamber was used in the experiments. The samples were placed in this chamber which was then flushed with dry nitrogen. The amine was injected into the chamber and the reaction allowed to proceed at a controlled temperature for a predetermined length of time. Determination of the germanium content of the sample was performed on a General Electric Company XRD-6 wavelength-dispersive XRF instrument. The Ge-K_α line at 36.33° (2θ) from a LiF crystal was used as the analytical line.

Initially, laboratory-synthesized samples were used in the development of this procedure. These samples were prepared by placing 2 to 10 µL of solutions containing ∿10 µg/µL H_2SO_4 or NH_4HSO_4, or ∿50 µg/µL $(NH_4)_2SO_4$ on Mylar or filter substrates.

The reagent, trimethyl-3-aminopropyl-germane, proved to be a good choice. It does not decompose at its normal boiling point of 157°C. After several months of working with the compound, there was no indication of sensitivity to air, light, or temperature. After a large number of cycles (∿100) involving the introduction, vaporization, and flushing of the amine in the neutralization chamber, no visible signs of a residue were observed. However, one of the difficulties encountered with the reagent was its low vapor pressure. It is estimated that, at room temperature, the reagent's vapor pressure is ∿3 to 4 torr. This increases to ∿20 torr at 50°C and ∿150 torr at 100°C.

The first phase of the work was devoted to finding a suitable set of operating conditions for the neutralization process. The primary requirements are quantitative reaction with the strongly acidic protons in H_2SO_4 and NH_4HSO_4, and minimum response to $(NH_4)_2SO_4$ and other species in atmospheric samples.

At room temperature and 1-atm pressure, the reaction time required for the neutralization was very long. Even after 30 minutes, unacceptably low recoveries were obtained for the prepared samples. Upon partial evacuation of the neutralization chamber (to increase the rate of reagent mass transfer), good recoveries were obtained for H_2SO_4 with a reaction time of 15 minutes. However, the recoveries for NH_4HSO_4 were erratic and ranged from 30 to 70%. Response to $(NH_4)_2SO_4$ was generally low (equivalent to 10% or less of the NH_4^+ ion) but was as much as 60 to 100% at times. This sporadic behavior is not completely understood, but the primary cause appeared to be insufficient drying of the sample before introduction of the amine into the neutralization chamber.

It was hypothesized that residual water in the sample acted as a proton transfer agent allowing an exchange of the organic amine for ammonia which is a weaker base in aqueous solution. An experiment was carried out to test this hypothesis. In this experiment, several samples of ammonium bisulfate were prepared and neutralized with TAPG without drying. The reaction with ammonium ion was quantitative under these conditions as indicated by an average germanium recovery of 202% relative to the acid expected in the samples.

This result demonstrated a need for a reliable method of drying the samples prior to neutralization. Oven drying of synthetic samples was tested and gave good results from the standpoint of reducing reaction with ammonium ion, but low recoveries of H_2SO_4 were obtained even for low oven temperatures (40°C). Often, low H_2SO_4 recovery was accompanied by strong discoloration of the substrate. We believe that the H_2SO_4 losses were due to either volatilization or reaction of the sulfuric acid during the drying step. After some experimentation, it was determined that storing the samples overnight in a desiccator charged with silica gel would result in complete drying without loss of H_2SO_4.

A series of synthetic standards dried in this manner were neutralized with TAPG to better define the neutralization conditions. For these tests, the samples were placed in the neutralization chamber and TAPG (∿100 μL) was injected into the chamber. All stopcocks on the chamber were tightly closed and it was placed in a drying oven at a preset temperature for 30 minutes. After this time, the chamber was removed from the oven to a laboratory hood and flushed with dry air (dried over molecular sieves) to remove the excess reagent. For efficient removal, a heat lamp illuminated the chamber while it was flushed out. After approximately 15 minutes flushing time, the samples were removed, fixed with a drop of collodion in ethyl acetate and subjected to XRF analysis.

Using this procedure, average recoveries for several series of synthetic samples were determined using neutralization temperatures of 89°C and 50°C. The results were:

Recovery of Acid by XRF

Temperature	H_2SO_4	NH_4HSO_4	$(NH_4)_2SO_4$	
89°C	64%	101%	2.7%	as NH_4^+
50°C	92%	100%	1.0%	

The low recovery of H_2SO_4 at the higher temperature is probably due to losses of the acid by volatilization or reaction prior to its neutralization by the TAPG reagent. A neutralization temperature of 50°C was used in all subsequent experiments. Since the results demonstrated that a usable procedure for synthetic samples had been obtained, work was begun to evaluate the method's performance with field-type samples.

The field samples used for this evaluation were archive samples of sulfate aerosol collected on Mylar with a Lundgren impactor as part of another program. Acidic samples were desired for the study, so samples were selected from a time period corresponding to an acidic episode as indicated by FTIR analysis. The samples were in the form of a line of impacted material ∿40-mm long on Mylar strips ∿3-mm wide. For each sample used, ∿15 mm was taken for FTIR analysis which provided a value for the total sulfate (as micromoles SO_4^{2-}), as well as the relative acidity of the sulfate (*e.g.*, more acidic or less acidic than bisulfate). The remaining sample was divided into several sections which were used for determination of the proton acidity by neutralization with the TAPG reagent or by measuring the pH change of a weakly acidic (pH ∿4.5) leach solution upon addition of the sample. This reference pH method for proton acidity was shown to be reliable for strong-acid synthetic samples (H_2SO_4 and NH_4HSO_4) deposited on Mylar.

The data obtained through the various methods for the field samples are summarized in Table 4. In order to simplify comparison of the data, the values in Table 4 are generally given in terms of micromoles or microequivalents per millimeter of sample. This was done because the sample-size requirements differ among the methods so that varying sample lengths had to be used.

Table 4. Summary of Data from Analysis of Field Samples of Sulfate Aerosol

Sample Identification	Method		
	FTIR	ΔpH	XRF - Ge
	μmol SO_4^{2-}/mm	μeq H^+/mm	μeq H^+/mm
IPS-102-IV-15	0.0335	0.0332	0.0318
			0.0352
IPS-102 After-Filter	None Detectable	<0.0003 (per mm^2)	<0.0003 (per mm^2)
IPS-102-IV-14	0.0268	0.0307	0.0308
		0.0260	0.0602
IPS-102-IV-13	0.0305	0.0269	0.0860
			0.0412
			0.0492
			0.0451
IPS-102-IV-12	0.0178	--	0.0526
			0.0349
			0.0538

The FTIR results indicated that the sulfate acidity of all the samples was near that of bisulfate. This observation is supported by the close correspondence between the microequivalents of acid found by pH measurement and the micromoles sulfate by FTIR. Some caution is advised in comparing these results too closely, however, for two reasons. First, the precision of either method at this range of sample size is not better than 15%. Second, some inhomogeneity or unevenness exists in the distribution of the sample on the Mylar substrate, as evidenced by microscopic examination of the samples and the failure of different sections of the sample to give duplicate results even within 15%.

Initial results from the XRF method were extremely encouraging. For the first field sample that was analyzed, IPS-102-IV-15, very good agreement among all three methods was obtained. Next, a sample from the impactor after-filter of IPS-102 was used, and values from all three methods fell below their respective limits of detection. This result was also interpreted as good agreement.

The second impactor sample, IPS-102-IV-14, gave mixed results. The values for pH measurement, from FTIR analysis, and one XRF result agreed satisfactorily. However, the other XRF result was high by a factor of about two. It appeared that sample inhomogeneity was affecting the data. Because all three methods employed here are destructive and it was not possible to reexamine the samples already run, a more carefully controlled experiment was planned for the next set of samples.

In this experiment, a permanent record of the appearance of the samples was first obtained by optical micrography. Examination of the photomicrographs showed:

(1) The impacted material was not evenly distributed along the length of the line on the substrate.

(2) Material on the Mylar substrate was not restricted to the vicinity of the line; a thin layer of wet-looking material coated the Mylar to varying widths, sometimes reaching to the edges of the Mylar strip.

(3) Droplets and smears of a viscous, colorless liquid were visible over broad areas of the sample. The distribution of these droplets was often localized and by no means homogeneous.

Once they were photographed, the samples were placed to dry in a desiccator over silica gel over the weekend. Surprisingly, drying in this way changed the sample's microscopic appearance very little. In particular, the size and location of the liquid droplets remained the same. The Mylar strip was then divided into several sections for analysis. Neutralization with TAPG resulted in total drying of the liquid material on the sample. Wherever a particularly large droplet had been, a lump of crystalline material was found. XRF measurement of the deposited germanium gave recoveries that ranged from 150 to 300% of the expected values (samples IPS-102-IV-12 and -13 in Table 4). In view of the problems with sample drying that were encountered in our early work with synthetic samples, and based on the results of the microscopic examination of the samples, we first suspected that these high recoveries might be due to incomplete water removal by the silica gel desiccant. We reasoned that perhaps the desiccant had been used too long and was ineffective. To test this possibility, a second desiccator charged with a fresh batch of silica gel was prepared. Synthetic samples from an aqueous solution of NH_4HSO_4 were dried in both the old and new desiccators and neutralized with TAPG. In both cases, the salt appeared dry when removed from the desiccator. The acid recoveries (determined by XRF) from the old and new desiccators were 107% and 104%, respectively, and demonstrated that the desiccant was not the source of the problem.

The fairly reproducible recoveries within each set of samples lead us to believe that the problems encountered are a reflection of some real property of the samples rather than merely an erratic malfunction in the neutralization process. The occurrence of high results in these samples is best classified as an interference effect. At the present time, the sources of this interference have not been identified, but some possibilities may be suggested:

(1) The interference may be due to reaction with ammonium ion. It is conceivable that, although silica gel is an adequate desiccant for pure sulfates, a mixture of H_2SO_4 and NH_4HSO_4 might retain water more efficiently than either pure compound. This water could allow reaction with NH_4 as described earlier. Alternatively, H_2SO_4 may serve as an efficient proton transfer agent if it is present in the samples in an unneutralized state. Some light might be shed on these possibilities by characterizing the liquid found in abundance in the deviant samples.

(2) The interference may be due to weak acids present in the samples. Weak acids would not dissociate in the acidic leach solution used for the reference method, but may react with the relatively strong TAPG base. Possible candidates are bisulfite ion, HS^-, or amphoteric metal ions such as Al^{3+} or Fe^{3+}. We have looked at the samples by X-ray fluorescence and have not found any indication of heavy metals. FTIR analysis of these and similar samples have not indicated the presence of bisulfite, HS^-, or of organic acids. However, these examinations have not ruled out the presence of weak acids in these samples.

(3) The interference may be due to complex chemical reactions between the TAPG reagent and sample constituents; such reactions could be catalyzed by the seemingly inert components of the aerosol particulates such as soot.

b. Filter Samples

The TAPG neutralization method for sulfate acidity was also investigated using laboratory-generated aerosol samples deposited on Fluoropore filters. In these experiments, a Kevex Model 7000 energy-dispersive X-ray spectrometer and data system was used for the XRF measurements. Germanium on the filters was determined using the Ge-K_α line at 9.88 KeV; excitation was from the Br-K_α line at 11.9 KeV of a KBr secondary target. In addition, a titanium secondary target was employed for determining sulfur using the S-K_α line at 2.31 KeV. The ability to determine sulfur with the Kevex XRF instrument provides a useful internal standard for the germanium measurements associated with the TAPG method. Comparison of the germanium deposited on the filter during neutralization against the sulfur present on the filter provides a simple indicator of the apparent relative acidity of the sulfate aerosol.

The XRF sulfur measurement was calibrated using almost neutral sulfate aerosol deposited on 90-mm-dia Fluoropore filters. The aerosol samples were generated by thermal decomposition of ammonium sulfate in an acidic sulfate aerosol generator.[9] The filters were stored over silica gel and weighed prior to depositing the aerosol. After a sample was collected, the filter was dried over silica gel and reweighed. From the mass of material collected and the area of the filter, the concentration of sulfate (in µmol/cm^2) was calculated. Figure 10 shows a plot of the sulfur counts accumulated in 200 seconds *vs.* the concentrations of sulfate on the filters. The straight line in this plot is the calibration line used for sulfate measurement in subsequent experiments with unknown samples.

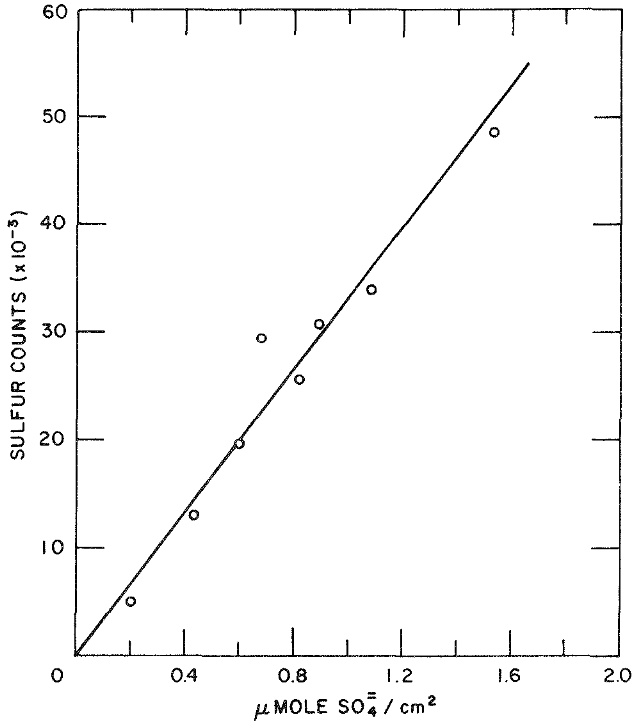


Fig. 10. Calibration of Filter Samples for Sulfur Determination by the XRF Method

The TAPG neutralization and germanium determination were evaluated using sulfuric acid aerosol samples produced by nebulizing 0.05N and 0.1N H_2SO_4 solutions. Samples from the nebulizer were collected at 15 L/min on 90-mm-dia filters. These filters were dried over silica gel and divided; portions were neutralized with TAPG and subjected to XRF analysis. As illustrated in Fig. 11, good correlation between the XRF germanium measurements and the corresponding sulfur results were obtained. This correlation is indicative of reproducible recovery of the acid in H_2SO_4 aerosol by the TAPG neutralization when the aerosol is collected on filters. However, the major difficulty encountered in applying the method to impactor samples was not that of achieving complete neutralization of sulfuric acid, but of controlling unwanted reaction with weak acids--particularly ammonium ion.

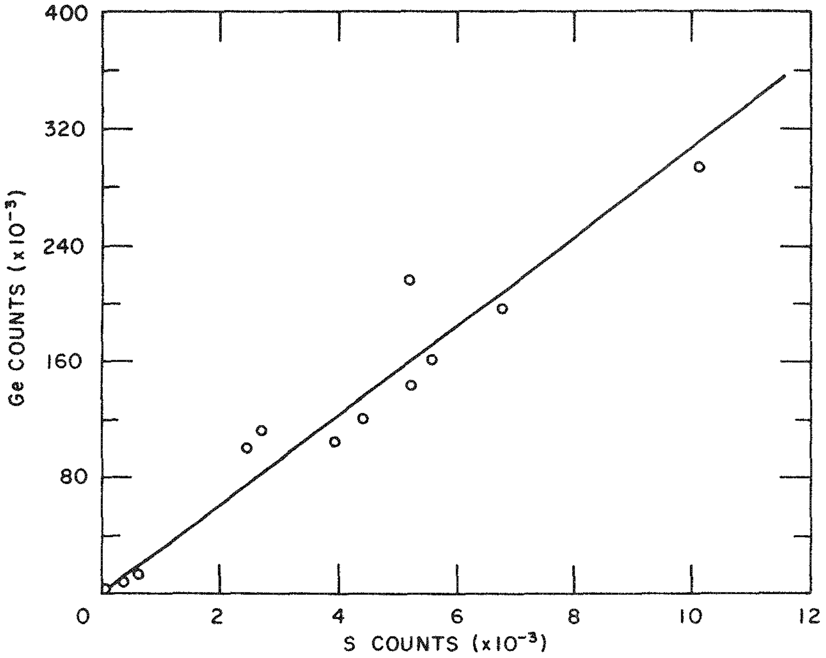


Fig. 11. Results of the Neutralization of Sulfuric Acid by TAPG on Fluoropore Filters

In order to test the possibility of ammonium ion interference when filter samples are neutralized with TAPG, a series of filters of varying acidity were prepared using the acidic sulfate aerosol generator. These filters were neutralized in the flanged-glass chamber previously employed with the impactor-type samples. The results of this experiment are shown in Table 5. The data presented there include the amount of sulfate on each filter as determined by XRF, the acidity of the sulfate measured by the pH change of a leach solution, the ammonium ion obtained by difference, the germanium found by XRF after TAPG neutralization, and the percent NH_4^+ that must have reacted to account for the difference between the acid on the filter and the germanium recovered. On the average, 64% of the NH_4^+ present reacted with the TAPG reagent. Clearly, under the neutralization conditions used in this experiment, interference by ammonium ion in the filters is excessive. Apparently, the material collected on filters is much more reactive than that deposited by drying of solutions or by impaction, and the conditions established using samples prepared by these latter methods are too severe for neutralization of the filter samples.

Consequently, an alternative neutralization procedure was tested in which the TAPG reagent was injected into a stream of clean, dry air flowing through the filter sample. The injection port, a glass tee fitted with a rubber serum cap, was heated to approximately 100°C to speed up vaporization of the amine reagent. Following injection of the amine, the air flow was continued for a few minutes to ensure removal of excess TAPG from the filter.

Table 5. Results of Analysis of Synthetic Sulfate Aerosol on Filters Neutralized with TAPG in a Closed Chamber

Sample No.	H^+,[a] μeq/cm^2	SO_4^{2-},[b] μmol/cm^2	NH_4^+,[c] μeq/cm^2	Ge,[d] μeq/cm^2	NH_4^+ Reacted, %
WSJ-1	0.277	0.566	0.835	0.928	78
-2	0.043	0.415	0.787	0.536	63
-6	0.235	0.447	0.659	0.741	77
-8	0.019	0.030	0.041	0.049	73
-9	0.001	0.006	0.011	0.009	73
-10	0.004	0.006	0.008	0.009	63
-11	0.0	0.003	0.006	0.002	33
-12	0.002	0.008	0.014	0.009	50
-13	0.032	0.096	0.160	0.137	66
-14	0.0	0.010	0.020	0.010	50
-15	0.188	0.503	0.818	0.910	88
-16	0.011	0.187	0.363	0.213	56

[a] By pH change of leach solution after sample addition.

[b] By sulfur XRF.

[c] By difference: $NH_4^+ = 2SO_4^{2-} - H^+$

[d] By Ge XRF after TAPG exposure.

The results obtained with a series of weakly acidic samples using the flow-through procedure are presented in Table 6. For these samples, reaction with ammonium ion was much less pronounced than for samples neutralized in the closed chamber. Nevertheless, the interference resulting from an average 12% reaction of the NH_4^+ on the filters was sufficient to obscure any relationship between the germanium recovered and the acidity of the samples.

No other modifications of the neutralization procedure have been investigated. It is possible that optimization of the conditions for exposing the filters to TAPG might reduce the interference to acceptable levels. The probability of achieving a viable procedure appears to be higher for filter samples than for impactor samples.

3. Summary

A new procedure for determining the proton acidity of atmospheric aerosol samples has been examined. In this method the collected sample is exposed to a vapor-phase, tagged proton acceptor, and the amount of the tag element in the neutralized product is then measured by X-ray fluorescence.

Table 6. Results of Analysis of Synthetic Sulfate Aerosol on Filters Neutralized with TAPG in Flow-Through Procedure

Sample No.	H^+,[a] μeq/cm^2	SO_4^{2-},[b] μmol/cm^2	NH_4^+,[c] μeq/cm^2	Ge,[d] μeq/cm^2	NH^+ Reacted, %
WSJ-31	0.150	0.924	1.697	0.258	6
-32	0.085	0.884	1.683	0.108	1
-33	0.009	0.767	1.525	0.111	7
-34	0.0	0.151	0.302	0.070	23
-40	0.248	1.463	2.679	0.323	3
-41	0.213	0.583	0.953	0.320	11
-42	0.027	1.018	2.010	0.314	14
-44	0.006	0.398	0.789	0.275	34

[a] By pH change of leach solution after sample addition.

[b] By sulfur XRF.

[c] By difference.

[d] By Ge XRF after TAPG exposure.

On the basis of desirable physical and chemical properties, trimethyl-3-aminopropyl-germane was selected as the proton acceptor. Tests were conducted with both impactor-collected and filter-collected samples. It was found that both the response of the method to proton acidity and the extent of interference from the NH_4^+ ion were strongly affected by sample preparation and neutralization conditions. These conditions could be optimized for synthetic samples containing H_2SO_4, NH_4HSO_4, and $(NH_4)_2SO_4$. However, these optimized conditions were still not suitable for samples collected in the field, for which the procedure gave almost quantitative response for the NH_4^+ ion, as well as for the H^+ ions present. The detailed nature of this interference has not yet been determined.

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