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An Intermethod Comparison of X-ray Photoelectron Spectroscopic (ESCA) Analysis of Atmospheric Particulate Matter

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A comparison of ESCA with wet chemical and other analytical techniques has demonstrated agreement within about a factor of 2 for sulfate and carbon but gave much larger deviations for nitrate and ammonium in analysis of atmospheric particulate samples collected in California's South Coast Basin. Analyses for nitrate and ammonium were low by a factor of 5 to 10 relative to the wet chemical methods. Loss of volatile ammonium- and nitrate-containing materials under the high vacuum and localized X-ray beam-induced heating conditions of ESCA was the most reasonable explanation of the discrepancy. Detailed temperature programmed ESCA studies support this conclusion and suggest the significance of highly volatile nitrate (e.g. nitric acid) and ammonium compounds in the atmospheric particles.

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INTRODUCTION

Efforts to characterize atmospheric aerosols often involve determination of aerosol composition as a function of particle size and time of day. This requires analytical methods of high sensitivity since loadings for specific elements in the range of a few nanograms/cm² are frequently encountered. As a result, highly sensitive instrumental techniques such as neutron activation analysis,¹ X-ray fluorescence analysis (XRFA)² and electron spectroscopy for chemical analysis (ESCA)³ are being used.

The present report focuses on efforts to validate sulfate, nitrate, ammonium and carbon data as obtained by ESCA in a program to characterize California atmospheric aerosols. These materials are all important constituents in atmospheric aerosols and are associated with deleterious effects on human health or reduced atmospheric visibility. Analytical methods of proven accuracy and precision are needed for these chemicals both to assess the need for control strategies and to measure the effectiveness of such strategies.

In addition to high sensitivity, ESCA has other inherent advantages including the frequent absence of interferences from the substrate (because of its restriction to the sample surface), and its ability to provide, from a single analysis, data on a number of different oxidation states of a given element. The difficulties with ESCA for aerosol analysis include the following:

- 1) Peaks in ESCA spectra corresponding to species in the same oxidation state for a given element are often only poorly resolved. For atmospheric samples peak assignments are empirical, being based upon comparison with chemical shifts for a limited set of pure, reference materials.

- 2) To obtain quantitative results by ESCA, an element in the sample must be analyzed by another technique and other species determined by ratio to this internal standard. In our study, Pb, determined by XRFA, served as the internal standard. Since XRFA analyses more deeply into a given particle or surface because of less absorption, Pb values so obtained may not be relevant to the ESCA spectra.

- 3) ESCA analyzes only the outer 50–150 Å of the exposed particles. So, for example, with 1 micron spherical particle, ESCA analyzes only the outer 0.5–1.5% and thus may not yield analyses representative of the average composition of the particle. On the surface of a filter or impaction medium, particles lying shielded by other particles may not be analysed due to absorption and scattering. Similarly, particles which penetrate into the pores or beneath the fibres of a filter will probably not be analyzed. Since the degree of penetration as well as composition may be a function of particle size, such penetration may lead to biased data.

4) ESCA requires maintaining the sample in vacuum (10^{-7} – 10^{-9} torr). Furthermore, while the samples are typically maintained at around room temperature as in this intermethod comparison, X-ray bombardment may produce localized heating of the sample. With or without such heating, there is the possibility of loss of volatile species such as nitric or sulfuric acid and ammonium nitrate.

This paper is intended to assess the combined effect of these and other unrecognized sources of error. To determine the accuracy of ESCA in the absence of standard reference materials, data obtained by ESCA were compared with those obtained by other instrumental or wet chemical techniques. Since the sensitivity requirements were beyond the range of conventional wet chemical methods, new techniques were developed and validated. These will be outlined briefly.

EXPERIMENTAL

A. Sampling and analysis strategy

Samples were collected on 47 mm Gelman GA-1 cellulose acetate filters for sulfate analysis and on 47 mm, 1.2 μ pore size silver membrane filters for carbon and nitrogen species analysis. The sampling rate was 3.0 cfm with the membrane filters being changed at 2-hour intervals throughout 24-hour periods. In addition samples were collected on Hi-volume cellulose filters (Whatman 41) sampling continuously during the same 24-hour period.

ESCA analyses were conducted only on the membrane filters while, depending on sensitivity, wet chemical methods employed either the 2-hour or 24-hour Hi-volume filters.

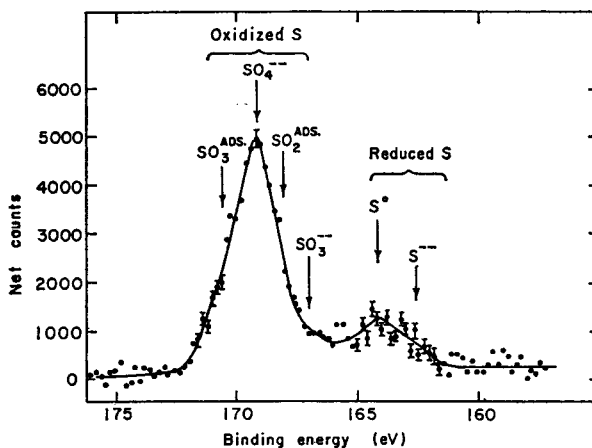
Intermethod comparisons included, therefore, both direct and indirect comparisons. Direct comparisons involved analyses of sections from the same filters while indirect comparisons required comparison of calculated 24-hour average values from ESCA analysis of 12–2-hour filters with the wet chemical analysis of the Hi-volume filter.

B. X-ray Photoelectron spectroscopy (ESCA)

Extensive reviews of X-ray photoelectron spectroscopy have been given in the literature¹¹ and therefore only a brief description of the method will be given here. ESCA measures the kinetic energies of photoelectrons expelled from a sample irradiated with monoenergetic X-rays. The kinetic energy of a photoelectron E_{kin} , expelled from a subshell i , is given by $E_{\text{kin}} = hv - E_i$ where hv is the X-ray photon energy and E_i is the binding energy of an electron in that subshell. If the photon energy is known the determination of the

kinetic energy of the photoelectron peak provides a direct measurement of the electron binding energy.

The electron binding energies are characteristic for each element which enables the method to be used for elemental analysis. The binding energies for a given element are modified by the valence electron distribution. Thus the binding energy of an electron subshell in a given atom depends on the atom's chemical environment (e.g. different oxidation states). These differences in the electron binding energies are known as the "chemical shift". The binding energies for oxidized species are greater than for the neutral configuration (a positive shift), while the binding energies show a negative shift for reduced species.



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FIGURE 1 Sulfur (2p) photoelectron spectrum of an ambient particulate sample. Expected positions of sulfate, sulfite, neutral sulfur and sulfide are indicated. In addition the expected line positions for adsorbed SO_3 and SO_2 are also shown.

The ESCA technique can, therefore, be used for both elemental analysis and for determination of chemical states.

Because of the limited resolution at the time of this study ESCA spectra were analyzed only for total oxidized sulfur on a routine basis (c.f. Figure 1). This includes adsorbed SO_2 , sulfite as well as sulfate.¹³ Based upon more detailed studies of a limited set of samples, sulfate typically represents at least 70% of this total.

In ESCA analysis for nitrate, nitrate proved to be the only discernible oxidized nitrogen species making total oxidized nitrogen a good approximation for determining this species.

ESCA analysis for ammonium was hampered by the presence of a second reduced nitrogen component. Indeed in the room temperature spectra, NH_4^+ nitrogen sometimes represented as little as 10–20% of this second species. This proportion was highly variable, however, making quantitative comparison difficult. Nevertheless, wet chemical ammonium ion determinations have been compared to ESCA values taking the total reduced nitrogen as an upper limit to the true ammonium value.

Intermethod comparison of carbon analysis employed total carbon making resolution of discrete species or oxidation states unnecessary.

C. Wet chemical sulfate analytical methods

1) SRI microchemical⁴—In a procedure developed at the Stanford Research Institute samples are extracted with hot water and all soluble sulfur compounds, presumed to be principally sulfate, reduced to H_2S by hydrogenation followed by coulometric titration. The sensitivity was sufficient to permit analysis of aliquots of the same 2-hour filters analyzed by ESCA.

2) Barium chloride turbidimetric analysis^{1,5}—Because of limited sensitivity this method could not be used on 2-hour samples. The method was used to analyze 24-hour Hi-volume samples which were then compared to the average of twelve 2-hour low-volume filters collected sequentially throughout this 24-hour period and analyzed by ESCA.

3) AIHL microchemical¹⁰—Because the SRI procedure lacks specificity for sulfate a new procedure was developed and validated in this laboratory. The procedure employs an excess of a barium-dye† complex in an acetonitrile-water solution, and is based upon suggestions from the literature.⁶ A decrease in absorbance by formation of BaSO_4 provides a sensitivity of 1 $\mu\text{g}/5$ ml solution.‡ The procedure was validated by analyzing aqueous extracts from atmospheric samples by this and two methods requiring larger samples (“macro-methods”) including the BaCl_2 turbidimetric procedure and a barium titrimetric method (Table I).

The two macro-methods, employing 200–1500 $\mu\text{g}/\text{aliquot}$ agree generally within 10%. At 3–5 $\mu\text{g}/\text{aliquot}$, the micro method results are low by about 50% relative to the macro-methods while at ≥ 6 $\mu\text{g}/\text{aliquot}$ (samples 4 and 5), values agree within 10–20%. Considering the uncertainties in ESCA analysis, the micro-method was considered adequate for comparison above the 3 $\mu\text{g}/\text{aliquot}$ level. It was applied to aliquots of the same 2-hour filter samples analyzed by ESCA.

†Dinitrosulfanazo-III.

‡A micropercolation procedure was employed for extraction of filter samples into 5 ml of water.⁷

D. Wet chemical nitrate and ammonium analytical methods

The microchemical procedure for nitrate employed permitted analysis of the same 2-hour samples analyzed by ESCA. This was the conventional 2,4 xylenol method⁵ increased in sensitivity by a 5-fold increase in path length for determining absorbance values and other minor modifications. An extract obtained by the previously mentioned micropercolation procedure⁷ was used.

A comparison of the micro- and conventional 2,4 xylenol method in the 1–20 and 50–80 $\mu\text{g}/\text{aliquot}$ ranges, respectively, with atmospheric samples yielded average agreement in concentration within 10%. Furthermore, the precision of the micro-method was $\pm 10\%$ or better even at 1 μg per aliquot.

TABLE I
Comparison of micro- and macro-sulfate analyses of particulate samples^a

Sample	Micro SO_4 ^{a,b} $\mu\text{g}/\text{ml}$	Titrimetric SO_4 ^{a,b} $\mu\text{g}/\text{ml}$	Turbidimetric SO_4 ^{a,c} $\mu\text{g}/\text{ml}$
1	7.3 \pm 0.4	11.4 \pm 0.1	10.5 \pm 0.3
2	7.0 \pm 0.6	11.6 \pm 0.2	10.2 \pm 0.3
3	11.6 \pm 0.7	17.1 \pm 0.4	14.8 \pm 1.0
4	20.3 \pm 0.4	22.9 \pm 0.7	24.2 \pm 0.4
5	30.0 \pm 1.1	32.7 \pm 1.0	36.2 \pm 0.3
Sample Range $\mu\text{g}/\text{aliquot}$:	3.5–8.1	570–1535	205–723

^aData shown represent mean and 1 σ values for 3 replications of each sample.

^bA titration with barium ion in 2:1 v/v acetone-water to a dinitrosulfanazo-III spectrophotometric endpoint, as developed at AIHL.

^cReference 15.

Lacking a suitable micro-method for ammonium ion, ESCA data averaged over 12, 2-hour filters were compared to those from the corresponding 24-hour Hi-volume filter collected simultaneously at the same location and analyzed by the indophenol blue procedure.⁸

E. Combustion analysis for carbon

Samples collected on silver membrane filters were analyzed by combustion to CO_2 with quantitation by gas chromatography as detailed by Mueller *et al.*⁹

F. Control studies on volatile losses under ESCA instrumental conditions

ESCA measurements were performed as a function of the sample temperature in the range from -150°C to 350°C . The sample was first cooled in dry nitrogen (at atmospheric pressure) to low temperature. The cold sample was then introduced into the spectrometer vacuum and spectra taken at -150°C and consecutively higher temperatures.

The experiments were performed with ammonium sulfate, ammonium nitrate, nitric acid and a number of ambient air particulate matter samples.

RESULTS

A. Sulfate

Table II lists the results of the comparisons of ESCA sulfate determinations with those by the SRI and AIHL microchemical methods and by the BaCl_2 turbidimetric method. Except as noted, ESCA data were obtained on the Gelman GA-1 filter samples.

TABLE II
Sulfate analyses by ESCA compared to microchemical and turbidimetric methods

Wet Method	No. of Samples	ESCA Range for Sulphate ($\mu\text{g}/\text{m}^3$)	Wet Method Range for Sulfate	Ratio of Wet Method to ESCA ^e
SRI Microchemical ^{a, b}	12	3.3–19	0.6–16	0.5 ± 0.1
AIHL Microchemical ^a	8	3.6–30	2.5–9.7	0.7 ± 0.2
BaCl_2 Turbidimetric ^c	4 ^f	1.1–6.4	1.0–5.9	1.0 ± 0.4
BaCl_2 Turbidimetric ^d (Ag. membrane)	4 ^f	1.8–17.1	4.4–19.0	0.9 ± 0.2

^aCarried out on sections from the same 47 mm Gelman GA-1 cellulose ester filters after sampling for 2 hours at 3.0 cfm.

^bThe uncertainty in these analyses are not currently available. The standard error of the ratio of means was calculated assuming a standard error of 10% for each determination by the SRI method.

^cESCA values are mean results from 12-2 hour Gelman GA-1 filters sampling at 3.0 cfm while BaCl_2 turbidimetric data are from analysis of a 24-hour Hi-volume filter collected simultaneously at the same sampling site.

^dESCA values are mean results from 12-2-hour Selas 1.2 μm Ag membrane filters sampling at 3.0 cfm while BaCl_2 turbidimetric values are as in footnote c.

^eThe uncertainty stated is the standard deviation of the ratio of the means.

^fRefers to the number of 24-hour Hi-volume filters.

For the comparison of ESCA and the SRI microchemical procedure analyzing sections from the same filter samples, the range in ratios of results was from 0.1 to 0.8 with the ratio of means about 0.5, ESCA yielding higher values. In a similar comparison of ESCA with the AIHL micro-chemical procedure, the ratio of means was 0.7 indicating average agreement within better than a factor of two. The indirect comparison of ESCA and the barium chloride turbidimetric values for sulfate indicates good agreement, on the average. The effect of filter medium was explored by comparing ESCA results for samples collected on silver membrane filters with the BaCl_2 turbidimetric method as previously described. The results for sulfate were not significantly different from those with the Gelman membrane filters. We conclude that ESCA provides sulfate analyses which are correct within a factor of two.

B. Nitrate and ammonium

Table III compares ESCA to wet chemical analyses for nitrate and ammonium employing determinations conducted on the same filters and the indirect procedure outline above. With nitrate, using both comparative techniques, the ESCA results were lower by a factor of nearly 5.

Using total reduced nitrogen as an approximation to ammonium the ESCA values appear to agree well with that by the indophenol blue procedure. However, this agreement is fortuitous since the ammonium ion represented as little as 10–20% of the total reduced nitrogen making ESCA values low by as much as a factor of 5 to 10. We discuss below a probable cause of the apparent agreement between wet chemical NH_4^+ and total reduced nitrogen by ESCA.

It is unlikely that the wet chemical methods are subject to significant interference with these samples. A far more likely source of error is the loss of volatile nitrate and ammonium in the ESCA spectrometer vacuum. Relevant control studies are detailed below.

C. Carbon

Twenty-nine samples collected on Ag membrane filters were analyzed for total carbon both by ESCA and by a combustion technique.⁹ ESCA values ranged from 8.09 to 146 $\mu\text{g}/\text{m}^3$ with a mean ratio of combustion to ESCA results of 0.9 ± 0.1 . These results suggest average carbon analyses by ESCA to be reasonably accurate. However the degree of agreement for carbon analysis should also be influenced by the evaporation of the more volatile organic materials under ESCA conditions. The present agreement implies that most of the carbon was nonvolatile.

D. Volatile losses under ESCA instrumental conditions

Synthetic aerosols of ammonium sulfate were found to be stable in vacuum at 25°C for time intervals normally used to complete the analysis of air samples; no detectable decrease of either ammonium or sulfate photoelectron peak intensity was observed between -150°C and 25°C. However, upon further heating at higher temperatures (NH₄)₂SO₄ appeared to decompose to NH₄HSO₄, the ammonium peak decreasing noticeably at $\geq 80^\circ\text{C}$, while the sulfate peak remained approximately constant until 150°C. At 150°C, NH₄HSO₄ appeared to be the species present. At higher temperatures both NH₄⁺ and sulfate sulfur decreased at the same rate.

TABLE III

Ammonium and nitrate analysis by ESCA compared to wet chemical methods

Species	Wet Method	No. Samples	ESCA Range ($\mu\text{g}/\text{m}^3$)	Wet Method Range ($\mu\text{g}/\text{m}^3$)	Ratio of Wet Method to ESCA ⁱ
NO ₃ ⁻	Micro-2,4 xylenol ^{a, b}	9	2.2-26.5	2.4-133	4.6 ± 0.7
NO ₃ ⁻	2,4 Xylenol ^{c, d}	3 ^e	0.9-7.1	5.6-36.4	4.9 ± 1.3
NH ₃ ^{+f}	Indophenol Blue ^{c, g}	4 ^h	2.8-16.0 ^e	2.3-16.4	1.0 ± 0.1 ^f

^aSee text.

^bCarried out on sections from the same 47 mm 1.2 μ Ag membrane filters run for 2 hours at about 3 cfm.

^cMethod detailed in Reference 5.

^dESCA values are mean results from 12-2-hour 1.2 μ Selas Ag membrane filters sampling at about 3 cfm while the wet chemical analysis for nitrate was conducted on 24-hour Whatman 41 Hi-volume filters collected simultaneously at the same sampling site.

^eUpper limits as discussed in text.

^fWith ESCA the NH₃⁺ analysis is taken to be 100% of the total reduced nitrogen observed while NH₄⁺ could be as low as 10-20% of this value. See text.

^gESCA values are mean results from 12-2-hour 1.2 μ Selas Ag membrane filters sampling at about 3 cfm. The wet chemical analysis was conducted on 24-hour Whatman 41 Hi-volume filters collected simultaneously at the same sampling site.

^hRefers to number of 24-hour Hi-volume filters.

ⁱThe uncertainty stated is the standard deviation of the ratio of the means.

Ammonium nitrate proved to be more volatile in vacuum than ammonium sulfate. It decomposed completely at temperatures above about 100°C with equivalent loss of anion and cation. Even at normal sample temperatures of about 25°C a decrease in both nitrate and ammonium peak intensities was observed at a rate of about 15 per cent per 12 hour period. A decrease of much less than 5 per cent was observed for ammonium nitrate between sample temperatures of -150°C and 25°C. Since 12 hours (at room temperature) is the maximum time that an ambient sample was kept in vacuum, an underestimation of ≤ 15 per cent is to be expected for ammonium nitrate concentration determination.

Nitric acid samples were prepared¹⁴ by exposing polycrystalline graphite

to NO_2 and moisture in air.† Intense nitrate photoelectron peaks were observed at -150°C . However, most of the nitric acid was lost when the sample was heated up to 25°C .

Figure 2 details typical results of variable temperature ESCA studies conducted with ambient aerosol samples. The ESCA spectrum of the nitrogen 1s region taken with the sample at -150°C is shown in Figure 2a. Nitrate and ammonium photoelectron peaks are seen in addition to a peak, labelled N_x , believed to be due to surface amine and/or amide compounds.^{3,13} The amount of ammonium, as reflected in the photoelectron peak intensity,

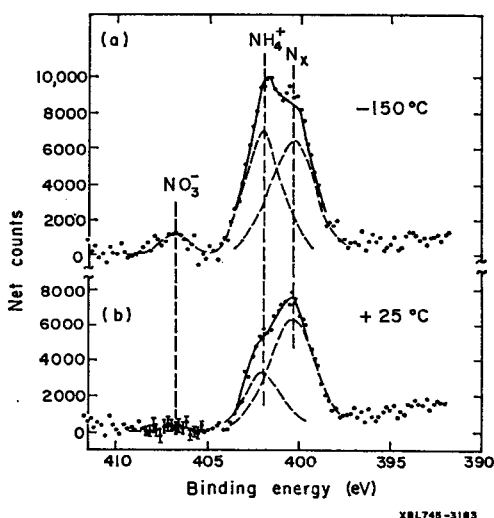


FIGURE 2 (a) Nitrogen (1s) photoelectron spectrum of an ambient particulate sample measured at -150°C . The positions of nitrate, ammonium and of N_x species are indicated. (b) Nitrogen (1s) spectrum of the same sample measured at $+25^\circ\text{C}$.

exceeds the nitrate peak intensity by a factor of about 6. Therefore at most about 15% of the total ammonium present in the sample at -150°C could be associated with nitrate (i.e. as NH_4NO_3). The remaining 85% of the ammonium could be in the form of ammonium sulfate or in the form of some other ammonium containing compound.

Figure 2b shows the nitrogen 1s spectrum of the same sample taken after it was heated up to 25°C . This spectrum reveals only a trace of the original nitrate and a decrease of about 60 per cent in ammonium peak intensity. The amount of ammonium nitrogen apparently lost by volatilization is

†Nitrous acid was not observed but would be detectable if present.

about three times the original nitrate nitrogen observed at -150°C . Therefore, the volatile ammonium cannot be principally ammonium nitrate.

Based on these results, the inconsistency between ESCA (at 25°C) and wet chemical determinations for ammonium probably cannot be explained by volatile losses of ammonium sulfate, ammonium bisulfate or ammonium nitrate. The inconsistency for nitrate can similarly not be explained by the volatilization of ammonium nitrate. The results with nitric acid, however, indicate that only a small fraction of any nitric acid initially present would have been observed by ESCA at 25°C . Thus if a large fraction of nitrate exists as HNO_3 on the filter, this would explain, qualitatively, the low nitrate values by ESCA.

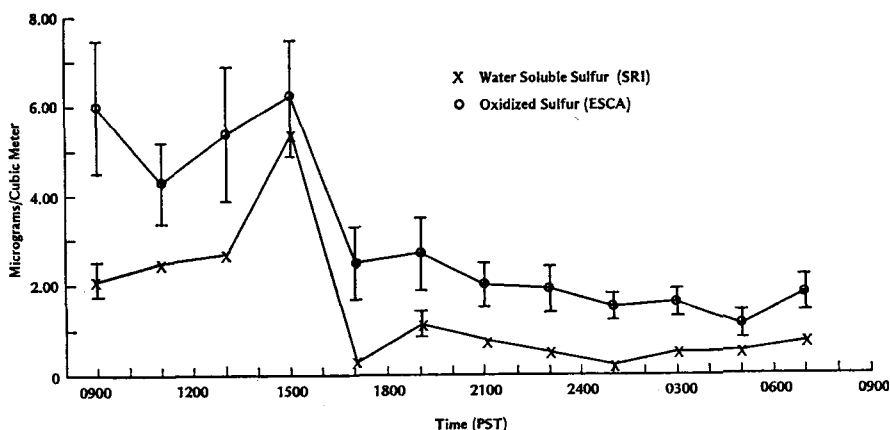


FIGURE 3 Diurnal Pattern for Sulfate (as Sulfur) by ESCA and the SRI Microchemical Methods, Pomona, California, October 24-25, 1972.

The limited volatility of the ammonium salts and the behavior of the ambient samples suggest that the major fraction of ammonium on aerosol particles is present in a hitherto unrecognized volatile form perhaps produced by chemisorption of ammonia. Indeed, ammonia was found to adsorb on, for example, combustion-produced carbon particles, to form a volatile carboxyl-ammonium salt.^{1,2}

It is notable that the volatile ammonium species is found in concentrations similar to the concentration of the other reduced nitrogen species (i.e. N_x), at least for the ambient air samples which have been examined at low temperatures by ESCA. Because these ESCA measurements were performed at 25°C , the total reduced particulate nitrogen is largely in the form of N_x . This might explain the apparent agreement between the results of wet

chemically determined concentrations of ammonium and ESCA concentrations of total reduced nitrogen.

E. Precision of ESCA determinations

The preceding discussion has emphasized the accuracy of ESCA determinations. A qualitative indication of the precision of ESCA is obtained by comparing diurnal patterns for species determined both by ESCA and by alternate procedures. Figure 3 depicts diurnal patterns for sulfate analyses as measured by both ESCA and the SRI microchemical procedure applied to 2 hour low-volume filters. The data is that for a 24-hour moderate smog episode at Pomona, California. ESCA and the SRI procedure yield strikingly similar diurnal patterns suggesting sufficient precision for the ESCA method to permit useful interpretation.

SUMMARY AND CONCLUSIONS

A comparison of ESCA with wet chemical and other analytical techniques has demonstrated agreement within about a factor of 2 for sulfate and carbon but yielded much larger deviations for nitrate and ammonium analysis in the analysis of atmospheric samples from California's South Coast Basin. For these species ESCA analysis performed at 25°C was low by a factor of at least 4.

Detailed ESCA studies with temperature programming from -150°C to 350°C demonstrated that loss of ammonium sulfate, ammonium bisulfate and ammonium nitrate are probably minor contributors to this discrepancy. The data are consistent with loss of a more volatile nitrate (e.g. nitric acid) and ammonium species the latter perhaps arising from chemisorption of ammonia on particulate matter.

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References

1. F. A. Iddings, *Environ. Sci. and Tech.* **3**, 132 (1969); W. H. Zoller and G. E. Gordon, *Anal. Chem.* **42**, 257 (1970); R. Darns, *et al.*, *Anal. Chem.* **42**, 861 (1970); K. Rahn, J. J. Wesolowski, W. John and H. R. Ralston, *Air Poll. Cont. Assoc. J.* **21**, 7 (1971).

2. T. R. Dittrich and C. R. Cothorn, *J. Air Poll. Cont. Assoc.* **21**, 716 (1971); R. D. Giauque, *et al.*, *Anal. Chem.* **45**, 671 (1973).
3. T. Novakov, P. K. Mueller, A. E. Alcocer, and J. W. Otvos, *J. Coll. and Interface Sci.* **39**, 225 (1973).
4. F. L. Ludwig and E. J. Robinson, *Coll. Sci.* **20**, 571 (1965); F. L. Ludwig and E. J. Robinson, *Atmos. Environ.* **2**, 13 (1968).
5. *Intersociety Committee Methods of Air Sampling and Analysis*, American Public Health Association, 1972.
6. B. Budesinsky and L. Krumlova, *Anal. Chim. Acta.* **39**, 375 (1967); D. Klockow and G. Röncke, *Atmos. Environ.* **7**, 163 (1973).
7. H. W. Hermance, C. A. Russell, E. J. Bauer, T. F. Egan and H. V. Wadlow, *Environ. Sci. and Tech.* **5**, 781 (1971).
8. M. W. Weatherburn, *Anal. Chem.* **39**, 971 (1967).
9. P. K. Mueller, R. W. Mosley and L. B. Pierce, *J. Coll. Interface Sci.* **39**, 235 (1972).
10. Private communication from E. L. Kothny, 1973.
11. S. H. Hercules and D. M. Hercules, *Environ. Anal. Chem.* **1**, 169 (1972); T. Novakov, in "Proceedings of the Second Joint Conf. on Sensing of Environ. Pollutants", p. 197, published by Instr. Soc. of America, Pittsburgh (1973).
12. S. G. Chang and T. Novakov, *Atmos. Environ.* **9**, 495 (1975).
13. N. L. Craig, A. B. Harker and T. Novakov, *Atmos. Environ.* **8**, 15 (1974).
14. W. R. Forsythe and W. F. Giauque, *J. Am. Chem. Soc.* **64**, 48 (1942).
15. "Selected Methods For the Measurement of Air Pollutants," Public Health Service Publication No. 999-AP-11, 1965.