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ELECTRON SPECTROSCOPY

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Lawrence Berkeley Laboratory University of California/Berkeley
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IDENTIFICATION AND DETERMINATION OF PARTICULATE COMPOUNDS:
ELECTRON SPECTROSCOPY*

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ABSTRACT

The application of X-ray photoelectron spectroscopy (ESCA) to the chemical characterization of atmospheric particulates is described. The experimental results reviewed involve the measurement of chemical shift and determination of relative concentrations and physical properties such as thermal stability and volatility of particulate species. The application of multiplet splitting to the determination of oxidation states of certain transition metals is also described. The use of photoelectron spectroscopy has helped to uncover several previously unsuspected chemical species associated with particulates and to provide the first information about their surface composition.

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I. INTRODUCTION

It is desirable that wet chemical and other microanalytical procedures be complemented by nondestructive physical methods. X-ray photoelectron spectroscopy, also known as ESCA (Electron Spectroscopy for Chemical Analysis),¹ whose application to chemical characterization of pollution particles is described in this chapter, is one such method. For example, application of this method has helped to uncover the presence of significant concentrations of reduced nitrogen species other than ammonium in ambient aerosol particles.² This group of species contains, among others, certain amines and amides³ which are not soluble in water or such solvents as benzene and therefore could not be detected by wet chemical methods. Most analyses of pollution aerosol particles have employed wet chemical methods; and on the basis of this kind of measurement, different workers have concluded that the principal particulate nitrogen species are ammonium and nitrate ions⁴ and have suggested that the most likely combination of these is ammonium nitrate and ammonium sulfate.⁵ The species uncovered with the aid of electron spectroscopy have thus escaped observation by means of wet chemistry.

In this chapter we will describe the use of X-ray photoelectron spectroscopy for chemical characterization of ambient and source-enriched aerosol particles. These analyses involve measurement of the chemical shift, core electron level splitting, relative concentrations, and volatility (in vacuum) of different particulate species. Because the method of photoelectron spectroscopy has been described in great detail in a number of papers and monographs, only the fundamentals of the technique relevant to

this topic will be reviewed here. Because most of the mass of airborne pollution particles consists of compounds of carbon, nitrogen, and sulfur, special emphasis will be placed on characterization of C, N, and S species. Attempts to chemically characterize some trace metals such as lead and manganese, both originating in fuel additives, will also be described.

II. X-RAY PHOTOELECTRON SPECTROSCOPY

X-ray photoelectron spectroscopy is the study of the kinetic energy distribution 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 $E_{\text{kin}} = h\nu - E_i$, where $h\nu$ 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, experimental determination of the photoelectron kinetic energy provides a direct measurement of the electron binding energy.

The electron binding energies are characteristic for each element. The intensity of photoelectrons, originating from a subshell of an element, is related to the concentration of atoms of that element in the active sample volume. In principle, this feature enables the method to be used for quantitative elemental analysis. The binding energies, however, are not absolutely constant but are modified by the valence electron distribution, so that the binding energy of an electron subshell in a given atom varies when this atom is in different chemical environments. These differences in electron binding energies are known as the chemical shift. The origin of the chemical shift can be understood in terms of the shielding of the core electrons by the electrons in the valence shell. A change in the charge of the valence shell results in a change of the shielding which affects the

core electron binding energies. For example, if an atom is oxidized, it donates its valence electrons and thus becomes more positively charged than the neutral configuration. Some of the shielding contribution is removed, and in general the binding energies of the core electron subshells are increased. Conversely the binding energies will show an opposite shift for the reduced species. Therein lies the usefulness of chemical shift determinations in the analysis of samples of unknown chemical composition. In practice, the measurements of the chemical shifts are complemented by the determination of relative photoelectron intensities, from which the stoichiometric information can be inferred.

The relation $E_{\text{kin}} = h\nu - E_i$ is unambiguous for gaseous samples. In solid samples, however, the photoelectron has to overcome the potential energy barrier at the surface of the sample. This potential energy barrier is known as the work function of the sample, ϕ_{sample} . However, if the solid sample is in electrical contact with the electrically "grounded" spectrometer, the Fermi levels of the sample and of the spectrometer are equalized. On entering the spectrometer a photoelectron is accelerated by $e[\phi_{\text{sample}} - \phi_{\text{spect}}]$, and as it reaches the detector, it acquires the kinetic energy $E_{\text{kin}} = h\nu - E_{i,f} - \phi_{\text{spect}}$. In the experiment, therefore, the kinetic energy is determined by the spectrometer work function, ϕ_{spect} , and by the binding energy referenced to the Fermi level of the spectrometer, $E_{i,f}$.

We shall briefly describe some of the theoretical results on chemical shifts that relate to the chemist's intuitive conception of bonding and molecular structure and to the subject of analytical applications of photoelectron spectroscopy.

In the early stages of photoelectron spectroscopy, it was realized that the chemical shifts can be related to the oxidation state of the atom in a molecule. Subsequently, attempts to correlate the binding energy shifts with the estimated effective atomic charges were made. Electronegativity difference methods,^{6,7} the extended Hückel molecular orbital method,⁸ and the CNDO method⁹⁻¹¹ were used to calculate the effective charge. Only rough correlations were obtained, however. It was subsequently found that the poor correlations result from neglect of the potential generated by all charges in the molecule.

Chemical shifts can be adequately described by the electrostatic potential model in which the charges are idealized as point charges on atoms in a molecule. The electron binding energy shift, relative to the neutral atom, is equal to the change in the electrostatic potential resulting from all charges in the molecule as experienced by the atomic core under consideration. Different approaches to the potential model calculations were used by Gelius et al.,^{12,13} Siegbahn et al.,^{7,14} Ellison and Larcom,¹⁰ and Davis et al.¹¹ Detailed theoretical analysis of the potential model were given by Basch¹⁵ and Schwartz.¹⁶

In practice, line broadening and the small magnitude of the chemical shifts may make the determination of even the oxidation state difficult in some cases. Because of this difficulty in cases of transition metal compounds, the "multiplet splitting" effect can be employed to infer the oxidation state. Multiplet splitting of core electron binding energies¹⁷ is observed in the photoelectron spectra of paramagnetic transition metal compounds. In any atomic or molecular system with unpaired valence electrons, the 3s-3d exchange interaction affects the core electrons differently,

according to the orientation of their spin. This causes the 3s core level to be split into two components. For example, in an Mn^{2+} ion whose ground state configuration is $3d^5 6s$, the two multiplet states will be $7S$ and $5S$. In an Mn^{4+} ion having the ground state configuration $3d^3 4F$, the two spectroscopic states will be $5F$ and $3F$. In the first approximation, the magnitude of the multiplet splittings should be proportional to the number of unpaired 3d electrons. Hence the Mn(3s) splitting will be greatest for Mn^{2+} ions and least for Mn^{4+} .

Because of the low energy of photoelectrons induced by the most commonly used Mg or Al X-rays, the effective escape depth for electron emission without suffering inelastic scattering is small. Recent studies have given electron escape depths of 15 to 40 Å for electron kinetic energies between 1000 and 2000 eV.¹⁸ This renders the ESCA method especially surface sensitive and thus useful in surface chemical studies. Because of the high energy resolution, the electrons which have escaped the solid sample without energy loss are well separated from the lower energy electrons whose energy has been degraded by the inelastic collisions. The chemical shift measurements are performed only on electrons with no energy loss.

III. ESCA AS AN ANALYTICAL TOOL

The principal sources of uncertainty and error in ESCA analyses are related to: 1) electron energy loss processes, 2) electron escape depth variations, 3) binding energy calibration procedures, and 4) sample exposure to vacuum and X-rays during analysis. The first two of these problems may have major repercussions for the determination of concentrations of elements and species in chemically heterogeneous samples. The third problem influences

the validity of the assignment of chemical states through the determination of chemical shifts. Finally, the spectrometer vacuum and heating of the sample by the X-ray source may be the cause of losses of volatile species.

In this section experimental results and conclusions on some of the problems that relate to the analytical application of ESCA will be reviewed. These results deal with different specific objectives which are felt to be equally applicable to the topics of this chapter.

Wagner¹⁹ has determined a table of relative atomic sensitivities which enables the conversion of photoelectron peak intensities to relative atomic concentrations of elements in a sample. Wagner's study, as well as the one by Swingle,²⁰ indicates that ESCA can be used as a semiquantitative ($\leq 50\%$ relative error) or even as a quantitative ($\leq 10\%$ relative error) method when comparing chemically similar samples. Unfortunately, both of the above authors found that the relative photoelectron intensities obtained with chemically dissimilar samples show wide variations. For example, Wagner's¹⁹ data on the Na(1s)/F(1s) intensity ratios (corrected for stoichiometry) for a number of sodium and fluorine containing compounds were found to vary by as much as a factor of 2.

Swingle²⁰ has attributed the observed variations in the apparent sodium and fluorine atomic sensitivities to the differences in the structure of the photoelectron energy loss spectrum. In cases of chemically similar samples, however, the same mechanism should be responsible for inelastic electron scattering.

The effect of the chemical form of an atom on the relative intensity of the photoelectron peak arising from that atom has been studied in detail by Wyatt, Carver, and Hercules.²¹ They have demonstrated that different

lead salts show different atomic sensitivities and have suggested that the escape depth for lead salts depends on the crystalline frame surrounding the lead cation and its coordination number, because the observed differences in sensitivities could not be accounted for by inelastic electron scattering alone. These findings imply that elemental analysis must be done with great caution unless the chemical form of the elements in the sample is well defined.

The bulk sensitivity of ESCA can be estimated at approximately 0.15% based on bulk percentage. Therefore ESCA is not a "trace element" technique in the usual sense. However, because of the possibility of detecting as little as 0.1% of a monolayer²² (about 10^{12} atoms), the absolute sensitivity of ESCA is in the picogram range. Thus ESCA is a unique trace method if the analysis is confined to preferentially surface located species.

The topics discussed so far in this section pertain essentially to the determination of relative concentrations of elements and species. The importance and uniqueness of ESCA, however, are in its capability to measure the chemical shifts which contain implicit information about the molecular forms. The principal difficulty encountered in chemical shift measurements pertains to the calibration procedure used to account for the electrostatic charging of the sample. Hercules and Carver²³ list four basic calibration approaches which have been used. These make use of 1) contamination carbon, 2) admixed species, 3) vapor deposition of noble metals, and 4) sample constituents as internal calibration standards.

IV. APPLICATION OF ESCA TO CHEMICAL ANALYSIS OF PARTICULATES

A. Effect of Sample Composition at Relative Intensities

It is important to assess the usefulness of 1) photoelectron peak intensities for inferring the likely stoichiometry of certain compounds, for example, to distinguish between ammonium sulfate and ammonium bisulfate; and 2) the relative photoelectron peak intensities for determination of relative concentrations of elements and chemical species in particulate matter. Dod et al.²⁴ have investigated the possible effects of the chemical composition and the surrounding matrix on photoelectron peak intensities, using heterogeneous samples that reasonably simulate the situation found in ambient particulates.

The first set of these experiments investigated the constancy of the intensity ratios of S(2p) and N(1s) photoelectron peaks, corrected for stoichiometry, for a number of pure sulfur and nitrogen containing compounds. The mean value for peak intensity ratios of these samples is 1.65 ± 0.21 (1 σ). The results indicate that within an uncertainty of $\pm 15\%$ the photoelectron peak intensities of nitrogen and sulfur reflect the relative abundances of these atoms in compounds.

The second set of experiments²⁴ investigated the effects of matrix dilution on photoelectron peak intensities of nitrogen and sulfur from ammonium bisulfate. Activated carbon, lead chloride, and graphite mixtures were used as the diluent matrix. As before, such mixtures were assumed to simulate the conditions normally found in atmospheric particulates. The results of these dilution experiments demonstrated a constancy in the sulfate to ammonium peak ratio to within $\pm 10\%$, i.e., well within the error limit for peak intensity determination.

Thus, based on these results, it seems justifiable to use relative photoelectron peak intensities to infer the apparent stoichiometry of sulfur and nitrogen containing compounds of the kind commonly associated with air pollution particulates. It will be shown later in the text that photoelectron peak intensities can be used to determine the concentration ratios of certain elements and species.

Before outlining the results for chemical states of sulfur, nitrogen, and carbon species in atmospheric particulates, we shall first justify the use of apparent carbon (1s) binding energy to correct for sample charging. As discussed later in more detail, carbon peaks from atmospheric particulates appear essentially as a single peak with a binding energy corresponding to a neutral charge compatible with condensed hydrocarbons and/or soot-like material. Since carbon is by far the most abundant element in particulates, practically the entire ESCA C(1s) signal is due to the sample itself, rather than to hydrocarbon contamination of the sample in the spectrometer.

In order to test the validity of using the carbonaceous content of a sample as the internal binding energy reference, the apparent binding energies of C(1s) and Pb(4f_{7/2}) from a number of ambient samples collected near a freeway were determined. (The samples were collected in 1972 in the course of the Aerosol Characterization Experiment of the California Air Resources Board.) The results are shown in Figure 1 where these binding

(Figure 1)

energies are plotted against time of day corresponding to sample collections. (The samples were collected for 2 hours on silver membrane filters.) The figure shows that the variations in the carbon and lead peak positions are similar. Assuming that the chemical composition of lead and carbon species

are similar throughout the episode, we can conclude that the binding energy error caused by the use of C(1s) as the reference should not exceed ± 0.25 eV. It appears, therefore, that use of the C(1s) peak binding energy as an internal reference is adequate to determine the chemical states of major species associated with atmospheric particulates.

B. Chemical States of Particulate Sulfur and Nitrogen

The feasibility of using X-ray photoelectron spectroscopy for the chemical characterization of particulates was first explored by Novakov, Wagner, and Otvos.²⁵ These authors have determined the elemental composition of the particulate samples and have found that most of the particulate nitrogen is in the reduced chemical state. The observed nitrogen (1s) photoelectron lines were of complex structure, indicating the presence of several different reduced nitrogen species. The sulfur (2p) peak appeared to have a single component, consistent with sulfate.

A more systematic ESCA study of the chemical states of sulfur and nitrogen as a function of particle size and time of day was performed by Novakov et al.² The particle separation was accomplished by use of a Lundgren cascade impactor. The samples for analysis were collected on Teflon films covering the rotating impactor drums. Two "size cuts," 2.0-0.6 μm and 5.0-2.0 μm , corresponding to the fourth and third impactor stages, were used in this experiment.

The sulfur (2p) spectra indicated the presence of two components which were assigned to sulfate and to sulfite. The 6+ and the 4+ state were present in both size ranges. Their relative abundance changed with particle size and time of day, however.

The ESCA spectra from this study have revealed the presence of four different chemical states of particulate nitrogen: nitrate, ammonium, and two reduced species tentatively assigned to an amino-type and a heterocyclic nitrogen compound. The nitrate was observed only in the larger particle size range but not in the smaller one.

Hulett et al.²⁶ used ESCA for chemical characterization of coal fly ash and smoke particles. These authors have analyzed specimens of smoke particles collected on filter paper from coal burned in a home fireplace, and found three distinct components in the sulfur (2p) peak: a single reduced state assigned to a sulfide and two species of higher oxidation, corresponding to sulfite and sulfate. The sulfur (2p) peak of fly ash particles was also found to consist of two components. These were assigned to sulfates and/or adsorbed SO_3 , since their binding energies were much higher than those for sulfite ions.

Araktingi et al.²⁷ used ESCA to analyze particulates collected in Baton Rouge. A number of elements were identified in this work, the most abundant of which were sulfur, nitrogen, and lead. The N(1s) peak appeared to consist of at least two components with binding energies at about 399.4 and 401.5 eV. The authors did not propose an assignment to these peaks. It would appear, however, that these are similar to the nitrogen peaks identified in Pasadena samples by Novakov et al. The S(2p), according to these authors, was entirely in the form of sulfate.

In summary, these early experiments have demonstrated that there is a considerable variety in the chemical states of sulfur and nitrogen associated with air pollution particulates. For example, particulate sulfur may exist in both oxidized (sulfate, adsorbed SO_3 , and sulfite) and reduced

(sulfide) states, while nitrogen species include nitrate, ammonium, and two other, previously unrecognized, reduced forms. This obviously suggests a more complex situation than the one inferred from wet chemical results, i.e., that the only significant sulfur and nitrogen species are sulfate, nitrate, and ammonium ions.

Craig et al.²⁸ have attempted to formulate an "inventory" of chemical states of particulate sulfur based on their examination of ESCA spectra of more than a hundred samples collected at various sites in California. The samples used in that study were collected both with and without particle size segregation. All samples were collected for 2 hours as a function of time of day. The sulfur spectra of these samples were of varying degrees of complexity, sometimes covering a wide range of binding energies. The binding energies deduced from the analysis of particulate samples were assigned to certain characteristic chemical states with the help of ESCA results obtained with a number of pure compounds and with certain surface species produced by the adsorption of SO_2 and H_2S on several solids.

The chemical states of particulate sulfur identified in the work of Craig et al. are, in terms of the chemical shift, equivalent to adsorbed SO_3 , SO_4^{--} , adsorbed SO_2 , SO_3^{--} , S^0 , and possibly two kinds of S^{--} . The assignment of S^0 as neutral (elemental) sulfur was made because of the similarity of its binding energy to that of elemental sulfur. It is possible, however, that sulfur in species designated by S^0 is actually in the -2 oxidation state. Differences in binding energies between different sulfides are expected because of the differences in the corresponding bond ionicity. Naturally not all of these species did occur at all times and locations. In all instances, sulfates were found to be the dominant species, although

concentrations of other forms of sulfur were at times comparable to the sulfate concentrations.

As we mentioned earlier, ESCA analyses of ambient particulates uncovered the existence of previously unsuspected reduced nitrogen species² whose binding energies are similar to certain amines and/or heterocyclic nitrogen compounds. For simplicity we shall denote these species by N_x . Further studies on the chemical structure of N_x species were performed by Chang and Novakov³ by means of temperature-dependent ESCA measurements. The experimental procedure consisted in measuring ESCA spectra of ambient samples and gradually increasing sample temperatures. The samples were collected on silver membrane filters which could withstand the temperatures used in the experiment.

The results of one such measurement for an ambient particulate sample, collected in Pomona, California, during a moderate smog episode (24 October 1972), are shown in Figure 2. The spectrum taken at a sample temperature

(Figure 2)

of 25°C shows the presence of NO_3^- , NH_4^+ , and N_x . At 80°C the entire nitrate peak is lost, accompanied by a corresponding loss in the ammonium peak intensity. The shaded portion of the ammonium peak in the 25°C spectrum represents the ammonium fraction volatilized between 25 and 80°C. The peak areas of the nitrate and the volatilized ammonium are approximately the same, indicating that the nitrate in this sample is mainly in the form of ammonium nitrate. The ammonium fraction still present at 80°C but absent at 150°C is associated with an ammonium compound more stable than ammonium nitrate, such as ammonium sulfate. At 150°C the only nitrogen species remaining in the sample is N_x . At 250°C the appearance of another peak,

labeled N_x' , is seen. The intensity of this peak continues to increase at 350°C. The total $N_x + N_x'$ peak area at 150, 250, and 350°C remains constant, however, indicating that a part of the N_x is transformed into N_x' as a consequence of heating.

N_x' species will remain in the sample even if its temperature is lowered to 25°C, provided that the sample has remained in vacuum. However, if the sample is taken out of vacuum and exposed to the humidity of the air, N_x' will be transformed into N_x . It was concluded that N_x' species are produced by dehydration of N_x :

Based on the described temperature behavior and on laboratory studies³ of reactions (see below) that produce species identical to those observed in the ambient air particulates, N_x was assigned to a mixture of amines and amides. (N_x photoelectron peaks are broad indications of the presence of more than one single species.) Dehydration of the amide results in the formation of a nitrile, N_x' .

Application of temperature-dependent ESCA measurement^{3,29} also revealed the presence of a hitherto unrecognized form of ammonium characterized by its relatively high volatility in vacuum. Temperature-dependent studies have also indicated that nitrate in ambient samples may occur in a volatile form different from common nitrate salts. Tentatively, such a nitrate is assigned to nitric acid adsorbed on the filter material and/or on the particles.

These conclusions are illustrated with the aid of the spectra shown in Figure 3. The spectrum shown in Figure 3a (collected in 1973 in West Covina, California) has been obtained with the sample at -150°C . The sample was kept at a low temperature in order to prevent volatile losses in the ESCA spectrometer vacuum. It will be shown later that volatilization in vacuum was suspected as one reason for the apparent inconsistency between the ammonium and nitrate determination by ESCA and by wet chemical techniques. Individual peaks corresponding to nitrate, ammonium, and N_x (amines and amides) are clearly seen in the spectrum.

Figure 3b shows the same spectral region of the same sample after its temperature was raised to 25°C . This spectrum shows only a trace of the original nitrate and about a 60% decrease in the ammonium peak intensity. Considering the nitrate and ammonium peak intensity in the lower temperature case, it is estimated that at most about 15% of the total ammonium could be associated with nitrate as NH_4NO_3 . The volatile ammonium component is therefore not ammonium nitrate. Ammonium sulfate and ammonium bisulfate were found to be stable in vacuum at 25°C during time intervals normally used to complete the analysis. Furthermore, since no detectable decrease in the sulfate peak was observed over the same temperature range, it was also concluded that ammonium sulfate (and/or bisulfate) is not being volatilized in the spectrometer vacuum.

The limited volatility of ammonium salts and the behavior of the ambient samples suggest that a major fraction of ammonium in these samples is present in a previously unrecognized form. The volatility properties of nitrate in this and other samples suggest the possibility of the

existence of adsorbed nitric acid in accordance with the wet chemical results of Spicer and Miller.³⁰

ESCA analysis of particulates enables not only the possibility of detection of specific ions and functional groups, but also their mutual relationship. This is achieved by the measurement of the ESCA chemical shift augmented by the determination of relative concentrations and by study of the volatility properties of certain particulate species.

The capability of ESCA for a straightforward differentiation of different forms of atmospheric sulfates was recently demonstrated by Novakov et al.^{31,32} Figure 4 shows the nitrogen (1s) and sulfur (2p) regions in

(Figure 4)

ESCA spectra of two ambient samples. One was collected in West Covina, California, in the summer of 1973, and the other was collected in St. Louis, Missouri, in the summer of 1975. The peak positions corresponding to NH_4^+ , $-\text{NH}_2$, and SO_4^{--} are indicated. The solid vertical bar indicates the ammonium peak intensity expected under the assumption that the entire sulfate is in the form of ammonium sulfate. Obviously, the observed ammonium content in the West Covina sample is insufficient to account for the sulfate by itself. This is in sharp contrast with the St. Louis sample where the observed ammonium intensity closely agrees with that expected for ammonium sulfate.

These results demonstrate that ammonium sulfate in the aerosols can easily be distinguished from other forms of sulfate such as the one found in the West Covina case. However, wet chemical analyses³³ performed on West Covina samples collected simultaneously with the ESCA samples resulted in ammonium concentrations substantially higher than those suggested by the ESCA measurements. As mentioned earlier, this apparent discrepancy

between the two methods was subsequently explained by the volatility of some ammonium species in the ESCA spectrometer vacuum. That these volatile losses are not caused by the volatilization of ammonium sulfate is evidenced by the St. Louis case, where no volatile losses were observed. Similarly, ammonium nitrate (negligible in these samples) and ammonium bisulfate were found to be stable in vacuum during the time periods usually required to complete the analysis. Therefore, species other than these have to be responsible for the apparent loss of ammonium in vacuum.

That the volatile ammonium is not necessarily associated with sulfate or nitrate ions is illustrated by means of results^{31,32} represented in Figure 5. Here the changes in the nitrogen (1s) spectrum of a sample

(Figure 5)

collected in a highway tunnel are shown as a function of the sample vacuum exposure time. Obviously, the ammonium peak intensity decreases with the vacuum exposure time of the sample. The amino-type nitrogen species intensity remains constant, however. The amount of nitrate in this sample was negligible compared with ammonium. The maximum ammonium peak expected under the assumption that the entire sulfate is ammonium sulfate is indicated by the solid vertical bar in Figure 5. It is obvious, therefore, that the counterions for this ammonium are neither nitrate nor sulfate.

Figure 6 summarizes the findings about ammonium volatility in the

(Figure 6)

three samples discussed above. The shaded bars at the far left of the figure indicate the expected ammonium intensity based on the assumption that all of the sulfate in the sample is in the form of ammonium sulfate. It is evident from the figure that only the St. Louis sample contains ammonium

sulfate, while the West Covina and the tunnel samples contain a different kind of ammonium which volatilizes in the spectrometer vacuum.

Novakov et al.^{31,32} have applied this procedure routinely to analyze a number of ambient samples. The results of such measurements for six St. Louis samples are shown in Figure 13 where the ratio of the observed ammonium peak intensity to the peak intensity expected of the ammonium in the form of ammonium sulfate is plotted as a function of the sample vacuum exposure time. From inspection of this figure, it is evident that in addition to the cases of practically stoichiometric ammonium sulfate (samples 913 and 914), there are cases where the observed ammonium is found in excess of ammonium sulfate. The excess ammonium consists of volatile ammonium species which decay away until ammonium sulfate is the only ammonium species left (sample 917).

The anions corresponding to the volatile ammonium species cannot be identified with certainty at this time. One possibility is that these species are produced by the adsorption of ammonia on fine soot particles to form carboxyl- and hydroxyl-ammonium complexes which have been shown to have similar volatility properties to ambient particulates.³ Another possibility is that these species could be due to ammonium halides which are also volatile in vacuum.

In conclusion, ESCA analysis of ambient samples allows for a straightforward differentiation of different forms of atmospheric sulfate and ammonium containing species. The following distinctly different cases have been identified:

- 1) Ammonium sulfate accounts for the entire ammonium and sulfate content of the sample.

2) Ammonium appears in concentrations above those expected for ammonium sulfate (and nitrate). The "excess" ammonium is volatile in vacuum.

3) Ammonium appears mostly in a volatile form independent of sulfate and nitrate.

C. Chemical Characterization of Particulate Carbon

ESCA has also been used in attempts to chemically characterize particulate carbon.³ In most instances the carbon (1s) peak of ambient particulates appears essentially as a single peak with a binding energy compatible with either "elemental" carbon or condensed hydrocarbons or both. As seen in Figure 7, where the carbon (1s) spectrum of an ambient

(Figure 7)

air particulate sample is shown, chemically shifted carbon peaks, due to oxygen bonding, are of low intensity compared with the intense neutral chemical state peak.

From the standpoint of air pollution, it is important to distinguish the volatile hydrocarbon type (mostly secondary species) carbon from the mostly nonvolatile soot-like (primary species) carbon.

Chang and Novakov³ have attempted to distinguish these species by comparing the carbon (1s) peak obtained with the sample at 25°C to the carbon (1s) peak with the sample at 350°C. The difference between the low-temperature and the high-temperature runs should give the fraction of volatile carbon. Figure 7 shows the result of one such experiment for a sample collected in 1975 from West Covina. This experiment suggests that most of the ambient particulate carbon is nonvolatile in vacuum at 350°C.

Assuming that the secondary hydrocarbons will have a substantial vapor pressure at 350°C, the authors have suggested that a substantial fraction of the total particulate carbon is of a primary (soot-like) nature. The conclusion about a high nonvolatile carbon content could be erroneous if a large fraction of particulate carbon volatilizes even at 25°C in vacuum. This seems unlikely, however, because reasonably good agreement has been found between the total carbon concentration as measured by ESCA and a combustion technique²⁹ (see below).

D. Chemical States of Trace Metals in Particulates

The application of chemical shift measurements to the chemical characterization of metals has encountered difficulties because of the small differences in binding energies between different metal compounds. Chemical characterization of particulate lead species was attempted by Araktingi et al.²⁷ These authors have attempted to determine the relative abundance of lead oxide and lead halide in samples collected in Baton Rouge, Louisiana. Because of the small chemical shift between oxide and halide, the two suspected components could not be resolved, however.

Harker et al.³⁴ used ESCA to determine the chemical state of manganese in particulate emissions from a jet turbine combustion burning 2-methyl cyclopentadiene, manganese tricarbonyl (MMT) as jet fuel additive. The oxidation state assignment was made by examining the multiplet splitting of the (3s) core level in the exhaust sample and some manganese compounds. In addition to oxides, MnF_2 was also studied since it is the most ionic compound of divalent manganese, and therefore its Mn^{2+} ion should exhibit the largest possible (3s) splitting.

In Figure 8 comparative (3s) spectra for MnF_2 , exhaust particulates, (Figure 8)

and MnO_2 are shown. Based on the magnitude of the splitting, it is concluded that the oxidation state of the manganese in the combustor exhaust is +2 as MnO . Other +2 manganese compounds are eliminated by the fact that oxygen is the only negatively charged species present in sufficient concentrations to balance the manganese.

E. Intercomparison of ESCA with Other Analytical Methods

An intermethod comparison of ESCA with analytical methods of proven accuracy and precision was undertaken by Appel et al.²⁹ in order to validate the quantitative aspects of ESCA analysis. This work focused on validation of sulfate, nitrate, ammonium, and carbon data as obtained by ESCA in a program to characterize ambient California particulates.

Samples for this study²⁹ were collected on 47-mm Gelman GA-1 cellulose acetate filters for sulfate analysis and on 47-mm, 1.2 μm pore size silver membrane filters for carbon and nitrogen species analysis. Two-hour samples were collected in addition to 24-hour high-volume (Whatman 41) filters.

ESCA analyses were conducted only on the membrane filters while, depending on sensitivity, wet chemical methods employed either the 2-hour or 24-hour high-volume filters. Direct comparisons involved analyses of sections from the same filters, while indirect comparison required comparison of calculated 24-hour average values from ESCA analysis of twelve 2-hour filters with the wet chemical analysis of the high-volume filter.

Three wet chemical methods²⁹ were used:

- 1) Stanford Research Institute (SRI) used a microchemical method, which measures total water-soluble sulfur, to analyze 2-hour filters.

2) Barium chloride turbidimetric analysis was used to analyze water-soluble sulfate in high-volume samples.

3) Air and Industrial Hygiene Laboratory (AIHL), California State Department of Health, uses a method for 2-hour samples which employs an excess of a barium-dye complex in acetonitrile-water solution. A decrease in absorbance due to the formation of barium sulfate is measured.

ESCA analysis included the determination of relative concentrations of sulfate and lead from the measured peak areas corrected for elemental sensitivity. Relative concentrations were converted to $\mu\text{g}/\text{m}^3$ of sulfate by normalization to lead concentrations (in $\mu\text{g}/\text{m}^3$) which were determined by XRF analysis.³⁵

Table I lists the results of the comparisons of ESCA sulfate determinations with those by the SRI and AIHL methods and by the BaCl_2 turbidimetric method. The ratio of means between wet chemical methods and ESCA varies from 0.5 to 1.0. It was concluded that ESCA provides sulfate analyses which are correct within a factor of 2. A qualitative indication of the precision of ESCA results is obtained by comparing the diurnal patterns for sulfate determined both by ESCA and by alternate procedures.

Figure 9 shows sulfate diurnal patterns as measured by ESCA and by

(Figure 9)

the SRI method. The data are for a 24-hour sampling period during a moderate smog episode in Pomona, California. ESCA and SRI procedures yield strikingly similar diurnal patterns suggesting a sufficient precision for the ESCA method.

More recently, Harker³⁶ compared the results of ESCA sulfate analysis to the results obtained by XRF and a wet chemical method. A number of 4-hr samples were collected in the Los Angeles area of fluoropore filters. The

results of Harker's study are shown in Figure 10 and 11. These results

(Figure 10)

(Figure 11)

obviously prove that the ESCA technique can give a good representation of the bulk composition of atmospheric particulates in spite of its surface sensitivity.

Carbon analysis by ESCA has also been validated, and the results are described in the above-mentioned paper by Appel.²⁹ Twenty-nine samples collected on silver membrane filters were analyzed for total carbon, both by ESCA and by a combustion technique. A mean ratio of 0.9 ± 0.1 was found between the combustion method and ESCA, suggesting that average carbon analyses are reasonably accurate.

The results of ESCA analyses for nitrate were also compared with the results of wet chemical procedures conducted on the same filters and on 24-hour filters.²⁹ With nitrate, using both comparative wet chemical techniques, the ESCA results were lower by a factor of about 5. This result is consistent with the volatilization of adsorbed nitric acid, as discussed above.

Similarly, ESCA analyses systematically underestimate the ammonium concentrations. The reasons for this discrepancy are related to the volatility of certain ammonium species in vacuum.

V. CONCLUSIONS

X-ray photoelectron spectroscopy is a viable analytical tool for the chemical characterization of atmospheric particulates. Analysis by this method is nondestructive and requires no sample preparation. The only requirement for the sampling substrate material (filters or other collection media) is that it cannot contain the same elements as those found in the particulates.

Ample experimental evidence suggests the justification of using relative photoelectron peak intensities to infer the apparent stoichiometry of certain molecular species commonly associated with particulate matter.

Determination of chemical shifts, together with information concerning stoichiometry and volatility, allow for a complete characterization of the principal sulfur and nitrogen containing compounds. Multiplet splitting, to determine the oxidation state of certain transition metals, can be used in cases where the chemical shift by itself does not appear to be sensitive enough.

Use of X-ray photoelectron spectroscopy has led to a better understanding of the chemical composition of atmospheric particulates; this is illustrated by the following observation and results:

- 1) Particulate sulfur may exist in a variety of chemical states, under certain atmospheric conditions.
- 2) Substantial concentrations of previously unsuspected reduced particulate nitrogen species of the amine, amide, and nitrile type have been identified.
- 3) Ammonium species associated with anions other than sulfate and nitrate have been identified.

4) Much of the particulate nitrate may be present in the form of adsorbed nitric acid.

5) The relative surface concentrations of sulfate, lead, and particulate carbon are similar to their bulk concentration.

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Table I. Comparison of sulfate data, ESCA vs wet chemistry.^a

$\mu\text{g}/\text{m}^3$ sulfate				
		ESCA Cellulose ester filters vs $\bar{x}$ 2-hour low volume	Wet chemistry Whatman 41 24-hour high volume	
Site	Date	High vol. wet chemistry	$\bar{x}$ 2-hr low vol. ESCA	High vol./ $\bar{x}$ 2-hr low vol.
San Jose	8-17-72	1.6 $\pm$ 0.4	1.1 $\pm$ 0.2	1.5 $\pm$ 0.5
San Jose	8-21-72	1.0 $\pm$ 0.2	1.4 $\pm$ 0.3	0.7 $\pm$ 0.2
Fresno	8-31-72	4.2 $\pm$ 1.0	4.0 $\pm$ 1.1	1.1 $\pm$ 0.4
Riverside	9-19-72	5.9 $\pm$ 1.5	6.4 $\pm$ 4.6	0.9 $\pm$ 0.7
Ratio of means = 1.0				
Spearman's ρ = 0.80				
Linear regression slope = 1.0				
(intercept $\equiv$ 0)				

^aFrom Ref. 29.

FIGURE CAPTIONS

Figure 1. Apparent binding energies (not corrected for sample charging) of carbon (1s) and lead ($4f_{7/2}$) photoelectrons from a number of 2-hour samples collected near a freeway. The apparent binding energies are plotted against time of day corresponding to sample collection.

Figure 2. Nitrogen (1s) photoelectron spectrum of an ambient sample as measured at 25, 80, 150, 250, and 350°C (from Ref. 3).

Figure 3. a) Nitrogen (1s) photoelectron spectrum of an ambient sample as measured at -150°C.

b) The spectrum of the same sample as measured at 25°C (from Ref. 3).

Figure 4. Nitrogen (1s) and sulfur (2p) regions in X-ray photoelectron spectra of two ambient samples. The peak positions corresponding to NH_4^+ , $-\text{NH}_2$ (N_x), and SO_4^{--} are indicated. The solid vertical bar represents the ammonium intensity expected under the assumption that the entire sulfate is in the form of ammonium sulfate. The difference in the relative ammonium content of the two samples is obvious. The sulfate and ammonium intensities in the St. Louis sample are compatible with ammonium sulfate. The ammonium content in the West Covina sample is insufficient to be compatible with ammonium sulfate. Both samples were exposed to the spectrometer vacuum for about one hour (from Ref. 32).

Figure 5. The variation in the observed ammonium peak intensity with vacuum exposure for a sample collected in a highway tunnel. The decrease in the peak intensity is caused by the volatilization of the ammonium species present in the sample. The solid vertical bar

represents the ammonium intensity expected under the assumption that the sulfate in this sample is in the form of ammonium sulfate. The nitrate in this sample is also small compared to ammonium. The ammonium in this sample is considerably in excess of that expected for ammonium sulfate or ammonium nitrate (from Ref. 32).

Figure 6. Volatility properties of West Covina, St. Louis, and automotive ammonium aerosol. The shaded bars on the far left of the figure indicate the expected ammonium intensity if the entire sulfate were ammonium sulfate (from Ref. 32).

Figure 7. Carbon (1s) photoelectron spectrum of an ambient sample as measured at 25 and 350°C. The shaded area represents the difference between low and high temperature spectra. The apparent volatile losses are mainly confined to the chemically shifted component of the carbon peak (from Ref. 3).

Figure 8. Manganese (3s) spectra of MnF_2 , exhaust particles, and MnO_2 showing the multiplet splitting of the 3s core level (from Ref. 34).

Figure 9. Diurnal variations of sulfate as measured by ESCA and by a wet chemical method (SRI). The data are for a 24-hour sampling period during a smog episode in southern California (from Ref. 29).

Figure 10. Comparison of quantitative particulate sulfate analyses by ESCA and X-ray fluorescence spectroscopy (from Ref. 36).

Figure 11. Comparison of quantitative particulate sulfate analyses by ESCA and a colorimetric wet chemical procedure (from Ref. 36).

XBL7610-4092

Figure 1

XBL746-3532

Figure 2

XBL745-3183

Figure 3

Figure 4

00004500594

XBL 763 2537

Figure 5

XBL 763-2536

Figure 6

XBL 745-3308

Figure 7

XBL 767-8541

Figure 8

XBL7310-4278

Figure 9

XBL 769-4834

Figure 10

0 0 0 0 4 5 0 8 5 9 6

45

LBL-5290

XBL 769-4835

Figure 11

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