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DETERMINATION OF THE CHEMICAL STATES OF SULFUR IN AMBIENT POLLUTION AEROSOLS BY X-RAY PHOTOELECTRON SPECTROSCOPY*

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Abstract:

The chemical states of sulfur present in ambient particulate matter have been identified by use of x-ray photoelectron spectroscopy (XPS-ESCA). Seven separate chemical species of sulfur were found in atmospheric samples taken in California. These are SO_3, $SO_4^{=}$, SO_2, $SO_3^{=}$, S^o and two kinds of sulfides. Sulfates were found to be the dominant species, although reduced forms of sulfur were at times comparable to the sulfate concentrations.

I. Introduction

It has been established that sulfur compounds, gaseous and suspended, are directly involved in the formation of atmospheric aerosols (Bufalini, 1971). The suspended sulfur compounds are known to be associated with particles having a diameter less than 2μm, which are primarily responsible for the reduction of visibility because of light scattering (NAPCA, 1969). This size range also puts the sulfur compounds in the respirable fraction of ambient aerosols. These factors point out the importance of further studies

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into the mechanisms of formation and the behavior of these suspended sulfur compounds in pollution aerosols.

Most studies have determined only the sulfate content of ambient aerosols, with use of conventional wet chemical techniques (see for example Wagman et al, 1967). This has been the case since it is believed that the major reactions of sulfur dioxide in the atmosphere led to the formation of suspended sulfates. As the first step in a more comprehensive project dealing with heterogeneous atmospheric chemistry, we have undertaken a study whose aim is to establish a complete inventory of the sulfur compounds present in ambient particulate matter. This project was carried out through the study of a large number of pollution particulate samples using x-ray photoelectron spectroscopy as the analytical tool. Formulating such an "inventory" of ambient chemical species is a prerequisite for gaining an understanding of the atmospheric transformations of sulfur-containing compounds.

The method of x-ray photoelectron spectroscopy, also known as XPS and ESCA, has been shown to be a convenient and useful technique for the determination of chemical states of atoms in molecules (see Hollander and Jolly, 1970 and references therein). It has also been demonstrated that this method has a potentially significant application to the chemical characterization of pollution aerosols. For example, Novakov et al. (1972) have applied this method for the determination of lead and the determination of the chemical states of sulfur and nitrogen in smog particles as a function of particle size and time of day. Two oxidized states of sulfur were identified in their work; the more oxidized form was assigned to the sulfate species, while it was suggested that the other corresponds to an oxidation state of 4^+, i.e. sulfite or adsorbed sulfur dioxide.

Hulett et al. (1971) used XPS to study sulfur compounds in fly ash and smoke particles. They reported three chemical states of sulfur present on coal smoke particles. These included a single reduced state, which was assigned to hydrogen sulfide or a mercaptan, and two species in higher oxidation states corresponding to sulfate and sulfite. The sulfur in the fly ash was tentatively identified as a sulfate.

In the course of our work on the electron spectroscopy of ambient aerosols we have carefully examined the spectra of more than a hundred samples containing different particle size classes, collected at various sites in California at different times of day. (The aerosol samples were collected during the ARB sponsored study of the Aerosol Characterization summer 1972.) The sulfur XPS spectra were of varying degrees of complexity, sometimes covering the entire range of known sulphur binding energies. In this paper we describe how individual binding energies, characteristic of definite sulfur species, were determined by a comparative study of a large number of specimens. These binding energies are assigned to characteristic chemical states, with the help of XPS results obtained with a number of simple sulfur compounds and with SO_2 and H_2S adsorbed on various solids. It is shown that the ambient particulate-sulfur spectra can be explained in terms of $SO_4^=$, $SO_3^=$ and $S^=$ ions, neutral sulfur, and surface bonded SO_2 and SO_3. Thanks to the measurable differences in binding energies between the bulk-type ions and the surface species, these can be distinguished in favorable cases.

II. Experimental Technique

Extensive reviews of x-ray photoelectron spectroscopy have been given

in the literature and therefore only a brief description of the method will be given here. XPS consists of the measurement of 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 $E_{kin} = h\nu - Ei$ where $h\nu$ is the x-ray photon energy and E_b is the binding 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, which is the main observable in this type of spectroscopy.

The electron binding energies are characteristic for each element, which enables the method to be used for elemental analysis. The binding energies are not, however, absolutely constant, but they are modified by the valence electron distribution, so that the binding energy of an electron subshell in a given atom varies when the atom is in different chemical environments. These differences in the electron binding energies are known as the "chemical shift".

In the early stages of photoelectron spectroscopy it was realized that the chemical shifts can be related to the oxidation state of the element studied. Subsequent studies have shown that the electron binding energy shifts are correlated to a high degree with the effective charge which the atom possess in the molecules. Therein lies the usefulness of chemical shifts in the analysis of unknown molecular structures. The chemical shift can be adequately described by using a simple electrostatic model in which the charges are idealized as point charges on atoms in a molecule (Lindberg et al. 1970) and the electron binding-energy shift relative to the neutral atom is equal to the change in the electrostatic potential, as experienced by the atomic core under consideration, resulting from all charges in the molecule. This model predicts a practically linear relationship between the binding

energy shift and the effective charge. In short, the binding energies will be greater than the ones for the neutral configuration for positive effective charges, i.e. for oxidized species. Similarly the binding energies will show a negative shift for reduced species.

Good correlations between the estimated charges, based on the electrostatic model, and measured binding energy shifts have been obtained for a large number of sulfur compounds (Lindberg et al. 1970). The existence of this type of theoretical and experimental background facilitates our task in identifying the sulfur species in the ambient aerosol.

All measurements reported in this paper have been made with an AEI ES200 procedure for analyzing the systematic occurrence of peaks at certain binding energies.

Let us examine in more detail the individual spectra in Figure 1. Spectrum I consists of a single, well defined peak occurring at a binding energy of 169.2 eV. This peak is easily recognizable in all spectra (I through VII). This peak is denoted by A in Figure 1 and is assigned to the sulfate ion (see below). Spectrum II reveals an additional peak at a binding energy higher than that of the sulfate, which we denote as B. This peak must correspond to a sulfur species with a higher positive effective charge than that in $SO_4^=$ ion. Peak B is also apparent in spectra V and VII. Spectrum III shows the existence of a component at a binding energy of 168.1 eV which is marked C and which is also seen in spectra VI and VII. An indication of the presence of a component (D) at a binding energy of about 167 eV is found in spectrum VII: namely, if the high binding energy group consisted only of peaks A, B and C, then one would expect a much more pronounced valley between this group and the low binding energy group, centered around 162 eV. We tentatively place component D at 167 eV.

Components A, B, C and D represent various oxidized forms of sulfur seen in ambient aerosol samples. In addition the occurrence of reduced sulfur species is seen in spectra V, VI and VII. By way of contrast we refer to spectrum IV, in which no trace of reduced sulfur is visible. Peak E with a binding energy of 164.2 eV is clearly seen in spectra V and VII. The same peak is only partially resolved in spectrum VII, where in addition two states, even more reduced, are evident. These are marked by F and G. Altogether we can distinguish at least seven different states of sulfur (four oxidized and three reduced) in the ambient aerosol specimens.

In order to assign these individual sulfur 2p binding energies we have determined the sulfur binding energies of several common sulfur compounds, by using the same spectrometer and the same experimental procedure used for the ambient samples. The sulfur 2p binding energies of Na_2SO_4, Na_2SO_3 and ZnS, for example, were found to be 169.0, 167.0 and 162.2 eV respectively. These values are indicated in Figure 1 together with the literature value for elemental sulfur. Obviously these binding energy values correspond closely to the peaks A, D, E and F of the ambient spectra, which we therefore assign to $SO_4^{=}$, $SO_3^{=}$, S^o and $S^{=}$ respectively.

Let us now turn to the assignment of peaks C and B. As a result of our measurements of SO_2 sorption on metal oxides (Siekhaus et al. 1973) these are assigned to SO_2- and SO_3-type surface species respectively. One feature of the sorption data is shown in Figure 2. Here in the upper part of the figure we show the sulfur 2p spectrum of MgO exposed to SO_2 measured at room temperature immediately after insertion of the sample in the spectrometer. The other spectra in Figure 2 are of the same sample measured subsequently at elevated temperatures. Three binding energies are revealed:

171.0, 169.7 and 167.9. The peak seen at a binding energy of 169.7 is that of the sulfate. Its intensity stays constant upon heating. In contrast, the intensities of the other two peaks decrease markedly with temperature, indicating that they represent loosely bound surface species. The binding energy of one of them is consistent with the published value of 168.3 eV (Lindberg et al. 1970) of presumably frozen SO_2. The other desorbable peak appearing at about 3 eV higher binding energy (hence higher positive charge) probably corresponds to a surface species of the SO_3 type. The binding energies of these two surface species are indicated in Figure 1, from which it can be seen that they correspond well with peaks C and B in the ambient spectra.

In some ambient spectra, like the one in Figure 1-VII, an indication is found for the existence of a sulfur form (peak G) possessing a more negative charge than that of the common metal sulfides such as ZnS. It is of interest to note that H_2S adsorbed on CaO for example, probably producing calcium sulfide, yielded a sulfur binding energy about 1 eV lower than ZnS. Shifts between different sulfides can be expected because of the corresponding differences in electronegativities. We are therefore inclined to assign peak G of the ambient spectra to an extremely negative sulfidic sulfur involving cations with lowest electronegativity. The results described here are also presented in tabular form in Table I.

IV. Discussion

In the preceeding section we have described how seven distinctly different chemical species of sulfur were identified in pollution aerosols (sampled in the San Francisco and Los Angeles areas), by using the technique of x-ray photoelectron spectroscopy. These are SO_3, $SO_4^{=}$, SO_2, $SO_3^{=}$, S^0 and two kinds of

$S^{=}$. Naturally not all of these seven species occur generally at all times and at all locations. In most instances, sulfates are found to be the dominant species, although concentrations of reduced forms of sulfur were at times comparable to the sulfate concentrations.

From these results stem several implications of significance to both analytical and physical aerosol chemistry. For example, finding that sulfur species other than sulfates are often present in significant quantities makes it necessary to reexamine certain analytical methods for sulfate determination. Some of these methods implicitly presume that the sulfates are the only sulfur compounds present in the aerosol samples. Methods based on the reduction of sulfates to H_2S are in this category.

It is therefore desirable to account separately for sulfates and non-sulfates. Our experiments indicate that XPS provides a practical way to accomplish this objective. Care has to be taken, however, in interpreting the relative concentrations determined by XPS because of the semisurface nature of the method: the photoelectrons detected by XPS have an escape depth of only several tens of Ångstroms for solid samples. The majority of atoms are not, however, in the outermost layer and therefore it is important to perform bulk analysis in addition to examining the surface, as a check on the method. We are presently carrying out a separate study of the quantitative analytical aspects of XPS, the results of which will be published elsewhere.

This inventory of chemical species of sulfur in atmospheric aerosols provides an empirical picture of the "real world" which theoretical and laboratory models must recognize. One obvious question is, for example: can this variety of species be explained by the interactions of a few input gases such as SO_2 and H_2S with other constituents of the polluted atmosphere?

Finally, it is significant to learn that surface SO_2 and SO_3 can be distinguished from their counterpart ions $SO_3^{=}$ and $SO_4^{=}$, in spite of the fact that both pairs are in 4+ and 6+ oxidation states respectively. We are currently pursuing the possibility of applying this feature of XPS to the study of surface interactions of SO_2 with both ambient and laboratory aerosols.

Acknowledgments

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TABLE I.

Sulfur 2p Binding Energies

Ambient aerosol samples		Surface species produced by SO_2 and H_2S adsorption			Sulfur Compounds	
Peak Assignment	Binding Energy (eV)	Species Designation	Binding Energy (eV)	System	Compound	Binding Energy (eV)
"A" sulfate	169.2 ± 0.2	$SO_4^{=}$	169.7 ± 0.2	$MgO+SO_2$	Na_2SO_4	169.0 ± 0.3
"B" SO_3	170.6 ± 0.3	SO_3	171.0 ± 0.3	$MgO+SO_2$		
"C" SO_2	168.1 ± 0.3	SO_2	167.9 ± 0.3	$MgO+SO_2$		
"D" sulfite	≈ 167				Na_2SO_3	167.0 ± 0.3
"E" elem. S	164.2 ± 0.3				S	164.2 (Lindberg 1970)
"F" sulfide	162.6 ± 0.3				ZnS	162.2 ± 0.3
"G" sulfide	160.5 ± 0.6	$S^{=}$	161.0 ± 0.3	$CaO+H_2S$		

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Figure Captions

Figure 1. Sulfur 2p photoelectron spectra of ambient pollution-aerosol samples. The samples were collected at various locations in California. The spectra are arranged in order of increasing complexity. Sulfur 2p binding energies derived from ambient spectra are indicated together with sulfur 2p binding energies of some simple compounds and sulfur species produced by adsorption of SO_2 on MgO and H_2S on CaO. The binding energies of ambient samples are assigned to SO_3, $SO_4^{=}$, SO_2, $SO_3^{=}$, S^o and two kinds of $S^{=}$ ions.

Figure 2. Sulfur 2p spectrum of MgO exposed to SO_2 measured at room temperature, immediately after insertion of the sample in the spectrometer (upper part of figure). The other two spectra are of the same sample measured at elevated temperatures. The sulfate peak intensity remains constant upon heating, while the intensities of SO_3 and SO_2 peaks decrease markedly with temperature.

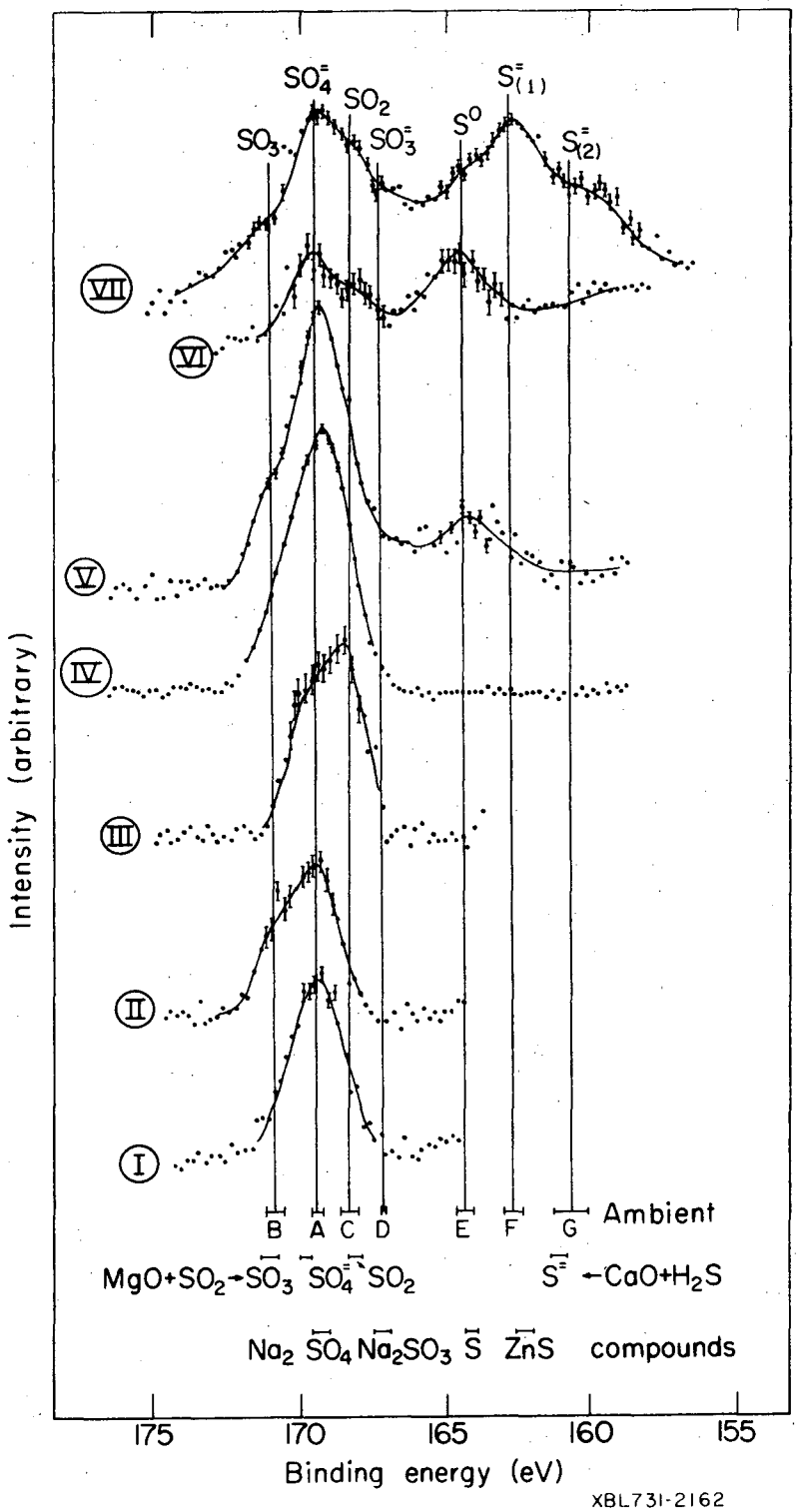
SO4=
SO2
S=(1)
SO3
SO3=
S0
S=(2)
VII
VI
V
IV
III
II
I
Intensity (arbitrary)
B A C D E F G
Ambient
MgO+SO2→SO3 SO4= SO2
S= ←CaO+H2S
Na2 SO4 Na2SO3 S ZnS compounds
175
170
165
160
155
Binding energy (eV)
XBL731-2162

Fig. 1

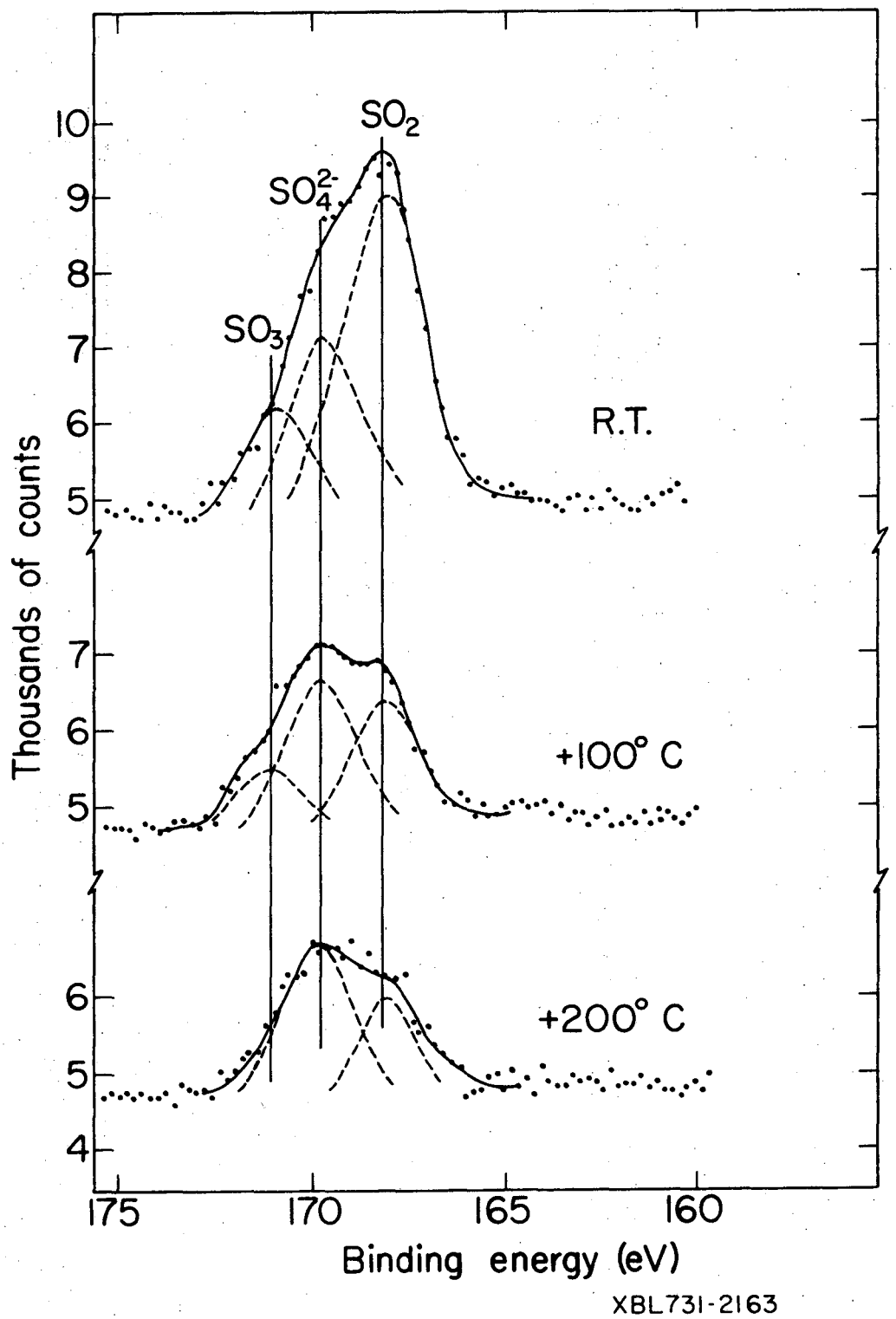
SO2
SO4 2-
SO3
R.T.
+100° C
+200° C
Thousands of counts
10
9
8
7
6
5
7
6
5
6
5
4
175
170
165
160
Binding energy (eV)
XBL731-2163

Fig. 2

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