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Presented at the 76th National
AICHE Meeting, Tulsa, Oklahoma,
March 10-13, 1974.

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April 1974

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

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LBL-2693

Paper presented at the 76th National AICHE Meeting, Tulsa, Oklahoma, March 1974. Session on Applications of Surface Science and Technology in Air Pollution Control. To be published in AICHE Symposium series.

CATALYTIC OXIDATION OF SO_2 ON CARBON PARTICLES*

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April 1974

*Work supported by the National Science Foundation-RANN and the United States Atomic Energy Commission.

ABSTRACT

This paper discusses the role of finely divided, high surface area soot particles in the oxidation of SO_2 to sulfate. It is found that these particles are efficient and from the air pollution standpoint realistic catalyst for SO_2 oxidation. The proposed oxidation mechanism is based on X-ray photoelectron spectroscopic (ESCA) measurements of ambient pollution particulates, on ESCA studies of SO_2 adsorption on activated charcoal, graphite and on propane soot particles.

I. INTRODUCTION

Sulfates in pollution aerosols have been the subject of considerable interest, because they are associated with particles that are most effective in scattering visible light, and more importantly because they are detrimental to health. Much of the past research, in laboratory and in field conditions, has centered on the formation of sulfuric acid droplets and suspended ammonium sulfate $(NH_4)_2 SO_4$ (1-4) particles, through photochemical and solution chemical reactions of gaseous SO_2.

Recent field studies in California (5) have shown, however, that these two mechanisms alone cannot adequately account for the observations (6). This could be an indication that some heterogeneous catalytic mechanism, involving gas-particle interactions, is involved in the oxidation of SO_2. The question of just what is the actual catalyst was left open, however.

Our studies of ambient aerosol samples from certain urban locations in California (7) have shown that (in these samples) liquid H_2SO_4 and $(NH_4)_2 SO_4$ are not the dominant sulfate form. We have also observed correlations between the diurnal patterns of sulfate and particulate carbon, indicating the need for investigation of heterogeneous non-photochemical, sulfate forming reactions involving carbon particules, which constitutes about 50% of the total particulate emissions in urban atmospheres (8). In this paper we propose such a mechanism, according to which pollution particulate sulfates are formed catalytically on carbon particles. This is concluded from experiments dealing with: chemical characterization

of ambient aerosols and with chemisorptive formation of sulfates on carbon particles.

II. EXPERIMENTAL TECHNIQUE

Extensive reviews of X-ray photoelectron spectroscopy have been given in the literature (9) and therefore only a brief description of the method will be given here. ESCA or XPS is the study 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 $E_{kin} = h\nu - E_i$ 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 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.

Because of the low energy of photoelectrons produced by Mg or Al Kα x-rays, which are most commonly used as photon sources, the effective escape depth for their emission without suffering inelastic scattering is small. Recent studies (10) have given an electron escape depth of 15 - 40 Å for electron kinetic energies between 1000 and 2000 eV. This renders the ESCA method especially sensitive to the surface conditions of solids and thus the technique is useful in the study of catalysis.

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 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 compounds. The existence of this type of theoretical and experimental background facilitates our task in identifying the species in aerosols.

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

III. RESULTS

III. 1. Ambient Studies.

The ambient aerosol particles discussed here were sampled on September 19 and 20, 1972 near the Harbor Freeway in Los Angeles (5) ard are representative of an urban atmosphere with primary automotive and other anthropogenic pollutants, with reduced local visibility, but with low photochemical oxidant and low relative humidity levels.

The dominant elements in these particles are carbon, lead, nitrogen and sulfur. The measurements were made on 2 hr. total filters (TF), without particle-size segregation, and on 2 hr. after filters (AF) at a Lundgren impactor, containing mainly submicron particles. Concentrations were derived by normalization of ESCA results to the lead concentrations determined by X-ray Fluorescence (11). Carbon concentrations are the averages of determinations by ESCA and by a combustion technique (12). The diurnal concentration variations of sulfate (7) (TF and AF), carbon (TF) and lead (TF and AF), obtained from a set of 2 x 12 filters covering a 24 hour period are shown in Figure 1a. An examination of Figure 1a shows that: a) there is a similarity between the patterns of sulfate and of carbon, while the lead pattern shows a different trend; b) changes in both sulfate and carbon concentrations are related to the wind direction, indicating sulfate and carbon sources that are both to some extent spatially localized; c) the difference between TF and AF sulfate trends can be explained by the influx of predominantly larger particles carried by the changed wind direction; and d) because of the changing wind direction the contribution of the

Harbor Freeway is not the only significant factor in this episode.

Two alternative mechanisms can be invoked to explain the similarity between the diurnal variations of sulfate and carbon. Either there esists a "chemical" link between sulfate and carbon particles, or these are carried separately and noninteractively in the same air mass. In the latter case the sulfates, produced by photochemical and solution chemical processes, would be mainly in the form of H_2SO_4 or $(NH_4)_2\ SO_4$ if the ambient ammonia concentrations are high enough.

ESCA measurements indicate that the sulfates, in this episode, do not occur primarily as $(NH_4)_2SO_4$ (7). Figure 1b shows the nitrogen (1s) and sulfur (2p) ESCA spectrum of a sample of pure $(NH_4)_2SO_4$. Figure 1c shows the same spectral region for an ambient filter (TF 1200 PST). If all of the sulfate were present as ammonium sulfate, the corresponding nitrogen peak would appear as indicated by the dashed line in Figure 1c. The ammonium content in this, and other samples of the episode, is too low to account for the entire sulfate content. The dominant nitrogen peak corresponds to a species, seen in all the spectra of ambient samples, which possesses a more negative charge than that of ammonium nitrogen (13). ESCA Spectrum of an overnight TF sample collected in Berkeley (primary pollutants during the summer fog season is seen in Figure 1d. Even in this situation of high humidity, which should enhance the

formation of $(NH_4)_2SO_4$, there is not sufficient ammonium present to account for all the sulfate. It appears instead that the ammonium is associated with nitrate in the ration 1:1, as in NH_4NO_3 (Fig. 1e). ESCA measurements at elevated temperature indicate a sulfate form less volatile than liquid H_2SO_4.

III. 2. Catalytic Oxidation of SO_2 on Carbon

Because of the outlined results and because our ESCA measurements on ambient samples at elevated temperatures have shown that up to 80% of the ambient particulate carbon is non-volatile, probably in bulk elemental form, we have performed SO_2 adsorption measurements on activated charcoal, graphite and propane soot particles representing different forms of elemental carbon.

In Figure 1f, a representative sulfur (2p) ESCA spectrum is shown of activated charcoal exposed to SO_2 (at STP). These data (7) show that most of the sulfur remaining on the charcoal surface, after gaseous SO_2 has been pumped away, is in sulfate form. In some experiments, a small amount of reduced sulfur was also seen.

When clean graphite (that is, showing no trace of oxygen) was exposed to about 10^{-6} torr-sec SO_2, the ESCA spectrum after this treatment revealed only a reduced sulfur species. On the other hand, if the graphite surface was initially oxygenated and subsequently exposed to SO_2, under similar conditions sulfate formation occurred. (7). The oxidation (or oxygenation) was achieved by in situ exposure of a hot graphite surface to water vapor or by cutting the crystal in air to expose the fresh surface

to oxygen and moisture.

The interaction of SO_2 with graphite particles was also studied with the setup shown in Figure 2, which produces small, fresh surface graphite particles (diameters ≈ 20, μm). These particles can be collected on a filter after they have interacted with SO_2. ESCA spectrum of graphite particles exposed to SO_2 reveals two sulfur (2p) peaks corresponding to sulfate (binding energy of 168.4 eV) and to sulfide. Blank filters without graphite particles, under identical SO_2 exposure conditions, do not produce measureable amounts of sulfate (or sulfide). These experiments show that even graphite particles in air are oxidizing SO_2 to sulfate analogously to activated carbon.

The equivalency of soot particles to graphite with respect to SO_2 oxidation is demonstrated by the following experiment. Soot specimens from a premixed propane-oxygen flame were prepared on (silver membrane) filters. In order to assure the equivalency of soot substrates to be used for experiments with different SO_2 exposure conditions, small sections of each filter were cut and used in the apparatus shown in Figure 3. Dry and prehumidified particle free air or nitrogen was used with SO_2 concentration of about 300ppm and an exposure time of 5 minutes. The entire chamber was kept at about 150°C to prevent water condensation. Typical ESCA spectra of SO_2 exposed soot samples are shown in Figure 3. Sulfate peaks were found to be always more intense in the case of prehumidified air, than in the case of dry air. Blank filters without soot particles exposed to SO_2 and prehumidified air under identical conditions showed at most only low, background level

sulfate peaks. Dry and prehumidified nitrogen, when used instead of air, produced identical but very low levels of sulfate. This indicates that in addition to soot particles the oxygen in air is importnat for SO_2 oxidation. Water molecules enhance the observed sulfate concentration in the air + SO_2 + soot system. The only possible competing mechanism of relevance to the described experiment is SO_2 oxidation via dissolved molecular oxygen in water droplets. This alternative is ruled out by the experiment with blank filter and prehumidified air, which does not result in significant sulfate formation. Furthermore, the elevated temperature prevents the formation of liquid water droplets.

For a constant relative humidity and SO_2 exposure the sulfate yield (measured as the sulfate S to C ratio) is within the experimental error proportional to the inherent O:C ratio (determined by the oxygen to fuel ratio of the flame) of the soot substrate before SO_2 exposure. Evidently, the efficiency of the sulfate formation is related to the active surface area which is reflected in the O:C ratio of the unexposed soot.

Decrease in SO_2 concentration Δ (SO_2) on account of sulfate formation on propane soot particles was studied with the apparatus shown in Figure 4. Decrease in SO_2 concentration is observed when the flame is placed in the intake position. Removal of the flame will cause the SO_2 concentration to rise to its initial value. The plot in Figure 4 shows Δ (SO_2) as function of O_2/fuel ratio, for two initial $(SO_2)_i$ concentrations of 5.5 and 9.9 ppm.

For a given combustion regime Δ (SO_2) is practically independent on $(SO_2)_i$, and it increases with O_2/fuel ratio. The former feature is related to the saturation of the active sites on soot particles, while the latter effect reflects the increasing number of very small but high surface area particles produced in oxygen rich flame. The fraction Δ $(SO_2)/(SO_2)_i$ is higher for lower $(SO_2)_i$. These data also show that the SO_2 concentrations used in the previously described exposure experiments were well above the saturation levels. The possibility of reaction of water molecules with SO_2 to yield sulfurous acid, thorugh three body collision process, was examined by introducing steam into the system through the intake funnel. The SO_2 concentration did not detectably change however.

Gaseous species will suffer about 10^8 collisions on the path between the flame and the SO_2 input. It can therefore be expected that the reactive radical species produced in combustion will be largely neutralized by the time they reach the SO_2 input, again suggesting the important role of soot particles in SO_2 oxidation.

IV. CONCLUSION

In summary, our findings demonstrate that finely divided, high surface area soot particles are efficient and from the pollution standpoint realistic catalyst for SO_2 oxidation. More specifically, we have found that: 1) Most of the ambient particulat carbon is present in form of "elemental" carbon or soot; 2) different forms of carbon, such as activated charcoal, graphite and soot particles catalytically oxidize SO_2 in presence of oxygen; 3) soot catalyzed oxidation is a major form of SO_2 oxidation even in presence of flames and combustion produced gases; 4) oxidation on soot particles shows a saturation effect, i.e. after the saturation of the active sites is achieved the excess SO_2 will not be further oxidized; 5) the genetic relation of sulfate to carbon is manifested in the correlation between their diurnal concentration variations.

Because of the availability of reactive carbon particles in combustion processes, it can be expected that sulfate-bearing particles are emitted into the atmosphere as primary pollutants from sources including their immediate vicinity, if the fuels contain trace amounts of sulfur. This sulfate emission occurs in competition with the emission of gaseous SO_2. The SO_4^{--}/SO_2 ratio at the source would depend on the combustion regime, i.e. particle size, surface area, etc. Catalytic sulfate formation would also be expected to occur in the open atmosphere on reactive carbon particles. The chemisorptive mechanism outlined here may play a dominant role in urban situations that are characterized by large particulate carbon concentration.

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FIGURE CAPTIONS

Figure 1 - a) Diurnal variations of sulfate, carbon and lead (concentrations in $\mu g/m^3$ of element) Total-Filter (TF) data were obtained with samples collected without particle size segregation. Lundgren impactor after-filter (AF) samples contain only submicron praticles. Sampling was done in Los Angeles, near the Harbor Freeway on September 19-20, 1972. The wind direction relative to the freeway and relative humidity are shown on the figure.

b) ESCA spectrum of nitrogen (N1s) and sulfur (2p) of ammonium-sulfate

c) ESCA spectrum of the same region of an ambient Los Angeles TF sample (1200 PST).

d) ESCA spectrum of the same region taken with a sample from Berkeley, Calif.

e) Nitrogen (N1s) ESCA spectrum of ammonium-nitrate

f) Sulfur (2p) spectrum of sulfate produced by SO_2 chemisorption on activated charcoal.

g) Sulfur (2p) spectrum of sulfate produced by SO_2 chemisorption on propane smoke particles. (From Ref. 7)

Figure 2 - Experimental arrangement used to study the interaction of SO_2 with graphite particles. The rotation of the stainless steel rotor produces fresh surface graphite particles, which can be collected on a filter after they have interacted with SO_2. ESCA spectrum of graphite particles reveals two sulfur

2p peaks corresponding to sulfate and to sulfides.

Figure 3 - Apparatus used to study the interaction of SO_2 with soot particles collected on filters from a premixed propane-oxygen flame. Dry or prehumidified particle free air was used with SO_2 concentrations of about 300ppm and an exposure time of 5 minutes. The entire chamber was kept at about 150°C to prevent water condensation. Typical ESCA spectra of SO_2 exposed soot are also shown. Sulfate peaks were found to be always more intense in the case of prehumidified air. Blank filters, that is without soot particles, exposed to SO_2 and prehumidified air under indentical conditions showed only low, background level sulfate peaks.

Figure 4 - Apparatus used to study the decrease in SO_2 concentration on account of SO_2-sulfate conversion. Decrease in SO_2 concentration Δ (SO_2) is observed when the flame is placed in the intake position. The plot shows Δ (SO_2) as function of O_2/fuel ratio for two initial SO_2 concentrations, $(SO_2)_i$, of 5.5 and 9.9 ppm. For a given combustion regime Δ (SO_2) is independent on $(SO_2)_i$, indicating the saturation of active sites on soot particales. Δ (SO_2) increases with O_2/fuel ratio reflecting the increasing number of very small but high surface area soot particles.

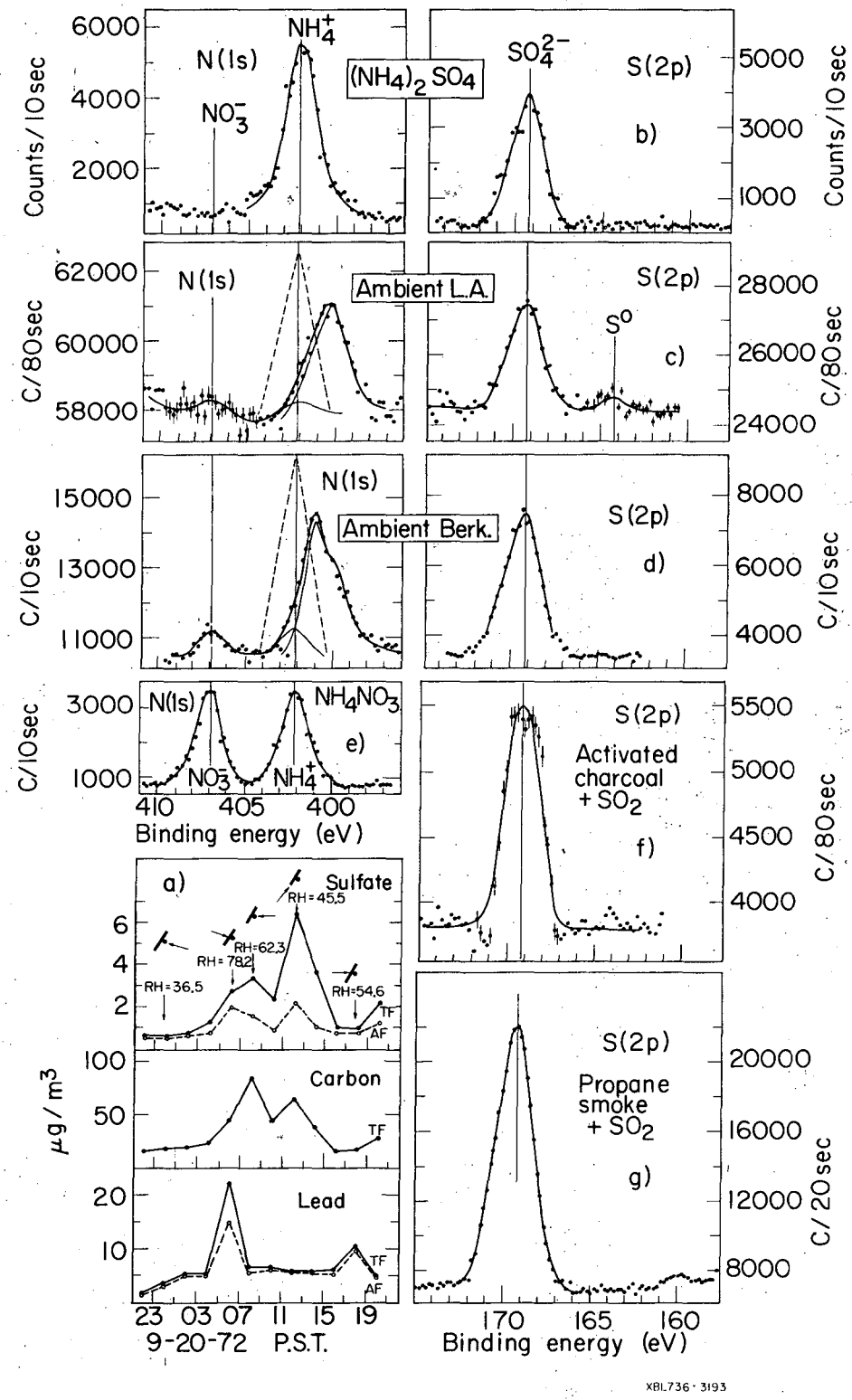

N(1s)
NH_4^+
NO_3^-
$(NH_4)_2SO_4$
SO_4^{2-}
S(2p)
b)
Counts/10sec
Ambient L.A.
S^0
c)
C/80sec
Ambient Berk.
d)
C/10sec
NH_4NO_3
e)
Binding energy (eV)
Activated charcoal + SO_2
f)
a)
Sulfate
RH=45.5
RH=62.3
RH=78.2
RH=36.5
RH=54.6
TF
AF
Carbon
Lead
$\mu g/m^3$
9-20-72 P.S.T.
Propane smoke + SO_2
g)
C/20sec
XBL736-3193

Fig. 1.

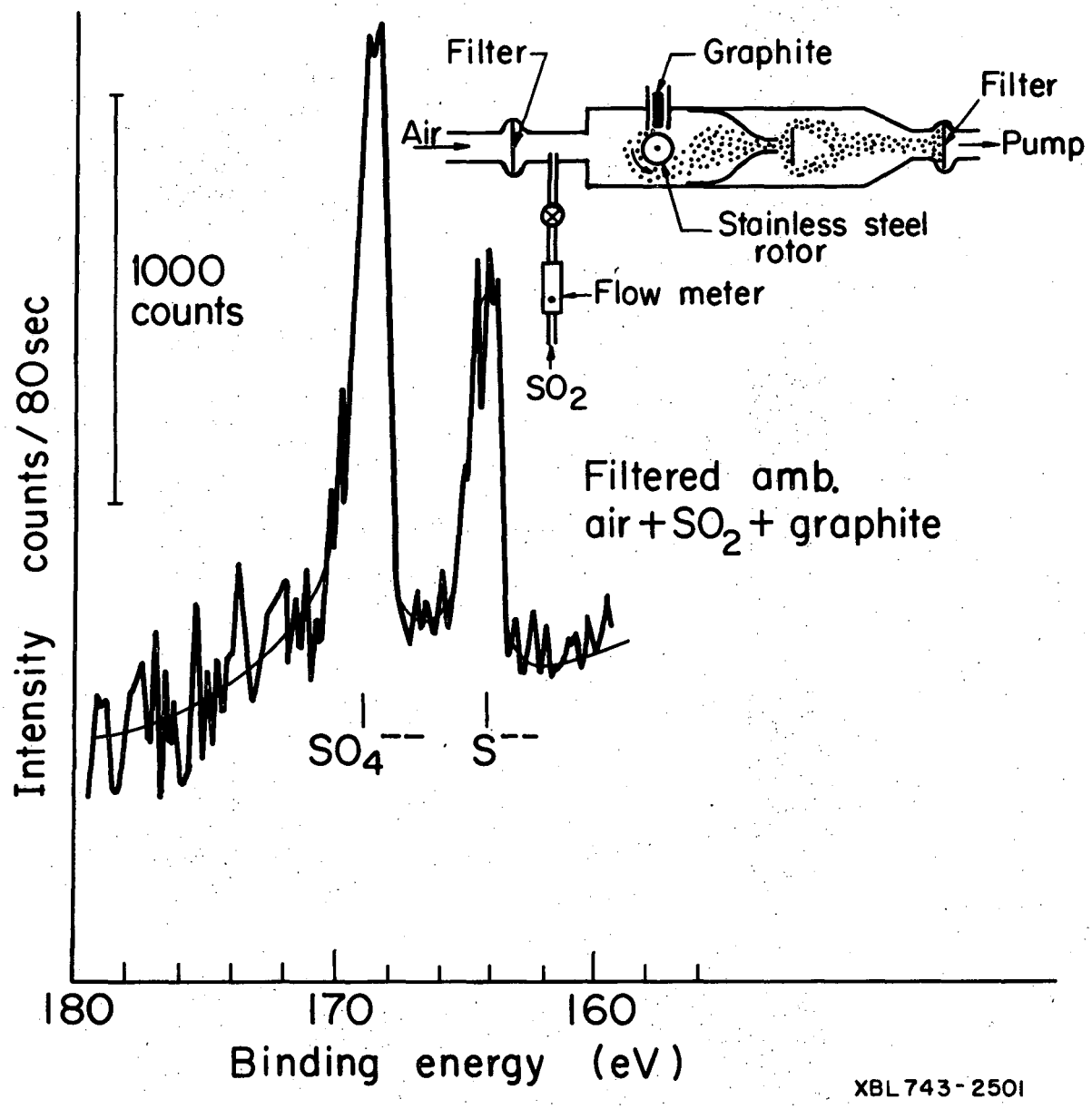

Filter
Graphite
Filter
Air
Pump
Stainless steel rotor
Flow meter
SO_2
1000 counts
Intensity counts/80sec
Filtered amb. air + SO_2 + graphite
SO_4^{--}
S^{--}
180
170
160
Binding energy (eV)
XBL743-2501

Fig. 2.

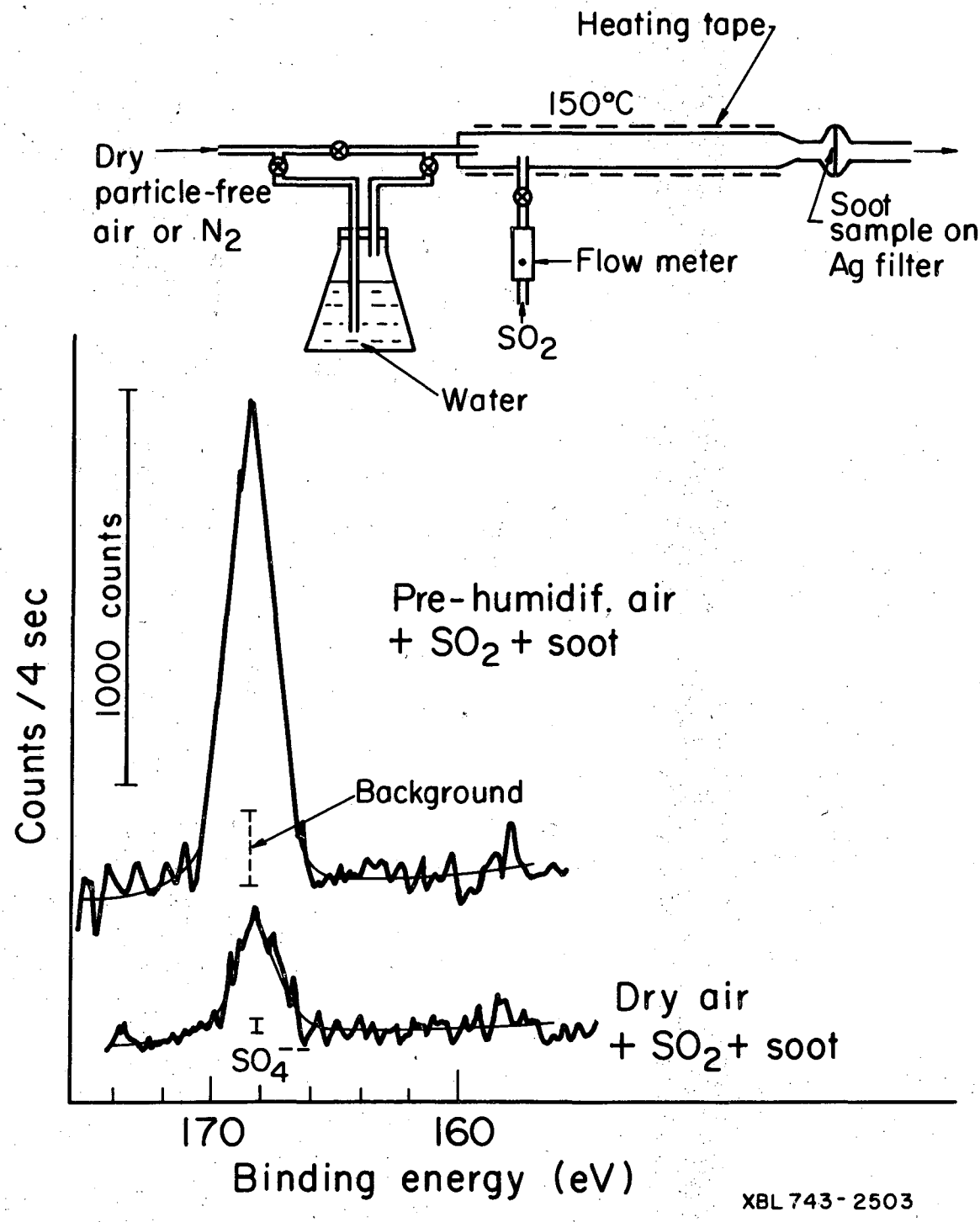
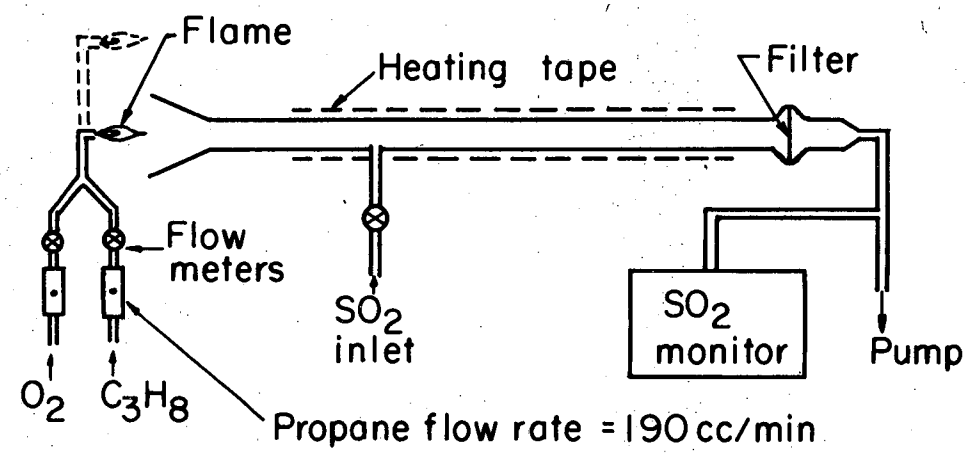

Heating tape
150°C
Dry particle-free air or N_2
Soot sample on Ag filter
Flow meter
SO_2
Water
1000 counts
Counts /4 sec
Pre-humidif. air + SO_2 + soot
Background
Dry air + SO_2 + soot
SO_4^{--}
170
160
Binding energy (eV)
XBL 743-2503

Fig. 3.


Flame
Heating tape
Filter
Flow meters
SO_2 inlet
SO_2 monitor
Pump
O_2
C_3H_8
Propane flow rate = 190 cc/min

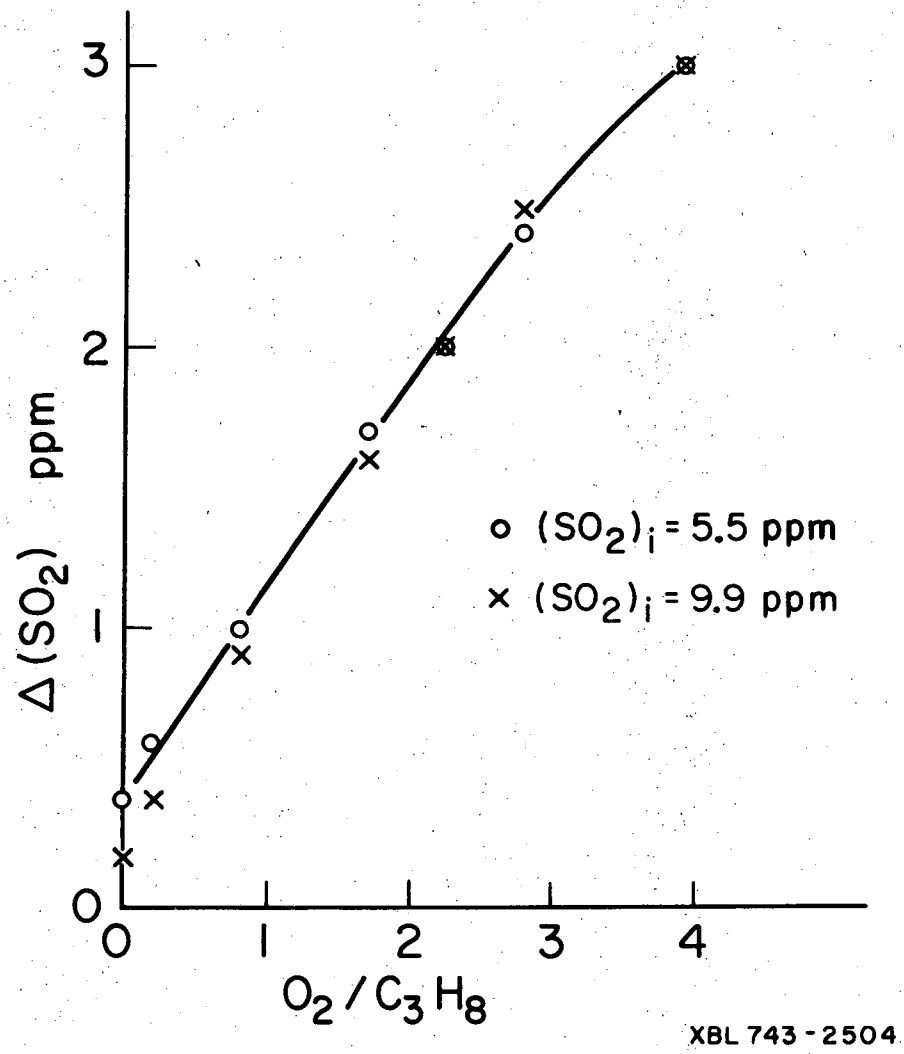

$\Delta(SO_2)$ ppm
O_2 / C_3H_8
o $(SO_2)_i$ = 5.5 ppm
× $(SO_2)_i$ = 9.9 ppm
XBL 743-2504

Fig. 4.

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