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SULFATES IN POLLUTION PARTICULATES

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SULFATES IN POLLUTION PARTICULATES*

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May, 1974

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ABSTRACT

The body of information presented in this paper is directed to those interested in the oxidation of sulfur dioxide to sulfate in polluted atmosphere. Experimental evidence is presented which demonstrates that combustion generated carbon particles in form of finely divided soot, are efficient catalyst involved in SO_2 oxidation. The main conclusions are: (i) most of the ambient particulate carbon is nonvolatile soot; (ii) photoelectron spectroscopic measurements support the view of basic similarity between soot and graphite; (iii) both soot and graphite particles in air catalytically oxidize SO_2; (iv) soot catalyzed oxidation of SO_2 plays a major role even in presence of combustion produced gases; (v) soot catalyzed oxidation shows a pronounced saturation effect; (vi) sulfate species produced on carbon particles are nonvolatile in vacuum but they are water soluble and when dissolved increase the acidity of the solution; (vii) the results of field studies are compatible with this oxidation mechanism. The main experimental tool used is X-ray Photoelectron Spectroscopy (ESCA).

I. INTRODUCTION

This paper addresses itself to one aspect of heterogeneous atmospheric chemistry, namely to the problem of catalytic oxidation of sulfur dioxide on pollution particulate carbon. Experimental evidence will be presented which demonstrates that carbon particles, in the form of finely divided soot, are efficient - and from the air pollution standpoint certainly realistic - catalyst involved in SO_2 oxidation. It will be also shown that results of field studies are compatible with this oxidation mechanism.

The proposed mechanism of SO_2 oxidation on carbon particles has evolved from our work on X-ray photoelectron spectroscopy (ESCA) of ambient pollution particulates. Since we have first applied this technique to the chemical characterization of aerosol particles we have examined about 400 samples collected in various regions of California. In the course of this work we have become increasingly aware of systematic correlation that exists between the diurnal concentration variations of sulfate and particulate carbon. In addition, we have also concluded from a series of experiments performed by means of our newly developed method of measuring ESCA spectra as function of sample temperature, that a large fraction of the total particulate carbon, perhaps as high as eighty percent, is nonvolatile in vacuum at temperatures of about 400°C. Because ESCA spectra reveal a neutral charge on the carbon core, we assume that most of the nonvolatile carbon is elemental carbon or soot. It is known, however, that soot particles are of essentially graphitic structure, with some fine soot particles consisting of only a few elemental

cells, thus possessing extremely high surface area. Because catalytic properties of activated carbon are well known and because similar catalytic properties can be expected of soot, we have undertaken a laboratory study with the aim of establishing wheather soot particles are catalytically and/or surface chemically active when interacting with common pollutant gases such as SO_2, NO_x and NH_3. In this paper the results dealing with SO_2 oxidation to sulfate will be described,as well as some other results which may help in assessing the relative importance of soot particles in the chemistry of polluted atmosphere. Because the technique of X-ray photoelectron spectroscopy is relatively new as a research tool in the field of aerosol chemistry the basic principles of the method will be also described.

II. EXPERIMENTAL TECHNIQUE

X-ray photoelectron spectroscopy,[1] also known as ESCA (Electron Spectroscopy for Chemical Analysis), 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 photoelectron kinetic energy 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, while the photoelectron intensity is related to the concentration

of atoms of that element in the active sample volume. This 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 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. Subsequent studies have shown that the binding energy shifts are correlated to a high degree with the effective charge which the atom possesses in the molecule. Therein lies the usefulness of chemical shifts in the analysis of unknown molecular structures. Chemical shifts can be adequately described by a simple electrostatic 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, 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, binding energies will be greater, than the ones for neutral configuration, for positive effective charges, that is for oxidized species and similarly, the binding energies will show a negative shift for reduced species.

Because of the low energy of photoelectrons induced by Mg or Al X-rays, which are most commonly used, the effective escape depth for their 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. This renders the ESCA method especially surface sensitive and thus useful in the 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 low energy electrons whose energy has been degraded by the inelastic collisions. The chemical shift measurements are performed only on electrons with no energy loss. In some cases, however, the study of the energy distribution of the inelastically scattered electrons may provide useful information which is complementary to the chemical shift measurement. Namely, the photoelectrons will loose energy in producing collective excitation, interband or intraband transitions of the latice electrons. The energy loss structure will thus be characteristic of the material. We have applied this phenomenon to show that soot and graphite have similar electronic structure.

III. RESULTS

Chemical States of Particulate Carbon. In this section we will present evidence that ambient particulate carbon is to a large extent elemental carbon, i.e., soot. We will also show that photoelectron spectroscopy can be used to demonstrate the basic structural similarity of soot and graphite.

Photoelectron spectra of ambient particulates reveal that carbon (1s) photoelectron peak appears essentially as a single peak with a binding energy corresponding to a neutral charge stae, compatible with either elemental carbon or hydrocarbons or both. Chemically shifted carbon peaks

due to oxygen bonding, when observed, are generally of low intensity as compared with the main hydrocarbon + elemental carbon peak. Such measurements rule out carbonates as a significant form of particulate carbon for example. Other less positive carbon species such as carboxyls for example are identifiable although again their proportion to nonoxidized carbon is quite low. (Figure 1)

Unfortunately, because of the nature of the chemical bonding in hydrocarbons, they can not be distinguished from elemental carbon by core electron chemical shift under realistic sample conditions. We had therefore to employ other suplementary, although somewhat indirect, measurements to estimate the relative abundance of elemental carbon. This was achieved in one series of experiments by comparing the carbon ESCA peak intensity with the sample at normal operating temperature of 25° to the peak intensity obtained with the same sample at 350 - 400° C. The difference between the low and high temperature runs should give the fraction of the volatile carbon compounds, under assumption that organic compounds will have vapor pressures above 10^{-6} torr, i.e., higher than the spectrometer pressure, at the temperatures employed. We have performed such measurements on a number of ambient particulate samples collected on silver membrane filters, and have found that in these samples at least 80% of the total carbon is nonvolatile, i.e., presumably elemental. The result of one such measurement is shown in Figure 1, where the carbon (1s) peak measured at 25° C and at 350° C is shown. A decrease in the peak area (peak area is proportional to the carbon atom concentration) of 5% is observed in this particular sample, collected on 8/29/73 in West Covina, CA. The decrease in intensity is confined to the chemically shifted carbon.

The conclusion about the very high nonvolatile carbon content could be erroneous if a large fraction of the particulate carbon volatilizes in vacuum even at low temperatures, thus leading to the underestimation of the volatile content. This would seem unlikely, however, because a reasonably good agreement has been found between the total carbon concentration as measured by ESCA and by a combustion technique.[2] Actually the concentrations determined by ESCA were in most cases higher than the concentrations obtained by combustion. Furthermore, measurements employing thermal analysis in nitrogen at atmospheric pressure in conjunction with combustion analysis show that on the average at least 50% of the total carbon is nonvolatile.[3]

In the discussion that follows we shall assume that the nonvolatile carbon fraction is largely in the form of soot, which we think of as a microcrystalline form of graphitic carbon, as evidenced by electron microscopic and X-ray difraction analysis.[4] That soot is indeed a form of graphite can be also demonstrated by electron spectroscopy,[5] i.e., by observing the discrete energy losses suffered by carbon (1s) photoelectrons in the process of escaping from the solid sample. Figure 2a shows the energy loss structure associated with carbon (1s) photoelectrons of a polycrystalline graphite sample with contaminated surface. As expected, the energy loss structure becomes more pronounced after the sample is heated to 350° C, that is after the volatile surface contaminants have been removed. This is shown in Figure 2b. In Figures 2c and 2d we show similar spectra of propane soot as observed with an untreated sample and after the soot sample was heated in vacuum at 350° C. The energy loss features are similar for both graphite and for soot suggesting the basic similarity of

these materials.

Catalytic Oxication of SO_2 on Carbon Particles in Air. Carbon constitutes about 50% of total particulate emissions in urban situations. This fact alone, and especially in conjunction with the foregoing discussion about the chemical and physical properties of particulate carbon, makes the assessment of its chemical role in the chemistry of air pollution imperative. In spite of the fact that catalytic properties of activated carbon are known the relevance of soot catalyzed reactions to the atmospheric chemistry has not been appreciated.

In this section we describe experiments which under laboratory conditions demonstrate the feasibility of SO_2 oxidation in air on both graphite and soot particles.[6] These will be presented in such an order as to reflect the increasing complexity of the experimental systems used. We will first describe experiments in which the possibility of interfering and competing oxidation mechanisms is essentially eliminated, and after that we will describe experiments, also involving soot particles, but this time in the presence of possibly reactive combustion produced gases. In addition we will also describe the chemical properties of sulfate produced by soot - SO_2 interaction.

The interaction of SO_2 with graphite particles was studied with the apparatus shown schematically in Figure 3. The rotation of the stainless steel rotor against which a piece of polycrystalline graphite is placed produces small, initially fresh surface graphite particles with diameters of about 20 μm. These particles are collected on a filter after they have been exposed to SO_2 and particle free air of low relative humidity. The

SO_2 concentrations used were of the order of 100 ppm. ESCA spectrum of these particles reveals two sulfur (2p) photoelectron peaks corresponding to sulfate (binding energy 168.4 eV) and to sulfide. In a separate experiment[7] we were able to show that SO_2 will produce sulfide by chemisorption on atomically clean trigonal plane of a graphite single crystal under UHV conditions. Consequently, the sulfide induced on graphite particles in the above experiment is an indication of the presence of "clean" surface portions. On the other hand surfaces which have reacted with oxygen and water will achieve a surface coverage with carbon-oxygen complexes, which give rise to the catalytically active graphite. Actually, the main chemical difference between graphite and soot stems from the differences in their surface composition.

Blank filters, that is without graphite particles, under otherwise identical SO_2 exposure conditions do not produce measureable amounts of sulfate (or sulfide). This experiment shows that even relatively clean graphite particles in air are to some extent oxidizing SO_2.

The equivalency of soot particles to graphite with respect to SO_2 oxidation is demonstrated by the following set of experiments. 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 4. Dry and prehumidified particle free air or nitrogen was used with SO_2 concentration of about 300 ppm 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 4. Sulfate peaks were found to be more intense in the case of prehumidified air, than in the case of dry air (Table 1A). Blank filters without soot particles exposed to SO_2 and prehumidified air 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 important 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 (Table 1B). 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.

It is of interest to assess the role of soot catalyzed oxidation in or near combustion devices where both SO_2 and soot concentrations are always the highest. Here, however, the SO_2 oxidation may be, at least in principle, caused by reactions with reactive combustion produced radical

species. The experimental arrangement is shown in Figure 5. Soot samples were prepared by introducing a constant SO_2 flow (300 ppm, 4 minutes) through ports #1 through #4, while the propane flame was on. The amounts of sulfate detected on filters are shown in the graph in Figure 5 and in Table 1C. Similarity of the sulfate concentrations produced when SO_2 was passed over the flame and when introduced outside (downstream) of the flame envelope indicates the relatively minor singificance of the homogeneous gas phase oxidation. The somewhat higher sulfate formation efficiency achieved when SO_2 was introduced through inputs #1 and #2 as compared with inputs #3 and #4 can probably be attributed to the higher particle surface area in their growth stage and to temperature effects.

We have also studied the SO_2 oxidation on propane soot particles by observing the decrease in the gaseous SO_2 concentration Δ (SO_2), occuring on account of sulfate formation (Figure 6). SO_2 concentration is adjusted to the desired initial value $(SO_2)_i$, with the flame removed from its position in front of the intake funnel. Decrease in SO_2 concentration Δ (SO_2) is observed within the instrument response time, when the flame is placed in the intake position so that combustion generated aerosol gets in contact with SO_2. Removal of the flame will cause the concentration to rise to its initial value. Because gaseous species will suffer about 10^8 collisions on the path between the flame and the SO_2 input, it can be expected that reactive radical species will be largely neutralized by the time they reach the SO_2 port. This and other evidence described earlier suggests that the observed decrease in SO_2 concentration is caused by the action of soot particles. The possibility that the removal is related

to the formation of sulfurous acid was eliminated by a separate experiment, in which combustion generated aerosol was replaced by steam. No detectable change in SO_2 concentration was observed in this case.

The plot in Figure 6 shows the amount of SO_2 converted to sulfate as function of the oxygen to fuel ratio, for two initial concentrations of 5.5 and 9.9 ppm. For a given combustion regime Δ (SO_2) is independent on $(SO_2)_i$. This feature is probably related to the saturation of active sites on soot particles. Δ (SO_2) increases, however, with O_2/fuel ratio, reflecting the increase in the number of very small, high surface area particles produced in oxygen rich flame.

The results just described show, among other, that SO_2 concentrations used in the experiments with soot and graphite under static conditions were well above the saturation level.

Sulfate species in samples prepared by the described procedures are nonvolatile in vacuum at room temperature. ESCA study of these samples as function of sample temperature shows that sulfate concentration decreases very slowly in a quite specific manner. The sulfate species are water soluble with accompanying increase in the acidity of the solution. These results indicate that the sulfate produced by soot - SO_2 interaction is in the form of adsorbed, surface bonded, sulfuric acid.

Surface Reactions of Ammonia and Nitric Oxide with Carbon Particles. For the sake of completeness and because of the relevance to the better understanding of the catalytic properties of carbon particles we will outline the recent results obtained by Chang and Novakov[8] on the interactions of graphite and soot with NH_3 and NO. The main factor determining the

catalytic or surface properties of soot is the nature and abundance of surface carbon oxygen complexes. These inherently exist on soot particles and can be readily formed on graphite by exposure to oxygen and humidity. The relative amount and the nature of these surface complexes depend significantly on temperature, i.e., the history of soot formation, or as in the case of graphite on the temperature during the pretreatment with O_2 and/or H_2O. It was demonstrated, by the use of X-ray photoelectron spectroscopy, that interaction of either NO or NH_3 with soot or graphite at room temperature in air results in the formation of volatile ammonium like surface species. On the other hand the same reaction at elevated temperature yields reduced nitrogen species, which manifest itself by photoelectron peaks possessing lower binding energies that the binding energy of ammonium, indicating a core charge more negative than the core charge on nitrogen in ammonium ion. The same authors have also shown that these reduced species have chemical properties identical with nitrogen species also observed in ambient particulates. These are identified as amines, amides and nitriles, and it is proposed that they are produced in a series of reactions with, for example, surface carboxyl groups.

In so far as the oxidation of SO_2 is concerned it is of interest to note that carbon particles on which the amines and amides have been formed, by one of the above mentioned reactions, seize to be catalytically active for SO_2 oxidation. These species are poisoning the carbon catalyst, probably by engaging the same active sites. This example illustrates the importance of the surface conditions for the catalytic activity of

carbon particles.

IV. DISCUSSION

Experimental results described in the preceeding section can be summarized as follows:

(i) Most of the ambient particulate carbon in nonvolatile soot.

(ii) Electron spectroscopic measurements support the view that soot is basically of graphite structure. The chemical equivalency of soot and graphite is further demonstrated by their reaction with SO_2, NH_3, and NO.

(iii) Both soot and graphite particles catalytically oxidize SO_2 in air. Soot catalyzed oxidation of SO_2 plays a major role even in the presence of combustion produced gases and vapors.

(iv) Soot catalyzed SO_2 oxidation shows a pronounced saturation effect. Catalytic activity of soot will ~~seize~~ cease once the soot surface becomes saturated with the sulfate product. Carbon particle catalyst can be also poisoned by products of other surface reactions which compete for the same active sites. Catalytic activity of carbon particles is determined by their surface conditions.

(v) Sulfate species produced on carbon particles are nonvolatile in vacuum at room temperature. They desorb, however, at elevated temperatures monotonically in a specific manner.

(vi) Sulfate species on carbon are water soluble, and when dissolved increase the acidity of the solution.

We can not, at this time, describe the exact step-by-step mechanism of the sulfate formation on carbon particles. From the phenomenological point of view, however, it is clear that the essential ingredients for the oxidation process are oxygen and water molecules, in addition to carbon particles. Experimental findings are consistent with the idea that the role of carbon particles is to catalyze $SO_2 + O_2$ reaction, with the latter reactant being adsorbed on active sites provided by carbon surface. The role of water molecules is probably to produce surface adsorbed sulfuric acid as the end product of catalyzis. This would explain the ~~seiz~~cess ation of the catalytic activity after a certain sulfate concentration has been reached on particle surfaces, as well as the solubility of sulfate on carbon.

As with other processes whose feasibility has been demonstrated under laboratory conditions, the assessment of the relevance of the catalytic sulfate formation to the polluted atmosphere, has to be established through correlations in the field data expected from the proposed process.

The proposed process is based on abundant presence of finely divided, high surface area, soot particles in the polluted atmosphere. The experimental results obtained with ambient particulates support this assumption, which is logical in view of the fact that most of urban air pollution is combustion generated and that even seemingly complete combustion under realistic conditions always produces significant amounts of soot. The small particle size of soot would naturally prevent its visual observation.

If a significant fraction of pollution sulfates is produced catalytically on carbon particles, there should be a high degree of

correlation between the diurnal concentration variation of ambient particulate sulfate and carbon. An example of such correlation 1, 6 we show the diurnal plots of sulfate, total particulate carbon and lead obtained on twelve samples without particle size segregation, collected in downtown Los Angeles on September 20, 1972. The similarity between carbon and sulfate pattern is obvious. Other similar correlations have been obtained more recently, actually not one exception to this rule was found to date. The validity of carbon sulfate correlation extends to submicron particles. In Figure 7 we show a plot obtained by Hidy et al.,[9] for the summer of 1973, of the submicron sulfate (as fraction of the gaseous sulfur oxides) vs. the submicron particulate carbon. The high degree of correlation is evident from the figure.

That the sulfate on carbon hypothesis is also consistent with analytical results obtained on ambient sulfate is evident from the following: Namely, pollution particulate sulfates are believed to exist in one or more of the following forms, i.e., sulfuric acid, ammonium sulfate, ammonium acid sulfate and sulfate salts with metals. Since ambient sulfates are fairly nonvolatile in vacuum, it is not likely that they are actually in liquid sulfuric acid form during analysis. Ammonium sulfate although present is not necessarily always the major sulfate form (1). Sulfate salts with metals can be ruled out as significant because the amounts of metals found in particulates are small to act as major sulfate cations.[10] The properties of sulfate produced catalytically on carbon are compatible with all of these results. For example, upon disolving in water its acidity will increase as with sulfuric acid, but because of its

bonding to the carbon surface. sulfate on carbon will be much less volatile in vacuum then liquid sulfuric acid. Acturally in a series of experiments we have found that the ambient sulfate exhibit the same characteristic desorption in vacuum as function of the sample temperature, as the sulfate produced by SO_2 - soot interaction. Furthermore because of the solubility of these sulfates it is conceivable that they can be neutralized by ambient ammonia to form ammonium sulfate. It appears, therefore, that the chemical properties of sulfate on carbon are consistent with the chemical properties of ambient sulfates.

Finally, the saturation effect observed for sulfate formation on carbon particles is qualitatively consistent with the saturation behavior reported for ambient sulfate.[11]

Catalytic sulfate formation on soot particles can be expected to occur in the open atmosphere and especially in or near combustion sources, where both SO_2 and soot concentration are highest. Although the described sulfate formation mechanism could occur in addition to other reactions we believe that it plays a major role in urban situations characterized by large particulate carbon concentrations.

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TABLE 1

SUMMARY OF RESULTS ON SULFATE FORMATION BY SOOT + SO_2 INTERACTION

	Experimental Conditions	Relative atomic concentrations (C-100) C	O	S (sulfate)	O:S	Remarks
A)	Soot substrate before SO_2 exposure	100	18.0±2.0	-	-	See Figure 4 - note the sulfate O:S stoichiometry for the case of prehumidified air
	Identical soot substrate + dry air + SO_2	100	35.0±3.0	4.0±.5	8.7	
	Identical soot substrate + prehumidified air + SO_2	100	91.0±9.0	21.0±2.0	4.3	
B)	Soot substrate #1	100	3.4±0.4	-	-	Resulting sulfate concentration is proportional to the O:C ratio on soot before SO_2 exposure
	Soot substrate #1 + SO_2 + 1.h. air	100	14.0±2.2	2.0±0.4	7.0	
	Soot substrate #2	100	17.1±2.2	-	-	
	Soot substrate #2 + SO_2 + 1.h. air	100	27.1±2.5	3.5±0.2	7.7	
	Soot substrate #3	100	20.4±6.0	-	-	
	Soot substrate #3 + SO_2 + 1.h. air	100	27.3±5.0	4.4±0.2	6.2	
C)	SO_2 input through port #1 5 cm upstream from flame	100	220.±20	60.0±6.0	3.7	See Figure 5 - note that O:S ratio is about 4 for this high humidity case
	SO_2 input through port #2 15 cm downstream from flame	100	240.±25.	54.0±15.0	4.4	
	SO_2 input through port #3 28 cm downstream from flame	100	150.±15.	31.0±3.0	4.8	
	SO_2 input through port #4 58 cm downstream from flame	100	156.±15	37.0±4.0	4.2	

FIGURE CAPTIONS

Figure 1: Carbon (1s) photoelectron peak of an ambient particulate sample as measured at 25° C and at 350° C. The shaded area represents the loss of volatile species.

Figure 2: The energy loss structure associated with the carbon (1s) photoelectron peak for: a) graphite with a contaminated surface, b) the same sample heated to 350° C, c) propane soot sample measured immediately after collection and d) same soot sample after heating in vacuum at 350° C. The similarity of graphite and soot energy loss structure is evident. (Ref. 5)

Figure 3: ESCA spectrum of graphite particles exposed to SO_2 and filtered ambient air reveals the presence of both sulfate and sulfide on those particles. Sulfate is produced by catalytic oxidation of SO_2 on graphite particles. Sulfide peak is the result of SO_2 chemisorption on parts of particle surfaces which are "atomically" clean. Apparatus used for production of small graphite particles and for their exposure to SO_2 and filtered air is also shown. (Ref. 6)

Figure 4: Soot particles exposed to prehumidified particle free air and SO_2 produce sulfate concentrations about five times higher than in the case of dry air, for the same SO_2 concentration. Blank filters without soot particles exposed to SO_2 and prehumidified air showed only background level sulfate. The exposure chamber was kept at elevated temperatures to prevent condensation of liquid water droplets. (Ref. 6)

Figure 5: Set of four soot samples was prepared with the setup shown in the figure. Constant flow of SO_2 was introduced, while the premixed propane-oxygen flame was on, through ports #1 through #4 which are placed at the indicated distance from the flame. The resulting sulfate concentrations are plotted vs. the SO_2 introduction port distances from the flame. The somewhat higher sulfate formation efficiency achieved when SO_2 was introduced through ports #1 and 2, as compared with inputs #3 and 4 can probably be attributed to the higher particle surface area in the particle growth stage and/or temperature effects. (Ref. 6)

Figure 6: Apparatus used to study the decrease in SO_2 concentration Δ (SO_2) on account of sulfate formation on propane soot particles. SO_2 concentration is adjusted to the desired value $(SO_2)_i$ with flame removed from its position in front of the intake funnel. Decrease in SO_2 concentration 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. For a given combustion regime Δ (SO_2) is independent on $(SO_2)_i$ and it is increasing with O_2/fuel ratio. The former effect is related to the saturation of soot particle surface area, while the latter reflects the increase in the number of ultrafine, high surface area particles. (Ref. 6)

Figure 7: Diurnal variation of particulate sulfate, carbon (ref. 3) and lead (ref. 12) concentrations. The sampling was done in downtown Los Angeles on September 20, 1972, (ref. 9). The similarity between carbon and sulfate patterns is obvious.

Figure 8: Scatter diagram of particulate sulfate Sp (as fraction of gaseous sulfur Sg) and carbon in particles <0.6 μm diameter (from ref. 9).

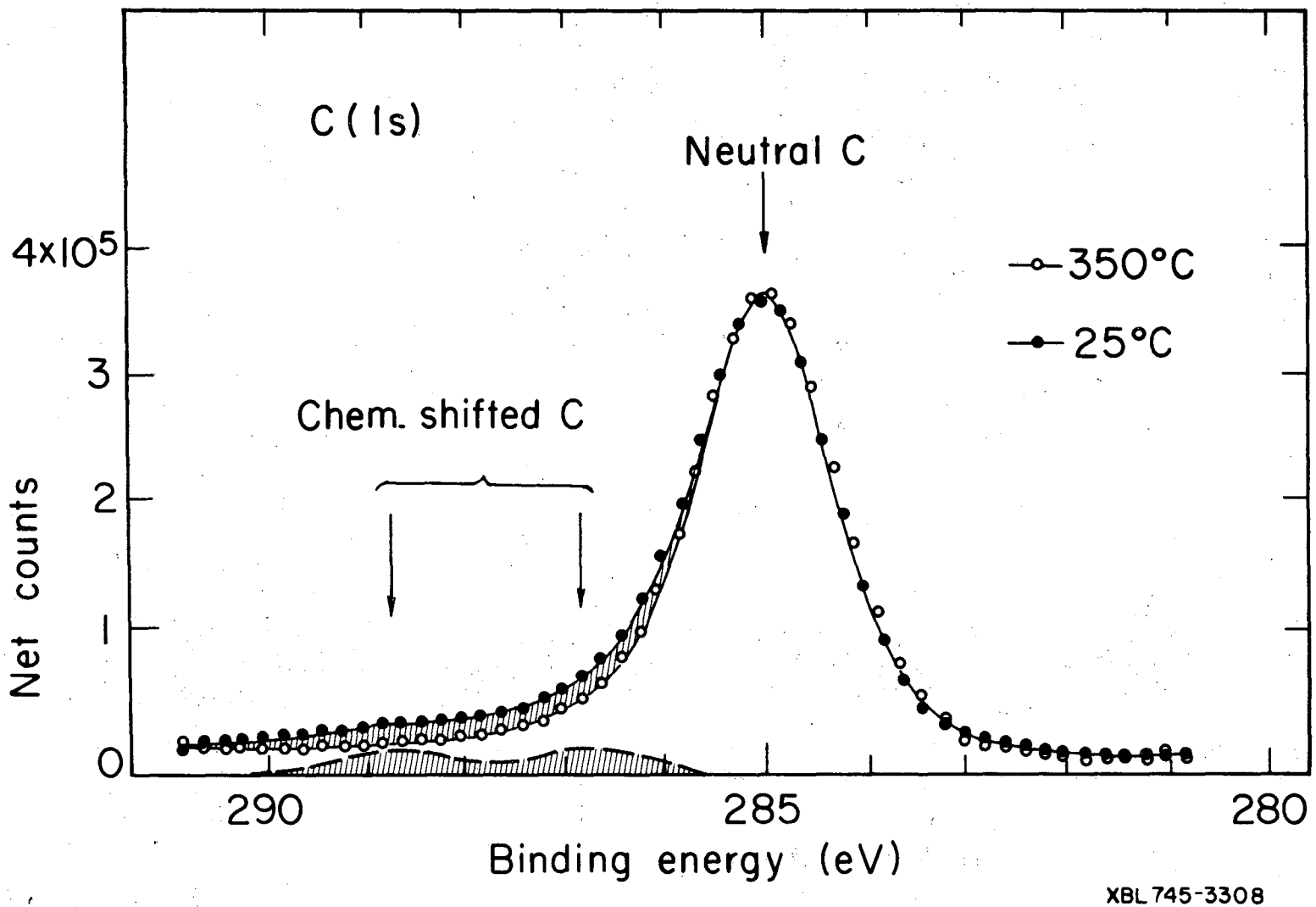
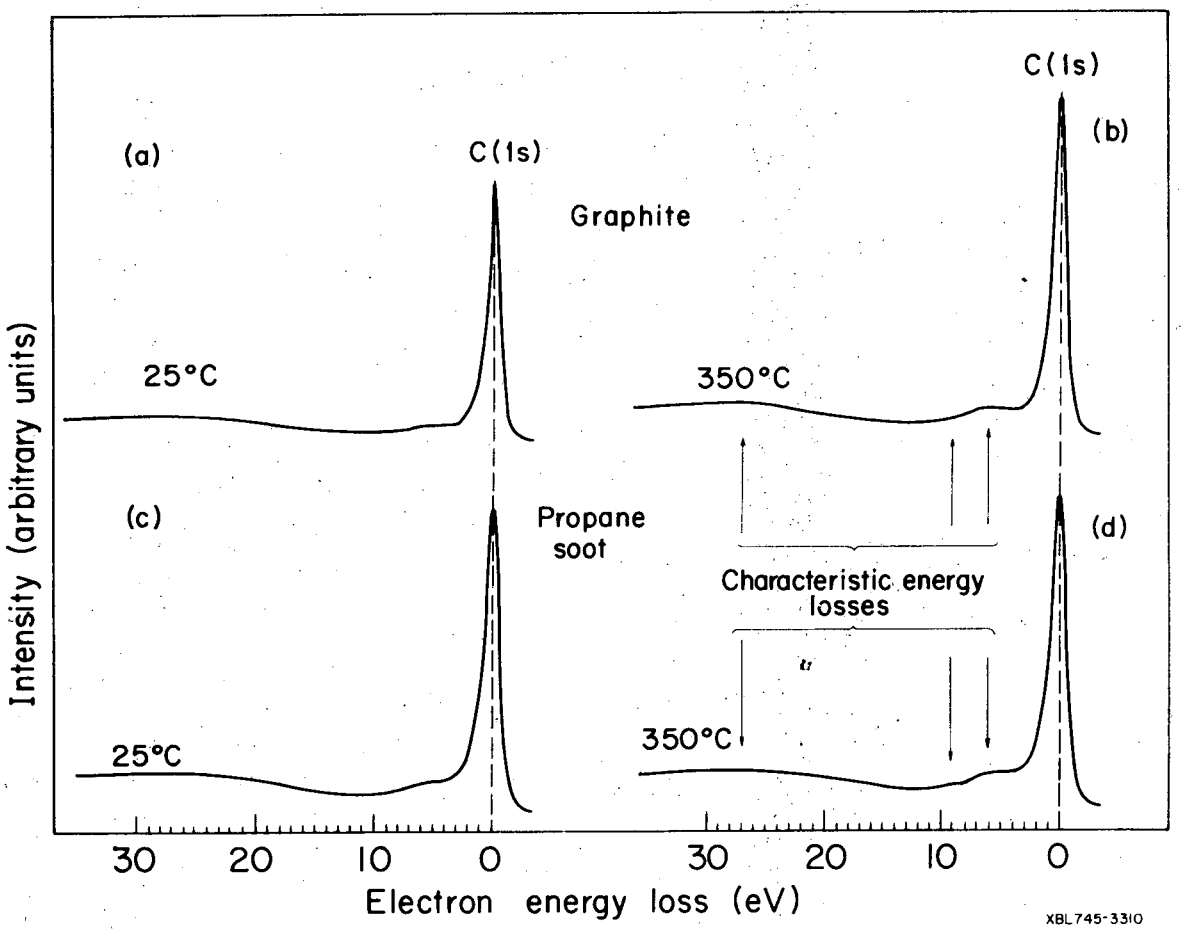

C (1s)
Neutral C
Chem. shifted C
350°C
25°C
4x10^5
3
2
1
0
Net counts
290
285
280
Binding energy (eV)
XBL 745-3308

Fig. 1.


C(1s)
(a)
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350°C
(c)
Propane
soot
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Characteristic energy
losses
350°C
(d)
Intensity (arbitrary units)
30
20
10
0
30
20
10
0
Electron energy loss (eV)
XBL745-3310

Fig. 2.

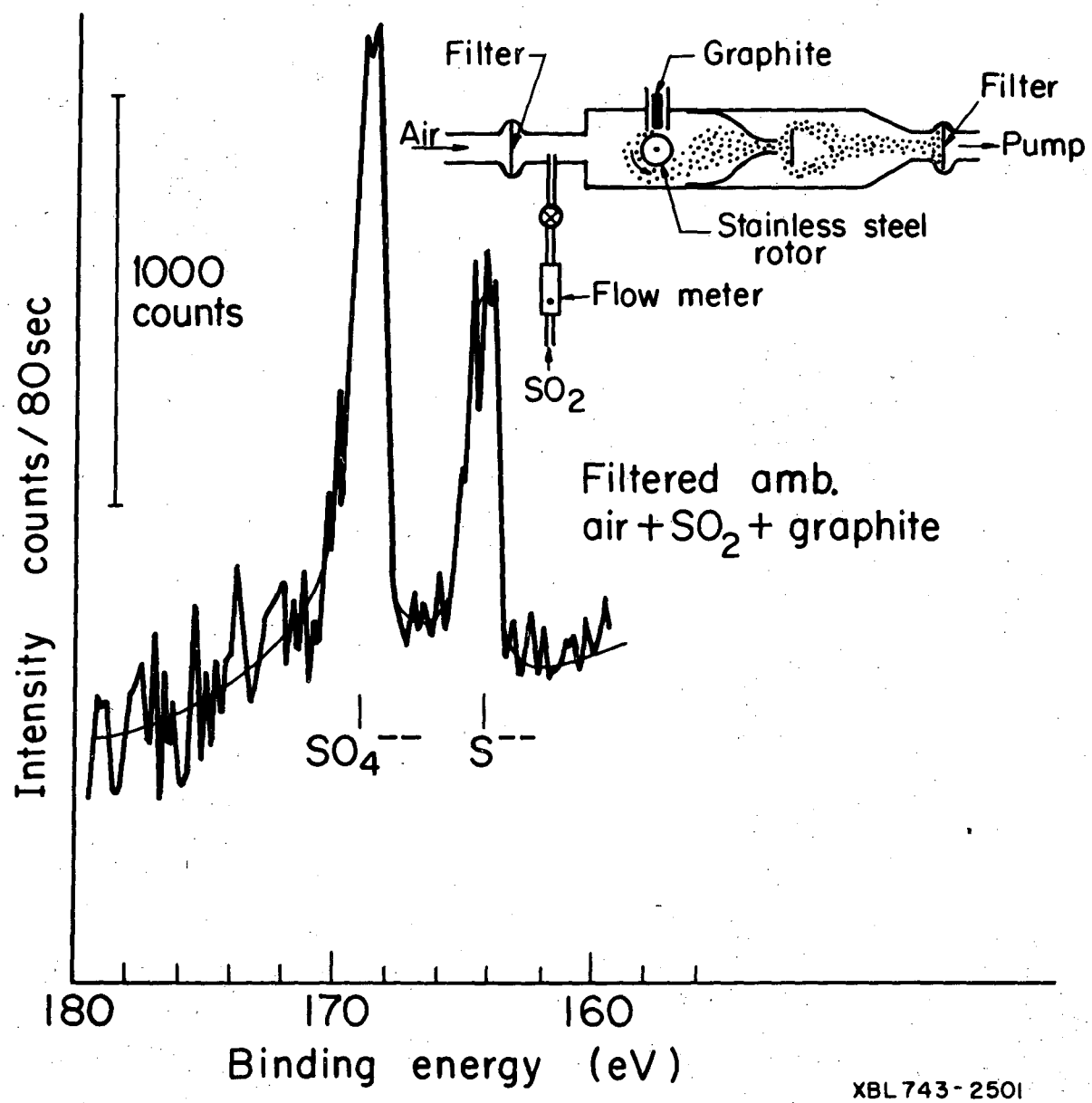

Filter
Graphite
Filter
Air
Pump
Stainless steel rotor
Flow meter
SO_2
1000 counts
Intensity counts/80sec
Filtered amb. air + SO_2 + graphite
SO_4^{--}
S^{--}
180
170
160
Binding energy (eV)
XBL 743-2501

Fig. 3.

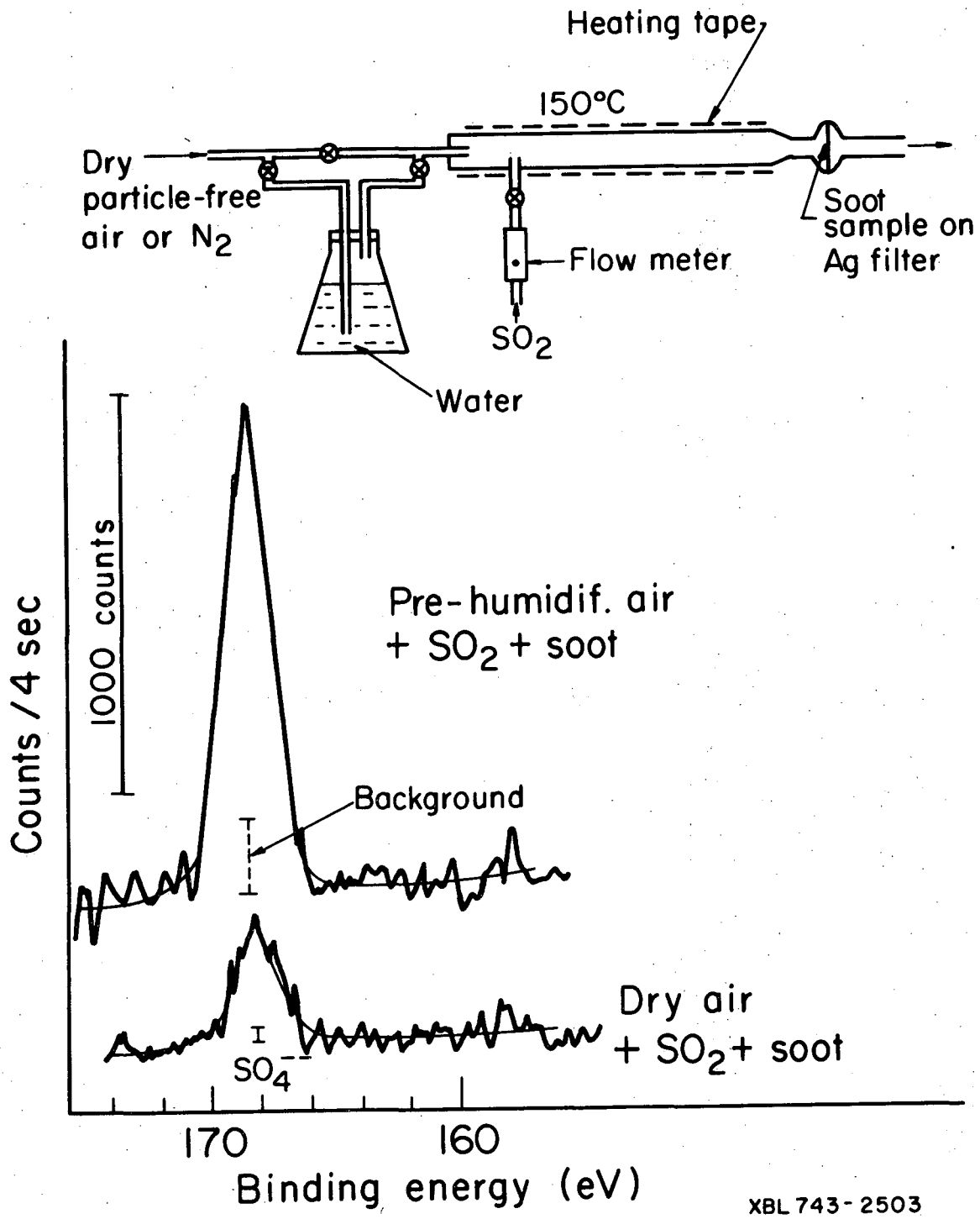
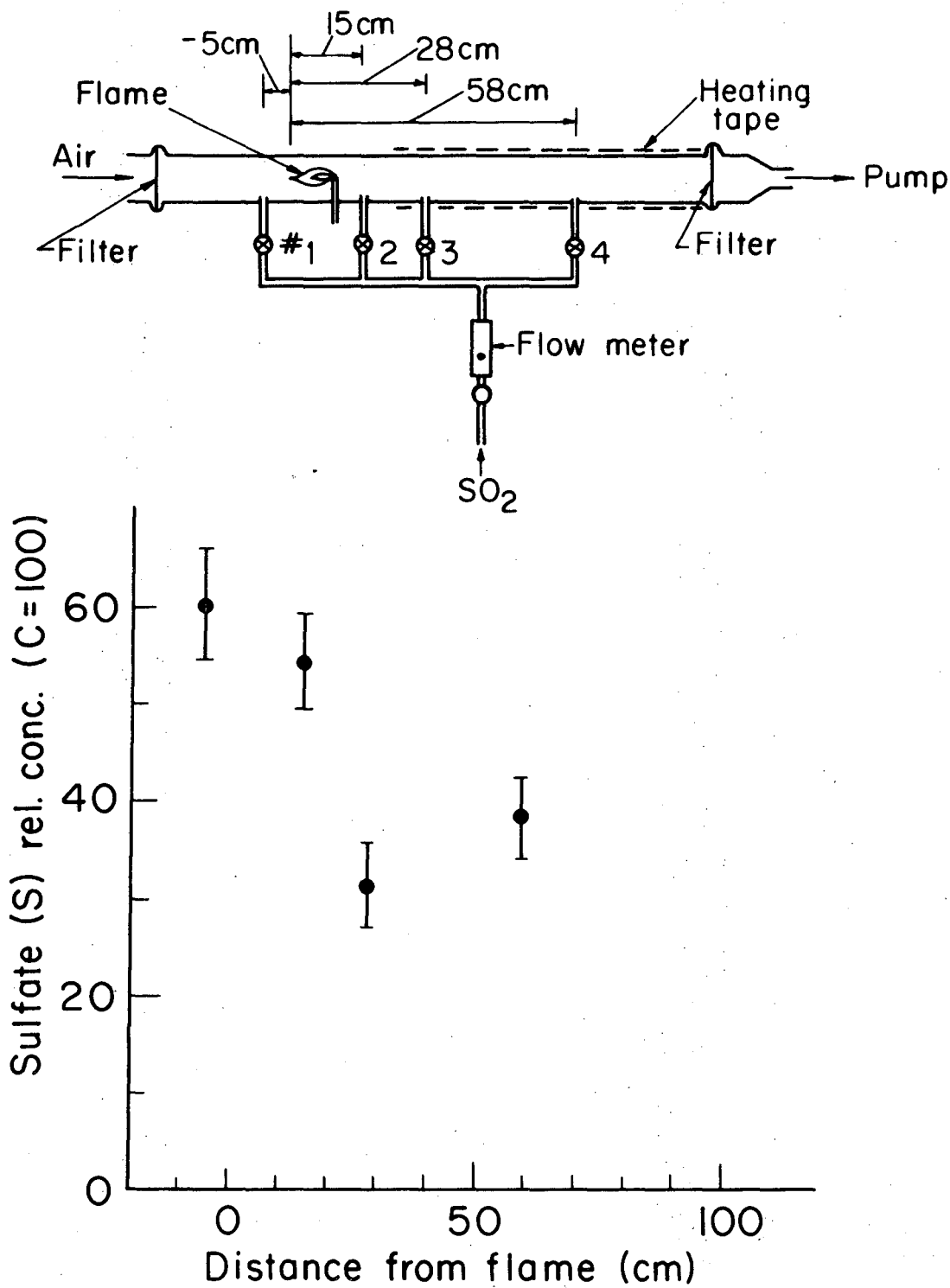
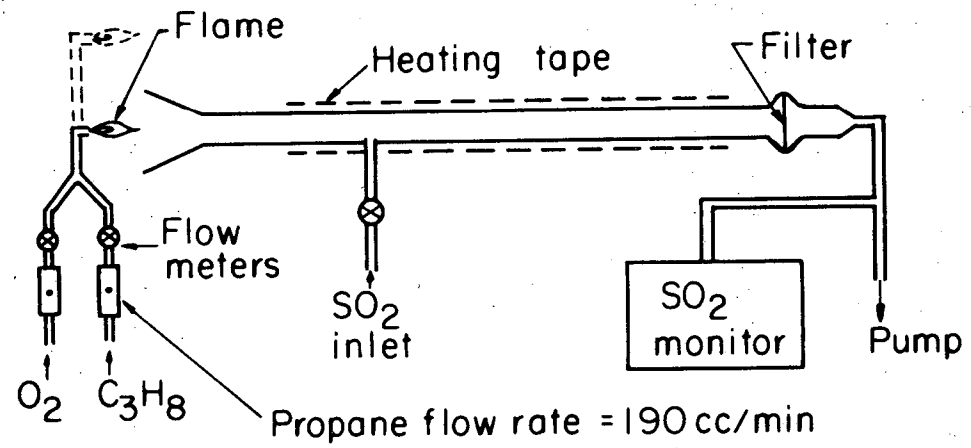

Heating tape
150°C
Dry particle-free air or N_2
Soot sample on Ag filter
Flow meter
SO_2
Water
1000 counts
Counts /4 sec
Pre-humidif. air + SO_2 + soot
Background
Dry air + SO_2 + soot
SO_4^{--}
170
160
Binding energy (eV)
XBL 743-2503

Fig. 4.



XBL743-2505

Fig. 5.


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

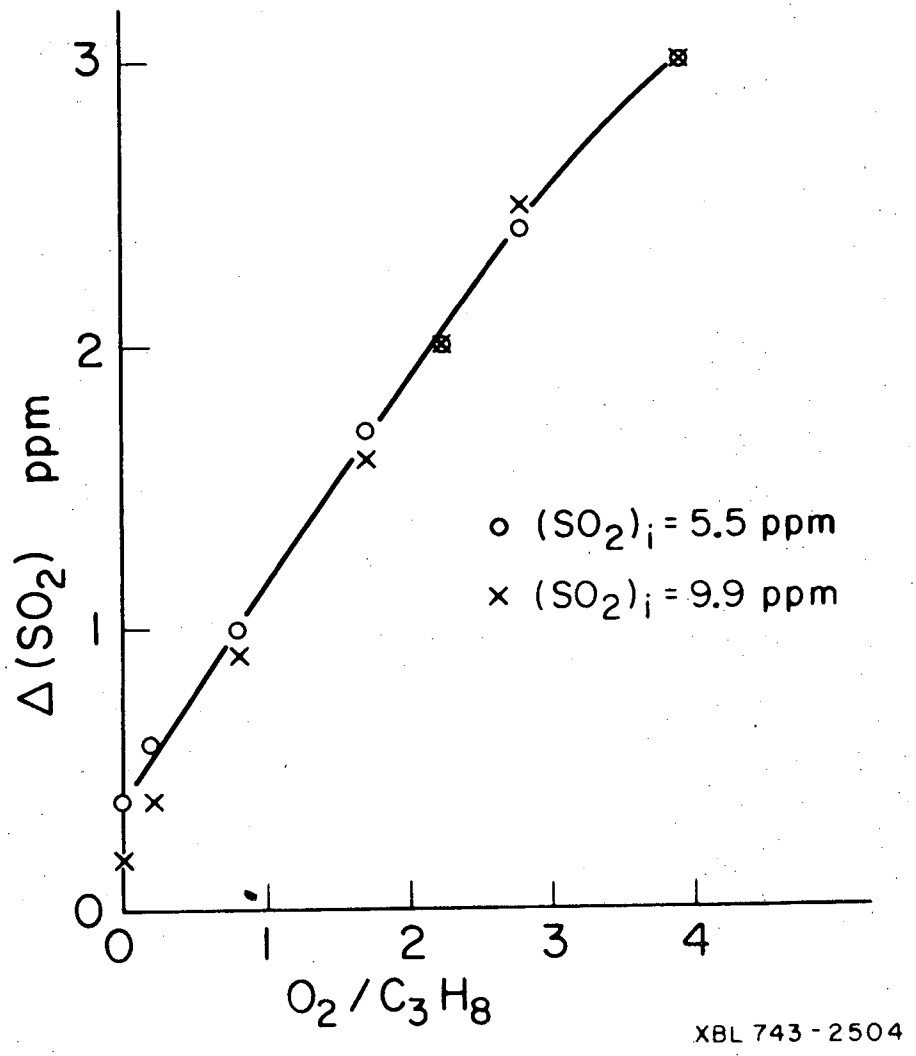

$\Delta(SO_2)$ ppm
O_2 / C_3H_8
o $(SO_2)_i$ = 5.5 ppm
× $(SO_2)_i$ = 9.9 ppm
XBL 743-2504

Fig. 6.

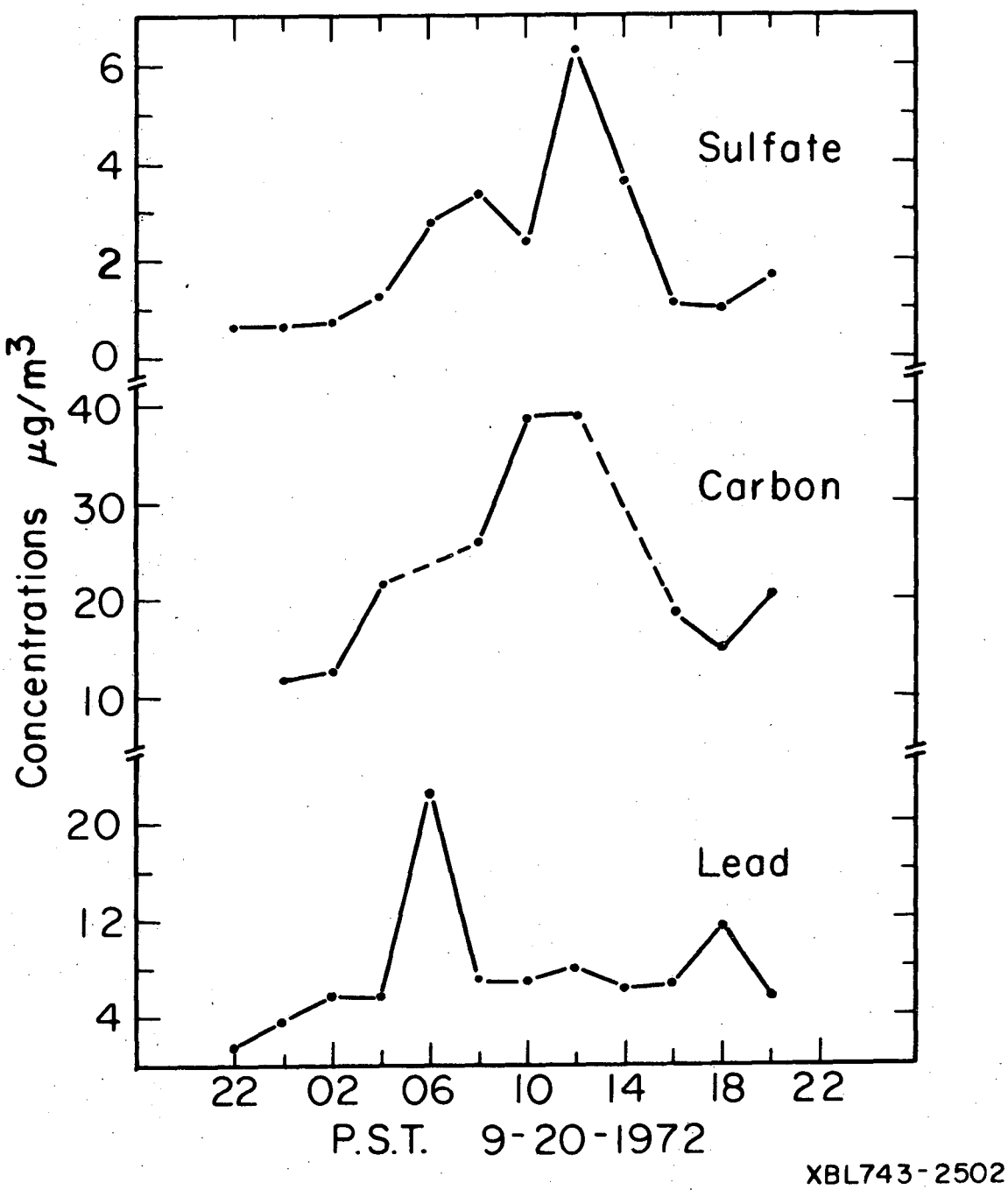

Sulfate
Carbon
Lead
Concentrations μg/m3
6
4
2
0
40
30
20
10
20
12
4
22
02
06
10
14
18
22
P.S.T. 9-20-1972
XBL743-2502

Fig. 7.

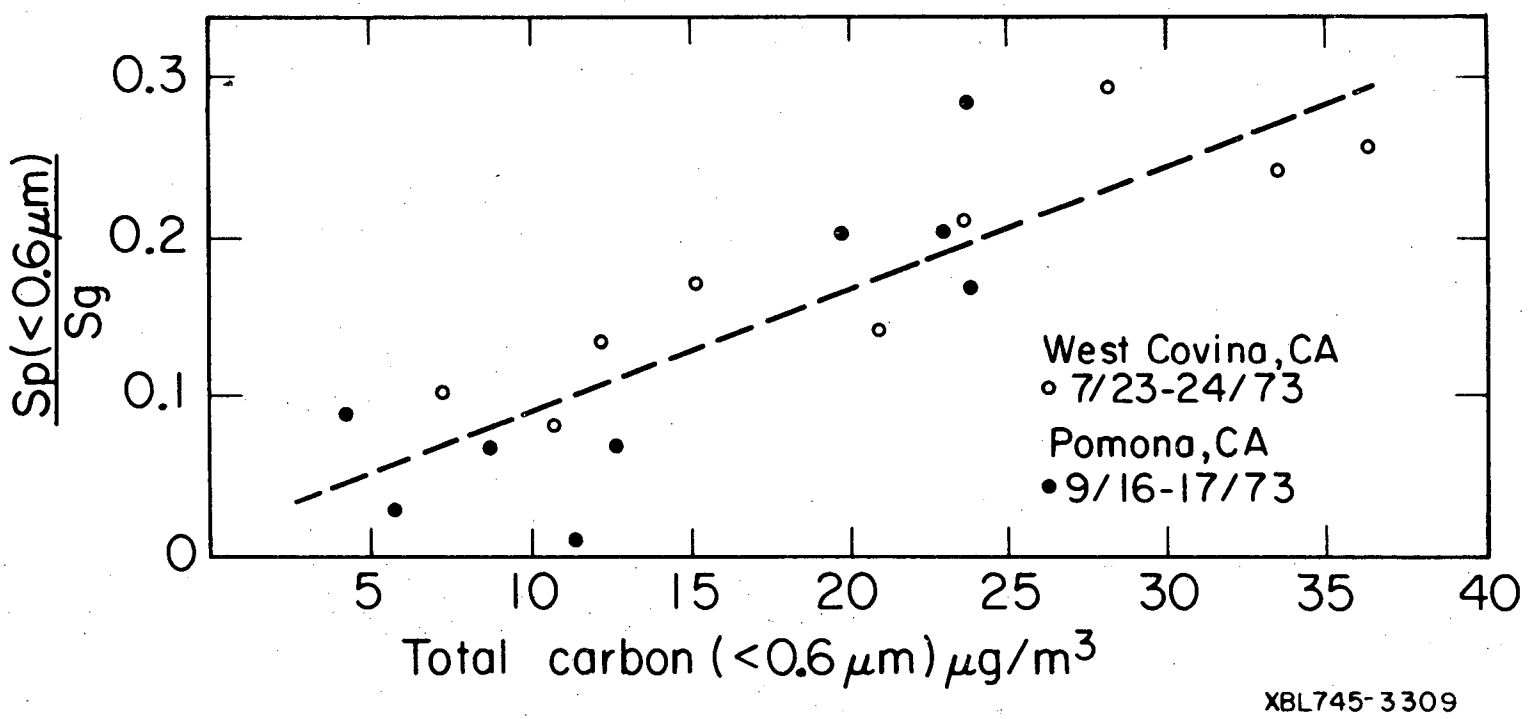

0.3
0.2
0.1
0
Sp(<0.6μm)/Sg
5
10
15
20
25
30
35
40
Total carbon (<0.6 μm) μg/m3
West Covina, CA
∘ 7/23-24/73
Pomona, CA
• 9/16-17/73
XBL745-3309

Fig. 8.

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