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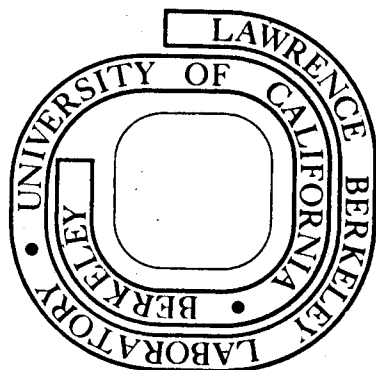
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SULFATES IN POLLUTION PARTICULATES: CATALYTIC FORMATION

ON

CARBON (SOOT) PARTICLES*

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June 1974

ABSTRACT

This paper discusses the role of finely divided carbon (soot) particles in the catalytic oxidation of sulfur dioxide to sulfate in polluted atmospheres. Experimental evidence is presented which shows that carbon particles may play a major role in SO_2 oxidation. The experiments deal with oxidation of SO_2 on graphite particles and combustion produced soot particles. The chemical properties of sulfate produced by SO_2 -soot interaction were also studied. The results obtained with laboratory produced sulfates are compared with properties and behavior of ambient sulfates. The proposed SO_2 oxidation mechanism is qualitatively consistent with field observations. Most experiment reported in this work were performed with the aid of x-ray photoelectron spectroscopy (ESCA).

Because of adverse effects of sulfate particles in polluted atmosphere the study of oxidation of sulfur dioxide to sulfate is occupying one of the central places in air pollution research. Most attention in the past has been devoted to the photochemical and solution chemical oxidation of SO_2 . There is, however, increasing evidence that these two kinds of processes alone cannot adequately account for the observations, meaning that perhaps some catalytic reaction on suspended particulates is involved. The possible role of suspended metal oxides, for example, was examined by some workers⁽¹⁾. Such oxides are found in small concentrations, however. This paper addresses itself to the role that a common pollutant and a catalyst abundantly present in the atmosphere in form of finely divided carbon (soot) particles, plays in the oxidation of SO_2 . Even though the surface chemical and catalytic properties of carbon are known^(2,3) the relevance of soot catalyzed reactions to air pollution chemistry has not been appreciated. We will show that soot catalyzed oxidation of SO_2 to sulfate is an important process in qualitative agreement with the field observations. The experiments reported here were performed with the aid of X-ray photoelectron spectroscopy, ESCA.

Carbon is the most abundant element associated with pollution particulates. Actually carbon constitutes about 50% of the total particulate emissions in urban atmospheres such as those in California⁽⁴⁾. From our ESCA studies of ambient particulates, we find that, perhaps as high as 80%, of particulate carbon is in the form of soot. Soot is basically carbon with graphite-like structure, with some small soot particles consisting of only a few elemental cells⁽⁵⁾ and thus possessing extremely high surface area.

We will first demonstrate the feasibility of SO_2 oxidation on graphite and soot particles. This will be followed by a discussion of

evidence which suggests the relevance of the proposed process to atmospheric pollution.

The interaction of SO_2 with graphite particles was studied with the setup shown in Figure 1a, which produces small, fresh surface graphite particles (diameters $\approx 20 \mu\text{m}$). ESCA spectrum of graphite particles exposed to SO_2 reveals two sulfur (2p) peaks corresponding to sulfate and to sulfide⁽⁶⁾. 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.

The similarity of soot particles to graphite with respect to SO_2 to oxidation is demonstrated by the following experiments. Soot specimens from a premixed propane-oxygen flame collected on (silver membrane) filters were used for experiments with different SO_2 exposure conditions, in the apparatus shown in Figure 1b. Dry and prehumidified particle free air or nitrogen was used with SO_2 concentration of about 300ppm and an exposure time of 5 minutes. ESCA spectra of SO_2 exposed soot are shown in Figure 1b. Sulfate peaks were always more intense in the case of prehumidified air, than in the case of dry air. Blank filters 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. Although water molecules enhance the observed sulfate concentration in the air + SO_2 + soot system, the contribution of sulfate produced by SO_2 oxidation via dissolved molecular oxygen in water droplets is not significant. This alternative is ruled out by the experiment with blank filter and prehumidified air, which does not

result in significant sulfate formation.

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 highest. Here, however, the SO_2 oxidation may be, at least in principle, caused by reactions with reactive combustion produced radical species⁽⁷⁾. The experimental arrangement is shown in Figure 1c. Soot samples were prepared while a constant SO_2 flow (300 ppm, 4 minutes) was introduced through ports #1 through #4, while the flame was on. The amounts of sulfate detected on filters are shown in the graph in Figure 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 significance of the homogeneous gas phase oxidation in this system.

We have also studied the SO_2 oxidation on propane soot particles by observing the decrease in the gaseous SO_2 concentration $\Delta(\text{SO}_2)$, occurring on account of sulfate formation (Figure 1d). SO_2 concentration is adjusted to the desired initial value $(\text{SO}_2)_i$, with the flame removed from its position in front of the intake funnel. Decrease in SO_2 concentration 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 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 the 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 1d 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 $\Delta (\text{SO}_2)$ is independent on $(\text{SO}_2)_i$. This feature is probably related to the saturation of active sites (8) on soot particles. $\Delta (\text{SO}_2)$ 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.

In summary, laboratory experiments show that: 1) Both graphite and soot particles oxidize SO_2 in air; 2) soot catalyzed SO_2 oxidation plays a major role even in presence of flames and combustion produced gases; 3) soot catalyzed oxidation shows a prominent saturation effect, and 4) in separate experiments it was determined that sulfate species on carbon are stable in vacuum at room temperature, they are water soluble and when dissolved they increase the acidity of the solution.

That the described sulfate formation process is consistent with ambient air results is evident from the following. Pollution particulate sulfates are believed to exist mostly in the form of sulfuric acid and/or ammonium sulfate⁽⁹⁾. Because soot- SO_2 interaction leads to sulfate which is water soluble and which could conceivably be neutralized by ambient ammonia its chemical properties are consistent with ambient sulfate properties in the analytical sense. More evidence is found from our finding that ambient and laboratory produced sulfate exhibit the same characteristic desorption in vacuum as function of sample temperature. Saturation effect reported for ambient sulfates⁽¹⁰⁾ is also consistent with the proposed process. Finally, a marked correlation between the diurnal concentration variation of ambient carbon and sulfate should be expected. An example of such correlation is

shown in Figure 2. Other similar correlations have been observed more recently for other sites and pollution episodes⁽¹¹⁾.

Catalytic sulfate formation on soot particles is expected to occur in the open atmosphere and especially in or near combustion sources, where both SO_2 and soot concentrations 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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REFERENCES AND NOTES

- *) Work supported by the National Science Foundation-RANN and the United States Atomic Energy Commission
- +) Present address: Science Center, Rockwell International, Thousand Oaks, CA 91360
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FIGURE CAPTIONS

Figure 1a - ESCA spectrum of graphite particles exposed to SO_2 and filtered ambient air reveals 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.

Figure 1b - Soot exposed to prehumidified air and SO_2 produce sulfate concentrations higher than in the case of dry air. Blank filters, without soot particles, exposed to SO_2 and prehumidified air show only background level sulfate.

Figure 1c - 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 located at the indicated distance from the flame. The resulting sulfate concentrations are plotted vs the SO_2 introduction port distances from the flame.

Figure 1d - SO_2 concentration is adjusted to the desired value $(\text{SO}_2)_i$ with flame removed from its position in front of the intake funnel. Decrease SO_2 concentration, $\Delta (\text{SO}_2)$ is observed when the flame is placed in the intake position. For a given combustion regime $\Delta (\text{SO}_2)$ is independent on $(\text{SO}_2)_i$ and it is increasing with O_2/fuel ratio. The former effect is related to the saturation of active sites on soot particles, while the latter reflects the increase in the number of ultrafine, high surface area particles.

Figure 2 - Diurnal variation of particulate sulfate, carbon (ref. 12) and lead (ref 13) concentrations. The sampling was done in downtown Los Angeles on September 20, 1972, (ref 14). The similarity between carbon and sulfate patterns is obvious.

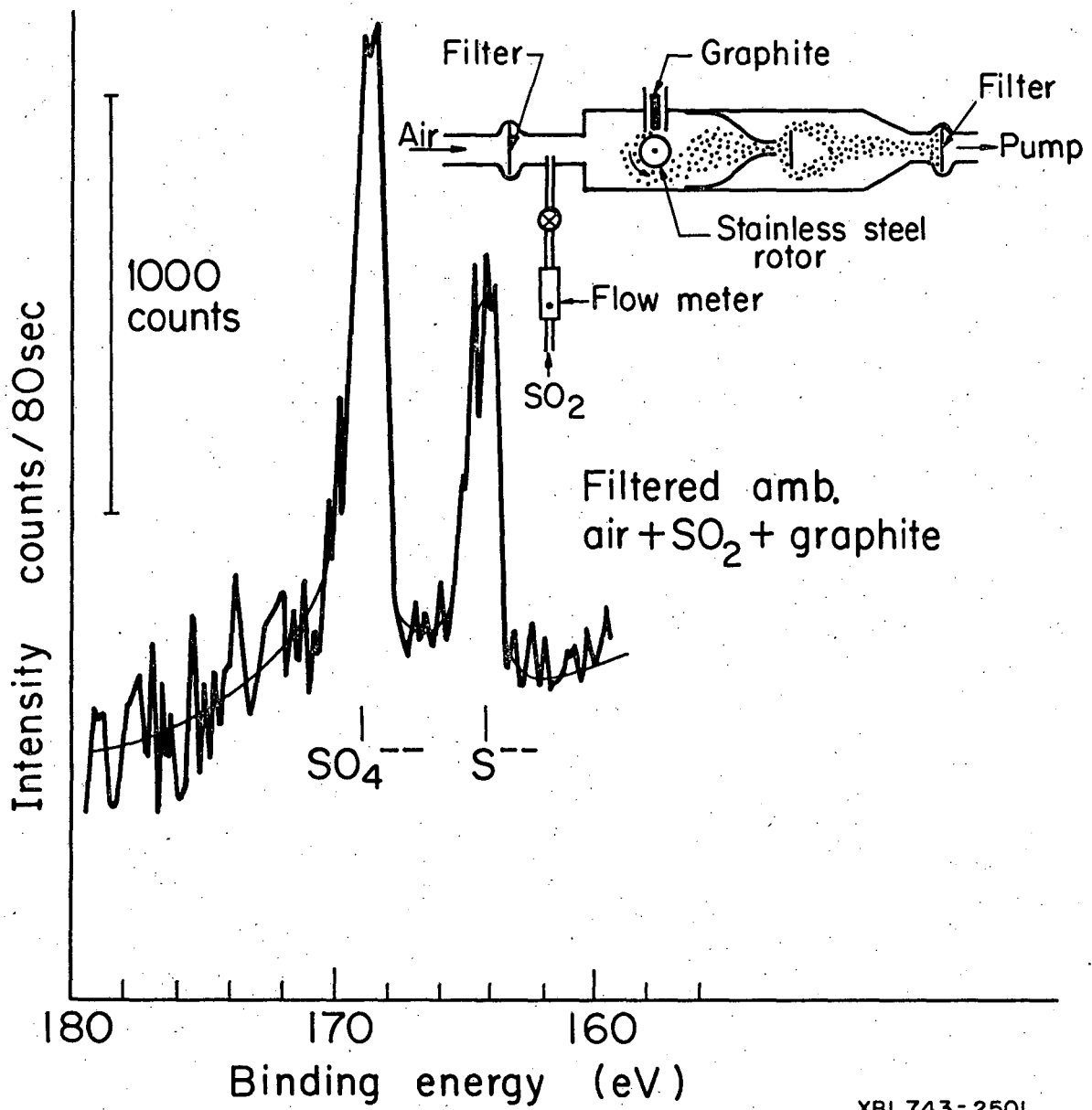
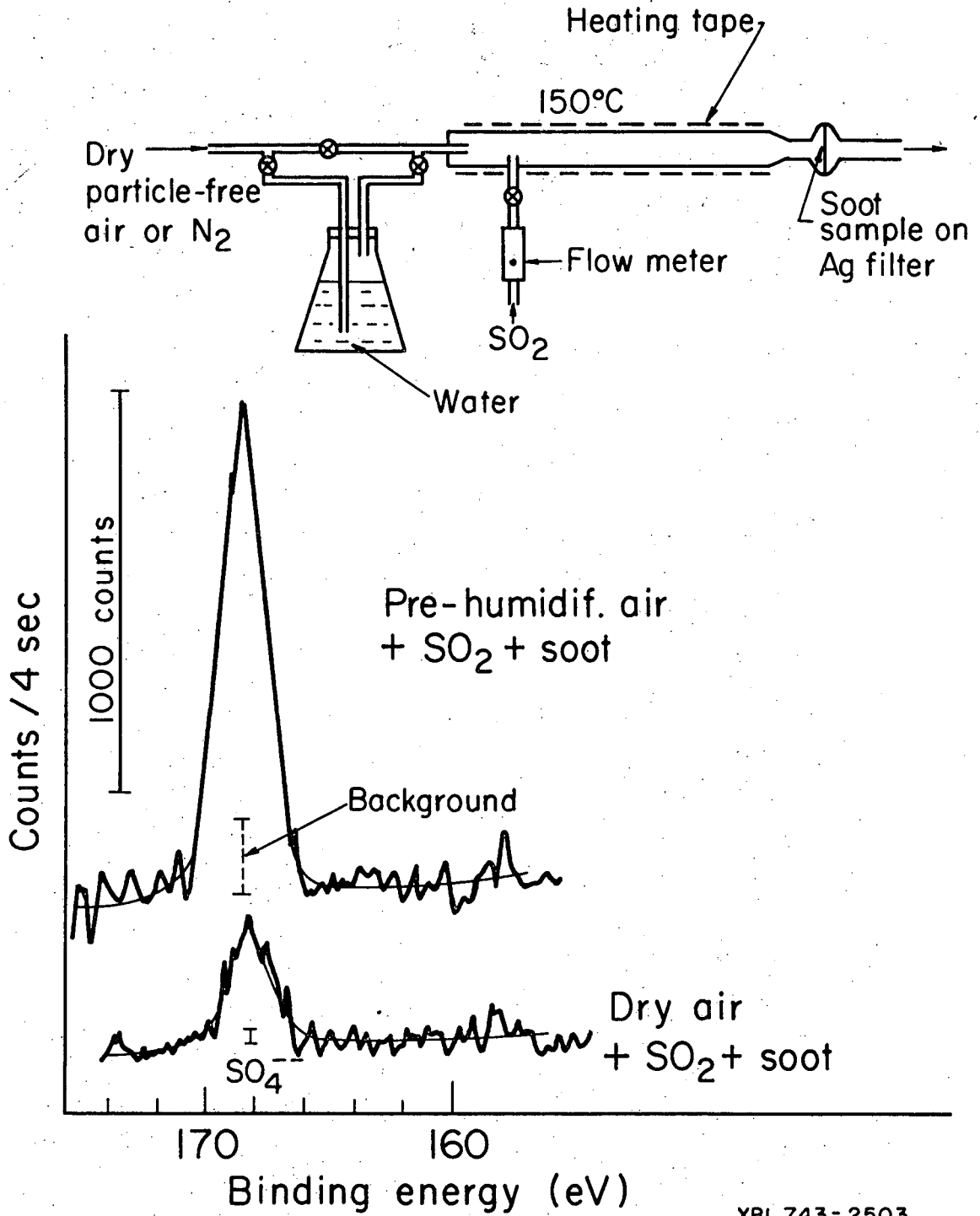
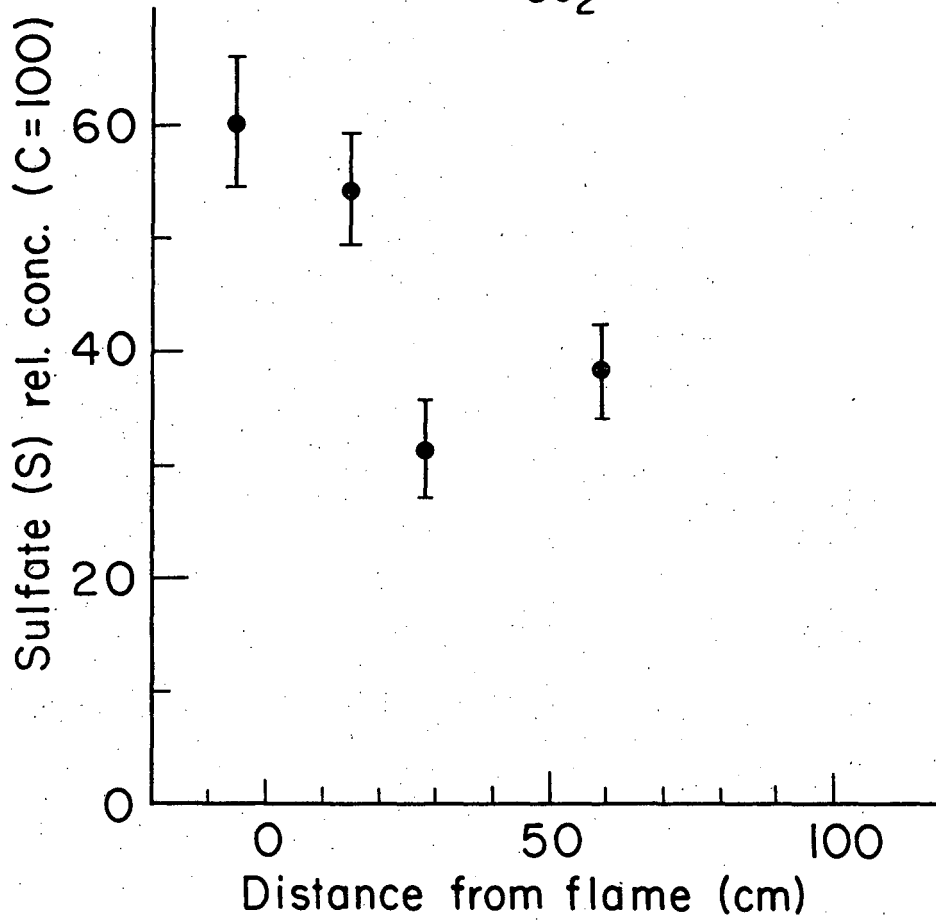
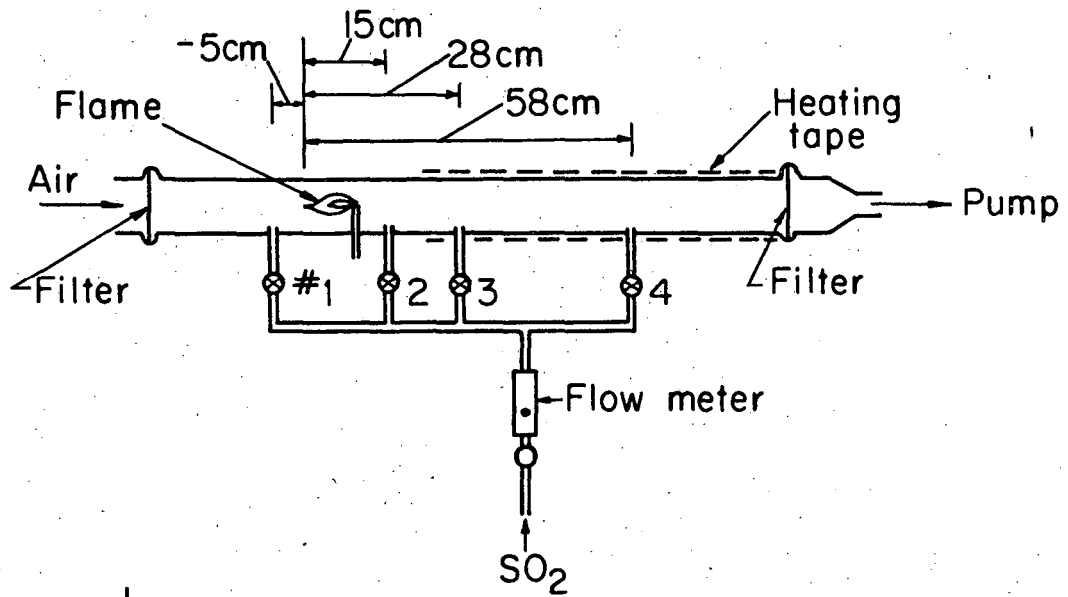


Fig. 1a.



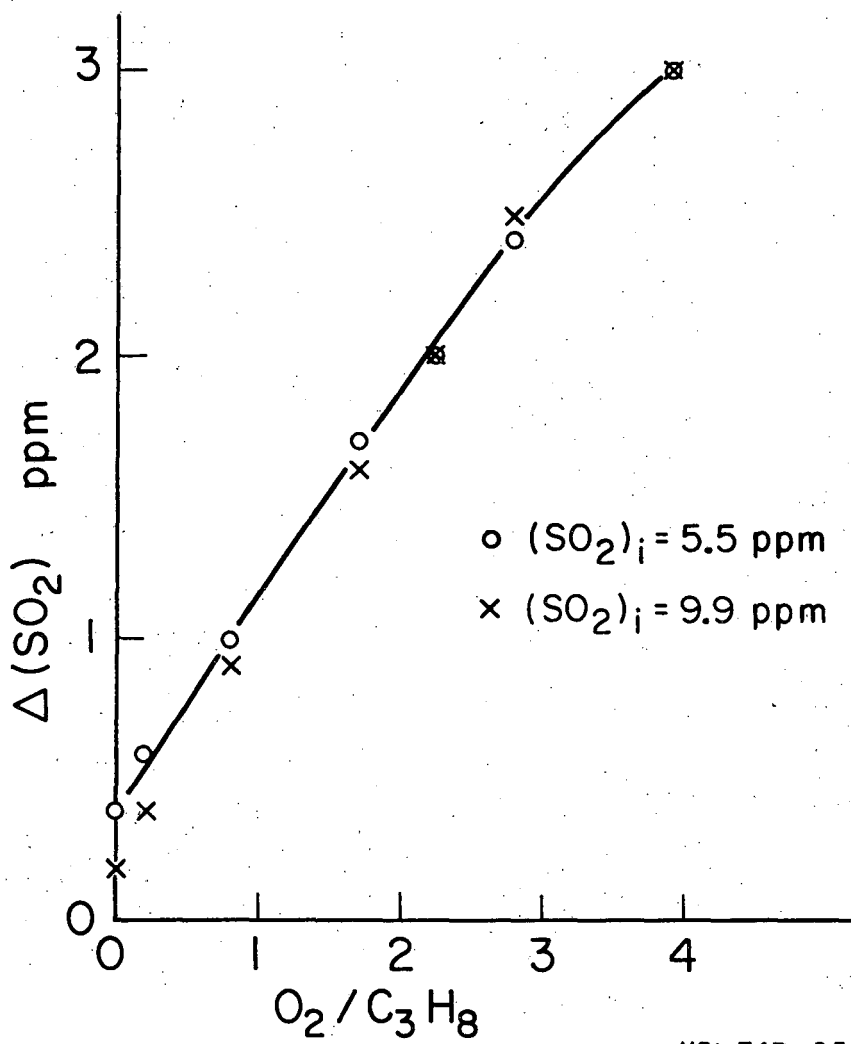
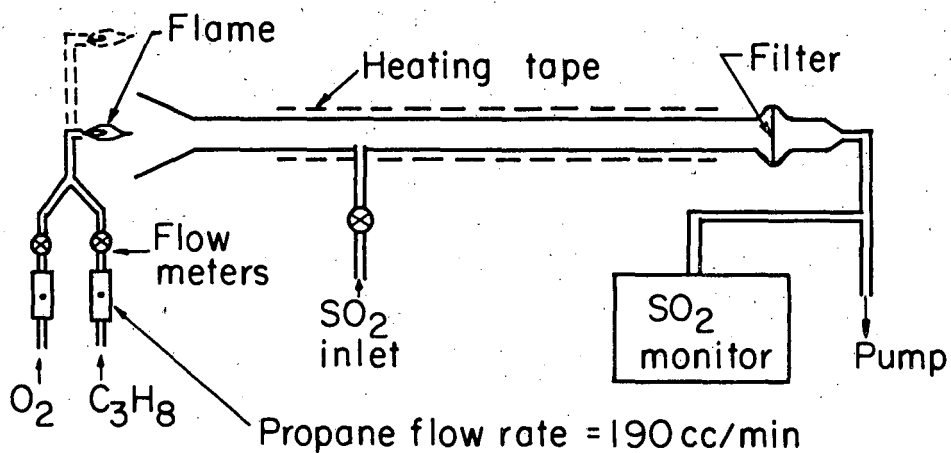
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Fig. 1b.



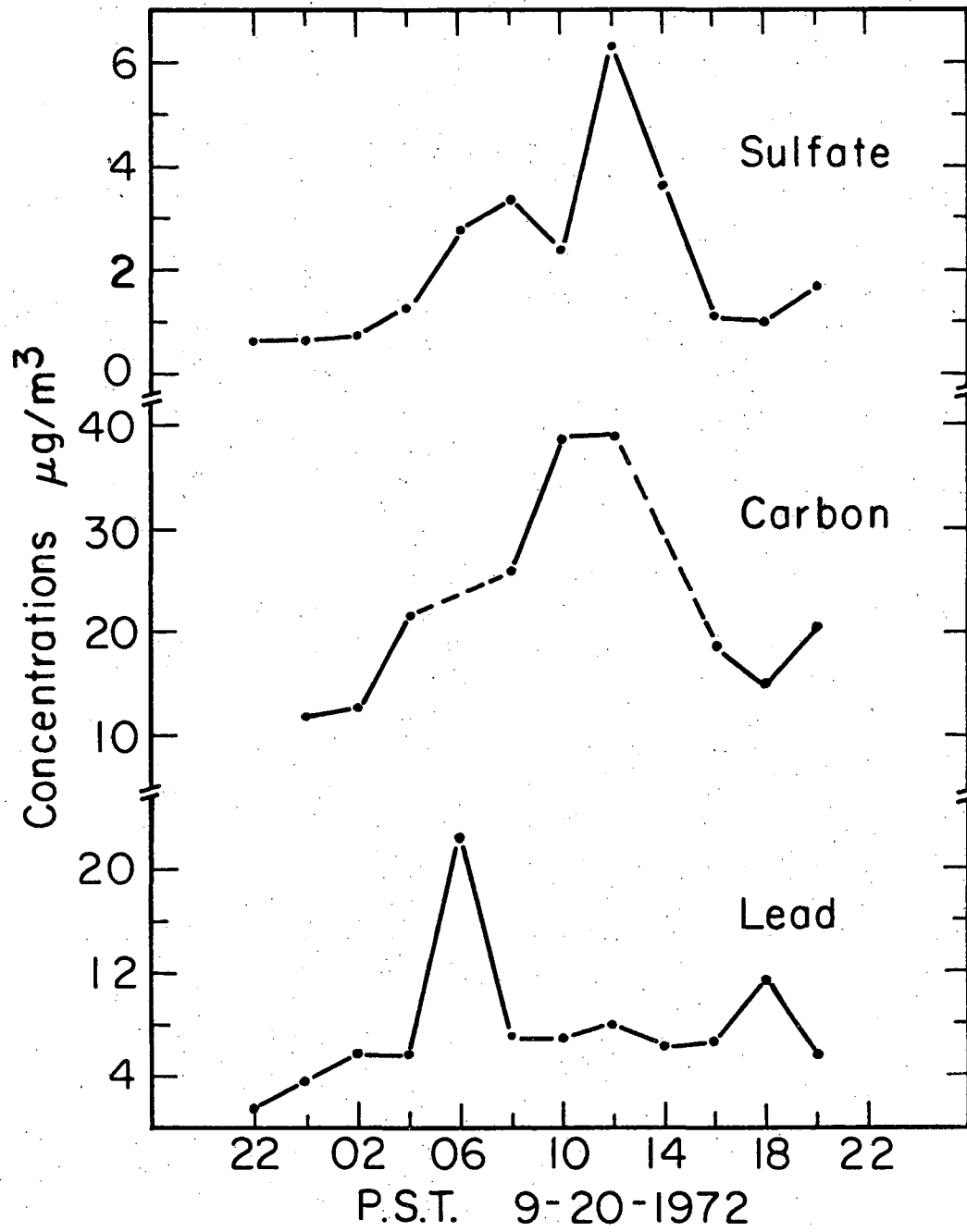
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Fig. 1c.



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Fig. 1d.



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Fig. 2.

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