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SULFATES IN POLLUTION PARTICULATES: CHEMICAL CHARACTERIZATION, FORMATION BY SO_2 CHEMISORPTION ON OXIDIZED CARBON PARTICLES AND THEIR EFFECT ON LIGHT SCATTERING

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Sulfates in Pollution Particulates: Chemical Characterization, Formation by SO_2 Chemisorption on Oxidized Carbon Particles and their Effect on Light Scattering*)

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ABSTRACT

A non-photochemical mechanism of chemisorptive formation of pollution sulfates on oxidized carbon particles is proposed. The proposed hypothesis is based on: a) photoelectron spectroscopic (ESCA) measurements of ambient pollution aerosols; b) ESCA studies of SO_2 chemisorption on graphite, activated charcoal and propane-smoke particles; and c) light-scattering measurements on propane-smoke particles coated with sulfates produced by SO_2 chemisorption.

One of the most objectionable manifestations of air pollution is the reduction of visibility, caused by the scattering of visible light by suspended atmospheric particles (aerosols). The role of sulfur compounds in the formation of these aerosols has been the subject of considerable interest, since urban sulfates are associated with the particles that are most effective in scattering visible light. (1)

Much of the past research has centered on the formation of sulfuric acid (H_2SO_4) aerosols via secondary processes from gaseous SO_2 (2). Two kinds of sulfate-formation mechanisms have received most attention: photochemical reactions (3) and reactions in aqueous solutions (4). H_2SO_4 aerosols produced by these mechanisms can react with ambient ammonia to produce dispersed ammonium sulfate, $(NH_4)_2SO_4$. There is little information about heterogeneous reactions, in sources and in the open atmosphere, involving SO_2-solid particle reactions. It is known, however, that even in the absence of sunlight, SO_2 is readily oxidized in the presence of finely divided metal-oxide particles (5). It is also known that photochemical reactions taking place in the presence of particles occur largely on their surfaces (6).

Our studies of ambient aerosol samples from several urban locations in California have shown that $(NH_4)_2SO_4$, while present, is not in fact the dominant sulfate form in these aerosols. On the other hand, work of other investigators (14) has failed to provide a conclusive proof for the presence of H_2SO_4 aerosols in polluted California air. In our ambient studies we have also observed correlations between the diurnal concentration patterns of sulfate and of carbon. These observations indicated to us the need for further investigations of non-photochemical sulfate-forming reactions involving solid particles, particularly carbon particles, which are so abundantly present in urban air.

This paper summarizes the results of a number of experiments dealing with (a) chemical characterization of ambient urban aerosols, (b) chemisorptive formation of sulfates on surfaces of oxidized carbon particles and (c) the effect of SO_2 chemisorption on the light scattering (visibility reduction) properties of these carbon particles. The chemical characterizations of both ambient and laboratory aerosols were made with the use of photoelectron spectroscopy (ESCA) (7); the light scattering measurements (8) were performed with an integrating nephelometer.

Ambient Studies. The measurements on ambient aerosols discussed here were made on samples collected on September 19 and 20, 1972, near the Harbor Freeway in downtown Los Angeles, CA. (9). Our results and conclusions therefore apply to an urban atmosphere characterized by automotive and other anthropogenic pollutants, with reduced local visibility, but with low oxidant and low relative humidity levels.

The dominant elements in these aerosols are carbon, lead, nitrogen and sulfur, appearing with maximum concentrations of about 80, 22, 12 and 7$\mu g/m^3$, respectively. ESCA measurements were made on 2hr. total filters (TF), without particle-size segregation, and on 2hr. after-filters of a Lundgren impactor (AF), containing mainly submicron particles. Absolute concentrations were derived by normalization of ESCA measurements to the lead concentrations determined by X-Ray fluorescence (10). Carbon concentrations are the averages of determinations by ESCA and by a combustion technique (11).

The sulfur spectra showed that sulfates were dominant in all cases, although in some samples reduced forms of sulfur -neutral and sulfides- were found in concentrations comparable to the sulfates (12). In this paper, however, we will be concerned only with sulfates.

The diurnal variations of sulfate concentrations in total and after filters obtained from a set of 2 x 12 filters covering a 24 hour period are shown in Figure 1a. Also shown are the variations of total carbon (TF) and lead (TF and AF) concentrations. The wind directions at sampling intervals are shown schematically in the same figure. 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; d) most of the sulfates are found in larger particle sizes (TF); and e) because of the changing wind direction the contribution of the Harbor Freeway is not the only significant factor in this episode. The early morning rise (0600 PST) in sulfate concentration, in addition to evidence just mentioned, the essential absence of $(NH_4)_2SO_4$ (see below) and low oxidant levels, suggests that this sulfate is not produced by photochemical reactions.

Two alternative mechanisms can be invoked to explain the similarity between the diurnal patters of sulfates and carbon, and our data allow a choice to be made between them. Either there exists a "chemical link" between sulfates and carbon particles, or the carbon and sulfate particles were carried separately and noninteractively in the same air mass. In the latter case the sulfates, produced by photochemical and solution chemical processes, would be in the form of either H_2SO_4 or $(NH_4)_2SO_4$ or both. Contrary to this expectation our data indicate that in the cases studied the majority of sulfates were in neither of these forms. The sulfate content did not decrease significantly when the sample was heated to 450° C in vacuum, indicating a sulfate form less volatile

than liquid H_2SO_4. Also, attempts to identify characteristic H_2SO_4 droplets in California aerosols by electron microscopy have failed (14). Our ESCA measurements indicate that the sulfates do not occur primarily as $(NH_4)_2SO_4$.

The ESCA analysis procedure is illustrated in Figures 1b, c and d. Figure 1b shows the nitrogen (1s) and sulfur (2p) ESCA spectrum of a sample of pure $(NH_4)_2SO_4$. The photoelectron peak positions (i.e. their binding energies) correspond to the ammonium and sulfate ions, respectively. The nitrogen/sulfur peak intensity ratio of about 1.4 reflects the atomic ratio of 2N/1S for this compound. 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. In fact, the ammonium content in this, and other samples of the episode, is too low to account for the entire sulfate content. Rather, 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). It is possible that these nitrogen species could be mistaken for ammonium by conventional wett chemical techniques.

A similar analysis of an overnight TF sample collected in Berkeley during the summer fog season is seen in Figure 1d. Nitrate and ammonium are recognizable in addition to other reduced nitrogen species. Even in this situation of high humidity, which should enhance the formation of $(NH_4)_2SO_4$, (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 ratio 1:1, as in NH_4NO_3 (Fig. 1e).

<u>SO_2 Chemisorption Studies</u>. The results outlined thus far indicate the possibility of heterogeneous chemisorptive sulfate formation on carbon particles.

Since our ESCA measurements on ambient samples at elevated temperatures (up to 450°C) 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 with anhydrous grade SO_2 on activated charcoal, propane smoke particles and graphite, representing different forms of elemental carbon.

In Figure 1f, a representative sulfur (2p) ESCA spectrum is shown of activated charcoal degassed in vacuum at 400° C and exposed to SO_2 (at STP). These data 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.

Similar experiments with smoke particles generated from propane were made with a flow system and SO_2 concentrations of 100 - 800 ppm. The apparatus, shown in Figure 2a was used both for sample preparation and for light scattering experiments.

Intense sulfate peaks were observed when SO_2 was introduced in the system <u>upstream</u> from the flame. A sulfur (2p) spectrum of a sample produced in this manner is shown in Figure 1g.

When the SO_2 was introduced <u>downstream</u> from the flame, 6 to 8 times lower sulfate intensities were obtained for a given SO_2 concentration.

An insight into the mechanism of this surface-catalyzed conversion of SO_2 to SO_4^{--} was obtained by a study of SO_2 adsorption on single crystal graphite surfaces in UHV. Clean graphite (that is, showing no trace of oxygen) was exposed to about 10^{-6} torr-sec SO_2, and the ESCA spectrum after this treatment revealed only sulfur, analogous to the reduced sulfur seen on some ambient and charcoal samples. On the other hand, if the graphite surface was initially oxygenated and subsequently exposed to SO_2, under conditions otherwise similar to the oxygen-free graphite, sulfate formation occurred. 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.

Both propane-smoke and graphite experiments indicate that elemental carbon becomes efficient in converting SO_2 to sulfate when its surface is covered with oxygen, probably from surface OH^- groups. Evidence against consideration of liquid water as the cause of this conversion is provided by the flame experiments. Water condensation on the carbon particles is expected to occur rapidly downstream from the flame, where no sulfate conversion was obtained. A rough estimate of the efficiency of the propane smoke for removing SO_2 was obtained by monitoring the gaseous SO_2 concentration by infrared spectroscopy. This indicated (under one set of conditions where the initial SO_2 concentration introduced upstream from the flame was 244 ppm) that the propane flame reduced the SO_2 concentration to one-third of its original value.

Light-scattering experiments were performed with an integrating nephelometer. Large increases in the scattering coefficient b_{scat} were observed between bare smoke particles and particles produced in the flow system when SO_2 entered the system <u>upstream</u> from the flame. Virtually no effect on light scattering was visible when SO_2 was introduced <u>downstream</u> from the flame. Figure 2b showns the nephelometer response to the introduction of about 150 ppm of SO_2 upstream from the flame. The value of b_{scat} is about twenty times that of bare smoke particles.

The effect of preferential chemisorption on fresh particles is illustrated in Figure 2c. A constant flow of SO_2 was periodically switched from the upstream to the downstream input. The upstream introduction occurred at points I, III and V, while the downstream introduction was at points II, IV and VI. The SO_2

flow was discontinued at point VII. The downstream input had very little, if any, effect on the value of b_{scat}. The interaction of SO_2 with particles before water condensation occurs, appears to be essential for both efficient oxidation and for an increase in light-scattering.

Scanning electorn micrographs of the particulates formed in these experiments indicate that the increase in light scattering (visibility reduction) is caused by coagulation and agglomeration of primary submicron smoke particles (diameters < 0.1μ) induced by surface sulfate formation.

Our experimental results are summarized as follows:

1. Most of the ambient particulate sulfate (downtown Los Angeles, 19-20 September, 1972) is present in a form other than the usually assumed ammonium sulfate, $(NH_4)_2SO_4$.

2. Diurnal variation of ambient sulfate concentration resembles the diurnal variation of particulate carbon, which was found to be largely non-volatile.

3. Laboratory-produced carbon particles with oxidized (oxygenated) surfaces are efficient catalysts for SO_2 to SO_4^{--} conversion.

4. Chemisorption of SO_2 on reactive submicron carbon particles produces large increases in the light scattering coefficient, b_{scat}. This increase is caused by agglomeration of sulfate-coated smoke particles.

5. The chemisorptive formation of sulfate and related increases in b_{scat} occur on oxidized carbon particles and cannot be explained by condensation of liquid water on the particles.

Because of the availability of reactive carbon particles in combustion processes, it can be expected that sulfate-bearing particles are emitted into the atmosphere from primary sources, 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 observed strong effect of SO_2 chemisorption on b_{scat} is an indication that sulfate-coated carbon particles are, at least in part, responsible for visibility reduction in the polluted urban atmosphere. The process of sulfate formation that we propose here could occur in addition to other reactions, such as photochemical. We believe, however, that the chemisorptive mechanism outlined here may play a dominant role in urban situations that are characterized by large particulate carbon concentration. This implies that reductions of gaseous pollutants, such as NO_x and hydrocarbons in the case of automobiles, alone may not have the desired effect in improving visibility if fuels with sulfur content, as at present, are used and if no efficient primary submicron particulate reduction is achieved.

The proposed chemisorptive sulfate-forming mechanism is in qualitative agreement with the features that we have observed in our studies of ambient sulfates and carbon.

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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 particles. 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.

Figure 2:

a) Flow system used for SO_2 chemisorption studies on propane smoke particles. The same apparatus was used for both sample preparation for ESCA measurements and for the study of the effects of SO_2 chemisorption on light scattering with an integrating nephelometer.

b) The nephelometer response to the introduction of 150 ppm of SO_2 upstream from the flame.

c) A demonstration of the preferential chemisorption on fresh particles as evidenced by the light scattering. The upstream introduction of SO_2 occurred at points I, III, and V, while the SO_2 flow was switched to the downstream input at points II, IV and VI. The SO_2 flow was discontinued at point VII. Downstream input had virtually no effect on the increase of b_{scat}.

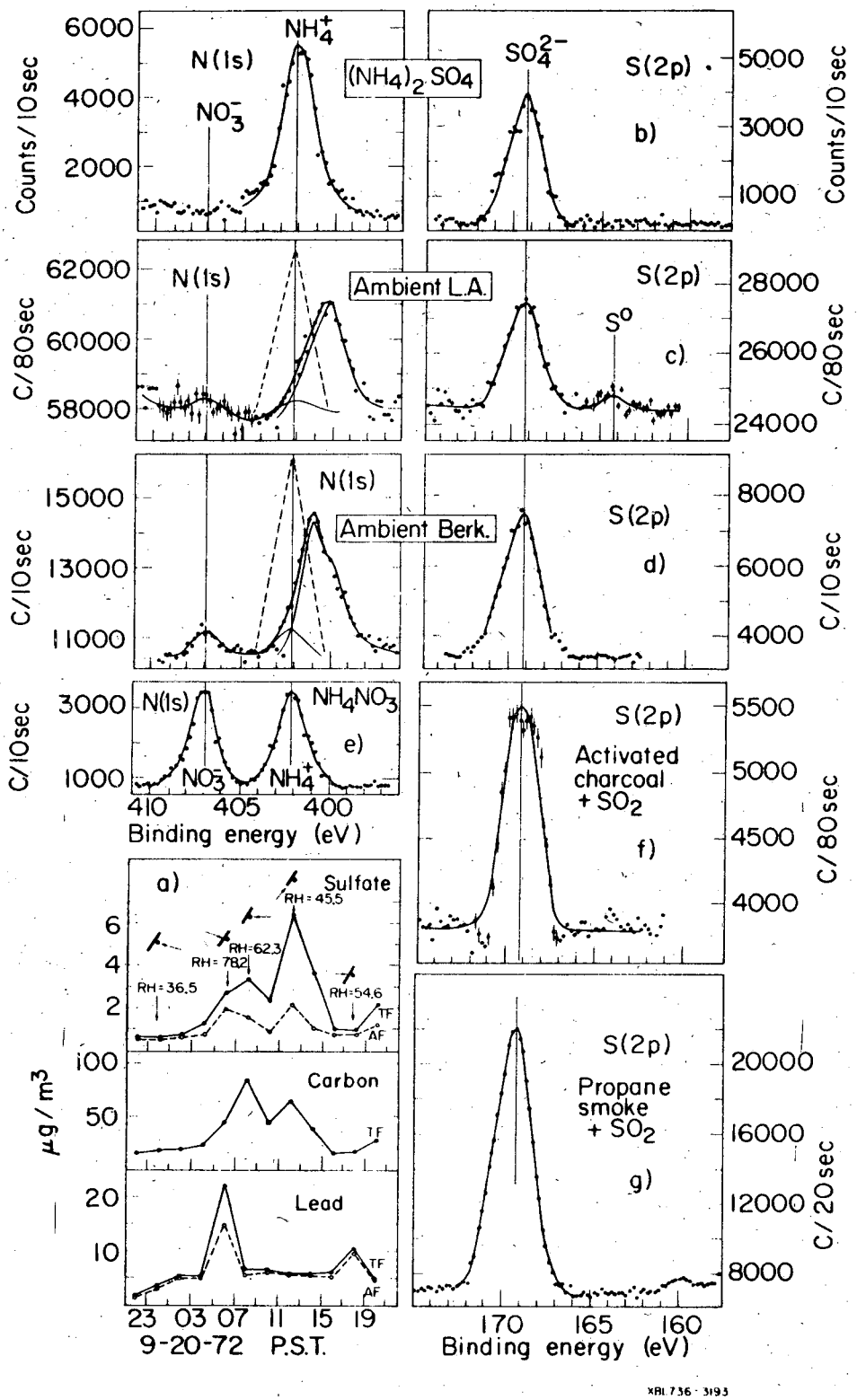
N(1s)
NH_4^+
NO_3^-
$(NH_4)_2SO_4$
SO_4^{2-}
S(2p)
b)
Counts/10sec
Ambient L.A.
S^0
c)
C/80sec
Ambient Berk.
d)
C/10sec
NH_4NO_3
e)
Binding energy (eV)
Activated charcoal + SO_2
f)
a)
Sulfate
RH = 45.5
RH = 62.3
RH = 78.2
RH = 36.5
RH = 54.6
TF
AF
Carbon
Lead
$\mu g/m^3$
9-20-72 P.S.T.
Propane smoke + SO_2
g)
C/20sec
XBL 736-3193

Fig. 1

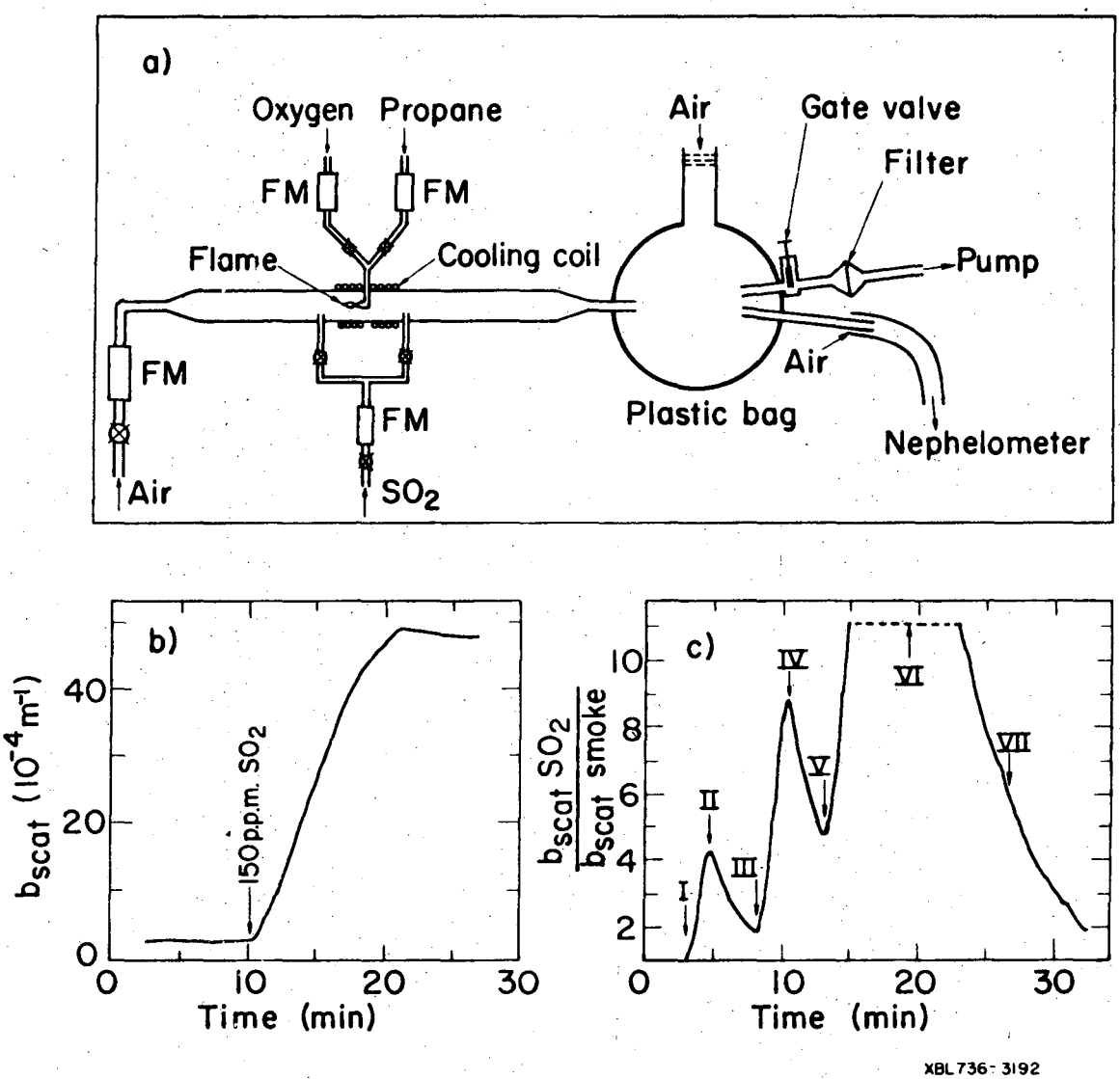
a)
Oxygen
Propane
FM
FM
Flame
Cooling coil
FM
FM
Air
SO2
Air
Gate valve
Filter
Pump
Air
Plastic bag
Nephelometer
b)
bscat (10-4m-1)
150p.p.m. SO2
Time (min)
c)
bscat SO2 / bscat smoke
I
II
III
IV
V
VI
VII
Time (min)
XBL 736-3192

Fig. 2

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