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OXIDATION OF SO_2 IN FOG DROPLETS BY PRIMARY OXIDANTS

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Abstract

Experiments described in this paper demonstrate that incomplete combustion is a source of gas-phase oxidants. These species, when dissolved in water, are manifested predominantly as H_2O_2 and, to a lesser degree, as organic peroxides. Experiments involving a fog chamber show that these primary oxidants oxidize SO_2 to sulfuric acid or sulfate in fog droplets. Drying such fog droplets results in suspended sulfate particles. For a constant SO_2 concentration and amount of fuel combusted, the amount of SO_2 oxidized and the amount of oxidant produced depend critically on the combustion conditions, being highest for incomplete combustion and negligible for stoichiometric flames.

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Introduction

Deposition of acidic forms of rain, fog, and particulate sulfate is one of the outstanding contemporary environmental problems. An understanding of the relationship between SO_2 emissions and the chemical composition of rain, fog, and cloud droplets could lead to control strategies that reduce acidic deposition; but, at present, this relationship is largely unknown. Because specific catalysts and/or oxidants are required in aqueous SO_2 oxidation pathways, the amount of SO_2 oxidized will depend not only on the SO_2 concentration but, under many circumstances, may also depend critically on the availability and origin of the oxidants and catalysts. Greater knowledge of the types and sources of SO_2 oxidants is crucial to solving this problem.

Certain catalytic materials such as soot and transition metals are co-emitted into the atmosphere with SO_2 from the same combustion sources. The atmospheric concentrations of these catalysts are directly related to source emissions and are therefore, in principle, controllable at the source. However, one of the most important oxidants for SO_2 oxidation is hydrogen peroxide (H_2O_2) (Penkett, 1979; Martin, 1981; Kuren, 1983; Schwartz, 1984; Hoffmann, 1975), which is believed to be produced entirely in the atmosphere by a series of photochemical reactions that involve many reactants not emitted directly from sources. Thus, the occurrence of H_2O_2 in the atmosphere is essentially unrelated to source emissions and is therefore uncontrollable at the source.

In this paper, we present evidence that incomplete combustion, besides being a source of particulate catalysts, is also a source of primary oxidants, which in the aqueous phase are mostly present as H_2O_2 and, to a lesser extent, organic peroxides. The amount of oxidant produced by flames depends on combustion conditions, production being highest for incomplete combustion and negligible for stoichiometric flames. We also demonstrate the role of these primary oxidants in the oxidation of SO_2 in fog droplets and the formation of suspended sulfates under laboratory conditions.

The origin of the primary oxidants is the precombustion reactions between fuel molecules and oxygen, with reaction intermediates (Sturgis, 1955; Heicklein, 1976). During perfect combustion, these species will be oxidized to CO_2 and H_2O. When the reacting mixture does not ignite or when some portions of it fail to ignite, the intermediate species produced by precombustion reactions will appear in the combustion effluent. These facts are known from combustion research but have not been fully appreciated by the atmospheric chemistry community. Emission of primary oxidants ties atmospheric chemistry to not only how much fuel is burned but also how fuel is burned, and this realization may have an effect on our understanding of the formation of acid precipitation, including acid fog and approaches to its control.

Experimental Methods

The apparatus used to study the interaction of combustion effluent with SO_2 and to demonstrate the emissions of primary oxidants is schematically shown in Fig. 1. It consists of a

glass chimney containing an axially positioned torch where gaseous fuels such as propane, natural gas, CO, and H_2 could be combusted with adjustable fuel-to-O_2 ratios. The flame is electrically ignited and can burn continuously or intermittently (e.g., 5 sec on, 5 sec off). This latter combustion regime is used to produce the most incomplete turbulent combustion. The walls of the chimney were maintained at least 5°C above the dew point of the effluent (General Eastern, chilled mirror dew point sensor). The flow rate of air through the chimney was held constant at 6 ℓpm. SO_2 can be introduced directly into the chimney above the flame to study gas and particle reactions or after the filter (Fluoropore) to study only the gas-phase processes. The filter also prevented the combustion-generated soot particles from reaching the SO_2 detector (TECO, pulsed fluorescence) or the bubblers in which the combustion gases and SO_2 could be dissolved for subsequent anion and total peroxide analysis.

The apparatus used in the fog chemistry experiments, schematically represented in Fig. 2, consists of two main parts: the glass chimney with the combustor, and the fog chamber itself. The chimney, identical to the one described above, is the source of gaseous combustion effluent, water of combustion, and combustion-generated particles. These particles also serve as fog condensation nuclei. The fog chamber is a plexiglass cylinder through which cooled nitrogen is passed to provide a temperature below the dew point of the incoming combustion gases. The combustion products are fed through heated tubing (50°C) into the chamber through an opening in the center of the bottom flange of the chamber. The actual inlet is slightly heated (50°C) to prevent water condensation. The flow rates of cold N_2 (6 ℓpm) and combustion gases (5 ℓpm) produced a fog at room temperature. The source of the water that condenses onto the combustion particles is principally from the flame and, to a small degree, from water vapor in the room air that enters through the chimney. Fog droplets are collected with an impactor, designed to provide a cut-off size of about 7 μm, situated near the top of the chamber.

Fog water was collected during runs having different flame conditions with and without added SO_2. The SO_2 was introduced into the system at a point between the chimney and the chamber. The collected fog water was analyzed for anions (NO_3^-, $SO_3^=$, $SO_4^=$), H_2O_2, and pH. Anions were quantitated by ion chromatography (Dionex Corp., model 12) using AS1-type columns and a 3 mM HCO_3^- + 3 mM $CO_3^=$ eluent at 2.3 ml min^{-1}. H_2O_2 was determined by iodometric titration after ammonium molybdate was added to catalyze the reaction between I^- and H_2O_2 (Johnson, 1970). A miniature pH electrode was used to measure $[H^+]$.

The apparatus shown in Fig. 2 was also used to study the formation of particulate sulfate. Sulfate particles were collected by quartz fiber filters at the two sampling points indicated in the figure: at the top of the chimney and after a drying denuder located on the top of the fog chamber. Sampling from the fog chamber was performed with and without fog present in the chamber. The principal difference between sampling directly from the chimney and from the fog chamber is in the gas temperature relative to the dew point of the combustion effluent. In the chimney, the gas temperature was 70°C, well above the 40-45°C dew point. In the fog

chamber, the temperature was 20°C. In the chimney, the temperature was above the dew point and precluded formation of visible fog droplets; while in the fog chamber, because of additional cooling, the fog readily occurred. Propane (110 ml min^{-1}) was burned as a steady diffusion flame. The filter samples were collected for 10 minutes, and the water-soluble anions were extracted with sonication into deionized water, refiltered through 0.22-μm-pore Millipore filters (pre-extracted, type GS) and analyzed by ion chromatography.

Results and Discussion

Three types of experiments are described in this section, dealing with (1) demonstrating that SO_2 reacts with gas-phase products of incomplete combustion, which when dissolved in water are effective oxidants for aqueous-phase SO_2; (2) acidifying of fog droplets by the oxidation of SO_2 by primary oxidants; and (3) forming particulate sulfate from acidic fog droplets.

Evidence for primary oxidants. When SO_2 is introduced into the air flow (Fig. 1) in the chimney at a rate that maintains its concentration at ∿ 1 ppm, an instantaneous decrease in this concentration is observed when a fuel such as sulfur-free propane (110 ml min^{-1}) is ignited in the torch. For a diffusion flame, the SO_2 concentration decreases approximately 80%.

This observation is essentially similar to one observed before (Novakov, 1974) and can be explained by one or more of the following processes: (1) SO_2 is scavenged by the condensed combustion-generated water; (2) SO_2 is converted to sulfate by oxidation or adsorption on combustion-generated particles; (3) the SO_2 detector is subject to a negative interference by some of the combustion effluents; or (4) SO_2 reacts in the gas phase with combustion products to produce gaseous sulfur species not detected by the SO_2 detector.

The first possibility was eliminated or at least minimized by maintaining the entire system at a temperature above the maximum measured dew point; furthermore, when H_2 was burned at a flow rate designed to produce the same concentration of H_2O vapor as that produced by the propane flame, only a small (5%) reduction in $[SO_2]$ was noted. The second possibility was eliminated when filter samples collected at the top of the chimney while a flame was burning showed that particulate sulfur could not account for the observed decrease in $[SO_2]$. The possibility that the observed SO_2 decrease was caused by species interfering with the SO_2 detector is unlikely. Consultation with the manufacturer of the SO_2 detector (TECO) indicated that no known interfering species cause a decrease in the apparent SO_2 signal: all known interferents, such as fluorescent hydrocarbons, are positive interferents.

This leaves the fourth possibility, that a gas-phase reaction between SO_2 and certain products of incomplete combustion occurs. It became evident that this reaction is a gas-phase reaction when similar decreases in $[SO_2]$ were observed when SO_2 was added after the filter. (This filter eliminated essentially all combustion-generated particles.) It also became evident that the reaction is fast because the residence time between the SO_2 injection point and the detector was 5 seconds. The reactant must be a product of incomplete combustion because

a steady (2-min) diffusion flame produced a smaller reduction in $[SO_2]$ than did a 4-minute intermittent flame (5 sec on, 5 sec off for 4 min) that burned the same total amount of fuel. When propane was premixed with air before combustion, the reduction in $[SO_2]$ was less; and premixing with O_2 caused essentially no reduction in $[SO_2]$.

The experiments described thus far suggest a free-radical-type reaction whose product is a gaseous, i.e., nonfilterable, species not detected by the pulsed fluorescence SO_2 detector. At this time, neither the reactive species nor the reaction product is known with any certainty However, the experiment that we describe next will demonstrate that products of incomplete combustion when dissolved in water act as potent oxidants for SO_2 oxidation and that most of this oxidant is H_2O_2.

The conclusion that combustion is a source of primary oxidant was reached by experiments using water bubblers to collect SO_2, the combustion gases, and any SO_2 reaction products (Fig. 1). When SO_2 alone was drawn through the bubbler, 100% of the expected SO_2 was recovered — 95% as S(IV) and 5% as $SO_4^{=}$. When filtered combustion gases and SO_2 were sampled through the bubbler, 90% of the gas-phase sulfur was recovered, but only 10% of the aqueous S was detected as S(IV); the remaining 90%, as $SO_4^{=}$. The dissolved combustion gases caused a large fraction of the SO_2 to be oxidized to $SO_4^{=}$.

Filtered combustion gases (without added SO_2) were also sampled in the bubbler. S(IV) in the form of HSO_3^- was then added to the bubbler solution so that the diluted final concentration was several ppm. This S(IV), upon immediate analysis, was found to have been oxidized to $SO_4^{=}$. This finding is shown in Fig. 3, where ion chromatograms of an S(IV) solution, of dissolved combustion effluent, and a combination of the two solutions are shown.

The fraction of S(IV) that was oxidized in the bubbler can be related to flame conditions and fuel type. For comparable amounts of fuel burned, S(IV) oxidation decreases in this order: intermittent flame > steady flame > air-premixed flame > O_2-premixed flame = CO = H_2. The combustion gases contain NO_2, but ion chromatographic analysis of the bubbler solution indicated that NO_2^- was not involved in S(IV) oxidation under these conditions.

The principal oxidizer for S(IV) oxidation in these solutions is H_2O_2, as is evident from Fig. 4. In this figure, the amount of S(IV) oxidized is plotted as a function of H_2O_2 lost. It is obvious that the quantities are correlated and that it takes between 1 and 2 moles of H_2O_2 to oxidize one mole of S(IV). Having in mind the uncertainties in the measurement of H_2O_2 below 10^{-4} M using titanium complexation (Johnson, 1980) in these preliminary experiments, we concluded that the results in Fig. 4 reflect that S(IV) oxidation by H_2O_2 follows approximately a one-to-one stoichiometry.

<u>Oxidation of SO_2 in fog droplets.</u> Because H_2O_2 is believed to be the principal oxidant involved in fog and cloud acidification and because, as we have just shown, incomplete combustion is a source of H_2O_2, it seemed logical to hypothesize that fog could be acidified by exposure to combustion products.

To test this assumption, experiments with a fog chamber (Fig. 2) were performed. The previously described experiments with bubbler solutions dealt with a bulk aqueous reaction system, and in contrast the fog chamber experiments deal with a dispersed droplet reaction system. The results obtained with the fog chamber are summarized in Table 1 for three different flame conditions: intermittent diffusion flame, steady diffusion flame, and steady premixed (air) flame. Propane was used as the fuel in all these experiments.

The results in Table 1 show that an intermittent flame of propane with minimal sulfur content produced fog with a pH of 2.7 and a trace of sulfate. This sulfate is due to the trace amounts of sulfur in the propane. The H_2O_2 concentration in this experiment was determined to be 21 mM. Adding about 20 ppm SO_2 (corresponding to propane with $\sim$ 0.1% sulfur content) to the combustion effluent lowered the pH value from 2.7 to 1.9 and increased the sulfate concentration by a factor of 700 over the sulfate concentration without additional SO_2. No detectable H_2O_2 was found (detection limit of the method used is $\sim 1 \times 10^{-4}$ M) because it was consumed by reacting with dissolved SO_2. We have also established that > 10% of the available SO_2 was converted to sulfate almost instantaneously. The results in Table 1 show similar trends for other flame conditions; but, as expected, the droplets contain progressively smaller absolute concentrations as conditions are adjusted to produce more efficient combustion.

Formation of particulate sulfate. That liquid water is essential for the formation of solid particulate sulfate is evident from the following experiments. As seen in Fig. 2, particulate sulfate could be sampled at two sampling points: from the chimney and from the fog chamber after the fog droplets were dried by a diffusion denuder. The results of these experiments are presented in Table 2. As this table shows, essentially no sulfate was detected in the samples collected directly from the chimney. The sulfate concentrations were highest in the dried fog + SO_2 sample. Samples collected from the fog chamber, but without fog, showed about three-quarters of the sulfate observed when the fog was present.

These experiments clearly demonstrated the role of liquid water in the sulfate formation. The highest concentrations of particulate sulfate were produced when the conditions for aqueous reactions were present. The sulfate production was greatest when visible fog was observed; however, even in the absence of visible fog, sulfate was formed as long as the temperature was at or below the dew point. At this temperature, a relatively thin layer of water could condense on combustion particles, which was sufficient to enable the aqueous SO_2 oxidation reactions to occur.

At this time, we don't have solid direct evidence about the concentrations and role of primary oxidants in polluted atmospheres. However, some preliminary experiments that we have performed and also data in the literature have shown that internal combustion engines in general (Sturgis, 1955; Heicklein, 1976), and diesel engines in particular, are a significant source of primary oxidants. For example, approximately one-third of sulfur from diesel fuel is oxidized to sulfate when the diesel engine exhaust is sampled in a water bubbler. Based on

such measurements, it was estimated that a diesel passenger car under idling conditions emits $\sim$ 10 μg of H_2O_2 per liter of exhaust (McKinney, 1984). A possible direct field observation of combustion-produced H_2O_2 was made by Kok et al. (1978), who observed an increase in ambient H_2O_2 during a local grass fire.

The results of early combustion studies corroborate our observation that hydrocarbon flames are sources of peroxides. Satlerfield and Reid (1955) demonstrated that precombustion reactions in cool propane flames produce large quantities of hydrogen peroxide. They showed that under certain conditions as much as 35 mole percent of the fuel became hydrogen peroxide. Bawn and Skirrow (1955) reported similar findings for propylene, butene, and heptene.

Conclusions

The experiments described above have demonstrated that incomplete combustion is a source of reactive species. These species readily react with SO_2 in the gas phase, forming a compound not detected by a pulsed fluorescence SO_2 detector. Reactive gas-phase combustion products, when dissolved in water, are manifested predominantly as H_2O_2 and, to a lesser extent, as organic peroxides.

These primary oxidants oxidize SO_2 to sulfate or sulfuric acid in either bulk or dispersed (fog) aqueous systems. For a constant SO_2 concentration and amount of fuel combusted, the amount of SO_2 oxidized depends critically on the combustion conditions, being highest for incomplete combustion and negligible for stoichiometric flames.

The evidence just outlined and our laboratory work suggest that primary oxidants may play a role in atmospheric SO_2 oxidation, particularly in formation of acid fog by involvement of automobile-emitted oxidants and in the formation of particulate sulfate in environments characterized by poor combustion technology. The primary oxidant mechanism may help to explain the observed systematic sulfate-soot correlation (Novakov, 1984), especially under winter conditions, because soot is also a product of incomplete combustion, co-emitted with primary oxidants. As soot is also a catalyst for SO_2 oxidation, sulfate may also be produced in part by its catalytic action. It is thus possible that both gaseous and particulate products of incomplete combustion play a role in atmospheric SO_2 oxidation.

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Table 1. Results of fog water analysis. Propane combustion was the source of primary oxidant and combustion water.

Flame type	$[SO_2]^a$	pH	H^{+b}	$H_2O_2{}^b$	$NO_3{}^{-b}$	$SO_4{}^{=b}$	$\frac{H^+}{NO_3^- + SO_4^=}$
Intermittent	0	2.7	2.0	21	1.4	0.013	1.4
" "	20	1.9	13.0	ND	1.3	9.1	1.3
Diffusion	0	3.0	1.0	0.48	0.36	0.013	2.7
" "	4.7	2.7	2.0	ND	0.7	0.27	2.1
Premixed	0	2.8	1.6	ND	0.83	0.009	1.9
" "	4.7	2.8	1.6	ND	0.61	0.057	2.4

[a] Concentrations in ppm.
[b] Concentrations are millimolar.

Table II. Collection of flame particles after treatments.

Conditions			
Fog	SO_2 added[a]	Location of filter	$\mu g\ SO_4^{=}/\ell$[f]
No	No	Chimney top[d]	.1
Yes[b]	No	Fog chamber[e]	.1
No[c]	Yes	Fog chamber[e]	.8
Yes[b]	Yes	Fog chamber[e]	1.2

[a] SO_2 added between chimney and fog chamber, $[SO_2]$ = 10 ppm.

[b] Cold N_2 added into fog chamber to cause condensation.

[c] Room-temperature N_2 added into fog chamber; no visible fog.

[d] Heated filter.

[e] Diffusion denuder located upstream of filter.

[f] All data on same basis: $\mu g\ SO_4^{=}/\ell$ of chimney effluent. Diluent N_2 added into fog chamber ignored for fog chamber calculations.

Figure Captions

Figure 1. Experimental setup used to observe the loss of SO_2 during combustion and for the collection of combustion gases in bubblers. (XBL 834-173)

Figure 2. Apparatus for condensing combustion water onto combustion particles to produce fog droplets. (XBL-844-1470)

Figure 3. Ion chromatograms of bubbler samples. (XBL 834-175)

Figure 4. Comparison of S(IV) oxidized by bubbler samples to amount of H_2O_2 reacted. (XBL 844-1469)

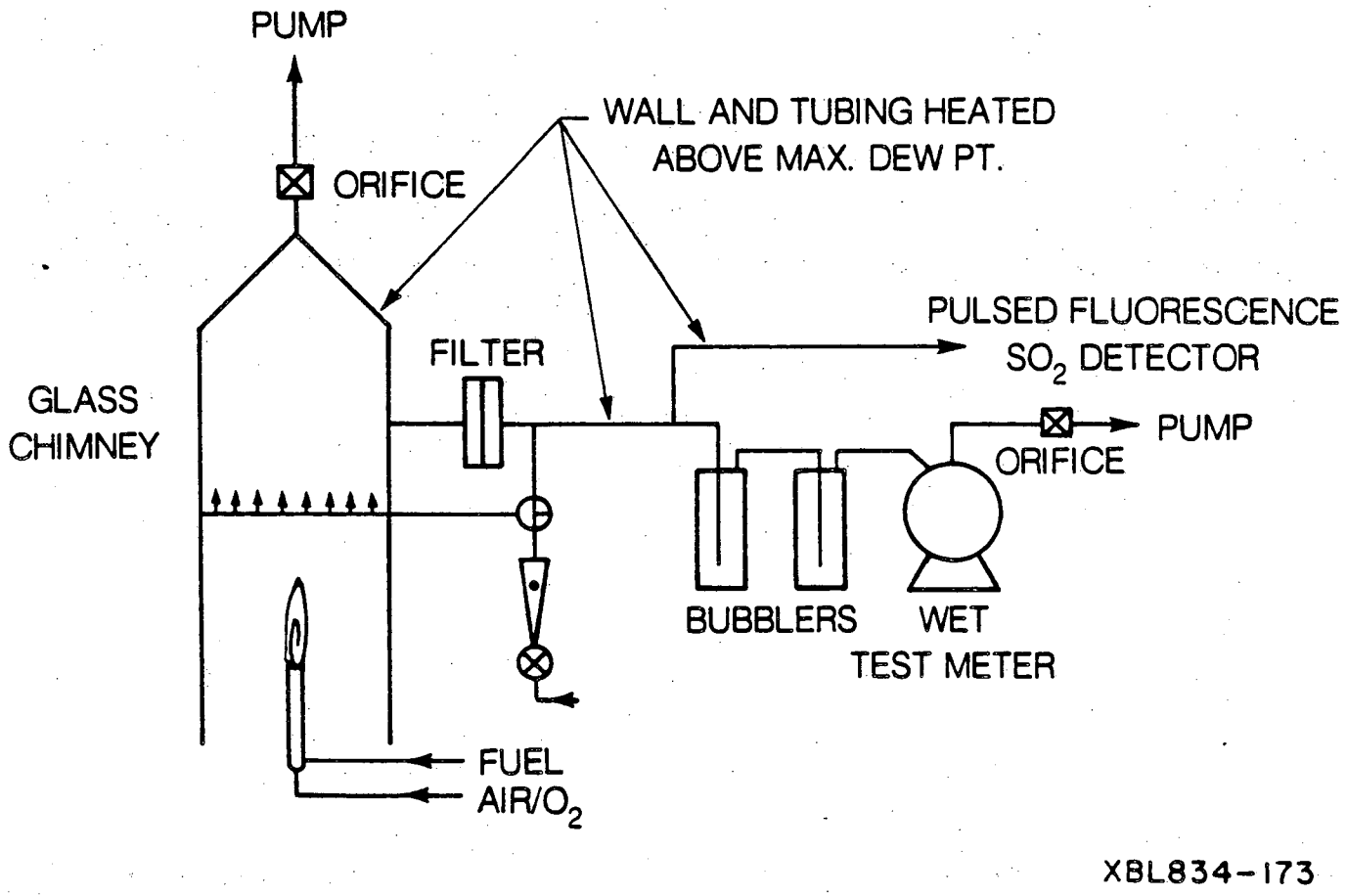
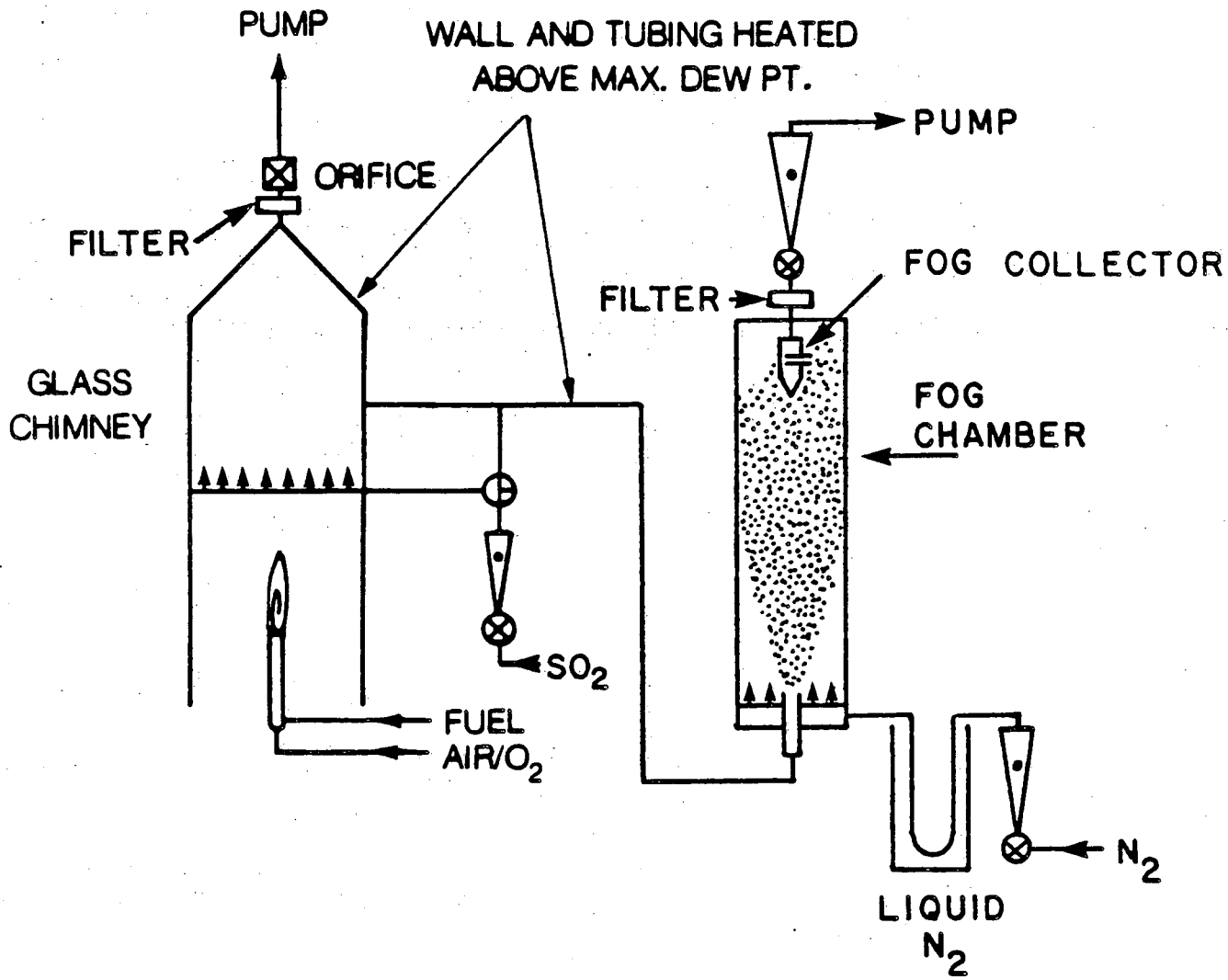

PUMP
ORIFICE
WALL AND TUBING HEATED
ABOVE MAX. DEW PT.
PULSED FLUORESCENCE
SO_2 DETECTOR
FILTER
GLASS
CHIMNEY
PUMP
ORIFICE
BUBBLERS
WET
TEST METER
FUEL
AIR/O_2
XBL834-173

Figure 1


PUMP
WALL AND TUBING HEATED
ABOVE MAX. DEW PT.
PUMP
ORIFICE
FILTER
FOG COLLECTOR
FILTER
GLASS
CHIMNEY
FOG
CHAMBER
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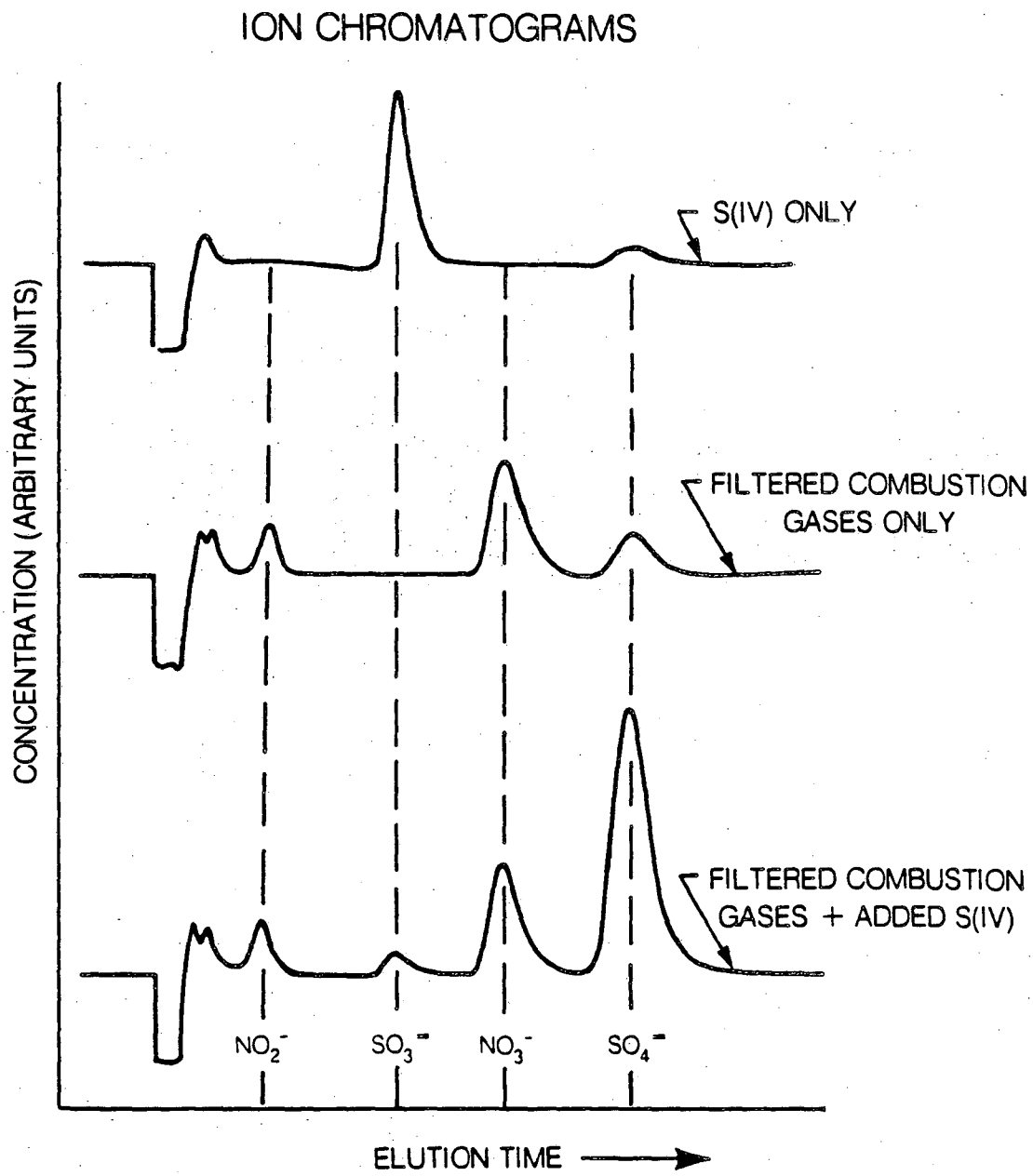
FUEL
AIR/O_2
N_2
LIQUID
N_2

Figure 2



XBL 834-175

Figure 3

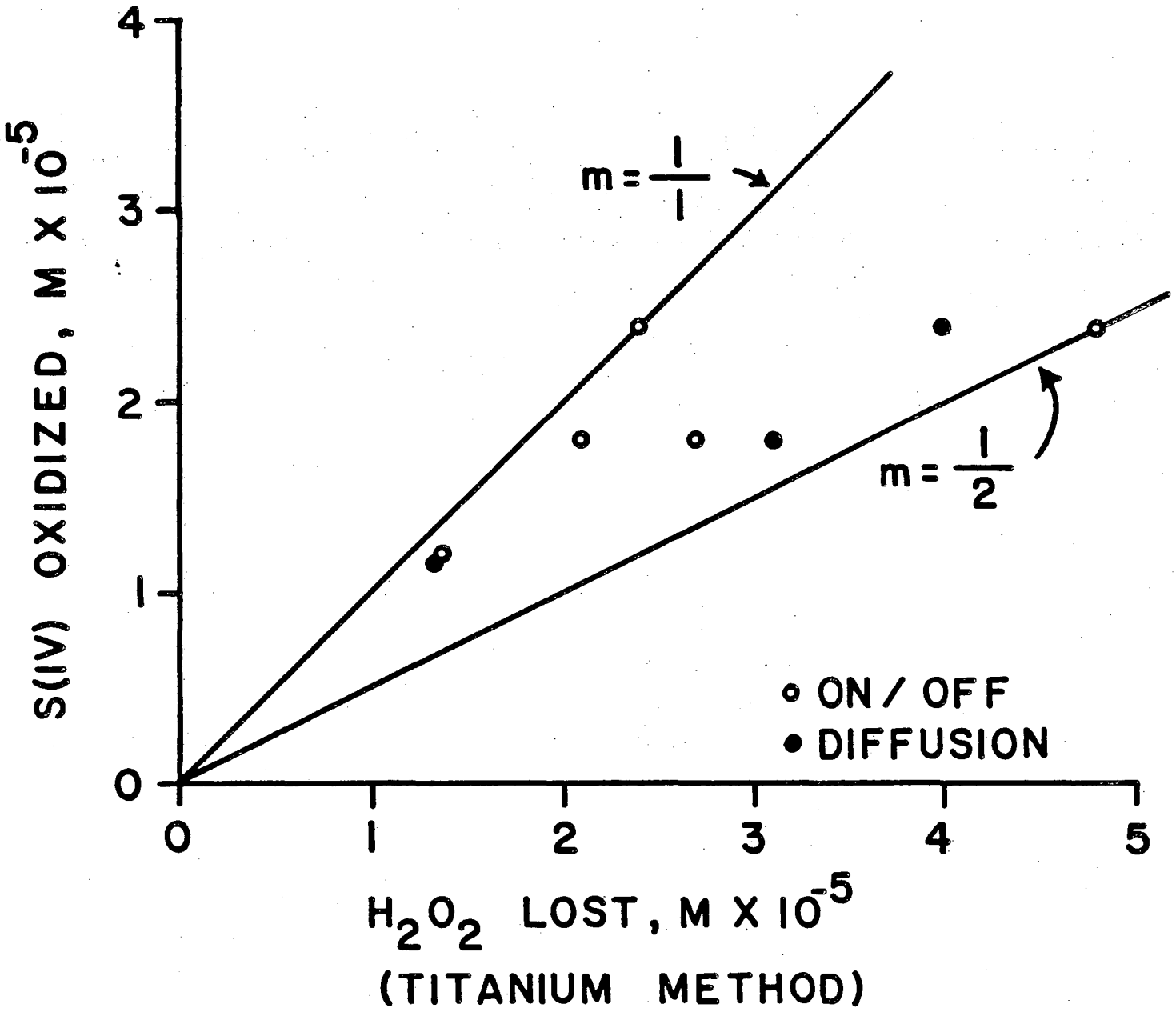

S(IV) OXIDIZED, M X 10^-5
H2O2 LOST, M X 10^-5
(TITANIUM METHOD)
m = 1/1
m = 1/2
ON / OFF
DIFFUSION
0
1
2
3
4
5

Figure 4

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