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MEASUREMENT OF SULFUR DIOXIDE IN THE POST-COMBUSTION ENVIRONMENT

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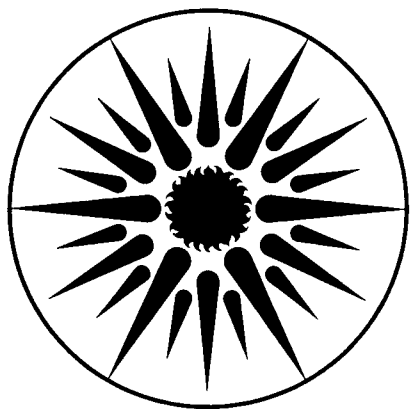
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MEASUREMENT OF SULFUR DIOXIDE IN THE  
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Measurement of Sulfur Dioxide in the Post-Combustion Environment

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## ABSTRACT

Tunable Atomic Line Molecular Spectroscopy (TALMS) has been used to measure sulfur dioxide in the post flame region of an atmospheric pressure stoichiometric methane/air flame. The technique is sensitive and highly selective and thus is useful for research and commercial applications. Response is linear to 20,000 ppm in a 7 cm path length, with a limit of detection of ~2000 ppm at 1500 K and ~40 ppm at 300 K. Ultraviolet absorption spectra of SO<sub>2</sub> were recorded in the 205 to 220 nm range at various temperatures, and reveal significant broadening due to rotational redistribution at the higher temperatures, and no interference from other combustion products. TALMS signal dependence on magnetic field strength confirms that the same transition is observed in the flame as at room temperature. Fluorescent quenching of SO<sub>2</sub> by combustion products were measured in a Thermo Electron model 40 analyzer. Plots of  $S_0/S - 1$  are linear and yield relative quenching coefficients which increase in the order: Ar, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, CO, and C<sub>6</sub>H<sub>6</sub>. Significant quenching corrections are needed to accurately determine SO<sub>2</sub> concentrations in combustion mixtures, especially for the case of rich combustion, where large concentrations of CO, unburned hydrocarbons, and aromatic soot precursors may be present.

## INTRODUCTION

Sulfur dioxide is a major combustion generated air pollutant, which is a precursor to atmospheric sulfate formation. The emission rate of  $\text{SO}_2$  from anthropogenic sources in 1973 was estimated<sup>1</sup> to be on the order of 30 megatons/year with stationary source combustion accounting for nearly 3/4 of the inventory.

The origin of sulfur containing pollutants from combustion is the fuel. Sulfur is present in gaseous fuels, fuel oils, and in coal<sup>2,3</sup>. The amount of sulfur in gaseous fuels is quite low and is frequently removed by pre-treatment. In contrast, the sulfur content of heavier oils ranges from 0.5 to 5% while sulfur can account for up to 10% of the coal mass.

Sulfur combustion chemistry has been reviewed by Levy et al.<sup>4</sup>, Cullis and Mulcahy<sup>5</sup>, and most recently by Levy<sup>6</sup>. Although much remains to be known of sulfur combustion chemistry, measurements of product concentrations from the combustion of fuels with known sulfur contents indicate nearly complete conversion of the sulfur to  $\text{SO}_2$  for lean and stoichiometric combustion. The ultimate fate of sulfur in rich combustion is more complicated since other sulfur containing species are present in the products, and these have not all been identified or quantified.

In order to understand sulfur combustion chemistry, assess control technologies, and evaluate the relationship between source emissions and acid deposition, it is important to be able to measure  $\text{SO}_2$  under combustion and exhaust stack conditions. Prior to the mid-seventies, the most commonly used techniques for measuring  $\text{SO}_2$  involved difficult sampling procedures and wet chemistry, and frequently were not selective<sup>7</sup>. Mass spectroscopy was also used<sup>6</sup>, but few investigators were willing to subject multi-purpose instrumentation to highly corrosive sulfur compounds. Results of early studies of  $\text{SO}_2$  fluorescence in the wavelength regions between 190 and 230

nm regions by Okabe and his colleagues<sup>7-10</sup> and by Zolner et al.<sup>11-12</sup> form the basis for the fluorescent detection of SO<sub>2</sub> which has been widely used since 1978. The technique of laser induced fluorescence was used by Muller et al.<sup>13</sup> to detect SO<sub>2</sub> and other product sulfur compounds in premixed laminar flames. In these LIF studies, Muller et al. used narrow band detection in a wave length region close to the exciting lines to provide a tractable method for making quenching corrections.

In this paper we report on spectroscopic techniques useful for measuring SO<sub>2</sub> in combustion mixtures. These techniques all employ excitation wavelengths in the 190 to 220 nm region. Tunable Atomic Line Molecular Spectroscopy (TALMS) is applied to the measurement of SO<sub>2</sub> in the post flame region of atmospheric pressure, premixed methane/air stoichiometric flames doped with SO<sub>2</sub>. This non-intrusive line-of-sight absorption technique is sensitive and very selective. The TALMS technique is based upon the Zeeman effect, which allows for magnetic tuning of an atomic line into resonance with a molecular absorption<sup>14</sup>. The technique has been successfully applied to the detection of small molecules which exhibit sharp rotational structure<sup>15</sup>, and to SO<sub>2</sub> detection under ambient conditions<sup>16</sup>. Cuellar and Brown<sup>17-18</sup> have recently applied the technique to detect S<sub>2</sub>, and have demonstrated the suitability of the technique for NO quantification in combustion mixtures<sup>19</sup>. The TALMS results we report for SO<sub>2</sub> measurements are the first for a triatomic molecule in combustion mixtures. Ultraviolet absorption spectra of SO<sub>2</sub> were also measured to help clarify our interpretation of the TALMS measurement. In addition to our absorption measurements, we also report a series of quenching corrections for various gases important in combustion system. These corrections are required for quantitative measurements of SO<sub>2</sub> in combustion mixtures using

the pulsed fluorescence Thermo Electron SO<sub>2</sub> analyzer.

### EXPERIMENT

Sulfur dioxide is measured by the Tunable Atomic Line Molecular Spectroscopy (TALMS) technique in the post-flame region of an atmospheric premixed methane/air flame doped with SO<sub>2</sub> and in a quartz cell electrically heated to fixed temperatures. The ultraviolet absorption spectrum of SO<sub>2</sub> is also measured between 205.0 and 220.0 nm.

The TALMS technique is an in situ, line of sight technique that uses a Zeeman-tuned atomic emission lamp as the light source for differential absorption measurements. The basis for detection of molecules by TALMS is the splitting and polarization of atomic emission lines by an external magnetic field. In a direction parallel to the magnetic field the Zn line at 213.8 nm ( $^1S_0 \rightarrow ^1P_1$  transition) is split into two circularly polarized components. The two components are very close in frequency ( $\sim 20$  GHz), but differ in polarization, with the  $\Delta M = +1$  transition right circularly polarized, and the  $\Delta M = -1$  transition left circularly polarized. Detection of SO<sub>2</sub> is accomplished by varying the strength of the magnetic field to tune one of the Zeeman components into resonance with a discrete absorption in SO<sub>2</sub>. Any background absorption present will be absorbed equally by the two Zeeman components. A differential measurement of the two components provides a quantitative determination of SO<sub>2</sub> in the optical path. Both beams traverse an identical optical path, thus permitting good correction of the signal in highly scattering or absorbing systems, such as those encountered in flames and other combustion systems.

A schematic diagram of the experimental apparatus is shown in Fig. 1. Except for the light source, the TALM spectrometer is identical with the



instrument described in detail previously<sup>18</sup>. The lamp uses zinc wire packed into an unfired boron nitride holder as the cathode and a stainless steel screw as the anode. The zinc is excited by an electric (AC and DC) discharge sustained with argon at ~0.2 torr flowing through the lamp during operation. The lamp is housed between the poles of a Varian electromagnet. Light emerges parallel to the magnetic field, and is focused with a quartz lens to a 2mm diameter spot above the burner surface. The variable phase retardation plate is used with a linear polarizer to alternately transmit the matched and unmatched Zeeman components through the monochromator to the detector. The monochromator is used to eliminate other lines emitted from the lamp and stray light rather than effecting a separation of the Zeeman components. The output of the photomultiplier tube is electronically processed and then recorded by a Hewlett-Packard 3497A data logger controlled by an HP 85 computer.

A deuterium lamp replaced the TALMS lamp as the light source to obtain ultraviolet absorption spectra of SO<sub>2</sub> in the 205 to 220 nm range. Scan rates were 0.5 nm/min. Intermediate temperature spectra were obtained by flowing SO<sub>2</sub>/N<sub>2</sub> mixtures through a 7 cm quartz cell heated by nichrome wire. A small gas flow was maintained to minimize reaction at the higher temperatures. Gas temperatures were determined by introducing pure nitrogen at the desired flow rate and measuring its temperature with a bare chromel-alumel thermocouple inserted into the cell.

Methane (Matheson C.P. grade) and air were supplied in high pressure gas cylinders. Sulfur dioxide was introduced as pure gas (Matheson anhydrous grade) or as 1.50% SO<sub>2</sub> in nitrogen (Matheson primary standard), depending on the final concentration desired. Calibration gases were SO<sub>2</sub> in nitrogen (Matheson certified standard) at 98 and 410 ppm concentrations. Gas flows were controlled by rotameters that have been calibrated for the

particular gas measured. Two cylindrical stainless steel mixing chambers, 30 cm long and 4.8 cm diameter and packed with glass beads, were used in series to mix the gases. Cold flow experiments were performed using Brooks high precision flowmeters and a Thermo Electron SO<sub>2</sub> analyzer to insure adequate mixing. Measured SO<sub>2</sub> concentrations in the calibration gases and SO<sub>2</sub>/N<sub>2</sub> mixtures prepared in the laboratory were within 3%.

The burner was operated at a total flow rate of 30,000 sccm, corresponding to a linear velocity of 17.7 cm/sec. At this flow, stable flames could be obtained at equivalence ratios ranging from 0.75 to 1.75.<sup>19</sup> Measurements presented here were performed at an equivalence ratio of 1.0, where the survival of sulfur dioxide through the flame should be quantitative<sup>5</sup>. Temperature profiles were measured with a Pt/Pt-13% Rh thermocouple. Vertical and radial temperature profiles measured previously<sup>19</sup> reveal negligible thermal gradients in the post flame region. Corrosion caused by the addition of the sulfur dioxide altered the appearance of the flame slightly, but did not significantly affect the post flame region.

Quenching measurements are made using a Thermo Electron Model 40 pulsed fluorescent SO<sub>2</sub> analyzer. Mixtures of SO<sub>2</sub> in nitrogen were doped with varying amounts of third body gases found in combustion environments using the same flow measuring equipment described above. After passing through the mixing chambers a portion of the room temperature gas mixture is routed to the analyzer to maintain a constant flow in the photolysis cell. Pressures throughout the system were monitored and maintained at a constant value through the use of fixed pressure relief valves. No restrictions or capillaries were placed in the flow path, insuring that a uniform composition mixture was being sampled. The analyzer was calibrated

between quenching measurements with the same SO<sub>2</sub>/N<sub>2</sub> mixtures used in the TALMS experiments.

## RESULTS AND DISCUSSION

We have used spectroscopic techniques to detect SO<sub>2</sub> in the ultraviolet in the wavelength region from 190 to 220 nm. There have been numerous studies of SO<sub>2</sub> spectroscopy under ambient conditions in this wavelength region<sup>20-22</sup>. The room temperature spectrum has been discussed by Duchesne and Rosen<sup>23</sup>, who have shown by vibrational analysis that vibronic transitions between two and probably three electronic states occur in this region. Due to the complexity of the electronic transitions of SO<sub>2</sub> in the 200.0 to 220.0 nm region and because the rotational structure has not been fully resolved, we cannot assign the 213.8 nm TALMS absorption to any particular transition.

In this section, results of the TALMS experiments are presented and discussed. Ultraviolet absorption spectra were measured to clarify and help interpret the TALMS results. Results of quenching measurements for several gases frequently present in combustion systems are also presented.

### 1. TALMS Measurements

The dependence of the TALMS signal strength on magnetic field for SO<sub>2</sub> differential absorption is shown in Fig. 2. Typical line shifts are approximately 2 GHz/kg<sup>24</sup>, and magnetic tuning over a range of 60 GHz can be achieved with a small electromagnet with a maximum field strength of 30 kG. Maximum sensitivity occurs at a magnetic field strength of 14.5 kgauss, and this value is used for all subsequent TALMS measurements. Data obtained at 1500 K show the same dependence of signal strength on magnetic field as that obtained at 300 K, indicating that the same transition is measured in

the flame system as under ambient conditions.

The response of the TALM spectrometer to varying  $\text{SO}_2$  concentrations in the flame system is shown in Fig. 3. The TALMS signal is linear with  $\text{SO}_2$  concentrations below 20,000 ppm in the 7cm diameter burner. The deviations from linearity noted for  $\text{SO}_2$  concentrations at this path length will be discussed subsequently.

The sensitivity of the TALMS technique varies with the temperature of the sample. For a 7cm path length at 1 atmosphere, the minimum detectable concentration is  $\sim 40$ ppm at 300K, and  $\sim 2000$ ppm at 1500K. The room temperature determination was made in the quartz cell using mixtures of  $\text{SO}_2$  in nitrogen, and the high temperature value was determined in the presence of combustion products in the post flame region. Density differences in the combustion system account only for a factor of 5 in sensitivity.

Ultraviolet spectra of  $\text{SO}_2$  were taken at various temperatures in a heated quartz cell for  $\text{SO}_2/\text{N}_2$  mixtures of fixed concentration and in the post flame region of the  $\text{SO}_2$  doped methane/air flame to determine the cause of the lowered sensitivity. The ultraviolet absorption spectrum of  $\text{SO}_2$ , measured as a function of temperature in the 297 to 803 K range, is shown in Fig. 4. Each curve has a different zero level to avoid overlapping the spectra. The discrete absorption features gradually broaden as the temperature increases, and the underlying continuum becomes even more absorbing when corrected for density differences. The ultraviolet spectrum of  $\text{SO}_2$  at 1500 K, taken in the post flame region shows continuing broadening, with no evidence of absorption by other species. The resolution in these spectra is on the order of 0.2 nm, much coarser than the resolution in the TALMS apparatus, which has a resolution of  $< 0.003$  nm. Higher resolution ( $< 0.05$  nm) spectra of  $\text{SO}_2$  in the post flame region revealed no additional structure<sup>25</sup>. The broadening of the absorption

features shown in Fig. 4, and noted at 1500 K, is largely due to redistribution of the rotational level populations at the elevated temperatures, with the particular transition probed by the zinc line in the TALMS experiment suffering a corresponding loss of population in the initial state. This results in decreasing sensitivity with increasing temperature since there are fewer molecules in the state excited by the Zn line. Pressure broadening due to the presence of other species may also contribute to the loss of sensitivity noted under post flame conditions, but the steady broadening noted as temperature increased from 300 to 800 K in the cell experiments where only  $N_2$  and  $SO_2$  are present indicates strongly that the loss of sensitivity is dominated by rotational redistribution. Also, the magnetic field dependence of the TALMS signal indicates no significant perturbation of the energy levels at the higher temperatures.

The ultraviolet absorbance at approximately the same wavelength as the TALMS experiments, shown in Fig. 5, is linear at concentrations as high as 30,000 ppm. This indicates that the fall-off in the TALMS signal is not attributable to self absorption or deviations from Beer's law, but is inherent to the TALMS technique. This behavior has been observed previously in the measurement of NO in combustion systems<sup>19</sup>. The non-linear region can be avoided by the proper choice of path length.

The TALMS technique is well suited for measurements in combustion environments. The selectivity of the technique, due to the high resolution light source, reduces interferences to those molecules that have a differential absorption at the same wavelength as  $SO_2$ . Any interference of this type can be detected by measuring the TALMS absorption as a function of magnetic field strength, and can often be eliminated or reduced by changing the magnetic field strength. The range of concentrations that can

be measured by the TALMS technique make it an attractive method for measuring SO<sub>2</sub> in combustion exhausts at utility sites where the emission levels must be monitored. At temperatures below 750 K and path lengths on the order of 1 meter, SO<sub>2</sub> concentrations below 40 ppm can be detected. Simple absorption measurement techniques can also be used effectively for measuring SO<sub>2</sub>, but only in systems which have no interferences such as other absorbing and/or scattering species.

## 2. Fluorescence Measurements of Sulfur Dioxide

Another method for measuring SO<sub>2</sub> uses pulsed fluorescence in the 190-230 nm region. In combustion exhausts, with high concentrations of combustion products, the signal from such an instrument must be corrected for the effects of third body quenching of the SO<sub>2</sub> fluorescence.

When the SO<sub>2</sub> concentration is low, and the optical path relatively short, the signal S obtained in the presence of the third body relative to the unperturbed signal S<sub>0</sub> is

$$\frac{S}{S_0} = \frac{1}{1 + \phi M_i}$$

where  $\phi$  is the Stern-Volmer quenching coefficient and  $M_i$  is the mole fraction of the third body species. A plot of  $S_0/S - 1$  as a function of the third body mole fraction at a constant SO<sub>2</sub> concentration should yield a straight line with a slope of  $\phi$ .

Such plots for species of interest in combustion are shown in Fig. 6. Quenching efficiencies were found to increase in the following order: Ar, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, CO, and C<sub>6</sub>H<sub>6</sub>. Table I lists the quenching gases measured, the range of concentrations covered, the quenching coefficients  $\phi$ , and the standard deviation of the straight line fit. Also listed are the values of  $\phi$  provided by the manufacturer of the Thermo Electron analyzer. No information is given about the experimental apparatus, range

of concentrations, or uncertainties in the measurements<sup>26</sup>, so it is difficult to make further comments about their results. Okabe<sup>10</sup> also examined the quenching of SO<sub>2</sub> fluorescence excited at 216 nm. It is not possible to directly compare our numerical results since quenching corrections are dependent on the excitation wavelength; however, there is agreement on the ordering of the quenching species. Okabe found O<sub>2</sub> more effective than CO<sub>2</sub> as we did, and N<sub>2</sub> and CO<sub>2</sub> quite similar. Michels et al.<sup>27</sup> also investigated the fluorescent quenching of SO<sub>2</sub> following broad band excitation between 200 and 250 nm. They report that O<sub>2</sub> is more effective than N<sub>2</sub>, in agreement with our results. Although quenching results frequently can be ordered with regard to molecular complexity of the quenching gas<sup>28</sup> this is not the case for SO<sub>2</sub>. The fluorescence of SO<sub>2</sub> is decidedly more complex than NO due to complex interaction in the SO<sub>2</sub> manifold and the large number of electrons in the molecule. Zolner also states that water should not be a problem in combustion systems as long as the sample is diluted sufficiently to prevent condensation, because the internal dryer in the TECO instrument reduces the water vapor concentration to ~2000 ppm, with this concentration resulting in a 3.2% lower SO<sub>2</sub> signal<sup>26</sup>. However, this should be checked in any system where high concentrations of water exist. It should be noted that rich combustion, where the concentrations of CO and unburned hydrocarbons may be significant, will have the largest quenching effects.

## CONCLUSIONS

We have shown that Tunable Atomic Line Molecular Spectroscopy (TALMS) can be used to measure sulfur dioxide in the post flame region of an atmospheric pressure stoichiometric methane/air flame. The technique is sensitive and highly selective and thus is useful for research and commercial applications. Response is linear to 20,000 ppm in a 7 cm path length, with a limit of detection of ~2000 ppm at 1500 K and ~40 ppm at 300 K. Ultraviolet absorption spectra of SO<sub>2</sub> were recorded in the 205 to 220 nm range at various temperatures, and reveal significant broadening due to rotational redistribution at the higher temperatures, and no interference from other combustion products. TALMS signal dependence on magnetic field strength confirms that the same transition is observed in the flame as at room temperature. Fluorescent quenching of SO<sub>2</sub> by combustion products were measured in a Thermo Electron model 40 analyzer. Plots of  $S_0/S - 1$  are linear and yield relative quenching coefficients which increase in the order: Ar, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, CO, and C<sub>6</sub>H<sub>6</sub>. Significant quenching corrections are needed to accurately determine SO<sub>2</sub> concentrations in combustion mixtures, especially for the case of rich combustion, where large concentrations of CO, unburned hydrocarbons, and aromatic soot precursors may be present.

## ACKNOWLEDGEMENTS

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Table I

Quenching Coefficients

<u>Species</u>	<u><math>\phi</math></u>	<u>Standard Deviation</u>	<u>Concentration Range(%)</u>	<u><math>\phi</math> (from ref. 26)</u>
N <sub>2</sub>	0	(defined)		
Ar	-0.005	0.0007	0 - 21.4	
CH <sub>4</sub>	0.084	0.004	0 - 21.7	
C <sub>5</sub> H <sub>6</sub>	0.49	0.10	0 - 9.7	
CO	0.100	0.004	0 - 21.7	0.0920
CO <sub>2</sub>	0.016	0.0013	0 - 20.3	0.01436
H <sub>2</sub>	0.033	0.0025	0 - 20.3	
O <sub>2</sub>	0.029	0.0016	0 - 20.2	0.02139

### Figure Captions

Figure 1. Schematic diagram of the TALMS apparatus.

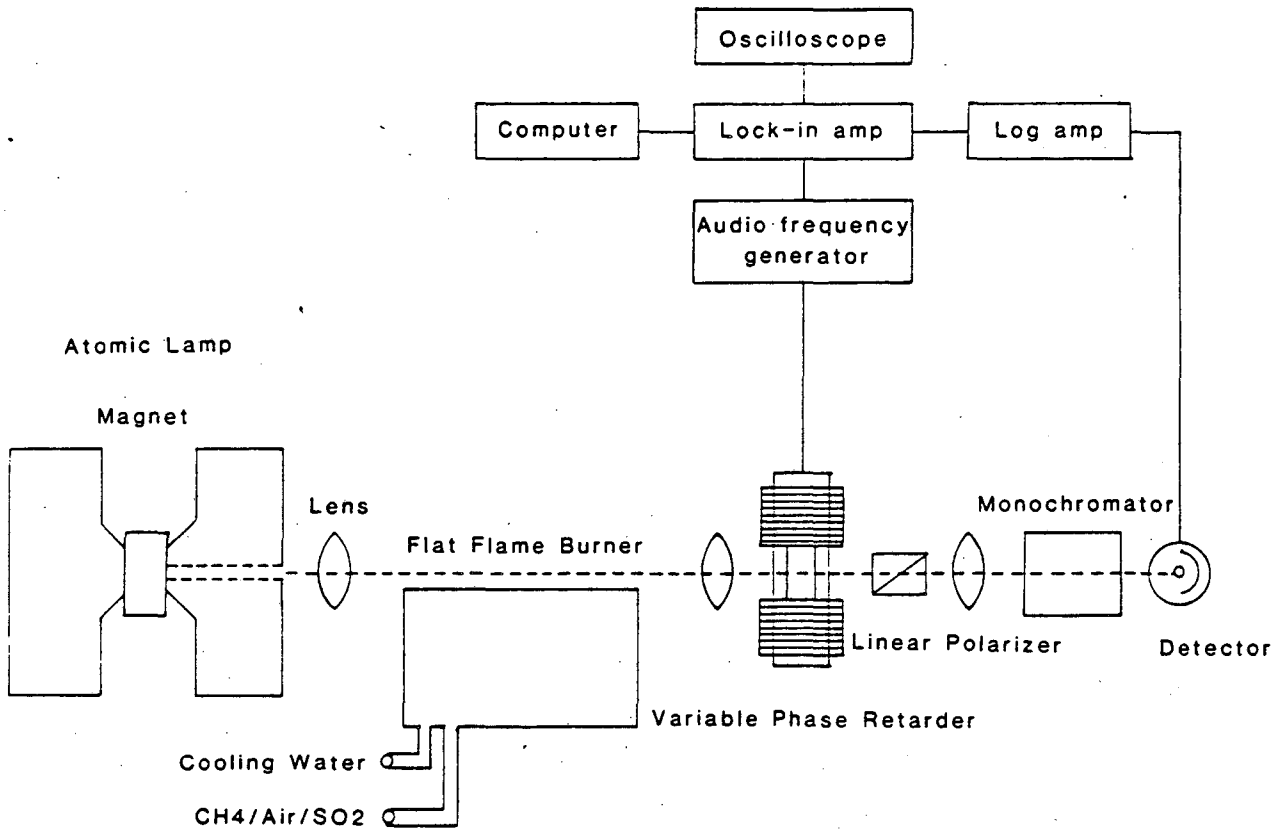
Figure 2. SO<sub>2</sub> TALMS signal as a function of magnetic field strength.

Figure 3. TALMS signal as a function of added SO<sub>2</sub> in the post flame region of a methane/air flame.

Figure 4. SO<sub>2</sub> absorption spectra in the 205 to 220 nm region as a function of temperature.

Figure 5. The 213.8 nm ultraviolet absorption as a function of added SO<sub>2</sub> in the post flame region of a methane/air flame.

Figure 6. Relative quenching of SO<sub>2</sub> by combustion products in a Thermo Electron Model 40 SO<sub>2</sub> analyzer.

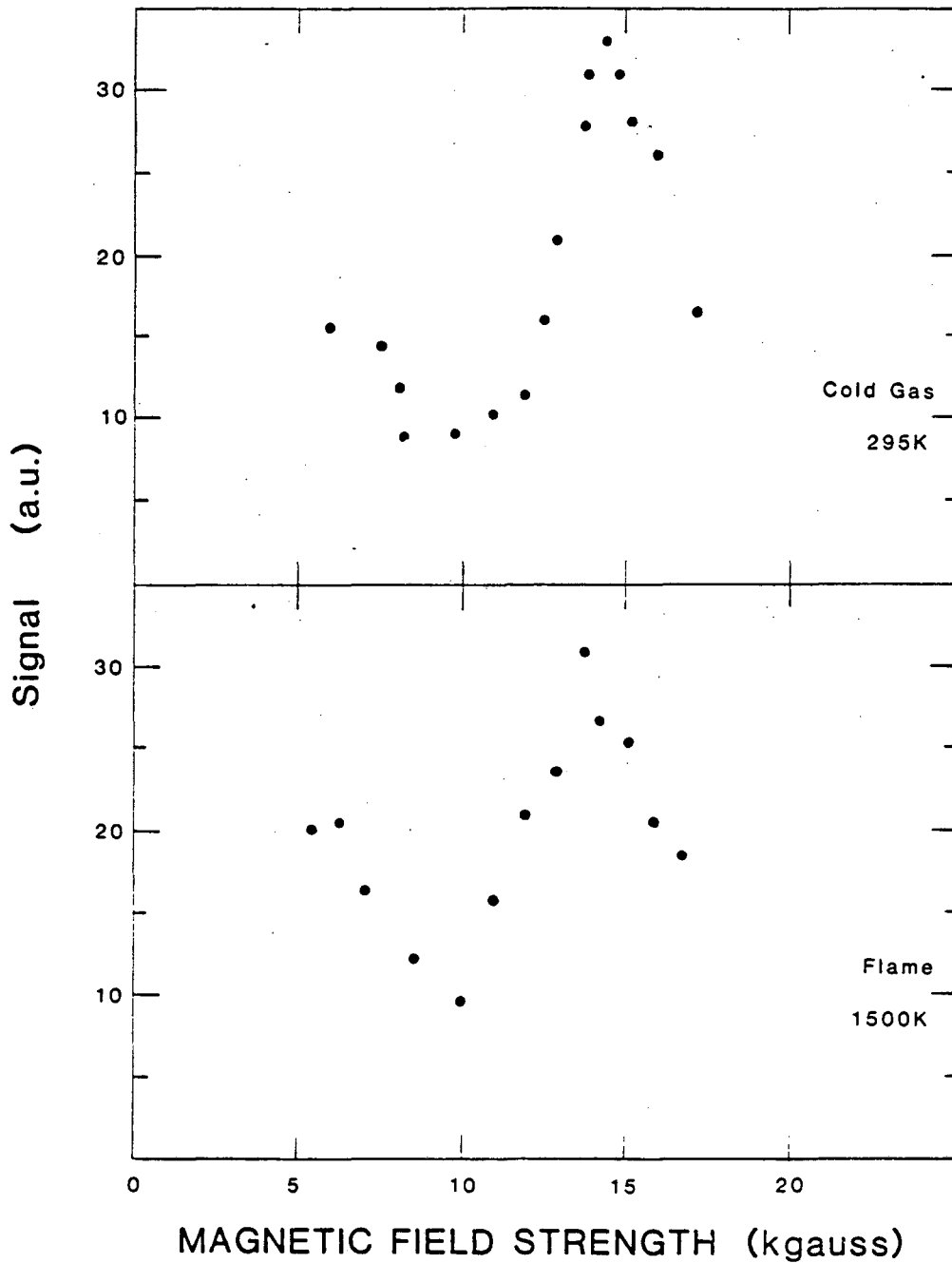


**SCHEMATIC OF TALMS APPARATUS**

XBL 839-11800

Fig. 1

# SO<sub>2</sub> TALMS vs. Magnetic Field



XBL 839-11799

Fig. 2

# TALMS SIGNAL vs. SO<sub>2</sub> CONCENTRATION

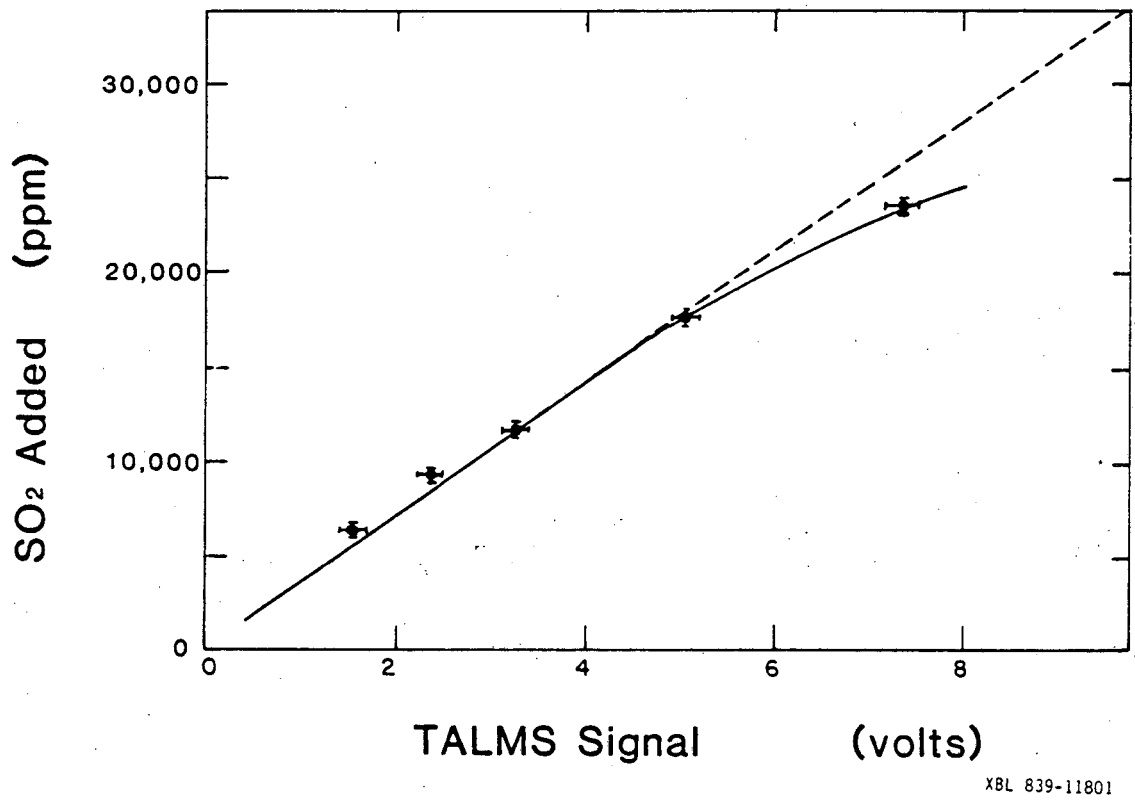
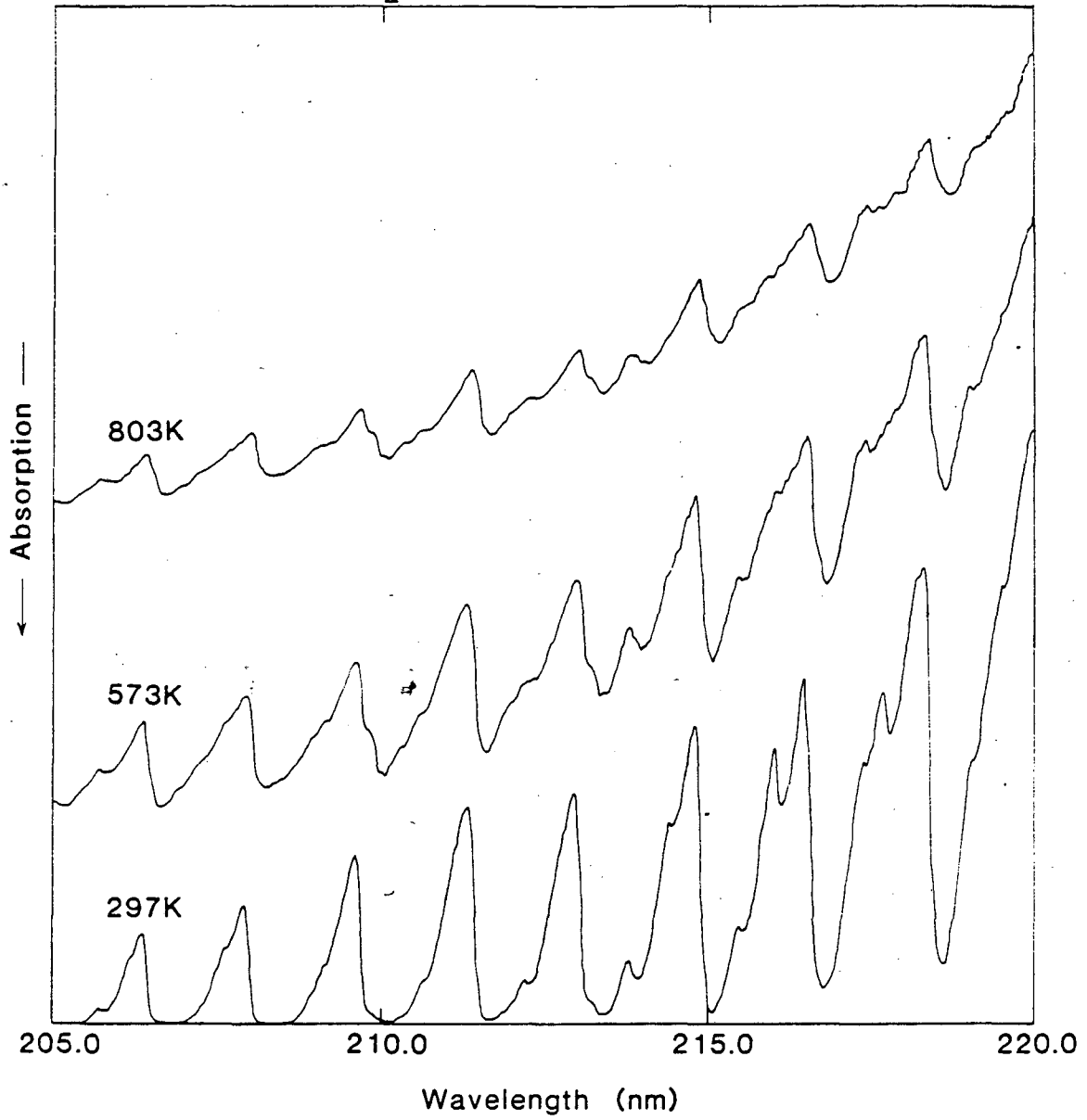


Fig. 3

SO<sub>2</sub> UV ABSORPTION SPECTRA

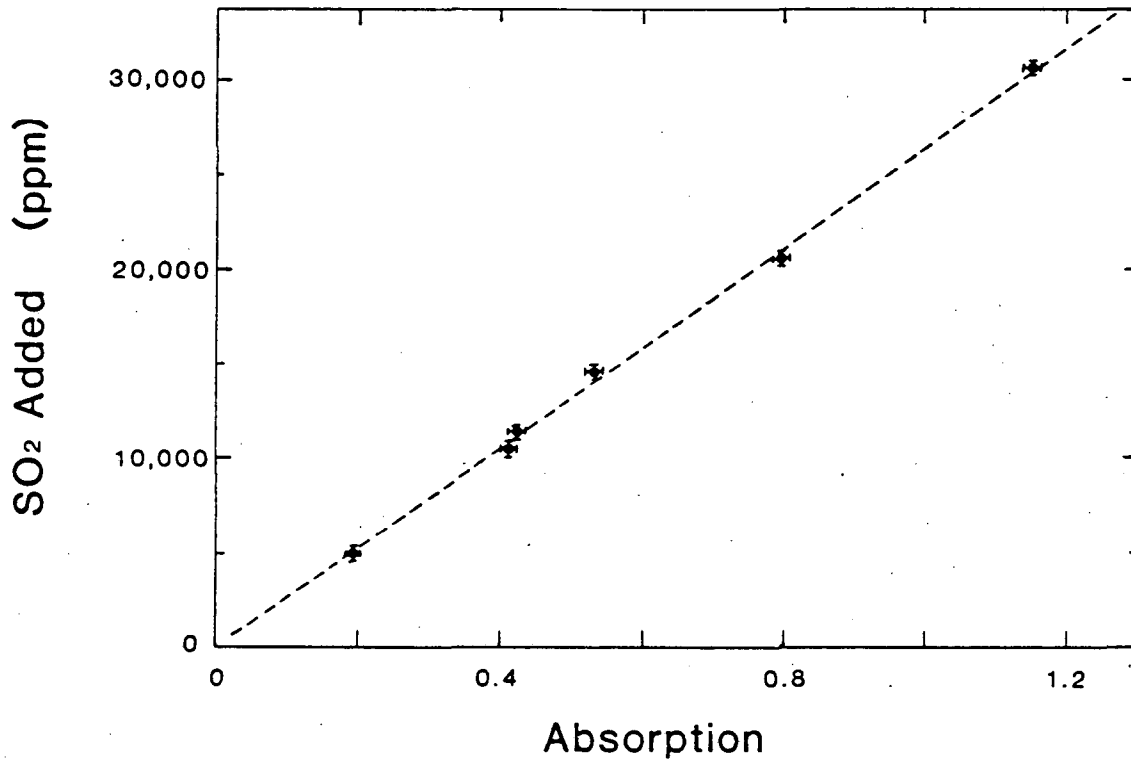


XBL 639-11803

Fig. 4

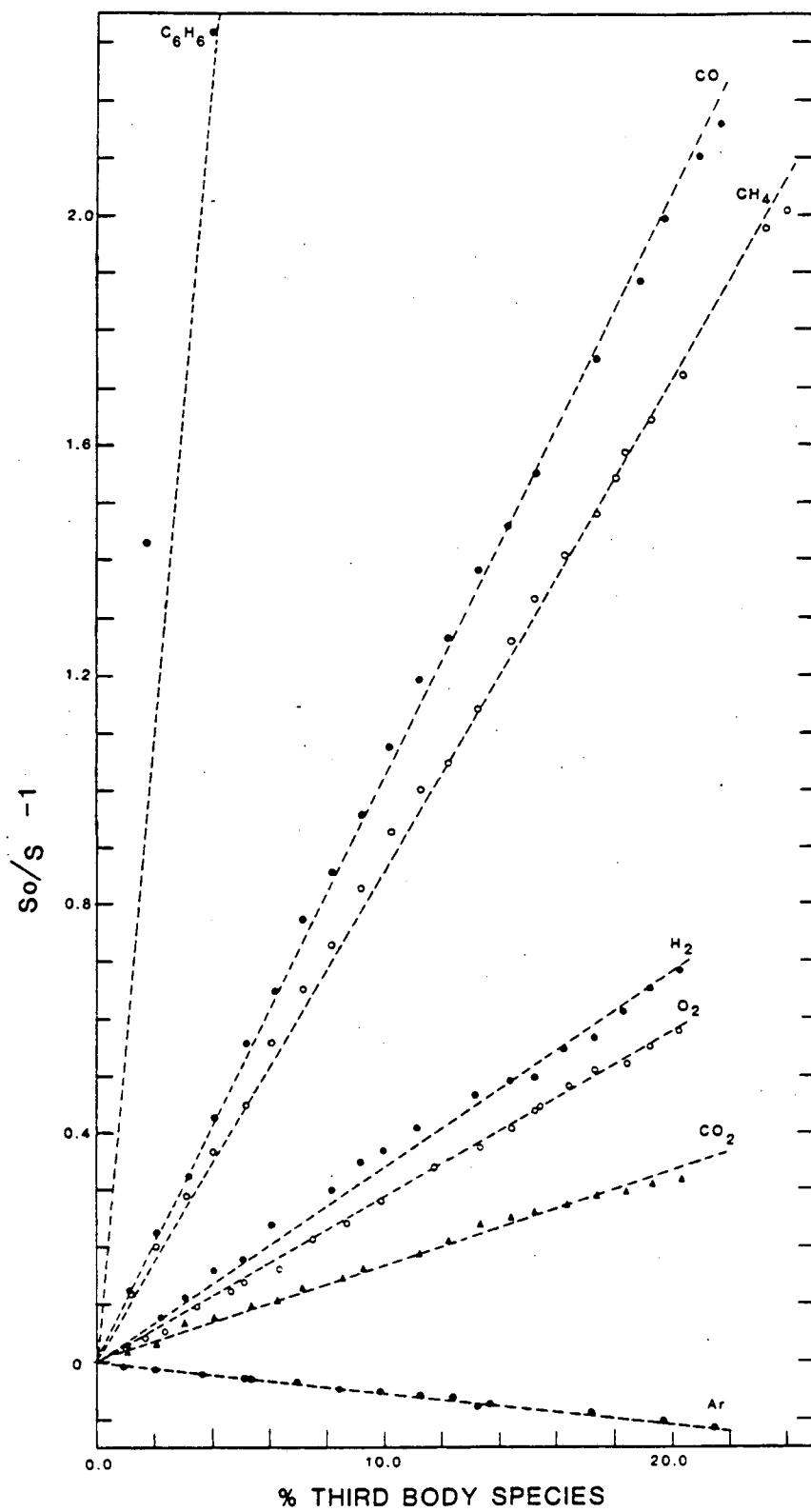


# 213.8 nm ABSORPTION vs. SO<sub>2</sub> CONCENTRATION



XBL 839-11802

Fig. 5



NBL 8312-2532

Fig. 6

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