

## SULFUR TRIOXIDE FORMATION IN HIGH SULFUR RESIDUAL OIL FLAMES

Peter M. Walsh, Walter F. Farmayan,\* Thomas Kolb,† János M. Beér

Energy Laboratory and Department of Chemical Engineering  
Massachusetts Institute of Technology  
Cambridge, MA 02139

### INTRODUCTION

Heavy residual fuel oils usually contain between 1 and 4 wt% sulfur. Although  $\text{SO}_2$  is the principal product of fuel sulfur oxidation, as much as 8 to 10 mol% of the sulfur oxides are present as  $\text{SO}_3$  in the flue gas arriving at the cold end of the convective section in an electric utility boiler. Sulfur trioxide is quantitatively converted to sulfuric acid vapor in the presence of typical flue gas water vapor concentrations at temperatures below about 500 K (Halstead and Talbot, 1980). Condensation of sulfuric acid on surfaces at temperatures below the acid dewpoint is responsible for corrosion of cold end components, especially the air preheater. The accumulation of unburned carbon particles on the wet surfaces and reentrainment of their agglomerates is the source of acid smuts (Blum, Lees and Rendle, 1959; Conolly and Kelsell, 1982). The adsorption of sulfuric acid on ash and unburned carbon may make a significant contribution to the mass of stack gas particulates.

The most severe acid deposition and sulfate emissions problems are associated with catalytic oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  over vanadium-containing deposits on tubes in the convective section. However, 1 to 2 mol% of the sulfur oxides are thought to be present as  $\text{SO}_3$  in the furnace exit gas. Reidich and Reifenhäuser (1980) reported 2 mol% of the sulfur oxides as  $\text{SO}_3$  (25 mol ppm of total gas) at the furnace exit in a 300 MW, tangentially fired boiler operated at 0.6 mol% excess  $\text{O}_2$  with 2 wt% sulfur fuel. This is an amount sufficient to cause troublesome acid deposition and make a significant contribution to particulate loading, even in the absence of additional  $\text{SO}_3$  formation in the convective section. Experience has shown that  $\text{SO}_3$  formation can be controlled by reducing excess air, but this is accompanied by an increase in unburned carbon (coke cenospheres). Sulfur trioxide formation in the furnace is one component of a set of coupled processes making contributions to acid deposition and stack particulates (Cunningham and Jackson, 1978; Harada, Naito, Tsuchiya, and Nakajima, 1981).

Substantial progress has recently been made in the quantitative description of sulfur chemistry in flames (Muller, Schofield, Steinberg, and Broida, 1979; Kramlich, Malte, and Grosshandler, 1981; Smith, Wang, Tseregounis, and Westbrook, 1983; Wendt, Wootan, and Corley, 1983). Squires (1982) combined a detailed chemical kinetic description of reactions in the furnace with a global model for heterogeneous oxidation of  $\text{SO}_2$  over tube deposits in the convective section. The predictions of this model were in good agreement with observed levels of  $\text{SO}_3$  in the flue gases of 500 MW and 60 MW boilers. The present paper describes the initial steps of an investigation in which the results of fundamental kinetic studies are applied to the interpretation of direct measurements of  $\text{SO}_3$  in boiler-type turbulent diffusion flames.

\*Present address: Chemical Engineering Department, Shell Development Co., Westhollow Research Center, Houston, TX 77001

†Present address: Engler-Bunte-Institut, University of Karlsruhe, West Germany

Table 1. Experimental Conditions.

Run No.	Fuel Treatment	Atomizer Location w.r.t. Air Nozzle (mm)	Comb. Swirl No.	Air Mole Fraction $O_2$ in Flue Gas (%)	Excess Air (%)	Air Velocity at Nozzle (m/s)	Fuel Temperature (K)	Fuel Pressure (MPa)	Atomizing Air Pressure (MPa)
212	None	-25	0.9	1.5	7.3	49	389	1.48	1.48
213	Additive B	+25	0.9	1.5	7.3	49	389	1.51	1.51
214	None	+46	0.5	1.0	4.7	48	389	1.25	1.14
215	Additive D	+46	0.5	1.0	4.7	48	389	1.25	1.14
216	Additive E	+46	0.5	1.0	4.7	48	389	1.25	1.14
217	7.0% Water Emulsion	+46	0.5	1.0	4.7	48	391	1.25	1.14
218	Additive B	+46	0.5	1.0	4.7	48	389	1.25	1.14
219	Additive F	+46	0.5	1.0	4.7	48	389	1.25	1.14
220	Additive C	+46	0.5	1.0	4.7	48	389	1.25	1.14
		±0.5		±0.1			±3	±0.04	±0.04

## EXPERIMENTAL

The measurements were made in the 1.2 x 1.2 m combustion tunnel in the MIT Combustion Research Facility (Beér, Jacques, Farmayan, and Taylor, 1981). The fuel was a mixture of residual oils produced by the Exxon refinery at Aruba. Its analysis was (wt%): carbon 85.80, hydrogen 10.86, nitrogen 0.47, sulfur 2.15, oxygen 0.57, and ash 0.10. Asphaltenes (IP 143/57) were 10.5 wt%, and the metal contents (wt ppm) were: vanadium 421, nickel 51, iron 15, sodium 9.8, calcium 20, and magnesium 4.8. The heating value was 42.5 MJ/kg and viscosity was 213 Saybolt Furol seconds at 50°C. The fuel was heated to 389 K, fired at 0.05 kg/s (2 MW thermal), and atomized by a 70° (full angle) six-hole "Y" jet nozzle with air as the atomizing medium. Combusting air was preheated to 560 K and supplied through a 0.176 m diameter duct to a 50° (full angle) divergent quarl mounted flush with one end wall of the combustion chamber. Several parameters were varied in order to examine their effects on carbon burnout and SO<sub>3</sub> formation: atomizer position, atomizing air/fuel ratio, combustion air swirl, and excess air. Five different commercial preparations designed to promote carbon burnout were added to the fuel; these contained compounds of the metals iron, zirconium, and cerium. One run was made with fuel emulsified with 7 wt% water. The experimental conditions are given in Table 1.

Gas temperature and composition (O<sub>2</sub>, CO<sub>2</sub>, CO, SO<sub>2</sub>, NO) were determined using standard techniques. The axial component of the gas velocity was measured using a two-hole impact probe. A representative set of gas temperature, velocity, and composition profiles is shown in Fig. 1. Axial positions are measured from the exit of the 0.176 m diameter combustion air nozzle. For calculation purposes, the temperature, velocity, and carbon monoxide profiles in the region following the peak flame temperature at  $z = z_0 = 0.95$  m were fit by the following relations, shown as solid lines in Fig. 1:

$$T = T_0 - \alpha(z - z_0) \quad 1)$$

$$u = \beta/z \quad 2)$$

$$X_{CO} = X_{CO,0} \exp[-\gamma(z - z_0)] \quad 3)$$

Table 2. Data used in the calculations. The mole fractions of CO<sub>2</sub>, O<sub>2</sub>, and SO<sub>2</sub> are calculated flue gas values (wet) based on the fuel analysis and air/fuel ratio.

Run No.	T <sub>0</sub> (K)	α (K/m)	β (m <sup>2</sup> /s)	X <sub>CO,0</sub>	γ (m <sup>-1</sup> )	X <sub>CO2</sub>	X <sub>O2</sub>	X <sub>SO2</sub> (ppm)
212	2005	175	16	.0133	1.517	.131	.0133	1220
213	2045	172	16	.0319	1.499	.131	.0133	1220
214	2000	138	15	.0435	1.992	.134	.00885	1250
215	2000	131	15	.0319	1.859	.134	.00885	1250
216	1975	130	15	.0291	1.829	.134	.00885	1250
217	1985	143	15	.0319	1.925	.133	.00878	1240
218	2005	133	15	.0368	1.906	.134	.00885	1250
219	2000	130	15	.0338	1.776	.134	.00885	1250
220	1990	133	15	.0338	1.776	.134	.00885	1250

Values of the parameters are given in Table 2. A mean gas residence time of 1 s, typical of a tightly designed oil-fired utility boiler, is reached at a distance of about 2.9 m from the combustion air nozzle.

$\text{SO}_3$  in the flame gases was determined using the Severn Science Ltd./Marchwood Engineering Laboratories (Central Electricity Generating Board, UK) continuously recording  $\text{SO}_3/\text{H}_2\text{SO}_4$  monitor (Jackson, Hilton, and Buddery, 1981). This instrument is intended primarily as a flue or stack gas monitor. The 2 m long heated sampling probe supplied with the instrument was adapted for sampling in the flame by enclosing it in a water-cooled sheath. The glass sampling tube was replaced with one made of quartz. The indicated mole fractions of  $\text{SO}_3$  along the flame axis are shown in Fig. 2.

After making a measurement, brown, orange, black, and yellow deposits were observed over 60 mm of the inside wall at the tip of the quartz sampling tube. Most of the deposit was soluble in 0.05 M  $\text{H}_2\text{SO}_4(\text{aq})$ . If this deposit contains vanadium it may catalyze the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$ . Even though the composition and physical properties of the probe deposit have not been determined, the available information can be used to place some approximate limits on the change in  $\text{SO}_3$  content of the gas during sampling. Kinetic studies of related systems have been reviewed by Urbanek and Trela (1980), although most of this work has been conducted at relatively high  $\text{SO}_2$  and  $\text{O}_2$  (order of 10 mol%) and in the temperature range (650 to 850 K) over which conversion of  $\text{SO}_2$  to  $\text{SO}_3$  is greatest in flow reactors. The portion of the sampling tube coated with deposit was treated as a one-dimensional tubular reactor with catalytic wall. The wall temperature was assumed to decrease linearly from a value equal to the gas temperature at the probe tip to the melting point of  $\text{V}_2\text{O}_5$  (943 K) at the end of the deposit. The sample enters the quartz tube at high temperature and with  $\text{SO}_3$  at greater than equilibrium concentration. Conversion near the tube entrance was assumed to be controlled by boundary layer diffusion of  $\text{SO}_3$  to and from the deposit surface, where  $\text{SO}_3$  is in equilibrium with excess amounts of  $\text{SO}_2$  and  $\text{O}_2$ . The composition of the bulk gas then shifts until it is equal to the equilibrium composition at the deposit. When the entering gas is at 1625 K and contains 10 mol ppm  $\text{SO}_3$ , 1250 mol ppm  $\text{SO}_2$ , and 1 mol%  $\text{O}_2$ , this occurs at a distance of 20 mm into the probe, at which point the mole fraction of  $\text{SO}_3$  has decreased to 7 mol ppm. Production of  $\text{SO}_3$  from this point onward is assumed to be kinetically controlled, with a rate proportional to the deposit geometric surface area. The mechanism of Mars and Maessen (1968) was used with activity per unit area estimated from the total areas and effectiveness factors reported by Livbjerg and Villadsen (1972). This calculation resulted in  $\text{SO}_3$  equal to 27 mol ppm at a distance of 60 mm from the tube entrance. Therefore, in the event that the deposit has an activity comparable with that of an industrial alkali-promoted vanadium catalyst whose kinetic parameters are the same at 1400 K as at 800 K,  $\text{SO}_3$  could be altered by the sampling procedure. Inspection of the  $\text{SO}_3$  profiles shows that amounts of about 10 mol ppm were observed in 6 of the 9 runs under the conditions of the above calculation ( $z = 3$  to 4 m). This indicates that the greatest errors would have occurred if  $\text{SO}_3$  in the entering gas had actually been near equilibrium, with most of the observed  $\text{SO}_3$  produced in the probe. Based on these observations the limits of error in the measurements are tentatively estimated to be plus 100% and minus 50% of the indicated values. Further study of this problem is warranted, not only by its importance to the sampling technique, but because the situation is analogous to that encountered in the convective section of a boiler, where vanadium and alkali metal tube deposits catalyze the oxidation of  $\text{SO}_2$  as the flue gas is cooled.

#### CALCULATIONS

Notwithstanding the uncertainty in the accuracy of the  $\text{SO}_3$  measurements, it is worthwhile to compare the observations with calculations based on a simple set of assumptions. The objective is to determine if  $\text{SO}_3$  in the furnace exit gas of a

utility boiler might be correlated with flame characteristics which are known or can be estimated, such as fuel sulfur content, peak flame temperature, furnace exit gas temperature, excess air, and carbon monoxide.

A set of reactions which might account for the behavior of  $SO_3$  in the present system is (Kramlich, Malte, and Grosshandler, 1981):



The rate coefficient for Reaction 1 is given by Troe (1978); that for Reaction 2 by Smith, Wang, Tsergounis, and Westbrook (1982). The reverse of Reaction 2 has a negligible rate under the conditions of interest here. Reaction 3 is neglected in the present calculation, although Kramlich et al. provide evidence that it is important in lean hydrocarbon combustion. The concentration of third bodies, M, is taken equal to the total gas concentration, C (but see Kramlich et al., 1981). The net rate of  $SO_3$  production, apparently quite small over much of the region of the measurements, is then:

$$r_{SO_3} = k_1 C_{SO_2} C_O C - k_{-1} C_{SO_3} C - k_2 C_{SO_3} C_O \approx 0 \quad 4)$$

$$\frac{C_{SO_3}}{C_{SO_2}} = \frac{X_{SO_3}}{X_{SO_2}} \approx \frac{k_1 C_O C}{k_{-1} C + k_2 C_O} \quad 5)$$

Under the above assumptions the ratio of  $SO_3$  to  $SO_2$  is limited to the range

$$K_1 C_{O,eq} \leq \frac{X_{SO_3}}{X_{SO_2}} \leq \frac{k_1}{k_2} C \quad 6)$$

as long as the system is not frozen. The total equilibrium mole fractions of  $SO_3$ , shown as dashed lines in Fig. 2, are everywhere less than the measured values, which are, in turn, much less than the right hand side of Equation 6, especially near the furnace exit. In order to apply Equation 5 we require an estimate of the oxygen atom concentration. In discussing this same problem Merryman and Levy (1979) suggested that an estimate of the oxygen atom concentration might be obtained by assuming equilibration of the principal reactions by which they are formed during CO oxidation:



$$C_0 = \frac{K_4 C_{CO} C_{O_2}}{C_{CO_2}} \quad 7)$$

The mole fractions of  $O_2$ ,  $CO_2$ , and  $SO_2$  were taken constant and equal to the outlet values, given in Table 2. Sulfur trioxide mole fractions calculated using Equations 1, 3, 5, and 7 are shown as solid lines in Fig. 2.

The calculated profiles satisfactorily reproduce the magnitude of the  $SO_3$  measurements near a mean residence time of 1 s ( $z = 2.9$  m) in most of the lower excess  $O_2$  (1 mol%) cases. Large discrepancies are observed in two instances (Runs 212 and 213); these are distinguished by low temperature (212), high levels of  $CO$  (213), and high excess  $O_2$  (both). The calculated values are especially sensitive to temperature. Most important is the fact that the calculation predicts  $SO_3$  increasing with distance near the furnace outlet, while most of the measurements show a tendency of  $SO_3$  to approach equilibrium. The assumption of equilibration of Reaction 4 was not originally intended by Merryman and Levy (1979) to be applied at points so far into the postflame region, but at shorter times. As the rate of  $CO$  oxidation slows, due to  $CO$  consumption and decreasing temperature, Equation 7 becomes a progressively poorer approximation. The  $CO$  mole fractions at  $z = 3.1$  m are in the range 320 to 950 ppm, no longer sufficient to maintain significant super-equilibrium concentration of oxygen atoms against competition with recombination, for example, by Reactions 1 and 2 themselves. Because the calculation is least reliable near the furnace exit, it would be unwise to use this approximation to estimate  $SO_3$  in furnace exit gas. The steady state approach (Equation 5) might still be useful however, if the decay of oxygen atoms at long times can be related to  $CO$  and stable species concentrations.

#### SUMMARY

Mole fractions of sulfur trioxide were measured along the axis of a confined turbulent diffusion flame, under conditions simulating those in electric utility boilers. The fuel was a No. 6 residual oil containing 2.2 wt% sulfur, fired at the rate of 0.05 kg/s or 2 MW(thermal). The sulfur trioxide mole fractions were in the range from 3 to 25 mol ppm; representing 0.2 to 2% of the total sulfur. An estimate was made of the contribution of catalytic  $SO_3$  formation by ash constituents deposited in the probe. The uncertainty introduced from this source was estimated to be plus 100% and minus 50% of the indicated value. The observed mole fractions were approximately steady and everywhere greater than the local total equilibrium values. Sulfur trioxide mole fractions were calculated by assuming that the steady state is determined by atomic oxygen reactions, with atomic oxygen in partial equilibrium with carbon monoxide, carbon dioxide, and molecular oxygen. The results of this calculation approximately reproduced the experimental measurements under most, but not all, sets of conditions investigated. Because of its sensitivity to temperature, carbon monoxide, and oxygen this approximation is not recommended for the estimation of  $SO_3$  in furnace exit gases.

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## NOMENCLATURE

C	total gas concentration, kmol/m <sup>3</sup>
C <sub>i</sub>	concentration of gaseous species i, kmol/m <sup>3</sup>
k <sub>j</sub>	rate coefficient of Reaction j in forward direction, various units
k <sub>-j</sub>	rate coefficient of Reaction j in reverse direction, various units
K <sub>j</sub>	equilibrium constant for reaction j, = k <sub>j</sub> /k <sub>-j</sub>
r <sub>i</sub>	net rate of production of species i by chemical reaction, kmol/m <sup>3</sup> s
Sw	combustion air Swirl Number
T	temperature, K
u	axial component of gas velocity, m/s
X <sub>i</sub>	mole fraction of species i
z	axial distance from the combustion air nozzle, m
α	mean temperature gradient along the flame axis, Equation 1, K/m
B	gas velocity decay constant, Equation 2, m <sup>2</sup> /s
γ	carbon monoxide decay constant, Equation 3, m <sup>-1</sup>

## Subscripts

o	evaluated at z = z <sub>o</sub> = 0.95 m from the combustion air nozzle
eq	total equilibrium concentration

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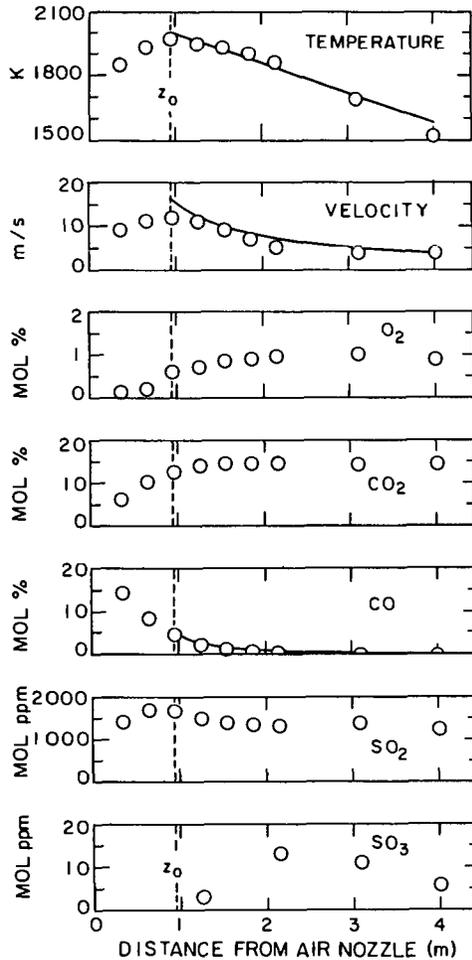


Figure 1. Measurements of gas temperature, axial component of gas velocity, and mole fractions (dry basis) of  $O_2$ ,  $CO_2$ ,  $CO$ ,  $SO_2$ , and  $SO_3$  along the axis of a 2 MW residual oil spray flame. Run No. 214, combustion air Swirl No. = 0.5. The location of the peak flame temperature,  $z = 0.95$  m, is taken as the starting point for calculations. Solid lines are fits of Equations 1, 2, and 3 to the data points.

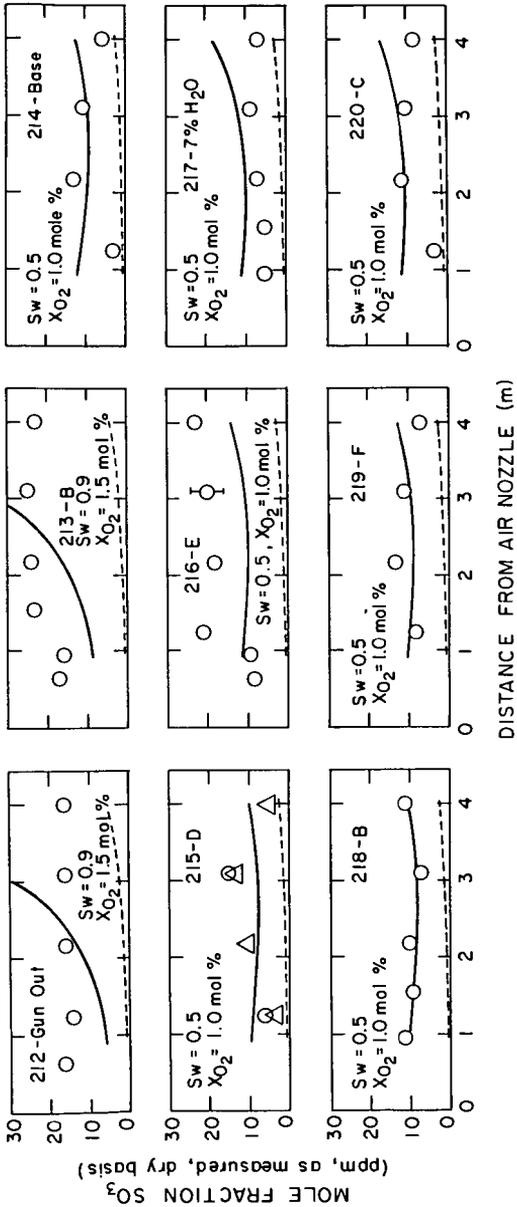


Figure 2. Mole fractions (dry basis) of  $SO_3$  measured along the flame axis and comparison with calculations. The combustion air Swirl No. and flue gas  $O_2$  mole fraction (dry) are indicated in each figure. A distinguishing feature of each run is indicated after the run number. The letters B to F correspond to various fuel additives designed to promote carbon burnout.

Circles: measured value  
 Triangles: duplicate measurements in separate trial  
 Dashed line: calculated, total equilibrium  
 Solid line: calculated, steady state, with oxygen atoms in partial equilibrium with  $CO$ ,  $CO_2$ , and  $O_2$ .

## RAMAN STUDIES OF HALON FIRE RETARDANTS.

J. H. May, F. S. Allen, M. R. Ondrias, R. E. Tapscott,  
H. D. Beeson, and D. M. Zallen.

Chemistry Department, and New Mexico Engineering Research Institute,  
University of New Mexico, Albuquerque, New Mexico 87131.

Raman spectroscopy can be used as a passive probe for the study of active systems. Various types of analytical determinations can be made with-out perturbing the system under study. Of interest is the elucidation of the extinction processes employed by Halon type extinguishing agents. Raman has in the past been used to study molecules such as  $H_2O$ ,  $N_2$ , and  $CO_2$  in flames (1). Halons and pyrolyzed products, having vibrations that are more polarization sensitive than the above molecules, should then be readily analyzed in flames. As an initial approach to this problem we are studying the pyrolysis of Halon 2402 (1,2 dibromotetrafluoroethane). The pyrolysis products are isolated using vacuum line techniques, and identified using GC/MS and Raman. A library of the Raman spectra from each component is being formed for subsequent use in flame analysis.

Experimentally, we use a tube furnace with a specially designed tube, having detachable nitrogen traps on each end, and also capable of holding a vacuum. To simulate the combustion process, Halon 2402 is frozen in one of the nitrogen traps, and the whole system is brought to high vacuum. The Halon is then allowed to vacuum transfer through the pyrolysis tube, which is at approximately  $790^\circ C$ , to the other nitrogen trap. This process is repeated several times. The products are then vacuum distilled, capturing fractions as they come over, in different, sealable cuvettes. Presently all fractions are studied in the gas phase at room temperature.

The Raman data are collected on an instrument made up of:

- 1) An EG&G Princeton Applied Research model 1420 intensified silicon photodiode array tube coupled with its model 1218 solid state detector controller, and the model 1215 computer console.

- 2) A SPEX model 1877 triplemate monochromater.

- 3) A Coherent model CR-4 Argon ion laser, capable of producing over 3 watts of continuous wave power at the 488.0 nm. line.

Spectra, in the range of  $100\text{ cm}^{-1}$  to  $1000\text{ cm}^{-1}$  can be obtained at a single setting of the monochromater. Since Raman spectra of many of the thermal degradation products are not available, we have used a Finnigan, series 4900, GC/MS to identify the products that are obtained from the pyrolysis experiment. Raman spectra collected on these components will subsequently form a spectral library of the pyrolysis products.

Figures 1. and 2. are the Raman spectra of the first fraction collected from the vacuum distillation process on the pyrolyzed 2402. The complexity of the spectra suggests that more than one component is present. The GC/MS revealed that the gas contained only tetrafluoroethylene, and bromotrifluoromethane (Halon 1301) in significant concentrations. Figures 3. and 4. are the Raman spectra of pure 1301, and it is evident that its spectral bands match many of the bands in the distilled fraction.

Pure tetrafluoroethylene will be examined to identify its spectral contribution to pyrolysis products spectra. The vacuum distillation was done at 500 millitorr, later distillations using higher pressures should provide better separation of the fractions.

Each of these spectra took thirty minutes to collect, fifteen minutes for the signal spectra, and another fifteen for the background ( Raman spectra normally require the subtraction of the background spectra, taken with the excitation source off, from the signal spectra. This is especially true for photodiode array detectors.). Accurate spectra, to within 2  $\text{cm}^{-1}$ , of all but the weaker bands can be taken in a minute or less if desired ( This includes background spectra.). Using pulsed, or higher intensity C.W. lasers, spectra could be taken in less time with even better signal to noise ratios.

As a result of these preliminary studies, we will build a library of Raman spectra for the stable products produced by the simulated combustion of the Halon 2402 in a vacuum, as well as in oxidizing and reducing environments. This library will then be used in subsequent studies to identify which of the products are present in flames near extinction due to the presence of Halon 2402.

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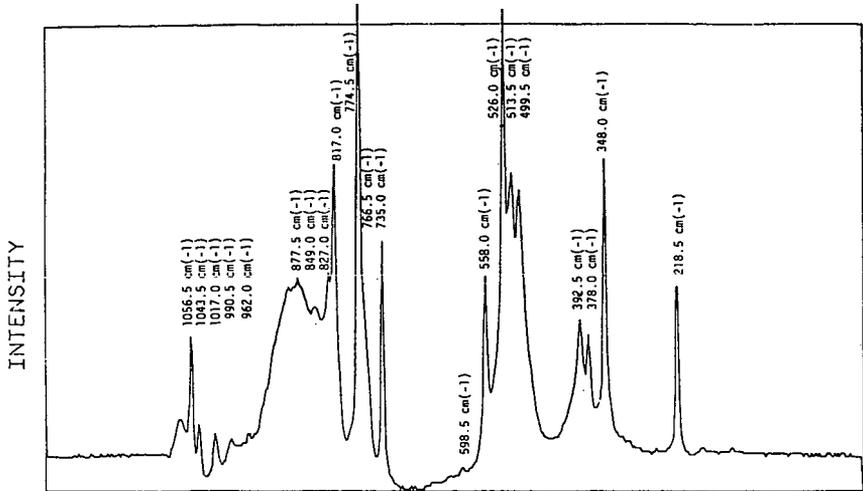


Figure 1. Raman spectrum of the first fraction collected from the vacuum distillation process, for the products of the pyrolyzed Halon 2402.

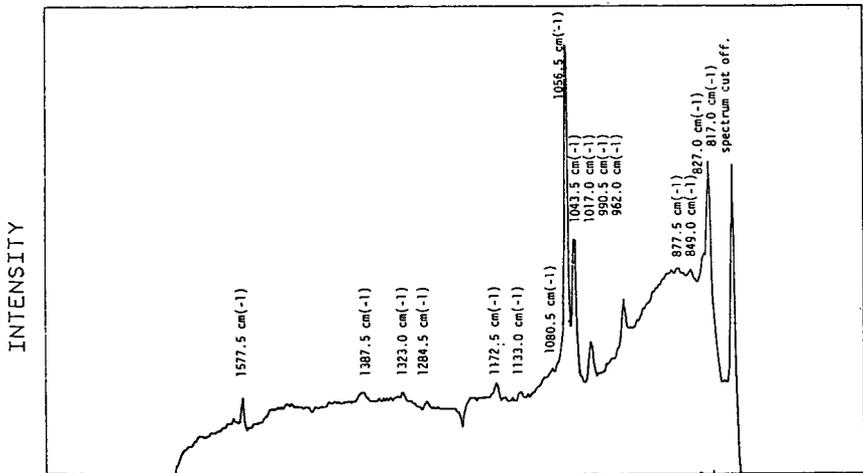
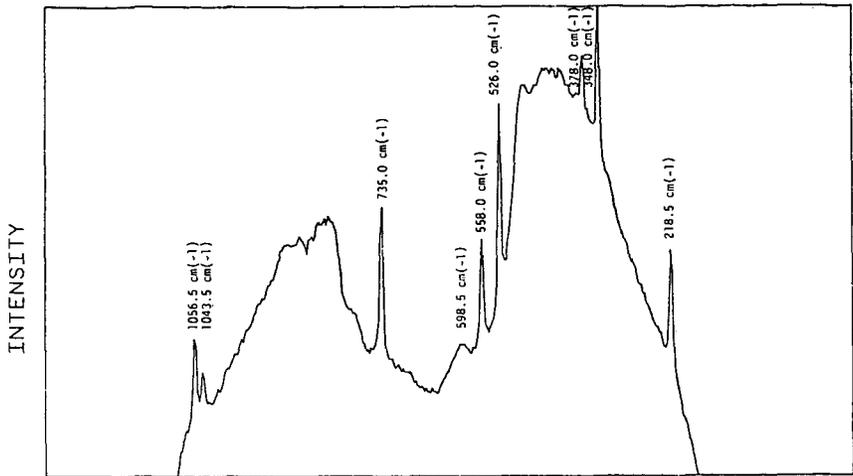
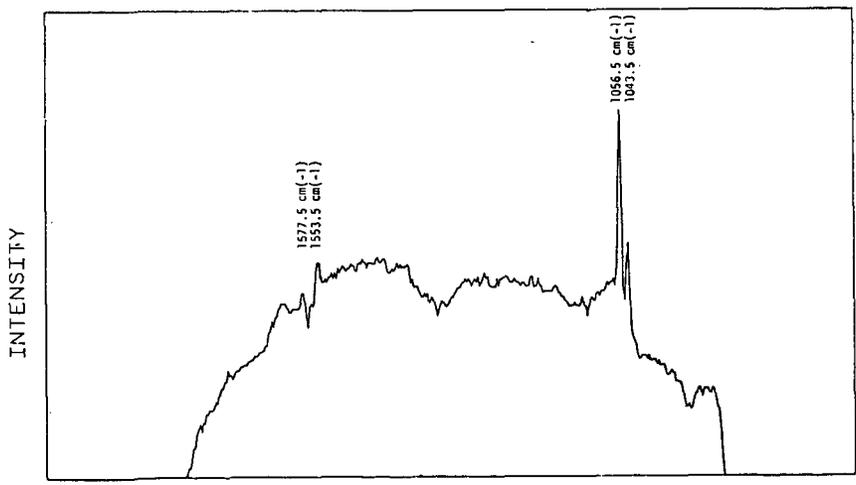


Figure 2. Raman spectrum of the first fraction collected from the vacuum distillation process, for the products of the pyrolyzed Halon 2402. Y axis has been expanded.



←--- WAVENUMBERS CM<sup>-1</sup> .  
 Figure 3. Raman spectrum of pure Halon 1301 ( Bromotetrafluoromethane ).



←--- WAVENUMBERS CM<sup>-1</sup> .  
 Figure 4. Raman spectrum of pure Halon 1301 ( Bromotetrafluoromethane ).  
 Y axis has been expanded.