Short Communication

Near-continuous measurement of hydrogen sulfide and carbonyl sulfide by an automatic gas chromatograph

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ABSTRACT

An automatic gas chromatograph with a flame photometric detector that samples and analyzes hydrogen sulfide and carbonyl sulfide at 30-s intervals is described. Temperature programming was used to elute trace amounts of carbon disulfide present in each injection from a Supelpak-S column in a single peak at the end of 15-min runs. The system was used to study the high-temperature fuel-rich sulfur capture reactions of hydrogen sulfide and carbonyl sulfide with injected calcium oxide sorbent, necessitating the nearly continuous measurement of these gaseous sulfur species. The hydrogen sulfide concentration ranged from 300 ppm to 3000 ppm and the carbonyl sulfide from 30 ppm to 300 ppm. The system was also used to monitor sulfur dioxide levels under fuel lean conditions, and the results compared very closely with sulfur dioxide measurements made simultaneously with continuous UV sulfur dioxide instrumentation.

INTRODUCTION

The combustion of coal produces acid rain precursors such as SO_2. Dry calcium based sorbent injection is a potential method for reducing SO_2 emissions from existing coal-fired boilers. A great deal of study has been devoted to the fuel lean SO_2 reaction [1–3]:

$$CaO(s) + SO_2 + \tfrac{1}{2} O_2 \rightarrow CaSO_4(s)$$
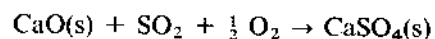
The study of this reaction is facilitated by use of continuous analyzers for the measurement of SO_2 which is the predominant sulfur species present at the high temperatures usually studied. Although the reaction is very fast, the high molar volume of calcium sulfate ($CaSO_4$) quickly plugs the porous CaO structure, and utilization of calcium is theoretically limited to *ca.* 50%.

The fuel rich reactions:

$$CaO(s) + H_2S \rightleftharpoons CaS(s) + H_2O$$

$$CaO(s) + COS \rightleftharpoons CaS(s) + CO_2$$
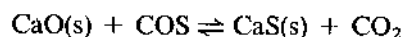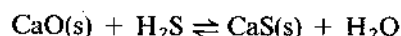
are kinetically faster than the SO_2 reaction [4] and the molar volume of CaS is so much less than $CaSO_4$ that complete calcium utilization is possible. The fuel rich reactions have not been extensively studied particularly under combustion conditions. One difficulty in studying the fuel rich reactions is having to continuously analyze the reduced sulfur species at the concentration levels of interest (up to 3000 ppm or higher).

Reduced sulfur species have been continuously measured with the Barton coulometric titrator and the DuPont Model 460 UV SO$_2$ analyzer. The Barton instrument uses bromine as the active reagent; however, erroneously high readings are possible because of reactions with other materials such as terpenes and other hydrocarbons [5]. With the DuPont instrument, the reduced sulfur species are oxidized and measured as SO$_2$. Thus, information about the relative amounts of various reduced sulfur species is lost.

Gas chromatography (GC) offers a reliable and accurate method for measuring concentrations of various sulfur gases. The use of grab samples, however, provides only periodic analyses, which are not well-suited for the study of sulfur capture reactions. Variations in sorbent feed rate result in fluctuating final sulfur levels requiring multiple samples to obtain an average value. Automatic gas chromatographs have been described in the literature. Huber and Obbens [6] and De Souza [7] have both described automatic GC techniques for monitoring reduced sulfur species. These techniques were designed for lower sulfur levels (1 to 100 ppm), and a complex mix of sulfur species such that 6 to 10 min were required to complete the analysis. The present paper describes an automatic GC technique for measuring moderate levels (up to 3000 ppm) of H$_2$S and COS at 30-s intervals. Temperature programming was used to elute trace amounts of CS$_2$ present in each injection in a single peak at the end of 15-min runs.

EXPERIMENTAL

The top portion of a natural gas fueled (26.4 kW) furnace was operated substoichiometrically to study high temperature (1100 °C) sulfur capture reactions of entrained limestone particles under fuel rich conditions at various levels of sulfur concentration and calcium to sulfur molar ratio (Ca/S). Twenty-five per cent excess air was added to the bottom portion of the furnace, and the ultimate fuel lean sulfur capture was simultaneously measured. A detailed description of the furnace and an analysis of the results can be found elsewhere [8].

An automatic GC sampling system was constructed which allowed nearly continuous monitoring of H$_2$S and COS levels in the rich zone and is

depicted in Fig. 1. The GC apparatus used was a Varian 3700 equipped with a dual flame Aerograph Flame Photometric Detector and a pneumatically controlled gas sample valve. The dual flame photometric detector separates the region of sample decomposition from the region of light emission to be measured. The response from this type of flame photometric detector is independent of the molecular form of the sulfur species and much less susceptible to hydrocarbon quenching than single flame photometric detectors [9].

The high temperature gas sample was taken from the furnace through a 0.75 m × 1.6 cm O.D. stainless steel, water-cooled phase discrimination probe. The core flow was 10 to 15 times the sample flow. The probe tip was designed so that the sample stream would have to flow back against the core flow direction as shown in Fig. 2; thus, most of the sorbent particles stayed in the core flow. The sample stream flowed along a water-cooled wall, which quickly quenched any reaction with remaining sorbent particles. The temperature of the sample stream was monitored and maintained above 120°C to prevent any condensation. The stream was then thoroughly filtered through heated submicron filters so that no sorbent or carbon black particles would contaminate the GC analytical system. The gas sample was delivered to the GC system via a 10 m × 0.4 cm heated PTFE tube. As much PTFE as possible was used in the sulfur gas sampling systems; however, the use of stainless steel in the probe construction and filter housings was unavoidable. Problems of H$_2$S adsorption on the stainless steel were minimized by heating the stainless surfaces (above 120°C) and sampling at a moderately high rate (1.4 std l/min dry; the flow was measured after the water was condensed out and corrected to 0°C and 1 atm). A small sample (ca. 25 ml/min) was drawn by vacuum through the GC sampling system from the main sample stream. The GC sampling and calibration system was made entirely of PTFE including all valves, fittings, and sample loop. H$_2$S adsorption was not a problem and, after a few minutes of sampling, the H$_2$S level would stabilize.

The GC sampling system consisted of three PTFE solenoid valves and a sample valve actuator all under timer controle. Solenoid valve V1a (see Fig. 1) was used when calibrating the GC (V1b closed), and V1b was used when sampling from the
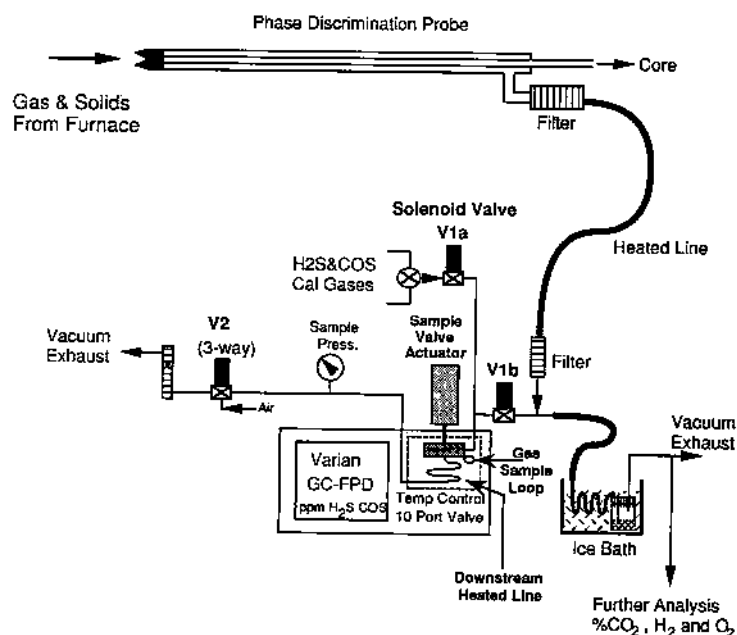
Fig. 1. Schematic of the fuel rich sampling system showing the phase discrimination sampling probe and the automated GC sampling system.

furnace (V1a closed). The distance between V1b and the gas sample valve was only 15 cm of 3.2 mm O.D. (1.6 mm I.D.) PTFE tubing so that very little flow was needed to get fresh sample into the sample loop.

The sampling cycle proceeded as follows: V1b and V2 would both be open for 10 s to allow fresh sample to be drawn into the gas sample loop (ca. 0.03 ml). Then V1b would close and V2 would switch allowing air to flow back toward the sample

Fig. 2. Detail of phase discrimination probe and water jacket.

loop and pressurize the loop from about 660 mmHg to atmospheric (760 mmHg). A piece of 1 m of heated 3.2 mm O.D. PTFE tubing (2.0 ml volume) immediately down stream from the sample loop ensured that the flow back into the sample loop did not modify the sample (the sample loop volume was small compared to the volume of the downstream line; the heated PTFE prevented modification due to reaction, adsorption, or condensation; and the length of the downstream line prevented modification by diffusion). The sample system required 12 s to equilibrate to atmospheric pressure. The sample was then injected into the GC column with the sample valve actuator and 8 s were allowed to sweep out the sample loop. The sample valve would then return to the "load" position and V1b and V2 would open and again allow fresh sample to be drawn into the sample loop. Thus, the gas was sampled every 30 s.

Because of the high concentration of H_2S to be measured, a very small sample loop was required. The sample loop used was approximately 6.4 cm × 0.08 cm I.D. for a sample volume of about 0.03 ml. The column used was a Supelco (Bellefonte, PA,

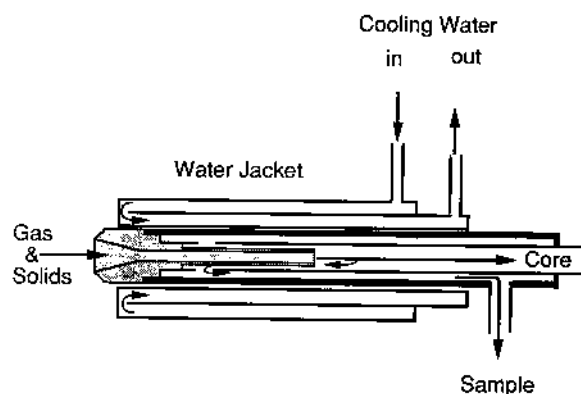USA) Supelpak-S [46 cm packed (80/100 mesh) × 3.2 mm O.D. PTFE]. This column contains an acetone-washed porous polymer packing which requires no liquid phase. A distinct advantage of this column was that moisture in the sample did not degrade the packing so the analysis could be done on a hot, wet sample [10].

Calibration

Standard calibration gases of H_2S and COS mixtures were obtained from Scott Specialty Gases (Plumsteadville, PA, USA) and were used as received to calibrate the GC flame photometric detection (FPD) system. Three different mixtures of H_2S/COS were used: 1025 ppm : 310.5 ppm, 1448 : 150.6, and 2980 : 75.39. These gases were certified to ± 1% except for the 1025 : 310.5 gas which was ±2%. Barometric pressure was monitored and corrections were made for any changes measured assuming the concentration in the sample loop was the same as that in the bottle when the sample loop pressure was 760 mm Hg absolute.

Table I shows the conditions used in the operation of the GC FPD. The FPD apparatus was operated at the lowest sensitivity setting available and was set for square-root output mode. For the sample loop used, the highest concentration of H_2S measurable was *ca.* 1500 ppm when using the normal optimal operating conditions for the FPD. To measure H_2S concentrations up to 3000 ppm the sensitivity of the dual flame photometric detector was decreased by increasing the air rate to the upper emission producing flame (air No. 2) from 170 ml/ min to *ca.* 190 ml/min. The additional oxygen in the emission flame probably prevented optimal conversion of the sulfur species to the detected excited diatomic sulfur species [9], thus reducing the sensitivity by a factor of 2.

Fig. 3 shows typical calibration curves (peak area *vs.* ppm sulfur gas in the sample loop) for both the normal and low sensitivity settings. For the normal settings using the square-root output mode, there is a linear response passing through zero and both the COS and H_2S data all fall on the same straight line. This indicates that with the dual flame photometric detector at normal operating settings the theoretical square-root FPD response [9] was achieved. For the low sensitivity setting and the square-root output mode, there was a linear response for concentra-

TABLE I

GC CONDITIONS USED

Carrier gas	30 ml/min N_2
Sample volume	≈0.03 ml
Sample temperature	150°C
Detector temperature	150°C
Detector gas flows (dual flame)	
H_2	140 ml/min
Air No. 1	80 ml/min
Air No. 2	170 ml/min, normal
	190 ml/min, low sensitivity
Temperature programme	
H_2S/COS	70°C for 15 min; increase linearly to 140°C over 2 min (35°C/min); hold at 140°C for 1 min
SO_2	90°C for 15 min; increase linearly to 140°C over 2 min (25°C/min); hold at 140°C for 1 min

tions 300 ppm and greater; however, the line does not pass through zero and the lower COS concentration data did not show a linear trend. This indicates that the theoretical square-root FPD response was not achieved with the low sensitivity settings.

The GC system was calibrated before and after each series of three sulfur capture runs, which on average took 1½ h to complete. Under normal FPD
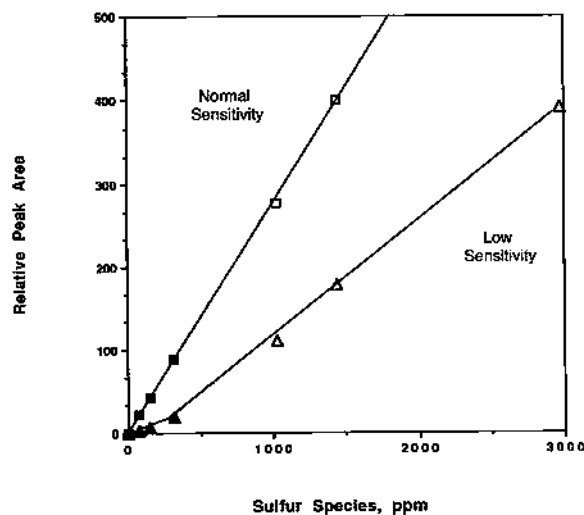

Fig. 3. Typical GC calibration curve. Open symbols: H_2S; solid symbols: COS.

conditions, the calibration for COS was taken as the linear regression fit of the three COS calibration points plus the point (0,0). The H_2S calibration was taken as the linear regression fit of the two H_2S calibration points, the highest COS calibration point and the point (0,0). Under the low sensitivity FPD conditions, the calibration for COS was taken as a cubic fit to the three calibration points, which were forced through the point (0,0). The H_2S calibration was taken as the linear regression fit of the three H_2S calibration points plus the highest COS calibration point. During the 3000 ppm sulfur capture runs, the concentration of H_2S never dropped below ca. 800 ppm.

RESULTS AND DISCUSSION

The H_2S and COS peaks were well separated using the Supelpak-S column at 70°C and 30 ml/min N_2 carrier. The retention time for H_2S and COS was 30 and 45 s, respectively. Just under 30 s were required for both peaks to completely elute which allowed multiple sample injections at 30-s intervals. Fig. 4 shows a typical GC trace for a sulfur capture run. There are 11 H_2S peaks before sorbent injection, 10 peaks during sorbent injection, and 10 peak after. The small, broad peak at the end is CS_2. The small amount of CS_2 in each injection did not elute during the 15 min of 70°C isothermal operation. At the end of each run a temperature program was

started: 35°C/min for 2 min. The CS_2 from each injection eluted at this time.

The GC sampling and analysis technique could also be used to monitor SO_2 levels in the lean zone where SO_2 was the only sulfur species present. Fig. 5 shows a typical GC trace for SO_2 samples from the lean zone ca. 0.1 s after the addition of the excess air. This trace shows 8 peaks before, 12 peaks during and 8 peaks after sorbent injection. The retention time for SO_2 was 47 s, and a 30-s sampling interval allowed adequate time for each peak to elute. The same GC conditions as before were used for this analysis except that the initial isothermal temperature was raised to 90°C.

The lean SO_2 level was also measured simultaneously by a continuous UV analyzer that sampled from a point ca. 0.9 s after the addition of the excess air. Fig. 6 shows a comparison of the SO_2 levels as measured by each technique during simultaneous measurements. There is good agreement in the two curves in both the absolute level of SO_2 measured and trends due to variation in the sorbent feed rate. Very similar results were obtained in five other runs. These tests indicate that the rapid sample GC technique used in this study is an accurate method for nearly continuous monitoring of H_2S/COS or SO_2 in high temperature flue gases. The simultaneous lean SO_2 results also indicate that the fuel rich to fuel lean transition reactions are complete in less than 0.1 s.
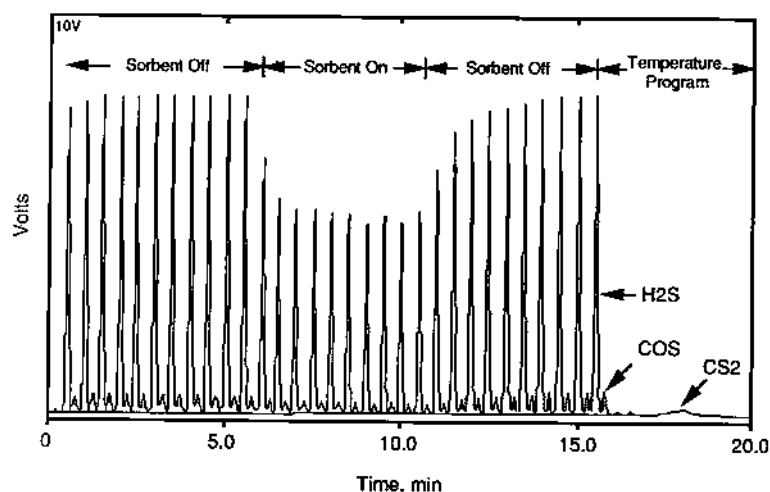

Fig. 4. Typical GC trace for a fuel rich sulfur capture run at Ca/S = 3.0. The H_2S and COS concentrations are reduced from 1430 ppm and 105 ppm to 910 ppm and 60 ppm, respectivley, for an overall fuel rich sulfur reduction of 37%. The GC conditions used are shown in Table I for H_2S/COS measurement at normal sensitivity.
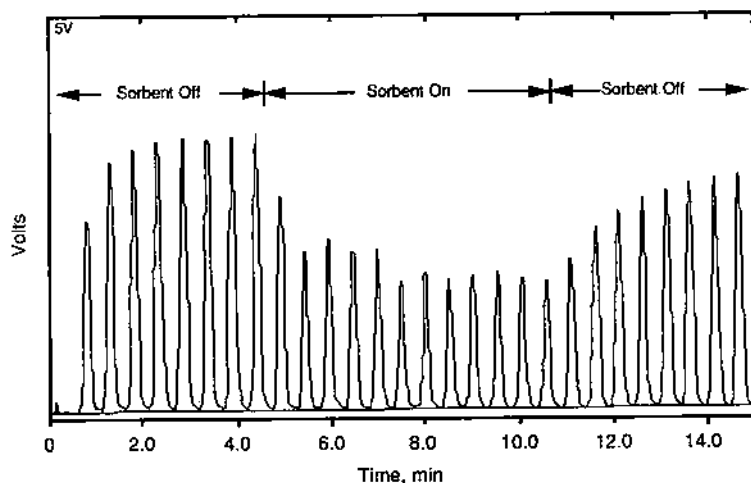
Fig. 5. Typical GC trace for measurement of fuel lean sulfur capture for Ca/S = 3.0. The SO_2 concentration is reduced from 1050 ppm to 475 ppm for an ultimate sulfur reduction of 55 percent. The GC conditions used are shown in Table 1 for SO_2 measurement at normal sensitivity.
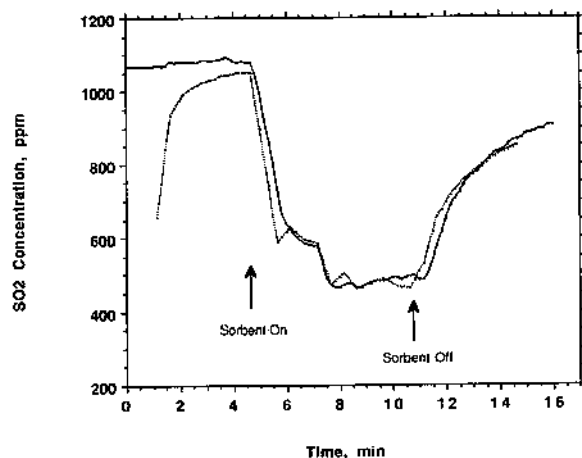
Fig. 6. Comparison of simultaneous SO_2 sulfur capture measurements. ——— = Continuous analyzer; ---- = by GC.

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