

The Determination of Sulfur Gases in Point Source Emissions of a Pulp Mill

GC/MS

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Introduction

The production of Kraft pulp is an important industrial process. At a typical Kraft pulp mill, this process involves the reaction of wood fiber with cooking liquor (sodium hydroxide, sodium sulfide, and sodium carbonate). The byproducts of the bleaching process, which need to be surveyed according to environmental regulations, are hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyl disulfide.

The point source emission of all of these sulfurous byproducts at the mill's location are controlled at the emission regulatory levels shown in Table 1.

Table 1

Site	Total Sulfur
Recovery Boiler	5 ppm
Lime Kiln	10 ppm

While several different analytical techniques are used for the analysis of these compounds at the parts per million level, the Saturn ion trap GC/MS has been employed for the determination of the four compounds listed above.

Experimental

The source samples were collected in Tedlar™ bags at the end of a heated probe which is inserted into the stack gas stream. The probe is fitted with a cooled phosphoric acid trap to remove excess water.

A Varian Saturn Ion Trap GC/MS was used in the analysis of the sulfur gases. A 1.0 mL sample volume was introduced via a 6-port heated gas sampling valve, connected to the sample inlet and SPI injector by means of PEEK (polyetherether-ketone) tubing. PEEK tubing has been found to be compatible with the sulfur gases being analyzed in this application.

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Instrumentation

Gas Chromatograph

Column: SPB-1 (Sulfur column) 60M x 0.32 mm, 4µ film
Flow rate: 1 mL/min He
Column oven: 40°C/3 min, 10°C/min to 140°C/hold
Valve oven: 260°C
Injector: 170°C, isothermal

Mass Spectrometer

Mass Range: 33-150 m/z
Scan Rate: 2/sec
Temperature: 260°C
AM voltage: 3.8V

Results and Discussion

The SPB-1 Sulfur column (Supelco) is a special purpose column developed for the analysis of sulfur gases and other volatile sulfur compounds. It has a very thick film but a low column bleed. Figure 1 displays a chromatogram of a sample from the recovery boiler. Peak symmetry for all the components is satisfactory.

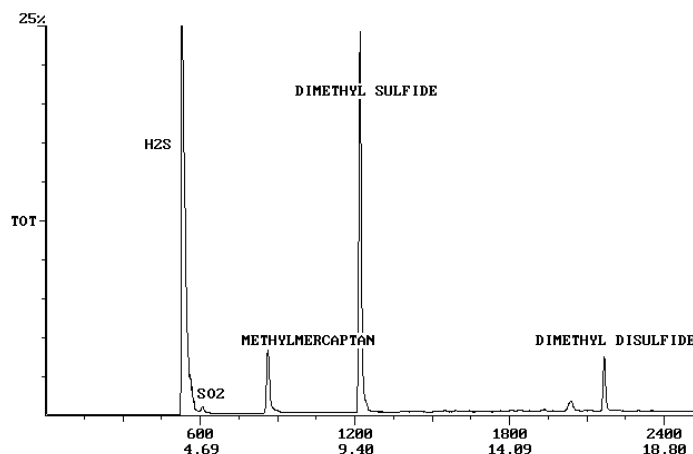
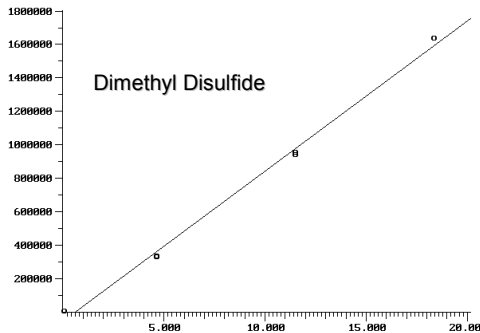
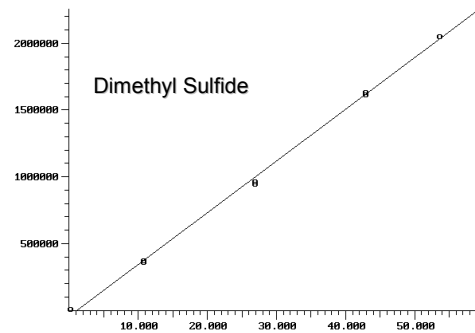
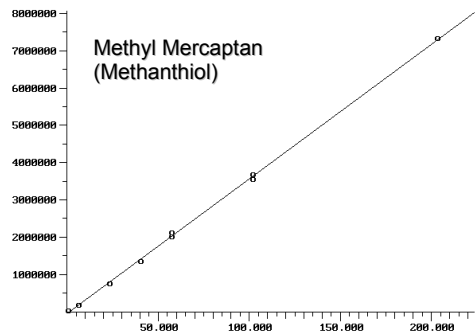
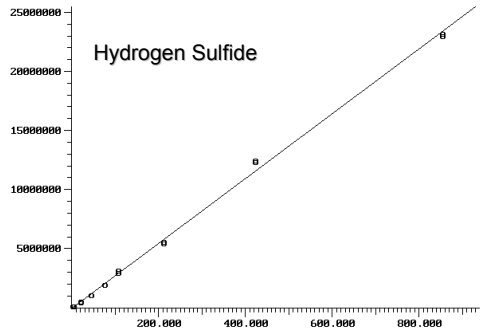


Figure 1. RTICC of 1.0 mL Sample from the Recovery Boiler

Calibration standards for the hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide were prepared over varying concentration ranges and the plots of concentration versus response of the quantitation ions are shown in Figure 2. The quantitation ions selected were m/z 34, 47, 62, 94 respectively.



The spectra of the four sulfur gases are shown in Figure 3 with NIST search parameters.

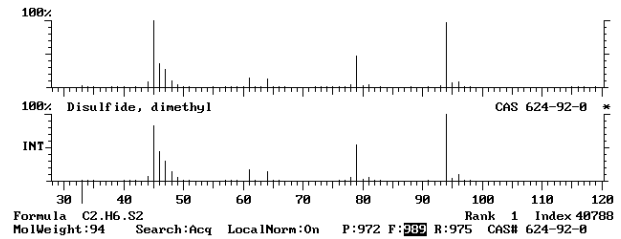
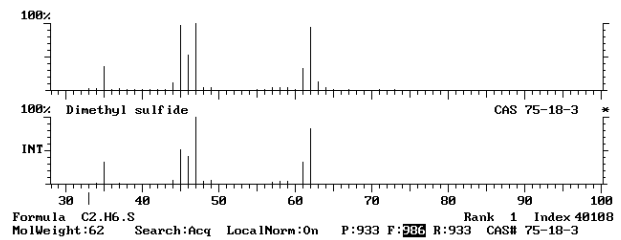
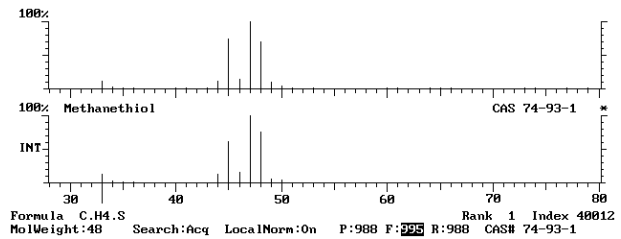
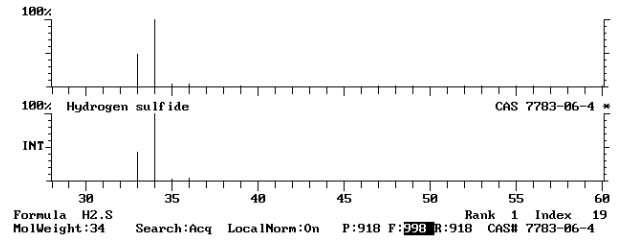


Figure 2. Linearity of Response in the 1-800 ppm Range Peak Area of Sample vs. Amount of Sample Injected

Figure 3. Spectra and NIST Library Search of the Sulfur Compounds Analyzed

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