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ATMOSPHERIC MICROWAVE-INDUCED PLASMA DETECTOR FOR THE GAS CHROMATOGRAPHIC ANALYSIS OF LOW-MOLECULAR-WEIGHT SULFUR GASES

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SUMMARY

New methodology has been developed for the analysis of low-molecular-weight sulfur compounds such as SO₂, COS and H₂S. The method employs gas chromatographic separation with specific element detection using emission spectroscopy. The emission spectroscopic source is a helium microwave-induced atmospheric plasma which is interfaced directly to the gas chromatographic column. Utilizing the vacuum ultraviolet sulfur emission line at 182.04 nm, detection limits of COS, H₂S and SO₂ are 50, 100 and 100 ppb*, respectively. Because of its specificity, other matrix components eluting with the peaks of interest have virtually no effect on the detectability of the sulfur species.

INTRODUCTION

The analysis of low-molecular-weight sulfur compounds such as SO₂, COS and H₂S has become increasingly important for both environmental monitoring and process control. Gas chromatography (GC) provides an acceptable means of isolating each sulfur compound from the others as well as from the diluent matrix. Until recently, however, GC analysis on these gaseous sulfur compounds has proven to be a difficult and time-consuming method due to the lack of adequate GC detectors. This is particularly true when determinations are required at the low ppm or ppb* concentration levels. In general, most conventional detectors, including flame ionization (FID), thermal conductivity (TCD) and electron capture, either do not have adequate sensitivity or are adversely affected by the diluent matrix due to their lack of specificity. If separation is not totally achieved between the diluent, such as air and the compounds of interest, the large excess of diluent can easily obscure the chromatographic peaks of interest. Flame photometric detectors (FPDs) provide good sensitivity and specificity for sulfur analysis but can suffer from non-linearity, are compound dependent, and can be somewhat cumbersome to use. In addition, the lack of versatility of FPDs, when compared to FIDs or TCDs, makes it incompatible to

* Throughout this article, the American billion (10⁹) is meant.

many other applications, thus making it necessary to have a GC system dedicated to sulfur analysis or require time-consuming detector changes on a single GC unit.

The utilization of atomic emission spectroscopy as an element-specific detector for GC offers an attractive alternative to both conventional detectors and FPDs for low-molecular-weight sulfur compounds. Several emission sources exist that are or may be adaptable to interfacing with a gas chromatograph. Among these sources are the inductively coupled plasma (ICP), the d.c. arc plasma and the microwave-induced plasma (MIP). The MIP has to date received the greatest attention for element-specific GC detection. McCormack *et al.*¹ first described a low-pressure microwave plasma employed for the analysis of compounds eluting from a gas chromatograph. The detection of sulfur compounds utilizing the low-pressure MIP has also been described²⁻⁴.

Recently attention has been drawn to the use of an atmospheric microwave plasma as an atomic emission source for gas chromatographic detection. Since Beenakker described the construction and use of a microwave cavity able to support both a helium and argon plasma at atmospheric pressure^{5,6}, an increasing amount of work is taking place to apply it to a wide range of GC problems⁷⁻¹⁰.

The atmospheric microwave plasma possesses several important advantages over other atomic emission sources: (1) the atmospheric pressure MIP is extremely well suited for gaseous analysis; (2) the small quartz plasma tube is easily interfaced with GC columns while both d.c. and ICP sources require somewhat elaborate plumbing arrangements to assure the integrity of the eluted peak; (3) in addition, the MIP is extremely stable, easily tuned and relatively inexpensive to construct and operate.

The work described here is aimed at utilizing atomic emission spectroscopic detection for the analysis of low molecular weight sulfur-containing gases. A helium atmospheric MIP was chosen as the emission source. The GC microwave-cavity interface is described. This study was restricted to the analysis of H₂S, COS and SO₂ in air, although sulfur compounds such as CS₂ and small-chain mercaptans should be equally applicable. Generally detection limits have been found to be in the fractional ppm to ppb range. Because the most sensitive emission lines for sulfur appear in the vacuum ultraviolet, a study of the emission spectra between 170.0 and 200.0 nm was undertaken in order to characterize the discharge in this region. Since other elements of interest, such as phosphorus and carbon, emit strongly in this region, a characterization such as this can be extremely useful for other applications not discussed here.

EXPERIMENTAL

Gas chromatographic system

A Fisher/Victoreen series 4400 gas chromatograph was equipped with a 6 ft. × 1/8 in. O.D. Teflon (FEP) Chromosil 310 column (Supelco, Bellefonte, PA, U.S.A.). Helium was employed as the carrier gas at a flow-rate of 12 ml/min. All separations were carried out at a constant temperature of 50°C. Standard injection volumes were 1.0 ml utilizing Pressure-Lok gas syringes (Supelco).

Standard gas mixtures were made from commercially obtained cylinders of 0.5% H₂S and COS, and 0.5% SO₂ (Linde Division, S. Plainfield, NJ, U.S.A.). Utilizing 500-ml round-bottom flasks equipped with side-arms to which septums could be attached, the appropriate amounts of each gas were delivered into the vessel

through the septum. Prior to introduction of gas samples, the vessels were purged with nitrogen. To assure rapid mixing, *ca.* twenty 1/8-in. acrylic mixing balls were placed in the flask which was then vigorously shaken. Standard concentrations as low as 0.10 ppm were successfully prepared utilizing this procedure. Samples to be analyzed were injected without dilution or any other sample handling.

Microwave plasma detector system

A schematic diagram of the microwave plasma detector system is shown in Fig. 1. The microwave cavity was an all-copper Beenakker-type cavity^{5,6}. The cavity was equipped with a type N coaxial cable connector. The original cavity tuning screws described by Beenakker were removed and not used at any time. The microwave power supply was the Model MPG 4M microwave generator supplied by Ophthos, Rockville, MD, U.S.A. The generator was equipped with both forward and reflected power meters and operated at a frequency of 2450 MHz.

Tuning was accomplished by a coaxial/stub stretcher Model SL-03N (Micro-lab/FXR, Livingston, NJ, U.S.A.) attached between the microwave cavity and coaxial line leading to the cavity. In addition a microwave circulator CT3487-N (UTE Microwave, Asbury Park, NJ, U.S.A.) and termination TB-7MN (Micro-lab/FXR) were placed in the coaxial line just prior to the microwave cavity. The termination was continually cooled by a small 3-in. fan. The combination of circulator and termination acted to reduce or eliminate reflected power from reaching the generator which can cause both damage and instability in the generator. At powers less than 70 W the circulator proved to be nearly 100% efficient in eliminating reflected power to the generator. At powers in excess of 70 W a minimal amount of reflected power could be observed at the generator. At the typical operating power of 100 W, reflected power was only 4 W. This could be reduced to zero but only at the expense of plasma stability.

The plasma tube assembly was simply a 1.3 mm I.D. \times 6 mm O.D. quartz tube which was inserted in the microwave cavity at its center. The entire plasma cavity was

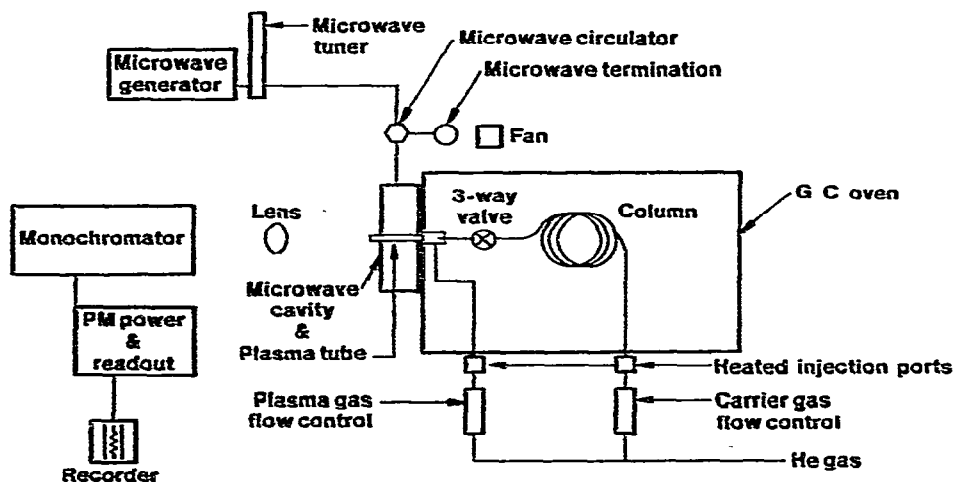


Fig. 1. Schematic diagram of GC atmospheric microwave plasma detector.

attached directly to the GC oven side wall with a series of four nut-and-bolt assemblies. The quartz plasma tube when inserted into the cavity would extend into the GC oven through an access hole provided in the GC oven wall. The plasma discharge was operated in helium at a total flow-rate of 50 ml/min. This helium was supplied to the discharge via two routes; *ca.* 12 ml/min was supplied by the carrier gas of the column, and the remainder through a secondary injection port on the gas chromatograph. This port was sealed off from use except for providing the plasma support gas. A 1/8-in. stainless-steel line was silver-soldered into a hole drilled into a 1/4-in. Swagelok union. This line was then attached to the rear of the injection port while the plasma tube was placed into one end of the Swagelok union. This provided control of the plasma support gas by rotometers already supplied with the gas chromatograph. In addition all lines servicing the plasma were maintained within the GC oven providing easy access and preheating of gases which might contact the GC effluent.

A three-way electrically actuated switching valve with a 1/8 in. bore was mounted between the plasma tube and GC column (1-43-90; General Valve Corporation, East Hanover, NJ, U.S.A.). The valve was actuated by the operator and provided dumping of any column effluent prior to reaching the microwave discharge. This was important when large injections were employed where the solvent eluting from the column caused plasma instability or extinction.

Optical system

The optical system used to monitor the emission from the plasma consisted of 0.25-m Ebert monochromator Model 82-410 (Jarrell-Ash, Waltham, MA, U.S.A.) and a 15-mm diameter, 25-mm focal length fused-silica lens. An optical bench was constructed from a 1/4-in. aluminum plate to which all optical components were mounted. This was then attached directly to the GC wall by an angle iron (Fig. 2). This provided excellent stability of alignment between the microwave plasma and other optical components.

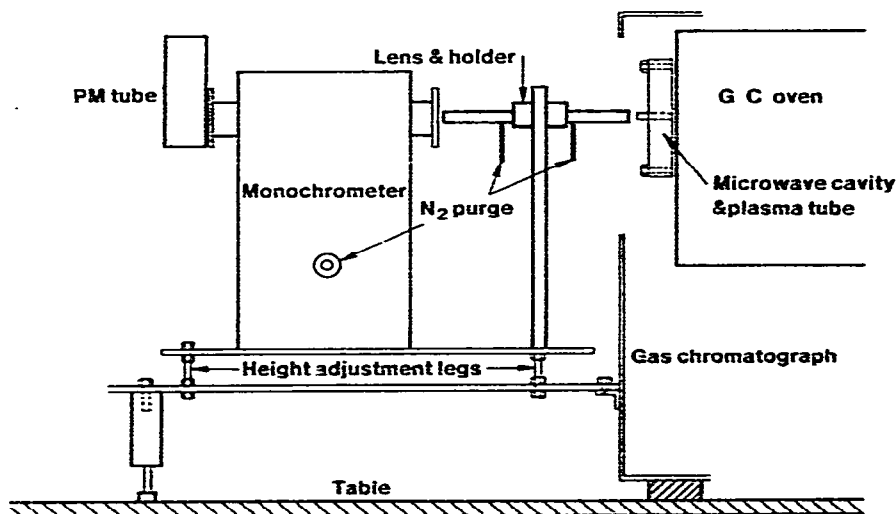


Fig. 2. Optical emission detector arrangement showing nitrogen purge.

The monochromator was equipped with a dual grating. The grating utilized in this work has 2360 grooves/mm, 300.0 nm blaze angle, and the system provided a linear dispersion of 1.65 nm/mm. Both entrance and exit slits were 150 μm . A standard RCA 1P28 photomultiplier (PM) tube operating at -750 V was used. Both photomultiplier power and readout were supplied by a Model 124 digital photometer (Pacific Photometric Instruments, Emeryville, CA, U.S.A.). A Model 1202 Linear recorder (Linear Instrument Corporation, Hackensack, NJ, U.S.A.) was used to record all chromatographic peaks.

Because nearly all of the sensitive sulfur emission lines are located in the vacuum ultraviolet, the optical system was modified to incorporate nitrogen purging of both the optical path and monochromator. Glass tubes, equipped with 1/3-in. side-arms, were mounted on either side of the lens directly onto the lens holder. These tubes extended to the entrance slit of the monochromator on one side and to within 5 mm of the plasma tube on the opposite side. Nitrogen was introduced through the side-arms. In addition, the glass tubes were blackened to minimize light loss or light scattering from overhead lights.

The monochromator was purged by drilling and tapping a 1/4-in. hole in its top and mounting a 1/4-in. pipe-to-Swagelok adaptor to it. A nitrogen bleed was provided by a line attached at this point. A period of *ca.* 24 h was given to purge the system completely and then a bleed of 200–400 ml/min of nitrogen was maintained at all times. For convenience, liquid nitrogen was used.

RESULTS AND DISCUSSION

Spectral characteristics

The spectral characteristics of the atmospheric pressure helium MIP have not been widely documented to date. Considerably more work has been directed towards development of methodology for adapting the MIP as a GC detector than towards examining it phenomenologically. Tanabe *et al.*¹² have developed a wavelength table for emission lines of non-metallic elements for a helium atmospheric MIP. However, this study does not extend below 190 nm.

With the primary concern of our investigation aimed at developing a sensitive tool for the quantitation of low molecular weight sulfur compounds, the spectral region below 190 nm was of interest. In this region three of the most sensitive sulfur emission lines exist at 180.73, 182.04 and 182.63 nm.

The effect of possible nitrogen entrainment into the discharge was of concern. Nitrogen band systems are known to extend into the vacuum ultraviolet, in particular the Far Ultraviolet System and the Lyman–Birge–Hopfield System, arising from N_2^+ and the neutral molecule N_2 , respectively.

Fig. 3 shows a wavelength scan between 170.0 and 200.0 nm which was taken while a constant bleed of 10 ppm COS in N_2 was maintained to the plasma. It is interesting to note that a nearly identical spectrum was obtained when no sample was added except for the absence of the sulfur peaks. The majority of the spectrum between 183.0 and 200.0 nm was attributed to nitrogen bands most likely being the N_2^+ band system. It is fair to assume that the nitrogen flushing of the optical path just in front of the discharge tube was causing an appreciable amount of N_2 entrainment into the plasma. In addition to nitrogen band structure, the carbon emission

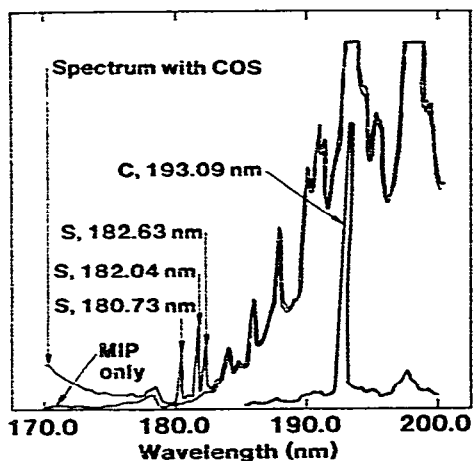


Fig. 3. Wavelength scan between 170.0 and 200.0 nm during continuous bleed of 10 ppm COS into plasma and with no COS bleed. Carbon emission line shown at 193.09 nm on a reduced scale.

line at 193.09 nm was identified and is shown in Fig. 3, where the scale has been substantially reduced. The presence of carbon was attributed to hydrocarbon impurities in the helium gas supply.

Of the three prominent sulfur emission lines, the 182.04-nm line was chosen for the balance of the analytical work due to its slightly better sensitivity than either the 180.73 nm or the 182.63 nm line.

Operational characteristics of the MIP

Several variables were considered important in obtaining both a stable and reproducible plasma and in interfacing the MIP to the gas chromatograph. Among the variables studied were power to the plasma, total helium flow-rate to the plasma, tuning variability of the plasma cavity, and plasma tube size.

Previous experience with atmospheric microwave plasmas has shown that ignition and tuning of the cavity can sometimes be difficult with seemingly large variations in day-to-day performance. In an attempt to alleviate this difficulty several additional components were added to the tuning circuit which had previously consisted of a single coaxial stub stretcher tuner. In addition to the tuner a microwave circulator and termination were added to the circuit. The circulator acts as a shunt for power which is being reflected back towards the generator due to impedance mismatching between the microwave cavity and generator. The circulator allows power to flow from the generator to the cavity but reflected power is diverted to a dummy load termination where it is dissipated as heat. The addition of these components had two significant effects on the operation of the plasma. First the tuning and ignition of the discharge were greatly simplified. Once the tuning position on the coaxial stub stretcher was found, no further tuning was required. This was due to the fact that, prior to plasma ignition, a small impedance mismatch occurred which normally requires retuning, however, with the additional circuit components this mismatch was removed. The second important effect was the reproducible plasma conditions obtained from day to day. With the tuning performance improved, plasma conditions

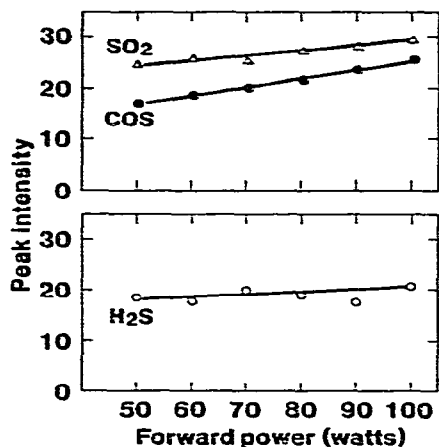


Fig. 4. Relative peak intensity *versus* forward microwave power applied to plasma for COS, H₂S and SO₂ at 100 ppm each in nitrogen.

were stable with reproducibility better than 98% and background drifts during an 8-h period of operation being less than 1%.

The choice of the plasma tube inside diameter was based on the need for the GC effluent to contact the plasma to the largest degree possible. It was found that with quartz tubes of 1–1.5 mm the plasma would fill the entire tube cavity at powers ranging from 60 to 100 W. Larger plasma tube cavities produced a noticeable localization of the discharge, with the plasma growing to fill the cavity only at powers exceeding 100 W.

The work reported here was carried out with a quartz plasma tube of 1.3 mm I.D. The ability of the plasma to fill the quartz tube at relatively low powers produced a remarkable low dependence on power input *versus* analytical performance of the system for the low molecular weight sulfur gases studied. Fig. 4 shows the variation of peak height *versus* power for COS, SO₂ and H₂S. Peak height was found to be an acceptable measure of response in most cases due to the sharp narrow bands ob-

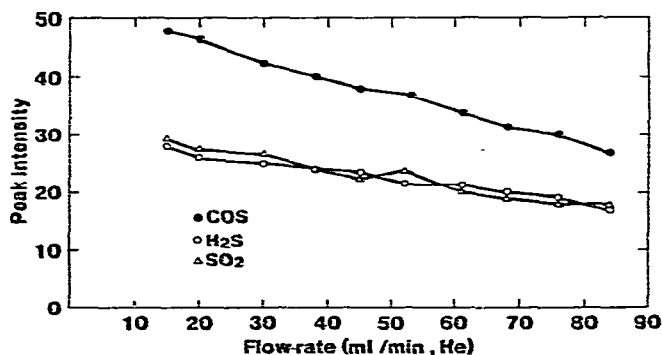


Fig. 5. Relative peak intensity *versus* helium flow-rate to plasma for COS, H₂S and SO₂ at 100 ppm each in nitrogen.

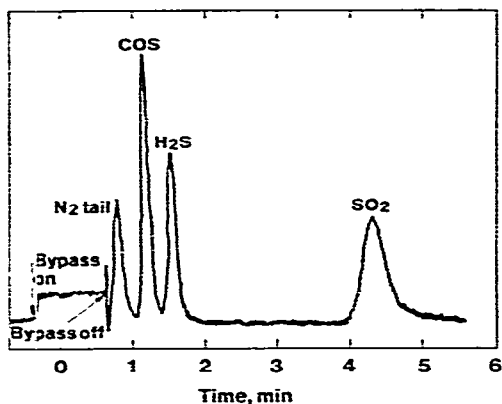


Fig. 6. Chromatogram of 5 ppm each of COS, H₂S and SO₂ in nitrogen. Operating conditions: 1 ml injection; column temperature, 60°C; column flow-rate, 15 ml/min He; total flow-rate to plasma, 60 ml/min He; forward microwave power, 100 W; reflected power, 4 W; sulfur emission line, 182.04 nm.

served. All analytical quantitations however were based on peak area. Although there seemed to be little gained by operating at higher powers, it was also found that the discharge was more stable at higher powers when the introduction of a large sample volume was necessary. In addition, plasma ignition was significantly easier at powers above 70 W. A general operating power of 100 W was maintained.

Total helium flow-rate to the discharge had a greater effect on detector response than power as can be seen in Fig. 5, where the relative peak intensity is shown *versus* total flow-rate. The combination of helium column carrier gas and plasma support gas comprised the total helium flow-rate to the plasma. The plasma can be maintained over a wide range of flow-rates, although at flow-rates less than 25–30 ml/min the discharge exhibited some instability. A flow-rate of 50 ml/min was chosen in order to provide good sensitivity while maintaining excellent plasma stability.

A typical chromatogram of a 5 ppm mixture of COS, H₂S and SO₂ is shown in Fig. 6. It was found that when sample volumes greater than 0.1 cc were utilized there was a tendency for the matrix gas, in this case nitrogen, to extinguish the plasma. In

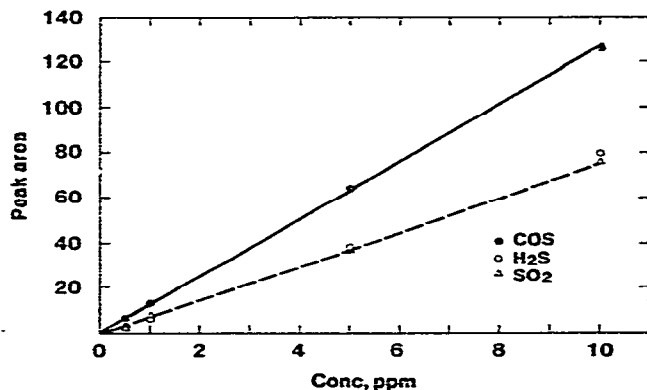


Fig. 7. Calibration curves for COS, H₂S and SO₂. Operating parameters same as Fig. 6.

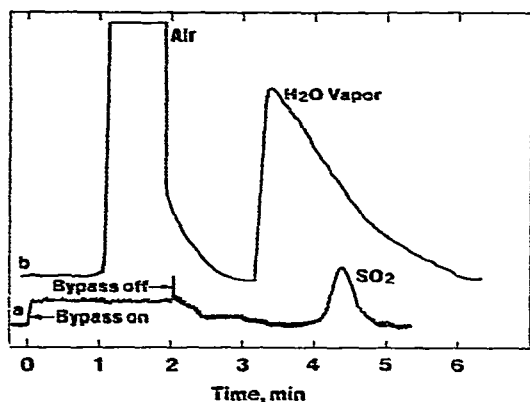


Fig. 8. (a) Chromatogram of atmospheric SO_2 with significant water vapor content using MIP detection. Operating parameters: 1 ml injection; column temperature, 60°C ; column flow-rate, 15 ml/min He; total flow-rate to plasma, 60 ml/min He; forward microwave powers, 100 W; reflected power, 4 W; sulfur emission line, 182.04 nm. (b) Chromatogram of SO_2 analysis under identical chromatographic conditions with a TCD.

addition, the matrix gas was of significant concentration to produce large background changes in the spectrum which could imitate a true sulfur compound being eluted.

To solve this problem a bypass valve was placed between the column and the MIP discharge tube similar to that reported by Quimby *et al.*⁹. Prior to injecting a sample the valve was activated causing effluent from the column to bypass the MIP. Because the helium flow-rate to the plasma was also slightly diminished, the observed background increased. Enough time was allowed for the solvent to elute from the column, at which time the valve was deactivated allowing the effluent from the column to pass into the MIP. Due to the proximity of the trailing edge of the N_2 peak to the COS peak, the valve was deactivated slightly before total elution of N_2 had

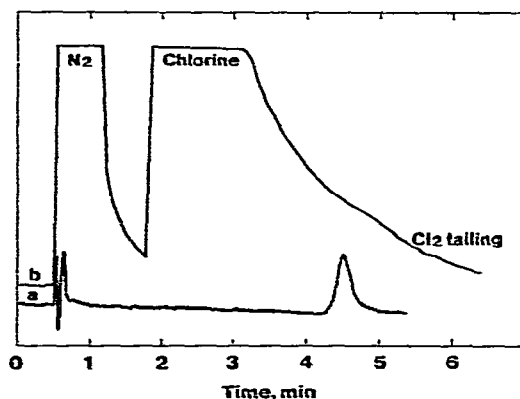


Fig. 9. (a) Chromatogram of SO_2 containing large amounts of N_2 and Cl_2 . Operating parameters same as Fig. 6, 0.1-ml sample injection used and bypass valve not employed. (b) Chromatogram of SO_2 under identical conditions using a TCD.

taken place. In this case a false peak resulted from the small amount of N_2 still eluting which caused a background shift in the plasma. This, however, had no effect on our ability to resolve or quantitate COS or H_2S .

Typical calibration curves for COS, H_2S and SO_2 are shown in Fig. 7. Detection limits were determined based on the equivalent concentration at a signal-to-noise ratio of 2. The detection limits for COS, H_2S and SO_2 were 50, 100 and 100 ppb, respectively. Linear dynamic ranges, assuming the detection limits as the lowest quantitative concentration, were 2.5 for COS and 3.5 for both H_2S and SO_2 .

To demonstrate the specificity of the atmospheric microwave plasma as a GC detector, a series of determinations were run for SO_2 in air samples. All samples contained large amounts of water vapor. An attempt was made to use a thermal conductivity detector but as can be seen in Fig. 8b, the water vapor eluting from the column obscures the SO_2 peak. Fig. 8a shows an identical analysis utilizing the MIP as the detector. Since only emission from sulfur is observed, the SO_2 peak is completely unaffected by the water vapor, although in reality they are eluted together.

A similar application involved the determination of SO_2 in a gas which contained large amounts of chlorine. Once again an analysis failed to detect SO_2 when a TCD was employed because of the large tailing peak due to chlorine (Fig. 9). The MIP detector was not responsive to the chlorine gas and essentially no problem was encountered in performing this analysis.

In conclusion, a system using an atmospheric microwave plasma detector for GC can be extremely useful for the determination of low molecular weight sulfur compounds. This is especially true when concentrations are low and large solvent peaks obscure the sulfur peaks of interest when conventional GC detection is used.

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