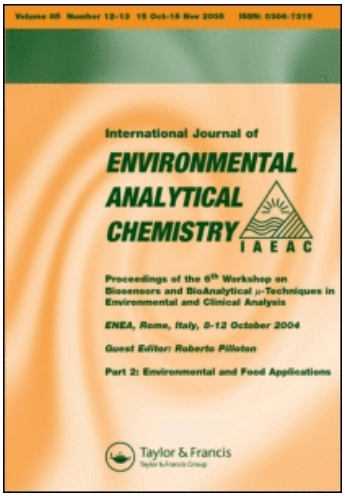

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ANALYSIS OF VOLATILE TRACE SULFUR COMPOUNDS IN WATER WITH GC-SCD BY DIRECT AQUEOUS INJECTION

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A method of direct aqueous injection analysis of volatile trace sulfur compounds in waste or contaminated water is reported. The detection limits of H_2S, COS, and several mercaptans range from several ng/mL to several tens of ng/mL. The method precision is approximately 10%. Contamination problems, standard curve preparation, injection volume and several problems related to the method development and sample analysis are also addressed in this paper.

KEY WORDS: Volatile trace sulfur compounds, GC, sulfur chemiluminescence detector, direct aqueous injector.

INTRODUCTION

The importance of volatile and semi-volatile trace sulfur compounds in the environment continues to be a critical environmental issue worldwide. For example, the measurement and removal of sulfur compounds from waste water generated by industries, such as graphics, mining, paper, rubber, petroleum and viscose industries, have been conducted by many scientists[1–4]. Also, the contribution of sulfur compounds, such as H_2S, COS, CH_3SH, CS_2, CH_3SCH_3 (DMS), SO_2, and C_3H_7SH, etc., to the global sulfur budget and to the sulfur flux in the atmosphere has been well studied[5–11]. In nature, there is an exchange of volatile sulfur compounds between surface water and the atmosphere. This exchange can contribute a significant amount of volatile sulfur compounds to the atmosphere[12].

From an environmental point of view, there is an increasing concern about waste water from the petroleum industry processes as petroleum supplies are becoming increasingly sour and new environmental regulations are requiring petroleum products with lower sulfur contents. Therefore, monitoring of volatile sulfur compounds in waste water from the petroleum industry and other industries is becoming more important.

The traditional techniques for analysis of volatile trace sulfur compounds in water use pre-concentration methods, such as purge-and-trap and solvent extraction. Although low detection limits can be achieved by the purge-and-trap technique[13], it is very tedious and not accurate for many non-purgable or poorly purgable compounds in water. Solvent extraction can only be used for extraction of some volatile sulfur compounds in water, but cannot be used to extract compounds, such as H_2S, from water. Thus solvent extraction and purge-and-trap techniques prevent the accurate assessment of many aqueous environmental samples.

A direct aqueous injection technique for the analysis of volatile organic compounds in water has been in use in the analytical field for many years[14–18]. The advantages of the direct aqueous injection technique have been summarized by Gurka *et al.*[18]. It can provide faster, lower cost analysis and eliminate the use of toxic extraction solvents.

This study reports a gas chromatographic method for direct aqueous injection analysis of volatile trace sulfur compounds in waste water or contaminated water. Due to using the high sensitivity flameless sulfur chemiluminescence detector (SCD), the method detection limits of H_2S, COS, and several mercaptans can range from several ng/mL to several tens of ng/mL. The method precision is around 10%. Several other problems related to the method, such as contamination problems, the decay of volatile trace sulfur compounds in water, the injection volume, and the standard curve preparation, etc., have also been addressed in this paper.

EXPERIMENTAL

Instrumentation

A Shimadzu GC-9A (Shimadzu Corporation, Kyoto, Japan) and a Siever Model 355 SCD (Siever Instruments Inc., Colorado, USA) was used. The data handling system was a Varian Star Work Station (Varian, Walnut Creek, CA, USA). The column used in this study was a J & W (J & W Scientific, Folsom, CA, USA) DB-1 megabore capillary column (15 m × 0.53 mm × 5 μm df.) The column was connected to the GC injector, which was modified for on-column injection. A piece of on-column injection sleeve (Varian CAT NO. 2–3630) was cut to fit in the injector (Figure 1). The injector temperature was 200°C. Helium was used as the carrier gas; the flow rate was 4.0 mL/min. The detector was operated at the conditions suggested by the manufacturer, namely, air flow rate 40 std mL/min, H_2 flow rate 100 std mL/min, temperature 780°C, and vacuum pressure 265 torr. The column temperature was held at 0°C for 1 min, then programed to 30°C at 10°C/min, and finally programed to 250°C at 20°C/min.

Standard solution preparation

H_2S, COS, CH_3SH (Matheson, Gas Products Canada), C_2H_3SH, C_3H_7SH, C_4H_9SH (Supleco, sulfur compounds kit 71), deionized (DI) water, and 2-propanol (Fisher Scientific, Nepean, CA, USA, purified grade) were used to prepare standard solutions.

Before preparation, the DI water was purged with helium for about 2 hours. A small amount of C_2H_5SH, C_3H_7SH and C_4H_9SH was dissolved in 2-propanol to form a stock solution. At first, 200 uL of each gas phase of H_2S, COS and CH_3SH was injected into 50 gram of degassed DI water which was kept in a 60 mL glass vial (Supelco, CAT NO. 3-3109) with a Teflon-faced rubber septum (Supelco, CAT NO. 3-3200). After shaking about 30 min, the head space of the vial was analyzed to determine how much of the spiked gas phase sulfur compounds had dissolved into the DI water. Then, a calculated volume of the standard stock solution was spiked into the above DI water to form a standard solution. Several dilutions were subsequently made from the above standard solution.

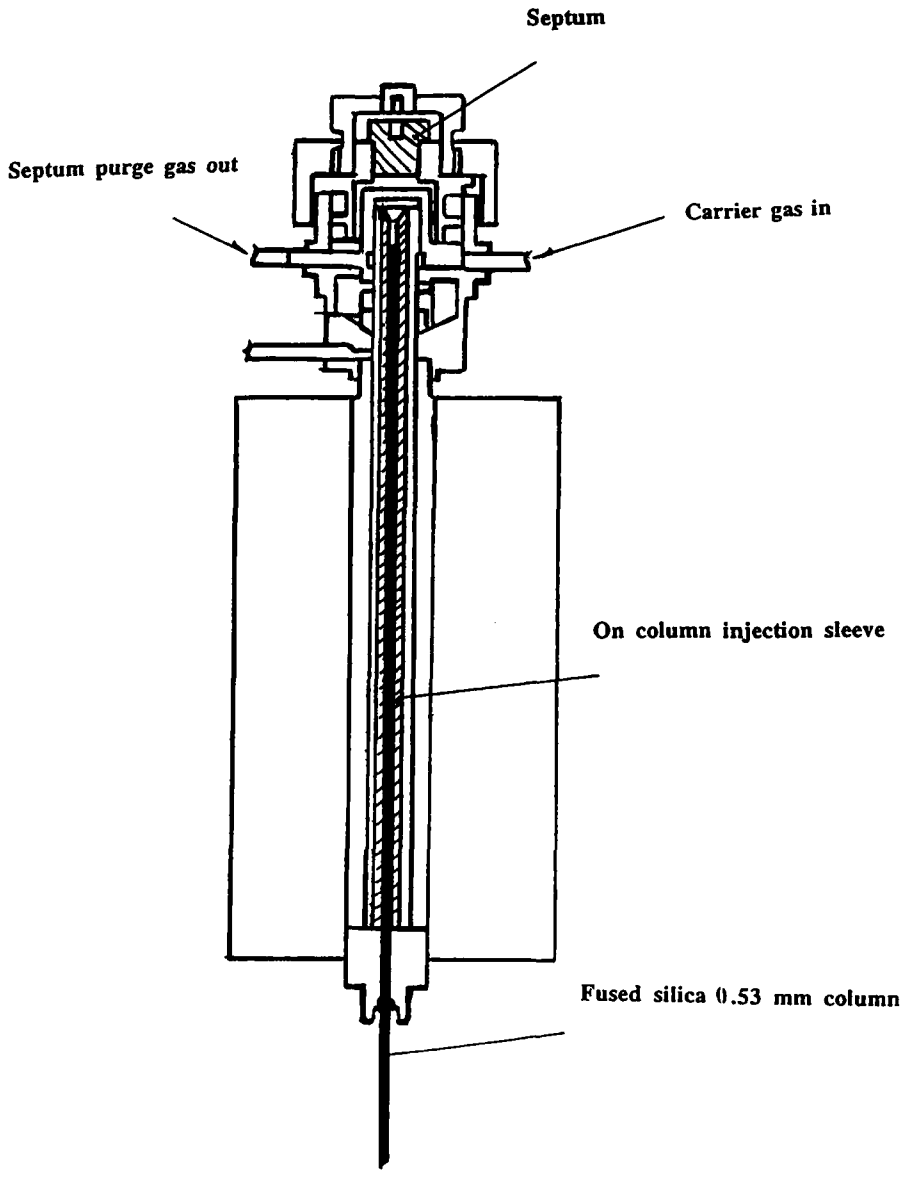

Figure 1 A schematic of the modified on-column injector from Shimadzu 9A.

Glassware and syringe cleaning

Due to strong adsorption of gaseous sulfide onto the glassware surface[19], all glassware was thoroughly cleaned and deactivated before use. The cleaning procedure was that described in reference 13. It includes soaking the glassware in chromerge and rinsing with DI water, then soaking in 10% HCl and rinsing with DI water, and finally drying

with acetone. The last step was silanizing the glassware. The reagent used was dimethyl dichlorosilane 5% (v/v) in toluene (Sylon CT, Supelco, Bellafonte, CA, USA). Methanol and dichloromethane (BDH Inc., Associate of E. Merck, Darmstadt, West Germany) were used to clean syringes.

RESULTS AND DISCUSSION

Typical chromatograms showing determination of the trace volatile sulfur compounds in water are shown in Figure 2; Figure 2-A is from a standard solution, and Figure 2-B is from a secondary outlet of a pulp mill. The resolution of H_2S and COS, and the peak shapes for all tested sulfur compounds are very good. The calibration curves obtained from standard solutions are shown in Figure 3. It can be seen that peak areas were linearly related to the amount of the spiked sulfur compound.

Experiments show that there are several factors which affect the quantitation.

Contamination problems. The Siever model 355 SCD is one of the most sensitive selective detector for the measurement of sulfur compounds. Potential contamination is, therefore, a serious problem. Gaines *et al.*[20] have conducted a comparison study of the SCD (Siever model 350) and FPD. They found that the SCD displayed a better day-to-day reproducibility than the FPD, but the SCD also displayed a larger standard deviation than the FPD from run-to-run. Their explanation for the larger standard deviation in SCD from run-to-run is that the column retained some analytes from each injection, and these analytes would become noticeable to an extremely sensitive detector. The sensitivity of Siever model 355 SCD is ten times higher than that of the Siever model 350 SCD. Therefore, the contamination problem when using the Siever model 355 SCD is more apparent. In order to eliminate the GC system contamination problem, several injections of degassed DI water should be conducted before any analysis to ensure that there are no ghost peaks appearing in the chromatogram.

Syringe contamination is another problem. It was found that needle-changeable syringes are more difficult to clean than needle-fixed syringes, and the small volume syringes, such as 1 μL syringes, can adsorb H_2S due to their larger metal surface than other type syringes. It was noticed that pretreatment of a 1 μL syringe with acetic acid resulted in a large peak for H_2S.

The fixed-needle syringe is preferred. The cleaning procedure after each sample injection employed in this study included: first rinsing syringes with CH_3OH 10 times, then using CH_2Cl_2 ten times, and finally rinsing the syringe with fresh CH_3OH an additional 10 times.

Water as a solvent. Water is a special solvent which can generate a very large vapor volume compared to many other popular organic solvents. Table 1 lists the volumes generated by several solvents at the injection temperature 280°C, column head pressure 101 *kpa*, and injection volume 1 μL. It can be seen that the volume generated from water is more than 7 times higher than that from hexane at the same conditions. High volume instantly generated in the injector can strongly affect the column head pressure, and consequently affect the split injection ratio and the method precision.

Figure 4 shows a comparison of standard deviations using a narrowbore (0.32 mm i.d.) and a megabore columns (0.53 mm i.d.) at a split ratio of 1 to 7 (n = 5, 2000 ng/mL standard solution). It can be found that using a megabore column can get better method precision. Megabore columns have less column resistance than narrowbore columns, and can be easily connected for on-column injection mode. It is not surprising that using megabore columns combined with on-column injection can generate better method precision.

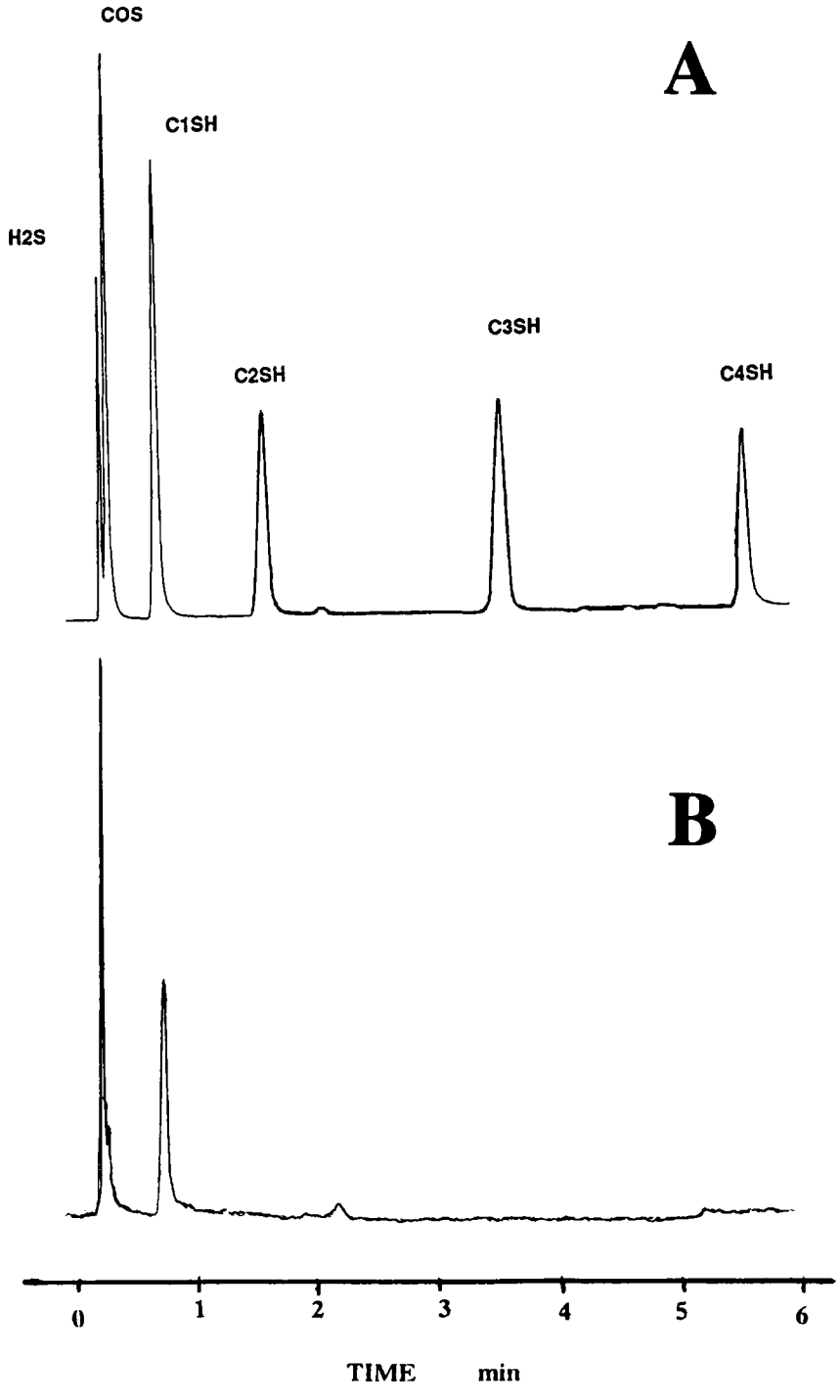

Figure 2 Chromatograms of several volatile sulfur compounds in water. A. Standard solution; B. Secondary outlet waste water from a pulp mill. Initiation: C1SH = CH_3SH, C2SH = C_2H_5SH, C3SH = C_3H_7SH, C4SH = C_4H_9SH. The same in the following figures.

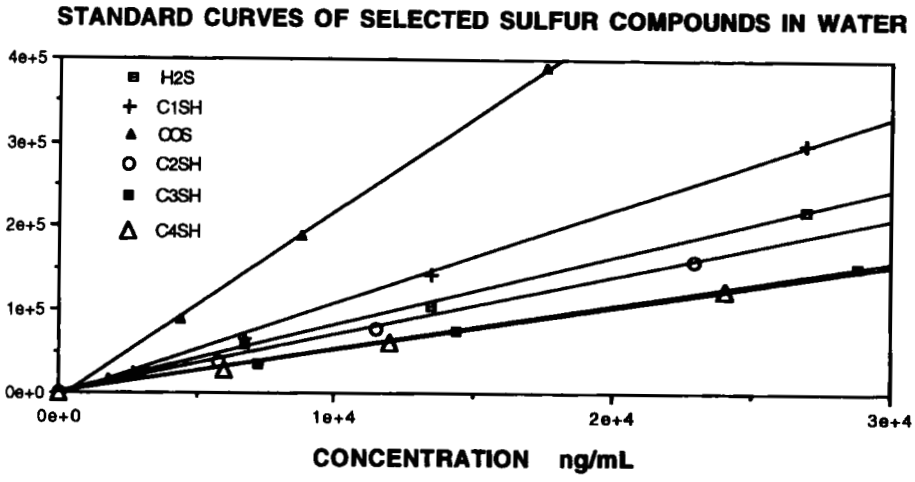

Figure 3 Standard curve of the selected volatile sulfur compounds in DI water.

Table 1 Comparison of vapor volumes of different solvents with 1 μL injection.

Solvents	*Volumes (μL)*
Hexane	174
Toluene	214
Methylene Chloride	355
Carbon Disulfide	377
Methanol	563
Water	1260

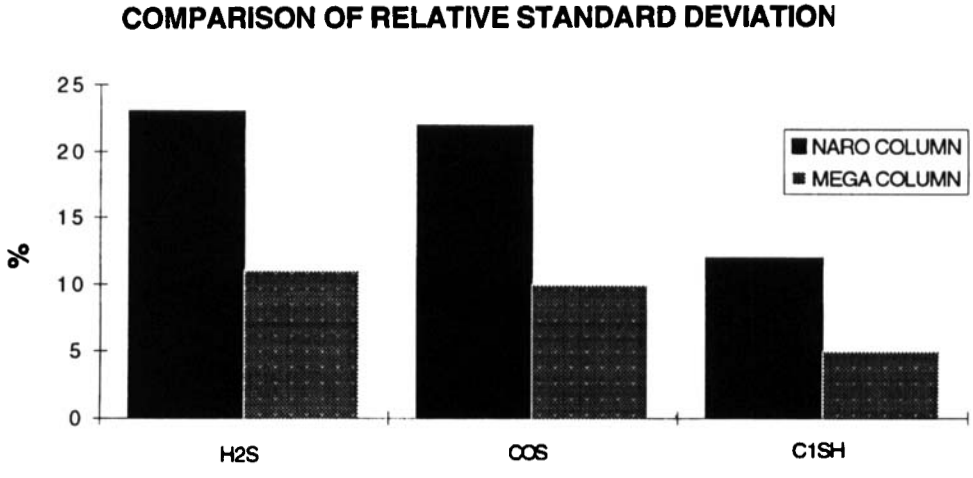

Figure 4 Comparison of relative standard deviations of the selected volatile sulfur compounds in DI water in different columns.

There is another big difference when using water as a solvent compared to other organic solvents. The boiling point of many volatile sulfur compounds in water are much lower than that of water. Thus, water will elute from the column much later than many other sulfur compounds in water. If the water remains in the column, it will cause serious trouble. Because there is no response for water in SCD, it is difficult to decide the retention time for water. The best way is to allow enough time between run to run for the water to elute from the column, especially for samples which are contaminated only be several very low boiling point compounds such as H_2S, COS and CH_3SH, where all the contaminants will elute within 1 or two minutes.

Injection volume. Experiments show that the responses of the Siever model 355 SCD are proportional to the water sample volumes injected into the GC (Table 2). Using a large sample volume can decrease the detection limits, but it is also noticed that the sensitivity of Siever model 355 SCD decreased after several large volume injections. This might be due to the strong polarity of water. In addition, traces of the stationary phase reacted with water elutes to the SCD, and causes fouling of the detector.

Detection limits. The method detection limits for different volatile sulfur compounds in water vary from several ppb to several tens of ppb (Table 3). The detection limits increase along with the increase of the molecular weights of the compounds. Table 4 lists the peak areas comparison of H_2S and COS. Compared to H_2S,

Table 2 Peak areas related to injection volume of a sulfur standard solution.

Volumes (μL)	*Peak areas*	
	H_2S	*CH_3SH*
0.4	1338	757
1.0	2878	1601
2.0	5478	3278

Table 3 Method detection limits for selected volatile sulfur compounds*.

Compounds	*Detection limits (ng S/mL)*
H_2S	8
COS	5
CH_3SH	8
C_2H_5SH	16
C_3H_7SH	24
C_4H_9SH	24

* Method detection limit is calculated based on the detectability (D = 4N/S) of the individual compound at 1 μL injection.

Table 4 Comparison of peak areas of H_2S and COS.

Compounds	*Concentrations (ng/mL)*	*Peak areas*	*Peak areas/(ng/mL)*
H_2S	480	22326	46
COS	260	25093	96

COS is less polar. Therefore, the solubility of COS in DI water is less than that of H_2S. The key point derived from Table 4 is that the peak area per unit of COS is larger than that of H_2S. This might reveal that H_2S. H_2O formed during the solution of H_2S in the water could not be completely decomposed when the water sample was injected into the injector even at 300°C.

Storage time of water sample. Caron and Kramer[18] found that the analytical results of volatile sulfur compounds in water varied with time of storage. Even if a microbial intoxicant m-cresol was added to some stored samples, concentrations of part of the measured sulfide still decreased with time. In this study, the same problem was met, especially for COS. The concentration of COS in the standard solution also rapidly decreased with time. It is believed that the decrease of the concentration of COS is due to its low solubility in water. This data further supports the conclusion[18] that water samples should be analyzed as quickly as possible.

CONCLUSIONS

The method of direct aqueous injection analysis of trace volatile sulfur compounds in waste water or contaminated water is suitable for practical use at ng/mL concentration. Use of a megabore column and on-column injection can yield better method precision. At optimized conditions, the detection limits for H_2S, COS and several mercaptans range from several ng/mL to several tens of ng/mL. Contamination and losses of the trace volatile sulfur compounds during analysis and sample preparation are a serious problem. Special care of glassware, syringe and GC system must be adhered to.

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