



ELSEVIER

Journal of Chromatography A, 726 (1996) 161–166

JOURNAL OF  
CHROMATOGRAPHY A

# Determination of volatile sulphur species in soil samples of interest for prospecting for metal sulphide deposits<sup>1</sup>

Rafel Simo, Joan O. Grimalt\*

*Department of Environmental Chemistry, CID-CSIC, Jordi Girona 18, 08034-Barcelona, Spain*

Received 23 May 1995; revised 17 July 1995; accepted 20 September 1995

## Abstract

A method for the determination of volatile reduced sulphur species, namely carbonyl sulphide, dimethyl sulphide, carbon disulphide and dimethyl disulphide, adsorbed in soil samples overlying sub-surface metal sulphide mineral deposits is described. Heating time and temperature and the headspace gas are critical parameters determining the final composition and yield of the desorbed mixtures. Heating at 95°C for 1 h with nitrogen in the headspace provided maximum yields of the compounds reflecting the desorbed species. Longer heating times generate mixtures of sulphur compounds that correspond to thermal decomposition of the soil organic matter with no value for prospecting purposes.

*Keywords:* Soil; Geological materials; Metal sulphides; Sulphides; Carbonyl sulphide; Dimethyl sulphides; Carbon disulphide

## 1. Introduction

Volatile sulphur compounds (VSC), namely carbonyl sulphide (COS) and carbon disulphide (CS<sub>2</sub>), have been detected in the neighbourhood of sulphide-bearing ore deposits [1–4]. Sulphide mineral weathering experiments have also shown that these gases, particularly COS, are related to the oxidation of pyrite, sphalerite and galena [5–8].

These findings have prompted the use of these gases as geochemical tracers in prospecting for

buried metal sulphide deposits. However, this approach is still hampered by gaps in the information on several of the geochemical processes influencing their generation and dispersion. Furthermore, the most adequate sampling and analytical conditions of VSC for exploration purposes are still to be determined.

COS is currently found adsorbed on soils [4,6]. This in practice impedes the use of probes for the direct study of the gas anomalies in overburden and requires the application of desorption methods for the determination of VSC trapped in soil samples. Several desorption mechanisms and conditions have been used but their implications in terms of the yields and composition of the evolved gases are still to be evaluated.

The present study is a contribution to the

\* Corresponding author.

<sup>1</sup> Presented at the XXIVth Annual Meeting of the Spanish Chromatography Group. 7.as Jornadas de Análisis Instrumental, Madrid, 3–6 April, 1995.

knowledge of the most reliable soil desorption conditions for the identification of significant VSC above mineral deposits. Furthermore, a chromatographic method allowing the determination of these compounds is also described. This method is based on analytical developments described in previous studies [9].

## 2. Experimental

### 2.1. Sample preparation, treatment and injection

Glass vials (40 ml) were kiln-fired at 350°C, rinsed with dilute HCl, distilled water and acetone and dried at 60°C. They were filled with homogenized soil sample up to 20 ml so that the remaining empty volume (headspace) was 20 ml. The exact sample mass was measured after introduction into the vials. These containers were stoppered with screw-caps provided with Teflon septa. When nitrogen had to be introduced to replace air, the open vials were left under a moderate nitrogen stream for 3 min and quickly stoppered.

The temperature treatments were started within a few minutes after sample preparation. The vials were placed in a programmable oven where temperature was set at the required value. Once the treatment was completed, each vial was removed from the oven and 2 ml of the air retained in the headspace was immediately removed with a gas-tight syringe and injected into the gas chromatograph.

### 2.2. Gas chromatography

The analysis of the VSC was performed with a gas chromatograph specially designed for this purpose [10]. This instrument was equipped with a flame photometric detector (Perkin-Elmer, Norwalk, CT, USA) and a Hewlett-Packard Model 3393A integrator. The optimum detector gas flow-rates were 95 and 170 ml/min for hydrogen (99.999% quality) and synthetic air, respectively. The carrier gas was 99.999% quality nitrogen, additionally purified by passage through molecular sieves, oxysorb and cryogenic

traps. The sulphur components were separated on a 1.4 m × 1/8 in (ca. 3 mm) O.D. FEP Teflon column packed with 40–60-mesh Carboxpack BHT 100 (Supelco, Bellefonte, PA, USA). Column heating and cooling were performed with Peltier elements. The column was conditioned overnight at 100°C with carrier gas at a flow-rate of 20 ml/min. An almost baseline separation of H<sub>2</sub>S, COS, CH<sub>3</sub>SH, (CH<sub>3</sub>)<sub>2</sub>S, CS<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>S<sub>2</sub> was achieved using temperature programming from 50 to 100°C at 30°C/min, with an initial 0.5-min delay and 8-min hold at the end. The carrier gas flow-rate was 20 ml/min.

### 2.3. Calibration

Calibration was performed using certified permeation tubes containing H<sub>2</sub>S, COS, CH<sub>3</sub>SH, (CH<sub>3</sub>)<sub>2</sub>S, CS<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>S<sub>2</sub> (Vici Metronics, Santa Clara, CA, USA). The gaseous standards were obtained in a permeation apparatus, keeping the tubes in glass vessels at a constant temperature of 30.0 ± 0.1°C and under a continuous nitrogen flow. Variable volumes of the outcoming nitrogen stream were taken with gas-tight syringes and injected through the septum of the injector into a Teflon line connected to the column of the gas chromatograph.

## 3. Results and discussion

The VSC species encountered in the thermal desorption experiments performed in this study are COS, (CH<sub>3</sub>)<sub>2</sub>S, CS<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>S<sub>2</sub> (Fig. 1). The chromatographic system and conditions used for the analyses allow the baseline separation of compounds having similar retention times such as (CH<sub>3</sub>)<sub>2</sub>S and CS<sub>2</sub> and COS and CO<sub>2</sub> (which is recorded as a small peak with the flame photometric detector). This resolution allows the determination of all the VSC found in the soil samples situated above sulphide mineral deposits.

### 3.1. Headspace gas

The chromatograms shown in Fig. 1 corre-

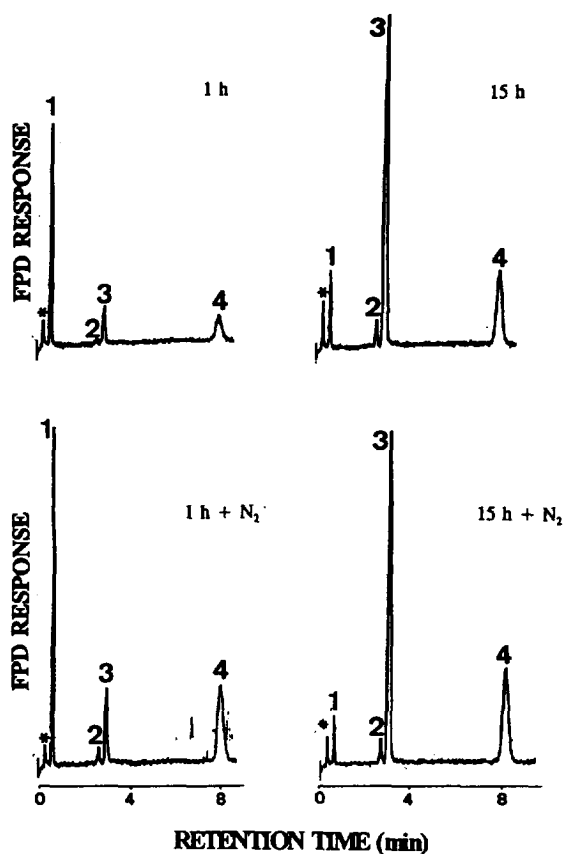


Fig. 1. Representative gas chromatograms of the volatile sulphur species desorbed from soil samples situated above sulphide mineral deposits. Peaks: \* =  $\text{CO}_2$ ; 1 =  $\text{COS}$ ; 2 =  $(\text{CH}_3)_2\text{S}$ ; 3 =  $\text{CS}_2$ ; 4 =  $(\text{CH}_3)_2\text{S}_2$ .

spond to the same soil sample heated at  $95^\circ\text{C}$  for 1 or 15 h with air or nitrogen in the headspace of the desorption vial. The quantitative values corresponding to two replicates of these conditions are given in Table 1.  $\text{COS}$  and  $\text{CS}_2$ , the two VSC commonly related to the occurrence of sub-surface sulphide deposits [1–4], are the major species in the mixtures desorbed in the presence of air. However, when air is replaced by nitrogen as the headspace gas,  $(\text{CH}_3)_2\text{S}_2$  is the major species and the dominant compound in some experiments.

To the best of our knowledge, nitrogen has not been used as a headspace gas in previous studies on the potential of VSC for mineral exploration. The simple replacement method used in the

Table 1  
Yields of volatile sulphur compounds (ng S/g) under air or nitrogen (temperature  $95^\circ\text{C}$ )

Compound	1 h (air)	1 h ( $\text{N}_2$ )	15 h (air)	15 h ( $\text{N}_2$ )
$\text{COS}$	1.1	1.9	0.65	0.54
	1.3	2.5	0.78	0.49
Mean	1.2	2.2	0.72	0.52
$(\text{CH}_3)_2\text{S}$	0	0.35	0.60	0.66
	0	0.67	0.51	0.85
Mean	0	0.51	0.55	0.75
$\text{CS}_2$	0.59	1.2	4.6	3.9
	0.65	1.7	4.9	4.1
Mean	0.62	1.5	4.8	4.0
$(\text{CH}_3)_2\text{S}_2$	0.81	2.5	1.9	2.2
	0.90	4.0	2.0	3.0
Mean	0.85	3.2	1.9	2.6

present study does not eliminate completely the effects of oxygen during desorption because of the air trapped in the soil matrix. However, the replacement is very significant in terms of both qualitative and quantitative composition. As illustrated in Table 1, the yields of all VSC after 1 h of thermal desorption increase considerably when nitrogen is used. The difference is particularly significant for  $(\text{CH}_3)_2\text{S}$  and  $(\text{CH}_3)_2\text{S}_2$ . The former is not detected in the presence of air and the latter becomes the dominant compound on desorption under nitrogen. These differences are not so important at longer desorption times (15 h). Most probably, the larger amount of VSC generated after 15 h of heating reacts and eliminates a substantial amount of the oxygen contained in the vial headspace.

### 3.2. Temperature

Table 2 summarizes the results obtained in the desorption of several soil samples situated above sulphide deposits at  $70$  and  $95^\circ\text{C}$  (desorption time 15–17 h). In all cases, the yields obtained with all compounds are considerably higher at  $95^\circ\text{C}$ . Even the yields obtained at  $95^\circ\text{C}$  with only 1 h of heating are significantly higher than those obtained at  $70^\circ\text{C}$  during 17 h of desorption. Heating at temperatures lower than  $70^\circ\text{C}$  (results

Table 2  
Yields of volatile sulphur compounds (ng S/g) at 70 and 90°C with nitrogen as headspace gas

Sample	70°C/17 h				95°C/15 h				95°C/1 h			
	COS	(CH <sub>3</sub> ) <sub>2</sub> S	CS <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> S <sub>2</sub>	COS	(CH <sub>3</sub> ) <sub>2</sub> S	CS <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> S <sub>2</sub>	COS	(CH <sub>3</sub> ) <sub>2</sub> S	CS <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> S <sub>2</sub>
A	0	0	0	0	0	0	2.4	0	5.0	0	1.1	0
	0	0	1.2	0	0	0	2.4	0	4.5	0	1.1	0
Mean	0	0	0.62	0	0	0	2.4	0	4.8	0	1.1	0
B	1.8	0	0	0	0	0	1.0	0	2.7	0	0	0
	0	0	0	0	2.3	4.1	2.6	0	3.0	0	0	0
Mean	0.92	0	0	0	1.1	2.0	1.8	0	2.9	0	0	0
C	0	0	0	0	0	0	1.8	0	2.4	0	0	0
	0	0	0	0	0	0.89	2.5	0	2.7	0	0	0
Mean	0	0	0	0	0	0.45	2.2	0	2.5	0	0	0
D	0	0	0	0	0	0	1.0	0	0	0	0	0
	0	0	0	0	0	0	1.2	0	0	0	0	0
Mean	0	0	0	0	0	0	1.1	0	0	0	0	0
E	2.5	0	1.6	0	3.6	1.7	25	0.97	5.1	0	2.4	0
	0	0	1.4	0	1.8	0	14	0	2.6	0	1.7	0
Mean	1.2	0	1.5	0	2.7	0.87	19	0.49	3.9	0	2.0	0
F	0	0	0	0	0	0.97	3.6	3.7	4.0	0	1.3	0
	0	0	0	0	1.7	1.1	3.9	2.7	2.8	0	0	0
Mean	0	0	0	0	0.88	1.0	3.7	3.2	3.4	0	0.64	0

not shown) does not give rise to measurable amounts of VSC. These experiments point to 95°C as the most adequate temperature for desorption, which agrees with the results obtained in other studies [4].

### 3.3. Desorption time

As shown in Table 1, in the presence of air as headspace gas the concentrations of most VSC increase at longer desorption times. These results are coincident with those corresponding to another experiment in which heating at 1, 5 and 15 h was compared (Table 3). The changes are also qualitative, involving a decrease in the relative concentration of COS (from 45–73 to 9–10%) and an increase in (CH<sub>3</sub>)<sub>2</sub>S (from 0 to 2.2–6.9%) and CS<sub>2</sub> (from 23–27 to 60%) at longer times.

In the presence of nitrogen, the desorption time differences are not so important in terms of

total VSC concentration (Tables 1 and 2) but they are still very significant in relation to the qualitative composition. Strong decreases in the relative proportion of COS are generally observed at longer desorption times (from 30–100 to 0–23%) and CS<sub>2</sub> is the compound showing the largest increase with longer desorption (from 0–34 to 36–100%).

Further insight into the geochemical significance of these desorption conditions can be obtained by comparison of the results of two successive desorption periods of 15 h at 95°C for the same sample aliquots. Table 4 summarizes the results corresponding to this experiment of sequential desorption using nitrogen as headspace gas. Surprisingly, more VSC are found in the second desorption period and a similar qualitative composition is found in the evolved gases in both steps. This distribution is significantly different from the composition of the same samples after 1 h of heating which, consistent with the results in Tables 1–3, is characterized by

Table 3  
Effects of desorption time on the yield of desorbed volatile sulphur compounds (ng S/g) (temperature 95°C, headspace air)

Compound	Time (h)		
	1	5	15
COS	1.7	1.1	0.75
	1.8	1.1	0.85
	1.9	1.3	0.84
Mean	1.8	1.1	0.81
R.S.D. (%)	5	8	6
(CH <sub>3</sub> ) <sub>2</sub> S	0	0.10	0.16
	0	0.17	0.17
	0	0.16	0.19
Mean	0	0.14	0.17
R.S.D. (%)	0	21	6
CS <sub>2</sub>	0.54	2.0	4.7
	0.92	2.2	5.0
	0.53	2.4	4.4
Mean	0.66	2.2	4.7
R.S.D. (%)	27	6	5
(CH <sub>3</sub> ) <sub>2</sub> S <sub>2</sub>	0	0.44	2.0
	0	0.41	2.3
	0	0.43	2.2
Mean	0	0.43	2.2
R.S.D. (%)	0	4	8

a higher relative concentration of COS (60% vs. 1.3–4.8% at 15 h).

The generation of more VSC after a first desorption of 15 h indicates that there is a VSC reservoir that is not exhausted in the first long heating period. These VSC are very unlikely to correspond to adsorbed species. Conversely, they

Table 4  
Successive desorption of volatile sulphur species (ng S/g) after prolonged heating (15 h + 15 h) of a soil sample at 95°C

	COS	(CH <sub>3</sub> ) <sub>2</sub> S	CS <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> S <sub>2</sub>
<i>First desorption</i>				
	0.11	0.55	1.6	3.5
	0.05	0.76	1.3	4.1
Mean	0.08	0.66	1.4	3.8
<i>Second desorption</i>				
	0.96	2.2	5.3	10
	0.23	0.68	2.9	2.2
Mean	0.59	1.4	4.1	6.1

appear to be de novo synthesized compounds from the decomposition of soil organic matter constituents such as sulphur-containing amino acids [11,12]. Hence the uniform VSC distributions obtained after a long heating period of 15 h probably represent the gas mixtures generated by thermal degradation reactions and not VSC truly adsorbed on the mineral matrix. These results suggest the use of short desorption periods, e.g. 1 h, to avoid the mixing of the adsorbed VSC with the authigenic compounds generated by thermal decomposition.

#### 4. Conclusions

The study of the VSC desorbed from soil samples situated above sulphide mineral deposits confirms that some VSC, particularly COS, are gases that can be used for prospecting purposes. These gases are adsorbed on the soil matrices and can be determined by gas chromatographic analysis of the VSC accumulated in the headspace after heating in Teflon-capped vials. However, the composition of the desorbed mixtures depends on the heating conditions (time and temperature) and also on the gas used to fill the headspace. The most suitable conditions found in the present study correspond to heating at 95°C for 1 h using an inert gas, nitrogen, to fill the headspace. These conditions correspond to the maximum yield of COS and in terms of heating temperature and time are in agreement with those obtained in other studies [4]. However, the use of nitrogen as headspace gas represents a considerable improvement in terms of VSC yields. Long heating times at 95°C give rise to uniform VSC distributions resulting from the thermal decomposition of the soil organic constituents. These distributions cannot be related to the gases adsorbed on the soil matrices having no value for prospecting purposes.

#### Acknowledgements

This paper greatly benefitted from discussions with Mr. Luis Ocaña (Tecnología y Recursos de

la Tierra, TRT, Madrid, Spain). Financial support is acknowledged.

## References

- [1] M.E. Hinkle and J.A. Kantor, *J. Geochem. Explor.*, 9 (1978) 209.
- [2] T.K. Ball, R.A. Nicholson and D. Peachey, *Trans. Inst. Min. Metall., Sect. B*, 94 (1985) B181.
- [3] R.A. Nicholson, D. Peachey and T.K. Ball, *Trans. Inst. Min. Metall., Sect. B*, 97 (1988) B57.
- [4] B.W. Oakes and M. Hale, *J. Geochem. Explor.*, 28 (1987) 235.
- [5] C.H. Taylor, S.E. Kesler and P.L. Cloke, *J. Geochem. Explor.*, 17 (1982) 165.
- [6] S.E. Kesler and M. Gardner, *J. Geophys. Res.*, 91 (1986) 12339.
- [7] M.E. Hinkle, J.L. Ryder, S.J. Sutley and T. Botinelly, *J. Geochem. Explor.*, 38 (1990) 43.
- [8] D.H. Stedman, M.Z. Creech, S.E. Kesler and M. Gardner, *Geophys. Res. Lett.*, 1 (1984) 858.
- [9] R. Simo, J.O. Grimalt and J. Albaiges, *J. Chromatogr. A*, 655 (1993) 301.
- [10] W. Haunold, H.-W. Georgii and G. Ockelmann, *LC·GC Int.*, 5 (10) (1992) 2445.
- [11] W.L. Banwart and J.M. Bremner, *Soil Biol. Biochem.*, 7 (1975) 359.
- [12] S.O. Farwell, *Soil Biol. Biochem.*, 11 (1979) 411.