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Short communication

Quantitation of volatile sulphur compounds in polluted waters

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Abstract

A study on the linear dynamic range of a combined cryogenic trap-gas chromatographic method with flame photometric detection (FPD) has shown that quantitation of volatile sulphur compounds (VSCs) in heavily polluted waters, in the order of hundreds of nanograms, is possible. A correct calibration of the FPD is needed for this purpose. Calibration over 2.5–3 orders of magnitude requires the determination of three different linear equations extending over this mass range. Equations for hydrogen sulphide, carbonyl sulphide, methanethiol, dimethyl sulphide and carbon disulphide are given. The intervals corresponding to each linear equation are determined from the inflexion points in the calibration plots. The changes in sign of the relative error resulting from re-calculation of the VSC mass after use of one single calibration curve for the whole mass range interval provide a secondary criterion of interest. © 1997 Elsevier Science B.V.

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1. Introduction

Volatile sulphur compounds (VSCs), namely hydrogen sulphide (SH_2), carbonyl sulphide (COS), methanethiol (CH_3SH), dimethyl sulphide [$(CH_3)_2S$], carbon disulphide (CS_2) and dimethyl disulphide [$(CH_3)_2S_2$], may be present in water streams as consequence of industrial spillages or natural reduction processes in the presence of high amounts of organic matter and sulphate [1–5]. These compounds may be toxic. Thus, the immediately dangerous to life and health (IDLH) values for SH_2, CH_3SH and CS_2 range from 300–500 ppm in air [6]. However, their odor thresholds are about 3 to 5 orders of magnitude lower than these IDLH levels which means that, in practice, their environmental implications are essentially concerned with bad odor nuisances.

The direct study of VSCs in waters provides useful information on source input, e.g., direct spillages vs. redox processes, which is important for the design of adequate remediation strategies. In a previous study [7], a combined cryogenic trapping-gas chromatographic method allowing the determination of VSC mixtures in waters was described. However, the determination of these mixtures in the presence of high concentrations of one of these VSC species, the current case in polluted waters, is difficult due to the short linear range of the flame photometric detector and saturation of the cryofocussing trap.

Changes in the cryogenic trap procedures and adequate calibration of the flame photometric detection (FPD) system allow the quantitative determination of VSC composition even in these unfavorable cases. In the present study, these changes are

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described and the performance and calibration requirements of FPD for quantitation of large amounts of VSCs are investigated.

2. Experimental

2.1. Sampling and purging

Water samples were collected in high-density polyethylene bottles that were filled completely to minimize headspace. The samples were analysed within 1–8 h after sampling.

A glass bubbling flask was used for the stripping of volatiles from water. The flask was provided with a PTFE-capped side-port through which the sample was introduced and with a fritted glass diffuser through which the sparging gas (nitrogen, 99.999% quality) was supplied.

Aliquots of 1–50 ml were filtered through GF/F (Whatman, Maidstone, UK) and injected into the flask. In the case of small sample volumes, these were brought to 50 ml by dilution with degassed Milli-Q water.

The traps for cryogenic preconcentration were U-shaped borosilicate glass tubes (20 cm×6 mm I.D.× 10 mm O.D.). The lower portion of the tubes was packed with quartz wool to increase the condensation surface. The traps were conditioned before use by nitrogen flushing. Series of five U-tubes were connected to two six-way PTFE tubings. One position was short-circuited, allowing the loops to be closed without interrupting the gas flow. During preconcentration with nitrogen at a flow-rate of 150 ml/min during 20 min, the traps were immersed in liquid argon (−186°C). A Nafion dryer (Perma-Pure, Toms River, NJ, USA), with a countercurrent of dry air at a flow-rate of 300 ml/min, was located between the purge flask and the cryogenic trap to avoid ice blocking on the trap loop.

2.2. Cryofocusing and injection

Once sparging was completed, the cryotrap was connected to the gas chromatograph by means of the six-port valves. Desorption was performed by quickly placing the loop in hot water (70–80°C). The desorbed volatiles were cryofocused in a second, smaller cryogenic trap (W-shaped, 25 cm×1/8 in.; 1 in.=2.54 cm), also immersed in liquid argon, located at the inlet of the chromatographic column. The chromatograph was already in operation at this step to record the signal of major VSCs that could overload this second loop. After a desorption/cryofocusing time of 90 s, the valves of the collection cryotrap were short-circuited so that the carrier gas flowed directly through the cryofocusing loop to the column. Injection proceeded by quickly placing the cryofocusing loop in hot water. This cryofocusing step prevented peak widening caused by the difference in the diameters between the cryotrap and the column. It also allowed the separation of the water not removed by the Nafion dryer by adequate control of the desorption time (90 s) and temperature (<90°C) between the cryotrap and the cryofocusing loop.

2.3. Gas chromatography

The analysis of VSCs was performed with a gas chromatograph especially designed for this purpose [7]. It was equipped with a FPD system (Perkin-Elmer, Norwalk, CT, USA), a 1.4 m×1/8 in. PTFE (FEP) column filled with Carbopack BHT-100 (Supelco, Bellefonte, PA, USA) and heated/cooled with Peltier elements. The optimum detector gas flow-rates were 85 and 110 ml/min for hydrogen (99.999% quality) and synthetic air, respectively. The carrier gas was 99.999% quality nitrogen, additionally purified by passage through an oxygen trap, a moisture gas-cleaner and a cryogenic trap. The column was conditioned overnight at 100°C with carrier gas at a flow-rate of 20 ml/min. Baseline separation of SH_2, COS, CH_3SH, $(CH_3)_2S$, CS_2 and $(CH_3)_2S_2$ was achieved holding the column temperature at 5°C for 1 min, then programming to 50°C at 30°C/min, holding 2 min, and finally programming to 100°C at 30°C/min with 7 min final holding time. The carrier gas flow-rate was 20 ml/min. Peak areas were recorded with a Hewlett-Packard 3393A integrator.

2.4. Calibration and quantitation

Calibration was performed using certified permeation tubes containing SH_2, COS, CH_3SH, $(CH_3)_2S$,

CS_2 and $(CH_3)_2S_2$ (Vici Metronics, Santa Clara, CA, USA). The gaseous standards were obtained in a permeation chamber, 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 out-coming nitrogen stream were taken with gas-tight syringes and injected through the septum of the injector into a PTFE line connected to the column of the gas chromatograph. Interpolation on linear log (peak area)/log (mass) plots for every compound allowed quantification.

The water standards were prepared by injecting variable volumes of the gaseous standards mixed in the permeation chamber into glass containers closed with screw-caps provided with PTFE septa and completely filled with Milli-Q water.

3. Results and discussion

3.1. Cryofocusing and quantitation

Representative chromatograms of the VSC composition in the waters of Besos River (Catalonia, Spain) are shown in Fig. 1. The high content of organic matter and sulphate in these river waters enhances the activity of sulphate-reducing bacteria and the generation of large amounts of hydrogen sulphide. The above-mentioned VSCs are also present in minor proportions. As shown in these chromatograms, part of the hydrogen sulphide present in the waters overloads the secondary 25 cm×1/8 in. loop and is recorded in the gas chromatograph during cryofocusing. Diverse tests using the above-described VSCs have shown that the capacity of these cryogenic loops is overloaded for absolute amounts above 100 ng per individual VSC.

The introduction of large amounts of one single compound in the packed column of the chromatograph is reflected in decreases of the separation efficiency but a priori does not impede quantitation. Luckily, the problems of generation of high VSC concentrations associated to high pollution loads are reflected in the dominance of one single species. Obviously, if more than one species would to be found in high concentration the efficiency losses due to lack of cryofocusing would prevent quantitation.

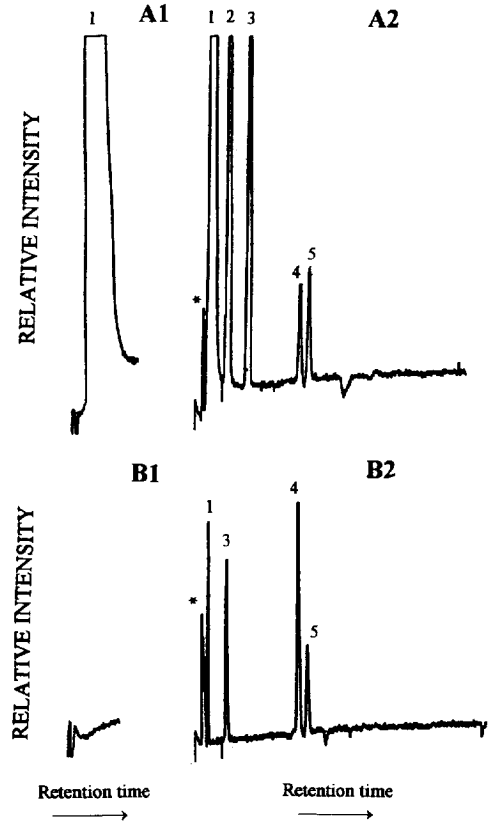

Fig. 1. Representative chromatograms of the VSC composition in the waters of Besos River. (A) Sample corresponding to high sulphate reduction: A1, hydrogen sulphide overloading the cryogenic trap; A2, VSCs retained in the cryofocusing trap. (B) Polluted river sample without sulphate reduction: B1, lack of hydrogen sulphide overloading; B2, standard VSC profile. Peak assignment as follows: (1) hydrogen sulphide; (2) carbonyl sulphide; (3) methanethiol; (4) dimethyl sulphide; (5) carbon disulphide. (*) carbon dioxide.

3.2. FPD calibration

VSC chemiluminescence in FPD is generally proportional to $[S]^n$, where S is the amount of sulphur reaching the detector and n ideally equals 2 [8]. Linearized plots of log (area) vs. log $[M]$ are used for quantitation. These plots have been determined for the VSC species of interest in the present study (Fig. 2). Log $[M]$ refers to the logarithm of absolute VSC amounts and ranges among 2.5–3 orders of magnitude.

As shown in Fig. 2, all the plots exhibit significant

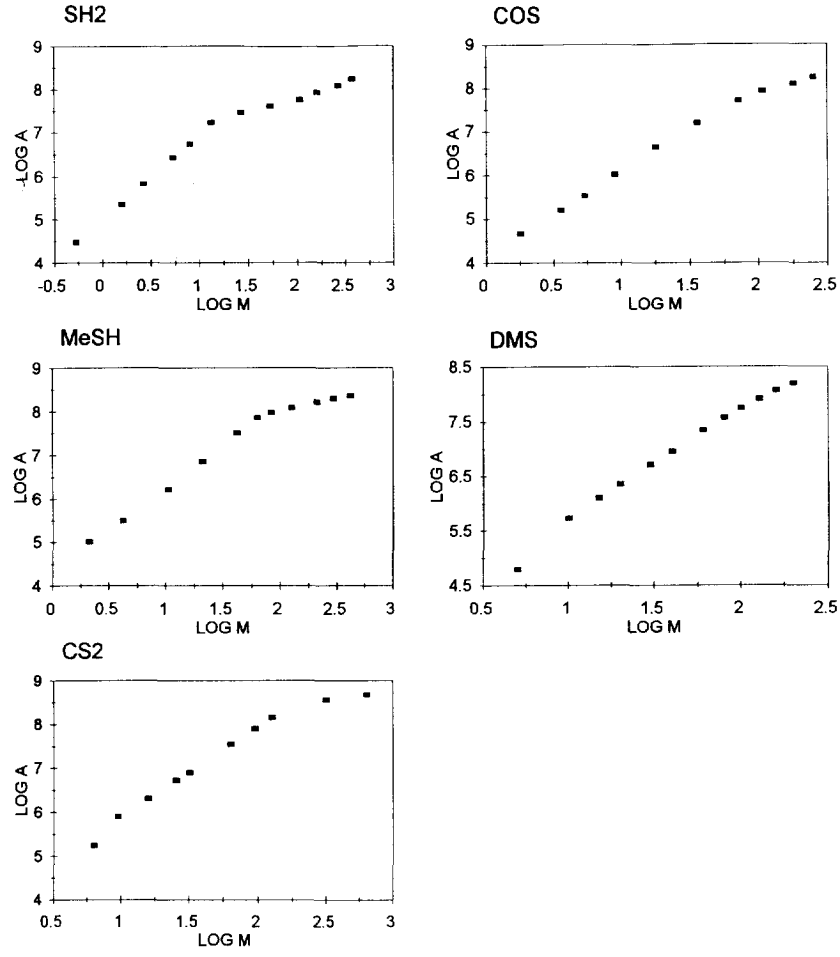

Fig. 2. Log (area) vs. log [M] plots showing the response of the FPD with increasing VSC amounts. Log (area) is in arbitrary units and log M refers to the logarithm of VSCs in nanograms.

slope changes at different concentration ranges. These changes may reflect diverse degrees of autoquenching when large amounts of sulphur species reach the flame. However, it is interesting to note that the log (area) vs. log [M] curves can be decomposed in series of linear sectors that can be used for quantitation.

The linear calibration lines that can be defined from Fig. 2 plots are summarized in Table 1. As it may be observed the linear regression coefficients are always higher than 0.9 (and higher than 0.99 in most cases). In all compounds, the consideration of VSC ranges over 2.5–3 orders of magnitude and involves the use of three equations for calibration.

One important aspect to be elucidated is the criterion for curve-fitting and eventual use of different calibration equations along the log (area) vs. log (amount) plots. In some cases, well-defined inflexion points can be recognized in the plots (Fig. 2) and obviously these discontinuities prompt for calibration line changes. However, in other plots the overall curve is smooth and an objective criterion is not so easy to establish. In this respect, the results the slopes of the successive calibration lines corresponding to each compound can be compared by means of the t-test (Table 2). In some cases, the slope differences between two successive calibration curves are very significant (level of 95% or even 99%) but in others the significance is low (<90%).

The evaluation of the relative error generated as

Table 1
Straight lines for the calibration of volatile reduced sulphur species in gas chromatography

Compound	Lines	y-Intercept	Slope	Coefficient	Range (ng)
SH_2	1	−2.5	0.50	0.9989	0.5–13
	2	−11	1.6	0.9895	13–110
	3	−6.9	1.2	0.9920	110–370
COS	1	−2.1	0.50	0.9982	1.8–36
	2	−3.0	0.63	0.9912	36–110
	3	−6.9	1.1	0.9916	110–250
$(CH_3)SH$	1	−2.5	0.57	0.9945	2.1–10.5
	2	−2.3	0.52	0.9903	11–130
	3	−13	1.9	0.9925	130–420
$(CH_3)_2S$	1	−0.81	0.32	0.9970	5.1–10
	2	−1.9	0.51	0.9992	10–160
	3	−2.8	0.62	0.9270	160–200
CS_2	1	−0.59	0.27	0.9882	6.4–9.6
	2	−1.9	0.49	0.9992	9.6–130
	3	−8.25	1.3	0.9766	130–640

consequence of one single linear calibration curve provide further insight into this question. As shown in Fig. 3, the sign of the relative error changes along the log (area) vs. log (amount) curves. These points of change are very clear and may be used as secondary tools for the elucidation of the amount ranges at which a different calibration line is required. The diagrams shown in Fig. 3 also illustrate the strong decrease in relative errors resulting from the use of three instead of one calibration equation.

4. Conclusions

Quantitation of large amounts of VSCs, in the order of hundreds of nanograms, the concentrations characteristic of heavily polluted waters, is possible even under conditions of saturation of the cryofocusing loop provided that only one sulphur species is present at these high concentrations, and that the FPD system is calibrated adequately. FPD calibration over 2.5–3 orders of magnitude requires the determination of three different linear equations corresponding to diverse mass ranges. The mass ranges under which these equations are operative can be determined from the inflexion points in the calibration plot, log (area) vs. log $[M]$. The changes in sign of the relative error resulting from re-calculation of the VSC mass after use of one single calibration curve for the whole mass range interval is also useful for this purpose.

Table 2
Degree of significance of the t-test evaluation of the slope differences between the successive calibration lines of each compound (Table 1 data)

Compound	Eqs. 1 and 2	Eqs. 2 and 3
SH_2	95%	90%
COS	–[a]	–
$(CH_3)SH$	–	90%
$(CH_3)_2S$	90%	–
CS_2	90%	99%

[a] Degree of significance of the slope difference lower than 90%.

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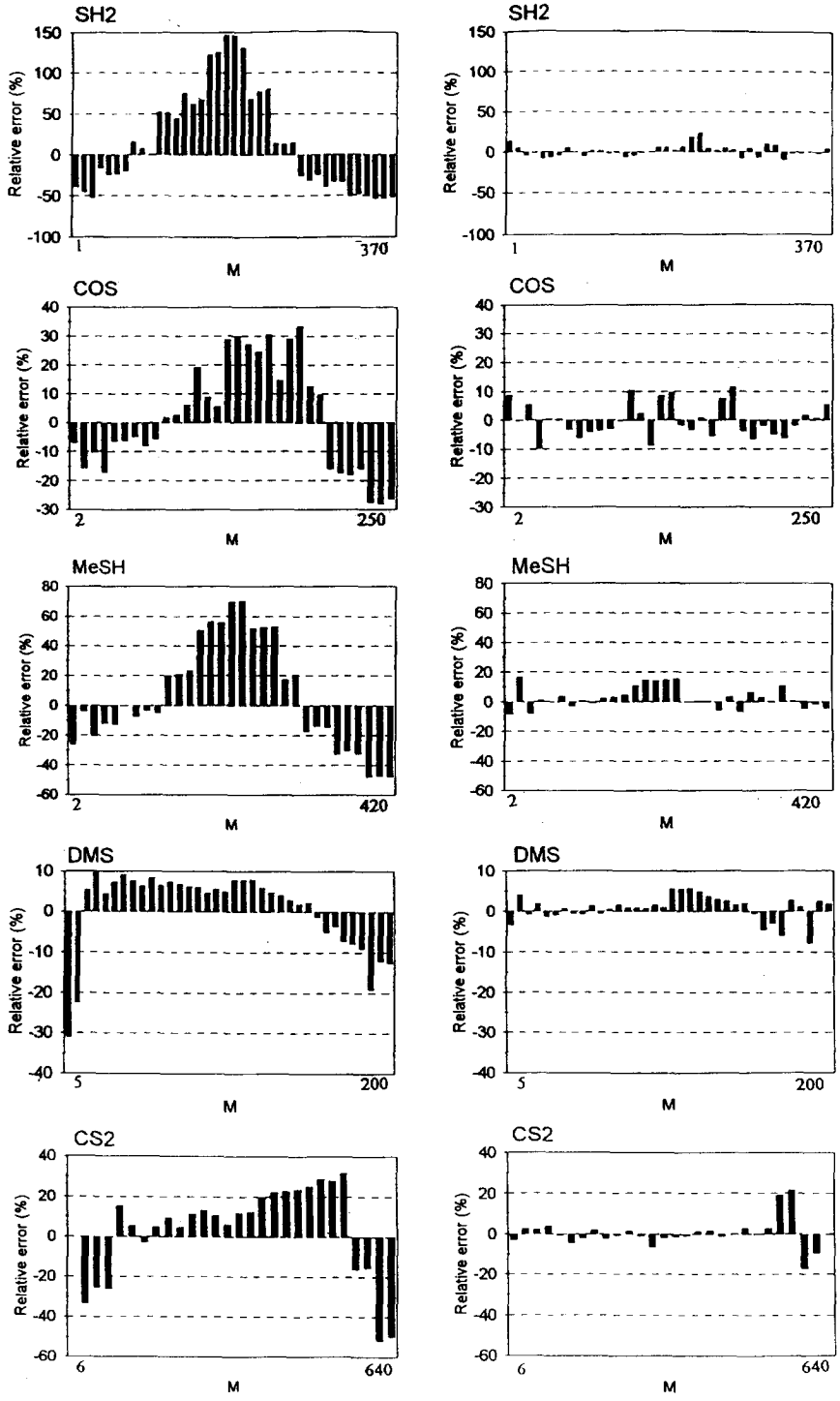

Fig. 3. Relative error—(calculated mass−real mass)/real mass—in the determination of VSC concentrations with (left column) one single calibration equation or (right column) the three calibration equations described in Table 2.

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