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Journal of Chromatography A, 830 (1999) 485–489

JOURNAL OF CHROMATOGRAPHY A

Short communication

Measurement of reduced sulphur compounds contained in aqueous matrices by direct injection into a gas chromatograph with a flame photometric detector

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Received 17 July 1998; received in revised form 20 October 1998; accepted 20 October 1998

Abstract

An analytical method was developed to measure the concentration of hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide contained in aqueous matrices (distilled water, tap water, kraft mill condensates and membrane bioreactor mixed liquor) by direct injection of aqueous samples into a gas chromatograph with a flame photometric detector. The analytical method requires a small sample volume (2 ml), sample preparation and analysis can be completed within 20 min and no complex sampling apparatus is needed. Consistent results and good recoveries were observed in all matrices investigated over the range of concentrations examined. The relationship between the normalized peak area obtained from GC–flame photometric detection and the concentration of the reduced sulphur compounds (RSCs) examined did not follow the theoretical power law exponent of two. The power law exponent appeared to decrease with the organic fraction associated with each RSC. The observed power law exponents for hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide were 1.92, 1.90, 1.66 and 1.72, respectively.

Keywords: Water analysis; Injection methods; Kraft pulp; Sulphur compounds; Dimethyl disulphide; Hydrogen sulphide; Methyl mercaptan; Dimethyl sulphide; Thioanisole

1. Introduction

A study was conducted to investigate the removal of reduced sulphur compounds (RSCs) from kraft pulp and paper mill condensates using a high-temperature membrane bioreactor (MBR). The performance of the MBR was monitored by measuring the batch biotic and abiotic removal rates for the RSCs (hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide) in the MBR. The rates were determined by withdrawing samples from the MBR and measuring the rate of change in the concentration of RSCs.

Gas chromatography with flame photometric detection (GC–FPD) is commonly used to measure the concentration of RSCs in aqueous samples [1–4]. However, the injection of aqueous samples directly into a GC–FPD system is not recommended because it can cause a number of problems. Primary, the injected water can extinguish the detector flame and non-volatile material contained in the aqueous sample can coat the GC injection port and column. To avoid these problems, most analytical methods

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0021-9673/99/$ – see front matter
PII: S0021-9673(98)00882-6

specify that the volatile compounds be separated from an aqueous sample before analysis by either purge and trap techniques or headspace gas sampling [2–7]. There are a number of disadvantages associated with purge and trap techniques when applied to the measurement of RSCs in aqueous matrices. First, a relatively complex and expensive purging and trapping apparatus is required [2–6]. In addition, gaseous sulphides strongly adsorb to glass, potentially leading to poor recoveries if the glassware used for purging and trapping the volatile RSCs is not properly cleaned and 'deactivated' [6]. Second, it is often difficult to ensure that 100% of a compound with low volatility has been entirely purged, again potentially leading to poor recoveries [4]. Third, it can take a number of hours to complete the purge-and-trap steps [4]. Some RSCs such as hydrogen sulphide and methyl mercaptan are relatively unstable [4,8]. Consequently, the characteristics of the sample can change during sample storage and analysis. Finally, a relatively large volume of sample, up to 100 ml, is required by purge-and-trap techniques [6]. This is of major disadvantage when many samples are to be withdrawn from a laboratory or bench-scale system within a short period of time, to assess the kinetics associated with the removal of RSCs. The main disadvantage associated with the injection of the head-space gas from a sample vial directly into a GC is that the relationships between the concentrations of volatile RSCs in the head-space and those of the aqueous sample (Henry's law) are highly influenced by the temperature of the sample [7,9]. Therefore, all samples must be analyzed at precisely the same temperature, requiring a constant temperature automatic sampler which can significantly add to the complexity and cost of the analytical apparatus. Also, equilibrium conditions must be assumed between the vapor phase and the aqueous phase for all compounds of interest.

An analytical method which consists of direct injection of an aqueous sample into a GC–FPD system was developed to address the inadequacies of the above techniques. The analytical method measures the concentration of hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide in aqueous matrices which consists of either distilled water, tap water, kraft pulp mill condensates or mixed liquor from an MBR.

2. Experimental

2.1. Sample preparation

The samples were prepared before analysis to remove particulate material. Approximately 2 ml of sample were collected with a 10-ml glass syringe and filtered through a 25-mm syringe filter holder (Gelman Sciences, Ann Arbor, MI, USA). Several filtering materials were investigated. Cellulose nitrate, cellulose acetate, nylon and paper filters all resulted in recoveries less than 75%. Glass microfibre filters (Whatman 934-AH; Whatman International, Maidstone, UK) resulted in satisfactory recoveries (see Section 3).

For the analysis, 0.5 ml of filtered sample was introduced into a 2-ml GC vial. A 10-μl aliquot of thioanisole (99% pure, Aldrich, Milwaukee, USA) solution, consisting of 25 μl thioanisole in 100 ml methanol (99% pure, Fisher Scientific, Fair Lawn, USA), was added to each GC vial to normalize the peak area for the RSCs (see Section 2.3). Thioanisole was selected because it was stable for an extended period of time and because the peak for thioanisole did not overlap with the peaks associated with the RSCs examined.

2.2. Gas chromatography

A gas chromatograph (HP5890-II with a HP3396 Series II Integrator; Hewlett-Packard, Avondale, USA) with a flame photometric detector (HP5890A Option 240; Hewlett-Packard) was used to measure the concentrations of RSCs. Although initially the detector flame was periodically extinguished by the injected water, an increase in the detector temperature to 250°C prevented the detector flame from being extinguished. Higher detector temperatures were not useful, because beyond 250°C, the baseline signal became highly variable.

A 1-μl volume of filtered sample was injected into the GC–FPD system with a split ratio of 10:1. The slow injection speed setting for the automatic sampler (HP 7673 GC/SFC Automatic Injector, Hewlett-Packard) was used. Split injection reduced the quantity of non-volatile material entering the column, reducing the chance of column blockage and/or ghost peaks. Perhaps most important, split in-

jection reduced the amount of water entering the column and, thereby, reduced the chances of extinguishing the detector flame. A wide bore capillary chromatography column (DBWAX 30 m×0.53 mm I.D., 1 μm film thickness; J&W Scientific, Folsom, CA, USA) was used. Helium (99.996% pure, Praxair, Mississauga, Canada; with Supelco 23800 Carrier Gas Purifier, Supelco, Bellefonte, USA) was used and the carrier gas flow-rate was 5.8 ml/min.

The oven temperature program used to separate the individual RSCs was 40°C for 5 min, followed by a temperature increase of 30°C/min to an intermediate temperature of 160°C, which was held for 3 min and finally a temperature increase of 40°C/min to 200°C. The hydrogen sulphide (1.16 min), methyl mercaptan (1.39 min) and dimethyl sulphide (1.66 min) peaks eluted at the initial temperature setting. The dimethyl disulphide (6.74 min) peak eluted during the transition to the intermediate temperature. The thioanisole (11.35 min) peak eluted at the intermediate temperature setting. The final temperature increase to 200°C was done to purge any remaining volatiles from the column.

The GC–FPD system was 'conditioned' before and after every sample series by increasing the temperatures of the injection port, the oven and the detector to 20°C above their maximum analytical temperature (i.e., 180°C for injector port, 220°C for oven and 270°C for detector) for approximately 2 h. Approximately 12–15 samples were analyzed per series. Since non-volatile material would remain in the sample following filtration, portions of such material could accumulate in the injection port and the column, potentially resulting in ghost peaks or plugging of the column. The injection port was cleaned approximately once per four to five sample series to remove accumulated non-volatile material by cleaning and deactivating the injector port glass insert as recommended by Caron and Cramer [6], cleaning the injector port with a cotton swab soaked in methanol and replacing the injector port O-ring and septum.

2.3. Calibration

A calibration curve was constructed using a standard mixture of RSCs prepared by injecting 200 μl of hydrogen sulphide (98.5% pure, Praxair) and 200 μl of methyl mercaptan (99.5% pure, Aldrich) gas, at room temperature and atmospheric pressure, into a 58-ml capped glass vial filled with distilled water. A 15-μl mixture of 30 μl of dimethyl sulphide (98% pure, Aldrich) and 30 μl of dimethyl disulphide (99% pure, Aldrich) in 2 ml of methanol was then injected into the 58 ml capped glass vial. All volumes were measured using a gas-tight syringe. The vial was then shaken for 30 min to allow the RSCs to fully dissolve. All glass vials were cleaned and deactivated prior too use as recommended by Caron and Kramer [6]. The resulting theoretical concentrations for hydrogen sulphide and methyl mercaptan, 4.87 and 6.88 mg/l, respectively, were below their respective solubility limits in water [10]. The resulting theoretical concentrations for dimethyl sulphide and dimethyl disulphide, 3.28 and 4.06 mg/l, respectively, were also below their solubility limits (a solubility test, in which dimethyl sulphide and dimethyl disulphide were injected into water, indicated that dimethyl sulphide and dimethyl disulphide were indeed soluble in water to concentrations in excess of 20 mg/l). The pH of the standard mixture was adjusted to approximately 3.5 with hydrochloric acid as required. The standard mixture was diluted 2, 5 and 10 times and analyzed to obtain data for the calibration curve. The resulting concentration of RSCs in the diluted samples corresponded to the range of interest for determining the removal rates for RSCs in an MBR.

To improve the accuracy and precision of the analytical method, thioanisole was added to each sample as previously described. The absolute peak areas for the RSCs were normalized against a common $\log_{10}$ peak area for thioanisole. The $\log_{10}$ peak area for thioanisole was calculated by averaging the $\log_{10}$ peak areas for thioanisole for all the samples analyzed in one series. The normalized peak area for each RSC was then calculated according to Eq. (1). Normalizing the peak areas before developing the calibration curve increased the coefficient of determination (r^2) and reduced the standard error of the estimate associated with the calibration curve, thus increasing the accuracy of the analytical method and also reduced the standard error associated with the slope of the $\log_{10}$–$\log_{10}$ calibration curve increasing the precision of the analytical method.

$$\text{Normalized peak area for RSC} = 10\exp\left\{\log_{10}(\text{Absolute peak area for RSC in sample}) \times \left(\frac{\log_{10}(\text{Absolute peak area for thioanisole in sample})}{\log_{10}(\text{Average absolute peak area for thioanisole in all samples analyzed})}\right)\right\} \quad (1)$$

3. Results and discussion

The chemiluminescence emitted in a flame photometric detector is theoretically proportional to the square of the amount of sulphur reaching the detector (i.e., linear relationship, with a slope of 2, between the $\log_{10}$ of the peak area obtained from GC–FPD and the $\log_{10}$ of the concentration of RSC injected) [11]. The calibration curves observed in the present study exhibited linear relationships between the $\log_{10}$ of the concentrations of each RSC injected and the $\log_{10}$ of their respective peak areas. However, the power law exponent (slope of $\log_{10}$–$\log_{10}$ calibration curve) for each RSC was less than 2. The deviation from the theoretical power law exponent of 2 is likely due to hydrocarbon quenching, which occurs when some of the light emitted by the sulphur species is adsorbed by the carbon dioxide present in the flame when organic sulphur compounds are injected into the GC–FPD system [12]. Power law exponents have been reported to vary from 1 (directly proportional to the concentration of sulphur species), to the theoretical exponent of 2 [1,2,12]. The power law exponent for the RSCs investigated in the present study appeared to decrease with an increase in the fraction of carbon associated with each RSC indicating that hydrocarbon quenching increased with the fraction of carbon associated with each RSC (Table 1). Self-quenching, which can occur when injecting high concentrations of sulphur compounds into a GC–FPD system, was not a problem over the range of concentrations investigated. Self-quenching results in a non-linear slope for the $\log_{10}$–$\log_{10}$ calibration curve [12].

The concentration of each RSC in a sample was calculated according to Eq. (2). The exponent P corresponds to the power law exponent for the individual RSCs examined.

$$\text{Concentration (mg/l)} = \left(\left(\frac{\text{Normalized peak area for sample}}{\text{Normalized peak area for standard}}\right) \times (\text{Concentration of standard (mg/l)})^{P}\right)^{(1/P)} \quad (2)$$

Good and consistent recoveries were observed for all RSCs, in all aqueous matrices examined and over the range of concentrations examined. The average recoveries for hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide, for samples collected from all matrices examined, were 105±15, 107±17, 101±12 and 97±9%, respectively ($n=16$; 90% confidence interval). The relationships between the concentration of RSCs and their respec-

Table 1
Calibration curve results

RSC	Range (mg/l)	Power law exponent[a] (–)	Confidence interval for the concentration measurements	
			($\log_{10}$ signal)[a,b]	(mg/l)[a,c]
Hydrogen sulphide	0.49–4.87	1.92±0.17	±0.26	±0.15–±1.52
Methyl mercaptan	0.69–6.88	1.90±0.16	±0.14	±0.12–±1.18
Dimethyl sulphide	0.33–3.28	1.66±0.15	±0.12	±0.02–±0.18
Dimethyl disulphide	0.41–4.06	1.72±0.20	±0.11	±0.06–±0.59

[a]The '±' corresponds to the 90% confidence interval from the five calibration curves using distilled water as solution matrix.
[b]Confidence interval (90%) for the concentration measurements expressed as $\log_{10}$ normalized peak area.
[c]Confidence interval (90%) for the concentration measurements expressed as mg/l, at the lower and upper range of concentrations examined.

tive normalized peak areas are not linear. Consequently, the 90% confidence interval for the concentration measurements of each RSC varies with the concentration of the RSC measured. The range of the 90% confidence interval for the concentration measurements of each RSC, over the range of concentrations investigated, is listed in Table 1. The precision of the concentration measurements for dimethyl sulphide and dimethyl disulphide is satisfactory. However, the precision of the concentration measurements for hydrogen sulphide and methyl mercaptan is significantly lower. The lower precision associated with the concentration measurements for these compounds is likely due to their highly volatile nature and the resulting effect on the sampling error. The precision can be improved by analyzing multiple samples.

Poor recoveries were initially observed for hydrogen sulphide, methyl mercaptan and dimethyl disulphide in tap water. The resulting recoveries for hydrogen sulphide and methyl mercaptan were less than 41 and 88%, respectively, and these decreased with the amount of RSCs injected. The recovery for dimethyl disulphide was greater than 160%. The low recovery for hydrogen sulphide was attributed to the reaction and precipitation of hydrogen sulphide with the copper contained in the tap water. The low recovery for methyl mercaptan and the high recovery for dimethyl disulphide was attributed to the oxidation of methyl mercaptan to dimethyl sulphide in tap water. Similar observations were reported by Saunders [4]. Good recoveries were observed when the tap water was purged with hydrogen sulphide and methyl mercaptan, to precipitate the copper and remove the oxidizing potential of the tap water, and then stripped of these gases prior to spiking with RSCs to determine the recoveries.

4. Conclusions

(1) Direct injection of aqueous samples into a CG–FPD system can be used to measure the concentration of RSCs in aqueous matrices. Consistent results and relatively good recoveries were observed for all aqueous matrices examined over the range of concentrations examined.

(2) The analytical method requires only a small sample volume (2 ml), sample preparation and analysis can be completed within 20 min and no complex sampling apparatus is required.

(3) Samples must be filtered with glass fiber filters to insure proper recoveries.

(4) The exponent in the power law relationship between normalized peak area and concentration is different for each RSC. The power law exponent appears to decrease with the organic fraction associated with each RSC. The power law exponent for hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide are 1.92, 1.90, 1.66 and 1.72, respectively.

(5) The combination of periodic cleaning of the injection port, split injection and the use of a wide-bore capillary chromatograph column prevented the detector flame from being extinguished and the occurrence of ghost peaks.

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