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Trace determination of sulphur mustard and related compounds in water by headspace-trap gas chromatography–mass spectrometry

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ABSTRACT

A method for trace determination of sulphur mustard (HD) and some of its cyclic decomposition compounds in water samples has been developed using headspace-trap in combination with gas chromatography–mass spectrometry (GC–MS). Factorial design was used for optimisation of the method. The trap technology allows enrichment and focusing of the analytes on an adsorbent, hence the technique offers better sensitivity compared to conventional static headspace. A detection limit of 1 ng/ml was achieved for HD, while the cyclic sulphur compounds 1,4-thioxane, 1,3-dithiolane and 1,4-dithiane could be detected at a level of 0.1 ng/ml. The method was validated for the stable cyclic compounds in the concentration range from the limit of quantification (LOQ: 0.2–0.4 ng/ml) to hundred times LOQ. The within and between assay precisions at hundred times LOQ were 1–2% and 7–8% relative standard deviation, respectively. This technique requires almost no sample handling, and the total time for sampling and analysis was less than 1 h. The method was successfully employed for muddy river water and sea water samples.

1. Introduction

One of the most employed chemical warfare agents (CWA) in history is the skin damaging agent bis(2-chloroethyl) sulphide (sulphur mustard, with military designation HD). HD was frequently used in World War I, and more recently in the Iran–Iraq war and during the campaign against the Iraqi Kurdish population in 1987–88 [1]. Today, one of the concerns related to HD is the large amount of sea dumped or abandoned weapons from World War II (WWII). In the Baltic Sea and along the coast of Japan, fishermen have snared mustard agents from old artillery with their nets, and been injured from contact with the agents [2]. In China, large amounts of abandoned CWA, including HD, were left behind during Japanese retreat in the closing stages of WWII. It has been estimated that abandoned CWA in China have caused two thousand casualties or fatalities since the end of the war [3]. After the Chemical Weapons Convention (CWC) entered into force in 1997, the production, storage and use of CWA have been prohibited [4]. In light of the CWC and the environmental concerns of abandoned CWA, the need of sensitive analytical methods for determination of HD and related compounds has increased.

HD has low aquatic solubility (1 g/l) and freezes at 14 °C [5]. The hydrolysis of HD in larger lumps is slowed down or completely prevented by formation of oligomeric and polymeric layers of the degradation products [6]. Hence, HD in sea dumped munitions can stay intact at the sea bed for a long time after the artillery shell is corroded. When dissolved in water, HD hydrolyses to a set of sulphides, disulphides, sulphoxides, sulphones, and thiols [7]. In addition, munition grade HD often contains impurities that survive in the environment longer than the agent itself. Thus, determination of several common degradation products and impurities in aqueous samples may act as a reliable proof of the original existence of HD. This study includes determination of HD, two of the most common degradation products 1,4-thioxane and 1,4-dithiane [7–9], and 1,3-dithiolane. The latter has been found in water and soil samples near an old destruction site of HD [10,11].

Gas chromatography–mass spectrometry (GC–MS) has been extensively used for the identification of HD and related compounds in environmental samples [12–15]. For determination of CWA in aqueous samples, a recommended protocol from sample treatment to final instrumental analysis is available [16]. Liquid–liquid extraction (LLE) or solid phase extraction (SPE) is recommended as sample preparation techniques. It has been shown that HD could be determined in aqueous samples with the LLE procedure [11], and with the SPE procedure [17] followed by

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GC–MS analysis. For the determination of non-volatile degradation products of HD, a derivatisation step must be included prior to the GC–MS analysis [18,19]. Recently, several microextraction techniques have been applied for HD determination in water, like the single drop microextraction (SDME) [20] and hollow fibre-mediated liquid-phase microextraction (HF-LPME) [21,22] followed by GC–MS analysis. The solid phase microextraction (SPME) technique, combined with GC and flame ionisation detection (FID) has also been used [23]. For the water-soluble non-volatile degradation products, liquid chromatography (LC) and MS with atmospheric pressure chemical ionisation (APCI) [24,25] or electrospray ionisation (ESI) [26] has gained increasing utility. Microcolumn LC with MS or flame photometric detection (FPD) with large volume injection and peak compression has also been applied for the water-soluble degradation products [27,28].

The headspace (HS) extraction and sample introduction technique has not been used extensively for determination of HD and related compounds. However, Wils et al. have employed dynamic HS followed by GC–MS to determine the hydrolysis product bis(2-hydroxyethyl) sulphide (TDG) in water and urine, where TDG was converted to HD prior to the determination [29,30]. In addition, HS has been used in combination with SPME for determination of HD and related compounds in soil, where water was added to the soil to form a slurry prior to analysis [10,31]. In the present study, the headspace-trap (HS-trap) technique in combination with GC–MS is applied for the first time for determination of CWA. The HS-trap technique patented by Tippler and Mazza [32] is an enhanced static headspace system which was commercialised in 2004. The technique has shown a great potential for determination of various volatile organic compounds in water [33–35].

2. Experimental

2.1. Chemicals

HD (98.5%) was purchased from Netherlands Organisation for Applied Scientific Research (TNO, Delft, The Netherlands). 1,4-Thioxane (98%) and 1,3-dithiolane (97%) were obtained from Sigma–Aldrich Inc., MO, USA, while 1,4-dithiane was obtained from Sigma–Aldrich, U.K. 1,2,4-Trimethylbenzene (1,2,4-TMB) (98%) was purchased from Acros Organics, NJ, USA. Ultra resi-analysed acetone (≥99.4%) was obtained from J.T. Baker, Deventer, The Netherlands. Analytical grade sodium chloride (≥99.5%) was purchased from Merck, Darmstadt, Germany. Laboratory type II water (classified according to the American Society of Testing and Materials, D1193-91) was delivered in-house by RIOS 30 Laboratory-Grade Water Systems from Millipore, France.

2.2. Preparation of solutions

Stock solutions of HD were prepared by diluting 1 μl of the neat agent in various amounts of acetone, to concentrations of 0.1–0.3 mg/ml. Further dilutions were made in acetone, while the final working solutions of 0.5–400 ng/ml were made in type II water. Due to the instability of HD in water, the final solutions were prepared directly in the HS-vials 1–2 min prior to analysis. 1,4-Thioxane, 1,3-dithiolane and 1,4-dithiane were prepared in joint stock solutions, by diluting 50–100 mg of the neat agents in acetone, resulting in concentrations of 1–2 mg/ml. Further dilutions were made in acetone, while the final working solutions were made in type II water at concentrations from 0.05 to 50 ng/ml. The validation solutions were made in the same way. 1,2,4-TMB was used as internal standard (IS), and a stock solution was prepared by diluting 200 mg in 100 ml acetone. This solution was further diluted in type II water to a final concentration of 4 ng/ml. All stock and intermediate solutions were stored at 4 °C.

2.3. Natural water samples

Three types of natural water samples were collected: (1) water from a rain pool, sampled approximately 1 h after raining had stopped. (2) River water with a relatively high content of mud; total residue on evaporation was $(2.7 \pm 0.3) \times 10^2$ mg/l ($n = 3$). (3) Seawater from Oslo harbour, collected 10-20 cm below the surface to avoid contamination from the water surface. All samples were kept in borosilicate glass 3.3 (Duran) bottles with screw caps having Teflon gaskets (Schott, Mainz, Germany), and stored at 4 °C. Two 100 ml aliquots of the samples were spiked with a solution of the cyclic sulphur compounds to concentrations of 0.7–1.2 ng/ml and 7.2–11 ng/ml, respectively. No sample cleanup or other sample preparation was performed. Three 2.00 ml replicates were transferred from each solution to HS-vials, and added 0.80 g NaCl. Finally, 20 μl of an IS solution was added. Headspace analyses were performed within 24 h after sample preparation.

Recoveries of the spiked cyclic sulphur compounds in the natural water samples were calculated from calibration curves, established for each compound. Calibration solutions of the compounds were prepared in Type II water, the same way as described for the working solutions in Section 2.2. Five concentration levels were prepared from 0.40 to 21 ng/ml for 1,4-thioxane, 0.23–12 ng/ml for 1,3-dithiolane and 0.35–18 ng/ml for 1,4-dithiane. The IS was added to each solution to a final concentration of 4 ng/ml.

2.4. Instrumentation

The HS-trap system works as a conventional static HS analyser in the first step, by heating the vial until the analytes approaches equilibrium between the sample matrix and the vapour phase (thermostatting). Thereafter, the vial is pressurised, and the pressure is released by leading the vapour phase through an adsorbent tube where the analytes are focused (trap load), as shown in Fig. 1. The water is then removed by purging helium through the adsorbent (dry purge). Finally, the trap is rapidly heated and backflushed (trap desorption), and the analytes are desorbed and

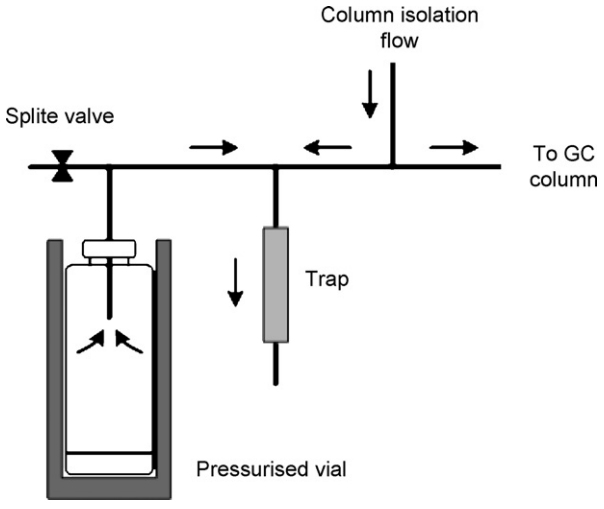

Fig. 1. Working principle of the HS-trap system, in trap load mode. The analytes in vapour phase are transferred from the pressurised vial and focused on the adsorbent. A column isolation flow prevents the sample from being introduced onto the column until the trap is heated and backflushed.

led into the chromatographic system. This way, a much larger fraction of the vapour phase is utilised compared to conventional static headspace, improving the sensitivity of the analysis considerably. Furthermore, the pressurising and trap load steps can be repeated to utilise an even larger fraction of the vapour phase.

The instrument used was the TurboMatrix HS 110 Trap connected to a Clarus 500 GC–MS with quadropole, both from PerkinElmer instruments, CT, USA. The HS-trap system was controlled by an internal graphical user interface, while the GC and MS were controlled by the Turbomass software, version 5.1.0. The adsorbent tube was a Tenax trap with a bed size of 2.7 × 25 mm, delivered by PerkinElmer. The GC column was a DB-5MS, 30 m × 0.25 mm ID and 0.25 μm film thickness, from J&W Scientific (Folson, CA, USA). The column was coupled directly to the HS through a heated transfer line, with a constant helium inlet pressure of 15 psi. This gave a flow rate of 1 ml/min at 100 °C. The transfer line temperature was set to 150 °C, in order to avoid sample condensation on possible cold spots at the connection between the transfer line and the HS sampler (recommended by the manufacturer). The GC temperature program was: 40 °C (1 min), then 10 °C/min to 140 °C (0 min) and 20 °C/min to 300 °C (1 min). The MS was operated in electron ionisation (EI) mode with ionisation energy of 70 eV. Mass spectra were collected over the *m/z* range 35–300 with a scan time of 0.2 s, and an inter-scan delay of 0.05 s.

Headspace vials (22 ml), together with septa of polytetrafluoroethylene (PTFE)/silicone were delivered by PerkinElmer. Preliminary experiments had shown poor repeatability for water analyses when the HS-vials were used several times. All method development and validation analyses were therefore performed with new HS-vials.

2.5. Experimental design

Factorial design experiments and a basic simplex optimisation procedure were employed in the method development and method validation. Statistical data from the factorial design experiments were treated in Minitab®, version 15.1.1.0.

3. Results and discussion

Because of the low stability of HD in water, separate methods were developed for determination of the cyclic sulphur compounds and for determination of HD. The optimised instrument parameter values for determination of the analytes in water are listed in Table 1.

3.1. Effect of salt saturation

Addition of salt to the water samples (salting out) is a widely employed technique in HS analysis to facilitate the extraction of analytes into the vapour phase [36,37]. Saturation of the sample is important to maximise the effect of the salt and also to avoid variations in salt concentrations from sample to sample, which may affect the repeatability of the analyses [38]. Fig. 2 shows the measured peak area of each analyte from samples where no salt was added, and samples saturated with NaCl.

With salt saturated samples, the recoveries increased three to four times for the cyclic sulphur compounds, and approximately forty times for HD. The half-life of HD in water is prolonged with increasing salt content [39]. Thus, the main reason for the large effect on recovery of HD was probably a considerable decrease in degradation during thermostatting. Due to the significant positive effect on the analytes, all samples were saturated with NaCl prior to analysis.

Table 1
Instrument parameter values for determination of the analytes in water. The values for determination of HD are given in parenthesis where the methods diverge.

	Parameter values
Trap parameters	
Trap low temperature	50 °C
Trap high temperature	280 °C
Dry purge time	7 min (HD: 5 min)
Desorption time	0.5 min
Trap hold time	3 min
Desorption pressure	30 psi
Needle purge split flow	13 ml/min
HS parameters	
Thermostatting temperature	80 °C
Needle temperature	90 °C
Transfer line temperaure	150 °C
Thermostatting time	15 min (HD: 2.5 min)
Pressurisation time	1.0 min
Decay (trap load) time	2.0 min
Number of cycles	2 (HD: 1 cycle)
Vial pressure	40 psi
Column pressure	15 psi
Shaker (on/off)	On

3.2. Trap settings

The trap adsorbent material (Tenax) is a porous polymer resin based on 2,6-diphenyl oxide. The adsorbent is widely used for trapping volatiles and semi-volatiles from air, and in purge and trap devices. Tenax has low water affinity, which makes it especially useful for purging and trapping of organic volatiles from water. The highest recommendable working temperature for the Tenax material is 280 °C. To avoid carry-over between samples, the analytes must be completely desorbed during trap desorption. Possible carry-over was checked with analyses performed at a trap high temperature of 280 °C, and desorption time of 3 min. No carry-over of analytes was observed when blank water samples were analysed subsequently to water samples containing the compounds.

The trap parameters should be set to give optimum sample transfer into the GC column, and to ensure an efficient removal of water from the trap. By closing the needle purge split flow during trap desorption, the sample transfer efficiency can be maximised. However, as this gives larger background signal and broader chromatographic peaks, it is not recommended by the manufacturer. Instead, the introduced sample amount is optimised by adjusting the desorption pressure and desorption time. A higher desorption pressure increases the amount of analyte introduced on the column, and thereby enhances the MS signal intensity. However, since the

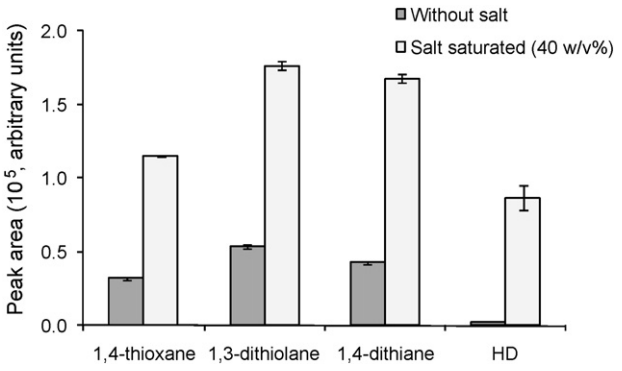

Fig. 2. Effect of salt saturation on extraction efficiency, shown as average peak areas ± one standard deviation ($n = 3$). Sample volume was 2.00 ml, and the concentrations were 0.04 μg/ml for 1,4-thioxane, 0.02 μg/ml for 1,3-dithiolane and 1,4-dithiane, and 0.4 μg/ml for HD. The HS-vials were thermostatted for 20 min at 60 °C.

Table 2
Two-level factorial design experiment for the thermostatting time, sample volume and thermostatting temperature. Concentrations were between 22 and 47 ng/ml for the cyclic sulphur compounds and 230 ng/ml for HD.

Thermostatting time (min)	Sample volume (ml)	Thermostatting temperature (°C)	Peak area (10^5)			
			1,4-Thioxane	1,3-Dithiolane	1,4-Dithiane	HD
15	2	50	0.90	1.46	1.34	1.82
30	2	50	0.87	1.42	1.33	0.70
15	10	50	0.43	0.71	0.67	0.91
30	10	50	0.39	0.65	0.59	0.20
15	2	80	3.12	3.93	3.89	nd[a]
30	2	80	3.10	3.99	3.98	0.07
15	10	80	1.49	2.12	2.07	nd
30	10	80	1.52	2.22	2.18	nd
22.5	6	65	0.87	1.43	1.25	nd
22.5	6	65	0.79	1.27	1.10	nd
22.5	6	65	1.01	1.60	1.53	nd
		SD (n = 3)	0.11	0.17	0.22	–

[a] Not detected.

desorption pressure also is activated during the dry purge step, a higher pressure affects the water removal in a negative manner. A desorption pressure of 30 psi was found to be a good compromise between these factors. The desorption time was set to 0.5 min, which was well above the observed critical low time of 0.3 min, needed to ensure a complete sample transfer into the GC column. The amount of water loaded on the trap was highly dependant on the HS thermostatting temperature and number of vial extractions. With the obtained HS conditions described in Table 1, a trap low temperature of 50 °C, and a dry purge time of 7 min (HD: 5 min) was necessary to achieve an acceptable water removal. It was assured that no loss of analytes occurred during the dry purge step at the present settings by comparing the extraction yields with those performed at a lower trap temperature (40 °C) and shorter dry purge time (4 min). No significant difference in peak areas was observed, and the relative standard deviations (RSDs) were below 2% at both settings (t-test at $\alpha = 0.05$, $n = 4$).

3.3. Headspace conditions

3.3.1. Sample agitation

Shaking of the sample helps to shorten the time needed to establish equilibrium between the sample and the vapour phase. It has been shown that sample agitation also improves precision when analysing soil/water slurry samples [40]. In the present study, shaking was activated in all experiments.

3.3.2. Temperature, time and sample volume

Among the parameters of most importance to the sensitivity in HS analysis are the thermostatting temperature, thermostatting time and sample volume. A two-level factorial design experiment was performed for the three parameters, and the parameter values and peak areas of each analyte are shown in Table 2. Three analyses were performed with intermediate values for the parameters to establish SD of the analyses, shown in the table.

The highest yield of the cyclic sulphur compounds were achieved at 80 °C thermostatting temperature, and with a sample volume of 2 ml. An increase in the thermostatting time from 15 to 30 min did not affect the peak areas, which indicated that equilibrium was achieved already after 15 min. For HD on the other hand, only one of the analyses performed at 80 °C gave detectable response. Considerably higher peak areas were achieved at 50 °C. The recoveries decreased at longer thermostatting time, probably due to degradation of HD during thermostatting. Because of the different behaviour of HD relative to the cyclic sulphur compounds, further optimisation of the conditions for HD determination was performed separately.

For the cyclic compounds, an increase in temperature from 80 to 90 °C resulted in larger variations, and only a slight increase in peak areas. The larger variations may be due to oxidation of the analytes at the higher temperature. Opstad and Tørnes showed that 1,4-dithiane was oxidised to the respective sulphoxide and sulphone after long time storage in seawater at 25 °C [41]. Even though Table 2 shows that a sample volume of 2 ml was preferable compared to 10 ml, the optimal sample volume may be between these values. However, an increase in sample volume from 2 to 4 ml resulted in lower extraction yield of all compounds (results not shown).

For determination of HD, a simplex optimisation procedure [42] was performed for the further investigation of the thermostatting time and temperature. The sample volume was kept at 2 ml. The starting simplex consisted of experiments at 40 °C/15 min, 50 °C/15 min and 50 °C/10 min. From this, the response increased continuously at decreasing thermostatting time and increasing temperature. The maximum extraction yield was achieved with a thermostatting time of 2.5 min and a temperature of 80 °C. This very short thermostatting time is presumably a compromise between the transfer rate into the vapour phase, and the rapid degradation of HD at 80 °C. Thus, the analyte is most probably not in equilibrium between the water and the vapour phase, as is the intention with the static HS extraction technique. The low stability of HD in water and at elevated temperature makes it not feasible, however, to achieve stable conditions with the present extraction technique in any way.

3.3.3. Repeated vial extractions

The pressurisation and trap load steps can be repeated up to four times, in order to achieve a more complete vapour extraction from the vial. Peak areas of the cyclic compounds from analyses with use of one, two and three successive vial extractions are shown in Fig. 3. A significant increase in peak area (between 60 and 75%) was observed with use of two vial extractions. A further increase (between 10 and 30%) was achieved with a third extraction. The SD also increased with use of repeated extractions, probably because the system was no longer in equilibrium. Further transfer of the analytes into the headspace should be expected during subsequent vial extractions, and the elapsed time between each trap load step was probably not sufficient to reach equilibrium between the sample and the vapour phase. Since the aim of the investigation was to develop a method for trace determination of the cyclic sulphur compounds, the sensitivity of the analysis was of higher importance than obtaining the best accuracy and precision. However, each successive extraction led to a prolonged analysis time, and introduced more water vapour onto the trap. Hence, a procedure with two vial extractions was preferred.

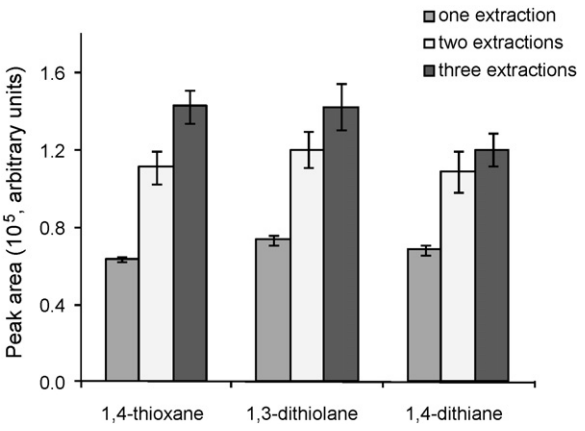

Fig. 3. Effect of successive vial extractions on signal intensities of the cyclic sulphur compounds, shown as average peak areas ± one SD ($n = 4$). Sample volume was 2.00 ml, and the concentrations were 8 ng/ml for 1,4-thioxane and 4 ng/ml for 1,3-dithiolane and 1,4-dithiane. The HS-vials were thermostatted for 15 min at 80 °C.

Determinations of HD with two vial extractions gave 30% higher recovery in average compared to one extraction, but large variations in peak area appeared. The variations could be due to further degradation of HD on the adsorbent during the second trap load step. Because of the large variations in peak area with two extractions, a procedure with one sample extraction was preferred.

3.3.4. *Vial pressure and decay time*

A higher vial pressure should improve the analyte transfer onto the trap, but also increases the risk of leakage between the septum and the vial, or in the septum puncture at the needle. An increase in the vial pressure from 30 to 45 psi gave 20 ± 3% ($n = 3$) higher peak areas of the cyclic compounds. Due to the limited effect of a higher pressure, and to prevent leakage, a vial pressure of 40 psi was chosen in the method. The decay time (trap load) must be long enough to just allow the vial pressure to be decreased to atmospheric pressure. The decay time is dependent on the vial pressure and sample volume, and was set to 2.0 min after calibration with a blank sample.

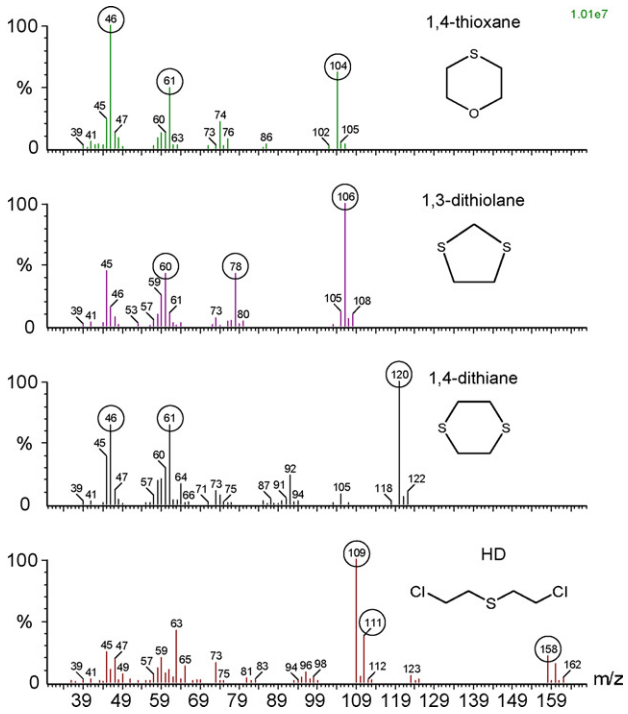

Fig. 4. Mass spectra and structures of the analytes, where the *m/z* ratios used for determination of LODs are indicated with circles. The mass spectra were obtained at analysis conditions as described in Table 1. Sample volume was 2.00 ml, and the concentrations were 21 ng/ml for 1,4-thioxane, 12 ng/ml for 1,3-dithiolane, 18 ng/ml for 1,4-dithiane and 42 ng/ml for HD.

3.4. *Method validation*

Method validation was performed for trace determination of the cyclic sulphur compounds in water. Because of the low stability of HD in water, quantitative measurements of high precision were of limited value, and only the detection limit (LOD) was investigated. The LODs were established from reconstructed ion chromatograms (RICs), extracted from the total ion current (TIC) chromatograms. The RICs were plotted as the sum of signals of three characteristic ions for each compound, shown in the mass spectra in Fig. 4.

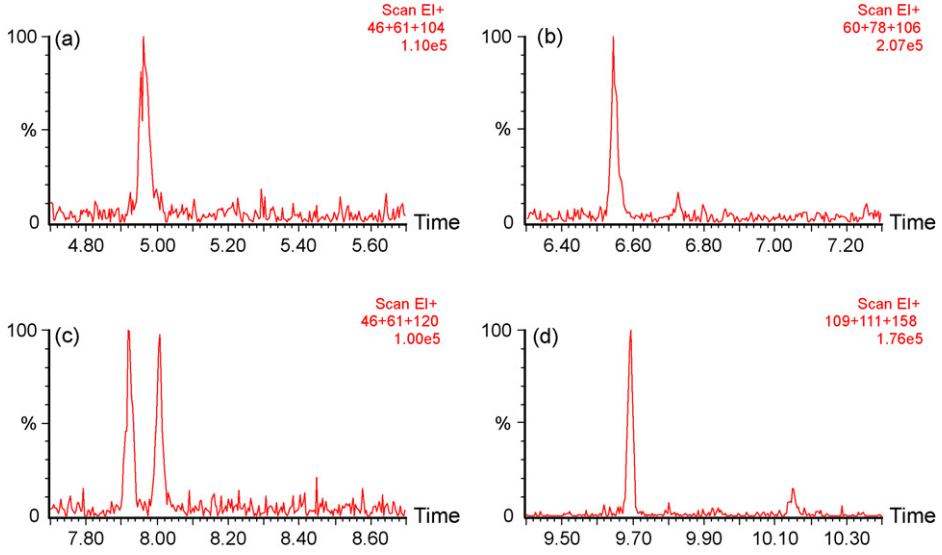

Fig. 5. RICs at the approximate LOD level of each compound, plotted as the sum of signals of three selected ions. (a) 1,4-thioxane, 0.15 ng/ml; (b) 1,3-dithiolane, 0.12 ng/ml; (c) 1,4-dithiane (the peak at 8.00 min), 0.10 ng/ml; (d) HD, 1.0 ng/ml. The S/N ratio of HD is higher than ten, since the molecular ion disappeared in the mass spectrum at lower concentrations.

Table 3
Data from method validation for determination of the cyclic sulphur compounds in water.

	1,4-Thioxane	1,3-Dithiolane	1,4-Dithiane
LOD (ng/ml)	0.14	0.08	0.12
LOQ (ng/ml)	0.42	0.24	0.36
Linearity (R^2) LOQ – 100·LOQ	0.997	0.998	0.998
Repeatability (RSD) (n = 6)			
LOQ			
Within assay	4.1	8.2	15
Between assay	7.0	7.4	15
100·LOQ			
Within assay	1.6	1.5	2.4
Between assay	7.4	7.1	7.9

The LODs were calculated as the concentrations giving a signal to noise (S/N) ratio of ten. In addition, a requirement was that all three ions should be visible in the mass spectrum at these concentrations. Fig. 5 shows the RICs at the approximate LOD level of each compound.

The LOD of HD was determined to 1.0 ng/ml, and was limited by the signal of the molecular *m/z* 158 ion, which disappeared in the mass spectrum at lower concentrations. An LOD as low as 1 ng/ml is comparable to what is achieved by the HF-LPME technique [21,22] (0.1–1 ng/ml) and SPME technique [23] (1.7 ng/ml). The HF-LPME technique is, however, not commercially available. Reported LODs of HD with the recommended LLE procedure followed by GC–FID [11], and SPE followed by GC–MS [17], are both 50 ng/ml.

The obtained LODs of the cyclic sulphur compounds are listed in Table 3. Few reports can be found on determination of the cyclic compounds in water, but the lowest LOD reported is 51 ng/ml for 1,4-dithiane [43]. The quantification limits (LOQs) were calculated as three times the detection limits. The linearity and repeatability of the method were investigated within the concentration range from LOQ to hundred times LOQ. The IS was added to the samples at a concentration of 4 ng/ml. Very good linearity was proven within the investigated range ($R^2 \geq 0.997$). RSDs of less than 10% were achieved, except for 1,4-dithiane which had 15% RSD at the LOQ level. Repeatability of <10% RSD should be regarded as fully acceptable, especially taken into consideration that a high sensitivity was preferred instead of the precision in method optimisation. Fig. 3 clearly shows that a higher precision could be achieved with use of one vial extraction instead of two.

Robustness of the method for determination of the cyclic sulphur compounds was investigated for three of the most important

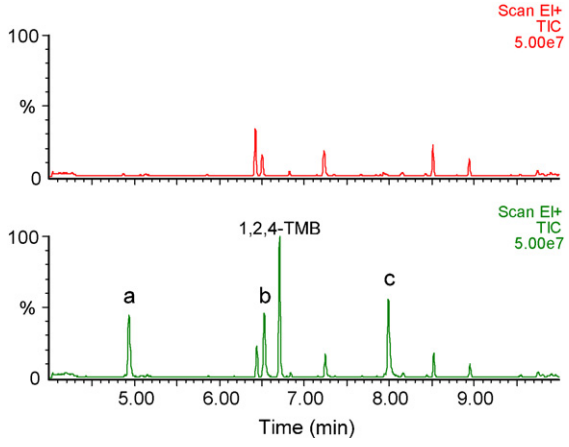

Fig. 6. TIC chromatogram of a rain water sample (lower chromatogram), spiked with (a) 1,4-thioxane, (b) 1,3-dithiolane and (c) 1,4-dithiane, at concentrations of 12, 7.2 and 11 ng/ml, respectively. 1,2,4-TMB was added as IS at 4 ng/ml. Analysis of a blank rain water sample is shown in the upper chromatogram.

Table 4
Recovery test of natural water samples. The samples were spiked with the cyclic sulphur compounds at concentrations of approximately three and thirty times the LOQ levels. Analysis conditions were as described in Table 1.

Compound	Spiking level (ng/ml)	% Recovery ± SD (n = 3)		
		Rain water	River water	Sea water
1,4-Thioxane	1.2	100 ± 2	90 ± 4	98 ± 2
	12	91 ± 3	89 ± 2	95 ± 2
1,3-Dithiolane	0.72	102 ± 5	93 ± 3	98 ± 5
	7.2	92 ± 2	89 ± 2	95 ± 1
1,4-Dithiane	1.1	104 ± 1	97 ± 4	101 ± 4
	11	90 ± 2	89 ± 3	96 ± 3

parameters, at concentrations of fifty times LOQ. A two-level full factorial design experiment was performed for the sample volume (±0.05 ml), thermostatting temperature (±2 °C) and vial pressure (±2 psi). No significant effect was observed from variations in sample volume and vial pressure with a confidence limit of 95%. Variations in the thermostatting temperature were just at the significance level, however, and hence the temperature should be kept well within ±2 °C.

3.5. Analyses of spiked natural water samples

The developed method for trace determination of the cyclic sulphur compounds was employed for analysis of three different types of natural water samples. Water from a rain pool, as well as muddy river water and sea water were investigated. The samples were spiked with the three cyclic sulphur compounds at concentrations of both three and thirty times the LOQs. Fig. 6 shows TIC chromatograms of a rain water sample spiked with the analytes at thirty times LOQ and a blank rain water sample. The peak present in the blank water sample at 6.5 min is coeluting with 1,3-dithiolane in the spiked sample. However, as the contaminant contains none of the selected ions characteristic for 1,3-dithiolane, it is not interfering with the detection and quantification of the compound.

Recoveries of the compounds are shown in Table 4. High recoveries were achieved, varying from 89 to 104%, even for concentrations at the ppb level. Thus, the method proved to be well suited for different types of water samples. As no filtration is included, the method is not vulnerable to a high particulate concentration, like that of the river water sample. Moreover, no concentration step which usually causes some loss of analytes is included in the method. In fact, the simplicity of the method allows direct field sampling into the HS-vials if these are added NaCl in advance.

4. Conclusions

Methods for trace determination of HD and related compounds in water by HS-trap GC-MS have been developed. The optimal conditions for HD determination differed considerably from those for the cyclic sulphur compounds, due to the low stability of HD in aqueous environment and at elevated temperatures. Therefore, separate methods were developed for determination of HD and for the cyclic compounds. By saturating the water samples with salt, the recovery of all analytes was considerably improved, with the greatest improvement achieved for HD. With application of the newly commercially available HS-trap system and utilisation of the matrix modification technique, HD could be determined at a concentration as low as 1.0 ng/ml. This is substantially better than what has been obtained by the recommended SPE or LLE procedures, followed by GC–MS or GC–FID. The present analysis technique showed to be even more sensitive for 1,4-thioxane, 1,3-dithiolane and 1,4-dithiane, with obtained LODs of approximately 0.1 ng/ml. Validation of the method for determination of the cyclic sulphur

compounds showed good linearity and repeatability within the investigated range from LOQ to hundred times LOQ. The technique proved to be very simple in use, as the only sample preparation needed was the addition of salt to saturate the water solutions. Thus, the total analysis time including sample handling was less than 1 h. This is a great improvement compared to the recommended SPE or LLE procedures followed by GC–MS analysis, which are both labour demanding and requires sample handling times of typically 4–5 h.

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