Short communication

Method development for trace analysis of heteroaromatic compounds in contaminated groundwater

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Abstract

An analytical method providing high sensitivity (limit of quantitation of 50 ng/l) with acceptable reproducibility (mean R.S.D. 19%) has been developed for determining heteroaromatic compounds in creosote-contaminated groundwater. The best technique (highest recovery and reproducibility) found between liquid–liquid extraction using either dichloromethane, diethyl ether or pentane and solid-phase extraction with reversed-phase bonded columns, was the classical liquid extraction with dichloromethane from weak basic solutions and GC–MS (selective ion monitoring) analysis of concentrated extracts.

Keywords: Water analysis; Environmental analysis; Extraction methods; Aromatic compounds; Heteroaromatic compounds; Creosote; Dichloromethane; Diethyl ether; Pentane

1. Introduction

Heteroaromatic compounds have their anthropogenic origin in creosote, oil, chemicals and pharmaceuticals [1,2]. Some occur naturally in plants, like the tryptophan-derived alkaloids [3]. Creosote is a very complex mixture that, apart from heteroaromatic compounds, mainly contains polyaromatic hydrocarbons (PAHs), phenols and monoaromatics (BTEX). The content of heteroaromatic compounds, comprising nitrogen, sulphur or oxygen in the cyclic π system (NSO compounds), ranges from 5 to 13% in creosote [1,4–7]. When the

subsurface is contaminated with creosote, the groundwater will be contaminated primarily with polar and mobile compounds, such as phenols, NSO, BTEX and some more water-soluble PAHs like naphthalene [8]. High concentrations (μg/l to several mg/l) of NSO compounds such as benzothiophene, dibenzothiophene, benzofuran, dibenzofuran, pyridines, quinolines, indole and carbazole, together with some oxygenated metabolites of quinoline and acridine, were found in creosote-contaminated groundwater at a wood-preserving facility in Pensacola, FL, USA and at a gasworks site in Seattle, WA, USA [9–13]. In biodegradation studies of creosote-contaminated groundwater, several oxygenated metabolites of N- and S-compounds have also been detected [14–16]. Therefore, potential metabolites are also of interest when considering ground-

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water pollutions. Typically, PAHs, BTEX and phenols are measured at creosote-contaminated sites, whereas analyses for NSO compounds are rarely done. Due to their high water solubilities (low K_{ow}, Table 1), toxicities [17,18] and adverse organoleptic characteristics, NSO compounds should be included in groundwater monitoring.

The aim of this study has been to develop a simple and very sensitive method for determining volatile and semi-volatile heteroaromatic compounds in groundwater. A detection limit of the order of ng/l was aimed at, because the acceptance criteria for toxic organic compounds in groundwater used for drinking water typically are 0.1–10 μg/l in Denmark. The classical sample preparation method for analysis of organic compounds in creosote-contaminated water is liquid–liquid extraction (LLE) using

dichloromethane (DCM) at varying pH [19–21]. It is a time-consuming method with use of large amounts of toxic solvent and with a high risk of contamination and sample loss. Alternative sample preparation methods, such as LLE with diethyl ether (DEE) and pentane commonly used for polar and non-polar compounds [19] and solid-phase extraction (SPE), are simpler to use and require minimal use of organic solvents [22,23]. Due to the complex nature of creosote-contaminated groundwater, the combination of gas chromatography–mass spectrometry (GC–MS) providing high resolution, sensitivity and selectivity was used for the analysis. The results of LLEs with three different solvents and of SPE are described and evaluated, and finally, an optimized sample preparation method based on LLE with DCM in combination with GC–MS analysis is validated.

Table 1
Physical and chemical data of heteroaromatic compounds and the selected ions (m/z) for GC–MS analysis

NSO Compound	M+ m/z	2nd ion m/z	M_r g/mol	b.p. °C	log K_{ow}	pK_a	Sw mg/l
Nitrogen-containing compounds:							
Pyrrole	67	41	67.1	131	0.75	<1	16 000
1-Methylpyrrole	81	80	81.1	113			High
2-Methylpyridine	93	66	93.0	129	1.06	5.97	High
2,4-Dimethylpyridine	107	79	107	157		6.99	High
Indole	117	90	117	254	2.00	<1	3000
Quinoline	129	102	129	238	2.03	4.92	6500
2-Methylquinoline	143	142	143	248	2.23	5.83	
Carbazole	167	139	167	355	3.71		1.2
Acridine	179	178	179	346	3.5	5.68	38.4
Sulphur-containing compounds:							
Thiophene	84	58	84.1	84	1.81		3600
Benzo[b]thiophene	134	–	134	221	3.12		130
Benzo[b]thiophene-2,3-dione	136	108	164	Sublim			
Dibenzo[b]thiophene	184	–	184	332	5.45		1
Dibenzo[b]thiophene-sulfone	216	187	216	Sublim			
Oxygen-containing compounds:							
Benzofuran	118	89	118	174	2.67		224
Dibenzofuran	168	139	168	285	4.12		10
Internal standards:							
1-Chlorobenzene	112	77	112	132			
1-Bromonaphthalene	206	208	207	240			

M+ (molecular ion): quantification ion m/z and second intense ion m/z. Sublim: the compound sublimes. Log K_{ow}: n-octanol–water partition coefficient. S_w: water solubility [8,34–37].

2. Materials and methods

2.1. Reagents

Solvents of chromatographic grade and freshly distilled DEE and pentane were used for extractions. Anhydrous sodium sulphate (Na$_2$SO$_4$) from Merck was cleaned by Soxhlet extraction for 24 h with methanol, DCM and afterwards was dried at 110°C. The solid-phase columns containing ethyl-, octyl-, octadecyl-, cyclohexyl-, phenyl-, and cyano-modified silica (500–1000 mg) were obtained from Waters and Varian.

All available reference substances were of very high purity from commercial sources. Benzothiophene-2,3-dione (BT-2,3-dione) and dibenzothiophene-sulfoxide (DBT-sulfoxide) were prepared by the methods published by Papa et al. [24] and Gilman and Esmay [25]. Further purification of these compounds was made by either extraction with DCM or by separation on a silica column. The purity of the synthesized products was confirmed by TLC, ^{1}H NMR and melting point measurements.

Standard solutions in Milli-Q water and DCM were prepared from a concentrated standard solution of NSO compounds in tetrahydrofuran; spiked water samples were also made by addition of this solution to tapwater or groundwater. Contaminated groundwater samples were collected from a former gasworks site in Fredericia, Denmark.

2.2. Methods

The effect of pH on extraction efficiency was examined. Tapwater, spiked with NSO compounds at five concentrations ranging from 0.07 to 25 mg/l, was extracted individually at acidic, neutral and basic pH with DCM and analysed by GC–MS in scan mode. The extraction ratio was 5:1 and the pH was adjusted with 10 M NaOH or 4 M H$_2$SO$_4$. Calibration curves based on pure standard solutions and extracts of standards solutions at acidic (pH<2), neutral (pH 7) and basic pH (pH>10) were established. The slopes of the four calibration curves, with correlation coefficients higher than 0.99, were used to determine the recovery of each NSO compound.

LLE, using either DCM, DEE or pentane, was studied by extracting spiked water (800 μg/l of each

compound) at pH 8 in the ratio of 6:1. The extracts were analysed by GC–flame ionization detection (FID). Recovery studies were done by comparing the results of extracted samples with the results of the pure standard solutions.

SPE was performed with an automatic sample preparation with extraction columns system (ASPEC) obtained from Gilson (Villiers Le Bel, France). Bonded phase columns were conditioned with methanol, eluting solvent and Milli-Q water. Spiked water samples (300 ml of 25 μg/l), pH 8, were loaded slowly (5 ml/min) onto the columns that successively were washed with 1 ml of Milli-Q water. The eluting solvent was added twice after a delay of 3 min (2×0.75 ml) at a flow-rate of 1 ml/min using pressurized air. The combined eluent was dried with Na$_2$SO$_4$ and analysed by GC–FID. The columns resulting in the highest recoveries were selected for further studies of eluent [DEE, acetone, DCM–acetone (2:1)] [23], and finally the best SPE condition (octyl material and elution with DEE) was tested on Milli-Q water and contaminated groundwater samples spiked at 25 and 50 μg/l with each NSO compound.

The optimized method for analysing the heteroaromatic compounds at the ng/l level was eventually performed as follows: pH of the water sample was adjusted to 8 using 10 M NaOH, and 900 ml of sample were extracted three times with 50–100 ml of DCM in a separating funnel. The combined DCM extract was filtered through anhydrous Na$_2$SO$_4$, then concentrated by rotary evaporation to 5–10 ml and eventually, under a slow stream of dry air, to 0.50 ml. Afterwards, 1-chlorobenzene and 1-bromonaphthalene were added, to correct for solvent evaporation in vials and injection volume errors of the volatile and semi-volatile compounds, respectively. The concentration step was performed carefully to avoid loss of volatile compounds, and blanks were made in the same way. Extracts were analysed by GC–MS; compounds were identified using relative retention times and by comparing the mass spectra with library reference spectra or with spectra of standard solutions (DCM), or by comparing the relative abundance of two characteristic ions (m/z) of each compound (Table 1). Quantification was done by the external standard method, with standard solutions spiked at five concentrations and extracted

and concentrated in the same way as samples. The area counts of each compound's base ion (Table 1) was used for quantification. The recovery and precision of the method were studied by spiking tapwater with the concentrated solution of NSO compounds at 0.20, 1.0, 2.5 and 25 μg/l of each compound, in triplicate.

2.3. Instrumental analysis

GC analyses of 2-μl extracts were performed using a Carlo Erba Mega gas chromatograph, equipped with an autosampler, a split–splitless injector (250°C) and a flame ionization detector (275°C). Separation was obtained on a CP-Sil 8 CB fused-silica column (25 m×0.32 mm I.D., 0.25 μm film thickness) with nitrogen (purity 99.999%) as the carrier gas, at an inlet pressure of 80 kPa and the following temperature program: initial temperature 35°C for 5 min, increased by 25°C/min to 130°C, isothermal for 4 min, then increased by 25°C/min to 240°C, isothermal for 4 min, then increased by 25°C/min to 280°C, then maintained at this temperature for 7 min.

GC–MS analysis was performed on a Carlo Erba gas chromatograph QMD 1000 coupled with a mass spectrometer and an autosampler. A J&W Scientific DB-5.625 fused-silica capillary column (25 m×0.25 mm I.D., 1 μm film thickness) was used with helium (99.9999%) as the carrier gas. The injection technique and temperature program were used as described above, while the temperatures of the injector, transfer line and ion source were 275, 250 and 200°C, respectively. Positive electron ionizations (EI) at 70 eV with scanning parameters ranging from 10 to 350 u in 0.90 s were used. The samples were analysed by GC–MS selective ion monitoring (SIM) with two descriptors of each compound (Table 1). The chromatograms were collected on a computer system and processed by Labbase chromatography software.

3. Results and discussion

3.1. Oxygenated metabolites

Due to thermolability and adsorption effects in the column or injection port at low concentrations,

problems were encountered with the capillary GC analysis of oxygenated heteroaromatic metabolites, viz. 2-hydroxyquinoline, oxindole, isatine, acridone, BT-2,3-dione and DBT-sulfoxide [26]. By differential thermal analysis (DTA), isatine and BT-2,3-dione were shown to decompose at 200°C (data not published). Even at extract concentrations higher than the 30–50 μg/l necessary to detect these compounds, peaks showed clear signs of decomposition. However, acceptable correlation coefficients of the calibration curve were obtained for BT-2,3-dione in standard solutions (DCM), while the results of DBT-sulfoxide were not reproducible, and it was therefore excluded in the validated method. To determine these oxygenated compounds, another instrumental method should be used, such as HPLC.

3.2. Liquid–liquid extraction

3.2.1. Influence of pH

The recoveries of LLEs of some NSO compounds are pH sensitive, as shown in Fig. 1 for the extraction with DCM at acidic, neutral and basic pH. The compounds influenced by pH were the S-metabolite BT-2,3-dione and the six-membered N-heterocyclic compounds. BT-2,3-dione was recovered to about 75% in acidic conditions, whereas it probably hydrolysed to mandelic acid in an alkaline solution [24]. The recovery of the basic compounds increased with the number of aryl substituents on the pyridine structure, due to their decreasing water solubility. The optimal pH for the extraction of heteroaromatic compounds (Table 1) was considered to be a basic environment, due to the base character of the N-containing heterocycles; thus, the pyridine-containing ring structures have pK_a values between 4 and 7 (Table 1), and they exist in their unprotonated form in basic aqueous solutions. Accordingly, no difference in extraction efficiencies was observed for the pyridines between pH 7 and 10. However, at high pH values metal hydroxides are precipitated from groundwater [22], and as that interferes with the phase separation, relatively weak basic conditions are preferred.

3.2.2. Solvent choice

The extraction efficiencies (% recovery) of NSO compounds in LLE with commonly used solvents in
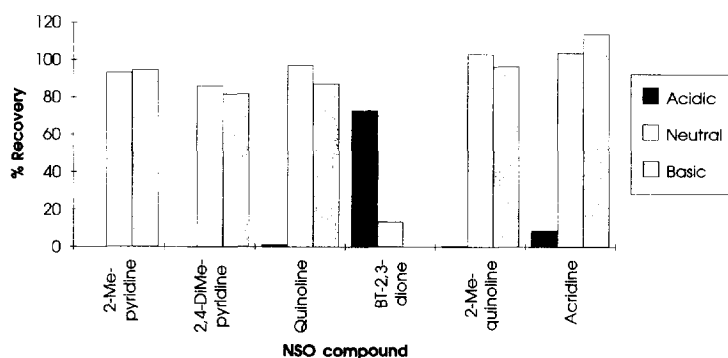
Fig. 1. Extraction efficiencies (recoveries) of pH-sensitive NSO compounds from aqueous solutions at various pHs using dichloromethane. Based on extracts of spiked water samples and standard solutions (DCM) at five concentration levels between 0.25 and 50 mg/l in the extracts and analyzed by GC–MS (scan mode). Abbreviations: Me, Methyl; BT, Benzothiophene.

weakly basic solutions are shown in Table 2. The NSO compounds were recovered in the highest amounts and most versatile with DCM. Thiophene was not measured due to coelution problems with DCM. Generally, the extraction efficiencies of neutral compounds such as benzofuran, dibenzofuran, benzothiophene, dibenzothiophene and carbazole were independent of the organic solvents used and were 100%. The basic and polar compounds such as pyrroles, pyridines, quinolines, acridine and DBT-

Table 2
Recoveries of NSO compounds from water using different extraction solvents

	DCM	DEE	Pentane
Thiophene	ND	100	103
1-Methylpyrrole	96	73	66
Pyrrole	61	50	4
2-Methylpyridine	79	21	0[a]
2,4-Dimethylpyridine	97	33	0[a]
Benzofuran	100	98	97
Benzothiophene	100	99	99
Quinoline	98	65	61
Indole	98	99	44
2-Methylquinoline	100	81	82
Dibenzofuran	100	100	100
Dibenzothiophene	100	100	99
Acridine	99	95	96
Carbazole	99	101	95
Dibenzothiophene-sulfone	93	75	43

Results from extraction of spiked water at pH 8. Analytical instrumentation: GC–FID. ND: Not detected.
[a] The pyridines had incompatibility problems with pentane.

sulfone were recovered in the highest quantities using DCM. Van Hoof et al. [27] observed the same with polar N-containing herbicides. DCM may be considered to be a versatile solvent, however, due to its toxicity, alternatives should be sought.

The GC–FID responses of standard solutions in DCM were higher by a factor 1.3 in peak area (R.S.D. 3.9%, n=32) than those of the DEE and pentane solutions, while no differences in response between the DEE and pentane solutions were observed. Extractions with DEE resulted in higher recoveries of the NSO compounds than those obtained with pentane. By extraction with mixtures of DEE and pentane, the recoveries of the N-containing compounds, in particular, were influenced by the pentane content (data not shown). Some pentane (<25%) in the solvent mixture reduced the aqueous solubility of the solvent. Extraction with DEE–pentane mixtures could easily be scaled up, but it showed no advantages compared with DCM extraction that resulted in the highest recoveries of all NSO compounds. With lower demands of detection limits (high μg/l), extraction with DEE–pentane mixtures could be beneficial due to the solvent density and therefore easier sample preparation.

3.3. Solid-phase extraction

The recoveries of heteroaromatic compounds from several bonded reversed-phase materials are shown in Fig. 2. The highest recoveries were obtained with
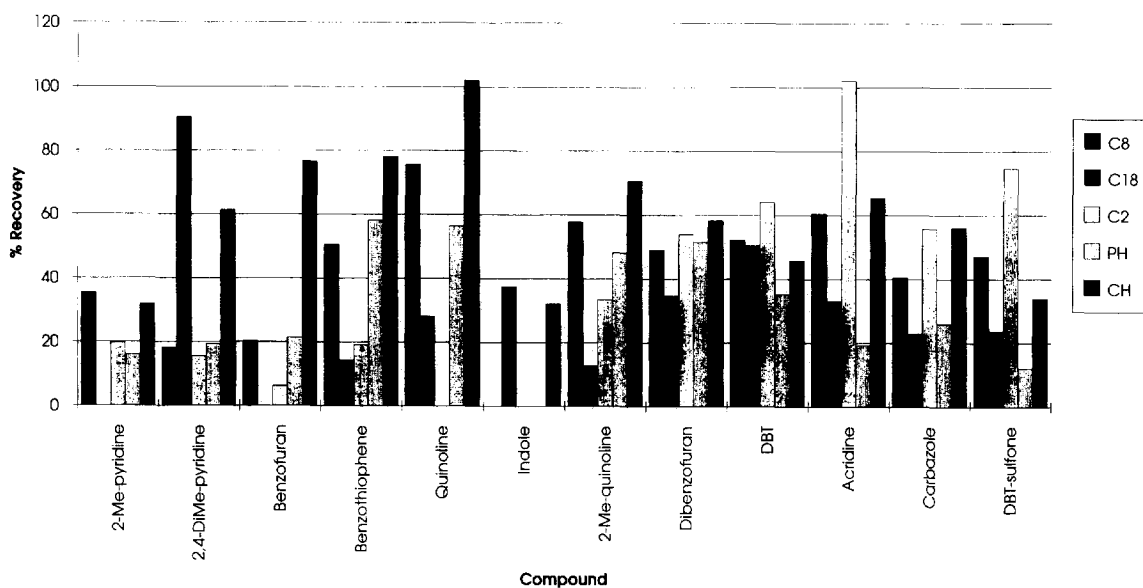
Fig. 2. Recoveries (%) of NSO compounds for various SPE cartridges. The solid phases were octyl- (C_8), cyclohexyl- (CH), phenyl- (PH), ethyl- (C_2), cyanopropyl- (CN) and octadecyl- (C_{18}), which were loaded with 300 ml of spiked water (25 μg/l) and eluted with diethyl ether. Analysis was by GC–FID. Abbreviations: Me=methyl; DBT=dibenzothiophene.

the octyl-, phenyl- and octadecyl-bonded phases. Recoveries from cyano-bonded columns were less than 15% and are not included in Fig. 2. The pyrroles were not absorbed by any of the phases tested, and the pyridines were only minimally absorbed, probably due to their volatility and high aqueous solubility. Generally, the affinity of five-membered N-heterocycles was low, especially in comparison to the more water-soluble six-membered N-compounds. Rostad et al. [23] studied the SPE of creosote compounds, including some NSO compounds, in groundwater and found that the cyclo-hexyl-bonded phase was a poor choice for N-heterocyclics and that the octadecyl-bonded phase provided the highest recoveries of the neutral heterocyclics. In this study, the higher-molecular-mass polar N-compounds were recovered in similar amounts as the neutral compounds, with an average efficiency of 50–60%. The lower recoveries with octadecyl- than with the octyl-bonded phases could be explained by the fact that the column was no longer "wetted" due to the high aqueous sample through-put. This problem might have been overcome by adding 1–3% methanol to the sample

before processing, as this would have maintained the equilibrium between the stationary and mobile phases [28,29].

The selection of adequate solvents was limited due to GC separation problems with the volatile NSO compounds. By using DEE, highest recoveries were achieved on the octyl phases compared with the phenyl-bonded phase (data not shown). The eluting efficiency of the solvents, DEE, acetone and a DCM–acetone mixture (2:1, v/v) was very similar on the octyl material (data not shown), and hence the octyl phase with DEE as the eluent was chosen for optimization. The recoveries and relative standard deviations of extractions of spiked groundwater and Milli-Q water samples at two concentration levels are shown in Table 3. Somewhat lower recoveries of the basic compounds were obtained from spiked groundwater samples, probably due to their peak tailing and more unstable baselines. The standard deviation decreased with increasing concentration level. In general, the SPE technique was useable for two thirds of the NSO compounds, and the recoveries and reproducibilities were acceptable in comparison with US Environmental Protection

Table 3
Recoveries (%) and R.S.D. (%) of NSO compounds by optimized SPE

Matrix	Ground water				Milli-Q water			
Spiked level	25 μg/l (n=2)		50 μg/l (n=8)		25 μg/l (n=5)		50 μg/l (n=4)	
	E.E. (%)	R.S.D. (%)	E.E. (%)	R.S.D. (%)	E.E. (%)	R.S.D. (%)	E.E. (%)	R.S.D. (%)
Thiophene	7	7.3	8	0.2	8	1.7	8	1.2
1-Methylpyrrole	0	–	0	–	0	–	0	–
Pyrrole	0	–	0	–	0	–	0	–
2-Methylpyridine	21	17	20	1.4	15	13	17	9.6
2,4-Dimethylpyridine	15	21	59	6.0	83	7.5	62	6.4
Benzofuran	28	11	38	4.1	36	1.5	37	2.7
Benzothiophene	53	28	60	4.5	74	7.1	69	9.4
Quinoline	71	20	74	2.6	94	9.8	86	13
Indole	11	5.0	13	2.1	13	1.5	13	1.5
2-Methylquinoline	65	12	65	6.1	81	8.5	75	11
Dibenzofuran	56	12	48	1.5	69	7.8	60	13
Dibenzothiophene	54	7.1	36	1.4	50	5.6	44	8.5
Acridine	50	13	39	2.8	27	2.7	32	6.8
Carbazole	96	13	57	6.1	83	9.5	72	16
Dibenzothiophene-sulfone	60	19	41	2.4	59	12	52	13

SPE of 250 ml of spiked water samples at two levels using C_8 material and elution with 1.5 ml ether. Analytical instrument: GC–FID. E.E. and R.S.D.: extraction efficiency and relative standard deviation.

Agency (EPA) methods. However, the retention of compounds by the column material was not very high and for ultimate use of this technique, a concentration factor of 2000 was required. Therefore, higher sample through-put was necessary, but when up to 1000 ml of sample was loaded, washout of compounds from the bonded phase became a problem, resulting in poor reproducibilities (data not shown). This made the SPE method inapplicable for analysis of NSO compounds at the ng/l level.

In comparison with LLE, the recovery of the SPE was lower, and the very soluble and volatile compounds could not be analysed by SPE techniques. However, for the semi-volatile heteroaromatic compounds, viz. benzothiophene, quinoline, 2-methylquinoline, dibenzofuran, dibenzothiophene, carbazole and dibenzothiophene-sulfone, recoveries were higher than 50%. Compared with the EPA 525 SPE method, the results obtained with the optimized SPE method for the semi-volatile compounds were acceptable, and analyses at high μg/l level seem possible. Alternatively, the solid-phase microextraction (SPME) technique might be used. With this technique, other solid-phase materials are available than with SPE; SPME has been used successfully for

analyses of other creosote compounds, such as BTEX, phenols and naphthalenes in water [30–32], and a study on trace analysis of heteroaromatic compounds in water by SPME is now in progress.

3.4. Final optimized method

Among the studied sample preparation techniques, LLE with DCM provided the highest recoveries of all NSO compounds, with good reproducibility, and scaling the method up was easy. The application of sample preparation methods other than the classical DCM extraction method was not advantageous at this stage, however alternative techniques should still be investigated, as DCM is a toxic solvent. The technique for optimization was therefore LLE using DCM in a weakly basic environment. By using larger sample volumes, a concentration factor of 1800 could be obtained. The analytical parameters of the optimized method are listed in Table 4, including retention time (t_R), relative retention time (rel. t_R) (against 1-bromonaphthalene), % recovery, relative standard deviation (R.S.D.), limit of detection (LOD) and a range of linearity with the calibration curve

Table 4
Analytical characteristics of the optimized method

Number	Compound	t_R (min)	Rel. t_R	E.E. (%)	S.D.	R.S.D. (%)	LOD (μg/l)	Range (μg/l)	Calibration curve		
									Slope	Intercept	r^2
1	Thiophene	2.67	0.17	27	6.8	25	0.04	0.05–10	0.176	−0.003	0.9998
2	1-Methylpyrrole	3.94	0.24	42	17	42	0.05	0.05–25	0.068	0.012	0.9997
3	Pyrrole	4.32	0.27	14	2.9	21	0.20	0.20–25	0.019	0.003	0.9991
4	2-Methylpyridine	6.17	0.38	30	14	46	3.0	3.0 –50	0.035	0.037	0.9909
5	2,4-Dimethylpyridine	8.24	0.51	41	3.6	8.8	3.0	3.0 –50	0.154	0.141	0.9919
6	Benzofuran	9.15	0.56	74	20	27	0.04	0.05–10	0.639	−0.006	0.9999
7	Benzothiophene	11.93	0.74	66	18	27	0.03	0.03–25	1.309	−0.074	0.9993
8	Quinoline	12.76	0.79	69	15	22	0.04	0.05–10	0.488	−0.007	0.9999
9	Indole	13.72	0.85	59	5.6	9.4	0.04	0.05–25	0.385	−0.017	0.9991
10	2-Methylquinoline	14.01	0.86	77	11	14	0.03	0.05–25	0.711	−0.137	0.9998
11	Benzothiophene-2,3-dione	16.33	1.01	20	6.4	31	2.5	2.5 –50	0.0075	0.0001	0.9994
12	Dibenzofuran	16.58	1.02	75	8.6	11	0.03	0.05–25	0.659	0.015	0.9999
13	Dibenzothiophene	18.61	1.15	88	11	13	0.03	0.03–25	0.962	0.031	0.9999
14	Acridine	19.01	1.17	85	18	21	0.05	0.05–10	0.328	−0.004	0.9999
15	Carbazole	19.27	1.19	58	16	27	0.04	0.05–10	0.219	−0.004	0.9998
16	Dibenzothiophene-sulfone	22.13	1.37	62	21	33	0.10	0.15–25	0.265	−0.106	0.9990

Results from water spiked at four concentrations ranging from 0.1 to 50 μg/l (triplicates). t_R =retention time in min; rel. t_R =relative retention time to 1-bromonaphthalene. E.E., extraction efficiency; S.D., standard deviation (n = 12); R.S.D., relative standard deviation. LOD, limit of detection range; linearity of SIM–GC–MS analysis. Correlation coefficients: r^2.

parameters: slope, intercept and correlation coefficient (r^2). Fig. 3 illustrates a total ion chromatogram and a SIM chromatogram of tapwater spiked at 10 and 0.25 μg/l, respectively. The GC separation of the spiked NSO compounds was good, but some unknown peaks were detected both in spiked and blank tapwater samples, and the basic pyridines, quinolines and acridine showed some peak tailing. Linearity of standards extracted from spiked water extended for more than two decades and had correlation coefficients that were mostly above 0.999. No differences were observed between recoveries and standard deviations at the different concentration levels, and therefore the accumulated means of recovery (%) and R.S.D. are shown in Table 4. The recoveries ranged from 30–90%, which is less than in the first study of DCM extraction (Table 2) and is a result of the upscaled sample preparation. Loss of compounds happened during rotary evaporation, filtration and transfer between bottles. The R.S.D. ranged from 8 to 46% with an average of about 19%. The recovery and reproducibility were poorest for the volatile compounds, such as thiophene, and for the very water-soluble compounds, like the pyrroles.

The limit of quantification, defined as the minimum concentration of a compound in spiked groundwater that gave a well defined peak (area >100 000 or a signal-to-noise ratio >3), was generally at the ng/l level. The SO compounds and the higher-molecular-mass N-compounds were quantified at 50 ng/l. Pyrrole was quantified at 0.2 μg/l, while the S-metabolites, dibenzothiophene-sulfone and BT-2,3-dione, were detected at 0.10 and 2.5 μg/l, respectively. The high detection limit of BT-2,3-dione was a result of its thermolability and pH instability.

When the validated data of the optimized method were compared (detection limit and R.S.D.) to that of standard methods of the EPA for determination of organic compounds in water (Method 500–600), the method was acceptable. The most applied EPA analyses [33] include DCM extraction and compared with these, the detection limit was improved in our study by achieving higher concentration factors and using capillary GC. Unfortunately, several relevant oxygenated biodegradation products of NSO compounds could not be analysed by this method in realistic concentrations, due to thermal decomposition and chromatographic interactions.
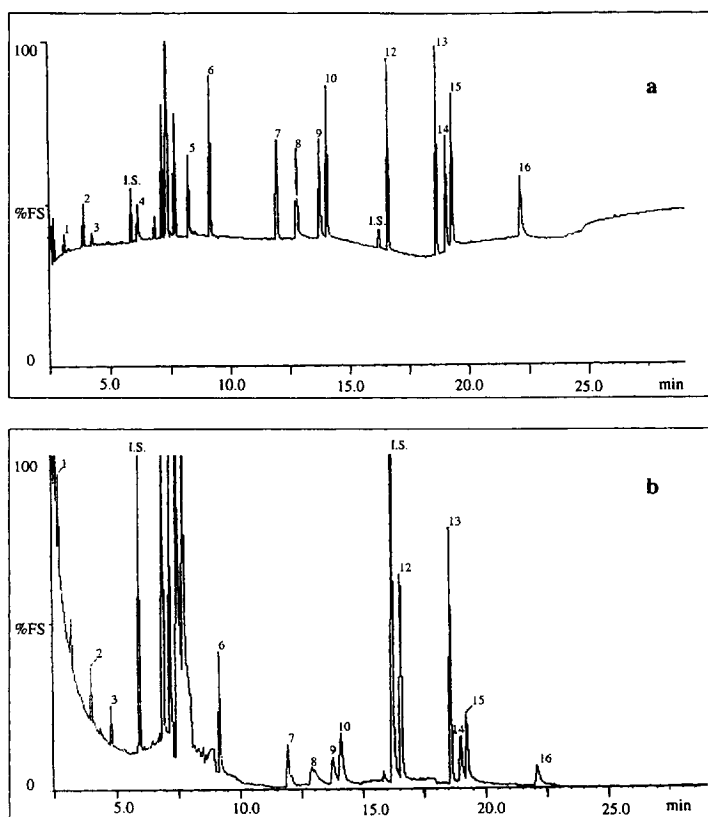
Fig. 3. Total ion chromatogram (a) and a selective ion monitoring chromatogram (b) of tapwater spiked with NSO compounds at 10 and 0.25 μg/l, respectively, obtained by the final optimized dichloromethane extraction method. The response is normalized to 100% full scale (FS), and each peak is numbered according to the compounds in Table 4.

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