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Gas chromatographic and mass spectrometric determination of nitroaromatics in water

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ABSTRACT

Several methods for the extraction of nitroaromatic compounds from water were compared. High recoveries were achieved with discontinuous or continuous extraction of water with dichloromethane and by adsorption on Amberlite XAD-2, -4 and -8 resins (1:1:1) and elution with dichloromethane. The recoveries obtained with solid-phase extraction using cyano-, phenyl- or octadecyl-bonded phases varied, depending on the compounds studied, and were often low. Nitroaromatic compounds were determined by gas chromatography using an electron-capture or a chemiluminescence detector (thermal energy analyser) and by mass spectrometry using electron impact and positive- and negative-ion chemical ionization.

INTRODUCTION

Nitroaromatic compounds are widely used in the chemical industry, *e.g.*, for the production of explosives, dyes, pesticides and polyurethane foam, which may lead to their partial release into the environment. Nitroaromatics are toxic. They are readily adsorbed by skin contact and may lead to methemoglobinemia, anemia or liver damage [1]. Thus the LD_{50} value (rat) for 1-chloro-2-nitrobenzene is as low as 288 mg/kg and the LC_{50} value for goldorfe 5-10 mg/l [2].

Several nitroaromatic compounds are listed as priority pollutants by the U.S. Environmental Protection Agency [3] (nitrobenzene, 2,4-dinitrotoluene, 2,6-dinitrotoluene, 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol and 4,6-dinitro-2-methylphenol) and by the European Community [2] (1-chloro-2-nitrobenzene, 1-chloro-3-nitrobenzene, 1-chloro-4-nitrobenzene, 4-chloro-2-nitrotoluene, 4-chloro-2-nitroaniline and parathion ethyl). Nitrobenzene, nitrotoluene isomers and chloronitrobenzenes have been observed repeatedly in samples from the river Rhine [4]. Acute pollution of the river Main led to concentrations of chloronitrobenzene isomers of *ca.*

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[a] This paper is based on the Ph.D. Thesis of J. Feltes, University of Bonn, 1988.

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80 μg/l [5], which led to cessation of the withdrawal of Rhine water for drinking water supplies in The Netherlands.

In the past, relatively few studies have been exclusively directed towards the determination of nitroaromatic compounds in water. Explosives and related compounds have attracted particular attention. These compounds are usually determined by gas chromatography (GC) with flame ionization detection (FID) [6,7] or more selectively and sensitively using electron-capture detection (ECD) [8–13]. The use of chemiluminescence detection (thermal energy analysis, TEA) should be advantageous. This type of detection has been used for the selective GC determination of nitroaromatics in biosludge [14]. GC methods for the determination of nitroaromatics in water (in particular munition plant wastewater) [6,7,12] and sea water [10,11] have been published and the determination of nitrotoluidines (aminonitrotoluenes) in water by GC has been described [13].

Alternatively, high-performance liquid chromatography (HPLC) can be employed for the determination of nitroaromatics in water (mainly wastewater [15–18]).

In most instances the water samples were extracted by liquid–liquid extraction (using mainly benzene or toluene) [6-11,13]. Alternatively, resin adsorption using Porapack R, Porapack S or XAD-4 was used for sample extraction [12,18].

Nitrophenols represent a specific class of nitroaromatic compounds. They are usually determined using methods optimized for phenols, as reviewed by Tesarova and Pacakova [19]. Owing to their high polarity, the GC of these compounds may be difficult and they are often first derivatized [19]. Nitropolycyclic aromatic hydrocarbons represent another class of nitroaromatic compounds for which specific analytical schemes have been developed, as reviewed by White [20].

The methods discussed above were usually based on a few compounds and in general tested only with spiked water samples.

We report here the optimized determination of a large number of nitro compounds with a variety of functional groups. Analysis is performed by GC with ECD and TEA or by combined GC–mass spectrometry (MS) using electron impact (EI), positive-ion chemical ionization (PICI) or negative-ion chemical ionization (NICI). Nitrophenols are discussed only briefly as they have been considered in detail elsewhere [21–23]. Nitropolycyclic aromatic hydrocarbons have also been dealt with elsewhere [24].

EXPERIMENTAL

Instrument

All GC measurements were carried out on a Varian Model 3700 instrument equipped with a Varian ^{63}Ni electron-capture detector and a Model 543 chemiluminescence detector (TEA) from Thermedics (Woburn, MA, U.S.A.). Pyrolysis was effected at 950°C. The pressure in the reaction chamber was 0.8 Torr. Separation was achieved on both a DB-17 and an OV-225 column (30 m × 0.32 mm I.D., d_f 0.25 μm) with a column temperature of 70°C for 1 min, then raised from 70 to 250°C at 3°C/min, using nitrogen (ECD) or helium (TEA) as the carrier gas.

Mass spectrometric measurements were carried out on a Finnigan Model 4500 and a Vacuum Generator Model VG70 SQ instrument using an electron energy of 70 eV and a source temperature of 120°C (Finnigan) or 200°C (VG). PICI was achieved with methane (0.5 Torr) or isobutane (0.05 Torr) as reagent gas and both methane and argon were used for NICI (0.5 Torr). Samples were introduced via the GC system using a DB-5 column with a temperature of 70°C for 1 min, then increased from 70 to 260°C at 3°C/min.

Extraction

Discontinuous extraction was carried out with a separation funnel using 1 l of water spiked with the internal standards and shaking three times with 30 ml of dichloromethane. The combined organic phases were dried over anhydrous sodium sulphate and reduced in volume to *ca.* 1 ml in a rotary evaporator after exchange of the solvent (methanol instead of dichloromethane). Concentration to 1 ml at 40°C and reduced pressure does not lead to evaporation losses as determined by recovery studies (recovery >96%).

Continuous extraction was carried out for 5 h in a rotary perforator using 0.5 l of water and dichloromethane as solvent followed by concentration and solvent exchange as described above.

Solid-phase extraction was performed using Amberlite (residue-free) XAD-2, XAD-4, XAD-8 resins from Alltech and Rohm & Haas, C_{18} phases (500-mg cartridges) from Baker (Baker 10 SPE), Analytichem (Bond-Elut) and Merck (Adsorbex), phenyl phases (500-mg cartridges) from Baker (Baker 10 SPE) and Analytichem (Bond-Elut) and cyano phases from Baker (Baker 10 SPE). XAD resin (2.5 g) was filled into a 15 × 1 cm I.D. glass column plugged with silanized glass-wool and flushed with methanol and water prior to use by forcing the solvent through the column with nitrogen at enhanced pressure. After forcing 1 l of the sample through the column at a flow-rate of 30 ml/min, the column was dried in a stream of nitrogen for about 15 min and eluted twice with 15 and 10 ml of dichloromethane. The C_{18}, phenyl and cyano cartridges were eluted with 1 ml of dichloromethane at reduced pressure. Drying, concentration and solvent exchange were carried out as described above.

Chemicals

Nitroaromatic reference compounds of 97–99% purity from Merck, Fluka, Riedel-de Haën and Aldrich were used without further purification. Solvents were purchased from Baker and Rathburn Chemicals.

RESULTS AND DISCUSSION

Gas chromatography

Nitroaromatic compounds were determined by GC with either ECD or TEA. In the TEA detector nitro compounds are pyrolysed to form $NO^{\bullet}$ radicals that react with ozone to form triplet excited NO_2, which relaxes to the ground state with emission of light in the near-infrared region (>0.6 μm), which is monitored. Slightly polar (DB-17) to moderately polar columns (OV-225 or DB-225) are well suited for the separation of nitroaromatics. Fig. 1 compares the chromatograms of 40 nitroaromatic compounds obtained on a DB-17 column with ECD (upper part) and TEA (lower part), and in Fig. 2 the chromatogram (ECD) of a mixture of explosives and their metabolites is presented. In Tables I and II retention times and capacity factors (k')

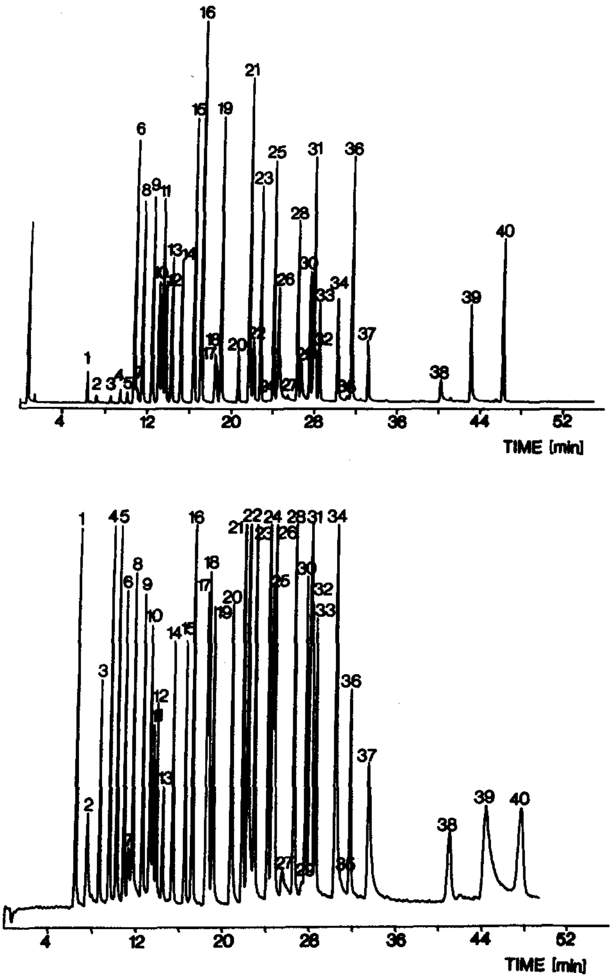

Fig. 1. Gas chromatograms of 40 nitroaromatic compounds on a DB-17 column (top, ECD; bottom, TEA). For peak assignment, see Table I.

are summarized for the DB-17 and OV-225 columns. 1-Chloro-2,4-dinitrobenzene and 2,2'-dinitrobiphenyl were used as internal standards. With the TEA detector substantial peak broadening is observed at high retention times, probably owing to adsorption within the transfer line.

Nitroaromatics can be determined by ECD as a result of their high electron affinity. However, Fig. 1 reveals that the response for nitroaromatics depends strongly on the individual compound. Thus, for instance, the ECD response of 3,4-dinitrotoluene is 61 times that of 2-nitrotoluene. On the other hand, the TEA response is more similar for all the compounds, as is evident from Fig. 1 (the response of 3,4-dinitrotoluene is 3.4 times that of 2-nitrotoluene). A low response is observed for the nitrophenols. This is particularly true for the dinitrophenols, such as 2,4-dinitro-6-*sec.*-butylphenol (dinoseb), which is probably due to irreversible adsorption of the

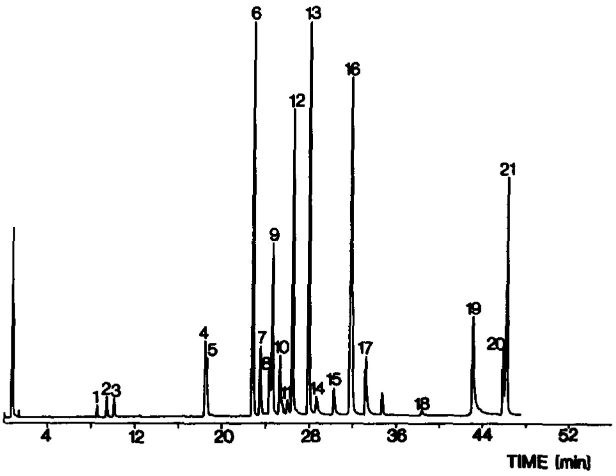

Fig. 2. Gas chromatogram of 21 nitroaromatic compounds used in ammunition production (including the degradation products) (ECD). For peak assignment, see Table II.

phenol at the active centres of the column. Hence it is preferable to derivatize nitrophenols [19].

The TEA detector responds specifically to nitro and nitroso compounds and is therefore better suited for the analysis of complex environmental samples than ECD, which is less selective. On the other hand, the selectivity of GC with ECD can be enhanced if the samples are chromatographed on two columns with phases of different polarities. As stated above, DB-5 and OV-225 (DB-225) are well suited for this purpose.

The linearity of the detectors for nitro compounds was studied using both ECD and TEA for five compounds. The results in Fig. 3 show that the ECD response (top) levels off at concentrations > 10 ng, whereas the TEA detector (bottom) shows good linearity even at higher concentrations.

The detection limit of the detector (defined at three times the standard deviation of the noise) is summarized for 15 compounds in Table III for both ECD and TEA. With ECD the detection limit ranges from $0.8 \cdot 10^{-14}$ to $109 \cdot 10^{-14}$ g/s and that with TEA from $6 \cdot 10^{-11}$ to $34 \cdot 10^{-11}$ g/s. Hence ECD is about three orders of magnitude more sensitive than TEA.

Gas chromatography–mass spectrometry

A mass spectrometer is a considerably more specific GC detector than either electron-capture or TEA detectors. Nitroaromatic compounds were determined using EI, PICI and NICI. Mass spectrometry is particularly suitable for the analysis of this class of compounds as their ionization leads to the formation of structure-specific fragments, as summarized in Table IV for all three ionization methods. Under EI conditions, nitroaromatic compounds fragment predominantly by loss of $NO^{\bullet}$ or NO_2. In general, loss of NO_2 prevails. An *ortho* effect may lead to an abundant loss of $OH^{\bullet}$ [25] if a methyl or amino group is in an *ortho* position to the nitro group. In addition, dinitro and trinitro derivatives show in part the loss of two nitro groups. An

TABLE I

ELUTION ORDER, RETENTION TIMES AND CAPACITY FACTORS OF NITROAROMATIC COMPOUNDS CHROMATOGRAPHED ON A DB-17 AND OV-225 COLUMN

Compound	DB-17			OV-225		
	Elution order	t_R (min)	k'	Elution order	t_R (min)	k'
Nitrobenzene	1	6.32	13.04	1	5.94	17.56
2-Nitrophenol	2	7.16	14.91	2	6.70	19.94
2-Nitrotoluene	3	8.50	17.89	3	7.46	22.31
3-Nitrotoluene	4	9.42	19.93	4	8.71	26.22
4-Nitrotoluene	5	10.07	21.38	5	9.70	29.31
1-Chloro-3-nitrobenzene	6	10.74	22.87	9	12.06	36.69
3-Methyl-6-nitrophenol	7	10.94	23.31	6	10.34	31.31
1-Chloro-4-nitrobenzene	8	11.52	24.60	7	10.57	32.03
1-Chloro-2-nitrobenzene	9	12.45	26.67	5	9.70	29.31
2-Chloro-5-nitropyridine	10	13.08	28.07	11	13.66	41.69
4-Chloro-2-nitrotoluene	11	13.41	28.80	9	12.06	36.69
6-Chloro-2-nitrotoluene	12	13.74	29.53	8	11.50	34.94
5-Chloro-2-nitrotoluene	13	14.31	30.80	10	12.68	38.63
2-Chloro-4-nitrotoluene	14	15.20	32.78	12	13.98	42.69
1,4-Dichloro-2-nitrobenzene	15	16.41	35.47	13	15.58	47.69
1,2-Dichloro-4-nitrobenzene	16	17.12	37.04	13	15.58	47.69
1,3-Dichloro-4-nitrobenzene	16	17.12	27.04	14	15.84	48.50
2-Nitroanisole	17	18.45	40.00	15	19.27	59.22
4-Nitroanisole	18	18.59	40.31	15	19.27	59.22
4-Nitrobenzonitrile	19	19.00	41.22	16	21.31	65.59
2-Nitroaniline	20	20.67	44.93	20	23.93	73.78
1,4-Dinitrobenzene	21	21.71	47.24	19	23.84	73.50
1,3-Dinitrobenzene	22	22.15	48.22	21	24.93	76.91
3-Nitrophenol	22	22.15	48.22	32	34.10	105.56
2,6-Dinitrotoluene	23	22.84	49.76	18	23.63	72.84
2,4-Dinitrophenol	24	23.56	51.36	17	22.48	69.25
1,2-Dinitrobenzene	25	24.12	52.60	25	28.06	86.69
3-Nitroaniline	26	24.61	53.69	27	29.75	91.97
2,4-Dinitrotoluene	26	24.61	53.69	23	27.27	84.21
4-Nitrophenol	27	25.49	55.64	35	40.50	125.56
1-Chloro-2,4-dinitrobenzene[a]	28	26.44	57.76	26	29.35	90.72
2-Methyl-3-nitrophenol	29	26.79	58.53	28	30.71	94.97
1-Nitronaphthalene	30	27.61	60.36	22	26.24	81.00
3,4-Dinitrotoluene	31	27.94	61.09	30	32.23	99.72
4-Chloro-2-nitroaniline	32	28.09	61.42	29	31.66	97.94
2-Nitronaphthalene	33	28.55	62.44	24	27.78	85.81
4-Methoxy-2-nitroaniline	34	30.27	66.27	31	33.05	102.28
4-Nitroaniline	34	30.27	66.27	33	37.70	116.81
Dinoseb	35	31.23	68.40	32	34.10	105.56
2,6-Dichloro-4-nitroaniline	36	31.65	69.33	32	34.10	105.56
2-Methyl-4-nitroaniline	37	33.22	72.82	34	39.42	122.19
Parathion ethyl	38	40.26	88.47	38	51.60	160.25
2,4-Dinitroaniline	39	43.16	94.91	37	51.49	159.91
2,2'-Dinitrobiphenyl[a]	40	46.24	101.76	36	47.23	146.59

[a] Internal standard.

TABLE II

ELUTION ORDER, RETENTION TIMES AND CAPACITY FACTORS OF NITROAROMATICS USED IN AMMUNITION PRODUCTION (INCLUDING POSSIBLE METABOLITES)

Compound	DB-17			OV-225		
	Elution order	t_R (min)	k'	Elution order	t_R (min)	k'
2-Nitrotoluene	1	8.50	17.89	1	7.46	22.31
3-Nitrotoluene	2	9.42	19.93	2	8.71	26.22
4-Nitrotoluene	3	10.07	21.37	3	9.71	29.34
2-Nitroanisole	4	18.45	40.00	4	19.25	59.16
4-Nitroanisole	5	18.59	40.31	4	19.25	59.16
2,6-Dinitrotoluene	6	22.84	49.76	5	23.64	72.88
2-Methyl-6-nitroaniline	7	23.51	51.24	6	25.63	79.09
4-Methyl-2-nitroaniline	8	24.33	53.07	7	27.25	84.16
2,4-Dinitrotoluene	9	24.61	53.69	7	27.25	84.16
5-Methyl-2-nitroaniline	10	25.28	55.18	8	28.32	87.50
2-Methyl-3-nitroaniline	11	25.96	56.69	10	30.23	93.47
1-Chloro-2,4-dinitrobenzene[a]	12	26.44	57.76	9	29.28	90.50
3,4-Dinitrotoluene	13	27.94	61.09	11	32.23	99.72
2-Methyl-5-nitroaniline	14	28.65	62.67	12	32.94	101.94
4-Methoxy-2-nitroaniline	15	30.27	66.27	12	32.94	101.94
1,3,5-Trinitrobenzene	16	31.80	69.67	15	39.75	123.22
2,4,6.Trinitrotoluene	16	31.80	69.67	13	37.96	117.63
2-Methyl-4-nitroaniline	17	33.20	72.78	14	39.43	122.22
2,4,6-Trinitrophenol	18	38.40	84.33	17	49.50	153.69
2,4-Dinitroaniline	19	43.13	94.84	18	51.52	160.00
N,2,4,6-Tetranitro- -N-methylaniline	20	45.93	101.07	19	51.89	161.16
2,2'-Dinitrobiphenyl[a]	21	46.24	101.76	16	47.25	146.66

[a] Internal standard.

abundant molecular ion is usually observed under EI conditions. As expected, this ion is of low abundance with dinitrotoluenes and absent (< 1% relative abundance) with trinitrotoluene.

Only a few nitroaromatic compounds have been studied previously under PICI

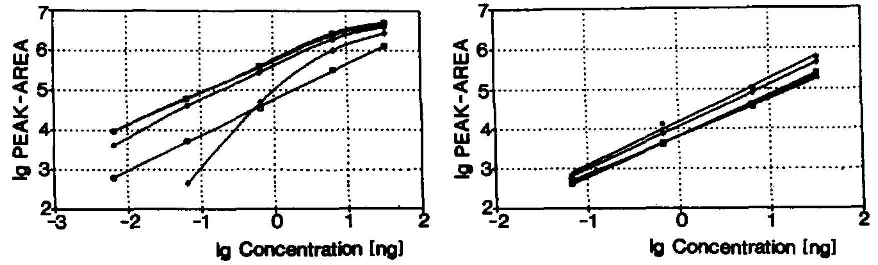

Fig. 3. Linearity of the detectors (left, ECD; right, TEA). □, Nitrobenzene; ○, 1-chloro-2-nitrobenzene; ■, 1,4-dichloro-2-nitrobenzene; ●, 2,6-dinitrotoluene; +, 2-nitroaniline.

TABLE III

DETECTION LIMITS OF THE ELECTRON-CAPTURE AND TEA DETECTORS

Compound	ECD		TEA	
	Detection limit (g/s)	R.S.D. (%)	Detection limit (g/s)	R.S.D. (%)
Nitrobenzene	$2.33 \cdot 10^{-13}$	8.1	$1.35 \cdot 10^{-11}$	7.8
2-Nitrophenol	$1.09 \cdot 10^{-12}$	6.2	$3.43 \cdot 10^{-11}$	6.5
3-Nirotoluene	$5.44 \cdot 10^{-13}$	3.9	$1.09 \cdot 10^{-11}$	7.1
1-Chloro-3-nitrobenzene	$1.18 \cdot 10^{-14}$	4.9	$1.42 \cdot 10^{-11}$	12.3
1,4-Dichloro-2-nitrobenzene	$8.28 \cdot 10^{-15}$	7.6	$1.12 \cdot 10^{-11}$	3.3
6-Chloro-2-nitrotoluene	$2.87 \cdot 10^{-14}$	5.2	$2.50 \cdot 10^{-11}$	9.2
4-Nitroanisole	$1.15 \cdot 10^{-13}$	9.7	$1.85 \cdot 10^{-11}$	4.7
2-Nitroaniline	$9.92 \cdot 10^{-14}$	11.2	$1.98 \cdot 10^{-11}$	8.8
2,4-Dinitrotoluene	$3.80 \cdot 10^{-14}$	7.9	$1.77 \cdot 10^{-11}$	4.9
1-Nitronaphthalene	$2.32 \cdot 10^{-14}$	2.2	$1.15 \cdot 10^{-11}$	6.6
2-Methyl-6-nitroaniline	$6.08 \cdot 10^{-14}$	5.8	$2.42 \cdot 10^{-11}$	7.5
4-Chloro-2-nitroaniline	$1.44 \cdot 10^{-13}$	8.4	$1.14 \cdot 10^{-11}$	9.2
Parathion ethyl	$2.25 \cdot 10^{-13}$	10.8	$1.62 \cdot 10^{-11}$	13.1
2,4-Dinitroaniline	$4.85 \cdot 10^{-14}$	9.2	$6.54 \cdot 10^{-12}$	18.5
2,4,6-Trinitrotoluene	$2.70 \cdot 10^{-14}$	5.6	$9.89 \cdot 10^{-12}$	7.2

conditions [26,27]. In this study methane and isobutane were used as reactant gases. Under PICI conditions with methane the protonated molecule is usually the most abundant peak, as shown in Table IV. This is even the case for the very labile trinitrotoluene. An abundant loss of NO$^\bullet$ from $[M + H]^+$ is observed in almost all instances whereas the loss of NO_2 is less pronounced or often absent. Further fragments are due to loss of O$^\bullet$ or H_2O from the protonated molecule. NO$^\bullet$ loss allows a rapid structure assignment.

Nitroaromatic compounds have a relatively high electron affinity and therefore they can be readily ionized with electron-capture NICI. In this study both methane and argon were used as buffer gases. Characteristic fragments are summarized in Table IV. The NICI spectra of some of these compounds were reported previously [28]. It is evident from Table IV that fragmentation under NICI conditions is low except for dinitro compounds. Losses of OH$^\bullet$, NO$^\bullet$ and NO_2 lead to characteristic fragments. Further fragmentation occurs by loss of H_2O or O$^\bullet$. Unfortunately, not all compounds show the structure-specific loss of NO$^\bullet$, which makes a structure assignment of unknowns difficult. The fragmentation is further reduced if argon instead of methane is used as a buffer gas. The response factors of nitroaromatic compounds under NICI conditions vary substantially. As expected, dinitro compounds such as dinitrobenzene and dinitrotoluenes in general have a higher response than the mononitro compounds, although exceptions are observed. Thus, 1,4-dinitrobenzene has a five times higher response than 1,3-dinitrotoluene.

Mass spectrometric detection limits (signal-to-noise ratio = 3) were determined for several compounds, as summarized in Table V. These detection limits were determined on the Finnigan 4500 quadrupole instrument. It is conceivable that they would

TABLE IV

MAIN FRAGMENTS OBTAINED WITH EI, PICI AND NICI

The Table represents the m/z values and in parentheses the relative abundance.

Compound	EI				PICI (CH_4)			NICI (CH_4)			
	M^+	M−OH	M−NO	$M-NO_2$	MH	MH−NO	$MH-NO_2$	M^-	M−OH	M−NO	$M-NO_2$
Nitrobenzene	123 (80)	–	93 (15)	77 (100)	124 (100)			123 (100)	106 (20)		
2-Nitrotoluene	137 (20)	120 (93)	107 (2)	91 (70)	138 (100)	108 (70)		137 (100)	120 (30)	107 (<1)	
3-Nitrotoluene	137 (80)	–	107 (10)	91 (100)	138 (100)	108 (72)		137 (100)	120 (5)	107 (<1)	
4-Nitrotoluene	137 (95)	–	107 (18)	91 (100)	138 (100)	108 (70)		137 (100)	120 (5)	–	
2-Nitroaniline	138 (100)	121 (5)	108 (8)	92 (50)	139 (100)	109 (30)		138 (100)	121 (30)	–	
3-Nitroaniline	138 (95)	–	108 (8)	92 (85)	139 (100)	109 (85)		138 (100)	121 (30)	–	
4-Nitroaniline	138 (100)	–	108 (28)	92 (35)	139 (96)	109 (100)		138 (100)	121 (4)	–	
4-Nitrobenzonitrile	148 (70)	–	118 (10)	102 (100)	149 (30)	119 (100)	–	148 (85)	–	118 (50)	102 (5)
2-Methyl-6-nitroaniline	152 (100)	135 (10)	122 (5)	106 (35)	153 (100)	123 (25)	107 (6)	152 (100)	135 (10)	122 (<1)	–
4-Methyl-2-nitroaniline	152 (100)	135 (4)	122 (4)	106 (50)	153 (100)	123 (30)	107 (6)	152 (100)	–	–	–
5-Methyl-2-nitroaniline	152 (100)	135 (65)	122 (2)	106 (30)	n.d.[a]			152 (100)	135 (20)	–	–
2-Methyl-5-nitroaniline	152 (100)	–	122 (4)	106 (63)	153 (100)	123 (66)	107 (8)	152 (100)	135 (25)	122 (<0.5)	–
2-Methyl-4-nitroaniline	152 (100)	–	122 (30)	106 (30)	153 (100)	123 (73)	–	152 (100)	–	–	–
2-Methyl-3-nitroaniline	n.d.				153 (100)	123 (82)	107 (10)	152 (100)	135 (13)	–	–
2-Nitroanisole	153 (80)	136 (<1)	123 (36)	107 (5)	154 (100)	124 (90)	108 (4)	153 (100)	136 (10)	123 (2)	107 (2)

(Continued on p. 30)

TABLE IV *(continued)*

Compound	EI				PICI (CH_4)			NICI (CH_4)			
	M^+	M − OH	M − NO	M − NO_2	MH	MH − NO	MH − NO_2	M^-	M − OH	M − NO	M − NO_2
4-Nitroanisole	153 (100)	–	123 (30)	107 (10)	154 (95)	124 (100)	108 (6)	153 (100)	136 (2)	123 (8)	107 (12)
1-Chloro-2-nitrobenzene	157 (80)	–	127 (22)	111 (80)	158 (100)	128 (97)	–	157 (100)	140 (2)	127 (4)	–
1-Chloro-3-nitrobenzene	157 (73)	–	127 (7)	111 (100)	158 (100)	128 (78)	–	157 (100)	140 (5)	127 (<1)	–
1-Chloro-4-nitrobenzene	157 (94)	–	127 (35)	111 (93)	158 (68)	128 (100)	112 (2)	157 (100)	140 (5)	–	–
1,4-Dinitrobenzene	168 (100)	–	138 (1)	122 (26)	169 (75)	139 (28)	123 (30)	168 (100)	–	138 (50)	122 (12)
1,2-Dinitrobenzene	168 (100)	–	138 (2)	122 (2)	169 (100)	139 (7)	123 (11)	168 (100)	151 (2)	138 (95)	122 (20)
1,3-Dinitrobenzene	168 (100)	–	138 (2)	122 (30)	169 (100)	139 (11)	123 (14)	168 (100)	151 (5)	138 (68)	122 (6)
1,2-Dichloro-4-nitrobenzene	191 (95)	–	161 (60)	145 (70)	192 (71)	162 (100)	–	191 (100)	–	161 (30)	145 (2)
1,3-Dichloro-4-nitrobenzene	191 (98)	–	161 (30)	145 (100)	192 (73)	162 (100)	–	191 (100)	–	161 (2)	–
1,4-Dichloro-2-nitrobenzene	191 (100)	–	161 (6)	145 (95)	192 (100)	162 (100)	146 (12)	191 (100)	–	161 (50)	145 (10)
4-Chloro-2-nitrotoluene	171 (36)	154 (100)	141 (3)	125 (28)	172 (70)	142 (100)	126 (3)	171 (100)	154 (4)	141 (<1)	–
5-Chloro-2-nitrotoluene	171 (40)	154 (100)	141 (1)	125 (30)	172 (100)	142 (85)	126 (5)	171 (100)	154 (4)	141 (1)	–
6-Chloro-2-nitrotoluene	171 (36)	154 (100)	141 (1)	125 (30)	172 (100)	142 (80)	126 (3)	171 (100)	154 (4)	141 (1)	– –
2-Chloro-4-nitrotoluene	171 (100)	–	141 (18)	125 (80)	172 (100)	142 (60)	–	171 (100)	154 (5)	–	–

2,4-Dinitrotoluene	182 (12)	165 (100)	–	136 (1)	183 (100)	153 (12)	137 (15)	182 (100)	165 (50)	152 (54)	136 (14)
3,4-Dinitrotoluene	182 (100)	–	152 (4)	136 (1)	183 (100)	153 (6)	137 (10)	182 (100)	–	152 (32)	136 (10)
2,6-Dinitrotoluene	182 (2)	165 (100)	–	136 (<1)	183 (100)	153 (22)	137 (20)	182 (100)	165 (35)	152 (85)	136 (20)
1-Nitronaphthalene	173 (80)	–	143 (12)	127 (100)	174 (70)	144 (100)	128 (2)	173 (100)	156 (2)	143 (<1)	–
2-Nitronaphthalene	173 (90)	–	143 (2)	127 (100)	174 (85)	144 (100)	128 (3)	173 (100)	–	–	–
1-Chloro-2,4-dinitrobenzene	202 (100)	–	172 (8)	156 (8)	203 (100)	173 (15)	157 (18)	202 (100)	185 (4)	172 (50)	156 (10)
2-Chloro-4-nitroaniline	172 (100)	155 (4)	142 (7)	126 (56)	173 (100)	143 (21)	127 (6)	172 (100)	155 (10)	142 (5)	126 (<1)
2,6-Dichloro-4-nitroaniline	206 (100)	–	176 (50)	160 (50)	207 (73)	177 (100)	161 (3)	207 (85)	190 (60)	–	–
4-Methoxy-2-nitroaniline	168 (100)	151 (1)	138 (1)	122 (40)	169 (100)	139 (42)	123 (10)	168 (100)	151 (25)	138 (2)	122 (1)
Parathion ethyl	291 (88)	–	261 (1)	–	292 (100)	262 (80)	–	291 (100)	274 (10)	–	–
1,3,5-Trinitrobenzene	213 (85)	–	–	167 (10)	214 (100)	–	–	213 (100)	–	183 (50)	167 (12)
2,4,6-Trinitrotoluene	227 (–)	210 (100)	197 (<1)	–	228 (100)	198 (5)	–	227 (100)	210 (36)	197 (42)	181 (10)
3-Nitrophenol	139 (100)	–	109 (2)	93 (50)	140 (100)	110 (20)		139 (100)	122 (30)	109 (6)	
2-Nitrophenol	139 (100)	122 (5)	109 (12)	93 (10)	140 (100)	110 (11)		139 (100)	122 (20)	109 (8)	
2-Methyl-3-nitrophenol	n.d.				154 (100)	124 (21)	108 (10)	153 (100)		123 (4)	
3-Methyl-6-nitrophenol	153 (100)	136 (4)	123 (20)	107 (5)	154 (100)	124 (12)	108 (5)	153 (100)	136 (35)	123 (8)	–
2,2′-Dinitrobiphenyl	244 (–)	–	–	198 (100)	245 (100)	–	199 (12)	244 (90)	227 (20)	214 (40)	198 (100)

[a] n.d. = not detected.

TABLE V

MASS SPECTROMETRIC DETECTION LIMITS (SIGNAL-TO-NOISE RATIO = 3) (pg)

Compound	EI (full scan)	EI (SIM[a])	PICI (isobutane)	NICI (methane)	NICI (argon)	NICE–SIM[a] (methane)	NICI–SIM[a] (argon)	NICI–SIM[b] (methane)
2-Nitrotoluene	21	7	44	3	2	0.6	0.3	n.d.
Nitrobenzene	43	4	206	2	3	0.3	0.3	n.d.
2,6-Dinitrotoluene	47	4	n.d.[c]	0.4	1	0.2	0.2	0.05
1,2-Dinitrobenzene	152	6	660	3	2	0.3	0.8	n.d.
2-Nitronaphthalene	32	17	7800	1	2	0.5	0.7	n.d.

[a] Ten masses are monitored.
[b] One mass is monitored.
[c] n.d. = not determined.

be one order of magnitude lower on modern sector field instuments. Whereas under full scan EI conditions an average detection limit of *ca.* 60 pg is achieved, the detection limit is higher by a factor of 2–200 under PICI conditions (isobutane). On the other hand, a substantial improvement in the detection limit is achieved under full-scan NICI conditions, ranging from 1 to 3 pg. Selective ion monitoring (SIM) using time windows with ten masses lowers the detection limit to below 1 pg, and a single mass can be monitored even at 0.05 pg.

If water samples are analysed for nitroaromatics by mass spectrometry, EI in general will be the method of choice as under these conditions abundant structure-specific fragments are formed and library searches can be carried out. NICI has the advantage of an at least ten times higher sensitivity and a substantially higher selectivity than EI and should be preferentially applied when traces of nitroaromatic compounds are to be determined in a complex aqueous mixture.

Extraction

Four different methods for the extraction of nitroaromatics from water were compared, *viz.*, discontinuous liquid–liquid extraction with dichloromethane, continuous liquid-liquid extraction with dichloromethane, solid-phase extraction with XAD resins and solid-phase extraction with octadecyl-, phenyl- and cyano-bonded phases. Moreover, the influence of different pH values and salt additions (sodium chloride) was studied. The most important results for the recovery of fifteen compounds are summarized in Table VI. The complete data are available on request.

The classical discontinuous extraction (separation funnel) with dichloromethane leads to good recoveries [$>78\%$, relative standard deviation (R.S.D.) $<11\%$]. Lowering the pH to 2.5 or increasing the salt content to 10 g/l NaCl does not influence the recoveries significantly. If the compounds are present in the sample at concentrations as low as 0.05 μg/l, they can still be recovered to a large extent ($>70\%$) although with higher R.S.D. Surprisingly, continuous extraction with dichloromethane for 5 h leads to poorer recoveries. The recovery of 2-nitrophenol is poor with both methods (46–49%). Poor recoveries were also observed for other nitrophenols.

Adsorption of nitroaromatic compounds on Amberlite XAD-2 and -4 resins leads to good recoveries ($>80\%$, R.S.D. $<7\%$) except for 2-nitrophenol (36%) and 2,4-dinitroaniline (58%). The recovery can even be enhanced for some compounds by using XAD-8. Solid-phase extraction (elution with dichloromethane) with phenyl- or octadecyl-bonded phases leads to recoveries that vary strongly from compound to compound. Although the recoveries are better with octadecyl- than phenyl-bonded phases (leading also to lower R.S.D.s), there are several compounds with unacceptably low recoveries, such as nitrobenzene, 2-nitroaniline and 1,2-dinitrobenzene. The recoveries are even poorer with cyano-bonded phases. Elution with other solvents such as methanol or diethyl ether does not improve the recovery. The poor recoveries observed for solid-phase extraction with phenyl- and octadecyl-bonded phases may be at least partially due to irreversible adsorption on the phase. If, after use, the C_{18} phase is extracted for 8 h with methanol in a Soxhlet the compounds with poor recovery can be obtained, although not quantitatively.

For the determination of the detection limit of the method, 1 l of water was spiked with 5, 50 or 500 ng/l of seventeen nitroaromatic compounds, extracted by adsorption with XAD-2 and -4 resins (1:1) and analysed by GC with ECD and TEA. If ECD is employed nitroaromatics can be determined at a concentration of 50 ng/l with recoveries comparable to those in Table VI and R.S.D. <9%. At 5 ng/l the R.S.D. rises to 10–30%. Similarly, nitroaromatic compounds can be detected with TEA with low R.S.D. (<10%) at a concentration of 500 ng/l, whereas 50 ng/l the R.S.D. rises to 10–30%. In favourable cases, detection at a level of 10 ng/l is possible. Thus, if the TEA detector is used the detection limit of the method is about one order of magnitude higher than if ECD is used. The relatively poor detection limit of the latter method is due to a substantial increase in the noise if a water sample is analysed.

Although TEA is less sensitive than ECD, compound assignment is more reliable as TEA is much more specific for nitroaromatic compounds than ECD (see below).

Analysis of surface water

A variety of surface waters were analysed for nitroaromatic compounds. Some results are reported below and additional data are available on request. The nitroaromatic compounds were extracted with Amberlite XAD-2, -4 and -8 resins (1:1:1). 1-Chloro-2,4-dinitrobenzene and 2,2′-dinitrobiphenyl were added as internal standards. The samples were chromatographed on both DB-17 and OV-225 columns. If

TABLE VI

RECOVERIES FOR THE EXTRACTION OF NITROAROMATIC COMPOUNDS FROM WATER[a]

Compound	Liquid–liquid extraction (continuous)[b]		Liquid–liquid extraction (discontinuous)[c]	
	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
Nitrobenzene	84	4	61	12
2-Nitrophenol	46	17	49	10
3-Nitrotoluene	83	3	77	6
1-Chloro-3-nitrobenzene	n.d.[e]		n.d.	
6-Chloro-2-nitrotoluene	78	6	66	11
1,4-Dichloro-2-nitrobenzene	97	5	86	5
4-Nitroanisole	94	9	82	3
2-Nitroaniline	91	7	74	8
1,2-Dinitrobenzene	93	5	78	4
1-Nitronaphthalene	92	5	78	6
4-Chloro-2-nitroaniline	105	6	89	3
Parathion ethyl	104	6	91	4
2,4-Dinitroaniline	94	11	55	9
2,4,6-Trinitrotoluene	n.d.		n.d.	
1-Chloro-2,4-dinitrobenzene	110	5	104	4

[a] Means of three determinations (relative to 2,2′-dinitrobiphenyl as internal standard, 2 μg/l per compound).

[b] pH 7.6 + 1 g/l NaCl.

[c] pH 7.6 + 0.5 g/l NaCl.

[d] pH 7.

[e] n.d. = not determined.

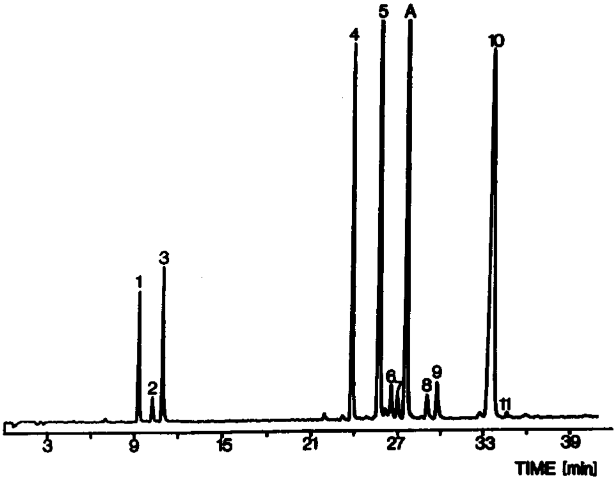

Fig. 4. Gas chromatogram (TEA) of a water sample taken from a brook near Hirschhagen/Waldhof (Hessia, F.R.G.). For peak assignment, see Table VII.

the retention times of unknown compounds coincide with those of reference compounds, the identification should be reliable, particularly if TEA is used.

Fig. 4 presents the chromatogram (obtained with TEA and a DB-5 column) of a

XAD-2/4^d		XAD-8^d		Phenyl^d		C_{18}^{d}	
Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
93	3	97	5	7	30	18	15
36	10	<1		<1		<1	
86	3	112	13	27	23	78	15
86	7	105	8	21	16	72	10
100	3	98	4	69	11	94	4
110	1	96	5	58	3	92	3
96	3	109	7	65	5	67	4
86	2	90	4	<1		16	3
80	5	89	5	13	18	23	7
85	4	99	3	100	5	104	4
97	3	91	6	25	14	74	9
96	5	109	8	80	11	103	7
58	20	88	4	<1		62	4
95	7	n.d.		n.d.		n.d.	
102	4	99	1	107	–	104	–

sample taken from a brook near Hirschagen/Waldhof (Hessia, F.R.G.) which rises in an area where ammunition was produced in World War II. The chromatogram reveals the presence of nitrotoluenes, dinitrotoluenes, trinitrotoluene and also several methylnitroanilines. While the former compounds are the direct remains of the ammunition production which was terminated over 45 years ago, the latter compounds are probably biodegradation products. The compound assignment was corroborated by running the sample on an OV-225 column. As the brook is contaminated by relatively few compounds, analysis can be achieved reliably using ECD.

The brook is highly polluted by nitroaromatic compounds. Trinitrotoluene has been observed at a concentration of 19 μg/l. High concentrations of nitroaromatics were also found in a second brook nearby and in the river Losse, into which these brooks flow. The quantitative results are summarized in Table VII. Results obtained with ECD and TEA usually agree to within ± 10%. As mentioned above, TEA leads to substantial peak broadening at higher retention times, so that this part of the chromatogram could not be used to identify compounds unequivocally. Thus, in combination with GC–MS (both EI and NICI), 2,6-dinitro-4-aminotoluene and 2,6-diamino-4-nitrotoluene could be identified.

Nitroaromatic compounds were also detected in two ponds (1–10 m in depth) (Pfauenteiche) near Clausthal-Zellerfeld (Lower Saxony, F.R.G.), which again are located near a former ammunition plant closed after World War II. Fig. 5 shows the chromatogram obtained with the TEA detector for one of these ponds (Unterer Pfauenteich). In contrast to the sample in Fig. 4, where dinitrotoluenes and trinitrotoluene dominated, mononitrotoluenes were more abundant in this sample. 2-Nitrotoluene was found at a concentration of 22 μg/l. Again, several methylnitroanilines were observed, which are probably biodegradation products. Small amounts of dinitrotoluenes were also found in the river Oder near Bad Lauterbach. The concentrations were near the detection limit (TEA). Table VIII summarizes these results. In addition, with GC–MS 2,6-diamino-4-nitrotoluene and 2,6-dinitro-4-aminotoluene were identified.

TABLE VII

CONCENTRATIONS OF NITROAROMATIC COMPOUNDS IN TWO BROOKS AND THE RIVER LOSSE NEAR HIRSCHAGEN/WALDHOF

No.	Compound	Concentration (μg/l)		
		Brook I	Brook II	River Losse
1	2-Nitrotoluene	7.4	0.4	1.2
2	3-Nitrotoluene	0.9	0.1	0.1
3	4-Nitrotoluene	4.5	0.3	0.4
4	2,6-Dinitrotoluene	7.6	4.1	0.1
5	2,4-Dinitrotoluene	13.0	3.1	0.5
6	5-Methyl-2-nitroaniline	6.7	3.5	0.2
7	2-Methyl-3-nitroaniline	2.5	0.5	<0.03
8	3,4-Dinitrotoluene	0.8	0.5	<0.03
9	2-Methyl-5-nitroaniline	1.2	0.3	0.3
10	2,4,6-Trinitrotoluene	19.0	12.0	0.7
11	2-Methyl-4-nitroaniline	0.4	0.1	0.1

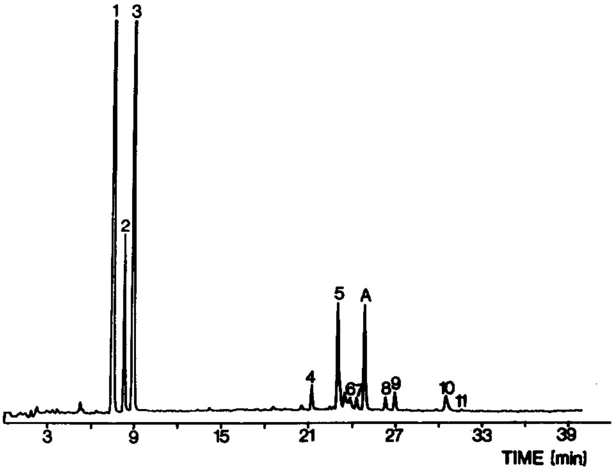

Fig. 5. Gas chromatogram (TEA) of a water sample taken form a pond near Clausthal-Zellerfeld (Lower Saxony, F.R.G.). For peak assignment, see Table VII.

Samples from several rivers in F.R.G. were analysed for nitroaromatic compounds. Fig. 6 compares the chromatograms of a sample from the Elbe (near Lauenburg) obtained using ECD (top) and TEA (bottom) on a DB-5 column. A variety of nitroaromatic compounds can be identified. Table IX summerizes the quantitative results. Compound assignment was again verified by running the sample on a second column (OV-225). As the river Elbe is a highly polluted surface water which contains many ECD-sensitive compounds, compound assignment and quantification based on the ECD chromatogram alone is not reliable. With ECD, a five times higher concentration of 2-nitrotoluene (as compared with TEA) was determined in this sample. In

TABLE VIII

CONCENTRATIONS OF NITROAROMATIC COMPOUNDS IN TWO PONDS AND THE RIVER ODER (HARZ)

No.	Compound	Concentration (μg/l)		
		Unterer Pfauenteich	Mittlerer Pfauenteich	River Oder
1	2-Nitrotoluene	22.0	0.4	<0.01
2	3-Nitrotoluene	1.5	0.1	<0.01
3	4-Nitrotoluene	4.8	0.2	<0.01
4	2,6-Dinitrotoluene	0.3	0.07	0.02
5	2,4-Dinitrotoluene	1.2	0.8	0.02
6	5-Methyl-2-nitroaniline	0.8	0.5	<0.01
7	2-Methyl-3-nitroaniline	0.7	0.1	<0.01
8	3,4-Dinitrotoluene	0.1	0.1	<0.01
9	2-Methyl-5-nitroaniline	0.2	0.2	<0.01
10	2,4,6-Trinitrotoluene	0.5	0.5	<0.01
11	2-Methyl-4-nitroaniline	<0.01	<0.01	<0.01

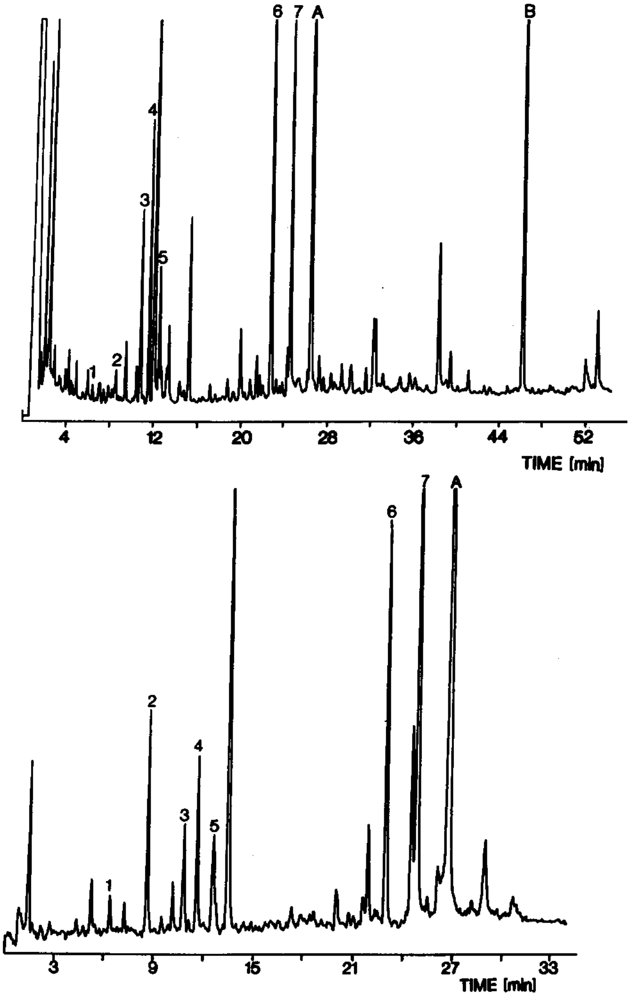

Fig. 6. Gas chromatogram of a water sample taken from the Elbe near Lauenburg (top, ECD; bottom, TEA). For peak assignment, see Table IX.

TABLE IX

CONCENTRATIONS OF NITROAROMATIC COMPOUNDS IN THE RIVER ELBE AT THREE LOCATIONS

No.	Compound	Concentration (μg/l)		
		Lauenburg	Brokdorf	Brunsbüttel
1	Nitrobenzene	0.1	0.03	0.02
2	2-Nitrotoluene	0.4	0.08	0.05
3	1-Chloro-3-nitrobenzene	0.2	0.04	<0.02
4	1-Chloro-4-nitrobenzene	0.3	0.1	0.04
5	1-Chloro-2-nitrobenzene	0.2	0.1	0.04
6	2,6-Dinitrotoluene	0.5	0.08	0.04
7	2,4-Dinitrotoluene	1.3	0.3	0.1

contrast, the much higher selectivity of the TEA detector allows a safe assignment of nitroaromatic compounds if reference compounds are available (The TEA chromatogram in Fig. 6 reveals the presence of an additional major unknown compound for which a reference compound was not available). With GC–MS the results in Table IX could also be corroborated.

CONCLUSIONS

Nitroaromatic compounds can be extracted from aqueous samples with high recoveries by liquid–liquid extraction with dichloromethane or by adsorption on Amberlite resins, while lower and strongly varying recoveries are found if solid-phase extraction with phenyl-, octadecyl- or cyano-bonded phases is employed. As a result of their high electron affinities, nitroaromatic compounds can be determined with high sensitivity by GC using ECD. If, however, highly polluted surface water is to be investigated, ECD is not sufficiently selective for an unambiguous compound assignment. In contrast, a chemiluminescence detector (TEA) is much more selective for nitro compounds, allowing a reliable peak assignment if reference compounds are available. The major disadvantage of the chemiluminescence detector is its lower sensitivity (compared with the electron capture detector), which precludes the analysis of weakly polluted water. Definite compound assignment can usually be achieved with GC–MS, where NICI is more sensitive and selective than EI, but gives fewer structure-specific fragments.

Some nitrophenols have also been studied. However, the analysis has not been optimized for this specific class of compounds, for which poor recoveries were observed with extraction as described above.

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