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Gas chromatographic determination of aromatic amines in water samples after solid-phase extraction and derivatization with iodine II. Enrichment

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Abstract

A procedure for the enrichment of aromatic amines via solid-phase extraction was developed. A HR-P phase based on styrene–divinylbenzene was used for the investigations, generally followed by derivatization with iodine and determination via GC–ECD. The recoveries of 53 aromatic amines in a drinking water matrix at pH 9 were determined. Most anilines showed relative recoveries between 80–120% with relative standard deviations of ≤5% at concentration levels between 10 and 20 μg l^{-1}. The comparison with a wastewater matrix led to similar results. The enrichment procedure was applied to real samples, e.g., samples of ammunition wastewater. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Solid-phase extraction; Sample preparation; Water analysis; Environmental analysis; Amines, aromatic

1. Introduction

Due to their high polarity and the corresponding high solubility in water the extraction of aromatic amines from water samples is difficult. In the past the enrichment of aminoaromatic compounds was performed by liquid–liquid extraction (LLE) using different solvents. Dichloromethane [1,2] as well as toluene [3] or isooctane [4] were used, but large volumes of solvent are necessary to reach sufficient recoveries. In each case the removal of solvent in a time and energy consuming step is necessary. In recent years LLE is increasingly replaced by solid-phase extraction (SPE) [5–7]. The advantages of SPE are the reduction of solvent requirement, the removal of matrix components and the facilitation of automation [8–10]. The enrichment of aromatic amines is possible on nonpolar solid phases at basic pH values. For this purpose, solid phases based on styrene–divinylbenzene copolymers, introduced by Junk et al. in 1974 [11], seemed especially promising because of their higher capacities and pH stability in comparison with common C_{18} phases. Some recent investigations describe the enrichment of a limited number of relatively nonpolar chloroanilines [12–14] as important degradation products of pesticides, others the enrichment of polar diamino- and amino-nitro compounds [15–19]. The use of these resins for the enrichment of nitroaromatic explosives was also shown [20].

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Our intention was the optimisation and investigation of the enrichment of aromatic amines via SPE using solid phases based on styrene–divinylbenzene copolymers. For the application of a method to real samples it is necessary to know if the influence of the matrix may falsify the results of a quantitative determination. Therefore the relative recoveries of the tested aromatic amines are determined in a drinking water matrix and in a wastewater matrix.

2. Experimental

2.1. Samples

Real water samples were taken from the drain of a waste disposal site and wells at the former ammunition plant Stadtallendorf, Hessen, Germany. The samples were stored at 4°C in brown glass bottles and analysed within four weeks. No differences in results were observed when determining the contents of aromatic amines after this period of time.

2.2. Chemicals and reagents

Reference substances were obtained from various suppliers [Aldrich (Steinheim, Germany), Fluka (Neu-Ulm, Germany), Merck (Darmstadt, Germany), Promochem (Wesel, Germany) and Riedel-de Haën (Seelze, Germany)] in the highest purity available. The compounds, their CAS numbers and the abbreviations used throughout the text are given in Table 1.

Pentane, amidosulfonic acid and hydrochloric acid were purchased from Riedel-de Haën, hydriodic acid from Aldrich, sodium sulphite, sodium nitrite, sodium hydroxide, phosphoric acid, potassium iodide, iodine, potassium dihydrogenphosphate and dipotassium hydrogenphosphate from Merck. The methanol (Baker) and water (Baker) used were HPLC grade.

Table 1
Aromatic amines used in this study with abbreviations and CAS Nos.

Compound	Abbreviation	CAS No.	Compound	Abbreviation	CAS No.
Aniline	–	62-53-3	4-Amino-2,6-dinitrotoluene	4A2,6DNT	19406-51-0
2-Nitroaniline	2NA	88-74-4	2,4-Diamino-6-nitrotoluene	2,4DA6NT	6629-29-4
3-Nitroaniline	3NA	99-09-2	2,6-Diamino-4-nitrotoluene	2,6DA4NT	59229-75-3
4-Nitroaniline	4NA	100-01-6	2,3-Dimethylaniline	23DMA	87-59-2
2,4-Dinitroaniline	2,4DNA	97-02-9	2,4-Dimethylaniline	24DMA	95-68-1
2,5-Dinitroaniline	2,5DNA	619-18-1	2,5-Dimethylaniline	25DMA	95-78-3
2,6-Dinitroaniline	2,6DNA	606-22-4	2,6-Dimethylaniline	26DMA	87-62-7
3,5-Dinitroaniline	3,5DNA	618-87-1	3,4-Dimethylaniline	34DMA	95-64-7
1,2-Phenylenediamine	1,2PDA	95-54-4	3,5-Dimethylaniline	35DMA	108-69-0
1,3-Phenylenediamine	1,3PDA	108-45-2	2,6-Diethylaniline	26DEA	579-66-8
1,4-Phenylenediamine	1,4PDA	106-50-3	2-Ethyl-6-methylaniline	2E6MA	24549-06-2
2-Methoxyaniline	2MOA	90-04-0	4-Isopropylaniline	4IPA	99-88-7
3-Methoxyaniline	3MOA	536-90-3	2-Aminobiphenyl	2ABP	90-41-5
4-Methoxyaniline	4MOA	104-94-9	4-Aminobiphenyl	4ABP	92-67-1
2-Aminotoluene	2AT	95-53-4	1-Naphthylamine	1NphA	137-32-7
3-Aminotoluene	3AT	108-44-1	2-Naphthylamine	2NphA	91-59-8
4-Aminotoluene	4AT	106-49-0	Benzidine	–	92-87-5
2,3-Diaminotoluene	2,3DAT	2687-25-4	4-Chloro-*N*-methylaniline	4CNMA	932-96-7
2,4-Diaminotoluene	2,4DAT	95-80-7	2-Chloroaniline	2CA	95-51-2
2,6-Diaminotoluene	2,6DAT	823-40-5	3-Chloroaniline	3CA	108-42-9
3,4-Diaminotoluene	3,4DAT	496-72-0	4-Chloroaniline	4CA	106-47-8
2-Amino-3-nitrotoluene	2A3NT	570-24-1	3,4-Dichloroaniline	3,4DCA	95-76-1
2-Amino-4-nitrotoluene	2A4NT	99-95-8	3-Chloro-4-methylaniline	3C4MA	95-74-9
2-Amino-5-nitrotoluene	2A5NT	99-52-5	3-Chloro-4-methoxyaniline	3C4MOA	5345-54-0
2-Amino-6-nitrotoluene	2A6NT	603-83-8	4-Chloro-2-methylaniline	4C2MA	95-69-2
4-Amino-2-nitrotoluene	4A2NT	119-32-4	4-Bromoaniline	4BrA	106-40-1
2-Amino-4,6-dinitrotoluene	2A4,6DNT	35572-78-2			

2.3. Sample preparation and enrichment procedure

Immediately before measurements, the samples were adjusted to about pH 9 with a concentrated sodium hydroxide solution (10 mol l^{-1} in water). If necessary, the sample was filtered through 0.45-μm cellulose nitrate membrane filters (Sartorius, Göttingen, Germany). A 100-ml volume of sample was filled in measuring cylinders for the subsequent enrichment step.

Polystyrene–divinylbenzene was used as the solid phase for extraction. Routinely used was HR-P phase from Macherey–Nagel (Düren, Germany) with a surface of 1300 m^2 g^{-1}. For comparison of suitable solid-phase materials of other suppliers [LiChrolut EN (Merck), Bond Elut ENV (Varian, Darmstadt, Germany), SDB 1 (Mallinckrodt–Baker, Griesheim, Germany), Restek Polymer (Restek, Sulzbach, Germany), Isolute ENV+ (ICT, Bad Homburg, Germany) and Envichrome P (Supelco, Deisenhofen, Germany)] were used.

Prefilled 3-ml polypropylene cartridges with 200 mg of each solid phase, which was kept between two polyethylene frits, were used for all extractions. For the HR-P phase used in most experiments batch-to-batch differences were not measurable, thus self-filling of cartridges with bulk material of one batch was not necessary.

The solid phase was conditioned on a vacuum manifold from Mallinckrodt–Baker two times with 1 ml of methanol and two times with 1 ml of acetonitrile, which was allowed to pass through the cartridge without the use of vacuum. Afterwards the cartridges were washed with two times 1 ml of distilled water, adjusted to pH 9, filled with 2 ml of water and connected to a peristaltic pump. Large-volume-samplers from Supelco, consisting of a 1/8 in. (1 in.=2.54 cm) PTFE tubing with a stainless steel mass on the sample side and a polypropylene adapter on the cartridge side, were used to connect samples and cartridges. Prefilling of the cartridges with water was necessary to prevent the solid phases from running dry when the pump was started. The pump rate was set to 60, which corresponds to a flow-rate of 10±0.2 ml min^{-1}.

Following sample application, the cartridges were washed with 2 ml of distilled water and then placed on the vacuum manifold again and dried under vacuum for 5 min. Elution was carried out three times with 1 ml methanol–acetonitrile (1:1, v/v), which was again allowed to pass through the cartridge without the use of vacuum. Between each addition of eluting solvent, the phases were dried for 10 s with the use of vacuum. The extracts were combined for the subsequent derivatization in 24-ml borosilicate glass vials and reduced in volume under a gentle stream of nitrogen at 40°C to less than 0.5 ml (exact measurement of the volume was not necessary).

2.4. Derivatization

To the extract 5 ml of water were added and the solution acidified with 0.2 ml of hydriodic acid. The solution was mixed with 0.5 ml sodium nitrite in water (10 g l^{-1}) and shaken. After a reaction time of 20 min, 1 ml amidosulfonic acid in water (50 g l^{-1}) was added to destroy the surplus of nitrite and the mixture was vigorously shaken for 45 min. The solution was heated for 5 min in a water bath, temperature 100°C, and afterwards cooled down in water to room temperature. The surplus of iodine was destroyed with 0.25 ml of a saturated aqueous solution of sodium sulphite. The solution was basified with 0.5 ml of a 10 mol l^{-1} sodium hydroxide solution and extracted for 15 min with 2 ml of pentane. During the extraction the vials were mechanically shaken with a SM shaker from Bühler. GC–electron-capture detection (ECD) or GC–MS analysis was carried out on aliquots of the extracts which had been filled in autosampler vials.

2.5. Gas chromatography

The GC system consisted of a gas chromatograph HP 5890 II+ and an autosampler unit HP 7673 (both from Hewlett-Packard, Waldbronn, Germany), equipped with an ECD system and a split/splitless injector. Control of the equipment and data acquisition was done with the personal computer program Gynkosoft V 5.32 (Gynkotek, Germering, Germany). Carrier gas was nitrogen, which was further purified using a Megasorb reactor by Messer-Griesheim (Frankfurt, Germany). The column pressure was set to 100 kPa. The temperatures of the injection block and the detector were 250 and 300°C, respectively.

Table 2
Comparison of various solvents for the use as elution agent

Substance	Elution with	Cumulative recovery (% after)			
		1st elution	2nd elution	3rd elution	4th elution
2AT	Methanol	16	52	91	100
	Acetonitrile	70	99	100	100
	Acetonitrile–methanol (1:1, v/v)	52	89	97	100
	Methanol–acetic acid (9:1, v/v)	10	59	93	100
2A6NT	Methanol	33	72	93	98
	Acetonitrile	73	100	100	100
	Acetonitrile–methanol (1:1, v/v)	54	89	99	100
	Methanol–acetic acid (9:1, v/v)	35	76	90	96
2A4NT	Methanol	24	59	86	97
	Acetonitrile	71	98	100	100
	Acetonitrile–methanol (1:1, v/v)	57	86	98	100
	Methanol–acetic acid (9:1, v/v)	31	72	87	95
4A2,6DNT	Methanol	24	63	92	99
	Acetonitrile	69	100	100	100
	Acetonitrile–methanol (1:1, v/v)	59	97	100	100
	Methanol–acetic acid (9:1, v/v)	17	65	86	95
2A4,6DNT	Methanol	15	39	74	93
	Acetonitrile	53	100	100	100
	Acetonitrile–methanol (1:1, v/v)	50	94	100	100
	Methanol–acetic acid (9:1, v/v)	13	49	82	95

The injection volume was 1 μl. For the separation of the analytes a (5%-phenyl)-methylpolysiloxane column, 30 m×0.25 mm I.D., 0.25 μm d_f (DB5 from J&W, Köln, Germany) was used. The separation was started at an oven temperature of 135°C. After 21.5 min the temperature was raised using a rate of 12.5°C min^{-1} to 235°C and then held for another 8.5 min.

2.6. High-performance liquid chromatography (HPLC)

The HPLC analyses were performed with the following HPLC equipment: M 480 pump, on-line degasser GT-103, auto sampler GINA 50 and diode array detector UVD 340-S (all Gynkotek). A RP-18 column (25 cm×3 mm I.D.) was used for separations. The column temperature was 30°C, the flow-rate was 0.5 ml min^{-1}. For the separation of the standard mixtures a methanol–buffer (pH 6.4) gradient was used. The buffer was a solution of 15 mmol potassium dihydrogenphosphate and 15 mmol dipotassium hydrogenphosphate in 1 l of deionized water. After 10 min in an ultrasonic bath the solution was filtered through a 0.45-μm cellulose nitrate membrane filter. The elution started with 20% methanol and was linearly shifted to 80% in 40 min followed by a 10 min isocratic run and 15 min of equilibration. The eluates of the solid phases were diluted (1:5) with reagent water and 50 μl injected.

3. Results and discussion

3.1. Choice of eluting solvent

Methanol, methanol–acetic acid (9:1, v/v), acetonitrile and methanol–acetonitrile (1:1, v/v) were tested as elution agents. To include possible matrix interferences, leachate water with a high content of total organic carbon (around 30 mg/l) was used in these experiments. Ten ml of the water were extracted as described above. 5×1 ml of each solvent were used for the elution of the analytes. Each ml

was separately collected, derivatized and analysed via GC–ECD.

The analytes occurring in the sample and their measured values are given in Table 2. It can be seen that acetonitrile and methanol–acetonitrile (1:1, v/v) give the best results. The main part of analytes was eluted in the first two fractions. Three ml of solvent are sufficient for the complete elution of the analytes. With methanol and methanol–acetic acid (9:1, v/v) at least 4 ml of solvent were necessary to elute the main part of amines. It was tested if 3 ml of eluting solvent would influence the following derivatization. Therefore three identical standard mixtures were derivatized: the first one without addition of solvent, the second with addition of 3 ml acetonitrile and the third with addition of 3 ml methanol–acetonitrile (1:1, v/v). In Fig. 1 the measured values of 4-amino-2,6-dinitrotoluene are shown as an example. The use of acetonitrile as eluting solvent showed a higher influence on the derivatization than methanol–acetonitrile (1:1, v/v). Therefore methanol–acetonitrile was chosen as eluting agent and the eluates were concentrated to ≤0.5 ml before derivatization. Due to losses of volatile analytes the complete evaporation of solvent was not possible.

3.2. Variation of pH

During the first investigations the water samples were adjusted to pH 12 before extraction. The adjustment of real samples to pH 12 led to colloid precipitates, which had to be filtered through a membrane filter. The filtration was time consuming because the filter was rapidly clogged and had to be replaced several times for the enrichment of higher sample volumes. Therefore we investigated if the enrichment at lower pH values would lead to the same results. A mixture of the standard solutions of 25 aromatic amines was prepared (concentrations between 1–5 μg ml^{-1}). A 1-ml volume of this mixture was filled up to 100 ml with wastewater from a well of the former ammunition plant in Stadtallendorf. The obtained water sample was adjusted to pH 12 and extracted as described. The enrichment at pH 10 and 9 was carried out in the same way. The eluates were derivatized and analysed via GC–ECD. The measured values are shown in Table 3.

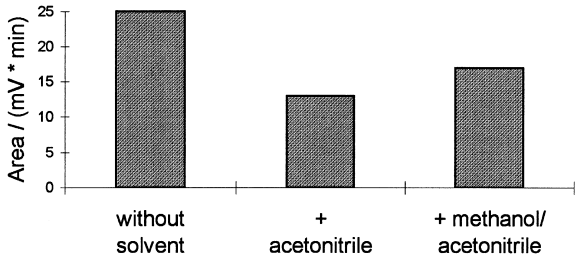

Fig. 1. Influence of eluting solvent on the derivatization of amines, comparison of measured values of 4A2,6DNT after derivatization with and without addition of 3 ml solvent followed by determination with GC–ECD.

For most of the analytes no significant differences of the measured values were found at the different pH values. The advantage of adjustment to pH 9 was that no formation of colloid precipitates was observed and therefore filtration of the samples was not necessary. So the enrichment at pH 9 was chosen for our further studies.

3.3. Relative recoveries with different matrices

The relative recoveries of the 53 aromatic amines were determined in a drinking water matrix (see Table 4). Three mixtures of standard solutions were prepared since it was not possible to separate all compounds in one GC run. One of the standard mixtures (standard mix 1) contained 33 aromatic amines, which could be separated in one GC run after derivatization using the described temperature program (see Part I [21]). Three aliquots of each mixture were filled up to 100 ml with drinking water and extracted as described (concentrations between 10–20 μg l^{-1}). The analytes were subsequently derivatized and analysed by GC–ECD. The measured values were compared with values of derivatized aliquots of the mixtures without prior dilution and extraction. The relative recoveries obtained are listed in Table 4.

Most of the relative recoveries were between 80–120%. Some substances showed higher values up to 303% (2,5DMA). Ten amines had relative recoveries <80%. The relative standard deviations (R.S.D.s) were between 1–9%, for most compounds ≤6%. 1,4-Phenylenediamine could not be recovered at all.

To compare the relative recoveries of the analytes

Table 3
Peak areas after enrichment at different pH values followed by derivatization and determination with GC–ECD

Compound	Area (mV min)			Ratio	
	Mean pH 12 (R.S.D., %)	Mean pH 10 (R.S.D., %)	Mean pH 9[a]	pH 9/pH 12 (%)	pH 10/pH 12 (%)
Aniline	0.85 (17)	0.79 (8)	0.75	88	93
4AT	0.54 (15)	0.49 (7)	0.48	89	91
4CNMA	0.17 (12)	0.16 (5)	0.16	97	98
3,5DMA	0.29 (14)	0.29 (9)	0.28	98	99
2,6DMA	0.61 (15)	0.61 (9)	0.58	95	100
3,4DMA	0.23 (14)	0.22 (7)	0.23	99	93
4IPA	0.54 (13)	0.51 (8)	0.52	96	94
6E2MA	0.63 (14)	0.63 (8)	0.62	98	99
2,6DEA	0.62 (12)	0.61 (7)	0.64	103	98
1,3PDA	0.22 (9.0)	0.16 (3)	0.19	87	72
3NA	1.42 (4.0)	1.52 (4)	1.55	110	107
4NA	1.99 (3.0)	2.19 (5)	2.23	112	110
2A6NT	1.81 (4.0)	1.91 (4)	1.95	108	106
4A2NT	1.32 (3.0)	1.39 (4)	1.45	110	105
2,4-DT	1.52 (10)	1.23 (1)	1.45	96	81
2,6DAT	1.51 (10)	1.36 (2)	1.54	102	90
2A4NT	1.61 (3)	1.71 (4)	1.75	108	106
2NphA	1.25 (4)	1.27 (4)	1.38	110	101
1NphA	1.27 (5)	1.28 (5)	1.45	115	101
2,6DNA	0.42 (6)	0.52 (8)	0.54	130	123
4A2,6DNT	1.79 (4)	2.11 (5)	2.09	117	118
2A4,6DNT	0.94 (7)	1.39 (5)	1.41	149	147
2,4DA6NT	1.29 (3)	1.06 (7)	1.44	112	82
2,6DA4NT	0.95 (3)	1.00 (7)	1.03	109	105
Benzidine	1.77 (2)	1.69 (7)	1.98	112	95

[a] No R.S.D. determined, only duplicate measurement.

in a drinking water sample with their relative recoveries in a real water sample, ammunition wastewater was chosen as the second matrix. The relative recoveries of the 33 amines in standard mixture 1 were determined in the same way as it was done with the drinking water matrix. The results are listed in Table 4. The relative recoveries of most of the analytes were between 80–120% with R.S.D.≤7%, mostly ≤4%. The relative recoveries of most of the amines were in approximately the same magnitude in both matrices. Amines that had shown relative recoveries >120% in drinking water had even higher values in the wastewater matrix and vice versa. A general trend of higher or lower relative recoveries in comparison with the drinking water matrix could not be recognised. The influence of matrix components is relatively small for most of the analytes.

The relative recoveries of some of the aromatic amines could not be determined in the mentioned way because the derivatization of these substances did not work (1,2PDA; 2,3DAT; 3,4DAT; 2,4 DNA; 2,5DNA) (see part I [21]). These amines and the analytes which had shown relative recoveries >120% were distributed to three standard mixtures. An aliquot of each mixture was filled up to 100 ml with drinking water (concentrations: 75 μg l^{-1}), adjusted to pH 9 and extracted as described. The eluates were diluted (1:5) with reagent water and analysed by HPLC. The results are listed in Table 5. The relative recoveries were in the range of 90–120% with R.S.D.<5%. The values of the analytes, which had shown relative recoveries >120% after derivatization (up to 303%) and analysis with GC–ECD, were much lower, when the relative recoveries were determined via HPLC without derivatization. The reasons for these differences are still not understood. The high relative recoveries can not be attributed to superposition of compounds that could

Table 4
Relative recoveries after enrichment of aromatic amines in two different matrices followed by derivatization and determination with GC–ECD

Compound	Relative recovery (%) (R.S.D., %)		Compound	Relative recovery (%) (R.S.D., %)	
	Matrix: d.w.	Matrix: w.w.		Matrix: d.w.	Matrix: w.w.
Aniline	80 (7)	83 (7)	2,4DAT	52 (5)	48 (2)
2AT	231 (5)	n.d.	2,6DAT	80 (7)	104 (3)
3AT	151 (3)	n.d.	2A46DNT	81 (8)	86 (3)
4AT	80 (3)	111 (6)	4A2,6DNT	89 (7)	73 (2)
4ClNMA	120 (1)	107 (3)	2,4DA6NT	95 (6)	104 (1)
2,3DMA	257 (5)	n.d.	2,6DA4NT	109 (6)	130 (2)
2,4DMA	107 (5)	n.d.	2MOA	135 (11)	n.d.
2,5DMA	303 (5)	n.d.	3MOA	92 (10)	n.d.
2,6DMA	111 (4)	148 (5)	4MOA	67 (10)	n.d.
3,4DMA	66 (4)	107 (6)	2,6DNA	60 (8)	75 (4)
3,5DMA	99 (5)	127 (4)	3,5DNA	83 (7)	97 (4)
6E2MA	179 (4)	230 (4)	1NphA	79 (5)	100 (4)
2,6DEA	253 (5)	322 (4)	2NphA	82 (5)	87 (4)
4IPA	116 (3)	144 (5)	2ABP	80 (6)	84 (2)
1,3PhDA	35 (1)	23 (4)	4ABP	94 (6)	95 (2)
1,4PhDA	–	–	Benzidine	69 (6)	58 (3)
2NA	76 (2)	n.d.	2CA	71 (4)	n.d.
3NA	89 (6)	85 (2)	3CA	71 (4)	n.d.
4NA	97 (6)	100 (3)	4CA	85 (5)	n.d.
2A3NT	80 (9)	126 (2)	3,4DCA	100 (3)	89 (5)
2A4NT	91 (5)	91 (2)	3C4MA	94 (4)	n.d.
2A5NT	90 (6)	90 (2)	3C4MOA	106 (5)	91 (3)
2A6NT	88 (9)	92 (2)	4C2MA	144 (3)	134 (4)
4A2NT	84 (5)	60 (1)	4BrA	93 (6)	n.d.

d.w.=drinking water; w.w.=wastewater; n.d.=not determined.

Table 5
Relative recoveries of some amines after enrichment and determination via HPLC compared with relative recoveries after derivatization and determination via GC–ECD

Compound	Relative recovery (%) (R.S.D., %) (HPLC[a]), spike concentration: 75 μg l^{-1}	Relative recovery (%) (R.S.D., %) (GC–ECD[b]), spike concentration: 10–20 μg l^{-1}
1,2PDA	88 (4)	–
2,3DAT	96 (6)	–
3,4DAT	79 (4)	–
2,4DNA	118 (4)	–
2,5DNA	118 (5)	–
2,6DNA	100[c]	60 (8)
3,5DNA	117 (5)	83 (8)
2,3DMA	114 (5)	257 (5)
2,5DMA	107 (5)	303 (5)
2AT	115 (6)	231 (5)
3AT	93[c]	151 (3)
2E6MA	116 (4)	179 (4)
2,6DEA	115 (4)	253 (5)
4C2MA	115 (4)	144 (3)

[a] Analysis with HPLC.
[b] Analysis with GC–ECD after derivatization.
[c] No R.S.D. determined.

have been extracted out of the solid phase, because no signals are received after the enrichment of 100 ml of pure water. At the moment we suppose that the yield of derivatives of these amines is influenced in some way but the reason for this behaviour is still unclear. The enrichment and determination of these compounds is possible despite the high relative recoveries, because reproducible results are obtained for all analytes (see R.S.D.s in Table 4). However, HPLC might be used as an alternative separation method for the compounds with relative recoveries >120%.

3.4. Comparison of solid-phase materials of various suppliers

To compare the solid-phase materials of different suppliers the relative recoveries of 33 aromatic amines (standard mix 1) were tested. The used solid phases are mentioned in Section 2.3. All used materials were based on a styrene–divinylbenzene copolymer. The relative recoveries were determined as described. Two matrices were used: drinking water and wastewater. The results for the drinking water matrix are listed in Table 6. The few com-

Table 6
Comparison of the relative recoveries of 33 aromatic amines in drinking water after enrichment on polymer based solid phases of different suppliers in drinking water

Compound	Relative recovery (%) (R.S.D., %) after SPE with						
	Macherey–Nagel HR-P	Varian Bond Elut ENV	Supelco Envichrome P	Baker SDB 2	Restek Polymer	ICT Isolute ENV+	Merck LiChrolut EN
Aniline	80 (7)	69 (4)	78 (8)	47 (4)	59 (9)	71 (18)	85 (21)
4AT	80 (3)	55 (2)	64 (8)	43 (2)	58 (12)	75 (25)	76 (17)
2A3NT	80 (9)	86 (4)	106 (10)	84 (5)	90 (3)	96 (3)	105 (11)
2A4NT	91 (5)	90 (1)	95 (2)	87 (5)	87 (3)	88 (1)	102 (19)
2A5NT	90 (6)	87 (2)	92 (2)	89 (7)	90 (3)	90 (2)	105 (17)
2A6NT	88 (9)	89 (1)	94 (2)	88 (6)	88 (2)	90 (1)	100 (19)
4A2NT	84 (5)	88 (4)	92 (2)	85 (6)	83 (3)	85 (2)	96 (17)
2,4DAT	52 (5)	30 (4)	46 (2)	62 (7)	60 (9)	51 (4)	50 (7)
2,6DAT	80 (7)	23 (3)	52 (4)	78 (8)	48 (6)	60 (2)	63 (10)
2A4,6DNT	81 (8)	63 (1)	68 (2)	96 (6)	89 (8)	90 (5)	77 (11)
4A2,6DNT	89 (8)	84 (2)	91 (1)	87 (7)	86 (3)	86 (2)	102 (16)
2,4DA6NT	95 (6)	88 (3)	90 (5)	92 (8)	89 (2)	90 (1)	107 (14)
2,6DA4NT	109 (6)	90 (4)	93 (7)	97 (8)	97 (2)	100 (2)	117 (14)
2,6DMA	111 (4)	55 (3)	58 (9)	101 (7)	108 (13)	107 (9)	91 (13)
3,4DMA	66 (4)	36 (4)	42 (5)	30 (2)	58 (14)	79 (28)	59 (10)
3,5DMA	99 (5)	46 (2)	51 (7)	84 (6)	98 (13)	99 (6)	81 (10)
6E2MA	179 (4)	65 (2)	69 (11)	113 (9)	119 (16)	113 (9)	138 (20)
2,6 DEA	253 (5)	80 (2)	84 (12)	117 (11)	122 (18)	112 (10)	203 (34)
4IPA	116 (3)	65 (5)	87 (16)	46 (2)	70 (16)	85 (26)	111 (23)
3NA	89 (6)	87 (1)	93 (1)	85 (7)	84 (5)	83 (1)	101 (21)
4NA	97 (6)	92 (1)	94 (1)	89 (8)	88 (5)	87 (1)	108 (20)
2,6DNA	60 (8)	66 (5)	64 (3)	79 (3)	79 (1)	88 (5)	74 (14)
3,5DNA	83 (8)	70 (3)	70 (4)	98 (5)	96 (2)	100 (3)	88 (13)
1,3PhDA	35 (1)	9 (1)	35 (2)	58 (6)	15 (2)	33 (3)	38 (6)
1NphA	79 (5)	74 (5)	84 (8)	50 (4)	73 (12)	89 (19)	87 (17)
2NphA	82 (5)	72 (3)	88 (7)	49 (3)	71 (11)	83 (17)	87 (16)
2ABPh	80 (6)	83 (4)	99 (6)	61 (6)	81 (12)	90 (10)	93 (18)
4ABPh	94 (6)	87 (4)	96 (10)	74 (7)	89 (15)	97 (9)	104 (17)
Benzidine	69 (6)	81 (1)	91 (7)	76 (5)	76 (17)	78 (2)	89 (11)
4CNMA	120 (1)	122 (8)	128 (6)	106 (7)	112 (13)	116 (6)	132 (29)
4C2MA	144 (3)	123 (3)	131 (12)	110 (6)	119 (17)	120 (6)	149 (32)
3,4DCA	100 (3)	103 (0)	105 (6)	97 (9)	99 (5)	100 (2)	112 (21)
3C4MOA	106 (5)	108 (4)	120 (4)	106 (6)	114 (8)	100 (16)	122 (23)

pounds that had shown relative recoveries >120% with the HR-P phase showed similar high values with the LiChrolut EN phase whereas these compounds had relative recoveries between 80 and 120% with the solid phases of the other suppliers. However, the best results for most of the amines were obtained with the HR-P phase (relative recoveries mostly ≥80%, R.S.D.s mostly ≤6%), because lower relative recoveries or higher R.S.D.s were achieved with the other materials. Similar results were obtained, when a waste water matrix was used. Therefore the HR-P phase was used for all studies.

3.5. Application to water samples

The developed SPE procedure was applied to real samples from a disposal, a gas plant and from former ammunition plants in Stadtallendorf and Mecklenburg-Vorpommern. The eluates were derivatized and analysed by GC–ECD. In Fig. 2 a chromatogram of a water sample from a groundwater measuring point is shown. A 250-ml volume of water was enriched, derivatized and analysed by GC–ECD. As it was suspected, nitroaromatic amines were found as transformation products of trinitrotoluene and its by-products.

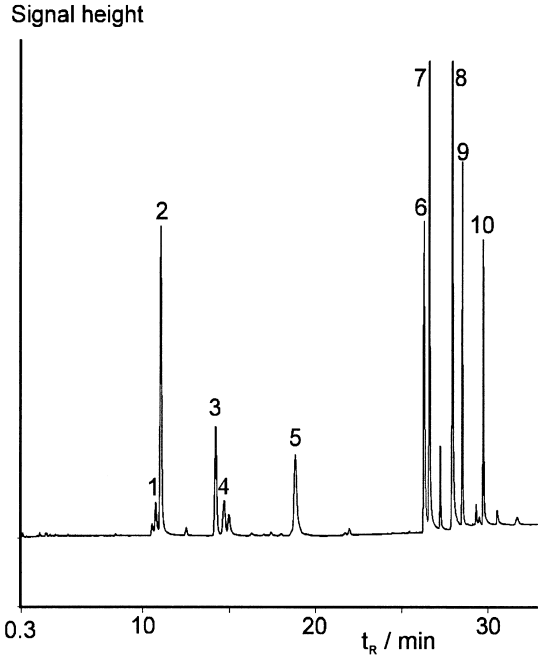

Fig. 2. GC–ECD chromatogram of a ground water sample from a measuring point of a former ammunition plant in Mecklenburg-Vorpommern after enrichment of 100 ml water, followed by derivatization; Peak identification: 1=3NA (1.4); 2=2,6-dinitrotoluene; 3=2A6NT (1.8); 4=4A2NT (1.3); 5=2A4NT (9.1); 6=3,5DNA (12); 7=4A2,6DNT (85); 8=2A4,6DNT (71); 9=2,4DANT (9.9); 10=2,6 DANT (3.9). Concentrations of analytes in $\mu g\ l^{-1}$ given in parentheses.

4. Conclusions

SPE of aromatic amines on phases based on styrene–divinylbenzene is a efficient method for the enrichment of these compounds. Most of the 53 studied analytes had a relative recovery of 80–120% in drinking water or wastewater compared to results obtained from a derivatized standard mixture in reagent water, which is a requirement for the application on real water samples.

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