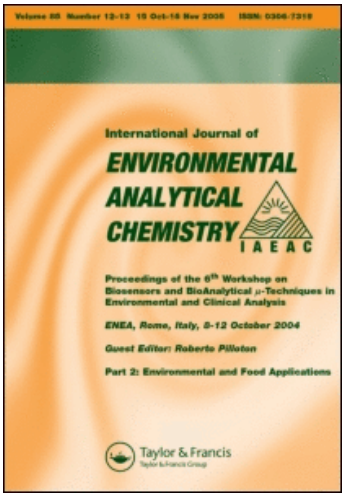

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DETERMINATION OF AROMATIC AMINES IN GROUND AND WASTE WATER BY TWO NEW DERIVATIZATION METHODS

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Two derivatization methods for aromatic amines are presented that are based on the halogenation of the aromatic ring. Bromination yields brominated anilines, in which all hydrogens in *ortho-* and *para*-positions are replaced by bromine via an electrophilic substitution. In contrast, iodination yields the corresponding iodobenzenes, in which all amino groups are substituted by iodine. Separation of at least 30 derivatives in a single gaschromatographic run in 30 min is possible with each method. Detection in routine analysis was done with an electron capture detector, but some findings with GC-MS and GC with atomic emission detection are also presented.

Both methods were applied to real samples of different origin and the results are compared. In industrial wastewater and ground water from a landfill and a former ammunition plant, about 20 aromatic amines were found to be present in the µg/L concentration range. In the case of the former ammunition plant, most analytes observed were degradation products of nitroaromatic explosives. In both other cases aniline and methyl anilines were the main pollutants found.

Keywords: Water analysis; aromatic amines; anilines; derivatization; GC-ECD; GC-AED; GC-MS

INTRODUCTION

Aromatic amines are important industrial chemicals[1], and rather high amounts are released to sewage plants where they are not completely degraded. Besides, aromatic amines are generated in the environment via the degradation of pesticides[2–4], nitroaromatics[5–7] and azo dyes[8–10]. Aromatic amines are of consid-

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erable interest in environmental analytical chemistry due to two factors. First they are very polar and water soluble. Thus they are easily transported to and in aquifers[11]. Secondly, the amino group is capable of unique sorption processes with soil particles, either due to covalent binding[12, 13] or to ion exchange processes[14–16]. Because of their wide-spread distribution and their mobility it does not surprise that a wide range of aromatic amines has been found in environmental matrices by several investigators, for example in river water[17–24] and ammunition wastewater[25–36]. Another important factor is the high acute and chronical toxicity of many aromatic amines. Therefore a reliable risk assessment is necessary, which demands accurate analytical methods at a trace level for a wide variety of aromatic amines.

Because of their polarity, many of these compounds are difficult to analyze. Our aim was to develop a method, which might be used in the routine analysis of water samples for a wide range of aromatic amines. For this, we used solid-phase extraction of the analytes, followed by halogenation for decreasing the polarity of the anilines and improving the detection in terms of selectivity and sensitivity by using gas chromatography/electron capture detection (GC-ECD). Halogenation was done either by bromination in an acetic acid medium or iodination in an acidic aqueous medium. The results of a prior investigation of 12 methylanilines in ammunition watewater with bromination[35] and iodination[36] were promising, so we decided to study in detail the derivatization of more than 50 aromatic amines and to explore the use of the methods for other water samples. Details of the method development are already described elsewhere[37,38], in this contribution we will emphasize the use and comparison of both methods in the analysis of real water samples of different origin, and present first results with an GC-AED.

EXPERIMENTAL SECTION

Samples

Real water samples were taken from four different locations: two were in the vicinity of former ammunition plants in the states of Hessen and Mecklenburg-Vorpommern (Germany), one was on the site and near a former landfill and one from an industrial sewage plant. The matrix ranged from highly contaminated, deep yellow and smelling leachate water to drinking water wells. The samples were stored at 4 °C in brown glass bottles and analyzed within four

weeks. No significant differences in results were observed when determining the contents of aromatic amines during this storage time.

Chemicals and reagents

Reference substances were obtained from various suppliers [Aldrich (Steinheim, Germany), Fluka (Neu-Ulm, Germany), Merck (Darmstadt, Germany), Promochem (Wesel, Germany), Mallinckrodt-Baker (Griesheim, Germany) and Riedel-de Haën (Seelze, Germany)] in the highest purity available. All in all, 56 aromatic amines were studied, which are listed in Table I.

TABLE I Aromatic amines used in this study with corresponding CAS-no. and peak-no. of the derivatives in the following chromatograms

Compound	*CAS-no.*	*Peak-no. of derivative in chromatograms*
Aniline	62–53–3	13
1,2-Phenylendiamine	95–54–5	-
1,3-Phenylendiamine	108–45–2	14
1,4-Phenylendiamine	106–50–3	15
2-Nitroaniline	88–74–4	16
3-Nitroaniline	99–09–2	17
4-Nitroaniline	100–01–6	18
2,4-Dinitroaniline	97–02–9	52
2,5-Dinitroaniline	619–18–1	53
2,6-Dinitroaniline	606–22–4	50
3, 5-Dinitroaniline	618–87–1	51
2-Aminotoluene	95–53–4	2
3-Aminotoluene	108–44–1	3
4-Aminotoluene	106–49–0	1
2,3-Diaminotoluene	2687–25–4	-
2,4-Diaminotoluene	95–80–7	4
2,6-Diaminotoluene	823–40–5	6
3,4-Diaminotoluene	496–72–0	-
2-Amino-3-nitrotoluene	570–24–1	24
2-Amino-4-nitrotoluene	99–55–8	9
2-Amino-5-nitrotoluene	99–52–5	25
2-Amino-6-nitrotoluene	603–83–8	7
4-Amino-2-nitrotoluene	119–32–4	5
2-Amino-4,6-dinitrotoluene	35572–78–2	12
4-Amino-2,6-dinitrotoluene	19406–51–0	10

Compound	*CAS-no.*	*Peak-no. of derivative in chromatograms*
2,4-Diamino-6-nitrotoluene	6629–29–4	11
2,6-Diamino-4-nitrotoluene	59229–75–3	8
o-Anisidine	90–04–0	21
m-Anisidine	536–90–3	22
p-Anisidine	104–94–9	23
2,3-Dimethylaniline	87–59–2	26
2,4-Dimethylaniline	95–68–1	27
2,5-Dimethylaniline	95–78–3	28
2,6-Dimethylaniline	87–62–7	29
3,4-Dimethylaniline	95–64–7	30
3,5-Dimethylaniline	108–69–0	31
N,N-Dimethylaniline	121–69–7	54
Diphenylamine	122–39–4	55
1-Naphthylamine	134–32–7	33
2-Naphthylamine	91–59–8	34
Benzidine	92–87–5	35
2-Aminobiphenyl	90–41–5	36
4-Aminobiphenyl	92–67–1	52
4-Isopropylaniline	99–88–7	37
2,6-Diethylaniline	579–66–8	38
2-Ethyl-6-methylaniline	24549–06–2	39
4-Chloro-N-methylaniline	932–96–7	40
2-Chloroaniline	95–51–2	41
3-Chloroaniline	108–42–9	42
4-Chloroaniline	106–47–8	43
3,4-Dichloroaniline	95–76–1	44
4-Chloro-2-methylaniline	95–69–2	45
3-Chloro-4-methylaniline	95–74–9	46
3-Chloro-4-methoxyaniline	5345–54–0	47
3-Chloro-4-fluoraniline	367–21–5	48
4-Bromoaniline	106–40–1	49

- : no derivatives detectable with GC-ECD or GC-MS

Pentane, sodium nitrite and glacial acetic acid were purchased from Riedel-de Haën, hydroiodic acid (ACS reagent, unstabilized, 55%) and amidosulfonic acid from Aldrich, sodium sulfite, sodium hydroxide, phosphoric acid, potassium iodide, iodine and bromine from Merck, all in the highest purity available.

Enrichment

Immediately before measurements, the samples were adjusted to about pH 9 with a concentrated sodium hydroxide solution (c = 10 mol L^{-1} in water). If necessary, the sample was filtered through 0.45 µm cellulose nitrate membrane filters (Sartorius, Göttingen, Germany) prior to the enrichment with a polystyrene-divinylbenzene [HR-P-phases from Macherey-Nagel (Düren, Germany)].

Prefilled 3-mL-polypropylene-cartridges with 200 mg of the solid phase, which was kept between two polyethylene-frits, were used for all extractions. The solid phase was conditioned two times with 1 mL of methanol, followed two times by 1 mL of acetonitrile, and washed two times with 1 mL of destilled water, adjusted to pH 9. The sample was passed through the cartridge with a peristaltic pump, set to a flow rate of 10 ± 0.2 mL min^{-1}.

After washing with distilled water, the cartridges were dried under vacuum for 1 min and eluted 3 times with 1 mL methanol/acetonitrile 1/1 (v/v). For the subsequent derivatization the eluates were transfered to 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).

Derivatization with iodine

To the eluate 5 mL of water were added and the solution was acidified with 0.2 mL of hydriodic acid. The solution was mixed with 0.5 mL sodium nitrite in water (c = 10 g L^{-1}) and shaken. After a reaction time of 20 min, 1 mL amidosulfonic acid in water (c = 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 sulfite. The solution was basified with 0.5 mL of a sodium hydroxide solution (c = 10 mol L^{-1}) and extracted for 15 min with 2 mL of pentane. During the extraction the vials were mechanically shaken. GC-ECD, GC-MS or GC-AED analysis was carried out on aliquots of the extracts which had been filled in autosampler vials.

Derivatization with bromine

The eluate was mixed with 3 mL glacial acetic acid and 0.25 mL of the bromination solution (consisting of 50 mL bromine in 200 mL glacial acetic acid) were added. The mixture was vigorously shaken, then 15 min were allowed for the reaction to complete. The surplus of bromine was destroyed with 0.5 mL of a sat-

urated solution of sodium sulfite. After addition of 5 mL of water the solution was basified with 7 mL of a sodium hydroxide solution (c = 10 mol L^{-1}). The alkaline solution was cooled down to room temperature in a water bath and extracted for 15 min with 2 mL of pentane. During the extraction the vials were mechanically shaken. GC-ECD, GC-MS or GC-AED analysis was carried out on aliquots of the extracts which had been filled in autosampler vials.

Gas chromatography

The gas chromatographic 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 and a split/splitless injector. Control of the equipment and data acquisition was done with the PC 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 make-up-gas flow to approx. 20 mL min^{-1} and the split ratio to 1:120. The temperatures of the injection block and the detector were 250 and 300 °C, respectively. The injection volume was 1 or 5 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. For the separation of the brominated derivatives the following temperature program was used: starting temperature 170°C, held for 18 min, temperature raising at 10°C/min to 230 °C, held for 20 min. The separation of the iodobenzenes was started at an oven temperature of 135°C. After 20.5 min the temperature was raised using a rate of 12.5 °C/min to 235 °C and then held for another 8.5 min.

The GC-MS investigations were carried out with a VG Trio 2 in the EI mode (70 eV). The same type of capillary column as mentioned above was used. Carrier gas was helium with a column pressure of 50 kPa. The temperatures of the injection block and the transfer line were 250 and 230 °C, respectively. For GC-MS the following temperature program was used: 40 °C (1 min), 15 °C/min to 270 °C. Injection was on-column with 1 µL.

The GC-AED measurements were done with a HPG 2350A Atomic Emission Detector coupled to a HP 6890 gas chromatograph with an autosampler unit HP 6890. The injector temperature and the cavity temperature were 250 °C. Injection was done in the split mode (split ratio 1:10) with 1 µL. For the separation of the analytes a methylpolysiloxane column, 25 m, 0.32 mm i.d., 0.17 µm d_f (HP1 from Hewlett-Packard) was used with the following programme: 40 °C (2 min), 8 °C/min to 250 °C. In addition, a pressure ramp was programmed from 20 psi for 2 min with 10 psi/min to 10 psi. Iodinated derivatives were detected at 183 nm, brominated derivatives at 478 nm.

TABLE II Comparison of main properties of the two derivatization methods

Parameter	*Derivatization Method*	
	Bromination	*Iodination*
Analytes investigated	56	56
Analytes derivatized	50	50
By-products	few except for polynuclear aromatic amines	very few
Selectivity	only electron-rich aromatics needed, but no interference of e.g. phenols observed	very good, only aromatic amines react, hydrolysis of precursors during derivatization possible
Separation	moderate tailing of a few peaks	difficult for positional isomers, interference of dinitrotoluenes
detection limits GC-ECD (3 σ, injected amount)	0.9 – 250 pg	0.5 – 50 pg
LOQ for 100-mL-enrichments GC-ECD (calibration data, according to [40])	1.2 – 40 μg L^{-1}	0.5 – 7.8 μg L^{-1}
Mass spectrometry	easily reveals substitution in *ortho*- and *para*-positions of the amino-group via the bromine isotopic pattern of the derivative	reveals number of amino groups in a molecule via the number of iodine atoms in the derivative
Time needed for derivatization/ percentage shaking or standing time	25 min / 80 %	80 min / 90 %
Sensitivity towards water	yes, if water content > 20 %	no
Toxicity of chemicals	especially bromination solution problematic, large amounts of sodium hydroxide needed	only minor amounts of hydriodic acid solution

LOQ: Limit of quantitation

RESULTS AND DISCUSSION

Analytical methods

The development of the solid-phase extraction and the influence of several parameters on the extraction efficiency are described elsewhere[39].

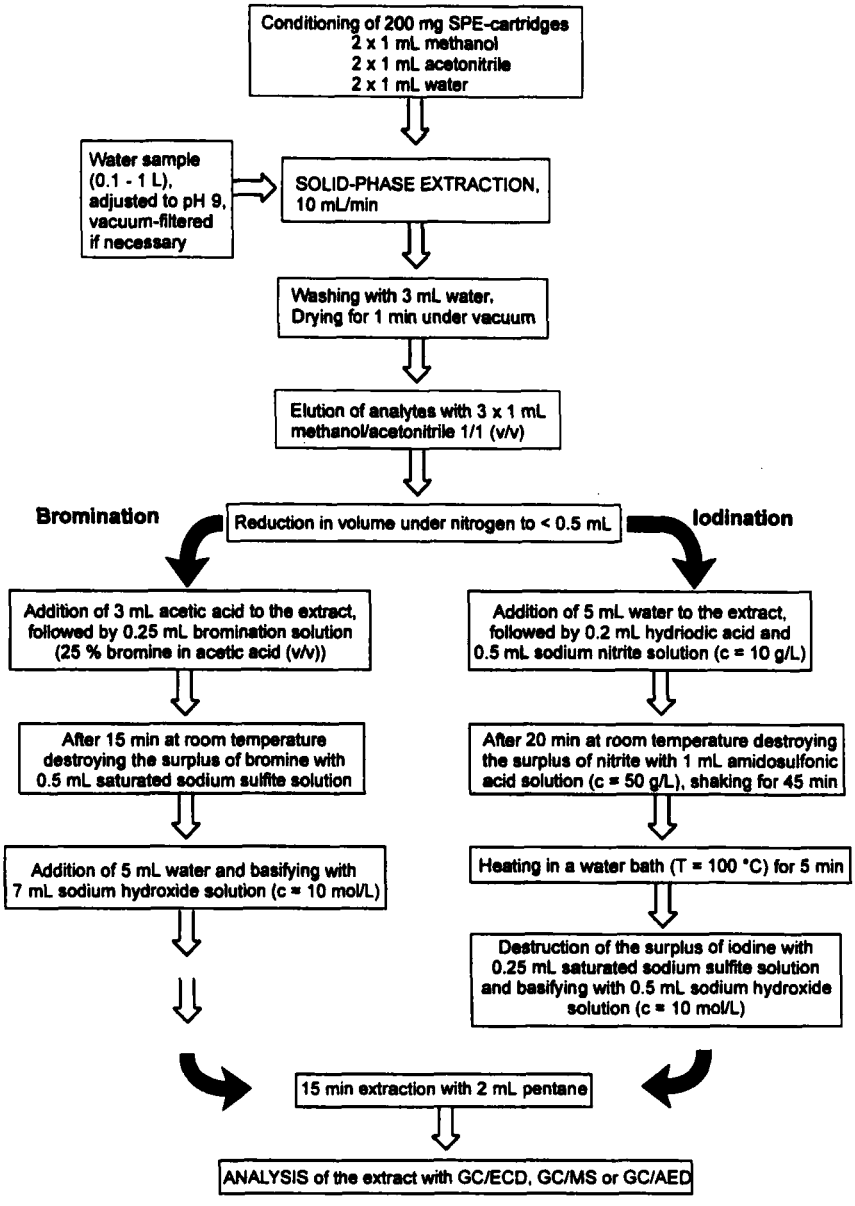

FIGURE 1 Scheme of the analytical method for the extraction and derivatization of aromatic amines from aqueous matrices applied to the samples in this study

The two derivatization methods are based on the halogenation of the aromatic ring. Bromination yields brominated anilines in a one-step reaction, in which all hydrogens in *ortho-* and *para*-positions are replaced by bromine via an electrophilic substitution. Iodination takes place in a two-step reaction, which comprises the diazotization of the amines and the subsequent substitution of the diazo group with iodine, and gives the corresponding iodobenzenes, in which all amino groups are substituted by iodine. The analytical procedure used in this study is depicted in Figure 1. Some real samples were only investigated with one of the two derivatization methods. With both methods the separation of at least 32 derivatives in a single chromatographic run is possible, which is shown in chromatograms of two different standard mixtures after bromination (Figure 2a) or iodination (Figure 2b). Hence, they seemed suitable for the simultaneous analysis of a wide range of aromatic amines in water samples.

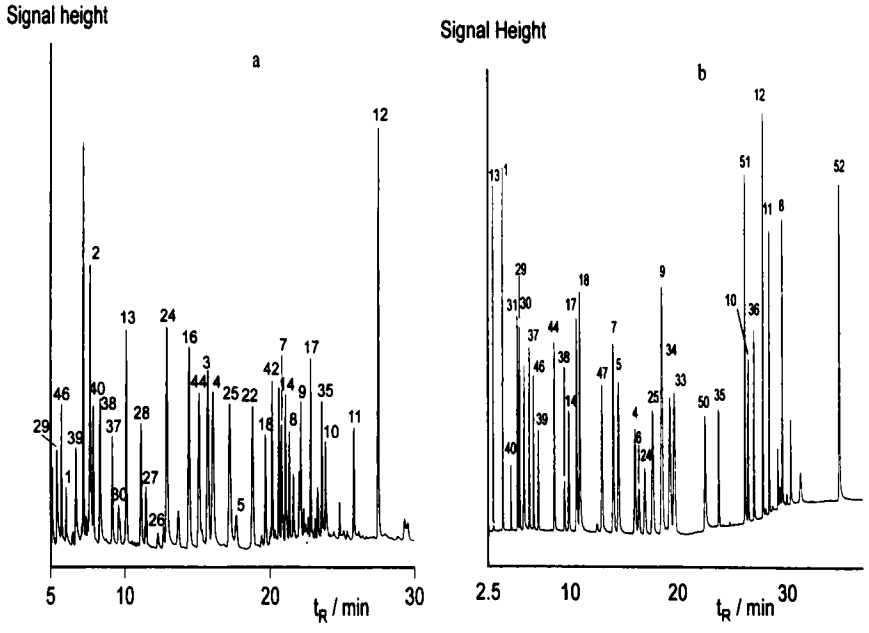

FIGURE 2 Gas chromatographic separation of 32 brominated derivatives (a) and 33 iodinated derivatives (b) of aromatic amines after enrichment on HR-P phases Detector: ECD. Concentration of analytes between 10 and 50 μg L^{-1}, prior to the solid-phase extraction. Peak assignment in Table I

Comparison of the two derivatization methods

In Table II, the main properties of both derivatization methods are summarized, some of which will be discussed here.

With both methods 50 of the investigated 56 aromatic amines were derivatized. The *ortho*-diamino compounds 1,2-phenylendiamine, 2,3-diaminotoluene and 3,4-diaminotoluene were not derivatized with either method. In addition, bromination did not yield derivatives with 2,6-dinitroaniline, 3,5-dinitroaniline and benzidine, iodination with 2,4-dinitroaniline, 2,5-dinitroaniline and diphenylamine.

The mass spectrometric data were especially easy to interpret for the brominated derivatives since the number of free *ortho*- and *para*-positions to the amino function can directly be elucidated from the isotopic pattern of bromine. GC-MS of the iodinated derivatives resulted in complementary data because the number of iodine atoms in the derivative represent the number of amino groups in the analyte.

The limits of detection given inTable II were calculated with the 3σ method from the measurements of diluted standard solutions, the limits of quantitation (LOQ) were calculated according to the German Standard Procedures for Water Analysis[40] from the analysis of spiked water samples (100 mL). The limits of detection, given as the absolute amount of analyte (refering to the aromatic amine) injected, do not depend on the injection volume whereas the limits of quantitation may still be lowered via the enrichment of larger sample volumes, larger injection volumes or different injection techniques (e.g. on-column or large-volume injection). Besides, the LOQ depend on the method standard deviation and are always higher than the 6σ values often given in literature.

Iodination is favourable concerning the formation of by-products, the selectivity towards aromatic amines, the limits of detection and quantitation reached, the sensitivity of the derivatization procedure towards water and the toxicity of the chemicals used. Bromination is advantageous concerning the ease and speed of derivatization and the possibility of separating positional isomers (e.g. the *ortho*-, *meta*-, and *para*-isomers of aminotoluene).

None of the methods was superior for all purposes and analytes, therefore both methods were applied to several real samples. If only one method was used due to limited time or sample volume, iodination was generally chosen.

Water samples from former ammunition plants

Both methods were applied to the determination of aromatic amines in ammunition wastewater from two different locations in Hessen and Mecklenburg-Vorpommern. The ammunition wastewater from Stadtallendorf/Hessen was previously studied in our group concerning the contents of nitroaromatic explosives and some major metabolites[35,36]. Now we were able to analyze a wider range of aromatic amines in the same water samples and in well water from

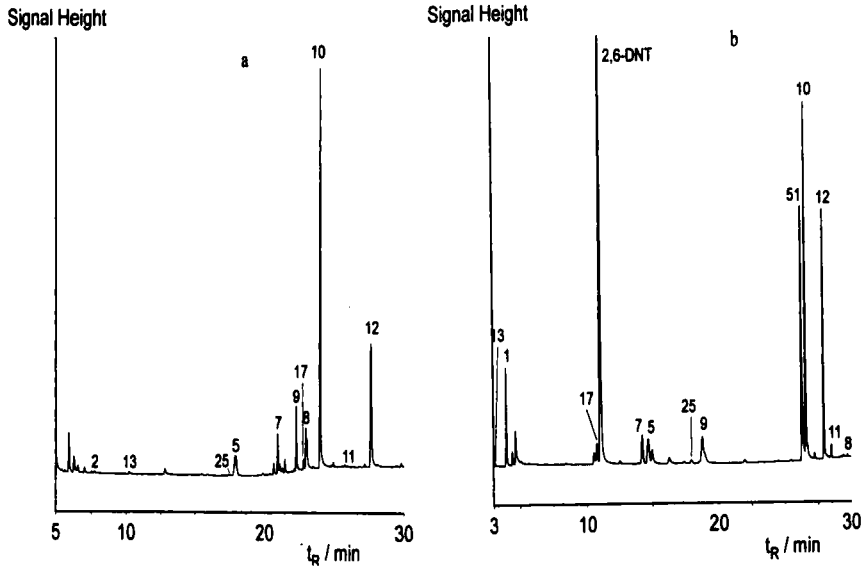

FIGURE 3 GC-ECD-chromatograms of a ground water sample from a former ammunition plant in Mecklenburg-Vorpommern after SPE and bromination (a) and iodination (b); 2,6-DNT: 2,6-dinitrotoluene. Peak assignment in Table I

another ammunition plant. Typical GC-ECD chromatograms of a well water sample are shown in Figure 3a (bromination) and Figure 3b (iodination). Peak 1 in Figure 3b represents the sum of the 3 iodotoluene isomers, since separation was not possible. The sample contained mainly aminonitrotoluenes from the microbial reduction of nitrotoluene explosives. Of this class of compounds, 9 metabolites were identified with both methods, 2-amino-3-nitrotoluene in a concentration $< 0.3\ \mu g\ L^{-1}$ only with iodination. Besides, aniline and 3-nitroaniline were found with both methods, 3,5-dinitroaniline with iodination (because it does not yield a brominated derivative). These three analytes are probably metabolites of nitrobenzene, 1,3-dinitrobenzene and 1,3,5-trinitrobenzene, respectively, which are well known pollutants in ammunition wastewater. In Figure 3b one can see the interference of the nitroaromatics themselves: 2,6-dinitrotoluene is eluted at the same time as 4-nitro-iodobenzene (derivative of 4-nitroaniline). The interferences are important only for the dinitrotoluenes when using iodination as derivatization method. Other nitroaromatics are either not extracted into pentane from the basic solution (2,4,6-trinitrotoluene) or are eluted earlier than the derivatives (nitrotoluenes). With bromination the latter is also the case with the dinitrotoluenes. In Table III the concentration range of aromatic amines in four well water samples from the two former ammunition plants, measured by GC-ECD, is given.

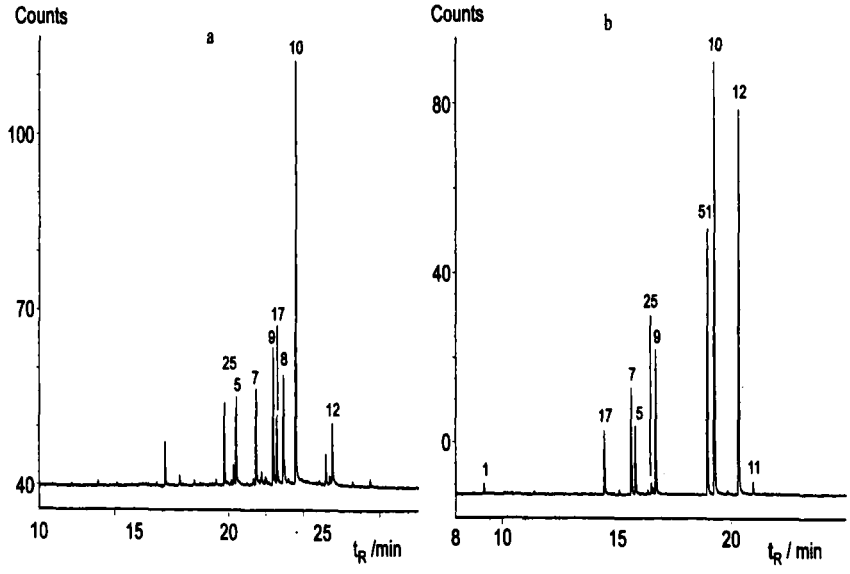

FIGURE 4 GC-AED-chromatograms of a ground water sample from a former ammunition plant in Mecklenburg-Vorpommern after SPE and bromination (a) and iodination (b). Peak assignment in Table I

TABLE III Aromatic amines in well water samples from former ammunition plants

Compound	*Concentration range / (µg L^{-1})*	
	Bromination	*Iodination*
Aniline	< LOQ – 0.1	0.20 – 0.40
3-nitroaniline	0.44 – 21	< LOQ – 1.5
3,5-dinitroaniline	-	1.0 – 17
2-amino-3-nitrotoluene	< LOQ	< LOQ – 0.30
2-amino-4-nitrotoluene	< LOQ – 8.3	0.02 – 14
2-amino-5-nitrotoluene	< LOQ – 1.5	0.03 – 0.43
2-amino-6-nitrotoluene	< LOQ – 5.3	0.03 – 2.5
4-amino-2-nitrotoluene	0.18 – 8.5	0.15 – 9.2
4-amino-2,6-dinitrotoluene	1.8 – 66	1.8 – 85
2-amino-4,6-dinitrotoluene	0.25 – 36	0.61 – 71
2,4-diamino-6-nitrotoluene	< LOQ – 2.5	0.06 – 9.9
2,6-diamino-4-nitrotoluene	< LOQ – 6.5	< LOQ – 3.9

LOQ: limit of quantitation; -: detection not possible

Some of the samples were investigated with GC-MS after derivatization. The presence of all analytes listed in Table III except aniline, 2-amino-3-nitrotoluene and 2-amino-5-nitrotoluene was confirmed via the mass spectra of their derivatives. The three analytes that could not be found with GC-MS were only present in small concentrations, and – at least under standard ionization conditions (EI, 70 eV) – GC-MS was much less sensitive than GC-ECD.

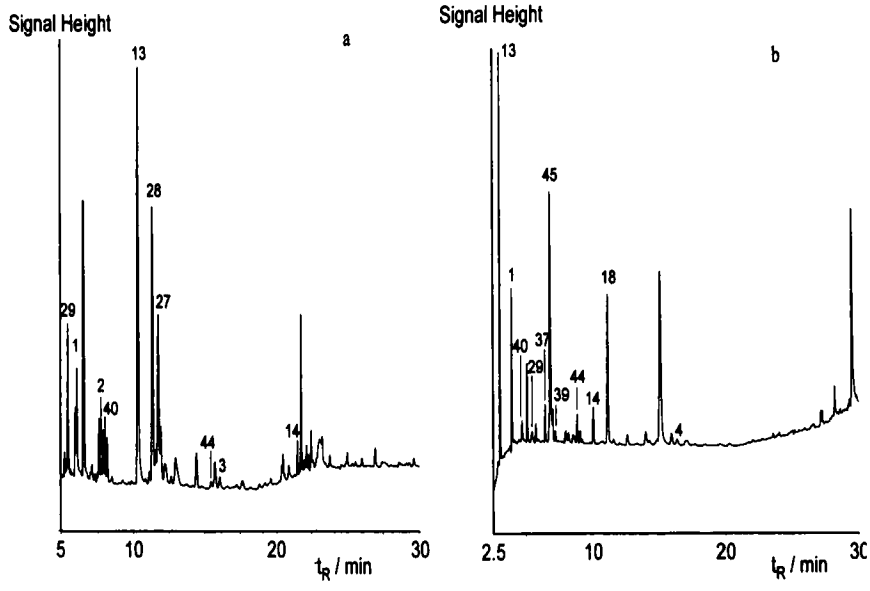

FIGURE 5 GC-ECD-chromatograms of a ground water sample from a former landfill in Hessen after SPE and bromination (a) and iodination (b). Peak assignment in Table I

Because of our prior detailed investigation of samples from former ammunition plants we chose these for first experiments with GC-AED. In Figure 4a a chromatogram of the brominated derivatives is shown, monitored at the bromine emission wavelength of 478 nm. In Figure 4b the corresponding chromatogram of the iodinated derivatives, monitored at the iodine emission wavelength of 183 nm is given. The number of main peaks in the chromatograms 3a and 4a (brominated derivatives) and 3b and 4b (iodinated derivatives) is nearly the same, and even the relative size of the peaks is similar. That suggests that no interfering halogenated analytes were present in the samples. The one prominent exception shows the main advantage of the AED: its very high selectivity. The interfering peak of 2,6-dinitrotoluene seen in Figure 3b has vanished in Figure 4b

and only iodinated compounds remain. The baseline in the GC-AED chromatograms is even flatter compared with the GC-ECD chromatogram and thus the sensitivity might be improved as well.

Water samples from a former landfill

From a former landfill in Hessen 15 ground water samples were studied with both derivatization methods. Quantitative determination was done for 32 and 25 substances with iodination and bromination, respectively. Figure 5a (bromination) and Figure 5b(iodination) show chromatograms from a sample with a rather high content of aromatic amines. With both methods aniline, methylanilines, 1,3-phenylendiamine, 3,4-dichloroaniline and 2,6-dimethylaniline were found. 4-chloro-2-methylaniline and 4-nitroaniline were detected in rather high amounts after iodination, 2,4-dimethylaniline and 2,5-dimethylaniline after bromination. Since these four analytes were only found with one method it remains uncertain at the moment if the results are reliable. However, first results with GC-MS indicate that at least 4-chloro-2-methylaniline is indeed present in the sample.

In all 15 samples, the pollution pattern was similar. The main pollutants were aniline, methylanilines and several chloroanilines, which were found in most samples with both derivatization methods. Interestingly, the polynuclear aromatic amines studied here (1-naphthylamine, 2-naphthylamine, 2-aminobiphenyl and benzidine) were either all present (5 samples) or not at all (10 samples). The measured concentrations of aromatic amines ranged from 0.14 to 12.5 $\mu g\ L^{-1}$ (iodination) or 0.94 to 7.4 $\mu g\ L^{-1}$ (bromination). The differences between the results obtained with both methods in the investigation of these samples were in general greater than for ammunition wastewater.

Water sample from an industrial sewage plant

To test if the derivatization of aromatic amines can be applied to even more complex matrices we investigated a water sample from an industrial sewage plant. This sample was only investigated with iodination. A chromatogram after enrichment and derivatization is shown in Figure 6. In the industrial wastewater, aniline, methylanilines, 2,4-dimethylaniline, four aminonitrotoluene isomers, 2,4-diaminotoluene and 3,5-dinitroaniline were found. Besides, there are a lot of unidentified peaks in the chromatogram, especially in the later half. The identification of 2-amino-4,6-dinitrotoluene and 2,6-diamino-4- nitrotoluene in this region is rather dubious. Unfortunately, we were not able to obtain mass spectra

of the analytes for the identification of unknown peaks, due to the rather low concentrations of the aromatic amines and interferences with other pollutants.

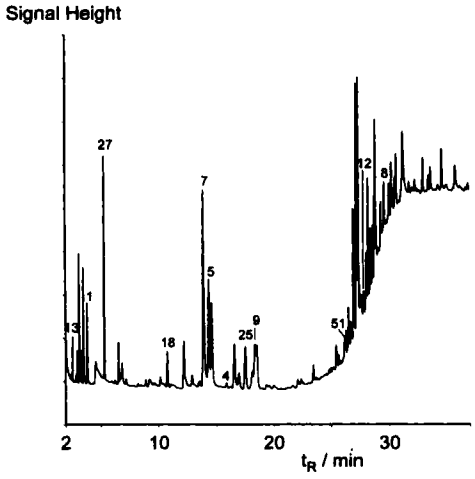

FIGURE 6 GC-ECD-chromatogram of a water sample from an industrial sewage plant after SPE and iodination. Peak assignment in Table I

CONCLUSIONS

The analytical procedure described in this contribution is well suited for the determination of aromatic amines in the aqueous environment. GC-ECD analysis of the derivatives is especially useful in routine analysis or for target analysis of distinct compounds because of its high selectivity and sensitivity. Thus matrix components do hardly interfere. A non-target analysis with GC-MS is possible if matrix components or interfering analytes are removed during the procedure. This was the case with samples from ammunition wastewater but not with the samples from the industrial sewage plant and the former landfill. For these samples a more selective sample preparation is needed. First results with a GC-AED indicate a gain in selectivity and sensitivity compared to GC-ECD. Further investigations will therefore concentrate on the use of GC-AED for a more selective detection. Furthermore, we want to find out, how differences obtained in the analysis of real samples with both derivatization methods can be explained, and if the methods may also be applied to the analysis of soil eluates.

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References

[1] P. F. Vogt and J. J. Geralis, in: *Ullmann's Encyclopedia of Industrial Chemistry,* Vol. A 2 (VCH, Weinheim, 1985) 5th ed., pp. 37–56.
[2] K.H. Domsch, *Pestizide im Boden* (VCH, Weinheim, 1992).
[3] E. M. Lores, D. W. Bristol and R. F. Moseman, *J. Chromatogr. Sci.,* **16**, 358–362 (1978).
[4] A. de Kok, Y. J. Vos, C. van Garderen, T. de Jong, M. van Opstal, R. W. Frei, R. B. Geerdink and U. A. Th. Brinkman, *J. Chromatogr.,* **288**, 71–90 (1984).
[5] J. C. Spain (Ed.), *Biodegradation of Nitroaromatic Compounds* (Plenum Press, New York, 1995).
[6] R. A. Larson and E. J. Weber, *Reaction Mechanisms in Environmental Organic Chemistry* (Lewis, Boca Raton, 1994).
[7] W. Neumeier, R. Haas and E. von Löw, *Forum Städte-Hygiene,* **40**, 32–37 (1989).
[8] E. A. Clarke and R. Anliker, in: *Handbook of Environmental Chemistry,* Vol. 3A (O. Hutzinger, ed., Springer, Heidelberg, 1980), pp. 181–215.
[9] G. L. Baughman and E. J. Weber, *Environ. Sci. Technol.,* **28**, 267–276 (1994).
[10] E. J. Weber and R. L. Adams, Environ. Sci. Technol., **29**, 1163–1170 (1995).
[11] G. Böer, C. Schlett and H.-P. Thier, *Vom Wasser,* **80**, 59–63 (1993).
[12] G. E. Parris, *Environ. Sci. Technol.,* **14**, 1099–1106 (1980).
[13] E. J. Weber, D. L. Spidle and K. A. Thorn, *Environ. Sci. Technol.,* **30**, 2755–2763 (1996).
[14] M. E. Essington, *Soil Sci.,* **158**, 181–189 (1994).
[15] S. B. Haderlein, K. W. Weissmahr and R. P. Schwarzenbach, *Environ. Sci. Technol.,* **30**, 612–622 (1996).
[16] O. P. Homenauth, M. B. McBried, *Soil Sci. Soc. Am. J.,* **58**, 347–354 (1994).
[17] R. C. C. Wegman and G. A. L. de Korte, *Intern. J. Environ. Anal. Chem.* **9**, 1–6 (1981).
[18] B. Scholz and N. Palauschek, *Fresenius' Z. Anal Chem.,* **331**, 282–289 (1988).
[19] V. Coquart and M.-C. Hennion, *Chromatographia,* **37**, 392–398 (1993).
[20] D. Bethmann, F. Sacher and H.-J. Brauch, *Vom Wasser,* **87**, 171–185 (1996.)
[21] H. Börnick, V. Hultsch, T. Grischek, D. Lienig and E. Worch, *Vom Wasser,* **87**, 305–326 (1996).
[22] S. Müller, J. Efer and W. Engewald, *Fresenius' J. Anal. Chem.,* **357**, 558–560 (1997).
[23] S. Paul, D. Lienig and E. Worch, *Vom Wasser,* **88**, 273–283 (1997).
[24] R. Haas, *Konzepte zur Untersuchung von Rüstungsaltlasten* (Erich Schmidt, Berlin, 1992).
[25] K. Levsen, P. Mußmann, E. Berger-Preiß, A. Preiß, D. Volmer and G. Wünsch, *Acta hydrochim. hydrobiol.,* 21, 153–166 (1993).
[26] P. Mußmann, A. Preiß, K. Levsen and G. Wünsch, *Vom Wasser,* **82**, 79–90 (1994).
[27] P. M. Gates, E. T. Furlong, T. F. Dorsey and M. R. Burkhardt, *Trends Anal. Chem.,* **15**, 319–325 (1996).
[28] U. Lewin, J. Efer and W. Engewald, *J. Chromatogr. A,* **730**, 161–167 (1996).
[29] A. Preiß, K. Levsen, E. Humpfer and M. Spraul, *Fresenius' J. Anal. Chem.,* **356**, 445–451 (1996).
[30] L. Wennrich, U. Lewin, J. Efer and W. Engewald, *Vom Wasser,* **86**, 341–352 (1996).
[31] U. Lewin, L. Wennrich, J. Efer and W. Engewald, *Chromatographia,* **45**, 91–98 (1997).
[32] K. Spiegel and T. Welsch, *Fresenius' J. Anal. Chem.,* **357**, 333–337 (1997).
[33] T. C. Schmidt, M. Petersmann, L. Kaminski, E. v. Löw and G. Stork, *Fresenius' J. Anal. Chem.,* **357**, 121–126 (1997).
[34] T. C. Schmidt, D. Meinzer, L. Kaminski, E. v. Löw and G. Stork, *Chromatographia,* **46**, 501–506 (1997).
[35] T. C. Schmidt, R. Haas, K. Steinbach and E. v. Löw, *Fresenius' J. Anal. Chem.,* **357**, 909–914 (1997).

[36] R. Haas, T. C. Schmidt, K. Steinbach and E. v. Löw, *Fresenius' J. Anal. Chem.*, **359**, 497–501 (1997).
[37] T. C. Schmidt, M. Leß, R. Haas, K. Steinbach, E. v. Löw and G. Stork, *J. Chromatogr. A*, **810**, 161-172 (1988).
[38] T. C. Schmidt, R. Haas, K. Steinbach and E. v. Löw, *Chromatographia*, in print.
[39] M. Leß, T. C. Schmidt, E. v. Löw and G. Stork, *J. Chromatogr. A*, **810**, 173-182 (1998).
[40] DIN 38402, in: *Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung* (Beuth, Berlin, 1986), part 51.