

A method based on microextraction by packed sorbent-programmed temperature vaporizer–fast gas chromatography–mass spectrometry for the determination of aromatic amines in environmental water samples

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Abstract We report a sensitive method for the determination of 15 aromatic amines in environmental water samples. They have been included in the list of priority pollutants in surface water by the European Union. The method is based on analyte enrichment using microextraction by packed sorbent (MEPS) and later analysis using programmed temperature vaporizer–gas chromatography–mass spectrometry (PTV-GC-MS). All MEPS steps were carried out manually. The detection limits were of the order of nanograms per liter for most of the compounds. The results were compared with those obtained without MEPS using the method exclusively based on direct injection of the sample into the PTV-GC-MS. External calibration in ultrapure water was used in the determination of the compounds studied in five types of water samples (sea, river, tap, influent, and effluent waste water) since no significant matrix effect was found. The results obtained can be considered highly satisfactory and they revealed the presence of aniline in the sea and the influent and effluent waste water samples.

Keywords Aromatic amines · Microextraction by packed sorbent · Gas chromatography · Mass spectrometry · Water samples

Introduction

Owing to their toxicity, carcinogenicity, and persistence, aromatic amines constitute a significant class of environmental water pollutants. These compounds are used in the production of dyes, pesticides, and pharmaceuticals, among others, and they may be released into the environment directly as a result of industrial discharge from factories, or indirectly through the degradation of compounds such as azo-dyes and pesticides [1].

Aromatic amines are highly soluble in water and they can permeate through soil and contaminate groundwater. Their widespread use and perniciousness mean that their analysis in environmental matrices is important. The European Union [2] has listed the priority pollutants in surface water to be monitored regularly, including aromatic amines.

Sample preparation helps not only to achieve detection limits that are as low as that required by current legislation but also to clean up the sample matrix. Some techniques used in the determination of these compounds in water samples are solid-phase extraction (SPE) [3–7], solid-phase microextraction (SPME) [8–12], stir-bar sorptive extraction (SBSE) [13], liquid-phase microextraction [14–18] and liquid–liquid extraction (LLE) [19, 20]. Microextraction by packed sorbent (MEPS) is a technique for sample preparation [21, 22] based on the miniaturization of conventional SPE and it was introduced in 2004 by the group of Abdel-Rehim [23]. In MEPS, a small amount of sorbent is placed in a syringe as a plug or between the barrel and needle as a cartridge and sample extraction is achieved in the packed bed. The small amount of sorbent used in the cartridges (1–4 mg) makes

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it possible to reuse them (up to 400 times) by optimizing the cleaning steps [21]. High solvent volumes would be required in order to perform the cleaning of SPE columns, which are generally single-use only. Furthermore, MEPS reduces the handling time by about 30 and 100 times [21] as compared with SPME and SBSE, respectively, saving time and resources. MEPS can be connected on-line to the analytical instrument for automated methods or it can be used for on-site sampling where the portable syringe, containing the analytes, is carried back to the laboratory for desorption and analysis [22]. This extraction technique has mainly been used in bionalysis [24–26] and environmental water analysis [27–29]. According to “green” analytical chemistry [21], it uses small amounts of hazardous chemicals and reduces energy costs and wastes.

Gas chromatography coupled with different detectors [3–9, 11, 12, 18, 20, 30, 31], high-performance liquid chromatography [10, 13–17], and capillary electrophoresis [19, 32, 33] have been used to determine aromatic amines in water samples. In many cases, GC-MS [5–8, 11, 12, 18, 20, 30, 31] is the preferred technique.

The present work describes the development and validation of a new method for the determination of 15 aromatic amines in water samples from different sources. The method is based on analyte enrichment by MEPS and later introduction of the sample into a programmed temperature vaporizer (PTV) inlet, followed by fast capillary gas chromatography coupled to mass spectrometry (PTV-GC-MS) in synchronous selected ion-monitoring (SIM)/scan data acquisition mode. The results are compared with those obtained with the method based exclusively on PTV-GC-MS. This is the first time that this methodology (MEPS-PTV-GC-MS) has been applied for the determination of these compounds in such matrices

Experimental

Reagents

The aromatic amines studied (aniline, *o*-toluidine, *o*-anisidine, *o*-chloroaniline, *m*-chloroaniline, *p*-chloroaniline, 3,5-dichloroaniline, 2,4-dichloroaniline, 3,4-dichloroaniline, 3,5-dimethylaniline, 2-chloro-4-methylaniline, 2,4,5-trichloroaniline, 2,4,6-trichloroaniline, diphenylamine and *o*-nitroaniline) were supplied by Sigma-Aldrich (Steinheim, Germany). All of them were analytical standards $\geq 99\%$ pure, except for 98 % 3,5-dichloroaniline, 3,4-dichloroaniline, 3,5-dimethylaniline, 2-chloro-4-methylaniline and *o*-nitroaniline. The solvent used was 99.9 % CHROMASOLV® Plus, for HPLC ethyl acetate (Sigma-Aldrich). Ultrapure water was obtained using a Wasserlab water purification system (Noain, Spain).

Stock solutions

Stock solutions (1,000 mg L⁻¹) of the 15 aromatic amines were prepared in ethyl acetate and stored at 4 °C. Working solutions containing the 15 compounds studied were prepared by appropriated dilutions of the stock solutions in ultrapure water and ethyl acetate for the methods based on MEPS-PTV-GC-MS and PTV-GC-MS, respectively. These solutions were employed to obtain the calibration curves, the detection and quantification limits and to spike the water samples.

Samples

The water samples analyzed were collected on December 2011 and kept under refrigeration at 4 °C until analysis. The samples included tap water from the city of Salamanca, water from the river Tormes taken in the city of Salamanca, influent and effluent water taken at the sewage treatment plant in Salamanca, and sea water collected from Miño (La Coruña, Spain). Samples were previously filtered through a 0.45 μm filter. Influent and effluent wastewater samples were diluted at a proportion of 1:25 and 1:20 with ultrapure water, respectively.

MEPS conditions

In the MEPS procedure, the analytes were retained in a sorbent packed inside a cartridge placed directly in a syringe, between the barrel and the needle. The assembly is called barrel insert and needle (BIN); it was provided by SGE Analytical Science (Griesheim, Germany) and contains 4 mg of a solid-phase silica-C18 material (mean particle size 45 μm ; pore size 60 Å). A hand-held automated analytical syringe coupled to a 500 μL MEPS syringe from SGE Analytical Science was employed. Ten different flow rates can be selected ranging between 18 and 300 $\mu\text{L s}^{-1}$.

The optimum conditions were as follows: the sorbent was first conditioned with 500 μL of ethyl acetate and then with 500 μL of ultrapure water at the lowest allowed flow rate (18 $\mu\text{L s}^{-1}$). Next, 0.2 g mL⁻¹ of NaCl was added to the sample and this was extracted by drawing and discarding (eight cycles of 500 μL at a flow rate of 18 $\mu\text{L s}^{-1}$). Then, the sorbent was washed once with 500 μL of ultrapure water to remove possible interfering substances and the cartridge was dried by pumping air through it (10 \times 500 μL) at the highest flow rate (300 $\mu\text{L s}^{-1}$). The analytes were eluted with 100 μL of ethyl acetate; this volume was pumped through the cartridge and injected into the vial. After elution, the cartridge was washed with two cycles, each containing 500 μL of ethyl acetate and 500 μL of ultrapure water. This latter process was performed to wash out the sorbent and prevent memory effect problems. The time

needed for each MEPS extraction was about 13 min. As stated before, all MEPS steps were carried out manually.

PTV-GC-MS conditions

All experiments were carried out with a PTV inlet (CIS-4, Gerstel, Baltimore, MD) using the solvent-vent injection mode; 10 μL of sample was injected. A liner (71 mm \times 2 mm) packed with deactivated glass wool was used. The injector venting temperature was 25 $^{\circ}\text{C}$. Venting flow was adjusted to 125 mL/min and venting pressure to 5.0 psi (34,474 Pa). After 0.30 min, the split valve was closed and the liner was flash-heated at a rate of 12 $^{\circ}\text{C}/\text{s}$ to 325 $^{\circ}\text{C}$. The analytes were transferred from the liner to the capillary column (1.0 min). The split valve was then opened (split flow 125 mL/min), and the liner temperature was held at 325 $^{\circ}\text{C}$ for 6.0 min. Cooling was accomplished with liquid CO_2 .

Gas chromatography was performed on a low-polarity DB-VRX capillary column (20 m \times 0.18 mm \times 1 μm) using an Agilent 6890 gas chromatograph. The initial oven temperature was 40 $^{\circ}\text{C}$ for 2.0 min; this was increased at a rate of 37 $^{\circ}\text{C}/\text{min}$ to 175 $^{\circ}\text{C}$ and then further increased at 40 $^{\circ}\text{C}/\text{min}$ to 250 $^{\circ}\text{C}$ and held for 2.50 min. The total chromatographic run-time was 10.02 min. The carrier gas was helium N50 (99.995 % pure, Air Liquide), and the flow rate was 1.3 mL/min.

The detector was a quadrupole mass spectrometer (HP5973N) equipped with an inert ion source. It was operated in electron-impact mode using an ionization voltage of 70 eV. The ion source temperature was 230 $^{\circ}\text{C}$, and the quadrupole was set at 150 $^{\circ}\text{C}$. The analyses were performed in synchronous SIM/scan mode which allowed collection of both SIM and full scan data in a single run. Full scan (45–200 m/z , 14.04 scans/s) was used for identification and SIM for quantification, selecting the characteristic ions in each case (Table 1), with a dwell time of 10 ms. The different compounds were identified by comparison of the experimental spectra with those of the NIST'08 database (NIST/EPA/NIH Mass Spectral Library, version 2.0).

Data analysis

Data collection was performed with the Enhanced ChemStation from Agilent Technologies [34].

Results and discussion

Preliminary study of methods

MEPS parameters

C18 and M1 (80 % C8 and 20 % strong cationic exchange) were tested as sorbent material for MEPS. In case of M1,

different pH values, ranging between 3 and 5, were studied to ensure that most of the aromatic amines were in their protonated form, according to their pK_a (Table 1). The highest signals were obtained when C18 was used.

Sample extraction was carried out in three different ways. In the first case, the sample was pumped up once and discarded into the waste (carrying out this operation with several aliquots of fresh sample) [28]. In the second case, it was pumped up and down several times, ranging between 12 and 24, from the same vial (multiple draw-eject mode) [26]. Finally, in the last strategy tested, the sample was divided into eight different vials and each aliquot was pumped up and down twice. No significant differences were observed with the three extraction strategies and the first option was chosen, which reduces the mechanical stress of the MEPS syringe and consequently increases its life time.

The effect of sample volume was studied using increasing volumes (1.0–7.0 mL) of spiked ultrapure water (8 $\mu\text{g L}^{-1}$ for all the compounds). The amount of all the analytes extracted increased with the sample volume. Recoveries were determined by comparison of the responses (peak areas) obtained by MEPS versus the responses obtained for a standard in ethyl acetate injected directly into the PTV-GC-MS system at an equivalent concentration. Figure 1 shows the recovery and the analytical signal for 2-chloro-4-methylaniline and 2,4-dichloroaniline when the sample volume was increased. Assuming that the use of larger volumes could improve the detection limits, 4 mL was chosen as the sample volume since recovery decreased for higher volumes and the time needed for each MEPS extraction increased. Similar plots were obtained for the rest of the compounds. The recoveries are shown in Table 2. In general, compounds with low octanol/water distribution coefficients are more difficult to extract than those with less polarity. The recoveries ranged between 16 and 84 % for all the compounds except for aniline, which was poorly extracted in the sorbent.

The influence of ionic strength on extraction was explored. Solutions containing different concentrations of NaCl ranging between 0 and 30 % (w/v) were studied. For most of the compounds, the analytical response was enhanced after salt addition. The addition of high amounts of salt must be avoided in order to prolong the life of the cartridge, since we observed that suspended particles partially blocked it. Consequently, NaCl was fixed at 20 % (w/v) for the experiments.

The elution volume was found to be a critical step for the analysis and was also evaluated. Different ethyl acetate elution volumes (1 \times 300, 1 \times 150, 1 \times 100, and 2 \times 50 μL) were tested and 1 \times 100 μL elution was chosen as optimum because it provided the best analyte responses.

The carry-over was tested by injecting blank after the highest concentration level used in the calibrations. To eliminate the memory effect, the sorbent was washed with two cycles,

Table 1 Retention times, m/z ratios selected in SIM mode, octanol/water distribution coefficients and pK_a of the compounds studied

Analyte	Retention time (min)	Quantification ion	Qualifier ions	Log K_{ow}	pK_a
Aniline (No. 1)	5.522	93	66, 65	0.90	4.60
<i>o</i> -Toluidine (No. 2)	6.029	107	106, 77	1.32	4.45
<i>o</i> -Chloroaniline (No. 3)	6.298	127	129, 65	1.92	2.66
<i>o</i> -Anisidine (No. 4)	6.483	80	108, 123	1.02	4.52
3,5-Dimethylaniline (No. 5)	6.496	121	106, 120	2.17	4.89
<i>m</i> -Chloroaniline (No. 6)	6.582	127	65, 129	1.88	3.52
<i>p</i> -Chloroaniline (No. 7)	6.600	127	65, 129	1.83	3.97
2-Chloro-4-methylaniline (No. 8)	6.750	141	140, 106	2.27	4.05
2,4-Dichloroaniline (No. 9)	7.151	161	163, 63	2.78	2.00
3,5-Dichloroaniline (No. 10)	7.386	161	163, 63	2.90	2.50
<i>o</i> -Nitroaniline (No. 11)	7.446	138	65, 92	1.85	0.26
2,4,6-Trichloroaniline (No. 12)	7.499	195	197, 199	3.52	0.07
3,4-Dichloroaniline (No. 13)	7.511	161	163, 63	2.69	2.90
2,4,5-Trichloroaniline (No. 14)	7.954	195	197, 199	3.45	0.96
Diphenylamine (No. 15)	8.261	169	168, 167	3.50	1.03

each containing 500 μL of ethyl acetate and 500 μL of ultrapure water. The carry-over was less than 0.7 % for all the compounds studied (Table 2), except for aniline (6.4 %). The carry-over did not decrease upon performing more cycles. The same high value for aniline was also obtained when MEPS was not used, which means that this memory effect depends exclusively on the strong retention of the compound in the glass wool-packed liner in the PTV, although it was cleaned after injections (a temperature of 325 $^{\circ}\text{C}$ was maintained for 6.0 min at a flow rate of 125 mL min^{-1}).

PTV parameters

The variables studied in the injection process with solvent-vent were the venting temperature, the venting flow and

time, and the injection time; 10 μL of spiked ultrapure water (8 $\mu\text{g L}^{-1}$) was injected in all the experiments. Different venting temperatures (15–65 $^{\circ}\text{C}$) were assayed, and 25 $^{\circ}\text{C}$ was selected as a final temperature because it allowed the removal of ethyl acetate while the compounds of interest were retained in the liner during the venting step. The analytical signal of the compounds decreased when the venting temperature was higher than 25 $^{\circ}\text{C}$. Regarding the flow of the purge gas, values between 50 and 300 mL min^{-1} were studied. It was decided to work at 125 mL min^{-1} since this permitted the analysis of all the compounds under conditions in which most of the solvent is removed in the venting process. For higher flow rates, a decrease in the signals occurred and the solvent fraction removed did not increase. In the case of 50 mL min^{-1} , a poor shape of the

Fig. 1 Analytical signals and recoveries obtained by extracting increasing sample volumes with a C18 BIN sorbent for 2-chloro-4-methylaniline (a) and 2,4-dichloroaniline (b)

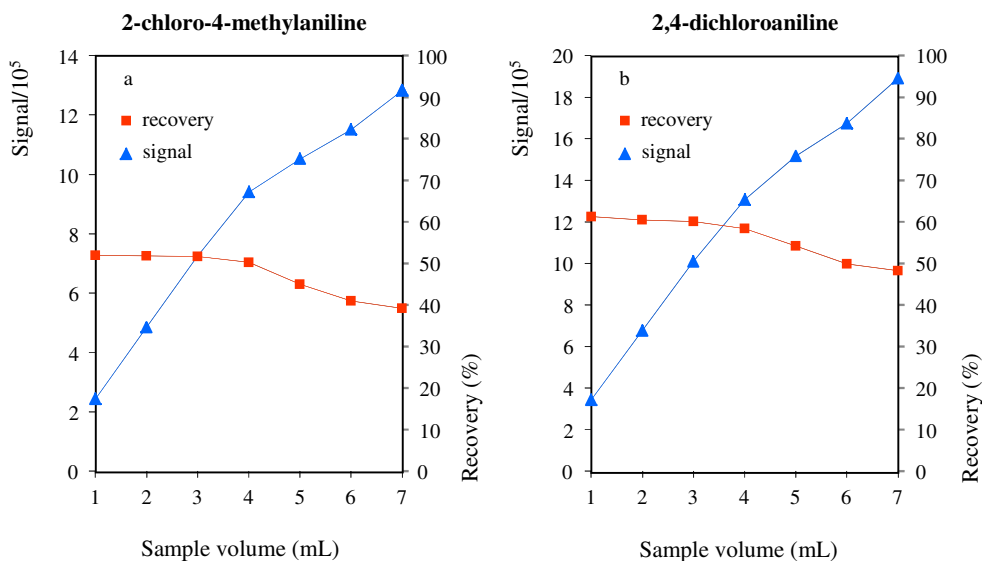


Table 2 Analytical characteristics of the two methods studied

Analyte	PTV-GC-MS				MEPS-PTV-GC-MS					
	Linearity		Level ($\mu\text{g L}^{-1}$)		Linearity		Level ($\mu\text{g L}^{-1}$)		Carry-over %	Recovery %
	Range ($\mu\text{g L}^{-1}$)	R^2	Low	High	Range ($\mu\text{g L}^{-1}$)	R^2	Low	High		
1	DL-2.0	0.9939	0.50	2.0	DL-1,6	0.9915	0.40	1.6	6.4	4
2	DL-16	0.9941	0.50	16	DL-4,0	0.9987	0.25	4.0	0.6	26
3	DL-127	0.9977	0.50	16	DL-0,80	0.9987	0.20	0.80	0.4	38
4	DL-8.0	0.9964	0.50	8.0	DL-3,2	0.9964	0.20	3.2	0.4	26
5	DL-32	0.9989	0.50	16	DL-6,4	0.9999	0.10	1.6	0.5	47
6+7	DL-256	0.9988	0.50	16	DL-6,4	0.9995	0.40	6.4	0.3	16
8	DL-64	0.9991	0.50	16	DL-6,4	0.9998	0.10	1.6	0.5	50
9	DL-64	0.9997	0.50	16	DL-0,80	0.9996	0.05	0.80	0.4	58
10	DL-16	0.9987	0.50	16	DL-6,4	0.9997	0.10	1.6	0.4	60
11	DL-48	0.9969	1.5	48	DL-4,8	0.9967	0.60	4.8	0.3	17
12	DL-64	0.9990	1.0	32	DL-2,8	0.9988	0.09	1.4	0.6	77
13	DL-16	0.9978	0.50	16	DL-2,1	0.9958	0.13	2.1	0.7	54
14	DL-16	0.9984	0.50	16	DL-2,1	0.9986	0.07	1.1	0.5	81
15	DL-64	0.9993	0.25	8.0	DL-0,50	0.9987	0.03	0.50	0.5	84

Analyte concentrations corresponding to low and high levels were used later to evaluate repeatability, reproducibility and accuracy

chromatogram was obtained. The venting time was studied within a range of 0.30 and 0.60 min. Maximum signals for all the compounds were obtained for a value of 0.30 min. For higher values, a decrease in the signals occurred since a fraction of the analytes was eliminated with the solvent. Three different injection times (from PTV to GC) were studied (0.5, 1.0, and 1.5 min). The injection time finally chosen was 1.0 min. When this time was shorter, desorption of the analytes retained in the liner was incomplete. An increase in this variable did not elicit any significant increase in signal for the analytes studied.

Fast GC parameters

In order to separate the analytes, different initial temperatures (ranging between 40 and 50 °C), initial times (within the 2.0–4.0 min range) and temperature ramps (ranging between 20 and 60 °C min⁻¹) were tested. Figure 2a shows the total ion chromatogram obtained on analyzing a solution containing all the compounds with the optimized method described in the “Experimental” section. Nine of 15 compounds appear completely separated from the others, and the other 6 are seen in three partially overlapping pairs. The retention times are shown in Table 1. The partial overlapping of these compounds does not prevent their individual chromatographic quantification using the extracted ion chromatograms, as may be seen for the pairs of compounds *o*-anisidine/3,5-dimethylaniline (see Fig. 2b) and 2,4,6-trichloroaniline/3,4-dichloroaniline (see Fig. 2d). The mass

spectra of the *m*-chloroaniline/*p*-chloroaniline isomers were identical, and complete separation was not achieved (see Fig. 2c) under any of the experimental conditions described above. The use of a different stationary phase with a higher degree of polarity than that used here would improve the separation of both isomers.

All peaks indicated in Fig. 2 had widths at half height ($W_{1/2}$) of less than 1 s (ranging from 0.60 s for *o*-anisidine to 0.73 s for diphenylamine). In fast GC, the usual value [35] for peak widths at half height is 0.2–3 s and the typical run-times range from 1 to 10 min. Thus, this case is a fast GC application for the compounds studied. Peak symmetry at 10 % height for all the compounds was within 0.95 and 1.05 except for the aniline (0.79).

MS parameters

Different dwell times (1–100 ms) in the SIM mode were assayed. A dwell time of 100 ms afforded a bad peak definition due to the few points defining it. However, 1 ms of dwell time increased the noise. A compromise for both parameters was found when a dwell time of 10 ms was used.

Evaluation of the methods

Solutions of the 15 aromatic amines were prepared in ethyl acetate at six different concentrations (see Table 2) and were analyzed with the method based on PTV-GC-MS. Ultrapure aqueous solutions of the analytes were also prepared at six

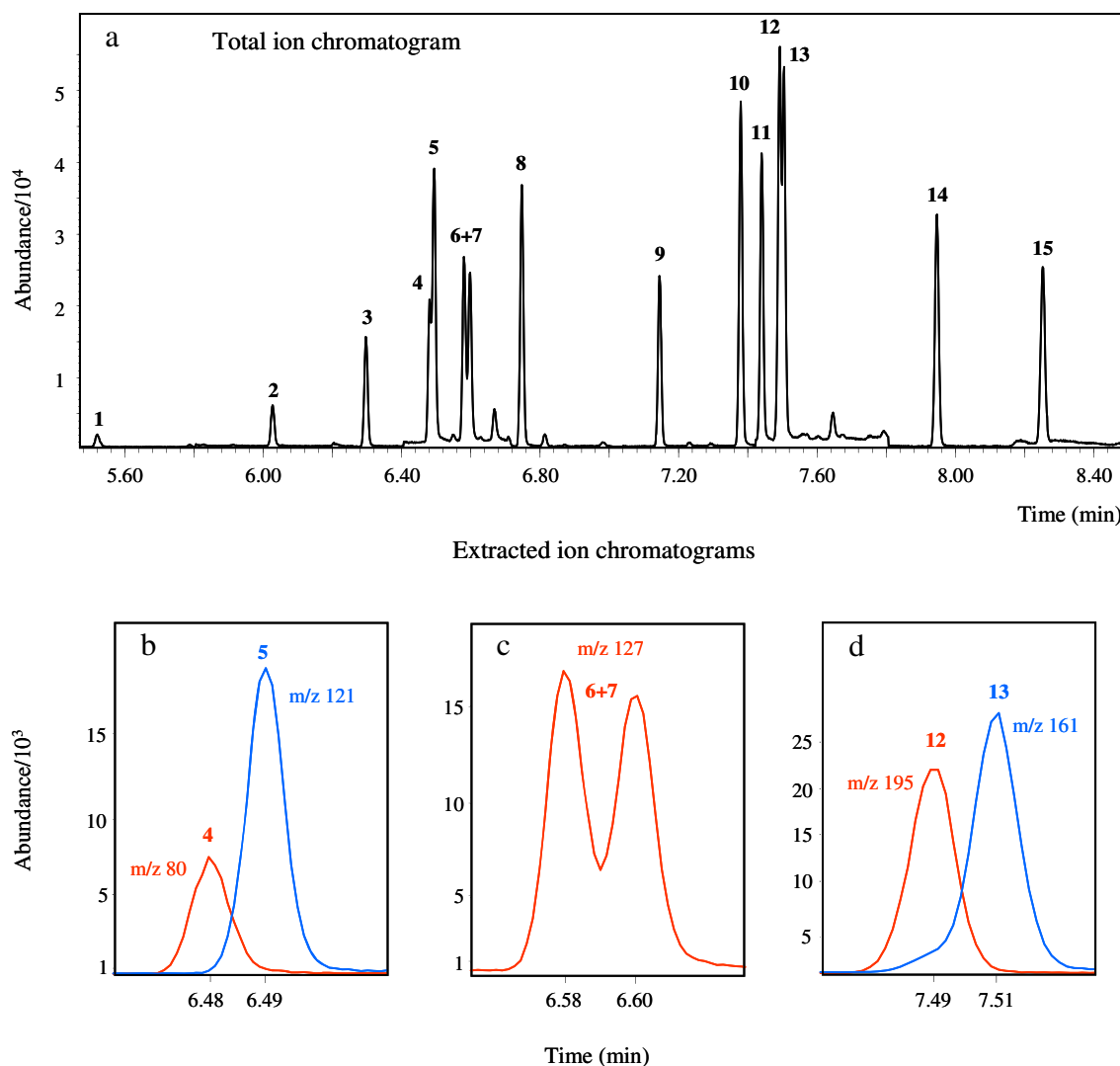


Fig. 2 a Total ion chromatogram for a laboratory-prepared solution containing the 15 aromatic amines in ultrapure water. **b–d** Extracted ion chromatograms corresponding to the pairs of compounds *o*-anisidine (No. 4)/3,5-dimethylaniline (No. 5), *m*-chloroaniline (No. 6)/*p*-

chloroaniline (No. 7) and 2,4,6-trichloroaniline (No. 12)/3,4-dichloroaniline (No. 13). The compounds are labeled with numbers according to Table 1

different concentrations (see Table 2) and were subjected to the extraction procedure prior to the PTV-GC-MS analysis. In both cases, triplicate measurements were made for each calibration standard. The analytical signals used for the calibration curves were the peak areas of the compounds in the extracted ion chromatograms (SIM mode) for the quantification ions shown in Table 1. The quantification of *m/p*-chloroaniline was performed using the total area corresponding to the sum of the individual areas of each isomer. It should be recalled that individual quantification may be inaccurate in the case of samples containing different concentrations of both isomers. All calibrations showed good linear behavior and the values of the coefficient of determination (R^2) were satisfactory for all the compounds using both methods, as shown in Table 2. The models did

not show lack of fit. The limits of detection and quantification were calculated as three and ten times, respectively, the standard deviation of a standard solution ($n=6$) that provided an S/N ratio of approximately 3, divided by the slope of the calibration straight line. The limits of detection in ultrapure water (Table 3) were within the 6 and 350 ng L⁻¹ range for the method in which MEPS was used and ranged between 63 and 928 ng L⁻¹ in the other case (PTV-GC-MS). The improvement in the quantification limits ranged between 2- and 12-fold for 13 of the compounds studied and 50-fold for 2,4,6-trichloroaniline when MEPS was used in comparison to the method exclusively based on PTV-GC-MS. Similar limits were obtained with both methods for aniline (No. 1), which was poorly retained in the sorbent. Repeatability and reproducibility were determined at two

Table 3 Repeatability, reproducibility and detection (DL) and quantification limits (QL) in ultrapure water for the two methods studied

Analyte	PTV-GC-MS				DL (ng L ⁻¹)	QL (ng L ⁻¹)	MEPS-PTV-GC-MS				DL (ng L ⁻¹)	QL (ng L ⁻¹)
	Repeatability		Reproducibility				Repeatability	Reproducibility	DL (ng L ⁻¹)	QL (ng L ⁻¹)		
	RSD %		RSD %									
	Low level	High level	Low level	High level			Low level	High level				
1	5	5	6	6	254	770	3	4	4	4	301	911
2	7	3	7	7	379	1148	2	5	9	5	150	454
3	7	2	11	7	164	498	5	4	9	6	53	161
4	6	4	6	7	117	354	8	7	8	8	69	210
5	9	3	11	8	164	496	5	4	9	4	18	55
6+7	4	2	4	6	176	534	3	3	3	3	53	162
8	6	3	8	8	126	380	5	2	10	5	70	213
9	5	3	6	7	77	234	2	3	7	5	7	20
10	5	3	7	6	93	281	5	2	6	4	17	50
11	8	3	6	7	928	2811	5	5	21	17	350	1060
12	7	2	10	8	283	858	2	1	7	6	6	17
13	6	2	11	7	164	496	5	1	5	4	22	66
14	6	3	7	8	85	258	3	3	7	6	14	42
15	7	2	11	7	63	190	3	2	9	6	8	24

Repeatability and reproducibility were studied at two different levels (low and high) according to Table 2

concentration levels (Table 2). Repeatability was evaluated by performing the extraction and injection (or only the injection when MEPS was not used) six times for each level on the same day. The relative standard deviation (RSD) was lower than or equal to 9 % for both methods (Table 3), indicating good precision. To determine reproducibility, extraction and injection (or only the injection when MEPS was not used) was performed six times per day on two non-consecutive days. In all cases, the RSD was lower than or equal to 11 % (Table 3), except for *o*-nitroaniline (No. 11, RSD 21 %), indicating the good reproducibility of the methods.

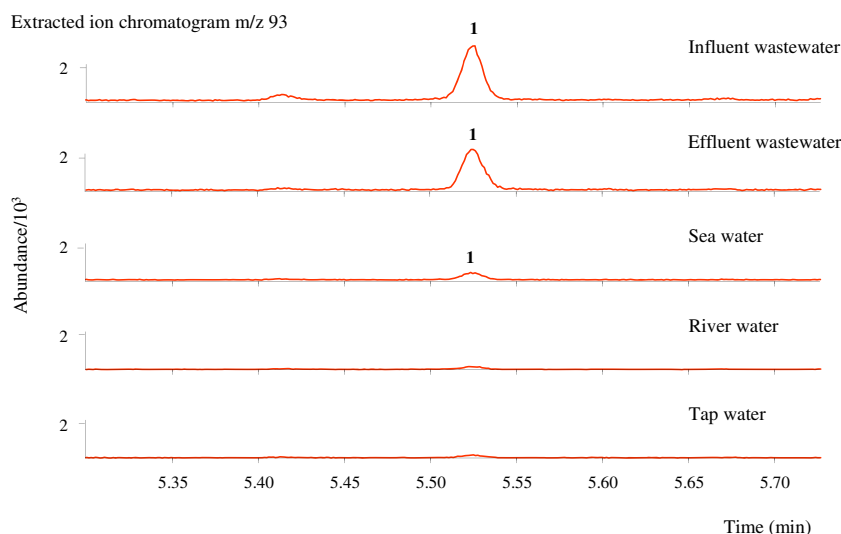
Some methods for the determination of aromatic amines in water samples used different preconcentration techniques (SPE, SPME or SBSE among others) and derivatization reactions [6, 11, 12, 18, 20, 30]. Although better detection limits were reported in some cases [5–8, 11, 16, 18, 20, 30], these methods showed important disadvantages in comparison with that proposed here. Compared with SPE, the proposed MEPS method has some advantages, mainly the reduction in sample volume, solvent consumption and analysis time. Regarding SPME and SBSE, a higher extraction time is required in comparison to MEPS. The use of a derivatization reaction increases the analysis time, sample preparation, and the error associated with such steps. The LLE-GC-MS method [20] has the lowest detection limits (low nanograms per liter) found in literature but it required

sample extraction and derivatization involving more than 1.0 h, chloroform as the extractant, and long chromatographic run-time (50 min).

Determination of aromatic amines in different environmental water samples

The determination of aromatic amines using MEPS-PTV-GC-MS was carried out in five different environmental water samples: sea water, tap water, river water, influent, and effluent water from a sewage plant. To check the possible existence of a matrix effect, all the samples and the ultrapure water were spiked with a solution of the compounds at different concentration levels. In addition, the influent wastewater sample was diluted at a proportion of 1:3 with ultrapure water, because this sample was complex, and dilution extended the life of the cartridge and problems with the blanks were reduced. The signals for the ultrapure water and the water samples were similar, and no important matrix effect was observed. Aromatic amines were predicted using external standard calibration in ultrapure water. Aniline (No. 1) was found in the sea water samples ($0.8 \pm 0.1 \mu\text{g L}^{-1}$) and in the influent ($16 \pm 1 \mu\text{g L}^{-1}$) and effluent wastewater ($12 \pm 1 \mu\text{g L}^{-1}$). Owing to the high concentration of this compound in the influent and effluent wastewater, they were diluted at a proportion of 1:25 and 1:20, respectively. Figure 3 shows the extracted ion chromatogram for

Fig. 3 Extracted ion chromatograms for all the environmental water samples studied. Aniline (*No. 1*) was found in influent and effluent wastewater and in sea water



the base peak of aniline ($m/z=93$) in the five samples studied. None of the other compounds were found. The detection limits in the different samples were calculated following the same strategy described in “Evaluation of the methods” and they were very similar to those obtained in ultrapure water (Table 2). To check the possibilities of the methodology, all samples were spiked with the 15 compounds studied at the low and high concentration levels shown in Table 2 (columns 8 and 9). Table 4 shows the predictions, their confidence intervals (95% probability) and accuracy for the low concentration level. Accuracy ranged between 80 and 120 % for most of the compounds. Similar results were obtained when samples were spiked at the high concentration level. In case of aniline in sea water and influent and

effluent waste water, accuracy was obtained by comparison of the amount added with the difference between the results obtained with and without the addition. The precision ($n=5$) was satisfactory, with a RSD lower than 10 % in most cases. These results reveal the applicability of the proposed methodology for the quantification of these compounds in water samples.

Conclusions

A new sensitive method for the determination of 15 aromatic amines in water samples has been implemented based on the capacity for the concentration of MEPS and on the

Table 4 Added and predicted concentrations and accuracy (*A*) in the environmental water samples using the method based on MEPS-PTV-GC-MS

Analyte	Added ($\mu\text{g L}^{-1}$)	Sea water		River water		Tap water		Sewage effluent water		Sewage influent water	
		Found ($\mu\text{g L}^{-1}$)	<i>A</i>	Found ($\mu\text{g L}^{-1}$)	<i>A</i>	Found ($\mu\text{g L}^{-1}$)	<i>A</i>	Found ($\mu\text{g L}^{-1}$)	<i>A</i>	Found ($\mu\text{g L}^{-1}$)	<i>A</i>
1	0.40	0.49±0.06	123	0.48±0.06	120	0.48±0.09	120	0.46±0.06	115	0.53±0.04	133
2	0.25	0.30±0.02	119	0.29±0.03	115	0.33±0.04	131	0.25±0.01	99	0.24±0.02	95
3	0.20	0.248±0.009	124	0.23±0.01	115	0.22±0.01	110	0.216±0.009	108	0.187±0.003	94
4	0.20	0.19±0.01	95	0.15±0.02	75	0.19±0.01	95	0.19±0.01	95	0.179±0.007	90
5	0.10	0.097±0.006	97	0.086±0.005	86	0.071±0.009	71	0.077±0.005	77	0.11±0.01	110
6+7	0.40	0.42±0.02	105	0.38±0.01	95	0.41±0.02	103	0.38±0.01	95	0.39±0.03	98
8	0.10	0.100±0.007	101	0.094±0.007	95	0.09±0.01	91	0.11±0.01	111	0.100±0.007	101
9	0.05	0.048±0.002	95	0.045±0.001	89	0.047±0.002	93	0.055±0.006	109	0.052±0.003	103
10	0.10	0.102±0.002	102	0.083±0.002	83	0.081±0.002	81	0.119±0.002	119	0.100±0.003	100
11	0.60	0.5±0.1	83	0.61±0.08	102	0.6±0.1	100	0.61±0.08	102	0.61±0.08	102
12	0.09	0.07±0.01	79	0.070±0.009	79	0.07±0.01	79	0.107±0.008	121	0.112±0.009	127
13	0.13	0.08±0.01	60	0.09±0.01	68	0.08±0.01	60	0.11±0.01	83	0.15±0.02	113
14	0.07	0.065±0.003	97	0.067±0.004	100	0.055±0.004	82	0.076±0.004	113	0.074±0.004	110
15	0.03	0.037±0.001	116	0.029±0.003	91	0.026±0.001	81	0.044±0.002	137	0.040±0.003	125

coupling of a PTV, which allowed large volume injection, to a GC-MS system.

Good results were achieved for all the compounds in terms of repeatability and reproducibility. The detection limits were at nanograms per liter for most of the compounds, which suggests the use of the method for the determination of these analytes in different types of water samples. The improvement in the quantification limits ranged between 2- and 12-fold for 13 of the compounds studied and 50-fold for 2,4,6-trichloroaniline when MEPS was used in comparison with the method exclusively based on PTV-GC-MS. Aniline was poorly retained in the sorbent. Only one C18 MEPS BIN has been used in this work and it still works properly; this can be considered a proof of high robustness and stability.

Aromatic amines in sea, river, tap and influent and effluent waste water samples were predicted using calibration standards in ultrapure water since no matrix effect was observed. Because there was no significant variability in either sample preparation or in sample injection, no internal standard was used. The method allowed the quantification of all the aromatic amines studied with a satisfactory accuracy and precision.

Fully automated MEPS-PTV-GC-MS could improve detection limits since the total eluted volume can be injected directly into the PTV injector.

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