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Journal of Chromatography A, 1010 (2003) 243–253
JOURNAL OF CHROMATOGRAPHY A
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Determination of aromatic primary amines at μg l^{-1} level in environmental waters by gas chromatography–mass spectrometry involving *N*-allyl-*N′*-arylthiourea formation and their on-line pyrolysis to aryl isothiocyanates

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Received 29 November 2002; received in revised form 15 May 2003; accepted 18 June 2003

Abstract

Derivatization of aromatic primary amines to *N*-allyl-*N′*-arylthioureas by reaction with allyl isothiocyanate and GC–MS of the derivatives, when pyrolysis to aryl isothiocyanates occurs in the heated injector, has been used to determine aromatic amines in the range 0.5–50 μg l^{-1} with a correlation coefficient, *r*, in the range 0.9902–0.9992. The limit of detection ranged 8 to 30 ng l^{-1} when 60 ml of sample were preconcentrated, after derivatization, on a styrene–divinylbenzene copolymer sorbent. The pyrolytic cleavage of *sym*- and *unsym*-diaryl or alkyl-/arylthioureas has been rationalized. The chromatography of isothiocyanates is much superior to that of aryl amines and the specific mass fragmentation permits positive identification of amines. The method has been applied to spiked drinking water, groundwater and river water samples, when the recovery ranged from 84 to 109% with RSD of 5–9%, and to detect aromatic amines formed by reductive cleavage of azo dyes in effluents when the recovery of amine was in the range 81–95% with RSD 8–15%. The method is not applicable to nitroanilines.

Keywords: Water analysis; Environmental analysis; Pyrolysis; Derivatization, GC; Amines, aromatic; *N*-allyl-*N′*-arylthioureas; Aryl isothiocyanates

1. Introduction

Aromatic amines such as aniline and related derivatives constitute an important class of environmental water pollutants owing to their toxicity and carcinogenic nature [1,2]. Substituted aromatic amines have been widely used in the chemical industry as intermediates in the production of dyes, pesticides, pharmaceuticals, paints, etc. They may be released into the environment directly as a result of industrial discharge from factories or indirectly as a result of degradation of phenylcarbamates, phenylurea and anilide herbicides and azo dyes [3–5]. Due to their high solubility in water, aromatic amines can easily permeate through soil and contaminate ground water [6,7]. They can be present at trace levels in drinking water and commercial products such as soft

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0021-9673/03/$ – see front matter
doi:10.1016/S0021-9673(03)01123-3

drink beverages, hard candies and other food products [8].

The European Union (EU) has included many anilines in the list of priority pollutants which should be monitored in environmental waters. Limits of detection as low as 0.1 μg l^{-1} are required in order to comply to EU regulations for drinking water quality, and to study the fate and transport of pollutants in aquatic media [9]. Chromatographic separation and quantification of primary amines is hampered by their polarity, which can cause tailing and irreversible adsorption [10–12]. The mass spectra of primary amines are often not ideal for their characterization, especially if these compounds are present in low concentration [13]. Several methods have been proposed for the derivatization of amines [13,14]. Nuclear halogenation with bromine [12,15,16] and replacement of the amino group by iodine [10,11] have been used with GC–electron-capture detection (ECD). Benzoylation and GC–MS have found application to a wide range of analytes including amines [17]. Conversion to isothiocyanates has been reported in the literature [18], the sequence of reactions used being formation of dithiocarbamic acids with carbon disulfide and their decomposition on heating with lead nitrate. The reaction is tedious and environmentally unfriendly as large quantity of toxic lead salt is used. Dithiocarbamic acids, resulting from the reaction of aliphatic amines with carbon disulfide, yield isothiocyanates when injected into the heated injector of a gas chromatograph [19]. β-Aryl-substituted alkylamines directly form isothiocyanates when reacted with carbon disulfide at room temperature; thus, amphetamine forms β-phenylisopropyl isothiocyanate [13].

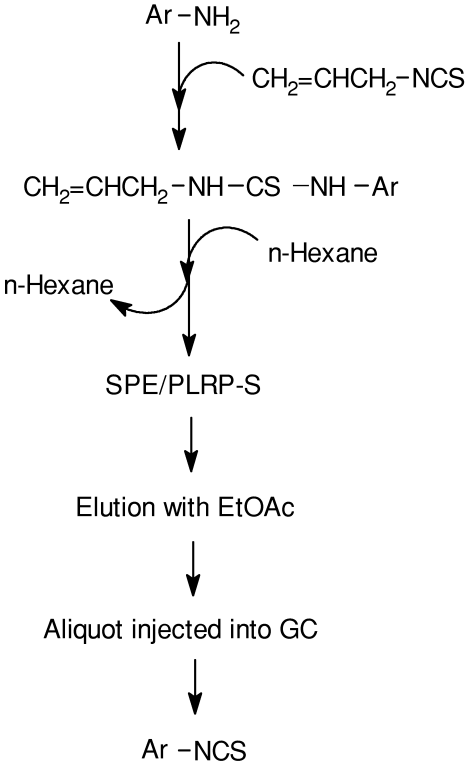


Fig. 1. Reaction scheme and analytical steps.

A pre-concentration step is necessary before the chromatographic analysis at μg l^{-1} level can be performed. Off-line pre-concentration using liquid–liquid or solid-phase extraction (SPE) has been employed [20–24]; low recoveries are usually obtained for many anilines on a number of sorbents and severe losses of the more volatile anilines take place during the solvent removal step. Liquid-phase microextraction that uses only a drop of organic solvent has also been used subsequently for analysis by GC [25–27]. Dithiocarbamic acid formation cannot be a suitable derivatization reaction since these compounds, being polar, are not suitable for SPE and are unstable at ambient temperature.

In the present work a new thermolysis method, the pyrolysis occurring in the GC injector, is proposed for the determination of aromatic primary amines as their isothiocyanates. Aromatic amines were derivatized to *N*-allyl-*N*′-arylthiourea by reaction with allyl isothiocyanate. Pyrolysis of the derivative always produced the corresponding aryl isothiocyanate and the total process can be regarded as a straightforward conversion of the aromatic primary amines into their isothiocyanates. Derivatization in the aqueous phase solves the problem of early breakthrough during trace enrichment, while the chemical conversion in the hot injector helps to prevent tailing peaks. The extraction efficiencies are high and the derivatives have good stability and practically no loss due to vaporization during the whole SPE procedure. The general strategy for the analysis of real world samples consisted of derivatization and SPE of analytes followed by GC–MS under full scan conditions (Fig. 1).

2. Experimental

2.1. Instrumentation

The GC–MS instrumentation used consisted of a Hewlett-Packard (Avondale, PA, USA) G1800B GCD system (HP 5890 Series II gas chromatograph with a quadrupole mass detector) having a HP-5 (5% phenyl-substituted methylpolysiloxane) 30 m×0.25 mm I.D. (0.25 μm film thickness) capillary column. Helium (99.999%), at a flow-rate of 1 ml min^{-1}, was used as carrier gas. The injector temperature was 250 °C. The GC oven temperature was held at 60 °C for 3 min and then programed to 180 °C at 9 °C min^{-1}, held for 0.5 min and then increased to 260 °C at 20 °C min^{-1}, held for 2 min. The GC–MS transfer line was maintained at 300 °C, and the mass spectrum was scanned from m/z 45 to 450. Electron energy of 70 eV and splitless injection mode was used. Chromatographic data were acquired using HP ChemStation software G1074B version A.01.00 (Hewlett-Packard). A sample volume of 1 μl was injected into the GC system. The configuration of the off-line SPE system is given in Fig. 2. Off-line SPE cartridges (10 mm×3 mm I.D.) were packed in the laboratory with a slurry in methanol of PLRP-S (styrene–divinylbenzene co-polymer, particle size 8 μm, Polymer Labs., Shropshire, UK) sorbent. Cartridge packing tools and column holder were obtained from the Free University, Amsterdam, The Netherlands. A Shimadzu (Kyoto, Japan) HPLC (LC-2A) pump was used for the activation of SPE sorbent, sample loading and washing. Solid-phase extraction cartridges, 2.8 ml, packed with C_{18} sorbent (500 mg) (Alltech Associates, Deerfield, USA) were used. An all-glass 0.45 μm membrane filter unit (Millipore-India, Mumbai, India) was employed for filtration of water samples.

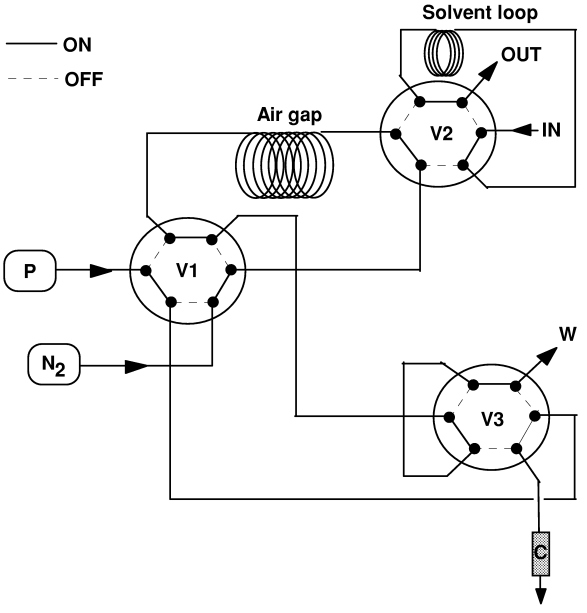


Fig. 2. Experimental set-up for the off-line SPE of *N*-allyl-*N′*-arylthioureas. V1–V3 = Rheodyne 7010 6-port valves; P = HPLC pump; C = SPE (10 3 mm I.D.) cartridge packed with PLRP-S; and W = Waste. Solvent loop was 200 μl, and air gap PTFE tubing (7 m×0.8 mm I.D.).

2.2. Reagents and materials

HPLC-grade methanol, acetonitrile, ethyl acetate, *n*-hexane and water (Merck, Mumbai, India) were used for sample preparation. Anhydrous sodium sulfate was from Merck. Amines used in this work were aniline, 2-toluidine, 3-toluidine, 4-toluidine, 2-chloroaniline, 4-chloroaniline, 2-anisidine, 3-anisidine, 4-aminobiphenyl, 1-naphthylamine, 3-nitroaniline (BDH, Dorset, UK), 2-aminobiphenyl (Fluka, Buchs, Switzerland), 2,6-dimethylaniline, 3,5-dimethylaniline and 3-chloroaniline (Aldrich, Gillingham, UK). Standard solution (2000 mg l^{-1}) of each aromatic amine was prepared in acetonitrile and stored in a refrigerator when not in use. Working solutions were prepared by sequentially diluting the stock solutions. The reagent solution was prepared by diluting a 5 ml aliquot of allyl isothiocyanate (Merck, Darmstadt, Germany) to 100 ml with acetonitrile. *sym*-Thioureas were synthesized by condensation of aromatic amines with carbon disulfide [18] and *unsym*-thioureas by condensation of alkyl or aryl isothiocyanates with aromatic amines [28].

2.3. Real samples

Real water sample, viz., Yamuna river water (Mathura), Ganga river water (Hardwar), Ganga river water (Kolkata), Narmada river water (Jabalpur), underground water (Jabalpur) and dye factory effluents (Jabalpur) were analyzed. All real samples

were filtered through a 0.45 μm membrane filter (Millipore-India, Mumbai) prior to analysis.

2.4. Determination of primary aromatic amines

The time program of events is given in Table 1 for off-line SPE of sample clean-up and enrichment. The SPE cartridge (10×3 mm) containing about 100 mg of PLRP-S sorbent was activated with 2 ml of methanol, and conditioned with 2 ml water, both at a flow-rate of 1 ml min^{-1}. A 60 ml portion of the sample was mixed with 0.5 ml of allyl isothiocyanate, shaken vigorously, and heated at 50 °C for 20 min. The mixture was cooled to room temperature, mixed with 2 ml of *n*-hexane, shaken vigorously and then the hexane layer was separated. The aqueous extract from separation was passed through the SPE cartridge at a flow-rate of 4 ml min^{-1} (pre-concentration step). After sample loading, the sorbent was washed with 2 ml of water (flow-rate 1 ml min^{-1}). The cartridge was dried with nitrogen (30 ml min^{-1}) for 15 min. The analytes were eluted from the SPE cartridge with 100 μl of ethyl acetate containing 3-nitroaniline as the internal standard (2 mg l^{-1}). Eluent was collected over about 50 mg of anhydrous sodium sulfate, kept for 5 min to remove any moisture, and a 1 μl aliquot was injected into the gas chromatograph.

2.5. Detection of aromatic amines in azo dye effluents based on their cleavage

The colored effluents were filtered through a 0.45 μm membrane filter and a 2 ml portion of filtrate was passed through a SPE cartridge (2.8 ml, packed with 500 mg of C_{18} sorbent) that was previously conditioned by passing in sequence 2 ml of methanol and 2 ml of deionized water. The sorbent was washed with 1 ml of deionized water, drained, and the retained azo dye was eluted with 2 ml of methanol. The extract was treated dropwise with tin(II) chloride solution [4 g of tin(II) chloride dissolved in 10 ml of concentrated hydrochloric acid] with periodic heating in a boiling water bath until the dye was fully decolorized. The solution was cooled in ice and treated with 10% (w/v) sodium hydroxide until the first formed precipitate of tin hydroxide redissolved. The cold solution was extracted with two 10 ml portions of diethyl ether. The combined ether extract was treated with 0.5 ml of 0.1 *M* hydrochloric acid and evaporated under a gentle stream of nitrogen. The residue was dissolved in 20 ml of water and subjected to derivatization and GC–MS as before.

3. Results and discussion

3.1. Pyrolysis of substituted thioureas

The chemistry of the reaction of *sym*-diarylthiourea with hot concentrated hydrochloric acid has been described [18]. *sym*-Diarylthioureas are partly converted into the aryl isothiocyanate. Hydrogen sulfide is evolved in the side reaction forming a diarylcarbodi-imide intermediate which undergoes subsequent nucleophilic addition with aromatic amine, also produced in a side reaction, to yield triarylguanidine. Thus, *sym*-diphenylthiourea forms phenyl isothiocyanate and triphenylguanidine when subjected to this reaction.

Since dithiocarbamates of amines form isothio-

Table 1
Time programme for SPE of derivatized aromatic amines

Step	Time (min)	Event	Valve position		
			V1	V2	V3
1	0–2	Flushing SPE cartridge with 2 ml methanol (1 ml min^{-1})	On	On	On
2	2–4	Flushing SPE cartridge with 2 ml water (1 ml min^{-1})	On	On	On
3	4–19	Loading 60 ml of sample (4 ml min^{-1})	On	On	On
	19–21	Cleaning air gap with nitrogen			
4	21–23	Washing SPE cartridge with 2 ml water (1 ml min^{-1})	On	On	On
5	23–38	Drying SPE cartridge with nitrogen (30 ml min^{-1})	On	On	Off
6	38–46	Eluting sample from SPE cartridge with ethyl acetate (0.2 ml min^{-1})	Off	Off	Off

cyanates [29] both in solution by reaction with a heavy metal salt [18] and in gas phase by pyrolysis [19] it was thought to utilize the above chemistry in the determination of aromatic primary amines involving derivatization to substituted thioureas, pyrolysis in the heated injector of GC and on-line chromatography of isothiocyanates formed. However, there was much uncertainty with the pyrolytic cleavage reaction of unsymmetrically substituted thioureas. A series of *unsym*-diaryl-, aryl-, alkyl- and monosubstituted thioureas were therefore subjected to a study on their pyrolysis and identification of products by GC–MS under the conditions as described in the Section 2.

The following observations were made (i) *sym*-diphenyl thiourea gave phenyl isothiocyanate and diphenylcarbodi-imide, the latter escaped nucleophilic addition with aniline in the gas phase, (ii) all *sym*-diaryl thioureas, other than *sym*-diphenyl thiourea, and *unsym*-diaryl thioureas yielded isothiocyanates but none produced diarylcarbodi-imide, (iii) all *N*-allyl-*N*′-aryl thioureas and monosubstituted aryl thioureas produced only aryl isothiocyanates; and (iv) both *N*-methylthiourea and *N,N*′-diethylthiourea eluted unchanged whereas *N*-allyl thiourea decomposed to many unidentified products. Chromatograms of pyrolysis products of *sym*-diphenyl thiourea and *N,N*′-bis(2-anisyl)thiourea are given in Fig. 3, along with the mass spectra of typical derivatives. Results for the pyrolytic products of substituted thioureas are summarized in Table 2.

The reason why only *sym*-diphenyl thiourea, and not other *sym*- or *unsym*-diarylthioureas, produces carbodi-imide is not clear. With fair certainty it is the

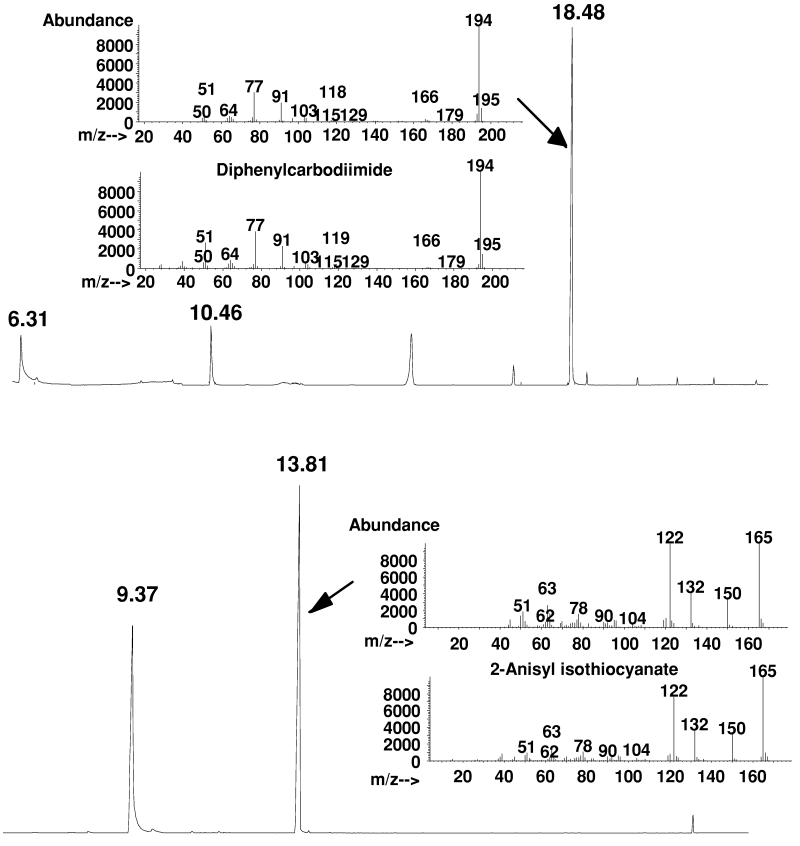
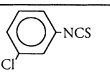
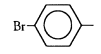
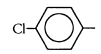
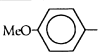
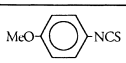
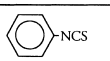
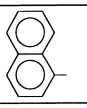
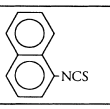
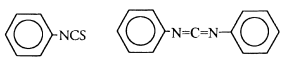
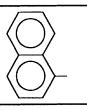
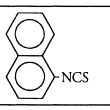
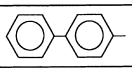
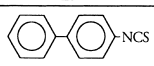
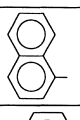
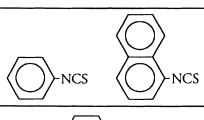
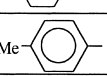
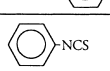
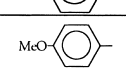
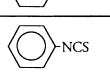
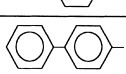
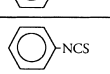


Fig. 3. Chromatograms for the pyrolysis of *sym*-diphenyl thiourea (upper trace; peak/min at 6.31 = aniline, 10.46 = phenyl isothiocyanate, and 18.48 = diphenylcarbodi-imide) and of *N,N*′-bis(2-anisyl)thiourea (bottom trace; peak/min at 9.37 = 2-anisidine and 13.81 = 2-anisyl isothiocyanate). Experimental conditions in the text.

Table 2
Pyrolytic products of substituted thioureas

R—NH—C(=S)—NH—R'		Product
R	**R'**	
		
	CH_2=CH-CH_2-	
		
	CH_2=CH-CH_2-	
	H-	
	H-	
	H-	
		
	CH_2=CH-CH_2-	
	CH_2=CH-CH_2-	
		
		
		
		

weak base substituent on *unsym*-diaryl or alkyl/arylthiourea that is converted into the corresponding isothiocyanate. Aromatic amines are weaker bases than allyl amine and thus *N*-allyl-*N′*-arylthioureas produced aryl isothiocyanates on pyrolysis. This observation suggested a route for the conversion of primary aromatic amines into their isothiocyanates, i.e., reaction with allyl isothiocyanate and pyrolysis of *N*-allyl-*N′*-arylthiourea. Secondary amines also react with allyl isothiocyanate to give *N*-allyl-*N′*-diarylthioureas but the latter do not form aryl isothiocyanates on heating.

3.2. Benefits of derivatization

Pre-column derivatization of aromatic primary

amine to *N*-allyl-*N′*-arylthiourea had the advantage of high breakthrough volume in the SPE, increased retention of aryl isothiocyanates and improved chromatography.

The electron impact mass spectrometric fragmentation of primary aromatic amines is complex. The molecular ions are often of low intensity. A large number of fragment ions are formed but none are good tracer ions; their intensity is low and diagnostic value is usually modest. In aryl isothiocyanates, the different charge distribution stabilizes the molecular ions and favors the formation of usually two high intensity fragments, the molecular ion, $M^{+\cdot}$, and $[M\text{-}58]^{+}$ that results due to the loss of isothiocyanate group. These ions can be monitored during a chromatographic run with a pre-focused mass detector (selected ion monitoring, SIM) or can be extracted (extracted ion chromatography, EIC) after full acquisition (total ion currect, TIC), enabling limits of detection in the ng l^{-1} range.

A disadvantage was noted with amines having electron-deactivating groups, such as nitroanilines, which are too weak nucleophiles to undergo thiourea formation on reaction with allyl isothiocyanate in aqueous medium. Thus, these compounds cannot be determined by this method.

3.3. Optimization of derivatization

The variation in peak areas (ratio to that of internal standard) for derivatized aromatic amines vs. the volume of reagent (0.1 to 1 ml of 5% allyl isothiocyanate used) was investigated to optimize the volume of the reagent. Optimum peak areas were obtained when 0.5 ml of the reagent was used; thus, this volume was used in subsequent experiments. It was expected that the reaction would be faster and quantitative in basic medium since free amines are more nucleophilic than their protonated species. In solutions of pH≥8, two broad peaks identified as *N,N′*-diallylurea and *N,N′*-diallylthiourea were observed due to the hydrolysis and subsequent side-reactions of allyl isothiocyanate. Thus, the aqueous samples should not be too acidic or basic; optimum reaction was found over a pH range 5 to 6.5. Derivatization was far from completion at ambient temperature even after 1 h of standing. Heating for 20 min at 50 °C gave optimum peak areas; no increase was found for additional 30 min heating.

3.4. Solid-phase extraction

Allyl isothiocyanate that was left after reaction was removed by liquid–liquid extraction with *n*-hexane and the aqueous phase from extraction was subjected to SPE on PLRP-S sorbent. The selection of sorbent for pre-concentration of analytes was based on three parameters, the retention capacity of sorbent, shorter drying time and ease of elution of the analytes. C_{18} and C_8 had lower breakthrough volumes, longer drying time and larger elution volumes. PLRP-S sorbent was the best sorbent found. Allylarylthioureas were found to have better retention than their corresponding anilines, as confirmed by extraction recovery that was in the range 96 to 102%. Recoveries >100%, as found here and in Section 3.7, are positive bias of the method and this phenomenon has been observed earlier [11,12,15–17]. Analyte losses during drying the SPE cartridge were insignificant as confirmed by increasing the drying time up to 1 h when peak area ratios were unaffected.

To study the breakthrough volume for SPE, 40 ml of 50 μg l^{-1} of each aromatic amine was diluted with 0, 20, 40 and 60 ml of HPLC-grade water and subjected to SPE as described before. There was no significant change in peak area ratios of analytes when up to 80 ml of sample was loaded, however, a 15% decrease was observed with 100 ml of sample. Therefore, up to 80 ml of sample can be loaded without any breakthrough of analytes at a sampling flow-rate of 4 ml min^{-1}.

3.5. Conditions for chromatography and detection

Fig. 4 shows the chromatogram obtained in the derivatization–SPE–pyrolysis–GC–MS of 60 ml of HPLC water spiked with 20 μg l^{-1} aromatic amines. Mass spectra of all tested compounds agreed well (95–98% matching) with the standard NBS and Wiley mass spectral libraries. Complete merging of 3- and 4-chloroaniline was observed and attempts to separate them using various temperature programs were unsuccessful. The two compounds have identi-

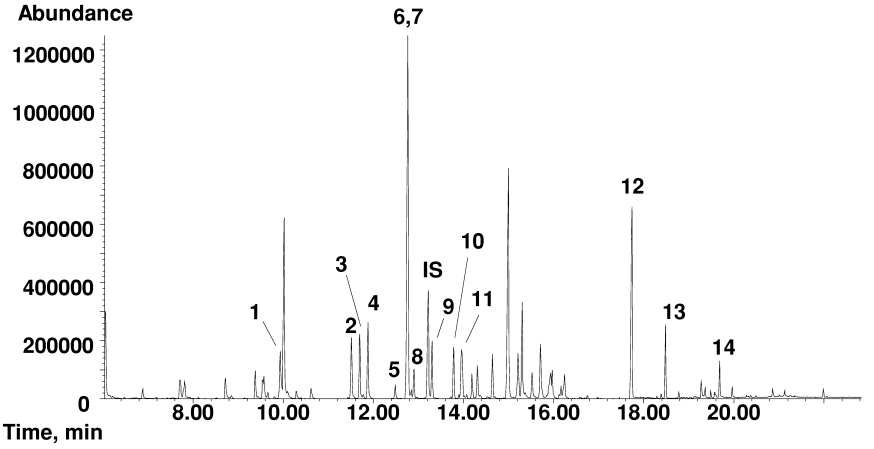


Fig. 4. Total ion chromatogram for the derivatization–SPE–GC–MS of 60 ml of HPLC water spiked with 20 μg l^{-1} of aromatic amines. Peaks identification (as isothiocyanates): 1 = aniline; 2 = 2-toluidine; 3 = 3-toluidine; 4 = 4-toluidine; 5 = 2-chloroaniline; 6 = 3-chloroaniline; 7 = 4-chloroaniline; 8 = 2,6-dimethylaniline; 9 = 3,5-dimethylaniline; 10 = 2-anisidine; 11 = 3-anisidine; 12 = 1-naphthylamine; 13 = 2-aminobiphenyl and 14 = 4-aminobiphenyl. I.S. = 3-nitroaniline. Column: HP-5, 30 m × 0.25 mm I.D., 0.25 μm film thickness; carrier gas, helium, flow-rate, 1 ml min^{-1}; sample volume, 1 μl.

cal mass spectra which precluded their separate quantification. Peaks for isothiocyanates of aniline, 3-anisidine and 4-aminobiphenyl also eluted near impurities (mostly by-products). All other peaks were well resolved. EIC on the basis of specific ions was used for quantification.

3.6. Calibration graph and detection limits

The dependence of the chromatographic signal on the concentration for all aromatic amines was determined under optimum conditions of derivatization and GC–MS. A rectilinear graph was obtained between the amount of analyte and the peak area of their isothiocyanate derivatives in the range 0.5–50 μg l^{-1}, the correlation coefficient, r, varied from 0.9902 to 0.9992. Though detection was not critical, the method did not give good linearity for amines below this concentration level. The EU guideline of 0.1 μg l^{-1} is set for individual pesticides and it is apparently not so low for aromatic amines in general. The figures of merit for the present method using a sample volume of 60 ml are summarized in Table 3, limits of detection ($S/N = 3$) ranged from 8 to 30 ng l^{-1} and the RSD was in the range 1.4–10.2%.

3.7. Application to environmental samples

The proposed method was applied to the determination of aromatic amines in environmental samples. Real samples, viz., Yamuna river water (Mathura), Ganga River water (Hardwar and Kolkata), Narmada river water (Jabalpur) and underground water (Jabalpur) were tested. All water samples were filtered through a 0.45 μm membrane filter to remove the particulate matter. For validation of the present method, real samples were spiked with known amounts (20 μg l^{-1}) of aromatic amines and analyzed. Recoveries were 84–109% (RSD of 5–9%) as compared to the recovery of the same amounts spiked to HPLC-grade water. A typical chromatogram obtained is given in Fig. 5.

Chromatograms obtained for the detection of aromatic amines found after cleavage of azo dyes in dyeing factory effluents are given in Fig. 6. The method was validated on azo dyes synthesized in the laboratory, viz., 1-(1′-naphthylazo)-2-naphthol, 4-(3′-chlorophenylazo)resorcinol and 4-(4′-anisylazo)-1-naphthol. Known amounts (about 1 mg) of dye dissolved in methanol were subjected to reductive cleavage. The liberated aromatic amine was derivatized and determined. The theoretical value was calculated on the basis of 1 mole of amine being

Table 3
Features of merit in the determination of aromatic amines as their isothiocyanate (range 0.5–50 μg l^{-1})

Compound	t_R (min)	m/z[a]	r[b]	LOD[c] (ng l^{-1})	RSD (%)[d] ($n=6$)
Aniline	9.94	77, 135	0.9924	25	2.7
2-Toluidine	11.54	117, 149	0.9980	20	6.7
3-Toluidine	11.43	91, 149	0.9940	18	1.6
4-Toluidine	11.92	91, 149	0.9976	16	1.4
2-Chloroaniline	12.51	111, 169	0.9975	30	8.3
3-Chloroaniline/ 4-chloroaniline	12.78	111, 169	0.9959	8	6.1
2,6-Dimethylaniline	12.92	163	0.9945	25	10.2
3,5-Dimethylaniline	13.32	148, 163	0.9950	21	8.3
2-Anisidine	13.80	122, 165	0.9990	26	1.9
3-Anisidine	13.98	122, 165	0.9867	28	6.3
1-Naphthylamine	17.74	127, 185	0.9902	14	5.5
2-Aminobiphenyl	18.50	178, 211	0.9919	18	4.3
4-Aminobiphenyl	19.70	152, 211	0.9913	22	3.0
3-Nitroaniline[e]	13.27	92, 138	0.9985	24	3.5

[a] Ions, m/z, selected for quantification.
[b] Based on seven concentration levels over the calibration range.
[c] LOD = limit of detection.
[d] RSD (%) found for 20 μg l^{-1} spike of each compound.
[e] Used as the internal standard.

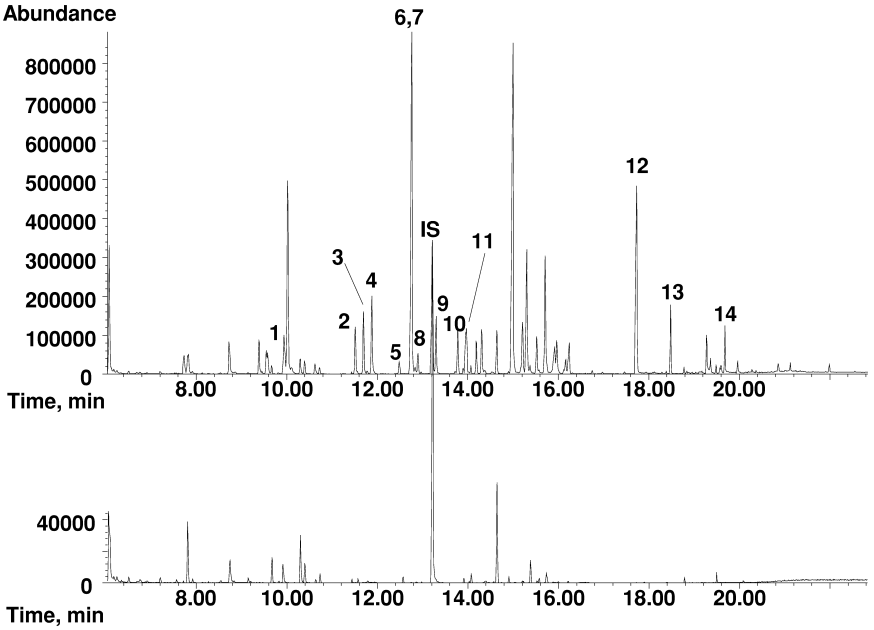


Fig. 5. Total ion chromatogram of Ganga River water (Hardwar, Uttaranchal State, India) sample blank with internal standard, lower trace, and that spiked with 20 μgl^{-1} of aromatic amines, upper trace. Peak identification and chromatographic conditions as in Fig. 4.

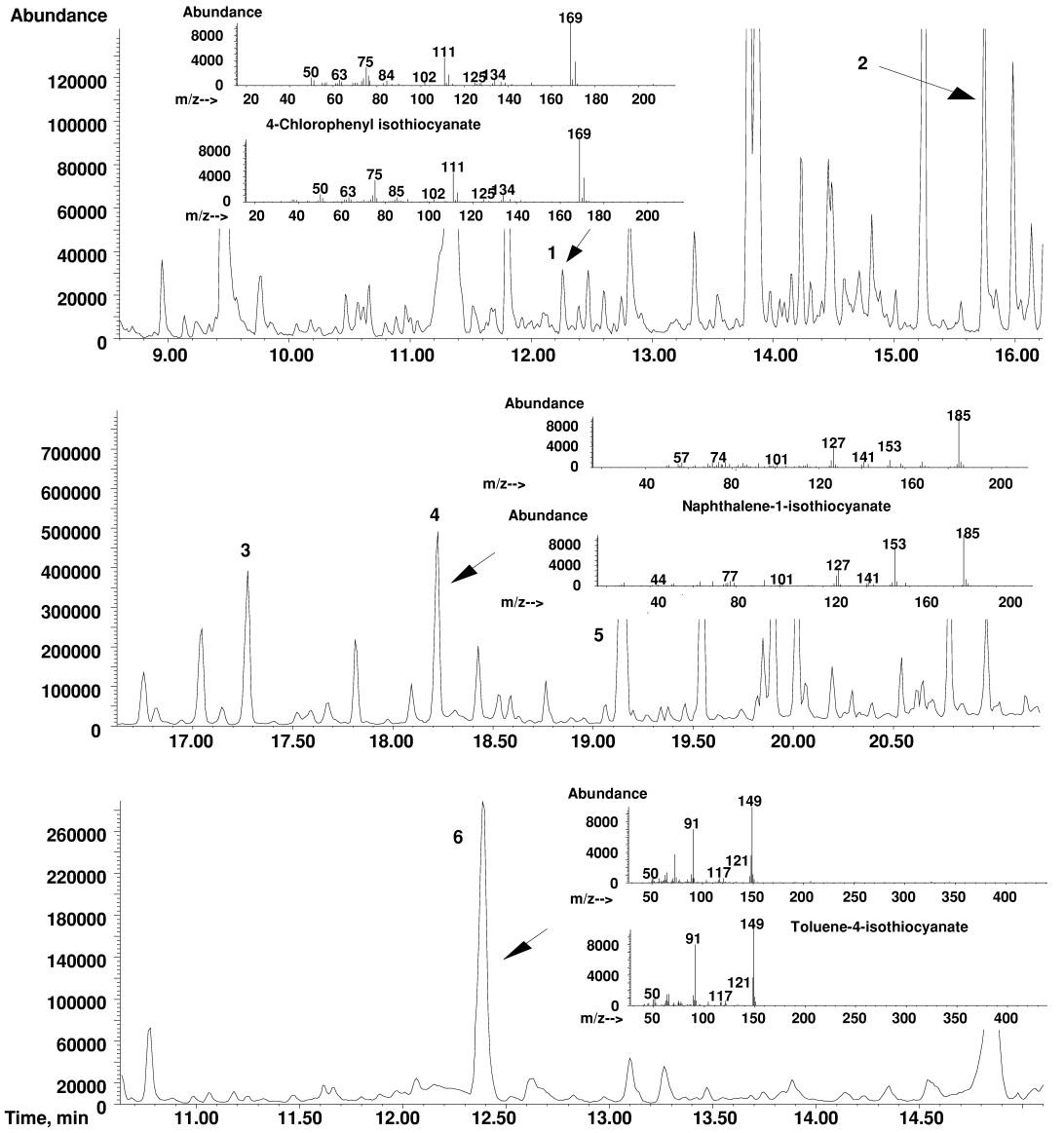


Fig. 6. Total ion chromatogram of aromatic amines (as isothiocyanates) produced after cleavage of azo dyes, and other compounds found in dyeing factory effluents. Peaks: 1 = 4-chlorophenylisothiocyanate; 2 = benzophenone; 3 = *N*-(1-naphthyl)ethylamine; 4 = 1-naphthylisothiocyanate; 5 = 3-methyl-benzo[*f*]quinoline; and 6 = toluene-4-isothiocyanate. Chromatographic conditions as in Fig. 4.

produced by each mole of the azo dye. The recovery of amine was in the range 81–95% (RSD 8–15%).

4. Conclusions

The proposed method using pre-column derivatization to *N*-allyl-*N′*-arylthioureas and their thermolytic conversion into aryl isothiocyanates in the GC injector has been found to be convenient and selective to determine aromatic amines in their complex mixtures in aqueous samples. During pyrolysis, the allyl group was decomposed leaving aryl isothiocyanate. Thus, the amino group of aro-

matic amines was exchanged for the thiocyanate group of allyl isothiocyanate. PLRP-S was a suitable sorbent owing to its higher retention efficiency and shorter drying time after sample loading. The specific mass fragmentation pattern of aryl isothiocyanates can be used for positive identification of aromatic amines. The described analytical method is rapid and together with the SPE clean-up can be automated and applied to control the water quality of environmental waters. It is also possible to use sulfur-sensitive detection and obtain still clean chromatograms. The derivatization/pyrolysis can be studied further for their synthetic value in the preparation of aryl isothiocyanates.

Acknowledgements

V.S. thanks the Council of Scientific and Industrial Research, New Delhi, for the award of a senior research fellowship. We gratefully acknowledge the support from the European Union (grant No. Cl1*-CT94-0049).

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