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Simultaneous determination of ammonia, aliphatic amines, aromatic amines and phenols at μg l^{-1} levels in environmental waters by solid-phase extraction of their benzoyl derivatives and gas chromatography-mass spectrometry

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Low concentrations of phenols and amines in environmental waters and their low breakthrough volume during solid-phase extraction (SPE) hinder the detection of phenols and aromatic amines, whereas ammonia and aliphatic amines are not suitable for SPE. Pre-column derivatization to arylbenzoates and *N*-alkyl- or *N*-arylbenzamides and their GC-MS is proposed to separate and determine phenols and amines in aqueous samples in the range 0.1–100 μg l^{-1} with correlation coefficients in the range 0.9910–0.9992. The limit of detection ranged from 7 to 39 ng l^{-1} for most analytes (90 ng l^{-1} for 2,3,6-trichlorophenol and 20 μg l^{-1} for ammonia) when 80 ml of sample were preconcentrated, after derivatization, on a styrene–divinylbenzene copolymer sorbent. The developed method was applied to spiked drinking water, groundwater and river water samples, and was used to detect halo-phenols in paper mill effluents. The average recovery ranged from 96 to 110% with RSD of 4–12%. The described method is rapid and can be applied to control the water quality of environmental waters with respect to three important classes of organic pollutants and ammonia.

Aliphatic amines, aromatic amines and phenols are substances of environmental concern owing to their toxicity and persistence. In the European Union (EU), the maximum allowable concentration (MAC) is 0.5 μg l^{-1} for the sum of phenols and amines and 0.5 mg l^{-1} for ammonia. Thus, detection limits at low μg l^{-1} levels are required for monitoring these compounds in drinking water. Chlorophenols represent a major class of contaminants that are released into the environment through many industrial processes and also as a result of degradation of pesticides such as phenoxyalkanoic acids and hexachlorobenzene. Higher chlorinated phenols are used as fungicides for wood preservation. Even small amounts of phenolic compounds can have a significant effect on water quality that may be detrimental to aquatic life[1] and impair the taste and odour of drinking water. Disinfection with chlorine has been associated with the formation of chlorinated phenols.[2] A number of chlorophenols are listed in the EU Directive 76/464/CEE, and in the US EPA list of priority pollutants 11 members are phenolic compounds.[3–6]

Aromatic amines are suspected carcinogenic compounds.[7,8] Substituted aromatic amines have been widely used in the chemical industry as intermediates in the production of dyes, pesticides, pharmaceuticals, paints, *etc*.[9] They may be released directly into the environment as a result of industrial discharge or indirectly through degradation of phenylcarbamates and phenylurea herbicides.[10] Aromatic amines, owing to their high solubility in water, can easily permeate through soil and contaminate groundwater.[11] The EU has included many anilines in the list of priority pollutants which should be monitored in environmental waters. Aliphatic amines have a wide range of industrial applications. These substances are emitted into the atmosphere from anthropogenic sources such as waste incineration, sewage treatment and various industries. Aliphatic amines are well known for their odour and as precursors of *N*-nitrosamines which are carcinogenic substances.[12] Aliphatic amines exhibit poor chromatographic performance and do not have any structural feature that could allow their detection without derivatization. They undergo α-cleavage resulting usually in a base peak at *m*/*z* 30 (CH_2=NH_2^+) that provides little scope for confirmation of identity or quantification through selected ion monitoring (SIM).[13] Separation of phenols by GC is often inadequate and characterized by the occurrence of broad and tailing peaks.[14–16] Although it is possible to minimize the problem of peak tailing due to interactions of aromatic amines with active sites in the injector or the column, it is tedious to maintain good peak shape.[17–19] Derivatization is therefore recommended to enhance extraction efficiency and improve chromatographic performance.[20]

Acetylation is the most common derivatization method for the determination of phenols by GC-FID[14,15] or GC-MS.[16,21] Nuclear bromination of aromatic amines[19] or replacement of the amino group by iodine[17,18] has been used with GC-ECD. Iodinated aromatic compounds have much greater electron affinity, at least by a factor of 150,[17] than other haloaromatics.[20] Dithiocarbamates, resulting from the reaction of primary amines with carbon disulfide, yield the corresponding isothiocyanates when injected into the heated injection port of a gas chromatograph; in electron impact (EI)-MS of alkyl isothiocyanates the molecular ion was the base peak.[13] Derivatization reactions for the determination of amines by GC have been reviewed.[22]

Since there is often a need for monitoring ammonia, aliphatic amines, aromatic amines and phenols in environmental samples, the aim of the present work was to develop a GC-MS method for these substances using a single derivatization reagent and determine them simultaneously. The method consisted in pre-column formation of benzoate esters and benzamides under the conditions of the Schotten–Baumann procedure[23] with benzoyl chloride and solid-phase extraction (SPE) of the derivatives. This technique was found to give positive identification of analytes and their sensitive detection.

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Experimental

Equipment

The GC-MS instrumentation used consisted of a Hewlett-Packard (Avondale, PA, USA) G1800B GCD System (HP 5890 Series II with a quadrupole mass analyzer). The gas chromatograph was fitted with a HP-5 (5% phenyl substituted methylpolysiloxane) capillary column (30 m × 0.25 mm id, 0.25 μm film thickness) and helium (99.999%), at a flow rate of 1 ml min^{-1} (inlet pressure 272 kPa), was used as carrier gas. The injector temperature was maintained at 250 °C and all injections were made in the splitless mode. The GC oven temperature was held at 60 °C for 3 min and then programmed to 225 °C at 25° C min^{-1}, held for 3 min and then increased to 250 °C at 45° C min^{-1}. The GC-MS transfer line was maintained at 280 °C, and the mass spectrum was scanned from *m*/*z* 45 to 450. Chromatographic data were acquired using HP ChemStation software G1074B version A.01.00 (Hewlett-Packard). A sample volume of 1 μl was used for injection. Off-line SPE cartridges (10 × 3 mm id) were packed in-house with a slurry in methanol of PLRP-S (styrene–divinylbenzene copolymer, particle size 8 μm, Polymer Laboratories, Shropshire, UK) sorbent. The cartridge packing tools and column holder were obtained from the Free University, Amsterdam, The Netherlands. The configuration of the off-line SPE system is given in Fig. 1. A Shimadzu (Kyoto, Japan) HPLC (LC-5A) pump was used for the activation of the SPE sorbent, sample loading and washing.

Reagents and standards

HPLC-grade methanol, acetonitrile, ethyl acetate and water (Merck, Mumbai, India) were used for sample preparation. Anhydrous sodium sulfate and sodium hydrogencarbonate were from Merck, and benzoyl chloride was from J. T. Baker, Phillipsburg, NJ, USA. Phenol (Sarabhai, Vadodara, India), 4-chlorophenol (Hopkin & Williams, Dagenham, Essex, UK), 3-nitrophenol, 4-nitrophenol and 2,3,6-trichlorophenol (Aldrich, Milwaukee, WI, USA), 2,3-dichlorophenol, 3,4-dichlorophenol, 2,5-dichlorophenol, 2,6-dichlorophenol, 4-bromo-2,6-dimethylphenol, 2,4,6-trimethylphenol, (Aldrich, Gillingham, Dorset, UK), 2,4-dichlorophenol, aniline, 2-toluidine, 3-toluidine, 4-toluidine, 2-chloroaniline, 4-chloroaniline, 3-anisidine, 4-anisidine (BDH, Dorset, UK), 2-anisidine (Riedel-de Haen, Hannover, Germany), 4-aminoacetophenone, and 2-aminobiphenyl (Fluka, Buchs, Switzerland) were used. All standards used had a purity in the range 98–100%. Standard solutions of phenols and amines (1000 mg l^{-1}) were prepared in acetonitrile and stored in a refrigerator when not in use. Working solutions were prepared by sequentially diluting the stock solutions. Stock solutions of ammonium chloride (Qualigens, BDH, Mumbai, India), methylamine, ethyl amine, (BDH, Poole, Dorset, UK), dimethylamine, isopropylamine, and diethylamine (Merck, Darmstadt, Germany) were prepared in methanol and diluted with methanol to give less concentrated solutions. Solutions of aliphatic amines were standardized by a previously established method.[24]

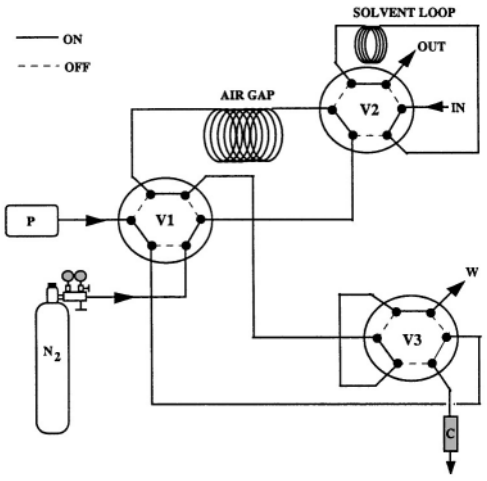

Fig. 1 Experimental set-up for the off-line SPE of benzoate esters and benzamides. V1–V3 = Rheodyne 7010 six-port valves; P = HPLC pump; C = SPE cartridge (10 × 3 mm id) cartridge packed with PLRP-S; and W = waste. Solvent loop volume was 200 μl, air gap was PTFE tubing (7 m × 0.8 mm id).

Standards of benzoate esters and benzamides

The Schotten–Baumann method[25] was used for the preparation of benzoate standards. About 0.5 g of analyte was separately taken in a well stoppered conical flask and dissolved in 3–5 ml of ethanol to which were added about 5 g of sodium hydrogencarbonate dissolved in about 40 ml of distilled water. This was mixed with about 0.5 ml of benzoyl chloride, and the flask was stoppered and shaken vigorously for 10–15 min so that the odour of benzoyl chloride completely disappeared. The solid derivatives were filtered off, washed thoroughly with ice-cold distilled water and recrystallized from ethanol–water.

Real samples

Real water samples, *viz*., Jabalpur city tap water, groundwater, paper mill water, Ganga river water (Kanpur) and Narmada river water (Jabalpur), were filtered through a 0.45 μm membrane filter (Millipore India, Mumbai, India) prior to their analysis.

Determination of phenols and amines

The SPE cartridge (10 × 3 mm) containing 100 mg of sorbent was activated with 3 ml of methanol, and conditioned with 3 ml of water, both at a flow rate of 1 ml min^{-1}. A 100 ml portion of the sample was mixed with about 1 g of sodium hydrogencarbonate and 0.3 ml of benzoyl chloride, and the mixture was shaken vigorously for 15 min. An 80 ml aliquot was passed through the SPE cartridge at a flow rate of 4 ml min^{-1} (the preconcentration step). During this period, nitrogen (30 ml min^{-1}) was passed through the air gap (Fig. 1). After sample loading, the sorbent in the SPE cartridge was washed with 2 ml of water (flow rate 1 ml min^{-1}). The switching valve V3 was actuated to dry the cartridge with nitrogen (30 ml min^{-1}) for 15 min. The solvent loop (200 μl) was filled manually with ethyl acetate containing the internal standard 2,4,6-trimethylphenyl-4′-nitrobenzoate; thereafter, the valves V1 and V2 were switched to elute the analytes. Water delivered by the HPLC pump pushed nitrogen into the air gap that in turn propelled the ethyl acetate through the SPE cartridge. The large air gap avoided the chances of water mixing with ethyl acetate. All the events are summarized in Table 1. The eluate was collected over anhydrous sodium sulfate and a 1 μl aliquot was injected into the gas chromatograph.

Results and discussion

GC-MS analysis

Fig. 2 shows the total ion chromatogram acquired over the range *m*/*z* 45–400 for benzoyl derivatives of phenols and amines.

2,4,6-Trimethylphenyl-4′-nitrobenzoate was selected as the internal standard. Mass spectra of benzamide (from ammonia), its *N*-substituted derivatives (from aliphatic amines and anilines), and benzoate esters (from phenols) agreed well with the EI mass spectra in the standard NIST and Merck mass spectral libraries. Mass spectra of many benzoyl derivatives of substituted phenols and anilines were compared with the spectra obtained for the authentic derivatives synthesized in our laboratory. A custom library was created for spectral matching. Derivatives were identified by their molecular ion peak and retention time. The molecular ion peak was strong for all benzamides but relatively weak for phenylbenzoates (Fig. 3). Thus, benzoylation was advantageous for individual aliphatic amines for which a molecular ion peak was recorded and it was helpful in characterization. For almost all derivatives the base peak was *m*/*z* 105 corresponding to $C_6H_5CO^+$. 2,4-Dichlorophenol and 2,5-dichlorophenol (peaks 13 and 14), as their benzoates, could not be separated. Acetylated derivatives of these two phenols could also not be separated in earlier reports.[26,27] Benzoylated 2-chloroaniline and 2-toluidine (peaks 16 and 17) also overlapped and 2,3-dichlorophenol (peak 15) was partly separated from them. In such cases quantification was performed on the basis of specific ions.

Sample preparation by SPE

Owing to their high polarity, aliphatic amines are not amenable to SPE, and most phenols and aromatic amines have low breakthrough volumes on conventionally used sorbents. To overcome this difficulty, phenols and amines were converted into their benzoyl derivatives, which are relatively less polar, and subjected to SPE on a PLRP-S sorbent. During derivatization, ammonia was converted to benzamide and thus it was also possible to determine ammonia along with amines and phenols. After drying the sorbent, the retained benzoyl derivatives were eluted with 200 μl of ethyl acetate containing the internal standard 2,4,6-trimethylphenyl-4′-nitrobenzoate.

Selection of derivatization reagent

The selection of benzoyl chloride was based on two main aspects: (i) its reaction rate under fairly mild conditions (room temperature), and (ii) its applicability to the three compound classes, and ammonia, under investigation. Tertiary amines of course do not react with benzoyl chloride. The peak areas for 100 μg l^{-1} analytes were optimum at 0.3 ml of benzoyl chloride, and the response was constant beyond that amount of the reagent. The derivatization reaction was validated by comparison of the retention times and mass spectra of the benzoyl derivatives of the analytes with those of the authentic samples, when the agreement was excellent.

Calibration graph and detection limit

The dependence of the chromatographic signal on the concentration of all the phenols and amines was determined under the optimum conditions of derivatization and SPE-GC-MS. The figures of merit for the present method using a sample volume of 80 ml are summarized in Table 2. A linear relationship was obtained between the amount of analyte and the peak area of its benzoyl derivative in the range 0.1–100 μg l^{-1}, the correlation coefficient, *r*, ranging from 0.9910 to 0.9992. The limit of detection (LOD) (S/N = 3) ranged from 7 to 39 ng l^{-1} except for 2,3,6-trichlorophenol (90 ng l^{-1}) and ammonia (20 μg l^{-1}); the RSD for the LOD was in the range 2.8–22.3%.

Table 1 Time programme for SPE of benzoate esters and benzamides

			Valve position		
Step	Time/min	Event	V1	V2	V3
1	0–3	Flushing SPE cartridge with 3 ml methanol (1 ml min^{-1})	On	On	On
2	3–6	Flushing SPE cartridge with 3 ml water (1 ml min^{-1})	On	On	On
3	6–26	Loading of 80 ml of sample (4 ml min^{-1})	On	On	On
	23–28	Drying air gap with nitrogen (30 ml min^{-1})			
4	26–28	Washing SPE cartridge with 2 ml water (1 ml min^{-1})	On	On	On
5	28–43	Drying SPE cartridge with nitrogen (30 ml min^{-1})	On	On	Off
6	43–50	Eluting sample from SPE cartridge with ethyl acetate (0.2 ml min^{-1})	Off	Off	Off

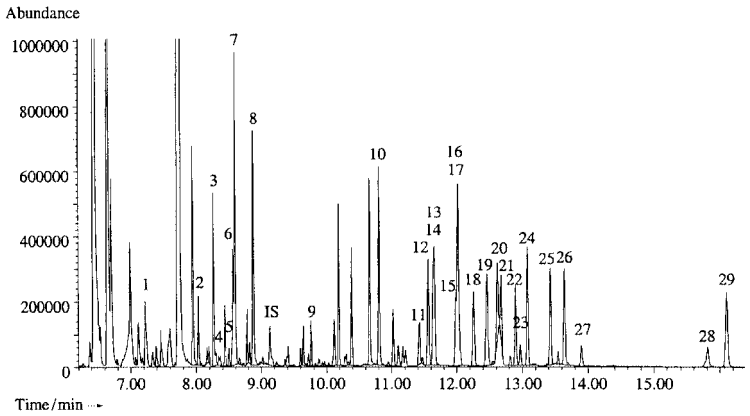

Fig. 2 Chromatogram of 80 μg l^{-1} of phenols and amines, as their benzoyl derivatives, by SPE-GC-MS in full scan mode (range *m*/*z* 45–400); sample volume for SPE, 20 ml. Peaks: 1 = 2,4,6-trimethylphenol; 2 = ammonia; 3 = dimethylamine; 4 = methyl amine; 5 = 4-bromo-2,6-dimethylphenol; 6 = ethylamine; 7 = isopropyl amine; 8 = diethylamine; IS = internal standard (2,4,6-trimethylphenyl-4′-nitrobenzoate); 9 = phenol; 10 = 4-chlorophenol; 11 = 2,6-dichlorophenol; 12 = aniline; 13 = 2,4-dichlorophenol; 14 = 2,5-dichlorophenol; 15 = 2,3-dichlorophenol; 16 = 2-chloroaniline; 17 = 2-toluidine; 18 = 3,4-dichlorophenol; 19 = 3-toluidine; 20 = 4-toluidine; 21 = 3-nitrophenol; 22 = 4-nitrophenol; 23 = 2,3,6-trichlorophenol; 24 = 3-anisidine; 25 = 4-chloroaniline; 26 = 2-anisidine; 27 = 4-anisidine; 28 = 4-aminoacetophenone; and 29 = 2-aminobiphenyl. Column: HP-5, 30 m × 0.25 mm id, 0.25 μm film thickness; carrier gas, helium; flow rate, 1 ml min^{-1}; sample injection volume, 1 μl.

Application to environmental waters

The proposed method was applied to real water samples. All the water samples were filtered through a 0.45 μm membrane filter prior to analysis. The present method was validated by analyzing these real samples spiked with known amounts (5–30 μg l^{-1}) of phenols and amines. Recoveries ranged from 96 to 110% (RSD in the range 4–12%) for all the water samples taking into consideration the amounts of analytes already present in such samples.

Ammonia was found within the MAC in all samples. Ganga river water (collected from Kanpur) and groundwater samples

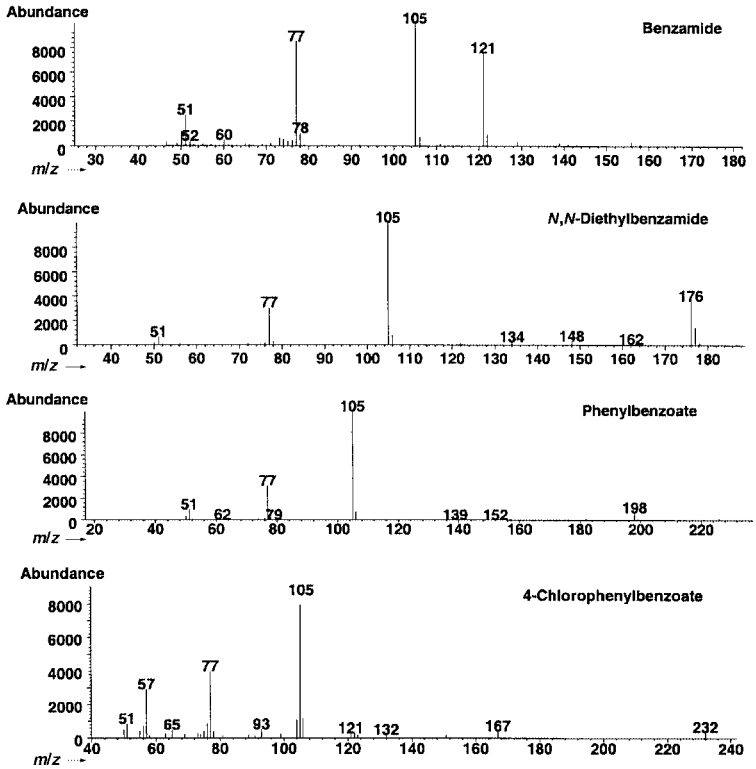

Fig. 3 Difference in molecular ion response between the benzamide and benzoate derivatives. Analyte concentrations, 1 μg l^{-1}.

Table 2 Figures of merit in the determination of ammonia, aliphatic amines, aromatic amines and phenols

Compound[a]	t_R/min	r	LOD /ng l^{-1}	m/z[b]	RSD (%)[c] (n = 6)
2,4,6-Trimethylphenol	7.23	0.9932	8	121, 136	6.1
Ammonia	8.05	0.9910	20[d]	121	4.3
Dimethylamine	8.23	0.9940	7	148, 149	6.1
Methylamine	8.30	0.9944	23	134, 135	6.9
4-Bromo-2,6-dimethylphenol	8.50	0.9945	10	200, 202	8.8
Ethylamine	8.56	0.9933	26	149	4.4
Isopropylamine	8.61	0.9953	21	163	5.1
Diethylamine	8.89	0.9959	9	176, 177	8.1
Phenol	9.14	0.9947	26	198	4.8
4-Chlorophenol	9.76	0.9952	8	232	6.9
2,6-Dichlorophenol	10.82	0.9916	24	133	6.8
Aniline	11.43	0.9989	16	197	5.7
2,4-Dichlorophenol	11.59	0.9983	13	133	8.6
2,5-Dichlorophenol	11.67	0.9981	25	133	8.0
2,3-Dichlorophenol	11.99	0.9974	30	133	9.1
2-Chloroaniline	12.03	0.9962	17	231	8.8
2-Toluidine	12.04	0.9928	20	211	3.8
3,4-Dichlorophenol	12.27	0.9990	39	133	9.6
3-Toluidine	12.49	0.9932	22	211	8.8
4-Toluidine	12.65	0.9945	23	211	9.6
3-Nitrophenol	12.69	0.9946	15	213	11.6
4-Nitrophenol	12.91	0.9924	20	213	7.5
2,3,6-Trichlorophenol	12.97	0.9930	90	169	12.3
3-Anisidine	13.10	0.9973	21	227	11.6
4-Chloroaniline	13.45	0.9967	22	231	5.2
2-Anisidine	13.66	0.9948	32	227	3.9
4-Anisidine	13.91	0.9952	22	227	5.6
4-Aminoacetophenone	15.82	0.9948	35	239	10.2
2-Aminobiphenyl	16.12	0.9992	23	273	4.2

[a] The linear range (μg l^{-1}) was 50–4000 for ammonia, 0.5–100 for 2,3,6-trichlorophenol and 0.1–100 for all other compounds. [b] Ions, m/z, selected for quantification. [c] RSD (%) found for 10 μg l^{-1} spike of each compound (50 μg l^{-1} for ammonia). [d] Concentration in μg l^{-1}.

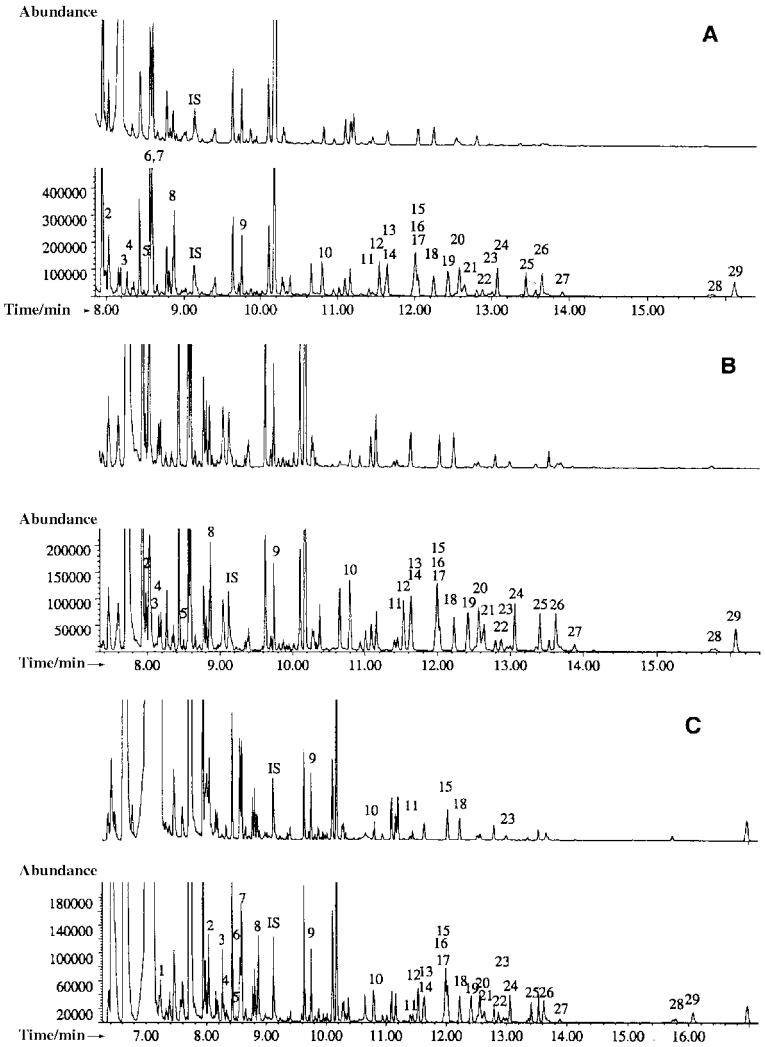

Fig. 4 Total ion chromatogram for Jabalpur city drinking water (A), Narmada river water (B) and paper mill treated effluent (C); sample volumes for SPE were 80, 40 and 20 ml, respectively. Upper traces, unspiked samples; lower traces sample spiked with 10 μg l^{-1} of each analyte. Peak designations as in Fig. 2.

(Jabalpur) showed the presence of diethylamine, at levels of 70 and 0.46 μg l^{-1}, respectively. Ammonia and diethylamine determined as benzamide and *N,N*-diethylbenzamide, respectively, showed good spectral matching with stored data in the NIST library. The Narmada river water (collected from Jabalpur) and Jabalpur city tap water had none of the target analytes present in these samples; some of the peaks such as 9, 14 and 18 in the unspiked samples had identical retention times but different mass spectra from the target compounds. Phenol and a number of chlorophenols were detected in treated paper mill effluents (Fig. 4).

Conclusions

Low concentrations of phenols and amines in environmental waters and their low breakthrough volumes during SPE hinder the detection of phenols and amines in routine chromatographic methods. The proposed method using pre-column derivatization to phenylbenzoates and benzamides and their GC-MS was used to determine phenols and amines in their complex mixtures in natural aqueous samples. Mass spectrometric detection coupled to SPE is a very sensitive technique; the limit of detection ranged between 7 and 39 ng l^{-1} when an 80 ml volume of sample was preconcentrated. PLRP-S was a suitable sorbent for enrichment of benzoyl derivatives owing to its high retention efficiency and short drying period with nitrogen. The developed method was applied to the determination of phenols and amines in spiked samples such as drinking water, groundwater and river water. The SPE clean-up procedure can be applied to the investigation of phenol and halo-phenols formed during the bleaching of paper pulp.

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