Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1045 (2004) 181–188
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Direct screening and confirmation of benzene, toluene, ethylbenzene and xylenes in water

A. Serrano, M. Gallego*

Department of Analytical Chemistry, Campus of Rabanales, University of Córdoba, E-14071 Córdoba, Spain

Received 6 April 2004; received in revised form 11 June 2004; accepted 16 June 2004

Abstract

A novel, straightforward sample screening method for benzene, toluene, ethylbenzene and xylene isomers (BTEX) in water is proposed. The method is based on the direct coupling of a headspace (HS) sampler with a mass spectrometer by using a chromatographic column heated to 200 °C as an interface. Samples are acidified and subjected to the headspace generation process, the resulting volatile fraction being directly introduced into the source of the mass spectrometer. The large number of samples to be analyzed and the wide range of *m*/*z* ratios scanned (75–110) suggest the use of chemometric approaches based on pattern recognition techniques (PRT). For sample classification purposes, the detection limit of the method (overall response 4.0 ng/ml BTEX) was selected as the cut-off level. The method proved highly reliable as no false negatives were obtained at the legally established concentration levels. Positive water samples were confirmed by using the same instrumental setup as in the screening method, but by heating the chromatographic column at 40–200 °C to separate the analytes.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Water analysis; Environmental analysis; Chemometrics; Pattern recognition; Benzene; Toluene; Ethylbenzene; Xylenes

1. Introduction

Benzene, toluene, ethylbenzene, *m*-, *p*- and *o*-xylene (BTEX) are important industrial chemicals, the contamination sources of which in water, include the massive use of petroleum and its derivatives, and that of solvents. The BTEX content in a standard gasoline blend is approximately 18% (w/w); benzene, which is the most toxic compound in BTEX, accounts for 11% of the total BTEX fraction in gasoline (26% toluene, 11% ethylbenzene and 52% total xylenes) [1]. The US Environmental Protection Agency (EPA) has included BTEX compounds on the list of National Primary Drinking Water Standards [2] and established a maximum contaminant level (MCL) of 5.0 μg/l for benzene and values over the range 0.7–10.0 mg/l for the other BTEX [2,3]. Also, the European Union has included benzene in the list of 33 priority pollutants in waters [4,5], and established an MCL of 1.0 μg/l for benzene in drinking water [6].

Sensitive, accurate analytical methods have been developed to detect pollutant concentrations below the maximum permitted levels; many use gas chromatography (GC) to determinate volatile organic compounds. Its coupling with various preconcentration/clean-up techniques such as purge and trap (P & T) [7–9], static headspace (HS) [9–12], solid-phase microextraction [10,12] and headspace–solid-phase microextraction [10–12], provides low enough limits of detection (LODs) for determining BTEX in water samples. In recent years, a number of direct sampling mass spectrometric (MS) methods have been developed for the analysis of environmental samples; such methods insert analytes directly into a mass spectrometer by using a simple interface and with minimal sample preparation and the need for no prior chromatographic separation. These methods entail the use of a protective barrier (an interface) between atmospheric pressure (where sampling is performed) and the high vacuum inside the instrument. There are four major types of inlets for direct sampling, namely: capillary restrictors, membrane introduction (MIMS), atmospheric pressure ionization and atmospheric sampling glow discharge ionization [13]. Some advances in sample introduction in MIMS involving a cryogenic trap

* Corresponding author. Tel.: +34 957 218616; fax: +34 957 218616.
E-mail address: qa1gafem@uco.es (M. Gallego).

0021-9673/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2004.06.028

or flow injection have provided very low detection limits [14–17]. The inlets used for this purpose have some disadvantages; thus, some air and water can penetrate into the spectrometer during sampling and the barrier may suddenly break and cause catastrophic failure of the instrument and call for the use of a complex pumping system [13].

The need for fast, reliable analytical methods for routine laboratories is unquestionable. Sample screening systems use expeditious analytical methodologies to identify and select, from a starting set, a group of samples containing one or more analytes at concentrations above a preset level [18,19]. Recently, a fast method for the characterization of cheeses using dynamic headspace mass spectrometry was reported; analysis were carried out following preconcentration of the volatile fraction on a Tenax TA trap [20]. Direct coupling of a headspace sampler with a mass spectrometer has been used for the detection of adulterants in olive oil [21], the characterization of olive oil classes [22] and the detection of hydrocarbon pollution in soils [23]. In all instances, chemometric techniques must be used to process the vast amount of data generated by the volatiles profile.

BTEX in drinking water are routinely determined by many laboratories in accordance with international standards. The development of a fast sample screening method for classifying water samples as contaminated or uncontaminated in relation to the low legally established levels is a top priority for such laboratories. However, a confirmation technique for determining the analytes found and their concentrations in those samples giving a positive response in the sample screening method is required. The novelty of the proposed method is the coupling of the screening and confirmation methods by using a chromatographic column as interface between the HS sampler and the MS instrument. The column temperature is set at 200 °C for sample screening and, if confirmation is required, an appropriate temperature program is used to separate the BTEX compounds. The proposed sample screening method is straightforward (it requires minimum sample preparation), expeditious (the throughput is 10 samples/h) and reliable (it provides no false negatives with respect to the legally established levels).

2. Experimental

2.1. Chemicals and standards

Benzene, toluene, ethylbenzene, *m*-, *p*-, *o*-xylene and fluorobenzene (internal standard, IS) were supplied by Sigma–Aldrich (Madrid, Spain); potassium chloride and nitric acid were purchased from Panreac (Barcelona, Spain) and methanol from Scharlau (Barcelona, Spain). Individual stock standard solutions were prepared at concentrations of 1.0 mg/ml in methanol and stored in amber glass stoppered bottles (without headspace) at 4 °C. Individual and cumulative working standard solutions were obtained by appropriate dilution of the stock in 50 ml of methanol and further diluted in ultrapure Milli-Q water to prepare solutions containing BTEX at the nanogram per milliliter level. The 1.0 mg/ml stock standard solutions were never stored for more than 3 months; intermediate standard solutions were prepared fortnightly.

2.2. Apparatus

For sample screening method, the experimental setup consisted of an HS autosampler HP 7694 and an HP 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with an HP 5973 mass-selective detector. The former was a 44-space autosampler for headspace vials equipped with a robotic arm and a headspace generation unit comprising with two parts, namely: an oven capable of holding six glass vials for heating the samples inside the vials and forming the headspace, and a six-port-injection valve with a 3 ml loop. The operating conditions for the HS autosampler were as follows: vial equilibration time, 20 min; oven temperature, 70 °C; vial pressurization time, 21 s; loop fill time, 9 s; valve/loop temperature, 110 °C. Helium (5.5 grade purity, Air Liquid, Seville, Spain), regulated with a digital pressure and flow controller, was used both to pressurize vials (124.0 kPa of flow pressure) and drive the formed headspace to the injection port of the chromatograph via a transfer line at 120 °C (13.8 kPa of flow pressure). Injection was done in the split mode (1:10 split ratio) for 1.0 min; an HP-5MS (5%)–phenyl–(95%) methylpolysiloxane capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness, J & W) was used with an oven temperature of 200 °C and an helium constant flow rate of 2.0 ml/min to transfer volatiles directly into the detector. Mass spectra were obtained at 70 eV in the electron impact ionization mode; the spectrometer was operated in the full scan mode over the mass range from *m*/*z* 75 to 110. The source and quadrupole temperatures were maintained at 230 and 150 °C, respectively. Total ion current chromatograms were acquired and processed using G1701CA Standalone data analysis software (Agilent Technologies) on a Pentium II computer that was also used to control the whole system.

Confirmation of positive water samples by HS–GC–MS was done under the same instrumental conditions as for the sample screening method, but using an appropriate temperature program for the chromatographic column. The GC conditions were as follows: inlet temperature, 200 °C; inlet mode, split operation with split ratio 1:15. The oven temperature was set at 40 °C (3 min) and raised to 60 °C at 5 °C/min, held for 1 min and raised to 200 °C at 20 °C/min. The final temperature was maintained for 2 min and the total run time was 17 min. Helium, at a constant flow rate of 1.8 ml/min was used as the carrier gas. The MS system was operated in the full scan mode, *m*/*z* 50–350. For identification, three characteristic ions per analyte were selected (the base peaks used for quantification are boldfaced): benzene 52, 77, **78**; toluene 65, **91**, 92; ethylbenzene 77, **91**, 106; xylene isomers **91**, 105, 106; fluorobenzene (IS) 50, 70, **96**.

Ten and twenty-milliliter glass flat bottomed vials for headspace analysis with 20 mm PTFE-silicone septa caps and a crimped aluminum closure (Supelco, Madrid, Spain) were also employed. Vials and septa were heated at 100 and 70 °C, respectively, overnight prior to use.

2.3. Sampling procedure

Samples were collected in amber glass bottles of 1 l without headspace and transferred to three amber glass bottles of 250 ml that were sealed airtight; no headspace volume was left in order to prevent air bubbles from passing through the samples. Samples were placed in a portable freezer for transfer to the laboratory, where they were stored at 0–4 °C until their analysis. All samples were analyzed within 2 or 3 days after collection to avoid storage losses.

2.4. Analytical procedure

For the *sample screening method*, 15 ml of water, 2.2 g of KCl and 300 μl of 5 M HNO_3 (sample medium 0.1 M HNO_3) were placed in a 20 ml glass vial that was tightly sealed. For the *confirmation method*, 15 ml of standard solutions or water samples containing between 0.5 and 750.0 ng/ml of each BTEX and 30 ng/ml of fluorobenzene (IS) were prepared as described above in 20 ml glass vials. In both cases, the sample was thermostatted under constant mechanical stirring at 70 °C for 20 min in order to equilibrate the gas phase and enrich it with BTEX compounds from the water. Then, the headspace of sample in the loop of the injection valve (3 ml) was introduced into the injection port of the gas chromatograph. For *sample screening*, the chromatographic column (used as an interface between the HS sampler and mass spectrometer) was kept at 200 °C, so that volatile compounds could reach the detector at once and a total ion current chromatogram, called the volatiles profile, be obtained for classification purposes. Positive samples were confirmed with the same instrument, but using an appropriate temperature program in the chromatographic column to separate BTEX compounds.

2.5. Chemometric treatment of sample screening data

The mass spectrum obtained from the volatiles profile required using a pattern recognition technique (PRT) to discriminate between BTEX contaminated and uncontaminated samples. We initially used unsupervised PRTs such as principal component analysis (PCA) and cluster analysis (CA) to identify the internal structure of the data and the best discriminant variables. Later, we used supervised PRTs such as soft independent modeling class analogy (SIMCA) and *K*-nearest neighbors (KNN) to construct an effective model to separate BTEX contaminated and uncontaminated samples in the training and prediction sets used to create and validate the model. The Euclidian distance, as similarity measure, and a 95% of confidence level were employed in all instances. This model was successfully applied to the screening of various types of water (drinking, lake, river, rain, ground, waste), both contaminated and uncontaminated. All chemometric analyses of the data were done with the statistical software package "Pirouette: Multivariate Data Analysis", developed by Infometrix Inc. (Woodinville, WA, USA).

3. Results and discussion

3.1. Optimization of the headspace generation conditions

The optimum conditions for HS generation were established by examining the influence of each individual parameter. Initially, optimization tests were performed at an oven temperature of 85 °C, a vial equilibration time of 30 min and a pressurization and loop fill time equal of 12 s. The effect of adding salt to the water samples in order to increase the ionic strength and reduce the solubility of the analytes was studied. For this purpose, 5 ml of sample containing 300 ng/ml (the concentration used in all optimization tests) of individual BTEX in glass vials of 10 ml was spiked with variable amounts of KCl (0–1.25 g). The salt was found to increase the signal abundance for all BTEX compounds. Benzene was the compound most strongly affected on account of its highest solubility in water; thus, it required 150 mg of KCl per ml of sample, which was used for all BTEX. Influence of the sample pH was studied over the range 1–9 by adjusting the saline solution of each BTEX with dilute HNO_3 or NaOH as required. The optimum pH range was wider (1–9) for toluene, ethylbenzene and xylene than for benzene (1–4). Water samples contain metals and organic matter, which can precipitate and hinder evaporation of BTEX. In order to increase the selectivity of the proposed method, all sample solutions were made in 0.1 M nitric acid to avoid the precipitation of metals and facilitate the destruction of organic matter. The influence of the sample volume was examined from 4 to 7 ml (in 10 ml vials) and from 8 to 16 ml (in 20 ml vials). The signal abundance increased with increasing sample volume up to 14 ml (above which it remained constant) as the likely result of the increasing BTEX concentration in the headspace. A sample volume of 15 ml (in 20 ml glass vials) was adopted as it provided better repeatability (relative standard deviation, R.S.D. = 5%, $n = 5$) than 14 ml (R.S.D. = 7%, $n = 5$).

The instrumental parameters most closely related to the BTEX concentration in the headspace were the oven temperature and the vial equilibration time; their effects were studied over the ranges 60–90 °C and 10–40 min, respectively. An oven temperature of 70 °C was chosen to minimize the evaporation of the water, and a vial equilibration time of 20 min was selected to expedite analyses. Once the headspace was generated and enriched with BTEX compounds, its individual injection into the mass spectrometer through the interface (the column, heated at 200 °C) was

done in two steps, namely: vial pressurization and filling of the 3 ml loop of the injection valve by venting the vial. Pressurization times between 3 and 30 s caused negligible changes in abundance signal for the least polar analytes (ethylbenzene and xylene); by contrast, they increased for the most polar analytes (benzene and toluene) up to 21 s, beyond which the signals leveled off. The venting time had no effect above 9 s. Thus, a value of 21 s for the pressurization time and 9 s for the venting time were chosen as optimal.

3.2. Sample screening method

The primary objectives of sample screening systems were to obtain a reliable response, to reduce the preliminary operations of the conventional analytical process and to minimize the need for permanent use of instrument. Therefore, a reliable screening method will be used mainly as a "filter" to select those samples in a starting set containing the analytes above a preset concentration level [18,19]. The cut-off level was a critical parameter for the screening method; such a level is normally imposed by legal requirements when related to toxic compounds for human health. However, the detection limit of the technique used should also be taken into account. The detection limits of the proposed method for BTEX in water samples were calculated on the basis of the standard deviation of residuals ($S_{y/x}$) [24] by constructing calibration graphs from individual standard solutions containing benzene, toluene, ethylbenzene or xylene at concentrations between 1 and 50 ng/ml and an *m/z* ratio of 78 for benzene and of 91 for toluene, ethylbenzene and xylene for quantification. The detection limits, expressed as three times the $S_{y/x}$ divided by the slope of calibration graphs, were 1.0 ng/ml for benzene, 0.9 ng/ml for toluene and 0.8 ng/ml for ethylbenzene and xylene; similar results were obtained by using 12 blank samples (ultrapure water containing KCl at pH 1) and their signal standard deviations to calculate LODs. For drinking water, only benzene is limited to very low concentrations (MCL, 1.0 ng/ml in European regulations [6] and 5.0 ng/ml for EPA [2,3]); the MCLs for the other BTEX compounds are much higher (~1 μg/ml). The presence of benzene in drinking water is associated with contamination by petroleum derivatives (mainly gasoline); a water sample contaminated with benzene exhibits increased amounts of toluene and xylene. Thus, the proposed sample screening method, which gives an overall response to BTEX, provides low enough detection limits to classify all water types (drinking waters included). An individual concentration of 1.0 ng/ml of each BTEX (overall response 4.0 ng/ml) was selected as the cut-off level for the classification of water samples. The sample screening method uses

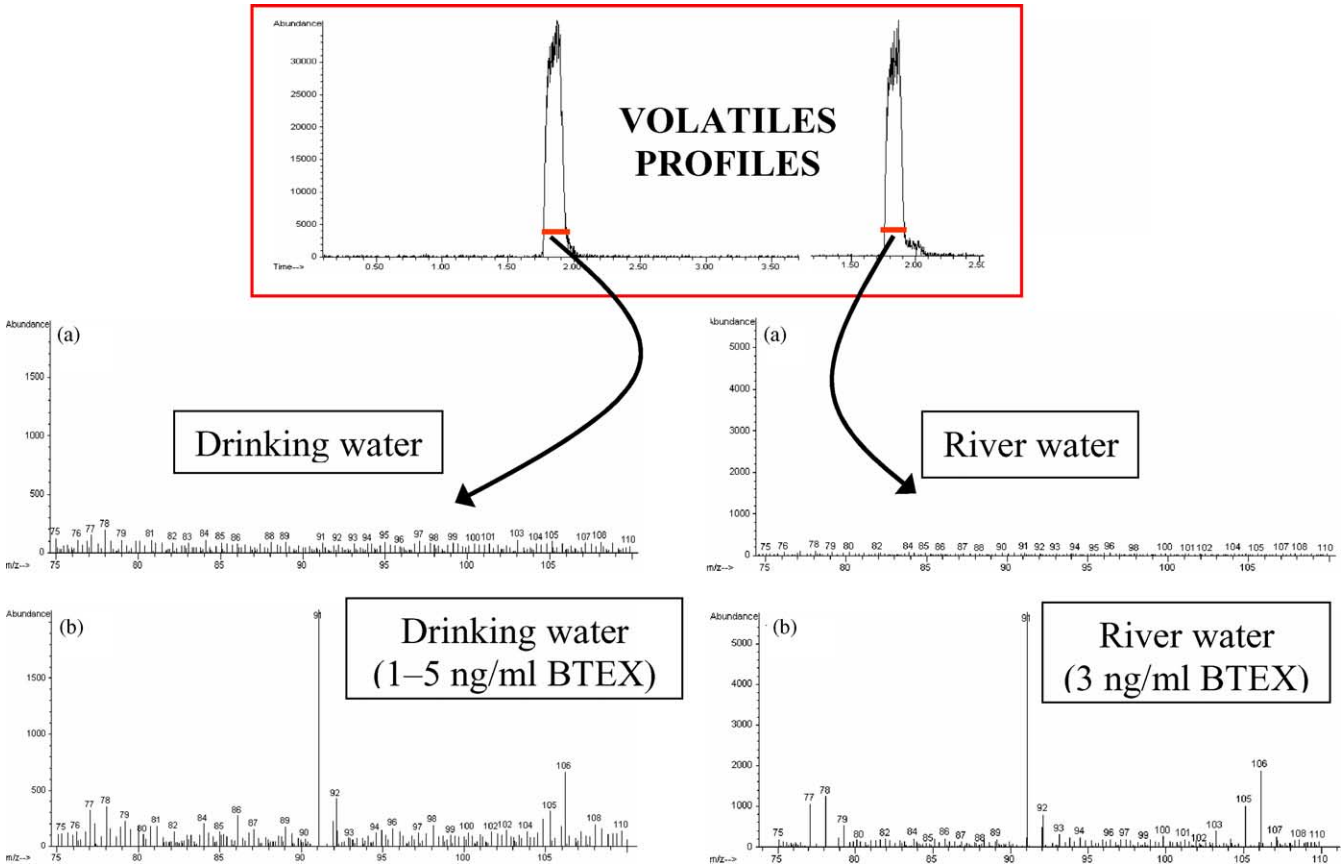

Fig. 1. Volatiles profiles and mass spectra for uncontaminated (a) and contaminated (b) drinking and river water samples. For details, see text.

the mass spectrum obtained from the volatiles profile to discriminate between contaminated and uncontaminated water samples. Fig. 1 shows the volatiles profile for a drinking water and river water, being similar for contaminated and uncontaminated water; the contribution of the BTEX compounds can not be distinguished from that of the other volatile compounds. BTEX can, however, be discriminated by using the mass spectrum for uncontaminated (Fig. 1a) and contaminated (Fig. 1b) water samples containing 1, 3, 1 and 5 ng/ml benzene, toluene, ethylbenzene and xylene, respectively, based on their ratio in gasoline (drinking water) and with 3 ng/ml of each BTEX (river water). As can be seen, the most characteristic *m*/*z* values for BTEX (77, 78, 91, 92, 105 and 106) are clearly discriminated from background noise in contaminated samples.

3.3. Data analysis for sample classification

Preliminary tests were conducted on 100 samples (30 uncontaminated and 70 contaminated with BTEX at variable concentrations), using unsupervised PRT such as CA and PCA. The dendrogram of Fig. 2, which was obtained by CA, showed two distinct groups of samples; uncontaminated and contaminated samples clustered with a similarity index of 0.48 and 0.56, respectively. PCA revealed that the most discriminant original variables were the *m*/*z* ratios 77, 78, 91, 92, 105 and 106, which correspond to the major mass fragments for BTEX compounds; all other variables only represented background noise (with a high mutual correlation). Finally, the *m*/*z* ratios 75, 80, 88 and 100, which represent background noise, together with the six most characteristic *m*/*z* values for BTEX, were selected to construct KNN and SIMCA models. Internal structure tests involving PCA of only such 10 variables yielded results identical with those previously obtained with CA.

3.3.1. K-nearest neighbors (KNN)

KNN is based on the distance between samples in a space of as many dimensions as variables are explored; only the *K*-nearest samples are used to make the assignment. The class to which the sample is assigned is that of the samples in the training set that are closest to it [22]. The classification model was constructed from a training set of 155 uncontaminated and contaminated water samples. Drinking, river,

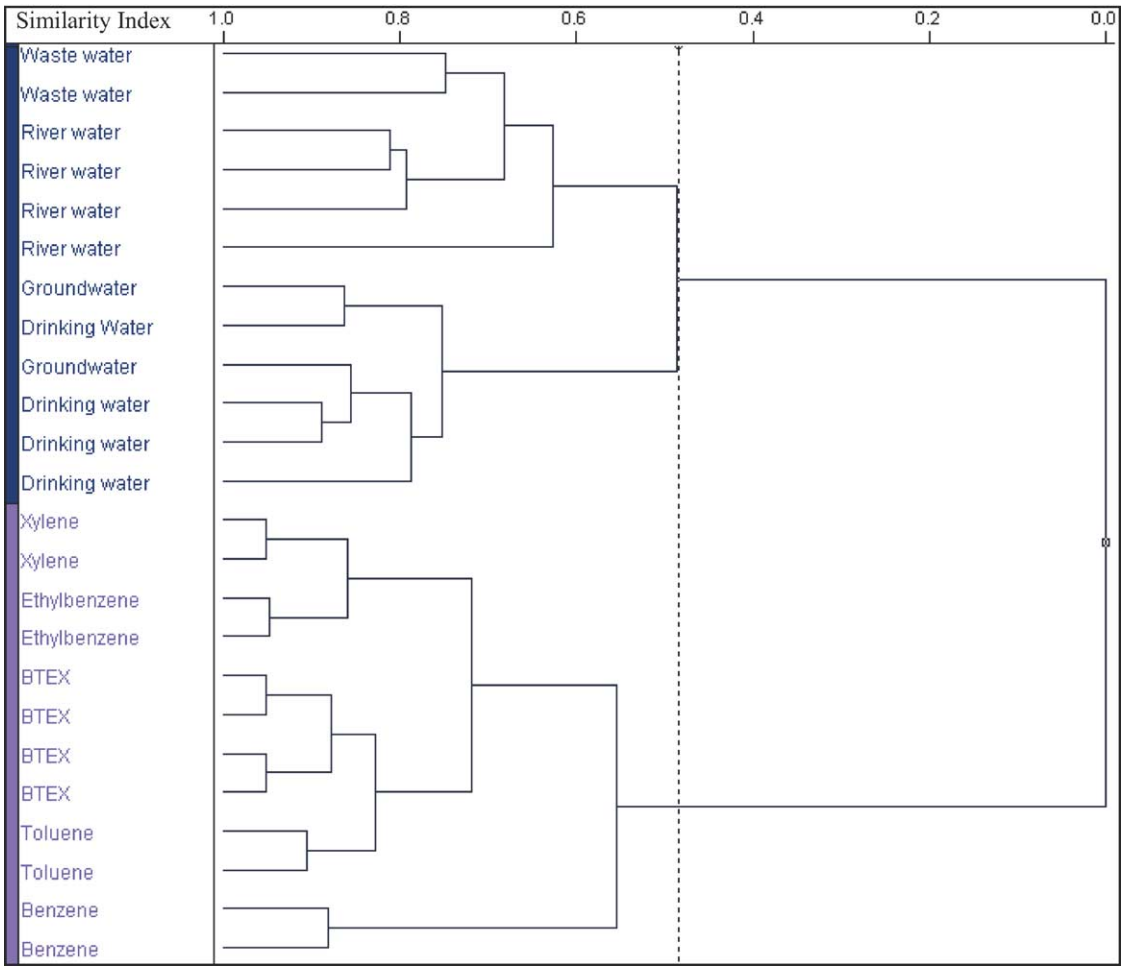

Fig. 2. Dendrogram for drinking, river, ground and waste water, and contaminated drinking water samples (containing individual concentrations of 3 ng/ml and an overall concentration of 4 ng/ml BTEX).

rain, ground and waste water were used as uncontaminated samples; and single, binary and ternary mixtures of BTEX compounds spiked to drinking water at concentrations ranging from 1 to 250 ng/ml were used as contaminated samples. *K* was optimized by determining classification ability and the number of misclassifications using *K* values between 1 and 15; the best results were achieved with $K = 3$. Autoscaling and normalization of the data were used as preprocessing techniques and transformations. Table 1 shows the results provided by the KNN classification model for uncontaminated and contaminated water samples in a classification matrix. All samples were correctly classified, so the classification ability was 100% for each class. Models were validated by using a prediction sample set consisting of 25 uncontaminated blank samples (drinking, river and ground water) and 25 contaminated drinking water samples [15 spiked with 1 ng/ml (the chosen cut-off level) of each BTEX and 10 spiked with 1, 3, 1 and 5 ng/ml of benzene, toluene, ethylbenzene and xylene (the BTEX concentration ratios in blended gasoline standard), respectively]. Based on the results listed in Table 1, the KNN classification technique allows one to separate BTEX contaminated and uncontaminated water; in fact, all test samples were correctly classified (no false positives or negatives were obtained).

3.3.2. Soft Independent modeling of class analogy (SIMCA)

SIMCA, based on an independent PCA model of each class and critical distances, is a class modeling technique that creates frontiers between each class and the rest of the universe. PCA is used to define the delimited region of the space for each class on the basis of a mathematical model created from a training set of samples. Each sample is assigned to a class if it falls within the boundaries of only one class-box and considered to be an outlier for that class if it falls outside the class-box [22,23]. The same water types and the spiked BTEX mixtures used as uncontaminated and contaminated samples to build the KNN model were employed to construct the SIMCA model. Using normalized data, a SIMCA classification model was constructed with two principal components for the uncontaminated samples class and three for the contaminated samples class; this ensures effective separation and allowed an adequate proportion of cumulative variance to be accounted for (98.6% for the uncontaminated samples class and 98.7% for the contaminated samples class). As can be seen in Table 1, the "No match" column in the classification matrix represents unclassified dubious samples (viz. samples that were not classified as either uncontaminated or contaminated). Like KNN, SIMCA can be used as a pattern recognition technique for the separation of BTEX contaminated and uncontaminated water samples. No false negatives were obtained with this model as unclassified samples were considered to be positive. The SIMCA model was validated with the same prediction set as the KNN model. Fig. 3 shows the scores plot obtained by applying the SIMCA classification model to the prediction set; the space region bounded by each class (encircled and dotted) and the separation between both classes are clearly seen. As can be seen, the 50 samples (dashed points) used for prediction were included in the corresponding space region. The uncontaminated sample class was assigned a small space region, so the presence of false negatives was reduced.

Table 1
Classification and prediction matrix for KNN and SIMCA

	Classes[a]	KNN		SIMCA		
		1	2	1	2	No match
Classification	1 (46)	46	0	46	0	0
	2 (109)	0	109	0	108	1
Prediction	1 (25)	25	0	25	0	0
	2 (25)	0	25	0	25	0

[a] 1 corresponds to uncontaminated samples and 2 to contaminated samples. In brackets the number of water samples used.

The reliability (proportion of correct binary responses) of a screening method is basically related to the absence of false negatives. The KNN model classifies all samples (even the dubious ones), so it can give false positives and negatives. By contrast, the SIMCA model does not classify dubious samples (which are given as no match and therefore considered to be positive samples in the proposed method); this excludes false negatives and increases the reliability of the SIMCA model.

The sample screening method was applied to 78 water samples, namely: drinking (30 samples), lake (10 samples), river (10 samples), rain (10 samples), ground (10 samples) and waste (8 samples) water. Only one river water, one rain water and two waste water samples were classified as positive by the SIMCA model.

3.4. Confirmation method

The same, optimum headspace conditions for the sample screening method were used in the confirmatory method,

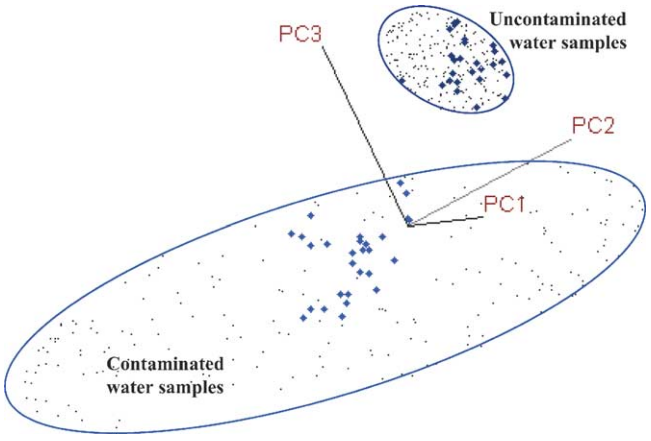

Fig. 3. Scores plot obtained by applying the SIMCA classification model to the uncontaminated and contaminated samples in the prediction set. For details, see text.

Table 2
Analytical figures of merit of the determination of BTEX compounds (sample volume 15 ml)

Compound	m/z[a]	Regression equation[b]	Linear range (ng/ml)	LOD (ng/ml)	R.S.D. (%)
Benzene	78	$y = 12 \times 10^{-4} + 395 \times 10^{-4}x$	0.6–750	0.20	4.2
Toluene	91	$y = 19 \times 10^{-4} + 470 \times 10^{-4}x$	0.6–750	0.19	3.3
Ethylbenzene	91	$y = 24 \times 10^{-4} + 680 \times 10^{-4}x$	0.5–750	0.14	3.9
$m + p$-Xylene	91	$y = 23 \times 10^{-4} + 620 \times 10^{-4}x$	0.5–750	0.15	4.6
o-Xylene	91	$y = 16 \times 10^{-4} + 630 \times 10^{-4}x$	0.5–750	0.15	4.1

[a] m/z quantitation value.
[b] y: analyte area-to-internal standard area, x: concentration (ng/ml).

Table 3
Evaluation of the goodness of fit and linearity of calibration graphs

Compound	Correlation coefficient, r	Determination coefficient, R^2	Lack-of-fit test, F_{LOF}[a]	Intercept significance, P-value
Benzene	0.997	0.993	1.43	<0.05
Toluene	0.998	0.995	2.15	<0.05
Ethylbenzene	0.998	0.996	1.07	<0.05
$m + p$-Xylene	0.998	0.996	1.93	<0.05
o-Xylene	0.998	0.996	1.22	<0.05

[a] $F_{crit,95\%} = 3.89$.

the chromatographic column being heated at temperatures between 40 and 200 °C as described in Section 2.2. Several calibration curves for each BTEX compound in drinking water were run. The figures of merit of the calibration graphs are summarized in Table 2. Fluorobenzene (30 ng/ml) was used as internal standard, on account of its similarity with the analytes and absence from the water samples. Detection limits were calculated on the basis of standard deviation of residuals and can be seen in Table 2, the limit of quantification (LOQ) taken to be the lowest concentration in the linear range. An evaluation to check the goodness of fit and linearity has been included in Table 3 [25]. The precision of the method, expressed as relative standard deviation, was checked on 12 drinking water samples containing a 5 ng/ml concentration of the analytes and was found to be ∼4% (within-day precision) and ∼5% (between-day precision). The recoveries of the confirmation HS–GC–MS method were assessed by adding, to each water type previously analyzed with the sample screening method, 1.0 ng/ml benzene, 3.0 ng/ml toluene, 1.0 ng/ml ethylbenzene, 4.0 ng/ml $m + p$-xylene and 1.0 ng/ml *o*-xylene (consistent with the BTEX ratios in gasoline). Each sample was spiked five times and then analyzed using the proposed method (HS–GC–MS). All compounds were correctly identified and the average recoveries obtained 92–98% (±3%)—waste water 85–95%, were acceptable for all types of water.

The positive water samples detected by the sample screening method were confirmed by HS–GC–MS. River and rain water samples were collected in the vicinity of a petrol station. The results obtained are listed in Table 4. The confirmation method allowed the individual identification and quantification of all BTEX compounds present in the samples. As can be seen, benzene was undetected or found at the lowest levels, probably as a result of environmental degradation—it is the most volatile—, as well as its low concentration in petroleum derivatives. Toluene and xylenes were found in all water samples, at concentrations higher than those of other analytes. This is consistent with their higher concentration in petroleum derivatives (mainly gasoline). In addition, both compounds are widely used as solvents.

Table 4
Determination of BTEX by HS–GC–MS in positive prescreened samples

Compound	Concentration found (ng/ml)[a]			
	River water	Rain water	Waste water 1	Waste water 2
Benzene	<0.6	n.d.	1.5 ± 0.1	n.d.
Toluene	2.6 ± 0.1	1.7 ± 0.1	6.7 ± 0.3	9.8 ± 0.5
Ethylbenzene	0.8 ± 0.1	1.4 ± 0.1	2.9 ± 0.2	0.6 ± 0.1
(*m*+*p*)-Xylene	2.0 ± 0.1	5.5 ± 0.3	7.5 ± 0.3	2.2 ± 0.2
o-Xylene	1.8 ± 0.1	3.3 ± 0.2	5.2 ± 0.3	1.8 ± 0.2

n.d.: not detected.
[a] ±Standard deviation, $n = 6$.

From the foregoing it follows that the proposed screening/confirmation method classifies/quantifies drinking water samples with respect to the legally established levels. Although HS–GC–MS provides adequate sensitivity, the P & T–GC–MS method is the most sensitive. Therefore, the cut-off level can be lowered by using the latter technique maintaining the same column temperature program and chemometric data treatment.

Acknowledgements

This work was supported by grant CTQ2004-02798 from Spain's DGICyT. A. Serrano would like to thank Spain's Ministerio de Educación, Cultura y Deporte for award of a predoctoral grant.

References

[1] L.M.L. Nollet (Ed.), Handbook of Water Analysis, Marcel Dekker, New York, 2001 (Chapter 33).
[2] http://www.epa.gov/safewater/consumer/mcl.pdf, 4 June 2004.
[3] http://toxics.usgs.gov/definitions/btex.html, 4 June 2004.
[4] Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000, Off. J. Eur. Commun. 327, 22 December 2002.
[5] Decision 2455/2001/EC of the European Parliament and of the Council of 20 November 2001, Off. J. Eur. Commun. 331, 15 December 2001.
[6] Directive 98/83/EC of the Council of 3 November 1998, Off. J. Eur. Commun 330, 5 December 1998.
[7] E. Martínez, S. Lacorte, I. Llobet, P. Viana, D. Barceló, J. Chromatogr. A 959 (2002) 181.
[8] A.D. Nikolaou, S.K. Golfinopoulos, M.N. Kostopoulou, G.A. Kolokythas, T.D. Lekkas, Water Res. 36 (2002) 2883.
[9] S. Lacorte, L. Olivella, M. Rosell, M. Figueras, A. Ginebreda, D. Barceló, Chromatographia 56 (2002) 739.
[10] J.C. Flórez Menéndez, M.L. Fernández Sánchez, J.E. Sánchez Uría, E. Fernández Martínez, A. Sanz-Medel, Anal. Chim. Acta 415 (2000) 9.
[11] Z. Wang, K. Li, M. Fingas, L. Sigouin, L. Ménard, J. Chromatogr. A 971 (2002) 173.
[12] A. Alonso, M.A. Fernández-Torroba, M.T. Tena, B. Pons, Chromatographia 57 (2003) 369.
[13] M.B. Wise, M.R. Guerin, Anal. Chem. 69 (1997) 26A.
[14] S. Bauer, Trends Anal. Chem. 14 (1995) 202.
[15] M.A. Mendes, R.S. Pimpim, T. Kotiaho, M.N. Eberlin, Anal. Chem. 68 (1996) 3502.
[16] P. Bocchini, R. Pozzi, C. Andalò, G.C. Galletti, Anal. Chem. 73 (2001) 3824.
[17] R.M. Alberici, C.G. Zampronio, R.J. Poppi, M.N. Eberlin, Analyst 127 (2002) 230.
[18] M. Valcárcel, S. Cárdenas, M. Gallego, Trends Anal. Chem. 18 (1999) 685.
[19] M. Valcárcel, M. Gallego, S. Cárdenas, Chromatographia 53 (2001) S149.
[20] C. Pérès, C. Denoyer, P. Tourmayre, J.L. Berdagué, Anal. Chem. 74 (2002) 1386.
[21] I. Marcos Lorenzo, J.L. Pérez-Pavón, M.E. Fernández Laespada, C. García Pinto, B. Moreno Cordero, J. Chromatogr. A 945 (2002) 221.
[22] F. Peña, S. Cárdenas, M. Gallego, M. Valcárcel, J. Am. Oil Chem. Soc. 79 (2002) 1103.
[23] J.L. Pérez Pavón, M. Nogal Sánchez, C. García Pinto, M.E. Fernández Laespada, B. Moreno Cordero, A. Guerrero Peña, Anal. Chem. 75 (2003) 2034.
[24] N.J. Miller, J.C. Miller; Statistics and Chemometrics for Analytical Chemistry, fourth ed., Prentice Hall, NJ, 2002.
[25] L. Kirkup, M. Mulholland, J. Chromatogr. A 1029 (2004) 1.