http://dx.doi.org/10.5935/0103-5053.20130194

J. Braz. Chem. Soc., Vol. 24, No. 9, 1530-1536, 2013.
Printed in Brazil - ©2013 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Application of Solid Phase Microextraction and Gas Chromatography for the Determination of BTEX in Solid Petroleum Residues

Morgana Frena,* Alessandra Emanuele Tonietto and
Luiz Augusto dos Santos Madureira

Departamento de Química, Universidade Federal de Santa Catarina,
CP 476, 88040-900 Florianópolis-SC, Brazil

Este trabalho descreve um método simples e rápido para a determinação de BTEX (benzeno, tolueno, etilbenzeno e xileno) em resíduos sólidos e soluções lixiviadas de resíduos sólidos aplicando a Norma Brasileira ABNT NBR 10004/2004. O método proposto possibilita a detecção direta de BTEX usando microextração em fase sólida e cromatografia a gás com detector por ionização em chama (HS-SPME GC/FID). Os limites de quantificação obtidos para BTEX evidenciaram que o método é adequado para a classificação de resíduos sólidos.

This work describes a simple and fast method for the determination of BTEX (benzene, toluene, ethylbenzene and xylene) in solid waste and solutions obtained from leaching applying procedures detailed in the ABNT NBR 10004/2004 Brazilian standard for the classification of solid residues. The proposed method allows the direct detection of BTEX using solid-phase microextraction and gas chromatography with a flame ionization detector (HS-SPME GC/FID). Limits of quantification for BTEX showed that the developed method is suitable for the classification of solid wastes.

Keywords: benzene, BTEX, gas chromatography, HS-SPME, solid waste

Introduction

In the literature, solid waste is defined as any garbage, refuse, sludge (from a water supply, wastewater treatment plant or air pollution control facility) or other discarded solid material containing liquid, semi-solid or gaseous materials. Such wastes originate from industrial, commercial, mining and agricultural operations as well as domestic activities.[1]

Due to the associated risks, in terms of environmental pollution and public health, the method of disposal of a solid waste is selected following an assessment of its composition. In Brazil, residues containing solid wastes are classified based on their hazardous contents according to the ABNT NBR 10004/2004 Brazilian standard,[2] and decisions regarding to the final destination, which can involve their reuse (e.g. in agriculture), disposal in industrial landfills or incineration, are based on chemical analysis.[3]

Benzene, toluene, ethylbenzene and xylene (BTEX) are volatile compounds commonly associated with petroleum products. One of the most common sources of BTEX contamination in soil and groundwater are spills involving the release of petroleum products, such as gasoline, diesel fuel and lubricating and heating oil, from leaking oil tanks. Because of the polarity and solubility characteristics of BTEX compounds, they are able to enter environmental (soil and groundwater) systems and cause serious pollution problems[4] since they all have acute and/or long-term toxic effects.[5,6] Because of the toxic effects to both the environment and human health, benzene is classified by the World Health Organization as a strong carcinogen, occupying the 6th place on the list of dangerous substances.[7] The Brazilian standard (ABNT NBR 10004/2004)[2] for solid waste sets a maximum limit of 0.5 mg L^{-1} for benzene extracts obtained in leaching tests. Exposure to these hazardous substances can have damaging effects on liver, kidneys, heart, lungs and nervous system, reduces bone marrow function and provokes cancer.[4,8]

A bibliographical search revealed that several researchers have studied BTEX in different matrices including soils,[9,10] water,[4,11-13] urine[14] and effluent samples.[15] Official methods for the determination of volatile organic analytes include various techniques through which these

---

*e-mail: morganafrena@hotmail.com

compounds may be introduced into a gas chromatograph (GC) or gas chromatograph-mass spectrometer (GC/MS) system. Automated static headspace for solids[16] and purging and trapping for solid, waste oil[17] and aqueous[18,19] samples are the most commonly used techniques. However, no method to determine BTEX in solid waste, in particular that originating from petroleum refining, by solid-phase microextraction (SPME) has been reported in the literature.

Due to its simplicity and high sensitivity, SPME is extensively employed for the determination of volatile and semi-volatile compounds. It is a fast and efficient extraction method which integrates sampling, isolation and enrichment into one step, allowing the quantitative determination of contaminants in a wide variety of matrices.[20] In view of this facility and the great complexity of solid residues, the aim of this work is to describe the use of a SPME method, followed by GC/FID, for the determination of BTEX in solid waste samples comprised of petroleum residues.

Experimental

Reagents and solutions

A stock solution of BTEX containing benzene, toluene, ethylbenzene and xylene, each at 2 mg mL^{-1} in methanol, was obtained from AccuStandard (New Haven, CT, USA). Working solutions were prepared by diluting stock solutions with nanograde methanol (Tedia, Rio de Janeiro, RJ, Brazil). Analytical grade sodium chloride (Vetec, Rio de Janeiro, RJ, Brazil) was used to adjust the ionic strength of the working solutions. Acetic acid (Nuclear, São Paulo, SP, Brazil), sodium hydroxide (Vetec), both analytical grade, and high purity distilled and deionized water (Milli-Q Millipore Bedford, MA, USA) were used to prepare the extraction solution (pH 4.93) as recommended by the ABNT NBR 10005/2004 Brazilian standard.[21] Buffer solutions at pH 4.00 ± 0.02 and pH 7.00 ± 0.02 (Nalgon, São Paulo, SP, Brazil) were used for the pH meter calibration. Nanograde dichloromethane was obtained from Tedia. All extractions were performed in 40 mL SPME vials (Supelco, Saint Louis, MO, USA).

Instrumentation

Chromatographic analysis was performed using a Shimadzu GC-2014 gas chromatograph with a flame ionization detector (FID), equipped with a split/splitless injector. Hydrogen (purity 99.995%) was used as the carrier gas. The capillary column was an Rtx-5MS (30 m × 0.25 mm i.d. × 0.25 mm d_f) (Restek, Bellefonte, PA, USA). The column temperature was held at 35 ºC (5 min) and then increased at a rate of 10 ºC min^{-1} up to 220 ºC and held for 1 min. The temperature of the injector was 280 ºC for CAR/PDMS (carboxen-polydimethylsiloxane) and 250 ºC for PDMS (polydimethylsiloxane) and PDMS/DVB (polydimethylsiloxane-divinylbenzene) fibers, applying the splitless mode with an initial time of 1 min (split ratio was fixed at 1:50). The time of desorption of the fiber in the injection port was 5 min. No carryover effect was observed. The detector temperature was 300 ºC. A thermal bath (Microquimica, Florianopolis, SC, Brazil) was used in this study to control the temperature. SPME fibers were obtained from Supelco.

Sampling and laboratory fortified matrix (LFM)

Solid waste samples from a petroleum hydroprocessing unit were extracted with 5 mL of dichloromethane and placed on a heating plate (80 ºC) in order to remove any organic traces and the remaining volatile compounds. All extractions were performed in triplicate. These LFMs were analyzed exactly as the samples and used for the method optimization and recovery tests.

Leaching of the solid waste

The leaching process was carried out according to the procedures recommended in the Brazilian standard (ABNT NBR 10005/2004).[21] In summary, to a sample aliquot of 25.0 g, 500.0 mL of the appropriate extraction solution containing 0.57% v v^{-1} glacial acetic acid and 6.43% v v^{-1} sodium hydroxide (1.00 mol L^{-1}) at pH 4.93 ± 0.05 were added. This solution is suitable for the extraction of volatile compounds. The mixture was submitted to stirring by rotating at 30 ± 2 rpm with an appropriate stirrer (TE-743, Tecnal, Piracicaba, SP, Brazil) for 18 h and the leachate was then ready for analysis.

Method optimization

Method optimization was carried out by the multivariate method. Two Doehlert designs[22] for three variables were employed to generate the response. Five levels of the variable mass of solid waste and extraction time and three levels of the variable water and ionic strength were studied, totalizing ten experiments (including a triplicate center point). All response surfaces were mathematically best described by a quadratic model consisting of 10 coefficients rather than linear models. All of the generated quadratic equations had at least 6 degrees of freedom and the determination coefficients (R) was better than 0.9. The Statistica® computer program

(Stat Soft, Inc., 2001; version 6) was used throughout the study to process the data obtained.

Fiber coating optimization

Three different fibers were tested: CAR/PDMS fiber film with 75 µm thickness, PDMS fiber film with 100 µm thickness and PDMS/DVB fiber film with 65 µm thickness (Supelco). Assays were performed using 30.0 mg of the previously extracted solid waste and enriched with the analytes at 100.0 µg g^{-1}. The extraction procedure consisted of extracting at 25 ºC for 30 min in the headspace mode. Prior to use, the fibers were conditioned in a GC injector port in accordance with the supplier instructions. PDMS and PDMS/DVB were conditioned at 250 ºC for 30 min, while CAR/PDMS was conditioned at 300 ºC for 60 min.

HS-SPME mode optimization

The extraction conditions were optimized applying a multivariate method. The BTEX compounds were extracted by SPME from the sample headspace. HS-SPME was performed with three commercially available fibers housed in a manual holder obtained from Supelco. A blank solid waste sample spiked with a known amount of the analytes was used for method optimization and validation. The samples were weighed directly into the SPME sampling vials, spiked with the target analytes and sealed with screw caps with PTFE/silicon septa.

The first step consisted of studying the variable mass of solid waste (10.0-50.0 mg) and extraction time (10-50 min). In the second step, a Doehlert design[22] was used to study the effect of the addition of water (0.5-10.5 mL), considering the solid waste dried and in suspension, and the ionic strength by addition of sodium chloride (0-360 g L^{-1}).

Method validation and application

Validation of the method was carried out by obtaining the main figures of merit, namely, the linear range, linear correlation coefficient, selectivity, robustness and limits of detection and quantification. Precision was evaluated as the relative standard deviation of replicate analysis and the accuracy as recovered (%) in recovery tests.

Results and Discussion

Selecting the optimum fiber coating

The appropriate selection of the fiber coating is important because the type and amount of compounds extracted from the sample are dependent on the physicochemical characteristics of the fiber stationary phase. Three different commercial fibers were tested: PDMS, PDMS/DVB and CAR/PDMS. Furthermore, fiber optimization is a critical step in SPME method development,[23] as appropriate selection can improve both the sensitivity and selectivity of the extraction.

As shown in Figure 1, the most suitable fiber for the extraction of the studied compounds was CAR/PDMS. This fiber is coated with porous carbon which retains all small analytes that come into contact with the pores.[24] The CAR/PDMS fiber extracts these analytes by adsorption, as opposed to absorption, the extraction mechanism of fibers coated solely with liquid phase.[25] This result is consistent with previous publications in which the CAR/PDMS is usually recommended for extracting small analytes.[26] Moreover, Shirey[27] established that fibers containing adsorbents, such as CAR and DVB, provided greater extraction yield than fibers composed of a liquid stationary phase, such as PDMS. In addition, Popp and Paschke[28] reported that, in general, CAR was a more effective coating than DVB for low-molecular mass compounds, corroborating the findings of this study. The poorest results, as expected, were obtained with the PDMS fiber since this fiber is recommended for the extraction of non-polar analytes. Thus, the CAR/PDMS fiber was chosen for further optimization and validation studies.

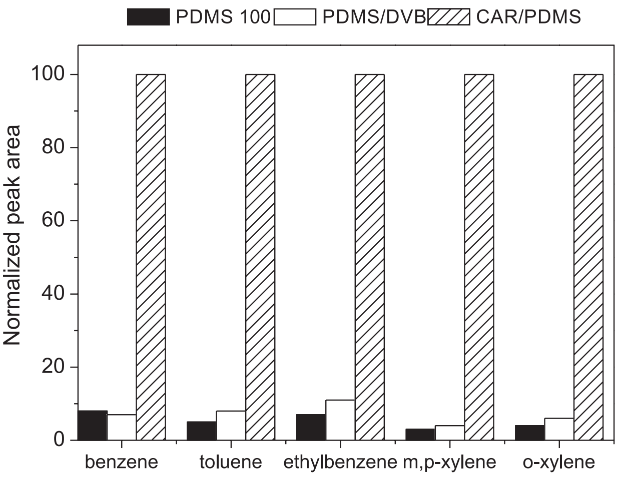

Figure 1. Comparison of the extraction efficiencies of the fibers PDMS 100, PDMS/DVB and CAR/PDMS obtained in the optimization of the method for the determination of BTEX in solid waste by HS-SPME.

Multivariate optimization

The mass of solid waste placed in the vial must be appropriate. If the mass is too small, sensitivity problems due to low chromatographic signals can occur. Similarly, the extraction time is a key factor since SPME is an equilibrium technique. In order to determine the influence of the sample mass and extraction time on the extraction efficiency, a Doehlert design was applied. As the compounds toluene, ethylbenzene, *o*-xylene and *p*-xylene showed similar behavior in terms of the response surface, these analytes are represented by *o*-xylene. Figure 2 shows the response surface for the extraction time *vs.* mass of solid waste for benzene, *o*-xylene and the geometric mean of the analytes. As can be seen, no significant improvement in the signal was observed on using between 10.0 and 25.0 mg of solid waste. Based on these results, the amount of 20.0 mg was chosen to proceed with the study. In relation to the extraction time, it can be observed that for benzene, 10 min are sufficient to obtain a good response. However, the results obtained for *o*-xylene showed that the best extraction is achieved between 20 and 40 min, as expected since *o*-xylene is less volatile than benzene, requiring an increased extraction time. Hence, the time of 20 min was adopted.

It is well known that sorption processes are affected by the ionic strength of the sample, which is adjusted by addition of salt.[29] Thus, the effect of ionic strength on the extraction process should be studied. A Doehlert design was applied considering the addition of different amounts of water (between 0.5 and 10.5 mL) and the addition of NaCl in different concentrations, considering no salt, intermediate saturation and close to the saturation point (0, 180 and 360 g L^{-1}, respectively). Figure 3 illustrates the effect of the addition of water *vs.* the addition of NaCl on the extraction process. The response surfaces obtained for *o*-xylene and the geometric mean for the analytes showed that the extraction yield decreased with increasing water and salt additions. The maximum response was obtained when 0.5 mL of water and no salt were added to the system. The exception was benzene (Figure 3a), for which the addition of water and saturation with NaCl favored the extraction. Menéndez *et al.*[11] also showed that the addition of NaCl led to only slightly better results in the case of benzene, while for the other BTEX compounds, no favorable, or sometimes unfavorable, effects were observed, for aqueous BTEX samples. Consequently, no salt and no water were added in this study.

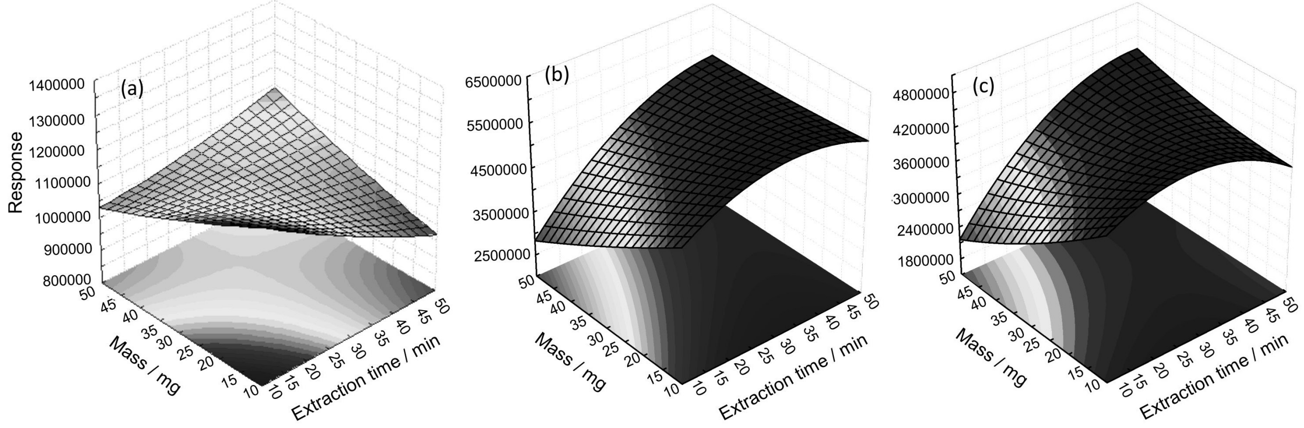

Figure 2. Response surface for extraction time *vs.* mass of solid waste for (a) benzene, (b) *o*-xylene and (c) the geometric mean for the analytes.

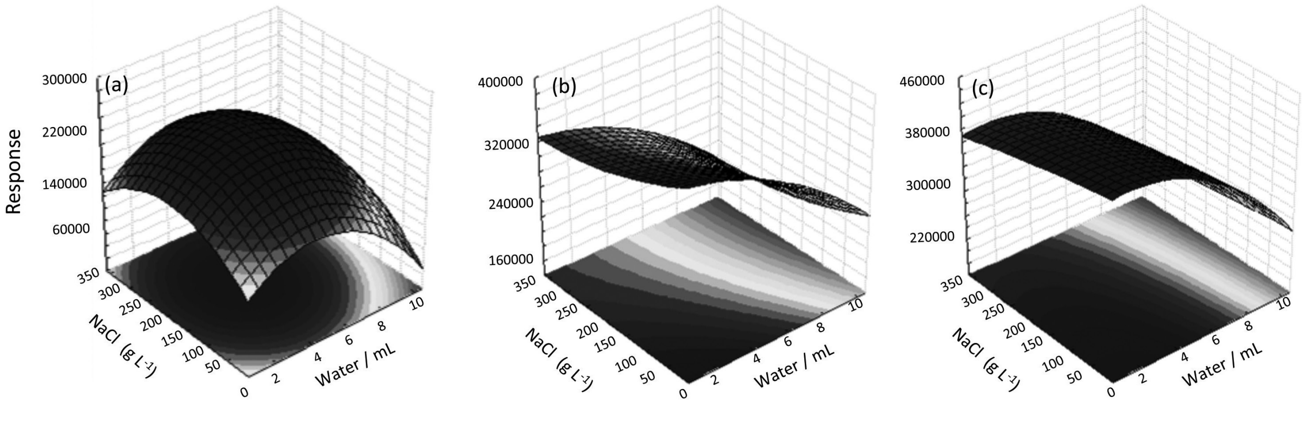

Figure 3. Response surfaces for addition of water *vs.* addition of NaCl for (a) benzene, (b) *o*-xylene and (c) the geometric mean for the analytes.

Analytical figures of merit

Several parameters were examined in order to validate the method for the determination of BTEX in solid waste proposed herein. The main analytical figures of merit obtained were: linearity, linear correlation coefficient, limits of detection and quantification, selectivity, robustness, precision and recovery tests. Results can be observed in Table 1.

The precision of the method, expressed as the relative standard deviation (RSD), was determined through the analysis of seven replicates of the solid waste spiked with BTEX at the concentration level of 100.0 ng mL^{-1}. Excellent values in the range of 1.3 to 7.0% were obtained. The linear correlation coefficients were between 0.9980 and 0.9999.

The limit of detection (LOD) was estimated as 3s/S, while the limit of quantification (LOQ) was estimated as 10s/S, where s is the standard deviation of the linear coefficient calculated from the calibration curve and S is the slope. The limit of detection obtained for the determination of BTEX in the solid waste varied from 1.8 to 21.0 ng mL^{-1} (Table 1), meaning that the proposed method has sufficient detection capacity to be used for waste classification, according to the ABNT NBR 10005/2004 Brazilian standard,[21] in which the stipulated limit for benzene is 0.5 mg L^{-1}.

The selectivity was evaluated by injecting a blank sample, without the addition of the analytes. The blank sample was injected seven times and no interfering compound eluted at the retention time of the analytes, showing that the proposed method is selective.

The robustness of the proposed method was also verified using three different quantities of the solid waste for the extraction by HS-SPME: 20.0, 35.0 and 50.0 mg. The obtained results revealed satisfactory RSD values, lower than 1.8% for all analytes.

As an application, solid waste samples comprised of petroleum residues were submitted to extraction by the proposed method for the determination of BTEX, aiming to classify the solid waste samples according to the standard.[21] Determined concentrations ranged from 18.9 to 429.1 ng mL^{-1} (Table 2).

In order to verify the accuracy of the method, recovery tests were carried out by spiking the samples of solid waste with different levels of BTEX. A comparison between leachates obtained using the method proposed in the Brazilian standard (ABNT NBR 10005/2004)[2] from solid waste samples spiked with different levels of BTEX was carried out (Figure 4). The results are shown in Table 3. Higher losses at a concentration of 250.0 ng mL^{-1} can be observed for the analytes benzene and *m*,*p*-xylenes, which can be assigned to the leaching procedure.

Table 1. Correlation coefficients, RSD, limits of detection and quantification obtained in the determination of BTEX in solid waste

Analyte	R	Linear range / (ng mL^{-1})	LOD / (ng mL^{-1})	LOQ / (ng mL^{-1})	RSD[a] / %
Benzene	0.9995	35.0-250.0	10.5 ± 0.5	34.9 ± 1.1	3.2
Toluene	0.9999	12.5-250.0	1.8 ± 0.1	6.0 ± 0.9	1.3
Ethylbenzene	0.9999	12.5-250.0	3.7 ± 0.2	12.3 ± 0.7	7.0
m,*p*-Xylene	0.9980	70.0-250.0	21.0 ± 0.8	70.0 ± 3.9	4.8
o-Xylene	0.9988	70.0-250.0	17.8 ± 0.9	59.3 ± 1.7	3.8

R*:* linear correlation coefficient; LOD: limit of detection; LOQ: limit of quantification; [a]RSD: relative standard deviation.

Table 2. Analyte concentrations (ng mL^{-1}) obtained in the determination of BTEX in solid waste originating from petroleum residues

Sample	Benzene	Toluene	Ethylbenzene	*m*,*p*-Xylene	*o*-Xylene
1	< 34.9 ± 1.1	61.8 ± 3.2	< 12.3 ± 0.7	< 70.0 ± 3.9	< 59.3 ± 3.7
2	< 34.9 ± 1.1	217.3 ± 10.8	429.1 ± 27.3	< 70.0 ± 3.9	< 59.3 ± 3.7
3	< 34.9 ± 1.1	39.7 ± 1.6	< 12.3 ± 0.7	< 70.0 ± 3.9	< 59.3 ± 3.7
4	< 34.9 ± 1.1	66.3 ± 3.9	65.7 ± 5.9	65.7 ± 5.8	< 59.3 ± 3.7
5	< 34.9 ± 1.1	43.8 ± 2.6	18.9 ± 1.6	< 70.0 ± 3.9	< 59.3 ± 3.7

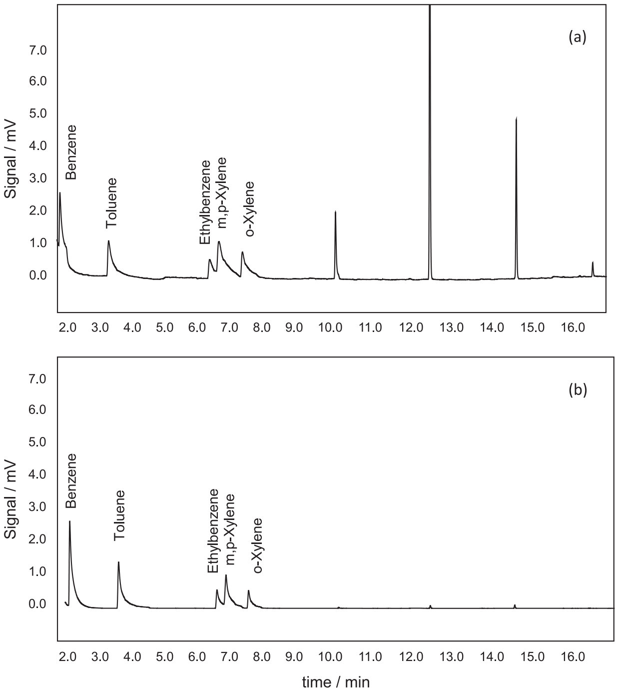

Figure 4. GC-FID chromatograms obtained from the HS-SPME analysis of (a) solid waste and (b) leachate spiked with BTEX.

Table 3. BTEX mean concentrations in spiked solid waste leachate and confidence interval 95% (n = 3)

Analyte	Leachate of solid waste spiked with 50.0 ng mL^{-1} of BTEX / (ng mL^{-1})	Leachate of solid waste spiked with 250.0 ng mL^{-1} of BTEX / (ng mL^{-1})
Benzene	50.5 ± 7.4	184.8 ± 12.7
Toluene	44.9 ± 8.9	212.5 ± 26.6
Ethylbenzene	46.5 ± 2.9	194.9 ± 27.3
m,p-Xylene	56.5 ± 3.6	155.2 ± 3.7
o-Xylene	58.1 ± 10.2	185.8 ± 11.9

Conclusions

A method was developed using HS-SPME for the determination of BTEX in solid waste. The use of an experimental design enabled the optimization of the extraction conditions. Maximum responses were obtained using a CAR/PDMS fiber, 20 min extraction time and sample mass of 20.0 mg. The developed method provides good performance in terms of precision (lower than 7% for all analytes), recovery, selectivity, robustness and LOD values (1.8 to 21.0 ng mL^{-1}), besides being fast and of low cost.

Acknowledgements

The authors are grateful to Petrobras for the financial support provided for this study. M. F. is grateful to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Brazil) for a scholarship.

References

1. http://www.dec.ny.gov, accessed in April 2013.
2. ABNT NBR 10004: *Resíduos Sólidos – Classificação*, Rio de Janeiro, Brasil, 2004.
3. Nemerow, N. L.; Agardv, F. J.; Salvato, J. A.; *Environmental Engineering: Environmental Health and Safety for Municipal Infrastructure, Land Use and Planning, and Industry*, vol. 1, 6th ed.; John Wiley & Sons, Inc.: Hoboken, USA, 2009.
4. Hosseinzadeh, R.; Tahmasebic, R.; Farhadi, K.; Moosavi-Movahedi, A. A.; Jouyban, A.; Madraghi, J.; *Colloids Surf., B* **2011**, *84*, 13.
5. Mazzeo, D. E. C.; Levy, C. E.; Angelis, D. F.; Marin-Morales, M. A.; *Sci. Total Environ.* **2010**, *408*, 4334.
6. Zhang, Y.; Mu, Y.; Liu, J.; Mellouki, A.; *J. Environ. Sci.* **2012**, *24*, 124.
7. Costa, A. S.; Romão, L. P. C.; Araújo, B. R.; Lucas, S. C. O.; Maciel, S. T. A.; Wisniewski Jr., A.; Alexandre, M. R.; *Bioresour. Technol.* **2012**, *105*, 31.
8. Durmusoglu, E.; Taspinar, F.; Karademir, A.; *J. Hazard. Mater.* **2010**, *176*, 870.
9. Ezquerro, O.; Ortiz, G.; Pons, B.; Tena, M. T.*; J. Chromatogr., A* **2004**, *1035*, 17.
10. Boonsaner, M.; Borrirukwisitsak, S.; Boonsaner, A.; *Ecotoxicol. Environ. Saf.* **2011**, *74*, 1700.
11. Menéndez, J. C. F.; Sánchez, M. L. F.; Uría, J. E. S.; Martínez, E. F.; Sanz-Medel, A.; *Anal. Chim. Acta* **2000**, *415*, 9.
12. Heleno, F. F.; Lima, A. C.; Afonso, R. J. C. F.; Coutrim, M. X.; *Quim. Nova* **2010**, *33*, 329.
13. Bianchin, J. N.; Nardini, G.; Merib, J.; Dias, A. N.; Martendal, E.; Carasek, E.*; J. Chromatogr., A* **2012**, *1233*, 22.
14. Fustinoni, S.; Rossella, F.; Campo, L.; Mercadante, R.; Bertazzi, P. A.; *Sci. Total Environ.* **2010**, *408*, 2840.
15. Gaujac, A.; Emídio, E. S.; Navickiene, S.; Ferreira, S. L. C.; Dórea, H. S.; *J. Cromatogr., A* **2008**, *1203*, 99.
16. Method EPA 5021: *Volatile Organic Compounds in Soils and other Solid Matrices using Equilibrium Headspace Analysis*, Ohio, USA, 1996.
17. Method EPA 5035: *Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples*, Ohio, USA, 1996.
18. Method EPA 5030 B: *Purge-and-Trap for Aqueous Samples*, Ohio, USA, 1996.
19. Method EPA 502.2: *Volatile Organic Compounds in Water by Purge-and-Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series*, Ohio, USA, 1989.
20. Eisert, R.; Pawliszyn, J.; *J. Chromatogr., A* **1997**, *776*, 293.

21. ABNT NBR 10005: *Procedimento para Obtenção de Extrato lixiviado de Resíduos Sólidos*, Rio de Janeiro, Brazil, 2004.
22. Ferreira, S. L. C.; dos Santos, W. N. L.; Quintella, C. M.; Barros Neto, B.; Bosque-Sendra, J. A.; *Talanta* **2004**, *63*, 1061.
23. Silva, E. A. S.; Pawliszyn J.; *J. Anal. Chem.* **2012**, *84*, 6933.
24. Mestres, M.; Marti, M.; Busto, O.; Guasch, J.; *J. Chromatogr., A* **1999**, *849*, 293.
25. Pawliszyn, J.; *Applications of Solid Phase Microextraction*, 1st ed.; The Royal Society of Chemistry: Loughborough, UK, 1999.
26. Elmore, J. S.; Mottram, D. S.; Hierro, E.; *J. Chromatogr., A* **2000**, *905*, 233.
27. Shirey, R. E.; *J. Chromatogr. Sci.* **2000**, *38*, 109.
28. Popp, P.; Paschke, A.; *Chromatographia* **1997**, *46*, 419.
29. Magdic, S.; BoydBoland, A.; Jinno, K.; Pawliszyn, J. B.; *J. Chromatogr., A* **1996**, *736*, 219.

Submitted: April 4, 2013