Headspace sorptive extraction coupled to gas chromatography-mass spectrometry for the determination of benzene, toluene, ethylbenzene and xylenes in finger paints

Marta Pastor-Belda, Pilar Viñas, Natalia Campillo, Manuel Hernández-Córdoba*

Department of Analytical Chemistry, Faculty of Chemistry, Regional Campus of International Excellence "Campus Mare Nostrum", University of Murcia, E-30100 Murcia, Spain

*Correspondence:

Prof. M. Hernández-Córdoba

 Department of Analytical Chemistry. Faculty of Chemistry. University of Murcia.

E-30100 Murcia. SPAIN

Tel.: +34 868887406

FAX: +34 868887682

e-mail: hcordoba@um.es

ABSTRACT

The presence of benzene, toluene, ethylbenzene and xylenes (BTEX) in dyes, paints and pigments is not still regulated but might be an indicator of contamination due to the well-known health risk of these compounds. An analytical procedure based on headspace sorptive extraction using a polydimethylsiloxane stir bar, was developed for the gas chromatographic determination of BTEX in finger paint samples. Univariate and multivariate designs were used to optimize experimental parameters, including equilibrium time, desorption time, saline effect and sample mass. Thirty minutes were necessary to absorb the analytes in the polydimethylsiloxane stir bar followed by a 5 min thermal desorption step. Limits of quantification of between 0.016 and 0.12 ng g^{-1} depending on the compound, were obtained. BTEX were found in the finger paint samples at levels between 0.14 and 12 ng g^{-1}.

1. Introduction

The fundamental principles and the knowledge of colors, dyes and pigments chemistry, as well as their contamination by organic compounds is an interesting topic [1]. Finger paints, which are a type of emulsion or water paint, are colored preparations, similar to pastes and/or gelatine, which can be applied directly to surfaces with fingers and hands, being especially designed for use by children. The paints consist of water, dyes, fillers, binders, humectants, surfactants, bitter agents and some organic compounds and are submitted to the safety requirements imposed by the European Toy Safety Directive (88/378/EEC) [2] and implemented by UNE-EN 71-7 [3].

Benzene, toluene, ethylbenzene and xylene isomers (BTEX) are usually used as solvents in consumer and industrial products and must be determined as contamination markers in biological fluids [4]. Since 1996, the European Comission has established rules related to the presence and the risk of some organic compounds in different types of paints and toys, to ensure child safety [5]. Thus, the risk of ingestion of finger paints is considered high, while prolonged skin contact is unavoidable. Studies in humans show that BTEX exposure is associated with effects on immune, metabolic, respiratory, and reproductive functioning, as well as on development. When chronically ingested, all BTEX may cause liver and kidney damage [6]. Consequently, the importance of analysing this type of paints and toys is clear, due to the fact that BTEX can present a risk to children health [5].

The use of headspace (HS) offers higher sensitivity for BTEX determination compared with direct injection techniques [7]. The static headspace (SHS)

technique is recommended by the Environmental Protection Agency (EPA) for the analysis of BTEX in some protocols [8] because it is inexpensive and uses simple instrumentation with no need for organic solvents. However, the limits of detection are not very low, making it more suitable for the analysis of samples containing high levels of volatile compounds [7]. Although HS has traditionally been applied for BTEX determination [9,10], microextraction techniques for sample preparation are gaining in importance. For example, BTEX analysis has been performed using liquid-phase microextraction (LPME), such as dispersive liquid liquid microextraction (DLLME) [11], hollow-fiber liquid phase microextraction (HF-LPME) [12] or single drop microextraction (SDME) [13–15]. In addition, techniques using a solid phase have also been used, including solid phase extraction (SPE) [14,16], dispersive solid-phase extraction (MSPE) [17-19] or headspace solid-phase microextraction (HS-SPME), this last being the most widely used with commercial fibers [7,20-23] or lab-made fibers [24-27], mostly in water or environmental samples [28]. Only one SPME-based procedure with an ionic liquid coated fiber [29] has been applied to the analysis of paint samples. These microextraction approaches are usually coupled with gas chromatography (GC) as the main alternative for the determination of BTEX with flame ionization [7,11,12,15,20,21,29] or mass spectrometry (MS) detection [13,17,22,23,25,30-32].

Stir bar sorptive extraction (SBSE) is a solvent-free sample preparation procedure based on the extraction of target compounds from different matrices into a stationary phase-coated stir bar. In headspace sorptive extraction (HSSE), the analytes are extracted by placing the bar in the headspace for a fixed time, after which the analytes are thermally desorbed by placing the bar

into a glass tube inserted in a thermal desorption system (TD) and a programmed temperature vaporizing (PTV) injector, and then analyzed by GC [33]. TD has been applied for BTEX analysis in ambient air using multibed adsorbents [31,32,34,35] and in other applications [30]. Both HSSE and HS-SPME are based on sorptive extraction, but HSSE provides better sensitivity due to the high volume of the polymeric coating, which achieves higher preconcentration factors, in addition to the higher robustness provided by the stir bar related to the fiber coatings. On the other hand, considering the extractant phase amount, HSSE should provide comparable or even better detection limits than those obtained with LPME techniques.

In this work, HSSE as sampling technique coupled to GC-MS is proposed for the first time for BTEX determination in finger paints. The results agreed this obtained by means of the classical SHS technique.

2. Materials and methods

2.1. Reagents

A commercially available mixture of BTEX (benzene, toluene, ethylbenzene and ortho, meta and para-xylene) at a concentration of 200 mg L^{-1} in methanol was provided by Sigma (St. Louis, MO, USA, www.sigmaaldrich.com). The solution was stored in darkness at -10 ºC. Eucalyptol from Sigma was used as internal standard. Working standard solutions were prepared daily by diluting with water from a Milli-Q water purification system (Millipore, Bedford, MA, USA, www.emdmillipore.com) and stored at 4 ºC.

2.2. Instrumentation

Commercial stir bars for sorptive extraction (Twisters®) coated with a 0.5 mm-thick layer of polydimethylsiloxane (PDMS) (24 µL), from Gerstel (Mullheim an der Ruhr, Germany, www.gerstel.es), were conditioned prior to use in an empty TD tube at 275 ºC for 0.5 h with helium at a flow rate of 50 mL min^{-1}. All the analyses were performed in 15 mL clear glass vials provided with a magnet in the stopper to hold the stir bar during the absorption step. The solutions were stirred with a magnetic stirrer (IKA RH KT/C, Supelco, www.ika.com) at 900 rpm using a PTFE magnetic stir bar (10 mm x 6 mm o.d). A laboratory-made heating system, built in the Central Laboratory Service of the University of Murcia and consisting of a drilled block provided with an electronic temperature control system was used for heating the sample solutions during the HSSE absorption step.

For thermal desorption injection, the sample introduction system consisted of a Thermal Desorption Unit (TDU-2) equipped with a multipurpose autosampler (MPS) and a Programmed Temperature Vaporization (PTV) Cooled Injector System (CIS-4) provided by Gerstel. The TDU was initially operated in solvent vent mode, maintaining a temperature of 50 ºC for 0.5 min. Next, a desorption program starting at 50 ºC and increasing to 210 ºC at 400 ºC min^{-1} and holding for 5 min was applied. The PTV was cooled to 10 ºC by a Peltier unit while the analytes were desorbed from the stir bar in the TDU. The PTV was equipped with a liner packed with Tenax (Gerstel). The PTV temperature program was as follows: start at 10 ºC, increase to 150 ºC at 870

ºC min⁻¹ and hold for 1 min, finally increase the temperature to 215 ºC at 540 ºC min⁻¹ and hold 2.5 min. A vent flow of 30 mL min⁻¹ and pressure of 7.05 psi were applied in the sample introduction system.

For gas injection, a MPS headspace unit provided by Gerstel was used. The samples were incubated and shaken at 750 rpm for 20 min at 70 ºC. Then, the MPS took a gas sample volume (750 µL) with a 2.5 mL syringe from the headspace above the sample for injection into the GC injector at 120 ºC in splitless mode. The whole process was fully automated and therefore can be considered very precise and reproducible.

The TDU and MPS units were installed in a 6890N gas chromatograph (Agilent, Waldbronn, Germany, www.agilent.com) coupled to a quadrupole mass selective spectrometrer (Agilent 5973) equipped with an inert ion source. A DB-5MS (5% diphenyl–95% dimethylpolysiloxane, Agilent) capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness) was used with a constant helium flow of 1 mL min⁻¹. The GC temperature program was: start temperature 40 ºC held for 5 min, increase to 50 ºC at 2.5 ºC min⁻¹ and maintain 1 min, finally increase to 280 ºC at 50 ºC min⁻¹, and hold 1 min. The retention time and the monitored ions are shown in Table 1. Benzene, toluene, ethylbenzene and o-xylene were well separated, while m-xylene and p-xylene were not totally resolved and were quantified together. The temperatures of the ion source, transfer line and quadrupole were 230, 300 and 150 ºC, respectively. The mass spectrometer was operated using electron-impact (EI) mode (70 eV). The compounds were quantified in the selected ion monitoring (SIM) mode in order to improve the limits of detection. Monitored target ions (*m/z*) were 78 for benzene and 91 for toluene, ethlybenzene and xylene isomers. Identification

was confirmed by the retention time and scan mass-spectra database for each compound.

2.3. Samples and analytical procedures

The finger paints were obtained from local shops and were from the same manufacturer. All the available colours were analyzed.

HSSE procedure. A 2 g sample was weighed into a 15 mL glass vial provided with a magnetic stopper, and eucalyptol was incorporated as internal standard at 5 ng g^{-1}. The mixture was diluted to 10 mL with water and manually shaken to homogenize. A magnetic stirrer was added to the mixture and a PDMS stir bar was placed in the headspace vial with the aid of a magnet placed in the stopper. The vial was heated to 30 ºC and stirred at 900 rpm for 30 min. The stir bar was removed from the stopper and dried with a lint-free tissue before being introduced into a glass desorption tube. The analytes were thermally desorbed from the stir bar, placing the desorption tube containing the stir bar in the TDU connected to the PTV injector and the GC-MS system.

SHS validation procedure. Into a 15 mL glass vial provided with a magnetic stopper, a 3.5 g sample was weighed, eucalyptol was incorporated as internal standard at 15 ng g^{-1} and the mixture was diluted to 10 mL with water and manually shaken to homogenize. The mixture was placed on the tray and automatically transported into the incubator with the magnetic stopper. The samples were incubatedat 70 ºC and orbital shaken at 750 rpm for 20 min. Afterwards, the MPS took a gas sample volume of 750 µL from the headspace above the sample and injected it into the GC-MS system in splitless mode.

3. Results and discussion

3.1. Optimization of the HSSE conditions

The HSSE procedure involves absorption of the analytes on the stir bar and their thermal desorption into the GC-MS. Extraction of the analytes from the sample solution was optimized in duplicate experiments for each variable using 1 g of white finger paint containing 10 ng g^{-1} of all the analytes.

Due to the high volatility of BTEX, stronger analytical signals were obtained for all the analytes when the stir bar was placed in the headspace rather than inside the solution. Therefore, the HSSE procedure was chosen. SBSE stir bars with different types of coating materials, such as the non-polar PDMS and the polar polyacrylate (PA) and ethylene glycol-PDMS copolymer (EG-Silicone), were tested. The PDMS coating provided higher extraction efficiency and better sensitivity for all the compounds, due to their non-polar nature, thus being selected.

Figure 1 shows the results obtained when varying other extraction conditions. The influence of the ionic strength was studied by adding different amounts of sodium chloride (0, 5, 10 and 15% w/v) and, as shown in Fig. 1A, this parameter did not affect the extraction efficiency of BTEX from paint samples, probably due to the non-polar character of BTEX. A similar behavior was observed by Liu *et al.* 2005 [29]. So, the addition of sodium chloride was discarded, and the effect of the presence of an organic modifier in the extraction medium was tested (five levels: 0, 10, 20, 35 and 50% v/v methanol). Fig. 1B

shows that the signals for all the analytes decreased when the methanol percentage increased, so this organic solvent was discarded. Different extraction temperatures (25, 30, 40, 50, 60 and 80 ºC) were assayed and sensitivity was highest for all the analytes at 30 ºC (Fig. 1C). Another important parameter affecting HSSE is the extraction time, which was investigated from 15 to 120 min (six levels: 15, 30, 45, 60, 90 and 120 min), equilibrium being almost reached for all the compounds at around 30 min (Fig. 1D), which was selected as optimal. Longer times improved sensitivity for some analytes, but obviously increased the analysis time.

The desorption step involves a high number of variables that are interrelated. For this reason, an experimental design based on a Plackett-Burman design (PBD) was used to identify the most important factors affecting the desorption step. The PBD (14 experiments, in duplicate) included the following variables: desorption time (5, 7.5 and 10 min), desorption temperature (160, 210 and 260 ºC), gas flow-rate (60, 90 and 120 mL min^{-1}), CIS time (4, 6 and 8 min) and CIS temperature (180, 215 and 250 ºC). The Pareto charts revealed that, due to the high volatility of BTEX, both the desorption temperature and desorption time of TDU, as well as the CIS temperature, were not relevant factors and values of 5 min for the TDU time, and 210 and 215 ºC for TDU and CIS temperatures, respectively, were chosen. On the other hand, the different interaction of the analytes with the CIS liner filling meant that both CIS time and helium flow were significant variables. A Taguchi multivariate design of two factors at four levels (16 experiments) was used to establish the optimal value of the helium flow (30, 60, 90 and 120 mL min^{-1}) and the CIS time (2.5, 5, 7.5 and 10 min). Maximum sensitivity was attained for all the

compounds with a 30 mL min^{-1} helium flow-rate and 2.5 min CIS time. The retention of the compounds in the PTV injector is strongly influenced by the temperature, which was fixed at 10 ºC by means of a Peltier unit. Moreover, trapping of the analytes in the PTV while they are being desorbed from the PDMS stir bar may be influenced by the nature of the filling in the PTV liner. Two different PTV liners with specific fillings for volatile compounds (Tenax and Carbotrap B) were tested. The Carbotrap B filling did not retain benzene, and the best results were obtained with the Tenax filling, which was selected.

The possibility of a matrix effect was evaluated by studying the influence of the paint mass in the 0.2-5 g range on the analytical signals of 10 ng g^{-1} BTEX. The greatest peak areas were obtained for all analytes when the paint sample mass increased up to 2 g, this value being selected.

Under the selected conditions, a complete desorption of the analytes was attained. However, to improve reproducibility the stir bar was reconditioned every five uses.

3.2. Optimization of SHS conditions

Different paint masses (0.5-5 g) diluted with water volumes in the 3.5-10 mL range were assayed, and best results were obtained 3.5 g sample diluted up to 10 mL. The most important parameters affecting SHS sensitivity are the incubation time and temperature. A central composite design (CCD, $\alpha = 1.5$, 4 cube points, 4 axial points and 4 central points, in duplicate) developed in the range 15-45 min for time and 40-80 ºC for temperature, was used to optimize

these variables simultaneously. Best results were obtained by heating at 70 ºC for 20 min, being selected.

3.3. Method performance

For studying the possible matrix effect, both direct calibration and standard additions calibration were carried out, at six concentration levels, between 0.04-8 ng mL^{-1} (0.2-40 ng g^{-1}) for HSSE. Eucalyptol, which showed similar chromatographic and chemical behaviour than the studied compounds, was used as internal standard at 1 ng mL^{-1} (5 ng g^{-1}). Moreover, all the studied samples were checked to be free of eucalyptol. Correlation coefficients were higher than 0.99 in all cases. The comparison of the slopes, using an ANOVA t-test applied at 95% confidence level, showed statistically significant differences between direct calibration with standard solutions and standard additions calibration, with p-values lower than 0.05 for all the compounds. However, there were no statistically significant differences between the standard addition slopes for the different paint samples. Therefore, matrix matched calibration using a blank sample slope was used for accurate quantification of the paint samples. These slope values were 0.53±0.04 for benzene, 0.78±0.03 toluene, 0.86±0.01 ethylbenzene, 0.68±0.02 m,p-xylene and 1.14±0.09 o-xylene.

Limits of detection (LOD) were calculated as three times the signal-to-noise ratio, values being 0.022 ng g^{-1} for benzene, 0.014 toluene, 0.011 ethylbenzene, 0.036 m,p-xylene and 0.015 o-xylene. The repeatability and reproducibility were calculated using the relative standard deviation (RSD) of the peak areas for 10 successive analyses carried out on the same day and on three different days,

respectively. Intra-day RSD values were in the 4.5-7.4 % range, while inter-day RSD values between 5.1-7.8 % were obtained.

Table 2 shows a comparison of the proposed method with others previously reported in the literature for paint and water samples based on headspace sampling. LODs for the HSSE method here presented are lower than those reported with HS-SPME for water and paint samples.

3.4. Analysis of paint samples

The proposed method was applied to the determination of the BTEX content in different colour (white, green, blue, red and yellow) paint samples. These were preconcentrated by HSSE and submitted to analysis. Comparison of the retention times and the MS spectra for the compounds in the standard mixture and the fortified samples allowed identification. Table 3 shows the BTEX contents (ng g^{-1}), obtained for all finger paint samples by HSSE and using the classical SHS methodology. A statistical comparison of the results obtained through both methods has been carried out using Mann-Whitney test, p values of 0.607, 0.848, 0.181, 0.914 and 0.463 being obtained for benzene, toluene, ethylbenzene, m,p-xylene and o-xylene, respectively. A chromatogram for the white paint sample fortified at 7 ng g^{-1} under the selected conditions for both methods is shown in Figure 2.

Since no reference materials were available for validation of the method, the accuracy was checked by recovery assays by fortifying two samples (white and green paint) at two concentration levels (0.5 and 10 ng g^{-1} for HSSE and 2.5 and 20 ng g^{-1} for SHS), which correspond to a low concentration and an

intermediate value of the linearity range. The average recoveries obtained for the different samples and spiking levels were 99±22 (n=20) for HSSE.

4. Conclusions

The need for sensitive analytical methods for BTEX control in finger paints can be fulfilled by using the solventless procedure based on HSSE technique coupled to GC-MS here discussed. The use of matrix-matched calibration instead of standard additions facilitates the sample quantification. HSSE afforded the lowest limits of detection, when compared to the classical SHS procedure. Most of the finger paints analyzed contained low levels of BTEX.

References

[1] P.-P. Zhan, Y. Zhang, J.-C. Liu, Y. Zhu, Y.-G. Zhao, Directly-coupled-column ultra-fast liquid chromatography with diode array detection method for the rapid quantification of allergenic disperse dyes in water preconcentrated by magnetic solid-phase extraction, J. Sep. Sci. 40

(2017) 4294–4302. doi:10.1002/jssc.201700578.

[2]   EC, Council Directive on the appoximation of the laws of the Member States concerning the safety of toys. (2008) 1–13.

[3]   EC, ISO 8124-7:2015 Safety of toys — Part 7: Requirements and test methods for finger paints.

[4]   A. Bahrami, F. Ghamari, Y. Yamini, F. Ghorbani Shahna, A. Koolivand, Ion-pair-based hollow-fiber liquid-phase microextraction combined with high-performance liquid chromatography for the simultaneous determination of urinary benzene, toluene, and styrene metabolites, J. Sep. Sci. 41 (2018) 501–508. doi:10.1002/jssc.201700685.

[5]   Z. Wang, Q. Zhang, H. Li, Q. Lv, W. Wang, H. Bai, Rapid and green determination of 58 fragrance allergens in plush toys, J. Sep. Sci. 41 (2018) 657–668. doi:10.1002/jssc.201700556.

[6]   N. Ramírez, A. Cuadras, E. Rovira, F. Borrull, R.M. Marcé, Chronic risk assessment of exposure to volatile organic compounds in the atmosphere near the largest Mediterranean industrial site, Environ. Int. 39 (2012) 200–209. doi:10.1016/j.envint.2011.11.002.

[7]   J. Flórez Menéndez, M. Fernández Sánchez, J. Sánchez Uría, E. Fernández Martínez, A. Sanz-Medel, Static headspace, solid-phase microextraction and headspace solid-phase microextraction for BTEX determination in aqueous samples by gas chromatography, Anal. Chim. Acta. 415 (2000) 9–20. doi:10.1016/S0003-2670(00)00862-X.

[8]   A.D. Hewitt, Comparison of sample preparation methods for the analysis of volatile organic compounds in soil samples: solvent extraction vs vapor

partitioning, Environ. Sci. Technol. 32 (1998) 143–149. doi:10.1021/ES970431Q.

[9] J.L. Pérez Pavón, A. Guerrero Peña, C. García Pinto, B. Moreno Cordero, Detection of soil pollution by hydrocarbons using headspace–mass spectrometry and identification of compounds by headspace–fast gas chromatography–mass spectrometry, J. Chromatogr. A. 1047 (2004) 101–109. doi:10.1016/j.chroma.2004.06.113.

[10] A. Serrano, M. Gallego, Direct screening and confirmation of benzene, toluene, ethylbenzene and xylenes in water, J. Chromatogr. A. 1045 (2004) 181–188. doi:10.1016/j.chroma.2004.06.028.

[11] M. Rahmani, M. Kaykhaii, E. Ghasemi, M. Tahernejad, Application of in-syringe dispersive liquid – liquid microextraction and narrow-bore tube dispersive liquid – liquid microextraction for the determination of trace amounts of BTEX in water samples, J. Chromatogr. Sci. (2015) 1–7.

[12] A. Sarafraz-Yazdi, A.H. Amiri, Z. Es'haghi, BTEX determination in water matrices using HF-LPME with gas chromatography–flame ionization detector, Chemosphere. 71 (2008) 671–676. doi:10.1016/j.chemosphere.2007.10.073.

[13] E. Aguilera-Herrador, R. Lucena, S. Cárdenas, M. Valcárcel, Ionic liquid-based single-drop microextraction/gas chromatographic/mass spectrometric determination of benzene, toluene, ethylbenzene and xylene isomers in waters, J. Chromatogr. A. 1201 (2008) 106–111. doi:10.1016/j.chroma.2008.06.010.

[14] H. Bagheri, M. Zare, H. Piri-Moghadam, A. Es-haghi, A combined micro-

solid phase-single drop microextraction approach for trace enrichment of volatile organic compounds, Anal. Methods. 7 (2015) 6514–6519. doi:10.1039/C5AY01077B.

[15] A. Sarafraz-Yazdi, A.H. Amiri, Z. Es'haghi, Separation and determination of benzene, toluene, ethylbenzene and o-xylene compounds in water using directly suspended droplet microextraction coupled with gas chromatography-flame ionization detector, Talanta. 78 (2009) 936–941. doi:10.1016/j.talanta.2008.12.069.

[16] H. Tabani, K. Khodaei, S.K. Movahed, A.Z. Moghaddam, F.D. Zare, S. Mirzaei, Evaluation of three dimensional high nitrogen doped graphene as an efficient sorbent for the preconcentration of BTEX compounds in environmental samples, RSC Adv. 6 (2016) 7198–7211. doi:10.1039/C5RA21397E.

[17] E. Fernández, L. Vidal, A. Canals, Zeolite/iron oxide composite as sorbent for magnetic solid-phase extraction of benzene, toluene, ethylbenzene and xylenes from water samples prior to gas chromatography-mass spectrometry, J. Chromatogr. A. 1458 (2016) 18–24. doi:10.1016/j.chroma.2016.06.049.

[18] L. Qin, G. Zeng, C. Lai, D. Huang, P. Xu, C. Zhang, M. Cheng, X. Liu, X. Liu, B. Li, H. Yi, "Gold rush" in modern science: Fabrication strategies and typical advanced applications of gold nanoparticles in sensing, Coord. Chem. Rev. 359 (2018) 1–31. doi:10.1016/j.ccr.2018.01.006.

[19] C. Lai, X. Liu, L. Qin, C. Zhang, G. Zeng, D. Huang, M. Cheng, P. Xu, H. Yi, D. Huang, Chitosan-wrapped gold nanoparticles for hydrogen-bonding

recognition and colorimetric determination of the antibiotic kanamycin, Microchim. Acta 184 (2017) 2097–2105. doi:10.1007/s00604-017-2218-z.

[20] I. Arambarri, M. Lasa, R. Garcia, E. Millán, Determination of fuel dialkyl ethers and BTEX in water using headspace solid-phase microextraction and gas chromatography–flame ionization detection, J. Chromatogr. A. 1033 (2004) 193–203. doi:10.1016/j.chroma.2004.01.046.

[21] J. Ji, C. Deng, W. Shen, X. Zhang, Field analysis of benzene, toluene, ethylbenzene and xylene in water by portable gas chromatography-microflame ionization detector combined with headspace solid-phase microextraction, Talanta. 69 (2006) 894–899. doi:10.1016/j.talanta.2005.11.032.

[22] M.R. Lee, C.M. Chang, J. Dou, Determination of benzene, toluene, ethylbenzene, xylenes in water at sub-ng l-1 levels by solid-phase microextraction coupled to cryo-trap gas chromatography-mass spectrometry, Chemosphere. 69 (2007) 1381–1387. doi:10.1016/j.chemosphere.2007.05.004.

[23] S. Tumbiolo, J.F. Gal, P.C. Maria, O. Zerbinati, Determination of benzene, toluene, ethylbenzene and xylenes in air by solid phase micro-extraction/gas chromatography/mass spectrometry, Anal. Bioanal. Chem. 380 (2004) 824–830. doi:10.1007/s00216-004-2837-1.

[24] R. Aranda-Rodriguez, A. Cabecinha, J. Harvie, Z. Jin, A. Marchand, R. Tardif, A. Nong, S. Haddad, A method for quantification of volatile organic compounds in blood by SPME-GC-MS/MS with broader application: From non-occupational exposure population to exposure studies, J.

Chromatogr. B. 992 (2015) 76–85. doi:10.1016/j.jchromb.2015.04.020.

[25] M. Behzadi, M. Mirzaei, Poly(o-anisidine)/graphene oxide nanosheets composite as a coating for the headspace solid-phase microextraction of benzene, toluene, ethylbenzene and xylenes, J. Chromatogr. A. 1443 (2016) 35–42. doi:10.1016/j.chroma.2016.03.039.

[26] R. Foroutani, V. Yousefi, S. Kangari, Synthesis of polyaniline-magnetite hollow nanocomposite as a novel fiber coating for the headspace solid-phase microextraction of benzene, toluene, ethylbenzene and xylenes from water samples, Anal. Methods. 7 (2015) 5318–5324. doi:10.1002/jssc.201401191.

[27] A. Sarafraz-Yazdi, A. Zendegi-Shiraz, Z. Es'haghi, M. Hassanzadeh-Khayyat, Synthesis and characterization of composite polymer, polyethylene glycol grafted flower-like cupric nano oxide for solid phase microextraction of ultra-trace levels of benzene, toluene, ethyl benzene and o-xylene in human hair and water samples, J. Chromatogr. A. 1418 (2015) 21–28. doi:10.1016/j.chroma.2015.09.044.

[28] N. Baimatova, B. Kenessov, J.A. Koziel, L. Carlsen, M. Bektassov, O.P. Demyanenko, Simple and accurate quantification of BTEX in ambient air by SPME and GC-MS, Talanta. 154 (2016) 46–52. doi:10.1016/j.talanta.2016.03.050.

[29] J. Liu, N. Li, G. Jiang, J. Liu, J.Å. Jönsson, M. Wen, Disposable ionic liquid coating for headspace solid-phase microextraction of benzene, toluene, ethylbenzene, and xylenes in paints followed by gas chromatography–flame ionization detection, J. Chromatogr. A. 1066

(2005) 27–32. doi:10.1016/j.chroma.2005.01.024.

[30] J.I. Cacho, N. Campillo, P. Viñas, M. Hernández-Córdoba, Gas chromatography-mass spectrometry using microvial insert thermal desorption for the determination of BTEX in edible oils, RSC Adv. 6 (2016) 20886–20891. doi:10.1039/C5RA26707B.

[31] M.R. Ras-Mallorquí, R.M. Marcé-Recasens, F. Borrull-Ballarín, Determination of volatile organic compounds in urban and industrial air from Tarragona by thermal desorption and gas chromatography-mass spectrometry, Talanta. 72 (2007) 941–950. doi:10.1016/j.talanta.2006.12.025.

[32] N. Yassaa, E. Brancaleoni, M. Frattoni, P. Ciccioli, Isomeric analysis of BTEXs in the atmosphere using b-cyclodextrin capillary chromatography coupled with thermal desorption and mass spectrometry, Chemosphere. 63 (2006) 502–508. doi:10.1016/j.chemosphere.2005.08.010.

[33] A. Prieto, O. Basauri, R. Rodil, A. Usobiaga, L.A. Fernández, N. Etxebarria, O. Zuloaga, Stir-bar sorptive extraction: A view on method optimisation, novel applications, limitations and potential solutions, J. Chromatogr. A. 1217 (2010) 2642–2666. doi:10.1016/j.chroma.2009.12.051.

[34] Ö.O. Kuntasal, D. Karman, D. Wang, S.G. Tuncel, G. Tuncel, Determination of volatile organic compounds in different microenvironments by multibed adsorption and short-path thermal desorption followed by gas chromatographic-mass spectrometric analysis, J. Chromatogr. A. 1099 (2005) 43–54. doi:10.1016/j.chroma.2005.08.093.

[35]   C.H. Wu, C.T. Feng, Y.S. Lo, T.Y. Lin, J.G. Lo, Determination of volatile organic compounds in workplace air by multisorbent adsorption/thermal desorption-GC/MS, Chemosphere. 56 (2004) 71–80. doi:10.1016/j.chemosphere.2004.02.003.
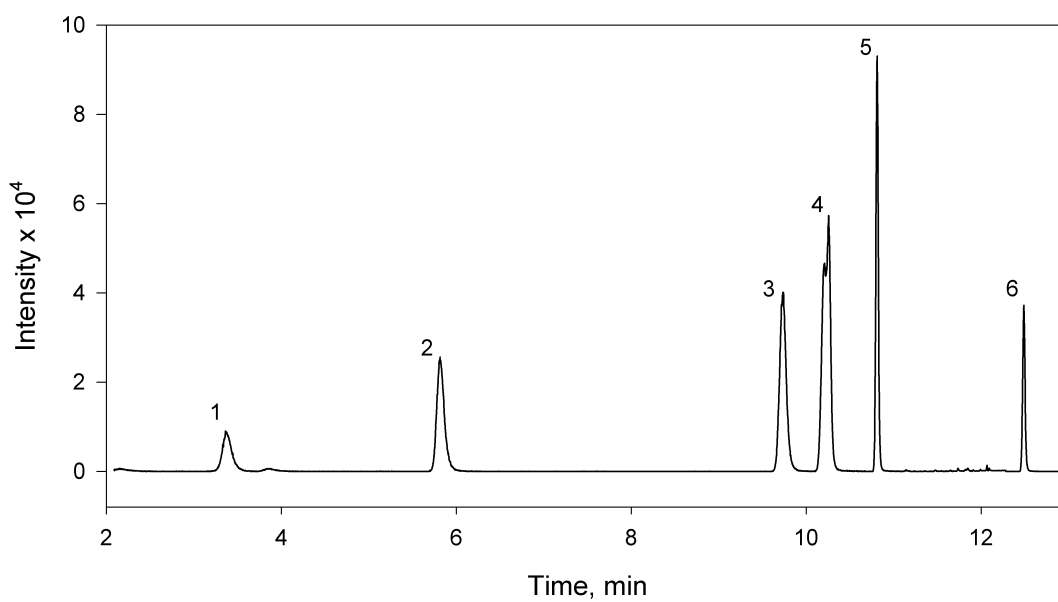
FIGURES
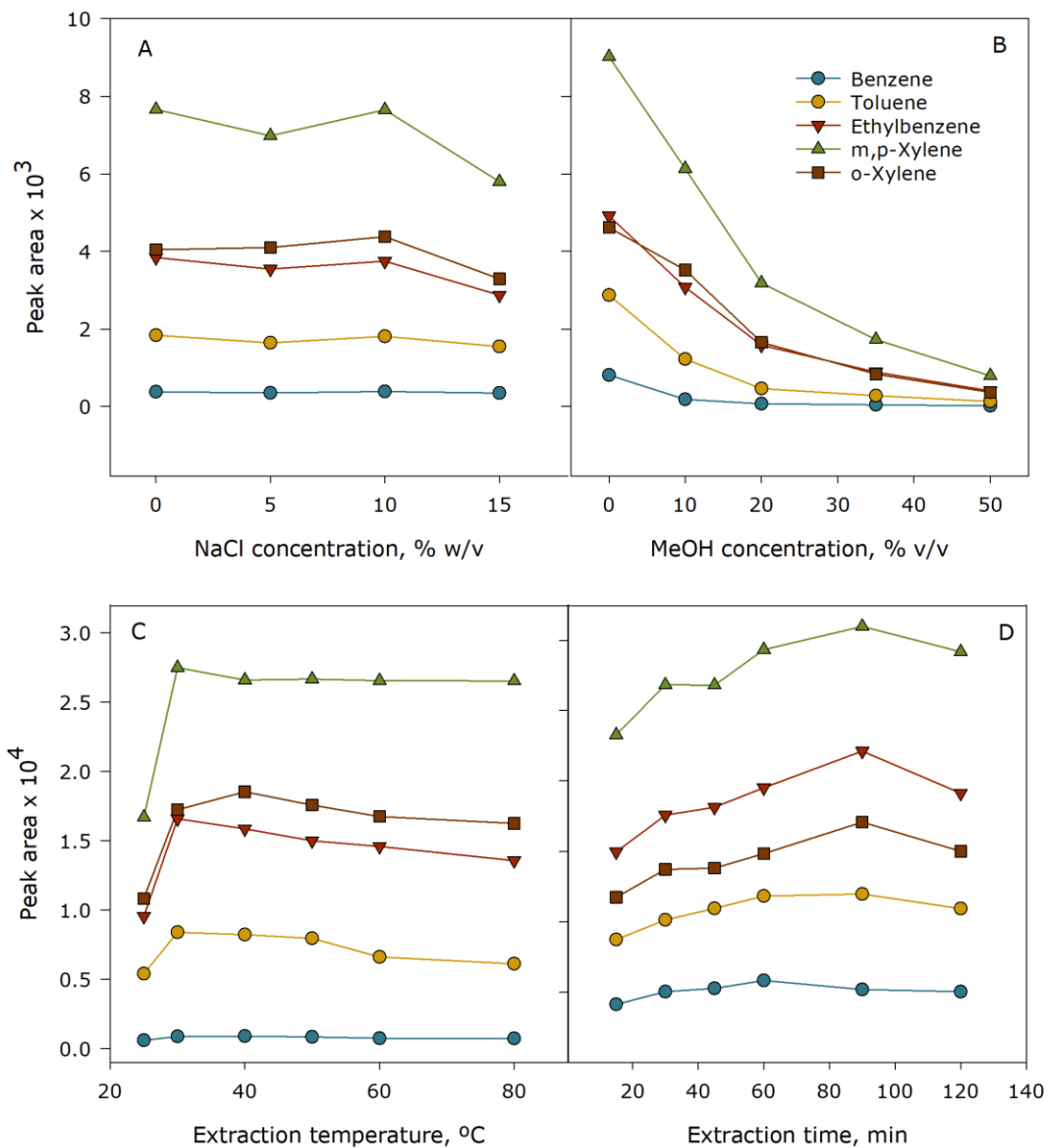
Fig. 1 Influence of ionic strength (A), methanol percentage (B), temperature (C)

and time (D) in the extraction stage for the HSSE method.

Fig. 2 Chromatogram obtained using HSSE combined with GC-MS in SIM mode for a white paint sample fortificated at 7 ng g^{-1}. (1) Benzene, (2) toluene, (3) ethylbenzene, (4) m,p-xylene, (5) o-xylene and (6) eucalyptol (internal standard).

Table 1 Retention times and target and qualifier ions for the analytes.

Compound	Retention time (min)	Target ion (m/z)	Q1[a] (m/z)	Q2[a] (m/z)
Benzene	3.2	78	50 (39)	77 (27)
Toluene	5.7	91	92 (56)	36 (26)
Ethylbenzene	9.7	91	106 (27)	77 (13)
m,p-Xylene	10.2	91	106 (44)	77 (18)
o-Xylene	10.9	91	106 (40)	77 (16)
Eucalyptol	12.5	108	139 (22)	154 (7)

[a] Values into brackets correspond to qualifier ion percentage.

12

Table 2 Comparison of methods using different preconcentration techniques.

Technique	Sample treatment	Sample type	LOD	Reference
GC-FID	HS-SPME (Poly (O-anisidine/GO fiber))	waters	0.01-0.05 ng mL^{-1}	25
GC-FID	SPE (3D-HND-G)	waters	0.5-1 ng mL^{-1}	16
GC-FID	MSPE (Fe$_2$O$_3$/ ZSM-5 zeolite)	waters	0.3-3 µg L^{-1}	17
GC-FID	HS-SPME (PDMS)	waters	0.08-0.6 ng mL^{-1}	6
GC-FID	HS-SPME (IL coated fiber)	paints	0.1- 0.8 µg mL^{-1} (10-80 µg g^{-1})	29
TD-GC-MS	HSSE (PDMS)	paints	0.011-0.036 ng g^{-1}	This method

IL, ionic liquid; GO, graphene oxide nanosheets; 3D-HND-G, three-dimensional high nitrogen doped graphene.

13

Table 3 BTEX content[a] in paint samples using HSSE and validation by SHS

Compound	HSSE (SHS) (ng g^{-1})				
	White	Green	Red	Blue	Yellow
Benzene	ND (ND)	ND (ND)	12.8±0.5 (10.2±0.4)	ND (ND)	0.39±0.07 (NQ)
Toluene	1.54±0.11 (1.42±0.05)	3.35±0.24 (3.15±0.1)	1.07±0.06 (0.80±0.05)	2.62±0.21 (2.43±0.09)	1.48±0.08 (1.68±0.05)
Ethylbenzene	0.29±0.02 (NQ)	ND (ND)	0.14±0.01 (ND)	0.61±0.03 (0.53±0.02)	0.27±0.02 (ND)
m,p-Xylene	0.54±0.05 (0.65±0.05)	ND (ND)	0.32±0.03 (NQ)	0.53±0.04 (0.64±0.02)	0.41±0.04 (NQ)
o-Xylene	0.52±0.02 (0.63±0.03)	ND (ND)	0.32±0.05 (0.44±0.06)	0.51±0.06 (0.57±0.01)	0.36±0.05 (0.41±0.03)

[a] Mean value ± standard deviation (n=3). ND, not detected. NQ, not quantified.

15

16