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Optimisation of Purge-and-Trap Gas Chromatography-Mass Spectrometry Analysis of Volatile Organic Compounds in Water

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This work presents the optimisation of the extraction process of 40 volatile organic compounds (VOC) from water samples with a manual purge and trap system (PT) that allows thermal desorption instruments to be used to analyse VOC in water. The purge device was a U shaped vessel with injection port, using as sorbent trap conventional Perkin–Elmer thermal desorption tubes filled with Chromosorb 106 and Tenax–GR. To avoid problems associated to humidity, a water trap was placed before sorbent tube and three desiccant agents (silica gel, CaCl_2 and NaCl) were tested. CaCl_2 was chosen since it absorbed water efficiently and selectively – without any losses in the content of volatile organic compounds; it also provided more precise results than NaCl . A thermostatic bath was used to control sample temperature during the purging step. Several parameters influencing this step were studied: gas flow rate, purge time, sample temperature, and salting effect. A Plackett–Burman model was applied to evaluate the influence of the above factors; however, it was statistically insignificant. Final conditions were fixed at: gas flow rate 50 mL min^{-1} , time 8 min, temperature 20°C , salinity (Na_2SO_4) 30 g L^{-1} . Analytes were thermally desorbed and analysed applying GC–MS. The proposed method was successfully applied to real tap and marine water samples.

W pracy przedstawiono optymalizację ekstrakcji 40 lotnych związków organicznych (LZO) z próbek wody, metodą „wypłukiwanie i wychwytywanie” (purge and trap, PT), pozwalającą na wykorzystywanie desorpcji termicznej do analizy LZO w wodzie. Do wypłukiwania zastosowano naczynie w kształcie litery U z wejściem iniekcyjnym, a do wychwytywania użyto klasycznych rurek Perkin–Elmera do desorpcji termicznej, wypełnionych

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Chromosorbem 106 i Tenaksem-GR. W celu uniknięcia problemów związanych z wilgocą przed złożem absorbującym umieszczono pochłaniacz wody. Przetes-towano trzy substancje osuszające: żel krzemionkowy, CaCl_2 oraz NaCl ; wybrano CaCl_2 , który dobrze pochłaniał wodę i zapewniał lepiej odtwarzalne wyniki. W celu kontrolowania temperatury próbki podczas etapu wypłukiwania zastosowano łaźnię termostatowaną. Prze-badano wpływ kilku parametrów wypłukiwania, tj.: przepływu gazu, czasu, temperatury oraz stopnia zasolenia. Do oceny zastosowano schemat Plaketta-Burmana; uzyskane zależ-ności były statystycznie nieistotne. Przyjęto następujące warunki eksperymentu: przepływ gazu 50 mL min^{-1} , czas 8 min, temperatura 20°C oraz stężenie soli (Na_2SO_4) 30 g L^{-1} . Anality były desorbowane termiczne i analizowane za pomocą GC-MS. Opracowaną metodę z powodzeniem zastosowano do badania próbek wody z kranu i wody morskiej.

Purge and trap technique was introduced to gas chromatography by Bellar and Lichtenberg in 1974 [1, 2]. Since that time they became a widely used technique for determination of VOCs in drinking water [3, 4], surface waters [5–7], groundwater [8], and marine water [9, 10].

The principle of the method is very simple. An inert gas is bubbled through the water sample, causing volatile species to move from the aqueous to the vapour phase. The continuous flow of the gas through the sample favours the extraction process leading to the improvement of LOD by a factor of 10–100 compared to LOD values available in static headspace techniques. The gaseous phase enriched with the analytes is passed subsequently through the sorbent trap, at which the analytes are retained. Then, the analytes are thermally desorbed and injected into the gas chromatograph. Three parameters basically control the extraction process: sample volume, the flow rate of the inert gas, and purging time. Other parameters that can be considered to improve the purging process are temperature and salinity of the sample, as they decrease the solubility of the analytes in the aqueous matrix [11–13]. This technique, however, has several disadvantages as *e.g.* foam formation; yet, the main problems are caused by the significant amount of water vapour that is purged with the analytes. Water can decrease the adsorption capacity of the sorbent bed, plug either the column or the trap at sub-zero temperatures (formation of ice), or affect both retention times and peak shapes of the compounds that are eluted close to water [14]. Moreover, water can damage mass spectrometer and electron capture detector. Several procedures have been applied to remove water: passing the wet gas through the permeable membrane tubes [15], condensing water vapour [10], purging the sorbent with a dry gas [13], or using inorganic salts or molecular sieves that absorb water [14].

In this work the optimisation of a PT-GC-MS method for the analysis of 40 VOCs has been presented. An appropriate drying system for water removal has been selected. The purging system used was compatible with a Perkin-Elmer ATD-400 external desorption unit. The proposed method can be successively applied for easy determination of VOCs in water in the laboratories equipped with a thermal desorption unit.

EXPERIMENTAL

Chemicals

Volatile organic compounds (Tab. 1) were supplied as pure substances by Supelco (Bellefonte, PA, USA), ChemService (West Chester, PA, USA) and Aldrich (Milwaukee, USA). Their purities exceeded 98%. Fluorobenzene (stock solution: 2000 $\mu\text{g mL}^{-1}$, Supelco) was used as an internal standard. 1,4-bromofluorobenzene and 1,2-dichlorobenzene- d_4 (stock solution: 2000 $\mu\text{g mL}^{-1}$, Supelco) were added to samples as surrogate standards. Individual stock standard solutions and multicomponental working standard solutions were prepared in ultra pure methanol (Romil, Cambridge, UK).

Table 1. Elution times, SIM windows, masses, and LODs of the analytes

| Compound | id | t_r , min | Ion mass | LOD, ng L ⁻¹ |
|-----------------------------------|----|-------------|----------|-------------------------|
| 1,1-Dichloroethene | 1 | 7.63 | 61 | 2.11 |
| Dichloromethane | 2 | 8.61 | 49 | – |
| <i>trans</i> -1,2-Dichloroethene | 3 | 9.22 | 61 | 0.71 |
| 1,1-Dichloroethane | 4 | 10.08 | 63 | 0.74 |
| Trichloromethane | 5 | 11.99 | 83 | 0.05 |
| 1,1,1-Trichloroethane | 6 | 12.48 | 97 | 2.57 |
| Tetrachloromethane | 7 | 12.88 | 117 | – |
| 1,2-Dichloroethane | 8 | 13.32 | 62 | 2.16 |
| Benzene | 9 | 13.32 | 78 | 0.24 |
| n-Heptane | 10 | 13.93 | 43 | – |
| Fluorobenzene | 11 | 13.93 | 96 | – |
| Trichloroethene | 12 | 14.82 | 130 | 0.24 |
| 1,2-Dichloropropane | 13 | 15.33 | 63 | 1.05 |
| Bromodichloromethane | 14 | 15.98 | 83 | 0.30 |
| 2-Chloroethoxyethene | 15 | 16.70 | 63 | 4.15 |
| <i>trans</i> -1,3-Dichloropropene | 16 | 17.11 | 75 | 0.40 |
| Toluene | 17 | 18.03 | 91 | 0.07 |
| n-Octane | 18 | 18.32 | 43 | 1.38 |
| <i>cis</i> -1,3-Dichloropropene | 19 | 18.53 | 75 | 1.54 |
| 1,1,2-Trichloroethane | 20 | 19.03 | 97 | 0.31 |
| Tetrachloroethene | 21 | 19.54 | 166 | 0.85 |
| Dibromochloromethane | 22 | 20.14 | 129 | 0.81 |

(Continuation on the next page)

Table 1. (Continuation)

| Compound | id | t _r , min | Ion mass | LOD, ng L ⁻¹ |
|------------------------------------|----|----------------------|----------|-------------------------|
| Chlorobenzene | 23 | 21.92 | 112 | 0.07 |
| Ethylbenzene | 24 | 22.22 | 91 | 0.10 |
| m+p-Xylene | 25 | 22.56 | 91 | 0.04 |
| o-Xylene | 26 | 23.75 | 104 | 0.40 |
| Styrene | 27 | 23.76 | 91 | 0.20 |
| Tribromomethane | 28 | 24.30 | 173 | 2.05 |
| Isopropylbenzene | 29 | 24.82 | 105 | 0.22 |
| p-Bromofluorobenzene | 30 | 25.29 | 174 | – |
| 1,1,2,2-Tetrachloroethane | 31 | 25.66 | 83 | 1.33 |
| n-Propylbenzene | 32 | 26.09 | 91 | 0.41 |
| 1,3,5-Trimethylbenzene | 33 | 26.61 | 105 | 0.13 |
| n-Decane | 34 | 26.68 | 57 | 2.92 |
| tert-Butylbenzene | 35 | 27.66 | 119 | 1.61 |
| 1,2,4-Trimethylbenzene | 36 | 27.80 | 105 | 0.17 |
| sec-Butylbenzene | 37 | 28.35 | 105 | 0.18 |
| 1,3-Dichlorobenzene | 38 | 28.71 | 146 | 0.76 |
| 1,4-Dichlorobenzene | 39 | 28.98 | 146 | 0.42 |
| 1,2,3-Trimethylbenzene | 40 | 29.14 | 105 | 0.20 |
| n-Butylbenzene | 41 | 30.07 | 91 | 0.40 |
| 1,2-Dichlorobenzene-d ₄ | 42 | 30.11 | 152 | – |
| 1,2-Dichlorobenzene | 43 | 30.20 | 146 | 0.63 |

Purge-and-trap device

Purging device (Fig. 1) consists of a U-shaped glass vessel (Supelco). One end of the vessel was connected to the gas supply. The gas line was equipped with a filter for retaining possible impurities from the gas or from the gas line. This filter was a Perkin–Elmer stainless-steel tube filled with a sorbent. The sample was placed in the other part of the vessel using an injection port. This part is equipped with a frit to break gas in small bubbles. The trap was placed at the top of this part. It consisted of two tubes connected in series joined with a 1/4" Swagelok unit. The first tube was a water trap and the second one – the sorbent trap.

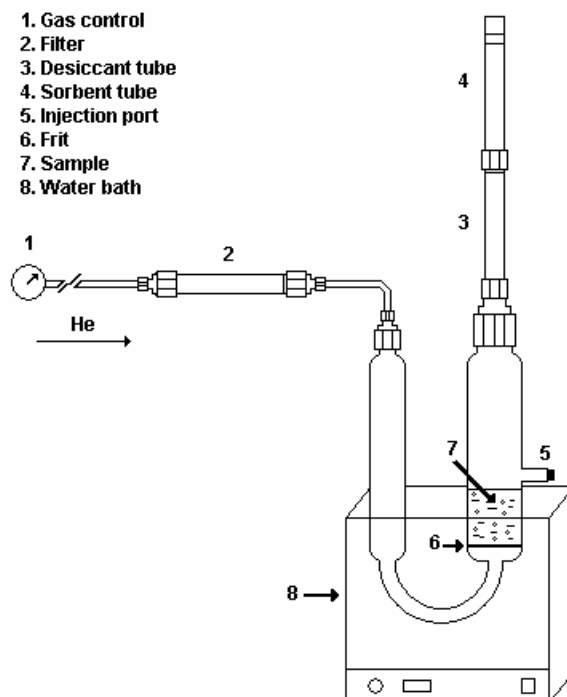


Figure 1. A scheme of the purge-and-trap system

Water trap was a glass tube (90 mm, ID = 5 mm; Perkin–Elmer, Norwalk, CT, USA) filled with a desiccant agent. Three substances were tested for this purpose: silica gel, NaCl and CaCl_2 . The sorbent trap was a stainless-steel tube (90 mm, ID = 5 mm; Perkin–Elmer) packed with a multibed system containing 140 mg of Tenax GR (60–80 mesh, $25 \text{ m}^2 \text{ g}^{-1}$; Chrompack Int, Middelbourg, NL) and 60 mg of Chromosorb 106 (60–80 mesh, $750 \text{ m}^2 \text{ g}^{-1}$; SKC Inc., Eighty Four, PA, USA), designed previously [16]. The sorbent tubes were conditioned by passing through a stream of ultra-pure helium at 60 mL min^{-1} and 210°C . The tubes were then capped with Teflon end-caps and stored in glass containers equipped with Teflon caps. The system was equipped with a thermostatic bath to control the sample temperature.

Instrumental analysis

Gas chromatography–mass spectrometry analyses were performed using a Perkin–Elmer Autosystem GC coupled with a Q–Mass 910 system and a ATD–400 thermal desorption unit (Perkin–Elmer, Norwalk, CT, USA). Two-step desorption was carried out. In the first step the tube was kept at 190°C for 5 min applying a stream of helium at the flow rate of 100 mL min^{-1} and desorbed analytes were trapped on a Tenax TA (60–80 mesh, $35 \text{ m}^2 \text{ g}^{-1}$; Perkin–Elmer, Norwalk, CT, USA) and cooled to -30°C . In the second step the trap was heated to 300°C and kept at this temperature for 4 min; after that the analytes were introduced into the chromatographic column. Two splitters were fixed at 0 and 3 mL min^{-1} to allow about 23% of desorbed analytes to enter the chromatographic system.

The column used was a HP–624 fused silica capillary, $60 \text{ m} \times 0.32 \text{ mm} \times 1.8 \mu\text{m}$ film thickness (Hewlett–Packard, Palo Alto, CA, USA). Helium served as a carrier gas at the flow rate of 1 mL min^{-1} .

The temperature of the chromatograph was kept at 40°C for 3 min, then it was raised to 210°C at the rate of 5°C min⁻¹, which took 34 min. Electronic ionisation was carried out at 70 eV. Multiplier voltage was fixed at 2200 V. The GC interface and ion source temperatures were set at 210°C and 230°C, respectively. Acquisition was performed in the selected ion monitoring (SIM) mode following the retention windows presented in Table 1.

RESULTS AND DISCUSSION

Selection of desiccant

Three types of water traps were prepared: silica gel (100 mg), NaCl (100 mg), and CaCl₂ (90 mg). Each water trap was tested running five purges with standards of 5 µg mL⁻¹. The silica gel trap retained most of the compounds and for this reason it was rejected. NaCl and CaCl₂ traps, in contrast, provided correct responses and satisfactory peak shapes and both behaved rather similarly. Finally CaCl₂ was selected as it ensured more reproducible results (RSD = 7%) than NaCl (RSD = 30%). The chromatogram obtained using CaCl₂ trap is presented in Figure 2.

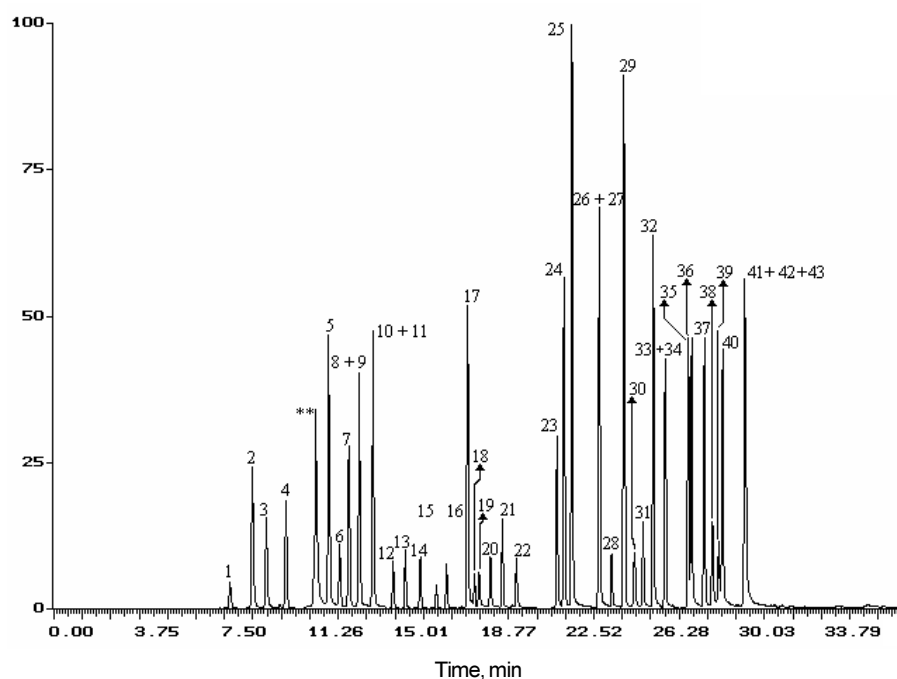


Figure 2. The effect of CaCl₂ on recoveries of VOCs

Optimisation of purging and trapping conditions

Once desiccant agent was selected, purge and trap conditions were optimised applying a multivariate approach. A two-level Plackett–Burmann design with three degrees of freedom was applied to find the variables that affect significantly the purging process. In Table 2 the studied variables and their lower and upper extremes are listed. Table 3 presents the matrix of the experimental design. Experiments were run five times by purging a standard containing each compound at the concentration of $5 \mu\text{g L}^{-1}$.

Table 2. Parameters of Plackett–Burman design

| Variable | Key | High (+) | Low (–) |
|--|-----|----------|---------|
| Purge gas flow (mL min^{-1}) | A | 30 | 80 |
| Purge time (min) | B | 8 | 30 |
| Sample temperature ($^{\circ}\text{C}$) | C | 20 | 40 |
| Salinity ($\text{Na}_2\text{SO}_4 \text{ g L}^{-1}$) | D | 30 | 120 |
| Dummy variable | E | + | – |
| Dummy variable | F | + | – |
| Dummy variable | G | + | – |

Table 3. Plackett–Burman designs for purging and trapping

| Experiment number | Variable | | | | | | |
|-------------------|----------|---|---|---|---|---|---|
| | A | B | C | D | E | F | G |
| 5 | + | + | + | – | + | – | – |
| 7 | – | + | + | + | – | + | – |
| 1 | – | – | + | + | + | – | + |
| 8 | + | – | – | + | + | + | – |
| 3 | – | + | – | – | + | + | + |
| 4 | + | – | + | – | – | + | + |
| 6 | + | + | – | + | – | – | + |
| 2 | – | – | – | – | – | – | – |

For the majority of compounds the influence of the studied experimental variables were statistically insignificant ($t_{\text{critical}} = 4.30$), except for tetrachloromethane. The extraction of this compound was significantly affected by the temperature, salinity, and gas flow rate. For the other compounds the influence of gas flow rate (variable A) was generally small and negative. This means that in the investigated range of flow rates an increase in the gas flow rate did not improve the extraction efficiency. Therefore, the medium value of 50 mL min^{-1} was selected. The influence of purging time (variable B) was very similar: small, yet positive. In order to make the experiment last as short as possible, the shortest time of 8 min was selected.

Salinity effects (variable D) were small and negative for most of the compounds. This was in contrast to the initial hypothesis stating that high salting-out effect would increase the efficiency of extraction. However, the foam formed at higher concentration of sodium sulfate could decrease purging efficiency. Thus, the addition of $30 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4$ was selected as an optimum value. Temperature (variable C) also caused small and negative effects on extraction efficiency. These negative effects should be attributed either to the dissolution of VOCs in water vapour condensed onto glass walls, or to the adverse effect that water has on the adsorption capacity of solid sorbents. For the above reasons lower temperature value (20°C) was selected.

Finally established experimental conditions were as follows: sample volume, 5 mL; gas flow, 50 mL min^{-1} ; purge time, 8 min; temperature, 20°C ; and salinity, 30 g L^{-1} of Na_2SO_4 .

Method performance

For the selected purging conditions calibration plots were constructed and the recoveries, relative standard deviations (RSDs), and detection limits (LODs) were calculated. Recoveries and RSDs were satisfactory for the most of compounds, except for dichloromethane, tetrachloromethane and n-heptane. For these species the recoveries exceeded 130% and RSD values were also high, possibly due to the background contamination that could not be eliminated. For the rest of compounds calibration plots were obtained in the concentration range of $0.1\text{--}10 \text{ }\mu\text{g L}^{-1}$. The corresponding LODs (Tab. 1) ranged from 0.04 ng L^{-1} for m+p-xylene to 4.15 ng L^{-1} for 2-chloroethoxyethene and were close to the literature values obtained for the SIM mode [8]. Applying an ATD-400 system satisfactory detection limits were achieved for 5 mL samples. This system was equipped with a low-flow cold trap that allows desorption from the sorbent tube at a low sample split, in contrast to automatic systems that utilise higher split flows to provide good peak shapes and satisfactory resolution.

Application to real samples

The developed method was applied to determine VOCs in drinking and marine water samples collected at the selected sites of the A Coruña harbour.

In drinking water, main compounds were those directly related to water chlorination processes as trihalomethanes: trichloromethane, bromodichloromethane and dibromochloromethane were detected at the concentration of $10 \mu\text{g L}^{-1}$, and tribromomethane at lower concentrations. Two other important compounds, 1,1,2-trichloroethane and chlorobenzene, were present at concentrations ranging between 1 and $2 \mu\text{g L}^{-1}$. Aliphatic hydrocarbons comprised only a small fraction of VOCs. The obtained concentration data were quite close to those given by Amaral *et al.* [17] for several drinking water samples from Catalonia (Spain), however, they were much lower than the values reported for more polluted areas as Taiwan. For these areas Kuo *et al.* [5] have determined concentrations of trichloromethane, bromodichloromethane and dibromochloromethane in the range $66\text{--}99 \mu\text{g L}^{-1}$.

Marine water samples were collected at two different sites of the harbour. The first sampling point was a closed dock with low water renewal where sailing and small fishing ships were berthed. At this sampling point, aromatic hydrocarbons: toluene, dichlorobenzenes, trimethylbenzenes and xylenes were the predominating compounds and appeared at the concentrations $2.5\text{--}4 \mu\text{g L}^{-1}$. Only trichloromethane was present at higher level ($13 \mu\text{g L}^{-1}$). The appearance of aromatic hydrocarbons was directly related to fossil fuels that could reach waters by means of combustion emissions and fuel leakages that are very common in harbours. Bianchi and Varney [9] have detected the same species, however aromatic compounds were present at the level of $30 \mu\text{g L}^{-1}$ and trichloromethane at the level of $14.6 \mu\text{g L}^{-1}$. In another sampling point, where marine undercurrents were stronger and water renewal was more efficient, the concentrations were lower, for toluene, n-octane, and chlorobenzene even lower than $0.6 \mu\text{g L}^{-1}$.

CONCLUSIONS

The proposed method has been applied to the analysis of 37 volatile organic compounds in water samples. Experimental conditions were: sample volume, 5 mL; gas flow, 50 mL min^{-1} ; purging time, 8 min; temperature, 20°C ; salinity, 30 g L^{-1} of Na_2SO_4 . CaCl_2 was selected as a desiccant due to its good water adsorption properties and reproducibility without VOC losses. The method shows good reproducibility, linearity, and satisfactory recoveries of the analytes. The obtained LODs were in the range from 0.04 to 4.15 ng L^{-1} . The method was successfully applied to the analysis of tap water, surface water, and sea water samples.

REFERENCES

1. Bellar T.A. and Lichtenberg J.J., *J. Am. Water Works Assoc.*, **66**, 739 (1974).
2. Bellar T.A., Lichtenberg J.J. and Kroner R.C., *J. Am. Water Works Assoc.*, **66**, 703 (1974).
3. Golfinopoulos S.K., Kostopoulou M.N. and Lekkas, T.D., *Water Res.*, **32**, 1811 (1998).
4. Golfinopoulos S.K., Lekkas T.D. and Nikolaou A.D., *Chemosphere*, **45**, 275 (2001).
5. Kuo H.W., Chiang T.F., Lo I.I., Lai J.S., Chan C.C. and Wang J.D., *Sci. Total Environ.*, **208**, 41 (1997).
6. Kostopoulou M.N., Golfinopoulos S.K., Nikolau A.D., Xilourgidis K. and Lekkas T.D., *Chemosphere*, **40**, 527 (2000).
7. Miermans C.J.H., Van der Velde L.E. and Fintrop P.C.M., *Chemosphere*, **40**, 39 (2000).
8. Buszka P.M., Rose D.L., Ozuna G.B. and Groschen G.E., *Anal. Chem.*, **67**, 3659 (1995).
9. Bianchi A.P. and Varney M.S., *Water Res.*, **32**, 352 (1998).
10. Huybrechts T., Dewulf J., Moerman O. and Van Langenhove H., *J. Chromatogr. A*, **893**, 367 (2000).
11. Djozan D.J. and Assadi Y., *J. Chromatogr. A*, **697**, 525 (1995).
12. Wittsiepe J., Wallschläger D., Selenka F. and Jackwerth E., *Fresenius J. Anal. Chem.*, **346**, 1028 (1993).
13. Wang J.L. and Chen W.L., *J. Chromatogr. A*, **927**, 143 (2001).
14. Janicki W., Wolska L., Wardencki W. and Namiesnik J., *J. Chromatogr. A*, **654**, 279 (1993).
15. Leckrone K.J. and Hayes J.M., *Anal. Chem.*, **69**, 911 (1997).
16. Fernández-Villarrenaga V., Fernández-Martínez G., López-Mahía P., Muniategui-Lorenzo S., Prada-Rodríguez D. and Fernández-Fernández E., *Design of a sorbent trap to analyse a mixture of VOC with a wide range of volatilities*, Proceedings of XXIX Scientific Meeting of the Group of Chromatography and Related Techniques, 12–14 July 2000, Alcalá de Henares, Madrid.
17. Amaral O.C., Otero R., Grimalt J.O. and Albaigés J., *Water Res.*, **30**, 1876 (1996).

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