Analysis of the volatile components emitted from cut tobacco processing by gas chromatography/mass spectrometry thermal desorption system

Qiang Gao [a,b], Yunfei Sha [b], Da Wu [b], Baizhan Liu [b], Chaoying Chen [b,*], Dingye Fang [a,**]

[a] School of Chemical Engineering, East China University of Science and Technology, 200237 Shanghai, PR China
[b] Technical Center, Shanghai Tobacco Group Co., Ltd, 200082 Shanghai, PR China

ARTICLE INFO

ABSTRACT

A sensitive and reliable method was developed for the determination of volatile components emitted from cut tobacco processing using thermal desorption (TD) followed by gas chromatography–mass spectrometry (GC–MS). In the work, to obtain the optimal sorbent, three commercial sorbents were compared in terms of adsorption efficiency. The carbotrap 349 was found to have the best performance. The desorption conditions were also studied. Validation of the TD-GC–MS method showed good sensibility, linearity and precision. Limits of detection ranges were from 0.20 to 3.6 ng. Calibration curves were obtained by plotting peak area versus concentration and the correlation coefficients relating to linearity were at least 0.9984. The analysis was reproducible, with relative standard deviation ($n=8$) within 6.5%. The target compound breakthrough examination showed no significant losses when about 1500 ng standards were prepared. In order to evaluate the performance of the analytical method in the volatile constituents of cut tobacco, samples were taken in industrial areas of cut tobacco processing. Recoveries ranged from 85.1% to 110% for all the compounds and good precision had been reached (RSD < 13.3). The results proved that TD-GC–MS was a simple, rapid and accurate method for the analysis of volatile compounds emitted from cut tobacco drying step.

1. Introduction

The chemical composition recipe is one of the core techniques of tobacco industry and cut tobacco is one of the necessary materials. Recently, studies on volatile constituents of tobacco and its smoke have been carried out, and hundreds of components have been reported [1–6], since their structures will provide information about the cigarette flavor. As we know, the drying process of cut tobacco is one of the key steps throughout the cigarette manufacturing. Since its baking temperature is up to 150 °C, this procedure could not only produce the flavor components due to a series of severe internal chemical reaction, but remove a portion of off-flavor and volatile nicotine in tobacco as well. Therefore, the analysis of volatile components emitted from cut tobacco during the drying course is significant for improving the cigarette quality. However, the related research has not been reported yet. In this work, for the first time, the analysis of volatile compounds from cut tobacco processing was performed.

The analytical procedures traditionally employed to identify and quantify the volatile components in tobacco samples collected on filters involve solvent extraction, followed by evaporation and gas chromatography-flame ionization detection (GC-FID) or gas chromatography–mass spectrometry (GC–MS) detection [7–12]. The above methods, although proven effective, suffer from a number of limitations such as toxic organic solvents, long extraction times and relatively large amounts of sample. As we know, thermal desorption (TD) techniques coupled with GC–MS can overcome these drawbacks [13–19]. TD is a technique that extracts volatiles from a non-volatile matrix by heating the matrix/sample in a stream of inert gas. The extracted volatiles are subsequently refocused onto a cold trap from which they are transferred in a narrow band to a gas chromatographic column for analysis. TD technique has been widely used for the extraction and analysis of the volatile organic compounds (VOCs) from numerous samples [13–26], including analysis of VOCs in tobacco samples [24–26]. For instance, Charles has collected VOCs and particulate emissions from commercial cigarettes on thermal sampling/desorption tubes packed with Tenax GR and Carbosieve SIII, and the samples were analyzed by GC/MS for 99 target VOCs as well as nicotine. However, the determination of the volatile components emitted from cut tobacco processing is still not reported in literatures.

In this study, TD technique followed by GC–MS was developed for the analysis of volatile components emitted from cut tobacco

* Corresponding author. Tel.: +86 21 6166 9401; fax: +86 21 6166 9950.
** Corresponding author. Tel./fax: +86 21 64251002.
E-mail addresses: chency@sh.tobacco.com.cn (C. Chen),
dyfang@ecust.edu.cn (D. Fang).

drying step. The sorbents in TD technique and desorption conditions were optimized, and the method validations were investigated.

2. Experimental

2.1. Chemicals and materials

Ten target chemicals (Table 1) were selected for this study, along with methyl eugenol as an internal standard (ISTD). All chemicals and solvents were purchased from commercial sources with purity equal to or greater than 98%. Standards were prepared in the following manner: the individual stock solution was prepared by accurately weighing the chemical in the 25 mg range into a 10 mL volumetric flask and diluted to the mark with methanol. Calibration solutions were prepared by appropriate dilution in methanol. The ISTD was prepared separately in the same way to a concentration of 150 ng μL^{-1}. Samples of cut tobacco emissions were acquired from Shanghai Cigarette Factory.

2.2. Multi-sorbent tubes

Carbotrap 300, carbotrap 317 and carbotrap 349 were obtained from Supelco (Bellefonte, PA, USA) as the sample tubes (6.35 mm outside-diameter and 89.9 mm long). The general guide to adsorbent selection was shown in Table 2. All sorbents were sufficiently hydrophobic to preserve the sample from water and could support desorption temperatures up to 400 °C [27].

Before the first use, tubes were conditioned by thermal cleaning (250 °C for 20 min, 300 °C for 20 min, 330 °C for 20 min, 350 °C for 20 min and 400 °C for 20 min) under a flow

rate of helium at 100 mL min^{-1}. For subsequent procedure, pre-conditioning at 400 °C for 15 min was applied. After conditioning, they were immediately sealed with Swagelock end caps.

2.3. Sample collection and quantitative tube preparation

The cut tobacco emissions during the course of drying process were absorbed in the sorbent tubes using a Supelco pump (Bellefonte, PA, USA), with an air stream for 10 min and a pumping flow calibrated by a rotameter at 200 mL min^{-1}. The scheme of the sample introduction is shown in Fig. 1. To reduce the dust from the exhaust pipe into the tubes at the sampling stage, a Teflon membrane was placed in front of the sampling tube. After collection, the tubes should be immediately capped with the storage caps to avoid losses. Sorbent tubes containing the samples were transferred to the laboratory and were immediately analyzed.

Quantitative tube preparation was performed as follows: to ensure the repeatability of the injection, 1 μL aliquots of the working standard solutions were spiked onto the tubes using a conventional gas chromatography with packed column injector. Quantitative tubes were connected to the injector through a stainless steel tube and Swagelock adapters. The injector was slightly heated at 30 °C and a flow stream of 90 mL min^{-1} of Helium was passed through the tubes. Tube loading time was 1 min. It was important to note that injected solution volumes should be accurately controlled to avoid vapors drag effects in the condensation step. The internal standard was handled in a similar way.

2.4. Analysis by TD-GC–MS

Analysis of the standards and samples was performed by automatic thermal desorption (ATD 50, Perkin–Elmer, Boston, MA, USA) coupled with GC–MS (HP 6890-5973, USA).

Thermal desorption of the sampling tubes was carried out at 240 °C with a flow rate of 50 mL min^{-1} for 15 min, during which the eluted emissions were swept from the tube to the internal trap (Tenax TA) maintained at −10 °C. After primary desorption, the cold trap was rapidly heated from −10 °C to 300 °C (secondary desorption) and then maintained at this temperature for 10 min. After the secondary desorption, the samples were injected into the capillary column (DB-wax, 60 m × 0.25 mm × 0.32 μm, provided by J&W, Folsom, CA, USA) via a transfer line heated at 230 °C. The column oven temperature was initially 40 °C for 1 min, increased to 230 °C at a rate of 6 °C min^{-1} and then maintained at 230 °C for 5 min.

The MS ion source was heated to 230 °C, and the quadrupole was kept at 150 °C. Their collision energy for MS fragmentation was at 70 eV, scanning from m/z 40 to 330 in one scan. Quantifying ion (Q) was selected for each analyte. The identification of the

Table 1
Chemical name, physical properties and GC–MS parameters of target compounds.

No.	Compound	CAS	Formula	Mw	GC–RT (min)	Q1 (m/z)
1	6-Methyl-5-hepten-2-one	110-93-0	$C_8H_{14}O$	126	21.846	108
2	Furfural	98-01-1	$C_5H_4O_2$	96	26.583	96
3	Benzaldehyde	100-52-7	C_7H_6O	106	28.845	106
4	Gamma-butyrolactone	96-48-0	$C_4H_8O_4$	86	32.449	86
5	Acetophenone	98-86-2	C_8H_8O	94	33.222	105
6	Furfuryl alcohol	98-00-0	$C_5H_6O_2$	98	33.403	98
7	Nicotine	54-11-5	$C_{10}H_{14}N_2$	162	40.005	84
8	Benzyl alcohol	100-51-6	C_7H_8O	108	40.019	108
9	Phenethyl alcohol	60-12-8	$C_8H_{10}O$	122	41.039	91
10	Phenol	108-95-2	C_6H_6O	94	43.487	94
ISTD	Methyl Eugenol	93-15-2	$C_{11}H_{14}O_2$	178	43.695	178

Table 2
The general guide to adsorbent selection.

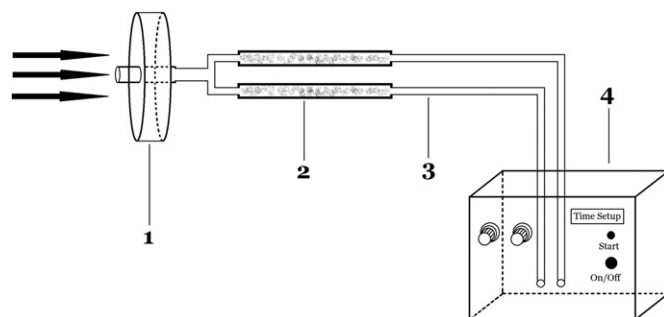| Sample tube	Sorbents	Specific surface area (m² g⁻¹)
Carbotrap 300	Carbopack C	10
	Carbopack B	100
	Carbosieve III	820
Carbotrap 317	Carbopack C	10
	Carbopack B	100
	Carboxen 1000	1200
Carbotrap 349	Carbopack Y	24
	Carbopack B	100
	Carbosieve 1003	1000

Fig. 1. Scheme of the sample introduction. 1—A teflon membrane; 2—sorbent tube; 3—silicone rubber hose; 4—a pump.

compounds was accomplished by comparing the retention time of the samples to that of the standards under the same conditions and the corresponding mass spectra.

3. Results and discussion

3.1. Selection of the sorbent materials

An ideal sorbent for preconcentrating the volatile components require four main properties, namely: infinite breakthrough volume, complete desorption of the target compounds at moderate temperatures, no generation of artifacts and no retention of water vapor [28]. No single available sorbent material met all of these criteria for a wide range of the volatiles. Thus, there was a tendency to explore multiple adsorbents.

Generally speaking, the greater specific surface area the adsorbent, the stronger the adsorption capacity. As for the wide boiling range of the abundant tobacco volatiles, different tubes (carbotrap 300, carbotrap 317 and carbotrap 349) containing three sections of sorbent materials (from low to high in adsorption capacity, Table 2) were selected for evaluating the adsorption efficiency. Fig. 2 shows the peak areas of the target compounds for the three different tubes at the same conditions. Carbotrap 349 indicated the best performance for these compounds by almost two or three times higher than that obtained with carbotrap 300, except for nicotine and phenol. This effect may be contributed to the proper specific surface area of each segment of sorbents in carbotrap 349. On basis of the above data, carbotrap 300 and carbotrap 317 were excluded for the following tests.

The carryover effect was determined by further investigation. Two sorbent tubes (carbotrap 349) connected in series were employed to sample an air volume of 2 L in the real sample application. The result demonstrated that no target compounds were found in the second tube, so the method was totally confirmed. This could be ascribed to its large surface area.

3.2. Optimization of TD conditions

The most adequate instrumental conditions for thermal desorption were studied for the selected carbotrap 349 tubes in order to achieve the highest desorption efficiency with no carryover. Sorbent tubes were injected with 1 μL of a methanolic solution containing 50 ng of each compound and then thermally desorbed and analyzed by GC–MS. The maximum desorption temperature permissible with the desorption unit was 400 °C. The abundance signal increased for all targeted compounds when the desorption temperature increased to 240 °C, above which it remained constant. The desorption time showed a similar influence on each compound at the critical point of 15 min. The focusing step of analytes using the cold trap and secondary desorption provided rapid injection and thus narrow bands. As can be expected at lower temperature, the compounds' recoveries increased. Therefore, the minimum temperature permissible for the cold trap with the desorption unit as −10 °C was selected.

To evaluate the good performance of target compounds desorption from sorbent tubes, three samples containing 1.5 μg of each compound were prepared, and analyzed. A subsequent re-analysis of the already desorbed tube was carried out at the same instrumental conditions and no remaining analytes were found.

3.3. Breakthrough

Concerning adsorption capacity, although breakthrough data were available for some materials [29,30], few data existed on multi-sorbent breakthrough. To examine the compounds breakthrough, two tubes were connected in series into the standards spiking system using a Swagelock. The injector was slightly heated at 30 °C and a flow stream of 90 mL min^{-1} was passed through the tubes for 1 min. The use of a dry purge gas (Helium, 99.999%) together with the good isolation of the injection system avoided the entrance of water into the standard tubes. A 1 μL aliquot of a 1500 ng μL^{-1} standard stock solution was injected
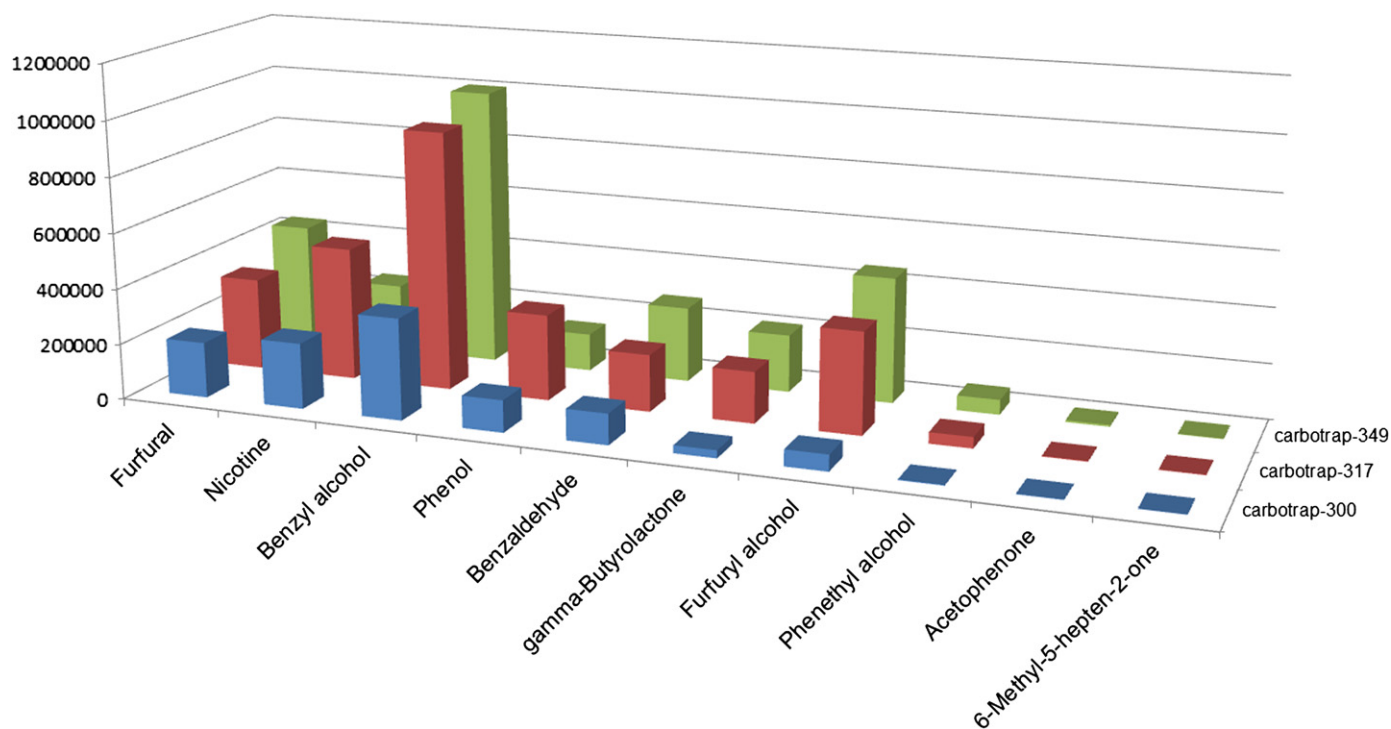

Fig. 2. Comparing three different commercial sorbent tubes (carbotrap 300, carbotrap 317 and carbotrap 349), for 10 target compounds fortification level in cut tobacco processing.

into the inlet end of the first tube. Individual analysis of each tube showed that no significant breakthrough (through measuring the compounds in the back tube) was observed for those compounds.

The safe sampling volume was also verified in our study. Triplicate tubes spiked with 1 μL of a 1500 ng μL^{-1} standard stock solution were flushed with clean air at the same sampling rate (200 mL min^{-1}) and analyzed for different flushing volumes (2, 4 and 6 L). The results showed that the standard normalized peak areas did not show a trend of decrease when the flushing volume increased except for nicotine (0.05%).

3.4. Validation of the method

Method validation results are presented and discussed below. The study was conducted by subsequent dilutions of working standard solutions. Limit of detection (LOD) and limit of quantification (LOQ) values were determined visually applying a standard deviation (SD) of the corresponding ratio of the standard established at 3 and 10, respectively [31]. LOD and LOQ values for each compound were shown in Table 3.

The linearity of the multi-point calibration was considered acceptable when R^2 (linear regression square coefficient) ≥ 0.99 and peaks showed a Gaussian shape. Linearity ranges for each compound together with their response factors are illustrated in Table 3. Gamma-butyrolactone and phenethyl alcohol showed relatively lower and higher response factors, respectively.

Precision study was conducted by consecutive analysis of 8 tubes spiked with the same amount of a standard work solution. Values of repeatability (%, relative standard deviation values, RSD) are also reported in Table 3. All the compounds showed RSD $\leq 6.5\%$, which suggested that the present method had a good precision.

3.5. Method performance

In order to evaluate the performance of the analytical method in the volatile constituents emitted from cut tobacco processing, samples were acquired in real industrial areas as presented in Section 2.2. The chromatogram of the sample is shown in Fig. 3.

The samples were collected at 200 mL min^{-1} up to 2 L and the mean value was considered to be representative of the compound concentration in the session. The precision was represented by RSD%, while the accuracy was expressed as the relative error between the average concentration found and the certified value. The concentration of spiked working standard solutions was laid on the basis of that in the real sample. All the data are given in Table 4. The precision of the method was reasonably good since the RSDs of the target compounds were less than 8.79%, except for nicotine which had RSDs inferior to 13.3%. The recoveries ranged from 85.1% to 110%. These results indicated that the method established in this study was quite appropriate for quantitative analysis of the target compounds.

Table 3
Summary of method validation data (standards; $n=8$).

Analyte	LOD (ng)	LOQ (ng; %RSD)	Linearity range	R^2	RF[a] (area/ng)
6-Methyl-5-hepten-2-one	0.63	2.1(1.2)	4.5–89.5	0.9992	41,080
Furfural	1.20	4.1(2.4)	5.9–117.4	0.9992	115,045
Benzaldehyde	1.90	6.4(2.4)	5.3–105.9	0.9993	151,862
Gamma-Butyrolactone	3.50	11(6.5)	12.8–256.1	0.9995	20,401
Acetophenone	0.20	0.67(1.9)	0.83–16.5	0.9998	207,381
Furfuryl alcohol	0.54	1.8(2.4)	5.6–112	0.9990	56,714
Nicotine	3.60	12(2.5)	8.5–170.5	0.9988	179,414
Benzyl alcohol	1.60	5.5(3.0)	10.4–208.5	0.9997	106,131
Phenethyl alcohol	0.91	3(6.1)	2.3–46.8	0.9984	218,507
Phenol	0.57	1.9(1.6)	1.7–33.8	0.9993	204,154

[a] Response factor, peak area per nanogram of analyte injected.

Table 4
Quantification of the volatile components emitted from cut tobacco processing ($n=6$).

| Analyte	Mean (ng)	RSD (%)	Recovery[a] (spiked amount, ng)
6-Methyl-5-hepten-2-one	13.1	1.94	104% (17.9)
Furfural	27.1	4.75	99.7% (23.48)
Benzaldehyde	25.7	6.79	98.9% (21.18)
Gamma-Butyrolactone	123	4.12	108% (51.22)
Acetophenone	2.77	7.09	106% (3.3)
Furfuryl alcohol	38.3	3.68	97.4% (22.4)
Nicotine	76.9	13.30	85.1% (34.1)
Benzyl alcohol	141	4.87	110% (41.7)
Phenethyl alcohol	15.7	4.41	110% (9.36)
Phenol	8.3	8.79	106% (6.76)

[a] Mean values of the target compounds.
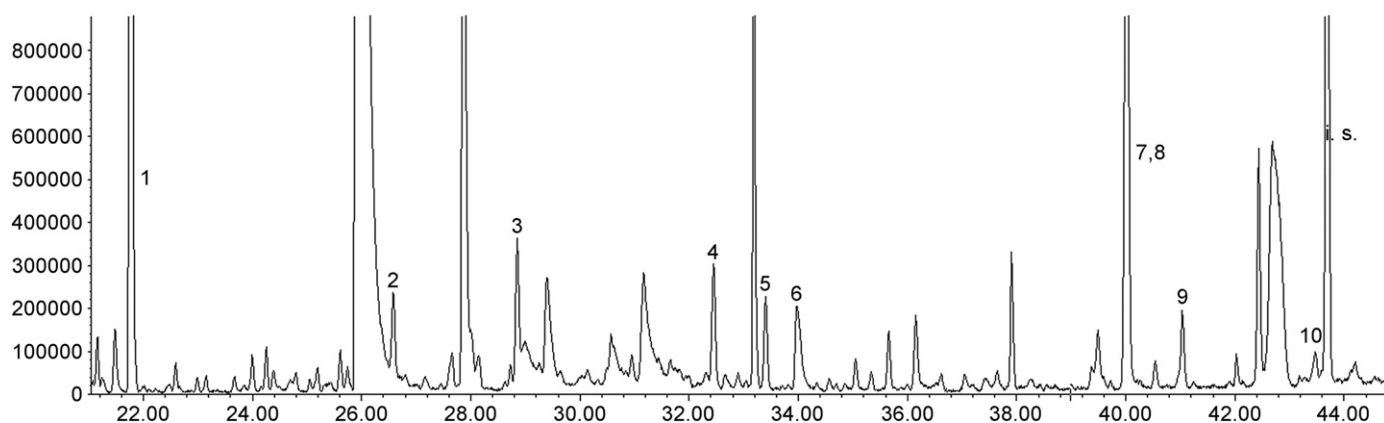
Fig. 3. GC–MS chromatogram of the volatile components emitted from cut tobacco processing. Peak identities are 1—6-methyl-5-hepten-2-one; 2—furfural; 3—benzaldehyde; 4—gamma-butyrolactone; 5—acetophenone; 6—furfuryl alcohol; 7—nicotine; 8—benzyl alcohol; 9—phenethyl alcohol; 10—phenol; and internal standard—methyl eugenol.

4. Conclusion

In this work, the TD-GC–MS method was successfully developed for the determination of the volatile components emitted from cut tobacco drying process. Carbotrap 349 was found to be the adsorbent providing the best adsorption efficiency. Method validation indicated that this technique was satisfactory sensitive and reproducible for all the target compounds. Furthermore, no significant breakthrough was detected when spiked standards in series tubes were examined. Method performance evaluation carried out on real samples also showed good adsorption efficiency and reproducibility for most of the compounds. Our study is the first one to survey the volatiles emitted from cut tobacco processing and also provides vital information on these compounds. Further investigation regarding the application of this methodology to the analysis of other organic compounds is ongoing.

References

[1] C. Masahiro, S. Yukio, T. Hirotoshi, J. Agric. Food Chem. 52 (2004) 7918–7924.
[2] C.M. Serban, K. Melissa, J. Chromatogr. A 114 (2007) 90–97.
[3] S. Elizabeth, S. Alan, A.S. Najat, Food Chem. Toxicol. 46 (2008) 1582–1590.
[4] Y. Li, T. Pang, Z.M. Guo, Y.L. Li, X.L. Wang, J.H. Deng, K.J. Zhong, X. Lu, G.W. Xu, Talanta 81 (2010) 650–656.
[5] K.P. Sudhir, K. Ki-Hyun, Trends Anal. Chem. 29 (2010) 804–819.
[6] Y. Li, T. Pang, Y.L. Li, X.L. Wang, Q.H. Li, X. Lu, G.W. Xu, J. Sep. Sci. 34 (2011) 1447–1454.
[7] L.F. Huang, K.J. Zhong., X.J. Sun, M.J. Wu, K.L. Huang, Y.Z. Liang, F.Q. Guo, Y.W. Li, Anal. Chim. Acta 575 (2006) 236–245.
[8] X.H. Lin, L. Sun, Y. Li, Z.M. Guo, K.J. Zhong, Q.C. Wang, X. Lu, Y.S. Yang, G.W. Xu, Talanta 82 (2010) 1571–1575.
[9] J.B. Cai, B.Z. Liu, P. Ling, Q.D. Su, J. Chromatogr. A 947 (2002) 267–275.
[10] J.C. Shen, X.G. Shao, Anal. Chim. Acta 561 (2006) 83–87.
[11] W.H. Liu, B. Ding, X.M. Ruan, H.T. Xu, J. Yang, S.M. Liu, J. Chromatogr. A 1163 (2007) 304–311.
[12] M. Sleiman, R.L. Maddalena, L.A. Gundel, H. Destaillats, J. Chromatogr. A 1216 (2009) 7899–7905.
[13] S.S.H. Ho, J.Z. Yu, Anal. Chem. 74 (2002) 1232–1240.
[14] S.S.H. Ho, J.Z. Yu, Environ. Sci. Technol. 38 (2004) 862–870.
[15] J. Caro, M. Gallego, Talanta 76 (2008) 847–853.
[16] S. Vainiotalo, V. Vaananen, R. Vaaranrinta, Environ. Res. 108 (2008) 280–288.
[17] S. Fahrenholtza, H. Hühnerfuss, X. Baur, L.T. Budnik, J. Chromatogr. A 1217 (2010) 8298–8307.
[18] P. Togyessy, B. Vrana, Z. Krascsenits, Talanta 87 (2011) 152–160.
[19] X.B. Pang, A.C. Lewis, J.F. Hamilton, Talanta 85 (2011) 406–414.
[20] E. Woolfenden, J. Chromatogr. A 1217 (2010) 2674–2684.
[21] N. Ochiai, S. Daishima, D.B. Cardin, J. Environ. Monit. 5 (2003) 997–1003.
[22] M. Harper, J. Chromatogr. A 885 (2000) 129–151.
[23] M. Clement, S. Arzel, B.L. Bot, R. Seux, M. Millet, Chemosphere 40 (2000) 49–56.
[24] J.Y. Liu, Y. Zhao, H.W. Yang, X.Q. Yin, X.L. Tan, Hunan Shifan Daxue Ziran Kexue Xuebao 34 (2011) 54–58.
[25] Y. Hou, L. Yang, B.X. Wang, J.C. Xu, Y. Yang, Y. Yang, Q.E. Cao, X.G. Xie, Se Pu 24 (2006) 601–605.
[26] S.M. Charles, C. Jia, S.A. Batterman, C. Godwin, Environ. Sci. Technol. 42 (2008) 1324–1331.
[27] K. Dettmer, W. Engewald, Anal. Bioanal. Chem. 373 (2002) 490–500.
[28] C.Y. Ma, J.T. Skeen, A.B. Dindal, C.K. Bayne, R.A. Jenkins, Environ. Sci. Technol. 31 (1997) 853–859.
[29] P.B.C. Forbes, E.R. Pohwer, Environ. Pollut. 157 (2009) 2529–2535.
[30] L.J. Lamm, Y. Yang, Anal. Chem. 75 (2003) 2237–2242.
[31] A.K. Attia, Talanta 81 (2010) 25–29.