Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Chromatography A, 985 (2003) 167–174
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Determination of triazines in soil by microwave-assisted extraction followed by solid-phase microextraction and gas chromatography–mass spectrometry

Gang Shen, Hian Kee Lee*
Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

Abstract

A method for determining triazine herbicides in soil samples that combines microwave-assisted extraction with solid-phase microextraction is described. Water containing 1% methanol was employed as extractant. The parameters of solid-phase microextraction and microwave-assisted extraction were investigated. In solid-phase microextraction, particular attention was paid to the negative effect of salt on fiber stability. Our experiments showed that this effect could be effectively reduced by simply washing the fiber with deionized water. The selected triazines could be efficiently extracted by the aqueous extractant at 105 °C for 3 min, with 80% output of maximum power (1200 W). The extraction procedure provided good precision (<7%) and recoveries (76.1–87.2%). The limits of detection were in the range 2–4 μg/kg. Compared with conventional liquid extraction, microwave-assisted extraction–solid-phase microextraction was more efficient, accurate and faster, and used a very small amount of organic solvent (only 250 μL methanol). The extraction of aged spiked soil samples indicated that, although the recoveries were lower than those of freshly spiked samples, they were nevertheless satisfactory for the quantitative analysis of real-world samples.

Keywords: Extraction methods; Soil; Triazines; Pesticides

1. Introduction

Triazines, important herbicides used in weed control, are ubiquitous environmental pollutants in soils and waters. Their use has caused great concern because they are mobile and soluble in water and can also be strongly sorbed onto soil. The study and survey of the widespread distribution of triazine herbicides in the environment require the availability of efficient analytical methods for monitoring both agricultural and non-agricultural areas. Generally, liquid–liquid extraction (LLE) methods, solid-phase extraction (SPE), and supercritical fluid extraction (SFE) are widely adopted [1–6]. These sample-preparation procedures, however, are time-consuming, expensive, and, for LLE, require large amounts of organic solvents.

In recent years, microwave-assisted extraction (MAE) has developed into a good alternative to traditional extraction methods and has become a popular routine technique in environmental analysis, especially in organic analysis [7]. MAE was first introduced by Ganzler and Salgo to isolate organic compounds from solid matrices [8]. Their work indicated that MAE was far more efficient than Soxhlet extraction. Frost [9] compared MAE, SFE, Soxhlet extraction and pressurized liquid extraction

*Corresponding author. Fax: +65-6779-1691.
E-mail address: chmleehk@nus.edu.sg (H.K. Lee).

0021-9673/02/$ – see front matter
PII: S0021-9673(02)01222-0

(PLE) procedures, and concluded that the advantages of MAE were that it was rapid and could handle multiple samples simultaneously.

Microwave heating is very efficient and involves two mechanisms: ionic conductance and dipolar rotation [10]. Therefore, polar solvents can effectively absorb and convert much more microwave energy. In order to improve the solvation characteristics, a mixture of solvents may be necessary [11,12]. For special cases, solvents with no dielectric constant may be used. In this case, solvents or materials that can absorb microwave energy and transfer the energy to the sample should be added, such as water or Welfon [13,14]. Water sometimes plays an important role in MAE, i.e. as moisture, as an extractant and in reactions with adsorption sites in solid matrices [15–17]. Xiong et al. [18] compared water, methanol, acetone–hexane (1:1) and dichloromethane in the extraction of triazines from soils, and indicated that water was as efficient as the organic solvents. Most important is that water is inexpensive, safe and environmentally friendly.

Unfortunately, after MAE, it is difficult to concentrate the aqueous extract because of the high boiling point of water. Additionally, MAE cannot separate the target analytes from other extractable interferences coexisting in the sample [19]. Thus an additional separation step is required. The advent of solid-phase microextraction (SPME) provides a solution to address the above drawbacks.

SPME is a solvent-free analytical process developed by Arthur and Pawliszyn [20] that includes simultaneous extraction and preconcentration of analytes from aqueous samples or the headspace of the samples. It is popularly used for the analysis of drugs, foods and environmental pollutants [21–23]. In most cases, SPME is carried out with direct immersion in aqueous samples. The direct use of SPME to extract an aqueous suspension of soil has also been studied [24–26]. In addition, the combination of SPME with other extraction methods to determine the analytes in soil or other solid matrices has been studied [27–31]. This technique provides efficient enrichment and cleanup, and also good selectivity and sensitivity.

Due to the ability of MAE to quantitatively extract both polar and nonpolar organics from solid matrices, and the success of SPME as a method for the quantitative determination of organics in the aqueous phase, the present study combines MAE with SPME–GC–MS to analyze triazines in soils. It offers further evidence of the applicability of MAE–SPME–GC–MS to the analysis of these compounds in soils, and provides a simple procedure to maintain the stability of the fiber. Some important extraction parameters of SPME and MAE were investigated.

2. Experimental

2.1. Chemicals

Methanol (HPLC grade) and acetone (pesticide grade) were from Fisher Scientific (Fair Lawn, NJ, USA). Atrazine (purity 98%), simazine (purity 99%), propazine (purity 98%), and prometryn (99.5%) were purchased from Supelco (Bellefonte, PA, USA). Stock standard solutions were prepared in acetone with concentrations of 500 μg/ml of each compound and stored in a freezer at about −20 °C. Working solutions prepared by dilution of stock standards with acetone or water prepared by a Nanopure water system (Barnstead, Dubuque, IA, USA) were used as standards for spiking the soil samples or as solutions for the SPME optimization. These solutions were prepared weekly and stored in the dark at 4 °C.

2.2. Preparation of soil samples

The soil samples (pH 6.5, organic matter content 4.0%, sand 72.5% and clay 18.4%) were air-dried, pulverized and sieved to a grain size of 2 mm. After homogenization, the soil sample was stored at 4 °C. There were no detectable levels of the target analytes in the soil before spiking.

Freshly spiked soil was prepared by adding an appropriate volume of spiking solution to the soil sample, then shaking carefully to homogenize it. This spiked soil sample was allowed to stand overnight to air-dry and was extracted directly thereafter.

For the preparation of the aged spiked sample (50 and 150 μg/kg), a known amount of soil was mixed with a suitable volume of acetone, containing a known concentration of triazines. The volume of acetone was large enough to form a slurry. The

slurry was stirred until most of the solvent had evaporated. The sample was allowed to stand overnight and then stored in the dark and aged for 60 days prior to extraction.

2.3. SPME

SPME fiber with 65 μm Carbowax–divinylbenzene (CW–DVB) was employed for the triazines. A manual SPME device was used in the present experiment. The fiber was conditioned before initial application in the hot GC injector at a temperature and period suggested by the supplier.

For SPME, a 4-ml vial was filled with 3 ml of aqueous sample containing 0.75 g NaCl. The vial was then sealed with a cap and PTFE-lined silicone septum. The extraction was carried out at room temperature (air conditioning at 25 °C) for 30 min with stirring at 1000 rpm by a magnetic stirring bar. The extracted triazines were desorbed for 4 min at 240 °C in the GC injector.

2.4. GC–MS analysis

Analysis of triazines was performed on a Shimadzu (Tokyo, Japan) QP5000 GC–MS system equipped with a split/splitless injector. The GC system was fitted with a DB-5 column (30 m×0.32 mm I.D., 0.25 μm film thickness) from J&W Scientific (Folsom, CA, USA). The following temperature programme was employed: 90 °C for 4 min; 25 °C/min to 160 °C, held for 2 min; then 2 °C/min to 180 °C; a further 20 °C/min to 280 °C, held for 7 min. The injector temperature was 240 °C, and all injections were made in the splitless mode. Ionization was by electron impact (EI). MS was scanned over the range m/z 50–500 to confirm the retention times of the analytes studied. For the determination of triazines, selected ion monitoring (SIM) was performed. The triazines used and their respective target and qualifier masses are listed in Table 1. The GC–MS interface temperature was set at 260 °C. Fig. 1 shows the GC–MS (SIM) chromatogram of a soil extract after MAE followed by SPME.

2.5. Microwave-assisted extraction of soil sample

Microwave-assisted extractions were performed on a MARS 5 (CEM, Matthews, NC, USA), 1200-W laboratory microwave accelerated reaction system configured with a 14-position carousel. The instrument can control either pressure or temperature. In the present work, only temperature control was employed. Pure water or organic solvent modified water (25 ml) was added to the MAE extraction vessel, which contained 1–10 g of spiked soil. Extraction was performed at 105 °C for 3 min at 80% power. After extraction, the vessels were cooled to room temperature. The aqueous extract was filtered through a Whatman No. 42 filter paper. The sample was further clarified by centrifugation at 4000 rpm for 4 min, and directly subjected to SPME using the procedure described above. For organic solvent extraction, 10 g of soil was extracted by dichloromethane–methanol (9:1) for 20 min at 115 °C. The microwave energy output was 950 W [31].

2.6. Liquid extraction of soil sample

Fifty grams of soil spiked at the 150 μg/kg level was extracted with 125 ml of acetonitrile–0.5%

Table 1
Physical properties of triazines, their target ions and relative intensities

Compound	Solubility in water (mg/l)	pK_a	Log K_{ow}	Target ions and relative intensity
Simazine	5.7	1.62[a]	2.18	201 (100), 186 (66), 173 (53), 158 (29)
Atrazine	28	1.65[a]	2.61	215 (100), 200 (192), 202 (63), 173 (65)
Propazine	8.6	1.85[a]	2.93	229 (100), 214 (155), 187 (54), 172(128)
Prometryn	48	4.05[a]	3.51	241 (100), 226 (61), 199 (30), 184 (115)

K_{ow}, octanol–water partition coefficient.
[a] These values are from the website of the U.S. Department of Agriculture: http//wizard.arsusda.gov/rsm/textfiles/.

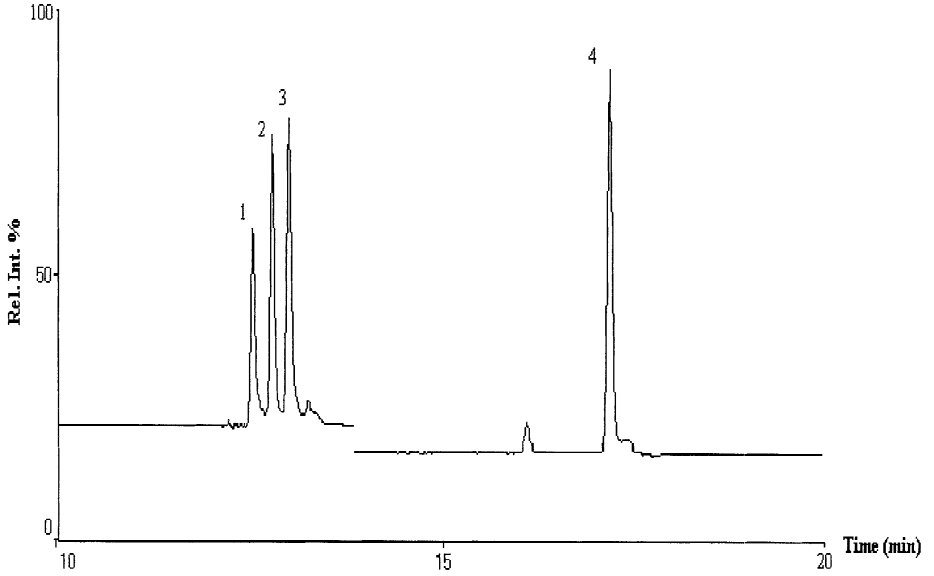

Fig. 1. GC–MS chromatogram (SIM mode) of a soil sample after MAE followed by SPME. Peaks: 1 = simazine, 2 = atrazine, 3 = propazine, 4 = prometryn.

ammonia in water (70:30, v/v) in a conical flask [32]. The flask was stoppered and the mixture was stirred for 30 min. After standing overnight, the sample was stirred again for 30 min and then filtered. The filtrate was made up to 250 ml by the addition of the acetonitrile and ammonia mixture solution in the above ratio. Subsequently, approximately 50 ml of the filtrate was evaporated off and the mixture was extracted three times with dichloromethane. The organic extract was allowed to dry, and 2 ml of hexane was employed to reconstitute the residue prior to GC–MS analysis.

2.7. pH

In experiments to determine the effect of pH on extraction, acidified or alkalized solutions were prepared and then added to the soil. The final pH values were obtained by measurement of the soil/water mixture.

3. Results and discussion

3.1. Development of SPME

A commercially available SPME fiber, CW–DVB, was employed in the present work. We paid particular attention to factors such as the extraction time, pH, and ionic strength of the sample solution. Although the recovery increased dramatically as the extraction time increased, it was not feasible from a practical point of view to use the equilibrium time, since the extraction time was too long (>120 min [27]). Generally, nonequilibrium extraction would be adopted only if the extraction was carefully timed in order to improve the extraction precision. Thus, 30 min was a reasonable extraction time to set. pH, ranging from 1.55 to 12, was investigated for its effect on SPME. The results indicated that pH values between 4.0 and 9.0 did not affect the adsorption of triazines significantly. Therefore, in this study, all solutions used were neutral for convenience.

The salting-out effect was investigated with different NaCl concentrations, 0, 10 and 25%, and a saturated solution. All triazines studied demonstrated a significant increase in extraction efficiency when the concentration of salt increased from 0 to 25% (see Table 2). Changing the concentration from 25% to saturation did not lead to a significant improvement. Thus 25% concentration was selected. However, one problem was that, at the beginning of the study, the lack of linearity and reproducibility was significant. The lifetime of the fiber was only around

Table 2
Effect of salt concentration on SPME

Compound	Salt concentration (w/v)			
	0	10%	25%	Saturated
Simazine	6592[a]	12 113	17 650	18 968
Atrazine	7662	12 590	20 473	21 907
Propazine	8648	12 842	22 386	23 125
Prometryn	4967	7288	13 924	14 536

[a] Peak counts.

15 extraction cycles, similar to previous reports [27,33]. This was possibly caused by salt deposited on the fiber, which made it fragile and readily breakable. Hernandez et al. [27] solved this problem by decreasing the salt concentration from 30 to 10%, although this led to a lower extraction efficiency. We overcame this problem by using pure water to wash the fiber after extraction and then inserting it into the GC injector for desorption. Intuitively, this can result in a loss of analytes, but our results indicated that the procedure had no adverse effects, which can be seen from the good linearity and repeatability. Using this procedure, we were able to achieve 100 extraction cycles with good precision. After optimization of all the variables, the optimum SPME parameters were: 3 ml of aqueous sample with the addition of 25% (w/w) salt, extracted for 30 min under magnetic stirring at 1000 rpm and desorption at 240 °C for 4 min.

3.2. Optimization of MAE of triazines in soils

Previous studies [17,18] showed that an aqueous extractant was efficient in extracting triazines from soil samples. However, the detailed parameters, such as temperature, extraction time, amount of soil sample, etc., were not optimized. Thus, in this study, we paid particular attention to optimization of the extraction parameters of MAE with water as extractant.

3.2.1. Temperature

Temperature is of prime importance in ensuring an efficient extraction. Hence, in this work, temperature was optimized first. Five temperatures were selected, 85, 95, 105, 115 and 130 °C, while the other parameters, such as power (1200 W at 80% output), time (10 min) and amount of soil (10 g), were kept

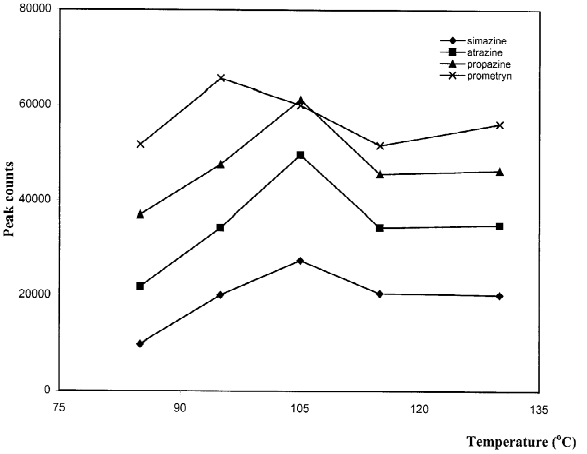

Fig. 2. Effect of temperature on MAE. Ten grams of soil extracted with 25 ml of water for 10 min. Energy output: 80%.

constant. As shown in Fig. 2, simazine, atrazine and propazine have the highest extraction efficiency at 105 °C, but that of prometryn was at 95 °C. A higher temperature was not useful to increase the extraction efficiency. Thus, 105 °C was optimum and for prometryn it was generally applicable.

3.2.2. Extraction time

This parameter was determined by extracting the analytes for 1–20 min with the other parameters kept constant (as in the temperature optimization experiments). The highest extraction was achieved at 3 min for all analytes (Fig. 3). In the time range from 3 to 15 min, the amount of analytes extracted did not

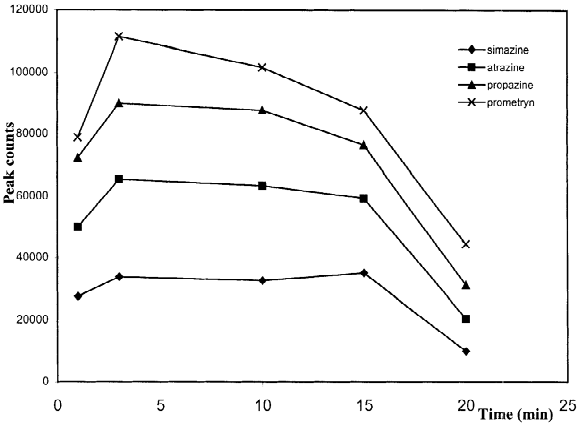

Fig. 3. Microwave-assisted extraction time profiles. Ten grams of soil extracted with 25 ml of water at 105 °C. Energy output: 80%.

change significantly, especially for simazine, atrazine and propazine. Longer extraction (>15 min) led to a decrease in the extraction efficiency. This may have been caused by degradation of the analytes under the relatively drastic conditions.

3.2.3. pH value of water

Triazines are weak bases. Thus the use of an acidic extractant should increase the extraction efficiency. According to the pK_a values listed in Table 1, various pH values (1.3, 7.0, 10.4 and 12.0, calculated after addition of water to the soil) were investigated. In theory, recovery should be highest under acidic conditions (pH 1.3), because the triazines would be in an ionic state and therefore more soluble in water. However, we observed that recovery at this pH was lower than that under neutral and basic conditions. One possible reason for this is that triazines may hydrolyze in acidic or basic aqueous environments, but are relatively stable under neutral conditions [34,35]. Although the hydrolysis rate is slow [35], the drastic conditions under MAE may enhance the reaction, making the triazines hydrolyze rapidly within a shorter time. Extraction with neutral water not only gives the highest extraction efficiency, but also the cleanest extracts. Thus, this was chosen as the optimum condition for extraction.

3.2.4. Effect of amount of soil sample

The final MAE parameter optimized was the amount of soil extracted. One, 3, 5 and 10 g soil samples were prepared. Other conditions were optimum as previously determined. The results indicated that the extraction efficiency decreased with an increase in the amount of soil. One gram of soil provided the best extraction efficiency. Thus 1 g of soil was selected as the optimum amount. The reason for this observation may be related to the bulk of the sample. For the same amount of extraction solvent and capacity of the extraction vessel, a smaller bulk of solid material is more completely immersed in liquid and extracted.

3.3. Modifiers in the aqueous extractant

The effect of organic solvent modifiers on the extraction efficiency was studied. In this study, methanol and acetone were tested. Since it has been reported for SPME that both the distribution of the analytes between the fiber and liquid phase and the long-term stability of the fiber are negatively affected by the addition of organic solvents [36,37], only small amounts of organic solvents were applied (1 and 5%, v/v) in the present work. As shown in Table 3, the addition of 1% methanol gave the maximum extraction efficiency compared with pure water and water mixed with other concentrations of modifiers.

3.4. Evaluation of the method

The method validation studies for spiked samples indicated that the present method provides good recoveries and reasonable precision for triazines in the range 10–500 μg/kg. As can be seen from Table 4, the recoveries from the MAE–SPME of triazines are 76.1–87.2% with good precision (<7%). The 10 μg/kg spiked soil sample gave relatively poorer RSD values and lower recoveries. This may be because this concentration is close to the detection limit of the method. The limits of detection of the MAE–SPME procedure calculated at $S/N = 3$ were from 2 to 4 μg/kg.

Additionally, conventional liquid extraction [37]

Table 3
Effect of organic solvent modifiers in the aqueous extractant on the MAE–SPME procedure

	Pure water	Methanol (%, v/v)		Acetone (%, v/v)	
		1	5	1	5
Simazine	288 152[a]	286 414	225 029	222 565	173 556
Atrazine	42 446	464 388	373 552	409 333	346 194
Propazine	530 213	544 898	467 860	505 226	503 300
Prometryn	507 956	561 435	519 854	532 659	523 457

[a] Peak counts.

Table 4
Recoveries, precision (RSD), and limits of detection (LODs) of the microwave-assisted extraction procedure followed by SPME of spiked soil samples

Compound	Recovery, % (RSD, %)				LOD[a] (μg/kg)
	Conventional liquid extraction (spiked at 150 μg/kg)	SPME ($n=3$)			
		500 μg/kg (spiked level)	50 μg/kg (spiked level)	10 μg/kg (spiked level)	
Simazine	71.7 (7.89)	87.2 (2.18)	84.1 (3.90)	81.6 (4.26)	4
Atrazine	70.5 (9.23)	85.7 (2.09)	82.5 (3.23)	76.6 (4.84)	3
Propazine	67.6 (11.4)	80.7 (3.88)	83.0 (4.97)	78.3 (6.67)	2
Prometryn	60.8 (8.65)	77.8 (3.17)	78.5 (5.36)	76.1 (4.73)	2

[a] Calculated from a soil sample spiked at the 10 μg/kg level.

was also performed in order to evaluate the MAE–SPME method. Compared with the present method, liquid extraction provided both lower recoveries and poorer precision (see Table 4). The reason for this might be the complex and tedious extraction and post-extraction treatment procedure. The comparison also indicates that, under the applied MAE conditions, there was no obvious degradation of the analytes by the microwave energy. Thus it can be concluded that the hot water produced by MAE is an excellent and efficient extractant. Also, the MAE extracts obtained by the aqueous extractant and conventional liquid extraction were clear and colorless, while the organic solvent extract exhibited a deep yellow color.

The MAE–SPME–GC–MS procedure developed above was finally used to analyze aged (60 days) spiked soil samples. Two concentrations, 50 and 150 μg/kg, were prepared. The results are given in Table 5. Compared with freshly spiked soil samples, the method provided similar precision but lower recoveries. In another study [37], triazines in an aged spiked soil sample were extracted by microwave-assisted extraction with dichloromethane–methanol as extractant. The results indicated that the recovery for the aged spiked sample was similar to that of a freshly spiked sample. Thus, after comparison, the low recovery from the aged spiked sample in the present study may be because the analytes were adsorbed more strongly on the soil active sites, which affected the extraction, or the analytes had undergone some degree of degradation during this period.

4. Conclusions

Microwave-assisted extraction using 1% methanol modified water as extractant followed by solid-phase microextraction has been developed to extract triazines from soil. The results indicate that this extraction procedure is efficient and precise. In this

Table 5
Recoveries and relative standard deviations of the MAE–SPME–GC–MS of aged (60 days) spiked soil samples ($n=5$)

Compound	MAE–SPME–GC–MS of aged spiked soil sample			
	150 μg/kg		50 μg/kg	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Simazine	82.2	1.98	77.0	4.77
Atrazine	70.7	1.16	74.4	2.40
Propazine	71.9	3.58	70.2	4.04
Prometryn	65.2	3.26	61.7	4.24

experiment, only small amounts of organic solvent were used for each extraction. The employment of SPME provided a labor- and time-saving procedure compared with evaporation of an aqueous extract. Finally, this combination provides excellent selectivity and sensitivity for the quantitative analysis of triazines in soil.

References

[1] G. Durand, D. Barceló, Anal. Chim. Acta 243 (1991) 259.
[2] K.A. Caldwell, V.M.S. Ramanujan, Z. Cai, M.L. Gross, Anal. Chem. 65 (1993) 2372.
[3] J.W. Pensabene, W. Jiddler, D.J. Domoghue, J. Agric. Food Chem. 48 (2000) 1668.
[4] R.E. Clement, G.A. Ericeman, C.J. Koester, Anal. Chem. 67 (1995) 221R.
[5] E.G. Vandervelde, M.R. Ramlal, A.C. Vanbeuzek, R. Hoogerbrugge, J. Chromatogr. A 683 (1994) 125.
[6] S. Papilloud, W. Haerdi, Chromatographia 38 (1994) 514.
[7] V. Camel, Trends Anal. Chem. 19 (2000) 229.
[8] K. Ganzler, A. Salgo, K. Valko, J. Chromatogr. A 371 (1986) 299.
[9] S.P. Frost, J.R. Dean, K. Evans, K. Harradine, C. Cary, M.H.I. Comberm, Analyst 122 (1997) 895.
[10] E.D. Neas, M.J. Collius, in: H.M. Kingston, L.B. Jassie (Eds.), Introduction to Microwave Sample Preparation, American Chemical Society, Washington, DC, 1988, p. 7.
[11] M.P. Llompart, R.A. Lorenzo, R. Cela, J.R.J. Pare, Analyst 120 (1997) 133.
[12] K.K. Chee, M.K. Wong, H.K. Lee, J. Chromatogr. A 723 (1996) 259.
[13] J.R.J. Pare, J.M.R. Belanger, S.S. Stafford, Trends Anal. Chem. 13 (1994) 176.
[14] K. Hummert, W. Vetter, B. Luckas, Chromatographia 42 (1996) 300.
[15] F.E. Onuska, K.A. Terry, Chromatographia 36 (1993) 191.
[16] S.J. Stout, A.R. daCunda, D.G. Allardice, Anal. Chem. 68 (1996) 653.
[17] T.R. Steinheimer, J. Agric. Food Chem. 41 (1993) 588.
[18] G.H. Xiong, B.Y. Tang, X.Q. He, M.Q. Zhao, Z.D. Zhang, Z.X. Zhang, Talanta 48 (1999) 333.
[19] N. Font, F. Hernandez, E.A. Hogendoorn, R.A. Baumann, P. van Zoonen, J. Chromatogr. A 798 (1998) 179.
[20] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
[21] C.L. Arthur, D.W. Potter, K.D. Buchholz, S. Motlagh, J. Pawliszyn, LC·GC 10 (1997) 656.
[22] Z. Zhang, M.J. Yang, J. Pawliszyn, Anal. Chem. 66 (1994) 847A.
[23] S. Megdic, J. Pawliszyn, J. Chromatogr. A 723 (1996) 929.
[24] C.G. Zambonin, F. Palmisano, J. Chromatogr. A 874 (2000) 247.
[25] C.G. Zambonin, F. Catucci, F. Palmisano, Analyst 123 (1998) 2825.
[26] A.A. Boyd-boland, J. Pawliszyn, J. Chromatogr. A 704 (1995) 163.
[27] F. Hernandez, J. Beltran, F.J. Lopez, J.V. Gasper, Anal. Chem. 72 (2000) 2313.
[28] K.J. Hageman, L. Mazeas, C.B. Grabanski, D.J. Miller, S.B. Hawthorne, Anal. Chem. 68 (1996) 3892.
[29] S.B. Hawthorne, C.B. Grabanski, K.J. Hageman, D.J. Miller, J. Chromatogr. A 814 (1998) 151.
[30] L. Wennrich, P. Popp, M. Möder, Anal. Chem. 72 (2000) 546.
[31] Y. Yang, M. Bonillar, H.M. McNair, J. High Resolut. Chromatogr. 20 (1997) 213.
[32] A.E. Smith, J. Agric. Food Chem. 29 (1981) 111.
[33] M. Möder, P. Popp, R. Eister, J. Pawliszyn, Fresenius J. Anal. Chem. 363 (1999) 6860.
[34] P.H. Howard (Ed.), Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Pesticides, Lewis, Boca Raton, FL, 1989.
[35] M.A. Kamrin, Pesticide Profiles: Toxicity, Environmental Impact, and Fate, Lewis, Boca Raton, FL, 1997.
[36] R. Eister, K. Levsen, Fresenius J. Anal. Chem. 351 (1995) 555.
[37] C. Molins, E.A. Hogendoorn, H.A.G. Heusinkveld, D.C. van Harten, P.L. van Zoonen, R.A. Baumann, Chromatographia 43 (1996) 527.