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Microwave-assisted solvent extraction and reversed-phase liquid chromatography–UV detection for screening soils for sulfonylurea herbicides

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Abstract

A multi-residue method for the rapid assay of cinosulfuron, thifensulfuron-methyl, metsulfuron-methyl, sulfometuron-methyl and chlorsulfuron in soil samples has been developed. The method involves microwave-assisted solvent extraction (MASE) prior to analysis by reversed-phase liquid chromatography (RPLC) and UV detection at 226 nm. MASE conditions were established providing efficient extraction without degradation of the analytes, furthermore selectivity can be enhanced by limiting the coextraction of interferences. Selected MASE conditions, including dichloromethane–methanol (90:10,v/v) as the extraction solvent, provided, in 10 min, a complete extraction of the analytes from soil samples. The extracts obtained with the developed MASE procedure are analysed by RPLC–UV in less than 15 min without additional cleanup; the overall procedure allows the determination of the analytes in soils to a level of at least 5 μg/kg. Method validation was performed by analysing freshly spiked soil samples and samples with aged residues at levels between 20 and 1000 μg/kg. Depending on the spiked level and the type of spiked sample recoveries were obtained between 70–100% with R.S.D.s between 1–10%.

Keywords: Extraction methods; Microwave-assisted solvent extraction; Soil; Environmental analysis; Pesticides; Sulfonylureas

1. Introduction

Sulfonylurea compounds are characterized by a very high herbicidal activity allowing low-dose rates of 10–40 g/ha for the control of many grasses and broadleaf weeds in the agriculture of crops [1]. This feature means, however, that under persistent conditions, e.g. high pH of soil, low temperatures, little rainfall and poor microbial activity, remaining low concentrations of these analytes can still affect the growth of susceptible plants [2]. Hence, in order to control carry-over from one growing season to the next, productive sensitive and selective methods are required for the determination of residues of sulfonylurea herbicides in soil.

A number of methods on the residue analysis of sulfonylurea herbicides in various matrices has been reported. Either capillary gas chromatography (GC) [3–8] or liquid chromatography (LC) [9–14] is used.

Because of the inherent high separation power and the availability of sensitive and selective detectors, GC is usually preferred in pesticide residue analysis. However, sulfonylurea herbicides are polar compounds (pK_a values about 3.5) with low vapor

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pressures requiring derivatisation techniques prior to GC analysis. Derivatisation has been performed with diazomethane [3,4,7,8] or pentafluorobenzyl bromide [5] prior to GC–MS [3–5], GC with nitrogen–phosphorus detection) (NPD) [4] or GC–electron-capture detection (ECD) [7,8].

An advantage of LC is that the separation of sulfonylurea herbicides can be performed without derivatisation. Reversed-phase liquid chromatography (RPLC) with UV detection has been applied for the determination of some sulfonylurea herbicides in soil and water [11–14].

Separation of sulfonylurea compounds without derivatisation can also be performed with capillary electrophoresis (CE) [15–17] or supercritical fluid chromatography (SFC) [18,19]. CE using micellar electrokinetic chromatography has been used to detect these herbicides in water and soil samples [15–17]. Supercritical fluid extraction (SFE) coupled to SFC has been used for metabolic studies of sulphonylurea herbicides in various solid matrices [18]. High-efficiency packed-column SFC coupled to various detection methods (UV, NPD and ECD) using on-line sampling enabled the determination of sulfonylurea herbicides in water samples at the sub μg/kg level [19].

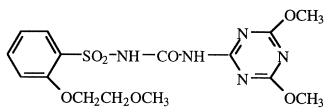
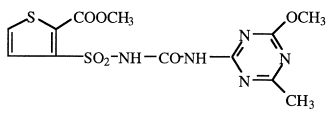
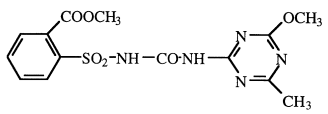
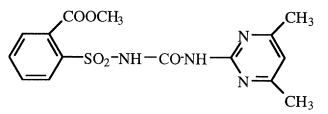
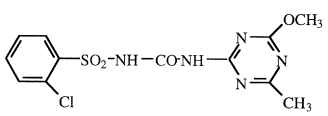
For the extraction of sulfonylurea residues in soil samples, several methods have been described. To enhance solubility of acidic analytes a basic aqueous solvent, viz. hydrogen carbonate solution, is frequently applied [3–5,8–10,13,14,17]. This step is usually followed by cleanup using either solid-phase extraction (SPE) [5,13,14] or liquid–liquid extraction (LLE) [8–10]. These procedures are rather time consuming and moreover, a basic aqueous extraction will liberate many acidic soil interferences, e.g. humic and fulvic acids.

The need for more efficient and more economical methods for the extraction of organic pollutants from soils has generated (semi) automated techniques such as supercritical fluid extraction (SFE), accelerated solvent extraction (ASE) and microwave-assisted solvent extraction (MASE). Among these techniques, SFE is widely adopted now and has also been used for the trace analysis of sulfonylurea compounds in water after sampling on solid-phase extraction disks [12] or from soil [14]. ASE and MASE have been recently introduced on the market and published work indicates that these are efficient techniques for the extraction of various kind of organic pollutants from soil samples [20–22]. In our laboratory MASE has been adopted and successfully applied for the extraction of triazines in soil samples [23,24].

The objective of this study was to investigate the feasibility of MASE in the development of an efficient extraction method for determination of sulfonylurea herbicides from soil samples. A crucial aspect of an extraction procedure is to determine its efficiency which cannot be obtained from freshly-spiked samples only. Therefore, samples with aged residues were prepared and tested with the developed MASE procedure.

For reasons of availability and possible agricultural application concerning the Netherlands and Spain, chlorsulfuron, cinosulfuron, thifensulfuron-methyl, metsulfuron-methyl and sulfometuron-methyl were selected as target analytes; structural information of these analytes is given in Table 1.

Table 1
Names and structural formula of sulfonylurea herbidides

1. Cinosulfuron	
2. Thifensulfuron-methyl	
3. Metsulfuron-methyl	
4. Sulfometuron-methyl	
5. Chlorsulfuron	

RPLC with UV detection was selected for instrumental analysis. UV detection is not very selective and concerning the trace analysis of these acidic analytes in soil extracts, matrix interferences can be expected. Therefore, a number of cleanup methods, viz. SPE and coupled-column RPLC were also investigated.

2. Experimental

2.1. Chemicals

All sulfonylurea herbicides with a purity >98% were obtained from Dr. S. Ehrenstorfer (Promochem, Wesel, Germany). Acetone, acetonitrile, dichloromethane and methanol, all of LC grade, were obtained from J.T. Baker (Deventer, Netherlands). Analytical-reagent grade hydrogencarbonate sodium ($NaHCO_3$), orthophosphoric acid (89%), hydrochloric acid (37%) were bought from Merck (Darmstadt, Germany). Demineralised water was purified in a Milli-Q (Millipore, Bedford, MD, USA) system to obtain LC-grade water for use in eluents and standard solutions.

Stock standard solutions (ca. 500 μg/ml) of the herbicides were prepared in acetonitrile. For LC analysis, the stock solutions were diluted with LC-grade water.

Extractions were performed with the MASE extraction solvent consisting of dichloromethane–methanol (90:10, v/v). Methanol–0.1% phosphoric acid in water, pH 3 (45:55, v/v) was used as the LC eluent.

2.2. Equipment

A Baker-10 system (J.T. Baker) was used to perform SPE. The LC system consists of a Model 231 autosampler, two isocratic pumps, a Model 305 from Gilson (Villiers-le Bel, France) and a Model 205 from Perkin-Elmer (Norwalk, CT, USA), and a Model 116 UV detector from Gilson. Separation was performed on a 100×4.6-mm I.D. column packed with 3-μm C_{18} Microspher (Chrompack, Middelburg, The Netherlands). For coupled column experiments two 50×4.6-mm I.D. columns packed with 3-μm C_{18} Microspher (Chrompack) were used. LC pumps and valves for column switching and eluent supply were controlled by the autosampler.

The columns were kept at 30°C with a laboratory-made column oven connected to a Model 1441 circulating-water system from Braun (Melsungen, Germany).

MASE extractions were performed with a MES-1000, 950-W laboratory Microwave Extraction System (CEM, Mathews, NC, USA) configured with a 12-position carousel. The instrument controls either pressure (P) or temperature (T), depending on which parameter reached its control set point first.

Quantitative measurements of peak heights were made with a Model 800 DP integrator from Fisons and UV spectra were recorded with a Model 1000S diode-array detector with a UV cell of 0.8 cm from ABI (Foster City, CA, USA).

2.3. Soil fortification

The two type of sandy soils A (humic-poor) and B (humic-rich) used were characterised by a clay content of 0.8 and 1.3%, a sand content of 91.5 and 77.5%, an organic carbon content of 0.37 and 1.68%, an organic matter content of 1.5 and 5.3%, and a pH of 4.6 and 4.2 for soil A and B, respectively.

Freshly-spiked soils were prepared by weighing 10.0 g of soil into a glass bottle followed by the addition of an appropriate volume (≤2 ml) of spiking solution; the samples were allowed to stand overnight before extraction. Fortifications were made at levels of 1000, 200, 20, 10 and 5 μg/kg, respectively.

Soils samples with aged residues were prepared by spiking the samples to levels of 100 and 20 μg/kg, respectively. After air-drying overnight, they were stored in a refrigerator at 4°C for 60 days.

2.4. MASE procedure

A 10.0-g spiked soil sample was transferred to the PTFE-lined extraction vessel. Next, 20 ml of MASE extraction solvent was added to the samples. Extractions were performed at 60°C for 10 min at 50% power and a pressure limit of 100 p.s.i.; the time required for reaching the installed temperature depends on the number and type of samples in the

carousel and is not included in the extraction time (1 p.s.i.=6894.76 Pa). After the extraction, the vessels were allowed to cool down to about 30°C before opening the instrument.

The extract was dried over sodium sulphate and collected in a glass tube with stopper. Five ml were transferred into a calibrated tube and evaporated to dryness under a gentle stream of nitrogen with a water bath at ca. 40°C. Shortly before the LC analysis, the residue was redissolved by the addition of 100 μl of acetonitrile followed by 900 μl of water.

2.5. RPLC–UV procedure

The mobile phase was adjusted to a flow-rate of 1 ml/min. From the extracts obtained, 200 μl were injected onto the 100×4.6-mm I.D. column. After 10 min a solvent switch to 100% methanol was made by means of the high pressure valve and the second LC pump set at a flow-rate of 0.5 ml/min. After rinsing the column for 2 min with 100% methanol, a solvent switch was made again and, prior to the next injection, the column was conditioned with the mobile phase for 5 min.

Detection of the analytes was performed with UV at 226 nm and quantification of the sulfonylurea herbicides was done by external calibration of peak heights with standard solutions of sulfonylurea herbicides in water.

3. Results and discussion

3.1. Selection of HPLC conditions

The first step in the set-up of a RPLC–UV method is to establish suitable chromatographic conditions and to assess the potential of UV detection. Sulfonylurea compounds are acidic compounds (pK_a values about 3.5), which can be separated on a C_{18} column using a mobile phase containing an acidic buffer. On a 100×4.6-mm I.D. column packed with 3-μm C_{18}, separation of the target analytes and capacity factors between 2 and 10 was obtained using a mobile phase of methanol–0.1% phosphoric acid (45:55, v/v).

Information on UV detectability was obtained with photodiode array detection. All analytes showed good sensitivity (ε range 15 000–18 000 l mol^{-1} cm^{-1}) at a wavelength of 226 nm providing under the selected LC conditions, a limit of detection (LOD, $S/N=3$) of approximately 2 ng for each compound.

In order to obtain a sensitivity aimed at a level of 5 μg/kg, an injection of the equivalent of about 500 mg of soil onto the column will be necessary. Based on earlier work [23,24], the amount of soil in the extract obtained after MASE is in the range of 2–5 g per ml solvent. Hence, an injection volume of a few hundred microliters will provide sufficient sensitivity. A sample injection volume of 200 μl was selected and tested with standard solutions. Initially, acidic aqueous standard solutions (pH of 2.5) were used in order to avoid band broadening of the acidic analytes during injection. However, as shown in Table 2, some compounds undergo degradation under acidic conditions. In comparison to a 20 μl injection and with or without acidifying the sample, no additional band broadening of analytes was observed for the 200 μl aqueous solution. Hence, it was not considered necessary to adjust the sample extracts to the mobile phase conditions by adding acid.

Table 2
Stability study in aqueous acidic solution (pH=2.5, T=20°C)

Herbicide	% of orginal concentration found				
	30 min	1 h 30 min	4 h 30 min	7 h	26 h
Cinosulfuron	96	98	96	96	86
Thifensulfuron-methyl	95	92	82	76	27
Metsulfuron-methyl	95	92	80	74	23
Sulfometuron-methyl	97	98	96	96	87
Chlorsulfuron	94	89	81	69	18

3.2. Selection of MASE conditions

In conventional extraction procedures [3,4,8–10] sodium carbonate solution (pH about 8.5) is used followed by washing with chloroform as a cleanup step. After acidifying the aqueous phase (pH about 3) the analytes are partitioned in toluene. Most of these procedures involve multiple extraction steps. Obviously, this is quite laborious and therefore a major goal of this study was to accelerate the process utilising MASE.

Aqueous extractions followed by washing or partitioning seem to be standard for this class of compounds, moreover the aqueous phase is compatible with RPLC analysis. Therefore the starting point in the MASE experiments was an aqueous two-solvent system of carbonate buffer (pH 8.5) and dichloromethane. In order to get a first impression of the efficiency of the extraction, rather clean soil samples (soil type A, see Section 2) were used, spiked with the analytes at relatively high levels (0.2–1 mg/kg).

Starting with the MASE settings applied for the determination of triazines in soil [23], viz. temperature (T) of 115°C, 100% power and an extraction time (t) of 20 min, recoveries of analytes in the aqueous phase were variable and low (range between 1–30%), most probably due to decomposition of the analytes. Hence, milder conditions such as lower temperatures, lower power and shorter extraction times were studied.

The results given in the left part of Table 3 clearly show that at temperatures below 70°C, recoveries above 70% are attainable. Hence, selecting 60°C as a safe extraction temperature, the influence of extraction time and the dichloromethane phase on the recovery was studied. The data given in Table 4 show that an increase in the extraction time (range 5–30 min) does not adversely affect the recovery under completely aqueous extraction conditions. It was established by analysing the dichloromethane phase that about 10–15% of the analytes were extracted into the organic phase. From the above data MASE conditions were selected, viz. T=60°C; t=10 min and 50% of power using an aqueous extraction.

Table 3
Effect of extraction temperature on recovery, solvent 0.1 *M* $NaHCO_3$–dichloromethane (2:1, v/v), extraction time 10 min

Herbicide	Recovery (%)			
	40°C	70°C	95°C	115°C
Cinosulfuron	75	78	65	31
Thifensulfuron-methyl	86	71	7	1
Metsulfuron-methyl	88	84	66	26
Sulfometuron-methyl	69	72	36	4
Chlorsulfuron	85	82	65	26

Table 4
Effect of the extraction time, solvent 0.1 *M* $NaHCO_3$, extraction temperature 60°C

Herbicide	Recovery (%)			
	5 min	10 min	20 min	30 min
Cinosulfuron	90	93	94	91
Thifensulfuron-methyl	89	89	87	81
Metsulfuron-methyl	91	91	91	89
Sulfometuron-methyl	88	89	91	87
Chlorsulfuron	88	88	89	88

Under these MASE conditions, the extracts of soil type A (organic carbon content, 0.37%) could be processed with RPLC–UV (226 nm) without any further sample pretreatment allowing the determination of the analytes to the 5 μg/kg level. However, determination of the analytes at this level was impossible in extracts from the soil type B (organic carbon content, 2.7%). The RPLC–UV trace of these soil samples using an acidic mobile phase was severely hampered by coextracted humic and fulvic acids eluting under acidic conditions as a broad hump. Addition of dichloromethane in order to wash the interferences from the aquous phase only slightly alleviated the problem.

Employing two C_{18} separation columns of 50×4.6 mm, the potential of coupled-column RPLC to perform an on-line cleanup was investigated. However, contrary to our experience in the determination of chlorophenoxy acids in water samples [25], a reduction of the broad hump originating from the soil samples was hardly observed making this approach not suitable.

3.3. Improvement of selectivity

The feasibility of SPE to improve cleanup was firstly investigated. Being very compatible with an aqueous extract (after acidifying) cartridges packed

with hydrophobic material offers the possibility to perform simultaneously, concentration and cleanup. Experiments using cartridges packed with 200 mg of C_{18}-bonded silica or SDB showed that volumes up to at least 20 ml can be loaded and that a cleanup with 2 ml of methanol–0.1% phosphoric acid in water (20:80, v/v) is possible without breakthrough of the analytes. However, SPE including the cleanup step did not substantially improved the selectivity.

Improvement of the selectivity can also be found in other extraction conditions; two options are available: changing the pH in the aqueous extraction or extraction by organic solvents. The stability of the compounds depends strongly on the pH, but partitioning the compounds simultaneously in an organic phase may circumvent this problem. Therefore, extraction with MASE using an acidic aqueous solution (0.1% phosphoric acid in water) combined with dichloromethane was investigated. Both the aqueous and organic phase (dichloromethane) were anlysed with RPLC–UV. The recovery of the analytes in the organic phase were in the range of 50%. No analytes were detected in the aqueous phase due to degradation of the analytes under acidic conditions (see also Table 2) under the mild MASE conditions used.

Atrazine and its polar metabolites can be recovered from soils with aged residues with MASE using dichloromethane–methanol (90:10, v/v) as the extraction solvent [23,24]. The use of this organic solvent provided a significant increase in selectivity in comparison to the basic aqueous solvent. This is clearly demonstrated in Fig. 1, showing the RPLC–UV analysis of MASE extracts from spiked soils (200 μg/kg). Under these conditions determination of the analytes in soil type B can be attained at a level of 5 μg/kg.

So far, injections of about 50 mg of soil were sufficient to adequately monitor the recovery experiments (spiked level≥200 μg/kg). During the RPLC–UV analysis of recoveries at low levels (injection of 500 mg of soil), a large variation in retention times of analytes (R.S.D.s about 20%) was observed. Apparently the high load of apolar matrix constituents was not removed efficiently under the chromatographic conditions used. Hence, the column was cleaned after the chromatophic run with a small volume of methanol (1 ml). This approach (see Section 2) provided acceptable variations of retention times (R.S.D.s<2%) of the analytes and a chromatographic run time of 17 min including the time for washing and reconditioning the column.

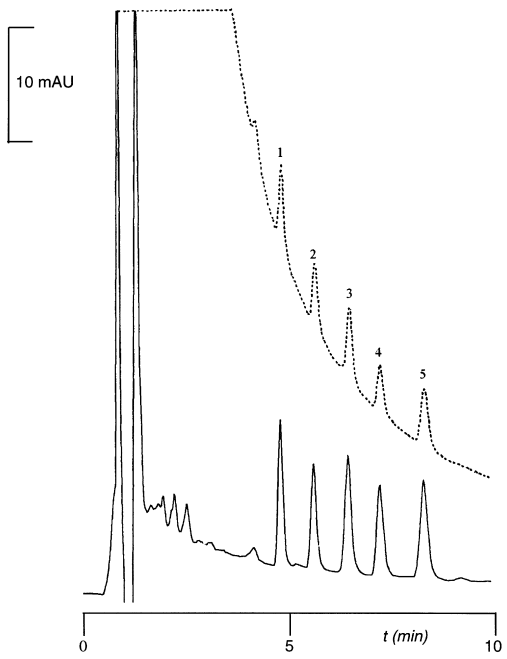


Fig. 1. RPLC–UV (226 nm) of extracts using different MASE solvents of soil samples (10 g) spiked with analytes at the level of 200 μg/kg. – – –, Extraction solvent, 20 ml of 0.1 *M* $NaHCO_3$ and 10 dichloromethane; ———, extraction solvent 20 ml dichloromethane–methanol (90:10, v/v). Injection 50 mg of soil; further LC and MASE conditions, see Section 2. Peaks: 1=cinosulfuron; 2=thifensulfuron-methyl; 3=metsulfuron-methyl; 4=sulfometuron-methyl; 5=chlorsulfuron.

4. Results

The response of the sulfonylurea compounds was linear for standards between 5 and 250 μg/l (n=5, r=0.999).

The multi-residue procedure was validated by analyzing a series of freshly-spiked samples and samples with aged residues (soil type B in both cases) fortified at three (1000, 200 and 20 μg/kg) and two (100 and 20 μg/kg) concentration levels, respectively. The recoveries and the relative standard

deviations given in Table 5 shows the performance data for this approach.

The recoveries obtained (≥90%) from the freshly-spiked samples show that the performance of the MASE method employing a organic solvent is comparable with existing procedures involving an aqueous basic extraction solvent [3,4,13,14,17].

Such a comparison cannot be made concerning the samples with aged residues because no data were found in the literature on these type of samples and/or samples with incurred residues. Both type of recovery experiments involve the same analytical procedure. This allows comparison of the data by making a pooled estimate of the standard deviation and employing the two-tailed *t*-test at the 5% level of significance [26]. This statistical evaluation showed that at the level of 100 μg/kg (compared with the 200 μg/kg freshly spiked) the residue recovered in the aged spiked samples was significantly lower for each herbicide according to the 5% level of confidence. Concerning the 20 μg/kg level a significant difference between freshly spiked and aged residues was only obtained for sulfometuron-methyl and chlorsulfuron.

Fig. 2 shows the RPLC–UV analysis of an extract of a soil sample (type B) spiked with the analytes at the level of 10 μg/kg. The figure shows that the procedure developed allows determination of the compounds in soil samples down to 5 μg/kg.

In combination with MASE, an efficient procedure is obtained providing a sample throughput of at least 24 samples per day.

UV detection at 226 nm is not very selective and, consequently, a confirmation method in case of positive samples should be available. A study is underway indicating that capillary column switching LC coupled to electrospray mass spectrometry (LC–LC–ES–MS) can be used for this purpose.

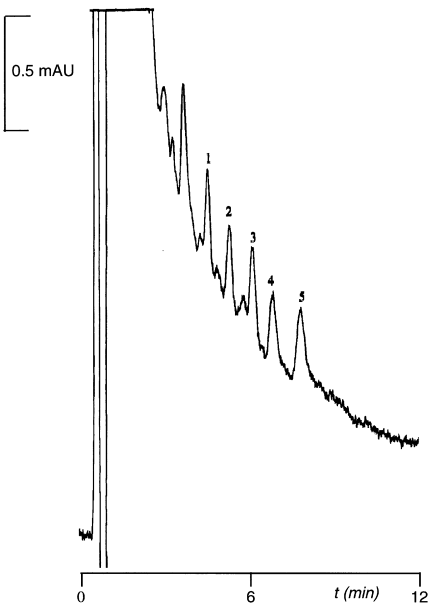


Fig. 2. RPLC–UV (226 nm) of an extract obtained with final procedure of a soil sample spiked with analytes at a level of 10 μg/kg. Injection 500 mg of soil. Procedure, see Section 2. Peaks: 1=cinosulfuron; 2=thifensulfuron–methyl; 3=metsulfuron–methyl; 4=sulfometuron–methyl; 5=chlorsulfuron.

5. Conclusion

This study illustrates that the combination of MASE and RPLC–UV is a convenient technique for

Table 5
Recoveries and R.S.D. (%) of freshly-spiked soil (B type) and aged residues (60 days at 4°C)

Herbicide	Recovery (%)				
	Freshly spiked			Aged residues	
	1000 μg/kg n=4	200 μg/kg n=4	20 μg/kg n=4	100 μg/kg n=5	20 μg/kg n=5
Cinosulfuron	101 (3)	102 (2)	78 (1)	91 (4)	75 (7)
Thifensulfuron-methyl	97 (3)	99 (2)	93 (1)	87 (3)	88 (9)
Metsulfuron-methyl	97 (2)	99 (2)	97 (6)	88 (4)	82 (4)
Sulfometuron-methyl	94 (3)	90 (3)	89 (6)	79 (3)	62 (9)
Chlorsulfuron	95 (2)	95 (2)	91 (1)	79 (3)	69 (6)

the multi-residue analysis of sulfonylureas herbicides at the low μg/kg level in soils. The benefits of MASE, shorter extraction times, reduction of solvent consumption, improved selectivity and the possibility of processing 12 samples simultaneously, make this technique a good alternative to conventional extraction procedures. Optimal extraction solvents for MASE cannot be deduced directly from those used in conventional procedures. For the less stable compounds one should ensure that the analytes are not decomposed during the extraction procedure. Solvent mixtures of dichloromethane and methanol seem to be very suitable for polar and medium-polar compounds.

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