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Journal of Chromatography A, 1058 (2004) 243–249
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Miniaturised pressurised liquid extraction of chloroanilines from soil with subsequent analysis by large-volume injection–gas chromatography–mass spectrometry

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Available online 19 June 2004

Abstract

A number of chloroanilines were extracted from soil by means of miniaturised pressurised liquid extraction (PLE). The extraction procedure was optimised for both large-volume on-column (LV-OC) and programmed-temperature vaporisation (PTV) injections combined with GC–MS. Hexane was the only extraction solvent suited for LV-OC and hexane/acetone gave the best results when using a PTV. Overall, the hexane/acetone-plus-PTV procedure shows better results than the hexane-plus-LV-OC method in terms of analyte recovery (36–109% versus 5–87%), repeatability (8–13% versus 4–31%) and detection limits. Both approaches allow detection of the chloroanilines in complex soil samples down to the 5–50 ng/g range. However, the PTV-based procedure is superior as regards robustness: over one hundred samples can be analysed without any maintenance being required.

Keywords: Pressurised liquid extraction; Soil; Programmed-temperature vaporisation; Chloroanilines

1. Introduction

Chloroanilines are a rather widespread class of pollutants that can reach the environment both as industrial by-products and as degradation products of phenylurea pesticides [1]. Their slight solubility in water (<1 g/l), extensive use and low biodegradability cause their ubiquitous presence in water, sediment and soil. Once in the environment, they can be adsorbed to soil, sediment or dissolved humic substances through electrostatic interactions, hydrophobic partitioning and covalent binding via their carbonyl group [2,3]. They are present in soil at relatively low concentrations, and because of their physico-chemical adsorption and binding to soil and humic material, chloroanilines persist for many years [4]. Due to their polarity extraction from soil is difficult. In addition, once extracted, the polar nature of the analytes easily plays an adverse role during injection and/or GC analysis. Two published procedures, report the extraction and analysis of chloroanilines from soil, using either solid–liquid partitioning with methanol under stirring, with subsequent SPE clean-up and LC–UV analysis [5] or headspace solid-phase microextraction (HS-SPME) and GC–ECD [6]. The first study only included a single chloroaniline. In the latter study, which discusses two chloroanilines, the recoveries were found to be highly matrix dependent and did not allow the quantification of chloroanilines in real samples. No method covering a large number of chloroanilines was found in the literature.

Soxhlet, the traditional extraction method for many pollutants from soil, normally requires large amounts of high-quality organic solvents, and long extraction times. In addition, clean-up and/or pre-concentration is required prior to GC analysis. Today, important alternative techniques are supercritical fluid extraction (SFE) [7,8], microwave-assisted extraction (MAE) [7,9,10] and pressurised liquid extraction (PLE) [11,12], which offer a better control of the extraction conditions, shorter extraction times

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doi:10.1016/j.chroma.2004.05.044

and higher selectivity. PLE has been applied for the extraction of a large variety of micro-contaminants, but not yet for chloroanilines. In 1995 PLE was accepted as a US EPA method for the extraction of water-insoluble or slightly water-soluble semivolatile organic compounds from soils, clays, sediments, sludges and waste solids [13].

The most important parameters affecting PLE efficiency are: extraction temperature, extraction time and extraction solvent. Several studies [11,14,15] have shown that pressure plays a minor role, and that a high pressure is used mainly to prevent the solvent from boiling at higher temperatures. As regards the solvent, hexane, dichloromethane, toluene and 1/1 mixtures of acetone/hexane and acetone/dichloromethane are frequently used [16].

Miniaturised PLE can be used to extract a rather small mass of sample (50–100 mg) with a small amount of solvent (a few 100 μl); the direct result is a rather dilute extract. However, if sufficiently large volumes of extract are injected, the desired limits of detection (LODs), typically 1–30 ng/g in the case of PAHs [14], can be reached without further pre-concentration and the risk of losing volatiles during evaporation.

The two main techniques for the introduction of large volumes of sample extracts are large-volume on-column (LV-OC) and programmed-temperature vaporisation (PTV) injection, with or without a solvent split. OC injection normally shows better repeatability for standards [17] and is the best technique when thermolabile or volatile analytes have to be determined. However, frequent analysis of samples with a high content of matrix constituents causes problems with high-boiling dirt remaining on the inner wall of the retention gap after the evaporation step which, in its turn, activates the retention gap and causes analyte adsorption, deterioration of peak shapes and poor long-term stability [18,19]. Consequently, the injected samples should be rather clean, which is usually true for tap and surface water extracts, but not for soil extracts, especially when no clean-up is performed. Therefore the latter are preferably analysed using a PTV injector, which largely prevents the (pre)column contamination, since the non-volatile matrix constituents remain in the liner which is easily exchangeable [20].

The main objective of this paper was to develop a miniaturised PLE procedure for the extraction of a number of chloroanilines from soil. Furthermore, it should be possible to directly analyse the extracts by GC–MS using either LV-OC or PTV injection.

2. Experimental

2.1. Chemicals

All chloroanilines were purchased from Aldrich Chemicals (Steinheim, Germany). The stock solution (1000 mg/l) was prepared in HPLC-grade acetonitrile (Merck, Schuchardt, Darmstadt, Germany). Hexane and ethyl acetate (both GC-grade) used for subsequent dilutions and extractions were purchased from Aldrich Chemicals and Riedel-de Haën (Seelze, Germany), respectively. Toluene (PA) was obtained from Riedel-de Haën and acetone (PA) from Merck. 4,4′-Difluorobiphenyl (100 μg/l, Aldrich Chemicals) was used as the internal standard.

The experiments for the optimisation of the extraction parameters were performed on an organic soil (C, 11.4%) sample collected in the gardens of the Free University (sieved to <53 μm) spiked at 500 ng/g with a solution of all target analytes in ethyl acetate. The spiking procedure consisted of spiking 1 g of soil with 1 ml of spiking solution, homogenising with a pestle for 5 min and allowing the solvent to evaporate for 24 h in a fume hood. The spiked soil was stored at $-18\,^{\circ}C$ until it was analysed. Two very polluted soils were taken from an industrial area in the Cengio region (north-western Italy).

2.2. PLE instrumentation and procedures

The PLE device used in this work was previously described in detail [14]. However, in the present application the 10 mm × 3.0 mm i.d. extraction cell was slightly modified to improve the robustness at high extraction temperatures. The cell had one wide open end for filling. The other end had a small hole to let the solvent through. Stainless-steel screens were placed at both ends of the extraction cell to prevent clogging of the tubing by soil particles. Additionally, a PEEK ring was positioned at the top of the cell, to seal it completely and avoid solvent leaks at the entrance of the cell. The exit was closed by a Valco connection. The cell is surrounded by a stainless-steel ring connected to a resistive wire for heating and to a thermocouple for temperature control. A ceramic ring around the cell provides thermal isolation. The temperature was programmed by the controller (made in house), which defined the starting temperature, the ramp rate to the final temperature and the hold time. The temperature programme was started manually at the beginning of each experiment.

A Phoenix 20 CU syringe pump (Fisons Instruments SPS, now ThermoFinnigan, Milan, Italy) was used to pump the extraction solvent into the cell. The tubing at the exit of the cell was connected to a 6-port automated Valco valve (Must HP6, Spark Holland, Emmen, The Netherlands) that allowed the switching from static to dynamic extraction conditions. All tubing was of stainless steel.

Extractions were performed by weighing 50 mg of soil into the extraction cell (85% of the total volume filled). The cell was then put into the holder and the extraction solvent was pressurised to the selected pressure in the constant pressure mode, to fill the cell and all the lines from the pump to the 6-port valve. Then the valve was closed and simultaneously the temperature programme was started. After the static extraction time, the valve was opened and the extract collected in a vial; next the internal standard was added and GC–MS analysis performed. The heating was switched off

and an additional volume of solvent was pumped through the cell and all the lines, to ensure proper cleaning. After emptying the cell, it was ultrasonically cleaned several times with fresh extraction solvent.

2.3. LV-OC–GC–MS

A GC 8000 equipped with an AS 800 autosampler, an on-column injector and a solvent vapour exit (SVE) and interfaced to a Fisons MD 800 mass spectrometer (all Fisons Instruments SPS, now ThermoFinnigan) were used. A diphenyltetramethyldisilazane-deactivated retention gap (5 m × 0.53 mm i.d.) was connected to a DB-XLB analytical column (30 m × 0.25 mm i.d., d_f 0.25 μm; Agilent Technologies, Palo Alto, CA, USA) and to an SVE valve through a glass Y-piece connector. Helium was used as the carrier gas at an inlet pressure of 150 kPa, which resulted in a flow rate of about 2.8 ml/min.

Hundred microlitres of sample were injected into the retention gap under partially concurrent solvent evaporation conditions, i.e. the injection speed was larger than the evaporation rate to ensure the formation of a solvent film on the inner wall of the retention gap in which the volatile analytes were trapped. The autosampler sent a signal to the SVE controller at the start of the injection; when most of the injected solvent had been evaporated and the carrier gas flow suddenly increased, the SVE controller actuated the closure of the SVE valve, and gave a start signal to the GC system [21]. For hexane this meant that 100 μl were injected at 12 μl/s and evaporated at 8.9 μl/s; this resulted in a total evaporation time and an SVE closure time of 11.2 s.

The GC temperature programme started at the standard boiling point of the solvent (69 °C for hexane; hold, 2 min), then at 10 °C/min to 280 °C (hold 21 min). The total run time was 44 min. The chloroanilines were quantified using extracted ion traces (*m/z* values are included in Table 1).

2.4. PTV–GC–MS

Cold split-less injections (20 μl) were performed on a Model 6890 GC equipped with an HP5972 MS (both from Hewlett-Packard, now Agilent Technologies) and a PTV injector (Optic 2-200, ATAS, Veldhoven, The Netherlands) provided with a multi-capillary liner. The initial injector temperature was 55 °C, which was kept for 30 s while venting the solvent; then the temperature was increased at 16 °C/s to 300 °C where it was kept until the end of the GC run. The split was opened after 97 s. GC separation was performed on a ZB-5 column (30 m × 0.25 mm i.d., d_f 0.25 μm; Phenomenex, Torrance, CA, USA). Helium was used as the carrier gas at an initial inlet pressure of 55 kPa; during the run the pressure increased gradually and reached 144 kPa at the end of the run. The oven temperature was programmed from 58 °C (hold, 2.5 min) to 190 °C at 30 °C/min, then at 10 °C/min to 300 °C (hold, 4 min); the total run time was 22 min. The chloroanilines were quantified using extracted ion traces or the selected ion monitoring (SIM) mode (*m/z* values are included in Table 1 below).

3. Results and discussion

3.1. LV-OC–GC–MS

Preliminary experiments for the optimisation of the extraction conditions were performed on an organic soil spiked with the chloroanilines at the 500 ng/g level. A combined static–dynamic extraction was considered the best option to ensure the removal of solvent remaining in the cell and washing of the soil and the capillary tubing.

When PLE is combined with LV-OC injection, not too much polar matrix material should be extracted. Ethyl acetate, toluene, hexane and hexane/acetone (1/1) were tested in preliminary experiments. However, after only three injections of extracts in ethyl acetate, obtained at extraction

Table 1
Analytical data for 100 μl injections of standard solutions of chloroanilines in LV-OC–GC–MS (extracted ion traces) and 20 μl injections in PTV–GC–MS (SIM)

Peak	Analyte	*m/z*	LV-OC		PTV	
			R^2	LOD (μg/l)	R^2	LOD (μg/l)
1	2-Chloroaniline	127	0.9996	0.05	0.9961	0.4
2	3-Chloroaniline	127	0.9984	0.2	0.9966	1.6
3	2,6-Dichloroaniline	161	0.9999	0.3	0.9964	0.4
4	2,4-Dichloroaniline	161	0.9999	0.4	0.9970	0.4
5	2,3-Dichloroaniline	161	0.9999	0.2	0.9971	0.3
6	3,5-Dichloroaniline	161	0.9999	0.2	0.9960	0.3
7	2,4,6-Trichloroaniline	195	0.9999	0.1	0.9972	10
8	2,4,5-Trichloroaniline	195	0.9996	0.3	0.9986	12
9	2,3,4-Trichloroaniline	195	0.9997	0.3	0.9973	11
10	2,3,5,6-Tetrachloroaniline	231	0.9993	0.1	0.9972	0.5
11	3,4,5-Trichloroaniline	195	0.9991	0.5	–	–
12	Pentachloroaniline	265	0.9986	0.1	0.9986	0.2

Table 2
Octanol/water partition coefficients, per cent recovery from soil spiked at 500 ng/g, and R.S.D. and LOD data for various PLE extractions with LV-OC or PTV injection

Peak	Analyte	$\log P_{ow}$	LV-OC		PTV		
			Hexane[a]		Ethyl acetate[b]	Hexane/acetone[c]	
			Recovery (%, R.S.D., $n = 6$)	LOD (ng/g soil)	Recovery (%, R.S.D., $n = 4$)	Recovery (%, R.S.D., $n = 8$)	LOD (ng/g soil)
1	2-Chloroaniline	1.90	56 (13)	1	37 (9)	46 (11)	1
2	3-Chloroaniline	1.88	5 (31)	35	22 (8)	36 (12)	2
3	2,6-Dichloroaniline	2.76	71 (7)	1	47 (12)	48 (11)	2
4	2,4-Dichloroaniline	2.78	47 (8)	2	68 (18)	79 (11)	0.2
5	2,3-Dichloroaniline	2.82	57 (5)	1	65 (18)	70 (13)	0.5
6	3,5-Dichloroaniline	2.90	14 (20)	8	46 (18)	50 (8)	1
7	2,4,6-Trichloroaniline	3.52	82 (5)	1	90 (24)	87 (13)	25
8	2,4,5-Trichloroaniline	3.45	61 (6)	3	110 (27)	109 (13)	3
9	2,3,4-Trichloroaniline	3.33	55 (8)	3	89 (22)	89 (11)	25
10	2,3,5,6-Tetrachloroaniline	4.10	87 (4)	25	99 (25)	92 (12)	0.5
11	3,4,5-Trichloroaniline	3.32	9 (30)	15	–	–	–
12	Pentachloroaniline	4.82	80 (13)	20	108 (26)	93 (12)	1

[a] Conditions: 60 °C, 20 min, 500 μl extracted, 100 μl injected; extracted ion traces.
[b] Conditions: 100 °C, 5 min, 100 μl extracted, 20 μl injected; SIM mode.
[c] Conditions: 100 °C, 10 min, 100 μl extracted, 20 μl injected; SIM mode.

temperatures of 60, 120 and 180 °C, respectively, and injected in that order, peaks became almost twice as broad and detectability became correspondingly poorer. At higher extraction temperatures, the extracts also became yellow, opaque or non-transparent. Moreover at temperatures above 120 °C, soil particles were flushed into the collection vial by the solvent, as was also observed by other authors [22]. Similar problems occurred when using hexane/acetone (1/1). The elution of soil particles can be the result of soluble material coagulating in the collection vial. Another possibility is that the exit screen in the extraction cell does not stay in place at high temperatures and lets particles pass between the screen and the extraction cell wall. The extracts obtained with toluene were even dirtier, which caused a larger loss of detectability. Because of the fast run-to-run peak deterioration and loss of detectability, it was impossible to determine the recoveries when extracting with ethyl acetate, toluene or hexane/acetone (1/1). If, on the other hand, hexane was used as solvent (temperature range, 35–100 °C), the extracts were clear and not coloured at any of the tested temperatures. Some peak broadening, however, still occurred after a few injections of extracts at temperatures above 60 °C. The latter temperature was therefore selected for further work.

The total volume of extract collected after the static and dynamic steps was optimised by collecting fractions of about 500 μl up to a total of 5 ml. Up to 90% of the analytes which can maximally be recovered was recovered in the first 500 μl of hexane. In the next fraction only a few per cent of the total amount of analyte was recovered and in further fractions only traces of analytes were detected. The extraction volume was therefore set to 500 μl. No attempts were made to reduce this volume, since adequate LODs could be obtained when injecting 100 μl and using extracted ion traces for quantification. As regards the extraction time, the analyte recoveries increased up to five-fold when increasing the static extraction period from 10 to 20 min. An extraction time of 30 min did not further improve the recoveries. Detailed results are given in Table 2.

As regards pressure, the range of 12–22 MPa was studied, but pressures above 12 MPa did not influence the extraction efficiency. Moreover, at pressures of over 20 MPa leaking occurred at the top of the extraction cell. To be on the safe side, the pressure was set to 15 MPa, as was also done earlier [14]. The optimum extraction conditions in combination with on-column injection were with hexane, extracting for 20 min at 60 °C and collecting 500 μl of solvent.

Calibration plots for standard solutions were linear in the range 0.5–250 μg/l. All had regression coefficients of 0.993 ($n = 6$) or higher and LODs of 0.5 μg/l or lower (Table 1). At the 1 μg/l level the relative standard deviations (R.S.D.s) were below 5%, with the exception of 3,4,5-chloroaniline (9%, $n = 3$).

Analyte recoveries from soil were satisfactory (47–87%) for all but three analytes (see below). The repeatability of the complete analytical procedure, that is, PLE plus LV-OC–GC–MS, was evaluated for six different extracts of one soil. The R.S.D.s were below 15% except for the three chloroanilines with the lowest recoveries, for which they were 20–30%. The relevant data are reported in Table 2, together with the octanol/water partition coefficients ($\log P_{ow}$) and the LODs in soil (1–35 ng/g). The widely different recoveries can only be partially related to the polarity of the analytes. Probably, the very low recoveries obtained for 3-chloroaniline, 3,5-dichloroaniline and 3,4,5-trichloroaniline can be explained by their chemical structure: they are the only three in the set of 12 which have no *ortho*-chlorine substitution. Because of a minimum of steric hindrance, they can more easily bind to the carbonyl

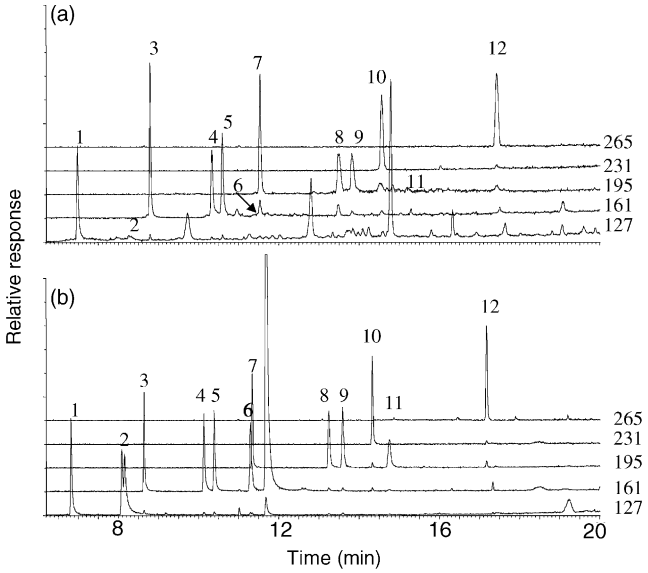

Fig. 1. (a) LV-OC–GC–MS ion traces of a soil extract spiked at 500 ng/g after PLE under optimimum conditions and (b) a 5 μg/l standard mixture of chloroanilines. For peak numbering, see Table 1.

groups of the humic acids present in the soil (11.4% carbon content), and will therefore need more drastic conditions, in terms of solvent and temperature, for efficient extraction. The co-injection of matrix constituents gives a more general explanation for the somewhat poor LODs and repeatability of the method. Fig. 1 shows ion traces of an organic soil extract, where the soil had been spiked at the 500 ng/g level and of a chloroaniline standard mixture (5 μg/l). The three analytes with the lowest recoveries can hardly be seen in the ion traces of the extract, while all others are easily identified.

When applying the procedure to a very polluted soil from a former industrial area in Cengio, Italy (soil 1), four of the target analytes were present at sufficiently high levels (2.7–13 μg/g) to be detectable in the TIC mode, while nine could be identified, at concentrations of 0.02–13 μg/g, by extracting the ion traces (see Table 3). In addition, several other ubiquitous pollutants, such as various chloro- and nitrobenzenes and chloro- and nitrotoluenes could be identified. When spiking part of the polluted soil at the 1 μg/g level before extraction and analysis, the additional concentrations found were much too high for several analytes. This indicates that ageing effects have to be considered for the present analyte/matrix combination, which is not unexpected [6,23]. Unfortunately, no certified reference material was available to further test and validate the analytical procedure.

Table 3
Quantification of chloroanilines in soil, in μg/g

Peak	Analyte	Soil 1		Soil 2
		LV-OC ($n = 3$)	PTV ($n = 2$)	PTV ($n = 2$)
1	2-Chloroaniline	7.5	2.8	5.6
2	3-Chloroaniline	7.5	3.0	6.2
3	2,6-Dichloroaniline	0.07	0.03	0.02
4	2,4-Dichloroaniline	13	1.7	3.5
5	2,3-Dichloroaniline	2.7	1.5	0.2
6	3,5-Dichloroaniline	1.0	0.4	0.5
7	2,4,6-Trichloroaniline	0.02	n.d.	0.06
8	2,4,5-Trichloroaniline	0.08	0.04	9.8
9	2,3,4-Trichloroaniline	0.02	0.01	0.09
10	2,3,5,6-Tetrachloroaniline	n.d.	0.004	0.01
12	Pentachloroaniline	n.d.	0.004	0.01

To our opinion, the method cannot be called fully satisfactory for routine analysis because of the occasionally poor repeatability but, mainly, the need for a frequent exchange of the retention gap. Under the present, rather gentle, extraction conditions (60 °C, 20 min, 15 MPa) disturbing peak broadening typically started to occur after some fifty injections.

3.2. PTV–GC–MS

Because the best injection technique for dirty samples is generally by means of a PTV, this technique was also studied. The current set-up could not be used for the injection of volumes larger than 20 μl. To make up for the loss of detectability compared with LV-OC, quantification was performed in the SIM mode instead of by using extracted ion traces. After fifteen 20 μl injections of extracts of a spiked garden soil, extracted with toluene at 180 °C, there was no peak broadening, and no loss of volatile analytes (monochloroanilines); this is evident from the SIM traces of Fig. 2. Since the only extracts that can be analysed by LV-OC–GC–MS were those in hexane, and the first

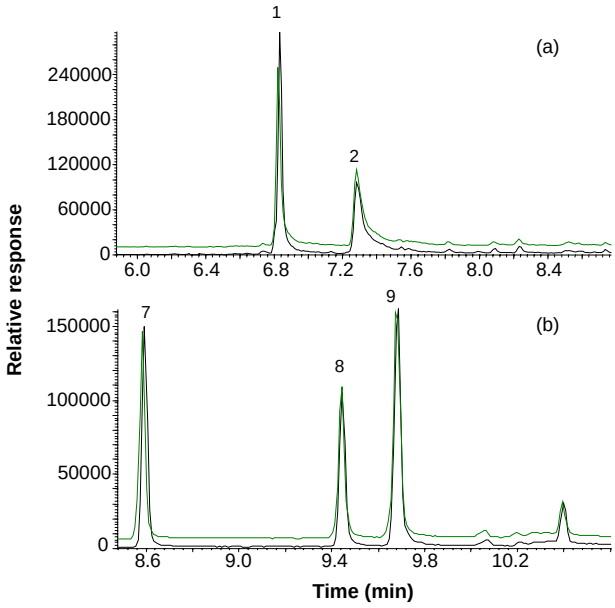

Fig. 2. SIM chromatograms for (a) monochloroanilines (*m*/*z* 127) and (b) trichloroanilines (*m*/*z* 195) isolated from a highly complex soil sample by PLE with toluene at 180 °C, and analysed by PTV–GC–MS. The traces for the first and the 15th injection are shown. For peak numbering, see Table 1.

results with PTV injection were promising, it was decided to further optimise the PLE procedure and analyse the extracts by PTV–GC–MS. In this case, only polar solvents (hexane/acetone (1/1) and ethyl acetate) were tested.

Static extractions were performed at 75, 100 or 125 °C and for 5, 10 or 20 min, but now by collecting fractions of about 100 μl and injecting 20 μl. Both solvents gave yellow-coloured extracts, but there were little or no problems with interfering peaks, no doubt partly because of quantification in the SIM mode. For hexane/acetone (1/1), 10 min PLE at 125 °C gave the highest recoveries (28–108%). At 100 °C (10 min) the recoveries were closely similar (36–109%), but the R.S.D.s were much better, that is 8–13% compared to 13–27% at the higher temperature. With ethyl acetate the best recoveries (22–110%) were found when extracting at 100 °C for 5 min. However, both the recoveries and the repeatability (8–27%) were poorer than with hexane/acetone (Table 2). Both solvents gave better recoveries than hexane for all analytes but 2,6-dichloroaniline, and especially for 3-chloroaniline and 3,5-dichloroaniline. No correlation was found between the recoveries and the chemical structures of the analytes. 3,4,5-Trichloroaniline could not be determined because of coelution with matrix interferences. When analysing several sequentially collected fractions, it was found that 100 μl was enough to quantitatively elute the analytes, irrespective of the extraction solvent used. The best extraction conditions were found when using hexane/acetone and extracting at 100 °C and 15 MPa for 10 min (Table 2).

With the PTV–GC–MS method, the LODs were similar to those obtained with the LV-OC method except for the trichloroanilines which had much higher LODs (10–12 μg/l, Table 1) because of a relatively high noise level for *m/z* 195 with the Model 5972 MS used. The linear regression coefficients of the calibration plots were slightly poorer than those obtained with LV-OC, but were all still above 0.996. The linear range was at least 20–1000 μg/l (2,4-dichloroaniline, 20–500 μg/l).

The LODs for the extraction from soil (with hexane/acetone) plus the PTV–GC–MS analysis were somewhat better than those for the on-column method (Table 2), namely 0.2–25 ng/g compared to 1–35 ng/g. The lower LODs can be explained by the combination of better peak shapes and a lower noise level because of the use of a PTV and analysis in the SIM mode instead of by extracted ion traces. No peak broadening was observed when using PTV injection and a single PTV liner could be used for hundreds of injections.

To test the hexane/acetone method on real samples, soil 1 (Cengio, Italy) was analysed by PLE plus PTV–GC–MS; the results were rather similar to those obtained with the hexane plus LV-OC method but, in most instances, lower (Table 3). This probably reflects the higher selectivity of the alternative procedure. Several chloroanilines were positively identified with both methods, but with the hexane/acetone method two more anilines could be identified, 2,3,5,6-tetrachloroaniline and pentachloroaniline. The hexane/acetone method was also used to analyse a second sample, from the same region, which contained even higher levels of chloroanilines (soil 2, Table 3). SIM-mode GC–MS chromatograms of a standard as well as soils 1 and 2, are shown in Fig. 3. Although the injected extracts in hexane/acetone (1/1) were much more contaminated than extracts in hexane, the performance of the hexane/acetone plus PTV approach was much better than that with hexane plus LV-OC injection.

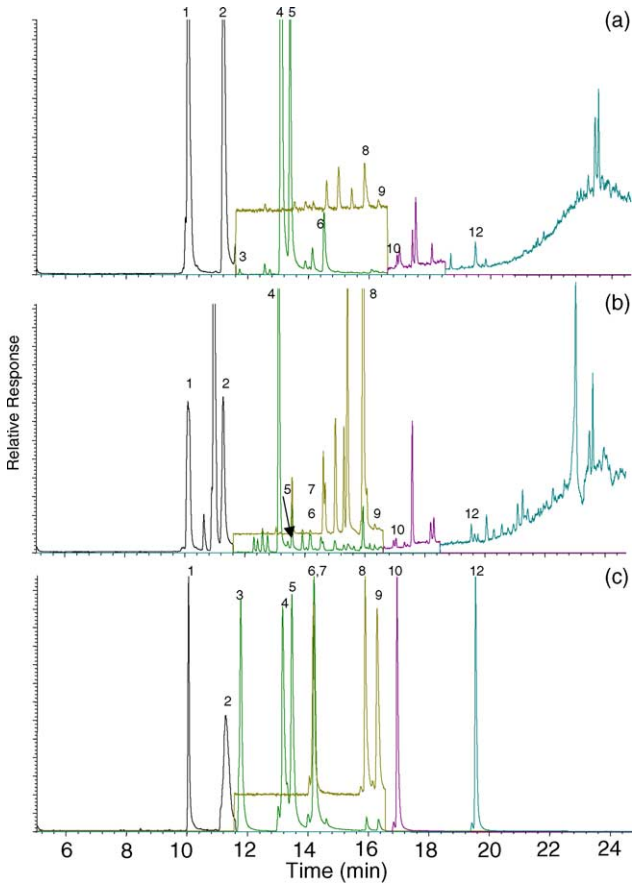

Fig. 3. PTV–GC–MS (SIM) chromatograms of sample extracts of (a) soil 1 and (b) soil 2 from Cengio, Italy, extracted with hexane/acetone (1/1) at 100 °C for 10 min, and (c) a standard at 500 μg/l. For peak numbering, see Table 1.

4. Conclusions

Miniaturised PLE offers the possibility to efficiently extract chloroanilines from soil. Compared to classical methodologies the amount of sample is reduced from 10 g to 50 mg and the solvent consumption from 20–200 to 0.1–0.5 ml. When combining PLE with LV-OC–GC–MS, the only suitable solvent was hexane. With this solvent, the recoveries were highly analyte dependent but even recoveries of about 10% allowed quantification of the analytes in soil at concentrations down to at least 50 ng/g. Unfortunately, the on-column method was not robust enough for the analysis of a large number of dirty extracts. When PLE

was optimised with more polar solvents and the extracts were analysed by PTV–GC–MS, the recoveries improved and became much less analyte dependent than with hexane. In addition, the repeatability improved. The LODs were, in most instances, similar to—or better than—obtained before, and almost all analytes could now be detected down to about 10 ng/g. The main advantage was, however, the distinctly increased robustness: more than one hundred sample injections could be made without any experimental or maintenance problem.

Acknowledgements

The authors thank the European Union for the support given to E.M.K. via a Training and Mobility of Researchers grant (no. FMBICT983012).

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