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Liquid chromatography–atmospheric pressure chemical ionization mass spectrometry for chlorinated phenolic compounds Application to the analysis of polluted soils

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Abstract

Liquid chromatography coupled to atmospheric pressure chemical ionization mass spectrometry (LC–APCI-MS) with negative ion detection was applied to the determination of chlorinated phenolic compounds in contaminated soils. A ternary mobile phase [ammonium acetate–acetic acid (5 m*M*, pH 4.5)]–acetonitrile–methanol (60:30:10, v/v/v) was used to separate 17 chlorophenols. MS conditions were optimized in order to achieve maximum sensitivity. The $[M-H]^-$ ion was the main ion for the low chlorinated phenols whereas the $[M-H-HCl]^-$ ion was the main one for the high (tri-, tetra- and penta-) chlorophenols. Abundant structure information can be obtained even at low extraction voltages from losses of HCl units. Detection limits for standard solutions between 0.1 and 10 ng injected and good linearity and reproducibility were observed. The optimum LC–APCI-MS conditions were applied to the analysis of chlorophenols in a contaminated soil.

Keywords: Environmental analysis; Soil; Organochlorine compounds; Chlorophenols; Phenols

1. Introduction

Chlorinated phenols (CPs) are widely known to be pollutants of environmental waters and soils as a results of a wide variety of industrial processes [1,2]. Liquid chromatographic methods have been developed in recent years using ultraviolet [3,4], electrochemical (ED) [5–10] and fluorescence [11,12] detection mainly for the determination of the 11 priority pollutant phenols listed by the US Environmental Protection Agency (EPA) with the advantage that no time-consuming derivatization procedures [13–16] as in gas chromatography (GC) are needed. In a previous work [17], we have demonstrated the capability of an LC–ED method for the determination of chlorophenols in polluted soils but environmental samples are very complex matrixes and there is a need for reliable identification of sample constituents that can be achieved only by mass spectrometry (MS), which has the advantage over these conventional detectors that it can provide information for confirmation or unambiguous identification.

Thermospray mass spectrometry (TSP-MS) has been used for the identification of some phenols in natural waters [18–21], but in the field of LC–MS coupling, there is much current interest in the use of atmospheric pressure ionization methods (LC–API-MS), i.e., electrospray (ES) and atmospheric pressure chemical ionization (APCI) due to their higher sensitivity compared to TSP or particle beam (PB). Some environmental applications of LC–API-MS methods have been reported. For example, chloronitrophenols [22] and pentachlorophenol [23] have

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been analysed by ES-MS and some polyphenolic compounds by APCI-MS [24]. The 11 EPA phenols have also been analysed by ES and APCI in water samples [25,26]. In a previous paper [27], ES-MS and APCI-MS were compared to test their applicability to the analysis of phenolic compounds in environmental waters thus concluding that a better performance can be achieved by using the APCI ion source.

To our knowledge, LC–APCI-MS has not been applied to the identification/determination of CPs in soil samples. So, the specific objectives of this work were: (i) to optimize the LC–MS parameters, (ii) to study the capability of the method to analyse CPs in polluted soils in terms of precision, linearity and detection limits and (iii) to apply the method to the identification/quantification of chlorophenols in a highly contaminated soil.

2. Experimental

2.1. Chemicals

The phenols studied were obtained from the following sources: 2-chlorophenol (2CP), 3-chlorophenol (3CP), 2,3-dichlorophenol (23DCP), 2,4-dichlorophenol (24DCP), 2,5-dichlorophenol (25DCP), 2,6-dichlorophenol (26DCP), 3,4-dichlorophenol (34DCP), 3,5-dichlorophenol (35DCP), 2,3,4-trichlorophenol (234TCP), 2,3,5-trichlorophenol (235TCP), 2,3,6-trichlorophenol (236TCP), 2,4,5-trichlorophenol (245TCP) and 2,4,6-trichlorophenol (246TCP) from Aldrich (Milwaukee, WI); 4-chlorophenol (4CP) from Carlo Erba (Milan, Italy); 2,3,4,6-tetrachlorophenol (2346TeCP), 2,3,5,6-tetrachlorophenol (2356TeCP) and pentachlorophenol (PCP) from Chem Service (West Chester, PA, USA) and 2,4-dibromophenol (24DBP) from Tokyo Kasei (Tokyo, Japan). Stock solutions (500 mg l^{-1}) of individual phenol standards were prepared in acetonitrile. A mixed stock solution (10 mg l^{-1} of each compound) containing all the standards was prepared from individual phenol standards by diluting with acetonitrile. Calibration standards were prepared by appropriate dilution with mobile phase. Acetonitrile and methanol (HPLC-grade) were from J.T.Baker (Deventer, Netherlands). The solvents *n*-hexane and acetone (residue analysis grade) and the ammonium acetate and acetic acid (analytical grade) were supplied by Merck (Darmstadt, Germany). All the solutions were passed through a 0.45-μm nylon filter before injection into the LC system.

2.2. Instruments and conditions

LC was performed using a LKB Pharmacia (Bromma, Sweden) Model 2520 and a Hewlett-Packard (Palo Alto, CA, USA) Series 1050 automatic injector. Separations were performed using a Shandon Hypersil Green Env C_8 column (5 μm particle size, 250×4.6 mm I.D.) from Shandon Scientific (Cheshire, UK) and a Pelliguard LC-18 (20 μm) pre-column (20×4 mm I.D.) from Supelco (Gland, Switzerland).

An isocratic ternary mobile phase of [ammonium acetate–acetic acid (5 m*M*, pH 4.5)]–acetonitrile–methanol (60:30:10, v/v/v) at 1.2 ml min^{-1} was used as described previously [17]. Separations were carried out at room temperature and 50 μl was injected into the LC–MS system.

MS was performed in a VG Platform II (Fisons Instruments, VG Biotech, Altrincham, UK) quadrupole mass spectrometer equipped with an APCI interface and using nitrogen as nebulising gas (150 l h^{-1}). Drying nitrogen was heated at 120°C and introduced into the capillary region at a flow-rate of 400 l h^{-1}. The capillary was heated to a temperature of 450°C. The corona voltage was held at a value of −2 kV for the negative mode. The extraction voltage ranged from −10 to −80 V. For data acquisition in full scan mode, the mass spectrometer was operated over a mass range of m/z 40–300 in the centroid mode at a cycle time of 1.00 s and an interscan time of 0.10 s. Quantitation was performed by using the time scheduled selected ion monitoring (SIM) mode at the masses given in Table 1, with a dwell time of 100 ms. The tuning and mass calibration was performed using a standard solution of phenols in mobile phase.

2.3. Sample analysis

The studied soil (CRM-530) is a reference material supplied by the Bureau Community of Reference (BCR) of the Commission of the European Com-

Table 1
Time-scheduled under SIM conditions using the LC–APCI-MS conditions described in Section 2.2

Compound	*m/z*	
	−30 V	−50 V
2CP, 3CP, 4CP	127, 129	91, 127, 129
23DCP, 24DCP, 25DCP, 26DCP, 34DCP, 35DCP	161, 163, 165	125, 161, 163, 165
236TCP, 245TCP, 236TCP, 245TCP, 246TCP	195, 197, 199	107, 159, 195, 199
2346TeCP, 2356TeCP	229, 231, 233, 195	195, 229, 231, 233
PCP	263, 265, 267, 195	195, 229, 231, 233

For abbreviations of chlorophenols, see Section 2.1.

munities (Brussels, Belgium). The CRM-530 is a high clay soil contaminated by chlorophenols, chlorobenzenes, chlorinated pesticides (e.g., benzene hexachloride, HCH), aromatic carboxylic acids, chlorinated dibenzo-*p*-dioxins and chlorinated dibenzofurans as a result of industrial processes. 0.2 g of the CRM-530 soil was accurately weighed and prewetted with 2 ml of 0.5 *M* H_2SO_4 for 2 h. The wetted sample was then transferred to a Soxhlet apparatus and extracted with 200 ml of a mixture of acetone–hexane (3:2, v/v) for 12 h. The extract was evaporated to ca. 2 ml after the addition of 2 ml of acetonitrile (boiling point 82°C) to avoid losses of phenols by evaporation. High recoveries (from 72 to 96%) were obtained with this procedure [17]. After the addition of 2,4-dibromophenol as the internal standard, the volume was made up to 5.0 ml with mobile phase. The extracts were analysed by LC–APCI-MS using the optimum working conditions for the 17 chlorophenols studied. To estimate the detection limits, a soil previously shown to be free of chlorophenols was spiked at low concentrations and treated similarly to the CRM-530 sample.

3. Results and discussion

3.1. Optimization of HPLC–MS parameters

Seventeen chlorophenols (2CP, 3CP, 4CP, 23DCP, 24DCP, 25DCP, 26DCP, 34DCP, 35DCP, 234TCP, 235TCP, 236TCP, 245TCP, 246TCP, 2346TeCP, 2356TeCP and PCP), which can be present in soils, were separated using an isocratic mobile phase [ammonium acetate–acetic acid (5 m*M*, pH 4.5)]–acetonitrile–methanol (60:30:10, v/v/v) at 1.2 ml min^{-1}. In Fig. 1 the total ion chromatogram (TIC) of a standard solution (1 mg l^{-1}, 50 μl injected) is given. To optimize the APCI-MS conditions, different parameters influencing mass spectra were investigated: the drying and auxiliary nitrogen flow-rates, the source and probe temperatures, and the corona and cone potentials were varied in flow injection analysis (FIA) experiments with 2CP, 34DCP, 245TCP, 2346TeCP and PCP. The optimum working conditions thus established were used throughout further experiments (Section 2.2).

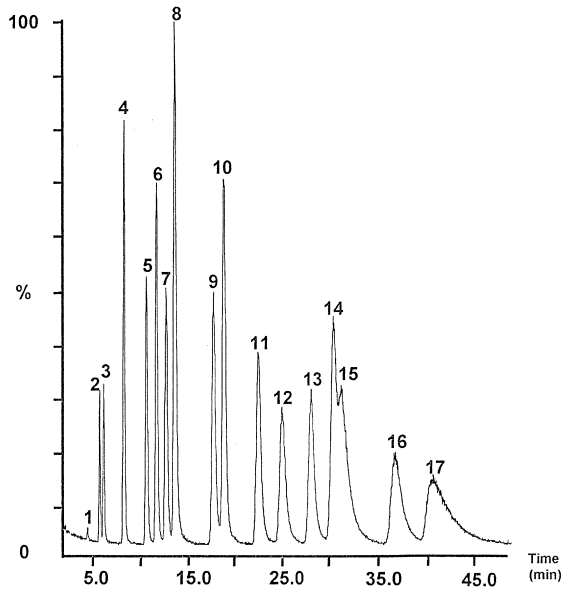

Fig. 1. TIC of a standard solution of 17 chlorophenols (1 mg l^{-1}, 50 μl injected) in mobile phase [ammonium acetate–acetic acid (5 m*M*, pH 4.5)]–acetonitrile–methanol (60:30:10, v/v/v) at 1.2 ml min^{-1}. LC–APCI-MS conditions as described in Section 2.2. Peaks: 1=2CP, 2=4CP, 3=3CP, 4=26DCP, 5=23DCP, 6=25DCP, 7=24DCP, 8=34DCP, 9=236TCP, 10=35DCP, 11=246TCP, 12=234TCP, 13=245TCP, 14=235TCP, 15=2356TeCP, 16=2346TeCP, 17=PCP. For abbreviations see Section 2.1.

Different source and probe temperatures were tested. At low values (80°C and 200°C, respectively), no fragmentation and a low signal-to-noise ratio were observed for the chlorophenols. Moreover, source contamination was produced after one day of work. For the improvement of the system performance and the prevention of source contamination, higher temperatures (120°C for the source and 450°C for the capillary) were used. The results showed more fragmentation with no source contamination after a working week.

In order to identify the main ions for every analyte, FIA was used to introduce the analytes (20 μl of a 1 mg l^{-1} individual standard solution) and then the mass spectra were obtained in full scan mode. The extraction voltage was then varied from −10 to −80 V in order to find the maximum response using the optimum LC–MS conditions described above (Section 2.2). The main ions obtained at two extraction voltages (−30 and −50 V) are given in Table 2. Low chlorinated phenols showed the $[M-H]^-$ ion as base peak in the MS spectra whereas the $[M-H-HCl]^-$ ion was detected with a relative abundance up to 95% depending on the compound and the extraction voltage. The high chlorinated phenols (tri-, tetra- and pentachlorophenol) demonstrated different behavior being the $[M-H-HCl]^-$ ion the base peak at all the studied extraction voltages (from −10 to −80 V). For all the studied compounds, typical losses of HCl and Cl were observed. Moreover, the spectra at −50 V for all the studied compounds except monoclorophenols had a pattern depending on the position of the substituents. For instance, 2346TeCP and 2356TeCP gave a quite different relative abundance for the $[M-H]^-$ ion and for dichlorophenols the relative abundance for the $[M-H-HCl]^-$ ion changes from 10 to 95%. This fact can be used to distinguish positional isomers.

In order to establish the optimum extraction voltage for all the compounds, normalized absolute abundances of the base peak for each compound vs. the extraction voltage were studied. Higher responses were obtained at −30 V for all the compounds so, this value was chosen for identification/quantification purposes. Additional structure information could be obtained by increasing the extraction voltage as can be seen in Fig. 2 where, as an example, the normalized absolute abundance (%) of the different ions for 25DCP and 2346TeCP at extraction voltages up to −80 V is given.

Therefore, for confirmation purposes, a higher extraction voltage (−50 V) was applied thus recording the characteristic ions (Table 1) of the previously identified compounds. This voltage was chosen as a compromise between the fragmentation and the sensitivity thus obtained.

3.2. Quality parameters

Calibration graphs were plotted (eight points) for standard solutions (between 25 pg and 50 ng injected). A wide range of linearity for all the phenols and good correlation coefficients (r^2 between 0.9910 and 0.9988) were obtained. For the study of the reproducibility of the LC–MS method, five replicate determinations on the same day of a standard solution (0.5 mg l^{-1} of each phenol) were carried out under the optimal LC–MS conditions (precision run-to-run). Moreover, five injections performed on three different days of that solution allowed day-to-day precision to be established. Relative standard deviations (R.S.D.s) ranged from 4 to 7% for the run-to-run precision and from 7 to 14% for the day-to-day precision, showing a good reproducibility of the method.

Limits of detection (LODs) for the 17 chlorophenols (SIM mode, −30 V, signal-to-noise ratio 3:1) were calculated using the base peak and ranged from 0.1 to 10 ng injected for standard solutions (Table 3). LODs for soils were estimated using a soil free of chlorophenols spiked at low μg g^{-1} and ranged from 0.01 to 0.7 μg g^{-1}. Comparing the LODs (based on ng injected) for standard solutions and soil samples, it can be deduced that matrix effects, even in complex samples with no clean-up, were not relevant when the described LC–APCI-MS technique is used.

3.3. Application

The method was applied for the analysis of chlorophenols in a candidate reference material CRM-530. Fifteen chlorophenols have been identified in the sample and then quantified using the external standard calibration method with 2,4-dib-

Table 2
Mass spectra fragments, relative abundances of chlorophenols using [ammonium acetate–acetic acid (pH 4.5, 5 m*M*)]–acetonitrile–methanol (60:30:10) as LC eluent and extraction voltages of −30 V and −50 V under the APCI-MS conditions in the FIA mode described in Section 2.2

Compound	M_r	m/z[a]	Tentative assignation	Relative abundance (%)	
				−30 V	−50 V
2CP	128	127	$[M-H]^-$	100	100
		91	$[M-H-HCl]^-$	–	20
3CP	128	127	$[M-H]^-$	100	100
		91	$[M-H-HCl]^-$	–	15
4CP	128	127	$[M-H]^-$	100	100
		91	$[M-H-HCl]^-$	–	25
23DCP	162	161	$[M-H]^-$	100	100
		125	$[M-H-HCl]$	–	40
24DCP	162	161	$[M-H]^-$	100	100
		125	$[M-H-HCl]$	6	95
25DCP	162	161	$[M-H]^-$	100	100
		125	$[M-H-HCl]$	2	77
26DCP	162	161	$[M-H]^-$	100	100
		125	$[M-H-HCl]^-$	5	10
34DCP	162	161	$[M-H]^-$	100	67
		125	$[M-H-HCl]^-$	8	100
35DCP	162	161	$[M-H]^-$	100	100
		125	$[M-H-HCl]^-$	5	65
234TCP	196	195	$[M-H]^-$	30	44
		159	$[M-H-HCl]^-$	100	100
		123	$[M-H-2HCl]^-$	7	94
235TCP	196	195	$[M-H]^-$	8	12
		159	$[M-H-HCl]^-$	100	100
		123	$[M-H-2HCl]^-$	3	60
236TCP	196	195	$[M-H]^-$	28	48
		159	$[M-H-HCl]^-$	100	100
		123	$[M-H-2HCl]^-$	4	50
245TCP	196	195	$[M-H]^-$	35	42
		159	$[M-H-HCl]^-$	100	100
		123	$[M-H-2HCl]^-$	5	80
246TCP	196	195	$[M-H]^-$	60	100
		159	$[M-H-HCl]^-$	100	65
		123	$[M-H-2HCl]^-$	–	45
2346TeCP	230	229	$[M-H]^-$	25	30
		193	$[M-H-HCl]^-$	100	100
		159	$[M-HCl-Cl]^-$	4	90
2356TeCP	230	229	$[M-H]^-$	4	6
		193	$[M-H-HCl]^-$	100	100
		159	$[M-HCl-Cl]^-$	–	90
PCP	264	263	$[M-H]^-$	1	-
		229	$[M-Cl]^-$	100	100
		193	$[M-HCl-Cl]^-$	7	100

[a] Only the first peak in the isotopic chloride pattern is given.

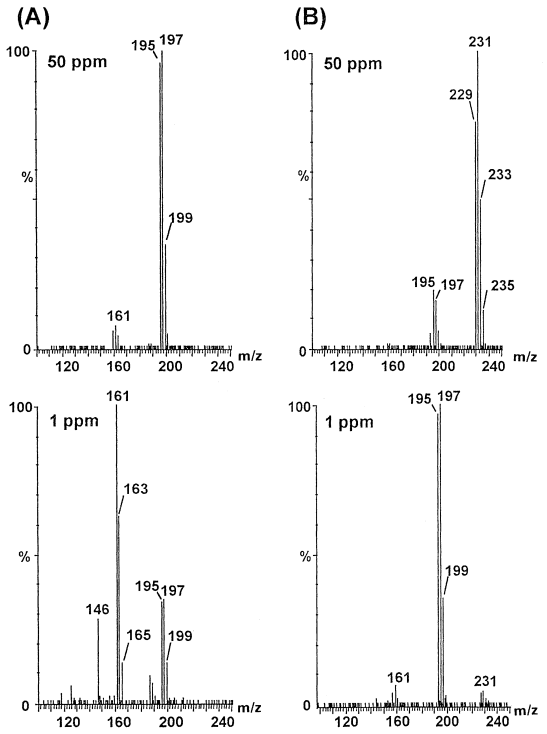

Fig. 2. Variation of the normalized absolute abundance (%) for some fragment ions vs. the extraction voltage for 2,5-dichlorophenol (A) and 2,3,4,6-tetrachlorophenol (B) using the LC–APCI-MS conditions described in Section 2.2. Tentative assignation of ions in (A) m/z 161, $[M-H]^-$; 125, $[M-H-HCl]^-$. Tentative assignation of ions in (B): m/z 229, $[M-H]^-$; 193, $[M-H-HCl]^-$; m/z 159, $[M-HCl-Cl]^-$.

romophenol as internal standard. The ion chromatograms are given in Fig. 3. In Table 4, the results corresponding to the quantification of the four certified chlorophenols (3CP, 34CP, 245CP and 2346CP) are presented. These results are in good agreement with the results obtained by our laboratory in the certification exercise of CRM-530 using LC with electrochemical (amperometric) detection and with the results of all the 14 participating laboratories. It can be observed that similar reproducibilities were obtained by using both modes of detection.

4. Conclusions

The application of LC-APCI-MS to the determination of chlorinated phenols in soil samples has been studied. Optimization of LC–MS parameters was performed in order to obtain maximum sensitivity. The mass spectra for 17 chlorophenols were studied showing typical losses of HCl and Cl units. Good linearity and reproducibility (run-to-run precision between 4 and 7% and day-to-day precision between 7 and 14%) and good detection limits (ranging from 0.01 and 0.7 $\mu g\ g^{-1}$ for soil samples) were obtained. The method has been validated by analysing a candidate reference material soil CRM-530 highly contaminated by other chlorinated compounds. The results obtained showed that the LC–APCI-MS method can be proposed for the analysis of chlorophenols in contaminated soils with the main advantages over the GC–electron-capture detection or GC–MS methods described in the literature that no clean-up and no derivatization were needed and over the LC–ED method previously reported [17] that the analytes could be unambiguous identified in the samples.

Table 3
Limits of detection for the 17 chlorophenols studied in standard solutions and in soil samples using the optimum LC–APCI-MS conditions described in Section 2.2

Compound	Limits of detection		
	Standard solutions[a] (ng)	Soil samples[b]	
		(ng)	($\mu g\ g^{-1}$)
2CP	7.5	10	0.7
3CP	1.2	5	0.3
4CP	1.2	5	0.3
23DCP	0.2	2	0.1
24DCP	0.2	0.2	0.02
25DCP	0.1	0.5	0.03
26DCP	0.1	1	0.07
34DCP	0.1	0.3	0.02
35DCP	0.1	0.7	0.05
234TCP	0.3	0.2	0.01
235TCP	0.4	1	0.07
236TCP	0.2	0.5	0.03
245TCP	0.3	0.1	0.01
246TCP	0.2	0.2	0.01
2346TeCP	0.2	0.1	0.01
2356TeCP	0.1	0.2	0.02
PCP	0.1	0.1	0.01

For abbreviations, see Section 2.1.
[a] In LC mobile phase.
[b] Estimated after Soxhlet extraction of 1.6 g of spiked non-contaminated soil. For more details, see Section 2.3.

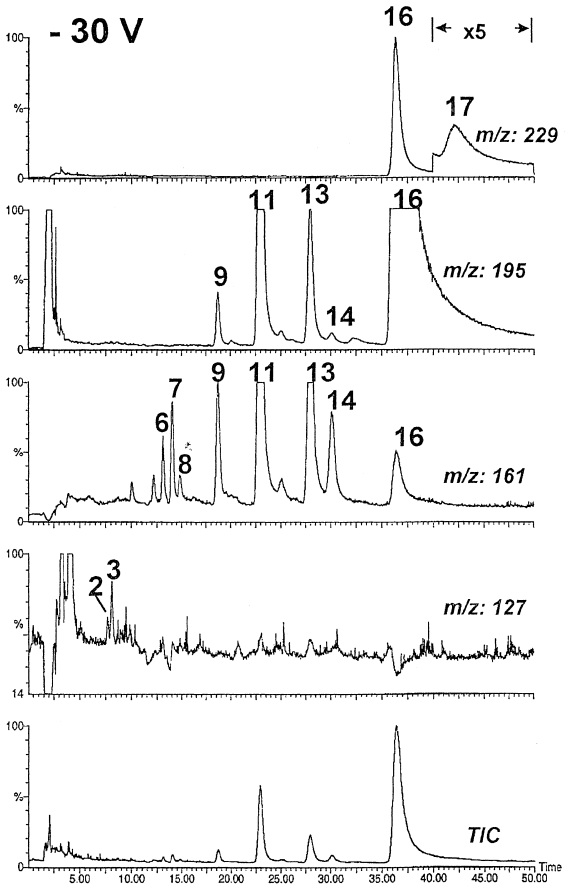

Fig. 3. LC–APCI-MS analysis (SIM) in negative mode at an extraction voltage of −30 V of chlorophenols in CRM-530 soil sample. Chromatographic conditions as in Fig. 1. LC–MS conditions described in Section 2.2. The lower trace is the TIC obtained by summing all ions above. Peaks: 1=3CP, 2=34CP, 3=245CP, 4=2346CP, 5=PCP. For abbreviations, see Section 2.1. Time scale in min.

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Table 4
Analysis of CRM-530 soil sample

Compound	Concentration ($\mu g\ g^{-1}$): mean±S.D.		
	LC–APCI-MS[a] ($n=2$)	LC–ED[b] ($n=6$)	Certification laboratories[c]
3CP	5.36±0.80	5.63±0.27	6.80±1.84
34DCP	5.54±0.21	5.06±0.25	7.04±1.73
245TCP	46.01±0.24	41.89±2.28	44.41±13.03
2346TeCP	73.44±9.70	77.79±3.84	82.57±17.62

[a] LC–APCI-MS conditions described in Section 2.2 for soil samples.
[b] LC with electrochemical (ED) amperometric detection at +1100 mV with a mobile phase [sodium acetate–acetic acid (30 m*M*, pH 4.5)]–acetonitrile–methanol (60:30:10, v/v/v) at 1.5 ml min^{-1} was used [23].
[c] Mean and standard deviation for the 14 participating laboratories in the certification exercise.

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