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Determination of linuron and related compounds in soil by microwave-assisted solvent extraction and reversed-phase liquid chromatography with UV detection

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Abstract

The combination of microwave-assisted solvent extraction (MASE) and reversed-phase liquid chromatography (RPLC) with UV detection has been investigated for the efficient determination of phenylurea herbicides in soils involving the single-residue method (SRM) approach (linuron) and the multi-residue method (MRM) approach (monuron, monolinuron, isoproturon, metobromuron, diuron and linuron). Critical parameters of MASE, viz. extraction temperature, water content and extraction solvent were varied in order to optimise recoveries of the analytes while simultaneously minimising co-extraction of soil interferences. The optimised extraction procedure was applied to different types of soil with an organic carbon content of 0.4–16.7%. Besides freshly spiked soil samples, method validation included the analysis of samples with aged residues. A comparative study between the applicability of RPLC–UV without and with the use of column switching for the processing of uncleaned extracts, was carried out. For some of the tested analyte/matrix combinations the one-column approach (LC mode) is feasible. In comparison to LC, coupled-column LC (LC–LC mode) provides high selectivity in single-residue analysis (linuron) and, although less pronounced in multi-residue analysis (all six phenylurea herbicides), the clean-up performance of LC–LC improves both time of analysis and sample throughput. In the MRM approach the developed procedure involving MASE and LC–LC–UV provided acceptable recoveries (range, 80–120%) and RSDs (<12%) at levels of 10 μg/kg (n=9) and 50 μg/kg (n=7), respectively, for most analyte/matrix combinations. Recoveries from aged residue samples spiked at a level of 100 μg/kg (n=7) ranged, depending of the analyte/soil type combination, from 41–113% with RSDs ranging from 1–35%. In the SRM approach the developed LC–LC procedure was applied for the determination of linuron in 28 sandy soil samples collected in a field study. Linuron could be determined in soil with a limit of quantitation of 10 μg/kg.

Keywords: Microwave-assisted solvent extraction; Extraction methods; Coupled columns; Soil; Environmental analysis; Linuron; Phenylureas; Pesticides

1. Introduction

Phenylurea compounds are used as selective and non-selective herbicides in agriculture in substantial amounts. The European Union (EU) council direc-

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tive 80/776/EEC (OJI.229 30.80) demanded the analysis of all pesticides in drinking water and drinking water sources at the 0.1 μg/l level. This has resulted in the availability of several methods of analysis for phenylurea herbicides in water [1]. In order to assess phytotoxicity, leaching and accumulation, suitable analytical techniques for the determination of these compounds in soils are mandatory.

Sample processing of soils usually requires extraction of the analytes followed by clean-up and concentration steps in order to increase selectivity and/or sensitivity of the analytical method. Current methodology frequently applies methods for the analysis of pesticides in soils involving liquid–solid extraction (LSE). A number of disadvantages have been noticed with LSE methods: they are laborious, time-consuming, expensive and are subject to problems arising from the formation of emulsions, the evaporation of large solvent volumes, and the disposal of toxic or inflammable solvents. Henze et al. [2] performed the extraction of linuron and its metabolites from soil samples by LSE with acetone followed by solid-phase extraction (SPE) clean-up and analysis by reversed-phase liquid chromatography (RPLC) with ultraviolet (UV) and amperometric detection. Performing LSE, Liegeois et al. [3] proposed a quantification procedure for isoproturon in soil samples using an enzyme-linked immunosorbent assay (ELISA) technique. Perez et al. [4] isolated chlorotoluron, isoproturon and metoxuron from soil samples by solvent extraction.

Nowadays, new extraction techniques like supercritical fluid extraction (SFE) [5], pressurised liquid extraction (PLE; Dionex tradename Accelerated Solvent Extraction) [6] and microwave-assisted solvent extraction (MASE) [7] are studied in order to facilitate sample pretreatment.

In accordance with other MASE studies [8–17] and based on our previous work [18–21], this technique appeared to be suitable for the extraction of pesticides with a wide range in polarity from soil samples. MASE permits a reduction of solvent consumption and extraction time, while obtaining good repeatability and reproducibility.

Besides the advantages of MASE, a few disadvantages can be named, such as limited selectivity, degradation of analytes, and the influence of the water content of the samples on the performance of MASE as a whole. Supported by previous experiments [18–22], temperature, water content and the extraction solvent are considered to be the most critical extraction parameters to be controlled during MASE. Although microwave radiation does not modify the molecular structure of the compounds, the temperatures that may be reached during extraction, due to local heating effects, may induce their degradation. This effect was observed by Font et al. [20], who studied the extraction of sulphonyl urea herbicides from soil samples by MASE.

The main objective of this study was to investigate the feasibility of the combination MASE and RPLC–UV in order to obtain an efficient method for the single-residue analysis of linuron in soil samples originating from a field study. Simultaneously, the potential of multi-residue analysis of a group of phenylurea herbicides, viz. monuron, monolinuron, isoproturon, metobromuron, diuron and linuron, selected on the basis of agricultural use in The Netherlands, was investigated. LC systems with and without column switching were compared in order to evaluate speed, selectivity and sensitivity of the analytical procedure.

2. Experimental

2.1. Reagents

3-(3,4-Dichlorophenyl)-1-methoxy-1-methylurea (linuron), 3-(4-chlorophenyl)-1,1-dimethylurea (monuron), 3-(3,4-dichlorophenyl)-1,1-dimethylurea (diuron), 3-(4-chlorophenyl)-1-methoxy-1-methylurea (monolinuron), 3-(4-isopropylphenyl)-1,1-dimethylurea (isoproturon) and 3-(4-bromophenyl)-1-methoxy-1-methylurea (metobromuron) were obtained from Dr. Ehrenstorfer (Promochem, Wesel, Germany) and had a purity >99%. Acetonitrile, methanol and dichloromethane, all HPLC-grade, were obtained from J.T. Baker (Deventer, The Netherlands). Demineralised water was purified in a Millipore system (Bedford, MA, USA) to obtain HPLC-grade water for use in eluents and standard solutions. Sodium sulphate (anhydrous) was purchased from Merck (Darmstadt, Germany).

Standard solutions were prepared by dissolving approximately 0.1 g pesticide in 100 ml methanol.

For spiking and high-performance liquid chromatography (HPLC) analysis, the stock solutions were diluted with a HPLC-grade methanol–water (50:50, v/v) mixture.

A dichloromethane–methanol (90:10, v/v) mixture was used for MASE.

In the one-column analysis (LC mode), the mobile phase consisted of acetonitrile–methanol–water (25:30:45, v/v/v). In column switching (LC–LC mode), acetonitrile–water (45:55, v/v) or acetonitrile–methanol–water (25:30:45, v/v/v) and acetonitrile–methanol–water (30:25:45, v/v/v) for the first (M-1) and second (M-2) mobile phases, respectively, were used.

2.2. Equipment

The LC system consisted of a Model 231 autosampler from Gilson (Villiers-le Bel, France) equipped with an additional six-way programmable high-pressure valve type 7010 of Rheodyne (Cotati, CA, USA), two Model 305 isocratic pumps from Gilson and a Model 116 UV detector from Gilson.

A 20×4.6 mm I.D. precolumn connected to a 150×4.6 mm I.D. analytical column both packed with 5 μm Suplex, pKb-100 of Supelco (Bellefonte, PA, USA) was used in the LC mode (one column separation) or as the second column (C-2) in column switching (LC–LC mode).

A 50×4.6 mm I.D. column packed with 3 μm C_{18} Microspher of Chrompack (Middelburg, The Netherlands) was used as the first column (C-1) in the LC–LC mode; a 10×3 mm I.D. precolumn packed with the same material was in the cartridge holder before the analytical column.

The LC columns were kept at 30°C with a laboratory-made column oven connected to a Model 1441 circulating water system of Braun (Melsungen, Germany). Quantitative experiments of peak heights were made with the PC-1000 integrator system of TSP employing a Model 800 DP integrator of Fisons.

MASE was 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 or temperature, depending on which parameter reaches its control set point first.

2.3. Soil samples

Available information on soil parameters of both standard soils and real soil samples is given in Table 1. Freshly spiked soil samples were prepared by weighing 5 g (10 g is optional) of a standard soil into a glass bottle followed by a spiking with a stock standard solution (volume=1 ml) at concentration levels of 10 and 50 μg/kg. The samples were allowed to stand overnight at ambient temperature and before extraction, 0.5 ml of water was added to 5 g of dried soil.

For the aged residue experiments, a few samples of each standard soil were spiked at a level of 100 μg/kg and after air-drying overnight at ambient temperature, they were stored in the dark for 40 days at about 4°C.

Table 1
Information on parameters of various types of soils

Type of soil	pH	Water content (%)	Organic matter content (%)	Organic carbon content (%)
Standard soils[a]				
Sand-1	3.9	16	1.7	0.4
Sand-2	5.5	9.2	5.3	1.4
Sea clay	7.9	17.9	3.8	1.2
Peat	5.8	6.0	30.4	16.7
Field-study samples				
Sand agricultural	5.3–6.0	12–26	1.5–6	0.4–1.6

[a] Sand-1, medium humic sand soil; sand-2, rich humic sand soil.

2.4. MASE procedure

After air-drying overnight at ambient temperature the 5.0 g portion of soil were transferred quantitatively to a PTFE-lined MASE vessel, and 0.5 ml of HPLC-grade water was added. Next, 20 ml of the dichloromethane–methanol mixture was added to the samples before the extraction vessels were closed. Extractions were performed at 70°C for 10 min at 100% power at a pressure of 690 kPa. After the extraction, the vessels were allowed to cool down to room temperature before they were opened. The organic solvent was dried over sodium sulphate and 8 ml of solvent (equivalent of 2 g of soil) was taken and evaporated to dryness. The residue was dissolved in 2 ml of a methanol–water (50:50, v/v) mixture.

In the processing of real samples, nine samples, one blank standard sand (medium humic) soil and two blank sand soils one spiked at level of about 10 and one at about 50 μg/kg, were extracted in the same MASE run.

2.5. RPLC–UV procedures

For both the LC mode and LC–LC mode the injection volume was 200 μl and the separation was performed by using analytical columns and isocratic elutions with flow-rates set at 1 ml/min. UV detection was carried out at 244 nm.

LC conditions as applied in the single-residue method (SRM) approach (linuron) or the multi-residue method (MRM) approach (six phenylurea compounds) are given in Table 2.

Quantification of the pesticides was performed by external calibration with standard solutions (concentration range, 0.010–0.10 μg/ml).

3. Results and discussion

3.1. Selection of LC conditions

RPLC–UV has shown to be an effective technique for the separation and detection of phenylurea pesticides [1,2]. Efficient elution is usually performed on an analytical C_{18} column with a mixture of water–methanol (and/or acetonitrile) as the mobile phase providing adequate retention and resolution (selectivity) by adjusting the eluotropic strength and/or (partially) the type of modifier.

Because of the difference in polarity between phenylurea compounds their separation is usually performed with a linear-gradient elution [1,2]. However, in trace analysis involving uncleaned soil extracts isocratic elution conditions are more favourable in order to reduce baseline disturbances by matrix interferences. Therefore, we investigated the possibility of an isocratic elution for the separation of the selected herbicides monuron, monolinuron, isoproturon, metobromuron, diuron and linuron.

Based on the conditions proposed by Henze et al. [2] adequate retention of the analytes, viz. $1<k<10$, and resolution between analytes ($R_s>1.2$) were obtained on the 5 μm Suplex pKb-100 column by employing a ternary mobile phase composition of acetonitrile–methanol–water (30:25:45, v/v/v). As shown in Table 2, this column/eluent combination was applied in our further experiments in the LC mode and as C-2/M-2 in the LC–LC mode.

Coupled-column RPLC employing a full size separation column as the first column (C-1) to perform high sample load and, moreover, an efficient clean-up has shown to considerably improve the selectivity/sensitivity and sample throughput in trace

Table 2
Information on applied LC conditions

Mode of analysis[a]	Type of column[b]		Type of mobile phase[c]		Volumes (ml) for	
	C-1	C-2	M-1	M-2	Clean-up	Transfer
LC, SRM and MRM	A	–	III	–	–	–
LC–LC, SRM	B	A	I	III	3.0	0.5
LC–LC, MRM	B	A	II	III	1.0	12

[a] SRM, single-residue method (linuron); MRM, multi-residue method (all compounds).
[b] A, 5 μm Suplex pKb-100 (150×4.6 mm I.D.); B, 3 μm Microspher C_{18} (50×4.6 mm I.D.).
[c] I, acetonitrile–water (45:55, v/v); II, acetonitrile–methanol–water (25:30:45, v/v); III, acetonitrile–methanol–water (30:25:45, v/v).

analysis of target analytes in various matrices, e.g., water [23,24] and soils [23,25].

Focused at the single-residue analysis of linuron and following the guidelines in LC–LC method development [23] a 3 μm C_{18} column (50×4.6 mm I.D.) and a binary mobile phase of acetonitrile–water (45:55; v/v) were successfully selected as C-1 and M-1, respectively. However, in multi-residue analysis the C-1/M-1 combination was not suitable. The change in selectivity as a result of the use of different modifiers in the mobile phases provided a reversed elution order of some of the analytes, e.g., isoproturon/metobromuron, hence, nullifying (almost) resolutions obtained on the individual columns. Therefore, in the MRM approach employing LC–LC, a ternary mobile phase M-1 was selected (see Table 2) corresponding very well with M-2 but with a slightly lower eluotropic strength in order to enhance the clean-up performance.

A wavelength of 244 nm was selected for the detection providing a limit of detection (LOD, $S/N=3$) of about 2 ng for each compound. In order to reach for linuron (and other compounds) a limit of quantification of 10 μg/kg in soil an injection volume of 200 μl of the soil extract was applied (200 mg of soil equivalent injected on column). Up to 400 μl could be injected without observing additional band broadening of the analytes.

3.2. Selection of MASE conditions

In order to select the appropriate MASE conditions, temperature, water content and extraction solvent (mixture), were studied. Based on our experience with the extraction of polar pesticides (triazines and metabolites, sulphonyl urea herbicides) from soil [18,20,22], the same solvent, dichloromethane–methanol (90:10, v/v), was firstly selected for the extraction of phenylurea herbicides from soil. The optimisation experiments were carried out in humic rich soil samples (sand-2), see Table 1. Table 3 shows recovery data obtained after 10 min extraction at different temperatures ($T=40$, 60, 70, 80 and 100°C). Maximum recoveries were in the temperature range 60–80°C, while lower recoveries were obtained for both higher and lower temperatures. These results were in agreement with Font et al. [20], who proposed possible analyte degradation when MASE was performed at too high temperatures. Based on these results, 70°C and 10 min were selected as appropriate starting conditions in the further optimisation of MASE.

Due to the nature of microwave heating [7], the presence of substances (as for instance methanol and water) with a high dielectric constant (ϵ) that readily absorb microwave energy and efficiently convert this energy to heat, greatly facilitates the heating up of the whole content of the extraction vessel. Thus, the presence of such a substance may be crucial for a successful MASE procedure. Therefore, the relation between both the water content of soil samples, the applied extraction solvent and the extraction efficiency and selectivity were studied.

Firstly, the effect on recovery when different percentages of water (0, 10, 20, 40 and 70%) were added to the dried soil before extraction was studied. Applying the MASE conditions as mentioned above, no differences in selectivity were observed, however as shown in Fig. 1, the recovery increased in the 0–10% range, and decreased when the amount of water was >10%. For all the assayed compounds, highest recoveries were obtained with the addition of

Table 3
Influence of MASE temperature[a] on the recovery of herbicides spiked at a level of 50 μg/kg to soil sand-2 samples

MASE temperature (°C)	Recoveries and RSDs (%)					
	Monuron	Monolinuron	Isoproturon	Metobromuron	Diuron	Linuron
40	62 (3)	66 (1)	67 (4)	70 (2)	67 (3)	67 (3)
60	101 (2)	100 (3)	97 (5)	98 (7)	80 (3)	105 (4)
70	93 (1)	100 (2)	107 (7)	106 (3)	95 (4)	109 (5)
80	82 (2)	103 (4)	91 (4)	104 (6)	87 (5)	106 (7)
100	11 (3)	59 (3)	22 (4)	84 (5)	10 (5)	85 (4)

[a] Other MASE conditions, 10 g soil, 20 ml dichloromethane–methanol (90:10, v/v), time 10 min, 100% power.

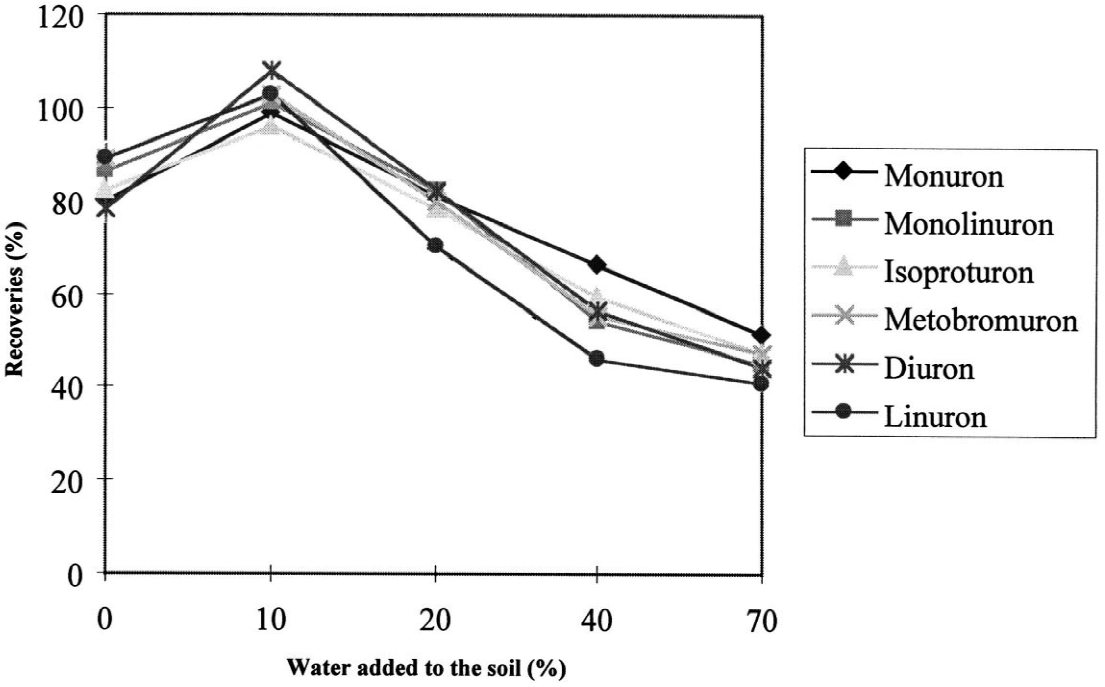

Fig. 1. Influence of water on the extraction efficiency of phenylurea herbicides from humic rich sandy soil samples. MASE conditions: time, 10 min; $T=70°C$; $P=690$ kPa; extraction solvent, 20 ml dichloromethane–methanol (90:10, v/v).

10% water to the dried soil samples and, hence, included in the analytical procedure.

Next, under the optimised MASE conditions the extraction solvent was varied. Table 4 shows the recoveries corresponding to extraction performed with different solvents.

The use of dichloromethane or dichloromethane–water (80:20, v/v) improved selectivity, however, relatively low recoveries were obtained. Methanol–water mixtures were evaluated as MASE solvent because of their compatibility with RPLC. However, extraction efficiency as well as selectivity were disappointing. Concluding, in comparison to other solvents the methanol–dichloromethane mixture is

Table 4
Influence of MASE solvent[a] on the recovery of herbicides spiked at a level of 50 μg/kg to soil sand-2 samples[b]

Solvent	Recoveries[c] and RSDs (%)					
	Monuron	Monolinuron	Isoproturon	Metobromuron	Diruon	Linuron
Dichloromethane	43 (3)	43 (5)	32 (6)	52 (6)	53 (1)	73 (4)
Dichloromethane–water (5:1)	56	54	36	51	47	42
Dichloromethane–methanol (9:1)	93 (1)	100 (2)	107 (7)	106 (3)	95 (4)	109 (5)
Methanol–water (7:3)	36	32	35	34	36	35
Methanol–water (9:1)	48	47	48	48	62	69

[a] Other MASE conditions, 10 g soil, 20 ml solvent, temperature 70°C, 100% power.
[b] For RSD data, $n=2$; other experiments, $n=1$.
[c] Without correction for miscibility of soil water content in case of water–methanol solvents.

most favourable concerning extraction efficiency of analytes and limited co-extraction of matrix interferences.

3.3. LC vs. LC–LC in the multi- and single-residue method approach

The LC modes listed in Table 2 were tested for suitability for multi-residue analysis (all six phenylurea herbicides) as well as single-residue analysis (linuron). In order to avoid unnecessary complexity of the analytical procedure, the possibility to process the soil extracts without column switching was firstly studied. Representing soil with a relatively high organic matter content and, hence, available matrix interference, humic rich sand samples (sand-2) were processed with the analytical procedure involving the LC mode.

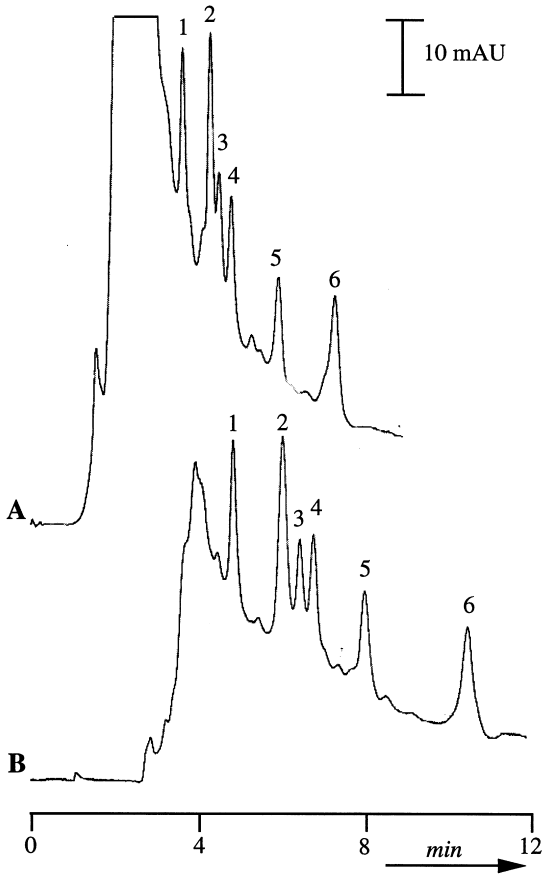

Fig. 2. RPLC–UV (244 nm) of an extract of a standard soil sand-2 sample (humic rich) spiked with phenylurea herbicides at a concentration level of 50 μg/kg employing different LC modes in the MRM approach (cf. Table 2). (A) LC mode (without column switching); (B) LC–LC mode (with column switching). Peaks: 1=monuron; 2=monolinuron; 3=isoproturon; 4=metobromuron; 5=diuron; 6=linuron.

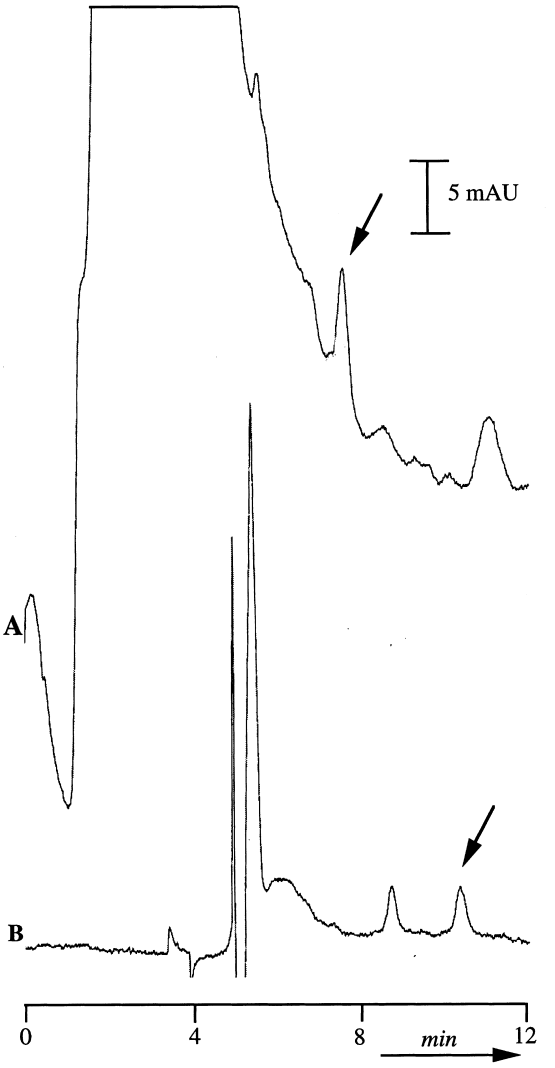

Fig. 3. RPLC–UV (244 nm) of an extract of a standard soil sand-2 sample (humic rich) spiked with linuron at a concentration level of 10 μg/kg employing different LC modes in the SRM approach (cf. Table 2). (A) LC mode (without column switching); (B) LC–LC mode (with column switching).

Not too surprisingly, in the LC–UV analysis of uncleaned soil extracts the baseline was severely elevated by matrix interferences making reliable quantification, especially in the first part of the chromatogram, difficult. However, a major drawback encountered in the LC mode was that strongly retained matrix constituents give rise to retention shifts of analytes and interferences in later chromatograms. Improvement can be expected when applying a cleaning of the column after elution of the last analyte with a strong eluent by means of a gradient elution. However, in the LC mode such a cleaning will considerably increase the time of analysis per sample.

In order to improve the analysis, the LC–LC mode was tested. As regards multi-residue analysis, Fig. 2 illustrates the performance of both the LC and the LC–LC mode for the RPLC–UV analysis of an extract of a soil (sand-2) sample spiked with the herbicides at a level of 50 μg/kg. As indicated by the profiles of the baselines, LC–LC (Fig. 2B) reduces the background signal caused by matrix interferences and slightly improves the separation of the individual compounds (especially for monolinuron, isoproturon and metobromuron). It must be noted that because of the difference in polarity between these compounds, a small clean-up volume and a large transfer volume have to be applied, hence, the clean-up performance is marginal. However, in the LC–LC mode no shifts in retention of analytes were observed during the processing of a series of soil extracts, and if necessary in case of late eluting interferences, flushing of the second column takes place while the C-1 is loaded for the next analysis.

The superior performance of LC–LC in the single-residue analysis is clearly displayed in Fig. 3 showing the RPLC–UV analyses of an extract of a sand-2 soil sample spiked with linuron at a level of 10 μg/kg. In comparison to LC, the LC–LC mode provides high selectivity as a result of optimised volumes for clean-up (large) and transfer (small) and the use of LC constituents of different selectivity.

3.4. Analysis of phenylurea herbicides in soil samples

The performance of the developed analytical procedure involving MASE and LC–LC–UV in the multi-residue method approach was tested with analysis of various types of standard soils (see Table 5) spiked at different levels with the six phenylurea compounds (including linuron). Besides freshly spiked samples, recovery experiments were carried out with aged residue samples (see Experimental).

Table 5
Recoveries of phenylurea herbicides from various type soils of freshly-spiked samples and aged residues samples

Soil type	Spiked level (μg/kg)	*n*	Recovery and RSD (%)					
			Monuron	Monolinuron	Isoproturon	Metobromuron	Diuron	Linuron
Sand-1	10	3	n.d.[b]	89 (1)	91 (8)	90 (16)	78 (2)	125 (6)
	50	3	88 (3)	97 (3)	98 (3)	99 (2)	94 (5)	100 (3)
	100[a]	2	93 (3)	99 (1)	94 (4)	100 (1)	97 (1)	105 (2)
Sand-2	10	3	80 (15)	n.d.[b]	148 (25)	138 (54)	102 (35)	89 (12)
	50	3	108 (2)	127 (20)	104 (1)	117 (3)	104 (12)	109 (3)
	100[a]	1	80	79	71	79	41	97
Clay	10	3	99 (6)	104 (14)	144 (23)	105 (25)	59 (7)	174 (12)
	50	1	89	89	92	88	73	104
	100[a]	2	49 (18)	50 (35)	70 (14)	71 (18)	86 (8.1)	83 (16)
Peat	100[a]	2	94 (2)	106 (7)	113 (3)	102 (7)	86 (7)	102 (4)

[a] Aged residue samples stored for 40 days at 4°C before analysis.
[b] n.d., not detectable due to matrix interference.

An overview of the results of the recovery experiments is made in Table 5.

It can be seen that at the level of about 50 μg/kg for almost all analyte/soil type combinations acceptable recoveries are obtained.

For two analyte/matrix combinations, viz. monuron/sand-1 and monolinuron/sand-2, quantification at the aimed 10-ppb level was not possible due to interferences.

For linuron the results at the 10 μg/kg level for both sandy soil types were satisfactory with mean recoveries ranging from 89–125% (range RSD, 6–12%) indicating the usefulness of the developed screening procedure.

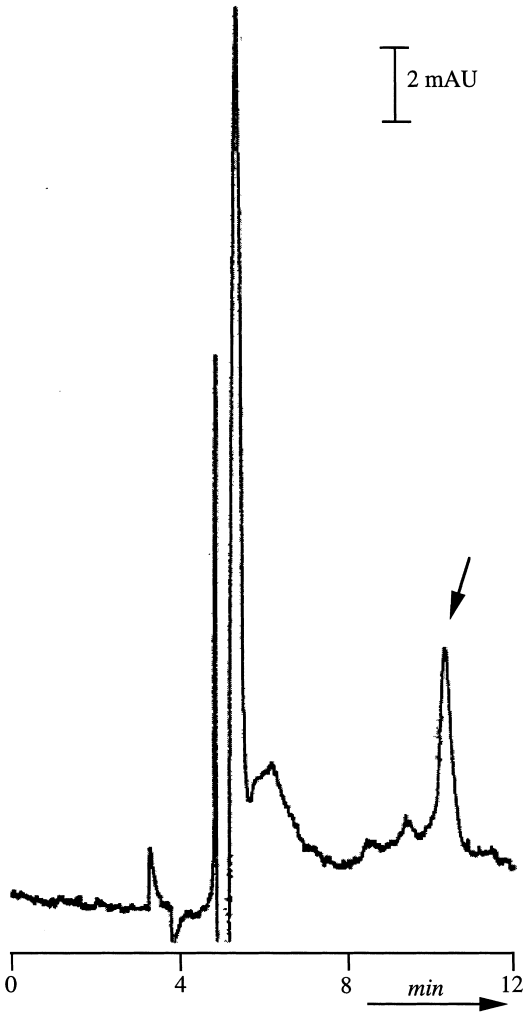

Fig. 4. LC–LC–UV (244 nm) in the SRM approach of an extract of a real soil sample containing an incurred residue of linuron of 18 μg/kg.

The mean recoveries of aged residue experiments ($n=7$) involving the analysis of the four different soil types spiked at a level of 100 μg/kg and stored over a period of 40 days (refrigerator), ranged between 41 and 113% (range RSD, 1–35%).

As part of a monitoring program ''Monitoring of potential accumulation of linuron in soil in The Netherlands'', 28 sandy soil samples (see Table 1) collected from seven different Dutch fields were analysed.

The obtained MASE extracts of these soil samples were firstly screened with RPLC–UV in the LC mode. Positive samples were re-analysed with LC–LC applying the SRM approach. The LC–LC–UV analysis of an extract of a collected field soil sample containing 18 μg/kg of linuron displayed in Fig. 4 clearly illustrates the ability of the developed technique to determine linuron at this concentration level.

4. Conclusions

MASE applied prior to RPLC analysis, is an efficient technique for the extraction of a group selected phenylurea herbicides from different soil types with ranging organic carbon content. By optimisation of MASE and RPLC parameters, most of the herbicides can be analysed at a concentration level of 10 μg/kg in the soils investigated. Also soil samples which contain aged residues are extracted efficiently.

In comparing the one column approach (LC mode) and the coupled-column approach (LC–LC mode) involving column switching for the determination of these compounds in soil samples, it is possible to conclude that (i) the LC mode can be used as screening method for six different phenylurea herbicides, (ii) the LC–LC can improve the determination of these compounds, by protecting the chromatographic system and reducing the time of analysis, and (iii) for single-residue determinations, LC–LC is superior to the LC mode regarding selectivity and reliable quantification.

The LC–LC mode was successfully applied for

the determination of linuron in soil samples collected in a field study.

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