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Comparison of various liquid chromatographic methods involving UV and atmospheric pressure chemical ionization mass spectrometric detection for the efficient trace analysis of phenylurea herbicides in various types of water samples

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Abstract

The performance of mass spectrometric (MS) detection and UV detection in combination with reversed-phase liquid chromatography without and with the use of coupled column RPLC (LC–LC) has been compared for the trace analysis of phenylurea herbicides in environmental waters. The selected samples of this comparative study originated from an inter-laboratory study. For both detection modes, a 50 mm×4.6 mm I.D. column and a 100 mm×4.6 mm I.D. column packed with 3 μm C_{18} were used as the first (C-1) and second (C-2) column, respectively. Atmospheric pressure chemical ionization mass spectrometry was performed on a magnetic sector instrument. The LC–LC–MS analysis was carried out on-line by means of direct large volume (11.7 ml) injection (LVI). The performance of both on-line (LVI, 4 ml of sample) and off-line LC–LC–UV (244 nm) analysis was investigated. The latter procedure consisted of a solid-phase extraction (SPE) of 250 ml of water sample on a 500 mg C_{18} cartridge. The comparative study showed that LC–LC–MS is more selective then LC–LC–UV and, in most cases, more sensitive. The LVI-LC–LC–MS approach combines direct quantification and confirmation of most of the analytes down to a level of 0.01 μg/l in water samples in less then 30 min. As regards LC–LC–UV, the off-line method appeared to be a more viable approach in comparison with the on-line procedure. This method allows the screening of phenylurea's in various types of water samples down to a level of at least 0.05 μg/l. On-line analysis with LVI provided marginal sensitivity (limits of detection of about 0.1 μg/l) and selectivity was sometimes less in case of surface water samples. Both the on-line LVI-LC–LC–MS method and the LC–LC–UV method using off-line SPE were validated by analysing a series of real-life reference samples. These samples were part of an inter-laboratory test and contained residues of herbicides ranging from 0.02 to 0.8 μg/l. Beside good correlation between the methods the data agreed very well with the true values of the samples. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Large-volume injections; Environmental analysis; Pesticides; Phenylureas

1. Introduction

Phenylurea herbicides are widely used in the Netherlands for weed control in agriculture and public greenery. The most important emissions to the aquatic environment are caused by atmospheric deposition, windburn spraying drift and, for some herbicides such as diuron, run-off from pavements. For example, the estimation of the total of these emissions in 1991 was $6 \cdot 10^3$ kg [1]. Phenylurea

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herbicides will also reach the Netherlands by atmospheric deposition of foreign origin and via transboundary rivers.

As a result of these emissions and the property of being slowly transformed, phenylurea herbicides are found widely spread in fresh waters as well as in marine waters [1]. Hence, quite an effort has been and will be spend in monitoring various types of water samples on the occurrence of these herbicides and, obviously, the availability of efficient and reliable analytical methodology is necessary.

Direct analysis of phenylurea compounds by gas chromatography (GC) is not feasible due to their polar and thermo labile properties, although derivatizations of the analytes prior to GC analysis [2,3] solve these problems.

Reversed-phased liquid chromatography (RPLC) with UV diode array detection (DAD) [4–14] and/or mass spectrometric (MS) detection [15–19] has shown to be an effective technique for the determination of these polar analytes in aqueous samples. A major advantage of RPLC is its compatibility with water samples allowing the on-line determination of phenylurea herbicides by means of column-switching [4–8,12,13,19] or automated solid-phase extraction (SPE) systems [16].

The long-term stability, scope of linear range, ease of use and low costs make DAD an attractive detection mode for screening and monitoring purposes [7–13]. The rather poor selectivity of UV can be improved significantly by using selective immunosorbents off-line [11] or on-line [13,14,16] with the analytical procedure.

The use of LC with selective MS detection for the trace determination of pesticides and metabolites in environmental water samples is a fast growing technique [20]. MS detection offers high selectivity and sensitivity and has been successfully applied for the rapid on-line determination of phenylurea herbicides in environmental waters [15–19].

Our current analytical methodology usually consists of off-line SPE of water samples and instrumental analysis of the extracts with coupled column RPLC (LC–LC) and UV detection [9]. The aim of this study was to compare the performance of our current approach with other attractive LC procedures involving direct large volume sample injection (LVI) in combination with UV or MS detection. In case of UV detection, a comparison was made between LC–LC and LC with the two columns connected in series without column switching.

The LC procedures were tested by analyzing reference material originating from our participation in an inter-laboratory study involving the determination of phenylurea herbicides in various types of environmental waters.

2. Experimental

2.1. Chemicals

Monuron, monolinuron, isoproturon, diuron, linuron, methabenzthiazuron, metoxuron and fluometuron (content >99%) were from Dr. S. Ehrenstorfer (Promochem, Wesel, Germany). Acetone, acetonitrile and methanol, all of HPLC-grade, were from J.T. Baker (Deventer, Netherlands). HPLC-grade water was obtained by purifying demineralized water in a Milli-Q system (Millipore, Bedford, MA, USA).

A stock standard solution (ca. 500 μg/ml) of each pesticide was prepared in acetonitrile. For spiking or LC analysis the stock solutions were diluted in acetonitrile–water (20:80, v/v). A solution of fluometuron (ca. 0.1 μg/ml) in methanol was used as an internal standard (I.S.) for the LC–MS analysis. The diluted solutions were kept in the refrigerator at 4°C.

Disposable 3 ml SPE cartridges containing 500 mg of C_{18} bonded phase (40 μm) were obtained from J. T. Baker. The cartridges were preconditioned with 3 ml of methanol, 3 ml of acetone, 3 ml of methanol and 6 ml of water, respectively.

2.2. Reference samples

As part of our participation in an inter-laboratory study organized by Kiwa Research and Consultancy (Nieuwegein, Netherlands) eight reference samples of one liter each were supplied consisting of three drinking water, three surface water and two ground water samples. Samples were only marked by a number, viz. both the type of sample and the spiking level of the analytes were unknown before analysis.

Information on type and amount of samples is included in Table 2.

2.3. Equipment

A Baker-10 system of J.T. Baker was used to perform SPE.

The LC–LC–UV 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, Rheodyne, Cotati, CA, USA) for column switching, two Series 1050 isocratic LC pumps from Hewlett-Packard (Waldbronn, Germany), and a Model 118 UV detector from Gilson.

In the LC–LC analysis a 50 mm×4.6 mm I.D. column and a 100 mm×4.6 mm I.D. column both packed with 3 μm C_{18} Microspher (Chrompack, Middelburg, Netherlands) were used as a first column (C-1) and second column (C-2), respectively. A precolumn (10×3 mm I.D.) packed with 3 μm C_{18} Microspher was installed before each column. In the LC analysis (one column approach) C-1 and C-2 were connected in series.

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

The LVI-LC–LC–MS system is schematically presented in Fig. 1 and consisted of a Model 480 gradient pump, GP, of Gynkotek (Germering, Ger-

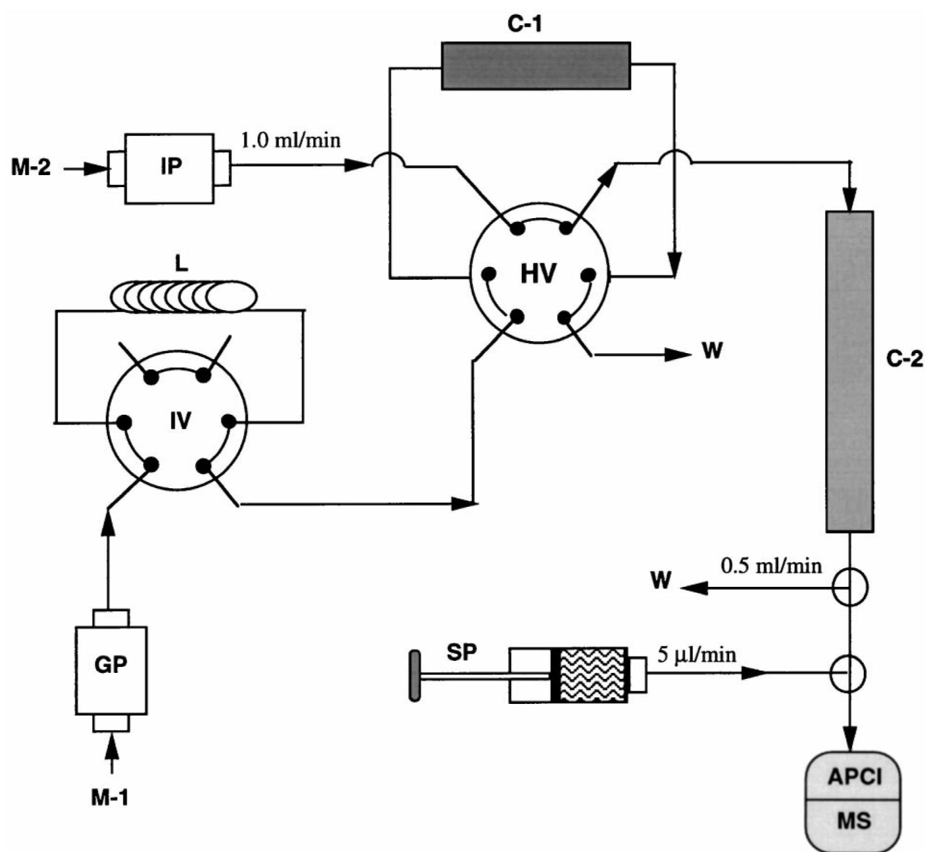

Fig. 1. Schematic representation of the LVI-LC–LC–APCI-MS system. M-1 and M-2, first and second mobile phase; C-1 and C-2, first and second separation column; IP, GP and SP, isocratic, gradient and syringe LC pump, respectively; IV injection valve with loop (L); HV, high-pressure valve; W, waste; APCI-MS, MS detector (for further explanation, see Experimental).

many), a Model 300 isocratic pump, IP, of Gynkotek (Germering, Germany), a Model 22 syringe pump, SP, of Harvard Apparatus (South Natick, USA), a manual injection valve, IV, Model 7725 of Rheodyne equipped with a laboratory-made loop, L, of 11.7 ml (coiled stainless steel tubing of 1 mm I.D.), a high-pressure valve, HV, type 710 of Rheodyne for column switching and a Finnigan MAT 95 magnetic sector mass spectrometer (Finnigan MAT, Bremen, Germany) equipped with an atmospheric pressure chemical ionization ion source.

2.4. Sample pretreatment

For SPE, a 250 ml water sample was percolated through a preconditioned 500 mg C_{18} cartridge at a flow of approximately 4 ml/min. After sampling, the cartridges were dried by passing air for 30 min and the analytes were desorbed with 2 ml of acetone. An aliquot of the acetone corresponding to 125 ml of sample was transferred in a tube and evaporated to dryness with a gentle stream of nitrogen. The residue was redissolved by adding first 0.20 ml of acetonitrile followed by 1.8 ml of LC-grade water.

In the case of LVI, a sample of about 20 ml was filtrated over an 0.45 μm filter prior to injection. For LVI-LC–LC–MS analysis the internal standard was added to the sample at a concentration level of 0.1 μg/l.

2.5. Analytical conditions and procedures

A brief description of the applied methods is given in Table 1. In all methods the mobile phase on the columns were adjusted to a flow-rate of 1 ml/min. For LC– and LC–LC–UV the mobile phase applied on the columns consisted of methanol–water (55:45, v/v). The LC–UV methods involved the determination of monuron, monolinuron, isoproturon, diuron and linuron.

The LC–MS method included the determination of monuron, monolinuron, isoproturon, methabenzthiazuron, metoxuron and diuron.

SPE+LC(–LC)–UV (methods Ia, Ib and II): 150 μl of extract obtained after the SPE procedure were injected. In case of column switching, the volumes for cleanup and transfer (fraction containing the analytes) were 1.3 and 3.4 ml, respectively.

LVI-LC(–LC)–UV (methods III and IV): 4.0 ml of sample were injected. In case of column switching, the volumes for cleanup and transfer (fraction containing the analytes) were 5.3 and 4.0 ml, respectively.

For the LC–UV methods quantification of the analytes was done by external calibration with standard solutions of the analytes in acetonitrile–water (20:80; v/v).

LVI-LC–LC–APCI-MS (method V, cf. Fig. 1): Samples were loaded and pre-concentrated on a 50 mm×4.6 mm I.D. column (C-1, Fig. 1) packed with 3 μm C_{18} Microspher (Chrompack). The mobile phase used for preconcentration consisted of methanol–water (10:90, v/v) and the flow-rate was 1.0 ml/min.

Fifteen minutes after injection, a linear gradient elution to methanol–water (60:40, v/v) in 6 min, was started. At the start of the gradient, the injection valve was switched to the load position to prevent

Table 1
Information on applied methods

Method	Abbreviation[a]	Volume injected	LOQ[b] (μg/l)	Storage[c] samples or extracts (days)
Ia	SPE+LC–LC–UV	150 μl (extract[d])	0.05	12
Ib	SPE+LC–LC–UV	150 μl (extract[d])	0.05	40
II	SPE+LC–UV	150 μl (extract[d])	0.05	41
III	LVI-LC–LC–UV	4.0 ml (sample)	0.1	280
IV	LVI-LC–UV	4.0 ml (sample)	0.1	281
V	LVI-LC–LC–APCI-MS	11.7 ml (sample)	0.01–0.2	80–90

[a] LC–LC, two columns with column switching; LC, two columns in series without column switching; LVI, large volume injection.
[b] Estimated limit of quantification (or range) of herbicides in reference samples (see Table 2).
[c] In refrigerator before instrumental analysis.
[d] Injection corresponds to an equivalent of 9.4 ml of water sample.

the passage of the gradient through the 11.7 ml injection loop. At the end of the gradient, the high-pressure valve was switched and the analytes were transferred to a 100 mm×4.6 mm I.D. 3 μm C_{18} Microspher (Chrompack) column (C-2, Fig. 1). Separation was carried out using a mobile phase consisting of methanol–water (60:40, v/v) at a flow-rate of 1.0 ml/min.

The effluent was split after C-2 allowing 0.5 ml/min to enter the MS system together with a solution of caffeine supplied by the syringe pump (SP) at a flow-rate of 5 μl/ml. The caffeine solution [1 ng/μl in methanol–water (60:40, v/v)] was used to provide a lock mass for correction of magnetic field strength drift.

Analytes were ionized by APCI using a vaporizer temperature of 300°C, a sheath gas (nitrogen) pressure of 3.5 bar and a corona current of 5 μA. The heated capillary was maintained at 175°C.

MS detection was performed in selecting ion monitoring (SIM) mode using the $[M+H]^+$ ions at 199.1/201.1, 207.1, 215.1/217.1, 222.1, 229.1/231.1 and 233.0/235.0 for monuron, isoproturon, monolinuron, methabenzthiazuron metoxuron and diuron, respectively. The $[M+H]^+$ ion of caffeine at 195.1 was used as lock mass. Integration time was 115 ms. The resolution of the mass spectrometer was set at 500.

Quantification of analytes in the sample was done by means of 5-point calibration plots obtained by the analysis of standard solutions (calibration solutions) in Milli-Q water containing 0.01–1.0 μg/l of the analytes and 0.1 μg/l of internal standard. Peak area ratio's of the analyte/internal standard were plotted against analyte concentration to determine the calibration functions. Concentrations of analytes in the samples were calculated using the calibration functions and analyte/internal standard peak area ratio.

3. Results and discussion

3.1. General aspects

The group of phenylurea compounds is a nice example of one of the few exceptions in which RPLC–DAD usually is the adopted technique of analysis. Despite the rather poor selectivity of UV detection, the favourable aspects of RPLC–UV make it an efficient technique for screening and/or monitoring purposes. However, in case of positive samples additional analytical methodology for the confirmation of analytes will be required.

LC–MS is a fast growing technique is this field of analyses demonstrating to provide both adequate sensitivity and selectivity. Particularly, the availability of atmospheric pressure ionization (API) interfacing has improved considerably convenient operation and robustness of the technique. Moreover, the improved sensitivity and the possibility to perform simultaneously confirmation are attractive features to perform high sample throughput. However, in comparison to LC–UV cost-effective analysis might be less favorable due the (still) high costs of the equipment.

In order to investigate the potential of LC–MS in comparison to our LC–UV approaches [9,21], a group of water samples originating from an interlaboratory study on the determination of phenylurea herbicides was analysed with the various LC methods and evaluated on their performance.

The LC methods are summarized in Table 1. Information on method development and performance will be given below.

3.2. LC–UV methods

For the determination of polar pesticides our methodology consists of LC–LC with off-line SPE [9] or with direct LVI of the sample [21]. Factors influencing the selection of the preferable method have been discussed [9]. For example, off-line SPE is attractive if storage of samples over a long period of time is necessary or convenient. For example in this study, we had to use off-line SPE (method Ia) because it was not possible to analyse the samples within two-weeks after their arrival at our Laboratory.

The main advantage of LC–LC is the use of separation power of the first column (C-1) to perform an efficient cleanup. As demonstrated in previous work [9,21], it eliminates effectively early eluting inferences allowing reliable quantification of analytes in the first part of the chromatogram. However, if column switching is not really necessary a one column LC system seems more attractive.

Therefore, we also investigated LC–UV without column switching (method II and IV, see Table 1).

Adequate LC conditions concerning separation and retention of the five phenylurea compounds were obtained by using a mobile phase of methanol–water (55:45, v/v) on both 3 μm C_{18} columns.

Fig. 2 shows the analysis of an extract of a reference surface water sample containing monuron (0.18 μg/l), monolinuron (0.70 μg/l) and diuron (0.20 μg/l) obtained by SPE with and without the use of column switching. Fig. 2 indicates that in comparison to a one column analysis (LC approach) LC–LC hardly improves the selectivity for this type of application.

For the on-line LVI approach a sample injection volume of 4 ml was selected providing limits of detection ($S/N=3$) of at least 0.1 μg/l for all analytes. The performance of on-line LVI with LC–LC (column switching) and LC (without column switching) for the analysis of the same surface water sample is illustrated in Fig. 3. In comparison to LC the LC–LC configuration substantially reduces matrix interferences providing improved determination of the analytes. A drawback encountered in LVI-LC

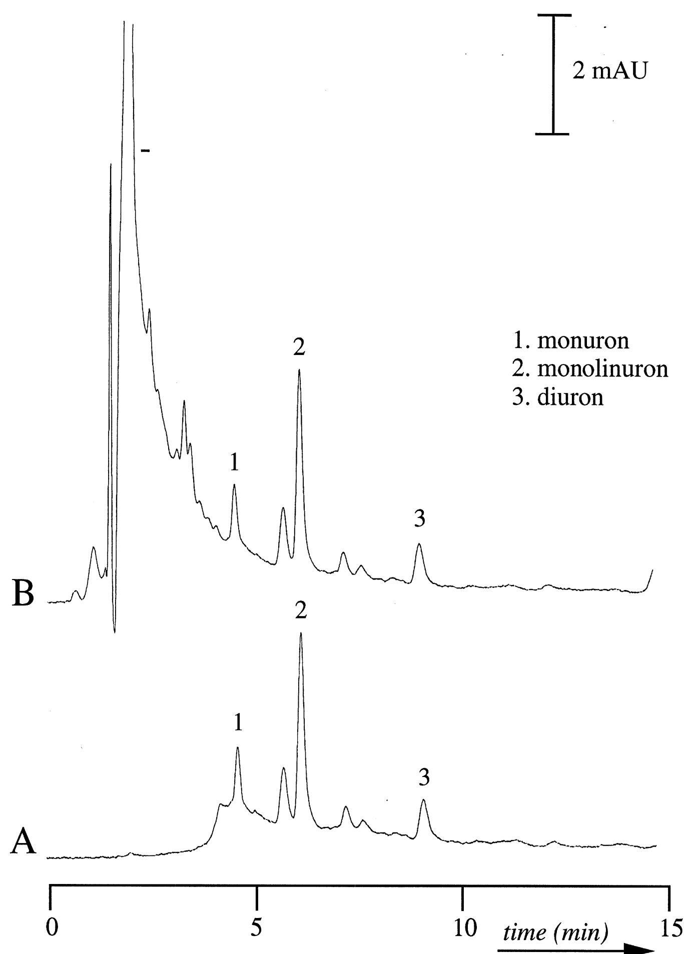

Fig. 2. Off-line SPE and LC(–LC)–UV (244 nm) of a SPE extract of surface water sample SW-3 (see Table 2) containing 0.18 μg/l monuron (1), 0.70 μg/l monolinuron (2) and 0.20 μg/l diuron (3). LC(–LC) conditions: C-1, 3 μm Microspher C_{18} (50×4.6 mm I.D.); C-2, 3 μm Microspher C_{18} (100 mm×4.6 mm I.D.); M-1 and M-2, methanol–water (55:45, v/v) both at 1 ml/min; injection of 150 μl of SPE extract; (A) LC–LC (column switching); cleanup volume, 1.3 ml; transfer volume 3.4 ml. (B) LC without column switching (C-1 and C-2 coupled on-line).

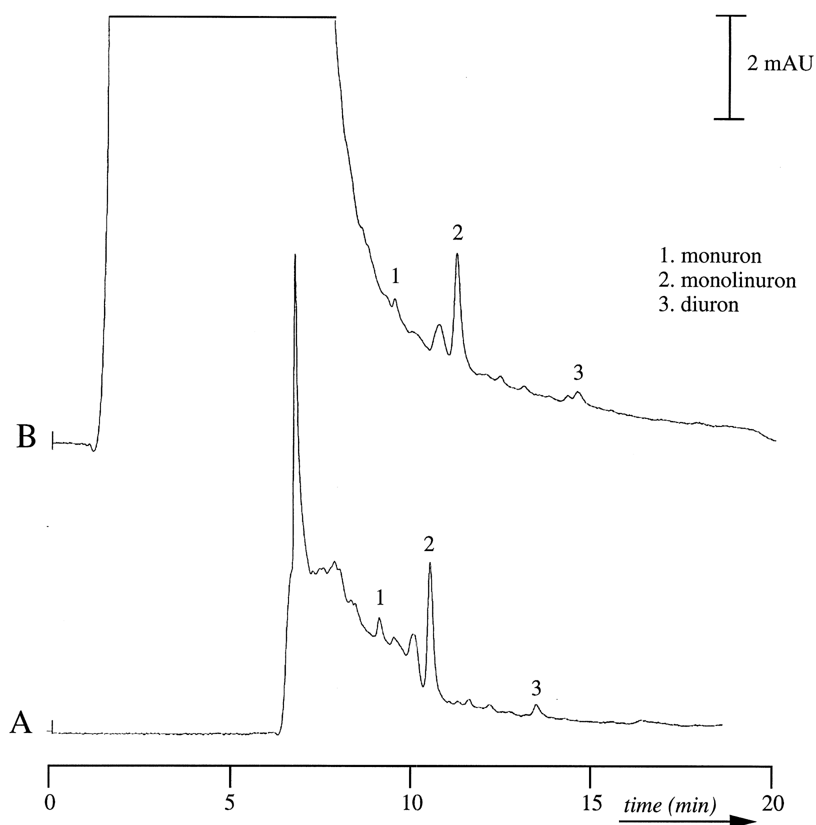

Fig. 3. LVI-LC(–LC)–UV (244 nm). Injection of 4 ml of surface water sample SW-3. (A) LC–LC (column switching); cleanup volume, 5.3 ml; transfer volume 4.0 ml. (B) LC without column switching (C-1 and C-2 coupled on-line). For further conditions, see Fig. 2.

was the rather high variability of the retention times of the analytes (>5%). It is assumed that this is caused by the large drop in column pressure during 6 min (ΔP_{max}=120 bar) as result of the injection of 4 ml of water.

The two LC–LC–UV methods are displayed in Fig. 2A (off-line SPE) and Fig. 3A (on-line LVI). Comparing these methods one can see that the SPE procedure offers higher selectivity and sensitivity. This is because of the sample pretreatment step providing some cleanup and higher sample load corresponding to an equivalent of 9.4 ml.

3.3. LVI-LC–LC–MS method

The use of LC with selective MS detection for the trace determination of pesticides and metabolites in environmental water samples is a fast growing technique [20]. At first sight, the hyphenation of LC–LC with selective MS detection would easily provide an overkill in separation power. However, based on our experience with the applied LC–MS contamination of the MS ion source, signal suppression by interferences such as ions and humic substances must be avoided as much as possible. LC–LC offers the possibility to perform efficient cleanup and to provide a highly stable flow-rate to the MS. These favourable LC–LC features were experienced before in the LC–MS analysis of β-agonists in body fluids [22,23].

The same columns were selected as used for LC–LC–UV and aiming at LODs below 0.05 μg/l a sample injection volume of about 10 ml was selected for the on-line analysis (see Fig. 1).

Applying an isocratic elution with methanol–water (60:40, v/v) on both columns (flow of 1 ml/min),

the feasibility of APCI-MS detection was investigated. However, despite the removal of a large part of interferences (cf. Fig. 3) the LC–LC–UV approach appeared not to be adequate when using the MS detection mode. Ions originating from the water samples were still entering the ion source causing contamination and signal suppression. Hence, a more efficient desalting step was necessary. This was accomplished by including a washing step after LVI and a linear gradient elution on the first column (see Experimental).

Because of a more stable signal and less ion source contamination the column effluent was split 1:1 after the second column. The loss of sensitivity caused by splitting the effluent was insignificant.

The identification criteria applied for the confirmation of phenylurea herbicides in a sample were: (a) retention time analyte must be within ±3 times the standard deviation of the retention time of the standard, (b) the ion current intensity must be ≥3 times the noise level, and (c) the ion current responses for chlorine containing analytes must reach maximum simultaneously.

The standard deviation of the retention time obtained for the standards was 1–4 s (relative standard deviation 0.2–0.6%). The natural isotope ratio of chlorine was not used as an identification criterion. The ion current ratio was calculated and compared with the natural isotope ratio in order to check whether interfering compounds were present.

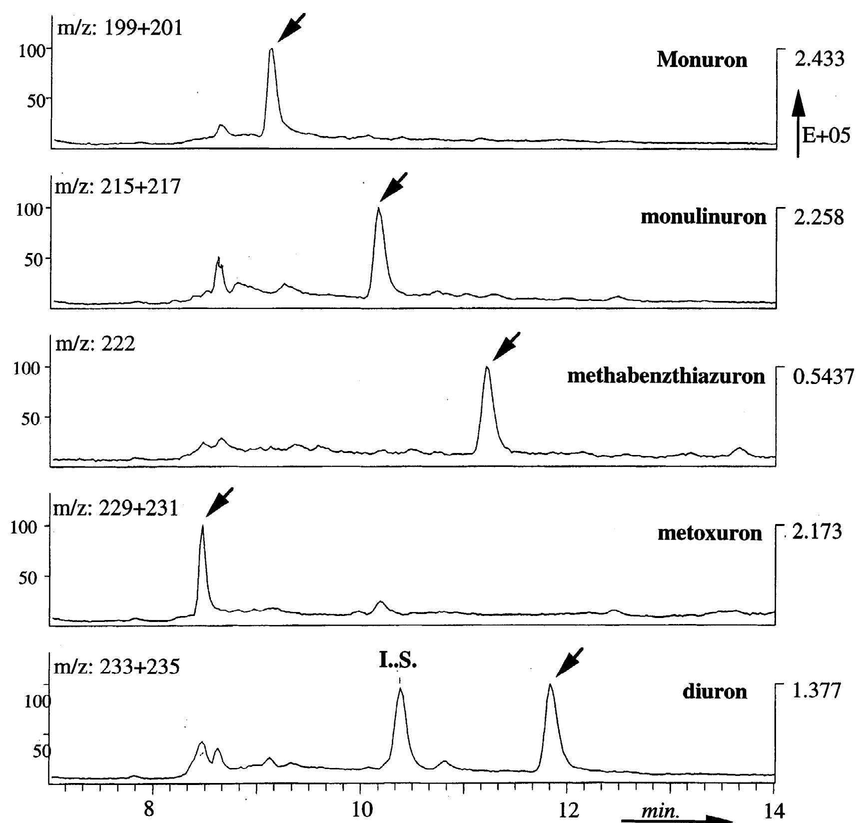

Fig. 4. Ion chromatograms of on-line LC–LC–APCI-MS of a surface water sample containing herbicides at a levels of about 0.1 μg/l. LC conditions: C-1, 3 μm Microspher C_{18} (50 mm×4.6 mm I.D.); C-2, 3 μm Microspher C_{18} (100 mm×4.6 mm I.D.); M-1, methanol–water (10:90, v/v) during 15 min followed by a gradient to methanol–water (60:40, v/v) in 6 min; M-2, methanol–water (60:40, v/v); flow-rates, 1 ml/min; sample injection volume, 11.7 ml; cleanup volume, 22 ml, transfer volume, 6.0 ml. Compounds at retention times: 9.07 min, monuron (0.09 μg/l); 10:09, monolinuron (0.63 μg/l); 11.12 min, methabenzhtiazuron (0.21 μg/l); 8.28 min, metoxuron (0.23 μg/l); 11.50 min, diuron (0.12 μg/l); 10.23 min, fluormeturon as internal standard (I.S.).

The ion chromatograms displayed in Fig. 4 of the surface water sample analysed before with LC(–LC)–UV (see Figs. 2 and 3) and containing the herbicides at levels between 0.1–0.2 μg/l clearly show that LVI-LC–LC–APCI-MS combines high selectivity/sensitivity with a high sample throughput.

A remarkable difference in sensitivity amongst the analytes was noticed. The APCI-MS sensitivity for monolinuron is approximately six times less than the sensitivity for monuron. The only difference in molecular structure of the analytes is the presence of an additional oxygen atom in monolinuron. The oxygen atom lowers the gas phase proton affinity, which is the explanation for the sensitivity difference. The sensitivity difference between diuron and linuron was of the same order of magnitude and has been reported by other authors as well [17].

All calibration plots were linear with R^2 of at least 0.993. The detection limits in Milli-Q water were approximately 0.005 μg/l for monuron, isoproturon, diuron, methabenzthiazuron and metoxuron, 0.025 μg/l for monolinuron and 0.1 μg/l for linuron.

4. Results

The reference samples of the inter-laboratory study were firstly analysed by Method Ia and these data were reported to the organizing Institute (Kiwa). Included were also the data of our home-made recovery experiments involving the analysis of drinking water samples ($n=6$) spiked with the five phenylurea herbicides at levels between 0.1 and 0.5 μg/l. Average recoveries ranged between 99 and 112% with RSD values between 4 and 9%.

Table 2 presents the true values provided by Kiwa and the results obtained by the various methods applied at different times (see Table 1). The residue data obtained by the various methods correspond very well. Beside the good correlation between methods for the spiked samples, no false positives were found with the LC–UV methods for the non-spiked samples indicating their usefulness for screening purposes.

On the basis of chromatogram inspection the limits of quantification (LOQs) for the analytes in the sample investigated with the LC–LC–UV methods were estimated to be 0.05 μg/l (off-line SPE) and 0.1 μg/l (on-line LVI), respectively.

From the signal-to-noise ratio obtained, the LOD ($S/N=3$) obtained by the LVI-LC–LC–APCI-MS method was 0.01 μg/l for all analytes except monolinuron and linuron. For these compounds LODs were approximately 0.05 and 0.2 μg/l, respectively. The favorable sensitivity/selectivity of the LC–MS method allowed to trace the incurred low residues of isoproturon (0.02 μg/l) in the surface water samples.

The identification criteria were met for all analytes. However, in some cases the isotope ratio differed more than 10% from the natural chlorine isotope ratio. For example, in surface water sample SW-3, the isotope ratio measured for monolinuron was 29% lower than the natural isotope ratio. Analysis of surface water sample SW-1, to which no monolinuron had been added, showed the occurrence of a peak at the retention time of monolinuron in the ion chromatogram of mass 215 but not in the ion chromatogram of 217. Thus, the surface water samples contained an interfering compound that contributed to the signal at 215. Since 215 was used as the quantitation mass, due to the interfering compound, the concentration of monolinuron determined by the LC–MS method was higher than the true value (Table 2). This case shows that it is significant to verify whether interfering compounds are present by calculating the isotope ratios. Unfortunately, not all phenyl urea herbicides contain chlorine. For these analytes MS–MS will be more adequate when interfering compounds are present in the samples. The data presented in Table 2 show that matrix interference was not a major problem. However, the limited number of samples gives only an indication about the significance of interfering compounds using the LVI-LC–LC–APCI-MS method.

The various experiments have been carried out over a 281 days period of time (see Table 1), hence, the data indicate stability of analytes in this type of water samples during storage in the refrigerator.

5. Conclusions

The comparative study on the determination of phenylurea compounds in water samples shows a good agreement between the tested five different LC

methods with UV and MS detection. Providing a total time of analysis of about 15 min LVI-LC–LC–UV is attractive for a fast (direct) screening of phenylurea herbicides in environmental waters to a level of 0.1 μg/l.

The combination of SPE and LC–LC–UV allows

Table 2
Analysis of reference water samples with different methods[a]

Compound	Sample[c]	Ref.[d]	Concentration of analyte (μg/l)[b]					
			Ia	Ib	II	III	IV	V
Monuron	DW-1	0.35	0.36					0.37
	DW-2	n.s.	<0.05	<0.05	<0.05	<0.1	<0.1	<0.01
	DW-3	0.22	0.23	0.22	0.22	0.23	0.21	0.25
	SW-1	n.s.	<0.05	<0.05	<0.05	<0.1	<0.1	<0.02
	SW-2	0.15	0.18	0.18	0.17	0.16	0.11	0.14
	SW-3	0.10	0.12					0.089
	GW-1	0.15	0.15	0.15	0.15	0.14	0.14	0.13
	GW-2	0.10	0.11					0.10
Monolinuron	DW-1	0.13	0.12					0.16
	DW-2	n.s.	<0.05	<0.05	<0.05	<0.1	<0.1	<0.05
	DW-3	0.19	0.19	0.18	0.18	0.17	0.16	0.20
	SW-1	n.s.	<0.05	<0.05	<0.05	<0.1	<0.1	<0.05
	SW-2	0.73	0.70	0.70	0.70	1.13	1.04	0.76
	SW-3	0.47	0.44					0.63
	GW-1	0.21	0.19	0.19	0.19	0.18	0.19	0.15
	GW-2	0.13	0.13					0.12
Isoproturon	DW-1	n.s.	<0.05					<0.01
	DW-2	n.s.	<0.05	<0.05	<0.05	<0.1	<0.1	<0.01
	DW-3	n.s.	<0.05	<0.05	<0.05	<0.1	<0.1	<0.01
	SW-1	n.s.	<0.05	<0.05	<0.05	<0.1	<0.1	0.025
	SW-2	n.s.	<0.05	<0.05	<0.05	<0.1	<0.1	0.024
	SW-3	n.s.	<0.05					0.019
	GW-1	n.s.	<0.05	<0.05	<0.05	<0.1	<0.1	<0.01
	GW-2	n.s.	<0.05					<0.01
Diuron	DW-1	0.30	0.30					0.32
	DW-2	n.s.	<0.05	<0.05	<0.05	<0.1	<0.1	<0.05
	DW-3	0.15	0.16	0.18	0.17	0.21	0.21	0.16
	SW-1	n.s.	0.05	0.07	0.07	<0.1	<0.1	0.060
	SW-2	0.15	0.20	0.22	0.21	0.17	0.19	0.19
	SW-3	0.08	0.13					0.12
	GW-1	0.08	0.07	0.09	0.09	<0.1	<0.1	0.075
	GW-2	0.15	0.16					0.15
Linuron	DW-1	n.s.	<0.05					<0.2
	DW-2	n.s.	<0.05	<0.05	<0.05	<0.1	<0.1	<0.2
	DW-3	n.s.	<0.05	<0.05	<0.05	<0.1	<0.1	<0.2
	SW-1	n.s.	<0.05	<0.05	<0.05	<0.1	<0.1	<0.2
	SW-2	n.s.	<0.05	<0.05	<0.05	<0.1	<0.1	<0.2
	SW-3	n.s.	<0.05					<0.2
	GW-1	n.s.	<0.05	<0.05	<0.05	<0.1	<0.1	<0.2
	GW-2	n.s.	<0.05					<0.2

Table 2. Continued

Compound	Sample[c]	Ref.[d]	Concentration of analyte (μg/l)[b]					
			Ia	Ib	II	III	IV	V
Methabenz-thiazuron	DW-1	0.10						0.14
	DW-2	n.s.						<0.01
	DW-3	0.06						0.073
	SW-1	n.s.						<0.01
	SW-2	0.15						0.19
	SW-3	0.20						0.21
	GW-1	0.20						0.21
	GW-2	0.27						0.37
Metoxuron	DW-1	0.07						0.093
	DW-2	n.s.						<0.01
	DW-3	0.18						0.25
	SW-1	n.s.						<0.01
	SW-2	0.13						0.15
	SW-3	0.20						0.23
	GW-1	0.45						0.49
	GW-2	0.25						0.30

[a] Methods Ia, Ib, II, III, IV and V (see text also and Table 1).
[b] No data, sample not analyzed with method.
[c] DW, drinking water; SW, surface water; GW, ground water.
[d] Ref., reference sample; n.s., sample not-spiked with herbicide.

determination of compounds to a level 0.05 μg/l, and the improved selectivity obtained by SPE makes it possible to perform screening without column switching.

For most analytes LVI-LC–LC–APCI-MS provides an LOD of 0.01 μg/l. The inherent high selectivity in combination with a total time of analysis of about 25 min makes this approach attractive for productive analysis.

The study indicated that for these types of analyte/matrices combinations the samples can be stored in the refrigerator over a 280 day period without degradation of the analytes.

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