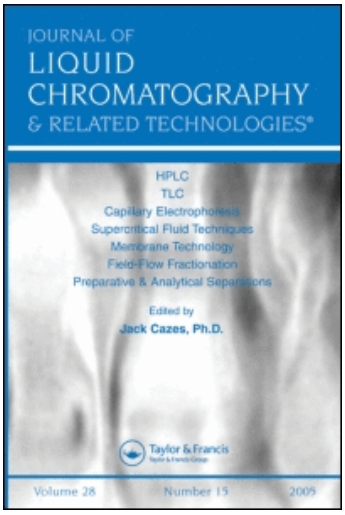

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ELECTROCHEMICAL DETECTION OF PHENYLUREA HERBICIDES IN LIQUID CHROMATOGRAPHY

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ABSTRACT

This paper describes the electrochemical detection of ten phenylurea herbicides after on-line trace enrichment on a small C18 precolumn and liquid chromatography on a C18 analytical column. The method presented shows sub-ppb sensitivity in surface water samples without extensive sample pretreatment. Electrode contamination occurs but does not seriously interfere in the routine analysis of such samples. Selective determination (at 1.0 V) of metoxuron in the presence of other phenylureas allows the detection of 30 ppt of the herbicide in surface water.

INTRODUCTION

Substituted phenylurea herbicides are frequently used in agriculture (1) and appear consequently in run-off and surface

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waters (2). Analysis of these compounds has been done by gas (GC) and liquid (LC) chromatography (3,4). The thermolability of the phenylureas is a serious disadvantage for GC analysis and makes derivatization procedures necessary (3,5,6). Direct determination of phenylureas in surface water by LC with UV absorbance detection is possible but the rather poor sensitivity and selectivity are a serious problem. Recently, our group described an automated LC method based on precolumn technology, for the determination of phenylurea herbicides in surface water in the presence of the corresponding anilines (7). Anilines, which interfere with the separation of the phenylureas are trapped on a platinum-loaded precolumn. The phenylureas themselves pass through and are enriched on a precolumn packed with C18 material; UV detection was done at 243 nm. In this study, we improved the performance of the quoted LC method by using direct electrochemical instead of UV detection for the phenylurea herbicides.

EXPERIMENTAL

Apparatus

The system used consisted of a Perkin Elmer (Norwalk, CT, USA) Series I pump equipped with a Kontron (Zürich, Switzerland) pulse damper, two Altex (Berkeley, CA, U.S.A.) Model 110 pumps, two home-made six-port switching valves and an electrochemical detector consisting of a Metrohm (Herisau, Switzerland) 1096/2 cell equipped with a glassy carbon working electrode (diameter, 3 mm), an Ag/AgCl/1 M LiCl (in 50% methanol) reference electrode, a platinum auxiliary electrode and a home-made potentiostat/amplifier. The volume of the detection cell was approx. 1 µl. For the purpose of comparison a variable-wavelength UV detector (Perkin Elmer LC-55) was used at 243 nm. Chromatograms were recorded on a Kipp and Zonen (Delft, the Netherlands) BD 40 recorder.

Chemicals

HPLC-grade methanol was obtained from J.T. Baker (Deventer, the Netherlands). LC-water was obtained by purification of demineralized water in a Milli-Q (Millipore, Bedford, MD, U.S.A.) filtration system. Sodium monohydrogen phosphate and phosphoric acid were analytical grade from Baker.

The phenylurea herbicides under investigation were gifts from the Food Inspection Service (Amsterdam, the Netherlands) and are listed in Table I. Stock solutions of these compounds were made in methanol and stored at -20°C. These solutions were diluted with LC-water to obtain standards at the ppm and ppb level.

Chromatography

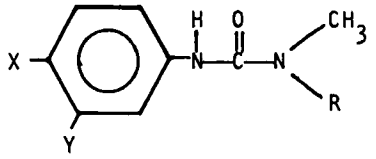
The herbicides were separated on a 100 x 3.0 mm I.D. glass column packed with 8 µm CP-Spher-C18 by Chrompack (Middelburg, the Netherlands). The mobile phase consisted of 0.02 M phosphate buffer (pH 7.0) - methanol (45:55) and was delivered at 0.4 ml/min. Under these conditions sufficient resolution was obtained (cf. Fig. 3 below). The home-made 11 x 2.0 mm I.D. precolumn used for the on-line trace enrichment was slurry packed by hand with 10 µm LiChrosorb RP-18 (Merck, Darmstadt, G.F.R.) as described elsewhere (8). This type of precolumn is commercially available from Chrompack.

Methods

The on-line trace enrichment, separation and detection were done using the experimental set-up schematically shown in Fig. 1. Compared to ref. 7 two changes were introduced: a third pump was used instead of a low-pressure solvent selection valve and all values were operated by hand instead of the microprocessor-controlled switching apparatus.

TABLE 1

Phenylurea Herbicides under Investigation



	Substituents		
Herbicide	X	Y	R
Fenuron	H	H	CH_3
Metoxuron	OCH_3	Cl	CH_3
Monuron	Cl	H	CH_3
Monolinuron	Cl	H	OCH_3
Metobromuron	Br	H	OCH_3
Chlortoluron	CH_3	Cl	CH_3
Diuron	Cl	Cl	CH_3
Chlorbromuron	Br	Cl	OCH_3
Linuron	Cl	Cl	OCH_3
Chloroxuron	4-Cl-C_6H_4O	H	CH_3

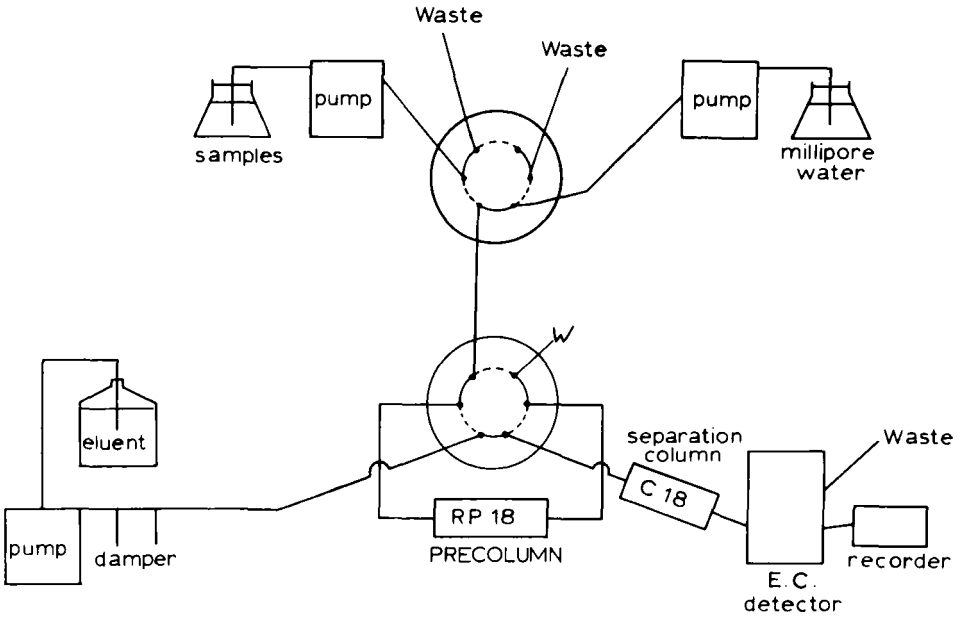


FIGURE 1. Experimental set-up for the on-line trace enrichment, separation and electrochemical detection of phenylurea herbicides. Precolumn, 11 x 2.0 mm I.D. packed with 10 µm LiChrosorb RP-18; analytical column, 100 x 3.0 mm I.D. packed with 8 µm CP-Spher-C18; eluent, 0.02 M phosphate buffer (pH 7.0) - methanol (45:55), delivered at 0.4 ml/min.

RESULTS AND DISCUSSION

Choice of oxidation potential

To determine the optimal detection potential, 24 µl of a mixture of eight herbicides (2 ppm each) were injected with a loop in the position of the precolumn (cf. Fig. 1) and chromatographed. The detection potential was varied from 0.9 to 1.4 V with 0.1 V increments. Peak areas were normalized per nMol of herbicide. The results shown in Fig. 2 indicate that metoxuron is quantitatively oxidized at 1.0 V, whereas the other herbicides

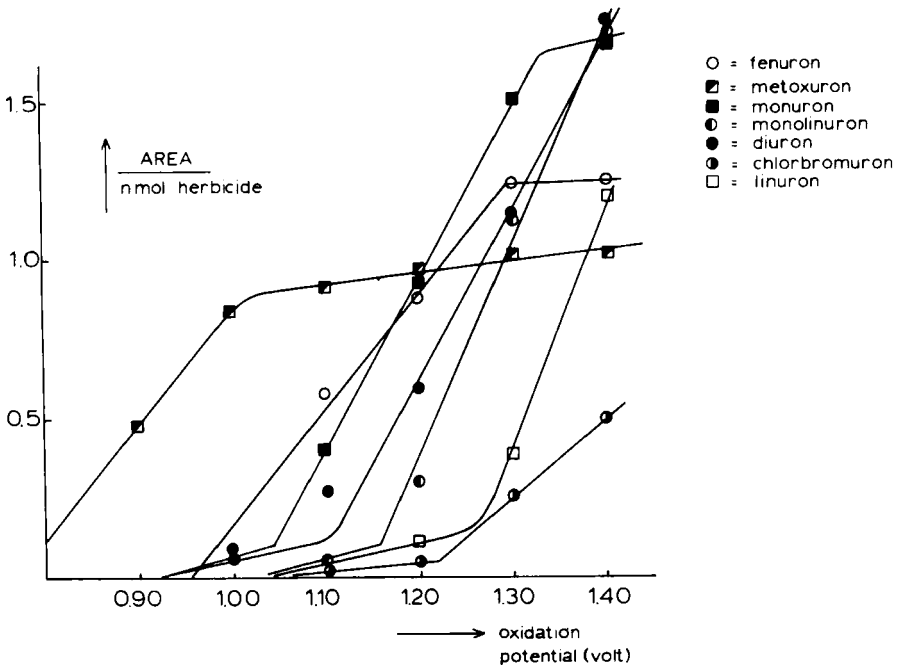


FIGURE 2. Signals per nMol herbicide for 24 µl loop injections of a standard solution at different oxidation potentials.

only start to give significant signals at about 1.2 V. This makes 1.0 V a suitable potential for the selective detection of metoxuron in the presence of other phenylurea herbicides and many other interfering compounds (see below). From Fig. 1 it is evident that if we want to oxidize all herbicides - and especially linuron and chlorbromuron - efficiently, the detection potential should be 1.4 V or even higher. However, at such a high detection potential the background current and noise are considerably increased. Therefore, a potential of 1.3 V seems to be a fair compromise.

The oxidation potential for a particular herbicide is strongly determined by its substituents. The methoxy group in

the para position of the benzene ring results in a decrease of the oxidation potential (metoxuron vs. fenuron). Electronegative substituents such as chlorine and bromine atoms cause an increase of the oxidation potential (diuron vs. monuron and linuron vs. monolinuron). Finally, if the methoxy substituent is on the non-aromatic nitrogen atom, the oxidation potential increases (linuron vs. diuron, monolinuron vs. monuron).

Analytical aspects

A standard solution of the herbicides in LC-water was used to determine the recovery of the trace enrichment procedure, and the linearity and the detection limits with the electrochemical detector set at 1.3 V. The concentrations of the individual herbicides in the standard solution ranged between 0.8 and 43 ppm to obtain roughly the same peak heights for all test compounds. Peak heights were compared for a 27 µl loop injection of this mixture and a 10-ml trace enrichment (sampling rate 1 ml/min) experiment with the same standard solution after its 500-fold dilution. The precolumn was eluted on-line during 6 min (2.4 ml) to ensure quantitative desorption and reconditioned with 10 ml LC-water before the introduction of the next sample. The experiment was carried out in duplicate. The recoveries of the trace-enrichment procedure, reported in Table II, are 94-98% for all phenylureas excepting fenuron. As is known from earlier results (7), the poor recovery for the latter herbicide is due to breakthrough during the preconcentration step.

The linearity of the trace-enrichment procedure was checked by plotting a calibration curve for 6 herbicide-containing solutions prepared by 500-20,000 fold dilution of the 0.8-43 ppm standard mixture. The calculated regression coefficients (0.9979-0.9999; cf. Table II) show the good linearity over the range tested, e.g., over at least one to two orders of magnitude around the 1-ppb level (from 0.04-1.6 ppb for fenuron, to 2.2-86

TABLE II

Recovery, Linearity and Repeatability of Herbicide Trace Enrichment with Determination by LC with Electrochemical Detection at 1.3 V*

Herbicide	Sample concn.		Recovery (%)	Regression coefficient (n = 6)	Rel. S.D. (%; n = 11)
	loop inj. (ppm)	trace enrich. (ppb)			
Fenuron	0.8	1.6	44	0.9979	6.0
Metoxuron	1.9	3.8	98	0.9985	3.5
Monuron	1.3	2.6	98	0.9992	3.0
Monolinuron	2.8	5.6	94	0.9991	5.5
Diuron	4.3	8.6	98	0.9997	5.0
Chlorbromuron	43.0	86	94	0.9999	6.0
Linuron	27.0	54	96	0.9999	5.5

*For all experimental details, see text

ppb for chlorbromuron). The repeatability was tested by preconcentrating and analyzing a 1-70 ppb standard mixture 11 times; the precolumn was reconditioned on-line with 10 ml LC-water after each experiment. The results which are included in Table II show that the rel. S.D. is between 3 and 6% for all herbicides, including linuron and chlorbromuron, which are only partly oxidized under the experimental conditions.

Fig. 3 shows a typical chromatogram obtained after preconcentration of a 10 ml standard solution containing ten herbicides at the low- and sub-ppb level. This chromatogram was used for calculating the detection limits with a signal-to-noise ratio of

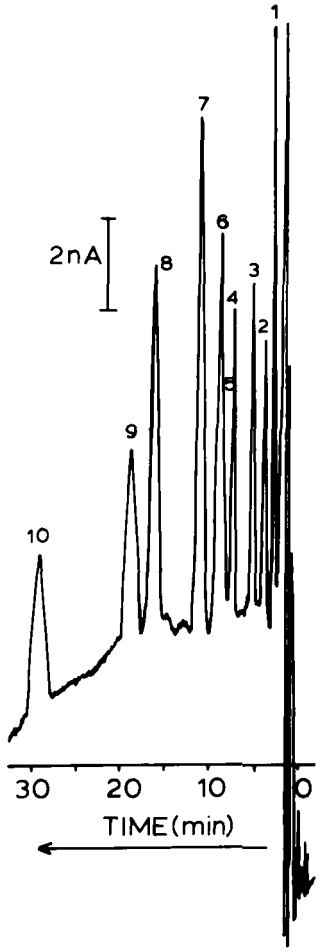


FIGURE 3. Trace enrichment and electrochemical detection of a 10 ml standard solution in LC-water using the set-up of Fig. 1; detection at 1.3 V. 1 = fenuron (0.32 ppb), 2 = metoxuron (0.40 ppb), 3 = monuron (0.30 ppb), 4 = monolinuron (0.50 ppb), 5 = metobromuron (0.80 ppb), 6 = chlortoluron (0.70 ppb), 7 = diuron (0.90 ppb), 8 = chlorbromuron (3.4 ppb), 9 = linuron (2.7 ppb) and 10 = chloroxuron (1.5 ppb).

TABLE III

Detection Limits for Phenylurea Herbicides

Herbicide	LC-El. chem. (this paper)*		LC-UV (ref. 7)*	GC-El. capture (refs. 5, 6)+
	ppb	ng	ppb	ppb
Fenuron	0.01	0.1	0.3	0.3
Metoxuron	0.02	0.2	0.3	0.1
Monuron	0.02	0.2	0.3	0.1
Monolinuron	0.04	0.4	0.4	0.1
Metobromuron	0.04	0.4	0.9	0.1
Chlortoluron	0.04	0.4	0.5	0.1
Diuron	0.05	0.5	0.3	0.1
Chlorbromuron	0.4	4.0	0.6	0.1
Linuron	0.3	3.0	1.0	0.1

*On-line trace enrichment of 10 ml sample.

+Extraction of 50-ml sample, hydrolysis and derivatization with heptafluorobutyric anhydride; 1 µl injection.

five. These detection limits are reported in Table III and compared with some literature data. One notes that - except for linuron, diuron and chlorbromuron - the present method is at least one order of magnitude more sensitive than the previously described LC-UV method and comparable or even more sensitive than capillary GC with electron capture detection, for which a 50 ml sample, was needed. The absolute detection limits in GC with electron capture detection are, of course, much lower (about 1 pg) than those recorded for LC with electrochemical detection (about

1 ng; cf. Table III). The limited injection volume of about 1 µl used in capillary GC, however, severely detracts from the sensitivity in concentration units of the GC method. Finally, one should notice that the present LC method allows direct introduction of the water samples without extraction, hydrolysis and derivatization.

Surface water samples and electrode contamination

Surface water (river Amstel, Amsterdam, the Netherlands) spiked with eight phenylureas at the 1.4-17 ppb level, was filtered over a 0.8 µm cellulose acetate membrane filter. Then, 10 ml were preconcentrated and analyzed as described above with detection at a potential of 1.3 V. As can be seen from Fig. 4, detection of metoxuron and fenuron is impossible because of the high background signal occurring in the early part of the chromatogram. All other herbicides can, however, easily be determined at low- and sub-ppb levels in this sample. Because of the low noise level, further increase of the detector sensitivity is, in principle, possible, but then monuron and monolinuron will also be hidden under the background peak. For the rest, if the electrochemical detection at 1.3 V is compared with the UV method (7) at 243 nm, the present method clearly shows better selectivity towards surface water samples.

The influence of contamination of the electrode surface on the sensitivity and repeatability was investigated as follows. 27 µl of a standard solution in LC-water were injected onto the separation column (i.e., without trace enrichment) and a chromatogram was recorded with the electrochemical detector equipped with freshly polished electrodes. A value of 100 was arbitrarily assigned to the peak heights so obtained. Then a 10 ml surface water sample was preconcentrated and analyzed. Next, another 27 µl injection of a standard solution in LC-water was done and the

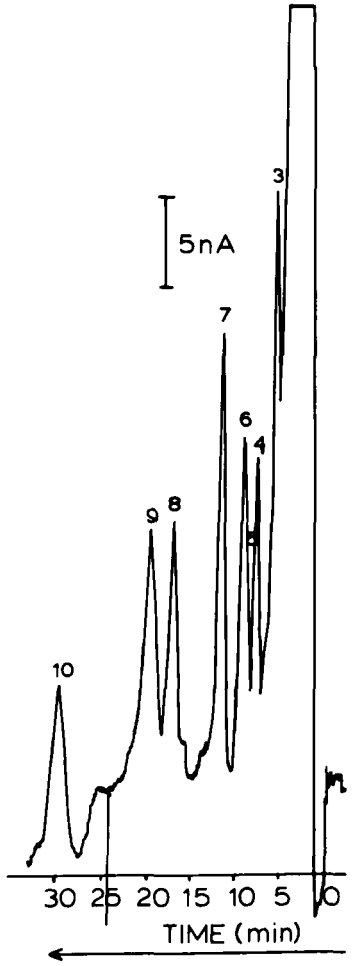


FIGURE 4. Trace enrichment and electrochemical detection of 10 ml river water spiked with the compounds of Fig. 3, except for fenuron and metoxuron. Concentrations: (3) 1.4 ppb, (4) 2.6 ppb, (5) 3.8 ppb, (6) 3.6 ppb, (7) 4.2 ppb, (8) 17.0 ppb, (9) 13.6 ppb and (10) 7.4 ppb. Other conditions as in Figs. 1 and 3.

TABLE IV

Influence of Electrode Surface Contamination on the Sensitivity and Repeatability of Standard Loop Injections

Herbicide	Concn. of standard (ppm)	Signal of 27 µl standard after passage of 10 ml surface water*	
		peak height	rel. S.D. (%)
Monuron	1.4	75	9
Monolinuron	2.8	65	11
Diuron	4.3	71	9
Chlorbromuron	17.0	56	9
Linuron	13.6	58	7
Chloroxuron	7.4	85	9

*7 cycles (i.e., latter 7 cycles of 9 cycles actually run; cf. text); average peak heights relative to those in clean-electrode situation which were set at 100.

peak heights now obtained were compared with those of the first 27 µl injection. This cycle was repeated 9 times and each time the comparison with the clean-electrode situation was made. The results are given in Table IV. It is evident that the signals decrease after the analysis of a surface water sample, probably due to deactivation of the electrode surface. It was observed that the system sensitivity - i.e., the peak height of the various 27-µl loop injections relative to that recorded in the clean-electrode situation - dropped rapidly in the first and second cycle but, next, became virtually constant at the values reported in Table IV. Substituting peak areas for peak heights gave the same results. In other words, the electrochemical detector can successfully be used for the analysis of a series of

TABLE V

Influence of Electrode Surface Contamination on the Sensitivity and Repeatability of 10-ml Surface Water Trace Enrichment

Herbicide	Sample concentration (ppb)	Signal of 10 ml surface water trace enrichment*			
		peak height	peak area	rel. S.D. (%) height	rel. S.D. (%) area
Monuron	0.7	46	53	11	11
Monolinuron	1.4	66	76	12	11
Diuron	2.2	87	111	10	10
Chlorbromuron	8.5	65	98	14	9
Linuron	6.6	79	88	13	15
Chloroxuron	3.7	67	92	13	13

*7 cycles (i.e., latter 7 cycles of 9 cycles actually run; cf. text); average signals relative to those recorded in Table IV.

samples, without in-between cleaning of the electrodes. It is interesting to note that the order of increasing loss of detection sensitivity parallels that of increasing oxidation potential recorded in Fig. 2.

In Table V, the peak heights and peak areas obtained after preconcentration and analysis of a series of 10-ml spiked surface water samples are reported, using the same model compounds and the same 9-cycle procedure as with Table IV. The peak heights and areas are corrected for the decrease in sensitivity recorded for the standard loop injections in Table IV. The peak height vs. peak area results indicate that the repeated passage of the sur-

face water samples causes additional band broadening in the LC system (pre- plus analytical column). Fortunately, however, resolution remained sufficiently high for satisfactory quantitative analysis.

From Table V one sees that for four out of the six herbicides studied, the results of the peak area measurements are, within the experimental error of about ± 10%, the same for trace enrichment and the 27 µl loop injections. A substantial difference is observed only for monuron and monolinuron. Since breakthrough during trace enrichment cannot explain this phenomenon (7), partly reversible deactivation of the electrode surface most probably explains these results. That is, the deactivation of the electrode caused by early eluting contaminants or their oxidation products (which affects the sensitivity for monuron and monolinuron) may well be restored via desorption phenomena before the other herbicides pass through the detector cell. Be that as it may, the more important conclusion from Table V is that the rel. S.D. shows values of between 9 and 15% for all test solutes and with both peak area and peak height measurements. That is low levels of all herbicides can indeed be safely determined in series of samples, despite the occurrence of (some) contamination of the electrode surface.

Selective detection of metoxuron

When discussing Fig. 2, attention was already called to the promising alternative of selective electrochemical detection of metoxuron at 1.0 V. At this potential, the selectivity towards surface water samples is strongly improved. In Fig. 4 the metoxuron peak was completely covered by the background signal. At a detection potential of 1.0 V, however, metoxuron can adequately be detected as is seen in Fig. 5. In this figure, the metoxuron spiking level is 0.6 ppb. The detection limit for this

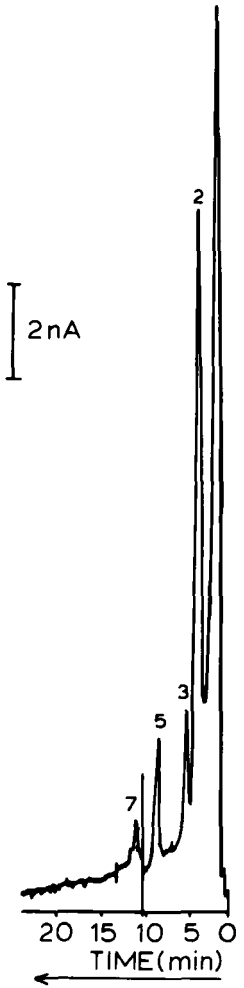


FIGURE 5 Selective detection of 0.6 ppb metoxuron at 1.0 V. after on-line trace enrichment from 10 ml river water. As regards the other phenylureas, small peaks show up only for monuron (1.4 ppb), metobromuron (3.8 ppb) and diuron (4.2 ppb). Other conditions as in Fig. 1.

widely used herbicide can be calculated to be about 30 ppt (signal-to-noise ratio, 5).

The area of the peak recorded with the 0.6 ppb spiked surface water sample was 84% as compared to the peak area of a preconcentrated standard solution. Since this sensitivity decrease is much less than that for monuron and monolinuron at 1.3 V, one may conclude that adsorption of surface water components on the electrode surface is less important at this lower potential.

CONCLUSIONS

The combination of liquid chromatography with precolumn switching techniques and electrochemical detection at 1.3 V offers a sensitive screening method for phenylurea herbicides in surface water samples without extensive sample pretreatment. In addition, the method can be easily automated as was done before (7).

In principle, all ten phenylurea herbicides can be determined at sub-ppb levels. With real (surface water) samples, however, fenuron and metoxuron are hidden beneath a steep background. This problem can possibly be solved by applying more selective precolumn techniques based on cation exchangers (9). Moreover, metoxuron can be selectively detected in real samples in the presence of other herbicides at 1.0 V with extremely high sensitivity (30 ppt).

When analyzing a series of surface water samples, detection sensitivity dropped by a factor of about two, due to contamination of the electrodes. Fortunately, however, this decrease in sensitivity occurred during the analysis of the first two samples. Subsequently, the detector sensitivity remained essentially constant. That is, the analysis of series of samples is not severely hindered.

ACKNOWLEDGMENT

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REFERENCES

1. Ashton, F.M. and Crafts, A.S., Mode of Action of Herbicides, Wiley, New York, 1973, p. 1.

2. Stöber, I. and Reupert, R., Vom Wasser, 51, 273, 1978.

3. de Kok, A., Roorda, I.M., Frei, R.W. and Brinkman, U.A.Th., Chromatographia, 14, 579, 1981.

4. Lawrence, J.F. and Turton, D., J. Chromatogr., 159, 207, 1978.

5. de Kok, A., Vos, Y.J., van Garderen, C., de Jong, T., van Opstal, M., Frei, R.W., Geerdink, R.B. and Brinkman, U.A.Th., J. Chromatogr., 288, 71, 1984.

6. de Kok, A., van Opstal, M., de Jong, T., Hoogcarspel, B., Geerdink, R.B., Frei, R.W. and Brinkman, U.A.Th., Int. J. Environ. Anal. Chem., 18, 10, 1984.

7. Goewie, C.E., Kwakman, P., Frei, R.W. and Brinkman, U.A.Th., J. Chromatogr., 284, 73, 1984.

8. Goewie, C.E., Nielen, M.W.F., Frei, R.W. and Brinkman, U.A.Th. J. Chromatogr., in press, 1984.

9. Nielen, M.W.F., Frei, R.W. and Brinkman, U.A.Th., J. Chromatogr., in press, 1984.