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Determination of herbicides in surface water by means of a supported liquid membrane technique and high-performance liquid chromatography

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Abstract

A technique for sample workup and enrichment using a supported liquid membrane (SLM) and high-performance liquid chromatography (HPLC) was used for the determination of basic herbicides in spiked lake water. The herbicides studied were propazine and simazine as triazine herbicides, and fenuron, monolinuron and diuron as phenylurea herbicides. The alkalized sample of water, as the donor solution, comes in contact with the liquid membrane into which analytes are extracted. On the other side of the membrane, analyzed compounds are trapped by dissociation in acidic acceptor solution. Enriched and cleaned up herbicides were injected into a HPLC system with ultraviolet detection. An increase of concentration after SLM extraction was observed only for triazine herbicides. The detection limit for enrichment of 40 ml of lake water was about 0.1 ppb.

Keywords: Membranes; Water analysis; Environmental analysis; Sample preparation; Pesticides; Phenylureas; Triazines

1. Introduction

Over the last few years triazine, carbamate and urea derivatives have become widely used as selective herbicides and insecticides, and there is a consequent need to determine these residues in a variety of matrices. They are extensively applied as the principal agrochemical control of broadleaf and grassy weeds, in croplands, on roads, on railways. Also because of their relatively high water solubility and persistence they are widely distributed in aquatic environments, including groundwater, rivers, lakes [1], estuaries [2] and rain [3]. Numerous methods have been published for extraction and preconcentration of herbicides from natural samples using such techniques as liquid [4,5], solid-phase [6], soxhlet and supercritical fluid [7] extraction or cation exchange [8].

Monitoring of herbicides at their usually low concentrations requires a selective and sensitive method. Gas chromatography with selective detection [2], HPLC and a combination of this technique with mass spectrometry [9,10] or even a combination of HPLC type precolumn trace enrichment and GC–MS analysis of triazines in real-life water samples [11] are possible methods. These sometimes sophisticated methods are expensive and complicated.

This paper describes a sample preparation technique using supported liquid membranes for analysis with satisfactory sensitivity by HPLC with UV detection, equipment available in most laboratories.

The liquid membrane technique developed for

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analytical purposes by Audunsson [12] has been applied to the analysis of amines in urine [13] in blood plasma [14], in ambient air [15] and rain water [16], carboxylic acids [17], organic acids in manure [18], acidic herbicides as phenoxy acids in humic rich water [19], sulfonylurea herbicides [20] and even metals [21]. The method has also been used for field sampling of herbicides from stream water [22,23]. An automated system for the trace analysis of organic compounds with SLM for sample preparation was applied also [24].

2. Experimental

2.1. Reagents and solvents

Propazine and simazine were obtained from Serva Feinbiochemica, Heidelberg (Germany), fenuron and diuron from the Institute of Organic Industry, Warsaw (Poland) and monolinuron from Pestanal Riedel de Haenag Seelze, Hannover (Germany). A stock solution of herbicides was prepared in methanol (Chemical Factory Oświęcim, POCh Gliwice, Poland) at concentrations of 0.1 mg/ml. A series of calibration solutions for HPLC–UV analysis in the range 100 ppm to 100 ppb were obtained by diluting the stock solution in methanol, and 0.1–100 ppb for extraction by diluting in water. Ammonium sulfate, sodium hydroxide, ammonium hydroxide 25% NH_3 and sulfuric acid were from POCh S.A. Gliwice (Poland). All chemicals were of analytical grade.

Organic solvents: di-*n*-hexyl ether (Sigma, St. Louis, MO, USA) and *n*-undecane (Merck, Darmstadt, Germany) were used for impregnation of membranes.

2.2. HPLC apparatus and chromatographic conditions

The HPLC instrument consisted of a HPP 4001 syringe pump (Laboratorni Pristroje Praha, Czechoslovakia), valve injector Reodyne (Berkeley CA, USA) equipped with a 20-μl loop and UV 254 nm detector (ELPAN, Lubawa, Poland). The chromatography was carried out on LiChrosorb 5-μm RP 18 (Merck, Darmstad, Germany) column (100 × 4 mm I.D.). Ammonium sulfate buffer, pH 7, and methanol (80:140, v/v) were used as mobile phase. For this purpose 8 ml of 25% ammonium hydroxide was diluted to 2 l, 8 ml of 0.5 *M* $(NH_4)_2SO_4$ was added to 200 ml of this solution, and the pH was adjusted to 7 with 0.5 *M* H_2SO_4. The mobile phase was filtered (17 G5 glass filter) and degassed for 5 min with a water vacuum pump to prevent bubble formation in the detector.

2.3. Extraction procedure

Sodium hydroxide and sample solutions were pumped by peristaltic pump into a mixing coil that consisted ca.1 m of 0.5 mm I.D. teflon tubing coiled with a diameter of 20 mm. Mixed solutions were passed over the liquid membrane in the membrane separator (Fig. 1a) which was made of two PTFE blocks (diameter 120 mm and thickness 8 mm) with machined spiral grooves facing each other (depth 0.25 mm, width 1.5 mm, length 250 cm and total volume ca.0.80 ml) (Fig. 1b) [22,23].

Aluminium blocks with 6 mm thickness were used to make the construction rigid. A porous PTFE membrane with polyethylene backing, was from Milipore FG (Ireland), (pore size 0.2 μm, total thickness 175 μm, of which 115 μm is polyethylene net, porosity 0.70). After impregnation by soaking for 15 min in *n*-undecan or dihexyl ether the membrane was placed between two PTFE blocks and the whole separator was damped together with eight screws. The excess of solvent on the surface of the liquid membrane was removed by pressing with water through both channels. In the separator the membrane separated the two channels: the donor for extraction of herbicides from alkaline solution into the membrane and the acceptor with stagnant sulfuric acid solution for reextraction of analytes from the membrane. After a pre-determined time of extraction, 20 μl or 10 μl of acceptor solution were injected into the HPLC.

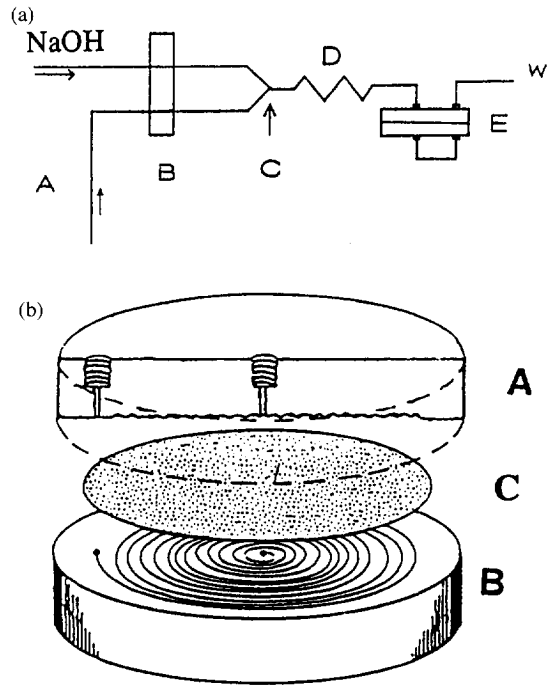

Fig. 1. (a) Set up for membrane enrichment of basic herbicides in water: A, herbicide sample; B, peristaltic pump; C, confluence point of sample and NaOH solution; D, mixing coil; E, membrane separator with stagnant acceptor solution; W, waste. (b) The membrane separator: A, aluminium backup; B, PTFE block with grooves like Archimedes' spiral; C, impregnated liquid membrane.

3. Results and discussion

3.1. Optimization of membrane extraction

To optimize the membrane performance the enrichment factor was plotted as a function of donor pH, acceptor pH and flow-rate of donor solution. The enrichment factor F_e is expressed as:

$$F_e = \frac{c_a}{c_d}$$

where c_a is the concentration of analyte in the acceptor solution after extraction and c_d is the concentration of analyte in the donor solution.

3.2. Influence of acceptor pH

Different acceptor solution pHs were obtained by adding different amounts of H_2SO_4. The influence of the acceptor pH on herbicide enrichment was investigated using dihexyl ether as the extraction solution in the liquid membrane. As a donor solution 0.1 *M* NaOH was chosen, containing 1 ppm of propazine, simazine, fenuron, monolinuron and diuron which was passed over the membrane with flow-rate F_d = 0.2 ml/min for 60 min. After extraction, 10 μl of acceptor solution was injected into the HPLC and the concentration of analytes was calculated.

Fig. 2 shows the influence of the pH of the acceptor solution on the enrichment factor. We observed only simple permeation of phenylurea herbicides through the membrane and the enrichment factor was ca. 1. Only simazine and propazine, which have weak basic properties, were preconcentrated nine and seven times more, respectively, in 0.5 *M* H_2SO_4 to compare with acceptor solution pH 4.

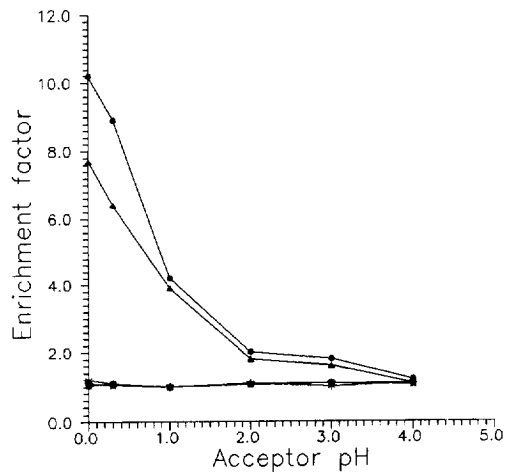

Fig. 2. Enrichment factor for fenuron (*), monolinuron (■), diuron (★), propazine (▲) and simazine (●) versus acceptor pH. Acceptor: different concentrations of H_2SO_4, extraction time of 60 min, membrane impregnated with di-hexyl ether, f_d=0.2 ml/min, donor was 0.1 *M* NaOH containing 1 ppm of herbicides.

3.3. Influence of donor pH

Solutions of the donor phase containing 1 ppm of herbicides with different pHs were prepared to examine the influence of acidity on the enrichment factor of investigated substances. For this purpose sodium phosphate buffer was used for the donor from pH 3 to pH 11; 0.1 *M* NaOH for pH 13 and 1 *M* NaOH for pH 14. The flow-rate of the donor was 0.2 ml/min, the time of extraction was 60 min and the acceptor was 0.5 *M* H_2SO_4. After the enrichment process, the acceptor solution was neutralized using 1 *M* NaOH and 20 μl was injected into the HPLC. The extraction of phenylurea herbicides did not depend on the pH of the donor (see Fig. 3). Propazine and simazine were enriched nine and eleven times, respectively, in the case of 1 *M* NaOH. Preconcentration starts from pH 4 because the pK_a value is 1.90 for simazine and 1.85 for propazine [25]. In this case we have observed simple carrier transport with chemical reaction of the permeant in the acceptor phase [26] because charged triazines are not soluble in the membrane and enrichment is achievable. Increasing the concentration of sodium hydroxide (pH 14) in the donor solution could increase the partition coefficient due to a salting out effect. When different amounts of herbicides were used in the donor solution it was found that enrichment showed a linear correlation with concentration in the range from 1 ppb to 1 ppm of triazines.

3.4. Influence of donor flow-rate

The influence of donor flow-rate on enrichment process of herbicides was also investigated. For this purpose *n*-undecane as a membrane solvent, 0.1 *M* NaOH with 1 ppm of herbicides as donor solution and 0.5 *M* H_2SO_4 as acceptor solution were used. flow-rates: 0.2 ml/min, 0.4 ml/min, 0.7 ml/min, 1.4 ml/min and 2.1 ml/min were applied for the 12 ml of donor. We have obtained different enrichment factors for triazines; lower values for higher flow-rates. For example, the enrichment factor was three times lower for simazine when a flow-rate was increased ca. ten times (Fig. 4). In the case of large

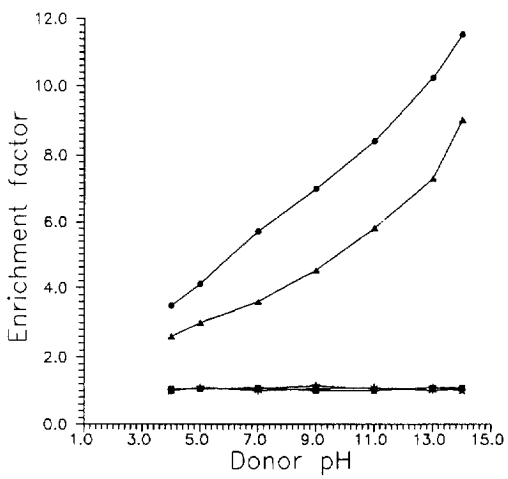

Fig. 3. Enrichment factor for fenuron (*), monolinuron (■), diuron (★), propazine (▲) and simazine (●) versus donor pH (sodium phosphate buffer pH 3-11, 0.1 *M* NaOH, pH 13; 1 *M* NaOH, pH 14. Acceptor was 0.5 *M* H_2SO_4. Liquid membrane impregnated with di-hexyl ether, f_d=0.2 ml/min, extraction time of 60 min.

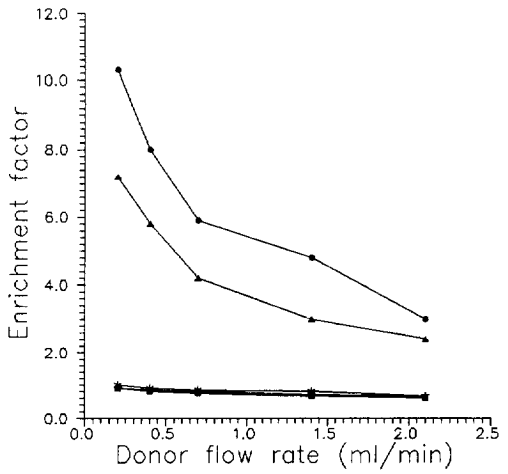

Fig. 4. The influence of donor flow-rate on enrichment factor. *n*-Undecane was used as the membrane solvent, 12 ml of 0.1 *M* NaOH with 1 ppm of herbicides was used as the donor solution pumped at different flow-rates, 0.5 *M* H_2SO_4 was used as the acceptor solution. The symbols are the same as in Fig. 3.

sample volumes the use of higher flow-rates is profitable because it permits to obtain a greater amount of analyte (in the same analysis time) in spite of the lower enrichment factor.

3.5. Calculation of extraction efficiency

Extraction efficiency E is expressed in percent of analyte extracted from the donor solution to the acceptor solution and was calculated from equation:

$$E = \frac{V_a \cdot h_a}{f_d \cdot t_e \cdot h_d} \cdot 100\%$$

where: V_a is the volume of the acceptor phase (ml); h_a is the peak height of analyte in the acceptor after enrichment, determined by HPLC; f_d is the flow-rate of the donor phase (ml/min); t_e is the time of extraction (min); h_d is the peak height of the analyte in the donor, determined by HPLC.

In our experiment we have used dihexyl ether, *n*-undecane and a dihexyl ether:*n*-undecane (1:1, v/v) mixture as extraction phases for herbicides in 0.1 *M* NaOH with a concentration of 100 ppb during 2 h of extraction, flow-rate: 0.2 ml/min. Acceptor phase was 0.8 ml of 0.5 *M* sulfuric acid. From these data the extraction efficiency calculated for propazine and simazine was 53% and 64%, for *n*-undecane; 68% and 76% for the 1:1 *n*-undecane and dihexyl ether mixture; 78% and 85% for dihexyl ether, respectively.

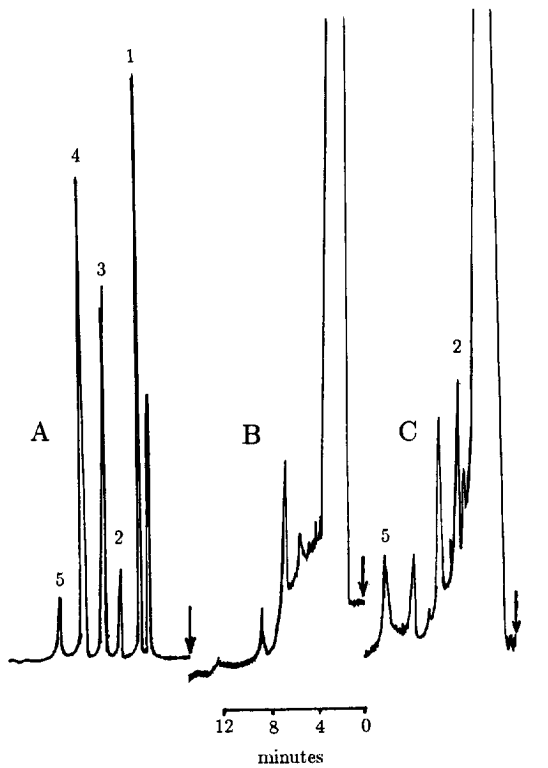

Fig. 5. Chromatograms of investigated herbicides: A, standard solution (1 fenuron, 2 propazine, 3 monolinuron, 4 diuron, 5 simazine); B, sample of 40 ml of lake water after SLM enrichment; C, sample of 40 ml of lake water spiked with 1 ppb of propazine and simazine. SLM extraction with di-*n*-hexyl ether was carried out with the donor at pH 14; flow-rate, 0.2 ml/min; acceptor, 0.5 *M* H_2SO_4. HPLC with UV detector at 254 nm; column, 100 × 4 mm I.D. with LiChrosorb 5-μm RP18; ammonium phosphate buffer (pH 7) and methanol (80:140, v/v) was used as the mobile phase.

3.6. Chromatograms

Using the above-mentioned chromatographic conditions, complete separation of fenuron (1), propazine (2), monolinuron (3), diuron (4) and simazine (5) was achieved in 10 min. Fig. 5A shows a typical run of a 500-ppb standard mixture, Fig. 5B shows 20 μl of acceptor solution after enrichment of 40 ml of lake water with the liquid membrane technique and Fig. 5C shows 20 μl of acceptor solution after enrichment of 40 ml of lake water spiked with 1 ppb of propazine and simazine. SLM extraction with di-*n*-hexyl ether was done with optimum donor (1 *M* NaOH), a flow-rate of 0.2 ml/min and acceptor (0.5 *M* sulfuric acid). Retention times of herbicides were inversely proportional to their polarity and their solubility in water. The shortest retention time was for fenuron and its solubility was 3850 mg/l, monolinuron was 735 mg/l, diuron 42 mg/l, simazine and propazine 5 mg/l. Only propazine had a shorter retention time than monolinuron and diuron probably due to protonation in the mobile phase [25].

3.7. Discussion

Enrichment of herbicides was observed only for propazine and simazine because phenylurea herbicides are hydrolyzed in alkaline and acid media [28]. As we can observe in Fig. 1C it is easy to detect even 0.1 ppb of triazines after enrichment of 40 ml of lake water. Changing the wavelength of UV detector to 220 nm, we can also decrease the limit of detection at least ten times because of the higher absorption of triazines at a shorter wavelength [26]. It is also possible to increase volume of the lake water to lower the limit of triazine detection to the ppt range, but unfortunately sampling time also increases by up to a few hours. Peaks of unknown substances appeared from the very complex matrix of natural lake water (Fig. 1B), probably organic amines or other basic substances which did not interfere with the substances investigated. The detection limit of triazines finally established was 0.1 ppb, which is ten times lower than the maximum residue limit in surface water [27].

4. Conclusions

The determination of basic herbicides in surface water by means of liquid-supported membrane technique and HPLC was investigated and it was shown that only triazines were successfully enriched.

The highest enrichment factor was achieved when 0.5 *M* sulfuric acid was used as the acceptor solution, 1 *M* sodium hydroxide as donor solution, flow-rate: 0.2 ml/min and when dihexyl ether was used for impregnation of the membrane. Maximum extraction efficiency was 78% for propazine and 85% for simazine.

The enrichment of triazines was proportional to their concentration in the range from 1 ppb to 1 ppm.

Using SLM technique and HPLC–UV analysis it was possible to determine 0.1 ppb of triazines in lake water.

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