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Determination of glyphosate and its metabolite aminomethylphosphonic acid in fruit juices using supported-liquid membrane preconcentration method with high-performance liquid chromatography and UV detection after derivatization with *p*-toluenesulphonyl chloride

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Abstract

The application of supported-liquid membrane (SLM) technique for effective extraction of *N*-(phosphonomethyl)glycine (glyphosate) and its primary metabolite aminomethylphosphonic acid (AMPA) from juices (orange, grapefruit, apple and blackcurrant) in combination with HPLC-UV detection after derivatization with *p*-toluenesulphonyl chloride (TsCl) is presented. The influence of various parameters such as the composition of acceptor phase, flow-rate, concentration of analytes, on the performance of extraction procedure, was studied. It was shown that by appropriate manipulation of SLM parameters the level of detection could be significantly improved. The influence of SLM conditions on extraction efficiency of studied compounds was also discussed. Selection of the optimal conditions enable detection of glyphosate and AMPA in juices at concentrations as low as 0.025 mg/l. The calculated recoveries for glyphosate were—71.1, 72.1, 93.6, and 102.7% and for AMPA—64.1, 64.6, 81.7, and 89.2%, for orange, grapefruit, apple and blackcurrant juices, respectively. The results suggest that the application of SLM extraction as a method for glyphosate and AMPA enrichment from complicated liquid matrices may be useful mean of routine analysis.

Keywords: Glyphosate; Aminomethylphosphonic acid; Supported-liquid membrane extraction; HPLC; Fruit juice; Pesticides

1. Introduction

Glyphosate (*N*-(phosphonomethyl)glycine) is a nonselective, post-emergence herbicide used for the control of a wide range of weeds [1]. It can be used on non-crop land as well as in a great variety of crops. Glyphosate is the active ingredient in the commercial herbicide Roundup®, marketed by Monsanto, and Touchdown, marketed by Zeneca Ag Products. It is an acid, but usually used in a salt form, most commonly the isopropylamine salt. Because of its relatively low toxicity to mammals, it has become one of the most widely used herbicides in the world. This widespread application generates problems with the contamination of the environment with this substance and therefore reliable methods are required for monitoring of this herbicide in crops, fruits and vegetables.

A great variety of analytical methods have been applied for determination of glyphosate. Both gas chromatography (GC) and liquid chromatography (LC) are used with various detection systems. GC analysis is performed after a derivatization procedure that converts glyphosate to a sufficiently volatile and thermally stable derivative [2–5]. In LC methods derivatization procedures, producing fluorescent derivatives, are often employed to enhance the sensitivity and selectivity of detection [6–9]. In many cases derivatization procedures are quite complicated and require special equipment. In recent years capillary electrophoresis (CE) has become a technique utilized for glyphosate determination more and more frequently [10–12]. While GC, HPLC and CE are well-developed methods for glyphosate analyses, enzyme-linked

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immunosorbent assay (ELISA) has become an alternative method [13–15].

In order to analyze low concentrations of glyphosate methods for enrichment and purification of analytes are required. They include such well-established techniques as: liquid-liquid extraction, solid-phase extraction as well as ion-exchange chromatography. Supported-liquid membrane extraction technique (SLM) can be considered as alternative for pretreatment of liquid samples containing herbicides.

SLM is a porous polymeric hydrophobic membrane with organic solvent immobilized in its pores. This membrane separates the aqueous (donor) phase and the receiving aqueous (acceptor) phase. During the extraction three simultaneous processes take place: extraction of the compound into the organic phase, its transport through the membrane and re-extraction into the acceptor phase. One of the main advantages of SLM is simultaneous extraction and clean-up of the compound of interest. Enrichment factors and the limits of detection obtained after SLM application are comparable to other extraction techniques, moreover, in many cases samples are much more cleaner.

SLM extraction has been successfully applied for separation and enrichment of various types of herbicides, such as, triazines [16,17], chlorophenoxyalkanoic acids [18], and chlorinated phenols [19]. There are two ways of operating the SLM system, which depend on the charge of the extracted analyte. In the case of acidic and basic compounds the enrichment is achieved by adjusting the pH of the donor and acceptor phases to appropriate values [20]. In order to extract multicharged compounds it is necessary to use a carrier incorporated into the membrane organic phase [21,22]. This carrier should bear a functional group with a charge opposite to the charge of the transported molecule. Such a carrier facilitates passage of the analyte through the liquid membrane by formation of neutral, organic phase soluble ion-pair complexes.

In comparison to all herbicides used in agriculture glyphosate is one of the most difficult to analyse. These difficulties originate from its chemical properties, namely high water solubility and polar nature, which limit the options for application of standard preparation methods, like solvent–solvent extraction. Its similarity to naturally occurring amino acids and small amino sugars contributes to the difficulty in determining residues of the compound in food samples. Many studies describing analysis of water samples for glyphosate presence have been published, but the number of publication where food samples have been analyzed is quite limited [2,4,23].

Our previous experiments showed that supported-liquid membrane extraction may be a very effective technique for simultaneous extraction and purification of herbicides of various structure from fruit juices [16]. There are reports in the literature describing extraction of glyphosate with SLM from water [24,25], but this technique has not been directly applied as preparation step for analysis of food samples.

The main goal of this work was a development of a simple analytical procedure involving SLM technique for the extraction and purification of glyphosate and AMPA from fruit juices followed by their determination with HPLC-UV after a simple derivatization procedure. It was also important that the detection limits reaches the maximum residue limits for the herbicide in food established in European Union, which is set at the level 0.1 mg/l (ppm) [26]. Various parameters affecting the analyte extraction, namely: flow-rate of phases, composition of acceptor phase and concentration of the studied compounds were examined and optimized.

2. Experimental

2.1. Chemicals

Aliquat 336-methyltrioctylammonium chloride was obtained from Janssen (Beerse, Belgium). Di-*n*-hexyl ether (DHE) used as the liquid membrane, and *N*-(phosphomethyl)glycine (glyphosate) was obtained from Sigma (St. Louis, MO, USA); aminomehtylphosphonic acid (AMPA) was obtained form ICN (Warsaw, Poland); the derivatization reagent, *p*-toluenesulphonyl chloride (TsCl) was from BDH (Poole, UK); acetonitrile for HPLC was from Chempur (Piekary Śląskie, Poland). Inorganic salts: KH_2PO_4, KOH, NaOH were purchased from POCh S.A. (Gliwice, Poland). All chemicals were of analytical grade. Water was purified with a Milli-Q-RO4 system (Millipore, Bedford, MA, USA).

All fruit juices are commercially available and are produced by Hortex Holding (Poland).

2.2. Membrane equipment

The membrane unit is composed of two circular PTFE blocks (120 mm diameter and 8 mm thickness) with grooves arranged as an Archimedes' spiral (0.25 mm depth, 1.5 mm width and 2.5 m length, with total volume of ca. 0.95 ml). To stabilize the whole construction aluminum blocks of 6 mm thickness were used on both sides of the PTFE blocks. A porous PTFE membrane with polyethylene backing (0.2 μm pore size, 175 μm total thickness with 115 μm backing and porosity 0.70 (Millipore FG, Millipore) was impregnated with 20% Aliquat 336 solution in DHE for 30 min. The membrane was then placed between two PTFE blocks and the whole construction was clamped tightly with six screws. After installation of the membrane, excess of organic solution on the surface was eliminated by pumping ca. 10 ml of water through both channels.

The water solutions and juices used in experiments were pumped with a peristaltic pump (Minipuls 3, Gilson Medical Electronics, Viliers-le-Bel, France) using acid resistance tubing (Acid Mainfold Tubing, Elkay Products, Shrewsbury, MA, USA) connected to the membrane unit with Altex screw

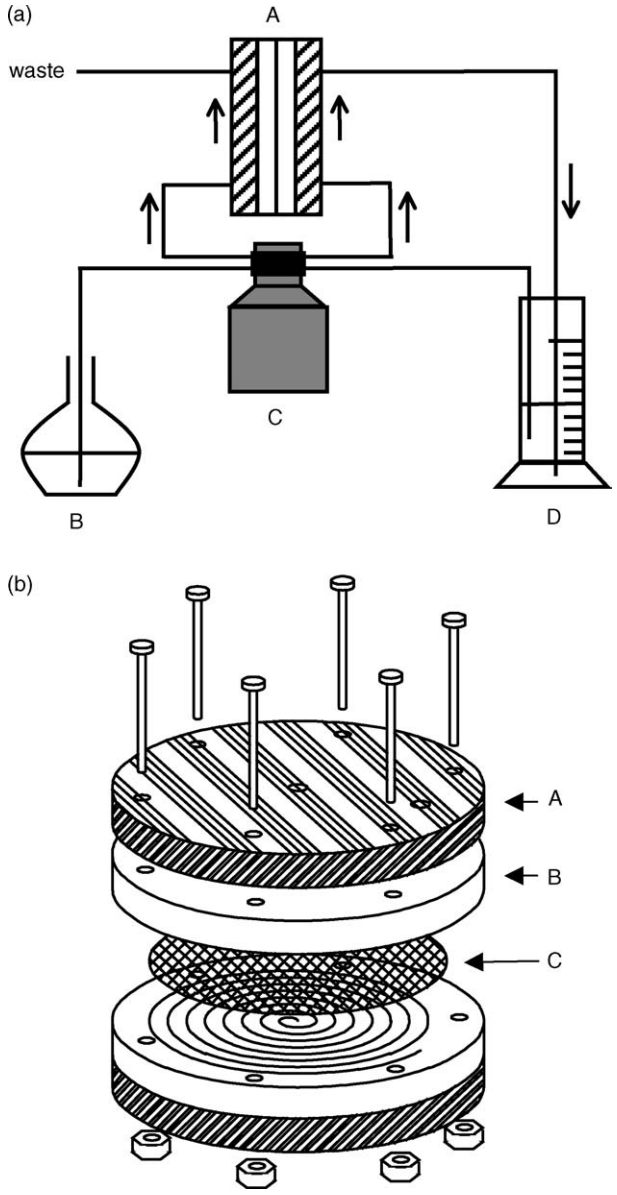

Fig. 1. (a) Set up of membrane enrichment of glyphosate and AMPA: A, liquid sample containing the analyzed compound (donor phase); B, SLM module; C, peristaltic pump; and D, circulating striping solution (acceptor phase). (b) SLM module: A. aluminum backup; B, PTFE block; and C, impregnated liquid membrane.

fittings. The schemes of SLM extraction and separation module are presented in Fig. 1.

2.3. Sample preparation and pre-concentration

All samples were collected in polypropylene bottles and care was taken to avoid that sample would come into contact with glass prior to the extraction step and derivatization, because of the possible adsorption of glyphosate and AMPA on glass surface.

Before every enrichment experiment 0.1 M HCl solution was pumped through the acceptor channel with simultaneous pumping of water through the donor to check the stability of membrane. Membrane was considered stable if the pH of waste-water from the donor was neutral.

Water samples spiked with the studied compounds were adjusted to pH 11 with 1 M NaOH. A 100 ml volume of sample solution was pumped through the donor channel. The acceptor phase consisting of 10 ml of 2 M NaCl or 0.1 M HCl was circulating in the acceptor channel with the same flow-rate as the donor phase during the extraction time. After the extraction, 1 ml of the acceptor phase was taken for derivatization. In the case of acid as the receiving phase, before derivatization 10 ml of acceptor was neutralized (pH 7) with concentrated KOH solution. Subsequently, both sides of liquid membrane were refreshed with ca. 10 ml of water before next experiment.

Juice sample spiked with an appropriate volume of a stock solution of glyphosate or AMPA (1 mg/ml in water, kept at +4 °C) was centrifuged (15,000 rpm, 20 °C, 10 min) to remove solid particles. The sample was than filtered through the paper filter, and treated using the same procedure as described above for water samples. All experiments were performed three times.

2.4. HPLC analysis

Derivatization procedure was adopted from Rios et al. [24]. Briefly, 1 ml of the acceptor phase was mixed with 0.5 ml of 0.4 M phosphate buffer (pH 11) and 0.2 ml of *p*-toluenesulphonyl chloride solution (10 mg/ml in acetonitrile) and heated in a water bath at 50 °C for 10 min.

The HPLC system used in this work consisted of a Varian-ProStar (Walnut Creek, CA, USA) model, equipped with ProStar 210 solvent delivery module and ProStar 325 UV–vis detector. Isocratic separation was performed on a 250 mm × 4.6 mm, Microsorb-MV, 100-5, C18 column at 25 °C. The eluent was a mixture of 0.06 M KH_2PO_4 buffer (adjusted to pH 2.3 with H_3PO_4) and acetonitrile (85:15, v/v). The eluent flow-rate was 1 ml/min. The sample was injected through 20 μl loop onto the column and elution was monitored at 240 nm.

Addition of the concentrated derivatized glyphosate and/or AMPA as internal standard to the sample allowed identification of peaks corresponding to these compounds. Quantification was carried out based on a calibration curve of water solutions with known concentrations of each compound after derivatization.

3. Results and discussion

3.1. Calibration of HPLC analysis

Calibrations for glyphosate and AMPA were performed by injection of water solutions spiked with these compounds after derivatization without applying of SLM sample preparation step. Calibration curve for glyphosate has been found

linear in the concentration range from 0.025 to 10 mg/l with the correlation coefficient of 0.9998. The limit of detection (LOD) was 0.01 mg/l calculated as three times signal-to-noise (*S*/*N*) ratio. Calibration curve for AMPA was also linear from 0.025 to 10 mg/l with the correlation coefficient 0.9993 and LOD of 0.01 mg/l. The curves were based on nine points with five injections for every standard solution.

3.2. Selection of extraction conditions

In recent years a number of papers describing application of the SLM technique for extraction of amino acids appeared in the literature [21,22]. Because of the structural similarity of glyphosate molecule to amino acids we have decided to use the same approach for sample preparation for analysis of this herbicide and its metabolite in fruit juices. The composition of the membrane phase and pH of the donor phase were taken from previous studies in our laboratory [25]. The selected membrane phase was 20% Aliquat 336 (v/v) in dihexyl ether and pH of donor phase set at 11.

In our previous experiments 2 M solution of sodium chloride has shown the best capability to trap glyphosate in the acceptor phase. In another work [24] authors described SLM enrichment of glyphosate, where 0.1 M hydrochloric acid solution was found to be effective acceptor phase for the stripping of this compound. Therefore, we decided to compare these two solutions as acceptor phases. Glyphosate recoveries of 93.5% ($n = 3$, RSD = 4.7%) and 89.5% ($n = 3$, RSD = 6.6%) were obtained using 2 M NaCl and 0.1 M HCl at flow-rate of 0.2 ml/min, respectively. The main role in glyphosate stripping plays presence of Cl^- anions in acceptor phase. They form the driving force of extraction, which is a gradient of the counter chloride anions from the acceptor to the donor phases. In the case of sodium chloride the concentration of the Cl^- anions plays a significant role. Whereas in the case of hydrochloric acid glyphosate is converted into the positively charged form in acceptor phase and cannot interact with carrier again to be re-extracted back into the donor phase. 0.1 M hydrochloric acid was further selected as acceptor phase, because high concentrated sodium chloride solution may have negative influence on the LC column.

Another important parameter in SLM is the flow-rate of pumped phases. For hydrophobic compounds high flow-rates are preferable [27]. In the case of hydrophilic compounds low flow-rates give better extraction efficiency. This parameter was therefore also examined (Fig. 2). At lower flow-rates the contact time between donor and membrane phases increases. As expected, this permits the carrier presented in membrane phase to interact with more amounts of analyte molecules and transport them to the acceptor. It is very important for glyphosate because it can be transported through the organic solution only by means of carrier. Therefore, 0.2 ml/min flow-rate was selected for further experiments.

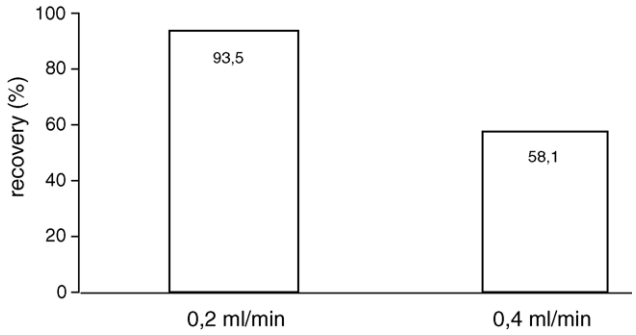

Fig. 2. Influence of flow-rate of both phases on extraction of glyphosate. Donor phase: 0.1 mg/l in water, 100 ml; acceptor phase: 10 ml, 0.1 M HCl; membrane phase: 20% Aliquat 336 in DHE.

Table 1
SLM extraction of glyphosate from water

Concentration of glyphosate in sample (mg/l)	Recoveries (%)			
	I	II	III	Mean
0.005	94.0	110.8	93.4	99.4
0.01	108.8	92.6	105.3	102.2
0.1	96.7	88.5	95.2	93.5
1	85.9	88.3	78.9	84.3
10	52.1	68.9	69.5	63.5

Donor: 100 ml of glyphosate from spiked water: acceptor phase: 10 ml, 0.1 M HCl; membrane phase: 20% Aliquat 336 in DHE; flow-rate of both phases: 0.2 ml/min.

3.3. Fruit juices analysis

Before application of the proposed preparation method to fruit juices it was desirable to test the extraction of glyphosate from pure water containing no interfering substances. Recoveries obtained in these experiments are presented in Table 1.

Table 2
SLM extraction of glyphosate and AMPA from spiked fruit juices ($n = 3$)

Type of studied juice	Recoveries of compounds (%) with RSD (in parenthesis (%))						
	Concentration of glyphosate in sample (mg/l)				Concentration of AMPA in sample (mg/l)		
	1	0.1	0.05	0.025	0.1	0.05	0.025
Orange	42.1 (8.2)	64.2 (4.7)	66.7 (4.0)	71.1 (21.0)	44.3 (8.6)	54.7 (7.7)	64.1 (5.0)
Grapefruit	52.1 (10.5)	68.2 (3.6)	75.2 (3.8)	72.1 (12.5)	46.1 (8.2)	56.8 (6.9)	64.6 (4.4)
Apple	64.6 (6.6)	78.9 (4.5)	79.3 (11.7)	93.6 (15.1)	63.0 (4.4)	70.1 (5.7)	81.7 (2.7)
Blackcurrant	54.8 (7.0)	75.8 (4.9)	82.2 (3.8)	102.7 (7.7)	64.8 (5.7)	74.9 (3.8)	89.2 (3.7)

Donor phase: 100 ml of juice; acceptor phase: 10 ml, 0.1 M HCl; membrane phase: 20% Aliquat 336 in DHE; flow-rate of both phases: 0.2 ml/min.

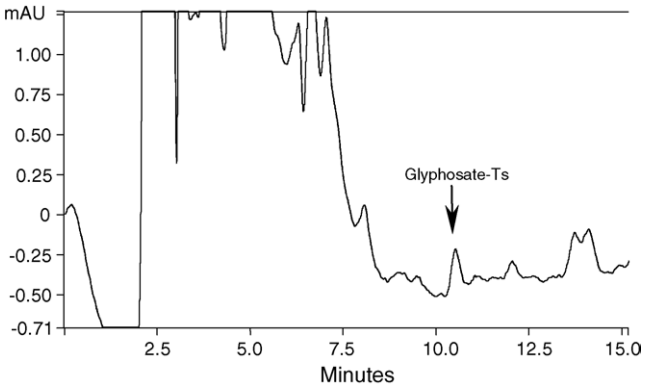

Fig. 3. Chromatogram of a sample after SLM extraction of glyphosate (0.025 mg/l) from 100 ml of orange juice (see Table 2 for conditions).

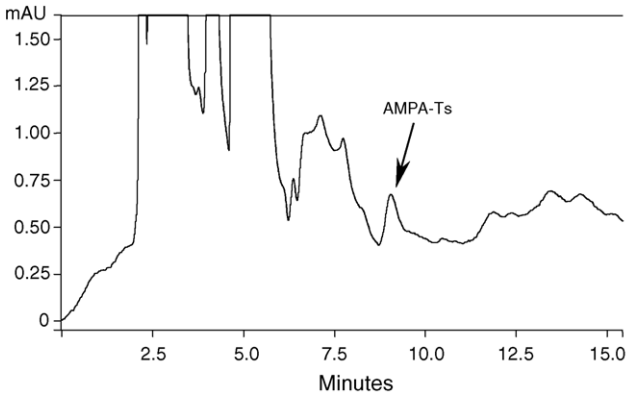

Fig. 4. Chromatogram of a sample after SLM extraction of AMPA (0.025 mg/l) from 100 ml of orange juice (see Table 2 for conditions).

From obtained results it can be concluded that in the examined range of glyphosate concentration the extraction efficiency rises up with the decreasing concentration of the compound in the sample. At the important for us concentration range (0.1 mg/l and lower) recoveries are not varied widely and equaled almost 100%.

Afterwards the developed SLM procedure with optimized parameters was used to extract glyphosate and AMPA from fruit juices. In Table 2 recoveries of these two compounds are shown. They vary with the kind of juice and the concentration of the compounds, but with few exceptions range from 40 to 100% for glyphosate, and from 45 to 90% for AMPA was obtained. Similarly as for water solutions, at lower concentrations the recovery was higher for both compounds. Moderate differences can be observed in recoveries of the herbicide and its metabolite in different juices. This can most likely derived from different composition of the samples. For instance, recoveries from orange and grapefruit juices were lower than from apple and blackcurrant juices in the case of both compounds. This may be explained by adsorption of glyphosate and AMPA on solid particles, which are present in orange and grapefruit juices and absent in remaining ones. It is worth pointing out that the extraction efficiency of AMPA was lower than of glyphosate at the same concentrations. This fact can be explained by differences in polarity between these two compounds. Even if AMPA interacts with the carrier in the same manner as glyphosate, the more polar AMPA molecule has a lower affinity to the organic phase than glyphosate. Therefore, smaller amounts of the metabolite molecules have time to interact with the carrier present in membrane phase. One of the important goals of the work was to develop procedure able to detect the herbicide at maximum residue limit (MRL) established in EU for food samples (0.1 mg/l). As it can be seen at concentration range (0.1 mg/l and lower) recoveries are equaled $70 \pm 10\%$. These are lower then for water, because of presence amino acid or other compounds of similar structure in juices, which can compete with the studied compounds in interaction with the carrier in membrane phase.

In Figs. 3 and 4 representative chromatograms of glyphosate and AMPA extracts from orange juice (at concentration of 0.025 mg/l) are presented. As it can be seen, chromatograms are sufficiently clear for precise determination of peaks corresponding to the studied compounds. This can be achieved by utilization of the SLM extraction as a preparation step. Fruit juices contain substances, which are hydrophilic and therefore have low affinity to organic solution of membrane phase. As it has been mentioned above, Aliquat 336 as a carrier showed a great ability to transport only amino acids and similar ionic compounds. Such specificity of this carrier prevents compounds with other structures to be collected in the acceptor phase. *p*-Toluenesulphonyl chloride, used for derivatization of glyphosate and AMPA before HPLC-UV determination, eliminated compounds, which do

Table 3
Extraction of mixture of glyphosate and AMPA from spiked juices

Concentrations and the type of compound	Recoveries (%)			
	Orange	Grapefruit	Apple	Blackcurrant
AMPA—0.025 mg/l	59.7	59.1	73.0	80.4
Glyphosate—0.1 mg/l	62.3	64.7	76.6	73.1
AMPA—0.1 mg/l	38.8	42.8	60.2	55.5
Glyphosate—0.025 mg/l	70.7	62.1	84.4	97.2
AMPA—0.025 mg/l	63.4	64.9	76.6	89.2
Glyphosate—0.025 mg/l	71.3	72.5	95.0	99.3

See Table 2 for conditions.

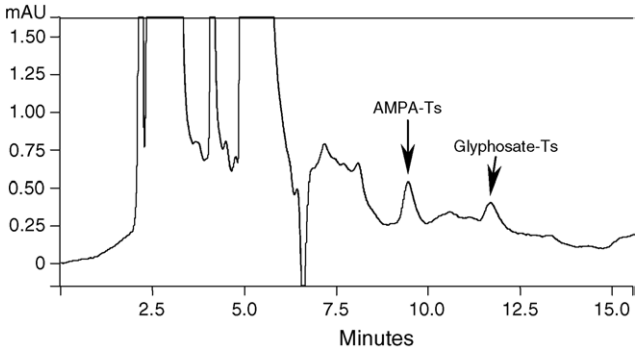

Fig. 5. Chromatogram of SLM extraction of mixture glyphosate and AMPA (0.025 mg/l) from 100 ml of orange juice (see Table 2 for conditions).

not have primary or secondary amino and hydroxy groups, from detection. All these factors allow obtaining clear chromatograms for all studied juices.

It is obvious that in real situation glyphosate is metabolized in fruits to aminomethylphosphonic acid. It was therefore important to check the applicability of the proposed analytical method for determination of the mixture of these two compounds in juices. In Table 3 results of these experiments are collected. It can be concluded that obtained recoveries for mixtures are at the same level as for individual compounds. Chromatograms are also clear and no interferences prevent identification of the studied analytes (Fig. 5).

In order to demonstrate the possibility of SLM preconcentration of glyphosate at lower concentrations (0.01 mg/l) the extraction from 200 ml of orange juice was carried out (Fig. 6). Calculated recovery was also in the same range (75.4%). Therefore, it is possible to improve significantly the limit of detection of both glyphosate and AMPA in fruit juices simply by increasing the volume of the pumped sample through the donor channel. However, if the task is only to detect glyphosate at the MRL it just can be achieved with lower volumes of the sample pumped through the donor channel, which makes the whole time of analysis shorter. According to our developed procedure the minimal volume of fruit juice, which is necessary to detect glyphosate at MRL is 20 ml.

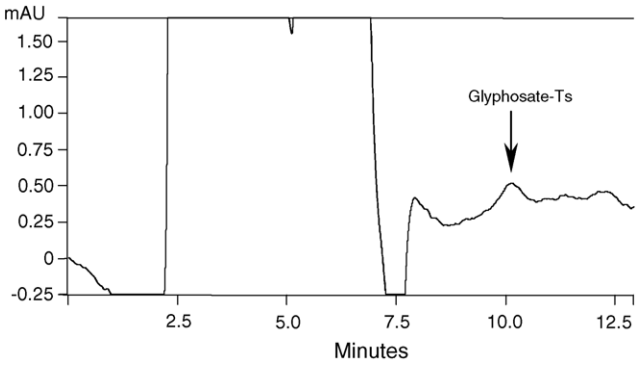

Fig. 6. Chromatogram of SLM extraction of glyphosate (0.01 mg/l) from 200 ml of orange juice (see Table 2 for conditions).

4. Conclusions

This study shows that SLM technique may be an effective extraction and preconcentration method for glyphosate and its major metabolite AMPA from complicated liquid samples, such as fruit juices. In combination with derivatization and HPLC-UV detection it offers a simple procedure for analysis of these compounds. The applicability of this method has been demonstrated with an example of most popular juices (orange, grapefruit, apple and blackcurrant). The developed procedure gives clear chromatograms, in which the herbicide and its metabolite can be easily identified and quantified. At the same time SLM was efficient in removing a large number of interfering compounds and concentrating the analytes. It was also shown that increasing the volume of juices pumped through the donor phase lowers the level of detection. The developed analytical procedure allows determination of glyphosate in food samples at the established maximum residue level.

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