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Application of solid-phase microextraction for determining phenylurea herbicides and their homologous anilines from vegetables

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Abstract

Residues of metobromuron, monolinuron and linuron herbicides and their aniline homologous were analyzed in carrots, onions and potatoes by solid-phase microextraction (SPME) performed with a polyacrylate fiber. A juice was obtained from food samples that were further diluted, and an aliquot was extracted after sodium chloride (14%) addition and pH control. At pH 4 only the phenylureas were extracted. A new extraction at pH 11 allowed the extraction of phenylureas plus homologous aniline metabolites. Determination was carried out by gas chromatography with nitrogen–phosporus detection (NPD) the identity of the determined compounds was studied by gas chromatography–mass spectrometry. Limits of quantification (LOQs) obtained with NPD and MS (selected-ion monitoring) were in the μg/kg order allowing determination of maximum residue levels (MRLs) established in the Spanish regulations. MRLs ranged from 0.02 to 0.1 mg/kg depending on the kind of food and herbicide. Under the proposed conditions matrix effects were low enough to permit calibration with samples proceeding from ecological (non-pesticide treated) crops. Twelve commercial samples of each carrots, onions and potatoes were analyzed and only three samples of potatoes contained residues of linuron at levels below MRLs.

Keywords: Food analysis; Vegetables; Phenylureas; Pesticides; Anilines

1. Introduction

Phenylureas are an important group of herbicides utilized in weed control. Phenylurea residues appear in the foods where they are applied [1–3], such residues are commonly determined by LC with UV [4–7], diode array [8,9] and mass spectrometry detectors. Atmospheric pressure ionization (API) with electrospray ionization (ESI) [8,10–12] and atmospheric pressure chemical ionization (APCI) [4] are the most popular interfacing techniques allowing the sensitive determination of intact phenylurea herbicides. Most methods for determination of phenylurea herbicides from foods based on LC techniques require cleanup processes either by using gel permeation chromatography and Florisil cartridges [5], strong anion-exchange cartridges and immunoaffinity columns [7], or a combination of gel filtration chromatography, strong anion-exchange cartridges and immunoaffinity columns [9]. The use of a large volume injection followed by LC–MS–MS allows reaching very good sensitivities with easy sample preparation that avoids the cleanup processes [10]. Solid-phase microextraction (SPME) is very useful for determining pesticide residues from water samples [13]. Direct SPME is limited to liquid aqueous matrices, only beginning studies to use it in non-polar matrixes have been done [14]. Although the fiber cannot be submerged in a solid, some applications of SPME to analyze pesticide residues in solid matrices have been reported. The problem of the solid state of the sample has been resolved by using headspace (HS)-SPME [15,16] or by obtaining an aqueous extract from the sample [17–25]. Direct SPME has been applied to determine pesticide residues in liquid foods as wine [11,26–28] and juice fruit [16,18,27] and, HS-SPME has been used in wines [29,30]. It has been reported that complex matrices such as soil [31], vegetables [22], fruits [17,18] and honey [19,21] can cause interferences in SPME. The use of deuterated surrogates or internal standard calibration may correct such matrix effects.

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Direct SPME with a polyacrylate (PA) fiber has been used to extract phenyl- and sulfonylurea herbicides from water [32]. Phenylureas are thermolabile and SPME is usually performed with automated instruments that are coupled with a gas chromatograph working at high temperatures. Under controlled conditions phenylureas can be determined from waters by SPME–GC in form of their respective derived anilines [32]. The gas chromatographic behaviour of the urea herbicides has been recently studied [33–35], the use of high temperatures at the injector port facilitates the degradation of the herbicide in a derived product, which depends on the solvent used for injection [36].

In the environment, the main metabolites of phenylurea herbicides are anilines. Anilines and other compounds have been analyzed from soil using a PA fiber by HS-SPME [31] and from water by direct SPME [37].

The Spanish legislation establishes maximum residue levels (MRLs) in foods [38] considering like residues the sum of all commercial phenylurea whose chemical structures are close giving the same aniline metabolites. Results must be expressed as the homologous aniline. For example, residues of linuron are the sum of diuron and linuron, expressed as 3,4-dichloroaniline.

Metobromuron, monolinuron and linuron are utilized in carrot (*Daucus carota*), onion (*Allium cepa*) and potato (*Solanum tuberosum*) crops and their MRL fixed in Spain for these foods ranged from 0.02 to 0.2 mg/kg. Monolinuron and linuron have been included in the black list of the Council Directive 76/464/EU as dangerous substances for aquatic environment [39]. Metobromuron and linuron have been considered herbicides of potential concern in the Mediterranean region.

We studied here the use of SPME coupled to GC for analyzing residues of phenylurea herbicides from vegetables seeing as no research in this field has been reported to date. In this way several advantages are attained; SPME allows rapid determination of the residues in such complex matrices without additional purification steps and couples to GC determination without further handling. In addition, GC conditions degrade and detect phenylurea herbicides in form of their corresponding anilines that is the way in which Spanish Legislation expresses results of MRLs. Since vegetables are foods with high water content, it is easy to obtain an aqueous extract (juice) from vegetables with a home juice extractor, in which the SPME fiber can be directly submerged, avoiding in this way the use of solvents.

2. Experimental

2.1. Materials

A PA fiber with a thickness film of 85 μm (Supelco, Bellefonte, CA, USA) was used with a SPME holder for an 8200 CX autosampler (Varian, Palo Alto, CA, USA). The fiber was previously conditioned in the injector port by heating it at 300 °C for 2 h, after that a stable baseline was obtained.

Ninety-eight percent sodium chloride, 98% sodium hydrogentartrate, and 99.5% sodium carbonate were purchased from Aldrich (Milwaukee, WI, USA).

Methanol (Suprasolv quality) was provided by Merck (Darmstadt, Germany). Ultra-pure water was obtained from a Milli-Q purification system (Millipore, Milford, MA, USA).

2.2. Standards

The herbicides buturon, diuron, linuron, metobromuron, monolinuron, monuron and neburon were purchased from Riedel-de Häen (Seelze, Germany) with purity up to 99%. 4-Bromoaniline, 4-chloroaniline and 3,4-dichloroaniline were purchased from Aldrich with purity up to 97%.

Stock solutions (1000 μg/l) of each phenylurea herbicide were prepared separately in methanol. These stock solutions were stored at 4 °C and diluted daily with ultra-pure water to prepare 100 μg/l intermediate solutions. Appropriate aliquots of intermediate solutions were used for spiking food samples. Methanol contained in such spiked samples was always below 0.1%.

2.3. Apparatus and conditions

Two gas chromatographs were used, the first was a Varian 3400 CX equipped with a nitrogen–phosphorous detection (NPD) system working at 3.2 A intensity with hydrogen at 4 ml/min, air at 175 ml/min and nitrogen at 30 ml/min, a septum programmable injector (SPI), a Varian 8200 CX autosampler with an SPME agitation accessory and a Varian Star 4.51 software to control the parameters. The SPME agitation accessory provides continuous contact of the fiber with fresh sample juice by vibrating the fiber protective sheath in the water solution without increasing temperature. A BP10 (30 m × 0.25 mm × 0.25 μm 14% cyanopropylphenyl + 86% dimethylpolysiloxane) column produced by Scientific Glass Engineering, SGE (Austin, TX, USA) was used with helium as the carrier gas at 1.5 ml/min. SPI and NPD system were kept at 300 °C. The oven temperature was programmed as follows; the initial temperature (100 °C) was increased by 10 °C/min to 240 °C and held for 15 min. The total GC run time was 29 min.

The second gas chromatograph was a Fisons 8000 series coupled with a Trio 1000 Quadrupole mass spectrometer (Fisons, Milan, Italy). The transfer line and source temperatures were 250 and 200 °C, respectively. The mass spectrometer worked in electron impact mode (−70 eV) by scanning from 50 to 450 amu for obtaining full spectra of the detected compounds or by selected-ion monitoring (SIM) for quantifying purposes. The spectra were handled with a LAB-BASE data station with NBS, Wiley 6 and US National Institute of Standards and Technology (NIST) spectral libraries. The

rest of the chromatographic conditions reproduced those of the Varian 3400 CX.

2.4. Sample preparation

Two kilograms of fresh vegetable (carrots, potatoes, and onions) was cut into small pieces and an aliquot of 50.0 g was processed. A liquefied juice was obtained by introducing the sample in a home juice extractor. The aqueous extract (ca. 39–44 ml) was made up to 50 ml with ultra-pure water. An aliquot of 5 ml was added with solid NaCl, and with solid sodium hydrogentartrate or with sodium carbonate, and was diluted to 25 ml with water. The final aqueous extract contained 14% (w/v) NaCl and pH 4 (for phenylurea determination) or 14% (w/v) NaCl and pH 11 (for phenylurea plus aniline metabolite determination).

To obtain fortified samples, ecological samples of vegetables (non-pesticide treated) without pesticides were cut and then spiked with known amounts of standards of phenylurea herbicides and/or anilines before the juice was obtained.

2.5. Analytical procedure

Autosampler vials (2 ml) were filled with 2 ml of the final aqueous extracts containing the appropriate buffer and 14% (w/v) sodium chloride and sealed with hole caps with PTFE-faced silicone septa (Supelco). The fiber was immersed in the sample for 60 min under needle agitation at room temperature ($22 \pm 2\,^{\circ}C$). After extraction the fiber was directly exposed to the hot injector port for subsequent analysis, and at this time the oven program was started. Thermal desorption of herbicides was held for 5 min. Experiences were performed in quadruplicate. A run with ultra-pure water was carried out after spiked food sample analysis to ensure the absence of memory effects.

3. Results and discussion

3.1. SPME

Some factors affecting SPME of phenylureas from water and soil have been already studied. The use of a PA fiber produces best extraction efficiency for phenylureas [32] and anilines [31] than polydimethylsiloxane. Equilibrium times for PA are typically near 90–120 min, but 60 min is usually enough for most analytical purposes. A large desorption time (5 min) and a high injector temperature ($300\,^{\circ}C$) reduces memory effects, such effects were not observed following the proposed procedure. Salting out effect is positive for improving extraction of urea herbicides except linuron that remains practically unaltered [32]. The pH of the sample extract affects the extraction of anilines that are basic compounds but not those of the phenylureas that are neutral substances. For example the main metabolites of linuron, metobromuron and monolinuron are 3,4-dichloroaniline (p*K* 2.97), 4-bromoaniline (p*K* 4.72) and 4-chloroaniline (p*K* 3.98). At pH 4 the ionic molecules of the anilines predominate largely over the non-ionic ones, thus at pH 4 only extraction of phenylureas was produced. At pH 11, the proportion between non-ionic and ionic molecules of anilines was sufficient to allow aniline extraction thus, at such pH both anilines and phenylureas were extracted.

Anilines can be found in foods proceeding from phenylurea herbicides but also from industrial activities. A double analysis of the sample performed at pH 4 and at pH 11 allows know separately the amount of phenylurea herbicides and the aniline residues in food.

SPME must be performed from aqueous solutions. Water contained in carrots, onions and potatoes is about 88.2, 88 and 77.8%, respectively; this fact allows obtaining a juice by liquefying easily the samples discarding the pulp in order to obtain an aqueous solution available to perform SPME. However, the presence of endogenous substances and solid particles affects the equilibrium fiber/water and the integrity of the fiber. It was observed that if the primary sample juice is directly extracted without further dilution, recoveries were 40–70% lower than with proposed method and the fiber deteriorates quickly. Dilution of the primary sample juice improved extraction and protected the PA fiber from deterioration but at the same time reduced sensitivity. A dilution of 1/5 was sufficient to reduce matrix interference and to reach enough sensitivity. Dilution was also chosen by other authors who extracted aqueous matrices with suspended matter such as fruits [17,18], vegetable [22] and honey [19,21].

3.2. Identity of the determined compounds

Phenylureas that were analyzed by SPME–GC were actually detected as the corresponding analogous anilines. The high temperature facilitated the degradation that occurred in the injector. Consequently, phenylurea herbicides with close structures giving the same derivative aniline cannot be distinguished. This analytical trouble is an advantage when analyzing samples for MRLs because the Spanish legislation indicates that linuron residue is the sum of diuron and linuron expressed as 3,4-dichloroaniline. The two commercial herbicides have analogous structures and were detected in form of 3,4-dichloroaniline in SPME–GC analysis. Neburon that has an analogous structure also generates 3,4-dichloroaniline. Similarly the residue of monolinuron is the sum of buturon, monolinuron and monuron expressed as 4-chloroaniline, those herbicides generated 4-chloroaniline in SPME–GC. Metobromuron is determined as 4-bromoaniline in SPME–GC. The identity of the determined compounds was known by inserting the PA fiber immediately after extraction in the injector of the Fisons gas chromatograph with mass spectrometric detector to obtain the full mass spectra. Our interest is focussed on phenylurea herbicides currently applied on carrots, onions and potatoes that are linuron, monolinuron and metobromuron. The rest of herbicides (diuron, monuron and neburon) are not applied

Table 1
Percent recoveries and relative standard deviations (in parenthesis, $n = 4$) for SPME–NPD of the selected herbicides (pH 4*) and anilines (pH 11**) from samples fortified at 0.020 mg/kg level

Compound	Carrots	Onions	Potatoes
Metobromuron*	88 (4)	89 (5)	83 (8)
Monolinuron*	92 (5)	90 (4)	76 (5)
Linuron*	90 (4)	87 (4)	79 (6)
4-Bromoaniline**	87 (6)	89 (5)	82 (7)
4-Chloroaniline**	94 (5)	95 (3)	81 (6)
3,4-Dichloroaniline**	95 (5)	89 (6)	85 (8)

on selected crops and buturon is not used in Spain, thus the three last herbicides were excluded of validation assays.

On the other hand, 4-bromoaniline, 4-chloroaniline and 3,4-dichloroaniline that were extracted at pH 11 do not degrade during injection into the GC system being determined as intact compounds as observed by mass spectrometry.

3.3. Validation of the analytical method

Samples of carrots, onions and potatoes proceeding from crops in which synthetic products were not applied were taken for studying analytical parameters.

SPME is not an exhaustive process, it is based in equilibrium between fiber and water governed by the K_{fw}, constant. Under similar conditions (pH 4, 14%, w/v, NaCl) phenylureas showed apparent K_{fw} corresponding to moderate to low affinities to the PA fiber [32]. For this reason, the same extractive conditions from ultra-pure water (pH 4, 14%, w/v, NaCl) were taken as reference (100% of recovery) to evaluate extraction from diluted juice extracts, being the quantification based on the peak areas. Hence, samples of selected matrixes were fortified with the selected herbicides at three levels and analyzed. Parallel analyses at the same levels of the herbicides and conditions were accomplished with ultra-pure water (pH 4, 14%, w/v, NaCl). Results of these assays performed with selected herbicides and with selected anilines at the 0.02 mg/kg spiking level are shown in Table 1, the results obtained at 0.25 and 1.25 mg/kg spiking levels were of the same order.

Recoveries (at pH 4) were greater than 76% for selected phenylureas and (at pH 11) greater than 79% for the corresponding anilines. Recoveries of anilines at pH 4 were below 4%. Recoveries for monolinuron, linuron and 4-chloroaniline from potatoes were slightly lower than those obtained from onions, carrots and carrots and onions, respectively. The R.S.D.s observed at any of the three levels of spike studied ($n = 4$) were lower than 10% for the selected herbicides at lower than 9% for anilines. Chromatograms corresponding to the SPME of an ecological carrot sample non-spiked (a) and spiked (b) with the selected herbicides are shown in Fig. 1. Some non-identified peaks were present but they did not interfere in herbicide determination.

Linearity was studied with NPD by analyzing fortified samples of carrots, onions and potatoes in quadruplicate at six levels (2.5, 25, 100, 250, 1000 and 2500 μg/kg). As seen in Table 2, the coefficients of correlation were better than 0.995 for the herbicides and better than 0.996 for the anilines.

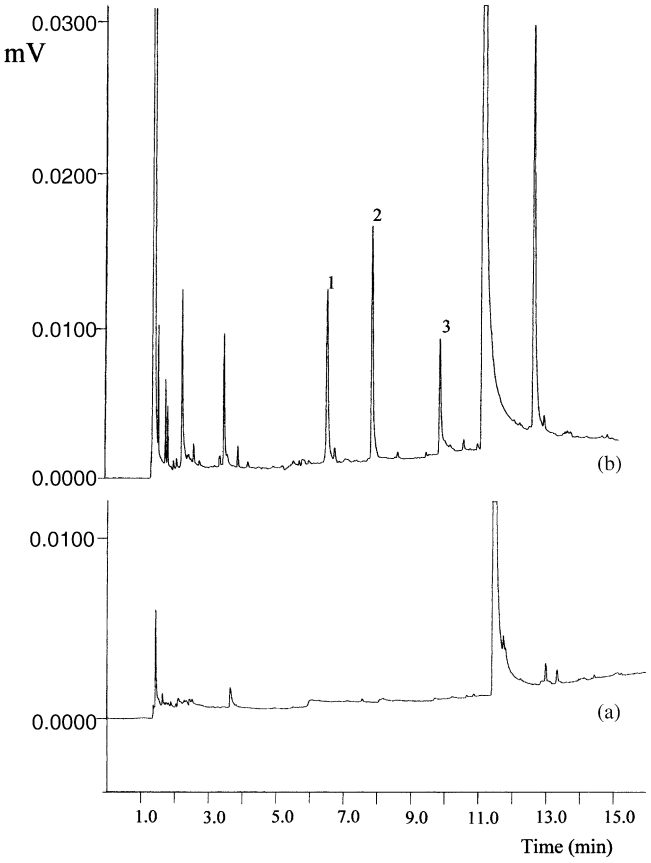

Fig. 1. GC-NPD chromatograms corresponding to the SPME of a pesticide-free carrot sample non-spiked (a), and spiked (b). Peak identification: monolinuron (30 μg/kg), 2: metobromuron (50 μg/kg) and 3: linuron (10 μg/kg).

Limits of quantification (LOQs) (S/N = 10) were evaluated for each herbicide and aniline with NPD and MS (SIM), results are shown in Table 2. The *m/z* ions monitorized were 161 and 163 to determine linuron residues as 3,4-dichloroaniline, 171 and 173 for metobromuron as 4-bromoaniline and 127 and 129 for monolinuron as 4-chloroaniline. The SIM program included the molecular mass of anilines that were also the base peaks. Fig. 2 shows the mass chromatograms corresponding to the analysis of a carrot sample spiked with the herbicides at very low levels. LOQs reached with NPD were good enough to determine residues at the MRL (Table 2). The injector of the Fisons gas chromatograph is not specially designed to be used with SPME fibers but LOQs obtained with MS (SIM) were better than those obtained with NPD.

Other authors that determined phenylurea herbicides in carrots and potatoes by performing extraction with solvents, followed by cleanup processes and LC–UV determination [5,7] reached LOQs of the 0.002–0.01 mg/kg order. Direct

Table 2
Limits of quantification (LOQ, S/N = 10 μg/kg), coefficients of regression (r^2) and maximum residue levels from Spanish regulation (MRL, ng/kg)

Compound	Carrots				Onions				Potatoes			
	LOQ		MRL	r^2*	LOQ		MRL	r^2*	LOQ		MRL	r^2*
	NPD	MS (SIM)			NPD	MS (SIM)			NPD	MS (SIM)		
Metobromuron	1.6	0.5	20	0.995	1.5	0.5	20	0.997	1.7	0.5	100	0.995
Monolinuron	1.9	0.6	50	0.999	1.9	0.6	50	0.998	2.2	0.7	50	0.997
Linuron	0.8	0.1	100	0.998	0.8	0.1	100	0.998	0.9	0.1	100	0.998
4-Bromoaniline	1.3	0.4	–	0.997	1.3	0.4	–	0.997	1.3	0.4	–	0.996
4-Chloroaniline	1.4	0.6	–	0.998	1.4	0.6	–	0.999	1.6	0.6	–	0.998
3,4-Dichloroaniline	0.8	0.1	–	0.999	0.8	0.1	–	0.999	0.9	0.1	–	0.999

MRL of monolinuron is the sum of buturon, monolinuron and monuron expressed as 4-chloroaniline
MRL of linuron is the sum of diuron and linuron expressed as 3,4-dichloroaniline
* 2.5, 25, 100, 250, 1000 and 2500 μg/kg, $n = 4$ for each point; obtained with NPD.

analysis of phenylurea herbicides has been reported from 1/10 diluted wine samples by in-tube SPME coupled to LC–ESI–MS obtaining LODs of 0.03–0.32 ng/ml [11]. The use of the more specific MS–MS detector coupled to LC permits to reach LODs of 0.5–2 μg/kg by injecting a large volume of sample vegetable extract without any cleanup step [10].

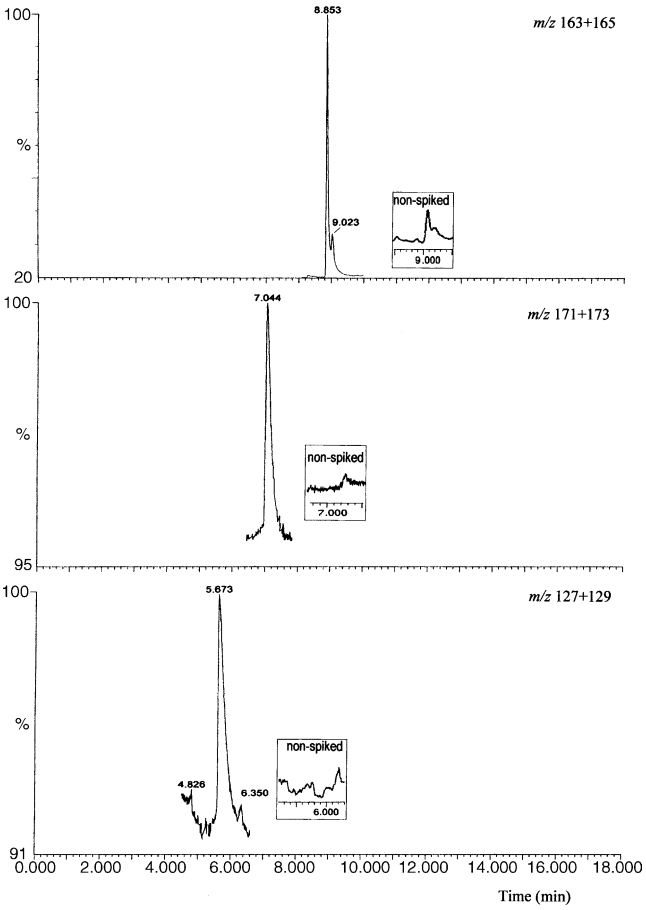

Fig. 2. Mass chromatograms corresponding to the SPME of a carrot sample spiked with 0.3 μg/kg of monolinuron (*m/z* 127 + 129), 0.3 μg/kg of metobromuron (*m/z* 171 + 173) and 0.1 μg/kg of linuron (*m/z* 163 + 165).

3.4. Analysis of commercial samples

Twelve commercial samples (2 kg) of each carrots, onions and potatoes were acquired from different markets of the Comunitat Valenciana (Spain). No herbicide residue was detected by SPME (NPD) at pH 4 in samples of carrots and onions. Residues of linuron expressed as 3,4-dichloroaniline were found by SPME (NPD) at pH 4 in three samples of

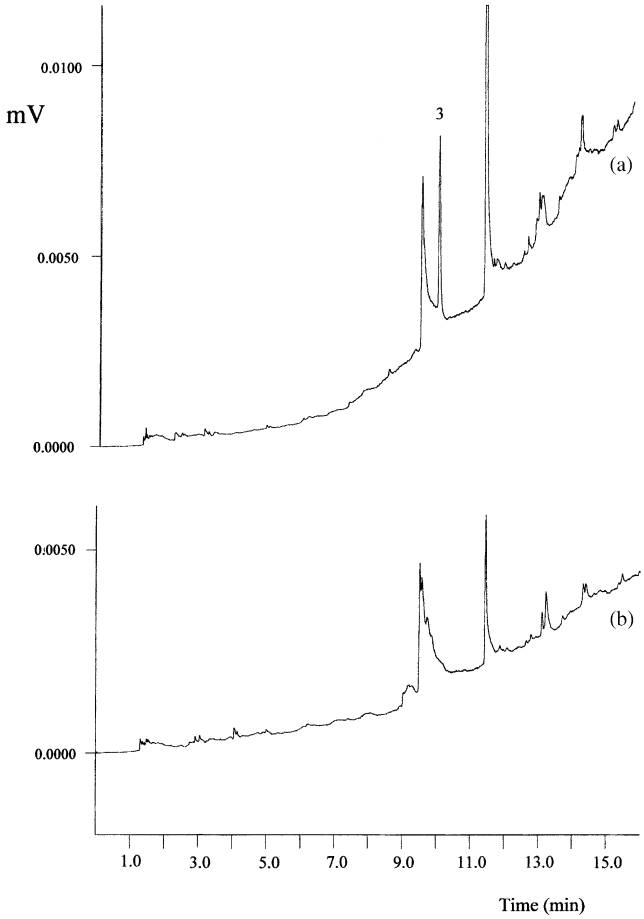

Fig. 3. SPME (NPD) analysis of a commercial potato sample containing 5 μg/kg of linuron (a) and a pesticide-free potato sample (b).

potato at 5, 9 and 4 μg/kg levels (below MRLs), calculation is based on peak area obtained from the diluted juices and the calibration curves for linuron. Such quantified residues did not proceed from aniline metabolites because new extractions of these samples at pH 11 quantified the same levels of linuron. Since diuron and neburon that could generate the same aniline are not applied on potato crops the quantified residues should be assigned to linuron. The linear equation obtained in the validation studies by spiking pesticide-free potatoes with linuron was used for quantifying linuron residues in commercial samples of potatoes. Results were qualitatively confirmed in such samples by MS (SIM). NPD profiles corresponding to the analysis of samples of potatoes No. 4 (c) and potatoes pesticide-free (d) are shown in Fig. 3.

Similar levels of residues of linuron (3 μg/kg) from carrots have been reported by other authors [10].

4. Conclusions

SPME coupled to a GC with NPD or MS detection allows determination of phenylurea herbicide residues from carrots, onions and potatoes according to Spanish regulation on MRLs exigencies. A juice must be obtained from the vegetable, diluted, added with sodium chloride and buffered. Such sample preparation is easy, economic, and solvent free. Once the sample is prepared the extraction and determination can be performed automatically. Environmental contamination of vegetable samples by anilines of industrial origin can be distinguished from phenylurea herbicide residues by performing two SPMEs, at pH 4 only phenylureas are determined and at pH 11 phenylureas plus anilines are quantified.

Very low levels of linuron were found in three of the twelve commercial samples of potatoes. Obtaining a juice from foods with high water content and diluting makes it possible to perform SPME of such kind of samples, nevertheless the influence of different matrices can affect the extraction process and should be particularly studied.

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