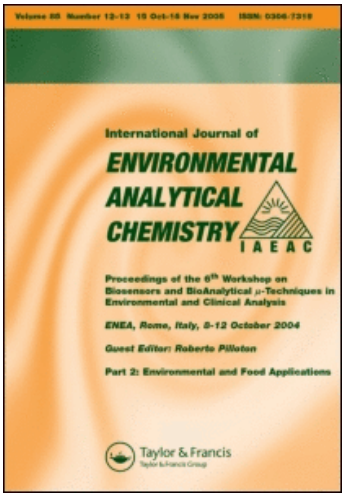


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

A new sample clean-up procedure, based on ion-pairing on RP-SPE cartridges, for the determination of ionizable pesticides

Konstantinos P. Prousalis[a]; Christos K. Kaltsonoudis[a]; Theodore Tsegenidis[a]
[a] Department of Chemistry, Section of Organic Chemistry, Biochemistry and Natural Products, University of Patras, 26500 Patras, Greece

To cite this Article Prousalis, Konstantinos P. , Kaltsonoudis, Christos K. and Tsegenidis, Theodore(2006) 'A new sample clean-up procedure, based on ion-pairing on RP-SPE cartridges, for the determination of ionizable pesticides', International Journal of Environmental Analytical Chemistry, 86: 1, 33 — 43
To link to this Article: DOI: 10.1080/03067310500246571
URL: http://dx.doi.org/10.1080/03067310500246571

Intern. J. Environ. Anal. Chem.
Vol. 86, Nos. 1–2, 15 January–15 February 2006, 33–43

Taylor & Francis
Taylor & Francis Group

A new sample clean-up procedure, based on ion-pairing on RP-SPE cartridges, for the determination of ionizable pesticides

KONSTANTINOS P. PROUSALIS, CHRISTOS K. KALTSONOUDIS and THEODORE TSEGENIDIS*

Department of Chemistry, Section of Organic Chemistry, Biochemistry and Natural Products, University of Patras, 26500 Patras, Greece

(*Received 3 October 2004; in final form 22 March 2005*)

Residues of ionizable pesticides in lemon extracts were isolated by a new solid-phase extraction method on reverse-phase cartridges. Cartridges were preconditioned with zwittergents such as cetyltrimethylammonium bromide for anionic pesticides and sodium dodecyl sulphate for cationic pesticides. Zwittergents and opposite charged analytes produce ion pairs that are stronger retained on the cartridge bed than the native analytes. Following washings of the cartridge, with an eluent of suitable concentration in organic solvent, resulted in interference removal. Finally, pesticides were eluted with acetonitrile. Based on the aforementioned procedure, two analytical methods were developed for the determination of acidic (2,4,5-trichlorophenoxyacetic acid, dichlorprop, and dinoseb) and basic (carbendazim and thiabendazole) pesticide residues in lemons. The analytes were separated on a reverse-phase C_{18} HPLC column and detected by UV.

Keywords: Solid-phase extraction (SPE); Ion-pair reagent; High-performance liquid chromatography (HPLC); Pesticides; Sodium dodecyl sulphate (SDS); Cetyltrimethylammonium bromide (Ctab)

1. Introduction

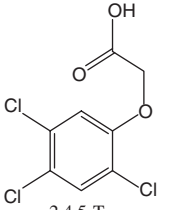
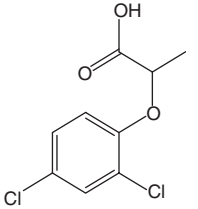
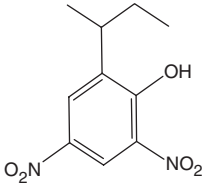
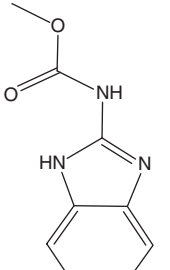
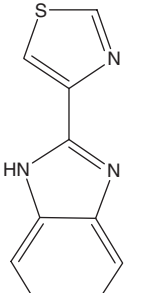
Solid-phase extraction (SPE) is a simple, fast, and inexpensive technique. It has been developed as an alternative to liquid–liquid extraction for the separation, purification, concentration, and/or solvent exchange of solutes. It is applicable to a great number of analytical methods concerning pesticide residue analysis in water, soil, grains, juices, drinks, fruits, vegetables, etc. The efficiency of SPE (sample clean-up and analyte recoveries) depends mostly on the selection of the appropriate sorbent.

Acidic herbicides, such as 2,4,5-trichlorophenoxy acetic acid (2,4,5-T), dichlorprop (2-(2,4-dichlorophenoxy)propionic acid), and dinoseb (2-sec-butyl-4,6-dinitrophenol) (table 1) are widely used for the control of broad-leaved weeds and other vegetation [1].

*Corresponding author. Fax: +30-2610-997152. Email: tsegen@upatras.gr

International Journal of Environmental Analytical Chemistry
ISSN 0306-7319 print: ISSN 1029-0397 online © 2005 Taylor & Francis
DOI: 10.1080/03067310500246571

Table 1. Chemical structures, pK_a and European maximum residue limits (MRL) of pesticides in lemons.

Structure	 2,4,5-T	 Dichlorprop	 Dinoseb	 Carbendazim	 Thiabendazole
pK_a[a]	2.83	3.1	4.62	4.2	4.64
MRL (mg/kg)	0.05	0.05	0.05	5	5

[a]Data obtained from the SRC PhysProp Database.

They usually exist as water-soluble salts (anionic form) at environmental pH values. After application, they easily pass into groundwater, streams, rivers, or lakes, so they may be critical contaminants of drinking-water resourses. The first two substances belong to the wider pesticide group of chlorophenoxy acids. The use of 2,4,5-T has been recently restricted by the European Committee, because 2,3,7,8-tetrachloro-di-benzo-*p*-dioxine is present as a by-product, during its industrial manufacturing [2]. Moreover, chlorophenoxy acids yield numerous toxic chlorophenols as intermediate metabolites of their decomposition [3]. Their residue analysis is attained mostly by SPE followed by high-performance liquid chromatography (HPLC) coupled with ultraviolet (UV) or mass spectrometric (MS) detection [4–9]. An immunoassay [10] and an electrochemical immunosensor [11] have been reported for 2,4,5-T determination. Dinoseb is a nitrophenol. Several analytical methods based on SPE-HPLC or gas chromatography [1, 12–14], and on voltametry [15], have been developed for its residue analysis.

Benzimidazole fungicides, carbendazim (methyl benzimidazol-2-ylcarbamate, MBC) and thiabendazole (2-(thiazol-4-yl) benzimidazole, TBZ) (table 1), are systemic pesticides, widely used for pre- or postharvest protection of various fruits and vegetables. These compounds have been used as pesticides since 1970, and many analytical methods have been developed for the determination of their residues in fruits and vegetables, which are considered as complex matrices from the analytical point of view. Moreover, two fungicides, benomyl and thiophanate methyl, can be determined as MBC after conversion [16]. Their residue analysis depends mostly on SPE-HPLC-UV or fluorescence detection (FLD) [16–26]. In addition, mass spectrometry after electrospray or atmospheric-pressure chemical ionization [27–31] and capillary electrophoresis [32] have been applied for their determination.

The present work describes an efficient and rapid sample clean-up procedure for the determination of some ionizable pesticide residues in lemons, using ion-pairing on reverse-phase SPE cartridges. The sorbent is saturated with a proper surfactant, forming ion pairs with the analytes, resulting in increased retention on the cartridge. The bulk of interferences are removed by washing with suitable eluents, and the analytes are obtained by elution with acetonitrile and determined by HPLC using UV detection.

2. Experimental

2.1. *Reagents, materials, and apparatus*

Sodium dodecyl sulphate (SDS, ≥99%) and cetyltrimethylammonium bromide (Ctab, >99%) were purchased from Sigma (Sigma Aldrich, Athens). Nonyltrimethylammonium bromide (Ntab, 96%) and dodecyltrimethylammonium bromide (Dtab, 99%) were purchased from Acrõs Organics (Techline, Athens). 2,4,5-T, dichlorprop, dinoseb, MBC, and TBZ standards (99% purity) were obtained from Riedel-de Haën (Sigma Aldrich, Athens). Oasis cartridges (30 mg, 1 mL) containing a hydrophilic–lipophilic balance (HLB) reverse-phase sorbent [poly(divinylbenzene-co-*N*-vinylpyrrolidone)] were purchased from Waters (Malva Ltd, Athens). Acetonitrile and methanol were of HPLC grade and were obtained from Merck (Merck-Hellas E.P.E, Athens). Trifluoroacetic acid, ethyl acetate, dichloromethane, petroleum ether

40–70°, hydrochloric acid (37%), ammonia solution (30%), anhydrous sodium sulphate, and sodium acetatate were of analytical reagent grade (Sigma Aldrich, Athens). Water was deionized and double-distilled.

Stock solutions (500 μg mL^{-1}) of the pesticides were prepared in methanol. Lemons were collected from local producers at Patras, Greece who had not used fungicides for the last five years. Lemons were chopped with an MR CA Type 4185 Braun mixer and homogenized with an Ultra Turrax T18 basic disperser (IKA Labortechnik, Staufen, Germany).

The chromatographic system consisted of a Pharmacia LKB-Gradient Pump 2249 (LKB Produkter AB, Bromma, Sweden) with a Rheodyne 7125 injector (Rheodyne Inc, Cotati, CA) and a 20 μL loop. UV detection was performed with a Hewlett-Packard 1100 Series variable wavelength detector (Hewlett-Packard Company, Waldbronn, Germany). Data were collected, stored, and integrated with an HP Chemstation. Separation of analytes was performed on a Supelcosil LC-18 reversed-phase column (25 cm × 4.6 mm i.d., 5 μm particle size, 100 Å pore size, Supelco Inc, Bellefonte, PA), at ambient temperature. The flow rate of the mobile phase was 1 mL min^{-1}.

2.2. *Extraction, sample clean-up and determination of acidic pesticides (2,4,5-T, dichorprop and dinoseb)*

A 2 g aliquot of homogenized lemon sample (spiked or free of fungicides), weighed in a 50 mL centrifuge tube, was extracted with 10 mL of dichloromethane/methanol (90 : 10, v/v) mixture, containing 0.1% (v/v) TFA, using homogenization (18 000 rpm, 3 min). The homogenate was centrifuged (3500 rpm, 10 min). The supernatant was collected in a 50 mL tube, while the residual solid was extracted twice with 2 × 10 mL of the extractant, as above. All supernatants were collected together and mixed with 10 mL of 0.01 mol L^{-1} HCl. The mixture was agitated and centrifuged (3500 rpm, 10 min). Two distinct liquid phases were formed. The lower phase (organic) was carefully transferred to another 50 mL tube, using a syringe equipped with a long metal needle. The extract was dried using anhydrous sodium sulphate, and the mixture was centrifuged (3500 rpm, 10 min). The supernatant was transferred to a 50 mL flask and concentrated to dryness, using a rotary evaporator. The residue was dissolved in methanol (0.15 mL) followed by the addition of 0.016 M ammonium hydroxide (0.85 mL). Residual solid was removed by centrifugation (12 000 rpm, 3 min). The supernatant (ca. 1 mL, 'sample extract') containing approximately 15% methanol was further purified by SPE.

An Oasis HLB cartridge (30 mg, 1 mL) activated with methanol and equilibrated with water was conditioned with 1% (w/v) Ctab aqueous solution (2 mL) and washed with 1 mL of water. The 'sample extract' was passed through the cartridge at a flow-rate of ca. 1 mL min^{-1}. The Oasis HLB cartridge was then washed with (1) 1 mL of a 15% (v/v) methanol 0.016 M ammonium hydroxide solution, (2) 1 mL of water, (3) 1 mL of a 30% acetonitrile aqueous solution, and (4) 1 mL of 0.5% TFA (v/v) aqueous solution. The washings were completely removed by passing air through the cartridge. The retained analytes were eluted with 1 mL of acetonitrile, using air pressure as above (final volume 1 mL). A 20 μL aliquot of the eluate was injected into the HPLC system. The analytes were separated on a Supelcosil LC-18 column, eluted with an 0.1 M sodium acetate/acetonitrile (70 : 30, v/v) mixture, and detected at 280 nm (figure 1). Under

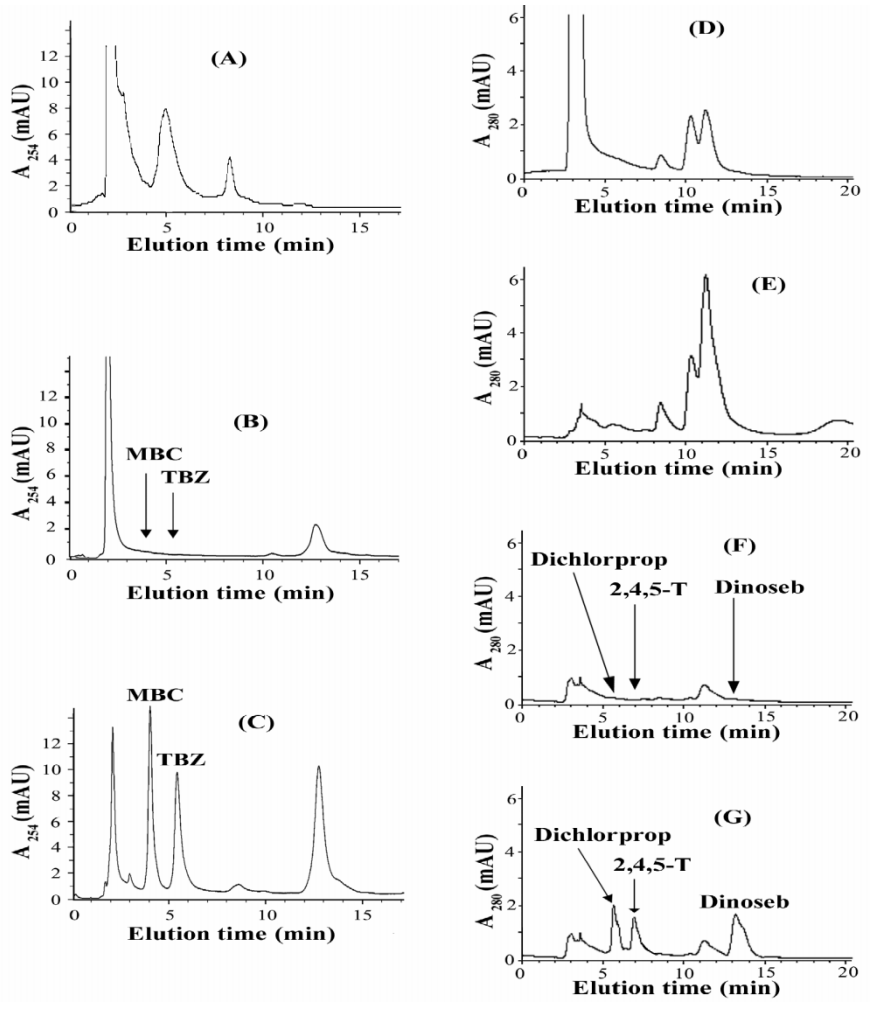


Figure 1. Liquid chromatograms of pesticide-free lemon samples or samples fortified with basic or acidic pesticides. (a) Pesticide-free lemon extract in 0.5% (v/v) TFA acetonitrile solution, purified on a RP-SPE cartridge by washing with 10% acetonitrile aqueous solution. (b) Same as (a), purified on the cartridge preconditioned with SDS and washed with 20% acetonitrile aqueous solution. (c) Lemon extract fortified with MBC and TBZ (5 mg/kg) and purified as in (b). (d) Pesticide-free lemon extract in dichloromethane/methanol (90 : 10, v/v) mixture, containing 0.1% (v/v) TFA. (e) Same as in (d), purified on the cartridge by washing with 10% acetonitrile aqueous solution. (f) Same as in (d), purified on the cartridge preconditioned with Ctab and washed with 30% acetonitrile aqueous solution. (g) Lemon extract fortified with 2,4,5-T, dichlorprop, dinoseb (6 mg/kg) and purified as in (f).

these conditions, dichlorprop was eluted at 5.5 min, 2.4.5-T at 6.9 min, and dinoseb at 13.2 min (figure 1g).

2.3. *SPE of the acidic herbicides (2,4,5-T, dichorprop and dinoseb) using various ion-pair reagents*

The effect of the length of ion-pair reagents' alkyl chain, on herbicides' retention, on the SPE cartridge, have been further studied, using three different surfactants. An Oasis

HLB cartridge (30 mg, 1 mL) was preconditioned with methanol and water. A second cartridge was preconditioned as above and saturated with Ntab by applying 2 mL of a 1% (w/v) aqueous Ntab solution. Finally, the sorbent was washed with 1 mL of 0.1 N NaOH aqueous solution and with 1 mL of water. Two more cartridges were treated in the same way. The only difference was the ion-pair reagent used: the first was saturated with Dtab and the second with Ctab. So, four cartridges were prepared: one containing no detergent and three others saturated with detergents, differing only in the length of their alkyl chain. One millilitre of an aqueous standard solution containing the three acidic herbicides (15 $\mu g\,mL^{-1}$ each) and 10% (v/v) methanol was applied to every one of the aforementioned cartridges. Withdrawal of the pesticides from the sorbent, was achieved by applying a set of eluents (1 mL of each one), in which the amount of acetonitrile gradually increased (10%, 15%, 20%, 30%, 40%, 50%, 60% aqueous acetonitrile solutions, v/v). Finally, 1 mL of pure acetonitrile was applied to every cartridge. Nine eluates (including the first eluate containing 10% methanol) of every cartridge were collected separately. A 20 µL aliquot of every eluate was injected into the HPLC system, and analyte determination was carried out as described in the previous paragraph. Percentage recoveries of the herbicides in the eluates, correlated with the percentage of acetonitrile in the eluents, are graphically presented in figure 2.

2.4. *Extraction, sample clean-up and determination of basic pesticides (MBC and TBZ)*

A 2 g aliquot of homogenized lemon sample (spiked or free of fungicides), weighed in a 15 mL tube, was extracted with 10 mL of acetonitrile acidified with 0.5% (v/v) TFA using homogenization (18 000 rpm, 3 min). The liquid phase was filtered through glass wool and collected in a 50 mL centrifuge tube. The residue was similarly treated with 5 mL of the extractant. The residual solid in the 15 mL tube and the sediment on the glass-wool filter were washed twice with 5 mL of ethyl acetate/petroleum ether (2 : 1, v/v). All filtrates and washings (ca. 25 mL) collected in the 50 mL centrifuge tube were mixed with 0.8 mL of ammonia solution 30% (w/v) and 3 mL of water. The mixture was agitated and centrifuged (3000 rpm, 5 min). Two distinct liquid phases were formed. The lower phase (aqueous) was carefully removed, using a syringe equipped with a long metal needle. The organic phase was washed with 5 mL of water with the same procedure and concentrated to dryness using a rotary evaporator. The residue was dissolved in acetonitrile (0.5 mL) followed by addition of 0.1% (w/v) SDS aqueous solution (2.5 mL). Residual solid was removed by centrifugation (12 000 rpm, 3 min). The supernatant (ca. 3 mL, 'sample extract') containing approximately 16% acetonitrile was further purified by SPE.

An Oasis HLB cartridge (30 mg, 1 mL) activated with methanol and equilibrated with water was conditioned with 1% (w/v) SDS aqueous solution (2 mL) and then with 0.1 $mol\,L^{-1}$ HCl (1 mL). The 'sample extract' was passed through the cartridge at a flow rate of ca. 1 $mL\,min^{-1}$. The Oasis HLB cartridge was then washed with (1) 1 mL of a 0.1% (w/v) SDS aqueous solution and (2) 2 mL of a 20% acetonitrile (v/v), 0.1% (w/v) SDS aqueous solution. The eluent was completely removed by passing air through the cartridge. The retained analytes were eluted with 1 mL of acetonitrile, using air pressure as above (final volume 1 mL). A 20 µL aliquot of the eluate was

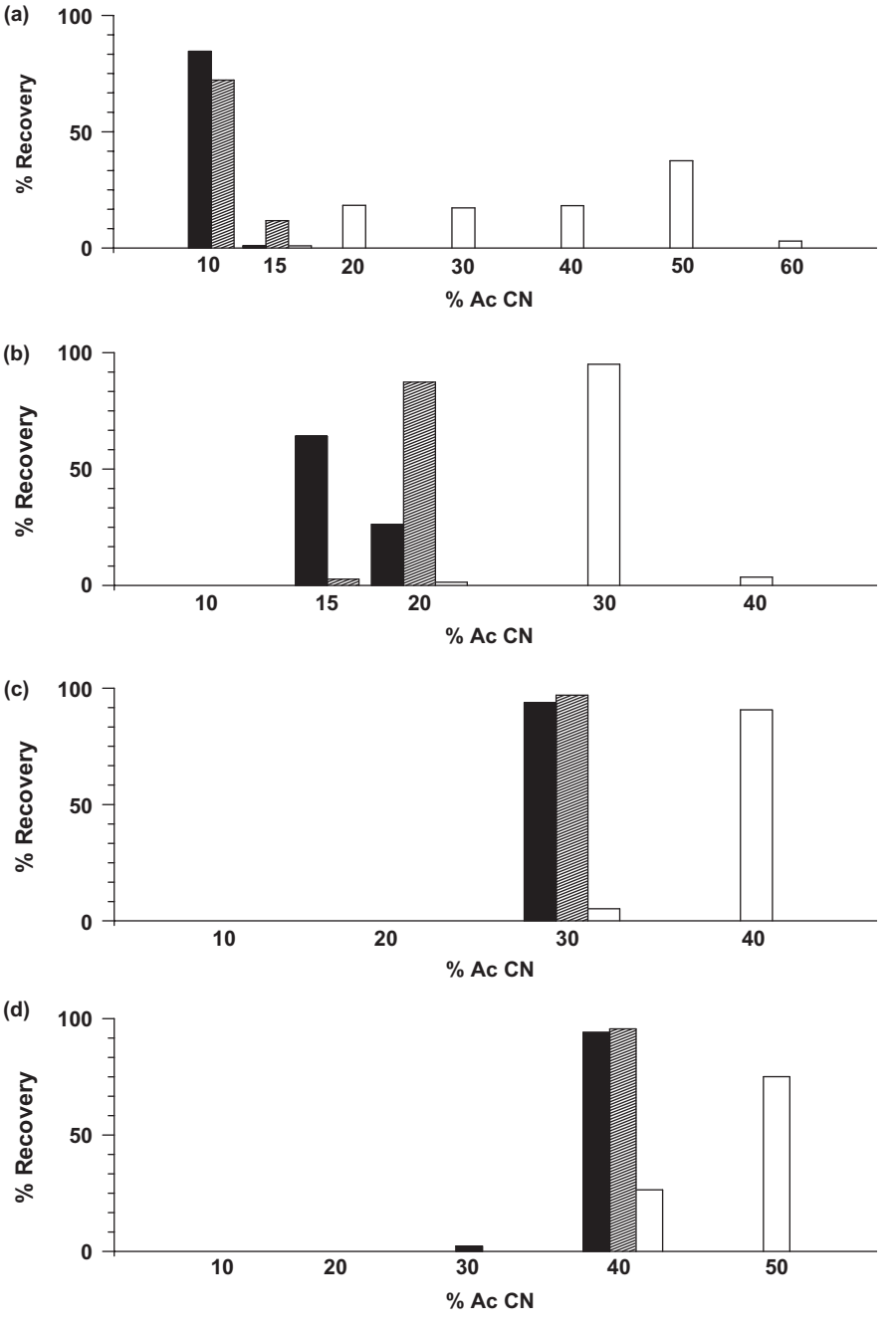


Figure 2. Histograms representing variations in acidic herbicides' retention on SPE cartridges, when no detergent (a) is applied to the sorbent or saturated with anionic surfactants containing: nine (Ntab) (b), 12 (Dtab) (c) or 16 (Ctab) (d) carbon alkyl chains. Percentage AcCN refers to the volume of acetonitrile in the eluates (aqueous acetonitrile solutions). Percentage recovery refers to the amount of each analyte determined in every eluate. Black bars: dichlorprop. Lined bars: 2,4,5-T. White bars: dinoseb.

injected into the HPLC system. The analytes were separated on a Supelcosil LC-18 column, eluted with an acetonitrile/water/ammonia solution 30% (39 : 60.5 : 0.5, v/v/v) mixture and detected at 254 nm. Under these conditions, MBC was eluted at 4.1 min and TBZ at 5.4 min (figure 1c).

3. Results and discussion

Quantitative extraction of both benzimidazoles was achieved with a 0.5% TFA acetonitrile solution. Additionally, the acidic herbicides were extracted with a dichloromethane/methanol (90 : 10, v/v) mixture, containing 0.1% (v/v) TFA. These extraction mixtures co-extract a large number of lemon ingredients which hinder HPLC determination of the analytes (figure 1d). Pilot experiments on spiked or pesticide-free lemon extracts revealed that an SPE clean-up step is essential for the removal of lemon ingredients. Studies were performed on Oasis HLB cartridges, containing a reverse-phase polymeric sorbent. These cartridges are applicable in many pesticide determination procedures, they exhibit increased chemical and physical strength, and they are stable in a wide pH range. Moreover, their performance is not affected by drying.

Initially, SPE experiments were carried out using pesticide-free lemon extracts on cartridges preconditioned with methanol and water. Washing of the cartridge with aqueous solutions containing less than 20% (v/v) acetonitrile does not improve the chromatogram (figure 1a and e). Effective withdrawal of interfering substances was achieved only when the sorbent was washed with aqueous solutions containing more than 20% acetonitrile (figure 1b and f). Tests on the retention of the analytes on the SPE sorbent using standard solutions of carbendazim, thiabendazole, 2,4,5-T, dichlorprop and dinoseb were carried out (table 2). They showed that a 20% acetonitrile aqueous mixture was able to remove almost quantitavely the pesticides from a cartridge, preconditioned with methanol and water. Under these conditions, it was not possible to remove interferences, without elution of pesticides, from the cartridge.

The introduction of ion-pair reagents to the sorbent proved to be successful way to increase the retention of the analytes. In the case of benzimidazoles, saturation of the cartridge with sodium dodecyl sulphate was achieved by elution with 1% (w/v) SDS aqueous solution. The sorbent was washed with 0.1 mol/L of HCl solution in order

Table 2. Retention characteristics of MBC, TBZ, 2,4,5-T, dichlorprop, and dinoseb on Oasis HLB cartridges.

Pesticide	Oasis HLB[a] % acetonitrile	Oasis HLB-SDS[b] % acetonitrile	Oasis HLB-Ctab[c] % acetonitrile
MBC	5	22	–
TBZ	20	25	–
2,4,5-T	15	–	40
Dichlorprop	15	–	40
Dinoseb	15	–	40

[a]Acetonitrile content, in the eluent, starting the elution of single pesticides. [b]Acetonitrile content, in the eluent, starting the elution of ion pairs with SDS. [c]Acetonitrile content, in the eluent, starting the elution of ion pairs with Ctab.

to transform $-SO_3^- Na^+$ groups of SDS to $-SO_3H$. This step requires a stable sorbent in strong acidic media. As the analytes pass through the cartridge, benzimidazoles are protonated, forming ion pairs with the $-SO_3^-$ groups of SDS, resulting in increased retention. Elution of benzimidazoles–SDS pairs was started with aqueous solutions containing more than 20% acetonitrile (v/v) (22% for MBC and 25% for TBZ, table 2), while the single ones were eluted with 5–20% (v/v) acetonitrile aqueous solutions (table 2). Finally, a washing step with an aqueous solution containing 20% acetonitrile (v/v) and 0.1% (w/v) SDS was applied. This solution removed a large number of co-extractives, without eluting the analytes. All the washing solutions contained a small quantity of SDS (0.1%, w/v) to replace the detergent removed during elutions. Eventually, quantitative elution of MBC and TBZ was achieved with 1 mL of acetonitrile. Therefore, both benzimidazoles were eluted concentrated in a small volume of organic solvent. Chromatograms of fortified and fungicide-free lemon samples, obtained with the developed extraction and clean-up procedure, are presented in figure 1b and c, respectively. HPLC analysis is not affected by the presence of SDS. The presence of some peaks (at about 3, 9, and 13 min), corresponding to unknown matrix substances, does not interfere with the determination of MBC and TBZ.

The method's repeatability and recovery for the benzimidazoles were estimated by six analyses of fortified samples at 5 mg/kg. The percentage RSD values and recoveries are presented in table 3. Recoveries achieved by this method (81–97%) are considerably higher than those recorded (60–80%) when benzimidazoles are extracted with ethyl acetate, and the clean-up is performed by liquid–liquid partitioning [18, 32] or SPE [16, 27, 28]. Moreover, similar recoveries, for the benzimidazoles, were achieved when two different SPE cartridges (or columns) were used for sample clean-up [19, 20]. As lower-cost alternative, we suggest a combination of an easy and fast liquid–liquid partitioning and RP-SPE [26].

In the case of the acidic pesticides (2,4,5-T, dichlorprop and dinoseb), cetyltrimethylammonium bromide (Ctab, 1% w/v) was applied to the cartridge in order to increase their retention. The analytes, in their anionic form, were introduced into the cartridge. As the analytes pass through the cartridge, ion-pair formation takes place between the $-N^+(CH_3)_3$ group of Ctab and the negative charged groups of the pesticides. Experiments with standard solutions of the herbicides on cartridges pretreated with Ctab (table 2) revealed that aqueous solutions containing at least 40% (v/v) acetonitrile are necessary for their elution, while elution of single pesticides starts with 15% (v/v) acetonitrile (table 2). Taking these results into account, a washing step with a 30% (v/v) acetonitrile aqueous solution was applied, and a large number of interfering lemon ingredients was removed. Finally,

Table 3. Average recoveries and % RSD values, from calculations based on data collected from analyses of fortified lemon samples ($N = 6$).

Pesticide	MBC	TBZ	Dichlorprop	2,4,5-T	Dinoseb
Fortification level of lemon sample (mg/kg)	5	5	6	6	6
Average recovery (%)	81.1	96.7	104	102	91.4
Repeatability (% RSD)	2.5	3.8	2.7	2.3	2.5

quantitative elution of the analytes was achieved with 1 mL of acetonitrile. Chromatograms of fortified and fungicide-free lemon samples, obtained with the developed extraction and clean-up procedure, are presented in figure 1f and g, respectively. The presence of some peaks (at about 3, 4, and 11.5 min), corresponding to unknown matrix substances, does not interfere with the determination of the herbicides. The presence of Ctab does not affect HPLC determination. The method's repeatability and recovery for the acidic pesticides were estimated by six analyses of fortified samples at $6\,mg\,kg^{-1}$ (table 3).

Finally, an effort to examine thoroughly the effect of surfactant size on analyte retention was carried out. Three cationic surfactants, differing only in the length of their alkyl chain were used: Ntab, Dtab, and Ctab with 9, 12, and 16 carbon alkyl chains, respectively. The amount of each pesticide detected in each eluate was compared with the amount of pesticide detected in the standard solution, before passing through the cartridge. In so doing, the percentage recovery values of the analytes were calculated and presented in figure 2. The use of surfactants with longer alkyl chain resulted in increased retention of the analytes. Thus, a greater amount of acetonitrile in aqueous eluting mixtures was necessary for the analytes' elution. Moreover, the range of acetonitrile concentrations in which analyte elution took place was remarkably shorter when an ion-pair reagent was used. Major differences were recorded for the elution of dinoseb. This was achieved with 20–40%, 30–40%, and 40–50% acetonitrile aqueous solutions, when Ntab, Dtab, and/or Ctab were used, respectively. However, the elution of this analyte started with a 15% acetonitrile solution and was completed with 60% acetonitrile, when no detergent was used. 2,4,5-T and dichlorprop exhibited a similar behaviour (figure 2). Taking into account these results, we can assume that when a surfactant is applied to the sorbent, the retention mechanism involves the following steps:

1. retention of the detergent on the SPE sorbent;
2. ion-pair formation between the analyte and the detergent;
3. elution of both the analyte and the detergent as ion-pair.

It is well known that retention of analytes on a RP-SPE sorbents is primarily governed by hydrophobicity. The more hydrophobic a molecule is, the stronger the retention. So, an increase in the length of surfactants' alkyl chain eventually results in enhanced retention of the analytes, which are able to form ion pairs with the specific surfactant.

4. Conclusions

A new, simple, and rapid sample clean-up procedure has been developed, based on ion-pair formation on cheap and disposable SPE cartridges. This concerns extraction, purification, and preconcentration of ionizable analytes from complex matrices, such as fruit or vegetable extracts. The great advantage of this procedure is the increase in analyte retention on a reverse-phase SPE cartridge, preconditioned with a proper surfactant. Sample extracts are efficiently purified by appropriate washings on the cartridge, and the analytes are quantitatively recovered in a small volume of pure organic solvents.

Acknowledgements

We thank the European Social Fund (ESF), Operational Programme for Educational and Vocational Training II (EPEAEK II), and particularly the Programme HERAKLEITOS, for funding the above work.

References

[1] M.J.M. Wells, L.Z. Yu. *J. Chromatogr. A*, **885**, 237 (2000).
[2] E.M.A. Lopez, A.M. Garcia-Campana, J.J. Aaron, L.C. Rodriguez. *Talanta*, **60**, 355 (2003).
[3] M. Czaplicka. *Sci. Total Environ*, **322**, 21 (2004).
[4] A.C. Hogenboom, M.P. Hofman, S.J. Kok, W.M.A. Niessen, U.A.Th. Brinkman. *J. Chromatogr. A*, **892**, 379 (2000).
[5] A. Di Corcia, M. Nazzari, R. Rao, R. Samperi, E. Sebastiani. *J. Chromatogr. A*, **878**, 87 (2000).
[6] R.K. Juhler, S.R. Sorensen, L. Larsen. *Wat. Res.*, **35**, 1371 (2001).
[7] E.A. Hoogendoorn, R. Huls, E. Dijkman, R. HoogerBrugge. *J. Chromatogr. A*, **938**, 23 (2001).
[8] J.L. Luque-Garcia, M.D. Luque de Castro. *J. Chromatogr. A*, **959**, 25 (2002).
[9] J. Patsias, E.N. Papadakis, E. Papadopoulou-Mourkidou. *J. Chromatogr. A*, **959**, 153 (2002).
[10] K. Morimune, Y. Yamaguchi, Y. Beppu, S. Miyake, S. Takewaki, M. Kawata, Y. Yuasa. *Anal. Chim. Acta*, **376**, 37 (1998).
[11] B.B. Dzantiev, A.V. Zherdev. *Biosens. Bioelectron*, **11**, 179 (1996).
[12] J. Hodgeson. *J. Chromatogr. A*, **659**, 395 (1994).
[13] C. Aguilar, I. Ferrer, F. Borrull, R.M. Marce, D. Barcelo. *J. Chromatogr. A*, **794**, 147 (1998).
[14] G. Fernadez-Salinero, M.E. Silva-Vargas, M.E. Leon-Gonzalez, L.V. Perez-Arribas, L.M. Polo-Diez. *J. Chromatogr. A*, **839**, 227 (1999).
[15] M. Sreedhar, T.M. Reddy, K.R. Sirisha, S.R.J. Reddy. *Anal. Sci. Int. J. Japan Soc. Anal. Chem.*, **19**, 511 (2003).
[16] A.D. Muccio, I. Cammoni, M. Ventriglia, D.A. Barbini, M. Mauro, P. Pelosi, T. Generali, A. Ausili, S. Girolimetti. *J. Chromatogr. A*, **697**, 145 (1995).
[17] Y. Kidata, M. Sasaki, K. Tanikawa. *J. Assoc. Off. Anal. Chem*, **65**, 1302 (1982).
[18] J. Garrido, M. de Alba, I. Jimenez, E Casado, M.L. Folgueiras. *J. Chromatogr. A*, **765**, 91 (1997).
[19] Y. Ito, Y. Ikai, H. Oka, J. Hayakawa, T. Kagami. *J. Chromatogr. A*, **810**, 81 (1998).
[20] A.D. Muccio, S. Girolimetti, D.A. Barbini, P. Pelosi, T. Generali, L. Vergori, G.D. Merulis, A. Leonelli, P. Stefanelli. *J. Chromatogr. A*, **833**, 61 (1999).
[21] N. Tharsis, J.L. Portillo, F. Broto-Puig, L. Comellas. *J. Chromatogr. A*, **778**, 95 (1997).
[22] M. Hiemstra, J.A. Joosten, A.D. Kok. *J. Assoc. Off. Anal. Chem.*, **78**, 1267 (1995).
[23] N. Aharonson, S.J. Lehotay, M.A. Ibrahim. *J. Agric. Food Chem.*, **42**, 2817 (1994).
[24] J.J. Jiménez, J. Atienza, J.L. Bernal, L. Toribio. *Chomatographia*, **38**, 395 (1994).
[25] M. Anastassiades, W. Schwack. *J. Chromatogr. A*, **825**, 45 (1998).
[26] K.P. Prousalis, D.A. Polygenis, A. Syrokou, F.N. Lamari, T. Tsegenidis. *Anal. Bioanal. Chem*, **379**, 458 (2004).
[27] M. Fernández, R. Rodríguez, Y. Picó, J. Mañes. *J. Chromatogr. A*, **912**, 301 (2001).
[28] C. Blasco, M. Fernández, Y. Picó, G. Font, J. Mañes. *Anal. Chim. Acta*, **461**, 109 (2002).
[29] E. Lacassie, M.F. Dreyfuss, J.L. Daguet, M. Vignaud, P. Marquet, G. Lachâtre. *J. Chromatogr. A*, **830**, 135 (1999).
[30] X. Pous, M.J. Ruíz, Y. Picó, G. Font. *Fresenius J. Anal. Chem.*, **371**, 182 (2001).
[31] C. Blasco, Y. Picó, J. Mañes, G. Font. *J. Chromatogr. A*, **947**, 227 (2002).
[32] C.K. Kaltsonoudis, F.N. Lamari, K.P. Prousalis, N.K. Karamanos, T. Tsegenidis. *Chromatographia*, **57**, 181 (2003).