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Short communication

Determination of pesticides in waters by capillary gas chromatography with atomic emission detection

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Abstract

Capillary gas chromatography with atomic emission detection (GC–AED) was successfully used to separate and quantify 14 pesticides (organochlorines, organophosphorus compounds and pyrethrins) in water samples after liquid–liquid extraction with ethyl acetate. Monitoring the emission lines for elements such as chlorine, bromine and sulfur ensures nearly specific chromatograms for these elements, and markedly increases selectivity. Calibration curves were obtained by plotting peak area versus concentration and the correlation coefficients relating to linearity were at least 0.999. Each chromatographic separation takes 21 min and, since two injections are necessary, it requires approximately 1 h to analyze one sample. The method shows a precision of 4.3–8.2% (RSD), depending on the compound. The application of liquid–liquid extraction with ethyl acetate led to recoveries from spiked samples ranging from 76 to 113%. The sensitivity and linearity for the elements chlorine, sulfur, nitrogen and phosphorus were checked under the optimized conditions at their customary emission wavelength. The sensitivity and linearity for these compounds decreased in the order (atom and emission wavelength) Cl (479 nm)>S (181 nm)>P (178 nm)>N (174 nm). A study of the GC–AED system's response to chlorine concentration in eight pesticide molecules was performed and a linear relationship was found with a correlation coefficient of 0.987.

Keywords: Water analysis; Liquid–liquid extraction; Pesticides; Pyrethrins; Organophosphorus compounds; Organochlorine compounds

1. Introduction

Pesticides, with their high degree of toxicity, constitute a very important group of target compounds in environmental samples. Those present in waters may have an agricultural, domestic or industrial origin, the most harmful effect being their inclusion in the so-called ''nutrition-chain'' [1]. Although the use of many organochlorine pesticides (OCs) has been restricted or even banned for several years because of their long residence times, their persistence and bioaccumulation, they can still be found in many environmental samples [2]. Organophosphorus (OPs) and carbamate pesticides have largely superseded organochlorines. The Environmental Pollution Agency (EPA) has compiled a list of priority organic pollutants which, if present at all, should only be found at very low levels in water [1]. This list includes five of the pesticides analyzed in this paper (lindane, *p,p′*-DDT, *p,p′*-DDD, *p,p′*-

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DDE and α-endosulfan). European Community directives on the quality of water intended for human consumption have set a maximum admissible concentration (MAC) of 0.1 μg l^{-1} for individual pesticides and 0.5 μg l^{-1} for total pesticides. These tolerance levels are more restrictive than the equivalent US regulations, which have established a MAC of 2 μg l^{-1} for the most toxic pesticides [1]. For wastewaters, typical concentrations ranging from 0.5 to 5700 μg l^{-1} have been found [3].

Chromatographic methods, particularly gas chromatography (GC) and liquid chromatography (LC), are preferred for determining pesticides. Since almost all pesticides contain heteroatoms, the most commonly used element-selective detectors for GC are nitrogen–phosphorus (NPD), flame photometric (FPD) and electron-capture detectors (ECD). On the other hand, atomic emission detectors (AED) can detect all elements, except helium, separately due to their multichannel ability and selectivity, making them more sensitive than the more commonly-used detectors cited above [3]. Regardless of the selectivity of the detector, mass spectrometry (MS), which is sensitive, also provides structural information. The usefulness of GC combined with AED for the selective detection of pesticides has been widely described [3–22].

Several extraction techniques must often be used when water samples are analyzed for pesticides with very different chemical properties. Liquid–liquid extraction (LLE) is one of the most frequently used preconcentration techniques for both inorganic and organic contaminants [8,11,16,23]. In this paper, we describe a reliable method for determining 14 pesticides in different water samples. The rapid and easy liquid–liquid extraction procedure and GC with atomic emission detection form a feasible analytical method.

2. Experimental

2.1. Chemicals

Standards of the pesticides (methamidophos, acephate, omethoate, chlorpropham, dimethoate, lindane, diazinon, chlorpyriphos, α-endosulfan, *p,p′*-DDE, *p,p′*-DDD, *p,p′*-DDT, permethrin and deltamethrin) (Dr. Ehrenstorfer, Augsburg, Germany) were used without further purification. Analytical-reagent grade acetone and ethyl acetate were purchased from Lab-Scan (Dublin, Ireland). Dichloromethane was supplied by Romil (Cambridge, UK). Sodium chloride was of analytical grade (Probus, Barcelona, Spain).

Stock standard solutions of 1000 μg ml^{-1} of each compound were prepared by dissolving 10 mg of the pesticide in 10 ml of acetone and stored in the dark at 4 °C. Working standard solutions were prepared freshly by diluting the stock solutions with acetone prior to calibration.

Helium, nitrogen, oxygen and hydrogen (99.9999% purity) were purchased from Air Liquide (Madrid, Spain).

2.2. Instrumentation

A G2350A microwave-induced plasma atomic emission detector (Agilent, Waldbronn, Germany) was coupled to a 6890 gas chromatograph. The GC was equipped with a 7683 automatic injector and a split–splitless capillary injection port (Agilent). Updated G2070AA ChemStation application with the G2360AA GC–AED software was used to control and automate many features of the GC and AED systems. Chromatographic separation was performed on a 30 m×0.32 mm I.D. HP-5, 5% dimethyl polysiloxane capillary column from Agilent with a 0.25 μm film thickness. The initial column temperature was set at 50 °C for 1.1 min, then increased to 150 °C (30 °C min^{-1}, 2 min hold), programmed to 170 °C (30 °C min^{-1}), to 185 °C (50 °C min^{-1}), to 205 °C (3 °C min^{-1}), to 250 °C (50 °C min^{-1}, 2.2 min) and then finally increased to 310 °C (30 °C min^{-1}, 2 min). Sample volumes of 5 μl were injected in splitless mode at an injection port temperature of 300 °C, applying a pressure pulse of 40 p.s.i. The flow-rate of the helium carrier gas was 3.2 ml min^{-1}. The solvent venting was switched on immediately after injection and switched off 4.5 min after injection. The final part of the GC column was used as a transfer line to the detector. The transfer line and the detector cavity were operated at 325 and 250 °C, respectively. The helium make-up flow was 40 ml min^{-1}. The scavenger gases were hydrogen

and oxygen at 15 and 20 p.s.i., respectively. The spectrometer was purged with nitrogen at 2.5 ml min^{-1}. Filter and back amount adjustment were set according to Agilent default specifications.

A Büchi vacuum V-500 rotatory evaporator R-200 coupled to a Büchi heating bath B-490 (Switzerland) was used to concentrate the sample extracts.

2.3. Sampling and extraction procedure

Fifteen sampling points to obtain tap, mineral, river, sea and sewage water samples were selected in different areas of Murcia (Spain). The water samples were collected in January and March 2002. Two 1-l volumes of water were collected in plastic bottles from each sampling site. Samples were stored at 4 °C prior to extraction, normally within 48 h.

For the extraction and preconcentration of pesticides from waters, a sample of 25 ml of non-filtered water, previously salted with 10% sodium chloride, was extracted with 125 ml ethyl acetate under mechanical shaking for 10 min in a separation funnel. The organic phases were separated from the aqueous phase using a phase separator paper (Albet 203 SF, 15 cm diameter) and the funnel was washed with 10 ml of ethyl acetate. The organic phases were collected in a flask and concentrated to dryness using a rotary vacuum evaporator at 35 °C. The dry extract was dissolved in 1 ml of acetone. No clean-up was necessary.

If methamidophos, acephate and omethoate are not being analyzed, dichloromethane can be used instead of ethyl acetate for extraction. For this purpose a sample of 100 ml of non-filtered water, previously salted with 10% sodium chloride, was extracted with 10 ml of dichloromethane under mechanical shaking for 5 min in a separation funnel. The organic phase was also separated from the aqueous phase using a phase separator paper and the funnel was washed with 10 ml of dichloromethane. The organic phase was concentrated to dryness and reconstituted in 1 ml of acetone.

2.4. Recovery assays

All water samples, except seawater, were salted with 10% sodium chloride and spiked by adding from 25 to 625 ng of the pesticides, depending on the compound, to 25 ml of water. The samples were allowed to equilibrate for 30 min prior to extraction and then processed according to the procedure which uses ethyl acetate. Three replicates were analyzed at each fortification level. If the dichloromethane extraction procedure was used, all water samples except seawater were salted and spiked by adding from 50 to 500 ng of the pesticides to 100 ml of water.

3. Results and discussion

With GC–AED it is possible to monitor every element in a pesticide, providing multiple channels of corroborative data, although, for technical reasons, it is not possible to detect all the elements simultaneously in one GC run. The elements can be in groups on the condition that close emission line wavelengths and the same scavenger gases are used. For this reason, three sequential chromatographic runs were required to obtain chromatograms for C, S, N, H, Cl, Br and P. The chromatograms for nitrogen (174 nm), carbon (179 and 193 nm) and sulfur (181 nm) were obtained simultaneously using oxygen and hydrogen as scavenger gases. While the emission lines for phosphorus lie in the same region (178 and 186 nm), this element required hydrogen as the sole scavenger gas and therefore had to be determined separately. The chromatograms for bromine (478 nm), chlorine (479 nm), hydrogen (486 nm) and carbon (496 nm) were obtained simultaneously using oxygen as the only scavenger gas. As the phosphorus emission line was not used for quantification, only two sequential runs were fully automated from the GC–AED system controller. Of particular interest are the chromatograms for sulfur, chlorine and bromine. Their presence, combined with the retention time, would usually be sufficient to identify a given pesticide. Quantification can be made using any (or all) of the elements present. This flexibility can be very useful if interfering compounds appear in one element channel, but not in another.

3.1. Optimization of GC parameters

The temperature program was optimized in order to elute the 14 pesticides in the shortest time

possible. Since carbon has an emission line at 193 nm which is common to all the analytes, it was monitored to study the GC parameters. The helium flow was varied between 0.5 and 4.5 ml min^{-1}, thus modifying the retention time and peak area values. Increasing the helium flow decreased the retention time and peak width and increased the peak area. The value selected was 3.2 ml min^{-1}, which reduced the analysis time necessary and produced no overlapping peaks. The effect of the injection temperature was studied for all pesticides between 225 and 325 °C. In the case of pyrethrins, permethrin and deltamethrin, the peak area increased up to 300 °C and then remained constant. For the other pesticides, temperatures below 300 °C did not affect the sensitivity, while higher temperatures slightly decreased the signals. Therefore, 300 °C was selected as the optimal injection temperature.

In order to increase the sensitivity of the chromatographic determination, large-volume injections were assayed. When injecting volumes larger than 3 μl in splitless mode, column performance rapidly decreases and pulsed injection is recommended [24]. A pressure is applied to the injector and the sample is introduced more rapidly into the column than when there is no pulse. When pressures of between 20 and 50 p.s.i. were applied to a 5 μl injection volume of a standard mixture of the pesticides, the best results were obtained with 40 p.s.i., where the sensitivity of the sulfur 181 nm emission line markedly increased.

3.2. Optimization of AED parameters

The detector operating parameters (reagent gas pressure and make-up gas flow-rate) were optimized to obtain the highest degree of sensitivity for the pesticides. For those emission lines which required two scavenger gases simultaneously, independent optimization of both the oxygen and hydrogen pressures was carried out. First, the hydrogen pressure was held constant at 8.9 p.s.i., the default value provided by the software, while oxygen was varied from 5 to 30 p.s.i. to determine the optimum oxygen pressure. For the S (181 nm) and C (193 nm) emission lines, an increase in oxygen pressure led to a decrease in peak area up to 15 p.s.i., which remained almost constant thereafter, while for N (174 nm), the oxygen pressure had hardly any effect on sensitivity. A pressure of 20 p.s.i. was adopted in order to avoid accumulation of elemental carbon in the AED discharge tube [13]. The oxygen reagent gas pressure was then held constant at its optimum value while the hydrogen pressure was varied from 5 to 25 p.s.i. A slight increase of sensitivity was observed at 15 p.s.i. in the S (181 nm) emission line for all pesticides, and this was the hydrogen pressure selected. For monitoring chlorine and bromine emission lines, oxygen was the only scavenger gas and a pressure of 20 p.s.i. was also selected, the behaviour being similar to that observed for the S (181 nm) emission line.

The supplementary helium added to the column flow prior to detection (make-up gas) affects the sensitivity and peak shape of the pesticides. To determine the optimum helium make-up gas flow-rate which provided the maximum sensitivity, a standard solution mixture of 5 μg ml^{-1} was injected and the flow-rate was varied from 20 to 100 ml min^{-1}. A flow-rate of 40 ml min^{-1} provided the maximum sensitivity for all pesticides at the Cl (479 nm), N (174 nm) and Br (478 nm) emission lines. Monitoring of the S (181 nm) and C (193 nm) emission lines showed very wide peaks and overlapping at flow-rates slower than the optimized value.

Under the optimized conditions, the pesticides determined eluted between 4.5 and 21 min in the following order: methamidophos (retention time 4.96 min), acephate (6.65 min), omethoate (7.81 min), chlorpropham (8.18 min), dimethoate (8.86 min), lindane (9.15 min), diazinon (9.5 min), chlorpyriphos (11.68 min), α-endosulfan (13.63 min), *p,p′*-DDE (14.75 min), *p,p′*-DDD (15.13 min), *p,p′*-DDT (15.66 min), permethrin (18.31 min) and deltamethrin (19.74 min). Elution profiles for the mixture at different channels are shown in Fig. 1.

3.3. Calibration, precision and detection limits

It is important to determine the sensitivity and linearity of the instrumentation for the so-called functional elements (Cl, S, N and P) because the potency or toxicity of pesticides is often generated by the functional groups containing these elements. For this experiment, chlorpyriphos (dursban) was selected because it contains the four functional

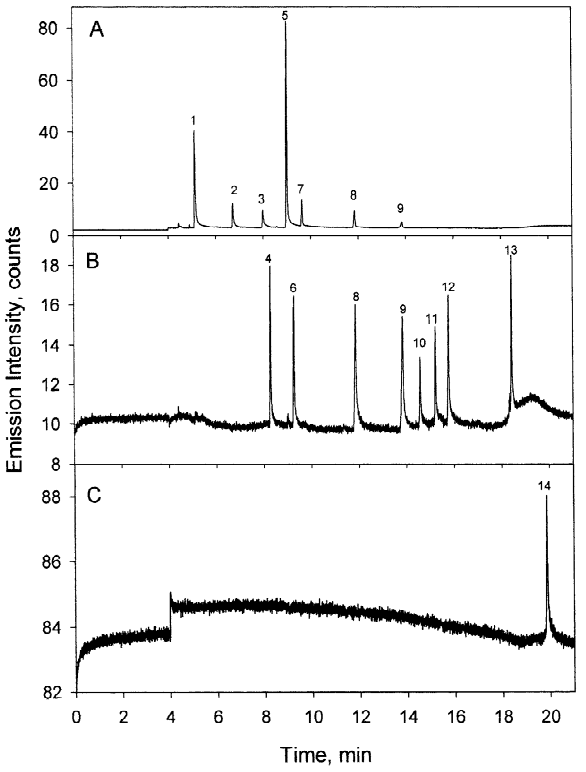

Fig. 1. GC–AED chromatograms of a standard mixture of pesticides by element wavelength: (A) S 181 nm, (B) Cl 479 nm and (C) Br 478 nm. 1, Methamidophos (600 ng ml^{-1}); 2, acephate (550 ng ml^{-1}); 3, omethoate (600 ng ml^{-1}); 4, chlorpropham (250 ng ml^{-1}); 5, dimethoate (550 ng ml^{-1}); 6, lindane (50 ng ml^{-1}); 7, diazinon (190 ng ml^{-1}); 8, chlorpyriphos (200 ng ml^{-1}); 9, α-endosulfan (110 ng ml^{-1}); 10, *p,p′*-DDE (60 ng ml^{-1}); 11, *p,p′*-DDD (60 ng ml^{-1}); 12, *p,p′*-DDT (100 ng ml^{-1}); 13, permethrin (200 ng ml^{-1}) and 14, deltamethrin (140 ng ml^{-1}).

elements [5]. Several solutions of chlorpyriphos in acetone were prepared at different concentrations ranging from 0.042 to 10.5 μg ml^{-1} (0.21–52.5 ng). Higher concentrations were not assayed because the practical value is lower in environmental analysis. The Cl (479 nm), S (181 nm), P (178 nm) and N (174 nm) emission lines were monitored. Each concentration was injected into the GC five times to improve the quality of the information. Table 1 shows the characteristics of the calibration graphs generated for each emission line. The results obtained show the following order of sensitivity: Cl (479 nm)>S (181 nm)>P (178 nm)>N (174 nm). Chlorine at 479 nm not only provided maximum sensitivity, but it also had the widest linear range (0.2–5 ng). Values for the sensitivity (expressed as the slope values) and the linearity ranges decreased for the other lines. The correlation coefficients derived from linear regressions and the standard errors of the estimates are also included in Table 1. The power of independent identity confirmation was clearly demonstrated with dursban. It was detected at all four target atomic emission lines with retention times that did not vary by more than 0.01 min.

Similar studies were carried out for the other pesticides and it was concluded that sulfur at 181 nm and chlorine at 479 nm were the most sensitive and selective emission lines, these being the monitored lines chosen for quantification (sulfur for methamidophos, acephate, omethoate, dimethoate and diazinon; chlorine for chlorpropham, lindane, chlorpyriphos, α-endosulfan, *p,p′*-DDE, *p,p′*-DDD, *p,p′*-DDT and permethrin), except for deltamethrin for which the bromine line at 478 nm was monitored. Linear calibration curves can be obtained by plotting peak areas versus concentrations and the linear relationships for the pesticides are shown in Table 2. Correlation coefficients are better than 0.999, showing a high degree of correlation between concentration and peak area for the 14 compounds studied. The precision of the method was demonstrated by repetitive analyses, calculating the average relative standard deviation (RSD) for 10 replicate injections of the pesticide mixture. The values are also given in

Table 1
Calibration parameters for chlorpyriphos at different emission lines

Parameter	Cl (479 nm)	S (181 nm)	N (174 nm)	P (178 nm)
Slope (ng^{-1})	19.53	15.56	1.24	5.27
Ordinate	−1.05	−1.47	−0.78	−0.95
Correlation coefficient	0.9989	0.9995	0.9987	0.9953
Standard error of estimate	2.17	1.32	1.76	1.32
Linearity range (ng)	0.2–5	0.5–5	2.5–50	0.5–5

Table 2
Analytical data for the target pesticides

Pesticide	Calibration curve[a] (correlation coefficient)	Linearity range (ng ml^{-1})	RSD[b] (%)	Detection limit[c] (pg)
Methamidophos	$y = -0.199 + 0.0823x$ (0.9994)	30–1000	8.2 (150)	50
Acephate	$y = 1.177 + 0.0297x$ (0.9993)	60–1500	5.2 (250)	100
Omethoate	$y = -5.379 + 0.0312x$ (0.9997)	60–1500	7.7 (350)	100
Chlorpropham	$y = 0.504 + 0.0538x$ (0.9990)	50–1000	4.6 (100)	100
Dimethoate	$y = 1.753 + 0.1421x$ (0.9995)	15–1000	5.1 (100)	22
Lindane	$y = 0.607 + 0.3125x$ (0.9992)	5–750	5.6 (50)	20
Diazinon	$y = -1.934 + 0.1047x$ (0.9998)	20–1000	5.9 (100)	30
Chlorpyriphos	$y = 1.446 + 0.1110x$ (0.9990)	20–1000	5.8 (100)	50
α-Endosulfan	$y = -0.100 + 0.2115x$ (0.9995)	10–1000	5.8 (50)	25
p,p'-DDE	$y = 3.466 + 0.1568x$ (0.9995)	15–1000	5.1 (50)	35
p,p'-DDD	$y = 0.293 + 0.1831x$ (0.9998)	10–1000	6.0 (50)	30
p,p'-DDT	$y = 2.274 + 0.1163x$ (0.9990)	10–1000	6.7 (50)	45
Permethrin	$y = -0.085 + 0.0505x$ (0.9997)	30–1000	5.7 (100)	100
Deltamethrin	$y = -0.226 + 0.0522x$ (0.9990)	25–1000	4.3 (100)	95

[a] Equations: y = peak area; x = concentration in ng ml^{-1}.
[b] Values in parentheses are the pesticide concentrations in ng ml^{-1}.
[c] Corresponding to $S/N = 3$.

Table 2. Detection limits were calculated using a signal-to-noise ratio of 3 for all investigated compounds and values are also given in Table 2 for the standards and for the water samples when using ethyl acetate as the organic extractant.

After confirming the linear response of the detector to the pesticide concentration at different emission lines, another experiment was carried out to demonstrate the linear response to the element concentration of the compounds. The eight pesticides with chlorine present were selected, each containing between one and six chlorine atoms per molecule. The pesticides chosen were chlorpropham, permethrin, chlorpyriphos, p,p'-DDE and p,p'-DDD, p,p'-DDT and lindane and α-endosulfan, which have one, two, three, four, five and six chlorine atoms per molecule, respectively. The concentration injected for each pesticide was different, with the total amount of pesticide varying from 3.0 to 4.0 ng. The response area was calculated as the mean area for 10 replicates divided by the amount of pesticide injected in ng [5]. The linear relationship between percentage chlorine concentration and response area led to the regression curve

$$\text{Area response} = -6.4874 + 0.9258\ \text{Cl}\%$$

showing a clear linear function with a correlation coefficient of 0.9875, which is a high value for this type of relation.

3.4. Optimization of the extraction procedure

Good results were obtained by liquid–liquid extraction (LLE). Preliminary experiments were carried out using several organic solvents (hexane, isoctane, toluene, diethyl ether, dichloromethane and ethyl acetate) and mixtures. Best recoveries were obtained using dichloromethane and ethyl acetate. The extraction procedure using dichloromethane provided excellent recoveries for all the pesticides except methamidophos, acephate and omethoate. In an attempt to improve the recovery efficiency by increasing the ionic strength of the sample, sodium chloride (10% w/v) was added to all the samples, which improved the extraction of those pesticides with a high degree of water solubility [25]. Higher sodium chloride concentrations did not improve extraction percentages.

The effect of the aqueous–organic phase ratio was studied by using 100 ml of a water sample and 2, 5, 10 and 20 ml of dichloromethane and shaking the mixture for 5 min. The extraction percentages obtained for the pesticides were optimal for a 10:1 water–dichloromethane ratio, although

methamidophos, acephate and omethoate were not extracted into this organic phase. Shaking times of 2, 5 and 10 min were assayed and 5 min was sufficient to obtain the highest extraction percentage. After extraction, the organic phase was evaporated to dryness and the dry extract dissolved with 1 ml of acetone (this is the minimum volume required to operate the injector). Thus, dichloromethane could be used for the extraction of the pesticides (excluding methamidophos, acephate and omethoate) providing a concentration factor of 100, and subsequently detection limits of between 0.04 and 0.2 ng ml^{-1}, depending on the compound.

The liquid–liquid extraction of all the pesticides was achieved using ethyl acetate. The effect of the aqueous–organic phase ratio was studied and a ratio of 1:5 was selected, which provided the best recoveries for all the pesticides. Water samples of 25, 50 and 100 ml were tested by using this extraction procedure in order to increase the sensitivity of the method, the first providing the best extraction percentages. The results obtained (extracting 25 ml of water sample spiked at 10 times the detection limit of each pesticide level with 125 ml of ethyl acetate) showed that 10 min were sufficient to achieve total extraction. Then, the ethyl acetate layer was concentrated to dryness and reconstituted with 1 ml of acetone, a concentration factor of 25 being achieved with this extraction procedure. The chromatograms were clean and no interfering peaks appeared in the areas of interest, meaning that no clean-up was necessary. The ethyl acetate extraction procedure was selected for the determination of the 14 pesticides under study. Detection limits for the pesticides in water samples were 25 times lower with the ethyl acetate extraction procedure than those directly obtained using the proposed GC–AED method.

3.5. Analysis of water samples and recovery study

Fifteen water samples were used to test the two methods of extraction (tap, mineral, river, sea and sewage waters). No pH adjustment was made since most of the studied compounds are stable in neutral media and below the pH of natural waters (pH 5 to 8). Only when the pH is higher than 8 does the hydrolysis rate of organophosphorus compounds increase steeply [26], but there was no risk of this in the analyzed waters. Filtering water samples previously fortified with the pesticides through 0.45 μm membrane filters led to recoveries of less than 50% and so the samples were not filtered. All the samples analyzed were free from the studied pesticides at the set detection limits. The standard addition method was used to investigate the possibility of a matrix effect. Each graph was constructed from four points, each point representing the mean of two injections. The slopes of the standard addition graphs were similar to those of standards directly prepared in acetone, confirming the absence of interferences by the matrix.

A recovery study was carried out by fortifying samples of tap, sewage and seawater samples at two concentrations (ranging from 1 to 25 ng ml^{-1}) with the 14 pesticides and using the ethyl acetate extraction procedure. Recoveries ranged from 76 to 113% with percent relative standard deviations of less than 13.2%. The recovery and RSD mean values obtained confirm that the applied extraction procedure can be considered as a validated analytical method [27]. Recoveries in the 83–107% range were obtained when dichloromethane was used as the extracting agent.

4. Conclusion

The proposed method using element-specific GC–AED permits the selective determination of 14 pesticides in water samples. Identification of the pesticides in environmental samples can be verified not only by one, but by all, characteristic element emission lines. Preconcentration of the water samples was carried out by a simple liquid–liquid extraction using ethyl acetate or dichloromethane, depending on the pesticides analyzed, with satisfactory results being achieved at minimum cost and with simple sample manipulation. The two methods provide good recovery and repeatability.

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References

[1] D. Pérez-Bendito, S. Rubio, Environmental Analytical Chemistry, Comprehensive Analytical Chemistry, Vol. XXXII, Elsevier, Amsterdam, 1999.
[2] S.N. Meijer, C.J. Halsall, T. Harner, A.J. Peters, W.A. Ockenden, A.E. Johnston, K.C. Jones, Environ. Sci. Technol. 35 (2001) 1989.
[3] L.L.P. van Stee, P.E.G. Leonards, R.J.J. Vreuls, U.A.Th. Brinkman, Analyst 124 (1999) 1547.
[4] P.L. Wylie, R. Oguchi, J. Chromatogr. 517 (1990) 131.
[5] C. Ting, P. Kho, J. Assoc. Off. Anal. Chem. 74 (1991) 991.
[6] S.M. Lee, P.L. Wylie, J. Agric. Food Chem. 39 (1991) 2192.
[7] M. Miyahara, T. Suzuki, Y. Saito, J. Agric. Food Chem. 40 (1992) 64.
[8] S. Pedersen-Bjergaard, T.N. Asp, T. Greibrokk, Anal. Chim. Acta 265 (1992) 87.
[9] H. Casabianca, Analusis 20 (1992) S9.
[10] R. Eisert, K. Levsen, G. Wünsch, J. Chromatogr. A 683 (1994) 175.
[11] N.L. Olson, R. Carrell, R.K. Cummings, R. Rieck, LC·GC 12 (1994) 143.
[12] H.J. Stan, M. Linkerhägner, Chem. Plant Prot. 12 (1995) 59.
[13] H.J. Stan, M. Linkerhägner, J. Chromatogr. A 750 (1996) 369.
[14] J.L. Bernal, M.J. del Nozal, M.T. Martín, J.J. Jiménez, J. Chromatogr. A 754 (1996) 245.
[15] S. Pedersen-Bjergaard, S.I. Semb, E.M. Brevik, J. High Resolut. Chromatogr. 20 (1997) 47.
[16] H. Casabianca, S. Dugenest, M.F. Grenier-Loustalot, Spectra Anal. 205 (1998) 17.
[17] A. Wenner, M. Wortberg, J. High Resolut. Chromatogr. 21 (1998) 661.
[18] T. Hankemeier, J. Rozenbrand, M. Abhadur, R.J.J. Vreuls, U.A.Th. Brinkman, Chromatographia 48 (1998) 273.
[19] J. Cook, M. Engel, P. Wylie, B. Quimby, J. Assoc. Off. Anal. Chem. Int. 82 (1999) 313.
[20] A.M. Carro, J.C. Cobas, J.B. Rodríguez, R.A. Lorenzo, R. Cela, J. Anal. At. Spectrom. 14 (1999) 1867.
[21] H.G.J. Mol, T. Hankemeier, U.A.Th. Brinkman, LC·GC 17 (1999) 544.
[22] H. Bagheri, M. Saraji, U.A.Th. Brinkman, Tech. Instr. Anal. Chem. 21 (2000) 211.
[23] D. Barceló, J. Chromatogr. 643 (1993) 117.
[24] A. Agüera, L. Piedra, M.D. Hernando, A.R. Fernández-Alba, M. Contreras, Analyst 125 (2000) 1397.
[25] F.J. López, J. Beltran, M. Forcada, F. Hernández, J. Chromatogr. A 823 (1998) 25.
[26] M. Eto, Organophosphorus Pesticides—Organic and Biological Chemistry, CRC Press, Boca Raton, FL, 1974.
[27] European Commission, Quality Control Procedures For Pesticide Residues Analysis, Guidelines for Residues Monitoring in the European Union, Brussels, 1997.