

Notes

Determination of Acrinathrin in Water Samples by Micro Liquid-Liquid Extraction and Gas Chromatography–Mass Spectrometry

Jose Luis VILCHEZ†, Pedro ESPINOSA, F. Javier ARREBOLA and Antonio GONZÁLEZ-CASADO

Department of Analytical Chemistry, University of Granada, E-18071 Granada, Spain

Keywords Acrinathrin, gas chromatography–mass spectrometry, water analysis, pesticides, pyrethroid

Acrinathrin [(*S*)- α -cyano-3-phenoxybenzyl (*Z*)-(1*R*, 3*S*)-2,2-dimethyl-3-[2-(2,2,2-trifluoro-1-trifluoromethylethoxycarbonyl)vinyl]cyclopropanecarboxylate] (Fig. 1) is an acaricide insecticide pyrethroid acting through contact and ingestion by such insects as phytophagous mites on citrus, cotton, fruit, hops, ornamentals, soyabeans, tobacco, vegetables, vines and greenhouse crops.^{1,2} Its half life in water is longer than other pesticides even under photolysis³ by natural sunlight.

Acrinathrin is manufactured by Roussel Uclaf under the tradename of Rufast (15% acrinathrin w/v). A method for the determination of acrinathrin residue in vegetables by gas chromatography was proposed by Fernández-Alba⁴ using electron capture detector (GC-ECD), with a determination limit of 0.001 mg kg⁻¹.

Here, we propose a method for the determination of acrinathrin in ground and sea water based in a hexane micro liquid-liquid extraction, a technique which has also been applied to the detection of some pyrethroids and endosulfans⁵ in water.

Experimental

Apparatus and software

A Hewlett-Packard system made of a 5890 GC fitted with a 7673 autosampler, a splitless injector for the HP-5MS fused silica capillary column (30 m×0.25 mm i.d.×0.25 μ m film thickness) and a 5971 mass spectrometer, a HP-UX Chemsystem computer and the proprietary software. The carrier gas was helium (purity 99.999%). The lack-of-fit test from Statgraphics software⁶ was applied to check the linearity of the calibration graphs according to the Analytical Methods Committee.⁷

Reagents

Acrinathrin (purity >99%) was supplied by Bayer. All other reagents were of analytical-reagent grade and came from Merck, Darmstadt, Germany, except the internal standard [⁸H₁₀]anthracene (Cromlab, Barcelona, Spain).

Stock solution: a solution of acrinathrin of 100 μ g ml⁻¹ in hexane was prepared, the working solutions being

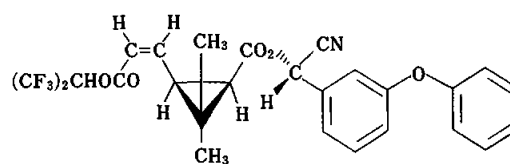


Fig. 1 Acrinathrin [(*S*)- α -cyano-3-phenoxybenzyl (*Z*)-(1*R*, 3*S*)-2,2-dimethyl-3-[2-(2,2,2-trifluoro-1-trifluoromethylethoxycarbonyl)vinyl] cyclopropanecarboxylate].

obtained by appropriate dilutions. Other pyrethroids were also used to check for possible interferences; the initial solutions were also of 100 μ g ml⁻¹ and were prepared with the product in question in hexane. All of them were stable for at least two weeks if stored in the dark at 4°C.

Internal standard solution: 3 μ g ml⁻¹ of [⁸H₁₀]anthracene in hexane (starting solution 100 μ g ml⁻¹) was stored also at 4°C.

GC-MS analysis

A 2 μ l aliquot of the extract was injected using the splitless mode with the split closed for 2 min. The GC-MS parameters are shown in Table 1. We chose 181 *m/z* (base peak) as target ion as well as 289, 208 *m/z* and 93 *m/z* as qualifiers in SIM analysis for acrinathrin and 187, 188 *m/z* for [⁸H₁₀]anthracene, respectively. The concentrations of the pesticide were calculated by the internal standard method.

Procedure

Sample treatment. Water samples were filtered through a cellulose acetate filter (Millipore HAWP 04700, pore size 0.45 μ m), collected in a glass bottle previously cleaned with HCl and stored at 4°C. The usual precautions were taken to avoid contamination.⁸

Determination of acrinathrin. 500 ml of water sample containing between 100 and 500 ng l⁻¹ of acrinathrin were transferred into a 500 ml separating funnel and then 0.5 ml of hexane containing 3 μ g ml⁻¹ of anthracene-*d*₁₀ were added.

The mixture was mechanically shaken for 2 min, after

† To whom correspondence should be addressed.

Table 1 GC-MS conditions

Gas chromatograph	
Total flow	100 ml min ⁻¹
Septum purge	3 ml min ⁻¹
Head column pressure	105 kPa
Purge-off time	2 min
Injector temperature	200°C
Injected volume	2 µl
Oven program	76°C (1 min), 30°C/min, 270°C (3 min)
Mass spectrometer	
Interface temperature	280°C
Electron multiplier voltage	between 1750 and 2100 V
Scan mode	SIM mode
<i>m/z</i> range	45–500
	Selected ion 93, 181, 208, 289

which the supernatant organic phase was brought up to the bottleneck of the separating funnel by the hydrostatic action of a communicating vase filled with deionized water by raising its level. Then the extract was collected at a Pasteur micropipette situated at the top of the above mentioned bottleneck, and was made ready to inject in the gas chromatograph.

Calibration graphs were constructed using solutions of acrinathrin at known concentrations.

Results and Discussion

We used micro liquid-liquid extraction (mLLE) selecting a 1000:1 ratio with hexane, the most adequate of 6 different solvents tried. Ionic strength was adjusted with NaCl or NaClO₄ and did not affect extraction efficiency, so salty waters might be monitored if wished. Figure 2 shows the chromatogram of acrinathrin spiked in water, together with pyrethroids and endosulfans currently employed in the agriculture practice.

The mass spectrum in scan mode is shown in Fig. 3. Notice that the molecular ion appear at 541 *m/z* and the base peak at 181 *m/z*.

Analytical parameters

The calibration graph for the samples treated according to the procedure described above, monitored using SIM mode, is linear for the concentration range 100 and 500 ng l⁻¹. To check the linearity of the calibration graph, the lack-of-fit test⁷ was applied for two replicates and three injections of each standard. Table 2 show the results for the intercepts (*a*), slopes (*b*), correlation coefficients (*R*²) and probability levels (*p*) deduced from the lack-of-fit test. The data yield a good linearity within the range 100 and 500 ng l⁻¹ as stated above.

In contrast with other analytical techniques, there is no agreement yet about how to get the detection limit (DL)⁹ and quantification limit (QL)¹⁰ from the blank standard deviation in gas chromatography. Moreover, IUPAC recommendations are seldom strictly used. We believe that our method for calculating DL and QL in pesticides in water¹¹ is more in line with the IUPAC recom-

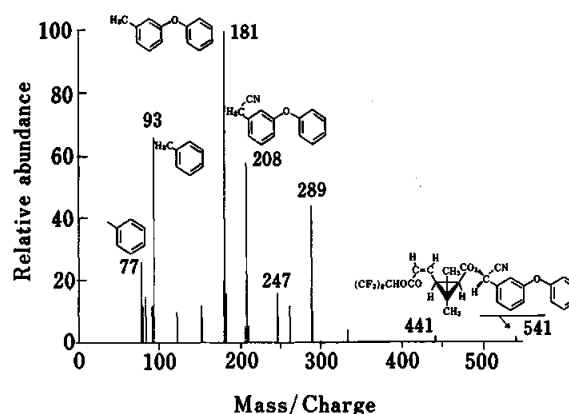


Fig. 2 Mass spectrum of [(*S*)- α -cyano-3-phenoxybenzyl (*Z*)-(*1R,3S*)-2,2-dimethyl-3-[2-(2,2,2-trifluoro-1-trifluoromethylethoxycarbonyl)vinyl]cyclopropanecarboxylate].

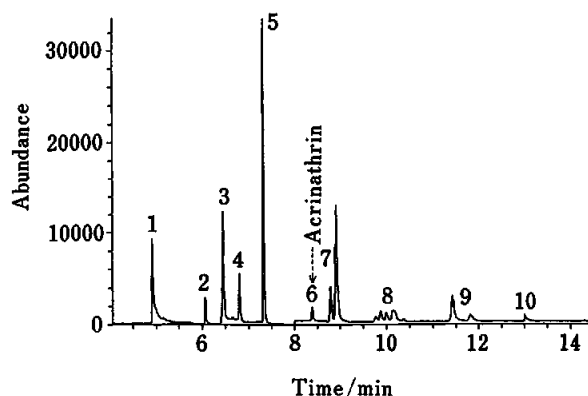


Fig. 3 Typical chromatogram of acrinathrin obtained in SIM mode, in presence of endosulfans and other selected pyrethroids using the proposed method: 1) Anthracene-*d*₁₀ (*t*_R=4.917); 2) α -Endosulfan (*t*_R=6.059); 3) β -Endosulfan (*t*_R=6.444); 4) Endosulfan-sulfate (*t*_R=6.800); 5) Bifenthrin (*t*_R=7.326); 6) Acrinathrin (*t*_R=8.391); 7) Permethrin (*t*_R=8.792, 8.918); 8) Cypermethrin (*t*_R=9.768, 9.876, 9.995, 10.134, 10.369); 9) Fenvalerate (*t*_R=11.430, 11.823); 10) Deltamethrin (*t*_R=13.010).

Table 2 Analytical parameters

Intercept (<i>a</i>)	0.0107
Slope (<i>b</i>)	0.0788
Correlation coefficient (<i>R</i> ²)	0.9998
Lack-of-fit test (<i>p</i> -value)	0.88
Linear dynamic range (ng l ⁻¹)	9–500
Linearity [1–RSD(<i>b</i>)] (%)	99.38
DL (ng l ⁻¹)	3
QL (ng l ⁻¹)	9
Precision (RSD) (%) [10% (9 ng l ⁻¹)–0.28% (500 ng l ⁻¹)]	

RSD (*b*), relative standard deviation of slope; DL, detection limit (ng l⁻¹); QL, quantification limit (ng l⁻¹).

Table 3 Numerical values of parameters SC, AC and YC

Parameter	SC	Addition C.		Youden C.	
		Ground water	Sea water	Ground water	Sea water
<i>n</i>	30	12	12	12	12
<i>a</i>	0.0107	4.0157	3.8167	0.1878	0.1628
<i>b</i>	0.0788	0.0776	0.0784	3.6933	3.7533
<i>S_{yx}</i>	0.1393	0.1147	0.2247	0.1476	0.0658
<i>t(b)</i>		1.1826 (<i>p</i> =24%)	0.3024 (<i>p</i> =76%)		

n, number of measurements; *a*, intercept; *b*, slope; *S_{yx}*, regression standard deviation; *t(b)*, statistic for slope; *p*, significance level for *t* test.

mendations. It relies in studying the blank standard deviation in an interval of time corresponding to the peak width in its base, extrapolated to zero concentration.

Here, DL and QL were estimated as in the above reference. Other analytical parameters summarized in Table 2 were established by applying the method proposed by Cuadros *et al.*¹²

Validation and applications of the method

We tried to find acrinathrin in ground water samples from Santa Maria farm, near Granada city and in seawater samples from Motril (Granada) itself. We did not find acrinathrin above our DL. Validation of the proposed method for water samples was carried out by using the standard addition method¹³ whereby three experiments are required to obtain the data set necessary to obtain the proposed statistical protocol. The same analytical procedure must be applied in each experiment to the 500 ml sample: a) standard calibration (SC) as described above; b) standard addition calibration (AC) obtained by standard additions of acrinathrin to sampled waters (0, 100, 200 and 300 ng l⁻¹); c) Youden calibration (YC).¹⁴ A calibration curve was made with the Youden method. Increasing amounts of sample volume (125, 250, 375 and 500 ml respectively) are checked three times for each of the above stated concentrations.

By applying linear regression analysis, the slope, the intercept, and the regression standard deviation for each of curves a, b and c, can be estimated for each sample and thus, the whole range of spiking concentrations can be estimated. The parameters obtained from the three methods: *i.e.* SC, AC and YC, are shown in Table 3. The student *t* test shows the similarity of the representative values of slopes of SC and AC and it can be concluded that the method is accurate. On the other hand the non-significative value of intercept in the YC reveals the absence of any matrix effect.

Finally the solubility in water of acrinathrin at 20°C was estimated by saturating three graduated flasks of 500 ml of distilled water with the insecticide. For that, we sonicated the mixture during 24 h. Then we filtered it twice through filter-paper of 0.45 µm and applied the extraction method. Solubility was found to be 11 ng ml⁻¹ at 20°C.

In conclusion, a simple, rapid, reproducible and

practical GC-MS method for the determination of residues of the pesticide acrinathrin in water samples (9 and 500 ng l⁻¹) is reported. Detection limit (3 ng l⁻¹) is about one order of magnitude below the actual European Community tolerance limits (100 ng l⁻¹). It was applied to natural waters samples from Granada (Spain) with good recovery rates.

This study was funded by the Comision Interministerial de Ciencia y Tecnologia (CICYT) Project AMB-94-0776 (Spain).

References

1. C. de Liñan, "Vademecum de Productos Fitosanitarios y Nutricionales", 94-95, ed. Embajadores, Madrid, 1995.
2. C. Tomlin, "The Pesticide Manual", 10^a ed. Crop Protection Publications, 1995.
3. A. R. Fernandez-Alba, A. Agüera, E. M. Almansa, S. Malato and J. Blanco, *Environ. Sci. Technol.* (in revision).
4. M. Sanchez-Alarcon, A. Valverde and A. Fernandez-Alba, *Book of Abstracts: 7th Symposium on Handling of Environmental and Biological Samples in Chromatography*. Lund, Sweden, 1995.
5. A. Fernández-Gutiérrez, J. L. Martínez-Vidal, F. J. Arrebola-Liébanas, A. González-Casado and J. L. Vilchez, *Fresenius' J. Anal. Chem.* (in revision).
6. Statgraphics version 6.0, Manugistics Inc. and Statistical Graphics Corporation, USA (1992).
7. Analytical Methods Committee, *Analyst* [London], **119**, 2363 (1994).
8. APHA-AWWA-WPCF, "Métodos Normalizados para el Análisis de Aguas Potables y Residuales", ed. Díaz de Santos S. A., Madrid, 1992.
9. IUPAC, "Nomenclature, Symbols, Units and Their Usage in Spectrochemical Analysis", *Pure Appl. Chem.*, **45**, 105 (1976).
10. Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry, *Anal. Chem.*, **52**, 2242 (1980).
11. A. González-Casado, L. Cuadros-Rodríguez, E. J. Alonso and J. L. Vilchez, *J. Chromatogr. A*, **726**, 133 (1995).
12. L. Cuadros-Rodríguez, A. M. García-Campaña, C. Jiménez-Linares and M. Román-Ceba, *Anal. Lett.*, **26**, 1243 (1993).
13. L. Cuadros-Rodríguez, A. M. García-Campaña, F. Alés-Barrero, C. Jiménez-Linares and M. Román-Ceba, *J. Assoc. Off. Anal. Chem.*, **78**, 471 (1995).
14. M. J. Cardone, *J. Assoc. Off. Anal. Chem.*, **66**, 1283 (1983).

(Received April 21, 1997)

(Accepted July 9, 1997)