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Comparison of various sample handling and analytical procedures for the monitoring of pesticides and metabolites in ground waters

A.R. Fernandez-Alba[a,*], A. Agüera[a], M. Contreras[a], G. Peñuela[b], I. Ferrer[b], D. Barceló[b]

[a]*Pesticide Residue Research Group, University of Almería, 04071 Almería, Spain*
[b]*Department of Environmental Chemistry, CID-CSIC, 08034 Barcelona, Spain*

Abstract

Various sample handling techniques such as liquid–liquid extraction off-line and on-line, solid-phase extraction followed by either gas chromatography (GC) with electron-capture, flame photometric or mass spectrometric detection, or liquid chromatography (LC) with diode array detection were applied in the determination of a selected group of insecticides and fungicides in ground water samples at sub-μg/l levels. An evaluation of the advantages and drawbacks in the application of the proposed methodologies for water monitoring studies is discussed. For the selected group of pesticides studied, off-line C_{18} or polymeric cartridges followed by GC–MS using an ion trap analyzer have been revealed as the more powerful technique. But very polar compounds such as methamidophos or acephate have not been recovered with this procedure. On the contrary, on-line C_{18} LC–DAD offered a few drawbacks for the trace determination of a large group of pesticides as a consequence of many important interferences in the chromatographic traces. Other techniques evaluated were LC–MS and GC–MS using a quadrupole analyzer, which offered complementary information and were useful for a limited range of analytes. An interlaboratory study was performed using all the methodologies evaluated in this work and the results obtained showed a good agreement between all the applied techniques. The various methodologies were for a ground water pilot survey study in Almeria (Spain). Endosulfan was the most ubiquitous pesticide detected in this area.

Keywords: Sample handling; Water analysis; Environmental analysis; Pesticides

1. Introduction

Monitoring of pesticides groundwater has been a topic of increasing importance over the last few years. In some important agricultural areas in the USA [1,2] and Europe [3,4], where pesticides have caused contamination in the hydrological system or its vulnerability is high, and where ground water is the primary source of drinking water, several water monitoring programmes have been developed to assess and evaluate pesticide concentration levels. The attention of these programmes has been focused on the most popular classes of pesticides, in terms of amount of production and appliance, i.e., carbamates, phenylureas, triazines and phenoxiacid derivatives. The number of published papers concerning the development and application of multiresidue environmental analysis on pesticides has increased enormously and has resulted in an extensive bibliography, mainly focused on herbicides [1,2,5]. But a noticeable fact is that until now, there is a lack of information about the presence of insectides and fungicides and their metabolites in natural water as their analytical characteristics are not well-studied compared to herbicides.

In Spain and in a broader sense in many Mediter-

*Corresponding author.

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ranean areas, due to the special characteristics of crop production and winter climate, pesticides used and so the target compounds in ground waters are insecticides and fungicides, i.e., organophosphorus pesticides (OPs) and organochlorine pesticides (OCs) [6]. For this reason there is a special interest to develop and to evaluate analytical methods for the analysis of a wide variety of fungicides and insecticides in water samples.

A few points have been carried out to evaluate the protocol of analysis.

1.1. Sample preparation

One of the main goals in pesticide water analysis is to reach determination limits of about 0.01 μg/l which cover all the requirements of the European Union (EU) Drinking Water Directives as well as the US National Pesticide Survey. Common and well-established multiresidue methods for ground water sample pretreatment are based on the use of either a liquid–liquid extraction (LLE) [6,7] or solid-phase extraction (SPE) [7–14] previous to chromatographic determination. Lately, in SPE the use of mini-extraction columns or extraction discs have gained importance, because of the wide variety of SPE materials developed recently, designed for polar as well as for semipolar compounds. Furthermore, this water sample preparation avoids the use of large amounts of organic wastes and allows an easy automation [15]. Techniques such as supercritical fluid extraction (SFE) or microextraction have also been applied, but to a lesser extent.

1.2. Chromatographic analysis

The sample preparation step, either off-line or on-line, is followed by gas chromatography (GC) and/or liquid chromatography (LC) separation. These techniques can offer several complementary advantages and the criterion for selecting one of them or both is based on the behaviour of the analyte in the GC or LC column [16]. The final determination can be achieved by coupling a series of selective detectors (electron-capture, nitrogen–phosphorus, UV, fluorescence) [10,11,17,18] or more universal detection systems like mass spectrometry (MS) [8–13]. Other developments are based on more complex coupling systems such as SPE–HPLC–GC, SPE–SFE–GC, etc., but we cannot consider these systems easily available for an average routine control laboratory. Undoubtedly MS is the best choice if we take into account the great number of compounds and metabolites to cover in each analysis as well as the high requirements in time and money to perform these analyses.

Normally the use of GC–MS is restricted to a confirmation technique [2] as a consequence of the low limit of detection (LOD) achieved in general with quadrupole analyzers (GC–Q-MS) operating in full scan mode. The use of ion trap analyzers (GC–IT-MS) can overcome this deficiency, making this technique a powerful primary screening tool rather than a secondary confirmation system [19,20]. In ion trap technology, switching from full scan electron impact ionization mode (EI) to chemical ionization (CI) can be achieved in a very easy way providing enough information for the identification and quantitation of pesticides and metabolites rapidly [21]. However, it is well-known that the produced spectra usually indicated a large percentage of EI spectra fragments overlapping the CI spectrum frequently [19,20].

Hyphenated LC–MS techniques allow the determination of a greater variety of polar compounds compared to GC–MS and can be extended to non-amenable ''GC pesticides''. Additional features of LC–MS are that typical GC pesticides can usually be analyzed by this technique and that be more easily coupled to SPE [14]. Nowadays atmospheric pressure chemical ionization (APCI) or electrospray (ESI) are the best options to provide an adequate sensitivity and structural information [22,23].

1.3. Applications

A very important item in the development of new pesticide analytical methods is the application to real samples. Even today a great part of new developed methods have only consisted of laboratory made applications. Difficulties related with the presence of metabolites which were produced environmentally to the more polar compounds than parent compounds [13] and the great variety of possible matrix effects can only be evaluated correctly by the analysis of a considerable amount of real samples.

The aim of this work is (i) to present a comparative evaluation of different sample handling by LLE and SPE and the analytical procedures GC–electron-capture detection (ECD), –flame photometric detection (FPD), GC–IT–MS, GC–Q-MS, LC–UV and LC–ESP-MS in their application to the analysis of insecticides and fungicides in ground waters of Almeria (Spain), which is one of the most important areas in crop production of Europe. (ii) The application of the various analytical methodologies to the evaluation of the behaviour of these compounds to leach the ground water of Almería during a pilot monitoring study.

2. Experimental

2.1. Materials and solvents

Pesticide-grade dichloromethane, ethyl acetate, cyclohexane, acetic acid and anhydrous sodium sulphate were supplied by Panreac (Barcelona, Spain), gradient HPLC grade acetonitrile, methanol and water were purchased from Merck (Darmstadt, Germany). Pesticide standards were obtained from Promochem (Wesel, Germany) and Riedel-de Haën (Seelze, Germany). The selected target pesticides were divided in two groups: insecticides/acaricides and fungicides. The first group included: acephate, acrinathrin, amitraz, aziphos methyl, bromopropylate, buprofezin, carbophenothion, chlorfenvinphos, chlorpyrifos ethyl, chlorpyrifos methyl, cypermethrin, deltamethrin, dichlorvos, dicofol, dimethoate, endosulfanI, endosulfan II, endosulfan sulphate, etrimfos, fenamiphos, fenitrothion, fenpropathrin, fenthion, lindane, malathion, mecarbam, methamidophos, mehtidation, methiocarb, mevinphos, monocrotophos, naled, omethoate, pharathion ethyl, parathion methyl, phosalone, pirimiphos mehtyl, prometryne, pyrazophos, pyridaphenthion, quinalphos, tebuconazole, tetrachlorvinphos, tetradifon, triazophos. The group of fungicides included: captafol, captan, chlorothalonil, chlozolinate, dichlofluanid, dicloran, folpet, iprodione, metalazyl, procymidone, vinclozoline.

ENVI-18DISK 47-mm and 6-ml, 500 mg Isolute ENV cartridges SPE materials were obtained from Suprelco (Bellefonte, PA, USA) and IST (Mid Glamorgan, UK), respectively.

2.2. Apparatus

2.2.1. Prospekt–LC–diode array detection (DAD)

LC–DAD analyses were performed with a Waters 600-MS solvent delivery unit with a 20 μl injection loop and a Waters 996 photodiode array detector (Waters–Millipore, MA, USA). The analytical column used was a 25 cm×4.6 mm I.D. packed with 5 μm octylsilica gel (Shandon).

Trace enrichment was performed on an automated SPE system (Prospekt). It consisted of a cartridge exchange module, a solvent delivery unit (SDU) (Spark Holland) and a low-pressure six-port valve, which was connected to the gradient pumps. Water samples were preconcentrated on 10 mm×2 mm I.D. disposable pre-columns of Prospekt (Spark, Emmen, Netherlands) prepacked with 40 μm C_{18} (Baker, Deventer, Netherlands). The gradient elution was performed as follows: from 35% A (acetonitrile) and 65% B (HPLC water) to 100% A and 0% B in 40 min at a flow-rate of 1 ml/min. Quantification was carried out with UV detection at 220 nm.

2.2.2. LC–APCI-MS

LC–APCI-MS with positive mode of operation was used for the determination of malathion. The eluent was delivered by a gradient system from Waters 616 pumps coupled to a Model Waters 600S controller (Waters, Milford, MA, USA). A VG Platform from Fisons Instruments (Manchester, UK) equipped with an APCI interface was used. The Platform APCI interface consists of a heated nebulizer probe and the standard atmospheric pressure source configured with a corona discharge needle. The LC eluents enter the probe at 1 ml/min where they are pneumatically converted into an aerosol and rapidly heated into the vapor/gas phase at the probe tip. The different operating parameters included a drying gas flow-rate of 250–300 l/h and a nebulizing gas flow-rate of 10 l/h. The cone voltage were set at 20 V and the corona voltage at 3.5 kV. The ion source was set at 180°C and the probe temperature was of 450°C. The gradient elution was performed in the same way as in LC–DAD with the only difference that acetic acid was added in the mobile phase

at 0.5%, in order to enhance the ionization of the analytes.

2.2.3. GC systems

A GC–IT-MS Saturn 3 system (Varian, Harbor City, CA, USA), consists of a Varian 3400 gas chromatograph, a Model 1093 septum-programmable injector (SPI) and a 8200 autosampler. Data acquisition and processing and instrument control were performed by Saturn GC–IT-MS workstation version 5.2 software loaded into a 486 DX, 66 MHz computer. A DB-5MS (J&W Scientific, Folsom, CA, USA) capillary column, 30 m×0.25 mm I.D., 0.25 μm film thickness was connected to the system. Operating GC conditions were: 1.0 μl injection volume; solvent plug 0.1 μl; 0.1 s needle hold time in port before injection; 60°C injection port for 0.5 s followed by ramping to 280°C at 150°C/min; 9 p.s.i (1 p.s.i.=6894.76 Pa). He column head pressure; oven temperature programme: 1.0 min at 60°C, 25°C/min to 180°C, 5°C/min to 280°C (4 min). Transfer line temperature, 280°C; detector manifold temperature, 230°C. IT–MS-EI mode operating conditions were as follows: 35 μA filament current; 1350-V electron multiplier tube and automatic gain control at 40.000. The mass spectra were monitored from 50 to 550 *m/z* and data acquisition was obtained from 4 to 25 min of the chromatogram.

For IT-MS-CI mode, the same conditions already described for EI mode were used. Acetonitrile was selected as reagent gas. The CI parameters were optimized as follows: maximum ionization time 2.5 ms, maximum reaction time 50 ms, ionization storage level 12.5 *m/z*, reagent ion eject amplitude 8 V and reaction storage level *m/z* 20.

GC–Q-MS Fisons MD 800 Micromass Instruments, Manchester, UK, consists of a Fisons 8000 gas chromatograph, a mass spectrometer (Fisons) and a 8200 autosampler.

2.3. Sample handling

2.3.1. LC

Stock standard solutions of 500 μg/l were prepared by weighing the solutes and dissolving them in methanol. A stock solution of 1 μg/l was used to spike ground water at the μg/l level for the preconcentration through the C_{18} cartridge and further construction of the calibration graphs.

A 150-ml volume of ground water sample was preconcentrated through the C_{18} cartridges at a flow-rate of 3 ml/min. Conditioning of the cartridges is described elsewhere.

2.3.2. GC

Stock standard solutions of 500 μg/l were prepared by weighing the solutes and dissolving in cyclohexane–ethyl acetate (9:1). A stock solution of 0.5 μg/l was used to spike ground water at the μg/l level for the preconcentration through the C_{18} disk or Isolute ENV cartridge and further construction of the calibration graphs.

A 800-ml sample of ground water was preconcentrated through the C_{18} disks or Isolute ENV cartridges at flow-rates of 50 and 5 ml/min, respectively. Conditioning of the disks cartridges is described elsewhere.

For the GC–IT-MS analysis, extraction and preconcentration of the samples was carried out. A dichloromethane LLE was applied in the following way: a 800 ml sample of water with 1.0 g of sodium chloride was extracted with 75×50 ml of dichloromethane. The combined organic extracts were filtered throughout a thin layer of anhydrous sodium sulfate and concentrated by a rotary evaporator until 2–3 ml. This extract so obtained was again evaporated to dryness with gentle N_2 stream and redissolved with sonication in 1 ml of cyclohexane–ethyl acetate (9:1) before injection.

Recovery studies were performed at the 0.5 and 5.0 μg/ml fortification levels with the extraction method proposed. With this aim, 1-l volumes of distilled water were spiked with aliquots of the stock standard solutions described above, and extracted at least three times at each fortification level.

The analyses were carried out between one to seven days after collecting, keeping the water samples dark and below 7°C. The delivery of water samples to Barcelona was done by courier in liquid state, adsorbed in C_{18} disks and polymeric cartridges, when duplicate water samples were analyzed in Almería and Barcelona for interlaboratory or monitoring studies.

3. Results and discussion

3.1. General considerations

Using information of several associations of farmers, exporters and local councils, we selected 58 pesticides as the most common compounds used in this area and possible leachers to ground water. These target compounds are 56 insectides and fungicides mainly included in the groups of OP and OC pesticides.

In a first stage, as a consequence of the need for a large scale screening of the list of pesticides mentioned, only LC–DAD and GC–ECD, –FPD and GC–IT-MS were applied to develop analytical methodologies to cover all these pesticides. The sample handling techniques used were automated SPE on-line by a Prospekt system with LC–DAD and LLE and SPE off-line either using disks and cartridges in the case of GC–ECD, –FPD and –IT-MS detectors. The analysis time that we considered optimum for a routine pesticide control was around 30–40 min. Analytical parameters for GC–IT-MS and LC–DAD are shown in Tables 1 and 2. Very similar results as for GC–IT-MS were obtained for GC–ECD and –FPD.

In a second stage, water samples for six selected wells were analyzed following the mentioned analytical methodologies over a six-month period in order to identify insecticides/fungicides. From these wells two polluted sites were located and selected as sampling sites for the pilot monitoring study. In addition, an interlaboratory study on ground water spiked with selected pesticides by using all the techniques was also carried out.

3.2. Large scale screening

3.2.1. Off-line LLE–SPE followed by GC–IT-MS in the EI mode

Table 1 indicates the identification ions and limits of detection of the studied pesticides using GC–IT-MS. GC–IT-MS in the EI mode was able to cover all screening requirements with an analysis time of 22 min. Several reasons make sample handling critical in the application of this technique.

From a practical point of view, classical dichloromethane LLE presents a matrix effect which can make their application tedious because of high requirements in maintenance of the ion trap system. Fig. 1 shows the chromatograms of ground water extracts after dichloromethane LLE and SPE using disks and cartridges. It is clear that the routine use of LLE has a very low selectivity and is quite troublesome.

On the other hand, identification scores are highly dependent on the used sample handling. Thereby, in the analyses of the pesticides at sub-μg/l levels, the fit values or concordance level between a spectrum obtained in the analysis and the same spectrum library are usually too low (<800, when 1000 represents 100% of concordance level) for LLE and very adequate for SPE by using C_{18} disks or polymeric cartridges. Fig. 2 presents the analysis of a real water sample at 0.15 μg/l of procymidone by using dichloromethane LLE and C_{18} disks, differences in fit values are observed, obtaining less than 300 for LLE and close to 1000 for SPE.

By preconcentrating 800 ml of ground water the recovery values were higher than 80% in most cases using C_{18} or polymeric cartridges. In the case of dimethoate only polymeric cartridges could be used. Very polar pesticides like acephate, methamidophos and omethoate were not recovered at all with the applied sample handling procedures as a consequence of their high water solubility. The LODs achieved were practically in all cases below the limits set by the EU Directive and in many cases several times below.

Using LLE and SPE followed by GC coupled with ECD or FPD yielded very similar results to GC–IT-MS, but they were considered to be time and money-consuming as a consequence of the needs to make several separate determinations for each group of compounds. Afterwards confirmation was always necessary by performing extra analyses especially when ECD is used.

3.2.2. On-line SPE–LC–DAD

The diode array detector for liquid chromatography was selected because of advantages such as the ability to detect oxo, sulfoxide and phenolic metabolites from different OPs (see Table 2). However, the disadvantages strongly outweighed the advantages for the target pesticides under study due to: (i) the screening had to be reduced to 17 compounds as a

Table 1
Identification ions (quantification ions in bold), detection limits and recovery values of all target pesticides by GC–IT-MS

	M_r	Identification ions			LOD (μg/l)	R.S.D. (%)
Acephate	183	94	**136**	143	0.15	0.12
Acrinathrin	541	**181**	289	441	0.06	0.051
Amitraz	293	132	147	**162**	0.10	0.08
Azinphos methyl	317	104	**132**	160	0.04	0.03
Bromopropylate	428	157	185	**341**	0.02	0.016
Buprofezin	305	105	**175**	249	0.04	0.03
Captafol	349	**79**	150	242	0.03	0.02
Captan	299	**79**	107	149	0.06	0.05
Carbophenothion	342	**157**	199	342	0.04	0.03
Chlorfenvinphos	358	**267**	295	323	0.04	0.03
Chlorothalonil	264	168	231	**266**	0.01	0.008
Chlorpyrifos ethyl	349	**197**	258	314	0.03	0.02
Chlorpyrifos methyl	321	109	125	**286**	0.01	0.01
Chlozolinate	331	188	**259**	331	0.03	0.02
Cypermethrin	415	127	163	**181**	0.10	0.08
Deltamethrin	505	**181**	209	253	0.13	0.1
Dichlofulanid	332	123	167	**224**	0.01	0.01
Dichloran	206	124	**176**	206	0.03	0.02
Dichlorvos	220	**109**	145	185	0.01	0.01
Dicofol	368	111	**139**	251	0.01	0.008
Dimethoate	229	**87**	93	125	0.06	0.05
Endosulfan I	404	195	241	267	0.02	0.015
Endosulfan II	404	195	**241**	267	0.02	0.018
Endosulfan sulphate	420	229	272	**387**	0.02	0.013
Etrimfos	292	153	181	**292**	0.02	0.019
Fenamiphos	303	154	260	**303**	0.30	0.24
Fenitrothion	277	125	**260**	277	0.03	0.02
Fenpropathrine	349	97	**181**	265	0.05	0.036
Fenthion	278	125	169	**278**	0.01	0.01
Folpet	295	104	130	**260**	0.03	0.025
Iprodione	329	187	245	**314**	0.04	0.034
Lindane	288	111	**183**	219	0.01	0.01
Malathion	330	93	127	**173**	0.03	0.02
Mecarbam	329	97	**131**	159	0.03	0.02
Metalaxyl	279	160	192	**206**	0.01	0.01
Methamidophos	141	**94**	126	141	0.07	0.058
Methidathion	302	85	93	**145**	0.03	0.02
Methiocarb	225	109	**153**	168	0.03	0.023
Mevinphos	224	**127**	164	192	0.05	0.04
Monocrotophos	223	109	**127**	192	0.05	0.04
Naled	380	**109**	145	185	0.11	0.09
Omethoate	213	110	141	**156**	0.05	0.04
Parathion ethyl	291	109	139	**291**	0.03	0.02
Parathion methyl	263	109	125	**263**	0.03	0.02
Phosalone	367	121	**182**	367	0.04	0.03
Pirimiphos methyl	305	180	276	**290**	0.01	0.01
Procymidone	283	96	255	**283**	0.01	0.01
Promethryne	241	184	226	**241**	0.03	0.02
Pyrazophos	373	**221**	232	265	0.05	0.038
Pyridaphenthion	340	188	199	**340**	0.09	0.069
Quinalphos	298	**146**	157	298	0.03	0.02
Tebuconazole	307	125	163	**250**	0.04	0.03
Tetrachlorvinphos	366	109	240	**329**	0.01	0.01
Tetradifon	354	**159**	229	356	0.05	0.04
Triazophos	313	162	172	**257**	0.05	0.04
Vinclozoline	285	178	198	**212**	0.01	0.01

Table 2
Detection limits (μg/l) and recovery values (n=5) of a group of selected insecticides and fungicides by SPE–LC–DAD

Pesticide	LOD (μg/l)	Recovery (%)
Azinphos methyl	0.06	98
Chlorfenvinphos	0.09	100
Chlorpyriphos ethyl	0.02	114
Chlorpyriphos methyl	0.02	90
Dichlorvos	0.10	106
Fenitrothion	0.20	99
Fenthion	0.07	101
Malathion	0.09	101
Methiocarb	0.07	95
Mevinphos	0.10	106
Parathion ethyl	0.50	100
Parathion methyl	0.03	98
Tetrachlorfenvinphos	0.04	84
Vinclozoline	0.04	98
Captafol	0.10	79
Captan	0.10	87
Chlorothalonil	0.06	90
Dichlofuanid	0.01	95
Folpet	0.02	78
Procymidone	0.02	98

consequence of important coelutions with matrix or other pesticides and time analysis requirements. (ii) Secondly, very important pesticides in this area, such as endosulfan or dimethoate, were not detected at all as a consequence of the absence of chromophores in the molecule. And (iii) finally the LOD achieved by using C_{18} 40-μm cartridges were too high for our purposes since the amount of each pesticide detected is usually lower than 0.1 μg/l.

3.2.3. Analysis of real samples

Water samples from seven selected wells were analyzed following the proposed methods during six months in order to identify insecticides/fungicides for further monitoring studies and to find two polluted sites to select them as sampling sites. The procedures mentioned were applied to the ground water samples.

By using SPE–LC–DAD only one positive finding of Malathion was detected along this time period. By using SPE combined with GC–ECD, –FPD and –IT-MS abundant positive findings of endosulfan I, II, sulphate, procymidone, vinclozolin and chlorothalonil were found.

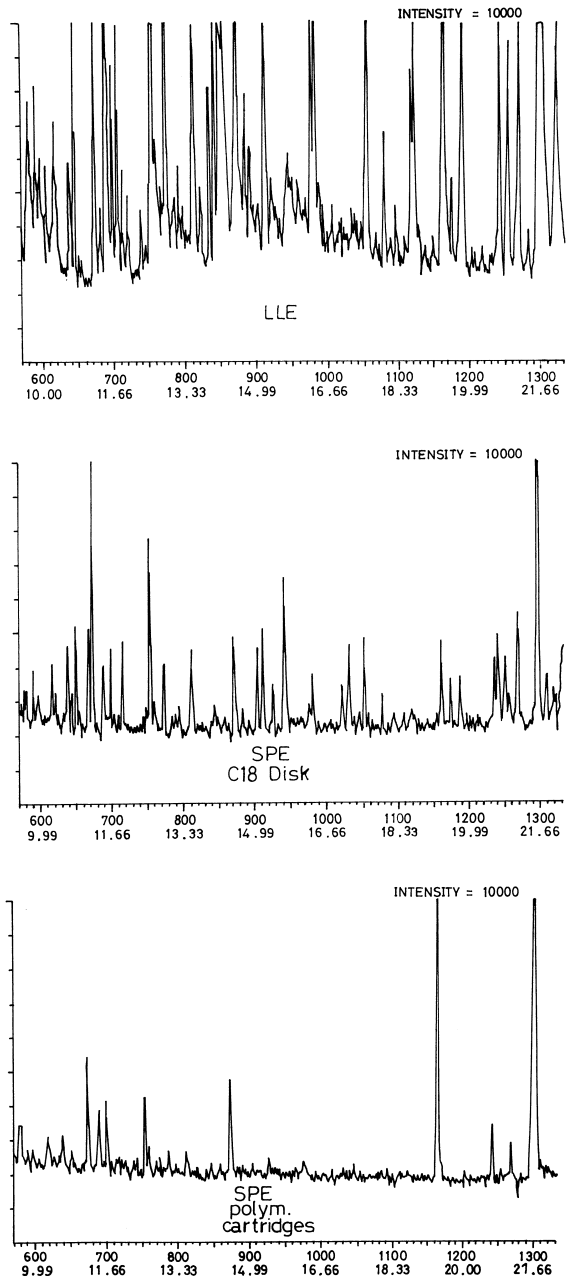
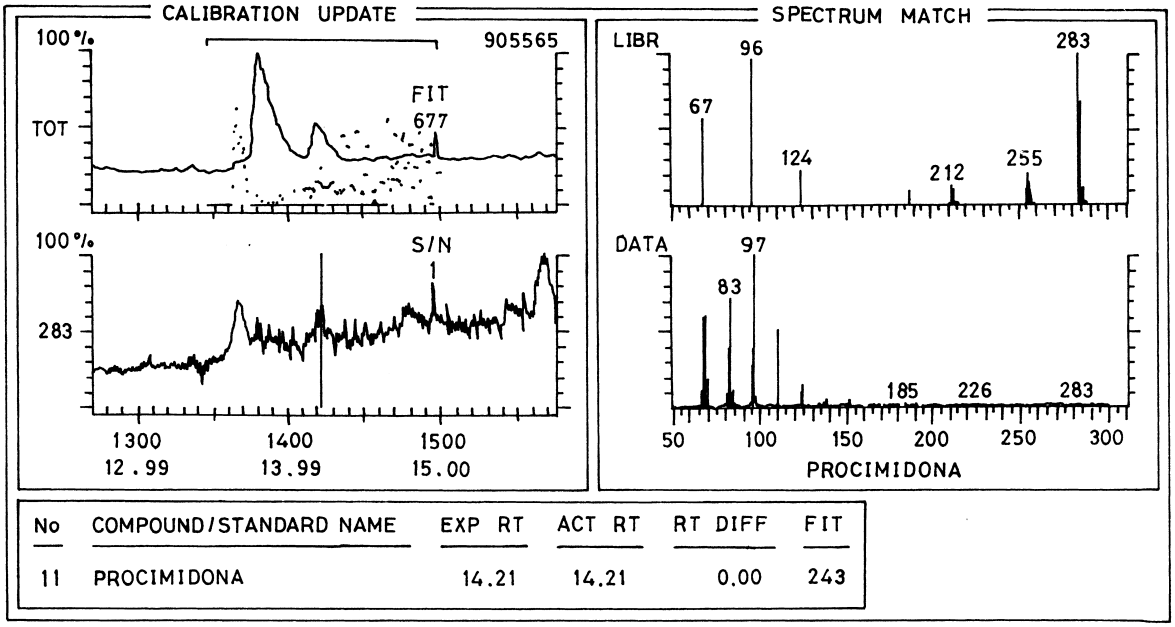


Fig. 1. Chromatograms of water samples obtained by GC–IT-MS in EI-mode after LLE, SPE using C_{18} disks and SPE using polymetric cartridges. x-Axis: scan No. (top) and retention time in min: s (bottom).



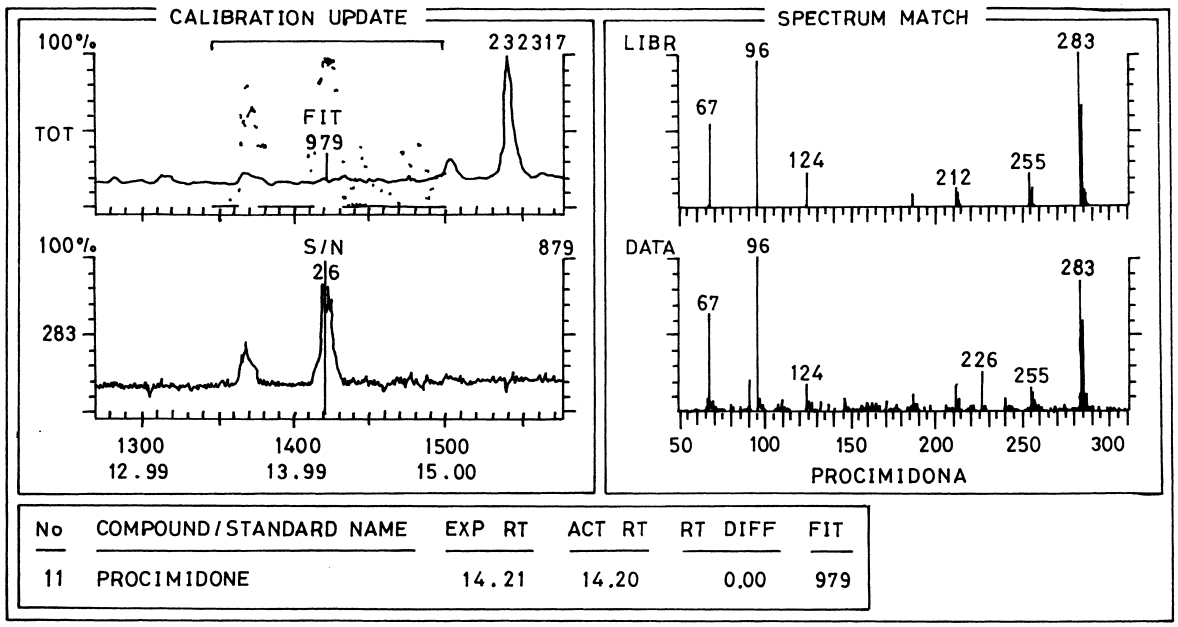


Fig. 2. Comparison of library mass spectra and obtained spectra by GC–IT-MS using (a) LLE and (b) C_{18} disks in the analysis of 0.15 μg/l of procymidone. *x*-Axis as in Fig. 1. Exp=Experimental; RT=retention time; ACT=actual; DIFF=difference.

3.3. GC–IT-MS in the PI mode

GC–IT-MS in chemical ionization PI with acetonitrile (AcN) as reagent gas was applied in order to study the improvement of selectivity and sensitivity of the analyses.

For some compounds protonated molecule ion was observed as base peak. Thereby in procymidone the M+1 ion (protonated molecule) was clearly the base peak (Fig. 3), and fragmentation is clearly lower with respect to EI. This fact obviously increased the sensitivity as a consequence of a better signal-to-noise ratio and a lower background as compared to EI (Fig. 3). But as reported in Ref. [24] the full scan CI spectra can produce hybrid EI and CI nature fragments under automatic reagent control (ARC). The contribution of typical EI fragments may be concentration dependant. These different contributions resulted in an adequate range for identification and quantification purposes in all cases studied except for malathion where the EI fragments contribution showed an unacceptable concentration dependence. Other pesticides such as cholorothalonil, lindane or endosulfan sulfate practically do not react with the reagent gas, so they are of no interest.

In Table 3, a comparative evaluation of the selected target pesticides between EI and CI modes is presented. An important increase of the LOD in the cases of dimethoate, procymidone, tetradifon and vinclozolin is noted when CI is used.

3.4. Interlaboratory study

An interlaboratory study on spiked ground water samples was carried out to compare the accuracy of the different techniques over the selected 12 pesticides. The results obtained are the average of three independent determinations by application of dichloromethane LLE and GC–ECD/FPD, off-line C_{18} disks and GC–IT-MS in EI and CI mode, off-line polymeric cartridges and GC–IT-MS in EI mode, on-line C_{18} cartridges and LC–DAD, off-line C_{18} disks and GC–Q-MS and on-line C_{18} cartridges and LC–APCI-MS. The results obtained are shown in Table 4. It is noted that all pesticides were covered when GC–IT-MS is applied and polymeric cartridges are used in the sample handling step. Other sample handling approaches like LLE or C_{18} disks do not allow an adequate recovery of dimethoate. In the case of LC-DAD, only four compounds were adequately identified as a consequence of matrix and pesticide coelution. GC–Q-MS in selected ion moni-

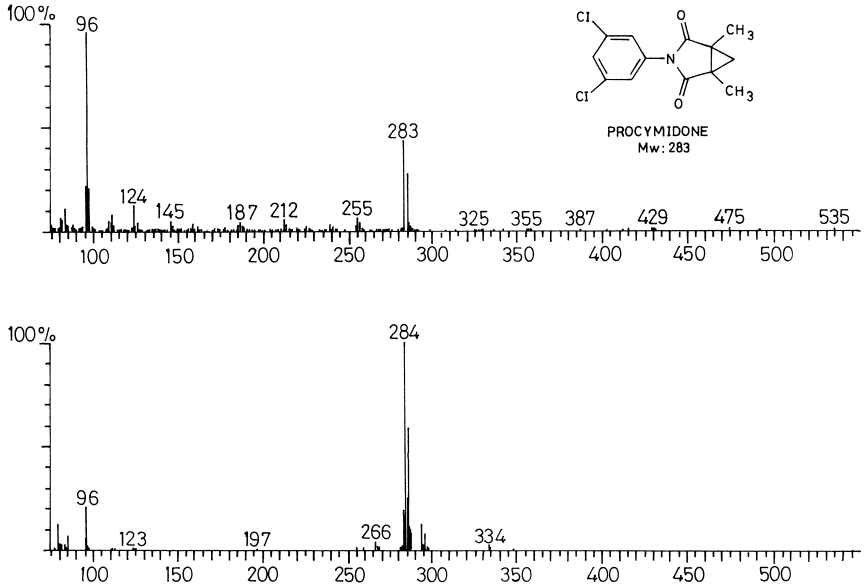


Fig. 3. Comparison of mass spectra obtained by GC–IT-MS in (a) EI mode and (b) CI mode using ACN in the analysis of 0.2 μg/l of procymidone. *x*-Axis: *m*/*z*; *y*-axis: abundance.

Table 3
Comparative evaluation of quantification ions, detection limits (μg/l) and reproducibility of the selected target pesticides between GC–IT-MS in the EI and CI modes

	EI				CI		
	M_r	QI	LOD	R.S.D. (%)	QI	LOD	R.S.D. (%)
Bromopropilate	428	341	0.02	5	411	0.01	12
Chlorotathalonil	264	266	0.01	7	266	–	–
Dichlofuanid	332	224	0.01	10	224	0.01	11
Dimethoate	229	87	0.06	9	230	0.01	9
Endosulfan I	404	241	0.02	5	406	0.03	12
Endosulfan II	404	195	0.02	5	406	0.03	9
Endosulfan sulphate	420	387	0.02	7	389	–	–
Lindane	288	183	0.01	9	219	–	–
Malathion	330	173	0.03	11	285	–	–
Procymidone	283	283	0.01	8	284	0.005	9
Tetradifon	354	159	0.05	9	355	0.01	12
Vinclozoline	285	212	0.01	6	286	0.005	8

toring (SIM) mode was only used for endosulfan and LC–APCI-MS only for malathion. All determinations by the different techniques applied coincided well and the relative standard deviations (R.S.D.s) were lower than 30% for all pesticides studied. The typical overestimation that can be expected and commented in the bibliography [24] by using GC–IT-MS in EI mode is clearly avoided by the use of SPE and a slow tendency to underestimation is noted. GC–Q-MS in the SIM mode yielded closer values to the spiking level with respect to GC–IT-MS. LC–APCI-MS has demonstrated its reliability for on-line analysis of ground water at sub-μg/l levels for instance in the determination of malathion, as can be seen in Fig. 4.

3.5. Pilot survey

All these techniques except LC–DAD and GC–ECD and –FPD were applied to a pilot monitoring

Table 4
Results and relative standard deviation (in parentheses) of interlaboratory studies in the analysis of spiked water samples with the selected target pesticides by using different analytical procedures

Pesticide	Level of fortification	GC–ECD/FPD[a]	GC–IT-MS, EI/CI[b]	GC–IT-MS[c] EI	LC–DAD	GC–Q-MS/LC–MS
Bromoprpylate	0.170	0.161 (14)	0.111 (10)/0.13 (16)	0.125 (9)	–	–
Chlorothalonil	0.180	0.138 (19)	0.188 (21)	0.130 (22)	0.226 (10)	–
Dichlofuanid	0.169	0.148 (11)	0.149 (10)/0.126 (12)	0.118 (10)	0.168 (7)	–
Dimethoate	0.194	0.027 (10)	**	0.179 (7)	–	–
Endosulfan I	0.191	0.134 (8)	0.164 (15)/0.140 (21)	0.178 (12)	–	0.217 (15)
Endosulfan II	0.174	0.134 (6)	0.159 (13)/0.140 (18)	0.152 (19)	–	0.165 (9)
Endo. sulphate	0.196	0.164 (14)	0.155 (14)	0.161 (8)	–	0.197 (8)
Lindane	0.186	0.109 (11)	0.142 (18)	0.149 (15)	–	–
Malathion	0.177	0.116 (5)	0.144 (16)	0.179 (10)	*	0.180 (21)
Procymidone	0.180	0.231 (7)	0.214 (8)/0.200 (8)	0.166 (6)	*	–
Tetradifon	0.174	0.156 (16)	0.148 (12)	0.145 (18)	0.198 (5)	–
Vinclozoline	0.196	0.186 (9)	0.173 (6)/0.16 (7)	0.158 (9)	0.232 (8)	–

* Coelution.
** Not detected.
[a] LLE extraction with DCM.
[b] Extraction with C_{18} disks.
[c] Extraction with polymeric cartridges.

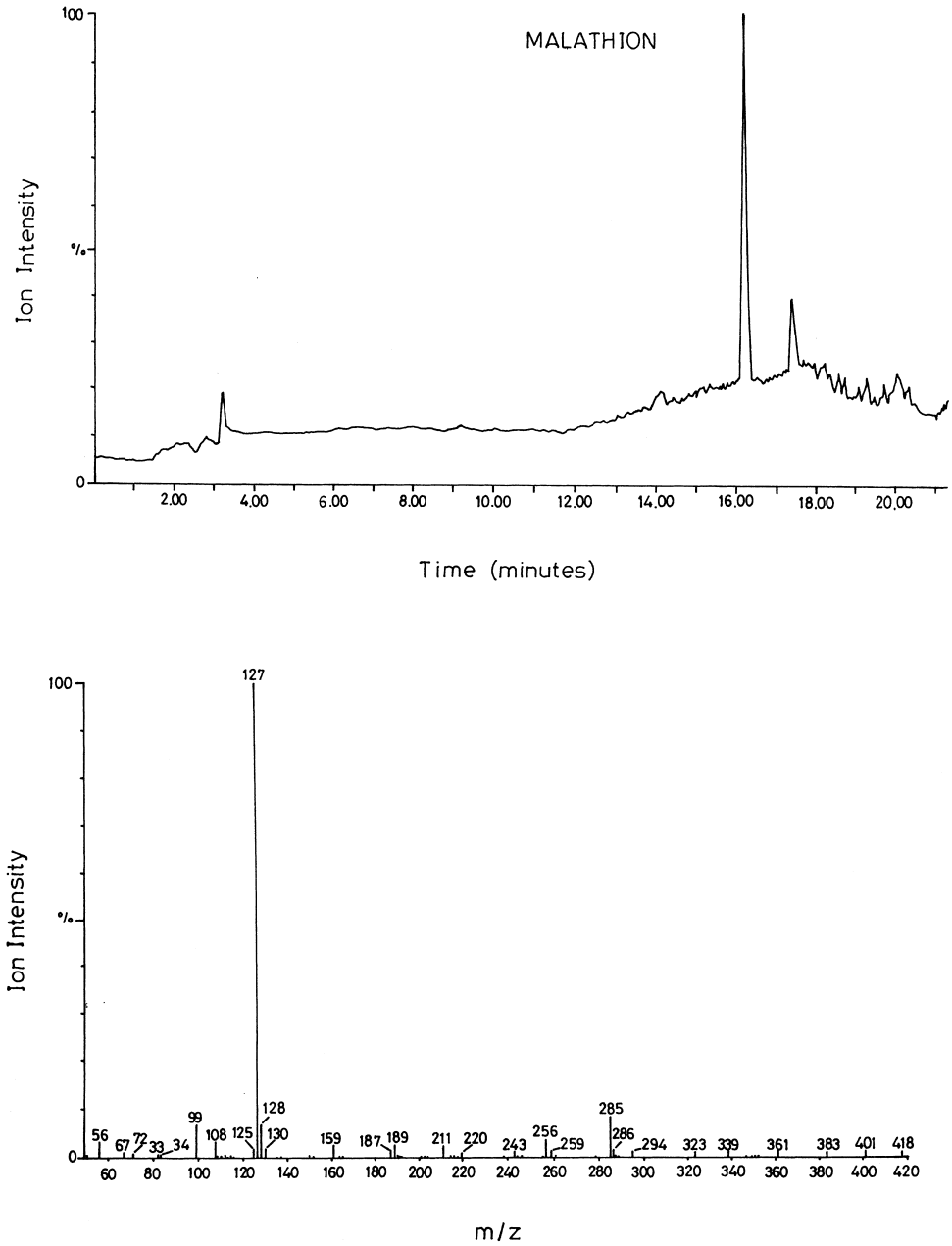


Fig. 4. Analysis of ground water containing malathion 0.2 μg/l: (a) chromatogram, (b) mass spectrum.

study over the 12 target pesticides in two selected sampling wells (D1 and CN6) where pesticide contamination was detected. The selected wells were 50 and 110 m in depth. Sampling was carried out monthly over a year (1996). The results were calculated as means of the values obtained by the different techniques applied. The total pesticide findings were 105. When looking at the seasonal variation of insecticide/fungicide concentration, it can be noted that two peaks occurred, one in

February/March and the other in October/November. Different pesticides were found during the whole year in a range from 0.01–0.35 μg/l. The pesticides found were chlorthalonil, vinolozolin, endosulfan, tetradifon, malathion and procymidone in well CN6 and chlorthalonil, vinclozolin, endosulfan, tetradifon and procymidone in well D1. Considering each pesticide individually, endosulfan was the main pollutant and it was present over the whole year in both cases. Malathion was only present in well CN6. Fungicides like chlorothalonil, procymidone and vinclozolin were usually present at concentrations lower than 0.1 μg/l

4. Conclusions

4.1. Sample handling

SPE disks or cartridges are necessary to achieve adequate identification scores at sub-μg/l levels when GC–IT-MS is used.

SPE polymeric cartridges can allow cleaner extracts and permit a broader range of recovered pesticides to be obtained than C_{18} extraction disks.

It is necessary to reach higher preconcentration values and cleaner extracts than those obtained by C_{18} when LC–DAD is used.

4.2. Analytical procedures

GC–IT-MS has been revealed as a more powerful technique than LC–DAD for large scale screening of insecticides/fungicides in ground waters.

The use of GC–IT-MS in the PI mode can improve the sensitivity and selectivity of the analysis, but a previous study of the behaviour of the target pesticides under CI conditions is necessary.

4.3. Monitoring data

OPs and OCs are important pollutants in water quality control in ground waters up to a depth of 100 m.

Insecticide/fungicide pollution levels sporadically exceeded the limits set by the EU directive on water quality.

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