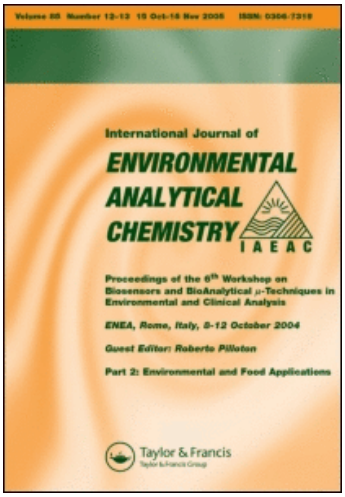

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article ColumÉ, Almudena , Diewok, Josef and Lendl, Bernhard(2004) 'Assessment of ftir spectrometry for pesticide screening of aqueous samples', International Journal of Environmental Analytical Chemistry, 84: 11, 835 — 844
To link to this Article: DOI: 10.1080/0306731031000149697
URL: http://dx.doi.org/10.1080/0306731031000149697

Intern. J. Environ. Anal. Chem.
Vol. 84, No. 11, pp. 835–844, 15 September 2004

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ASSESSMENT OF FTIR SPECTROMETRY FOR PESTICIDE SCREENING OF AQUEOUS SAMPLES

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(Received 29 October 2002; In final form 18 April 2003)

This article assesses the potential of Fourier transform infrared spectrometry (FTIR) to be used in pesticide screening and determination of selected pyrethroid and organochlorine pesticides in fresh water. FTIR spectra of 28 single pesticides in the dry state were recorded on a horizontal diamond attenuated total reflection (ATR) element. Hierachical cluster analysis of the recorded FTIR spectra (spectral range: 4000–500 cm^{-1}) showed that different pesticide groups could be distinguished. A representative of each main group (dichlofuanid, captan and fenpropathrin) was selected and their direct simultaneous determination in fresh water without using a chromatographic separation step investigated. The developed analysis procedure comprised a liquid–liquid extraction step with *n*-hexane, further automated clean-up and preconcentration by solid-phase extraction using a silica mini-column and final elution of the analyte with ethyl acetate. The extract containing the analytes was further concentrated and dried on the ATR element for spectrum acquisition. Using a partial least square (PLS) calibration it could be shown that all three analytes could be quantified in fresh water in a concentration range from 1.2 to 4.8 μg/L. Recoveries for dichlofuanid, captan and fenpropathrin from fortified tap and river waters ranged from 66.3 to 102.0% (captan was the pesticide providing the lowest values, 66.3 and 70.3%).

Keywords: Pesticide screening; Water; Solid-phase extraction; Liquid–liquid extraction; FTIR; PLS; Hierarchical cluster analysis

INTRODUCTION

The use of pesticides to prevent pests and plant diseases is a risk to human health. Pesticide residues remain on agricultural goods and are also transported from agricultural fields to fresh surfaces, drinking and ground waters. Pyrethroids and organochlorine pesticides (OCPs) are a wide group of fungicides and insecticides extensively used in many agricultural applications. In the European Union rigid limits for pesticides in drinking water have been established, being 0.1 μg/L for single pesticides and 0.5 μg/L for total pesticide concentration [1].

Pyrethroids and OCPs are usually determined by gas chromatographic (GC) techniques, using different detectors, such as electron capture detectors (ECD) [3,4] or

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ISSN 0306-7319 print: ISSN 1029-0397 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/0306731031000149697

mass spectrometry [3,5–7]. However, Fourier transform Infrared (FTIR) spectrometry has gained wide acceptance in this field by virtue of its remarkable usefulness for both qualitative and quantitative analysis, but is limited by the high concentration of analyte required for detection. In this context, a literature survey of available methods for the determination of pesticides using FTIR shows that many of them are applied to agrochemical formulations, [8–11] where these analytes are present at high concentration. Recently, automatic methods using flow analysis (FA) have been developed for pesticide formulation analysis [12,13]. Direct determination of dithiocarbamate pesticides in spiked soil samples by microwave-assisted extraction with chloroform and measurement in solution has also been investigated [14]. On the other hand, FTIR is also employed as detector in high-performance liquid chromatography [15], supercritical fluid chromatography [16] and gas chromatography [17–19]. The main advantage of chromatographic techniques is that they provide a chemical separation of a complex mixture of analytes prior to FTIR spectrometry, but this separation step is often time-consuming and costly.

The aim of this work was to assess the potential of FTIR spectrometry for screening of water samples for pyrethroid and organochlorine pesticides by combining FTIR with an SPE preconcentration step and avoiding a chromatographic separation. Two main aspects were taken into account in this work:

1. The evaluation of the information content of ATR-FTIR spectra of pesticides, using hierarchical cluster analysis, in order to determine which classes of pesticides can be, in principle, recognized. Based on this evaluation, three analytes from different clusters were selected for subsequent screening in water samples
2. The development of a technique based on a continuous solid-phase extraction (SPE) system, which allows recording of high quality ATR-FTIR spectra of trace amounts of pesticides in aqueous solutions, and establishing a PLS calibration for simultaneous determination of three pesticides. This technique comprises a liquid–liquid extraction step of water samples with *n*-hexane, clean-up and preconcentration of the *n*-hexane extracts with a flow system-based SPE step using a silica column, elution of the analytes with ethyl acetate and recording of FTIR spectra of the dried ethyl acetate extracts by means of a horizontal diamond ATR cell.

EXPERIMENTAL

Instruments and Apparatus

A Bruker IFS 66 FTIR spectrometer, equipped with a 9-reflection horizontal ATR cell (Dura SamplIR, SensIR Technologies, CT, USA) and a deuterated triglycine sulfate (DTGS) detector, was used. The spectrometer was controlled using the software package OPUS 3.0/IR (Bruker, Germany). All spectra were recorded in the region from 4000 to 500 cm^{-1}. Each spectrum was based on 128 co-added scans at a spectral resolution of 4 cm^{-1}. Hierarchical clustering was performed in OPUS 3.0 and the PLS calibrations were established with OPUS NT 3.1.

The flow system was constructed with a Gilson Minipuls-3 peristaltic pump (Villiers-le-Bel, France) furnished with Solvaflex pump tubing, two Rheodyne 5041 injection valves, PTFE tubing (0.5 mm i.d.) and commercially available connectors. The sorbent glass column (2 cm × 4 mm i.d.) was hand-packed with 50 mg of silica and sealed at

both ends with small cotton beads to prevent material losses. The sorbent column was sequentially conditioned with 0.5 mL of acetonitrile and 1 mL of *n*-hexane prior to running each sample. This column can be reused for at least three months, working daily, including a washing step with 0.5 mL of isopropanol before conditioning.

Chemicals and Standard Solutions

All chemicals and sorbents were of analytical grade or better. The following pesticides were studied: aldrin, captan, captafol, chlorbenside, chlordane, dichlofuanid, dichloran, dicofol, dieldrin, α-, β-endosulfan (3:1, w/w), endosulfan sulphate, endrin, hexachlorobenzene (HCB), heptachlor, iprodione, α-, β-, δ-, γ-hexachlorohexane (α-, β-, δ- and γ-HCH 1:1:1:1, w/w), methoxychlor, procymidone, vinclozolin, bifenthrin, λ-cyhalothrin, deltamethrin, fenpropathrin, fenvalerate (*cis* and *trans* isomers), permethrin (*cis* and *trans* isomers), cyfluthrin isomers, cypermethrin isomers, and piperonyl butoxide. All were obtained from Riedel-de-Haën (Seelze, Germany). The silica sorbent was obtained from Varian (Zug, Switzerland). HPLC grade solvents (ethyl acetate, *n*-hexane, isopropanol, acetonitrile) were purchased from Sigma-Aldrich (Vienna, Austria).

Stock standard solutions of each pesticide were prepared in acetone (except HCB, which was dissolved in dichloromethane) at concentrations of 5 mg/mL, and stored in glass stoppered bottles in the dark at 4°C. Working standard solutions were obtained by appropriate dilution with *n*-hexane or acetone.

Protocol for Pre-concentration, Clean-up and Measurement by ATR-FTIR Spectrometry

The continuous clean-up system designed is shown in Fig. 1. A volume of 10 mL of the *n*-hexane phase obtained from pesticide standards or aqueous samples after liquid–liquid extraction (see next section) was aspirated at 2 mL/min. Dichlofuanid,

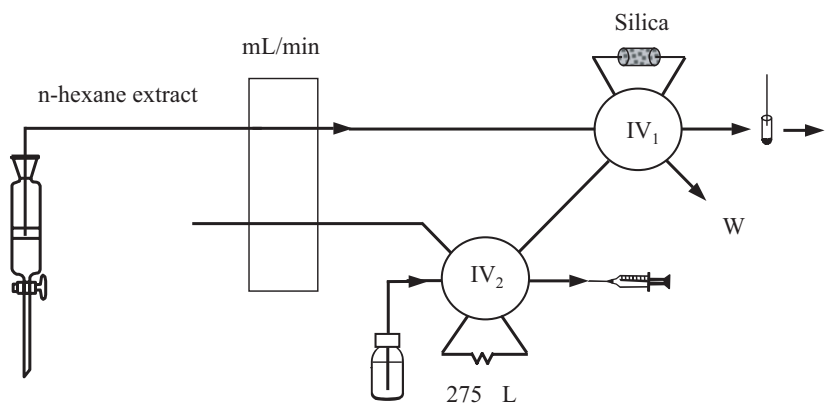

FIGURE 1 Experimental setup for screening of pesticides in water samples. P: peristaltic pump; IV: injection valve; W: waste; FTIR: Fourier transform infrared spectrometer. Step 1: Liquid–liquid extraction of water sample; Step 2: Clean-up and pre-concentration by continuous SPE system; Step 3: Recording of ATR-FTIR.

captan and/or fenpropathrin concentration in the *n*-hexane phase was 0.0–0.2 μg/mL. All pesticides were adsorbed on the 50 mg silica column located in the loop of injection valve 1 (IV_1), and the sample matrix was sent to waste. Simultaneously, the loop of the second injection valve (IV_2) was filled with ethyl acetate by means of a syringe. Any residual organic solvent remaining inside the column and the connectors was flushed by passing an air stream through the carrier line at 1 mL/min for 4 min. Next, IV_2 was switched to pass the loop contents (275 μL of ethyl acetate) at 1 mL/min through the column, in the opposite direction to the sample, in order to elute the pesticides. The whole organic extract was collected in a glass micro-vial, evaporated to dryness under a N_2 stream and re-dissolved in 10 μL of ethyl acetate. A 5 μL aliquot was transferred with a micro-pipette onto the ATR crystal and allowed to dry. Spectra were recorded after complete drying of the sample which was complete after 30 s as revealed by the disappearance of solvent bands in the spectra. For the next sample the ATR crystal was cleaned using pure solvent and a soft tissue and a new background spectrum was recorded. Between samples, the sorbent column was cleaned, without removal from the continuous SPE system, with 0.5 mL of isopropanol and then conditioned with 0.5 mL of acetonitrile and 1 mL of *n*-hexane. Under these conditions, the sorbent column was useable for about three months.

Water Sample Pre-treatment and Liquid–Liquid Extraction

Apart from the synthetic pesticide standards in *n*-hexane, aqueous samples were analysed with a previous liquid–liquid extraction step. Fresh water samples from Vienna rivers and tap water were collected in amber glass bottles. A volume of 1 mL of 0.1 M $Na_2S_2O_3$ per litre of water sample (final concentration of 10^{-4} M) was added on-site to suppress the interferences of chlorine and humic and fulvic acids. All samples were filtered through a Micro Separations Inc. 0.45 μm nylon filter (Westboro, MA, USA) to remove particulate matter. In order to avoid degradation of some of the pesticides under alkaline conditions [20], the pH of all water samples was adjusted to 5–6. Water samples were kept in the dark at 4°C from collection to analysis, being analysed within two days. A volume of 0.5 L of water sample was placed into an extraction funnel with 12 mL of *n*-hexane. The mixture was shaken for 10 min and allowed to settle. Then, 10 mL of the *n*-hexane phase were continuously aspirated into the flow system.

RESULTS AND DISCUSSION

Preliminary investigations were performed in order to optimize the recording of the FTIR spectra with the ATR cell (see Step 3 of the complete experimental protocol below) and to evaluate the information content and similarity of the FTIR spectra of 28 different organochlorine and pyrethroid pesticides.

Optimization of ATR Measurements

To remove the interfering absorbance of the solvent (ethyl acetate) [21], the samples were allowed to dry on the ATR crystal. In order to achieve the maximum sample volume which provides a homogeneous dry film on the ATR crystal, different volumes of ethyl acetate between 1 and 10 μL, containing 1 μg of dichlofuanid were tested.

Spectra were recorded and results showed that the maximum applicable volume was 5 μL. For higher volumes, spectra were less reproducible, as solvent evaporation forced the analyte to form a ring on the ATR crystal limits.

Hierarchical Cluster Analysis of FTIR Spectra of Pesticides

In order to perform hierarchical cluster analysis, FTIR spectra of 19 OCPs and 9 pyrethroid pesticides were recorded after transferring 1 μL aliquots of 1 mg/mL solutions in acetone onto the ATR crystal and allowing to dry. The FTIR spectra were vector normalized and Ward's algorithm was used for clustering and creating dendrograms. Different wavenumber regions from 4000 to 500 cm^{-1} of the normalized spectra were tested, and optimal results were obtained with the spectral region between 575 and 1850 cm^{-1}. The clustering results are shown in Fig. 2. As can be seen, using FTIR spectrometry the pyrethroid pesticides can be clearly distinguished from OCPs, whereas OCPs are divided into two subgroups.

Determination of Selected Pesticides in Water

According to the clustering results, one pesticide from each cluster was selected for consequent multianalyte determination by PLS calibration: dichlofuanid, captan and fenpropathrin. The corresponding spectra are shown in Fig. 3.

The proposed FTIR screening method of pesticides in waters can be divided into the following four analysis steps (see also Fig. 1):

1. Liquid–liquid extraction of water sample with *n*-hexane
2. Clean-up and pre-concentration of the *n*-hexane phase using a continuous SPE system

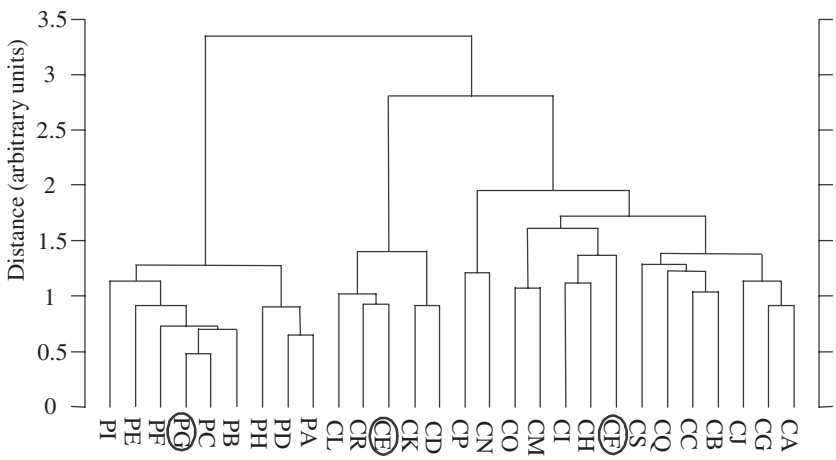

FIGURE 2 Dendrogram calculated from the normalized MIR spectra of 19 organochlorine pesticides and 9 pyrethroid pesticides. Pesticides selected for PLS are marked with a circle. CA: aldrin; CB: dieldrin; CC: endrin; CD: captafol; CE: captan; CF: dichlofuanid; CG: chlordane; CH: endosulfan sulfate; CI: α-,β-endosulfan; CJ: heptachlor; CK: procymidone; CL: vinclozolin; CM: chlorbenside; CN: dichloran; CO: Dicofol; CP: HCB; CQ: α-,β-,δ-, γ-HCH; CR: iprodione; CS: methoxychlor; PA: bifenthrin; PB: cyfluthrin; PC: deltamethrin; PD: λ-cyhalothrin; PE: permethrin; PF: fenvalerate; PG: fenpropathrin; PH: cypermethrin; PI: piperonyl butoxide.

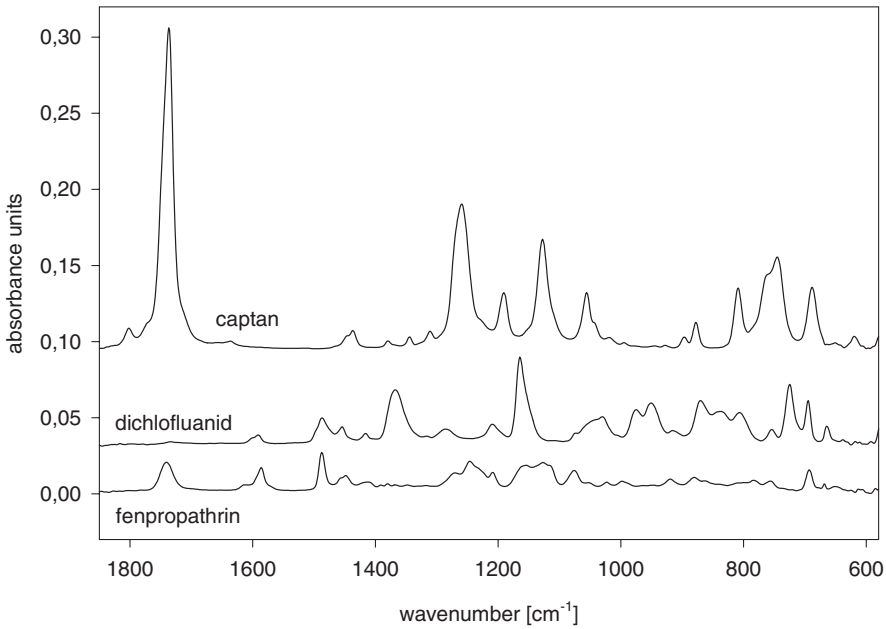

FIGURE 3 FTIR spectra of pesticides selected for PLS calibration: captan; dichlofuanid (offset: 0.03 a.u.) and fenpropathrin (offset: 0.09). 1 µL of 1 mg/mL solutions in acetone were transferred onto the ATR and allowed to dry.

3. Transfer of the pre-concentrated extract onto the ATR and recording of the FTIR spectrum of the dried extract
4. Quantitation based on PLS calibration (established using standards in *n*-hexane which have been treated as the samples following Steps 2 and 3).

In the next sections the optimization of the continuous SPE system, the establishing of the PLS calibration and the analysis of water samples including optimization of the extraction step will be described in detail.

Continuous SPE System

Recently, our working group has developed a method for the determination of organochlorine (OCPs) and pyrethroid pesticides in fruits and vegetables based on automated sample preparation and clean-up using a flow system and final separation and quantitation by GC-ECD [22,23]. In these investigations it was found that for sample clean-up a liquid–liquid extraction step with *n*-hexane followed by further SPE using a silica column and elution of the analytes with ethyl acetate was highly efficient. For the present study the experimental conditions optimized for GC-ECD detection had to be adapted to the needs of ATR-FTIR spectrometry. However, as the minimum amount of pesticide on the ATR needed to obtain satisfying FTIR spectra was between 0.1 and 0.2 µg the flow system was modified in order to handle bigger analyte amounts.

The sorbent capacity of the 50 mg silica column was evaluated in previous work [22,23] as ~14 µg of pesticide, which was sufficient for the present FTIR study. Therefore only the effect of the eluent volume had to be studied. The elution volume

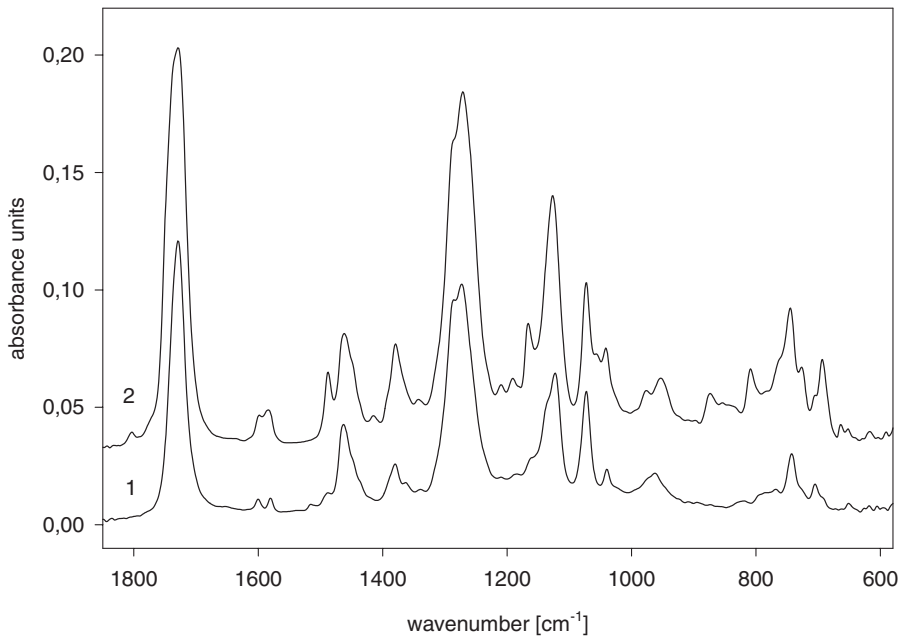

FIGURE 4 ATR-FTIR spectra of a 10 mL *n*-hexane blank (1) and a 10 mL pesticide standard (0.2 μg/mL dichlofuanid, captan and fenpropathrin) (2, offset: 0.03) after continuous SPE treatment and drying as described in the Experimental Section.

was varied in the range of 175 to 500 μL and the completeness of elution checked by a second elution step. Complete elution of analytes was obtained with a single injection of 275 μL of ethyl acetate.

In order to achieve maximum pre-concentration, *n*-hexane solutions of 5 to 20 mL (20 mL being the previously determined breakthrough volume [22,23] containing 2 μg of dichlofuanid, captan and fenpropathrin) were passed through the flow system. Results showed that despite using HPLC grade solvents, the solvents contained some impurities that were retained on the silica column and eluted with ethyl acetate. The bigger the *n*-hexane volume, the stronger was the influence of these impurities on the final spectra. Because of this solvent purity problem, a loaded *n*-hexane volume of 10 mL was selected as a compromise between maximum pre-concentration factor and optimal spectral quality.

Figure 4 shows the ATR-FTIR spectra of a 10 mL *n*-hexane blank and a 10 mL pesticide standard (0.2 μg/mL dichlofuanid, captan and fenpropathrin) after continuous SPE treatment and drying as described in the Experimental Section.

Partial Least Square Calibration

The PLS calibration set comprised the following samples (Table I): samples (nos. 1–8) of 10 mL *n*-hexane solutions containing all possible ternary combinations of the three selected pesticides at two concentration levels; samples (nos. 9–11) containing only one of the pesticides, samples (nos. 12–17) containing binary and ternary combinations at varying concentrations and solutions (nos. 18–20) without analytes (flow system blanks). All these solutions were in the range of 0.00 to 0.2 μg/mL for the analytes

TABLE I Analyte concentrations in *n*-hexane phase for the different mixtures of the calibration set

Sample number	*Concentration* (μg/mL)		
	Dichlofuanid	*Captan*	*Fenpropathrin*
1	0.2	0.2	0.2
2	0.2	0.2	0.05
3	0.2	0.05	0.2
4	0.05	0.2	0.2
5	0.2	0.05	0.05
6	0.05	0.05	0.2
7	0.05	0.2	0.05
8	0.05	0.05	0.05
9	0.1	0.0	0.0
10	0.0	0.1	0.0
11	0.0	0.0	0.1
12	0.1	0.1	0.05
13	0.1	0.05	0.2
14	0.07	0.1	0.07
15	0.0	0.1	0.07
16	0.2	0.0	0.1
17	0.05	0.07	0.0
18	0.0	0.0	0.0
19	0.0	0.0	0.0
20	0.0	0.0	0.0

(corresponding to 0.0 to 4.8 μg/L in 0.5 L water samples). 10 mL of all calibration standards were prepared and passed through the flow system in duplicate. Calibration models were validated by cross-validation, using a leave-one-out procedure.

Because of the influence of the solvent impurities in the spectra, it was important to select the optimal wavenumber range in the calibration method. Several ranges were tested starting with the full spectra. Then, ranges were selected taking into account spectral regions where the flow system blank spectrum exhibited lower absorptions and each analyte spectrum exhibited higher absorptions. Regions where the flow system blank spectrum dominated the total spectrum were excluded from calibration. For each pesticide separately, calibration models were constructed using different wavenumber ranges and their combinations, and original, first- and second-derivative data.

The results were always better using first-derivative data (Savitzky–Golay with 13 smoothing points) than original spectra, and the best model for each pesticide was constructed using a combination of different wavenumber ranges. Parameters for these optimal models are listed in Table II. The optimal number of PLS components was four to five in all cases, which was the same as the number of analytes plus the effect of solvent impurities. The root-mean-square error of cross validation (RMSECV) was acceptable, ranging between 0.015 and 0.019 μg/mL.

Application to Water Samples

Prior to the screening of water samples, the *n*-hexane liquid–liquid extraction step was optimized. For this purpose 0.5 L of water samples containing 10 μg/L of each pesticide were used. *n*-Hexane volumes from 10 to 50 mL and extraction times of 2 to 15 min were investigated. The minimum volume of *n*-hexane and minimum time required for

TABLE II PLS calibration parameters for the three selected pesticides, using first derivative pre-processing

Pesticide	*Wavenumber intervals* (cm^{-1})	*PLS components*	R^2	*RMSECV*
Dichlofuanid	1504–1476 990–920 990–920	4	0.937	0.017
Captan	1825–1789 700–540	4	0.952	0.015
Fenpropathrin	1423–1403 1355–1330 1000–990 890–785	4	0.927	0.019

TABLE III Mean recoveries (± RSD) in the analysis of tap and river water spiked at 2.4 μg/L ($n = 3$)

Water sample	*Dichlofuanid*	*Captan*	*Fenpropathrin*
Tap water	88 ± 4	66 ± 6	102 ± 7
River water	92 ± 3	70 ± 7	89 ± 3

complete extraction of the analytes were found to be 10 mL and 10 min, respectively. The extraction was performed manually.

The proposed system was applied to the screening of dichlofuanid, captan and fenpropathrin in tap and river waters. In all cases, the pH of the water samples ranged from 6.7 to 8.3. In order to avoid degradation, they were preconditioned with $Na_2S_2O_3$ and their pH was adjusted to the optimum range (5–6) with dilute HNO_3 as soon as possible after collection. No natural samples containing pesticide residues at detectable concentrations could be obtained, so a recovery test was carried out.

Recoveries of analytes were studied in tap and river water. For this purpose, volumes of 0.5 L of each water were pre-conditioned as described in the Experimental Section, and fortified with 1.2 μg of each selected pesticide from standard solutions in acetone. After the addition, the spiked water was slightly shaken and then analysed in triplicate, using the proposed method. Results are shown in Table III. In both cases, the lowest recoveries were obtained for captan, which can be ascribed to its being either partially irreversibly bound to the matrices or degraded during the contamination time, as shown in previous studies with water samples [3].

CONCLUSIONS

This study clearly showed the ability of FTIR spectrometry to group pesticides according to their chemical structure as well as to provide simultaneous quantitative determination in fresh water samples. For the latter purpose FTIR spectra of organic extracts obtained by a sequence of sample pre-treatment steps were recorded, thus avoiding the commonly used chromatographic separation step. A major difficulty encountered, however, was the strong spectral influence of remaining matrix molecules and solvent impurities. Nevertheless, owing to the high information content of FTIR

spectrometry, this technique promises to be useful in screening methods which would supply rapid qualitative information on the pesticide contamination of a sample and simultaneously provide information on the group of pesticides present. Development of such screening techniques is one of the current goals of modern analytical chemistry. These techniques are needed for fast decision making and to allow the efficient use of expensive and time-consuming standard methods for pesticide analysis, which mostly require a chromatographic separation step and subsequent sensitive detection of the separated analytes. Future work will therefore concentrate on improving the sample clean-up step which was identified as the key for successful screening analysis by FTIR spectrometry.

Acknowledgments

A. Columé is grateful for a training fellowship at the Marie Curie Training Site on Advanced and Applied Vibrational Spectroscopy (ADVIS) in Vienna. Also, S.D. and B.L. thank the Austrian Science Fund for further financial support within the project 13686.

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