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Short communication

Simultaneous determination of imidacloprid and carbendazim in water samples by ion chromatography with fluorescence detector and post-column photochemical reactor

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ABSTRACT

A new analytical method has been developed and validated for the simultaneous determination of pesticides from different classes using ion chromatography-online photochemical derivatisation-fluorescence detector (IC-*hv*-FD). Fluorimetric detection was performed at $\lambda_{ex}/\lambda_{em}=332$ nm/367 nm for imidacloprid and then detector was set at $\lambda_{ex}/\lambda_{em}=247$ nm/470 nm for carbendazim. The two pesticides imidacloprid and carbendazim were successfully separated isocratically on an IonPac® AS11 (250 mm × 4 mm i.d; 13 μm particle size, Dionex) anion-exchange column using 40 mM KOH with 10% (v/v) acetonitrile and pumped at a flow rate of 1.0 mL min^{-1}. Under the optimized conditions, the limit of detection (LOD, S/N=3) of imidacloprid and carbendazim were 7.8 μg L^{-1} and 67 μg L^{-1}, respectively. The experimental results showed that there was good linearity with a correlation coefficient (r)≥0.9966 over the range of 0.05–10 mg L^{-1} for imidacloprid and 0.2–15 mg L^{-1} for carbendazim. Good reproducibility with a relative standard deviation (RSD, $n=7$) less than 4.5%. Finally, the proposed method was applied with satisfactory results to the analysis of these pesticides in ground water, lake water and river water without any pre-treatment of samples. The average spiked recoveries were in the range of 90–104%.

1. Introduction

The use of pesticides in agriculture has increased dramatically and undeniably during the last few decades. Discharge of pesticides into the environment can cause their incorporation into various kinds of matrices such as soil, crops, water and this may be a serious threat to human health [1,2]. The pesticides affect the quality of the natural waters and it can become a severe environmental concern. Imidacloprid [1-(6-chloro-3-pyridylmethyl)-*N*-nitroimidazolodin-2-ylideneamine] is a neonicotinoid insecticide from a new group of active ingredients with novel mode of action, low toxicity for warm blooded animals, tremendous activity at very low application rates, admirable systematic properties and enduring action [3]. It acts as an agonist of acetylcholine by binding to postsynaptic nicotinic receptor in the insect central nervous system, causing the paralysis and death of insects [4].

Carbendazim or methyl-2-benzimidazole carbamate (MBC) is the most extensively used active ingredient in the benzimidazole carbamate class of fungicides. It is among the most influential systemic fungicides against various fungal diseases caused by *Basidiomycetes; Deutermycetes* spp. and *Asccomycetes* spp. in vegetable and fruits [5,6].

Gas chromatography (GC) remains the main basic analytical technique for pesticide residues analysis when combined with mass spectrometry (MS). Nevertheless, imidacloprid and carbendazim have low volatility, high polarity and thermolability so GC seems to be excluded as a determination method even by minimizing the temperature [7–9]. GC–Mass methods for the determination of imidacloprid in soil, water [9] and vegetables have been proposed [10]. Here, complex sample pretreatment is required to transform the pesticide into volatile compound by hydrolysis in basic medium, after which liquid–liquid extraction with chloroform is carried out.

Liquid chromatography (LC) with a diode array detector (DAD) and thermal lens spectrometric detection (TLS) method based on reversed phase separation on C_{18} column with isocratic elution for the analysis of trace amount of imidacloprid, thiamethoxam, thiacloprid and acetamiprid from river water and potato has been reported [11]. Prousalis et al. measured residual levels of carbendazim, thiabendazole and o-phenylphenol in lemons by HPLC-UV. Here, sample extraction is followed by a multi-step purification process with liquid–liquid partitioning after addition of an aqueous ammonia solution and finally an elution through a clean-up solid phase cartridge [12]. An HPLC-diode array detection technique was used for the determination of imidacloprid residues

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extracted from the vegetables by using acetone and C_{18} reverse phase cartridges [13]. The application of LC-based techniques to residue analysis is impeded mainly by problems in sample preparation because of unspecificity, insensitivity of DAD and enormous interference from the vegetable extracts [13–15]. These methods are characterized for developing particular sample handling procedures or sophisticated clean-up strategies. So, it can be hard to identify and quantitate the analytes in many commodities [13,15,16].

Sing et al. reported microwave-assisted extraction and HPLC-UV analysis for thiamethoxam, imidacloprid, and carbendazim residues in raw and cooked vegetable samples [17]. Recently, a capillary electrochromatograpy (CEC) with DAD detection method for the determination of imidacloprid and carbendazim in tomato samples has been proposed [18]. Liquid chromatography coupled to mass spectrometry (LC–MS) is also gaining acceptance for the analysis of pesticides in vegetable and fruits [19,20]. Although, LC–MS technique provides the sensitive and unambiguous detection, avoiding most of the matrix interferences but it requires the use of expensive instrumentation which is not in the access of many laboratories in developing countries, hence, it would appear desirable to develop an alternative, simpler, low cost and rapid method for the determination of pesticides.

Because of selectivity and high sensitivity, fluorescence detector (FD) combined with HPLC can be used for trace analysis [21]. The number of pesticides presenting an intrinsic fluorescence is limited. Various kinds of derivatisation techniques such as photochemical, chemical or electrochemical are recommended for analytes with no or weak native fluorescence for their conversion into strongly fluorescent species and then detection by FD [22–24]. The use of UV radiation to produce fluorescent photoproducts by direct irradiation of the liquid solutions containing the analyte is a valuable method for the speedy screening of non-fluorescent materials in pharmaceutical, clinical, biochemistry and environmental analysis [25]. From the analytical point of view the photochemical derivatisation has an advantage in that it is not necessary to identify the structure of the fluorescent compound (s) formed after UV irradiation, provided that reproducible photochemically induced fluorescence (PIF) signals are obtained [26].

Werkhoven-Goewie et al. were apparently the first to apply photochemically induced fluorescence (PIF) to liquid chromatographic analysis of chlorophenol pesticides in biological and water samples. Photolysed chlorophenols gave fluorescence signals which were linearly related to the amounts of analyte over 2 to 3 orders of magnitude [27].

Saleh et al. described a method for fluorescence enhancement of carbendazim in the presence of another macrocyclic host molecule, cucurbit [6] uril, in aqueous solution. It is chemical derivatisation which involved a tedious chemical process with the consumption of a large amount of chemicals [28]. Photochemical kinetics are relatively speedy and in most of the compounds, the photochemical reactions yield a photoproduct with an enhanced molecular absorption coefficient and/or higher fluorescence quantum yield relative to those of analytes [29].

The LC separation and fluorescence detection after photochemical derivatisation method has been established to determine imidacloprid and its metabolite (6-chloronicotinic acid) in honey bee samples. The methodology involves separation of the analytes by an Aquasil C_{18} column and further derivatisation by using a photochemical reactor in sodium hydroxide solution [30]. The imidacloprid gives the best fluorescence signals in basic medium at pH ~12, but silica based columns work well in the pH range of 2–8; therefore an alkaline solution was added to the effluent after the separation to perform the photochemical conversion of pesticide to generate the fluorescence signal. Mixing tee and an extra pump were required, which made the procedure more complex.

Ion chromatography (IC) has become one of the most renowned methods for determining cations, anions and small organic ions in aqueous samples [31,32]. Organic polymer based columns dominate in IC because of their rigidity and stability in extreme pH conditions (0–14). Moreover, these polymer based columns can work well in alkaline medium.

This paper presents, for the first time, a method developed for the simultaneous determination of imidacloprid and carbendazim with ion chromatography combined with online post-column photoactivation and fluorescence detection (IC-*hν*-FD). The separation of the pesticides is carried out in the anion-exchange column with a basic eluent. This analytical procedure has been applied to determine imidacloprid and carbendazim in natural waters. The elimination of complicated additional instrumental setup in the present methodology makes it more simplified and straight forward.

2. Experimental

2.1. Chemicals and materials

Analytical standards of Imidacloprid (95%, w/w) and carbendazim (98%, w/w) were obtained from Shanlong Qi Chun Ltd. (Hubei China). HPLC-grade acetonitrile (ACN) was purchased from Tidia company. The analytical grade reagents, sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate and sodium phosphate for analysis were bought from Aladdin Co. (Shanghai, China). LC grade water (<18 cm MΩ specific resistivity) was obtained by purifying demineralized water in a Milli-Q system (Millipore, Molsheim, France).

2.2. Solutions

Individual stock solutions (400 mg L^{-1}) of imidacloprid and carbendazim were prepared by exactly weighing and then dissolving corresponding amounts of compounds in a mixture of water-ACN (90:10) and stored in stained glass-stopper bottles. These solutions were stable for at least one month if stored in the dark at 4 °C. Working solutions of both compounds were freshly prepared daily by appropriate dilution of aliquots of the stock solution in water.

2.3. Instrument and software

The IC system was composed of a Dionex Ultimate 3000 series (Sunnyvale, CA, USA) equipped with a quaternary pump, temperature controlled column compartment and autosampler. Detection was performed with a model Ultimate 3000 RS fluorescence detector (Dionex, Sunnyvale, CA, USA). The IonPac® AS11 column (250 mm × 4 mm i.d; 13 μm particle size) preceded by an IonPac® AG11 guard column (50 mm × 4 mm i.d; 13 μm particle size) was used for separation. Data collection and analysis was performed with a personal computer equipped with Chromeleon® 7 software (Dionex, USA). For the pesticide and environmental analysis, laboratory-constructed instruments and modifications to commercially available instruments for measuring photochemical induced fluorescence in various methods have emerged in the last years. A home-made continuous flow photochemical reactor was constructed by freely coiling the knitted PTFE reactor (17 cm long × 1.5 mm o.d. × 0.5 mm i.d.) around a rod shaped low-pressure mercury lamp (18 W, 254 nm spectral emission line). It is placed into a PVC cylinder internally fixed with aluminum foil to allow the maximum reflectance of UV light and heat dissipation. Fig. 1. illustrates the arrangement of various components used in

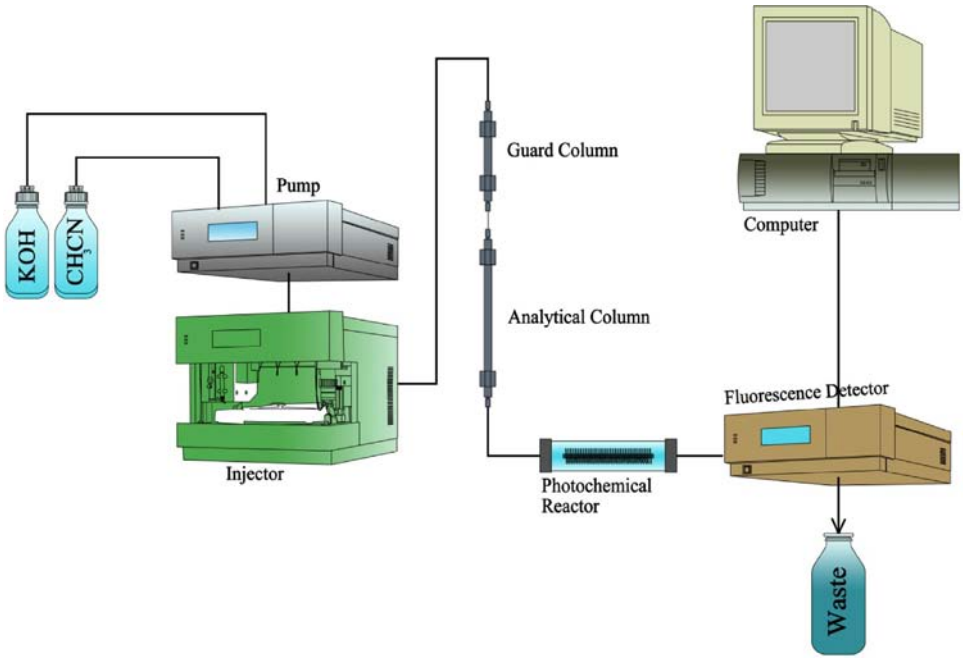

Fig. 1. A schematic diagram of IC-*hv*-FD instrumental setup used for the determination of imidacloprid and carbendazim in water samples.

the present study. A precise pH-meter (Mettler Toledo, FE20, China) was used for the pH measurements.

2.4. Treatment of samples

Water samples were filtered through a 13 mm membrane syringe filter (Xiboshi, pore size 0.45 μm, Tianjin Fuji Tech Co., Tianjin, China), and directly injected into the chromatographic system. These samples were stored in dark glass bottles at 4 °C for the future use.

2.5. Chromatographic technique

The IC separation of imidacloprid and carbendazim was conducted by using an anion-exchange IonPac® AS11 column combined with IonPac® AG11 guard column. The columns were operated at ambient temperature isocratically at a flow rate of 1.0 mL min^{-1}, using mobile phase 40 mM KOH-10% ACN (v/v, pH ~12). The injection volume was 20 μL. After separation of two target analytes photoactivation was performed in the UV photochemical reactor. The fluorimetric detection was carried out at an excitation wavelength (λ_{ex}) of 332 nm and at an emission wavelength (λ_{em}) of 367 nm for the imidacloprid and then the detector was changed at 7 min at an excitation wavelength (λ_{ex}) of 247 nm and emission wavelength (λ_{em}) of 470 nm for carbendazim.

3. Results and discussion

3.1. The selection of medium for the pesticides

It is known that imidacloprid does not show intrinsic fluorescence in the aqueous medium, but when its aqueous solutions are irradiated with UV light, a fluorescent signal is obtained. A former imidacloprid photodegradation study [33] enabled the fluorescing transformation product to be isolated and identified: 1-(6-chloro-3-pyridylmethyl)-2-hydroxyimino)-3,4-didehydroimidalozolidene. The optimization of excitation and emission wavelength for the photoderivatised product of imidacloprid was carried out according to a previously reported method [34]. Therefore, λ_{ex} and λ_{em} were 332 nm 367 nm respectively, which were nearly similar to the literature [34]. In the case of carbendazim, the excitation and emission maxima were determined by conducting experiments in our laboratory and observed at 247 nm and 470 nm. During these processes of emission and excitation wavelength determination, the concentration of each of the pesticide was taken 10 mg L^{-1}. A flow injection analysis was carried out to find the effect of concentration and type of bases used as reaction medium on the fluorescent signal of the pesticides. For this purpose the solutions of various kinds of bases were used in the concentration range of 5.0–100 mM. The experimental results are shown in Fig. 2 and 3. It was found that the impact of base type and concentration on imidacloprid photochemical fluorescence intensity was greater as compare to carbendazim. When strong bases, sodium hydroxide and potassium hydroxide solutions were used as reaction medium for imidacloprid, the photochemically induced fluorescence signals first increased then decreased with the increase of base concentration. The concentrations 30 mM and

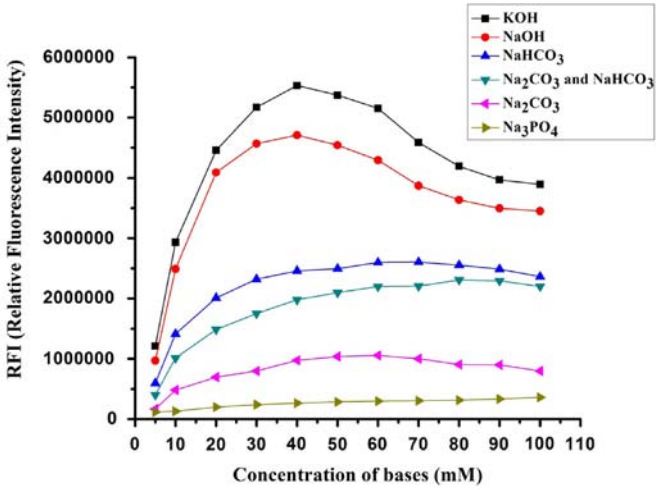

Fig. 2. The effect of base concentration on the photochemically induced fluorescence intensity of imidacloprid (10 mg L^{-1}). The fluorescence detection: $\lambda_{ex}/\lambda_{em}$=332 nm/367 nm; flow rate: 1.0 mL min^{-1}.

40 mM were found to be optimum for both bases, although at a concentration of 40 mM of potassium hydroxide solution, the signal produced was 17% higher than that produced in sodium hydroxide at the same concentration.

Solutions of the weak bases sodium carbonate and sodium bicarbonate were used separately as well as in the mixed forms, however, the photochemical fluorescence (PCF) signal first increased gradually then decreased with the increase of concentration. In an another basic medium, sodium phosphate, the fluorescence signals were comparatively weak and showed slowly increasing trend with the increased base concentration.

The other pesticide, carbendazim (pK_a=4.3) in the aqueous solution shows the properties of a weak base. It exists in the neutral form (pH > pK_a) and as a protonated form (pH < pK_a) [35]. In the high alkaline mediums it remained as a deprotonated form, which is more sensitive towards UV light [36]. Therefore, in the case of carbendazim, photochemical fluorescence response were similar to imidacloprid in strong bases but it showed slightly more in sodium hydroxide medium as compare to potassium hydroxide. In weak bases it showed comparatively less RFI, which increased with the increase of basic concentration and finally showed decreasing pattern. However, 40 mM KOH solution was selected as reaction medium for both pesticides because of their better separation on ion chromatographic column by addition of small amount of organic solvent.

3.2. Selection of separation system

The simultaneous separation and determination of these two pesticides is a real challenge because of their entirely different chemical and physical properties. The chemical structures of these compounds are provided below in Fig. 4.

Usually, the imidacloprid and carbendazim were eluted by reversed-phase high performance chromatography, with aqueous buffer and organic modifier [11–13]. The post column photochemical derivatisation technique was used for the determination of imidacloprid with RP-HPLC [30]. In this study the attempt was made to separate these analytes by using an anion-exchange column and elution with a base/acetonitrile mixture as eluent. Dionex anion-exchange columns, AS-15A, AS-16, were tested with potassium hydroxide and acetonitrile but unfortunately, both the pesticides were not eluted simultaneously. Another anion exchange column (IonPac® AS11 column, Dionex) was tested for separation of these pesticides with potassium hydroxide and by the addition of a small amount of organic solvent (acetonitrile). The selectivity of the IonPac® AS11 column can be altered by the addition of organic solvents; therefore, the suitable mobile phase for the separation and elution of these pesticides was 40 mM KOH plus 10% ACN. This column has highly cross-linked substrate material EVB/DVB polymer functionalized by alkanol quaternary ammonium functional groups and the diameter of the latex bead is 85 mm with an ion-exchange capacity of 45 μequiv column^{-1}. The retention of pesticides in the AS11 column is due to adsorptive interactions, which can be reduced significantly by the organic solvent in the eluent. Afterward the chromatographic conditions were optimized to avoid peak tailing and to improve the peak shape at a flow rate of 1.0 min mL^{-1} by using 20 μL volume of a mixed solution of pesticide having 1.0 mg L^{-1} concentration by fluorescence detector. The analytes were separated on an AS11 column without band broadening and with good peak shape in just 9.0 min. The chromatographic parameters, such as retention time, peak width at half peak height and asymmetric factor are given in the Table 1.

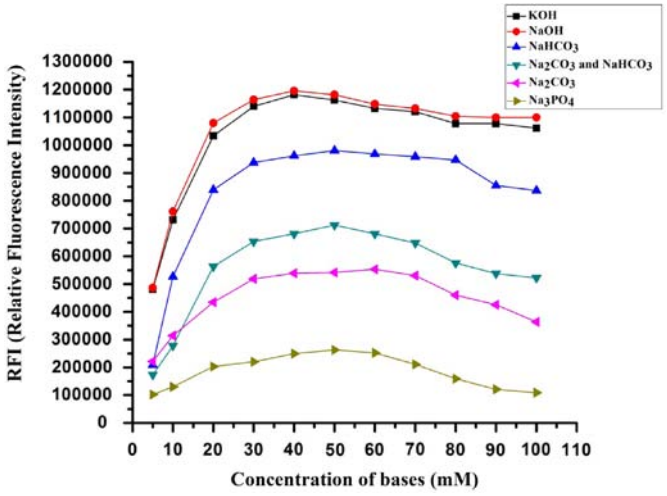

Fig. 3. The effect of base concentration on the photochemically induced fluorescence intensity of carbendazim (10 mg L^{-1}). The fluorescence detection: $\lambda_{ex}/\lambda_{em}$=247 nm/470 nm; flow rate: 1.0 mL min^{-1}.

3.3. Photochemical derivatisation of pesticide

The laboratory made photochemical reactor was used to study the effect of the UV light on the imidacloprid and carbendazim. Preliminary experiments have shown that in aqueous basic solution both the pesticides do not show fluorescent characteristics, but under the influence of UV radiation the fluorescent signals are observed. The knitted PTFE reactor was used and the optimum reaction time was 3.5 min to give the maximum RFI (Relative Fluorescence Intensity) by the pesticides in alkaline medium. It was noted that addition of acetonitrile as organic modifier in KOH solution to elute the analytes from the IC-column has no effect on the florescence signals. The chromatogram (Fig. 5) showed the separation and effect of UV radiation on the two analytes. It was

Table 1
Chromatographic parameters of pesticides.

[a]Analytes	Retention time (min)	Asymmetric factor	Peak width at half height (min)
Imidacloprid	5.18	1.11	0.28
Carbendazim	8.54	1.19	0.31

[a] The concentration of pesticides was 1.0 mg L^{-1}. The experiment parameters are same as mentioned in the Fig. 5.

1-(6-chloro-3-pyridylmethyl)-*N*-nitroimidazolidin-2-ylideneamine (Imidacloprid)

methyl-2- benzimidazole carbamate (Carbendazim)

Fig. 4. Chemical structures of imidacloprid and carbendazim.

observed that without UV light there was no signal thus no photochemical derivatisation occurred and with UV radiation both the pesticides had peaks.

3.4. Validation study

The quantitative measurement was based on the linear relationship between the concentration and peak area of the pesticides. The calibration curves were developed by analyzing six different dilutions of each pesticide in the mobile phase of the stock solution. The *lack-of-fit* test [37] was applied to analyze the linearity of the calibration curves. Three replicates were used for each of six standards to obtain the calibration curves. The regression data were obtained from the average of three replicates. The linear dynamic range for imidacloprid and carbendazim were from 0.05 mg L^{-1} to 10 mg L^{-1} and 0.2 mg L^{-1} to 15 mg L^{-1}, respectively. The regression equations were $y=35.127x-4417.2$ and $y=37.813x-21{,}236$ where y = concentration and x = peak area. Each species exhibited satisfactory linearity with significant values of correlation coefficient (r). The lower limit of detection (LOD) and quantification (LOQ) for the proposed pesticides were calculated based on signal-to-noise (S/N) of 3 and 10, respectively. The repeatability of the proposed method was evaluated by seven replicate measurements (1.0 μg mL^{-1}) of each analyte. The relative standard deviation and other analytical parameters (presented in Table 2) were proven to be satisfactory.

3.5. Application to real water samples

The performance of the method was evaluated by analyzing three kinds of water samples, including ground water (Hangzhou city), lake water (Xihu Lake, Hangzhou) and river water (Qiantang River, Hangzhou). As under the previously optimized chromatographic conditions, three water samples were run separately to verify the presence or absence of the target analytes. When no peak was found at the related locations, it means there was no pesticide in the water samples. In order to validate the method real water samples were fortified with imidacloprid and carbendazim at a concentration of 0.5 mg L^{-1} and analyzed and chromatograms are shown in Fig. 6.

The average recoveries were in the range of 90–104% from all the water samples for imidacloprid and carbendazim and the results are shown in Table 3. The proposed method was compared with other techniques reported in literature with respect to the determination of target analytes, as shown in Table 4. It can be observed that IC-*hv*-FD is better than the previously reported methods with high sensitivity. This study provided more simplicity in instrumentation and minor consumption of chemicals, as compared to previous reports [30].

4. Conclusion

This work presents a new multiresidue method for the simultaneous analysis of pesticides of different classes by using an IC-*hv*-FD technique. The combination of photochemical reactor and fluorescence detection with IC has resulted in an essential tool to achieve high specificity by subtracting the effect of interference from the total peak area. Validation parameters such as detection limit, quantification limit, linearity, repeatability, recovery rates were obtained and the results proved that this method is suitable for the detection of imidacloprid and carbendazim together in the

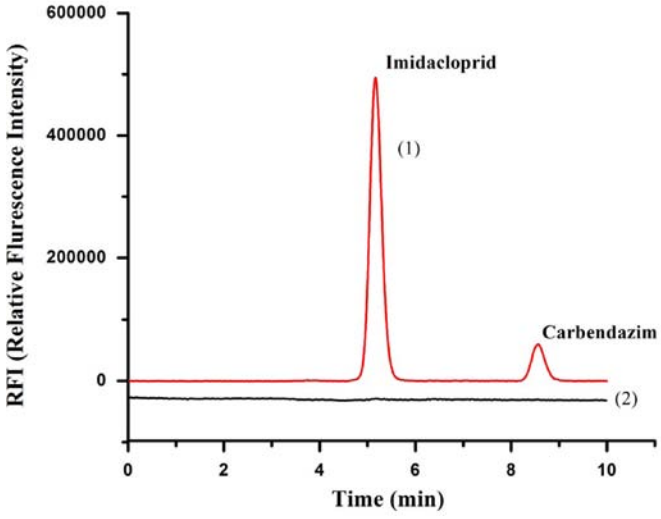

Fig. 5. Standard chromatograms of Imidacloprid and carbendazim (1.0 mg L^{-1}). Column: IonPac® AG11 (50 mm × 4 mm i.d; 13 μm particle size) and IonPac® AS11 (250 mm × 4 mm i.d; 13 μm particle size), Eluent: 40 mM KOH with 10% (v/v) ACN at flow rate of 1.0 mL/min, fluorescence detection at $\lambda_{ex}/\lambda_{em}$=332 nm/367 nm (for Imidacloprid) and $\lambda_{ex}/\lambda_{em}$=247 nm/470 nm (for carbendazim); (1) with UV and (2) without UV radiation.

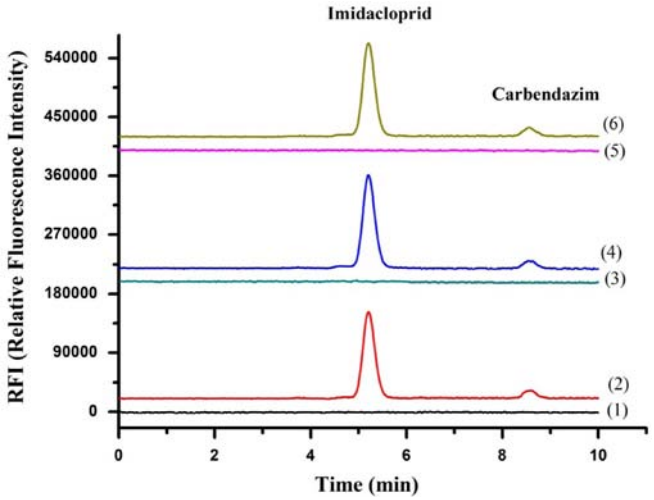

Fig. 6. IC-*hv*-FD chromatograms of real water samples. Spiked level 0.5 mg L^{-1}. Column: IonPac® AG11 (50 mm × 4 mm i.d; 13 μm particle size) and IonPac® AS11 (250 mm × 4 mm i.d; 13 μm particle size). Eluent: 40 mM KOH with 10% (v/v) acetonitrile at flow rate of 1.0 mL min^{-1}, fluorescence detection at $\lambda_{ex}/\lambda_{em}$=332 nm/367 nm (for Imidacloprid) and $\lambda_{ex}/\lambda_{em}$=247 nm/470 nm (for carbendazim). (1) Blank ground water and (2) spiked ground water.

Table 2
Analytical parameters of two pesticides in the standard solutions.

Pesticides	Intercept (S_a)	Slope (S_b)	r	Linear dynamic range (μg L^{-1})	LOD (μg L^{-1})	LOQ (μg L^{-1})	[a]RSD % (n=7)	Lack-of-fit test (P-value)
Imidacloprid	−4417.16 (618.4)	35.12 (1.4)	0.9966	50–10,000	7.8	26	4.5	0.28
Carbendazim	−21,236.37 (6206.1)	37.81 (0.2)	0.9990	200–15,000	67	225	3.9	0.30

[a] The relative standard deviations (RSD) were studied by seven replicates of analytes with concentration of 1.0 mg L^{-1}. S_a and S_b, the standard deviation of intercept and slope, respectively.

Table 3
Spiked recoveries (mean ± [a]SD) of imidacloprid and carbendazim in fortified water samples.

Samples	Imidacloprid			Carbendazim		
	Added (mg L^{-1})	Found ± [a]SD (mg L^{-1})	Recovery (%)	Added (mg L^{-1})	Found ± [a]SD (mg L^{-1})	Recovery (%)
Ground water	0.50	0.52 ± 0.01	104	0.50	0.51 ± 0.01	102
Lake water	0.50	0.47 ± 0.01	94	0.50	0.45 ± 0.02	90
River water	0.50	0.48 ± 0.01	96	0.50	0.46 ± 0.01	92

[a] The average of three determinations.

Table 4
Comparison between IC-*hv*-FD and other methods for the determination of target analytes in real samples.

Technique	Samples	Limit of detection	Reference
HPLC-DAD/TLS	River water and potato	27 μg L^{-1} for imidacloprid	[11]
HPLC-UV	Lemon	210 μg kg^{-1} for carbendazim	[12]
HPLC-DAD	Pepper, tomato and cucumber	10 ng g^{-1} for imidacloprid	[13]
IC-*hv*-FD	Ground water, lake water and river water	7.8 μg L^{-1} for imidacloprid and 67 μg L^{-1} for carbendazim	This work

natural waters without any matrix interference. Small amount of solvents is required for analysis by IC compared to previously reported conventional LC methods. The use of alkaline eluent with a small amount of organic modifier under the anion exchange mode eliminates the post column addition of buffer or alkaline solution, which makes the instrumental system very simple, more economical and convenient, without compromising sensitivity. In our view point, there is an ample scope to increase the application of IC-*hv*-FD for the analysis of pesticides in the future.

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