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Mendeleev Commun., 2014, **24**, 128–129
Mendeleev Communications

Determination of tetramethrin in water by liquid microextraction–capillary electrophoresis

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DOI: 10.1016/j.mencom.2014.03.022

A procedure for the rapid determination of tetramethrin in water by liquid–liquid microextraction–capillary electrophoresis with chemiluminescence detection is proposed.

The determination of poisonous substances in water is a problem of considerable current interest.[1–4] Tetramethrin is widely used in agricultural pest control, but aquatic arthropods are very sensitive to tetramethrin.[5] Liquid–liquid extraction (LLE) and solid phase extraction (SPE) are commonly used for the extraction of tetramethrin;[6,7] however, these methods are time-consuming and the former requires large amounts of toxic organic solvents.

Liquid phase microextraction (LPME) is a miniature liquid–liquid extraction technique using a drop of an organic solvent hanged on the tip of a microsyringe.[8] After the completion of extraction, the total amount of the drop is used in the subsequent analysis, which cannot cause secondary pollution, and is a kind of environmentally friendly sample preparation technology, but the suspension liquid drop falls easily off on account of water sample shaking. Hollow fiber membrane liquid phase microextraction (HF-LPME) overcomes the fault; the extraction organic solvents are fixed in a microporous structure of the hollow fiber membrane, and macromolecular matter, suspended particles and bacteria are filtered off by the hollow fiber membrane. Therefore, HF-LPME can be applied to the analysis of complex samples. LPME has been widely used as a sample preparation technique for the determination of chlorine-containing pesticides, organophosphorus pesticides, fungicides and herbicides.[9,10]

Capillary electrophoresis (CE) with UV-VIS, laser-induced fluorescence,[11,12] electrochemical,[11] electrochemical luminescence[13] and chemiluminescence (CL)[15,16] detection is a simple, efficient and rapid separation technique with inexpensive instrumentation. CL detection has considerable advantages over fluorescence and photometric detection techniques because it does not require an exciting light source and has a higher signal-to-noise ratio and sensitivity than those in fluorescence detection due to the absence of Rayleigh and Raman scattering noises.

The instrumentation included an MPI-B type CL analysis test system (Xi'an Remex Electronic Technology Co.), a PHS-3C acidometer (Shanghai Leici Analysis Instrument Factory) and a quartz capillary (Hebei Yong Nian Optical Fiber Factory). Commercial reagents of analytical grade and solvents were used. The stock solution (10 mg dm^{-3}) of tetramethrin (China Pharmaceutical and Biological Products Assay Institute) was prepared in twice-distilled water and stored in a refrigerator; it was diluted to a required concentration before the experiment.

Figure 1 shows the microextraction device. A buffer solution (2.0 ml) and a sample solution (total volume, 10.0 ml) were placed in a 10 ml vessel, and the contents were stirred with a Model 79-1 magnetic force heating stirrer (Huapuda Teaching Instrument Co., China). A 25 μl flat-cut HPLC syringe was used to fix a porous hollow fiber during extraction. The solution

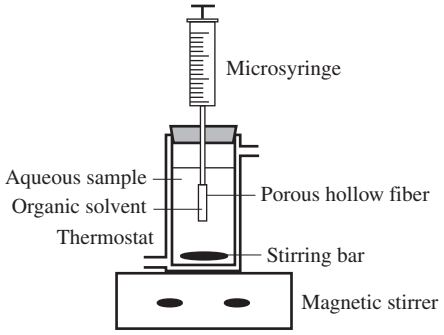

Figure 1 The device for porous hollow fiber based liquid–liquid microextraction (LLME).

was kept at a constant temperature by a Model CS-501 super thermostat. The porous hollow fiber of polypropylene (inner diameter, 800 μm; length, 5 cm; capacity, 25 μl; wall thickness, 200 μm) was purchased from Tianjin Motimo Membrane Technology Co. (China). Before the liquid–liquid extraction, the porous hollow fiber was ultrasonically washed with HPLC-grade acetonitrile for 15 s, dried in air and ultrasonically treated in methanol for 15 s. Then, a certain amount of an organic extractant (dibutyl phthalate) was added to the porous hollow fiber tube.

Figure 2 shows a CE-CL three-way connector. The inner diameter and the effective length of a separation capillary were 75 μm and 40 cm, respectively; the inner diameter and the length of a reaction capillary were 320 μm and 5 cm, respectively. The outer polyimide coatings of the separation and reaction capillaries were removed at the ends, and the ends were inserted into the three-way connector. The reagent pipe end was connected to a flow-limiting capillary (100 μm in inner diameter, 10 cm in length), and the chemiluminescence reagent luminol (Shanghai Chemical Reagent Corporation, China) passed through the reagent pipe into the connector. A test window about 1 cm long was located above a photomultiplier tube close to the end of the reaction capillary, and the whole connector and test window were placed in a cassette to avoid external light source interferences. The sample was injected at 15 kV×3 s, and the separation voltage

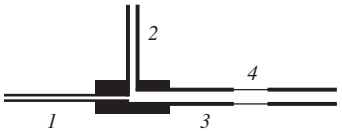

Figure 2 Schematic diagram of the three-way connector: (*1*) separation capillary, (*2*) reagent capillary, (*3*) reaction capillary and (*4*) detection window.

Table 1 The effect of extraction solvents on the extraction efficiency. Extraction time, 30 min.

Extraction solvents	Enrichment factor (%)	Extraction solvents	Enrichment factor (%)
Dibutyl phthalate	56.4	Toluene	45.2
o-Xylene	50.6	Benzene	41.8
Hexane	47.4		

Table 2 The effect of solvent volume on the extraction efficiency.

Solvent volume/μl	CL intensity/ counts	Solvent volume/μl	CL intensity/ counts
10	9.76	25	19.57
15	17.81	30	19.55
20	19.62	35	19.58

Table 3 The effect of extraction time on the extraction efficiency.

Extraction time/min	CL intensity/ counts	Extraction time/min	CL intensity/ counts
5	5.80	30	20.80
10	7.98	40	21.90
20	17.75		

was 15 kV. Before use, the capillary was washed with 0.1 mol dm^{-3} sodium hydroxide, water and 10 mmol dm^{-3} phosphate buffer solution for 5 min; all of the solutions should be filtered through a 0.22 μm hybrid fiber membrane. To keep the reproducibility, the high voltage of photomultiplier tubes should be set to 800 V.

Benzene, toluene, *o*-xylene, hexane and dibutyl phthalate can be used as solvents for the extraction of tetramethrin (Table 1), but dibutyl phthalate is an optimum extractant. Table 2 shows the results of tetramethrin extraction by various volumes of dibutyl phthalate for 30 min; it is evident that a proper extraction volume is 25 μl. Table 3 indicates that the CL intensity increased rapidly at the earlier stages of extraction. In order to reach high sensitivity and to save time, we chose an extraction time of 30 min. An optimum value was pH 10.0, at which the highest extraction efficiency was observed (Figure 3); thus, we used a 12.0 mmol dm^{-3} borax buffer solution (pH 10.0) to adjust the acidity of water samples. The optimal concentration of luminol was 5.0 mmol dm^{-3}, and the concentration of a potassium ferricyanide solution was 5.0 mmol dm^{-3}, which was prepared with 0.1 mol dm^{-3} sodium hydroxide. An optimal separation voltage of 15 kV was chosen.

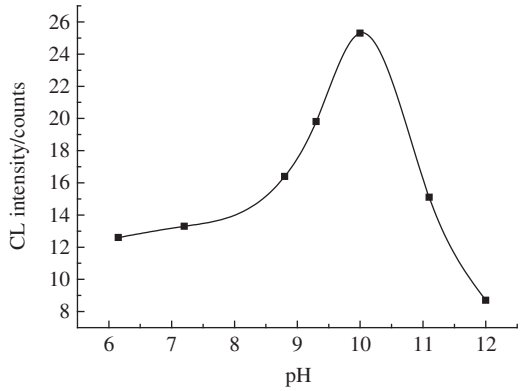

Figure 3 The effect of pH on the extraction of tetramethrin.

Table 4 Determination of tetramethrin in water (number of repeats, 5).

Added concentration of standard material/ μmol dm^{-3}	Found concentration of tetramethrin/ μmol dm^{-3}	Recovery ratio (%)	RSD (%)
0	5.6	—	0.19
10	15.5	99.4	0.20
20	25.8	100.8	0.18

The molecules of β-cyclodextrins (β-CDs) have a hydrophobic cavity, which can form inclusion complexes. The high electronic density of the β-CD cavity can activate the electrons of the inclusion complexes to change the optical properties of guest molecules and β-CDs. The addition of β-CDs to the buffer solution can enhance the strength of chemical luminescence. We found that an optimal β-CD concentration was 5.0 mmol dm^{-3}. The optimized conditions of electrophoresis were the following: running buffer of 12 mmol dm^{-3} borax, 4 mmol dm^{-3} sodium hydroxide containing 5 mmol dm^{-3} β-CD and 5 mmol dm^{-3} luminol; running voltage, 15 kV; sample injection time, 3 s in the motor-driven mode. The CE-CL method can be used for the direct determination of tetramethrin in water.

Under the optimal conditions, the strength of chemical luminescence was a linear function of tetramethrin concentration in a range from 1.0 to ~40 μmol dm^{-3}, and the linear regression equation was $y = 7280x + 19$, $r = 0.9988$. After the determination of 2.0 μmol dm^{-3} of tetramethrin repeated five times, the relative standard deviations (RSDs) of peak heights and migration times were 2.0 and 0.5%, respectively. The detection limit (3σ) was 0.06 μmol dm^{-3}. The sample recovery ratios varied from 99.4 to ~100.8% (Table 4).

This work was supported by the National Natural Science Foundation of China (project no. 21203003).

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Received: 8th October 2013; Com. 13/4223