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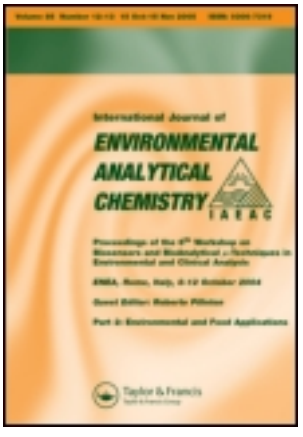

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A simple and rapid method using a microhotplate-based preconcentrator and an ion mobility spectrometer (IMS) is proposed for the detection of malathion in water. The preconcentrator is prepared by micro-electro-mechanical system (MEMS) process. Coated with Polydimethylsiloxane (PDMS), it has the advantages of solvent-less, low energy cost, self-heating and ease to combine with IMS. The operating conditions of the preconcentrator-IMS system, such as extraction time, extraction temperature, agitation speed and desorption temperature, were optimised. Using the preconcentrator, the sampling procedure can be simplified and the detection limit of the system can be decreased. A linear relationship between the IMS response and the concentration of the analyte solution was verified. The malathion detection limit based on 3 times the baseline noise is $0.43\,\mu g\,L^{-1}$ and the total analysis time is less than 30 minutes.

Keywords: preconcentrator; solid-phase microextraction; ion mobility spectrometer; malathion detection

1. Introduction

Pesticides are a group of chemicals used in agriculture to control pests and enhance agricultural production. Billions of pounds of pesticide are used in agriculture every year and a large portion of them are organo-phosphorus pesticides (OPPs) [1]. These compounds act as cholinesterase inhibitors in insects and mammals, and bring about a non-reversible phosphorylation of esterases in the organisms' central nervous system [2]. Along with the vast consumption, some of them are continually released into the water system through permeation and scouring. The water system, including underground and surface water, is often the source of drinking water. Therefore, it is crucial to develop rapid, sensitive and easily operated field methods to detect OPPs in environmental water [3]. At present, the most widely used methods for OPPs' detection involves gas chromatography (GC), high-performance liquid chromatography (HPLC), gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-tandem mass spectrometry (LC-MS-MS) [4–7]. Although these methods offer quantitative analysis with high sensitivity, they are time consuming, expensive, and have to be operated by highly trained technicians. Therefore, these methods are not suitable for field applications.

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Ion mobility spectrometry is an ion separation technique using the gas-phase mobility of ions in a weak electric field to characterise substances [8,9]. Because of its portability, high sensitivity and rapid determination, the ion mobility spectrometer (IMS) has been developed as a powerful tool for qualitative and quantitative analysis of explosives, illicit drugs and organo-phosphorus compounds [10,11]. OPPs have high proton affinities, and therefore can be easily protonated, even in the presence of several other constituents in ambient air [12]. Compared with conventional OPPs detection methods, IMS has the advantages of portability, avoid use of vacuum equipment, fast detection and easy operation. Thus, it is widely used in the detection of OPPs [13–15]. Until now, the detection limit is not as low as the conventional methods.

In order to improve the sensitivity of OPPs detection, sample preparation becomes a crucial step in the analytical process. A variety of pretreatment methods have been established for separation and preconcentration of OPPs including liquid-liquid extraction (LLE), solid-phase extraction (SPE), liquid-phase microextraction (LPME) and solid-phase microextraction (SPME). The conventional LLE often needs large amounts of toxic solvent and is a time-consuming procedure. Although SPE is less time-consuming than LLE and has been applied in many environmental fields, it still requires toxic organic solvent during the elution step [16]. SPME integrates sampling, extraction, concentration and sample introduction into a single step without the use of solvent. Polydimethylsiloxane (PDMS) is the most widely used coating for SPME. The coupling of SPME to IMS offers a rapid sampling and detection, and usually traditional SPME devices were used [17–21]. However, because of the large volume, large power consumption and fragile construction, SPME is not well suited to use with IMS. To overcome these shortcomings, some preconcentrators which facilitate the combination with IMS were reported [22–26]. Most of the devices were used for collecting vapours or aerosols, such as explosives, drugs and volatile organic compounds, in air, and none of them was used for OPPs in water.

In this work, a microhotplate-based preconcentrator was constructed. Malathion, one of the typical OPPs, was extracted from water using the preconcentrator and detected by coupling the preconcentrator to an IMS. The extraction and detection parameters, such as extraction time, extraction temperature and desorption temperature, were optimised.

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2. Experimental

2.1 *Materials and instruments*

Malathion (purity 90%) was purchased from Tianjin Huayu Pesticide Co. (Tianjin, China). PDMS (Sylgard 184 Silicone Elastomer) came from Dow Corning (Midland, MI, USA). Methanol (analytical grade) came from Beijing Chemical Reagent Co. (Beijing, China). Fresh stock solution ($1\,g\,L^{-1}$) was prepared weekly by dissolving 50 mg of malathion in 50 mL methanol and stored at 4°C. Before each experiment, the stock solution was diluted with deionised water to given concentrations.

The IMS system with a ^{63}Ni radioactive ionisation source was constructed in our laboratory. The operation conditions of the IMS used in this work was shown in Table 1. The ion mobility spectra were recorded by a signal processing system.

2.2 *Fabrication of the preconcentrator*

As shown in Figure 1a, the preconcentrator was composed of a hollow polytetrafluoroethylene (PTFE) cylinder, a PTFE printed circuit board (PCB) and a microhotplate

Table 1. Summary of the operation conditions.

Parameter	Setting
Drift tube length	4.3 cm
Electric field	233 V cm^{-1}
Kick-out pulse	0.2 ms
Drift tube temperature	205 ± 1°C
Drift tube pressure	755 torr
Detection mode	Positive ion mode (ammonium dopant)
Carrier gas	Air
Carrier gas flow	115 mL min^{-1}

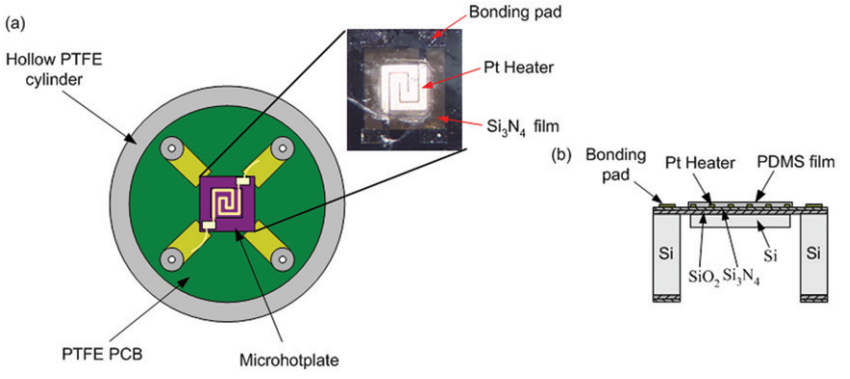

Figure 1. (a) The schematic diagram of the preconcentrator and the micrograph of the microhotplate. (b) The cross-sectional view of the microhotplate.

coated with PDMS. The microhotplate was packaged on the PTFE PCB, which was connected electrically with the power supply.

The microhotplate (shown in Figure 1b) with size of 3.5 mm × 3.5 mm was fabricated by MEMS process. The process mainly included thermal oxidation and low pressure chemical vapour deposition (LPCVD) to form SiO_2 and Si_3N_4 film; the lift-off step to form the Pt heater on the area of 1.35 mm × 1.35 mm. Deep reactive ion etching (DRIE) process was also included to form the windows of 2.35 mm × 2.35 mm in area and the silicon layer, which could improve the temperature uniformity of the heated area. The PDMS film was spin-coated on a PTFE plate and heat cured according to the manufacturer's literature. Film thickness was controlled by spin speed and calibrated by a surface profiler (ALPHA-STEP 500, KLA-Tencor Corp. Milpitas, CA, USA). A 110 μm of the film thickness was required. After stripping from the PTFE plate, the PDMS film was cut and glued to the microhotplate using a small amount of diluted PDMS and then purged with nitrogen at about 230°C for 2 hours before use.

2.3 *Procedure of malathion detection*

A 25 mL glass vial was used in which there are a 20 mL sample solution and a magnetic stirring bar. The preconcentrator was immersed in the aqueous phase and stirred at a

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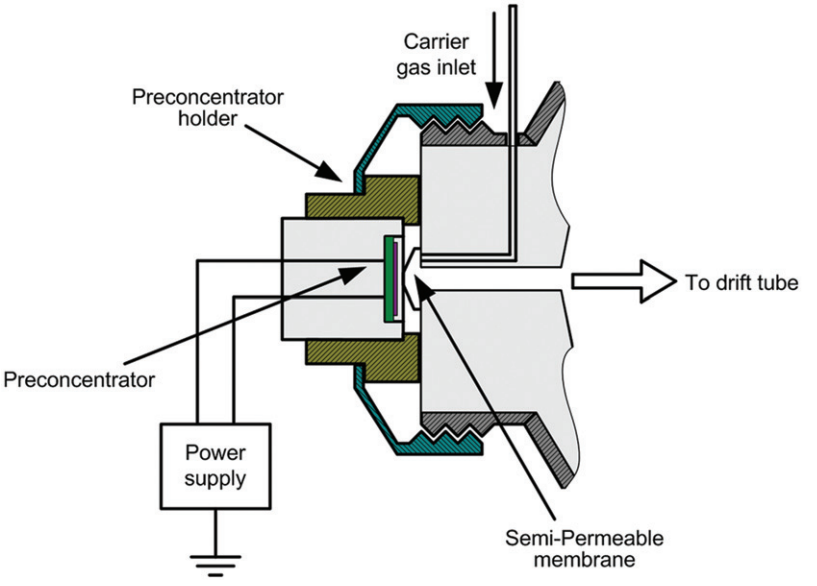

Figure 2. The schematic diagram of preconcentrator-IMS interface.

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moderate speed (~400 rpm) for 20 min at room temperature. After extraction, the preconcentrator was briefly dried with a tissue paper and then connected to the IMS (shown in Figure 2). When desorbing, a constant voltage was applied to the preconcentrator to reach the desorption temperature. The desorbed vapours were diffused into the IMS through a semi-permeable membrane which protects the detector from contaminations. The ion mobility spectra were recorded by the signal processing system when the IMS response reached a maximum and the product ion peak was detected by the home-made peak identification program. Then the preconcentrator was disconnected from IMS and heated to ~230°C for 5 min to clean the PDMS film. Three replicates were studied for each variable. As the method was supposed for field applications, simple operations were required; besides, the effects of pH and salt addition were small; and therefore, they are not discussed in this paper.

3. Results and discussion

3.1 *Reduced mobility of malathion*

Malathion was introduced into IMS to determine its reduced mobility value by two processes. An amount of 1 μL malathion solution with the concentration of 1 mg L^{-1} was pipetted on the microhotplate without a PDMS film. Using the interface shown in Figure 2, the sample solution was heated to 200°C to complete the detection. In the other introduction process, a preconcentrator was put into a 20 mL malathion solution with the concentration of 50 μg L^{-1} for 20 min for the extraction and then it was heated to 200°C to introduce the sample.

The ion mobility K is calculated according to Equation (1) [9]:

$$K = \frac{v}{E} = \frac{L^2}{Vt_d} \tag{1}$$

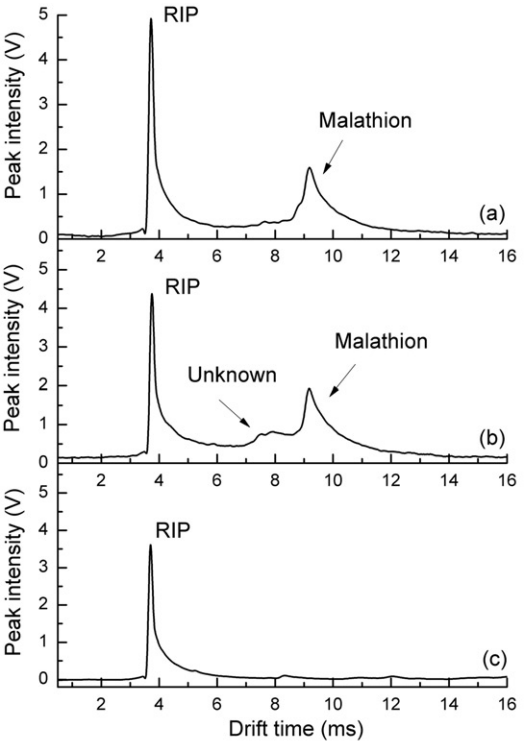

Figure 3. Ion mobility spectra of malathion introduced using the microhotplate with and without the PDMS. (a) 50 μg L^{-1} malathion solution with PDMS coating. (b) 1 mg L^{-1} malathion solution without PDMS coating. (c) Blank spectrum.

where L is the length of the drift tube, t_d is the drift time and V is the voltage applied across the ion drift region. The unit of K is $cm^2\ V^{-1}\ s^{-1}$. In order to correct the variations in temperature and pressure, the mobility is normalised to 273 K and 760 torr yielding a reduced mobiity (K_0), according to Equation (2):

$$K_0 = K \times \frac{273}{T} \times \frac{P}{760} \tag{2}$$

where T and P are the temperature and the pressure of the drift tube with the units of Kelvin and torr.

The ion mobility spectra of malathion introduced using the preconcentrator with and without the PDMS are shown in Figure 3.

The drift time of malathion is 9.18 ms. It can be seen that the drift times of malathion are the same in two introduction processes. According to Equations (1) and (2), the reduced mobility of malathion is $1.14 \pm 0.02\ cm^2\ V^{-1}\ s^{-1}$, close to the value reported in the literature [14,15,27] in which the malathion reduced mobility values of 1.17, 1.11 and 1.13 were reported.

3.2 *Extraction time*

An extraction time profile for malathion was obtained with the preconcentrator. Stock solution was diluted to 50 μg L^{-1} with deionised water. Extractions of 1, 3, 5, 10,

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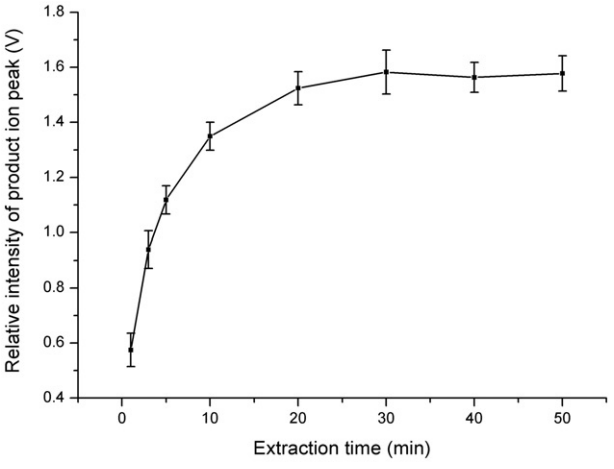

Figure 4. Product ion peak intensity vs. extraction time (room temperature extraction, desorption temperature ~200°C).

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20, 30, 40 and 50 min were performed at room temperature with moderate agitation (~400 rpm) for the solution. Each extraction was carried out with three replicates. The relative intensity of product ion peak was calculated by the intensity of product ion peak subtracting baseline which is the average of points corresponding to the malathion peak position in the blank. A graph of relative intensity of product ion peak as a function of extraction time was plotted in Figure 4. It can be seen that the product ion peak increased rapidly with the extraction time. At extraction times longer than 20 min, the curve approached a plateau region indicating the equilibrium of diffusion had been established between the sample solution and coating. Under perfect agitation conditions, the equilibrium time is determined by the diffusion of analyte in the coating and the thickness of the coating [28]. The diffusion is determined by the properties of coating and analyte. Under equilibrium conditions, the extraction time is proportional to the square of the coating thickness [28]. The thinner the coating, the shorter the equilibrium time is. As a thinner coating extracts less analyte, in order to balance the extraction time and the detectable amount of analyte, a 110 μm coating thickness and a 20 min extraction time were adopted.

3.3 *Extraction temperature*

The IMS responses at four different temperatures (room temperature (~20°C), 40°C, 60°C and 80°C) were evaluated by plotting the relative intensity of product ion peak versus the temperature of extraction (shown in Figure 5). From the figure it can be seen that the extraction efficiency increases as the solution temperature is increased from ~20 to 60°C; but a decrease in absorption capacity is observed when temperature increases up to 80°C. The temperature variation affects the solubility of analyte in both the polymer and water and leads to the change of the distribution constant. High extraction temperature enhances the mobility of the molecules, improves the extraction rate and, therefore, shortens the extraction time. However, because the absorption is an exothermic process, increasing the extraction temperature will decrease the distribution constant of the analyte

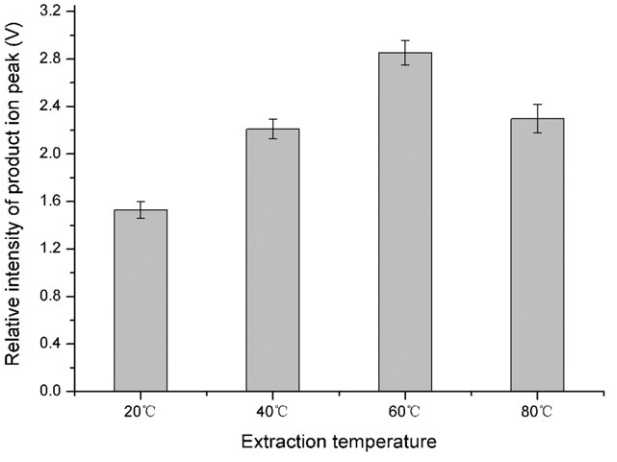

Figure 5. Extraction temperature profile for 50 μg L^{-1} malathion solution. (Extraction time 20 min, desorption temperature ~200°C, moderate speed agitation.)

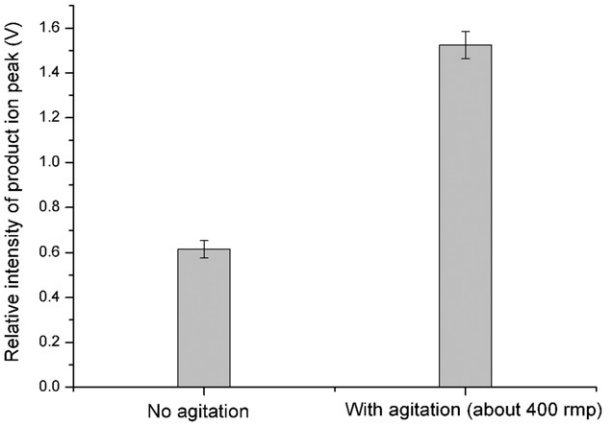

Figure 6. Effect of agitation on the relative intensity of product ion peak. (Extraction time 20 min, desorption temperature ~200°C.)

between aqueous solution and extraction phase. And the field applications also require simple operation. Therefore, room temperature was selected as the extraction temperature.

3.4 *Agitation effect*

Sample agitation plays an important role in reducing the extraction time and enhancing extraction efficiency. In this paper, two modes of agitation were investigated: no agitation and moderate speed agitation (~400 rpm). Figure 6 shows the IMS responses for 50 μg L^{-1} malathion with different agitation modes.

From Figure 6, it can be seen that the relative intensity of product ion peak increased greatly with the moderate speed agitation. There is an aqueous layer surrounding the extraction phase where the analyte has been depleted. The analyte has to penetrate the layer from the bulk water phase into the coating which limits the rate of mass transport

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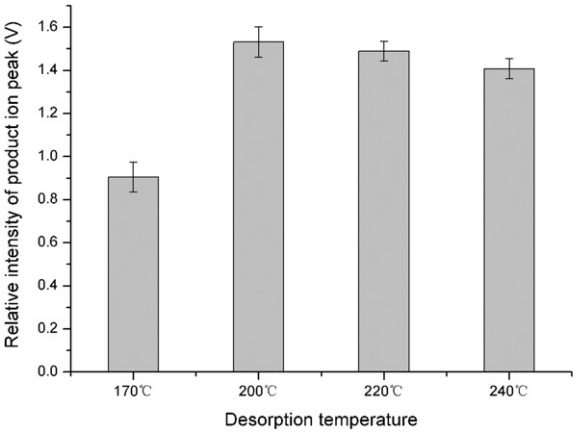

Figure 7. The relative intensity of product ion peak in IMS spectra recorded from 50 μg L^{-1} malathion solution at different desorption temperatures. (Extraction time: 20 min, extraction temperature: room temperature, moderate agitation.)

and slows down the extraction. Therefore, the extraction time with the unstirred solution is much longer than the one with the stirred solution. Sample agitation eliminates the depleted layer and accelerates equilibrium.

3.5 *Desorption temperature*

The temperature of microhotplate was calculated by measuring the heater's resistance. The relationship between temperature and resistance was calibrated using a resistance furnace.

Figure 7 shows the IMS response for the detection of 50 μg L^{-1} malathion solution with the desorption temperature of 170, 200, 220 and 240°C. The desorption time was 30 seconds. From the figure it can be seen that the relative intensity of product ion peak increases when the desorption temperature is raised from 170 to 200°C; then the response decreases when the desorption temperature increases to 240°C. With the increase of desorption temperature, the desorption rate of the malathion molecule is increased. This favoured the formation of a high concentration pulse in a short time and, therefore, to increase the response of IMS. However, due to the decomposition, the relative intensity of product ion peak declines when the desorption temperature exceeds 200°C. In addition, high desorption temperature may shorten the life-span of the polymeric coating. Thus, 200°C was adopted as the desorption temperature.

3.6 *Calibration*

The amount of the analyte extracted by the extraction phase n_1 is determined by the following equation [28]:

$$n_1 = \frac{KV_1V_2C_2^0}{KV_1 + V_2} \tag{3}$$

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Table 2. Sensitivity, Linear range, LOD and repeatability for the detection of malathion.

Slope (V/(μg L^{-1}))	Linear range (μg L^{-1})	Linearity (R^2)	LOD (μg L^{-1})	RSD (%)[a]
0.02685	1.0 to 70.0	0.9826	0.43	5.24

[a]RSD, Relative standard deviation, $n = 3$, at the concentration of 50 μg L^{-1}.

where K is the distribution constant of the analyte between extraction phase and aqueous solution. V_1 is the volume of the extraction phase, V_2 is the volume of sample solution, and C_2^0 is the initial concentration of the sample solution. It can be seen that the amount of analyte absorbed by the coating at equilibrium is proportional to the initial analyte concentration tested.

To validate the proposed method, malathion solutions with the concentrations of 1, 10, 30, 50 and 70 μg L^{-1} were tested. The relative intensity of product ion peak increases linearly along with the concentration of malathion solution ($R^2 = 0.9826$) ranging from 1 to 70 μg L^{-1}. Table 2 summarises the regression data for the detection of malathion. The limit of detection (LOD) is calculated to be 0.43 μg L^{-1} based on 3 times the baseline noise.

The enrichment effect of the preconcnetrator was investigated by comparing the IMS response while using the preconcentrator with an equilibrium extraction and the response without any preconcentration. In the latter measurement, 50 μg L^{-1} malathion solution (same volume as the PDMS film) was pipetted on the preconcentrator without PDMS. There was no malathion response in IMS spectra.

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4. Conclusions

This paper offers a simple and rapid method to detect malathion in water. A microhotplate-based preconcentrator is prepared by a MEMS process and a preconcentrator-IMS system is proposed based on the solid-phase microextraction. The preconcentrator integrates extraction, concentration and sample introduction into one single step and has the advantages of self-heating, low power consumption and ease of use. It can be integrated well with IMS for the detection of OPPs.

The operation condition of the preconcentrator-IMS system for the detection of malathion has been optimised. The moderate agitation (~400 rpm), 20 min extraction at room temperature are adopted on the absorption stage. The desorption temperature is 200°C to obtain a large IMS response. A linear relationship between the IMS response and the concentration of malathion solution is verified. The malathion detection limit is 0.43 μg L^{-1}.

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