Determination of cadmium in drinking and wastewater by dispersive liquid-liquid microextraction slotted quartz tube flame atomic absorption spectrometry system after complexation with a new imidazole based ligand

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Oral Presentation

Introduction

Cadmium is a widely used metal in various fields but it has the potential to cause serious health problems for humans. The Environmental Protection Agency (EPA) and World Health Organization (WHO) have therefore limited cadmium level in drinking water to 5.0 μg L^{-1} and 3.0 μg L^{-1}, respectively. Flame atomic absorption spectrometry (FAAS) is a robust analytical instrument for routine determinations but its sensitivity is not high enough to determine the limits set by EPA and WHO for cadmium (Fırat et al. 2017). Various microextraction techniques are present in literature and they can be used to preconcentrate analytes prior to determination. Dispersive liquid-liquid microextraction (DLLME) is a typical example which only requires a simple experimental set up to complete a rapid extraction and obtain high enrichment factors (Turan et al. 2017). Slotted quartz tube (SQT) is a simple material that can be cut and fitted onto the burner head of the FAAS. The SQT can be used to increase the residence time of atoms in the flame, thereby, enhancing sensitivity by 2-5 times depending on type of element (Özzeybek et al. 2017). The aim of this study was to preconcentrate cadmium using dispersive liquid-liquid microextraction after complexing with 2-(4-Methylphenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (2-MIP). An SQT was also coupled to the FAAS to further enhance the sensitivity for cadmium determination.

Materials and methods

An Analytik Jena NovAA 300 FAAS (air/acetylene) instrument was fitted with a slotted quartz tube (I.D: 16 mm, O.D: 18 mm) and used for cadmium determinations. Cadmium hollow cathode lamp was operated at 2.0 mA, 0.50 nm spectral bandpass and 228.8 nm analytical line. Background correction was done with a deuterium (D_2) lamp. Analytical grade reagents were used throughout the study. All working standard solutions were prepared from a 1000 mg L^{-1} Cd standard stock solution. 2-MIP stock solution, prepared in methanol was used for cadmium complex formation. Chemicals and reagents used in developing the DLLME method included ethanol, methanol, chloroform, carbon tetrachloride, dichloromethane, isopropyl alcohol, potassium chloride, potassium nitrate and sodium chloride, all obtained from Merck (Germany). A mixture of chloroform (0.40 mL) and methanol (3.0 mL) was injected into aqueous cadmium complex prepared by adding 1.0 mL 2-MIP and 0.50 mL buffer solution to 8.0 mL aqueous cadmium standard. The extraction solution was centrifuged for 2.0 min at 3461 *g*, and the organic phase totally evaporated and redissolved in concentrated nitric acid for FAAS determination.

Results and discussions

The method was developed in three optimization stages. Optimizations were made is a stepwise manner, varying one parameter at a time while keeping others fixed. The first stage was complex formation, where parameters such as pH and amount of buffer solution, ligand concentration and amount, and mixing period were optimized. In the second stage, parameters including types and amounts of extraction and dispersive solvents, salt effect, mixing type and period were optimized to obtain high DLLME output. The final stage was the optimization of SQT parameters including sample and fuel flow rates, and SQT height. Under optimum conditions (Table 1), the figures of merit of FAAS systems were determined as shown in Table 2. The detection limits fell below the WHO and EPA cadmium limits for drinking water. The applicability of the method to real samples was tested by performing recovery tests for tap, well and waste water, which yielded percent recoveries between 88% and 112%.

Table 1. Optimized parameters of the DLLME-SQT-FAAS.

Parameter	Value
pH of buffer solution (amount)	pH 9 (0.50 mL)
Ligand concentration (amount)	0.05% w/v (1.0 mL)
Mixing Period (complex formation)	15 s
Extraction solvent (amount)	Chloroform (400 µL)
Dispersive solvent (amount)	Methanol (3.0 mL)
Mixing type (period)	Hand shaking (0.50 min)
Sample/Acetylene flow rate (SQT height)	7.24 mL min^{-1}/40 L h^{-1} (2.0 mm)

Table 2. Analytical performance of the systems under study.

	LOD, µg L^{-1}	LOQ, µg L^{-1}	%RSD	Range, µg L^{-1}
FAAS	42	140	9.60	100-2000
SQT-FAAS	11.9	39.6	6.30	50- 1000
DLLME-FAAS	2.06	6.86	8.21	7.5- 125
DLLME-SQT-FAAS	0.57	1.90	4.17	2.0- 50

Conclusions

The DLLME-SQT-FAAS method only required simple and cheap materials but yielded an enhancement of about 74 times the conventional FAAS. The ligand (2-(4-Methylphenyl)-1H-imidazo[4,5-f][1,10]phenanthroline) was synthesized and used for the first time to form a metal complex for preconcentration. The method was applied to tap, well and waste water, and the percent recoveries obtained for different concentrations were appreciable.

References

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