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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Presentation Steps

General knowledge about Cadmium

How can we determine Cadmium?

What is the aim of our study
Cadmium is a widely used metal in various fields:
- Plating Industry
- Nuclear Reactors
- Rechargeable Batteries
Health Effects

Liver  Lungs  Kidneys  Central nervous system  Eyes  Brain
Maximum Allowable Limit of Cadmium

The Environmental Protection Agency (EPA) : \( 5.0 \, \mu g/L \) in drinking water

World Health Organization (WHO) : \( 3.0 \, \mu g/L \) in drinking water
Analytical Determination Methods

- Flame atomic absorption spectrometry
- Inductively coupled plasma mass spectrometry
- Inductively coupled plasma atomic emission spectrometry
- Atomic fluorescence spectrometry
- Spectrophotometry
Preconcentration Techniques

- Liquid-liquid extraction
- Solid-phase extraction
- Cloud point extraction
Microextraction methods

- Homogeneous liquid-liquid microextraction (HLLME)
- Single-drop microextraction (SDME)
- Solid phase microextraction (SPME)
- Dispersive liquid–liquid microextraction (DLLME)
Advantages of DLLME

- Less time-consuming
- High enrichment factors
- Lower cost
- Smaller amounts of organic solvents
SLOTTED QUARTZ TUBE (SQ T)
Optimization Parameters

- pH of buffer solution
- Ligand concentration
- Mixing Period (complex formation)
- Extraction solvent
- Dispersive solvent
- Mixing type (period)
- Sample/Acetylene flow rate (SQT height)
pH of buffer solution

pH: 5.0, 6.0, 7.0, 8.0, 9.0, 10, 11

pH Optimization
Ligand Concentration

0.20 – 0.50 – 1.0 – 2.0 g/L

Optimization of Ligand Concentration
Mixing Period (complex formation)

0.25 – 5.0 – 10 – 20 – 45 – 60 - 90 min
Extraction solvent type

- Chloroform
- 1,2 dichloromethane
- Carbontetrachloride

Optimization of Extraction Solvent

Absorbance

Types of Extraction Solvent

- chloroform
- 1,2dichloromethane
- CCl4
Extraction Solvent Amount

200, 250, 300, 350, 350, 400, 450 µL
Dispersive solvent

Methanol, Ethanol, 2-propanol

Optimization of Dispersive Solvent

Absorbance

Types of Dispersive Solvent

Methanol

Ethanol

2-propanol
Dispersive Solvent Amount

1.0, 2.0, 3.0, 4.0 mL

Optimization of Dispersive Solvent Amount

Absorbance

Amount of dispersive solvent, mL
Mixing type

Hand, Shaker, Vortex, Sonic

Optimization of Shaking Type

- Absorbance
- Type of shaking

![Bar chart showing absorbance for different shaking types: Hand, Shaker, Vortex, Sonication]
Optimization of Shaking Period

0.50 – 1.0 – 5.0 -10.0 min

Optimization of Shaking Time

Absorbance vs. Shaking Time, min

Graph showing absorbance values at different shaking times.
Sample/Acetylene flow rate (SQT height)

- 7.24 mL/min
- 40 L/h
- 2.0 mm
### Experimental Parameters of the Study

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand Concentration</td>
<td>0.05% (w/v) Phen-me</td>
</tr>
<tr>
<td>Ligand Amount</td>
<td>1.0 mL</td>
</tr>
<tr>
<td>pH of Buffer Solution</td>
<td>9.0</td>
</tr>
<tr>
<td>Amount of Buffer solution</td>
<td>0.5 mL</td>
</tr>
<tr>
<td>Extraction Solvent Type</td>
<td>CHCl₃</td>
</tr>
<tr>
<td>Extraction Solvent Volume</td>
<td>400 µL</td>
</tr>
<tr>
<td>Dispersive Solvent Type</td>
<td>CH₃OH</td>
</tr>
<tr>
<td>Dispersive Solvent Volume</td>
<td>3.0 mL</td>
</tr>
<tr>
<td>Mixing Type</td>
<td>Manuel Shaking</td>
</tr>
<tr>
<td>Mixing Period</td>
<td>15 s</td>
</tr>
<tr>
<td>Eluent Type</td>
<td>HNO₃ (65%)</td>
</tr>
<tr>
<td>Eluent Amount</td>
<td>150 µL</td>
</tr>
<tr>
<td>Acetylene flow rate</td>
<td>40 L/h</td>
</tr>
<tr>
<td>Sample Flow Rate</td>
<td>7.20 mL/min</td>
</tr>
<tr>
<td>SQT Height</td>
<td>2.0 mm</td>
</tr>
</tbody>
</table>
Calibration plot

\[ y = 0.0118x - 0.0038 \]

\[ R^2 = 0.9992 \]
## Analytical performance of the systems under the optimum conditions

<table>
<thead>
<tr>
<th>Method</th>
<th>LOD (µg/L)</th>
<th>LOQ (µg/L)</th>
<th>% RSD</th>
<th>Range</th>
<th>Sensitivity increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAAS</td>
<td>42.0</td>
<td>140.0</td>
<td>9.60</td>
<td>100-2000</td>
<td></td>
</tr>
<tr>
<td>SQT-FAAS</td>
<td>11.90</td>
<td>39.60</td>
<td>6.30</td>
<td>50-1000</td>
<td>3.53</td>
</tr>
<tr>
<td>DLLME-FAAS</td>
<td>2.06</td>
<td>6.88</td>
<td>8.21</td>
<td>7.50-125</td>
<td>20.39</td>
</tr>
<tr>
<td>DLLME-SQT-FAAS</td>
<td>0.57</td>
<td>1.90</td>
<td>4.17</td>
<td>2.00-50</td>
<td>73.68</td>
</tr>
</tbody>
</table>
## Recovery Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>10 µg L⁻¹</th>
<th>20 µg L⁻¹</th>
<th>40 µg L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste Water</td>
<td>100.56 ± 2.96</td>
<td>88.17 ± 0.64</td>
<td>88.58 ± 2.60</td>
</tr>
<tr>
<td>Tap Water</td>
<td>112.05 ± 3.29</td>
<td></td>
<td>103.01 ± 3.03</td>
</tr>
<tr>
<td>Ground Water</td>
<td>101.29 ± 12.99</td>
<td>105.02 ± 1.28</td>
<td>98.57 ± 1.58</td>
</tr>
</tbody>
</table>
Results

The DLLME-SQT-FAAS method only required simple and cheap materials but yielded an enhancement of about 73.68 times the conventional FAAS.

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%.

LOD, LOQ
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