Preconcentration Ultra Trace of Mercury (II) in Water Samples Using Dispersive Liquid-liquid Microextraction with Alanine Salicylaldehyde and Determination by CV-AAS

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Abstract: A simple method has been developed for the preconcentration of mercury based on Dispersive liquid-liquid microextraction (DLLME) technique was successfully used as a sample preparation method for cold vapor atomic absorption spectrometry (CV AAS). NADP (chelating agent) was rapidly injected by syringe into the water sample containing Mercury ions (interest analyte). At this stage, mercury reacts with alanine-salicylaldehyde (ALSA), and therefore, hydrophobic complex forms which is extracted into the fine droplets of carbon tetrachloride. Some effective parameters, such as extraction and disperser solvent type and their volume, extraction time, salt effect, pH and concentration of the chelating agent have been optimized. Under the optimum conditions, the enrichment factor 122 was obtained from only 5.00mL of water sample. The detection limit was of 1.3 ng L⁻¹. The relative standard deviation (R.S.D.) for ten replicate measurements of 20 ng L⁻¹ of Mercury was 2.9%.

Key words: Dispersive liquid-liquid microextraction; Preconcentration; Mercury; cold vapor atomic absorption spectrometry; Water analysis; alanine-salicylaldehyde (ALSA).

INTRODUCTION

In the past few decades there has been considerable emphasis on trace metal analysis. The determination of trace metals in metallurgical, agricultural, and environmental samples has become increasingly important. This has led to major developments in the field of trace metal analysis, with emphasis on the development of new and greener analytical methods. As a result there has been considerable growth in the analytical chemistry of various metals. Mercury is no exception to this. A rare element in the earth's crust, mercury is found either as a native metal or in cinnabar, cordierite, livingstonite and other minerals with cinnabar being the most common ore. Methyl mercury is a toxic compound that is widely found as a pollutant in water bodies and streams. Short-term exposure to high concentrations of mercury vapor causes harmful effects on the nervous, digestive, respiratory systems and the kidneys (Fergusson, 1990). Solid phase extraction is widely used for the removal of many toxic metal ions (Camel, 2003; Venkatesh, 2007; Tuzen, 2005; Moawed, 2004). The use of environment friendly sample treatment for speciation analysis has been reviewed in detail (Wrobel, 2003; Spivakov, 2006). Hg²⁺ is a soft acid and has good affinity towards sulfur containing ligands (Walcarius, 2005; Fontas, 2005; Starvin, 2004). Dithizone is one such ligand, which has been used in the preconcentration of many metal ions including mercury (Moghimi, 2006; Tehrani, 2005). A spectrophotometric method for the determination of trace level mercury using dithizone in micellar medium has been reported (Khan, 2005). The calibration graph was linear in the range 0.01-10µgL⁻¹ and the method was applied to water samples. silica gel-immobilized-dithiocarbamate derivatives modified by dimethylsulfoxide has been used for the separation and preconcentration of mercury (II) and the method has been tested in water samples with 98% recovery (Soliman, 2006; Moghimi1, 2006; Moghimi1, 2007). Micro columns packed with chlorella vulgaris immobilized on silica gel has been studied for mercury speciation and the method has been applied in spiked tap water samples with 96% recovery (Tajes-Martinez, 2006). Even though, a preconcentration factor of 200 could be achieved, strong acid was used for elution.

Most of the solid phase extraction methods for mercury involve either strong acids or toxic organic
solvents for elution. A survey of the literature reveals that solid phase extraction is one of the versatile methods for preconcentration. The inherent advantage of solid phase extraction is the high selectivity and preconcentration factor that could be attained. Inorganic adsorbents such as alumina and silica offer good advantages in terms of thermal, mechanical and chemical stability under various experimental conditions. Moreover, they offer good selectivity towards a particular metal ion.

In the previous researches, we demonstrated a novel microextraction technique, named dispersive liquid-liquid microextraction (DLLME), which was successfully used, for the extraction and determination of polycyclic aromatic hydrocarbons (PAHs), organophosphorus pesticides (OPPs) and chlorobenzenes in water samples (Rezaee, 2005; Berijani, 2006; Rahnama Kozani, 2007). DLLME is a miniaturized sample pre-treatment technique. On the other hand, cold vapor atomic absorption spectrometry (CV AAS) is a microamount sample analysis technique. Therefore, it makes it perfect when a combination of both DLLME and CV AAS is used. The applicability of the approach has been demonstrated for the determination of Mercury in water samples. This element was selected for evaluation of the procedure because Mercury is one of the principal heavy metals of analytical interest due to its extreme toxicity even at relatively low concentrations (Zhu, 2006; Kaewsarn, 2001).

2. Experimental:
2.1. Instrumentation:
The experiments were performed using a Shimadzu (Kyoto, Japan) atomic absorption spectrophotometer (AA 6300G) with a cold vapor furnace atomizer (CVA-EX71). A mercury hollow cathode lamp (Hamamatsu Photonics, Shizaoka, Japan), operated at a current of 8mA and a wavelength of 535nm with a spectral band pass of 0.7 nm was used. The sample injection volume was 20µL in all experiments. The good wetting of graphite by organic solvents promotes its penetration by the extracts that may give rise to signals of complicated shape. To prevent this undesirable effect, organic extracts can be added to electrothermal atomizer heated to the drying temperature and this will also prevent sample from spreading over the atomizer surface (Fernández, 2000). Therefore 20 µL of the sedimented phase was introduced 10 s after starting the drying step in all experiments. Argon 99.999% purchased from Air Products (West Sussex, UK) as sheath gas. The Centurion Scientific centrifuge (Model 1020D, UK) was used for centrifuging. The pH values were measured with a Metrohm pH-meter (Model: 691, Herisau, Switzerland) supplied with a glass-combined electrode.

2.2. Reagents and Solutions:
Alanine-salicylaldehyde Schiff base ligand was prepared as described previously 41. All solutions were prepared using ultra pure water (Ghazi Co., Tabriz, Iran). The stock solution of mercury (1000 mg L⁻¹ for atomic spectroscopy standard) was purchased from Merck (Darmstadt, Germany). Working standard solutions were prepared by serial dilutions of the stock solution with ultra pure water prior to analysis. The chelating agent, 0.020 g. L⁻¹ NADP solution, was prepared daily by dissolving the appropriate amount of NADP in ethanol (suprasolv, Merck). Other chemicals used were: carbon tetrachloride (analytical grade for determination with dithizone), chloroform (analytical grade for determination with dithizone) and carbon disulfide (for spectroscopy) as extraction solvent, ethanol (for spectroscopy), acetone (suprasolv) and acetonitrile (HPLC grade) as disperser solvent, HNO₃ (65%, suprapur), CH₃COONa (suprapur) and Na₂HPO₄ (suprapur) were obtained from Merck. The NaCl solution was prepared by dissolving the appropriate amount of NaCl (analytical grade, Merck) in ultra pure water and was extracted by carbon tetrachloride in the presence of NADP for further purification. All glass vessels used for trace analysis were kept in 0.1% Solution of NADP for at least 24 h and subsequently washed twice with ultra pure water and twice with acetone before use. Tap, sea and rivers water samples used for development of the method were collected in PTFE containers from the North of Iran and added appreciated amount of HNO₃ to adjust pH 3 and stored in dark at 4 °C and analyzed within 48 h of collection without previous treatment or filtration.

2.3. Dispersive Liquid-liquid Microextraction Procedure:
A 5.00mL of ultra pure water contains 50 µL HNO₃ (0.1N, suprapur) was placed in a 10mL screw cap glass test tube with conic bottom and spiked at levels of 20 ng L⁻¹ of mercury. Five hundred microliters of ethanol (disperser solvent) contains 34 µL of carbon tetrachloride (extraction solvent) and 0.00010 g NADP (chelating agent) was injected rapidly into a sample solution by using 0.50mL syringe (gastight, Hamilton, Reno, Nevada, USA). A cloudy solution (water, ethanol and carbon tetrachloride) was formed in a test tube.

In this step, mercury ions react with NADP and extract into the fine droplets of carbon tetrachloride. The mixture was then centrifuged for 2 min at 5000 rpm. After this process the dispersed fine droplets of carbon
Tetrachloride were sedimented at the bottom of conical test tube (25±1µL). Twenty microliters of this sedimented phase was removed using a sampler (eppendorf, Hamburg, Germany) and injected into cold vapor atomic absorption spectrometer. The volume of the sedimented phase was determined using a 50-µL microsyringe, which was about 25 µL.

**RESULT AND DISCUSSION**

In this research, DLLME combined with CV AAS was developed for the first time. Mercury was chosen as an example to study the possibility of this combination. In order to obtain a high enrichment factor, the effect of different parameters affecting the complex formation and extraction conditions, such as kind of extraction and disperser solvent and their volume, pH, concentration of the chelating agent, extraction time and salt addition were optimized. Eq. (1) was used for calculation of the enrichment factor.

\[
EF = \frac{C_{sed}}{C_0}
\]

where EF, C\text{sed} and C\text{0} are the enrichment factor, concentration of the analyte in the sedimented phase and initial concentration of the analyte in the aqueous sample, respectively. C\text{sed} was calculated from the calibration graph obtained by conventional LLE-CV AAS (extraction conditions: 5.00mL standard water sample in the concentration range of 0.5-3 µg L\text{−1} of Mercury, 5.00mL CCl\text{4}, 0.0050 g NADP and pH = 3).

3.1. Effect of Type and Volume of the Extraction Solvent:

Chloroform, carbon tetrachloride and carbon disulfide were compared in the extraction of mercury. A series of sample solution were studied by using 500 µL ethanol containing 0.00010 g NADP and different volumes of the extraction solvent to achieve 25µL volume of the sedimented phase. The solubility of the extraction solvents in water is different. Therefore to recover 25 µL volume of the sedimented phase at the bottom of the test tube, it is necessary to add an excess to account for this solubility. Thereby, 75, 50 and 34 µL of chloroform, carbon disulfide and carbon tetrachloride were used, respectively.

In this experiment chloroform, carbon disulfide and carbon tetrachloride as extraction solvents obtained enrichment factors of 128.9±8.6, 122.1±11.5 and 122.7±6.4, respectively. According to these results, variations of the enrichment factors using different extraction solvents are not statistically significantly different. Carbon tetrachloride forms a well stable cloudy solution, its sedimented phase can easily be removed by sampler to be introduced into the cold vapor and has less consumption volume, while chloroform forms an unstable cloudy solution and carbon disulfide is difficult to be removed by sampler. Therefore, carbon tetrachloride was the best to be used. To examine the effect of the extraction solvent volume, solutions containing different volumes of carbon tetrachloride were subjected to the same DLLME procedures. The experimental conditions were fixed and include the use of 500 µL ethanol containing 0.00010 g NADP and different volumes of carbon tetrachloride (34, 44, 54, 64, 74 and 84 µL). By increasing the volume of carbon tetrachloride from 34 to 84 µL, the volume of the sedimented phase increases from 25 to 75µL. Using less than 34µL volume of carbon tetrachloride decreases the volume of the sedimented phase to less than 25 µL. Therefore, removing the sedimented phase for injection into the CV AAS would be too difficult and accompany with systematic error. Fig. 1 shows the curve of enrichment factor versus volume of the extraction solvent (carbon tetrachloride). According to Fig. 1, enrichment factor decreases with increasing the volume of carbon tetrachloride, because of the volume of the sedimented phase increases. Subsequently, at low volume of the extraction solvent high enrichment factor was obtained. Thereby, the gain in sensitivity was achieved by using 34µL of carbon tetrachloride.

3.2. Effect of Type and Volume of the Disperser Solvent:

The main criterion for selection of the disperser solvent is its miscibility in the extraction solvent and aqueous sample. For this purpose, different solvents such as acetone, acetonitrile, ethanol and ethanol were tested. A series of sample solutions were studied by using 500µL of each disperer solvent containing 34µL of carbon tetrachloride (extraction solvent). Since the solubility of NADP in acetone and acetonitrile is low, in this experiment, an aqueous solution of NADP was prepared and added to water samples before the extraction.

The enrichment factors obtained for acetonitrile, acetone, ethanol and ethanol were 108.7±9.1, 122.6±8.8, 122.5±5.3 and 115.4±7.5, respectively. The results show no statistical significant differences between disperser solvents; however, the solubility of NADP in ethanol makes it a better choice.
The effect of the volume of ethanol on the extraction recovery was also studied. Since, variation of the volume of ethanol makes change in the volume of sedimented phase at constant volume of carbon tetrachloride (extraction solvent). Thereby, to avoid this matter and in order to achieve a constant volume of sedimented phase (25 µL) the volume of ethanol and carbon tetrachloride were changed, simultaneously. The experimental conditions were fixed and include the use of different volumes of ethanol 0.25, 0.50, 0.75, 1.00, 1.25 and 1.50mL containing 0.00010 g NADP and 33.0, 34.0, 35.0, 36, 37.5 and 39.0µL of carbon tetrachloride, respectively. Under these conditions, the volume of the sedimented phase was constant (25±1µL). The results showed that there was no considerable variation on extraction efficiency by using 0.25 and 0.50mL of ethanol as disperser solvent. The extraction efficiency slightly decreased when the volume of ethanol exceeded 0.50 mL. It is clear that by increasing the volume of ethanol, the solubility of complex in water increases. Therefore, the extraction recovery decreases. Thus, 500 µL of ethanol was selected as optimum volume in order to achieve better and more stable cloudy solution.

Fig. 1: Effect of the volume of extraction solvent (CCl₄) on the extraction efficiency of Mercury obtained from DLLME. Extraction conditions: water sample volume, 5.00 mL; disperser solvent (ethanol) volume, 0.50 mL; NADP amount, 0.00010 g; pH 3; concentration of Mercury, 20 ng L⁻¹.

3.3. Effect of the Extraction Time:
Extraction time is one of the most important factors in the most of extraction procedure. In DLLME, extraction time is defined as the time between injection mixture of disperser and extraction solvent, and starting to centrifuge. The effect of extraction time was examined in the range of 0-60 min with constant experimental conditions. The results showed that the extraction time has no significant effect on the extraction efficiency. It is revealed that after formation of cloudy solution, the surface area between extraction solvent and aqueous phase (water sample) is infinitely large. Subsequently, equilibrium state is achieved quickly, therefore, the extraction time is very short. This is the advantage of DLLME technique, i.e., short extraction time. In this method, the most time-consuming step is the centrifuging of sample solution in extraction procedure, which is about 2 min.

3.4. Effect of pH:
The separation of metal ions by dispersive liquid-liquid microextraction involves prior formation of a complex with sufficient hydrophobicity to be extracted into the small volume of the sedimented phase, thus, obtaining the desired preconcentration. pH plays a unique role on metal-chelate formation and subsequent extraction. The effect of pH on the complex formation and extraction of mercury from water samples was studied in the range of 1.3-8.1 by using HNO₃, CH₃COONa and Na₂HPO₄. The results illustrated in that the absorbance is nearly constant in the pH range of 2.8-8. As in Low pH, cations are less likely to precipitate, pH 3 seems a proper choice. Moreover, to make pH 3 adjustment, the use of buffer (which are sources of contamination) is not necessary and nitric acid can simply be used to make the pH adjustment.

3.5. Effect of NADP Concentration:
The effect of the NADP amount on the absorption is shown in Fig. 2. The absorption was increased by increasing the NADP amount, which is well expected. It seems that slight reduction of extraction in high concentration of NADP is due to the extraction of NADP itself, which can easily saturate the small volume of extraction solvent.
Also, at high concentration of NADP (0.0010 g) the background absorbance was increased. Therefore, the amount of 0.00010 g NADP was selected as the best choice to prevent any interference.

![Graph of NADP amount on the absorbance of Mercury obtained from DLLME.](image)

**Fig. 2:** Effect of NADP amount on the absorbance of Mercury obtained from DLLME.

### 3.6. Effect of Salt:
For investigating the influence of ionic strength on performance of DLLME, various experiments were performed by adding different amount of NaCl (0-5% (w/v)). Other experimental conditions were kept constant. By increasing the NaCl from 0 to 5%, the volume of sedimented phase increases slightly from 25 to 28µL. The results showed that salt addition has no significant effect on the enrichment factor. It is maybe because of two opposite effects of salt addition in DLLME of mercury. One of them is increasing the volume of sedimented phase that decreases the enrichment factor and another is salting-out effect that increases the enrichment factor. Therefore, the enrichment factor is nearly constant by increasing the amount of sodium chloride. These observations showed the possibility of using this method for separation of mercury from saline solutions up to 5%.

### 3.7. Effect of Coexisting Ions:
The effects of common coexisting ions in natural water samples on the recovery of mercury were studied. In these experiments, 5.00mL of solutions contains 20 ng L⁻¹ of mercury and various amounts of interfering ions were treated according to the recommended procedure. A given spices was considered to interfere if it resulted in a ±5% variation of the AAS signal. The results obtained are given in Table 1.

### 3.8. Figures of Merit:
The analytical characteristics of the optimized method, including linear range, limit of detection, reproducibility, and enhancement factor. The calibration graph was linear in the range of 2-21 ng L⁻¹ of mercury. The limit of detection, defined as \( C_L = 3 \cdot S_B / m \) (where \( CL \), \( SB \) and \( m \) are the limit of detection, standard deviation of the blank and slope of the calibration graph, respectively), was 1.3 ng L⁻¹. The relative standard deviation (R.S.D.) for ten replicate measurements of 20 ng L⁻¹ Mercury (II) was 2.9%. The enhancement factor was obtained from the slope ratio of calibration graph after and before extraction, which was about 100.

### 3.9. Analysis of Natural Waters:
The proposed DLLME-CVAAS methodology was applied to the determination of mercury in several water samples. Tap, sea and rivers water were collected from the North of Iran and were analyzed by DLLME combined with CV AAS for determination of mercury. The concentration of mercury in the tap, sea and rivers water samples were determined to be 15.1±0.4 ng L⁻¹, 6.9±0.3 ng L⁻¹, 7.1±0.4 ng L⁻¹ and 0.0 ng L⁻¹ (not detected), respectively (Table 2).

Tap, sea and rain water samples were spiked with mercury standards to assess matrix effects. The relative recoveries of mercury from tap, sea and rivers water at spiking level of 5 and 10 ng L⁻¹ were 99, 94, 97 and 96%, respectively (Table 2). These results demonstrated that the tap, sea and rivers water samples matrices, in our present context, had little effect on DLLME of mercury. Under the optimum conditions, the enrichment factor 122 was obtained from only 5.00mL of water sample.
Table 1: Effect of interferents on the recovery of 20 ng L⁻¹ Mercury (II) in water sample using DLLME-CV AAS.

<table>
<thead>
<tr>
<th>Interferent</th>
<th>Concentration (µg L⁻¹)</th>
<th>Interferent/Mercury (II) ratio</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>40,00,000</td>
<td>200,000,000</td>
<td>94.4</td>
</tr>
<tr>
<td>Li⁺</td>
<td>200</td>
<td>10,000</td>
<td>100.2</td>
</tr>
<tr>
<td>K</td>
<td>200</td>
<td>10,000</td>
<td>99</td>
</tr>
<tr>
<td>Ca (II)</td>
<td>200</td>
<td>10,000</td>
<td>98.6</td>
</tr>
<tr>
<td>Mg (II)</td>
<td>200</td>
<td>10,000</td>
<td>100.5</td>
</tr>
<tr>
<td>Ba (II)</td>
<td>200</td>
<td>10,000</td>
<td>98.4</td>
</tr>
<tr>
<td>Sr (II)</td>
<td>200</td>
<td>10,000</td>
<td>89.9</td>
</tr>
<tr>
<td>Mn (II)</td>
<td>200</td>
<td>10,000</td>
<td>95.6</td>
</tr>
<tr>
<td>Co (II)</td>
<td>200</td>
<td>10,000</td>
<td>96.7</td>
</tr>
<tr>
<td>Al (III)</td>
<td>200</td>
<td>10,000</td>
<td>98.6</td>
</tr>
<tr>
<td>Fe (III)</td>
<td>200</td>
<td>10,000</td>
<td>98.7</td>
</tr>
<tr>
<td>Ni (II)</td>
<td>200</td>
<td>10,000</td>
<td>66.4</td>
</tr>
<tr>
<td>Zn (II)</td>
<td>200</td>
<td>10,000</td>
<td>95.9</td>
</tr>
<tr>
<td>Pb (II)</td>
<td>200</td>
<td>10,000</td>
<td>96.5</td>
</tr>
<tr>
<td>As (III)</td>
<td>200</td>
<td>10,000</td>
<td>99</td>
</tr>
<tr>
<td>As (V)</td>
<td>200</td>
<td>10,000</td>
<td>98.5</td>
</tr>
<tr>
<td>Cd (II)</td>
<td>200</td>
<td>10,000</td>
<td>97.2</td>
</tr>
<tr>
<td>Cr (III)</td>
<td>200</td>
<td>10,000</td>
<td>74.4</td>
</tr>
<tr>
<td>Cr (VI)</td>
<td>200</td>
<td>10,000</td>
<td>63.7</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>200</td>
<td>10,000</td>
<td>65.3</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>200</td>
<td>10,000</td>
<td>65.3</td>
</tr>
<tr>
<td>CH₃ COO⁻</td>
<td>200</td>
<td>10,000</td>
<td>96.9</td>
</tr>
<tr>
<td>H₂PO₄⁻</td>
<td>200</td>
<td>10,000</td>
<td>98</td>
</tr>
</tbody>
</table>

Table 2: Determination of Mercury(II) in tap, sea and rivers water samples and relative recovery of spiked Mercury in tap, sea and rivers water samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration of Hg²⁺ mean ± S.D. a (ng L⁻¹)</th>
<th>Added Hg²⁺</th>
<th>Found Hg²⁺ mean ± S.D. a (ng L⁻¹)</th>
<th>ICP-AES</th>
<th>Relative recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water</td>
<td>15.23 ± 0.6</td>
<td>5</td>
<td>20.6 ± 1.3</td>
<td>20.3 ± 1.3</td>
<td>93</td>
</tr>
<tr>
<td>Sea water</td>
<td>7.4 ± 1.4</td>
<td>5</td>
<td>11.3 ± 1.2</td>
<td>11.4 ± 1.1</td>
<td>95</td>
</tr>
<tr>
<td>Rain water</td>
<td>7.3 ± 1.5</td>
<td>5</td>
<td>11.3 ± 1.2</td>
<td>11.6 ± 1.2</td>
<td>95</td>
</tr>
<tr>
<td>Tap water</td>
<td>9.9 ± 0.9</td>
<td>10</td>
<td></td>
<td>9.8 ± 1.9</td>
<td>96</td>
</tr>
</tbody>
</table>

Table 3: Characteristic performance data obtained by using DLLME and other techniques in determination of Mercury in water.

<table>
<thead>
<tr>
<th>Method</th>
<th>Calibration range (ng L⁻¹)</th>
<th>Time (min)</th>
<th>Sample consumption (mL)</th>
<th>Enrichment factor</th>
<th>R.S.D. b (%)</th>
<th>LOD a (ng L⁻¹)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>On-line solvent extraction-CV AAS</td>
<td>6-300</td>
<td>2</td>
<td>14</td>
<td>24.6</td>
<td>3.2</td>
<td>2.8</td>
<td>(Walcaius, 2005)</td>
</tr>
<tr>
<td>Co-precipitation-CV AAS</td>
<td>100-4000</td>
<td>&gt;30</td>
<td>100</td>
<td>100</td>
<td>3.2</td>
<td>2.9</td>
<td>(Fontas, 2005)</td>
</tr>
<tr>
<td>On-line SPE-CV AAS</td>
<td>20-200</td>
<td>4</td>
<td>3</td>
<td>59.4</td>
<td>1.3</td>
<td>1.3</td>
<td>(Mahmoud, 2000)</td>
</tr>
<tr>
<td>CPE-CV AAS</td>
<td>0-200</td>
<td>&gt;30</td>
<td>10</td>
<td>50</td>
<td>2.1</td>
<td>5.9</td>
<td>(Rudner, 1998)</td>
</tr>
<tr>
<td>SDME-CV AAS</td>
<td>10-1000</td>
<td>&gt;10</td>
<td>5</td>
<td>65</td>
<td>7.4</td>
<td>0.7</td>
<td>(Kera, 2005)</td>
</tr>
<tr>
<td>DLLME-CV AAS</td>
<td>21-Feb</td>
<td>&lt; 4</td>
<td>5</td>
<td>122</td>
<td>2.9</td>
<td>1.3</td>
<td>[Represented method]</td>
</tr>
</tbody>
</table>

3.10. Comparison to Other Methods:

A comparison of the represented method with other reported preconcentration methods is given in Table 3. In comparison with other reported methods, DLLME has low LOD (1.3 ng L⁻¹), high enrichment factor (122), short extraction procedure (less than 4 min) and low sample consumption (5 mL). These characteristics are of key interest for routine laboratories in trace metal ion analysis.
Conclusions:

Dispersive liquid-liquid microextraction combined with cold vapor atomic absorption spectrometry allows tackling the determination of mercury in natural waters in a simple way. The method is simple, rapid and inexpensive. High preconcentration factor was obtained easily through this method and a detection limit at sub ng L⁻¹ level was achieved with only 5.00mL of sample. In this method sample preparation time as well as consumption of toxic organic solvents was minimized without affecting the sensitivity of the method. Although the obtained results in this work are related to mercury determination, the system could be readily applied to the determination of other metals using various ligands, extractable by other organic solvents. Additional work is in progress on evaluating the performance of proposed method for the determination of other trace metal ions with spectrometric instruments.

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