

## Trace mercury determination in drinking and natural water after preconcentration and separation by DLLME-SFO method coupled with cold vapor atomic absorption spectrometry

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**Abstract.** A novel dispersive liquid–liquid microextraction based on solidification of floating organic drop (DLLME-SFO) for simultaneous separation/preconcentration of ultra trace amounts of mercury was used. A method based on amalgamation was used for collection of gaseous mercury on gold coated sand (Gold trap). The concentration of mercury was determined by cold vapor atomic absorption spectrometry (CV-AAS). The DLLME-SFO behavior of mercury by using dithizone as complexing agent was systematically investigated. The factors influencing, the complex formation and extraction of DLLME-SFO method such as type and volume of extraction and disperser solvents, pH, concentration of salt, centrifuging time and concentration of the chelating agent were optimized. The method was successfully applied to the determination of mercury in drinking and natural water and satisfactory relative recoveries (95–105%) were achieved. The proposed procedure was based on very low consumption of organic solvents. The other benefits of the system were sensitive, simple, friendly to the environment, rejection of matrix constituent, low cost, the time consuming and high enrichment factor.

**Keywords:** mercury; Dispersive liquid–liquid microextraction based on solidification of floating organic drop (DLLME-SFO); Dithizone; Cold vapor atomic absorption spectrometry (CV-AAS)

### Introduction

Mercury (Hg) is known as a harmful metal and its toxic effect has been known for centuries. A considerable amount of mercury comes from anthropogenic sources such as manufacture of plastic, paper, paint, pharmaceutical (Craig, 1986). Organometallic species of mercury are more toxic than inorganic, because of their high affinity to SH group of proteins and lipid issues (Pongratz et al, 1999). One of the routes of intake of this metal in to the human body is drinking water (Clifton, 2007); however, as the concentration of Hg in environmental and biological samples is very low, its direct determination is difficult even with highly sensitive and selective analytical techniques. Thus, a separation and pre- concentration steps prior to its determination is required. The widely used techniques for the separation and preconcentration of Hg are traditional liquid-liquid extraction (Gaona et al, 2003), solid phase

microextraction (SPE) (Hashempur et al, 2008), single drop microextraction (SDME) (Pena-Pereira et al, 2009), dispersive liquid- liquid microextraction (DLLME) (Gao et al, 2011)] and solidified of floating organic drop microextraction (López-García et al, 2010) have been recently developed.

A novel dispersive liquid–liquid micro extraction method based on the solidification of floating organic drop (DLLME–SFO) was introduced by Leong et al (2008). It is based on DLLME and the solidification of floating organic drop. In the DLLME-SFO procedure, selecting a perfect extraction solvent is vital. It should have low solubility in water, high affinity to analytes, low melting point below room temperature, and lower density than water. The large contact surface between the sample and the droplets of extractants speeds up mass transfer, as fast as DLLME and shorter extraction time than LLME-SFO. In this method there is no need to use conical bottom glass tubes, which are easily damaged and

hard to clean. The floated extractant is solidified and is easily collected for analysis. The advantages of DLLME-SFO method are simplicity of operation, rapidity, low cost, high recovery, and using extracting solvent with lower density rather than water and lower toxicity in contrast with DLLME. In this study, dithizone, the classical organic reagent was selected as chelating reagent and a new DLLME-SFO method combined cold vapor atomic absorption spectroscopy (CV-AAS) was developed for separation, enrichment and determination of mercury in water samples and fish. Factors affecting the extraction efficiency, such as solution pH, concentration of organic ligand, extraction time, sample volume, nature of organic solvent and its volume, and kind of disperser solvent and its volume were studied and optimized.

## Materials and Methods

All reagents were used of analytical reagent grades and were purchased from the Merck Company (Darmstadt, Germany). The pH of sample that containing proper amount of Hg was adjusted to ~7 by using HCl solution and NaOH solution. About 10 ml of the solution was transferred in to ~12 ml test tube and dithizone solution as complexing agent was added and mixtured, then extraction solvent and dispersive solvent was rapidly injected in to the aqueous sample. In this stage a cloudy solution was formed in a test tube the ions reacted with dithizone and were extracted in to extraction solvent in a few seconds. After centrifuging, the organic solution droplet was floated on the surface of the aqueous solution due to low density below water. The test tube was there after put into an ice bath for 5min. At this time the floated solvent was solidified because of the low melting point(24°C), then the solidified solvent was transferred in to a conical vial where it melted immediately, it was manually injected to gold trap cold vapor atomic absorption spectrometer system for the determination of mercury.

## Results and Discussion

In order to obtain a high enrichment factor, different parameters affecting the complex formation, extraction and analytes determination were optimized by using the uni variable approach. In DLLME-SFO procedure, selecting a perfect extraction solvent is vital. Accordingly, several extraction solvent, including 1-undecanol, 1-dodecanol, 1,10dichlorodecan and n-hexadecan were investigated. Suitable extraction solvent was recognized. The effect of the extraction volume on the extraction was also investigated.

Selection of the disperser solvent considers its miscibility with extraction solvent and water. In this experminet acetone, ethanol, methanol and acetonitrile were tested. With acetonitrile emulsion formed and separation of two phase was difficult and proper solvent was selected. The effect of the volume of disper solvent in the range of 50-400 $\mu$ L on the extraction efficiency of analytes was examined. The results show that by

increasing of the disperser solvent until 200 $\mu$ L the absorbance of analyte was maximized. At the low volume of disperser solvent, extraction solvent wasn't completely dispersed and the extract efficiency wasn't complet. In the volume of disperser solvent greater than 300 $\mu$ L, the extraction efficiency was decreased because of the increase in solution of complex of analytes in aqueous phase containing high percentage of disperser solvent. (Fig.1)

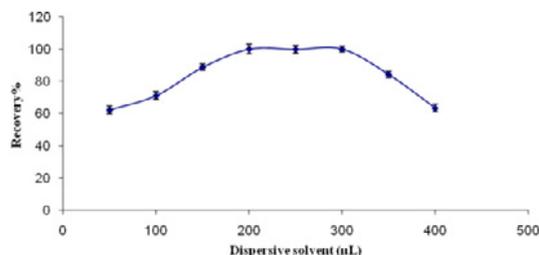


Fig. 1. Effect of disperser solvent volume.

The pH of the sample solution is one of the important factors affecting the formation of complex and subsequent extraction in DLLME -SFO. The effect of pH on the extraction of Hg with dithizone as a complex agent was studied by varying the pH within the range of 3-11. The pH was adjusted by using either HCl solution of 0.05mol l<sup>-1</sup> or NaOH solution 0.05mol l<sup>-1</sup>, while the other variable keeping constant. The results illustrated in Fig (2) demonstrating that the analytical signal is nearly constant in the pH range of pH 3-11.

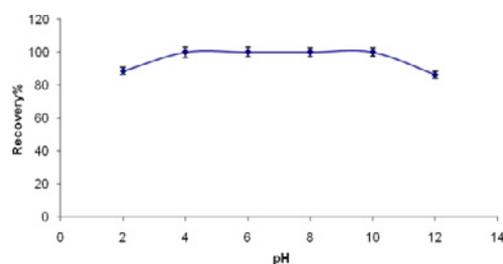


Fig. 2. Effect of pH.

An important parameter which influences the increase in the ratio of volume of aqueous phase to organic phase will result in significant increase in the enrichment factor, but an increase in sample volume may cause a decrease in extraction efficiency in a given time. The effect of sample volume on extraction of Hg from different sample volume (5-50ml), in a proper size vial, was investigated. The results Fig (3) showed that the extraction was quantitative with the aqueous phase volume in the range of 5-40ml and a decrease was observed with further increase in sample volume. Because of good sensitivity of CV-AAS for simple work, the volume of 10ml was used.

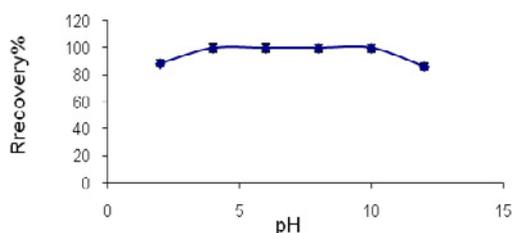


Fig. 3. Effect of sample volume

The effect of DZ concentration on the extraction efficiency was evaluated. Optimum concentration was selected for further studies.

In DLLME-SFO, extraction time is defined as the interval time between the injection of the solution of disperser and extraction solvent before starting to centrifuge. The effect of the extraction time was examined in the range of 0-5min with constant experimental conditions. As a result extraction time has no impact on extraction efficiency. In this method after the formation of a cloudy solution, the surface area between the extraction solvent and aqueous phase is very large. Thereby transition of the complex from aqueous phase to the extraction solvent is fast. Thus, the most important advantage of DLLME-SFO is time independence of the method. In this method time consuming steps are centrifuging of the sample solution in the extraction procedure, which is about 3min and solidified of 1-undecanol, which is about 5min.

Some metal ions also form stable chelates with dithizone, being a potential source of interference with the analytical procedure for mercury species. So the effect of common coexisting ions ( $\text{Cu}^{+2}$ ,  $\text{Zn}^{+2}$ ,  $\text{Pb}^{+2}$ ,  $\text{Cd}^{+2}$ ,  $\text{Al}^{+3}$ ) on mercury species analysis was investigated.

To examine the reliability of the recommended procedure, the method was applied for the determination of mercury in tap water, well water, spring water, sea water, river water and fish.

## Conclusion

It has been demonstrated that dispersive liquid liquid microextraction- solidified floating organic drop combined with gold trap CV-AAS can be used for separation/ enrichment and determination of ultra trace of mercury. Further DZ as chelating agent can be formation complex with mercury and extracted it to extraction solvent. Thus this method permits effective separation and concentration of Hg and final determination by CV-AAS and provide a novel route for trace determination mercury in several categories of natural waters. The most important advantages of DLLME-SFO are; lower time of detect, very short extraction time and ease of operation. It

is inexpensive and has higher enrichment factor.

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