Homogeneous liquid-liquid microextraction via flotation assistance for determination of trace amounts of manganese prior to inductively coupled plasma-mass spectrometry

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In the present study, homogeneous liquid-liquid microextraction via flotation assistance method is described for preconcentration of trace amounts of Mn(II). 1-(2-pyridylazo)-2-naphthol (PAN) is used as a ligand. The enriched analyte in the floated organic phase has been determined by inductively coupled plasma-mass spectrometry (ICP-MS). In this work, low density organic solvent is used and there is no need of centrifugation. Several factors influencing the microextraction efficiency, such as pH, the amount of chelating agent, nature and volume of extraction and homogeneous solvents have been investigated and optimized. Under the optimum conditions, the linear dynamic range is 1.0-500.0 ng L^{-1} with a correlation coefficient of 0.9998 and the detection limit of 0.1 ng L^{-1}. The proposed method has been successfully applied for separation and determination of manganese in different water samples.

Manganese (Mn) is recognized as both, an essential and a neurotoxic trace element. As an essential trace element, Mn plays an important role in bone and tissue formation, reproductive functions and the activation of many enzymes, which are involved in vital metabolic processes[1]. Element deficiency is not a common occurrence since dietary sources provide an adequate supply of 2–8 mg of Mn per day. However, toxic levels may be reached in workers or individuals leaving near mines, ore-processing plants or manufactures of varnish, pharmaceutical products, ceramics and pottery[1,2]. Manganese exists mainly in both Mn(II) and Mn(IV) oxidation states in ordinary aqueous environments. In aqueous environments Mn(IV) is a dominant chemical species, and exists in insoluble forms, such as particulate and colloidal MnO_2. However, Mn(II) ion is rather stable in aqueous environments, which are often linked with water pollution, especially for drinking water[3,4]. The greatest parts of dissolved manganese in environmental waters are thought to be Mn(II) ions[5]. The direct determination of trace Mn ions is generally difficult because of matrix interference problems and low concentration of metals in samples. These problems can be overcome by using preconcentration and separation procedures before the detection procedure. For this purpose, various methods for the separation and preconcentration of manganese have been reported, such as solid-phase extraction[6-8], cloud-point extraction[9] and liquid membrane[10] have been widely used. Featuring rapid extraction and high efficiency, since its first introduction by Rezaee et al.[11], dispersive liquid–liquid microextraction (DLLME) has been applied to the extraction of several compounds[12-16].

However, the limitation of using solvents with higher density than water as extraction solvents, (typically chlorinated solvents that are comparatively less environmentally friendly) for the convenient collection of organic extract (as the sedimented phase after centrifugation) is the main drawback of this method. To broaden the applicability of DLLME, several recent studies have focused on the use of organic solvents with lower densities than water by employing a home-designed and fabricated extraction vial[17-24].

Homogeneous liquid-liquid microextraction via flotation assistance (HLLME-FA) is an analytical technique recently developed by Haji Hosseini and co-workers[25,26]. The basic principle of this method is the mixture of extraction and homogeneous solvents are

injected into an aqueous sample to form in the initial state a homogeneous solution. To date, HLLME-FA has been applied for the analysis of various compounds[27-32]. Using air flotation in HLLME-FA omitted centrifugation, after the extraction procedure, organic solvent lighter than water accumulated at the top of the aqueous phase, followed by elevation of the floated organic solvent to the narrow part of the device. Phase separation was achieved by using air flotation. After the phases separated, the upper layer was moved into the narrow part of the device by adding a few distilled water into the glass tube on the side of the cell The present investigation has centered on the development of a reliable method for the determination of Mn in water samples. We for the first time use the new preconcentration method of HLLME-FA, which is combined with ICP-MS for the determination of Mn in water samples. The most effective variables on the HLLME-FA method could be considered as type and volume of extraction solvent, ionic strength, type and volume of homogeneous solvent, pH, concentration of ligand and time of extraction.

Materials and Methods

Chemicals and reagents

A standard stock solution of Mn(II) at a concentration of 1000 mg L^{-1} was prepared using manganese nitrate salt received from Tarbiat Modares University (Tehran, Iran). Working standard solutions were prepared in doubly distilled water. All the standard solutions were stored in a fridge at –4 °C and brought to ambient temperature just prior to use. N-hexane, n-heptane, toluene, 1-dodecanol, methanol, acetone, ethanol, acetonitrile and sodium chloride were obtained from Merck (Darmstadt, Germany). A solution of 1-(2-pyridylazo)-2-naphthol (PAN) (0.01 mol L^{-1}) was prepared by dissolving appropriate amounts of this reagent in ethanol. Youngling ultra pure water purification system (Aqua Max^{TM}-ultra, Korea) was used for purification of water. The pH of solutions was adjusted by dissolving proper amount of ammonium acetate in distilled water (2.5×10^{-3} mol L^{-1}) and drop wise addition of nitric acid (0.5 mol L^{-1}) and/or sodium hydroxide solutions (0.5 mol L^{-1}). In this work, an inductively coupled plasma mass spectrometry (ICP-MS) model Agilent-7500 was used for all determinations.

HLLME-FA procedure

Fig. 1 shows the schematic procedure of the proposed method. 0.5 mL methanol (as homogeneous solvent) containing 120 µL toluene (as extraction solvent) was injected into the home-designed extraction cell using a 5 mL syringe. 50 µL PAN (0.01 mol L^{-1}) as a ligand was added into the 22 mL saline aqueous solution which pH was adjusted at 7. An emulsion was formed in the cell. The emulsion separated into two phases by using air flotation and the extraction phase floated on the surface of the
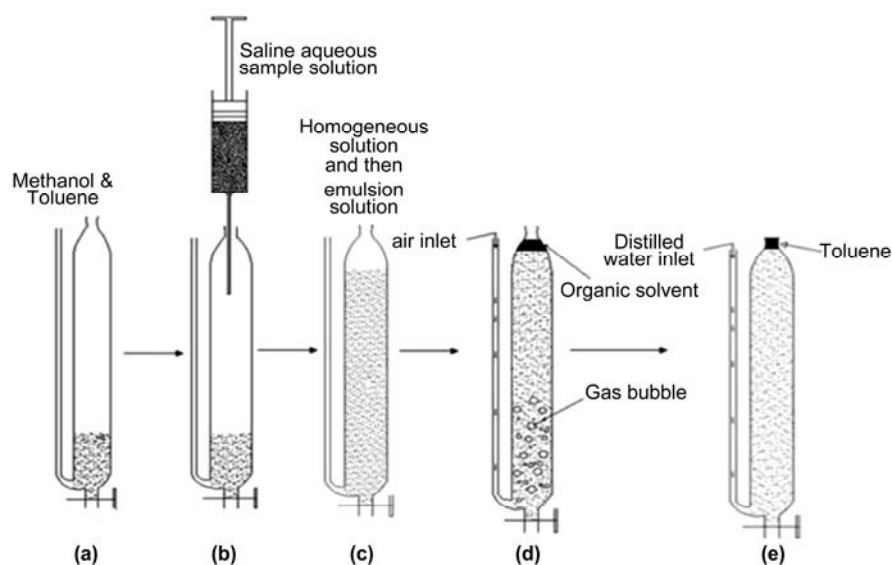

Fig. 1 — (a) Schematic for HLLME-FA procedure, (b) a mixture of 0.5 mL methanol containing 120 µL toluene was added to the extraction cell, (c) 22.0 mL of the saline aqueous solution was added into the extraction cell, (d) a homogeneous solution was formed in the cell using air flotation, organic solvent was moved to the top of the solution and (e) a small volume of distilled water was added into the glass tube on the side of the cell

solution. The collected extraction solvent was raised into the conical part of the cell by adding a few volumes of distilled water into the glass tube on the side of the cell. After evaporation of organic solvent, the residue was dissolved in the 0.5 mol L^{-1} HNO_3 and was injected into the ICP-MS instrument.

Results and Discussion

HLLME-FA combined with ICP-MS was developed for the determination of Mn in water samples. In order to obtain a high recovery, effects of different parameters such as the type and volume of the extraction and homogeneous solvents, pH, concentration of ligand, salt amount and extraction time were optimized.

Selection of extraction solvent

Certain factors need to be considered when choosing the optimal extraction solvent. First, it should be immiscible with water. Second, the density of the organic solvent must be lower than water. Third, it should be possible to extract the analyte with the extraction solvent. Several organic solvents with low water solubility meet these criteria, including 1-dodecanol, n-hexane, n-heptane and toluene. The results are depicted in Fig. 2. As shown in Fig. 2, toluene showed the highest extraction efficiency. It seems, because the structure of the PAN in the complex has benzene group and interaction with benzene group in toluene causes higher solubility of complex in toluene and better extraction efficiency. Thus, toluene was selected for subsequent experiments.

Selection of homogeneous solvent

The selection of a homogeneous solvent was also of great importance to the developed method. Miscibility of homogeneous solvent in extraction 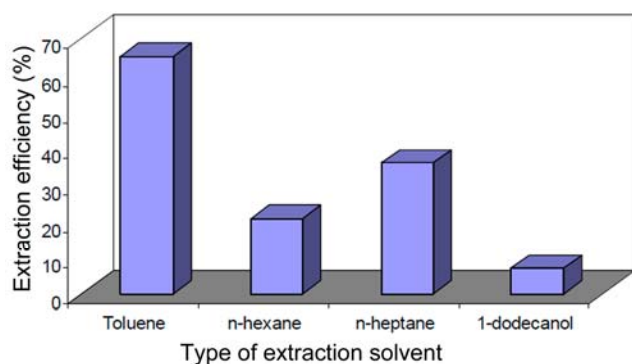solvent and aqueous phase is the main point for selection of homogeneous solvent. The effect of different homogeneous solvents including methanol, ethanol, acetone and acetonitrile were investigated. The relevant data was shown in Fig. 3. Methanol gave the highest value. It seems that by using methanol better homogeneous solution was obtained, hence, methanol was chosen as the best homogeneous solvent for the subsequent studies.

Selection of extraction and homogeneous solvent volumes

After selecting toluene as the extraction solvent, further experiments were performed to optimize the volume of extraction solvent, which is critical for the performance of HLLME-FA extraction. To determine the optimal volume of extraction solvent, different volumes of toluene (80, 120, 140, 160, and 180 μL) were used. The extraction efficiency of the analyte has increased with the increase in the volume of extraction solvent from 80.0 to 120.0 μL and then decreased at volumes higher than 120 μL (Fig. 4). On one hand, the reason may be that larger volume of extractant could extract more amounts of analyte, and therefore enhancing the extraction efficiency. On the other hand, the increasing volume of extractant could dilute the concentration of the analyte, hence decrease
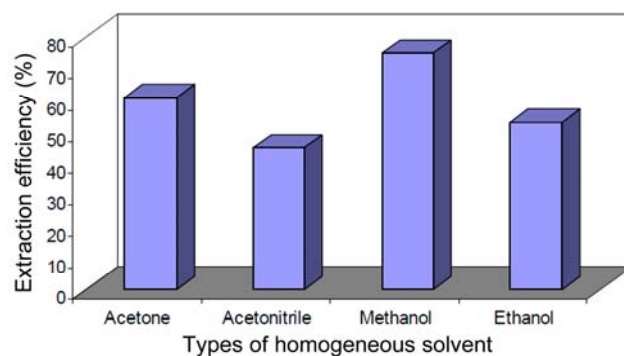
Fig. 3 — Effect of type of homogeneous solvent on the extraction efficiency
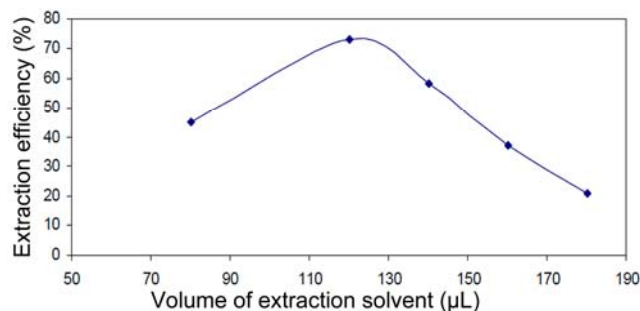
Fig. 4 — Effect of volume of extraction solvent on the extraction efficiency

Fig. 2 — Effect of type of extraction solvent on the extraction efficiency

the extraction efficiency. Therefore, a volume of 120 μL of toluene was selected for further experiments.

Subsequently, the effect of volume of methanol was also studied. A set of experiments were performed by keeping the volume of toluene constant (120 μL) and by varying the volume of methanol (0.5, 1.0, 1.5 and 2.0 mL). The results (Fig. 5) showed that with increasing of homogeneous solvent volume (methanol), the extraction efficiency are decreased; that is because of the increasing lipophilic characteristic in aqueous sample solution and decreasing the distribution constant. Thus, 0.5 mL methanol was chosen in this work.

Effect of pH

The pH plays a unique role on the metal complex formation and subsequent extraction. The separation of Mn(II) by the HLLME-FA method involves prior formation of a complex with sufficiently hydrophobic character to be extracted into the small volume of the extraction phase, thus obtaining the desired preconcentration. Extraction yield depends on the pH at which complex formation occurs. So, the effect of pH on the extraction of Mn(II) was studied by varying the pH within the range of 3–11. As shown in Fig. 6, the extraction recovery of Mn(II) increased from 3 to
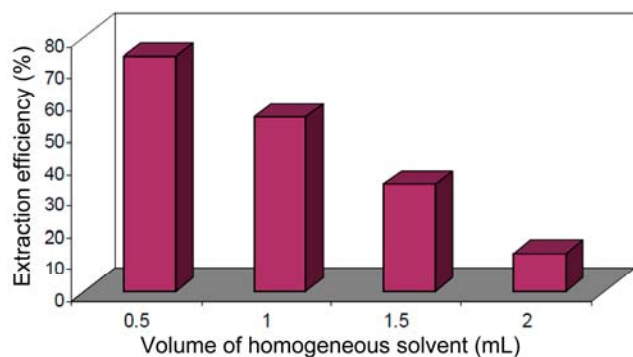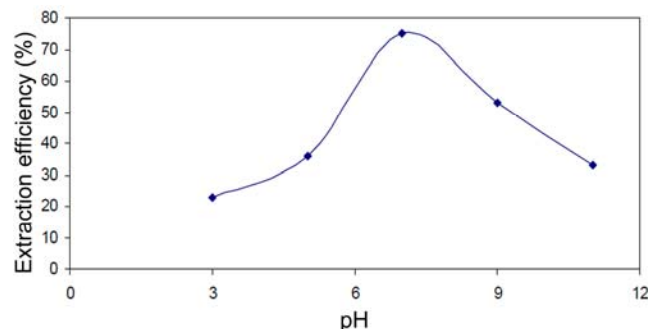
7, and then decreased with further increasing pH, because PAN activity decreases in the acidic qualification due to protonation of oxygen and nitrogen. Also metal settle up the form of hydroxide in alkaline perimeter. Therefore, pH 7.0 was selected for subsequent experiments.

Effect of reagent concentration

The influence of the PAN concentration on extraction recovery of Mn(II) was evaluated in the volume of 10 to 120 μL at the concentration level of (0.01 mol L^{-1}). The results are shown in Fig. 7. It can be observed that the extraction efficiency reached a maximum at the volume of 50 μL. Because, the mass of the chelating reagent present in the aqueous phase determines the amount of complex formed and hence the amount of analyte extracted. The strongest signal was obtained when 50 μL of PAN with the concentration of 0.01 mol L^{-1} was used. Also, it seems that slight reduction of extraction in high concentration of PAN is due to the extraction of PAN itself, which can easily saturate the small volume of the extraction solvent. Thus, for further studies, we used the volume of 50 μL of PAN with the concentration of 0.01 mol L^{-1}.

Effect of salt addition

Addition of salt can increase the ionic strength of the sample solution. It often improves the extraction of analyte in HLLME-FA due to the salting-out effect. For investigating the effect of the salt on the extraction efficiency, various experiments were performed by adding different amounts of sodium chloride (0.5–5.0 mol L^{-1}). In this study, with the increase of the amount of salt from 0.5 to 3.0 mol L^{-1}, the extraction efficiency of the analyte got increased, because in the extraction, the solubility of analyte in aqueous solutions decreases with increasing of ionic strength due to the salting out effect. When larger
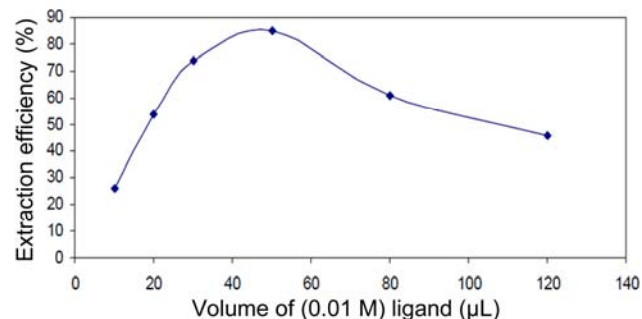

Fig. 5 — Effect of volume of homogeneous solvent on the extraction efficiency

Fig. 6 — Effect of pH on the extraction efficiency

Fig. 7 — Effect of volume of ligand (0.01 mol L^{-1}) on the extraction efficiency

amounts (>3.0 mol L^{-1}) of sodium chloride were added, lower extraction efficiency was observed (Fig. 8). It is possibly caused by the increased solution viscosity that reduces dispersion phenomenon. Therefore, sodium chloride of 3.0 mol L^{-1} concentration was added in subsequent experiments.

Effect of extraction time

In a HLLME-FA procedure, extraction time is defined as an interval time between beginning of the dispersion and the end of dispersion just before air flotation. The effect of time was examined in the range of 1–20 min. The obtained results show that transferring of the analyte from aqueous phase to extraction solvent is very fast. From these data it can be concluded that extraction time is not an important factor in this study. Therefore, 1 min was selected as optimum extraction time to achieve maximal extraction efficiency of the analyte.

Effect of coexisting ions

To investigate the selectivity of the developed method, the effect of foreign ions on the determination of Mn(II) was undertaken. An ion was considered as interfering, when it caused a variation in the extraction efficiency of the sample greater than 15%. These results (Table 1) show that the presence of common coexisting ions commonly present in water samples have no significant effect on the determination of Mn(II). These results show that Mn(II) can be successfully determined in various matrices.

Quantitative analysis

The characteristics of calibration curve were obtained under optimized conditions. Linearity was observed in the range of 0.5-500 ng L^{-1}. Correlation coefficient (r^2) was found to be 0.9998. The relative standard deviation (RSD, n=5) was calculated to be 3.7%. The limit of detection (LOD), based on signal-to-noise (S/N) of three was 0.1 ng L^{-1}.

Table 2 compares the proposed method with the other extraction methods for the determination of

manganese. Comparison of the proposed method with cloud point extraction[36] and ultrasound assisted emulsification microextraction based on solidification floating organic drop[33] for the extraction and determination of the analyte indicates that this novel method has a short extraction time for the determination of the manganese. Quantitative results of the proposed method such as detection limit and
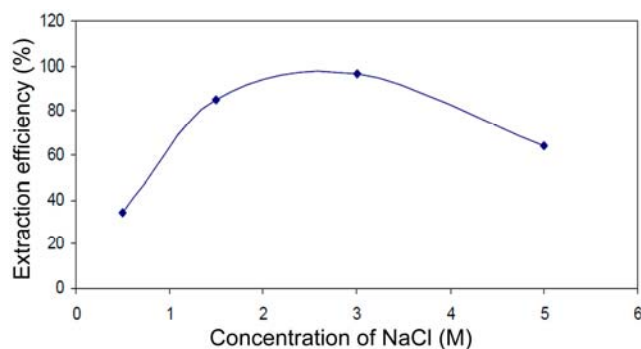

Fig. 8 — Effect of concentration of NaCl on the extraction efficiency

Table 1 — Effect of interference on pre-concentration and determination of metal ion

Interference	Interference to metal ion ratio	Recovery %
Ca^{2+}	100	87.3
Mg^{2+}	100	95.2
Na^+	100	103.5
K^+	100	101.8
Fe^{3+}	50	90.4
Zn^{2+}	50	89.6
Cd^{2+}	50	86.8
Al^{3+}	50	87.2
Co^{2+}	50	87.3
Ni^{2+}	50	89.6
Pb^{2+}	50	94.1
Sr^{2+}	50	92
Sn^{4+}	50	94.5
Rb^+	50	86.4
Cs^+	50	85.7
Be^{2+}	50	86.3
Ba^{2+}	50	89.8
$Li+$	50	88.7

Table 2 — Comparison of the proposed method with other extraction methods for the determination of manganese in water samples

Method	R.S.D.%	Dynamic linear range (ng L^{-1})	Limit of detection (ng L^{-1})	Extraction time (min)	Ref.
USA-EME-SFO[#]-GF-AAS	3.3	500-10000	300	5	[33]
DLLME-FAAS	3.3	10000-200000	3000	1	[34]
Ionic liquid based DLLME-ICP-OES	6	750-200000	1000	1	[35]
Cloud point extraction-FAAS	4.3	5000-120000	1000	25	[36]
HLLME-FA-ICP-MS	3.7	0.5-500	0.1	1	This work

[#]Ultrasound assisted emulsification microextraction based on solidification floating organic drop

Table 3 — Determination of manganese in tap, well, river and ground water and relative recovery of spiked manganese in them

Sample	Concentration of Mn (ng L^{-1}) ± SD^a, n=3	Added Mn (ng L^{-1})	Found Mn (ng L^{-1}) ± SD^a, n=3	Relative recovery (%)
Tap water[b]	6.4 ± 0.2	10.0	15.9 ± 0.4	95
well water[c]	9.9 ± 0.1	10.0	19.7 ± 0.5	98
River water[d]	19.7 ± 0.4	10.0	28.9 ± 0.8	92
Ground Water[e]	13.1 ± 0.5	10.0	22.0 ± 0.7	89

[a]standard deviation, [b]Was taken from our laboratory (Tehran. Iran), [c]Was taken from Tehran (Tehran. Iran), [d]Was taken from Anzali River (Gilan, Iran), [e]Was taken from Tehran (Tehran, Iran)

linear range are better than of ultrasound assisted emulsification microextraction based on solidification floating organic drop[33], dispersive liquid-liquid microextraction[34], ionic liquid based dispersive liquid-liquid microextraction[35] and cloud point extraction[36] methods. Also, the main advantages of the proposed method are this novel method does not need centrifugation to separate the organic phase and it is possible to use of low-density extraction solvents. In this research, a special extraction cell was designed to facilitate collection of the low-density solvent extraction. It is easy to design and made extraction cell in every laboratory. The extraction solvent (toluene) of this method has lower toxicity than DLLME, and thus this method is more environmental friendly. It is interesting to note that the HLLME-FA method can be performed with wide range of lighter solvents than water and the selection of extraction solvent is not limited to high-density solvents. Finally, it can be concluded that the proposed method is an efficient, rapid, simple and cheap microextraction method that can be a complement technique for DLLME method that have been used with organic solvents more dense than water for the determination of manganese in water samples.

Applicability of the proposed procedure for determination of Mn in water

The proposed procedure was applied for the determination of Mn in water samples. The results are shown in Table 3. Recoveries of Mn from water samples spiked with Mn(II) were also studied (Table 3). According to these results, the added Mn(II) ions can be quantitatively recovered from the water samples by the proposed procedure. These results demonstrate the applicability of the procedure for Mn determination in water samples.

Conclusions

This paper describes the application of the HLLME-FA method combined with ICP-MS for the determination of trace amounts of manganese in water

samples. The method is precise, reproducible and linear over a wide range and requires small volume of organic extractant. Moreover, the environmental impact of the procedure is low because it uses very small amount of organic solvent. In addition, it is important to point out that HLLME-FA is a low organic solvent consuming extraction technique, which turns it into a low cost technique. This technique acts as a selective and can be separated the analyte from interferences. The new procedure of HLLME-FA does not need centrifugation to separate the organic phase. In this method, air flotation was used to break up the organic-in water emulsion and to finish the extraction process. The performance of this procedure in manganese extraction from different water samples with various matrices was good and no matrix effect was observed.

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