Speciation of Fe(III) and Fe(II) in water samples by liquid-liquid extraction combined with low-temperature electrothermal vaporization (ETV) ICP-AES

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SPECIATION OF Fe(III) AND Fe(II) IN WATER SAMPLES BY LIQUID–LIQUID EXTRACTION COMBINED WITH LOW-TEMPERATURE ELECTROTHERMAL VAPORIZATION (ETV) ICP-AES

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The use of 1-phenyl-3-methyl-4-benzoylpyrazolone (PMBP) as extractant for separation of Fe(III) and Fe(II) and low-temperature vaporization of the Fe(III)–PMBP chelate into ICP-AES for their speciation analysis was investigated. The factors affecting the formation of $Fe(PMBP)_3$ chelate and its vaporization behavior were investigated in detail. PMBP was used not only as the extractant for the separation of Fe(III) and Fe(II) but also as the chemical modifier for the low-temperature ETV-ICP-AES determination of iron. Under the optimized conditions, the detection limit for iron(III) and iron(II) are both 3.2 ng/mL, with relative standard deviations of 3.9 and 4.5%, respectively. The proposed method was applied to the determination of trace iron in biological standard reference materials and the species in East Lake water samples, and the results obtained were satisfactory.

Keywords: Liquid–liquid extraction; Iron speciation; PMBP; Chemical modifier; Low temperature ETV-ICP-AES

INTRODUCTION

Iron is the fourth most abundant element in the Earth's crust: it is present in a variety of rock and soil minerals as both Fe(III) and Fe(II). Accurate and precise measurements of iron redox species are important in the study of the aqueous environmental chemistry of trace elements because aqueous speciation of trace elements is sensitive to the absolute concentrations of Fe(III) and Fe(II). Determination of the oxidation states of iron in a variety of natural water samples is important in light of studies that iron may be the limiting nutrient for phytoplankton growth in open oceans [1,2], and Fe(II) is probably the preferred nutrient for phytoplankton [3]. In addition, Fe(III) serves as an effective catalyst for the autoxidation of SO_2 to SO_4^{2-} in clouds [4,5].

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Iron is a significant factor in the evaluation of water quality, and its reactivity also drives numerous chemical processes in natural waters [6].

In recent years, the determination of the oxidation state of iron in a variety of natural water samples (e.g. sea water, lake water, river water, and atmospheric water) has been generally achieved by complexation, with separation and preconcentration technology followed by sensitive measurements [7–9]. The determination of the oxidation states of iron in natural waters with different methods was critically reviewed by Pehkonen in 1995 [10]. More recently, Pulido and his co-workers [11] used a modified optical sensor to determine the iron speciation. The addition of a mini-column containing the oxidizing reagent in the loop of an injection valve allows the determination of Fe(III) and total inorganic iron.

A specific and effective chelating reagent with Fe(III) or Fe(II) was usually used for the speciation of Fe(III) and Fe(II). Solvent extraction is one of the classical and well-rounded technologies of separation. It is simple, selective, rapid, and recoveries are high. A chelating extraction system has the advantage of high efficiency and large coefficient of separation, and the formed chelates are very stable. Among the chelating reagents, acetylacetone, benzoate, cupferron, dithizone, and phenanthroline have been used for a long time [12,13], with phenanthroline being used particularly widely [13]. Mono 2-ethylhexyl ester (PC-88A) in toluene has been reported for extraction separation of Fe(III). From the extracted complex species in the organic phase Fe(III) was stripped with inorganic acid and then determined by the thiocyanate spectrophotometric method [14]. In another paper, the N,N'-bis(2-hydroxy-5-bromo-benzyl)-1,2-diaminopropane (HBDAP)–chloroform extraction system and spectrophotometric determination were used for speciation of Fe(III) and Fe(II) in natural waters [15]. The extraction of Fe(III) from hydrochloric acid solutions has also been investigated using a mixed solvent system consisting of tributyl phosphate (TBP) and methyl isobutyl ketone (MIBK) [16].

Electrothermal vaporization inductively coupled plasma atomic emission spectrometry (ETV-ICP-AES) is a powerful technique in which the vaporizing and exciting processes of the analyte are carried out separately. Research has shown that the use of a chemical modifier can effectively suppress the formation of refractory carbides, eliminate the memory effect, and improve the detection limit and precision of determination. Halogenating reagents, such as halocarbons [17,18] and polytetrafluoroethylene (PTFE) [19–21], were used to improve the vaporization behavior of refractory metal elements.

Recently, a significant development was achieved in the exploration and application of organic chelating reagents as chemical modifiers in ETV-ICP-AES. Tao and co-workers [22–24] early reported the vaporization of oxinates of refractory elements, and these oxinates of V, Cr and Al could be introduced into ICP at about 1000°C. The application of PMBP chelates of rare earth elements in ETV-ICP-AES was investigated, and it was found that PMBP chelates of La, Y, Eu, and Sc could be vaporized from a graphite tube at 1000, 1200, 1200 and 900°C, respectively [25–27]. The method was applied successfully to determination of trace rare earth elements in environmental samples and high-purity zirconium dioxide. It should be noted that the range of application might be broadened because PMBP can be adapted as both chemical modifier and extraction reagent.

The use of organic chelating reagents as chemical modifiers in ETV-ICP-AES has some general characteristics: (1) refractory elements vaporize at lower temperatures,

which is beneficial in prolonging the lifetime of the evaporator; (2) refractory elements are introduced into ICP as volatile chelates from the evaporator; (3) the application range can be broadened and the determination sensitivity can be improved by combining the technique with a separation/preconcentration procedure [28]. The successful application of oxine, PMBP, and acetylacetone in ETV-ICP-AES indicates that this new technique has potential.

The aim of this work is to develop a new sensitive method by combining extraction separation with low-temperature ETV-ICP-AES for iron speciation analysis. Here, the intention was to use PMBP as both a chelating reagent for effective extraction of Fe(III) and as a chemical modifier for an ETV-ICP-AES determination. The total iron was determined after oxidizing Fe(II) to Fe(III) and the Fe(II) could be obtained by subtracting Fe(III) from the total iron. Formation conditions of the chelate and the factors affecting its vaporization and transportation were studied in detail. The proposed method was applied in the determination of trace iron in biological standard reference materials and water samples.

EXPERIMENTAL

Apparatus

The graphite furnace sample introduction device and ICP-AES instrument used in this work were identical with that reported previously [25]. An ICP spectrometric system (Beijing Broadcast Instrument Factory, Beijing, China) with a 2-kW plasma generator was used with a conventional silica plasma torch. A WF-1B-type heating device with a matching graphite furnace (Beijing Second Optics, Beijing, China) was used for analyte vaporization. The radiation from the plasma was focused as a 1:1 image on the entrance slit of a WDG 500-1A type monochromator (Beijing Second Optics, Beijing, China) having a reciprocal linear dispersion of $1.6 \, nm \, mm^{-1}$. Transient emission signals from the plasma were detected with a R456 type photomultiplier tube (Hamamatsu, Japan) fitted with a laboratory-built direct current amplifier, and recorded by a U-135C recorder (Shimadzu, Kyoto, Japan). The instrument operating conditions and wavelength used are given in Table I.

Standard Solutions and Reagents

All reagents used were of specpure or at least of analytical reagent grade. Doubly distilled water was used throughout this work. Iron is a ubiquitous element, so all

TABLE I   Operating conditions for determination of Fe

Wavelength (nm)	259.940
Incident power (kW)	1.0
Carrier gas (Ar) (L/min)	0.6
Coolant gas (Ar) (L/min)	16
Plasma gas (Ar) (L/min)	0.8
Observation height (mm)	12
Entrance slit-width (μm)	25
Exit slit-width (μm)	25
Drying temperature (°C)	100; ramp 10 s, hold 10 s
Vaporization temperature (°C)	900, 4 s
Sample volume (μL)	10

containers were soaked in 5% HNO_3 for at least 48 h before rinsing thoroughly with a large amount of doubly distilled water.

Fe(III) Stock Solution

Fe(III) (1 mg mL^{-1}) stock solution was prepared by dissolving 0.864 g FeNH$_4$(SO$_4$)$_2$ · 12H$_2$O in a 100-mL flask using 2.5 mL of 25% H_2SO_4 and doubly distilled water.

Fe(II) Stock Solution

Fe(II) (1 mg mL^{-1}) stock solution was prepared by dissolving 0.702 g Fe(NH$_4$)$_2$(SO$_4$)$_2$ · 6H$_2$O in a 100-mL flask using 0.2 mL of concentrated H_2SO_4 and doubly distilled water. This solution was freshly prepared just before use.

Hydrogen Peroxide Oxidizing Solution

A 1% (w/v) H_2O_2 solution was prepared by diluting 3.33 mL of 30% (w/v) H_2O_2 solution to a total volume of 100 mL with doubly distilled water.

PMBP Solution

A 0.03-mol L^{-1} PMBP solution was prepared by dissolving 0.835 g PMBP in 100 mL benzene.

Procedure

Liquid–liquid extractions were carried out by shaking equal volumes of aqueous and organic phases for the required time at 25°C. In most cases, distribution equilibrium was attained in less than 30 min. For speciation studies, two aliquots of sample solutions were acidified to pH 2.5 with hydrochloric acid. One was directly extracted by PMBP–benzene solution, while the other was extracted by PMBP–benzene solution after adding 1% H_2O_2. The former was used for determination of Fe(III) and the latter for determination of total iron. The Fe(II) was obtained by subtracting Fe(III) from total iron. All the extraction procedures used in the sample treatment were also applied to the standard solutions.

   After phase separation, 10 μL of organic phase was pipetted into the graphite furnace with a microsyringe. The sample inlet hole was sealed with a graphite cylinder before the graphite furnace heating cycle was started. The gaseous chelate produced by low-temperature ETV was carried into the ICP by argon carrier gas. The relative emission intensity of iron was recorded, and the peak heights were measured for quantification.

RESULTS AND DISCUSSION

Separation of Fe(III) and Fe(II) with PMBP Extraction

It is well established that PMBP can effectively extract Fe(III) at pH 2–8 while Fe(II) will remain in the aqueous phase [29]. In this work, a pH value of 2.5 was used for separation of Fe(III) and Fe(II) with PMBP extraction. Figure 1 shows the emission
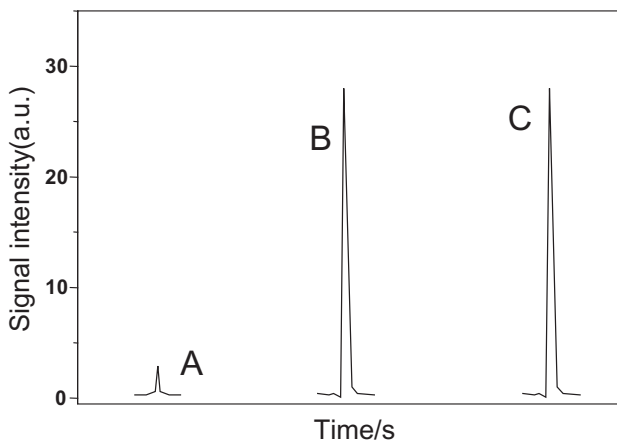
FIGURE 1   Separation of Fe(III) and Fe(II) with PMBP–benzene extraction: A, PMBP–benzene extracts 0.2 μg/mL Fe(II); B, PMBP–benzene extracts 0.2 μg/mL Fe(III); C, PMBP–benzene extracts 0.2 μg/mL Fe(III) and 0.2 μg/mL Fe(II). Conditions: drying, 100°C, ramp 10 s, hold 10 s; vaporization temperature, 900°C, 4 s.

signal profiles of Fe(III) and Fe(II) after extraction by equal volumes of PMBP–benzene solution. A strong signal intensity can be detected (Fig. 1B) in the organic phase after PMBP–benzene extraction of Fe(III). On the contrary, the signal of Fe(II) can hardly be detected (Fig. 1A) in the organic phase after PMBP–benzene extraction of the same amount of Fe(II). In order to verify this result, Fig. 1C is the signal profile obtained after PMBP–benzene extraction of 0.2 μg/mL Fe(III) mixed with 0.2 μg/mL Fe(II). It is obvious that the signal intensity obtained is the same as for PMBP extraction of an equal concentration of Fe(III) alone (Fig. 1B). This indicates that Fe(III) and Fe(II) can be effectively separated by PMBP extraction at pH 2.5.

The Effect of the Concentration of PMBP

To obtain a quantitative Fe(III) extraction from aqueous samples and the highest sensitivity for ETV-ICP-AES determination of Fe(III), the PMBP concentration should be optimized.

Figure 2 shows the effect of the concentration of PMBP on the signal intensity of iron. It was found that the signal intensity of iron strongly depended on the concentration of PMBP, and the maximum signal intensity was obtained after the PMBP concentration was more than 0.002 mol/L. As described previously, an excess of complexing reagent is usually required in low temperature ETV-ICP-AES to suppress the thermal decomposition of chelate during the vaporization process. Therefore, 0.003 mol/L of PMBP was used in this work.

Volatility of Chelate of Fe(III) and PMBP

It was found that the Fe(III)–PMBP chelate has good thermal stability and does not decompose at a temperature below 300°C [30]. This result demonstrates that low temperature vaporization of Fe(III) and PMBP chelate is possible using PMBP as a
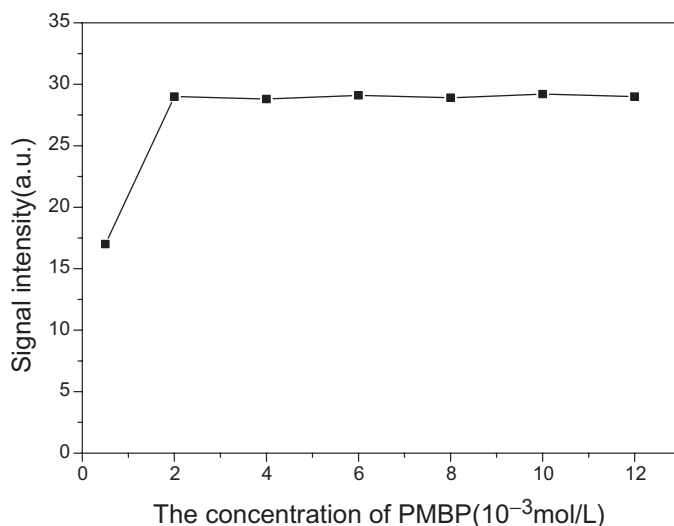
FIGURE 2 Effect of the concentration of PMBP on signal intensity. Conditions: Fe(III), 0.4 μg/mL; drying, 100°C, ramp 10 s, hold 10 s; vaporization temperature 900°C, 4 s.
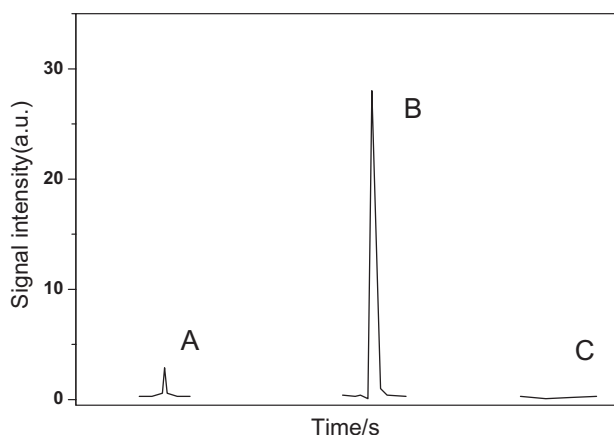

FIGURE 3 Signal profiles of Fe(III) vaporized at 900°C. A: only 0.1 μmol PMBP, B: 4 ng Fe(III) with 0.1 μmol PMBP, C: only 4 ng Fe(III).

chemical modifier. This possibility was further confirmed in this work. Figure 3 is a typical emission signal profile of Fe(III) obtained by low temperature ETV-ICP-AES with PMBP as chemical modifier. An intense and sharp emission signal profile was detected after the Fe(III) and PMBP chelate was formed in the graphite tube, and vaporized into the ICP at 900°C (Fig. 3B). On the contrary, no emission signal could be found for the same concentration of Fe(III) aqueous standard solution at the same vaporization temperature (Fig. 3C). Because iron is a widespread contaminating element, a very weak emission signal could be observed when PMBP–benzene was introduced into the graphite tube and vaporized into the ICP at 900°C (Fig. 3A). These results demonstrated that the analyte (Fe) was introduced into the ICP as the gaseous PMBP chelate.

Selection of Drying Conditions

There are many factors affecting the vaporization behavior of the Fe(III)–PMBP chelate, so it is necessary to investigate the influence of these factors and optimize the experimental conditions.

As mentioned above, the Fe(III)–PMBP chelate has good thermal stability below 300°C [28], so a drying temperature of 100° was selected. At the selected drying temperature, the effect of drying time on the vaporization behavior of the Fe(III)–PMBP chelate was investigated. It was found that the drying time had no significant influence on the signal intensity of the analyte and was constant after the drying time was more than 5 s. The drying time of 10 s was chosen in this work.

Optimization of Vaporization Conditions

The effect of vaporization temperature on signal intensity was studied and the result is shown in Fig. 4. At 350°C, a weak signal could be detected, showing that Fe(III)–PMBP chelate was formed and introduced into the ICP. As the vaporization temperature increased, the signal intensity increased markedly. At 800°C, the analytical signal intensity reached its maximum and remained constant at higher temperature.

Figure 5 shows the effect of vaporization time on the vaporization behavior of Fe(III)–PMBP chelate. The highest signal intensity was achieved after the vaporization time was longer than 3 s. Based on the above results, a vaporization temperature of 900°C and a vaporization time of 4 s were selected for this work.

Interferences

The influence of common metal ions, such as Na(I), K(I), Mg(II), Ca(II), and Al(III) on the determination of iron(III) were studied. The tolerance amounts of co-existing elements, which gave less than a 10% error for the determination of iron(III), were evaluated. The tolerance amounts of tested elements (absolute mass) are as follows:
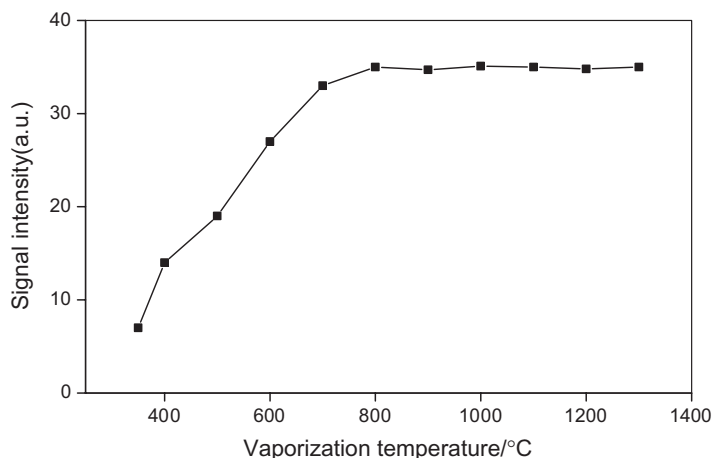

FIGURE 4 Effect of vaporization temperature on signal intensity. Conditions: Fe(III), 4 ng mixed with 0.1 μmol PMBP; drying, 100°C, ramp 10 s, hold 10 s; vaporization time, 4 s.
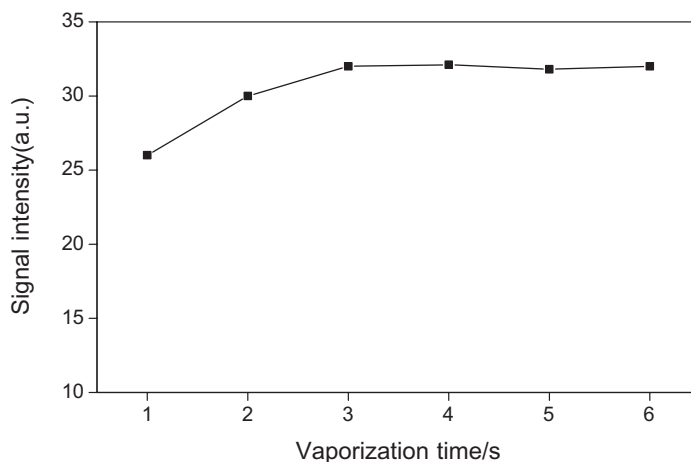
FIGURE 5   Effect of vaporization time on signal intensity. Conditions: Fe(III), 4 ng mixed with 0.1 μmol PMBP; drying, 100°C, ramp 10 s, hold 10 s; vaporization temperature, 900°C.

20 μg Na(I), 20 μg K(I), 4 μg Mg(II), 4 μg Ca(II), and 0.4 μg Al(III) are equivalent to 5000-, 5000-, 1000-, 1000-, and 100-fold of analyte (4 ng Fe(III)), respectively.

Detection Limit and Precision

The detection limit is defined as three times the standard deviation of background noise signal intensity. The detection limit of the proposed method was found to be 3.2 ng/mL for both iron(III) and iron(II). The calibration curves for iron(III) with the use of PMBP as chemical modifier was linear from 0.05 μg/mL to 20 μg/mL. The relative standard deviations measured at 0.2 μg/mL iron(III) and iron(II) were 3.9 and 4.5%, respectively ($n = 8$).

Samples Analysis

The developed method was applied to the determination of total iron in biological standard reference materials and Fe(III) and Fe(II) in water samples.

Rice Flour Reference Materials

For determination of total iron in biological standard reference materials (NIES No. 10-a, No. 10-b and No. 10-c), 0.5000-g rice flour samples (dried in an air oven at 85°C for 4 h) were weighed and transferred into separate 10-mL cleaned beakers. The samples were soaked in 7 mL concentrated nitric acid for 20 h, then 0.5 mL perchloric acid was added and the samples were digested by heating gently. The resulting solutions were evaporated to near dryness. The residue was dissolved in dilute nitric acid, and diluted to 2 mL with doubly distilled water. The final sample solutions were determined according to the procedure described previously. The analytical results (Table II) show that the determined values are in good agreement with the certified values. No significant difference was found at the 95% confidence level.

TABLE II   Analytical results for iron in rice flour reference materials

Sample	Measured value[a], μg/g	Certified value, μg/g
NIES No. 10-a	11.9 ± 0.4	12.7 ± 0.7
NIES No. 10-b	12.8 ± 0.8	13.4 ± 0.9
NIES No. 10-c	11.1 ± 0.5	11.4 ± 0.8

[a]mean $\pm$ sd, $n = 3$.

TABLE III   Analytical results for Fe(III) and Fe(II) in synthetic water samples (μg/mL)

Added		Determined[a]		Calculated
Fe(III)	Fe(II)	Fe(III)	Fe(III+II)	Fe(II)
1.00	1.00	1.02 ± 0.06	2.02 ± 0.05	1.01 ± 0.07
0.50	5.00	0.52 ± 0.03	5.51 ± 0.08	5.00 ± 0.06
5.00	0.50	5.03 ± 0.07	5.53 ± 0.04	0.50 ± 0.09

[a]mean $\pm$ sd, $n = 3$.

TABLE IV   Analytical results for Fe(III) and Fe(II) in East Lake water sample (μg/mL)

Fe(III)			Fe(II)		
Added	Determined[a]	Recovery, %	Added	Determined[a]	Recovery, %
0	0.15 ± 0.01	–	0	–	–
0.10	0.25 ± 0.01	99 ± 7	0.10	0.10 ± 0.01	100 ± 10
0.20	0.34 ± 0.02	97 ± 8	0.20	0.21 ± 0.02	105 ± 9

– not detected.
[a]mean $\pm$ sd, $n = 3$.

Synthetic Water Samples

Synthetic water samples were analyzed to check the accuracy and precision of the proposed method. The concentrations of Fe(III) and Fe(II) obtained (Table III) were in good agreement with the expected values in the concentration range 0.5 to 5.0 μg/mL.

Lake Water Samples

Lake water was collected in a 50-mL polyethylene container. Immediately after sampling, all water samples were filtered through a 0.45-μm filter membrane. The filtered samples were acidified to pH 2.5 with hydrochloric acid and determined by the procedure described previously. The analytical results of the samples together with the recoveries are listed in Table IV. Note that Fe(II) could not be detected in lake water.

CONCLUSION

This work developed a new method for the speciation of Fe(III) and Fe(II) using solvent extraction combined with low-temperature ETV-ICP-AES. The proposed

method is simple, rapid, sensitive, and reliable, and can be applied to the determination of Fe(III) and Fe(II) in a wide variety of water and other environmental samples.

Acknowledgements

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