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Ionic liquid-based extraction followed by graphite-furnace atomic absorption spectrometry for the determination of trace heavy metals in high-purity iron metal

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ABSTRACT

The analysis of high-purity materials for trace impurities is an important and challenging task. The present paper describes a facile and sensitive method for the determination of trace heavy metals in high-purity iron metal. Trace heavy metals in an iron sample solution were rapidly and selectively preconcentrated by the extraction into a tiny volume of an ionic liquid [1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide] for the determination by graphite-furnace atomic absorption spectrometry (GFAAS). A nitrogen-donating neutral ligand, 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPTZ), was found to be effective in the ionic liquid-based selective extraction, allowing the nearly complete (~99.8%) elimination of the iron matrix. The combination with the optimized GFAAS was successful. The detectability reached sub-μg g^{-1} levels in iron metal. The novel use of TPTZ in ionic liquid-based extraction followed by GFAAS was successfully applied to the determination of traces of Co, Ni, Cu, Cd, and Pb in certified reference materials for high-purity iron metal.

1. Introduction

The analysis of high-purity materials for trace impurities is important not only for their quality control but also for gaining insight into the synergistic action and correlation of the impurities. For example, iron metal exhibits different properties, depending on the impurities even at low μg g^{-1} or lower levels [1,2]. Such trace impurities can sometimes be directly determined by instrumental analysis, e.g., laser ablation-inductively coupled plasma-mass spectrometry [3,4]. Difficulties, however, lie due to heterogeneous ablation, insufficient introduction of ablated particles, and serious matrix-interferences.

Chemical pretreatment, including sample digestion and separation procedures, is thus beneficial to the precise and accurate analysis of iron metal for trace impurities [5]. Many techniques have been employed to separate elements of interest from the iron matrix: e.g., sorption [6–13], liquid–liquid extraction [14–19], precipitation [19–24], electrolysis [15,25,26], and volatilization [27,28]. However, these techniques are often tedious and time-consuming and they sometimes require volatile, flammable, and ill-smelling organic solvents or highly corrosive hydrofluoric acid. Special apparatus is also required for some techniques. Our research group has therefore studied less hazardous surfactant-mediated techniques for facile separation [10,12,17].

Ionic liquids are another candidate for a separation medium. They have emerged as an attractive alternative to conventional organic solvents because of the low volatility and flammability [29–32]. In addition to the safety, ionic liquids have a unique property of extracting charged species, which can be rationalized by ion-exchange and ion-pairing mechanisms [33]. Early examples include the extraction of alkali and alkaline-earth metal ions complexed with neutral ligands (e.g., crown ethers) [34–36]. Recently, we have reported the extraction of a cationic dye methylene blue [3,7-bis(dimethylamino)phenazathionium] for the spectrophotometric determination of trace S(-II) in water [37] and the extraction of heteropoly molybdic acids for the high-performance liquid chromatographic determination of traces of Si, P, and Si in high-purity iron metal [18].

Ionic liquid-based extraction can also be employed to determine trace metals in water by graphite-furnace atomic absorption spectrometry (GFAAS) [38–41]. The present paper describes a powerful combination of ionic liquid-based extraction and GFAAS for the determination of trace heavy metals in high-purity iron metal. After digesting an iron sample, traces of divalent heavy metals in the solution were selectively preconcentrated into an ionic liquid and subsequently determined by GFAAS. Because

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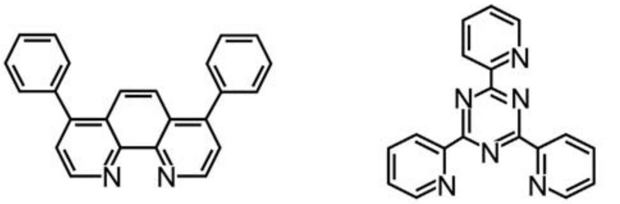
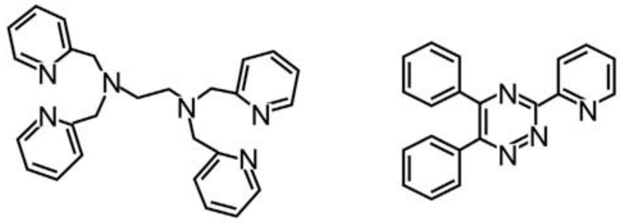


4,7-Diphenyl-1,10-phenanthroline (Diphen)

2,4,6-Tri(2-pyridyl)-1,3,5-triazine (TPTZ)



N,N,N′,N′-Tetrakis(2-pyridylmethyl)-ethylenediamine (TPEN)

3-(2-Pyridyl)-5,6-diphenyl-1,2,4-triazine (PDT)

Fig. 1. Chelating agents examined here.

the iron matrix can be oxidized to the trivalent state by commonly performed acid-digestion, the selective extraction was tried with N-donating neutral ligands (Fig. 1), which were expected to be less reactive with Fe(III) according to the well-accepted HSAB principle. These ligands were also expected to form the cationic chelates with other heavy metals, thus being promising for the selective extraction with an ionic liquid. In addition, GFAAS can allow the analysis of tiny volumes of sample solution and the elimination of the organic matrices (including solvent) at the drying and/or pyrolysis steps. The resulting advantages include no need for masking and back-extraction steps, decreased reagent usage, and no interference by the iron matrix. These advantages allowed the facile and sensitive determination with low risk of contamination.

2. Experimental

2.1. Apparatus and reagents

A Perkin-Elmer (Norwalk, CT, USA) AAnalyst 600 Zeeman graphite-furnace atomic absorption spectrometer equipped with an AS-800 autosampler was used for the determination of heavy metals under the following furnace operating conditions: The graphite tube was warmed for 1 s to 110 °C and held for 15 s to prevent bumping. The tube was further heated for 15 s to 200 °C and held for 15 s; it was then heated for 10 s to a pyrolysis temperature of 500 °C and held for 50 s. The tube was quickly heated to atomization temperatures of 2100 °C (Fe), 2400 °C (Co), 2300 °C (Ni), 2000 °C (Cu), 1500 °C (Cd), or 1900 °C (Pb) and held for 5 s. Clean-up was done at 2500 °C for 5 s. The wavelengths used were 248.3 nm (Fe), 242.5 nm (Co), 232.0 nm (Ni), 324.8 nm (Cu), 228.8 nm (Cd), and 283.3 nm (Pb). Hollow-cathode lamps were operated at 30 mA (Fe and Co), 25 mA (Ni), 15 mA (Cu), 4 mA (Cd), and 10 mA (Pb).

4,7-Diphenyl-1,10-phenanthroline (Diphen), 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPTZ), *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN), and 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazin (PDT) were purchased from Tokyo Kasei (Tokyo, Japan). The ionic liquids used were 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([BMIM][NTf_2], special grade for advanced material research, Kanto Kagaku, Tokyo, Japan) and 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([OMIM][NTf_2]), Nippon Gohsei, Osaka, Japan).

An iron(III) solution (10 mg mL^{-1} in 0.1 M HNO_3) was prepared from $Fe(NO_3)_3 \cdot 9H_2O$ (Wako Jun-yaku, Osaka, Japan); the concentration was checked by GFAAS. Certified reference materials for high-purity iron metal (chips), NIST 2168 and JSS 003-5, were obtained from National Institute of Standard and Technology (Gaithersburg, MD, USA) and Japan Iron and Steel Federation (Tokyo, Japan), respectively. Commercial standard metal solutions were purchased from Wako Jun-yaku and diluted to appropriate concentrations with 0.1 M HNO_3. A standard Pd solution (1.0 mg mL^{-1} in 1 M HNO_3) was purchased from Kanto Kagaku and used as a chemical modifier in GFAAS without dilution. Hydrochloric acid (12 M) and nitric acid (16 M) were of ultra-pure grade (Kanto Kagaku).

All reagents used were of reagent grade, unless otherwise stated. Water was purified with a Millipore (Billerica, MA, USA) Milli-Q Integral 5A-10 system.

2.2. Recommended procedure

A 500-mg iron sample was decomposed with 1.5 mL each of 12 M HCl and 16 M HNO_3 at a moderate temperature (50–80 °C) and diluted to 10 mL with water. A 1/100-aliquot (5.0 mg as Fe) of the solution was taken in a 15-mL centrifugation tube and it was diluted to 10 mL with water to give a pH around 2.0. The sample solution was vigorously shaken for 3 min with 150 μL of [BMIM][NTf_2] containing 0.10 M TPTZ. The ionic liquid phase (decreased to 90 μL due to the partial dissolution in the aqueous phase) was separated on the bottom by centrifugation at 7000 *g* for 5 min, collected in a graduated vessel with a microsyringe, and diluted to 1.0 mL with *N*,*N*-dimethylformamide (DMF). A 20-μL aliquot of the final solution (after dilution, if necessary) was subjected to the analysis for trace heavy metals by GFAAS with addition of 10 μL of Pd solution. The measurement was repeated three times and the obtained signals were averaged. Calibration curves were prepared using DMF containing metals of interest at sub- to low ng mL^{-1} levels.

3. Results and discussion

3.1. Ionic liquid-based extraction

Although ionic liquids can extract charged species, heavy metal ions were not extracted without chelating agents. Therefore, different chelating agents (Fig. 1) were examined by taking the extraction of Ni(II) as an example. A 200-ng amount of Ni(II) was added to 10 mL of water at pH 2.0 and it was extracted into 150 μL each of chelating agent-containing ionic liquids ([BMIM][NTf_2] and [OMIM][NTf_2]). However, Diphen and TPEN were scarcely dissolved in the ionic liquids. The other chelating agents (PDT and TPTZ) were soluble in the ionic liquids, thus being used at a near saturation level (0.10 M). Both ionic liquids provided similar recoveries: 35–37% for PDT and 99–100% for TPTZ. However, the ionic liquids differed in viscosity and solubility in water. Although [BMIM][NTf_2] was more water-soluble than [OMIM][NTf_2] (solubility at 25 °C, 0.72 and 0.09 wt%, respectively [31]), the former was less viscous and thus easier to handle. Therefore, [BMIM][NTf_2] containing TPTZ was used in the following studies. For comparison, ionic liquids were replaced by chloroform. Even with Diphen, TPEN, PDT, and TPTZ at 0.10 M, no extraction was observed, indicating that the use of ionic liquids was essential for the present method.

Fig. 2 shows the effect of pH and shaking time on the extraction of trace heavy metals [Co(II), Ni(II), Cu(II), Cd(II), and Pb(II)]. The simultaneous and nearly complete ($>96\%$) extraction was achieved at pH 1.8 or higher. The extraction was also, but slightly, affected by the shaking time. For all the heavy metals examined,

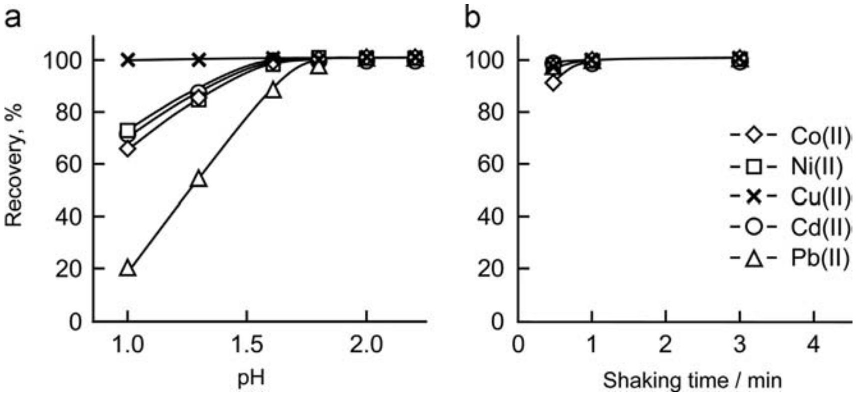


Fig. 2. Effect of pH (a) and shaking time (b) on the extraction of trace heavy metals. Co(II), Ni(II), Cu(II), Pb(II): 200 ng each. Cd(II): 20 ng. For (a), shaking time 3 min. For (b), pH 2.0.

the recoveries reached 90% or higher within 30 s and they were increased to 97% or higher at 1 min. The extraction was therefore performed by shaking for 3 min around pH 2.0 to ensure the simultaneous extraction of trace heavy metals.

The extraction did not require strict control of temperature; no difficulty was encountered at room temperatures of 15–30 °C. High ionic strengths, even 4.0 M NaCl (near saturation), caused no interference. The decrease in the concentration of TPTZ by half (0.05 M) led to the slight decrease in the recovery: e.g., 86% (pH 1.8) and 93% (pH 2.0) for Pb(II).

3.2. Determination by GFAAS

Although [BMIM][NTf_2] was less viscous, the direct injection into a graphite tube with the autosampler used was still problematic; incomplete injection was often observed. In addition, serious background absorption and distortion of the analytical signal occurred probably due to the insufficient elimination of the ionic liquid at the pyrolysis step. Therefore, the ionic liquid was diluted with DMF before the injection and the pyrolysis conditions were optimized. Although ethanol was also examined for the dilution, the reproducibility of the analysis sometimes deteriorated. The optimal temperature for the pyrolysis was around 500 °C. When the pyrolysis was done below 450 °C, the analysis was interfered by background absorption. Pyrolysis temperatures above 550 °C led to the decreased sensitivity, indicating the vaporization loss of the analyte. The time required for the sufficient pyrolysis was 40 s or longer. The pyrolysis was therefore done for 50 s to ensure the elimination of the interference source. The sensitivity did not change for at least up to 90 s. The use of a Pd modifier was essential, otherwise the sensitivity was decreased, especially for Cd.

Under the optimized conditions for GFAAS, at least up to 18 vol% of the ionic liquid in DMF did not interfere with the determination of trace heavy metals, except for Cu. The analytical signal of Cu was slightly (~10%) decreased in the presence of 16 vol% of the ionic liquid; the tolerance limit was 12 vol%. After the extraction, the ionic liquid phase was decreased to 90 μL due to the partial dissolution in the aqueous phase. The undissolved ionic liquid, into which metals of interest were extracted, was collected and diluted to 1.0 mL with DMF before the injection. The partial dissolution of the ionic liquid was reproducible, hence the ionic liquid in the final solution did not affect the determination of Cu. The chelating agent TPTZ caused no interference even at a near saturation level (0.030 M) in DMF.

When dealing with 20 mL of sample solution, the extraction of trace heavy metals was satisfactory. However, due to the dissolution in the aqueous phase, the ionic liquid phase was decreased to 30 μL, which was the practical lower limit for handling the undissolved ionic liquid. The dilution of the collected ionic liquid to 250 μL or more with DMF (ionic liquid, < 12 vol%) allowed the determination by GFAAS without interference, indicating that up to 80-fold preconcentration of trace heavy metals can be made for aqueous samples.

To find the required level of separation, the tolerance limit of Fe in the final solution was investigated. Up to 50 μg mL^{-1} of Fe did not interfere with the determination of trace heavy metals by GFAAS, except for Cd. The tolerance limit for the determination of Cd was 30 μg mL^{-1} of Fe in the final solution.

Table 1
Separation of trace heavy metals from Fe(III).

Fe(III) taken/mg	Recovery (%)					Fe found in the final solution/μg
	Co(II)	Ni(II)	Cu(II)	Cd(II)	Pb(II)	
5.0[a]	97	96	98	100	95	11
	95	96	94	98	100	9
5.0[b]	101	101	101	100	95	–[c]
	100	95	102	99	99	–[c]
7.0[a]	88	86	85	81	81	15
	98	87	84	80	75	14
10[a]	92	87	74	70	65	21
	91	88	66	88	74	19

[a] Co(II), Ni(II), Cu(II), Pb(II): 20 ng each. Cd(II): 2.0 ng.
[b] Co(II), Ni(II), Cu(II), Pb(II): 5.0 ng each. Cd(II): 0.50 ng.
[c] Not determined.

3.3. Analysis of synthetic and real samples

Milligram amounts of Fe(III) and nanogram amounts each of Co (II), Ni(II), Cu(II), Cd(II), and Pb(II) were added to 10 mL of water at pH 2.0. The resulting synthetic sample solutions were treated as described in *Recommended Procedure*. As given in Table 1, the Fe found in the final solution was 9–21 μg (~99.8% removal), which allowed the determination by GFAAS without interference. The simultaneous and nearly complete recoveries of trace heavy metals were obtained in the presence of 5.0 mg of Fe(III). Therefore, real samples (certified reference materials for high-purity iron metal) were analyzed by the proposed method. As given in Table 2, the analytical results were consistent with the certified or indicative values. The detection limits (in μg g^{-1}), based on the 3σ blank fluctuations, were 0.3 for Ni and Cu, 0.2 for Co and Pb, and 0.04 for Cd. The quantification limits (in μg g^{-1}), based on the 10σ blank fluctuations, were 1 for Ni and Cu, 0.6 for Co and Pb, and 0.2 for Cd. Owing to the low blanks, the sensitive determination

Table 2
Analytical results for high-purity iron metals.

Sample	Metal	Concentration in sample/μg g^{-1}	
		Determined[a]	Certified
NIST 2168	Co	6.1 ± 0.2	6 ± 2
	Ni	11.3 ± 0.5	10 ± 5
	Cu	5.2 ± 0.5	5 ± 2
	Cd	<0.04	(<1)[b]
	Pb	<0.2	(<1)[b]
JSS 003-5	Co	2.2 ± 0.1	2.2 ± 0.2
	Ni	0.4 ± 0.1	0.4 ± 0.1
	Cu	15.0 ± 0.6	15.4 ± 0.5
	Cd	<0.04	(<0.1)[b]
	Pb	<0.2	(<0.1)[b]

[a] Mean ± standard deviation, $n=4$.
[b] Indicative value.

was achieved, though the relative standard deviation for Ni in JSS 003-5 was somewhat large as a result of the low concentration near the detection limit. In the other cases, the reproducibility was satisfactory. The results obtained here demonstrate the practical applicability of the proposed method to the determination of trace heavy metals in high-purity iron metal. Without the matrix-separation procedure, the reliable determination at such trace levels cannot be made due to serious matrix-interferences.

4. Conclusion

In the present study, an N-donating neutral ligand, TPTZ, was found to be suitable for the ionic liquid-based selective extraction of trace heavy metals. Simply shaking a sample solution with a tiny volume of a TPTZ-containing ionic liquid allowed the rapid and selective preconcentration of trace heavy metals. The novel use of TPTZ in ionic liquid-based extraction, in combination with the optimized GFAAS, facilitated the analysis of high-purity iron metal with high sensitivity and low risk of contamination. The scope of the application may not be limited to the analysis of iron samples, but may encompass many other analytical fields, such as the determination of trace heavy metals in biological and environmental samples.

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