Matrix-precipitation for the Determination of Trace Impurities in High-purity Iron

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The present paper describes a facile method for the determination of trace impurities in iron metals. This method is based on the selective removal of the matrix element as hydroxide precipitate followed by the determination of desired trace elements left in the solution. To an iron sample solution were added ethylene glycol bis(2-aminoethyl ether)-*N,N,N',N'*-tetraacetic acid (EGTA) and diethylenetriamine. The iron(III) matrix was almost completely (>99%) precipitated at pH 9.5, while trace elements [Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II)] were left in the solution due to the complexation with EGTA and diethylenetriamine. The sufficient removal of the matrix element and negligible loss of trace elements allowed the sensitive determination at ng g⁻¹ levels by inductively coupled plasma-mass spectrometry.

KEY WORDS: matrix precipitation; iron(III) hydroxide; trace metals; high-purity iron; inductively coupled plasma-mass spectrometry.

1. Introduction

Iron metals are essential materials in various fields of industry. The properties of iron metals strongly depend on the impurities, even at low $\mu\text{g g}^{-1}$ or lower levels.^{1,2)} The analysis for trace impurities is thus important for the quality control and gaining further insight into the synergistic action and correlation of the impurities. Ishida and colleagues obtained the detection limits at 10 ng g⁻¹ levels by the combination of laser ablation and inductively coupled plasma-mass spectrometry (ICP-MS).³⁾ Difficulties in the direct analysis include heterogeneous ablation, insufficient introduction of ablated particles, and serious matrix-interferences. Therefore, trace analysis of high-purity iron metals generally requires chemical pretreatment steps,⁴⁾ in which the desired elements are separated from the matrix element to obtain accurate and precise results.

Many separation techniques, including sorption,^{5–12)} liquid-liquid extraction,^{13–18)} coprecipitation,^{18–22)} electrolysis,^{14,23,24)} and volatilization,^{25,26)} have been employed to determine impurities at ultratrace levels in iron and steels. However, these techniques are often tedious and time-consuming and they sometimes require volatile, flammable, and ill-smelling organic solvents or corrosive and hazardous acids. Special instruments are also needed for some techniques. The authors have therefore developed multielement separation techniques based on the selective removal of an iron(III) matrix with polyoxyethylene-type nonionic surfactants.^{9,16)} The sufficient removal was attained at high concentrations

of hydrochloric acid or lithium chloride, while various trace elements were left in the solution and determined by ICP-MS. Before the determination, however, the evaporation of the solution or the sorption and desorption of trace elements were required to eliminate the excess acid or salt, respectively.

Alternatively, selective precipitation of the matrix element, though scarcely applied to iron samples, is potentially useful for facile multielement separation. The determination of trace elements left in the solution can facilitate the trace analysis of several materials (e.g., copper, silver, and lead metals) for impurities.^{27–29)} However, the coprecipitation loss of trace elements is often problematic for iron samples. For example, Watanabe and colleagues removed the iron(III) matrix as hydroxide precipitate to determine Cr in steel.³⁰⁾ The recovery was not quantitative (84%) due to the coprecipitation, though the removal was satisfactory. Other elements such as Mn(II), Ni(II), and Cu(II) were almost completely coprecipitated.

In the present study, coprecipitation of trace elements was successfully controlled by complexation. The iron(III) matrix was selectively precipitated as the hydroxide, leaving trace elements [Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II)] in the solution. The direct analysis of the supernatant solution by ICP-MS offered the determination of impurities even at ng g⁻¹ levels in iron metals. The proposed separation method is simple and rapid and it employs no special instrument.

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2. Experimental

2.1. Apparatus and Reagents

An SPQ-6500 ICP-mass spectrometer (without a dynamic reaction cell, Seiko Instruments and Electronics, Ltd.) and an AA-1 Mark II atomic absorption spectrometer (Nippon Jarrell-Ash Co., Ltd.) were used for the determination of trace metals and iron, respectively. The operating conditions are summarized in **Table 1**. An MX-300 centrifuge (Tomy Digital Biology Co., Ltd.) was used for the separation of hydroxide precipitate at 7 000 g.

Ethylenediamine, diethylenetriamine, triethylenetetramine, and tetraethylenepentamine (Kishida Chemical Co., Ltd.) were dissolved each in water to give a concentration of 4.0 M. Aqueous 28% (w/w) ammonia (Wako Pure Chemical Industries, Ltd.) and 25% (w/w) tetramethylammonium hydroxide (TMAH, ultra-pure grade, Tama Chemicals Co., Ltd.) were diluted with water to appropriate concentrations. Iminodiacetic acid (IDA), nitrilotriacetic acid (NTA), ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA), ethylene glycol bis(2-aminoethyl ether)-*N,N,N',N'*-tetraacetic acid (EGTA), and diethylenetriamine-*N,N,N',N'',N''*-pentaacetic acid (DTPA) (Dojindo Laboratories) were dissolved each in a 2.5% (w/w) TMAH solution to give a concentration of 0.10 M.

An Fe(III) solution (100 mg mL⁻¹) was prepared by decomposing 2.00 g of iron metal (99.998% purity, powder, Johnson Matthey Plc) with 6.0 mL each of 12 M HCl and 16 M HNO₃ at 60–70°C and diluting the solution to 20 mL with water. Certified reference materials (CRM) for high-purity iron, JSS 001-6 and JSS 003-5 (chips), were obtained from Japan Iron and Steel Federation. Another CRM for high-purity iron, NIST 2168 (chips), was obtained from National Institute of Standards and Technology. Standard solutions of metals (1.0 µg mL⁻¹ in 1.0 M HNO₃) were prepared from commercial standard solutions (Wako Pure Chemical Industries, Ltd.). Mineral acids included nitric acid (16 M, ultra-pure grade, Kanto Chemical Co., Inc.) and

hydrochloric acid (12 M, ultra-pure grade, Kanto Chemical Co., Inc.).

All reagents used were of reagent grade, unless otherwise stated. Water was purified with a Milli-Q Gradient A-10 system (Nihon Millipore K. K.).

2.2. Recommended Procedure

A 1.00-g iron sample was decomposed with 3.0 mL each of 12 M HCl and 16 M HNO₃ at 60–70°C and diluted to 10 mL with water. A 1/20-aliquot (50 mg as Fe) of the solution was taken in a 15-mL centrifugation tube and diluted to 2.5 mL with water. After adding 1.25 mL of EGTA solution, the solution was mixed with 0.88 mL of diethylenetriamine solution to adjust the pH to 9.5 (if necessary, TMAH solution was further added). The solution was diluted to 5.0 mL with water, left to stand for 10 min, and centrifuged for 5 min to separate the precipitate of iron(III) hydroxide. The supernatant solution was analyzed by ICP-MS for trace metals. Calibration graphs were constructed as follows. In a 5.0-mL volumetric flask were taken 0.80 mL of 5 M HNO₃, 1.25 mL of EGTA solution, and 0.88 mL of diethylenetriamine solution. After adding metals of interest at pg mL⁻¹ to ng mL⁻¹ levels, the solution was diluted to the mark with water and introduced into the ICP-mass spectrometer.

3. Results and Discussion

3.1. Control of Coprecipitation by Complexation

First, the coprecipitation of trace metals was investigated with 5.0 mL of sample solution containing 50 mg of iron(III) and 250 ng each of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II). The pH was adjusted to 9.5 with an alkaline reagent TMAH to form the precipitate of iron(III) hydroxide. The iron and trace metals left in the solution were determined by atomic absorption spectrometry and ICP-MS, respectively. The iron was found to be 0.012 mg (99.98% removal), which did not interfere with ICP-MS. The trace metals, however, were less than 10 ng, which indicates that more than 96% of trace metals were lost by coprecipitation.

The loss of trace metals was partly prevented by adding an aminopolycarboxylate ligand before the precipitation. As given in **Table 2**, the losses of Cu and Cd were nearly negligible with EDTA, EGTA, and DTPA, while the other metals were still lost and insufficiently left in the solution. On the other hand, the removal of the iron matrix was interfered

Table 1. Operating conditions for ICP-MS and atomic absorption spectrometry.

<i>ICP-MS</i>	
Argon flow rate	
Outer	17 L min ⁻¹
Intermediate	0.8 L min ⁻¹
Carrier	1.0 L min ⁻¹
RF power	0.8 kW
Sampling depth	12 mm
Isotopes measured	⁵⁵ Mn, ⁵⁹ Co, ⁶⁰ Ni, ⁶³ Cu, ⁶⁴ Zn, ¹¹⁴ Cd, ²⁰⁸ Pb
<i>Atomic absorption spectrometry</i>	
Flame gas flow rate	
Air	7.0 L min ⁻¹
Acetylene	2.0 L min ⁻¹
Lamp current	10 mA
Wavelength measured	248.3 nm (Fe)

Table 2. Separation of trace metals with different aminopolycarboxylate ligands.

	Trace metals recovered, %							Fe remaining/ mg
	Mn	Co	Ni	Cu	Zn	Cd	Pb	
IDA	0	55	66	69	0	1	8	0.0066
NTA	28	54	52	76	68	88	3	0.68
EDTA	73	81	42	93	96	92	82	7.3
EGTA	64	68	62	96	62	97	52	0.011
DTPA	69	66	64	91	92	91	73	7.1

Trace metals 250 ng each, Fe 50 mg, aminopolycarboxylate ligand 25 mM, pH 9.5.

by the complexation with aminopolycarboxylate ligands, except for IDA and EGTA. Compared with IDA, EGTA was more powerful in controlling the coprecipitation, hence it was used in the following studies.

To completely control the coprecipitation, the pH was adjusted with an amine ligand, instead of TMAH, after the addition of EGTA. As given in **Table 3**, diethylenetriamine and tetraethylenepentamine were effective for all the trace metals tested. However, the latter was more reactive with iron than the former, leading to the one order of magnitude decrease in the removal efficiency. Therefore, the former was used together with EGTA. The iron remaining in the solution (0.13 mg, or $26 \mu\text{g mL}^{-1}$) did not interfere with ICP-MS.

3.2. Effect of Ligand Concentration and pH

The combination of EGTA and diethylenetriamine met the criteria of removing the iron matrix and leaving trace metals in the solution. The effect of the EGTA concentration was next investigated at a diethylenetriamine concentration of 0.70 M and pH 9.5 (optimal conditions, as described later). As given in **Table 4**, the appreciable loss of Pb was observed at 10 and 20 mM. On the other hand, the removal of the iron matrix was deteriorated at 30 mM because the unfavorable complexation with EGTA became not negligible. Holding the EGTA concentration constant (25 mM, optimal condition), the effect of the amine concentration was investigated. Because the pH varied with the amine

concentration, it was maintained at 9.5 by further adding TMAH or nitric acid, if necessary. As given in Table 4, the lower concentrations (0.20 and 0.40 M) led to the loss of Mn, Co, Zn, and Pb, while the higher concentrations (0.80 and 0.90 M) resulted in the gradual decrease in the removal efficiency for the iron matrix. Considering the results of the series of experiments, 25 mM EGTA and 0.70 M diethylenetriamine were employed in the following studies.

The effect of pH was shown in **Fig. 1**. The loss of trace

Fig. 1. Effect of pH on the separation of trace metals from iron matrix. Trace metals 250 ng each, Fe 50 mg, EGTA 25 mM, diethylenetriamine 0.70 M.

Table 3. Separation of trace metals with EGTA and different amine ligands.

	Trace metals recovered, %							Fe remaining/ mg
	Mn	Co	Ni	Cu	Zn	Cd	Pb	
Ammonia	82	78	79	103	86	103	88	0.015
Ethylenediamine	101	84	106	101	96	104	94	0.019
Diethylenetriamine	98	95	97	103	99	98	100	0.13
Triethylenetetramine	100	73	98	104	95	98	96	1.1
Tetraethylenepentamine	103	97	94	99	96	95	96	1.0

Trace metals 250 ng each, Fe 50 mg, EGTA 25 mM, amine ligand 0.70 M, pH 9.5.

Table 4. Effect of the ligand concentration on the separation efficiency.

EGTA added/ mM	Diethylene- triamine added/M	Trace metals recovered, %							Fe remaining/ mg
		Mn	Co	Ni	Cu	Zn	Cd	Pb	
10	0.70	91	96	102	102	95	97	75	0.032
20	0.70	100	96	99	103	96	104	87	0.042
25	0.20	82	82	96	98	89	103	72	0.038
	0.40	87	91	95	97	90	96	81	0.094
	0.60	97	98	97	100	96	100	99	0.11
	0.70	100, 102	97, 97	100, 103	99, 104	102, 104	99, 99	100, 101	0.10, 0.12
	0.80	96	97	95	99	100	101	100	0.29
30	0.90	100	99	95	101	96	101	96	0.47
	0.70	96	101	100	99	99	102	100	0.37

Trace metals 250 ng each, Fe 50 mg, pH 9.5.

Fig. 2. Simultaneous separation of trace metals from 50 mg of iron matrix.

metals was significant at lower pH's due to the insufficient complexation. The increase in pH made the complexation satisfactory and the coprecipitation was well controlled at pH 8.6–9.8 for all the trace metals tested. However, further increase in pH caused the modest loss of Mn, Co, Zn, and Pb because their hydrolysis became gradually dominant. On the other hand, the amount of iron remaining in the solution peaked at pH 8.3 and considerably decreased with increasing pH. Because of the high reactivity of iron(III) toward hydroxide ions,³¹⁾ the hydrolysis would be overwhelming above pH 8.3, providing the enhanced selectivity. The pH was fixed at 9.5 for the successful separation.

3.3. Analysis of Synthetic and Real Samples

A series of synthetic sample solutions was prepared to validate the proposed method at ultratrace levels. A high-purity iron metal was decomposed with a mixture of HCl and HNO₃. Concentrated acids were used, otherwise a longer time was required for the complete decomposition. Heating at excessively higher temperatures sometimes produced the black residue, hence the temperature was controlled at 60–70°C. Aliquots (50 mg as Fe) of the resulting solution were mixed with the known amount of trace metals and treated by the proposed method. As shown in Fig. 2, the relations between the amounts of trace metals added and found showed good linearity with slopes of 0.96–1.05, indi-

Table 5. Analytical results for high-purity iron metals.

Sample	Metal	Concentration in sample/ $\mu\text{g g}^{-1}$	
		Determined ^a	Certified
JSS 001-6	Mn	0.03 ± 0.03	$(0.03)^b$
	Co	0.37 ± 0.02	0.32 ± 0.05
	Ni	0.20 ± 0.04	$(0.2)^b$
	Cu	0.37 ± 0.02	0.36 ± 0.05
	Zn	2.0 ± 0.1	1.9 ± 0.3
	Cd	0.031 ± 0.003	— ^c
	Pb	0.18 ± 0.01	0.18 ± 0.02
JSS 003-5	Mn	27 ± 1	27 ± 1
	Co	2.0 ± 0.1	2.2 ± 0.2
	Ni	0.38 ± 0.02	0.4 ± 0.1
	Cu	16 ± 1	15.4 ± 0.5
	Zn	<0.07	$(<0.5)^b$
	Cd	<0.007	$(<0.1)^b$
	Pb	<0.02	$(<0.1)^b$
NIST 2168	Mn	4.6 ± 0.2	6 ± 4
	Co	7.1 ± 0.5	6 ± 2
	Ni	12 ± 1	10 ± 5
	Cu	4.3 ± 0.3	5 ± 2
	Zn	3.6 ± 0.3	$(<5)^b$
	Cd	0.022 ± 0.004	$(<1)^b$
	Pb	0.03 ± 0.01	$(<1)^b$

^a Mean $\pm$ standard deviation, $n = 4$.

^b Indicative value.

^c Not given.

cating the nearly complete recovery. For Mn, Ni, and Cu, the intercepts were not zero, which was ascribed to the trace impurities in the high-purity iron metal used. The concentrations (in $\mu\text{g g}^{-1}$) were calculated to be 0.46 (Mn), 0.17 (Ni), and 1.3 (Cu).

Finally, certified reference materials for high-purity iron (JSS 001-6, JSS 003-5, and NIST 2168) were analyzed. As given in Table 5, trace impurities at low $\mu\text{g g}^{-1}$ to ng g^{-1} levels were successfully determined. The obtained values were almost consistent with the certified or indicative values. The blank values through the whole procedure were $0.43 \pm 0.04 \mu\text{g g}^{-1}$ (mean $\pm$ standard deviation, $n = 6$) for Cu and undetectable for the other metals. The detection limits ($\mu\text{g g}^{-1}$) based on the 3σ blank fluctuations were 0.02 (Mn, Co, Ni, and Pb), 0.2 (Cu), 0.07 (Zn), and 0.007 (Cd). The proposed method is simple and rapid, and it would provide useful information for the quality control of high-purity iron metals and better understanding of the behavior of impurities at ultratrace levels.

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