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Determination of trace impurities in high-purity iron using salting-out of polyoxyethylene-type surfactants

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ABSTRACT

To an iron sample solution was added polyoxyethylene-4-isononylphenoxy ether (PONPE, nonionic surfactant, average number of ethylene oxides 7.5) and the surfactant was aggregated by the addition of lithium chloride. The iron(III) matrix was collected into the condensed surfactant phase in >99.9% yields, leaving trace metals [*e.g.*, Ti(IV), Cr(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II), and Bi(III)] in the aqueous phase. After removing the surfactant phase by centrifugation, the remaining trace metals were concentrated onto an iminodiacetic acid-type chelating resin. The trace metals were desorbed with dilute nitric acid for the determination by inductively coupled plasma-mass spectrometry or graphite-furnace atomic absorption spectrometry. The proposed separation method allowed the analysis of high-purity iron metals for trace impurities at low $\mu g\, g^{-1}$ to $ng\, g^{-1}$ levels.

1. Introduction

Ion-association extraction with oxygenic organic solvents (*e.g.*, diethyl ether and 4-methyl-2-pentanone) is a well-known separation technique for the determination of trace impurities in iron metals [1,2]. Iron(III) in hydrochloric acid solutions forms the chloro complexes, which are extracted by the proton-mediated interaction with the electron-donating oxygens of the solvent molecules. Various other elements remain in the aqueous phase, hence this extraction allows the facile multielement separation, though organic solvents are now considered unfavorable in view of user and environmental safety. Interest has thus been growing in organic solvent-free separation techniques. For example, a powerful method was developed using a cumulated bed of cation- and anion-exchange resins [3]. However, hazardous hydrofluoric acid was required for the multielement separation.

The use of polyoxyethylene-type nonionic surfactants can be an attractive alternative. Some anionic complexes [*e.g.*, $Co(NCS)_4{}^{2-}$, $AuCl_4{}^-$, and $GaCl_4{}^-$] were extracted into inert solvents (*e.g.*, halogenated hydrocarbons and benzenes) containing surfactants of the same class [4–7]. Similarly to the conventional extraction with oxygenic organic solvents, the interaction between the anionic complexes and the ethylene oxide chains of the surfactant was mediated by cations including proton, alkali metals, and alkaline earth metals. In our laboratory, polyoxyethylene-type surfactants were loaded on Amberlite XAD resin particles, which were used for the removal of the iron(III) matrix from 8 M hydrochloric acid solutions [8]. However, the preparation of the surfactant-loaded resin required several hours, and evaporation of the excess hydrochloric acid was also time-consuming.

Polyoxyethylene-type nonionic surfactants are known to be dehydrated by the addition of large amounts of electrolytes and then segregated from bulk water [9]. In the present study, such a salting-out effect was utilized. A nonionic surfactant was directly dissolved in an iron sample solution, into which a metal chloride (*e.g.*, M^+, Cl^-) was added as a salting-out agent. The metal chloride converted the iron(III) into the chloro complexes and provided them with the counter cations for the ion-association (*e.g.*, M^+, $FeCl_4{}^-$). As a consequence, the simple addition of a salting-out agent allowed the facile and rapid collection of the iron(III) matrix into the segregated surfactant phase without high concentration hydrochloric acid. Owing to the relatively low acidity, trace elements remaining in the aqueous phase were readily concentrated by solid-phase extraction (SPE). The proposed matrix-removal method was combined with inductively coupled plasma-mass spectrometry (ICP-MS) or graphite-furnace atomic absorption spectrometry (GFAAS) for the determination of trace impurities in high-purity iron metals.

2. Experimental

2.1. Apparatus

A Seiko (Chiba, Japan) SPQ-6500 ICP-mass spectrometer was used for the determination of trace metals. Because the deter-

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Table 1
Operating conditions for ICP-MS and GFAAS.

ICP-MS	
Argon flow-rate	
Outer	17 L min^{-1}
Intermediate	0.8 L min^{-1}
Carrier	1.0 L min^{-1}
RF power	1.0 kW
Sampling depth	12 mm
Isotopes measured	^{48}Ti, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{64}Zn, ^{114}Cd, ^{208}Pb, ^{209}Bi
GFAAS	
Furnace temperature	
Drying 1	110 °C (ramp, 1 s; hold, 30 s)
Drying 2	130 °C (ramp, 15 s; hold, 30 s)
Ashing	1000 °C (ramp, 10 s; hold, 20 s)
Atomizing	2300 °C (ramp, 0 s; hold, 5 s)
Clean-up	2450 °C (ramp, 1 s; hold, 3 s)
Wavelength	357.9 nm (Cr)
Sample injected	20 μL

mination of Cr was difficult due to serious spectral overlapping ($^{52}Cr^+$ and $^{40}Ar^{12}C^+$; $^{53}Cr^+$ and $^{37}Cl^{16}O^+$), Cr was determined using a Perkin-Elmer (Norwalk, CT, USA) AAnalyst 600 graphite-furnace atomic absorption spectrometer. The operating conditions are summarized in Table 1.

A Bio-Rad (Hercules, CA, USA) 680XR microplate reader was used for the spectrophotometric determination of iron because ICP-MS and GFAAS were not suitable in the presence of large amounts of salts. Surfactants were determined by high-performance liquid chromatography (HPLC) using a Jasco (Tokyo, Japan) PU-2080 pump, a Rheodyne (Rohnert Park, CA, USA) 7725i six-way injection valve with a 20-μL sample loop, a Merck (Darmstadt, Germany) Chromolith Performance RP-18e column (4.6 mm i.d. × 100 mm, packed with monolithic porous *n*-octadecylsilanized silica), and a Jasco UV-2070 spectrophotometric detector.

2.2. Reagents

Polyoxyethylene-4-isononylphenoxy ethers (PONPE) with average numbers of ethylene oxides of 7.5, 10, 15, and 20 were purchased from Tokyo Kasei (Tokyo, Japan). Polyoxyethylene-4-*tert*-octylphenoxy ethers with average numbers of ethylene oxides of 7.5, 9.5, 30, and 35 (Triton X-114, X-100, X-305, and X-405, respectively) were purchased from Nacalai Tesque (Kyoto, Japan). All the surfactants were used without purification. In the present study, the molecular weights were calculated based on the nominal numbers of ethylene oxides.

The salting-out agents examined (LiCl, KCl, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$, $AlCl_3 \cdot 6H_2O$, NH_4Cl, and $LiNO_3$) were dissolved in water to near saturation: 10 M (LiCl and $LiNO_3$), 5 M ($CaCl_2$), 4.5 M ($MgCl_2$), 4 M (NaCl and NH_4Cl), 3 M (KCl), and 2.5 M ($AlCl_3$). A lithium chloride solution was purified by the sorption with an iminodiacetic acid-type chelating resin, Amberlite IRC-748 (Rohm and Haas, Philadelphia, PA, USA). A 2.5-g amount of IRC-748 was dispersed in 250 mL of 10 M lithium chloride solution at pH 7 by stirring for 3 h and then removed by filtration. The sorption was repeated five times for the sufficient purification.

An iron(III) solution (100 mg mL^{-1} in 2 M HNO_3) was prepared from $Fe(NO_3)_3 \cdot 9H_2O$; the concentration was estimated by the phenanthroline method [10]. A high-purity iron metal (99.998%, Johnson Matthey, Ward Hill, MA, USA) was used for preparing synthetic sample solutions. Certified reference iron metals (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. A standard Cr(III) solution (1.0 mg mL^{-1}) was prepared from chromium metal (Nilaco, Tokyo, Japan). For other metals, commercial standard solutions (1.0 mg mL^{-1}) were used. Hydrochloric acid (12 M) and nitric acid (16 M) were of ultra-pure grade (Kanto Kagaku, Tokyo, Japan).

An acetate buffer (pH 7.0) was prepared by neutralizing 1 M acetic acid with 7.5 M aqueous ammonia and then purified with the IRC-748 chelating resin. Ammonium pyrrolidinedithiocarbamate (APDC, special grade for AAS, Nacalai Tesque) was dissolved in water to give a concentration of 30 mg mL^{-1}. An Empore disk cartridge (Teflon fiber disk containing polystyrene or iminodiacetic acid-type chelating resin, 10 mm in diam., 3 M Bioanalytical Technologies, St. Paul, MN, USA) was washed with ethanol, water, 2 M nitric acid, and water, successively. The cartridge was conditioned with 1 mL of acetate buffer before use. A 0.45-μm Durapore membrane filter [hydrophilic poly(vinylidene fluoride), Millipore, Billerica, MA, USA] was used with a Millipore filter holder (16 mm in diam.).

L-Ascorbic acid and 1,10-phenanthrolinium chloride monohydrate were purchased from Nacalai Tesque and used as 0.1 M and 10 mM solutions, respectively. Disodium ethylenediaminetetraacetate dihydrate (EDTA, Dojindo, Kumamoto, Japan) was used as a 50 mM solution.

All reagents used were of reagent grade (Wako Jun-yaku, Osaka, Japan), unless otherwise stated. Water was purified with a Millipore Milli-Q Gradient A-10 system.

2.3. Recommended procedure

A 500-mg iron sample was decomposed with 1.5 mL each of 12 M hydrochloric acid and 16 M nitric acid at 60–70 °C and diluted to 5.0 mL with water. A 1/10-aliquot of the solution was taken in a 15-mL centrifugation tube and diluted to 3.0 mL with water. After dissolving 1.1 g (2.0 mmol) of PONPE-7.5 in the solution, 7.0 mL of lithium chloride solution was added to cause the aggregation of the surfactant. The turbid solution was centrifuged at 7000 *g* for 5 min to form a condensed surfactant layer on the solution surface. The iron-rich surfactant phase was removed by filtration with a Durapore membrane filter and the filtrate was reserved for the determination of trace metals. The pH of the filtrate was adjusted to 7 with 1 and 7.5 M aqueous ammonia and the solution was passed through an iminodiacetic acid-type Empore disk to collect trace metals by the complexation. After washing with 5 mL of acetate buffer, the trace metals were desorbed from the Empore disk with 0.5 mL of 5 M nitric acid. The disk was washed with 0.5 mL of 5 M nitric acid followed by 3 mL of water. The combined solution was diluted to 5.0 mL with water and analyzed by ICP-MS (for Ti, Mn, Co, Ni, Cu, Zn, Cd, Pb, and Bi) and GFAAS (for Cr). Calibration graphs were constructed using 1 M nitric acid containing metals of interest at pg mL^{-1} to ng mL^{-1} levels.

2.4. Spectrophotometric determination of iron

The separation efficiency was evaluated by the phenanthroline method [10]. A volume lower than 500 μL of filtrate (obtained by centrifugation and filtration) was mixed with 80 μL of ascorbic acid solution, 80 μL of phenanthroline solution, and 160 μL of acetate buffer (pH 5.0), and diluted to 1.0 mL with water. After 10 min, the absorbance was measured at 490 nm for the reddish iron-phenanthroline chelate.

2.5. Determination of surfactant by HPLC

The salting-out effect was studied by determining the surfactant. To a 50-μL filtrate was added 200 μL of water, and 250 μL of EDTA solution was added to mask the iron(III). The solution was