# Thermoresponsive polymer-mediated extraction for graphite furnace atomic absorption spectrometric determination of trace metals in high purity iron

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A B S T R A C T

A thermoresponsive polymer-mediated extraction was designed for the selective separation of traces metal ions from high purity iron solutions. Traces metals were extracted into the coagulum of a thermoresponsive polymer, poly(*N*-isopropylacrylamide) as their dibenzyldithiocarbamate chelates, while Fe(III) matrix remained in the bulk aqueous solution as its water-soluble tartrate chelate. The coagulum was readily collected from the solution and then dissolved with a small amount of *N,N*-dimethylformamide for the introduction to a graphite furnace of atomic absorption spectrometer. The use of 0.5 g l$^{-1}$ poly(*N*-isopropylacrylamide), 2.0 mM sodium dibenzyldithiocarbamate, and 0.6 M diammonium tartrate (pH 10.7) allowed nearly complete (>99.9%) collection of Co(II), Ni(II), Cu(II), Cd(II), Pb(II), and Bi(III) with reducing Fe(III) concentration from 50 mg ml$^{-1}$ to $14 \pm 1$ μg ml$^{-1}$ being lower than the tolerance limits for the determination of traces of metals. Because of effective elimination of iron matrix, six metals at fractional μg g$^{-1}$ levels were successfully determined with high reproducibility. The accuracy and precision were evaluated by analyzing certified reference materials of high purity iron.

## 1. Introduction

In the area of material science, high purity iron is an interesting material, because of its unique physical and chemical properties such as high corrosion resistance and softness that are largely different from those of conventional iron metals [1–4]. The properties of high purity iron are largely dependent on the content of impurities even at μg g$^{-1}$ or lower levels. Therefore, the determination of trace impurities in high purity iron is an important analytical problem for the control of its quality as well as for a better understanding of the synergistic action and correlation of impurities.

Different metal impurities in high purity iron have successfully been determined by highly sensitive spectrometric methods such as graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), or inductively coupled plasma mass spectrometry (ICP-MS) [5]. Before these instrumental analyses, iron matrix should be eliminated from sample solution of trace metals [6,7]. Otherwise, highly concentrated iron significantly interferes with the determination of trace metals as well as irreversibly contaminates these instruments. Coprecipitation [8], electrodeposition [9], volatilization [10], liquid-liquid extraction [11–13], and sorption

(solid phase extraction and ion-exchange) [14–18] have been employed for separating iron matrix from trace metal impurities. However, such techniques are often tedious and time-consuming. Moreover, highly skilled handling is necessary for obtaining accurate and precise results. Irreversible sorption on solid sorbents in solid phase extraction and ion-exchange often reduces the recoveries of trace metals. Mutual solubility and viscosity of solvents in liquid-liquid extraction can interfere the reproducibility.

Previously, we have reported a simple extraction method based on the thermoresponsive coagulation of a water-soluble polymer, poly(*N*-isopropylacrylamide) [PNIPAAm], having lower critical solution temperature (ca. 32 °C). Hydrophobic compounds in aqueous solutions can readily be collected and highly concentrated into small volume of polymer coagulum [19,20]. By introducing chelating functionality, thermoresponsive polymer-mediated extraction can be designed for the concentration of trace metal ions in water for their sensitive determination with GFAAS [21–27]. Because of easy and nearly complete collection of the polymer coagulum as well as easy burning of the polymer materials during ashing stage of graphite furnace atomization, trace metal ions in aqueous samples can readily be concentrated and determined by GFAAS analysis with high reproducibility.

This technique is also applicable to eliminate water-soluble components that can hardly be incorporated into the polymer coagulum. If iron matrix can be converted into the water-soluble complex, it can be

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remained in the bulk aqueous phase and therefore eliminated from the polymer coagulum. In the present study, thermoresponsive polymer-mediated extraction was designed for selective concentration of traces of metals with eliminating iron matrix. Combined use of dithiocarbamate-type chelating agents and polyvalent carboxylic acids were examined. Experimental conditions for complete collection of trace metals and sufficient elimination of iron matrix were investigated. Accuracy and precision in the GFAAS determination of trace metals were evaluated by using reference standard materials of high purity iron.

## 2. Experimental

### 2.1. Materials

Poly($N$-isopropylacrylamide) [PNIPAAm, $M_w = 3.6 \times 10^5$, $M_n = 1.3 \times 10^5$ (GPC, polystyrene standard)], was prepared by aqueous radical polymerization of $N$-isopropylacrylamide with ammonium persulfate and $N,N,N',N'$-tetramethyethylenediamine at 0 °C [19,20]. It was purified by repeated coagulation and dissolution in aqueous ethanol solution followed by dialysis with Milli-Q water and freeze-drying to prepare 10.0 g l$^{-1}$ PNIPAAm solution. Certified reference materials of high purity iron were obtained from National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) and The Japan Iron and Steel Federation (Tokyo, Japan). Ammonium pyrrolidinedithiocarbamate (APDC), diammonium hydrogen citrate, hydrochloric acid (36%, ultrapur-100), and nitric acid (70%, ultrapur-100) were purchased from Kanto Chemical (Tokyo, Japan). Sodium dibenzyldithiocarbamate (SDDC) hydrate (Tokyo Chemicals, Tokyo, Japan) was dried in a vacuum desiccator for 24 h and dissolved with $N,N$-dimethylformamide to prepare 0.10 M solution. Diammonium (+)-tartrate, citric acid, ammonia solution (25%, for analysis of poisonous metals), tetramethylammonium hydroxide solution (25%, super special grade), iron(III) nitrate nonahydrate (99.999% Fe), standard solutions (1000 mg l$^{-1}$ in 0.1 M HNO$_3$) of Co (II), Ni(II), Cu(II), Cd(II), Pb(II), and Bi(III) were obtained from Wako Pure Chemical (Osaka, Japan). Water was purified with a Milli-Q Integral Water Purification System (Merck Millipore, Billerica, MA, USA). In order to eliminate trace metal impurities, aqueous solutions of PNIPAAm and diammonium tartrate were passed through an SDDC-modified solid-phase extraction cartridge (C18 Environmental, Waters, Milford, MA, USA).

### 2.2. LCST measurement

PNIPAAm solutions (0.5 g l$^{-1}$) containing prescribed amounts of diammonium tartrate or diammonium citrate (pH 10.7) were used. Temperature-dependent turbidity was measured as transmittance at 600 nm with a Jasco UV660 double-beam absorption spectrophotometer (Hachioji, Japan) with 1-cm quartz cells in a water-jacketed cell holder. Temperature was ramped with an EYELA CTP-201 recirculating chiller (Tokyo, Japan) at the rate of 0.5 °C min$^{-1}$.

### 2.3. Determination of trace metals in high purity iron samples

A 0.50-g portion of high purity iron (NIST2168, JSS001-6, or JSS003-5), placed in a 20-ml PTFE beaker, was dissolved in 10 ml of a 1 + 1 mixture of 6 M HNO$_3$ and 6 M HCl by heating at 60 °C. The solution was cooled to room temperature, transferred to a 10-ml PFA volumetric flask, and diluted to the mark with water to give a sample solution containing 50 mg ml$^{-1}$ of Fe(III). To 1.0 ml of the sample solution in a 30-ml glass vial were added 2.0 ml of 3 M diammonium (+)-tartrate, 2.5 ml of 10 M ammonia solution, and 3.0 ml of 25% tetramethylammonium hydroxide solution. With cooling the solution in an ice bath, 0.20 ml of SDDC and 0.50 ml of PNIPAAm solutions were added. The mixture was warmed at 40 °C in a water bath and shaken for inducing thermoresponsive polymer coagulation. The formed coagulum was collected using a PTFE micro-spatula, washed with warm (ca. 50 °C) 0.6 M

ammonium tartrate solution (pH 10.7), and placed into a 1-ml volumetric flask to be dissolved with $N,N$-dimethylformamide. A 20 μl-portion of the resulting solution was introduced into a graphite furnace of atomic absorption spectrometer (AAnalyst 600, PerkinElmer, Waltham, MA, USA). Operating conditions of GFAAS analysis for the respective metals were listed in Table 1.

## 3. Results and discussion

### 3.1. Thermoresponse of PNIPAAm under analytical conditions

Several investigators have studied the effect of salts on the LCSTs of PNIPAAm and related it to the Hofmeister series [24,28,29]. Buffer components and masking agents can influence the LCST of PNIPAAm. Because of the strong chaotropic effect, [30], citrate and tartrate may remarkably lower the LCST. Fig. 1 shows the LCST value of 0.5 g l$^{-1}$ PNIPPAm solution as a function of the concentration of diammonium citrate or diammonium tartrate. The LCST significantly lowered by the presence of citrate or tartrate. As described in the following section, 0.6 M of tartrate was necessary for sufficient elimination of Fe matrix. Therefore, the solution was cooled in an ice bath before heat-induced polymer coagulation.

### 3.2. Removal of iron matrix

Fig. 2 shows the effect of coexisting Fe on the GFAAS determination of 10 ng ml$^{-1}$ of Co, Ni, Cu, Cd, Pb, and Bi. The presence of 30 μg ml$^{-1}$ Fe gave positive error in the Pb determination while negative error in the determination of Co, Cd, or Bi. According these results, Fe(III) concentration should be reduced to be lower than 20 μg ml$^{-1}$. Since initial Fe(III) concentration is 50 mg ml$^{-1}$, >99.96% of Fe(III) has to be eliminated.

Tartrate and citrate can strongly complex with Fe(III) ions to form water-soluble chelates and utilized for the separation of iron matrix from trace metals in solid phase extraction [15,17]. Therefore, we used them in thermoresponsive polymer-mediated extraction. The effects of concentration of tartrate or citrate and solution pH on the extent of Fe(III) extraction from 50 mg ml$^{-1}$ of Fe(III) are shown in Fig. 3, where 2.5 mM of SDDC was added because it was a suitable chelating agent for trace metal ions (Section 3.3). Incorporation of Fe(III) into polymer coagulum was suppressed by the presence of tartrate or citrate (Fig. 3(A)). Especially, tartrate was effective for eliminating Fe(III). As shown in Fig. 3(B), pH was another important factor for lowering Fe(III) concentration. At pH 10.7, Fe(III) concentration in the final solution was 14 ± 1 μg ml$^{-1}$ being lower than the tolerance limits for the determination of traces of metals. In the following study, tartrate concentration and solution pH were settled to 0.6 M and 10.7, respectively.

**Table 1**
Operating conditions of GFAAS.

| Element [wavelenght] | Step | Temperature/°C | Ramp heating/s | Holding/s |
|---|---|---|---|---|
| Co[a] [242.5 nm] | Dry(1) | 110 | 1 | 15 |
| | Dry(2) | 130 | 15 | 15 |
| | Ash | 800 | 10 | 40 |
| | Atomize | 2400 | 0 | 5 |
| | Clean up | 2450 | 1 | 5 |
| Ni[a] [232.0 nm] | Ash | 600 | 10 | 40 |
| | Atomize | 2300 | 0 | 5 |
| Cu[a] [324.8 nm] | Ash | 600 | 10 | 40 |
| | Atomize | 2000 | 0 | 5 |
| Cd[a] [228.8 nm] | Ash | 500 | 10 | 55 |
| | Atomize | 1500 | 0 | 5 |
| Pb[a] [283.3 nm] | Ash | 800 | 10 | 40 |
| | Atomize | 1600 | 0 | 5 |
| Bi[a] [223.1 nm] | Ash | 800 | 10 | 40 |
| | Atomize | 1700 | 0 | 5 |

[a] Conditions for drying and cleaning up are the same as those for the Co detection.