Flow Injection On-line Column Separation for the Determination of Zinc in Steel by Atomic Absorption Spectrometry

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1. Introduction

It is currently recognized that the content of trace elements greatly affects the properties of steel products. To characterize the quality of the products, therefore, concentrations of the trace elements have to be determined by appropriate analytical techniques. Although several instrumental analyses, such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), etc., are effective to determine the trace elements in a water sample, the application of these methods to the determination of trace elements in a steel sample has been limited because the iron matrix often interferes with the analyses seriously. The separation of the elements from iron prior to the instrumental analyses is indispensable for the determination of trace element in steel.

Various separation techniques have been reported for the determination of the trace elements in steel. For example, in the case of the determination of selenium and tellurium in a steel sample, Ashino et al. reported a reductive coprecipitation technique, where both the elements were coprecipitated with palladium by adding ascorbic acid and were separated from the iron matrix.2) For the separation of boron from the iron matrix, Coedo et al. adopted a solvent extraction procedure, where acetylacetone was used as an extractant for iron(III).3) Tanaka and Ishii also used a solvent extraction technique, where acetylacetone was used as an extractant for iron(III).2) However, these methods, which were based on a chelating resin technique, could not be applied to the determination of zinc in a steel sample because iron(III) would be adsorbed on the resin. Judging from Kallmann’s report,4) the use of the anion exchange resin, instead of the chelating resin, would be promising for the determination of zinc in a steel sample by FI-AAS. The FI-AAS system with an on-line column packed with an anion exchange resin has not been reported yet.

This paper describes the FI-AAS system for the determination of zinc in a steel sample. The proposed system has a mini-column packed with a strongly basic anion exchange resin. The use of the column system enables not only the separation of zinc from the iron matrix but also the enrichment of zinc. The feasibility of the proposed system was evaluated by the analysis of zinc in a standard steel sample.

2. Experimental

2.1. Reagents

Stock solutions of iron(III) (1mol dm$^{-3}$) and zinc(II) (1×10$^{-3}$mol dm$^{-3}$) were prepared by dissolving ammonium iron(III) sulfate dodecahydrate and zinc(II) acetate dihydrate in 0.1mol dm$^{-3}$ nitric acid solution, respectively. A strongly basic anion exchange resin (Dowex 1X8–100, 50–100 mesh, chloride form, Sigma Aldrich) was used for separation of zinc(II) from iron(III).

All of the reagents were of analytical reagent grade and used without further purification. The water used to prepare the reagent was obtained by a Milli-Q water purification system (Millipore Co.).

2.2. Apparatus

A schematic diagram of the proposed system is shown in Fig. 1. A peristaltic pump (Eyela, MP-3) was used for pumping the solutions. Two six-way valves (Sanuki Kogyo, SVM-6M2) were used for injecting the sample solution and changing the stream. The flow lines were made of PTFE tubing (0.5mm i.d.) except for pump tubes (Tygon tube, 1.15mm i.d. for carrier, 2.15mm i.d. for eluent). A Hitachi (Model Z-6100) atomic absorption spectrophotometer was used for the determination of iron(III) and zinc(II). A mini-
column in the flow system was made of a PTFE tube (2 mm i.d., 5 cm) packed with the anion exchange resin. For the off-line studies, a glass column (Kontes Glass Co., FLEX-COLUMN, 7 mm i.d., 20 cm) loaded with 1 cm³ of the resin was used.

2.3. Procedure

2.3.1. Off-line Studies

Ten cubic centimeters of 1 mol dm⁻³ nitric acid was passed through the glass column loaded with the resin for washing, and then the same volume of a conditioning solution containing 10–100 g dm⁻³ sodium chloride and 0.01–1 mol dm⁻³ hydrochloric acid was passed through the column. Next, 10 cm³ of a sample solution containing 1×10⁻⁶ mol dm⁻³ zinc(II), 10–100 g dm⁻³ sodium chloride and 0.01–1 mol dm⁻³ hydrochloric acid was passed through the column, and then the column was washed with 10 cm³ of the conditioning solution. After 10 cm³ of 1.0 mol dm⁻³ nitric acid as the eluent was added to the column, the effluent was collected in a vial. The concentration of zinc(II) in the effluent was measured by AAS.

2.3.2. FI Method

At the valve position shown in Fig. 1a), a sample solution containing 0.18 mol dm⁻³ iron(III), 1×10⁻⁶ mol dm⁻³ zinc(II), 100 g dm⁻³ sodium chloride, 0.6 mol dm⁻³ hydrochloric acid and 0.65 mol dm⁻³ nitric acid was loaded into the sample loop. Then, V1 was turned to the position shown in Fig. 1c), zinc adsorbed on the resin was eluted with the eluent and then introduced into the AAS. After 3 min, both valves were turned to the position shown in Fig. 1a), then the carrier solution was pumped for one minute for conditioning the resin.

All experiments were carried out at room temperature (ca. 293 K).

3. Results and Discussion

In order to estimate the suitable concentration of chloride ion for separation of zinc(II) from iron(III), equilibrium distributions were calculated on the basis of the stability constants of the corresponding complexes. Figure 2 shows distributions of zinc(II) and iron(III) species in the presence of 10⁻²–10 mol dm⁻³ chloride ion. For the purpose of adsorptive separation of zinc(II) from iron(III) using an anion exchange resin, we have to choose a suitable chloride concentration that the zinc(II) forms anion species such as ZnCl₃⁻ or ZnCl₄²⁻, while iron(III) does not form such anion species. As shown in Fig. 2, zinc(II) forms anion species when the chloride ion concentration is above 0.1 mol dm⁻³, whereas iron(III) hardly forms the anion species in the examined concentration range. This result indicates that the zinc(II) can be separated from iron(III), if the adsorption on the resin is conducted under the experimental conditions containing chloride ion ranged from 0.1 to 3 mol dm⁻³.

Figure 3 shows the experimental results obtained by the off-line procedure described above. In this case, the effect of hydrochloric acid concentration on the adsorption percent (defined as \( \{(\text{the amount of the metal ion adsorbed on the resin})/(\text{the amount of the metal ion in the sample solution})\} \times 100 \)) of zinc(II) and iron(III) was examined under the two conditions of different sodium chloride concentrations: 10 g dm⁻³ (ca. 0.17 mol dm⁻³) NaCl and 100 g dm⁻³ (ca. 1.7 mol dm⁻³) NaCl. As expected from Fig. 3, the adsorption percent of zinc(II) increased with an increase in the chloride ion concentration, and reached the maximum
value at the 0.5 mol dm\(^{-3}\) HCl concentration in the presence of 100 g dm\(^{-3}\) NaCl. Although the adsorption percent became larger than 100%, which may be due to the contamination from reagents, it was found that the quantitative adsorption of zinc(II) was attained by the addition of 100 g dm\(^{-3}\) NaCl. On the other hand, the adsorption percent of iron(III) under the same condition was below 1%. The results indicated that the satisfactory separation of zinc from an iron matrix was achieved by using the mini-column packed with the anion exchange resin. From the above considerations, 0.6 mol dm\(^{-3}\) HCl containing 100 g dm\(^{-3}\) NaCl was adopted as the carrier solution. Nitric acid (0.65 mol dm\(^{-3}\)) was also added to the carrier solution in order to match the nitric acid concentration of the carrier solution with that of the sample solution. Nitric acid of 1.0 mol dm\(^{-3}\) was used as an eluent solution according to the literature.\(^{51}\)

In the flow system shown in Fig. 1, the effects of flow rate and sample volume were examined. Figure 4 shows the effect of flow rates of the carrier and eluent solutions. The absorbance increased with an increase in the flow rates, and attained to the maximum value, then decreased gradually. This behavior is interpreted as follows; the increase in the absorbance may be caused by the decrease in the dispersion of the sample segment, and the decrease in the absorbance may be due to the decrease in the contact time between zinc and the resin. In this system, the flow rates, 1.8 cm\(^3\) min\(^{-1}\) for carrier and 4.2 cm\(^3\) min\(^{-1}\) for eluent, which gave the maximum absorbance were used as the optimum conditions. Twelve samples an hour were able to be analyzed under the conditions. The effect of the sample volume was examined in the range from 0.1 to 2.5 cm\(^3\). A linear relationship between the sample volume and the absorbance was obtained. In this case, a 2.5 cm\(^3\) sample solution was injected in consideration of the zinc concentration of steel samples. The detection limit (3\(\sigma\) of the reagent blank) under the conditions used was 6.6\(\times\)10\(^{-6}\) mol dm\(^{-3}\) and the relative standard deviation for ten replicate analyses of 1.0\(\times\)10\(^{-6}\) mol dm\(^{-3}\) zinc was 4.1%.

The effect of foreign metal ions, cadmium(II), cobalt(II) and tin(II) which may form chloride complexes under the experimental conditions, was studied. Here, an error within \(\pm 5\%\) range on the determination of 1.0\(\times\)10\(^{-6}\) mol dm\(^{-3}\) zinc was considered to be tolerable. The tolerance limits for the three metals were as follows: 5\(\times\)10\(^{-5}\) mol dm\(^{-3}\) for cadmium(II); 1\(\times\)10\(^{-5}\) mol dm\(^{-3}\) for cobalt(II) and tin(II).

The proposed method was applied to the determination of zinc in a certified reference material of iron (JSS 001-4). The steel sample was dissolved as described previously,\(^{61}\) and then the chloride concentration was adjusted to that of the carrier solution by the addition of NaCl and HCl. A linear calibration graph (\(r=0.999\)) was obtained over the range 0–6\(\times\)10\(^{-5}\) mol dm\(^{-3}\) of zinc(II) by the flow system, and was used to determine the zinc concentration. Consequently, the obtained value, 1.0\(\times\)10\(^{-6}\) mol dm\(^{-3}\) of zinc(II) in the sample solution which corresponds to 6.6 \(\mu\)g g\(^{-1}\) in the steel sample, was in good agreement with the certified value, 6.8 \(\mu\)g g\(^{-1}\). The relative standard deviation for ten injections of the sample was 4.0%.

In conclusion, the FI-AAS system for the determination of zinc in a steel sample was developed. The proposed system, which had a mini-column packed with an anion exchange resin, enabled not only the separation of zinc(II) from iron(III) but also concentration of zinc(II). This method is simple, rapid and cost effective. The proposed system is expected to be a useful tool for the determination of zinc in steel samples.

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