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DETERMINATION OF COBALT IN ZINC ELECTROLYTE BY AN AUTOMATED FLOW-INJECTION SYSTEM

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Summary—A flow-injection method has been developed for the spectrophotometric determination of cobalt in zinc electrolyte using 2-(5-bromo-2-pyridylazo)-5-(*N*-propyl-*N*-sulphopropylamino)aniline (5-Br-PSAA) as chromogenic reagent. A sample solution is injected into a carrier containing hydrochloric acid, diammonium hydrogenphosphate and hydrogen peroxide. The sample is then merged with the stream of ammonium acetate solution and PSAA solution is synclonously injected into the sample zone. After mixing with $2M$ sulphuric acid, the absorbance of cobalt–PSAA complex is measured at 617 nm. The flow injection system proposed is fully controlled with a personal computer. The flow-injection system permits throughput of 12 samples per hour. The relative standard deviation ($n = 10$) for 0.1 μg Co/ml solution is 5.0%.

For preparation of zinc electrolyte in wet zinc refining, it is necessary to eliminate impurities originated from zinc concentrates (Sphalerite, Calamine and Smithsonite). In the stage of preparation of the electrolyte, zinc powder is commonly utilized to eliminate impurities by cementation.[1] Measuring the amount of cobalt, which is one of the impurities, has been used as an indicator for the total amount of coexisting impurities.

Flow-injection analysis (FIA) is a rapid and precise technique which has found wide application, especially in environmental, geological, clinical and pharmaceutical analysis,[2] and a number of automated FIA systems are commercially available. Although several methods for measuring cobalt with FIA have been published,[3,4] their applications to on-line process analyzers have scarcely been reported. We have investigated the determination of cobalt in high-salt concentration zinc electrolyte by FIA utilizing 2-(5-bromo-2-pyridylazo)-5-(*N*-propyl-*N*-sulfopropylamino)aniline sodium salt (5-Br-PSAA) as a chromogenic reagent for spectrophotometric detection. This reagent forms water-soluble complexes with cobalt, nickel, copper and iron, with high molar absorptivities (10^5 l. mole^{-1} cm^{-1}). A few applications have been reported using 5-Br-PSAA. Makino[5] have reported a direct colorimetric determination of copper in serum using 5-Br-PSAA. A flow-injection spectrophotometric determination of palladium in catalysis and dental alloy with 5-Br-PSAA have been reported by Sakai and Ohno.[6] Yamane and Koshino[7] have found a rate-enhancing effect of copper(II) on the complex formation reaction of cobalt with PSAA at pH 4.0.

In this paper, we developed an FIA system for the determination of trace cobalt in zinc electrolyte. To determine cobalt accurately and rapidly, the sample solutions were directly taken from a continuous flow process stream in zinc refining. Just before the determination of cobalt, chromogenic reagent alone was injected into the analytical system for the measurement of background absorbance at 617 nm, and the background absorbance was utilized for the correction of system variation. A calibration curve was constructed by using real sample solution, of which cobalt concentration had been determined by a combined solvent extraction[8] and GF-AAS method.

EXPERIMENTAL

Reagent

Chromogenic reagent solution. One gram of 2-(5-bromo-2-pyridylazo)-5-(*N*-propyl-*N*-sulphopropylamino)aniline, sodium salt (Dotite Laboratory, 5-Br-PSAA) was dissolved in 100 ml of water.

Standard cobalt(II) solution. Cobalt standard stock solution (1 mg Co/ml) was prepared by dissolving 1 g of cobalt (99.99% purity) in nitric acid, expelling out nitrogen oxides and diluting to 1000 ml with water. A working standard solution was prepared by diluting the stock standard solution appropriately.

Carrier solution. To prepare $1.0 \times 10^{-2}M$ diammonium hydrogenphosphate–0.1% (v/v) hydrogen peroxide–$0.5M$ hydrochloric acid solution, 1.3 g of diammonium hydrogenphosphate (Wako Pure Chemicals Co.) and 3.3 ml of 31% (v/v) hydrogen peroxide (Mitsubishi Gas Chemicals Co.) were dissolved in an appropriate amount of water, followed by addition of 42 ml of hydrochloric acid (Kanto Chemicals Co.) and dilution to 1000 ml with water.

Buffer solution. About 153 g of ammonium acetate (Kanto Chemicals Co.) was dissolved in 1000 ml of water to yield $2M$ ammonium acetate solution.

All reagents used were of analytical-reagent grade and all solutions were prepared with distilled water.

Apparatus

A MILTON ROY SPECTRONIC 3000 ARRAY photo-diode array spectrophotometer was used for batch-wise absorption measurements.

A Hitachi U-1000 ratio-beam spectrophotometer equipped with a 60-μl flow cell (20-mm path length) was used as a detector for the flow-injection system. Sanuki-kogyo DMX-2700T and DMX-2400T double plunger pumps were used for pumping the carrier and buffer solutions. Two types of peristaltic pumps, ATTO AC-2120 and EYELA MP-3S, were used to pump sample and reagent solutions, respectively. Sanuki-kogyo SVA-6M2H automated six-way valves, made of ceramics, were used for sample and chromogenic reagent introduction. Nippon-Seimitsukagaku NRB-15 reactor was used for heating reaction coils. Polytetrafluoroethylene (PTFE) tubing (1.0 mm i.d.) was used to construct the analytical manifold. The dimensions are specified in the discussion. All of the pumps, valves and spectrophotometer were controlled with an NEC PC-9801 personal computer, for which a control program written in our laboratory was used.

Measurement of absorption spectra

Measurement of absorption spectra were carried out by a batch-wise method as follows. Place 5 ml of sample solution containing 0.1–1.0 μg Co/ml in a 50-ml volumetric flask. Add 5 ml of a buffer solution containing $2M$ ammonium acetate and 5 ml of $0.01M$ diammonium hydrogenphosphate–$0.5M$ hydrochloric acid–0.1% (v/v) hydrogenperoxide mixture, and adjust the pH to 5. Add 2 ml of 1% (w/v) 5-Br-PSAA solution and mix well. Let the mixture stand for 5 min and add 5 ml of $6M$ sulphuric acid and measure the absorption spectra from 400 to 800 nm of the resulting solution against the reagent blank using 1-cm quartz cells.

Flow-injection analysis

Figure 1 shows a schematic diagram of the manifold used. Carrier solution C (diammonium hydrogenphosphate–hydrogen peroxide–hydrochloric acid) was pumped into the analytical line at the flow-rate of 1.5 ml/min by using the pump P1. The sample solution was collected from the zinc refining process with an on-line sampler, and introduced into the carrier stream with the six-way valve V1 (200 μl). After being merged with the buffer solution to adjust to a pH of 5.0 at a flow rate of 1.5 ml/min with pump P1, the chromogenic reagent (5-Br-PSAA) was introduced by the six-way valve V2 (65 μl) synchronously with the sample zone. Sulphuric acid solution ($2M$) was mixed to decompose the metal-5-Br-PSAA complexes except the cobalt complex, and the absorbance of the cobalt–5-Br-PSAA complex was monitored in the flow-through cell D at 617 nm. Just before the determination of cobalt, the chromogenic reagent alone was injected into the analytical system for the measurement of background absorbance, and the background absorbance

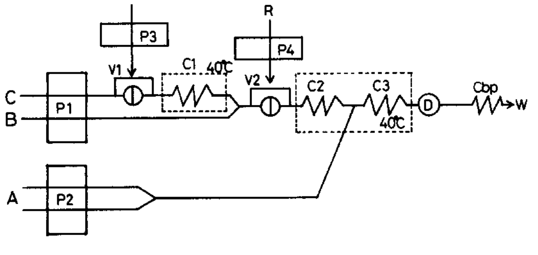

Fig. 1. Flow-injection system. C: Carrier solution; $0.01M$ $(NH_4)_2HPO_4$–0.1% (v/v) H_2O_2–$0.5M$ HCl, B: Buffer solution; $2M$ ammonium acetate, R: chromogenic reagent ($2.1 \times 10^{-3}M$ 5-Br-PSAA), Sample: zinc electrolyte, A: $2M$ H_2SO_4, P1,P2,P3,P4: pump, V1: sample injection valve, V2: reagent injection valve, C1,C2,C3: mixing coil (40°, C1: 1.0 mm × 1 m, C2: 1.0 mm × 3 m, C3: 1.0 mm × 5 m), D: spectrophotometer with flow cell, W: waste.

was utilized for the correction of system variation. Background corrected peak heights were rectilinearly related to cobalt concentration. Calibration curves were constructed by using solutions prepared by adding various increments of the standard cobalt solution to defined aliquots of the real sample solution of which the cobalt concentration had previously been determined by a combined solvent extraction[8]/GF-AAS.

Table 1. Composition of typical zinc electrolyte used for zinc refining

Element	Content (*μg/ml*)	Element	Content (*μg/ml*)
Ca	200	Cd	0.5
Co	0.1	Cu	0.1
Fe	15	K	5*
Mn	5*	Mg	8*
Ni	0.01	Pb	0.05
Sb	0.01	Zn	150 > *
SO_4^{2-}	ca.180*		

*mg/ml.

RESULTS AND DISCUSSION

The cobalt(II,III), copper(II), iron(II), nickel(II) and palladium(II) form water-soluble complexes with 5-Br-PSAA,[9] but the content of palladium(II) in zinc electrolyte is extremely low and zinc(II) does not form a complex with 5-Br-PSAA. In this form it is suitable for determination of trace cobalt in zinc electrolyte. Because the stability constants of cobalt-, copper-, nickel- and iron-5-Br-PSAA complexes are very high, EDTA or acids are added to improve selectivity. There are several reports[7,9] using EDTA for the decomposition of the nickel- and copper-5-Br-PSAA complexes. However, under the condition for the decomposition of the nickel- and copper-complexes with EDTA, zinc also reacts with EDTA. Then, it is necessary to add a high concentration of solution of EDTA to the sample solution in order to decompose these complexes. It is not appropriate for FIA to pump a high concentration solution, because analytical lines, pumps and/or six-way valves are clogged with the fine crystal of EDTA. Therefore, masking with EDTA is inapplicable to zinc-rich solutions. On the other hand, in acidic media, the nickel- and copper-5-Br-PSAA complexes are not stable, but the cobalt(II,III)- and iron(II)-5-Br-PSAA complexes are still stable. In this study, sulphuric acid was selected for acid medium to provide selectivity, because the sample solution originally contained a large amount of zinc sulphate and sulphuric acid (Table 1).

Absorption spectra of the 5-Br-PSAA complexes of cobalt(II,III) and iron(II) overlap with each other. It was necessary to mask iron(II) before introducing chromogenic reagent, because the sample solution usually contained 10 μg/ml levels of iron(II). We therefore studied masking techniques for iron(II), including masking with citric acid, tartaric acid, potassium periodide, diammonium hydrogenphosphate and the oxidation of iron(II) to iron(III) by irradiation of UV light. The most effective masking was observed using diammonium hydrogenphosphate in the presence of hydrochloric acid. In the case of using sulphuric acid instead of hydrochloric acid, the masking effect for iron(II) with diammonium hydrogenphosphate was not observed. We supposed that iron(II) was oxidized to iron(III) by hydrogen peroxide in the presence of hydrochloric acid and then iron(III) was complexed with phosphate ion. It is possible to mask iron(II) at less than 100 μg/ml using hydrogen peroxide, hydrochloric acid and diammonium hydrogenphosphate.

Optimization of flow-system

Effect of carrier concentration. The influence of the diammonium hydrogenphosphate was examined in the range of 0.001 to 0.1*M* and it was found that diammonium hydrogenphosphate of more than 0.01*M* was necessary to mask iron(II). However, the concentration of diammonium hydrogenphosphate at more than 0.05*M* cannot be employed because analytical lines are clogged with the precipitate of calcium phosphate. About 0.01*M* phosphate was enough to mask iron, where iron(II) was oxidized to iron(III) by hydrogenperoxide in the presence of hydrochloric acid and then iron(III) was complexed with phosphate ion. The effect of the concentration of hydrogen peroxide was then investigated and more than 0.05% (v/v) hydrogen peroxide is recommended for masking of iron(II). However, the evolution of bubbles was observed in the bottle of carrier solution when the hydrogen peroxide concentration was above 2.0% (v/v). For masking of iron(II) and dissolution of the fine precipitate of zinc sulphate in the sample solution, the concentration of hydrochloric acid was required to be 0.5*M* at the lowest. The mixture of 0.01*M* diammonium hydrogenphosphate–0.1% (v/v) hydrogen peroxide–0.5*M* hydrochloric acid was therefore chosen as the carrier stream.

Effect of pH and buffer concentration. The effect of the concentration of buffer solution was investigated by using acetate buffer with various pH values. The maximum absorbance was found when the pH of the mixture of the buffer and carrier solutions was between 4.0 and 6.0. Concentrations less than 0.5*M* cannot be employed because the buffer capacity is low for high salt concentration sample solutions. Then a buffer concentration of 2*M* and a pH of 5.0 were recommended for the buffer stream.

Effect of the concentration of sulphuric acid. It is necessary to use 2*M* sulphuric acid for rapid protonation of the cobalt(II,III) complexes. The concentration above 2*M* is not recommended, because the plunger seal of the pump P2 is damaged by sulphuric acid. We selected a concentration of sulphuric acid of 2*M* to protonate the cobalt complexes and decompose the other metal complexes involved in the sample solution.

Coil length. The effect of the length of the reaction coils (Fig. 1) was examined at the various flow-rates of the carrier and reagent solutions. The ratio of the flow-rate of the pump P1 to that of the pump P2 was fixed at 2, because it is necessary to use above 0.5*M* sulphuric acid in the final stream for the rapid protonation of the Co(II,III) complexes and the decomposition of the metal complexes except cobalt, and to avoid dilution of the sample stream. Firstly coils of 0, 1 and 3 m were tested for C1. No influence of the coil length was observed for the response of cobalt complexes, but complete masking of iron(II) cannot be accomplished without C1. The length of C2 was then varied from 1 to 5 m. The coil of 3 m gave the most sensitive and precise results. Finally coils of 1, 3 and 5 m were tested for C3. The flow-rate of the pump P1 is kept at 3.0 ml/min. Increasing the length of C3 enhanced the peak height and improved the reproducibility. The length of 5 m is necessary for C3 to protonate the cobalt complexes and decompose the other metal complexes in the sample solution. Thus the optimum lengths were 1 m for C1, 3 m for C2 and 5 m for C3.

Flow rate. The effect of the total flow-rate (P1, P2) on the peak height was studied in the range of 3.0 to 7.5 ml/min, by injecting 200 μl of cobalt standard solution and real sample solution which was spiked with cobalt standard solution to contain 0.6 μg Co/ml. The ratio of the flow rate of the pump P1 to that of the pump P2 was fixed at 2. The peak height increased steadily with increasing total flow-rate from 3.0 to 4.5 ml/min, reached a maximum at 4.5 ml/min and then slowly decreased with a further increase in the total flow-rate (Fig. 2). The optimum flow-rates of P1 and P2 were thus 3.0 and 1.5 ml/min, respectively.

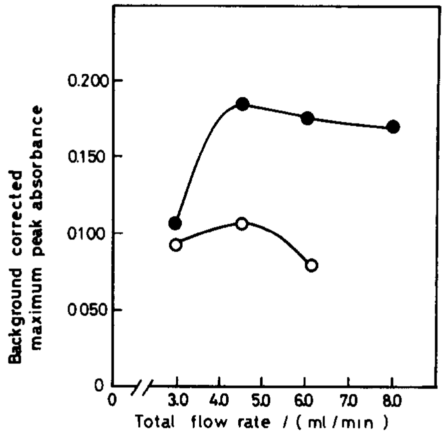

Fig. 2. Relationship between total flow rate and background corrected maximum peak height absorbance. ○: standard solution (Co 0.5 μg/ml), ●: sample solution (Co 0.63 μg/ml). The ratio of the flow rate of pump P1 to that of pump P2 was kept to 2.0.

Heating temperature of reaction coils. The effect of the temperature of the reaction coils was examined in the range of 20 to 140°, by injecting 200 μl of cobalt standard solution and real sample solution which was spiked with cobalt standard solution to contain 0.3 μg Co/ml. A constant response for cobalt were obtained, but the reagent blank absorbance increased steadily with increasing temperature from 20 to 140°. On the other hand, the absorbance change above the background was constant. We guess this fact to change the structure of 5-Br-PSAA. The heating temperature of reaction coils was chosen to be 40° to reduce the blank absorbance and to improve the reproducibility ascribed to the variation of environmental temperature.

Sample and chromogenic reagent injection volume. The influence of the sample volume on the absorbance was investigated by injecting varying volumes of cobalt standard solution (65–400 μl) and sample solution into the carrier stream at the recommended flow-rate and coil length, keeping the volume of the reagent solution at 65 μl. The injection volume affected the peak height and the reproducibility. Increasing

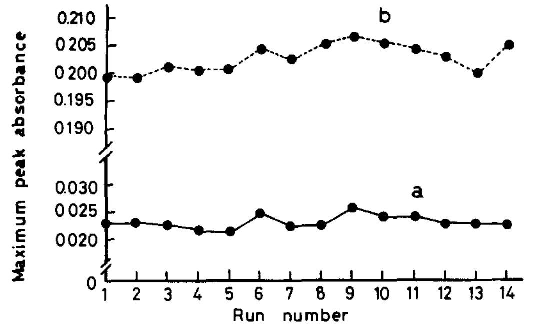

Fig. 3. Peak height absorbance on repeated runs. a: background corrected maximum peak absorbance (SD. = 0.0018, $n = 14$), b: non-background corrected maximum peak absorbance (SD. = 0.0024, $n = 14$), sample solution contained 0.11 μg Co/ml. Sample injected at constant intervals of 30 min.

the injection volume, however, spread the sample zone and led to the peak-split when the injection volume was more than 300 μl. Therefore, 200 μl was taken as a compromise. The chromogenic reagent volume was selected as 65 μl to reduce the consumption of expensive chromogenic reagent and also to reduce the blank absorbance of the chromogenic reagent.

Chromogenic reagent concentration. The effect of the 5-Br-PSAA concentration, ranging from 1.1×10^{-5} to $2.1 \times 10^{-3}M$, was tested, using 200 μl of sample and 65 μl of the reagent. The maximum and constant response for 0.5 μg Co/ml was obtained at the reagent concentration of above $1.6 \times 10^{-3}M$, so that $2.1 \times 10^{-3}M$ 5-Br-PSAA solution was used as the chromogenic reagent solution.

Injection sequence of sample and reagent solutions

If the proposed system is to be utilized as an on-line analyzer for cobalt in zinc electrolyte, the system should work regardless of the variation of environmental temperature. A spectrophotometer of laboratory use is affected by the variation of the surrounding temperature. On the other hand, the chromogenic reagent, 5-Br-PSAA, has an absorbance at 617 nm, which can be used to detect the fluctuation of the spectrophotometer. Therefore we utilized the blank absorbance of 5-Br-PSAA for the correction of the system variation. That is to say, the chromogenic reagent alone was injected into the analytical system prior to the determination of cobalt, and the background absorbance observed was utilized to correct the system variation. Figure 3 is the comparison of background corrected absorbance (a) and non-corrected absorbance (b) measured with the proposed system. The background corrected absorbance is more stable than the non-background corrected absorbance. The background correction is necessary to determine 0.1 μg/ml levels of cobalt.

Calibration curve

A calibration curve was obtained by the procedure described in the Experimental section. The calibration curve was linear over the range from 0.05 to 1.5 μg/ml for cobalt. The responses which were obtained by using solutions prepared by the addition of various increments of the standard cobalt solution to the real sample solution was 30% lower than those obtained by the standard cobalt solution. Therefore it was decided to prepare a calibration curve by the standard addition method. The mean values of the slope, the y-intercept, and the correlation co-efficient of the calibration curves were $y = (0.0937 \pm 0.0056)x + (0.0091 \pm 0.0023)$, $R = 0.9997 \pm 0.0002$ ($n = 3$).

Effect of foreign ions

The influence of foreign metal ions was studied. In the flow-injection spectrophotometric determination of 0.5 μg/ml of cobalt(II), the following ions when present in the amounts (μg/ml) shown in parentheses do not interfere: Cu^{2+}(100), Fe^{2+}(100), Fe^{3+}(100), Cd^{2+}(8000), Mn^{2+}(3600), Mg^{2+}(40000) and Ni^{2+}(1000). Alkaline metals, alkaline-earth metals, chloride, nitrate, and sulfate do not interfere at all. Oxalate and citrate, however, interfered seriously, probably owing to complex formation with cobalt.

Analysis of zinc electrolyte

The proposed flow-injection method was applied to the determination of cobalt in several

Table 2. Analytical results of cobalt in unrefined zinc electrolyte (μg/ml)

Sample No.	Proposed FIA method*	GF-AAS
1	0.08	0.08
2	0.10	0.09
3	0.86	0.85
4	0.11	0.09
5	0.17	0.18
6	0.12	0.11
7	0.10 ± 0.03†	0.11

*$n = 2$. †$n = 48$. Sample analyzed at regular intervals of 30 min.

samples. The results obtained for the high-salt concentration solutions of zinc electrolytes are given in Table 2, being in good agreement with the values obtained with a combined solvent extraction/GF-AAS method. The reproducibility has proved to be satisfactory with a relative standard deviation of less than 5.0% (0.1 μg Co/ml level, $n = 10$). The detection limit was 0.01 μg Co/ml. These results indicate that the proposed FIA method is suitable for the on-line sequential determination of traces of cobalt in the process stream of zinc electrolyte. The present FIA system has been operated as a process controller at the Akita zinc refinery of Mitsubishi Materials Co.

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