

Determination of ppb Level of Iron and Copper in Natural Waters and Boiler Waters in Steam Power Plant with 2-(5-Nitro-2-pyridylazo)-5-(N-propyl-N-sulphopropylamino)phenol by Flow Injection Analysis

Noriko Ohno^{1*}, Naoshi Nishikawa², Jiatai Wei², Norio Teshima² and Tadao Sakai²

¹Chemistry Laboratory, School of Business Administration, Asahi University, 1851, Hozumi, Hozumi-cho, Motosu-gun, Gifu 501-0296

²Department of Applied Chemistry, Aichi Institute of Technology, 1247, Yachigusa, Yakusa-cho, Toyota-shi, Aichi 470-0392

Abstract

A highly sensitive flow injection analysis for the determination of trace iron and copper is described. 2-(5-Nitro-2-pyridylazo)-5-(N-propyl-N-sulphopropylamino)phenol reacts with Cu(I), Cu(II) and Fe(II) to form water soluble compounds, but it does not react with Fe(III). When sodium metaperiodate is added, Cu(II) can be determined. In the presence of thiourea and reductant, iron can be determined. The calibration graphs are linear in the range of 1 ~ 10 ppb copper and iron. By amplifying the output of the detector, 0.4 ~ 1 ppb iron is detectable. The proposed FI method was applied to the determination of iron and copper in natural waters and boiler waters in the steam power plant.

Keywords: flow injection analysis, iron and copper at ppb level, 2-(5-nitro-2-pyridylazo)-5-(N-propyl-N-sulphopropylamino)phenol, natural water, boiler water

1. Introduction

Pyridylazo[1] and benzothiazolylazo[2] derivatives have been synthesized as photometric reagents for cobalt, iron and nickel and their molar absorptivities were reached to $10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ order. In the case mentioned above, the solvent extraction procedure was required for the spectrophotometric determination of metals because the solubility of complexes in water is poor. However, solvent extraction is troublesome and time consuming.

In order to eliminate the solvent extraction technique, water-soluble reagents such as 2-(3,5-dibromo-2-pyridylazo)-5-(N-propyl-N-sulphopropylamino)phenol[3] and 2-(3,5-dibromo-2-pyridylazo)-5-(N-propyl-N-sulphopropylamino)aniline (5-Br-PSAA)[4] have been synthesized and applied to the spectrophotometric analysis without solvent extraction. And also, 2-(5-nitro-2-pyridylazo)-5-(N-propyl-N-sulphopropylamino)phenol (nitro-PAPS) has been applied to the determination of iron in sera[5] and the each determination of iron, copper and zinc[6]. These water-soluble reagents are suitable for the determination of heavy metals with the flow injection system. Yamane et al. reported flow injection method for the determination of vanadium[7] and iron[8] using nitro-PAPS. In earlier papers, we reported the determination of palladium[9], iron and copper[10]

using 5-Br-PSAA and FI system. Wada et al.[11] synthesized 2-(2-thiazolylazo)-4-methyl-5-(sulphopropylamino)benzoic acid (TAMSPB) and applied to the flow injection analysis of copper. Although metals in the range of 10 ~ 100 ppb could be determined, the method described above was insufficient for the natural and boiler water analyses at a single ppb level.

The proposed method was successfully enhanced the sensitivity by using the low concentration of nitro-PAPS and iron at a sub-ppb level could be detected. The method was applied to the determination of trace amounts of iron and copper in natural and boiler water samples.

2. Experimental

2.1 Batchwise method

2.1.1 Apparatus

A Hitachi 124 double beam spectrophotometer with 10 mm quartz cells and 056X-Y recorder were used for measuring absorption spectra and absorbance. A Hitachi-Horiba F-7II pH meter was used.

2.1.2 Reagents

All reagents used were of analytical-reagent grade and distilled water was used throughout.

Standard Cu(II) and Fe(II) solutions: Commercially available standard solutions of Cu(II) and Fe(III) (Wako Pure Chemical Industries) were used. Working solutions were prepared by diluting the stock solution

* Corresponding author
e-mail: nohno@alice.asahi-u.ac.jp

with 0.01 mol l⁻¹ hydrochloric acid.

Nitro-PAPS solution (4.2 x 10⁻⁴ mol l⁻¹): A 0.021g of nitro-PAPS disodium dihydrate (Dojindo Laboratories) was dissolved in 100 ml of distilled water.

Buffer solution: A 0.1 mol l⁻¹ acetic acid-acetate buffer solution (pH 3 ~6) and a 0.3 mol l⁻¹ potassium dihydrogenphosphate-0.1 mol l⁻¹ sodium borate buffer solution (pH 6 ~ 10) were used.

Sodium metaperiodate solution (0.05%), L-ascorbic acid solution (1%) and thiourea solution (0.5 mol l⁻¹) were prepared by dissolving appropriate amounts in distilled water.

Thioglycolic acid solution (5 x 10⁻² mol l⁻¹) was prepared by dissolving a thioglycolic acid (Katayama Chemicals).

2.1.3 Procedure

An aliquot (1~3 ml) of 5 ppm iron, 1 ml of 1% L-ascorbic acid, 2 ml of 0.5 mol l⁻¹ thiourea, 2 ml of nitro-PAPS (4.2 x 10⁻⁴ mol l⁻¹) and 5 ml of buffer were placed into a 25 ml volumetric flask and diluted the mixture with water. The absorbance of iron-nitro-PAPS complex was measured at 580 nm against a reagent blank as a reference.

An aliquot (1~3 ml) of 5 ppm copper, 1 ml of 0.05% metaperiodate, 2 ml of nitro-PAPS (4.2 x 10⁻⁴ mol l⁻¹) and 5 ml of buffer were placed and diluted in the same manner described above. The absorbance of copper complex was measured at 565 nm.

2.2 Flow injection method

2.2.1 Apparatus and flow injection system

Soma Optics S-3250 double beam spectrophotometric detector fitted with the 8 μl flow cell and Toa Electronics FBR-251A recorder were used for the peak signals measurements. The solutions were delivered by a Sanuki Kogyo DMX-2300 double plunger micro-pump. A sample solution was injected into the carrier stream with a six-way rotary valve to which a volume control loop was attached. The PTFE tubing was 0.5 mm i.d. except for the back-pressure coil which was 0.25 mm i.d.

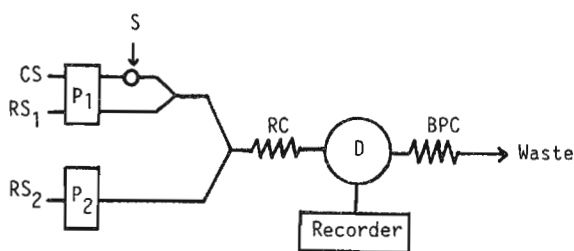


Fig. 1 Schematic diagram of FIA system

P₁ and P₂: pumps, S: sample injection (200 μl), RC: reaction coil, BPC: back-pressure coil (0.25 mm i.d. x 2m), D: spectrophotometric detector, CS: carrier solution, RS₁ and RS₂: reagent solutions prepared in 2.2.2.

The three-line manifold was assembled as shown in Fig. 1. The flow-rates of carrier and RS₁ were 0.5 ml min⁻¹, respectively and that of RS₂ was 1 ml min⁻¹. A

200 μl of sample solution was injected into the carrier stream and merged with RS₁ and RS₂.

A reaction coil length was 4 m for iron determination and it was 0.5 m for copper.

2.2.2 Reagents

Carrier solution (CS) was 0.01 mol l⁻¹ hydrochloric acid.

For Fe determination

Reagent solution 1 (RS₁, 0.15 mol l⁻¹ thiourea): A 5.71 g of thiourea was dissolved in 500 ml of water.

Reagent solution 2 (RS₂, 3.3 x 10⁻⁵ mol l⁻¹ nitro-PAPS + 0.1 mol l⁻¹ ascorbic acid, pH 4): 0.0083 g nitro-PAPS and 8.80 g of L-ascorbic acid were dissolved in 500 ml of 0.4 mol l⁻¹ acetic acid-acetate buffer solution (pH 4).

For Cu determination

Reagent solution 1 (RS₁, 0.1% metaperiodate): A 0.5 g of sodium metaperiodate was dissolved in 500 ml of water.

Reagent solution 2 (RS₂, 3.3 x 10⁻⁵ mol l⁻¹, pH 4): A 0.0083 g of nitro-PAPS was dissolved in 500 ml of 0.4 mol l⁻¹ acetic acid-acetate buffer solution (pH 4).

3. Results and Discussions

3.1 Characteristics of nitro-PAPS complex

Nitro-PAPS reacted with copper (I,II) and iron(II) to form colored complexes, but did not react with iron(III). The absorption maximum of the copper complex was at 565 nm and that of the iron complex was at 580 nm. Copper formed a 1:1 complex at pH 2.5~4.5 and a 1:2 complex at pH 8~9. The former molar absorptivity was 76000 l mol⁻¹ cm⁻¹ and the latter, 135000 l mol⁻¹ cm⁻¹. Iron(II) complex was formed at pH 3.4~9 and the molar absorptivity was 100000 l mol⁻¹ cm⁻¹.

Both copper and iron react with nitro-PAPS in the wide pH range of about 3~9, whereas some metals such as zinc, lead and cadmium react with nitro-PAPS to form a reddish complexes in alkaline media [12]. As a result, pH 4 was chosen for the selective determination of copper and iron.

3.2 Effect of masking reagents for iron determination

In the case, copper including in the sample solution gave a positive error on the determination of iron. To remove the copper interference, some masking reagents such as thiourea and thioglycolic acid were investigated by batchwise method. When 4 x 10⁻³ mol l⁻¹ thioglycolic acid was added, the absorbance of iron complex decreased. On the other hand, the iron-nitro-PAPS complex showed the same absorbance with and without 0.2 or 0.4 mol l⁻¹ thiourea. When 0.4 mol l⁻¹ thiourea was added, 0.4 ppm copper did not interfere for the determination of 0.2~0.6 ppm iron because of the masking effect.

In the FI method, 0.15 mol l⁻¹ thiourea was added to a carrier solution and the influence on the peak heights of iron was investigated. When the iron solution and/or the mixed solution of iron and copper were injected, each peak height was the same. It

means that copper is completely masked with thiourea and gave no influence of iron determination.

3.3 Effect of oxidants for the selective determination of copper

Iron (III) did not form a complex with nitro-PAPS. When an oxidant is added, only copper can be detected. The oxidants such as sodium perchlorate, potassium metaperiodate and sodium metaperiodate were added and their effects were studied. The concentration was varied from 0.005 to 0.08%. The results are shown in Fig. 2. Oxidation of iron(II) to iron(III) by sodium perchlorate was not sufficient. When over 0.005% of potassium metaperiodate and sodium metaperiodate were added, iron (II) was completely oxidized. In this work, to eliminate the influence of iron for the determination of copper, sodium metaperiodate was used because it was easily soluble in water.

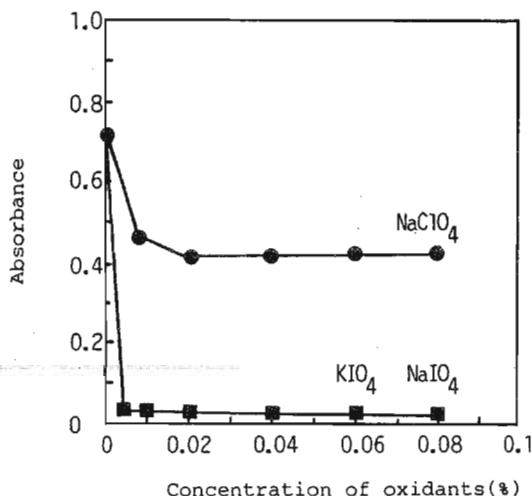


Fig. 2 Effect of oxidants
Fe: 0.2 ppm, pH: 4

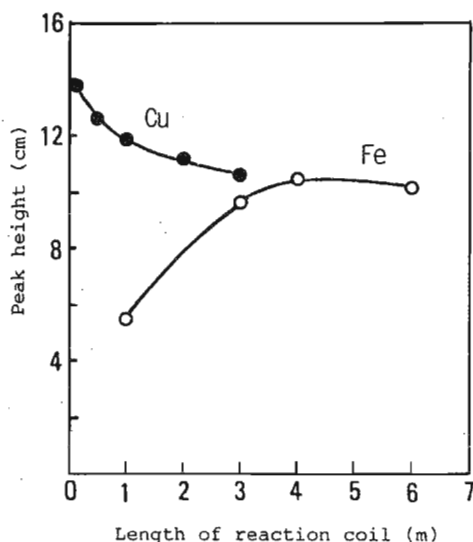


Fig. 3 Effect of reaction coil length
Fe and Cu: 20 ppb

3.4 Effect of reaction coil length

The reaction coil length was varied from 0.5 to 6 m (Fig.3). For iron, the largest peak was obtained at a length of 4 m. In the case of short reaction coil less than 4 m, the peak height was very low because the rate of chelate formation with nitro-PAPS was slow. Over 4 m, the peak height gradually decreased by dispersion of the sample zone.

Copper reacted with the reagent quickly to form a complex in RC. Peak heights decreased with increasing the length of RC. Accordingly, a 0.5-m long was used for the copper determination.

3.5 Effect of flow rate for the determination of iron

A carrier solution and a thiourea solution were propelled by pump 1 and the reagent solution 2 (nitro-PAPS + L-ascorbic acid) was delivered by pump 2. The 4 m reaction coil was set. Under these conditions, the influence of the flow rate was investigated. The peak heights slightly increased with increasing flow rate. In this experiment, the flow rates of CS, RS₁ and RS₂ were fixed at 0.5, 0.5 and 1 ml min⁻¹.

3.6 Effect of reagent concentration

The effect of nitro-PAPS concentration on the complex formation was investigated in the range of $1 \times 10^{-5} \sim 1 \times 10^{-3} \text{ mol l}^{-1}$. The peak heights were maximum and constant over $3.5 \times 10^{-5} \text{ mol l}^{-1}$ nitro-PAPS. The slight shorter peak was obtained at a lower concentration of nitro-PAPS. Since nitro-PAPS itself is colored, the use of higher nitro-PAPS causes base line to be noisy. The relationship between the output (absorbance unit, AU) in the detector and the concentration of nitro-PAPS was investigated. The result was shown in Fig. 4. When the concentration

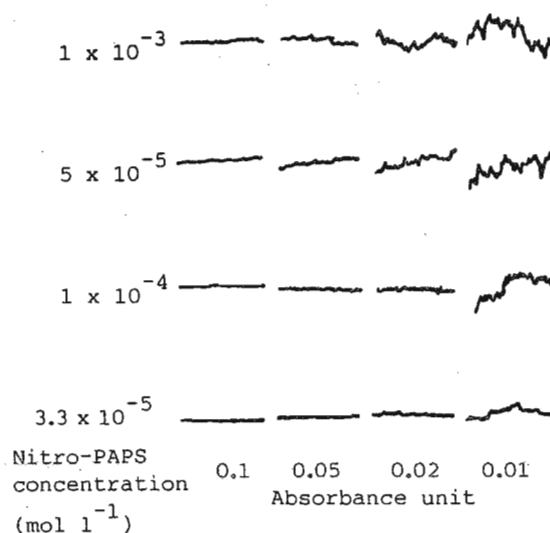


Fig. 4 Influence on base line caused by absorbance unit(AU) in the spectrophotometric detector and nitro-PAPS concentration

of nitro-PAPS was $3.3 \times 10^{-5} \text{ mol l}^{-1}$, the baseline was smooth. Even when AU 0.01 was used, the baseline did not give a significant influence on monitoring peaks. When the concentration was higher, the baseline was noisy. Therefore, AU 0.02 and $3.3 \times 10^{-5} \text{ mol l}^{-1}$ nitro-PAPS were preferable for the analysis of iron at single ppb level.

3.7 Calibration graphs

By delivering lower reagent concentration, iron and copper in the wide range from sub-ppb to ppm could be determined. The relative standard deviations(RSD) were 1 % for 5 determinations of 0.2 ppm iron and 1.7 % for 4 determinations of 3 ppb iron. Fig. 5 shows the flow signals in the range 1~7 ppb iron using 0.02AU. And also, a good linearity was obtained in the range 0.4~1 ppb iron using 0.02 AU in the detector. The calibration graph was linear over the range of 1~10 ppb copper, and the RSD was 1% for 3 determinations of 2 ppb copper.

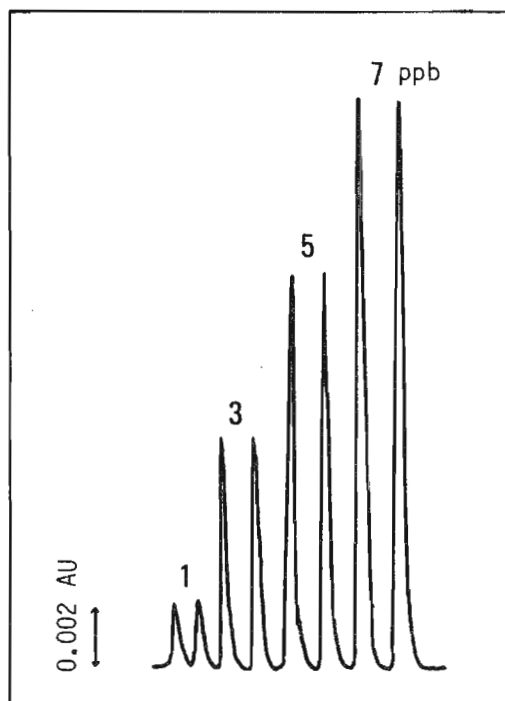


Fig.5 Flow signals for the determination of iron
Sample volume: $200 \mu\text{l}$, AU: 0.02.

3.8 Determination of iron and copper in natural waters and boiler waters at power plant.

Natural water was heated for 2 hrs at 80°C and HCl was added to give a final concentration of 0.01 mol l^{-1} . The results are summarized in Table 1. The proposed method is suitable for the determination of several ppb iron.

Table 1 Determination of iron in natural waters

Sample	Fe (ppb)
Natural water 1(Toyama)	4.3
Natural water 2(Toyama)	3.8
Natural water 3(Tsuwano)	4.0
Natural water 4(Shuho-do)	9.3
Top water 1(Hozumi)	4.9
Top water 2(Ogaki)	7.2

The boiler waters at the steam power plant were analyzed using the proposed FI system. After heating in the similar manner described above, a $200 \mu\text{l}$ of the sample solution was injected. These samples were also analyzed by ICP/AES and spectrophotometry using 2,4,6-tris(2-pyridyl)-s-triazine (TPTZ) for iron and by ICP/AES for copper. The iron concentration in the condensed boiler water (1) in the steam power plant was 3.5 ppb by FIA, 3.1 ppb by spectrophotometry and 4.7 by ICP/AES. For the same boiler water (2) in the different point, 4.0 ppb by FIA, 6.3 ppb by spectrophotometry and 6.0 ppb by ICP/AES were obtained. In the condensed boiler water(1), the result obtained by FIA was in a good agreement with the values by other methods, however, the latter showed a slight disagreement. The iron concentrations obtained by ICP/AES were slightly large because of difficulty of the iron detection.

For copper, 1 ppb by FIA and 0.9 ppb by ICP/AES were obtained. As can be seen, the proposed FI system is preferable for the determination of single ppb level of iron and/or copper and for the monitoring the boiler waters at steam power plants.

References

- [1] T. Katami, T. Hayakawa, M. Furukawa and S. Shibata, *Anal. Chim. Acta*, **188**, 289(1986).
- [2] T. Katami, T. Hayakawa, M. Furukawa and S. Shibata, *Analyst* [London], **110**,339(1985).
- [3] D. Horiguchi, M. Saito, K. Noda and K. Kina, *Anal. Sci.*, **1**, 461(1985).
- [4] D. Horiguchi, M. Saito, T. Imamura and K. Kina, *Anal. Chim. Acta*, **151**, 457(1983).
- [5] T. Makino, M. Kiyonaga and K. Kina, *Clin. Chim. Acta*, **171**, 19(1988).
- [6] N. Ohno and T. Sakai, *Bunseki Kagaku*, **46**,937(1997).
- [7] T. Yamane and Y. Yamaguchi, *Mikrochim. Acta*, **130**, 111(1998).
- [8] T. Yamane and H. Yamada, *Anal. Chim. Acta*, **308**, 433(1995).
- [9] T. Sakai and N. Ohno, *Anal. Chim. Acta*, **214**, 271(1988).
- [10] Sam Woo Kang, T. Sakai and N. Ohno, *Anal. Chim. Acta*, **261**, 1197(1992).
- [11] H. Wada, T. Ishizuki and G. Nakagawa, *Mikrochim. Acta*, 1983III, 235.
- [12] T. Yamane and Y. Yamaguchi, *Anal. Chim. Acta*, **345**, 139(1997).

(Received April 8, 2002)

(Accepted May 2, 2002)