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A CONTINUOUS MONITORING SYSTEM FOR THE DETERMINATION OF TOTAL IRON IN WASTE WATER BASED ON COMPLETELY CONTINUOUS FLOW ANALYSIS WITH SPECTROPHOTOMETRIC DETECTION

Rahmiana Zein, Durmawel and Edison Munaf*
Laboratory of Analytical Environmental Chemistry, Faculty of Mathematics and Natural Sciences, Andalas University, Padang 25163.

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ABSTRACT

An automated monitoring system based on "Completely continuous flow analysis" with spectrophotometric detection has been developed for monitoring the concentration of total iron in water. The method involves a continuous flow technique for sample reduction and complexation in small bore tubes (0.5 mm I.D.) at µL/min level. Sodium hydroxylamine hydrochloride containing acetate buffer (pH = 5.9) was used as the reducing reagent. While 1,10-phenantroline was used as the complexation reagent. The parameter of flow rate(s), reaction and reactor condition(s) was studied for on-line monitoring manifolds. The absorbance of the complex is detected at 526 nm. Under the optimal conditions, the present method could be successfully applied for the continuous monitoring of total iron in water.

Key words : Continuous monitoring system; total iron; waste water; spectrophotometric detection

*To whom correspondence should be addressed.

INTRODUCTION

Iron is the most abundant heavy metal in river water. The predominant oxidation state in oxygenated water is iron(III), which strongly reacts with different coexisting organic and inorganic matter to form colloidal and suspended particles. The determination of individual iron species offer

useful information for studied of the geochemical behavior and bioavailability of iron, which are toxic toward aquatic organisms.

Recently, the need for rapid determination of trace chemical e pollution monitoring has fostered the development of automated methods of analysis[1]. The unsegmented flow techniques offer a wide range of possible methodologies[2,3]. Thus conventional flow injection analysis (nFIA) allows analysis of pollutants with minimum consumption of the sample solution. Here the reagents demand the major expenditures for determinations. In cases such as wastewater analysis, reversed FIA (rFIA) is thus much more suitable to reduce the analytical cost. On the other hand, when continuous monitoring of the varied analyte concentrations in sample is required, the completely continuous flow method (continuous recording of the signal produced) is advantageous[4,5].

Several authors have described a flow injection technique for the quantification of iron in water[6,7]. Linch et al. described the determination of iron(II) and iron(III) with different reagents and detectors, using dual channel system[6]. On the other hand, Alonso et al. reported simultaneous determination of iron(II) and total iron using single channel system[8]. Yamane and Goto9,10 have described the use of single injection with only one detector for the determination of iron(II) and iron(III). Although the method seem to be has good recovery for iron(II) and iron(III), increased error was observed at lower concentrations. The different flow injection manifold has impact on the optimizing result for the determination of iron, as reported by Chalk and Tyson[11]. They found that manifold configurations would have different detection limit because of the practical consideration arising mainly from various noise sources.

Recently, we have reported the use of a continuous flow technique for the completely continuous determination of total mercury as well as the speciation of mercury compounds[12-17]. This paper present a continuous monitoring system for total iron based on completely continuous flow analysis, using hydroxylamine hydrochloride and 1,10-phenantroline as the reducing and complexing reagents, respectively. The method has been applied for on-line monitoring of total iron in water.

EXPERIMENTAL

Apparatus

A schematic diagram of the continuous flow analysis - spectrophotometry used in this work is shown in Figure 1. The operating conditions for the determination of total iron compounds are summarized in Table 1.

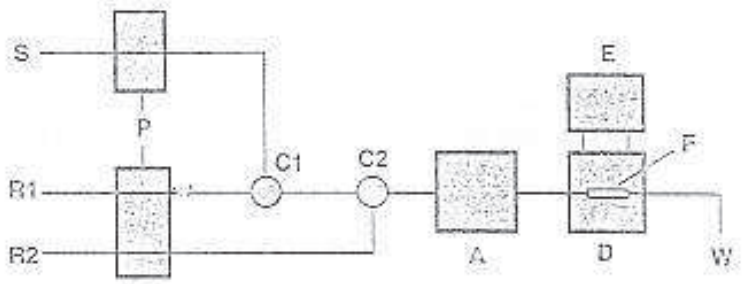

Figure 1. Schematic diagram of continuous microflow apparatus for the determination of total iron. S = sample, R_1 = reduction reagent, R_2= complexing reagent, C_1 = C_2 = mixing coil, A = aluminum block bath, D = detector, F = flow cell, E = recorder and W = waste.

Table 1. Operating conditions for the determination of iron.

Parameter/Components	Specification
Flow rate, S	400 µL/min
Flow rate, R_1	400 µL/min
Flow rate, R_2	300 µL/min
S	Sample or blank
R_1	Hydroxilamine hydrochloride + acetate buffer
R_2	o-phenantroline
Pump	Gilson Minipuls 2, France
Detector	Jasco model Uvidec, Inteligent UV/VIS spectrophotometer
Wavelength	526 nm
Recorder	Yokogawa Electric-Work Ltd, YEW type 3056.

Chemicals

All reagents employed in this work were obtained from E. Merck (Germany), unless otherwise noted. Hydrochloric acid was of special grade, ferric chloride, hydroxylamine hydrochloride, 1,10-phenantroline and acetate buffer were of reagent grade or better.

Procedure

The sample, hydroxylamine hydrochloride containing acetate buffer and 1,10-phenantroline reagent, are continuously flowed through peristaltic pumps at the flow rates of 400, 400 and 300 µL/min, respectively.

The sample stream is first mixed with the solution of hydroxylamine hydrochloride containing acetate buffer (pH 5.9) in a reduction reaction tube made of PTFE (0.5 mm I.D., 30 cm long), where the iron(III) in sample is reduced to iron(II). The reducing product then mixed with 1,10-phenantroline solution in complexing reaction tube made of PTFE (0.5 mm I.D., 1 m long) placed in an air bath with temperature of 45 °C, to perform the orange complex of iron(II) - phenantroline.

RESULTS AND DISCUSSION

Optimization of flow rate conditions

The flow rate(s) of solution(s) in the determination of total iron were optimized by using solution of 2 mg/L iron(III), 10% hydroxylamine hydrochloride in acetate buffer (pH 5.9) and 1% 1,10-phenantroline.

When the flow rate of the sample solution, i.e., 2 mg/L iron(III) was changed from 100 to 500 µL/min, almost constant response was observed at the flow rate higher than 400 µL/min (Figure 2A). Therefore, 400 µL/min was chosen as the flow rate of sample. In this experiment, the flow rate of reducing and complexing reagent were kept constant at 400 and 300 µL/min, respectively.

Figure 2B shows the effect of reducing reagent flow rate on the signal response. In this case the flow rate of sample and complexing reagent were kept constant at 400 and 300 µL/min, respectively. When the flow rate of reducing reagent solution was changed from 100 to 500 µL/min, the signal response increases with increasing the flow rates and remain constant at flow rates higher than 400 µL/min. this is because at flow rate of 400 µL/min, all the iron(III) solution was completely reduced to iron(II). Therefore, 400 µL/min was selected as the flow rate of reducing reagent.

Figure 2C, shows the relationship between the complexing reagent flow rate and the absorption response of the system iron(II) - phenantroline. When the flow rate of complexing reagent, i.e., 1% 1,10-phenantroline was changed from 100 to 400 µL/min, almost constant response was observed

during the experiment. For safety, 300 µL/min was chosen as the flow rate of complexing reagent.

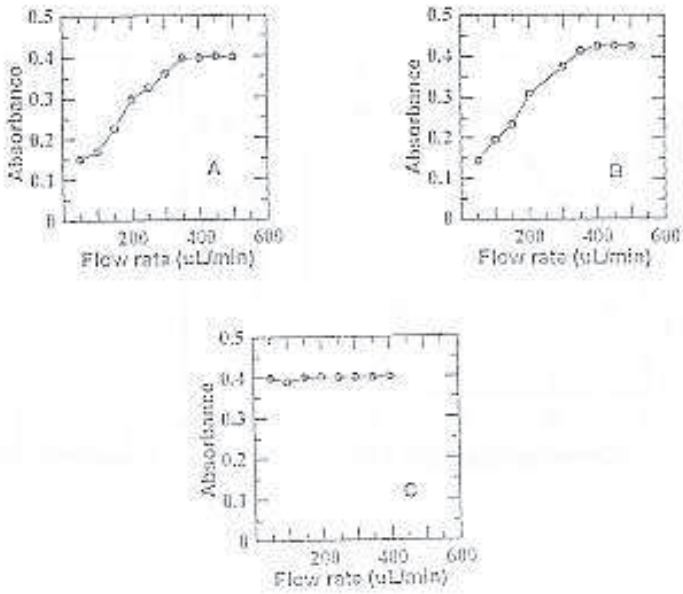

Figure 2. Optimization of flow rate conditions

Optimization of reaction conditions

In the present work, the effect of the concentration of reagent, i.e., hydroxylamine hydrochloride and 1,10-phenantroline were investigated. A 2.0 mg/L iron(III) standard solution and ultrapure water were alternately injected for 10 min.

The effect of hydroxylamine hydrochloride concentration as reducing reagent on the signal response of iron is shown in Figure 3A. In this case the concentration of 1,10-phenantroline was kept constant at 2%. As shown in Figure. 3A, when the concentration of hydroxylamine hydrochloride changed from 2 to 15 %, the sensitivity of iron increased up to the 10% and remained constant at the higher concentration. Consequently, 10% was selected as the optimum concentration.

Figure 3B shows the effect of the concentration of 1,10-phenantroline on the signal response of iron. No substantial change has been indicated when the concentration of 1,10-phenatroline is changed from 1 to 5%. For safety, 2 % of 1,10-phenantroline was selected as optimum.

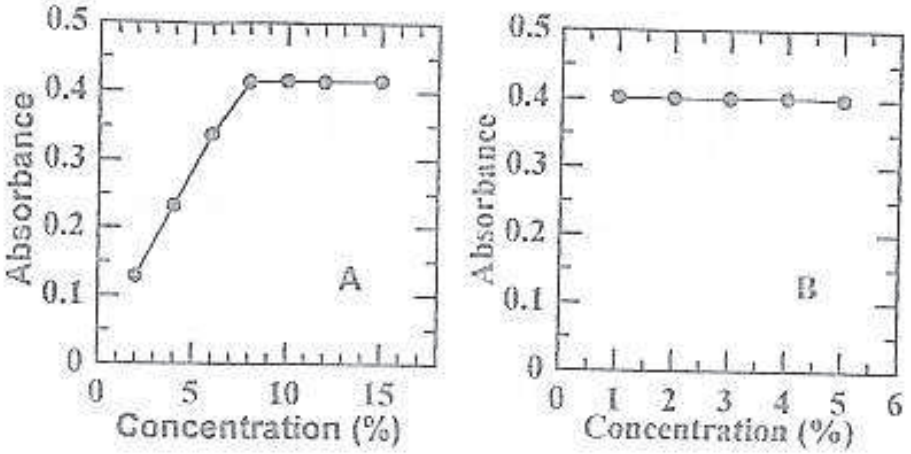

Figure 3. Optimization of reaction conditions

Optimization of reaction temperature

The effect of temperature on the signal response was investigated. When the reaction temperature was changed from 30 to 90 °C, the signal response slightly increasing with increased reaction temperature up to 45 °C and remained constant at higher temperature. Therefore for the further experiment, 45 °C was selected as reaction temperature.

Analytical figure of merits

Using the optimal conditions described above, the analytical figures of merit in iron determination by the present system were evaluated. In the concentration range of 0.5 - 2.5 mg Fe/L, the linear regression equation was $A = 0.0322\ [Fe] + 0.0005$, with the correlation coefficient = 0.95. The detection limit of iron estimated from the peak height measurement was 0.10 mg/L (S/N = 3). The standard deviation of the signal responses of total iron at 1.0 and 2.0 mg/L obtained by 3 replicate injection was ca. 1.9 and 2.2%.

Application to continuous monitoring

Continuous monitoring of total iron content in water, especially for industrial water is important for industrial waters quality control. For such purposes, the on-line monitoring is more desirable than the conventional discrete monitoring. On the basis of the studies described here, an on-line prototype monitoring system was constructed. Water was supplied through a pipe connected to the manifold S in Figure 1, and the sample was pumped continuously by using a peristaltic pump. The result is shown in Figure 4. Pumping a standard solution of 1.5 mg/L at the beginning of the measurements checked the stability of the iron signal. The present on-line monitoring system could be successfully performed for the determination of total iron. When iron(III) only want to determined, by replacing the reducing reagent with ultrapure water in Figure 1, the concentration of iron(II) could easily be determined.

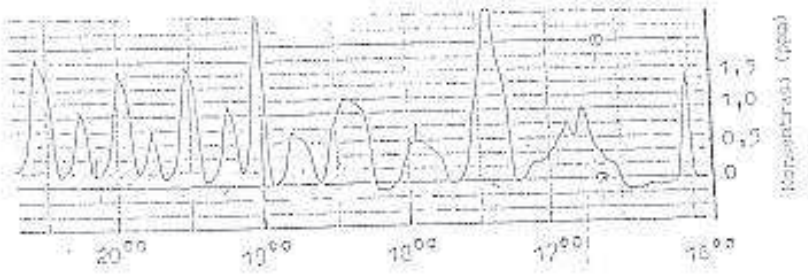

Figure 4. On-line monitoring of total iron present in water.

In conclusion, the proposed method allows on-line and automated monitoring of total iron in water. It should be noted that the amount of reagents required for the proposed system is much lower than the conventional automated one.

REFERENCES

1. Munaf, E., Takeuchi, T., Monitoring of university effluents, in : Korenaga, A. *et al.* (eds) *Hazardous waste control in research and education*, Lewis Publisher, USA 1994.
2. Goto, M., *Trends in Anal Chem* 4 : 92 – 94 (1983).
3. Ruzicka, J., Hansen, E. H., *Flow injection analysis*, 2nd ed, John Wiley and Sons, USA 1988.
4. Valcarcel M, Luque de Castro MD *Flow injection analysis. Principles and Applications*. Ellis Herwood, Chichester 1987.
5. Rujicka, J., *Analyst* 119:1925 – 1934 (1994).
6. Lynch, T.P, Kernogham NJ, Wilson JN *Analyst* 109:843 – 845 (1984).
7. Mortati J, Krug FJ, Pasenda LCR, Zagatto EAG, Storgaard Jorgensen S *Analyst* 107:659 – 663 (1982).
8. Alonso J, Bartroli J, Delvalle M, Barber R *Anal Chim Acta* 219:345 – 350 (1989).
9. Yamane T, Goto E *Anal Sci* 5:221 – 223 (1989).
10. Yamane T, Goto E *Anal Sci* 5:783 – 784 (1989).
11. Chalk SJ, Tyson JF *Anal Chem* 66:660 – 666 (1994).
12. Goto M, Munaf E, Ishii D *Fresenius Z Anal Chem* 332:745–749 (1989).
13. Munaf E, Goto M, Ishii D *Fresenius Z Anal Chem* 334:115 –117 (1989).
14. Munaf E, Takeuchi T, Goto M, Haraguchi H, Ishii D *Anal Sci* 6:313-314 (1990).
15. Munaf E, Haraguchi H, Ishii D, Takeuchi T, Goto M *Anal Chim Acta* 235:399 – 404 (1990).
16. Munaf E, Haraguchi H, Ishii D, Takeuchi T, Goto M *Sci Total Environ* 99:205-209 (1990).
17. Munaf E, Haraguchi H, Ishii D, Takeuchi T *Anal Sci* 7:605 – 609 (1991).