

## Reverse Flow Injection Analysis for Determination of Manganese(II) in Natural Water

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### ABSTRACT

A simple, rapid and sensitive reverse flow injection analysis (rFIA) method for determining the concentration of manganese in natural water has been developed. The analytical method is based on the reaction between Mn(II) and 4-(2-pyridylazo)resorcinol, which can be spectrophotometrically monitored at 495 nm. The chemical and flow injection variables were studied and optimized to make the procedure suitable for quantitating Mn(II) in water samples. The linear calibration curve is obtained in the range of 0.05-1.0 mg L<sup>-1</sup> Mn (II) with  $r^2 = 0.9993$ . The method has detection limit of 0.034 mg L<sup>-1</sup> and is capable of a sampling frequency of 180 h<sup>-1</sup>. The rFIA method provided good sensitivity and precision for determination of Mn(II) with a relative standard deviation of 0.8%. The procedure was applied successfully to the determination of Mn(II) in natural water, and the results were statistically compared with results determined by atomic absorption spectrometric method.

*Keywords:* Flow injection analysis, Manganese, 4-(2-pyridylazo) resorcinol

### INTRODUCTION

Trace metal ions have important roles in life because these metal ions are usually present in water. Wide spectrum of human activity may result in increasing level of contamination in the water. Manganese is one of three toxic essential elements. It exists mainly in both manganese(II) and manganese(IV) oxidation states. However, the greatest parts of dissolved Mn(II) is important due to its stability in aqueous environments. The uptake of high concentration of Mn(II) can cause human health such as nerve damage, Parkinson, lung embolism and bronchitis (Lenntech, 1998). Therefore, Mn(II) analysis in water has received attention strongly.

Several spectrophotometric methods have been used to determine Mn(II) in aqueous solutions (Kamburova, 1998; Ohura *et al.*, 2003) such as the reaction between permanganate and 4,4-tetramethyldiaminotriphenylmethane (Sandell, 1959). Disadvantages of this reaction are that the color is stable for only five minutes after develop fully, and that the determination must be carried out in a darkened room (Ahrland and Herman, 1975). The pyridylazo compounds are widely used for spectrophotometric reagents for metal ions because the sensitivities of these reagents for many metal ions are higher than those of other reagents but they are not selective (Ahrland and Herman, 1975; Munshi and Dey, 1964; Shibata, 1972). 4-(2-pyridylazo) resorcinol (PAR) can be used for many heavy metal species (Rocha *et al.*, 2001) with a very high absorptivity (Ahrland and Herman, 1975). This

reagent belongs to the same family as 1-(2-pyridylazo)naphthol (PAN), but has the added advantage of being soluble in water (Munshi and Dey, 1964; Ahrlund and Herman, 1975). A number of spectrophotometric procedures have been described for the analysis of Mn(II)-PAR complex has been reported (Ahrlund and Herman, 1975). However, this method could be sophisticated or time consuming as full color development or they could require expensive instrument. Recently, Flow injection analysis (FIA) is now widely used in analytical measurements because low reagent consumption, low cost of instrument and the simplicity of procedure as well as their speed, precision and accuracy (Ruzicka and Hansen, 1988).

In this work, a very simple, rapid and sensitive reverse flow injection analysis (rFIA) has been described for determination of manganese(II) in natural waters, with spectrophotometric detection using 4-(2-pyridylazo)resorcinol, PAR, as a complexing agent. The Mn(II)-PAR complex shows a maximum absorption at 495 nm in buffer solution pH 11. The operation conditions of rFIA procedure were investigated including reagent concentration, buffer solutions, injection loop, reaction coil and et al.

## EXPERIMENTAL

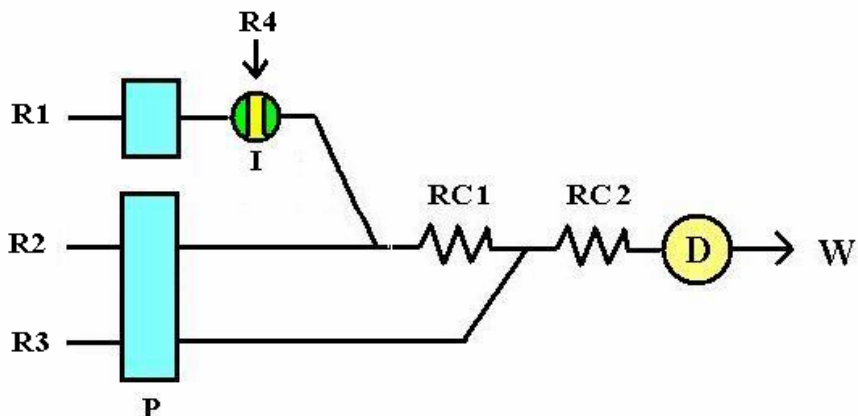
### Reagents

All the reagents used were of analytical grade, and the solutions were prepared in distilled and deionized water. A 1000 mg L<sup>-1</sup> of Mn(II) solution (Merck, Germany) was used as stock standard solution. Standard working solutions containing 1.0-4.0 mg L<sup>-1</sup> of Mn(II) were prepared by appropriate dilution.

A 5 × 10<sup>-3</sup> mol L<sup>-1</sup> 4-(2-Pyridylazo) resorcinol (PAR) (Fluka) solution was obtained by dissolving its sodium salt in deionized water. Universal buffer solutions containing borate, citrate, or phosphate with the pH adjusted within 7.0 and 12 were employed to obtain plots of peak area against pH.

### Apparatus and Procedure

A reverse flow injection system used in this work (Figure 1) consists of two pumps (FIAS300 Perkin Elmer, Germany), a six-way valve with a loop for sample injection with a UV-Vis spectrometer (Lambda2S, Perkin Elmer, Germany) as detector, has been described in a previous paper (Klamt, 2004). The rFIA procedure is based on a PAR reagent injection into the flowing carrier stream of 0.01 mol L<sup>-1</sup> NaOH, which was merged with sample solution and buffer solution at 2.2 and 0.9 ml min<sup>-1</sup>, respectively. The Mn(II) form complex with reagent in the reaction coil and the chelate shows an maximum absorption at 495 nm through a 1cm path length and 8 µL internal volume flow cell. PTFE tubing was used as flow lines and reaction coil in the system. A model UV-Vis diode-array spectrometer (Specord S100, Analytik Jena AG., Germany) was used to scan spectrum.

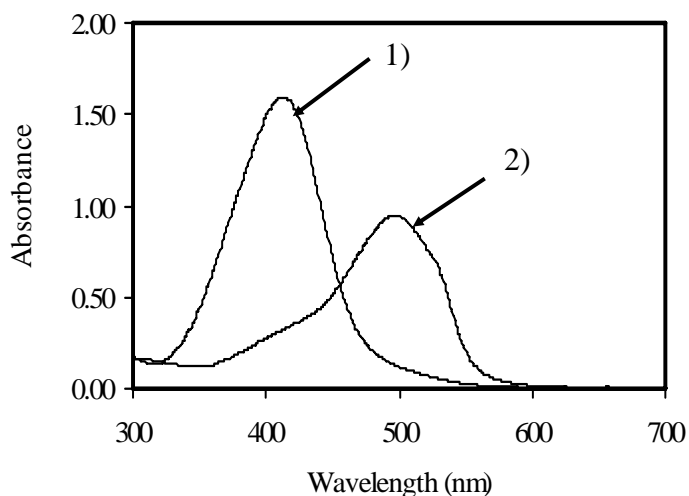


**Figure 1** The rFIA system. R1, carrier stream ( $0.01 \text{ mol L}^{-1} \text{ NaOH}$ ); R2, Sample stream, R3, Buffer solution; R4,  $3.0 \times 10^{-4} \text{ mol L}^{-1} \text{ PAR}$  solution; P, Peristaltic pump; I, Injection valve; RC1, reaction coil 1; RC2, reaction coil 2; D, Detector; W, Waste.

## RESULTS AND DISCUSSION

### Spectra characteristics

The spectrum of the Mn(II)-PAR complex was studied over the range 300-750 nm (Figure 2), which shows the maximum absorption at 495 nm. Therefore, this absorption wavelength was used for the following experiments.



**Figure 2** Absorption spectra of 1) PAR solution and 2) Mn(II)-PAR complex:  $C_{\text{PAR}} = 3.0 \times 10^{-4} \text{ mol L}^{-1}$ ,  $C_{\text{Mn(II)}} = 3.0 \text{ mg L}^{-1}$ , Buffer pH 11.

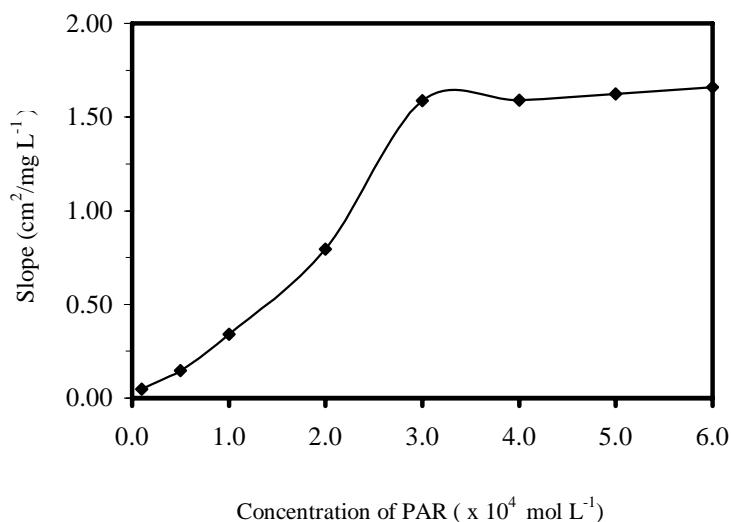
### Method optimization

To achieve the sensitive and selective determination of Mn(II) by rFIA method, the various parameters effecting the flow system were investigated and selected for a final method evaluation.

#### A. Optimization of chemical variables

Chemical parameter were varied while keeping the other flow injection variables constant, and were optimized by continuously introducing a standard solution containing Mn(II) ( $1.0\text{--}4.0\text{ mg L}^{-1}$ )

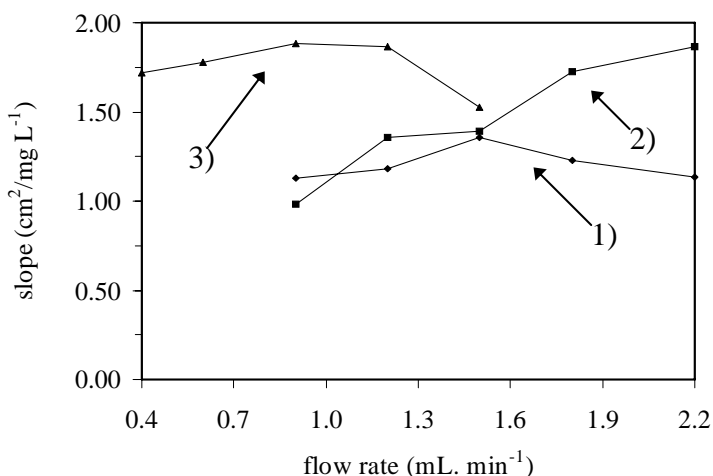
The influence of concentration of carrier stream and PAR reagent and pH of buffer solution was examined under flow condition. The different types of carrier stream, deionised water and NaOH concentration between  $0.01$  and  $0.10\text{ mol L}^{-1}$ , were determined. The results found that a  $0.01\text{ mol L}^{-1}$  NaOH concentration was found to be suitable for this determination. The PAR concentration was tested within the range of  $0.1\times 10^{-4}$  to  $6\times 10^{-4}\text{ mol L}^{-1}$ . The experiment results were shown in Figure 3. The results clearly demonstrated that the sensitivity increase with an increase of PAR concentration up to concentration  $3.0\times 10^{-4}\text{ mol L}^{-1}$ . Thus, a  $3.0\times 10^{-4}\text{ mol L}^{-1}$  PAR concentration was taken as optimum in order to favor sensitivity. The pH of buffer solution was studied over the range 9-12. An optimum value of pH 12 was observed for the buffer solution. This results showed small different with the results obtained by batch spectrophotometric methods (Ahrland and Herman, 1975; van Staden and *et al.*, 2003). This could be due to the differ of substances used for preparation of buffer solution.



**Figure 3** The effect of PAR concentration on the signal for the determination of Mn(II).

### B. Optimization of FIA variables

The flow injection variables were studied under the above optimum chemical variables. The flow rates of the various streams are very important in the flow injection techniques which were shown in Figure 4. The results indicated that the optimum of sensitivity is reached when rate of carrier stream flow, sample and buffer solution are 1.5, 2.2 and 0.9 mL min<sup>-1</sup>, respectively.



**Figure 4** The variation of slope with respect to flow rates of 1) 0.01 mol L<sup>-1</sup> NaOH 2) Sample solution and 3) Buffer solution pH 12

The volume size of reagent solution injected in the flow system was varied between 50 and 200  $\mu\text{L}$  by changing the length of the loop in the injection valve. The study showed that the sensitivity of the determination increases as a function of reagent volume due to increase dispersion of PAR in the sample zone. However, the signals of the injection volume above 50  $\mu\text{L}$  show distortions and a double-peak shape. Therefore, the volume of 50  $\mu\text{L}$  was used as an optimum volume for subsequent experiments.

The influence of the lengths and internal diameters of reaction coil was investigated between 100 and 500 mm with the internal diameter between 0.5 and 1.0 mm at a constant flow rate and injection volume. The length of RC1 has a slightly effect on the sensitivity, but an increase in the sensitivity of RC2 caused by a better mixing of sample-reagent and buffer, a maximum was reached at 300 mm and then, a decrease of sensitivity was observed, probably due to the dispersion of the sample into the reaction coil. In addition, the i.d. results of RC1 and RC2 were slightly decreased with increasing in diameter. Thus, lengths of 100 and 300 mm and diameters of 0.5 and 0.7 mm were selected as optimal reaction coils for RC1 and RC2, respectively.

### Analytical features

By taking into account the results of the variables study described above, the performance of the rFIA set-up have been evaluated under the conditions in Table 1. A calibration curve is linear up to  $1.0 \text{ mg L}^{-1}$ . The relationship between the peak area and the concentration is given by the equation  $y = 5.2496x + 12.608$ ;  $r^2 = 0.9993$  where  $y$  is the peak area and  $x$  is the concentration of Mn(II) in  $\text{mg L}^{-1}$ . The relative standard deviation of the peaks for repeated injections ( $n = 20$ ) of a number of  $0.30 \text{ mg L}^{-1}$  Mn(II) standard solutions were 0.8 %. The recovery results displayed in Table 2. The results shown a high recovery for the sample that added higher concentration of standard solution. The detection limit ( $2\sigma$ ) and sampling rate of the rFIA method for Mn(II) were determined to be  $0.034 \text{ mg L}^{-1}$  and  $180 \text{ h}^{-1}$ , respectively.

**Table 1** shows the range over which each parameter was determined and the optimal value obtained by a univariant approach.

Parameters	Range studied	Optimal value
NaOH ( $\text{mol L}^{-1}$ )	0.01- 0.10	0.01
pH of buffer solution	9-12	12
Concentration of PAR solution ( $\text{mol L}^{-1}$ )	$0.1 \times 10^{-4} - 6.0 \times 10^{-4}$	$3.0 \times 10^{-4}$
Flow rate ( $\text{mL min}^{-1}$ )		
- NaOH	0.8-2.2	1.5
- Sample	0.8-2.2	2.2
- buffer solution	0.4-1.5	0.9
Reagent volume ( $\mu\text{L}$ )	50-200	100
Reaction coil (mm)		
Length RC1	100-400	100
RC2	100-500	300
i.d. RC1	0.5-1.0	0.5
RC2	0.5-1.0	0.7

**Table 2** The Recovery Results

sample	Mn(II)			%recovery
	Found* ( $\text{mg L}^{-1}$ )	Added ( $\text{mg L}^{-1}$ )	Detected* ( $\text{mg L}^{-1}$ )	
1	0.31	0.10	0.39	83
2	0.31	0.30	0.59	94
3	0.31	0.50	0.79	95

\*  $n = 5$

The tolerable limit concentrations of several ions in the determination of Mn(II) were shown in Table 3. The levels of tolerated concentration of foreign ions was considered as maximum concentration found to cause a signal change lower than 5 % compared with the signal for Mn(II) solution without other metal ions. As can be seen from Table 3, Zn, Cd, Cu, and Pb ions interfered at positive direction with in the determination of 0.5 mg L<sup>-1</sup> Mn(II). The presence of Fe<sup>2+</sup> ion in Mn(II) sample more than 4.00 mg L<sup>-1</sup> is interfered for the determination of Mn(II). This result was in good agreement with the results showed by other researcher (van Staden *et al.*, 2003). Thus, the conditions for the determination of Mn(II) with this reagent must be strictly controlled to enhance its specificity. In the real water samples, the interferences from the other ions (Table 3) were negligible because of the presence of very low concentrations.

**Table 3** The tolerance limits of interfering ions

Species	Tolerance limit (mg L <sup>-1</sup> )
Zn <sup>2+</sup>	0.40
Cd <sup>2+</sup>	0.20
Cu <sup>2+</sup>	0.10
Pb <sup>2+</sup>	1.00
Fe <sup>2+</sup>	4.00

### Analytical application

Real samples from the different sites of ground water around the Naresuan University in Phitsanulok province were analysed by rFIA system. The concentration of Mn(II) in the sample solutions were determined from calibration curve obtained using standard solutions. The accuracy was evaluated by comparing the results obtained for the samples by atomic absorption spectrometry. The analytical results compared favorably, as seen from Table 4, with was proved with t-test to show that the results were not significantly different ( $t_{cal} = 0.11$  and  $t_{critic(95\%;5)} = 2.57$ ) between them.

**Table 4** Determination of Mn(II) in water by rFIA method compared with atomic absorption spectrometry

Sample	Concentration of Mn (mg L <sup>-1</sup> )	
	FIA	AAS
S1	0.036	0.022
S2	0.092	0.075
S3	0.034	0.035
S4	n.d	0.002
S5	n.d	0.004
S6	0.080	0.086
S7	0.014	0.018
S8	n.d	0.006
S9	0.156	0.158

N = 5

n.d. = not detectable

## CONCLUSION

In this paper, the rFIA method with spectrophotometric detection for the determination of Mn(II) has been studied. The chemical parameter and rFIA variables were optimized. The results provided good accurate and reproducibility for a concentration of Mn(II) at least 0.30 mg L<sup>-1</sup> with a relative standard deviation of 0.8% and a high sample throughput at the rate of 180 h<sup>-1</sup>. This method offers a linear detection range from 0.10 to 1.00 mg L<sup>-1</sup> and a detection limit of 0.034 mg L<sup>-1</sup>. The method was applied successfully to the analysis of different sites of water samples. The results obtained were in good agreement with that obtained by atomic absorption spectrometry.

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