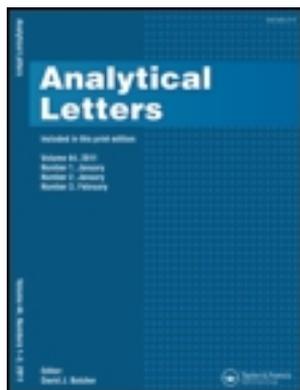


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THE DETERMINATION OF MN(II) IN WATER BY REVERSED FLOW INJECTION SPECTROPHOTOMETRY

Keywords: Manganese(II) determination, Spectrophotometry, FIA, Reverse flow

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ABSTRACT

This paper describes a reversed flow injection spectrophotometric method for determination of manganese(II) at low levels. A new chromogenic system TCMOPPH₂-Cd(II)-imidazole has been set up using a novel synthetic chromogenic reagent meso-tetra[4-(carboxymethylenoxy)phenyl]porphyrin [TCMOPPH₂] by a substitution reaction of Mn(II) and Cd(II)-TCMOPP complex. The linear range extends from 0.01 to 1.75mg·L⁻¹ with a sampling frequency of 90 h⁻¹. Co(II), Cu(II), Cr(III) and Fe(II) exert no interference until

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their concentrations are up to 30, 32, 15 and 23 times of that of Mn(II), respectively. The proposed method is proved to be simple, sensitive and suitable for on-line determination of Mn(II), and it has been used in analysis of Mn(II) in water samples of Liaohe Oil Field water treat plant during the on spot purification. The detection limit was $2.8\mu\text{g}\cdot\text{L}^{-1}$.

INTRODUCTION

In the water treatment plant of Liaohe Oil Field(Liaoning Province), the ground water under the depth of 400~500 m was used as the water supply with great benefit, but the content of minerals such as Fe(II) and Mn(II) are much higher than the drinking water standard. Manganese is one of the essential elements to human, plants and animals. It was considered that trace amount of manganese was necessary, however, it would bring much troubles when the concentration of Mn(II) was beyond a certain limit¹. It was obvious that the raw water is not suitable as drinking water, unless it is first purified.

Manganese exists in water at various valency states from +2 to +7. However, it will dissolve mainly in the +2 state in neutral ground water due to its stability and solubility.

The determination methods of manganese in water and wastewater have been reviewed²⁻³. Among all of these, spectrophotometry and atomic absorption spectroscopy were the primary methods, but their usefulness is limited. Flow injection analysis, which was used in an increasing number of applications in various fields of routine chemical analysis, has also been tested for the determination of Mn(II)⁴⁻⁷.

Porphyryns, acting as sensitive metallogenic reagents, have a strong absorption at the Soret band (400~500nm) with molar absorptivities of 10^5 to $10^6\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. The inherent weakness of porphyryns is that the coordination reactions of porphyrin ligands with metal ions are extremely slow at the room

temperature and the practical absorbance change due to complexation is small, thus limiting their usefulness⁸. There has been some reports in which porphyrins were used to determine Mn(II)⁹⁻¹¹.

In this paper, a system (TCMOPPH₂-Cd(II)-imidazole) was set up to detect trace amounts of Mn(II). There was a large shift of the characteristic absorption spectra between the ligand and the final product. Meanwhile, the adapted technique of flow injection provides on spot analysis.

EXPERIMENTAL

Apparatus

LZ--2000 Model Combination Flow Injection Analyzer (Shenyang, China); 7530 Model Spectrophotometer (Shanghai).

Reagents

TCMOPPH₂ was synthesized according to a previous publication¹².

TCMOPPH₂ stock solution: 0.0809g of TCMOPPH₂ was added into a solution of 0.1 M NaOH, then diluted accurately to the mark of 25.00mL in a brown volumetric flask. The concentration was 3.56×10^{-3} M; Mn(II) stock solution: 2.0×10^{-3} M; Cd(II)-imidazole solution: Transfer 3.00mL of 1.0×10^{-3} M Cd(NO₃)₂ solution into a 100mL volumetric flask, add 0.15 M imidazole solution to the mark; HCl solution: 0.01 M; All of the chemicals employed in the experiments were of analytical grade reagents; doubly distilled deionized water was used.

Recommended procedure

A schematic of the reversed flow injection system is shown in FIG.1. The following components were assembled into the proposed flow injection system: a peristaltic pump, a 8-port multi-functional sampling valve with a 30uL sampling

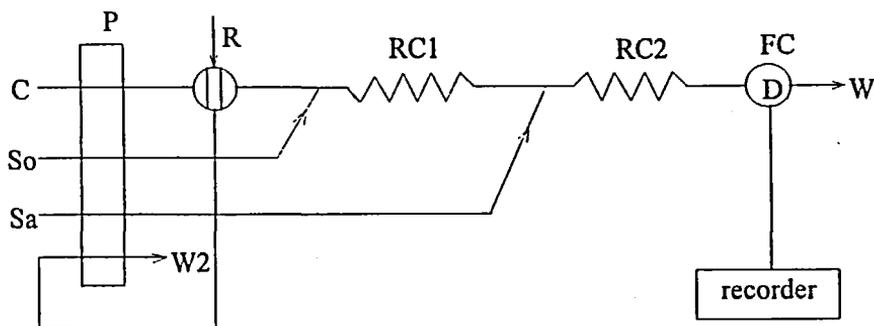


Fig. 1: The schematic plot of reversed flow injection system

P—Peristaltic pump; C—Carrier (H_2O); R—Reagent; So—Solution; Sa—sample; RC₁—Reaction coil 1; RC₂—Reaction coil 2; W₁—Waste1; W₂—Waste 2.

loop, reaction manifold systems and 7530 UV/Vis spectrophotometer equipped with a 10mm flow-through cell (volume 18uL). After the base line was stable, it was recorded as A_0 . Then, R (reagent, TCMOPPH₂) was pumped into the sampling valve. C (carrier stream solution was 0.01 M HCl), So (Cd(II)-imidazole solution) and Sa (sample solution containing Mn(II)) were pumped into flow system at flow rates of $3.62\text{mL}\cdot\text{min}^{-1}$, $0.58\text{mL}\cdot\text{min}^{-1}$ and $0.58\text{mL}\cdot\text{min}^{-1}$, respectively. Under these conditions, the reaction was carried out and absorbance A_i of reaction product was measured at 472.0nm.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of the Mn(III)-TCMOPP complex in the presence of imidazole (which played a role as an accelerator in the coordination reaction) is shown in FIG.2, together with those of TCMOPPH₂ and its relevant complexes.

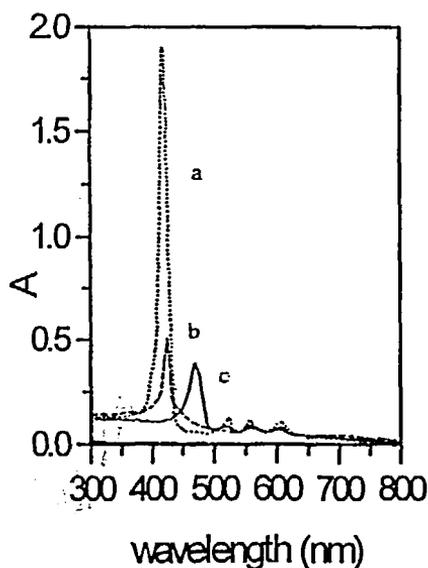


Fig. 2: The absorption spectra of ligand and its relevant complexes.

a---TCMOPPH₂; b---Cd(II)TCMOPP; c---Mn(III)TCMOPP contrast with TCMOPPH₂. [TCMOPPH₂]= 4.422×10^{-6} mol·L⁻¹; [Mn(II)]= 2×10^{-6} mol·L⁻¹; [Cd]= 1×10^{-3} mol·L⁻¹.

It can be seen that the Soret band of the manganese(III) complex, which was important for manganese(II) determination due to its high molar absorptivity, lay at 472.0nm and was different from those of TCMOPPH₂ at 418.6nm and the cadmium complex at 424.6nm. In the presence of air, the Mn(II)-TCMOPP complex was rapidly oxidized to Mn(III)-TCMOPP, which gave the characteristic absorption band around 472.0nm with ligand as the blank.

Carrier stream solution

The 0.1 M HCl selected as the carrier stream solution was compared to H₃BO₃-Na₂B₄O₇, HAc-NaAc, ClCH₂COOH-ClCH₂COONa and HCl, systematically, due to their acidity and composition, to obtain satisfactory results.

Flow rate

Flow rate of carrier stream

An increase in the flow rate of carrier stream solution from 0.58 to 5.20 mL·min⁻¹ caused the stability of the system to decrease, but the sensitivity of the measured signal increased. The result is shown in FIG.3. This is in agreement with the theory of Johnson¹³. The flow rate of carrier stream solution was set at 3.62 mL·min⁻¹.

Flow rate of Mn(II) solution

As shown in FIG.3, within the range of flow rate of manganese solution, 0.58 to 5.20 mL·min⁻¹, the sensitivity decreased with increasing flow rate. This was also in close agreement with the theory of r-FIA¹⁴, in which high sensitivity was achieved by the low axial dispersion of sample, since it was considered that 0.58 mL·min⁻¹ was an optimum flow rate in this experiment.

Flow rate of Cd(II)-imidazole solution

The relationship between the sensitivity and the flow rate of Cd(II)-imidazole solution is shown in FIG.4. As above, the high sensitivity was found to depend on the low dispersion, which corresponds with the low flow rate. In this experiment, 0.58 mL·min⁻¹ was chosen.

The volume of sampling loop

The volume of sampling loop was decided by all the following facts: the smaller the volume, the more stable the response value; the higher the sampling frequency, the less reagent used, and the lower the sensitivity. The results showed that a sampling loop volume of 300 μL gave an optimum performance for the Mn(II) analytes (FIG. 5).

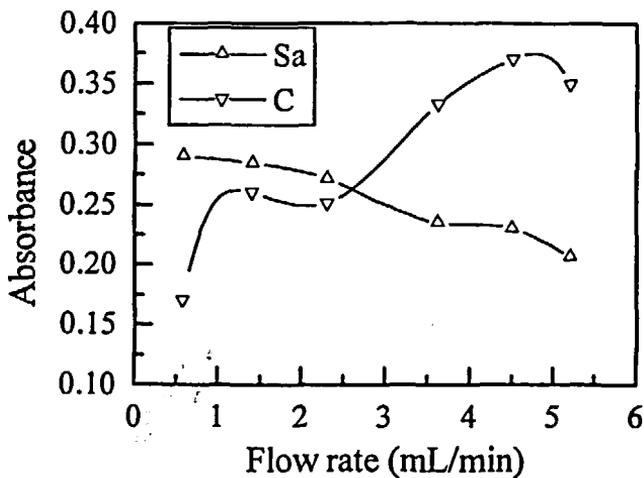


Fig. 3: The effect of flow rate on the absorbance.

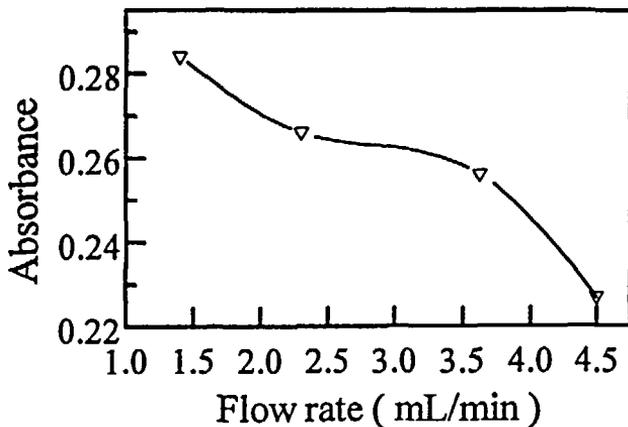


Fig. 4: The effect of flow rate of Cd(II)-imidazole solution on the absorbance.

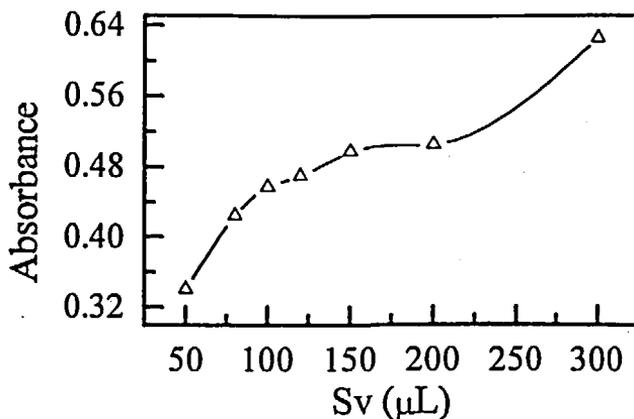


Fig. 5: The plot of absorbance against the volume of sampling loop.

The concentration of TCMOPPH₂

It was concluded that the sensitivity increased when the concentration of TCMOPPH₂ changed from 3.6×10^{-5} to 3.6×10^{-3} mol·L⁻¹. However, the responsible peak widened as the sensitivity enhanced. This would lead to an unnecessary carrying out when the sampling frequency was high. Moreover, the high concentration would waste the reagent. 7.2×10^{-4} M TCMOPPH₂ would achieve satisfactory results.

The length of reaction coil

The value of absorbance was recorded under various lengths of reaction coil covering the range of 100 to 1000cm with the other reaction conditions fixed. The plot of absorbance against L_{RC1} is shown in FIG.6. The maximum absorbance was obtained at 300cm coil length, so it was chosen and applied for all subsequent studies.

Similarly, the plot of absorbance against L_{RC2} is also shown in FIG.6. It was obviously that the absorbance decreases as the length of RC2 increased. The

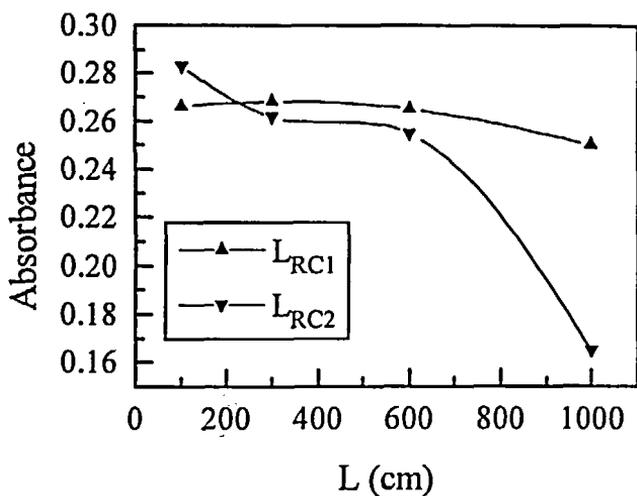


Fig. 6: The relationship of absorbance and the length of RC1.

result occurred from unnecessary dispersion. 100cm was appropriate on the base of the above facts.

Calibration, sensitivity and precise

The calibration graph was linear over the range of 0.01 to $1.75\text{mg}\cdot\text{L}^{-1}$ for Mn(II), the detection limit being $2.8\mu\text{g}\cdot\text{L}^{-1}$. The absorbance increased according to the equation: $A=1.854\times 10^4 C+0.001$ ($R=0.9991$). The RSD of 11 solutions whose concentration of Mn(II) was $1.0\times 10^{-5}\text{ M}$ was 0.3%, and the sampling frequency was 90 h^{-1} .

Effect of foreign ions

The effect of the system on the absorbance of 4 main kinds of foreign ions was investigated according to the composition and relevant reference. It was found that the four foreign ions were tolerated up to concentrations of Co(II),

TABLE 1. The results of samples analysis.

sample	standard value reported (mol·L ⁻¹)	Found(N=5) (mol·L ⁻¹)	RSD(N=5) (%)
1	1.00×10 ⁻⁵	9.90×10 ⁻⁶	0.31
2	2.06×10 ⁻⁵	2.00×10 ⁻⁵	0.29
3	3.09×10 ⁻⁵	2.99×10 ⁻⁵	0.28

Cu(II), Cr(III) and Fe(II) higher than 30, 32, 15 and 23 fold that of Mn(II), respectively.

Analytical applications

The recommended procedure was applied to the determination of Mn(II) in ground water of Liaohe Oil Field.¹⁵ The results are shown Table 1.

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