

## HIGHLY SENSITIVE FLOW INJECTION ANALYSIS

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### ABSTRACT

Highly sensitive flow injection analysis (FIA) was developed with a pulseless double plunger micro pump. Carrier and reagent solutions were emitted alternatively 4.9  $\mu$ l each. The whole manifold was kept at a constant temperature (25.0  $^{\circ}$ C) in an air bath. To eliminate a micro pulse, line filters, a reaction coil packed with glass beads and an air damper were equipped. The constant electric voltage was kept constant with an electric stabilizer. Iron of  $\mu$ g l<sup>-1</sup> (ppb) level could be determined by measuring the absorbance of Fe(II)-1,10-phenanthroline complex at 510 nm. The sensitivity could be enhanced up to 1000 times electrically.

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### INTRODUCTION

Double stream flow injection manifold has been widely employed in Japan and a pulseless double plunger micro pump is used to propel carrier and reagent solutions instead of peristaltic pump, because pulseless pumps are commercially available and the sample solution and reagent solution can be mixed accurately and rapidly. If the solutions are mixed completely and electrical pulses are small, the baseline on chart should be pulseless and stable. In such case, the peaks of sample are accurate and reproducible. However, the output is affected strongly by temperature change at high sensitivity, thus whole system should be kept at a constant temperature (25.0  $^{\circ}$ C). The absorbance of Iron(II)-1,10-phenanthroline complex was

measured at 510 nm and several ppb of Fe(II) could be determined with good reproducibility.

## EXPERIMENTAL

### Apparatus

PTFE tube (0.5 mm i.d.) was used for whole flow system except back pressure coil (0.25 mm i.d.). A pulseless double plunger micro pump (DM2M-1026, Sanuki Kogyo, Tokyo) was used. The plunger diameter was 2.5 mm and the stroke 1 mm. The suction and emission mode is shown in Fig. 1. With this pump any damper tube or air damper is not usually necessary, and sample and reagent solutions are mixed quickly in a reaction tube. Therefore a 50 cm of reaction coil was enough between the mixing joint and the flow cell. The flow rate of  $1.65 \text{ ml min}^{-1}$  was employed. A ceramic six-way

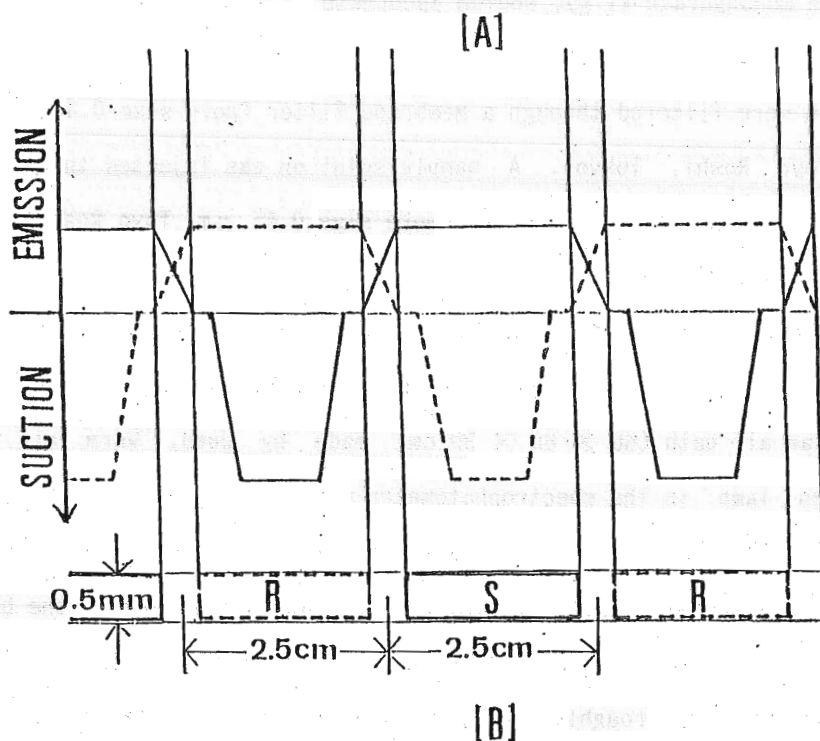


Fig. 1 Working mode of DM2M-1026 pump (A) and stream in PTFE tube (B).  
Solid line: sample solution, Broken line: reagent solution.

injector (STM-6M2L, Sanuki Kogyo) was used. The dead volume was 4  $\mu$ l, and the volume of injected sample solution was 188  $\mu$ l. A visible spectrophotometer (400~800 nm, S-3250, Soma Kogaku, Tokyo) with a titanium flow cell (0.5 mm i.d., light-path length 10 mm) was used. A recorder (Nippon Denshi Kogaku, U228, Tokyo) was used with chart speed 15 cm h<sup>-1</sup>.

#### Reagents

(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>FeSO<sub>4</sub>·6H<sub>2</sub>O (0.7022g) was dissolved in distilled water containing hydrochloric acid (1 ml) and sodium ascorbate (1 g), and the solution was diluted exactly to 1 l. This solution was containing 100 mg l<sup>-1</sup> Fe(II). The standard solution was diluted to prepare a series of 25, 20, 15, 10, 5 and 0 ppb Fe(II) solutions and another series of 10, 8, 6, 4, 2 and 0 ppb Fe(II) solutions for 500 times and 1000 times sensitivity, respectively. The reagent solution was composed of 1,10-phenanthroline chloride monohydrate (1 g), sodium ascorbate (1 g) and 0.1 ml hydrochloric acid in 1 l distilled water. Carrier (distilled water), and the reagent solution were filtered through a membrane filter (pore size 0.45  $\mu$ m, Toyo Roshi, Tokyo). A sample solution was injected through a disposable syringe filter Dismic-3CP (pore size 0.45  $\mu$ m, Toyo Roshi).

#### Highly Sensitive FIA

The FIA manifold used is shown in Fig. 2. To keep a constant temperature (25.0 °C) the spectrophotometer and the double plunger micro pump were set in an air bath (60 × 60 × 30 cm) made by wood. Warm air from a tungsten lamp in the spectrophotometer was blown to a radiator (25 × 9 × 3.5 cm) with a fan, in which lower temperature water circulated from a water bath outside the box, and another fan stirred air in the box. The temperature in the box was exactly adjusted to 25.0 °C by the outside water bath (below 25 °C) roughly and by controlling the circulating water speed finely.

To prevent a micro pulse from the pump, the carrier and reagent solutions passed through line filters which are made by sintered PTFE powder

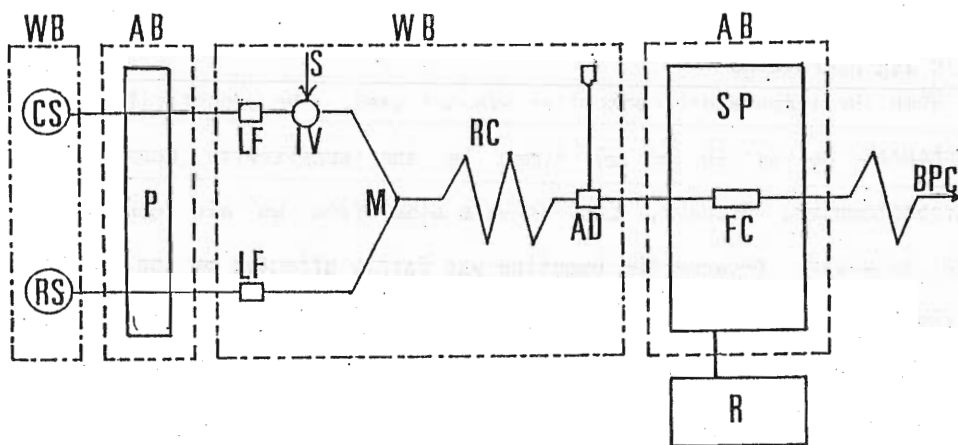


Fig. 2 Highly sensitive FIA manifold. CS: carrier solution, RS: reagent solution, P: double plunger micro pump, LF: line filter, IV: injection valve, S: sample solution, M: mixing joint, RC: reaction coil, AD: air damper, FC: flow cell, SP: spectrophotometer, R: recorder, BPC: back pressure coil (0.25 mm i.d.), WB: water bath (25.0 °C), AB: air bath (25.0 °C).

packings (diameter 4 mm, thickness 2 mm, GL Sciences, Tokyo). To eliminate a slight pulse, a 50 cm PTFE tube (1 mm i.d.) packed with glass beads (diameter 0.6 mm) was used as a reaction coil. After the reaction coil an air damper with 1 m PTFE tube (0.5 mm i.d.) was placed (Fig. 2). Line filters, mixing joint, reaction coil, air damper and injection valve were kept in a water bath (25.0 °C) together with carrier and reagent solution bottles.

To prevent electric noises, an electric stabilizer (SVC-1010, Matsunaga Manufacturing Co. Ltd.) was used, and the spectrophotometer, the pump and the recorder were earthed. When the baseline on a recording paper becomes constant and noiseless at elevated sensitivity of the detector, sample solutions were injected and reproducible and constant absorbances were obtained.

The sample solutions vessel was stoppered to prevent the contamination of iron from room air.

## RESULTS AND DISCUSSION

When the temperature controller was not used, the sensitivity could be enhanced up to 10 or 20 times by the sensitivity knob of the spectrophotometer. However, cool or warm wind from an air conditioner should be avoided, because the baseline was fairly affected by the temperature change.

Sample solution injected flows rapidly at the center of the tube but slowly near the tube wall. Therefore, the sample solution can be mixed with the reagent solution rapidly, and the mixing is complete even in a shorter reaction coil than 50 cm. When other commercially available pumps are employed, the emission volume at each stroke is about 100  $\mu$ l which occupies 50 cm of PTFE tubing (0.5 mm i.d.) and the mixing occurs only at the boundary. Thus the mixing may be incomplete if a 1 m PTFE reaction coil is equipped. The pump employed in this study emitted only 4.9  $\mu$ l solution at each stroke, that corresponds to 2.5 cm of tube. If the stable baseline and the reproducible peaks can be obtained, the highly sensitive detection can be performed when the out-put of the spectrophotometer is enhanced. By using the line filters, a reaction coil packed with glass beads, an air damper and the water bath and air bath, the reproducible peaks and stable base line were obtained.

By using this FIA system, iron at ppb levels was determined. The calibration outputs are shown in Fig. 3A and B. The correlation coefficients were A: 0.9999 and B: 0.9975, respectively. This method could be applied to the determination of ppb-level iron.

Sensitivity of FIA can be improved by employing this flow system, and sample at ppb levels can be determined correctly and rapidly.

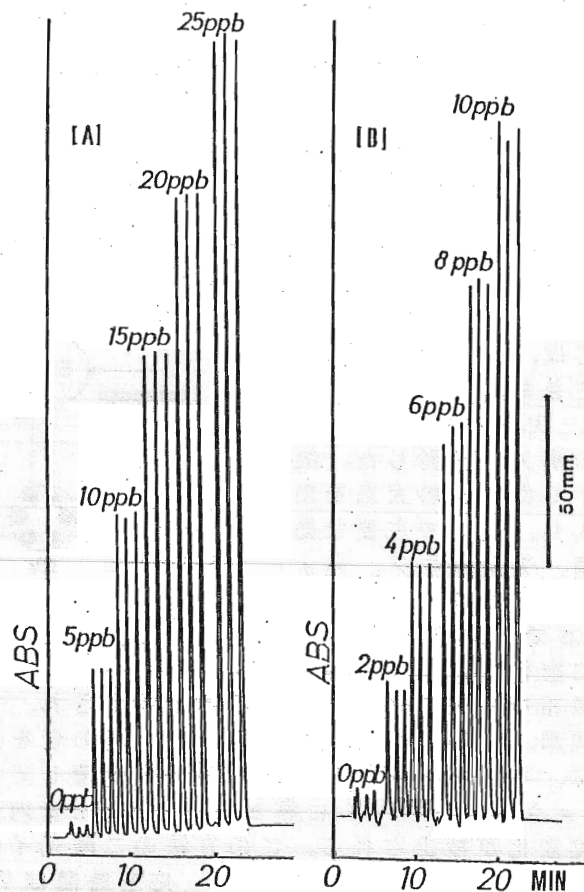


Fig. 3 Calibration graphs of Fe(II) by 1,10-phenanthroline.  
 A: 500 times , B: 1000 times.

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