—Communication—

Flow Injection Analysis of Chloride, Sulfate and Phosphate with a Displacement-Reaction Column

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1 INTRODUCTION

Flow injection analysis (FIA) has been widely used for the automation of chemical analysis. Many workers⁽¹⁾ have adapted a multi-manifold system for the determination of chloride, sulfate and phosphate; there are two or more pumps, flow streams and reaction coils in the system.

In this paper FIA combined with a single-line manifold and a new type of displacement-reaction column is described to analyze these anions; the samples react with the solid reagents in the reaction column according to a precipitation reaction. The apparatus is therefore very simple and the reagents can be easily exchanged. The usable working range of the method was extended to 0.01–3.1M ($M = \text{mol} \cdot \text{dm}^{-3}$) for Cl^- , 7×10^{-5} – 5×10^{-1} M for SO_4^{2-} and 1×10^{-5} – 1×10^{-2} M for PO_4^{3-} .

2 EXPERIMENTAL

The FIA was carried out using a Nihonbunkou HPLC pump (880-PU), a spectrophotometer (870-UV) and an electrochemical detector (840-EC) [working electrode: glassy carbon (0.16 cm^2); reference electrode: SCE; counter electrode: SUS-316] at room temperature. Stainless tubing (0.25mm i.d.) was used for the remainder of manifold. The manifold used is shown in Fig. 1.

Barium chloranilate and lanthanum chloranilate were obtained from Nacalai Tesque and Tokyo Kasei Kogyo, respectively. Hexacyanoferrate(III) was prepared by mixing AgNO_3 and $\text{K}_3[\text{Fe}(\text{CN})_6]$, and washed with water until the supernatant solution is free from silver ion. All other chemicals were of analytical-reagent grade.

A 100–300 mesh mixture of reacting reagents and matrix (cellulose or alumina) was fulfilled

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Fig. 1 Manifold of the FIA system with a displacement-reaction column. C, carrier; P, pump; S, sample injection; RC, reaction column; D, detector; R, recorder; W, waste.

into a HPLC stainless column (35mm x 4.6mm i.d.). The column was washed by carrier solutions for 30 min. Although a useful life-time depends on concentrations of samples, the column could be used for 50 or more injections without any change in response. The reaction efficiency was found to be 90% or more.

3 RESULTS AND DISCUSSION

3.1 Chloride determination

Although most flow injection procedures for Cl^- determination employ $\text{Hg}(\text{SCN})_2$ and $\text{Fe}(\text{III})$ as reactants⁽²⁾, $\text{Ag}_3[\text{Fe}(\text{CN})_6]$ has been investigated as an alternative. Displacement reaction occurs between $\text{Ag}_3[\text{Fe}(\text{CN})_6]$ and Cl^- , the reaction being:

An equivalent amount of $[\text{Fe}(\text{CN})_6]^{3-}$ is liberated, which is determined by electrochemical measurements or by spectrophotometrical ones.

Figure 2 shows an example of both the current (measured at +0.2V) and the absorbance (measured at 436nm) calibration curves for Cl^- determination. Samples as is concentrated were injected into the system without further dilution. In many cases, results for individual samples could be obtained within 40 s after injection. The proposed system could therefore perform routine replicate analyses at a speed of 150 or more samples/h. Well-established calibration graphs could be obtained for 0.1–25w/w% NaCl (0.01–3.1M Cl^-) concentrations. The relative standard deviation for 10 replicate injections of 3% NaCl was

Fig. 2 Calibration curves for NaCl. Carrier, 0.05M $\text{Ca}(\text{NO}_3)_2$; flow rate, 3ml/min; injection volume, 1μl.

ca. 2%. Bromide and iodide ions interfered with the proposed method.

3.2 Sulfate determination

It is well known that solid $\text{Ba}(\text{C}_6\text{Cl}_2\text{O}_4)_3$, when added to SO_4^{2-} solution, precipitates BaSO_4 and releases an equivalent amount of $\text{H}(\text{C}_6\text{Cl}_2\text{O}_4)^-$, which exhibits absorbance maxima in the visible (530 nm) and ultraviolet regions (330 nm)³⁾.

The reaction is dependent on pH. Calibration curves were tested at various pH values using acetic acid (pH 3.27), acetate buffer (pH 4.20), borax buffer (pH 7.66) and boric acid (pH 9.01).

The results are shown in Fig. 3. The sensitivity decreased with increasing pH. Although the highest sensitivity was obtained at pH 3.27, the column life-time was rather short. Hence, 0.02M acetate buffer solution (pH 4.20) was selected as the carrier solution. Changing a flow rate (0.5-2 ml/min) and an injection volume (5-50 μl) revealed that linear calibration curves could be obtained for 3 - 48000ppm (0.03 - 500mM) SO_4^{2-} .

The present method was applied to the determination of SO_4^{2-} in rain waters and in fresh concrete samples. The results obtained by this procedure were in good agreement with those by ion chromatography.

Fig. 3 Calibration curves for sulfate at various pH. Flow rate, 1ml/min; injection volume, 20μl.

3.3 Phosphate determination

$\text{La}_2(\text{C}_6\text{Cl}_2\text{O}_4)_3$ was used as a reaction reagent, the relevant reaction being:⁴⁾

Water-insoluble LaPO_4 is precipitated and the $\text{H}(\text{C}_6\text{Cl}_2\text{O}_4)^-$ liberated is also proportional to the initial amount of PO_4^{3-} in the sample.

A variety of carrier solutions were tested and 1mM ammonium succinate (pH 7) was selected. When the concentration of succinate was high, the solubility of $\text{La}_2(\text{C}_6\text{Cl}_2\text{O}_4)_3$ increased; a poor response was obtained. An example of recorder traces is shown in Fig. 4. It is possible to determine 1 - 300ppm (at 330nm) or 10 - 1000ppm (at 530nm) PO_4^{3-} with an accuracy of $\pm 2\%$ without interference from Cl^- or NO_3^- up to 400 ppm.

Phosphate in cola was determined by both the present method and the conventional molybdenum blue method. The results, expressed in gram per liter, were 1.02 and 0.99, respectively. Agreement between the two methods was excellent.

On the basis of the arguments presented above, the proposed FIA method is rapid and reliable. The principle of this method would have wide applicabilities in determining other anions.

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Fig. 4 Typical recorder traces for a 1-20ppm phosphate. Carrier, 1mM ammonium succinate; flow rate, 1ml/min; injection volume, 100μl.