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Specific and Selective Determination Method for Halide Anions by a Flow Injection Technique[1]

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A flow-injection analysis system is described for the determination of halide (chloride, bromide and iodide) anions. This method could be used as a post column detection method for these anions in water samples. The system is based on the specific and selective reaction between halide anion and fluorescein with an oxidant in an acidic flow. The product is detected at 530 nm in an alkaline flow. The detection limits of the three anions under the conditions tentatively established for the determination of bromide anion were as follows; Cl^-, 1×10^{-8} mol; Br^-, 1×10^{-10} mol; I^-, 1×10^{-10} mol.

Keywords——halide anion; fluorescein; flow-injection analysis; halogenated fluorescein derivative; visible absorption; bromovalerylurea

Specific and selective methods for the determination of trace amounts of halide anions are required in view of the ubiquitous occurrence of these anions in the environment. Among several methods hitherto proposed for the determination of halide anions, ion chromatography[2] which seems to be highly sensitive for many anions has been used for analyses of water samples. However, the method is subject to interference by other coexisting ions since the conductivity monitor used in the method shows no selectivity for halide anions.

Fluorescein, 9-(*o*-carboxyphenyl)-6-hydroxy-3*H*-xanthen-3-one, yields a characteristic colored compound, eosine, on reaction with bromine,[3] and this reaction has been used for sensitive and selective qualitative analysis of bromide anion (Br^-) in the presence of an oxidant. The authors have found that the reaction of fluorescein with chloride (Cl^-) and iodide (I^-) in acidic solution with $KBrO_3$ yields eosine-like compounds having a visible absorption spectrum different from that of fluorescein. Therefore, this reaction was considered to be a promising candidate for the specific and selective detection of halide anions in water samples.

A new analytical system, flow injection analysis (FIA),[4] has been recognized as a simple and convenient method. This system is advantageous as a post column detecting method in high performance liquid chromatography (HPLC). In this paper, we present a specific and selective determination method for halide anions using a flow system applicable as a post column determination system in HPLC.

Experimental

Reagents and Solutions——All chemicals used were of analytical grade. All HNO_3 solutions and NaOH solutions used in the FIA system were prepared at 50% (v/v) of the final concentration of ethanol. Fluorescein–$KBrO_3$ solutions were prepared at use by mixing fluorescein stock solution (0.1 M) and $KBrO_3$ stock solution (0.1 M) at 50% of the final ethanol concentration.

Apparatus and Procedure——Figure 1 shows a schematic diagram of the FIA system used in this study. Three single plunger-type micro-pumps, Seishin PSU-25, were used to obtain continuous flow of the three solutions from

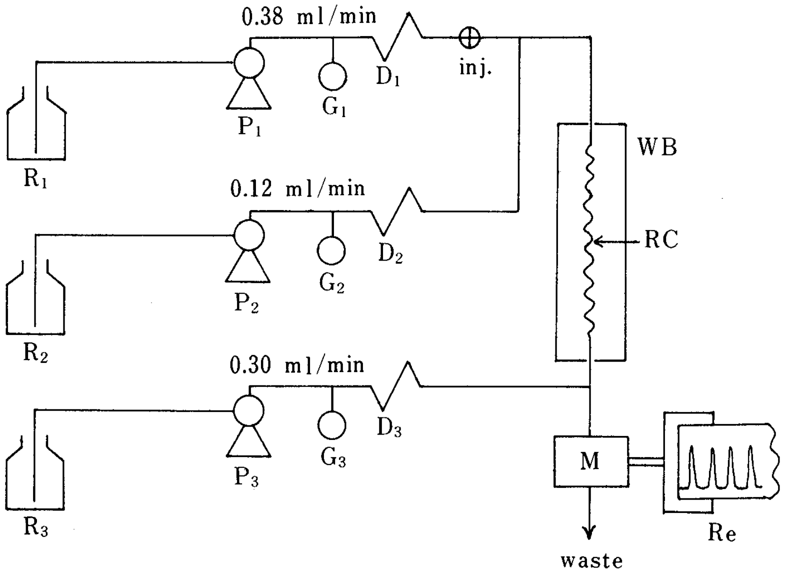

Fig. 1. Schematic Diagram of the FIA System

R_1, reservoir (HNO_3 solution); R_2, reservoir (fluorescein–$KBrO_3$ solution); R_3, reservoir (NaOH solution); P_{1-3}, pump; G_{1-3}, pressure gauge; D_{1-3}, damper coil; inj, injector; RC, reaction coil; WB, water bath; M, monitor; Re, recorder.

reservoirs. The flow rates of HNO_3 solution, fluorescein–$KBrO_3$ solution and NaOH solution were kept at 0.38, 0.12 and 0.30 ml/min, respectively. The sample solution was injected from a Seishin flow-injector with a capacity of 71.8 μl into the stream of fluorescein–$KBrO_3$ solution in coiled PTFE tubing (0.25 mm i.d.). The coil was heated in a thermostated water bath (Yamato BT-21). The absorbance at 530 nm of the reaction mixture was measured with a spectromonitor (Kyowa KLC-800). The other conditions of the FIA system were as described below.

Tentative Conditions for FIA——The concentration of HNO_3 solution was 0.1 M. The concentrations of the two components in the fluorescein–$KBrO_3$ solution were 1×10^{-4} and 1.5×10^{-3} M, respectively. The concentration of NaOH solution was 0.225 M. The residence time in the reaction coil was 1.14 min and the reaction temperature was fixed at 60 °C.

Results and Discussion

Suitable conditions for the determination of Br^- were tentatively selected on the basis of the following experiments. The effect of HNO_3 was examined only by changing the concentration of HNO_3. Figure 2(A) shows that the recorder response (reflecting the formation of the reaction product) decreased when the concentration of HNO_3 was increased above 0.1 M, although an acidic condition was necessary for the reaction to proceed. The concentration of HNO_3 should be kept at 0.1 M in order to obtain the maximum response. The effects of fluorescein concentration and $KBrO_3$ concentration were examined in the same manner as described above. The optimum concentrations of fluorescein and $KBrO_3$ were found to be 1×10^{-4} and 1.5×10^{-3} M, respectively (Fig. 2(B) and Fig. 2(C)).

Finally, the effects of reaction time and reaction temperature were examined in the same way. The formation of the reaction product (expressed as the recorder response) reached the maximum at 60 °C, although the range of optimum reaction time was rather limited to between 1 and 1.6 min (decomposition of the product might occur beyond this time range). The reaction at 40 °C gave less product than that at 60 °C, and required a longer time to reach the maximum (over 2 min, for example). The reaction at 40 °C showed no apparent product decomposition within the experimental time range investigated.

The absorbance at 530 nm of eosine was found to be much larger in alkaline solution ($pH > 8$) than in neutral or acidic solution. Therefore, the effect of NaOH was examined by changing only the concentration of NaOH to obtain the maximum response. The response did

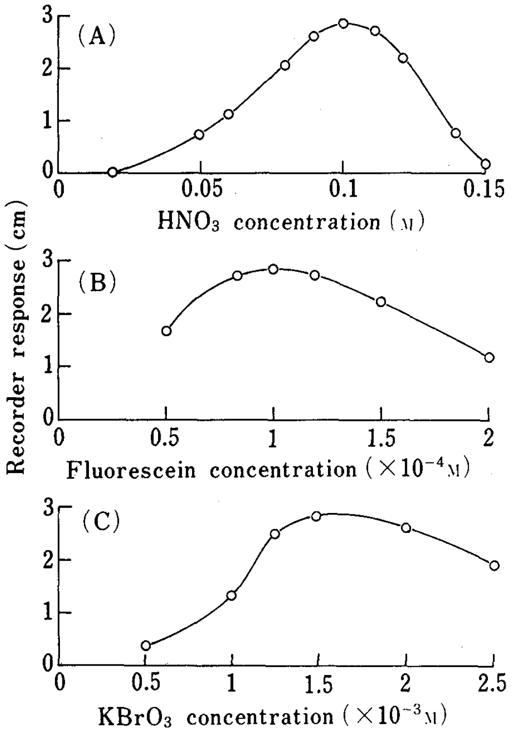

Fig. 2. Effects of Concentrations of HNO_3, Fluorescein and $KBrO_3$ on the Peak Height

The other conditions in each case were the same as described in "Tentative conditions for FIA."

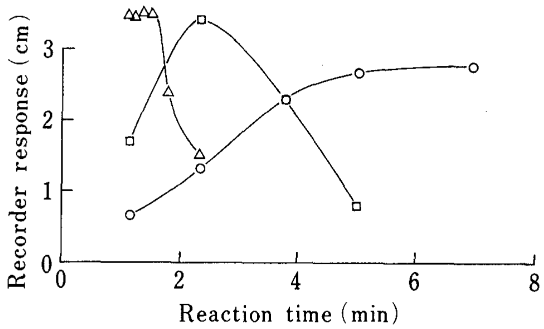

Fig. 3. Effect of Reaction Time at Various Temperatures on the Peak Height

○—○, 40 °C; □—□, 50 °C; △—△, 60 °C.
The other conditions were the same as described in "Tentative conditions for FIA."

not change from 1.75×10^{-1} to 2.75×10^{-1} M, and in our system, 2.25×10^{-1} M NaOH was used.

Calibration curves obtained with standard samples gave linear plots over the following ranges: Cl^-, 0.3×10^{-7}—4.3×10^{-7} mol ($r = 0.9994$); Br^-, 0.3×10^{-9}—5.0×10^{-9} mol ($r = 0.9999$); I^-, 0.3×10^{-9}—5.7×10^{-9} mol. The detection limits of the three ions were as follows; Cl^-, 1×10^{-8} mol; Br^-, 1×10^{-10} mol; I^-, 1×10^{-10} mol. The detection limits of Br^- and I^- by this method are compatible with those of ion chromatography. The response for Cl^- should be improved by modification of the conditions, since the values described here were obtained under the optimum conditions for Br^-.

Using the above reaction as a post column FIA detection system, bromide in bromovalerylurea (a bromine-containing pharmaceutical) was analyzed. Bromovalerylurea (0.1 g) was dissolved in 10 ml of 10% NaOH, and the solution was boiled for 5 min. After cooling to the room temperature, the solution was made up to 100 ml with water.[5] An aliquot of the solution was injected into the system. The analytical results are shown in Table I. The sample A, B and C were preparations of different grades (A was of ultrafine grade). The values of A obtained by this method were very close to the calculated values. The results indicate that this method is accurate and reliable. Samples B and C seemed to contain small amounts of impurities since the values obtained by this method are 2.6—5.8% lower than the calculated values.

The advantages of this method are as follows: (i) the volume of sample required is small (71.8 μl); (ii) the precision and reproducibility of the analytical results are good; (iii) all reagents used are inexpensive and readily available; (iv) a sampling rate of about 15 samples per hour can be achieved easily as the apparatus is based on the principle of continuous flow injection analysis; (v) the reaction is specific and selective to halide anions, so interference by

TABLE I. Analytical Data for the Determination of Br in Bromovalerylurea

Sample (g)		Analysis of Br (%)		Content of $C_6H_{11}BrN_2O_2$ (%)
		Calcd	Found[a]	
A	0.0995	35.8	35.6	99.8±0.4
	0.1041		35.9	
	0.1002		35.7	
B	0.1008	35.8	35.3	97.4±1.6
	0.1008		35.1	
	0.1027		34.2	
C	0.1015	35.8	34.8	94.2±3.1
	0.1008		32.6	
	0.0996		33.7	

a) Average of three determinations.

coexisting substances is minimized; (vi) the separation and determination of Cl^-, Br^- and I^- may be achieved when an anion exchange column is installed just after the sample injector. The determination of Cl^-, Br^- and I^- by HPLC and its application to the analysis of several samples will be reported elsewhere.

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