

## Quantitative Separation of $\text{Cl}^-$ , $\text{Br}^-$ , and $\text{I}^-$ Ions by Anion Exchange Chromatography Equipped with a Reflection Detector

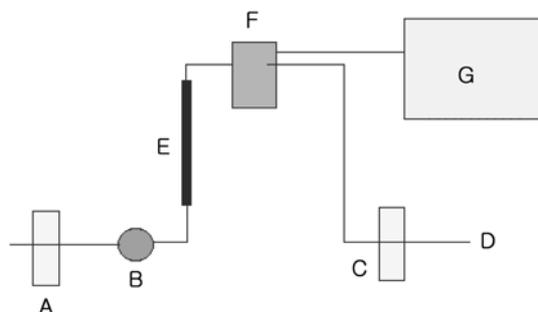
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Precipitation reactions of halide ions ( $\text{Cl}^-$ ,  $\text{Br}^-$  or  $\text{I}^-$  ion) with  $\text{Ag}^+$  ion produce precipitates of characteristic colors -  $\text{AgCl}$  (white),  $\text{AgBr}$  (creamy), and  $\text{AgI}$  (yellow). And such characteristic colors of silver halides can be used to identify the existence of each individual halide ion. However, it has not been easy to identify each constituent ion in solutions of various binary/tertiary mixtures of halide ions. While several methods for the separation and determination of halide ions in aqueous samples using electrochemical,<sup>1-3</sup> optical,<sup>4</sup> and chromatographic,<sup>5-7</sup> and capillary electrophoretic<sup>8</sup> techniques have been reported, they all require sophisticated devices and involve complex procedures. The proposed method presented in this paper involves a rather simple anion exchange chromatography equipped with a reflectance detector and especially shows its ability to achieve quantitative chromatographic separation of  $\text{I}^-$  ion from its mixtures with  $\text{Cl}^-$  and  $\text{Br}^-$  ions.

**Analysis System.** Figure 1 shows a schematic diagram of the anion exchange chromatography equipped with a reflectance detector. The first channel (A) from a HPLC pump (B) carries deionized water (1.0 mL/min) through a sample injection valve (C, Rheodyne 6-port sample injection valve) equipped with a sample loop of 0.50 mL into the anion exchange column (F, Dionex IonPac AS4A-SC). The effluent from the column meets with the stream of the second channel from a peristaltic pump (D, Ismatec MV) carrying 0.10 M  $\text{AgNO}_3$  solution (0.10 mL/min) at the mixing Tee. The precipitation reaction between halide ions in the effluent and  $\text{Ag}^+$  ion in the second stream begins to take place and is

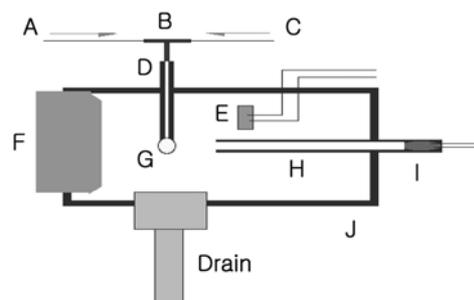


**Figure 1.** Schematic Diagram of Anion Exchange Chromatographic System Equipped With a Reflection Detector. A: channel for deionized water, B: peristaltic pump (0.10 mL/min), C: sample injection valve (Rheodyne), D: HPLC pump (1.0 mL/min), E: channel for 0.10 M  $\text{AgNO}_3$  solution, F: anion exchange column (Dionex), G: windowless optical detection system, H: recorder

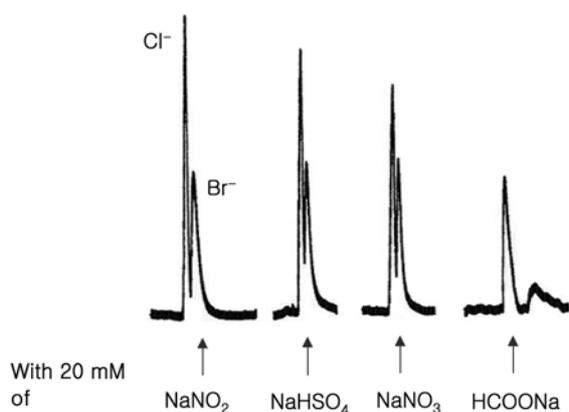
completed while the mixed solution flows through a delay line (Figure 2-B, PTFE tubing of 1 mm i.d., 5 cm in length). Then, the resulting solution containing fine silver halide precipitate particles is introduced into the optical detection system (Figure 2-D, windowless optical cell<sup>9</sup>). And the intensity of reflected light is recorded vs. time at a chart recorder (R).

**Windowless Optical Detection System.** Figure 2 shows the cross sectional view of the windowless optical detection system. The resulting solution containing fine silver halide precipitate particles formed by the reaction between the halide ions in the first stream (A) and  $\text{Ag}^+$  ion from the second stream (C) at the mixing T (B) is introduced through a delay line (D) into the optical detection system (housed in a black PVC compartment (J)). The formation and falling of droplets (E) of the solution occurs continuously at the bottom outlet of the delay line. The light from the radiation source (I, high luminescence blue light emitting diode) guided through a glass tubing (H, 4.5 mm i.d.) is shed over surface of each droplet (G) throughout its lifetime and the intensities of reflected light are measured at the radiation detector (F, a blue sensitive photodiode) placed on the same side with the radiation source. Two black PVC tubes are connected at the bottom of the compartment to be used for drain.

**Proper Eluent and Efficiency.** The eluent should meet a couple of requirements to be considered useful for the current chromatographic analysis. First, the anion of the eluent must exhibit sufficient affinity towards the anion exchanger used in this study. That is, since the selectivity order of the anion exchanger used in this study was ( $\text{I}^- >$

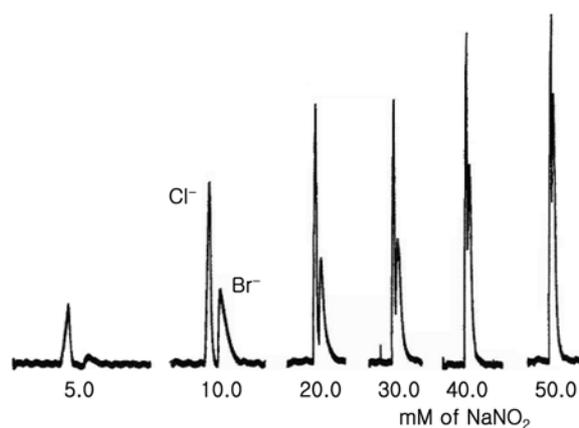


**Figure 2.** Schematic Diagram of a Windowless Optical Detection System. A: the eluent, B: mixing T, C: 0.10 M  $\text{AgNO}_3$  solution, D: delay line, E: black rubber plug, F: photodiode, G: droplet, H: light guiding tube, I: blue light emitting diode, J: black PVC compartment.

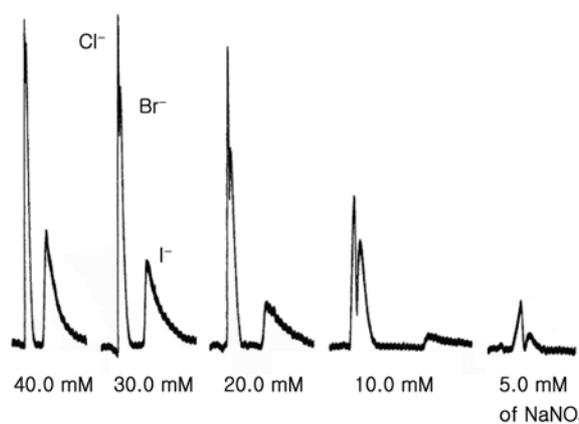


**Figure 3.** Chromatograms (the Intensity of Reflected Light vs. Time) Obtained From Separation of  $\text{Cl}^-$  and  $\text{Br}^-$  Ions in Their Equimolar (3.50 mM) Mixture with Various Eluents.

Phenolate >  $\text{HSO}_4^-$  >  $\text{ClO}_3^-$  >  $\text{NO}_3^-$  >  $\text{Br}^-$  >  $\text{CN}^-$  >  $\text{HSO}_3^-$  >  $\text{NO}_2^-$  >  $\text{Cl}^-$  >  $\text{HCO}_3^-$  >  $\text{IO}_3^-$  >  $\text{HCOO}^-$  >  $\text{Ac}^-$  >  $\text{OH}^-$  >  $\text{F}^-$ ), the eluent should contain an anion of relatively strong binding power towards the anion exchanger to effectively elute the most strongly binding  $\text{I}^-$  ion. The well-known and widely used ion chromatographic analysis using a bicarbonate/carbonate buffer as an eluent has not been applied for the separation and identification of  $\text{I}^-$  ion due to its high affinity towards the anion exchanger. Secondly, the anion of the eluent should not react with  $\text{Ag}^+$  ion so that the baseline of the chromatogram could be maintained at a minimum level of its magnitude. Based on the selectivity series of the anion exchanger and the two requirements discussed above, solutions of  $\text{KNO}_3$ ,  $\text{NaHSO}_4$ ,  $\text{NaNO}_2$ , and  $\text{HCOONa}$  were selected as tentative eluents and tested for eligibility. Figure 3 shows chromatograms (the intensity of reflected light vs. time) obtained by using 20.0 mM solutions of  $\text{KNO}_3$ ,  $\text{NaHSO}_4$ ,  $\text{NaNO}_2$ , and  $\text{HCOONa}$  as eluents and the sample solution containing an equimolar (3.5 mM) mixture of  $\text{Cl}^-$  and  $\text{Br}^-$  ions. According to chromatograms in Figure 3,  $\text{NaNO}_2$  solution was chosen as the most desirable eluent for its ability to produce the best efficiency and signals of the highest magnitudes. Figure 4 shows chromatograms obtained with 5.0, 10.0, 20.0, 30.0, 40.0, and 50.0 mM  $\text{NaNO}_2$  solutions as eluents for solution of an equimolar (3.5 mM) mixture of  $\text{Cl}^-$  and  $\text{Br}^-$  ions. And Figure 4 indicated that increasing the concentration of  $\text{NaNO}_2$  solutions would enhance the sensitivity of analysis while it would cause a lower efficiency of the separation. Therefore based on chromatograms shown in Figure 4, a compromise was made to select 20.0 mM for  $\text{NaNO}_2$  solution for the most desirable one for quantitative identification of  $\text{Cl}^-$  and  $\text{Br}^-$  ions of concentrations at current millimolar level in their mixtures. Figure 5 shows chromatograms obtained with 5.0, 10.0, 20.0, 30.0, and 40.0 mM  $\text{NaNO}_2$  solutions as eluents for solution of an equimolar (5.0 mM) mixture of  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  ions. According to Figure 4, the proper concentration of  $\text{NaNO}_2$  to achieve a baseline separation between  $\text{I}^-$  ion and the other halide ions ( $\text{Cl}^-$  and  $\text{Br}^-$ ) was to be 40 mM due to a very strong affinity of  $\text{I}^-$  ion towards the anion exchanger.



**Figure 4.** Chromatograms (the Intensity of Reflected Light vs. Time) Obtained From Separation of  $\text{Cl}^-$  and  $\text{Br}^-$  ions with Various Concentrations of  $\text{NaNO}_2$ .



**Figure 5.** Chromatograms (the Intensity of Reflected Light vs. Time) Obtained by Varying the Concentration of  $\text{NaNO}_2$  for an Equimolar (5.0 mM) Mixture of  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  Ions.

In summary, even though the proposed method require further works covering other concentration ranges of halide ions, the proposed method, as a simple anion exchange chromatographic system utilizing a windowless optical system as a detector which could separate and identify  $\text{I}^-$  ion from its mixtures with other halide ions, was proven a quite feasible one for quantitative identification of  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  ions from their various mixtures.

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