Note

Effect of eluent impurities and sample matrix on quantitative analysis by ion chromatography

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Conventional liquid chromatography is an impulse method[1] in terms of the mode of sample injection, *i.e.*, eluent is allowed to flow continuously, sample is injected into the flow as a pulse and a chromatogram is obtained. Conversely, when sample is allowed to flow continuously as in gas chromatography[1], and gas without a sample constituent is injected into the flow as a pulse, negative chromatography, *i.e.*, "vacancy chromatography"[2] is obtained. If the unknown sample is allowed to flow continuously and a reference sample is injected as a pulse, then if there are some differences in the constituent or its concentration between those two samples, positive and/or negative peaks can be observed. If there is no difference between the samples, no peak will appear on the chromatogram. This method is effective in recognizing clearly the difference between a standard and an unknown sample in which the latter contains constituents very close to those in standard sample. Gel permeation chromatography[2,3] for example, allows the detection of differences as small as 1% in the molecular weights of the components and it is useful for process control.

In ion chromatography, Okada and Kuwamoto[4] added various ions to the eluent in the process of examining the formation mechanism of a "dip peak", and concluded that "absent peaks" of those ions are one of the causes. However they suggested that the vacancy chromatogram, which is a mirror image of the normal chromatogram, is difficult to obtain because of the slow "transfer rate" of divalent ions such as sulphate.

It has been found that when an eluent mixed with sample is allowed to flow in a column continuously, and solution that contains no sample constituent is injected through the sample injection port as a pulse, a "vacancy chromatogram" can be obtained[5,6]. Also, the peak height or area depends closely on the amount and type of the solution to be injected. This means, in conventional ion chromatography, that if the component to be measured is present in the eluent as an impurity, a negative error corresponding to the vacant peak would appear, and its size would depend on the quality of the sample, *i.e.*, the concentration of the matrix in the sample.

In this paper, the effect of impurities in the eluent and of the matrix concentration in the sample on the accuracy of quantitative analysis is discussed.

EXPERIMENTAL

Apparatus

A conventional non-suppressed type of ion chromatograph consisting of a Hitachi Model L-6200 pump, a 2720IC packed column (cation-exchange resin, particle size 10 μm, capacity 0.01 mequiv./ml; 50 mm × 4 mm I.D.), an L-3700 conductivity detector, a 655A-52 column oven and a Rheodyne Model 7125 sample injector was used. The conductivity cell, with the column, was placed in the column oven. The temperature was set at 40°C.

Reagents

In order to separate alkaline earth metal ions, 0.5 mM tartaric acid–0.5 mM ethylenediamine solution (pH 4.8) with and without 1 ppm each of the alkaline earth metal ions, and to separate alkali metal ions, 1.6 mM nitric acid solution with 2 ppm each of the alkali metal ions, were used as eluents. The other reagents were commercially available guaranteed-reagent grade materials.

RESULTS AND DISCUSSION

Ion chromatography was performed on various standard sample solutions containing 1 ppm each of magnesium, calcium, strontium and barium. Fig. 1 shows chromatograms of the samples prepared by dissolving these alkaline earths in 0.5–20 mM tartaric acid–ethylenediamine (matrix) solutions for which the composition ratio was the same as that of the solute in the eluent. In Fig. 1, 0.5 mM means that the chromatogram of a sample of 1 ppm alkaline earth metal ions–0.5 mM tartaric acid–0.5 mM ethylenediamine solution is shown. The peak height of calcium ion decreases considerably with increasing matrix concentration, and at 5 mM, it is a negative peak. When the concentration reaches 20 mM, the peak becomes very broad and the peaks of magnesium and strontium cannot be distinguished.

The peak areas in these chromatograms are plotted in Fig. 2. It seems that the quantitative value at zero matrix concentration is the correct one and the other values
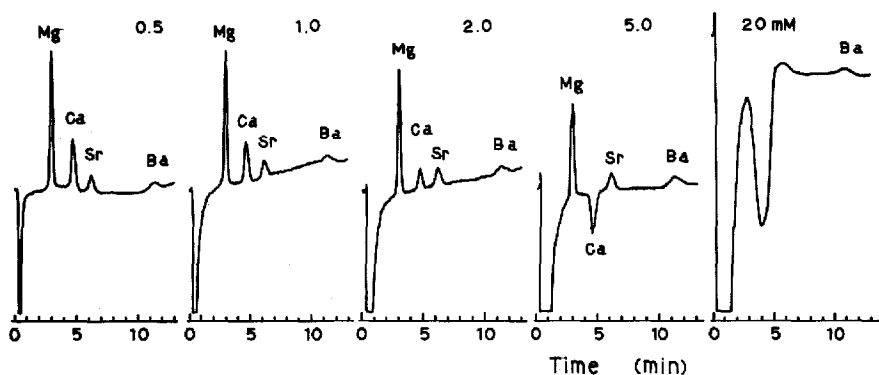

Fig. 1. Chromatograms of standard solutions. Samples, 1 ppm Mg, Ca, Sr, Ba–x mM tartaric acid–x mM ethylenediamine, 20 μl; column, Hitachi 2720IC packed column, 50 mm × 4 mm I.D., 40°C; eluent, 0.5 mM tartaric acid–0.5 mM ethylenediamine; flow-rate, 1.0 ml/min; detector, conductivity.
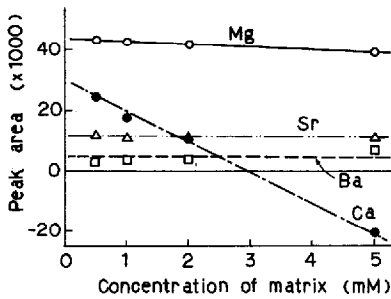
Fig. 2. Effect of sample matrix concentration on peak area for conditions as in Fig. 1.

contain negative errors. It is considered that a negative error that becomes larger with increasing matrix concentration is caused by a vacant peak, based on impurities such as magnesium and calcium in the eluent. The concentration of the impurities was measured using atomic absorption spectrometry. The eluent that remained in the vessel used before the eluent was transferred into the eluent container contained 16 ppb of calcium.

The chromatograms of the standard sample solutions using an eluent that contained 1 ppm each of alkaline earth metal ions were also obtained. The standard sample solutions which were 1 ppm (2 ppm in pure water) solutions of alkaline earth metal ions were injected in 20-μl volumes. Some of the chromatograms obtained are shown in Fig. 3. Only the standard sample dissolved in pure water gives a normal chromatogram, and when the matrix concentration is 0.5 mM, which is the same as the eluent, peaks of the sample constituents do not appear at all, and at higher concentrations negative, vacant peaks appear. This behaviour is shown in Fig. 4. The
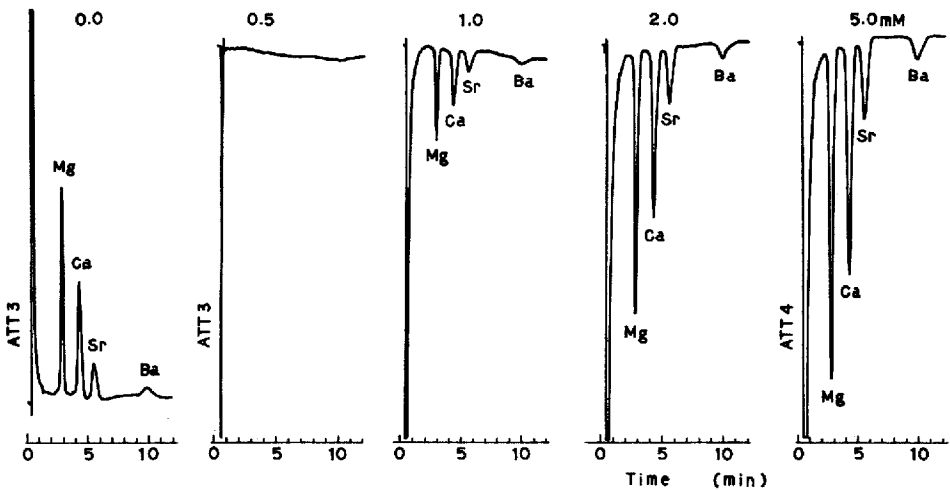

Fig. 3. Sample matrix concentration and chromatographic response profiles. Samples, 2 ppm Mg, Ca, Sr, Ba–water and 1 ppm Mg, Ca, Sr, Ba–x mM tartaric acid–x mM ethylenediamine, 20 μl; eluent, 1 ppm Mg, Ca, Sr, Ba–0.5 mM tartaric acid–0.5 mM ethylenediamine. Other conditions as in Fig. 1.
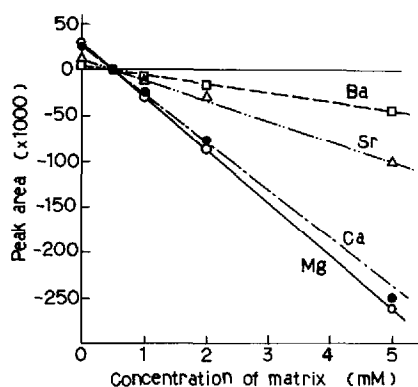
Fig. 4. Effect of sample matrix concentration on peak area for conditions as in Fig. 3.

relationship between matrix concentration and peak area is almost linear, but contamination by calcium is easy and there are large fluctuations of the data.

Samples that contained only matrix and no alkaline earths were injected. The results are shown in Fig. 5, with the vacant peak area plotted against matrix concentration, the same as above. Good linearity is found up to a matrix concentration of 20 mM. Typical chromatograms are shown in Fig. 6. When only water was injected, positive peaks corresponding to 0.02 ppm of magnesium and 0.1 ppm of calcium are detected. The cause is thought to be additional adsorption of alkaline earth metal ions in the eluent on the column owing to the change in equilibrium on dilution of the eluent.

Because the slopes of the lines in Figs. 4 and 5 are almost the same, and the relationship between concentration of impurity in the eluent and vacant peak area of the impurity is linear[5], the slope should indicate the amount of the impurity present in the eluent. Incidentally, the concentrations of magnesium and calcium in the eluent, as obtained from the slopes of the lines in Fig. 2, are 0.016 and 0.19 ppm, respectively. The
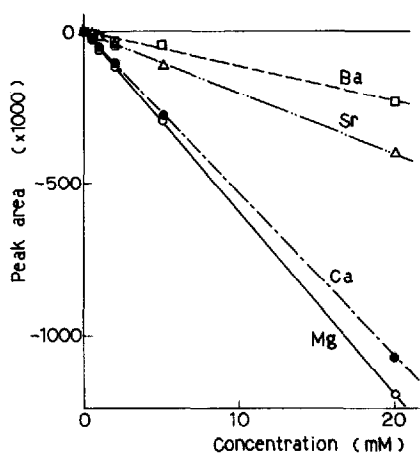

Fig. 5. Effect of sample matrix concentration on peak area for water and x mM tartaric acid–x mM ethylenediamine (no alkaline earth metal ions) as samples and other conditions as in Fig. 3.
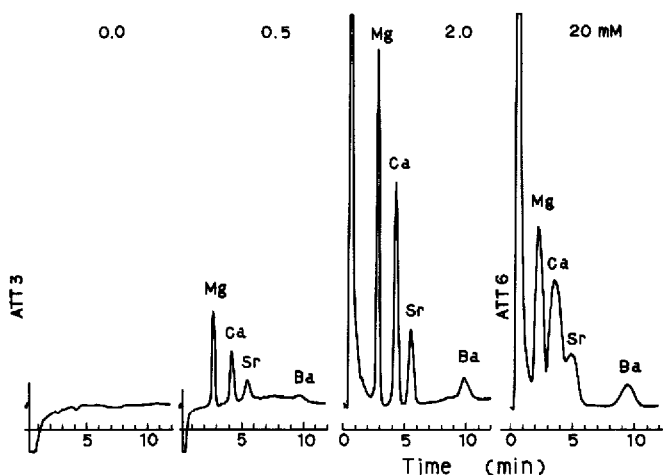
Fig. 6. Example of vacancy chromatograms. Conditions as in Fig. 5.

calcium value is about ten times higher than the initial one. This suggests that contamination arises from the chromatographic process.

The same phenomena were observed for the separation of alkali metal ions. In this instance 1.6 mM nitric acid with 2 ppm each of alkali metal ions was used as the eluent and 2 ppm each of alkali metal ions in hydrochloric acid of different concentrations as the samples. The results are shown in Fig. 7 as peak area $vs.$ concentration of hydrochloric acid (sample matrix). Positive peaks were observed when the concentration of hydrochloric acid in the sample was less than 1.6 mM and negative (vacant) peaks at concentrations above 1.6 mM.

The impulse chromatographic response, R_t, is given by the equation[1]

$$R_t = R_0 + \sum_j \frac{C_j}{\sqrt{2\pi}\sigma_j} \cdot \exp\left[-\frac{(t - t_{R_j})^2}{\sigma_j^2} \right] \tag{1}$$
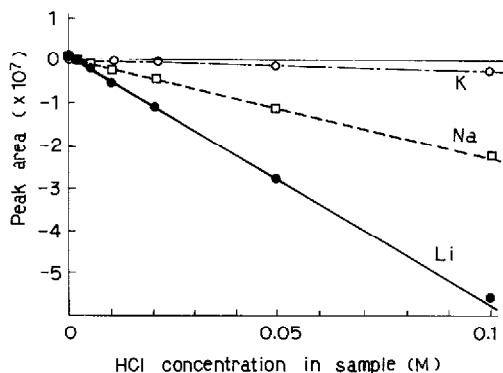

Fig. 7. Effect of hydrochloric acid concentration on vacant peak area. Sample, 2 ppm alkali metal ions–x mM hydrochloric acid, 20 μl; column, cation-exchange resin of $ca.$ 20 μequiv./ml, 50 mm × 4 mm I.D., 40°C; eluent, 1.6 mM nitric acid–2 ppm alkali metal ions; flow-rate, 1.5 ml/min; detector, conductivity.

where R_0 is the baseline response (steady-state value), σ is the peak standard deviation, t is time and t_{R_j} is the retention time of component j. The concentration can be expressed as

$$C_j = K(C_{js} - \alpha C_{je}) \qquad (2)$$

where K is a constant, C_{js} is the concentration of component j in the sample solution and C_{je} that in the eluent. When the matrix of the sample is the same as that of the eluent, $\alpha = 1$. Fig. 4 shows that if the sample matrix composition ratio is the same as the eluent but only its concentration is different, α will be equal to C_{e_0}/C_{s_0}, where C_{e_0} is the eluent concentration and C_{s_0} is the matrix concentration in the sample. In the other case, where the sample matrix component is different from the eluent, as shown in Fig. 7, α depends on the affinity of the sample matrix component to the column packing material. When C_j is positive a positive peak, when C_j is zero no peak and when C_j is negative a vacant peak are observed on the chromatogram.

It appears that the negative error might be attributed the fact that the impurities in the eluent enriched on the resin in a separation column are partially eluted at the front owing to the equilibrium between the concentration of the impurities in the resin in the column and that of the constituents in the matrix of the sample. The constituents of the sample were partially readsorbed on the resin in the equilibria between the resin and the eluent. Therefore, the concentration of constituents in the sample decreases and causes large negative errors in quantitative analysis. This negative error can be eliminated by complete removal of the impurities from the eluent and avoiding contamination.

Removal of the sample matrix component is also effective, as reported for the determination of alkali metal ions in hydrochloric acid, where the chloride ion as matrix was removed by using silver carbonate[7].

CONCLUSION

In ion chromatography, when components to be analysed are present in the eluent as impurities, the quantitative analytical results include a small positive error or a large negative error depending on the concentration of the sample matrix. Because the positive error does not exceed the concentration of the impurities in the eluent, the error may sometimes be negligible. The negative error, however, in an analytical system using an ion-exchange resin of very low ion-exchange capacity and a dilute eluent could reach more than 100 times the concentration of the impurity in the eluent. This problem is especially serious when using a resin of extremely low capacity, a low concentration of eluent and a high concentration of sample matrix. The solution is to improve the purification of the eluent. In some instances, it is effective to remove matrix components from the sample. Some instances in which a negative peak appears unexpectedly might be treated by assuming the appearance of this vacant peak.

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