Simultaneous Spectrophotometric Determination of Aluminum(III), Iron(III) and Beryllium(III) in Rainwater by a Matrix Method

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A rapid and accurate method for the simultaneous determination of aluminum(III), iron(III) and beryllium(III) is proposed. The method can be applied to the determination of aluminum(III), iron(III) and beryllium(III) in rainwater without any preliminary separation. The determinations are performed by a CPA matrix method with spectrophotometric detection using Chromazurol S. The results obtained in analyses of rainwater samples are reported in order to demonstrate the effectiveness of the proposed method.

Keywords Simultaneous determination, spectrophotometry, CPA matrix method, aluminum determination, iron determination, beryllium determination, water analysis

During these days of concern over environmental pollution, there has been an increasing need for a simple, rapid and precise method for determining low parts per billion (ppb) of aluminum(III), iron(III) and beryllium(III).

Many methods have been proposed for separate determinations of aluminum, iron and beryllium. Colorimetric and atomic emission or absorption methods are most commonly used. Although all of these methods are rapid and suitable, colorimetric methods are generally preferred, since they involve less expensive instrumentation and afford greater sensitivity when appropriate chromogenic reagents are employed. Numerous chromogenic reagents have been recommended for the determination of aluminum\(^1\),\(^2\), iron\(^3\),\(^4\) and beryllium\(^5\),\(^6\) individually; few of these are practical for the simultaneous determination of aluminum(III), iron(III) and beryllium(III).

In this paper we propose a new method for the simultaneous spectrophotometric determination of aluminum(III), iron(III) and beryllium(III) based on the CPA matrix method, and by using Chromazurol S as a color-developing agent and hexadecyltrimethylammonium bromide as a solubilizing agent. Details and characteristics of the new method are described. The analytical wavelengths and the various parameters which affect the simultaneous determination of aluminum(III), iron(III) and beryllium(III) were investigated. This method is simple, rapid and sensitive, and applicable to the simultaneous determination of ppb levels of aluminum(III), iron(III) and beryllium(III) in rainwater.

Theory

Spectrophotometric quantitative analysis is based on the Beer–Lambert law,

\[ A = abc, \]

where \( A \) is the absorbance, \( a \) the absorptivity, \( b \) the optical pathlength, and \( c \) the concentration.

For a multicomponent system, Brown et al.\(^7\) modified the Beer–Lambert law to

\[
\begin{bmatrix}
C_1 & C_1^* & \ldots & C_1^n \\
C_2 & C_2^* & \ldots & C_2^n \\
\vdots & \vdots & \ddots & \vdots \\
C_n & C_n^* & \ldots & C_n^n
\end{bmatrix}
\begin{bmatrix}
P_{11} & P_{12} & \ldots & P_{1n} & P_{10} \\
P_{21} & P_{22} & \ldots & P_{2n} & P_{20} \\
\vdots & \vdots & \ddots & \vdots & \vdots \\
P_{n1} & P_{n2} & \ldots & P_{nn} & P_{n0}
\end{bmatrix}
= \begin{bmatrix}
A_1' & A_1'' & \ldots & A_1^n \\
A_2' & A_2'' & \ldots & A_2^n \\
\vdots & \vdots & \ddots & \vdots \\
A_n' & A_n'' & \ldots & A_n^n \\
1 & 1 & \ldots & 1
\end{bmatrix}
\]

or

\[ \mathbf{C} = \mathbf{P} \mathbf{A}, \]

where \( \mathbf{C} \) is the matrix of the component concentrations in standard mixtures and \( \mathbf{A} \) is the absorbance matrix of standard mixtures; the \( \mathbf{P} \) matrix represents the proportionality between \( \mathbf{C} \) and \( \mathbf{A} \) and the last column of the \( \mathbf{P} \) matrix allows for a nonzero intercept; the \( \mathbf{A} \) matrix is augmented by the last row of 1's. We can solve for \( \mathbf{P} \) with the usual least-squares approach:
\[ P = C A (A A^T)^{-1} \]  
(4)

where, in this case, the sum of the squares of the differences between the observed and calculated concentrations has been minimized. The \( P \) matrix can be used directly to obtain the concentrations of unknown samples from the measured absorbances by the equation

\[ C = PA. \]  
(5)

**Experimental**

**Reagents**

All of the reagents were of analytical-reagent grade, and solutions were prepared with deionized water.

- Chromazurol S (CAS) solution, 0.1%.
- Hexadecyltrimethylammonium bromide (CTMAB), 0.1%.
- pH 6 potassium dihydrogenphosphate-sodium hydroxide buffer solution.

An aluminum(III) stock solution (1 mg/ml) was prepared from potassium aluminum sulfate, an iron(III) stock solution (1 mg/ml) from ferric nitrate, and a beryllium(III) stock solution (1 mg/ml) from beryllium sulfate. The standard solutions of aluminum(III), iron(III) and beryllium(III) were freshly prepared by diluting these stock solutions before each use.

**Apparatus**

A Model 721-100 spectrophotometer was used for the absorbance and spectral measurements. A Model ZD-2 pH meter with a saturated calomel-glass electrode system was used for pH measurements. A Sharp Model PC-1500 pocket computer was used for data treatment.

**Procedure**

Filter the rainwater sample through a sheet of Model 202 quantitative filter paper (medium filtration rate) in order to remove any turbidity. Pipet 5.00 ml of the sample into a 25-ml volumetric flask; then add 4 ml of a 0.1% CAS solution, 4 ml of a 0.1% CTMAB solution, 5 ml of a pH 6 buffer solution; finally, dilute to 25 ml with deionized water. Transfer the contents of the volumetric flask to a 1-cm cell and measure the absorbances at 590, 598, 618, 620 and 624 nm against a reagent blank, respectively. Treat the data and give the aluminum(III), iron(III) and beryllium(III) concentrations in the rainwater sample using the PC-1500 computer.

**Results and Discussion**

**Absorption spectra**

As shown in Fig. 1, the Al(III)-CAS-CTMAB, Fe(III)-CAS-CTMAB, Be(III)-CAS-CTMAB complexes and their mixture exhibit absorption maxima at 617, 640, 615 and 624 nm, respectively.

The most important parameter in the simultaneous determination of aluminum(III), iron(III) and beryllium(III) in mixtures by this method is the selection of the optimum wavelengths. According to the selection principle of analytical wavelengths proposed by Wang et al., 590, 598, 618, 620 and 624 nm were selected as analytical wavelengths in the work reported here.

**Effect of the pH**

The effect of the pH on the absorbance was investigated. As shown in Fig. 2, the optimum pH is completely identical for each ion and their mixture. Since

![Fig. 1 Absorption spectra. 1, Fe(III)-CAS-CTMAB complex (Fe(III) 0.16 µg/ml); 2, Al(III)-CAS-CTMAB complex (Al(III) 0.16 µg/ml); 3, Be(III)-CAS-CTMAB complex (Be(III) 0.08 µg/ml); 4, the ternary mixture (Al(III) 0.08+Fe(III) 0.16+Be(III) 0.08 µg/ml).](image)

![Fig. 2 Effect of pH. 1, Be(III)-CAS-CTMAB complex (Be(III) 0.08 µg/ml, \( \lambda = 615 \) nm); 2, Fe(III)-CAS-CTMAB complex (Fe(III) 0.16 µg/ml, \( \lambda = 640 \) nm); 3, Al(III)-CAS-CTMAB complex (Al(III) 0.16 µg/ml, \( \lambda = 617 \) nm); 4, the ternary mixture (Al(Ill) 0.08+Fe(III) 0.16+Be(III) 0.08 µg/ml, \( \lambda = 624 \) nm).](image)
the maximum absorbance was obtained at pH 6, subsequent determinations were performed at pH 6.

**Effect of the CAS amount**

The effect of the CAS amount on the absorbance for a mixture of aluminum(III), iron(III) and beryllium(III) was examined by varying the volume of 0.1% CAS while the other variables were held constant. As shown in Fig. 3, the absorbance is maximum and constant when the 0.1% CAS added to the mixture is in the volume range of 3–5 ml. In this work, 4 ml of 0.1% CAS solution was used.

**Effect of the CTMAB amount**

The effect of the CTMAB amount on the absorbance for a mixture of aluminum(III), iron(III) and beryllium(III) was examined. As shown in Fig. 4, the maximum, constant absorbance is obtained when the 0.1% CTMAB added to the mixture is in the volume range 3–5 ml. In this work, 4 ml of a 0.1% CTMAB solution was used.

**Effect of the reagent addition order**

The effect of the reagent addition order on the absorbance for a mixture of aluminum(III), iron(III) and beryllium(III) was investigated. As shown in Table 1, the optimum order of the reagent addition is No. 1.

**Developing time and color stability**

The developing reaction is completed immediately after a mixture of aluminum(III), iron(III) and beryllium(III) is mixed with CAS and CTMAB solutions, and the absorbance remains unchanged for thirty minutes.

**Effect of foreign ions**

The effect of foreign ions on the simultaneous determination of 70 ppb aluminum(III), 40 ppb iron(III) and 10 ppb beryllium(III) in mixtures was investigated. The experimental results show that 20 ppb hypochlorite, 38.4 ppb copper(II) and 30 ppm carbonate do not interfere.

**Standardization of the P matrix**

Six standard mixtures with different concentration ratios of Al(III):Fe(III):Be(III) were prepared. After development under the optimum conditions, the absorbances were measured at the selected analytical wavelengths. The measured absorbances were used to form the "known" absorbance matrix. This matrix and the corresponding matrix of concentrations were used to determine the P matrix by Eq. (4). The P matrix is as follows:

\[
P = \begin{bmatrix}
-86.82 & -144.93 & 115.92 & 295.65 & -22.43 & -11.50 \\
-163.32 & -324.00 & 147.26 & 317.23 & 57.00 & -7.94 \\
113.88 & 197.81 & -87.04 & -139.39 & -33.78 & 6.76
\end{bmatrix}
\]

**Analysis of rainwater**

The proposed method was used for a simultaneous determination of aluminum(II), iron(III) and beryllium(III) in rainwater samples (collected 18 April, 13 and 29 May, 1990, at Liaohua, China). The results obtained are shown in Table 2.

To investigate the applicability of this method to the simultaneous determination of aluminum(III), iron(III) and beryllium(III) in rainwater, recoveries of known
amounts of aluminum(III), iron(III) and beryllium(III) added to rainwater samples were examined by the above procedure. Table 3 presents the recovery results of aluminum(III), iron(III) and beryllium(III).

The recovery results indicate that this analytical method can be successfully applied to the simultaneous determination of the ppb levels of aluminum(III), iron(III) and beryllium(III) in rainwater.

The proposed method allows for the simultaneous spectrophotometric determination of aluminum(III), iron(III) and beryllium(III) using the CPA matrix method. The method is simple, rapid, sensitive, accurate and uses less sample and reagent. The validity of the method was demonstrated by simultaneously determining these parameters in rainwater.

Table 2 Determination of aluminum(III), iron(III) and beryllium(III) in rainwater by the proposed method

<table>
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<tr>
<th>Sample No.</th>
<th>Concentration, ppb</th>
<th>RSD, %</th>
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<tbody>
<tr>
<td></td>
<td>Determined</td>
<td>Mean</td>
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<tr>
<td>RW-1</td>
<td>Al 43.4, 43.4, 43.1, 24.5, 39.1, 140.5</td>
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<td>Fe 19.4, 19.6, 18.6, 18.0, 16.5, 18.2</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>Be 10.2, 10.0, 10.8, 10.4, 10.3, 4.54</td>
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<tr>
<td>RW-2</td>
<td>Al 53.4, 53.7, 52.7, 54.0, 54.2</td>
<td>53.6</td>
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<tr>
<td></td>
<td>Fe 28.9, 29.1, 28.1, 28.8, 30.1</td>
<td>29.0</td>
</tr>
<tr>
<td></td>
<td>Be 7.2, 6.9, 7.5, 7.1, 6.3</td>
<td>7.0</td>
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<tr>
<td>RW-3</td>
<td>Al 41.6, 41.7, 41.2, 41.3, 41.5, 41.3</td>
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<td>Fe 27.0, 26.9, 26.4, 27.0, 26.8, 27.0</td>
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<tr>
<td></td>
<td>Be 3.0, 3.1, 3.3, 3.0, 2.9</td>
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</table>

Table 3 Recovery of aluminum(III), iron(III) and beryllium(III) added to rainwater

<table>
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<th>Parameter determined</th>
<th>Concentration, ppb</th>
<th>Recovery, %</th>
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<td>48.0</td>
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<td></td>
<td>3.8 22.8</td>
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<td>6.0 24.8</td>
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References


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