Spectrophotometric Determination of Trace Amounts of Beryllium Using 1,8-Dihydroxyanthrone as a New Chromogenic Reagent

A. Beiraghi* and S. Babaee

Faculty of Chemistry, Tarbiat Moallem University, Mofatteh Ave., No.49, P.O. Box 15614, Tehran, Iran

A simple, rapid, and sensitive spectrophotometric method for the trace level determination of beryllium based on the formation of a 1:2 complex with anthralin (1,8-dihydroxyanthrone) as a new reagent is developed. A spectrophotometric method was used to determine the acidity constant and stepwise proton dissociation of the reagent. The experimental conditions for determining beryllium including the influences of pH, reagent concentration and time were evaluated and optimized. Under the optimum experimental conditions, the molar absorptivity of the complex is 0.47×10^4 l mol^{-1} cm^{-1} at 545 nm. Calibration graph was linear in the range of 0.04-1.04 µg ml^{-1} with a detection limit of 0.012 µg ml^{-1} and a %RSD of 0.43%, for 5 replicate determinations at 0.48 µg ml^{-1} of Be(II). The interferring effect of some cations and anions was also studied. The method was applied for the determination of beryllium in beryl, silicate rock and alloys. Ethylenediaminetetraacetic acid (EDTA) was used for masking interfering ions.

INTRODUCTION

Beryllium metal and its compounds are widely involved in present day technologies [1]. This element is a highly toxic metal and its toxicity is well documented in the literature [2]. The toxicity mechanism of Be involves the destruction of cellular membrane and decrease in enzyme activity. Also, Be is carcinogenic [3]. Over recent years numerous analytical techniques have been employed to detect Be(II) in different samples. These include spectrophotometric methods [4-7], spectrofluorimetric methods [8,9], flame atomic absorption spectroscopy (FAAS) [10], electrothermal atomic absorption spectroscopy (ET-AAS) [11-13], inductively coupled plasma atomic emission spectroscopy (ICP-AES) [14] and several other techniques [15-18]. In contrast to the majority of these

expensive and sophisticated analysis systems, spectrophotometric methods have been favored by analytical chemists due to their high sensitivity, moderate to high selectivity, good accuracy (RSD in the range of 0.1 to 3%) and convenience.

Triphenylmethanes [19] and azo reagents [20] are used in most spectrophotometric methods of beryllium analysis. Be(II) is selectively unreactive towards ethylenediaminetetraacetic acid (EDTA) and, therefore, in spectrophotometric determination of Be(II). However, it can be used as a masking agent for various metal ions [4-7,19-21].

Anthralin (1,8-dihydroxyanthrone) is a yellow amorphous solid which is readily soluble in water at alkaline pH [22]. According to the best of our knowledge, this reagent has not been reported in the literature as being used for any cation determinination. In this study, for the first time, we wish to report this reagent as a selective reagent in spectrophotometric

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*Corresponding author. E-mail: Beiraghi@Saba.tmu.ac.ir

determination of micro amounts of beryllium in different real samples.
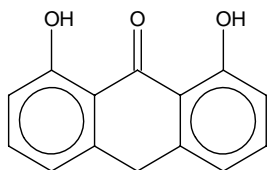
Anthralin

EXPERIMENTAL

Apparatus

All absorbance measurements were performed with a Milton Roy model 1201 single beam UV-Vis spectrophotometer connected to an IBM PCS-486 computer with Spectro software to convert absorbance data to ASCII format. A quartz cell of 1.0 cm was used for all spectrophotometric measurements. All spectral measurements were carried out using a blank solution as a reference. The pH measurements were taken by Metller E603 pH meter using a combined glass-calomel electrode.

Reagents

All the reagents employed were of analytical grade and the solutions were prepared with triply-distilled water. HPLC grade methanol (Caledon) and oxalic acid from Fluka were used. Anthralin from Sigma was used as received. Lithium hydroxide and succinic acid (Merck) were used without further purification, except for vacuum drying over P_2O_5 for 72 h, for the preparation of succinate buffer solution. Oxalate and succinate buffers were prepared according to the methods explained in the literature [23]. Standard solutions of beryllium were prepared by serial dilution of a 1000 μg ml^{-1} standard solution (Shimadzu pure chemical co. Ltd.) with distilled water. A stock solution of anthralin (3.0×10^{-3} M) was prepared by dissolving 68 mg anthralin in 10 ml NaOH (0.2 M) and diluted to the mark with distilled water in a volumetric flask (100 ml). A buffer of pH 11.3 was prepared from boric acid, potassium chloride and 0.2 M sodium hydroxide solution. A stock solution of EDTA (1.4×10^{-2} M) was prepared by dissolving appropriate amount of Na_2EDTA (Merck) in distilled water. $NaClO_4$, NaOH, H_2SO_4, HNO_3 and other salts (for interference study) were obtained from Merck Ltd., Germany.

Procedures

Acidity constant determining of anthralin. First, the pH meter was calibrated in various binary methanol-water mixtures by using the 0.01 M solutions of oxalate and succinate buffers [23]. Then, according to the procedure introduced by Asuero group for a di-protonic acid [24], the absorbance of a 2.0×10^{-4} M Anthralin in 50% methanol solution was taken in acidic and basic solutions. Finally, the absorbance measurements at λ_{max} of the basic forms *vs*. pH of the solution were made, while the anthralin solution was titrated with a concentrated sodium hydroxide solution in the same solvent mixture, using a precalibrated micropipette. All pH values are expressed in terms of activity. The acidity constants were evaluated from the non linear curve fitting of the absorbance-pH data to the equations which was resulted from substituting the [H$^+$] and absorbance values in the mass balances:

$$A = (A_0 + A_1 [H^+]/K_2 + A_2 ([H^+]^2/K_1K_2))/ (1+ [H^+]/K_2 + ([H^+]^2/K_1K_2)) \qquad (1)$$

where, A is the observed absorbance at each titration point, A_0, A_1 and A_2 are the absorbances of the basic, monoprotonated and diprotonated forms respectively. K_1 and K_2 are the first and second acidity constants.

Determination of beryllium. To a solution containing 1-26 μg of beryllium, 2.5 ml anthralin (3×10^{-3} M) and 4 ml EDTA (1.41×10^{-2} M) was added, respectively. The pH of solution was first adjusted to 11.3 by adding buffer solution (5 ml) and then diluted to volume with distilled water in a volumetric flask (25.0 ml). After 15 min, the absorbance of solution was measured at 545 nm using a 1.0 cm quartz cell, against a blank reagent that was prepared in a similar way without beryllium.

Sample Preparation

Tap water samples were collected from Tehran (Iran).

Each sample was acidified to pH < 2 with concentrated HNO₃ and filtered through a 0.45 μm PTFE filter. A portion of this solution (5 ml) was first spiked with appropriate amount of beryllium and then the pH was adjusted approximately to 5 by adding NaOH/HNO₃. This solution was subjected to the proposed method as described above.

In case of beryl, 0.10 g of it was fused with NaF (1.0 g) using a platinum crucible. It was cooled, concentrated H₂SO₄ (5 ml) was added and boiled until a clear solution was obtained. The content of crucible was transferred to a volumetric flask and the volume was made up to 100 ml with distilled water. An aliquot (ml) of the solution was diluted with distilled water and subjected to proposed method as described above.

Powdered rock sample (0.10 g) was weighed into a platinum crucible and after addition of 2 ml concentrated H₂SO₄ the crucible was heated on a sand bath for 20 min. 3 ml of concentrated HF was added drop by drop (avoiding from foam formation). After complete dissolution of the solid, the mixture was heated until its volume was reduced to 1-2 ml. The residue was transferred to a volumetric flask (100 ml) and the volume was adjusted to the mark by adding distilled water. An aliquot (ml) of this solution was diluted with distilled water before being subject to the proposed method.

Alloy sample solution was prepared by dissolving 0.5 g of standard sample (Be-Cu alloy 21C) in 8.0 ml of nitric acid (1:1), gradual addition of H₂O₂ (3 ml, 30%) and heating the solution. This solution was first diluted with distilled water (in order to bring the Be(II) concentration within the linear range of the calibration graph) and then subjected to procedure as described above.

RESULTS AND DISCUSSION

Preliminary Investigations

According to the sec 2.3.1 and by using a non-linear least-squares curve fitting program (KINFIT) [25], the pK_1 and pK_2 values for anthralin in 50% methanol were evaluated 6.20 ± 0.07 and 8.84 ± 0.02 respectively. In addition, study on the absorbance-pH curve is shown in Fig. 1. At a pH < 7.0, λ_{max} was 425 nm, which was shifted to 505 nm in the pH range 8.0-12. A break at 455 nm between pH 8.5 and 9.5 was noted and then λ_{max} remained constant between pH 10-12. As is obvious
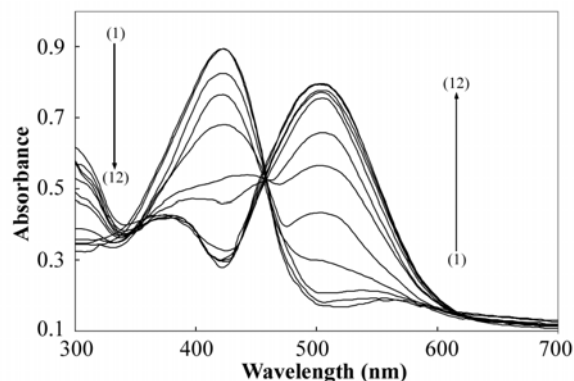
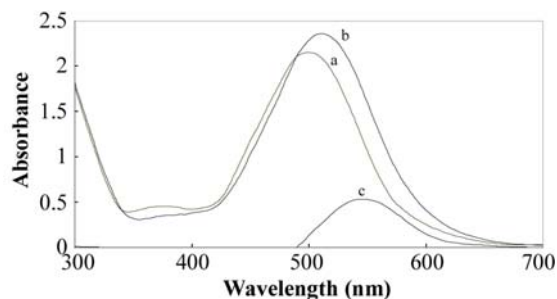**Fig. 1.** Effect of pH on the absorption spectra of anthralin. Conditions:anthralin, 2×10^{-4} M; medium, 50% methanol; T = 25 °C; pH: (1) 5.5, (2) 6.5, (3) 7.4, (4) 8.2, (5) 8.8, (6) 9.2, (7) 9.4, (8) 10.2, (9) 10.4, (10) 10.6, (11) 11.6, and (12) 12.0.

from Fig. 1, there are two isobestic points in the spectra indicating the existence of three species in equilibrium (i.e., H_2L, HL^- and L^{2-}), and so it can be concluded that the proton dissociation in anthralin occurs in two steps as follows:
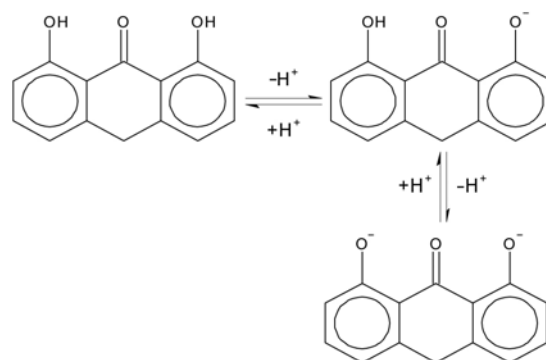
The absorption spectra, for the ligand (a) and for the complex (b) are shown in Fig. 2. The maximum absorbance of the anthralin and Be(II)-anthralin are being at 500 nm and 510 nm, respectively. The difference in absorptivity between the complex and free ligand is maximal at 545 nm, which is therefore chosen as the analytical wavelength. The molar

Fig. 2. Absorption spectra of (a) anthralin (b) Be(II)-anthralin and (c) Net Be(II)-anthralin *vs.* anthralin. Conditions: Be(II), 1.0 μg ml^{-1}; anthralin, 3 × 10^{-4} M; pH = 11.3 and T = 25 °C.
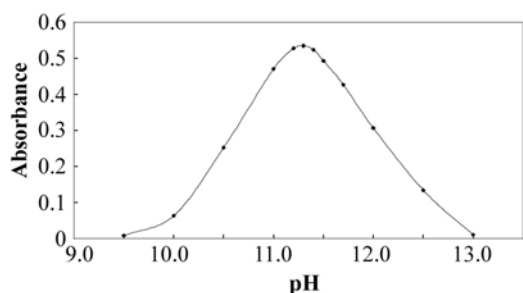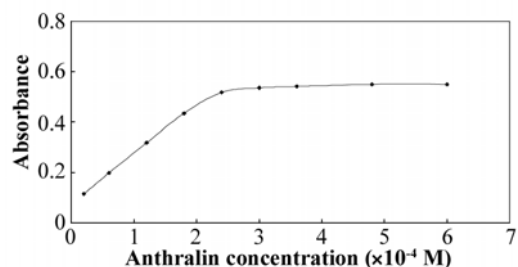

Fig. 3. Effect of pH on absorbance of Be(II)-anthralin complex at 545 nm, Conditions: Be(II), 1.0 μg ml^{-1}; anthralin, 3 × 10^{-4} M and T = 25 °C.

Fig. 4. Effect of anthralin concentration on complex absorbance at 545 nm, Conditions: Be(II), 1.0 μg ml^{-1}; pH = 11.3 and T = 25 °C.

Fig. 5. Effect of time on complex absorbance at 545 nm, Conditions: Be(II), 1.0 μg ml^{-1}; anthralin, 3 × 10^{-4} M; pH = 11.3 and T = 25 °C.

absorptivity of the ligand and complex were 7.2 × 10^3 and 4.7 × 10^3 (against ligand) l mol^{-1} cm^{-1}, respectively.
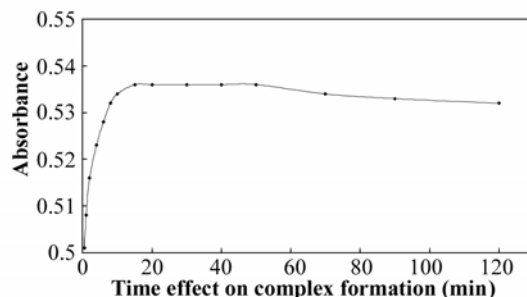
Effect of Different Variables

To take full advantage of the procedure, the reagent concentration and reaction conditions must be optimized. Various experimental parameters were optimized by setting all other parameters constant and optimizing one each time.

Effect of pH. The effect of pH variation on the formation of Be(II)-anthralin complex was investigated in the range 9.5-13. Considering molar absorptivity, quantitative complexation and color stability of the complex, the method was developed at pH 11.3. Figure 3 indicates that the absorbance is decreased at pH values lower than 11.3. This is due to low concentration of L^{2-} species which does not lead to the complete formation

of the complex. At pH > 11.3, Be(II) is mainly present as [Be(OH)$_4$]$^{2-}$, which does not form a complex with the ligand.

Effect of ligand concentration. Figure 4 shows the effect of anthralin concentration on the complexation reaction in the range 2.0 × 10^{-5}-6.0 × 10^{-4} M. It was observed that after reaching an anthralin concentration of 3.0 × 10^{-4} M, in a solution having a constant beryllium concentration (1.0 μg ml^{-1}), the absorbance was remained almost constant. Therefore, this concentration was selected as optimum value.

Effect of time. The effect of time on the stability of Be(II)-anthralin complex is shown in Fig. 5. As seen, a time interval of 15 min is required for quantitative complexation of Be^{2+} ion at room temperature. The absorbance of complex remained constant for more than 3 h.

Effect of EDTA concentration. The effect of EDTA

concentration, as a suitable masking agent for interfering cations, on the complexation reaction of Be (0.12 µg ml^{-1}) was studied in the range 0.0-3.5 × 10^{-3} M. It was found that EDTA^{2-} did not affect (causing less than ±4% negative deviation) beryllium determination unless it was present in over 170-fold molar ratio of beryllium. The addition of 4 ml EDTA solution (1.41 × 10^{-2} M) can effectively mask 56 µmol of any interfering cation (Table 2). Therefore, the method could be made selective in this way.

Stoichiometry of the complex. The stoichiometry and complex formation constant of Be(II)-anthralin complex were determined by the absorbance measurments at λ_{max} = 545 nm. The stoichiometry was determined to be 1:2 using both continuous variation (or Job's) method [26] (Fig. 6a) and molar-ratio [27] method (Fig. 6b). The complex formation constant (logK$_f$) was evaluated as 9.70 ± 0.03, using molar-ratio data and the non-linear least-squares curve fitting method.

Thus, based on the results discussed above, the following reaction mechanism at pH 11.3 is suggested:
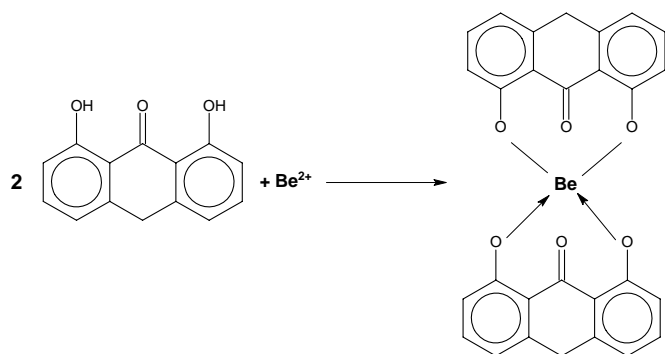
Analytical characteristics. Table 1 compares the analytical characteristics of the proposed method with those of the previously published spectrophotometric methods for the determination of Be^{2+}. In the proposed method, the calibration graph obeyes the equation A = 0.5267C$_{Be}$ + 0.007, which has a good regression coefficient (r = 0.9997) over a wide concentration range (0.04-1.04 µg ml^{-1}). The limit of detection, defined as C$_L$ = 3S$_B$/m (where C$_L$, S$_B$, and m are the limit of detection, standard deviation of the blank, and slope of the calibration equation, respectively) was 0.012 µg
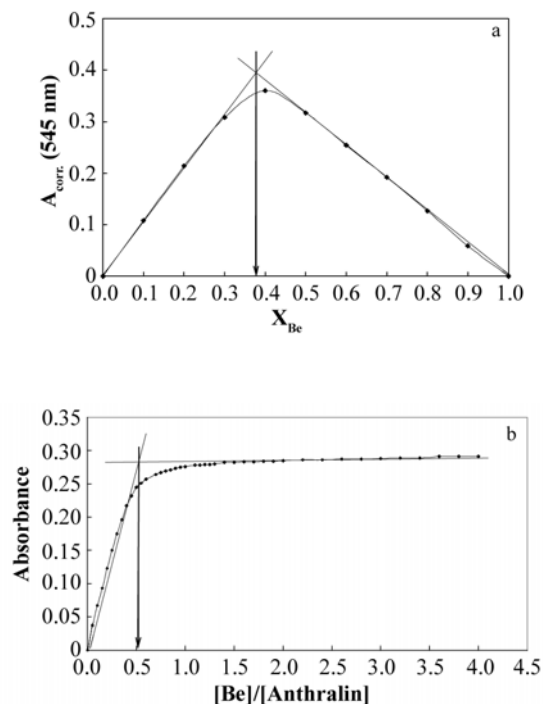
Fig. 6. (a) Job's method, and (b) Mole-ratio method for stoichiometry determination of the complex at 545 nm, Conditions: (a), [Be] = [L] = 3.0 × 10^{-4}, (b) [L] = 1.5 × 10^{-4} M and [Be] was varied from 0-6 × 10^{-4} M, pH = 11.3 and T = 25 °C.

ml^{-1} (n = 10) and RSD for 5 replicate determinations of Be (0.48 µg ml^{-1}) was 0.43%.

As it is obvious from the data given in Table 1, the analytical characteristics of the proposed method (e.g. LOD, LDR and molar absorptivity) are comparable with those reported for the previously published methods. The main advantage of our method is that the Al^{3+} does not interfere, when its concentration is up to 100-fold of Be(II), even without using EDTA, unlike other methods.

Effect of interfering ions. To study the selectivity of the proposed method, the effect of common ions (in silicate rocks and Cu-Be alloys) on the determination of beryllium (0.12 µg ml^{-1}) was tested under the optimum conditions. The results are given in Table 2. The tolerance limit was defined as the concentration of added ion causing less than ±5% relative

Table 1. Analytical Characteristics of the Proposed Method[a] and Comparison with Some Other Spectrophotometric Methods

Reagent	Condition (pH, Buffer)	LDR ($\mu g\ ml^{-1}$)	LOD ($\mu g\ ml^{-1}$)	ε ($l\ mol^{-1}cm^{-1}$)	λ_{max} (nm)	Ref.
Anthralin	11.3, Boric acid	0.04-1.04	0.012[b]	0.47×10^4	545	This work
Emodin	9.5, $Na_2B_4O_7$	0.036-0.18	0.007	0.79×10^3	530	[21]
Chrome azurol S	5.0, Hexamine	0.04-0.32	0.015	0.40×10^4	569	[28]
Thorin	10.0, Citrate/NaOH	0.2-1.5	Not reported	0.47×10^4	522	[29]
Alizarine fluorine blue	7.2, Tris/HCl	0.09-0.36	Not reported	0.53×10^4	480	[30]
1-Hydroxy-2-carboxy-anthraquinone	11.1, Ethylenediamine	0.040-0.4	0.009	0.84×10^4	463	[31]

[a]$A = 0.5267C_{Be} + 0.007$ (r = 0.9997), RSD = 0.43% (0.48 $\mu g\ ml^{-1}$ of Be, n = 5). [b]For ten replicate determination of the blank (n = 10).

Table 2. Tolerance Limits of Diverse Ions on the Be (0.12 $\mu g\ ml^{-1}$) Determination

Diverse cation	[Diverse ion]:[Be] ratio[a]		Diverse anion[b]	[Diverse ion]:[Be] ratio
Na^+, K^+ and Li^+	>1000	>1000	NO_3^-, Cl^-, BO_3^-,	
UO_2^{2+}, Al^{3+} and Ga^{3+}	100	270	SO_4^{2-} and HPO_4^{2-}	>1000
Ba^{2+}	17[b]	160	CN^-	50
Cr^{3+}	6[b]	150	$Citrate^{2-}$	50
Fe^{3+}	5	130	$Tartarate^{2-}$	40
Mn^{2+}, Co^{2+}	3	150	$Oxalate^{2-}$	30
Zn^{2+}, Sr^{2+} and Ca^{2+}	3[b]	166	$Picrate^{2-}$	75
Cd^{2+}	1[b]	140	F^-	30
Cu^{2+}	1[c]	158		
Mg^{2+}	0.5	148		

[a]$\leq 5.0\%$ Deviation in the absence (first column) and presence (second column) of EDTA (2.26×10^{-3} M).
[b]Negative deviation. [c]Precipitation observed at high concentration of diverse ion.

error. As can be seen, EDTA efficiently masked all these interfering species and, hence, Be(II) can be determined without any interference. It is noteworthy that a 100-fold molar excess of Al(III) did not inhibit beryllium determination even in the absence of EDTA.

ANALYTICAL APPLICATION

In order to evaluate the analytical applicability of the method, it was applied to the determination of beryllium in water samples. The results obtained for spiked water samples (tap water) are shown in Table 3. As seen, the recoveries for the addition of different concentration of Be to water samples are in the range of 97-102%. To assess the applicability of the method to other real samples, it was applied to the determination of beryllium in beryl, rock and alloy samples (Table 4) and the results were compared with those obtained using inductively coupled plasma-atomic emission spectrometry (ICP-AES). As seen, the results of two different methods are in satisfactory agreement.

Table 3. Determination of Beryllium in Spiked Water Samples

Sample[a]	Be^{2+} (μg ml^{-1})		
	Added	Found[b]	Errore (%)
1	0.04	0.041	+2.5
2	0.08	0.079	-1.25
3	0.12	0.122	+1.67
4	0.24	0.241	+0.42
5	0.36	0.35	-2.78
6	0.48	0.48	0
7	0.60	0.59	-1.67
8	0.72	0.72	0

[a]Tap Water containing Mg^{2+} (6 μg ml^{-1}) and Ca^{2+} (29 μg ml^{-1}). [b]Mean value of three determination (n = 3).

CONCLUSIONS

Spectrophotometric studies on anthralin shows two stepwise proton dissociations with pK_1 = 6.2 ± 0.07 and pK_2 = 8.84 ± 0.02. It forms a stable complex with Be(II) having a M:L ratio of 1:2 and $logK_f$ = 9.70 ± 0.03. This is the first time that this reagent is being used for the determination of beryllium. Be(II) can be determined in the presence of other cations if EDTA is used as a masking agent. Also Al(III) does not interfere, when its concentration is up to 100-fold of Be(II), even without using EDTA unlike other previous methods [4-6,32-34]. The proposed method is rapid, simple, and selective enough to be used for trace amount determination of beryllium in different type of samples such as beryl, rock, and alloys. Finally, the results obtained from proposed method and those of ICP-AES were in satisfactory agreement.

ACKNOWLEDGMENTS

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Table 4. Determination of Beryllium in Real Samples[a]

Samples	Beryllium content (%)			
	Conventional method	Standard addition method	ICP-AES method	Difference (%)[b]
Pegmatite	0.132 (±0.06)	0.137 (±0.07)	0.134 (±0.02)	-1.52
Beryl	3.58 (±0.12)	3.60 (±0.10)	3.54 (±0.08)	+1.12
Cu-Be alloy (21C)[c]	2.17 (±0.05)	2.14 (±0.08)	2.11 (±0.08)	+2.76

[a]Average of three determination (±Standard deviation). [b]Difference of conventional and ICP-AES methods. [c]Certificated beryllium content = 2.00-2.25%.

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