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KEYWORDS

Direct spectrophotometric determination; Beryllium; Beryl minerals; Chrome Azurol S (CAS); Absorbance; Wavelengths; Interference **Abstract** A developed, direct, rapid, and sensitive spectrophotometric determination of beryllium in beryl minerals with Chrome Azurol S (CAS) as a chromogenic reagent was developed in the present article. The determination was performed without either solvent extraction or ion exchange separation of beryllium from its matrix. The stable 1:1 Be-CAS complex was formed instantly with duration time of at least 24 h with constant absorbance. Different parameters such as wavelengths, pH, EDTA concentration and dye concentration were studied for the optimum determination of beryllium. Interference due to presence of high aluminum concentrations was overcome by adding 5% EDTA disodium salt solution. Maximum absorbance for Be-CAS complex was performed at λ_{max} 568 NM using acetate buffer at pH 4.6. Beer's law was obeyed in the range from 0.02 to 9 ppm with molar absorptivity $\varepsilon = 0.22 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ and an average standard deviation of 0.7. The R.S.D for 10 replicate measurements of 1 ppm Be was 1.2%.

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1. Introduction

Beryllium is indeed a strategic metal due to its vital importance and uses in several industries. In the earth's crust, Be is not found in the free state and its assay is about 6 ppm where it is more abundant than some other metals as U, Nb, Ag. Beryllium being one of the lightest known structural metals, it is

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used in a wide variety for both nuclear and non-nuclear applications. Its light weight makes it an obvious candidate for consideration in aerospace components, especially if certain nuclear characteristics are also desired. It is the combination of properties exhibited that result in being a very attractive material for use as neutron reflector. Physically, small nuclear reactors such as test/research reactors and those used in space applications, typically include neutron reflectors to more efficiently utilize the neutrons that are produced during reactor operation. In addition to being an excellent neutron reflector material, beryllium is also an attractive material as a neutron moderator, i.e. it effectively moderates or reduces the energy of neutrons. It is only two thirds as heavy as aluminum, yet about six times stiffer than steel and has a modulus of elasticity of one-third greater than steel (excellent strength-to-weight

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and stiffness-to-weight ratios), high specific heat, excellent thermal conductivity and retains its shape and strength at both elevated and cryogenic temperature. In addition, beryllium resists corrosion at high temperatures better than titanium or zirconium.

Most of the previous work for spectrophotometric determination of beryllium was usually preceded by their separation from the accompanying components (matrix) and interfering elements for increasing selectivity, sensitivity and accuracy. Methods of separation and preconcentration include solvent extraction, precipitation and co-precipitation with collectors, volatilization, or ion exchange separation (Minczewski et al., 1982; Mizuike, 1983; Zolotov and Kuz'min, 1990).

A number of classical and advanced methods for the determination of Be were described, these include gravimetric, volumetric, photonuclear activation, polarographic, atomic absorption, ICP-AES, infrared spectrometry, X-ray fluores-cence (XRF) and spectrophotometric methods.

The spectrophotometric method is convenient enough to be adopted and compared to other methods. Marczenko and Balcerzak (1998) mentioned that, owing to the presence of p-quinonoid rings, triphenylmethane reagents are intensely colored and provide the basis of spectrophotometeric methods for the determination of beryllium.

Katsube et al. (1961) used developed procedures for the spectrophotometric determination of trace amounts of beryllium, copper and iron (III) with sodium-2",6"-dichloro-4'-hydroxy-3,3'-dimethylfuchsone-5,5'-dicarboxylate. Some ions that interfere with beryllium determination were removed by oxine precipitation. Beer's law was applicable up to about 0.3 ppm of beryllium, about 4 ppm of copper and about 3 ppm of iron.

Kunita and Shibata (1963) studied the spectrophotometric determination of beryllium using beryllon II at maximum absorption of 620 nm. Beer's law was obeyed at the range from 0.02 to 0.5 ppm beryllium.

Keil (1972) has proposed a highly selective and rapid spectrophotometric determination of beryllium by thorin. The selectivity of spectrophotometric determination of beryllium by thorin has been essentially improved by simply masking the other cations with large quantities of EDTA and ammonium citrate. Over 60 cations and 20 anions have been investigated where they show no interference effect over a wide range of concentrations.

López et al. (1986) studied the colorimetric reaction between beryllium and leucoquinizarin for the determination of beryllium. The yellow chelate was formed at pH 5.3–5.5 in a medium containing 20% of ethanol, and the absorption is measured at 438 nm. The molar absorptivity ($\varepsilon = 1.2 \times 10^4 1 \text{ mol}^{-1} \text{ cm}^{-1}$) allows the determination of a range from 0.1 to 0.8 ppm beryllium.

Kaur and Gupta (1989) used carminic acid for the determination of beryllium complex at pH 4. The absorption was measured at 580 nm and the molar absorptivity value (ε) was 2.25×10^3 mol⁻¹ cm⁻¹. Beer's law was obeyed from 0.4 ppm to 1.6 ppm of beryllium. The effects of pH, reagent concentration and interferences from foreign ions have been studied.

Spectrophotometric investigations of Be complexes with eriochrome cyanineR(ECR) in the presence of cationic surfactants as benzyl dimethyl tetradecyl ammonium chloride (BDTA) and benzyl dimethyl cethyl ammonium chloride (BDCA) at pH 5.5–6.5 using acetate buffer solutions were studied. The main interfering cations Al (III), Fe (III) and Cu (II) are masked with EDTA and Ca-EDTA, respectively (Ivanova, 2001).

Saleh (1999) determined Be spectrophotometrically through calcion dye that reacts directly with Be to form a calcion-Be complex in a suitable aqueous media. The studied relevant factors include pH, concentration of the dye and the molar ratio. It was possible to determine beryllium between 0.04 and 1.35 ppm with molar absorptivity ε of 7.5×10^3 . The interference of accompanying elements has been studied in this work.

Bahram et al. (2007) have developed a new extraction method for preconcentration of ultra-trace quantities of beryllium as a prior step to its simultaneous spectrophotometric determination. Chrome Azurol S (CAS), cetyltrimethyl ammonium bromide (CTAB) and Triton X-114 were used as chelating agents, cationic surfactant for extraction and co-extraction agent, respectively. Linearity was obeyed in the range from 5 to 40 ng ml⁻¹ beryllium and 3–100 ng ml⁻¹ for aluminum. The detection limit of the method is 0.98 ng ml⁻¹ beryllium.

Afkhami et al. (2006) developed a new phase preconcentration method for separation of ultra-trace quantities of Be as a prior step to its colorimetric determination. Chrome Azurol S (CAS) and cetyltrimethylammonium bromide (CTAB) were used as chelating agent and cationic surfactant, respectively. Linearity was obeyed in the range from 0.9–18.0 ng ml⁻¹ $(1.00 \times 10^{-7} - 2.00 \times 10^{-6} \text{ mol } 1^{-1})$ Be. The detection limit of the method is 0.51 ng ml⁻¹ (5.66 × 10⁻⁸ mol 1⁻¹) Be. The interference effect of some anions and cations was also tested.

Chrome Azurol S (CAS) dye forms a colored chelate complex with beryllium and this has been used for the determination of beryllium. Eskinja et al. (1985) and Dong et al. (1991) stated that the Chrome Azurol S (CAS) method has been applied for determining Be in bronze and water. In the presence of surfactant, Eristavi and Brouchek (1968), Qiu et al. (1992), Nishada (1991) and Rudometkina et al. (1988) determined beryllium in minerals, sewage, coal dust and aluminum alloys, respectively. Sauerer and Troll (1983) has applied Eriochrome Cyanine R for determination of beryllium in water and silicates in weakly acidic or neutral medium (pH ~ 5, ± 0.5). Below this pH, the absorbance of CAS increases considerably, and above it the absorbance of the beryllium complex is decreased more by adding EDTA.

A simple, rapid, and sensitive spectrophotometric determination of trace amounts of beryllium using 1,8-dihydroxyanthrone as a new reagent was described by Beiraghi and Babaee (2007). The experimental conditions for determining beryllium include pH, reagent concentration and time. Under the optimum experimental conditions, the molar absorptivity ε was $0.47 \times 10^4 1 \text{ mol}^{-1} \text{ cm}^{-1}$ at 545 nm. Calibration graph was linear in the range from 0.04 to 1.04 µg ml⁻¹ with a detection limit of 0.012 µg ml⁻¹. The interfering effect of some cations and anions were also studied. The method was applied for the determination of Be in beryl, silicate rock and alloys.

2. Material and methods

2.1. Apparatus

A double beam UV–Visible spectrophotometer of high resolution power model Jasco V-530 with a wavelength ranging from

 Table 1
 Buffer pH variation effect on the Be-CAS complex formation at different wavelengths (nm).

λ (nm)	Absorbance (Å)							
	pH 3.0	pH 3.18	pH 4.0	pH 4.6	pH 4.9	pH 5.3	pH 5.78	
400	0.096	0.088	0.046	0.144	0.109	0.035	0.124	
420	0.133	0.10	0.06	0.17	0.12	0.09	0.169	
435	0.104	0.128	0.07	0.24	0.18	0.11	0.290	
450	0.90	0.118	0.08	0.36	0.23	0.13	0.370	
485	0.079	0.104	0.09	0.58	0.33	0.19	0.405	
505	0.054	0.092	0.122	0.72	0.34	0.28	0.468	
568	0.030	0.073	0.105	0.95	0.21	0.22	0.533	
625	0.024	0.054	0.081	0.64	0.19	0.28	0.600	
675	0.013	0.03	0.06	0.311	0.14	0.24	0.732	
700	0.009	0.011	0.034	0.109	0.099	0.198	0.729	

 Table 2
 Effect of EDTA concentration as masking agent on the formation of Be-CAS.

Absorbance (Å)								
EDTA 0.5%		EDTA 1%		EDTA 5%				
Be	Be+ 4 ppm Al	Be	Be+ 4 ppm Al	Be	Be+ 4 ppm Al			
0.559	0.748	0.320	0.486	0.300	0.302			
0.558	0.564	0.319	0.493	0.299	0.299			
0.557	0.685	0.318	0.492	0.298	0.293			
0.555	0.564	0.317	0.534	0.297	0.291			
0.548	0.465	0.309	0.562	0.294	0.281			
0.544	0.512	0.305	0.708	0.292	0.606			

190 to 1100 nm, computer controlled data analysis and reporting software was used in systematic study for determination of Be-CAS complex.

A pH meter model InoLab, Germany, was applied satisfactorily in the present work and calibrated daily by using two successive buffer solutions (pH 4 and 7 or 7 and 10).

3. Reagents and chemicals

Chrome Azurol S dye (CAS) ($C_{23}H_{13}C_{12}Na_3O_9S$) purchased from Sigma Co. (0.05%, w/v) stock solution was prepared by dissolving 0.05 g in double distilled water containing 0.2 g of Gum Arabic powder (Technolab Co.) and diluted to100 ml in a volumetric flask. Allow the solution to stand for several days, filter and store in dark bottle. The solution was stable and can be stored for several weeks.

Beryllium (Be) stock solution of 50 ppm was prepared by dissolving 0.9830 g of beryllium sulphate tetrahydrate (BeSO₄·4H₂O), (Merck Co.) in 200 ml of water and 50 ml of 10 M HCl and dilute to 1 liter volumetric flask. Different dilutions were performed for different experimental work.

Ethylene diamine tetraacetic acid disodium salt, EDTA-2Na (5%, w/v) (C₁₀H₁₄O₈N₂Na₂·2H₂O) supplied from Adwick Co. was prepared by dissolving 5 g of analytical grade in double distilled water and diluted in100 ml volumetric flask. Different dilutions were performed for different experimental work.

Acetate buffer solution with a pH of 4.6 was prepared by dissolving 59.5 g sodium acetate trihydrate (CH₃COONa·3H₂O, Adwick Co.) in 125 ml of double distilled water, 25.5 ml of glacial acetic acid (CH₃COOH) (Merck Co.), and diluted with water to 250 ml volumetric flask. A 5 ml aliquot of this solution diluted to 25 ml will give a recommended pH of 4.6.



Figure 1 Effect of CAS dye concentration on the absorbance of Be-CAS complex.

Sodium hydroxide (NaOH) (Merck Co.) solution 10% (w/v), for free acidity neutralizations, was prepared by dissolving 10 g of analytical grade NaOH with double distilled water and completed up to volume in100 ml volumetric flask.

Aluminum solution (50 ppm) was prepared by dissolving 0.0050 g of aluminum chloride hexahydrate (A1Cl₃·6H₂O) (Adwick Co.) in 100 ml volumetric flask and completed up to volume with double distilled water.

4. Analytical procedure

Different parameters such as wavelengths, pH, EDTA concentration and dye concentration were studied for the optimum determination of beryllium.

absorption method.						
Sample	Present modified method	Atomic absorption method				
1	55.6	56				
2	92.3	86.6				
4	135.16	127.5				
7	174.0	170				
8	166.3	156.8				
Kabo(1)	21.8	20.8				
Kabo(2)	9.60	8.9				

Table 3 Analytical results of Be (ppm) in six beryl samples bythe presently modified method in comparison to atomicabsorption method.

5. Dissolution of Beryl

Determination of beryllium in beryl minerals requires first the dissolution of the mineral then its spectrophotometric determination using CAS dye. Beryl samples were ground first to 0.074 mm in size, weighed, digested, and then analyzed. Dissolution of samples was carried out by dissolving 0.05 g of ground beryl (0.074 mm in size) in 20 ml hydrofluoric acid (HF) and 2 ml concentrated sulphuric acid (H₂SO₄) (Merck Co.) in a Teflon beaker. The solution was evaporated till no fumes were evolved. The final residue was dissolved in 15 ml of 5 M hydrochloric acid (HCl) (Merck Co.) and boiled till clear solution. The solution was completed to 100 ml volumetric flask.

6. Results and discussion

Several factors have been studied to optimize the formation of Be-CAS complex. These factors include pH and buffer solution, dye concentration, EDTA as a masking agent to overcome effect of interference of the accompanying elements.

6.1. Effect of pH and buffer solution on the formation of Be-CAS complex

Buffer solutions with different pH values ranging from 3 to 5.78 were studied within a range of wavelengths; 400–700 nm for obtaining maximum absorbance of Be-CAS complex formation. According to the obtained experimental data given in Table 1, it was found that acetate buffer at pH 4.6 is the most suitable, where it achieved the maximum absorbance value at λ_{max} 568 nm for Be-CAS complex formation.

6.2. Effect of CAS dye concentration on the absorbance of Be-CAS complex

The study of CAS dye concentration is important for optimum complex formation and its stability. A concentration of CAS dye, which is less than or higher than necessary, would cause deviation from Beer's law when constructing the calibration curve and overlapping of dye color spectra with the ion-dye complex. The optimization of the dye consumption and addition beside pH value would prevent, to a certain extent, the dye from the formation of complexes with other anions that may be present in the aqueous solution or absorb incident light. From the obtained data, it was found that the maximum stable absorbance for Be-CAS complex was observed at concentration of 2 ml dye (0.05% w/v) at maximum wave length of λ_{max} 568 nm as shown in Fig. 1.

7. Optimization of the masking agent (EDTA) for interfering ions

It was found that EDTA-2Na is the most common masking agent used for masking interfering ions by complexation in Be determination. It was added directly after sample solution

 Table 4
 Statistical calculation of Be determination in three beryl samples
 d^2 Samples no. Be content (ppm) Mean X (ppm) Standard deviation S (ppm) Standard error SE (ppm) d Accuracy Δ 0.57 1 56 55.66 0.329 1 1 0.55 55 0 0 56 1 1 91.5 2 92.33 0.76 0.439 1 1 0.7 0.25 0.5 92 5 93 1.5 2.25 4 134.5 135.16 0.76 0.439 1.5 2.25 0.7 136 1 1 135 0.5 0.25 7 174.5 174 0.50 0.289 0.5 0.25 0.5 174 0.5 0.25 173.5 1 1 0.5 0.25 8 166 166.33 0.28 0.161 0.29 166.5 0.5 0.25 166.5 0 0 Kabo(1) 21 21.8 0.76 0.439 1.5 2.25 0.7 22.5 1 1 22 0.5 0.25 Kabo(2) 10 9.16 0.76 0.439 1 1 0.7 2.25 9 1.5 8.5 0.5 0.25

because interfering ions form strong complexes with EDTA. whereas beryllium does not. It was usually used to mask the interfering ions accompanying beryllium during preconcentration, precipitation or classical separation. Addition of EDTA-2Na minimizes precipitation of aluminum, chromium and iron and further reduces co-precipitation of manganese, cobalt, nickel and zinc, via masking them during beryllium separation by precipitation. EDTA concentration should be optimized for complete masking of interfering ions, where its excess causes interference in the complex formation of Be-CAS dye. Aluminum represents the highest concentration percent in the Egyptian Beryl (Al₂O₃, 12-19%) while BeO ranges from 6% to 14%, hence it is the most deleterious interfering ion during beryllium spectrophotometric determination. The effect of EDTA concentration and volume on the color of beryllium complex was studied. The obtained results were listed in Table 2. It was found that Be-CAS complex absorbance when measured with EDTA decreases with increasing EDTA concentrations, which may be attributed to the complexation between Be cation and excess EDTA in most experiments, thus optimum concentration of EDTA must be added to overcome the interference effect of accompanying ions without any excess. On the other hand, it was found that 0.1-0.5 ml of 0.5% EDTA was optimum for complete masking of interfering ions, especially Al in the determination of beryllium.

Different sequences of additions were applied for the maximum absorption of Be-CAS complex formation. It was found that addition of Be, EDTA, buffer, NaOH, diluting with water to about 20 ml and dye solutions were the best sequence of addition.

8. Application of the modified method on some Egyptian beryl samples

In order to evaluate the analytical applicability of the proposed method, it was applied to seven Egyptian beryl minerals where beryllium concentration was determined in each of them, and at the same time they were analyzed by atomic absorption spectroscopy (AAS) technique for comparison of results by both techniques. The data were gathered and tabulated in Table 3.

9. Statistical evaluation of Be results

Although the systematic statistical analysis could not be performed on the results due to the small number of samples, an evaluation by appropriate statistical parameters was herein attempted to cast some light on the significance of the results (Table 4).

10. Conclusion

A developed method for the spectrophotometric determination of beryllium in beryl minerals with Chrome Azurol S (CAS) as a chromogenic reagent was developed in the present work. A stable 1:1 Be-CAS complex was formed with duration stability over 24 h. Different parameters were studied for the optimum determination of beryllium such as wavelengths, pH, EDTA concentration and dye concentration and interference due to presence of high aluminum concentration. Interference was overcome by adding 5% EDTA disodium salt solution. Maximum absorbance for Be-CAS complex was performed at λ_{max} 568 nm using acetate buffer at pH 4.6 with 2 ml CAS dye (0.05% w/v). Beer's law was obeyed in the range from 0.02 to 9 ppm with molar absorptivity $\varepsilon = 0.22 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ and an average standard deviation of 0.7. The RSD for 10 replicate measurements of 1 ppm Be was 1.2%.

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