

Spectrophotometric Determination of Beryllium with Chrome Azurol S -Application to Waters

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(Received 28/ 6 / 2011 ; Accepted 31 / 10 / 2011)

ABSTRACT

A simple, rapid and direct spectrophotometric method for the determination of beryllium II is described. The method is based on the reaction beryllium II with chrome azurol S in the presence of cetylpyridinium chloride at pH 5.0 forming a stable blue coloured complex which has an intense absorption at 620 nm. Beer's law was obeyed over the range of 0.25-100 µg/25 ml. The molar absorptivity and Sandal's sensitivity of the coloured complex are $1.02 \times 10^4 \text{ l.mol}^{-1}.\text{cm}^{-1}$ and $0.00883 \text{ µg.cm}^{-2}$, respectively. The interference caused by a number of common cations and anions can be removed by using EDTA as a masking agent. The method has been applied successfully to the determination of beryllium II in different water samples.

Keywords: Beryllium, Spectrophotometric method, Chrome azurol S; Cetylpyridinium chloride.

– (II)

5.0

620

25 /

100-0.25

2-

0.00883

1-

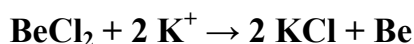
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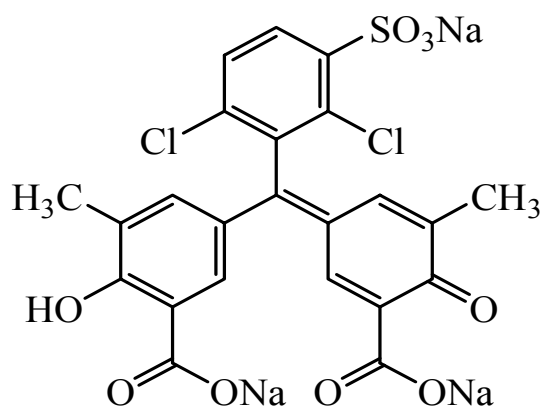
EDTA

INTRODUCTION

Beryllium is the chemical element with the symbol (Be) and atomic number (4) (Bailar and emeluse, 1975). The free element is a steel-gray, strong, lightweight brittle alkaline earth metal (IPCS, 1990). Structurally, beryllium's very low density, high melting point, high temperature stability and low coefficient of thermal expansion, make it in many ways an ideal aerospace material. It has been used in rocket nozzles and is a significant component of planned space telescopes. It is primarily used as a hardening agent in alloys, notably beryllium copper. Beryllium is found in 30 different minerals, the most important of which are bertrandite, beryl, chrysoberyl, and phenacite (Newman, 2003). Because of its relatively high transparency to X-rays and other ionizing radiation types (Whitehead et al., 2008), the isotope of beryllium -7 has half life 53.3 days, beryllium -9 is stable, but beryllium -10 has half life 2600000 years (Sujatha *et al.*, 2003). Commercial use of beryllium metal presents technical challenges due to the toxicity of beryllium-containing dusts. Beryllium produces a direct corrosive effect to tissue, and can cause a chronic life-threatening allergic disease called berylliosis in susceptible persons. Beryllium is a metal that can be very harmful when humans breathe it in, because it can damage the lungs and cause pneumonia (Breslin, 1966). Beryllium is a relatively rare element in both the earth and the universe. Friedrich Wohler and Antoine Bussy independently isolated beryllium in 1828 by the chemical reaction of metallic potassium with beryllium chloride, as follows (Hotzbecher *et al.*, 1976):



Chrome azurol S is a 5-[(3-carboxy-5-methyl-4-oxo-2,5-cyclohexadien-1-ylidene)-(2,6-dichloro-3-sulphophenyl)methyl]-2-hydroxy-3-methylbenzoic acid tri sodium salt (Sommer and Kuba, 1969). This reagent can be used for determination of some cations like titanium (Marczenko and Kalowska, 1982), iron (Qingji et al., 1993), aluminium (III) (Kennedy and Powell, 1986), europium(III) (Cattrall and Slater, 2000), and samarium (III) (Mustafa and Orhan, 2000), chrome azurol S (CAS) is a reagent that can be used to detect the mobilization of iron.



Chrom azurol S; $\text{C}_{23}\text{H}_{13}\text{Cl}_2\text{Na}_3\text{O}_9\text{S}$
M.wt = 605.29 gm/mol.

Different spectrophotometric methods have been proposed for the determination of beryllium. Aluminon reagent forms a coloured complex with beryllium in airborne dust samples (John, 1967). A microdetermination method at ng.ml^{-1} level for beryllium by solid-phase spectrophotometry has been developed, chrome azurol S is used as chromogenic reagent to form a blue complex which is easily and strongly sorbed and concentrated on a

dextran-type anion-exchange resin (Molina-Diaz *et al.*, 1998), also a new micelle-mediated phase preconcentration method for preconcentration of ultra-trace quantities of beryllium as a prior step to its determination by spectrophotometry has been developed. Chrome azurol S and cetyltrimethylammonium bromide are used as chelating agent and cationic surfactant, respectively, the method was applied to the determination of beryllium in spring water samples (Afkhami *et al.*, 2007). Beryllium has been determined in various samples using arsenazo III, alminon and erichrome cyanine R (Shekho, 2002). Other methods using different chromogenic reagent like titan yellow (Hong-Wen and Peng-Fei, 1994), haematoxylin (Dayananda *et al.*, 2007), 1,8-dihydroxyanthrone (Beiraghi and Babae, 2007). and xylenol orang in presence of cetyltrimethyl -ammoniumbromide (Madrakian *et al.*, 2005) have been reported. Fluorimetric methods has also been suggested for the determination of beryllium with 4-methyl-6-acetyl-7-hydroxycoumarin (Yoshida *et al.*, 1990). Also chromatographic methods have been used for determination of beryllium such as reversed-phase high-performance liquid chromatography (HPLC) with fluorometric detection using 2-(2'-hydroxyphenyl)-10-hydroxy -benzoquinoline as a precolumn chelating reagent (Matsumiya and Hoshino, 2003). High performance chelation ion chromatography (HPCIC), involving a chelating silica substrate bonded with aminomethylphosphonic acid, has been developed as a novel technique for the quantitative determination of beryllium in complex matrices (Shaw *et al.*, 2000). Ion chromatographic method has been used for the determination of beryllium in a number of water samples (Bashir and Paull, 2001).

The present work describes the determination of beryllium with chrome azurol S in the presence of cetylpyridinium chloride at pH 5.0, a blue, soluble and stable complex has been measured spectrophotometrically at 620 nm for the determination of beryllium in different water samples.

EXPERIMENTAL

Apparatus

The absorption spectra and absorbance measurements were recorded on a double-beam Shimadzu UV-Visible recording spectrophotometer UV-160 with 1.0 cm matched plastic cells. pH measurements were performed using HANNA Instrument pH 211 microprocessor pH meter.

Reagents

All chemical used were of analytical – reagent grade.

Stock beryllium (II) solution 100 µg / ml:

This solution is prepared by dissolving 0.1964 g of beryllium sulphate tetrahydrate (Hopkin and Williams) in distilled water and the volume was completed to the mark with distilled water in a 100 ml volumetric flask.

Working beryllium (II) solution 1 µg / ml:

This is prepared by diluting 2.5 ml of stock beryllium (II) solution to the mark in a 250 ml volumetric flask with distilled water.

Cetylpyridinium chloride (CPC) 1×10^{-3} M:

This is prepared by dissolving 0.1790 g of cetylpyridinium chloride (Fluka) in distilled water and the volume is completed to the mark in a 500 ml volumetric flask with distilled water.

Chrome azurol S 1×10^{-3} M:

This solution is prepared by dissolving 0.1513 g of chromogenic reagent chrome azurol S (Fluka) in distilled water, then complete the volume with distilled water to the mark in a 250 ml volumetric flask. The solution was then transferred to a dark bottle it is stable for at least one week.

Buffer solution (pH 5.0): is prepared by mixing 50 ml of 0.1 M potassium hydrogen phthalate and 22.6 ml of 0.1 M sodium hydroxide and the volume is diluted to the mark, with distilled water, in a 100 ml volumetric flask (Perrin and Dempsey, 1974).

Ethylenediaminetetraacetic acid (EDTA) 0.01M adjusted to pH =5.0: is prepared by dissolving 0.7306 g of ethylenediaminetetraacetic acid (disodium salt dihydrate) in distilled water then the pH of the solution is then brought to 5.0 with 1N NaOH, the volume is completed to the mark with distilled water in a 250 ml volumetric flask.

Procedure and calibration graph:

Aliquots of standard solution 0.25-120 μg of beryllium was transferred into a series of 25 ml volumetric flask. To each flask, 3 ml of masking agent solution, 2 ml of buffer solution, 2 ml of cetylpyridinium chloride (1×10^{-3}) M and 1 ml of chrome azurol S (1×10^{-3}) M were added, The reaction mixture were diluted to the mark with distilled water and mixed well. The absorbance of the produced coloured complex was measured at 620 nm against the corresponding reagent blank. A linear calibration graph (Fig.1) is obtained over the range 0.01-4.0 ppm with a molar absorptivity $1.02 \times 10^4 \text{ l.mol}^{-1}.\text{cm}^{-1}$ and sandell $0.00883 \mu\text{g}.\text{cm}^{-2}$.

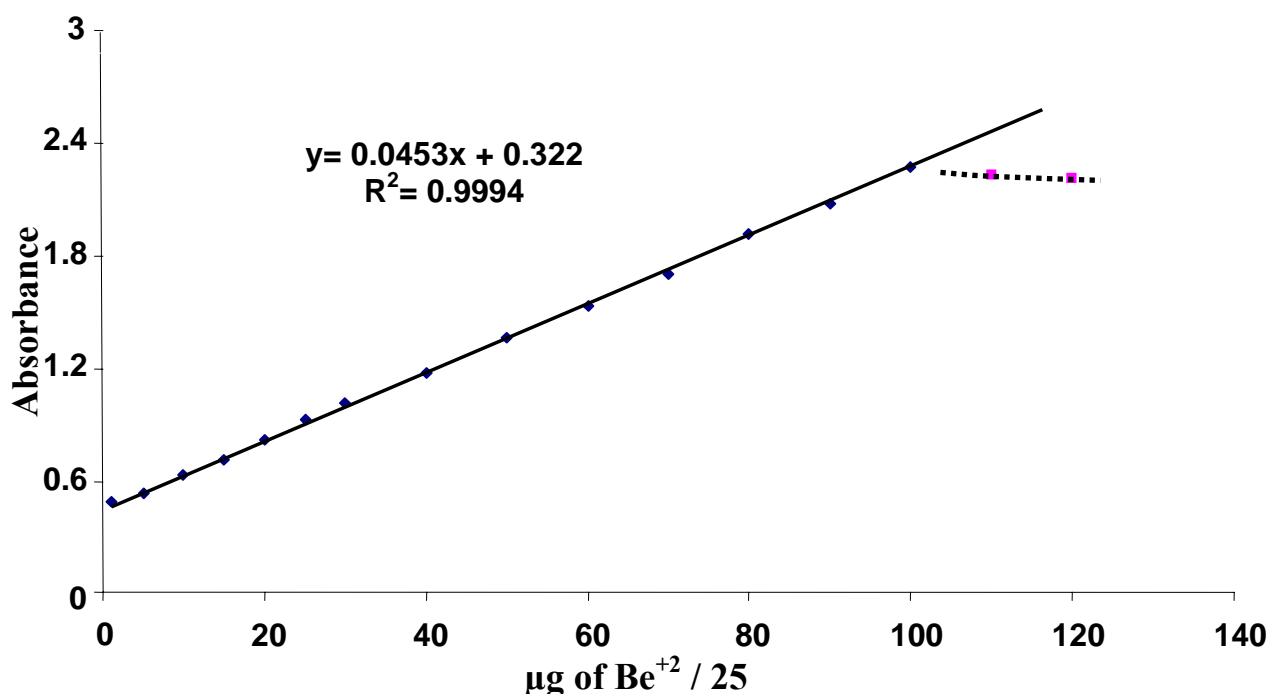


Fig. 1: Calibration graph of beryllium determination

RESULT AND DISCUSSION

Beryllium is complexed with chrome azurol S and CPC in presence of EDTA as a masking agent at pH 5.0, which form an intensely-coloured complex that shows an absorption maxima at 620 nm against reagent blank solution. The intensity of the coloured complex formed has been found to be proportional to the amount of beryllium originally present in solution.

Study of the experimental conditions

For the following investigations, 1 μg of beryllium is taken in 25 ml volumes.

Effect of pH:

The effect of pH on the intensity of coloured complex is studied by adding different amounts (0-3) ml of 0.001 M from both of sulphuric acid and sodium hydroxide solutions to an aliquot of solution containing 1 μg of beryllium. The intensity of absorption were measured against the reagent blank. The results are shown in Table 1 and 2:

Table 1: Effect of 0.001 M sulphuric acid.

ml of H_2SO_4 (0.001) M	Absorbance	λ_{max}	Final pH
0.0	0.310	615	5.70
0.1	0.389	617	5.50
0.3	0.396	619	5.27
0.5	0.436	619	5.10
1.0	0.314	619	4.80
1.5	0.295	618.5	4.63
2.0	0.239	617	4.47
2.5	0.204	618	4.39
3.0	0.189	618	4.26

Table 2: Effect of 0.001 M sodium hydroxide.

ml of NaOH (0.001) M	Absorbance	λ_{max}	Final pH
0.1	0.448	619	5.04
0.3	0.402	614	5.26
0.5	0.370	615	5.39
1.0	0.364	615	5.88
1.5	0.353	618	6.12
2.0	0.345	619	6.35
2.5	0.305	619.5	6.52
3.0	0.291	617	6.81

The results in Table 1 and 2 indicate that $\text{pH} \approx 5.0$ considered to be optimum. Several buffers (Purrin and Dempsey, 1974) of pH 5.0 are prepared and their effects on using different amounts are studied. The results are summarized in Table 3.

Table 3: Effect of buffer solutions.

ml of buffer	Absorbance */ ml of buffer added				
	Citric acid-NaOH	Sodium acetate-acetic acid	KH-phthalate-NaOH	Succinic acid-NaOH	Malic acid-Tris-NaOH
1	0.150	0.363	0.366	0.262	0.169
2	0.103	0.324	0.449	0.246	0.133
3	0.089	0.317	0.438	0.230	0.102
4	0.079	0.307	0.426	0.215	0.073
5	0.022	0.293	0.402	0.200	0.048

*Measured at $\lambda = 620$ nm.

** Tris= tris (hydroxymethyl) aminomethane.

The results in table 3 indicate that 2 ml of KH-phthalate-NaOH buffer gives maximum absorbance, hence, it is selected for the subsequent experiments.

Effect of masking agent:

Different amounts (0-5) ml of 0.01 M masking agent solution adjusted to pH 5.0 were examined. The results are shown in Table 4.

Table 4: Effect of masking agents.

ml of 0.01M masking agent adjusted to pH=5.0	Absorbance / ml of masking agent added				
	0.0	1.0	3.0	5.0	λ_{\max}
EDTA	0.451	0.519	0.523	0.492	620
NaF		0.097	0.054	0.022	619
NTA*		0.381	0.377	0.364	618
EGTA**		0.374	0.352	0.341	620
CDTA***		0.402	0.388	0.362	620

* NTA= Nitrilotriacetic acid.-bis(2-aminoethyl)-N,N,N,N-tetraacetic

**EGTA=Ethylenglycol-O,O acid.

***CDTA=Trans-1,2-diaminocyclohexane-N,N,N,N-tetraacetic acid monohydrate.

The results shown in table 4 indicate that the volume of 3 ml of 0.01 M EDTA solution is an optimum amount as it gives a sensitive reaction and lower blank value therefore, it is selected for the subsequent experiments.

Effect of reagent amount

Different volumes of 1×10^{-3} M chrome azurol S are added to 0.25-100 μg of beryllium (II) while other conditions being kept constant. A 1 ml of the reagent solution has been found to be optimum volume for 0.25-100 μg since the linearity (correlation coefficient) is good (0.998601) as shown in Table 5.

Table 5: Effect of reagent amount.

ml of 1×10^{-3} M chrom azurole S	Absorbance / μg of Be^{+2} in 25 ml							
	1	5	15	30	50	70	100	r^2
0.5	0.344	0.532	0.611	0.645	0.711	0.764	0.803	0.876739
1.0	0.498	0.62	0.81	1.09	1.56	2.02	2.522	0.998601
1.5	0.377	0.575	0.83	1.12	1.32	1.575	1.84	0.975092

Order of addition and stability of complex

To the metal ion solution (M), each of masking agent solution (M.A), buffer solution (B), hexadecylpyridinium chloride solution (CPC) and chrome azurole S solution (R) are added in possible orders. Experiment have showed that the order of addition (M+M.A+B+CPC+R) gives the best absorbance in each of the all order of additions tested, therefore this order is selected for subsequent experiments. The time for the absorbance of the coloured complex to reach a stable value is only 5 minutes, and the absorbance is then stable for at least 24 hours Table 6.

Table 6: stability of coloured complex.

Time, minutes	Absorbance / μg of Be^{+2} Present in 25 ml			
	1	5	10	50
1	0.511	0.556	0.665	1.508
3	0.517	0.564	0.675	1.510
5	0.519	0.567	0.677	1.511
10	0.519	0.571	0.680	1.511
20	0.519	0.571	0.683	1.511
30	0.519	0.571	0.680	1.511
40	0.519	0.571	0.680	1.513
50	0.519	0.570	0.680	1.511
60	0.518	0.571	0.680	1.511
70	0.519	0.571	0.682	1.511
80	0.519	0.571	0.680	1.509
100	0.519	0.571	0.681	1.511
120	0.519	0.571	0.680	1.511
24 hr.	0.517	0.571	0.681	1.511

Final absorption spectra

Absorption spectra of the coloured complex (beryllium-chrome azurole S-hexadecylpyridinium chloride) in presence of EDTA at pH 5.0 against its corresponding

reagent blank shows maximum absorption at 620 nm in contrast to the chrome azurol S reagent blank which shows a weak absorption at the same wave length as shown in Fig.2.

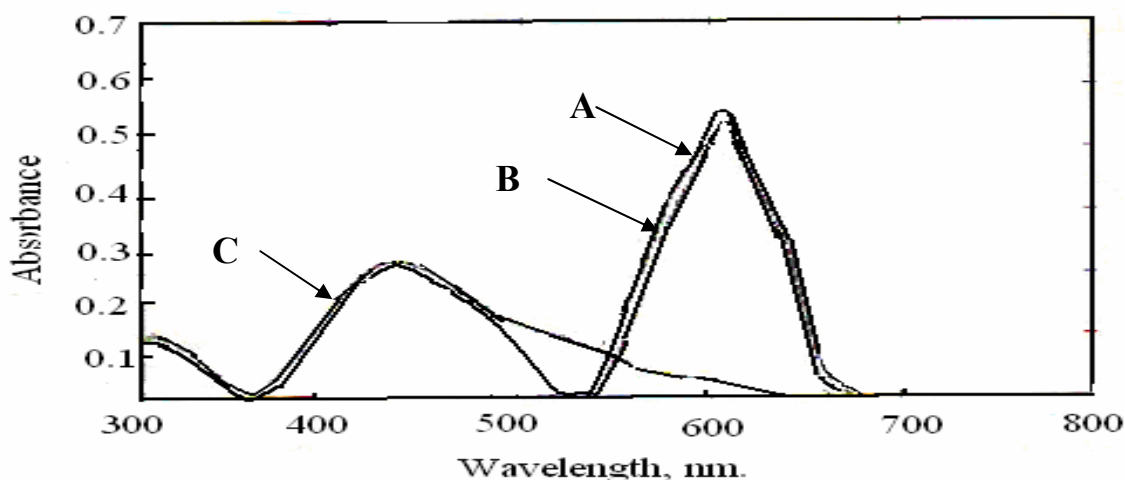


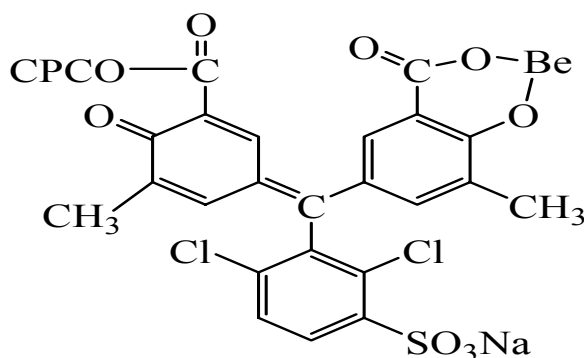
Fig.2: Absorption spectra of 1 μ g of beryllium /25 ml measured (A) against blank, (B) against distilled water, and(C) blank against distilled water.

Accuracy and precision

Under the experimental conditions which included in the recommended procedure, the recovery and precision of the method have been checked by performing five replicate determination for 1,5,10 μ g of beryllium the recovery and relative standard deviation are 100.46, 99.77, 99.98 and ± 0.0042 , ± 0.0023 , ± 0.0052 respectively, indicating the method has good accuracy and precision.

Nature of the coloured complex

Job's method of the continuous variations and mole ratio method have been used in the determination of the reaction ratio of beryllium with chrome azurol S reagent. The obtained results showed that the molar ratio of beryllium to chrome azurol S is found to be 1:1. The proportion of CPC in the complex is determined by measuring the absorbance of the mixtures containing beryllium and chrome azurol S in a 1:1 ratio and increasing amount CPC (in the same concentration of beryllium and reagent). Thus, the empirical formula of the coloured chelate may be written as below:



The Be-chrome azurol S-CPC complex

The average conditional stability constant of the coloured complex is found to be $0.16 \times 10^6 \text{ l.mol}^{-1}$.

Effect of foreign ions

The effect of many foreign ions on the determination of 1 μg beryllium per 25 ml of solution is examined under the experimental conditions used. The results obtain are summarized in table 7.

Table 7: Effect of foreign ions.

Foreign ion	Form added	Interference %			
		50	100	250	500
$\text{C}_2\text{O}_4^{=}$	$\text{Na}_2\text{C}_2\text{O}_4$	-0.82	-0.39	-0.78	-0.82
F^-	NaF	-74.86	-73.77	-73.91	-79.82
SO_3^{-2}	Na_2SO_3	-0.56	-0.59	-0.61	-0.66
NO_2^-	NaNO_2	-0.45	-0.49	-0.55	-0.67
NO_3^-	NaNO_3	-0.59	-0.61	-0.67	-0.71
$\text{CO}_3^{=}$	Na_2CO_3	-0.19	-0.34	-0.43	-0.46
Ca^{+2}	CaSO_4	-0.14	-0.23	-0.34	-0.41
Mg^{+2}	$\text{Mg SO}_4.7\text{H}_2\text{O}$	-0.32	-0.25	-0.14	-0.16
Li^+	$\text{Li}_2\text{SO}_4. \text{H}_2\text{O}$	Turbid	Turbid	Turbid	Turbid
Fe^{+3}	$\text{Fe}(\text{NO}_3)_3.5\text{H}_2\text{O}$	-49.82	-55.39	-56.78	-59.82
Fe^{+2}	$\text{FeSO}_4.7\text{H}_2\text{O}$	+0.47	+0.61	+0.86	+0.97
Al^{+3}	$\text{AlCl}_3.6\text{H}_2\text{O}$	+0.87	+0.91	+25.53	+40.83
$\text{S}_2\text{O}_3^{=}$	$\text{Na}_2\text{S}_2\text{O}_3.5\text{H}_2\text{O}$	-0.29	-0.41	-0.45	-0.52
PO_4^{-3}	$\text{NaH}_2\text{PO}_4.2\text{H}_2\text{O}$	-0.28	-0.39	-0.41	-0.45
Co^{+2}	$\text{Co}(\text{NO}_3)_2.6\text{H}_2\text{O}$	-0.66	-0.63	-0.97	-1.44
Hg^{+2}	$\text{Hg}(\text{NO}_3)_2. \text{H}_2\text{O}$	-0.55	-0.57	-0.60	-0.64
Cd^{+2}	$\text{Cd}(\text{CH}_3\text{COO})_2. \text{H}_2\text{O}$	+0.43	+0.68	+0.81	+0.89
Pb^{+2}	$\text{Pb}(\text{NO}_3)_2$	+0.56	+0.57	+0.69	+0.71
Bi^{+3}	$\text{Bi}(\text{NO}_3)_3.5\text{H}_2\text{O}$	-65.19	-67.65	-73.34	-77.19
Cr^{+3}	$\text{CrCl}_3.6\text{H}_2\text{O}$	-0.51	-0.66	-0.75	-0.93

The method seemed to be moderately selective, except toward Bi^{+3} , Fe^{+3} , F^- , which interfere seriously, perhaps this ions are masking of beryllium and avoid it to reacts with reagent, In case of the higher concentration of Al^{+3} , beryllium and its compound possess many properties similar to aluminium and its compounds. Thus organic and analytical reagents which are used for aluminium, frequently also find application in the analytical chemistry of beryllium ((Hotzbecher *et al.*, 1976).

Application of the method

The proposed method was applied to determine beryllium in different water samples. On applying procedure, good recovery is obtained as shown in table 8.

Table 8: Determination of beryllium in different water samples.

ml of water sample	Beryllium added μg	Recovery(%) of beryllium			
		Tap water	Tigris water	Sea water*	Well water**
2	1	100.62	99.86	98.41	100.12
4	1	99.13	100.36	97.98	99.75
6	1	99.86	96.79	98.87	99.15
2	10	100.13	98.66	100.76	99.24
4	10	100.29	100.19	98.41	100.50
6	10	99.98	100.28	97.99	98.56
2	30	100.39	100.55	98.84	100.53
4	30	97.89	97.81	100.77	97.85
6	30	99.27	99.27	97.88	99.24

* Sea water from middle east sea in lathiqya city /Syria.

**Well water from al-Shurra village in Mosul /Iraq.

The performance of the proposed method is assessed by calculating the student t-test with the literature method (Shekho, 2002). At the 95% confidence limit for five degree of freedom, the calculated t-values do not exceed the theoretical value (Table 9), indicating that there is no significant difference between the proposed method and the literature method (Shekho, 2002).

Table 9: The value of "t" test of natural waters.

Sample	Tap water	Sea water	Tigris water	Well water
The value of t-test	0.585	1.35	0.897	0.299

Comparison of methods

Table 10 shows the comparison of spectrophotometric methods for beryllium (II) determination.

Table 10: Comparison of methods.

Analytical parameter	Present method	Literature method (Pakalns, 1964)	Literature method (Uesugi, 1970)	Literature method (Beiraghi and Babae, 2007)	Literature method (Afkhami <i>et al.</i> , 2007)
pH	5.0	4.6	5.8–7.0	11.3	5.0
λ_{\max} (nm)	620	569	560	545	610
Reagent	Chrome azurol S	Chrome azurol S	Eriochrome brilliant violet B	1,8-dihydroxyant hrone	Chrome azurol S
prior step	-----	-----	-----	-----	Extraction
Beer's law range (ppm)	0.01 – 4.0	0-3.2	0.02–0.15	0.04-1.04	$(1 \times 10^{-7} - 2 \times 10^{-6} \text{ mol. L}^{-1})$
ϵ ($\text{l.mol}^{-1} \cdot \text{cm}^{-1}$)	1.02×10^4	0.406×10^4	0.595×10^4	0.470×10^4	-----
Masking agent	EDTA	EDTA	-----	EDTA	EDTA
Sandell's sensitivity	0.00883	-----	0.0002	-----	-----
RSD, %	$\pm 0.0023 - \pm 0.0052$	± 0.4	-----	± 0.43	-----
Interference	F^- , Fe^{+3} , Al^{+3}	Cr(III) , F^-	Cu(II) , Cd(II) , Ni(II) , Al(III) , Fe(III) , Cr(III) and the rare earth elements	Al(III) at high concentration	-----
Application of method	Various water samples	-----	-----	Beryl, silicate rock and alloys	spring water samples

It can be seen that the proposed method is one of the most sensitive method for beryllium determination.

CONCLUSIONS

The development of simple, sensitive, moderately selective and inexpensive spectro - photometric method for the determination of beryllium in different water samples has been carried out. The complex formed is stable, water soluble and has a maximum absorption at 620 nm with molar absorptivity of $1.02 \times 10^4 \text{ l.mol}^{-1} \cdot \text{cm}^{-1}$ and Sandall's sensitivity of $0.00883 \mu\text{g} \cdot \text{cm}^{-2}$. Beer's law is obeyed in the concentration range from 0.25-100 μg of beryllium in a final volume of 25 ml. the proposed method has been applied successfully to determination of beryllium in different water samples.

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