BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(2), 571—572 (1976)

The Spectrophotometric Determination of Beryllium with Chromazurol S and Polyoxyethylenedodecylamine

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(Received August 23, 1975)

Synopsis. A sensitive and selective method for the spectrophotometric determination of beryllium with Chro mazurol S (CAS) and polyoxyethylenedodecylamine(POEDA) in the presence of EDTA and perchlorate is proposed.

Sensitive methods for the spectrophotometric determination of beryllium with several triphenylmethane dyestuffs and cationic surfactants have been developed.[1-5] These methods are, however, subject to interferences from large anions, such as nitrate (above 4×10^{-2} mol/l) and perchlorate (above 4×10^{-4} mol/l), which precipitate easily by forming ion-pairs with the cationic surfactant.[2] In the present work, it is found that the effects of these anions can be appreciably eliminated by the use of a surfactant with a large polarity, such as polyoxyethylenedodecylamine {*N*,*N*-bis-(polyethylene glycol)-dodecylamine, abbreviated as POEDA}, and perchlorate in the spectrophotometric determination of beryllium with Chromazurol S(abbreviated as CAS).

Reagents and Apparatus. The standard beryllium solution (Be 1.00 mg/ml), the CAS solution (0.25%), the ethylenediaminetetraacetic acid disodium salt (abbreviated as EDTA) solution (1%), and the sodium acetate solution (1 mol/l) used in this work were the same as those described in previous papers.[2-4] POEDA solution (0.5%): the reagent (0.5 g) was dissolved in water containing 0.5 ml of 2 mol/l hydrochloric acid. The solution was adjusted to pH 4.5 with the sodium acetate solution and diluted to 100 ml with water. All the other chemicals used were of an analytical reagent grade. A Hitachi 139 spectrophotometer and 10-mm cells were used to measure the absorbance.

Recommended Procedure. A solution containing less than about 2 μg of beryllium was transferred into a beaker, there after 1 ml of the EDTA solution and 5 ml of a sodium perchlorate solution (5 mol/l) were added. The pH was adjusted to 4.5 with the sodium acetate solution, and the solution was evaporated to 5—10 ml.[3] By this procedure, interference from aluminum can be avoided by the easy complexing with EDTA. After cooling to room temperature, 1 ml of the CAS solution and 2 ml of the POEDA solution were added. The solution was transferred into a 25-ml volumetric flask and made up to volume with water. After the solution had then stood for 15 minutes, its absorbance was measured in a 10-mm cell at 605 nm against a reagent blank.

Effects of pH and Reagent Concentrations. The absorption maximum of the beryllium–CAS complex in the presence of POEDA is at 605 nm. The maximum absorbance is about four times higher than that in the absence of POEDA. The absorbance of the complex is almost constant over the pH range from 4.2 to 4.9.

A constant absorbance is obtained by the addition of more than 0.8 ml of the CAS solution (in the presence of 2 ml of the POEDA solution) and more than 1.5 ml of the POEDA solution (in the presence of 1 ml of the CAS solution). The addition of 1 ml of the CAS solution and 2 ml of the POEDA solution at pH 4.5 is, therefore, recommended.

A constant absorbance is also obtained by the addition of more than 0.8 ml of the EDTA solution. The maximum absorbance is obtained within 10 minutes after the color development and then remains constant for at least 10 hours.

Effect of the Concentration of the Perchlorate. A turbidity does not appear in the CAS–POEDA solution, even when 10 ml of a 5 mol/l sodium perchlorate solution are added. In the previous work, since the absorbance of the CAS–zephiramine solution increases with an increase in the ionic strength in the sample solution, the concentration of anions in the sample solution has to be held constant.[4] The effect of the concentration of anions on the absorbance of the CAS–POEDA solution is, therefore, examined. The effect of the concentration of perchlorate on the absorbance of the solution at pH 4.5 is shown in Table 1. The absorbance does not vary with the variation

Table 1. Effect of the concentration of sodium perchlorate on the absorbance of CAS-POEDA solution at pH 4.5

	Concentration of sodium perchlorate (mol/l)			
	0	0.5	1.0	2.0
Absorbance at 605 nm	0.228	0.230	0.230	0.234
	0.375[b]	0.250[a]	0.230[a]	0.230[e]
	0.425[d]	0.270[b]	0.232[b]	0.241[f]
	0.339[e]	0.276[c]	0.232[c]	0.232[g]
	0.350[h]	0.302[d]	0.248[d]	0.253[h]

Reference: water, Diverse anion added: a) nitrate (1 mol/l), b) nitrate (2 mol/l), c) chloride (1 mol/l), d) chloride (2 mol/l), e) sulfate (0.2 mol/l), f) sulfate (0.4 mol/l), g) acetate (0.1 mol/l), h) acetate (0.3 mol/l).

Table 2. Effect of the concentration of sodium perchlorate on the absorbance of the complex

	Concentration of sodum perchlorate (mol/l)				
	0	0.5	1.0	2.0	4.0
Absorbance at 605 nm	0.400	0.399	0.398	0.395	0.361

Reference: reagent blank, Be taken: 1.00 μg.

in the concentration of perchlorate. Up to 2 mol/l of nitrate and up to 1 mol/l of chloride in the presence of 1 mol/l of perchlorate also have no effect on the absorbance of the solution. The effect of the concentration of perchlorate on the absorbance of the complex is shown in Table 2. A constant absorbance is obtained by the addition of less than 10 ml of a 5 mol/l sodium perchlorate solution. The addition of 5 ml of the sodium perchlorate solution is, therefore, recommended.

Table 3. Effects of anions

Ion added (g)		Added as	Be found (μg)	Error (μg)
ClO_4^-	2.5	$NaClO_4$	0.99	−0.01
	7.5		0.90	−0.10
NO_3^-	1.5		0.99	−0.01
	3.0	$NaNO_3$	0.99	−0.01
	4.0		0.96	−0.04
Cl^-	1.0	NH_4Cl	0.99	−0.01
	2.0		0.97	−0.03
SO_4^{2-}	0.5		1.00	0
	0.7	Na_2SO_4	1.00	0
	1.0		1.09	+0.09
CH_3COO^-	0.10	CH_3COONa	1.00	0
	0.30		0.95	−0.05
F^-	0.003	NH_4F	0.95	−0.05

Be taken: 1.00 μg.

Table 4. Effect of cations

Ion added (mg)		Added as	Be found (μg)	Error (μg)
Ca^{2+}	1	$CaCl_2$	0.99	−0.01
Ba^{2+}	1	$BaCl_2$	0.99	−0.01
Mn^{2+}	1	$MnSO_4$	1.02	+0.02
Zn^{2+}	1	$ZnSO_4$	1.02	+0.02
Cd^{2+}	1	$CdSO_4$	0.98	−0.02
Pb^{2+}	1	$Pb(NO_3)_2$	1.00	0
Cu^{2+}	0.5	$CuSO_4$	1.03	+0.03
Ni^{2+}	0.5	$NiSO_4$	1.03	+0.03
Al^{3+}	0.2	$KAl(SO_4)_2$	1.01	+0.01
	0.5		1.10	+0.10
Fe^{3+}	0.3	$Fe(NO_3)_3$	1.03	+0.03
Mo^{6+}	0.1	$(NH_4)_6Mo_7O_{24}$	1.03	+0.03
V^{5+}	0.1	NH_4VO_4	1.03	+0.03

Be taken: 1.00 μg.

Effects of Diverse Ions. The effect of anions on the beryllium determination is shown in Table 3. Up to 2.5 g of perchlorate, 3 g of nitrate, 2 g of chloride, 0.7 g of sulfate, and 0.1 g of acetate do not interfere, but fluoride interferes seriously. The effect of cations on the beryllium determination is shown in Table 4. One mg of calcium, barium, manganese, zinc, cadmium and lead, 0.5 mg of nickel and copper, 0.3 mg of iron, 0.2 mg of aluminum, and 0.1 mg of molybdemum(VI) and vanadium(V) can be tolerated for the determination of 1 μg of beryllium, with a relative error of 3%.

Calibration Curve. As a result of the examinations described above, a procedure for the beryllium determination may be proposed. In the calibration curve obtained by the recommended procedure, Beer's law is obeyed over a concentration range up to at least 0.08 μg/ml and the apparent molar absorptivity at 605 nm is 9.0×10^4 l mol^{-1} cm^{-1}, which is 12% lower than that in the CAS–zephiramine method.[4]

The proposed method has the following merits compare with the CAS–zephiramine method:[4] it is adaptable to the beryllium determination in the sample solution containing perchlorate and nitrate as well as chloride, and it is unnecessary to hold the concentration of these anions constant within the range of concentrations described above.

References

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