Spectrophotometric Determination of Beryllium in Bronzes with Chrome Azurol S

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With 3 Figures

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There are many methods proposed in the literature for determination of beryllium¹. Among them spectrophotometric methods² are widely used due to their simplicity and sensitivity. However, most organic reagents used for spectrophotometric determination of metal ions are pH sensitive because they are usually present in different species depending on the pH and possibly complexing buffer ions. Thus, organometallic complex equilibria are manifold. Many analytical procedures and applications overlook the complexity of metal ion — ligand reactions in solutions. For example mixed ligand complexes can be formed by buffer components as potential ligands.

Analyzing some beryllium bronzes we found in the literature many controversial results and statements among different methods proposed. We decided to use for beryllium determination in bronzes a well known spectrophotometric reagent 3"'-sulpho-2",6"'-dichloro-3,3'-dimethyl-4-hydroxyfuchson-5,5'-dicarboxylic acid or its salts also known under names as Chrome Azurol S (CAS), Alberon, Solochrome Brilliant Blue B and Polytrop Blue R³⁻¹². The most detailed investigation of CAS application for beryllium determination was performed by Sommer and Kuban¹⁰,¹¹. It was shown that three different Be-CAS complexes are formed stepwise in solution containing a limited excess of CAS at three pH intervals i.e. BeRH⁻ at pH = 4.8—5.0, Be₂R₂⁴⁻ at pH = 6.4—7.0 and BeR(OH)₆⁻ at pH = 9.7—10.3. These authors preferred the procedure at pH = 6.5 ± 0.4 using
hexamethylenetetramine buffer in the presence of polyvinyl alcohol. Most other authors also prefer slightly acidic or neutral solutions\textsuperscript{3–12}, while Unemoto\textsuperscript{18} suggests the use of alkaline medium for determination of beryllium with CAS. To improve selectivity and sensitivity different masking agents and surfactants have also been proposed\textsuperscript{3–18} but in view of organometallic complex equilibria this represents additional complication despite the fact that under strict experimental control this can be of analytical use.

In this paper we demonstrate that CAS is very suitable reagent for reliable spectrophotometric determination of beryllium in bronzes and that the results obtained in alkaline medium are more reliable and less pH sensitive than those obtained in neutral or acidic medium, with only a very slight loss in sensitivity.

**Experimental**

*Chemicals and solutions.* All solutions used were of p. a. grade. Stock solution containing 4.69 \( \mu \)g/ml of Be was prepared from BeSO\(_4\).\( \cdot \)H\(_2\)O (Kemika). Beryllium content was determined by potentiometric titration using mercury indicator electrode\textsuperscript{16}. The solutions of 0.1 mol/l of Ca(NO\(_3\))\(_2\) (Kemika) and 0.001 mol/l of CAS (Merck) have been prepared by dissolving chemicals in bidistilled deionized water. Hexamethylenetetramine (\( c=1 \) mol/l) buffer was prepared by dissolving the reagent in small volume of water and adjusting the pH to 6.5 \( \pm \) 0.2 with HNO\(_3\) before dilution with water to 1 l. Polyvinyl alcohol (Merck) was used as 4% aqueous (w/v) solution. The ammoniacal buffer was used to adjust pH to 10.0 \( \pm \) 0.2.

*Instrumentation.* Electrogravimetric separation of Cu was performed by home made potentiostatic electrolyzer. Potentiometric titration and pH measurements were performed on Potentiometer E 436 (Metrohm). Visible spectra and absorbance measurements were performed on Spectrophotometer Acta III (Beckmann).

*Sample pretreatment.* A sample of about 1 g of bronze is accurately weighted and dissolved in 30 ml HNO\(_3\) (1 : 1), transferred to a volumetric flask (250 ml) and diluted with bidistilled water to the mark. An aliquot of 50 ml was electrolyzed at 2.5 V and 1.5 A for 45 min in order to separate Cu. To the aliquot 5 ml of HNO\(_3\) (conc.) and 1 g of urea were added and the electrolysis was performed at 60 \(^\circ\)C.

*Procedure for Be determination at pH=6.5 \( \pm \) 0.2.* To 5 ml of CAS (\( c=10^{-3} \) mol/l) and 10 ml of polyvinyl alcohol (4% w/v) in 50-ml volumetric flask add neutral or slightly acidic solution of sample containing from 5 to 130 ng Be. Dilute with water, add 2.5 ml of EDTA (\( c=0.1 \) mol/l), 3 ml of Ca(NO\(_3\))\(_2\) (\( c=0.1 \) mol/l) and 20 ml hexamethylenetetramine buffer (pH=6.5). Dilute with