Introduction

Mono- and bis-azo derivatives of chromotropic acid have been used for the spectrophotometric determination of plutonium\(^1\)\(^-\)\(^8\). Among them, Arsenazo III seems to give the most sensitive reaction\(^9\). The structure of Chlorophosphonazo III, 3,6-bis(4-chloro-2-phosphonophenylazo)-4,5-dihydroxynaphthalene-2,7-disulphonic acid, is analogous to that of Arsenazo III. Chlorophosphonazo III has two \(p\)-chlorophenylphosphonic groups as the functional groups, instead of the phenylarsonic groups in Arsenazo III. Nemodruk and others\(^2\)\(^,\)\(^4\) have suggested Chlorophosphonazo III as a reagent for the spectrophotometric determination of plutonium, but variables in the method have not been thoroughly examined.

The purpose of this investigation was to establish the optimal conditions for the determination of plutonium. The results obtained by the author differ considerably from those obtained by Nemodruk et al.\(^2\)\(^,\)\(^4\). Nevertheless, Chlorophosphonazo III is useful for the determination of \(\mu\)g amounts of plutonium.

Experimental

Reagents and Apparatus

Chlorophosphonazo III (Dojindo Co., Kumamoto-shi) was used without further purification.
Standard plutonium solution was prepared by dissolving 0.50 g of plutonium metal (U. S. NBS Standard reference material 949 b) in 100 ml of 1 M hydrochloric acid. Solutions containing 10 and 20 μg ml⁻¹ were obtained by diluting with 0.3 M hydrochloric acid. All other reagents were of analytical-reagent grade.

Absorbance measurements were made with a modified Shimadzu QB 50 spectrophotometer (1-cm cells) attached to a glove box. All the manipulations were carried out in glove boxes.

Recommended Procedure

To the sample containing 5 to 50 μg of plutonium in approximately 1 M hydrochloric acid, add 0.5 ml of 0.5 M hydroxylamine hydrochloride and heat for 30 minutes on a steam bath. After cooling, add 1 ml of 1 M potassium nitrite and allow to stand for 10 minutes. Transfer the solution to a 10-ml volumetric flask and add hydrochloric acid so that the acid concentration of the final solution is 1 M. Add 0.5 ml of 0.1% Chlorophosphonazo III solution and dilute to the mark with water. Measure the absorbance of the solution at 690 nm, using the reagent blank as the reference. Obtain the plutonium quantity from a calibration curve, which has been prepared with known amounts of plutonium.

Results and Discussion

Reagent. The synthesis of Chlorophosphonazo III was first described by Nemodruk et al. Later Ferguson et al. mentioned that they were unable to prepare Chlorophosphonazo III by the method of Nemodruk et al., and presented another method. The latter involves the use of 2-amino-5-chlorobenzenephosphonic acid. Buděšínský also recommended the latter method. Chlorophosphonazo III used in this work was synthesized by the method described by Buděšínský. Fig. 1 shows the absorption spectra of Chlorophosphonazo III in aqueous solution. The present curve agrees well with those presented by Ferguson et al. and Buděšínský et al.

Absorption spectra. Plutonium(IV) forms a green complex with Chlorophosphonazo III in dilute hydrochloric acid solution. As shown in Fig. 1, the complex has two absorption peaks at 630 and 685 nm; 690 nm was used for the determination.

Effect of acidity. The dependence of absorbance on the acidity was examined in the range 0.3 to 3 M in hydrochloric acid. Fig. 2 shows that the absorbance of the plutonium complex is almost constant in the range 0.5 to 2 M; 1 M was used in further in-