Accurate results are obtained in the pH range 4.8—6.0. pH 5.4 has been selected for further studies. One drop of indicator solution containing 5 μg of HDNZ in 100 ml of chloroform is sufficient to cause a sharp change of colour within a very short interval of time. A too large amount of indicator results in a too dark colour.

The following foreign ions did not cause any interferences: thiosulphate, borate, thiocyanate, chloride, bromide, iodide, citrate, tartrate, phosphate, fluoride, sulphate, perchlorate, nitrite, chromium, beryllium, barium, strontium and calcium. Out of the common anions only oxalate interferes. Attempts to mask mercury, zinc, copper, lead, nickel, cobalt and iron were unsuccessful.

The accuracy obtained by the proposed method is higher as compared to dithizone, whereas the sensitivity is comparable (0.0010 μg and 0.0012 μg for $\log I_0/I = 0.001$).

Recommended Procedure. An aliquot amount of EDTA (10 ml of 10^{-2} N) is taken in a Pyrex flask fitted with a ground glass stopper. A drop of indicator in chloroform and 10 ml of buffer (pH 5.40) is added. The whole mixture is titrated with the cadmium solution till the colour of the indicator changes from green to pink. The solution must be well shaken otherwise a stock of cadmium solution in presence of the indicator will be built up, thus causing a serious error in the titration. Addition of the drop of the indicator just near the end point helps in getting sharper end points.

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Complexometric Determination of Lead, Calcium and Phosphate in Ca- and Pb-Hydroxylapatites

Komplexometrische Bestimmung von Blei, Calcium und Phosphat in Ca- und Pb-Hydroxylapatiten

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A method for a rapid and accurate determination of lead, calcium and phosphate was desired in the course of physico-chemical investigations on synthetic solid solutions of calcium and lead hydroxylapatites. The complexometric procedure worked out is described below.

Procedure. Since the presence of phosphate interferes in the determination of calcium and lead by complexometric method, the phosphate was precipitated and separated first as ammonium phosphomolybdate [1]. The precipitate was dissolved in a minimum quantity of 0.1 M sodium hydroxide. In the presence of thymol-blue indicator it was reprecipitated as magnesium ammonium phosphate by the addition of a slight excess of 1 M magnesium sulphate at the appropriate pH obtained by the dropwise addition of 9.0 M ammonium hydroxide till the solution turned blue. It was separated by filtration, washed with 0.5 M ammonium hydroxide, dissolved in 5.0 M hydrochloric acid and a known excess of 0.05 M EDTA was added to it. The solution was then neutralised with 2 M sodium hydroxide and was finally titrated against 0.05 M magnesium sulphate at a pH $\sim$ 10 using Eriochrome Black T as indicator. From the volume of magnesium suphate consumed the amount of phosphate was calculated.

After the separation of phosphate calcium and lead were determined complexometrically. The filtrate was made up to a known volume. To a convenient volume of solution containing calcium and lead about 2.0 g of Rochella salt was added to suppress [2] the precipitation of lead as lead hydroxide in presence of buffer used (NH_4Cl/NH_4OH) to maintain pH $\sim$ 10 required for titration and the resulting solution was titrated against 0.05 EDTA using Eriochrome Black T as indicator. The total amount of lead and calcium was calculated from the volume of EDTA consumed.

The amount of lead in the same volume of aliquot used earlier could be determined by a similar titration masking calcium by the addition of ablut 2.0 g of ammonium fluoride [2]. The titration was carried out by using Eriochrome Black T as indicator at a pH $\sim$ 10. The amount of lead was calculated from the volume of EDTA consumed. The difference between the total amounts of calcium and lead obtained in the first titration and lead in the second titration gave the amount of calcium present in the aliquote.

When the method was applied to 0.6000 g of a synthetic solid solution of calcium and lead hydroxylapatites [$(Ca_{10}(PO)_4)_6(OH)_2 + Pb_{10}(PO_4)_6(OH)_2$] the weights found were: calcium, 0.1228 g; lead, 0.2331 g; and phosphorus, 0.0649 g; which gave a gram-atomic ratio per mole of (Ca + Pb)/P = 1.72 (theoretical value, 1.67).

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