COMPLEXOMETRIC DETERMINATION OF MAGNESIUM IN PRESENCE OF PHOSPHATE AND CHROMATE

SOLUTIONS containing $Mg(NO_3)_2$ with a large excess of H_3PO_4 and H_2CrO_4 are used for etching metals in electrochemical industry. Gravimetric determination[1] of magnesium after precipitation of Mg as $MgNH_4PO_4 \cdot 6H_2O$ is time consuming and cumbersome. Volumetric method using EDTA as a titrant is fast and sufficiently accurate for general determinations[2]. But this method is not practicable in the presence of large quantities of certain interfering anions like $(PO_4)'''$[3] and $(CrO_4)''$[4]. In the presence of $(PO_4)'''$, magnesium gets precipitated at the pH of the titration. Mg-EDTA complex being strong, titration can still be performed to a sharp end point. However, experiments in this laboratory have shown that EDTA titration of Mg^{2+} gives somewhat lower values (recovery $\approx 94\%$) when the solution contains $Mg(NO_3)_2 : H_3PO_4$ in the ratio 1 : 5. Titration of metal ions with EDTA is affected by the presence of a large concentration of chromate. Thus it is preferable to separate this from the solution before the titration.

Ion exchange method is suggested for removal of (PO_4''')[7]. Trial experiments have shown that small amounts of chromate can be removed by anion exchange resin—De acidite FF-IL.P; but at the level of concentrations used in etching solutions, a larger column would be necessary. The effluent from the resin was turbid and gave erratic titrations. Chromate at high concentrations attacks the resin. The following method is reliable and also rapid for monitoring magnesium in such solutions after separating both chromate and phosphate.

Experimental

Materials.—The reagents employed were of A.R. quality and the solulions were pepared and standardised by the usual methods.

Proposed method.—Six mixtures of different compositions with respect to chromic and phosphoric acid with known magnesium content were used for the analysis of magnesium. In all cases the content of magnesium nitiate $Mg(NO_3)_2$ was about 2% while the concentration of chromic acid varied from 0-20% and that of phosphoric acid varied from 0 10%. One solution containing about 2·5% magnesium nitiate, 20% chromic acid and 10% phosphoric acid was also employed. Magnesium content in these mixtures was determined by the following complexometric method:—

A suitable aliquot of the solution containing a known quantity of magnesium nitrate (0·2g) was taken in a 250 ml flask. Sufficient amount of 10% lead acetate was added in a thin stream while the flask was shaken. The pH of the solution was around 2·5. The solution was made up to 250 ml, shaken and was allowed to settle. The clear supernatant was filtered through a dry filter, the first 10–20 ml filtrate was rejected, the rest was collected in a clean, dry flask. A 25 ml aliquot was pipetted to a conical flask; 0·5 to 1·0 g of sodium diethyldithiocarbamate was added to complex the lead; about 10 ml of ammonia buffer of pH 10 was added; (a precipitate at this stage indicated lead in the original soluion); indicator methyl thymol blue complexone triturate was added; the solution was warmed to 40–50° and titrated with standard EDTA from blue to grey end point. Magnesium content in the original solution was calculated from the titre value. Recovery was found to be around 99·5% in all cases.

The magnesium content was also determined by two titrations, one for the sum of magnesium and lead at pH 10 and the second for lead only at pH 6. These values also agreed with the above titration results. However the authors prefer to mask lead and titrate for magnesium at pH 10 because titration for lead in acetate medium is likely to give low results[6].

Most metal phosphates have a low solubility but they do not get precipitated in acid medium because of the low dissociation constants of H_3PO_4 ($K_1 \approx 2$, $K_{12} \approx 7$ and $K_{13} \approx 12$)[8]. Least soluble of all the phosphates are those of Ce^{4+} [K_s of $Ce_3(PO_4)_4 \approx -90$] and Th^{4+} [K_s of $Th_3(PO_4)_4 \approx -78{\cdot}6$][8]. Of the more common metals, lead phosphate has the least solubility [K_s of $Pb_3(PO_4)_3 = -42{\cdot}10$][9]. Solubility products of lead phosphate and magnesium phosphate are so far separated that it is possible to precipitate phosphate as lead phosphate completely before magnesium is precipitated. Presence of at least 0·1 M lead ions in a solution of pH 2 or 0·005 M lead ions in a solution of pH 3 ensures that the phosphate content in solution is $< 10^{-4}$ M.

Lead chromate is also an insoluble salt (K_s of $PbCrO_4 \approx -13$, K_1 and K_{12} of H_2CrO_4'' are 6·57 and 4·15). Presence of at least 0·1 M lead ions in a solution of pH 2 or 0·002 M lead ions in a solution of pH 3 ensures that the chromate content in the solution $<10^{-4}$M.

Thus the removal of phosphate and chromate by precipitation with lead needs pH above 2·5. Most suitable pH range is 2·5–4·5. It is found that at pH values of the order of 5, the precipitate is very fine, does not settle easily and passes through the filter. In cases, where the final pH is nearly 5 it can be brought down by the addition of a little acetic acid or nitric acid as the condition needs.

In cases where magnesium is precipitated as magnesium ammonium phosphate the estimation of magnesium can be completed by volumetry by slightly modifying the above method. The precipitate is dissolved

in 10 ml of dilute nitric acid, the solution is transfered to a 250 ml volumetric flask with 10 ml of acetic acid. Lead acetate is added to precipitate the phosphate and the pH is adjusted to 2·5–3 and the determination of magnesium is completed by the above procedure. This method can also be used as an indirect method of estimating total phosphate content in any solution.

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Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, *February* 14, 1980.

S. K. VIJAYALAKSHAMMA.
H. S. SATYANARAYANA RAO.

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CHEMOTYPIC STUDIES IN NATURAL POPULATIONS OF *RAUVOLFIA SERPENTINA* FROM CERTAIN REGIONS OF KARNATAKA STATE, INDIA

Rauvolfia serpentina (L.), Benth. Ex-Kurtz, belonging to family *Apocyanaceae*, is recognised as an important source of reserpine contained in its roots. Reserpine is considered to be effective in treatment of hypertension all over the world. The plant is indigenous to India, growing wild in the lower hills and in the plains throughout the country. In view of its wide habitat it is natural to expect existence of its geographical races expressing variation in morphology and alkaloid content. With this objective in view, certain regions of South Kanara in the South-west of Karnataka and along its coastal area were surveyed in September–October, 1977, for collection of *R. serpentina* from its natural populations abounding in this area (Kazim)[1]. The regions falling between 12° and 16° N comprised Mangalore, Coondapur and Haliyal. The actual places of collection in each district/taluqua averaged about 10 and the number of plants collected from each place ranged from 15–20. During collection, whole plants were uprooted and their vegetative portion was cut off retaining only about 10 cm of the stem. Such cut plants were then planted in pots at Delhi and nursed. When 1½ years old (in February, 1979), these plants were taken out from the pots; roots were cut and bulked locality-wise. Thus, there were as many samples as the sites of collection in each district/taluqua. These bulked samples were used for the estimation of total alkaloid content. Other material included in the study consisted of 15 collections from Haldwani (U.P.), 17 seedlings from a grafted plant (with *R. tetraphylla* as root-stock and *R. serpentina* as scion) and a control (I.W. 1188–16) released earlier by Mital *et al.*[5]. In these studies, age of all the plants was the same (*i.e.*, 1½ year old) as in Karnataka collections excepting graft seedlings which were 3 years old. In the case of control, the population was small, and hence, only one bulk sample could be taken for analysis.

The bulk samples were analysed for total alkaloid content (*Indian Pharmacopoea*[1]), and their range, mean etc., were obtained as given in Table I.

TABLE I

Range of alkaloid content, mean, C.V. and S.D. in R. serpentina *collections*

Plant material	Range (alkaloid %)	Mean (alkaloid %)	C.V.	S.D.
Seedlings from graft	0·976–1·874	1·416	21·8	·310
Haldwani stock	1·266–1·874	1·516	25·9	·394
Haliyal material	1·402–1·922	1·621	13·6	·220
Mangalore material	1·295–1·735	1·516	9·4	·142
Coondapur material	1·526–2·034	1·806	9·9	·175
Control (IW 1188–16)	..	1·067	..	..

The data were further subjected to T-test as shown in Table II. (excluding the control since it consisted of only one sample).