the hydrogen bonding nature of chloroform and its possible interaction with the nitrogen of the amine group or the anion of the amine salt. This results in a decrease in the concentration of the extractant and the distribution ratio.

The authors wish to thank Dr A. K. Ganguly, Director (Retd), Chemical Group and Dr A. K. Sundaram, Analytical Chemistry Division for their interest and helpful suggestions.

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Spectrophotometric Determination of Niobium(V) as a Mixed Ligand Complex of Protocatechuic Acid & 1,2-Diaminocyclohexanetetraacetic Acid

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Niobium (V) has been determined spectrophotometrically as a mixed ligand complex with protocatechuic acid and trans-1, 2-diaminocyclohexanetetraacetic acid (DCTA). Measurements are carried out at 460 nm at pH 3.0, in tartrate medium, 30 min after the preparation of the solution at room temperature. The system obeys Beer's law over the range 0.37-9.66 μg of Nb/ml. The sensitivity of the method is 0.013 μg/ml of Nb. Interference due to many ions has been studied. Niobium has been also determined successfully in a few synthetic cationic mixtures.

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METHODS for the spectrophotometric determination of niobium are not many[1,2]. Some methods based on the color reactions with azodyes have been reported but these are quite unselective and many polyvalent metal ions interfere[3,4]. The present note describes a method for the determination of Nb(V) in the form of its mixed ligand complex with protocatechuic acid and DCTA in tartrate medium. Optimum conditions have been established for the determination of niobium singly and in the presence of foreign ions. A few synthetic cationic mixtures containing Nb have also been analysed.

A Bausch and Lomb Spectronic 20 spectrophotometer using 0.5″ matched cells and a Systronics pH meter (type 322-1) were used.

Niobium(V) solution (10^{-3} M) was prepared by fusing 26.6 mg of the specpure grade niobium pentoxide (Johnson Mathey) with 1 g of potassium bisulphate in a platinum crucible. After cooling the melt and dissolving it in 0.75% tartaric acid, the volume was made upto 100 ml. A 10^{-2} M solution of DCTA (K & K Labs) was prepared and a few drops of sodium hydroxide were added to get a clear solution. Freshly prepared 0.1 M solution of protocatechuic acid (BDH) in 15% aqueous alcohol and 0.75% tartaric acid (GR, Merck) were used.

Procedure — To an aliquot containing 9.0-240μg of Nb, protocatechuic acid solution (12 ml) and DCTA solution (7.5 ml) were added and the pH was adjusted to 3.0 ± 0.1 with hydrochloric acid or dilute sodium hydroxide. Volume was made up to 25 ml with distilled water of the same pH. The absorbance was measured, at 460 nm, 30 min after the preparation of the solution at room temperature. The amount of Nb present was calculated from a calibration graph.

Niobium in tartrate medium forms an yellow complex with protocatechuic acid in basic medium of pH 10 with λ_{max} at 325 nm and with DCTA alone colourless solution results. But when both the reagents are mixed with Nb and the pH adjusted to ~3.0, an intensely colored orange-red complex with λ_{max} at 460 nm results. Whereas most of the polyvalent metal ions form a similar yellow colored complex with protocatechuic acid in neutral medium, only niobium forms the orange-red colored complex under these conditions thus making the method a selective one. Formation of a similar complex by tantalum is suppressed by tartrate.

To study the effect of pH two different series of solutions were prepared, with and without DCTA, containing metal (1 ml) and protocatechuic acid (10 ml). The pH was varied between 1.0 and 8.0. From the observations it was clear that DCTA takes part in complexation only in a narrow pH region (2.0-4.0). Further, it was found that the absorbance values of the mixed complex remained constant between pH 2.6 and 3.6. So pH of 3.0 ± 0.1 was chosen as optimum for the present studies.

It was found that the formation of the mixed complex is complete within 25 min and the absorbance values remained constant for several days indicating the high stability of the complex. In all

the experiments absorbance values were noted 30 min after mixing the solutions at room temperature. The complex was found to be stable between 20 and 30°. Beyond these temperatures the absorbance values changed. Therefore all the readings in the present studies were taken at room temperature.

When protocatechuic acid in the range 11-13 ml, DCTA in the range 6-13 ml are mixed with 1 ml of metal solution at pH 3.0 and the total tartaric acid concentration maintained between 1.0 and 2.5 ml including the tartrate taken alongwith Nb (in tartrate medium), the absorbance values at 460 nm remain constant.

Beer's law and sensitivity — The optimum concentration range of Nb in the present method of estimation is 0.37-9.66 μg/ml and Beer's law is obeyed strictly in this region. The average molar absorptivity and Sandell sensitivity index are 7.15×10^3 moles/litre cm and 0.013 μg Nb/ml respectively.

Effect of foreign ions — The detailed interference study of various foreign ions is presented in Table 1.

Niobium was successfully estimated in the following synthetic mixtures using the present procedure.

TABLE 1 — INTERFERENCE STUDIES OF VARIOUS FOREIGN IONS

[Nb taken 37.16 μg]

Foreign ion added	Quantity added (μg)	Ratio of foreign ion to niobium	Niobium obtained (μg)	Difference
Ta(V)	180	5.0	37.16	0.0
"	221	6.0	37.16	0.0
"	442	12.0	27.16	—10.0
Ti(IV)	80	2.1	37.16	0.0
"	180	5.0	44.16	+7.0
Fe(III)	279	7.5	37.16	0.0
"	558	15.0	44.16	+7.0
"	558*	15.0	37.16	0.0
Sn(II)	237	6.4	37.16	0.0
"	474	12.8	29.16	—8.0
Cr(III)	47	1.3	37.16	0.0
"	94	2.6	45.16	+8.0
U(VI)	4760	120.0	38.16	+1.0
Th(IV)	3350	90.0	39.16	+2.0
Y(III)	1800	48.5	37.16	0.0
Be(II)	180	5.0	37.16	0.0
Cu(II)	635	17.0	37.16	0.0
Al(III)	270	7.3	37.16	0.0
Zn(II)	653	17.5	37.16	0.0
"	1306	35.0	43.16	+6.0
Zr(IV)	182	5.0	37.16	0.0
Sb(III)	1217	33.0	37.16	0.0
Ni(II)	293	7.9	37.16	0.0
Mn(II)	274	7.4	37.16	0.0
W(VI)	1286	34.6	37.16	0.0
Pb(II)	2072	56.0	37.16	0.0
Hg(II)	2000	54.0	37.16	0.0
Ca(II)	400	10.8	37.16	0.0
NH$_4$(I)	640	17.3	37.16	0.0
Na(I)	5700	154.0	37.16	0.0
K(I)	5700	154.0	37.16	0.0
Phosphate	1800	48.7	37.16	0.0
Sulphate	3000	81.0	37.16	0.0
Nitrate	3720	100.0	37.16	0.0
Chloride	2000	54.0	37.16	0.0

*Ascorbic acid (0.1 g) was added.

(i) Nb_2O_5 (53.14 μg) + ZrO_2 (6.16 μg) + U_3O_8 (241.1 μg).

(ii) Nb_2O_5 (44.34%) + Ta_2O_5 (8.05%) + TiO_2 (1.62%) + SiO_2 (0.22%) + SnO_2 (1.48%), Fe_2O_3 (14.77%) + CaO (0.94%) + MgO (0.03%) + Al_2O_3 (0.79%) + ThO_2 (1.21%) + Ce_2O_3 (0.8%) + Y_2O_3 (13.93%) + MnO (1.60%) + PbO (2.04%) + U_3O_8 (6.03%) Na_2O(0.29) + K_2O (0.21%) (corresponds to the composition of Samerskite mineral).

This method will be useful for the determination of niobium in minerals and alloys.

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Rapid Spectrophotometric Determination of Microgram Amounts of Cerium(IV) & Arsenic(III) with Tetrasulphonated Metal Phthalocyanine Complexes

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Cerium (IV) can be selectively determined spectrophotometrically in the presence of other rare earths by its reaction with excess of tetrasodium salt of cobalt(II) 4, 4′, 4″, 4‴-tetrasulphophthalocyanine 2-hydrate (Na$_4$CoPTS), nickel (II) 3′, 3″, 3‴-tetrasulphophthalocyanine [Na$_4$Ni(3-3″) PTS] or nickel(II) 4, 4′, 4″, 4‴-tetrasulphophthalocyanine (Na$_4$NiPTS). The decrease in the absorbance of Na$_4$ CoPTS, Na$_4$Ni (3-3″) PTS or Na$_4$NiPTS compared with the reagent blank is a measure of the amount of Ce(IV) present. The method has been successfully used for the determination of cerium in cerium alloys. Arsenic(III) has been indirectly determined.

MOST of the spectrophotometric methods for the estimation of cerium are not very sensitive and do not tolerate the interferences from associated foreign ions. The authors have now investigated the use of tetrasodium salts of cobalt(II) 4,4′, 4″,4‴-tetrasulphophthalocyanine 2-hydrate (Na$_4$CoPTS), nickel(II) 3,3′,3″,3‴-tetrasulphophthalocyanine [Na$_4$ Ni(3-3″)PTS] and nickel(II) 4,4′,4″,4‴-tetrasulpho-