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Synthesis and Ion-Exchange Behavior of a New Three-Component Ion-Exchange Material: Zirconium(IV) Arsenate Vanadate

Saidul Zafar Qureshi,* Mubeen Ahmad Khan, and Nafisur Rahman

Analytical Chemistry Division, Department of Chemistry, Aligarh Muslim University, Aligarh-202002, India

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Zirconium(IV) arsenate vanadate was prepared by adding a mixture comprising 0.05 M sodium hydrogen arsenate and 0.05 M sodium metavanadate to an aqueous solution of zirconium(IV) dichloride oxide (0.05 M) in different volume ratios at pH 1. The material possessed a good ion-exchange capacity of 1.20 and 1.30 meq g^{-1} of exchanger for the Na$^+$ and K$^+$ ion, respectively, and was fairly stable in dilute mineral acids, but insoluble in water, acetic acid, formic acid, ethanol, and 1,4-dioxane. The distribution coefficients of a large number of metal ions were determined in different solvent systems.

Analytical applications of synthetic inorganic ion-exchange materials with higher selectivities and resistance at moderately high temperature have now been well established.[1] Acidic salts of multivalent metals, prepared in combination with the anions of phosphate, arsenate, tungstate etc. as two-component ion exchangers have been studied most intensively.[2,3] Zirconium phosphate is directly used to remove ionic impurities from water at high temperature in pressurized-water reactors.[4,5] Moreover, they are very effective in removing trace inorganic constituents.[6] Phosphate and arsenate of zirconium show good thermal and chemical stabilities,[2,3] while only little work has been done on zirconium vanadate.[7]

In order to obtain reproducible characteristics of inorganic ion exchangers, various sets of conditions are employed for the preparations. These are (i) aging, (ii) pH control of the gel so formed, (iii) sequence of the addition of one reagent to another, (iv) refluxing etc. A study of the literature has shown that the three-component ion-exchanger possesses an increased ion-exchange capacity and selectivity compared to that of two-component materials.[8—22] The increased ion-exchange capacity can be explained in terms of a three-dimensional network of the ion-exchange material and pK_a values of acid anionic groups incorporated into the matrix.[17] In this manuscript we describe the preparation and properties of zirconium(IV) arsenate vanadate. It has been successfully used for the quantitative separation of Cr^{3+} from numerous metal ions.

Experimental

Reagents: Zirconium(IV) dichloride oxide (BDH), sodium hydrogen arsenate (E. Merck), and sodium metavanadate (E. Merck) were used for the synthesis of ion-exchange materials. All other chemicals used were of analytical grade.

Apparatus: A Toshniwal (India) single-electrode pH meter was used for pH measurements. Bausch & Lomb spectronic 20 and 1001 spectrometers as well as a Perkin–Elmer 137 spectrophotometer were used for spectrophotometric and IR studies, respectively. A Philips P.W-1140 diffractometer with nickel-filtered Cu $K\alpha$ radiation was used to obtain X-ray diffraction patterns of the material.

Synthesis: A zirconium(IV) arsenate vanadate ion-exchanger was prepared by mixing 0.05 M sodium hydrogen arsenate (1 M=1 mol dm^{-3}) and 0.05 M sodium metavanadate to 0.05 M zirconium(IV) dichloride oxide in different volume ratios at pH 1. The thus-formed gel was kept standing for 24 h at room temperature. It was then filtered and washed with distilled water several times in order to remove any excess reagent until a pH of 6 was obtained, and then dried at 40 °C in an oven. The material was broken into smaller particles by shaking in distilled water. The ion-exchanger granules, which showed cationic properties, were converted into the H$^+$ form by immersing in 1.0 M HNO_3 for 24 h. These granules were finally washed with distilled water until pH 6, and dried at 40 °C. The different samples prepared under different sets of conditions are named: ZAV_1, ZAV_2, ZAV_3, ZAV_4, ZAV_5. Sample ZAV_5 was chosen for further studies owing to its high ion-exchange capacity as well as thermal and chemical stability.

Ion-Exchange Capacity: A 0.50 g, exchanger in H$^+$ form was packed into a column (0.6 cm i.d.) with a glass-wool support. The ion-exchange capacity was determined as described earlier,[17] by passing a 1 M solution of different univalent and bivalent metal salts.

Chemical Stability: A 0.50 g exchanger material (ZAV_5) was equilibrated with 50 ml of the solution of interest at room temperature, and subsequently kept for 24 h with occasional shaking. Zirconium ions released in the solution were determined titrimetrically using Xylenol Orange as an indicator.[23] Arsenic and vanadium were deter-

Table 1. Synthesis and Properties of Zirconium(IV) Arsenate Vanadate

Sample No.	Mixing ratio Zr : As : V	pH	Appearance of precipitate	Composition	Ion exchange capacity for K^+ mequiv g^{-1} dry exchanger at pH 6.5
ZAV_1	1 : 1 : 1	1	Yellowish green gel	1.78 : 1 : 1.30	0.36
ZAV_2	1 : 1 : 2	1	Yellowish green gel	1.76 : 1 : 1.50	0.69
ZAV_3	1 : 2 : 2	1	Yellowish white gel	1.96 : 1.03 : 1	0.88
ZAV_4	1 : 2 : 1	1	Yellowish green gel	2.28 : 1.24 : 1	0.90
ZAV_5	1 : 3 : 1	1	Yellowish green gel	3 : 2 : 1	1.30

Samples were prepared from 0.05 M each of $ZrCl_2O$, Na_2HAsO_4, and $NaVO_3$. Color of beads after drying at 40 °C was almost the same as the gel but shiny.

mined spectrophotometrically using ammonium molybdate-hydrazinium sulfate[24)] and sodium tungstate[25)] as coloring reagents, respectively. The results are summarized in Table 3.

pH Titration: The pH titration of the ion-exchange material (ZAV_5) was carried out by the method of Topp and Pepper.[26)] Several samples of the exchanger (0.5 g) were equilibrated with 50 ml of 0.1 M KCl–KOH and 0.1 M NaCl–NaOH solutions.

Chemical Composition: For determining the chemical composition of the samples, 0.10 g of the exchanger was dissolved in hot concentrated sulfuric acid; the solution was then diluted to 100 ml with distilled water and zirconium, arsenic and vanadium were determined.[23—25)] The mole ratios of Zr, As, and V are given in Table 1.

Distribution Coefficient: The distribution coefficients for 21 metal ions in different solvent systems were determined. A 0.50 g exchanger in the H^+ form (40—50 mesh) was treated with 50 ml of a 1×10^{-2} M metal salt solution in a 250 ml Erlenmeyer flask. The mixture was then kept for 24 h at room temperature, and subsequently determined by titrating against the standard solution of EDTA. The K_d values were calculated according to the formula

$$K_d = \frac{[M_{ex}]}{[M_{aq}]},$$

where M_{ex} is mmoles of the metal ionic species in the exchanger phase/g of the exchanger and M_{aq} is mmoles of metal ionic species remaining in the aqueous phase/ml of the total volume of the resultant solution.

Separation of Metal Ions: A quantitative separation of metal ions was achieved on a 0.6 cm (i.d.) glass column using a 5.0 g exchanger (40—50 mesh) in the H^+ form. A metal-ion mixture was poured onto the top of the column. The flow rate of the effluent was maintained at 1 ml min^{-1} throughout the elution process.

Results and Discussion

Table 1 describes the preparation of samples of zirconium(IV) arsenate vanadate. It is apparent from this table that ion-exchange capacity of the material is strikingly dependent upon the ratio of Zr : As : V in the product; also, the molar ratio of Zr : As : V of the exchanger prepared under a different set of conditions was greatly dependent upon the mixing ratio of the component; that is, the arsenic content in the exchanger increased as the mixing ratio increased. Accordingly, the greater was the arsenic content, the higher was the capacity of the exchanger.

The ion-exchange capacities for alkali and alkaline earth metal ions were determined by a column method, and are reported in Table 2. It clearly indicates that the ion-exchange capacity increases along with a decrease in the hydrated ionic radii of the ingoing metal ions. This is in agreement with the findings of Nachod and Wood,[27)] who investigated the exchange of alkali and alkaline earth metal ions on a zeolite.

The stability of zirconium(IV) arsenate vanadate in different solvent system is given in Table 3. The ion-exchange material can be utilized to separate metal ions involving dilute mineral acids and neutral solutions. The material is also quite stable in moderate concentrations of organic acids, like acetic acid and formic acid.

Table 2. Ion Exchange Capacity (meq g^{-1} dry Exchanger) of Zirconium(IV) Arsenate Vanadate (Sample ZAV_5) for Various Cations at pH 6.5 and 25±1 °C

Sample No.	Cation	Hydrated ionic radius Å	Ion-exchange capacity (mequiv g^{-1} dry exchanger)
1	Li^+	10.0	0.87
2	Na^+	7.9	1.20
3	K^+	5.3	1.30
4	Mg^{2+}	10.8	0.65
5	Ca^{2+}	9.6	0.87
6	Sr^{2+}	9.4	0.88
7	Ba^{2+}	8.8	0.93

Table 3. Chemical Stability of Zirconium(IV) Arsenate Vanadate (ZAV_5) in Different Solutions

Solutions	Zirconium(IV) released mg/50 ml	Arsenic released mg/50 ml	Vanadium released mg/50 ml
1 M HCl	0.27	0.90	0.14
2 M HCl	0.03	0.80	0.18
4 M HCl	1.36	2.00	0.29
1 M HNO_3	0.22	1.10	0.00
2 M HNO_3	0.82	2.80	0.21
1 M H_2SO_4	3.19	3.00	1.20
2 M H_2SO_4	3.99	4.10	2.40
1 M $HClO_4$	0.22	0.13	0.00
2 M $HClO_4$	0.45	0.29	0.00
2.0 M CH_3COOH	0.13	0.15	0.12
1.0 M HCOOH	0.00	0.50	0.00
0.1 M NaOH	1.2	0.98	0.70
1.0 M NaOH	4.65	2.70	2.87
2.0 M NaOH	10.74	5.40	6.95
0.1 M aq NH_3	0.00	0.70	0.00
1-Butanol	0.00	0.02	0.00
DMSO	0.00	0.05	0.02

This sample is not soluble in H_2O, CH_3COOH (up to 1 M), ethanol, and dioxane.

It is also not soluble in water, ethanol and 1,4-dioxane. In aqueous sodium hydroxide there occurs a deterioration in its stability upon increasing the concentration of alkali.

The pH titration curve of zirconium(IV) arsenate vanadate shows (Fig. 1) two inflection points, which indicate that the exchanger is bifunctional. The first end point occurs at 1.30 and 1.20 meq g^{-1} and the second end point at 2.6 and 2.45 meq g^{-1} exchanger for K^+ and Na^+ ions, respectively.

The IR spectrum of zirconium(IV) arsenate vanadate in H^+ form shows a very strong peak in the region of 3400—2900 cm^{-1} with a maximum at 3300 cm^{-1}, which is the characteristic band of interstitial water, free water and OH groups. The strongly hydrogen-bonded OH or strongly coordinated H_2O also falls in the same region.[28] Another peak in the 1700—1580 cm^{-1} region is the characteristics of H–O–H bending vibration. The band which occurred in the 1000—750 cm^{-1} region was due to the presence of arsenate and vanadate.[29]

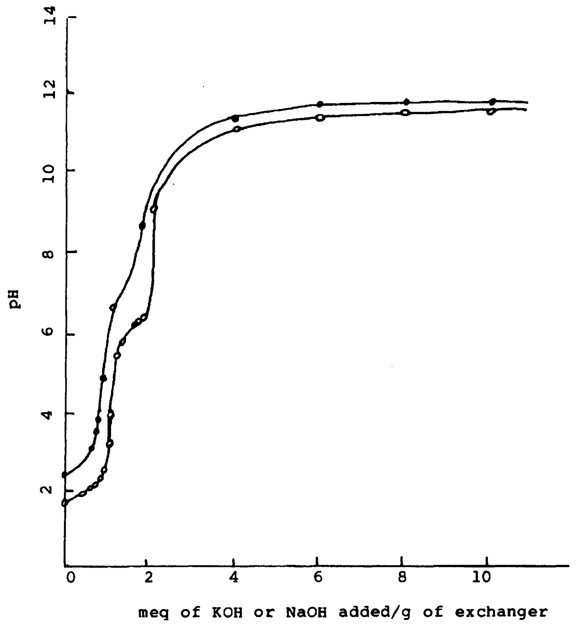

Fig. 1. pH titration curve of zirconium(IV) arsenate vanadate in H^+ form.

The X-ray diffraction (Fig. 2) pattern revealed that the exchanger was amorphous at room temperature, and that this behavior remained up to 600 °C. Crystallinity appeared above 600 °C, and there was an increase in the number of lines along with an increase in the temperature. It also showed a good X-ray pattern at 800 °C, and *d* values identical to those of a mixture of the corresponding ZrO_2, As_4O_6 and V_2O_5.

A thermogravimetric analysis of the sample ZAV_5 in the H^+ form was performed at a heating rate of 10 °C min^{-1}. The thermogram (Fig. 3) shows a continuous loss in weight up to 145 °C, which was due to the loss of external water molecules. The corresponding weight loss of the exchanger was 8.0%. Above a temperature of 370 °C, the weight became constant due to the formation of anhydrous zirconium(IV) arsenate vanadate.

Zirconium(IV) arsenate vanadate exchanger was prepared at pH 1. An elemental analysis indicated that the material had Zr : As : V ratio 3 : 2 : 1 (sample ZAV_5). From the aqueous chemistry of vanadium it could be seen that in an acidic medium vanadate exists according to the following equilibrium:[30]

$$3\ VO_3(OH)^{2-} + 3H^+ \rightleftharpoons V_3O_9{}^{3-} + 3H_2O$$

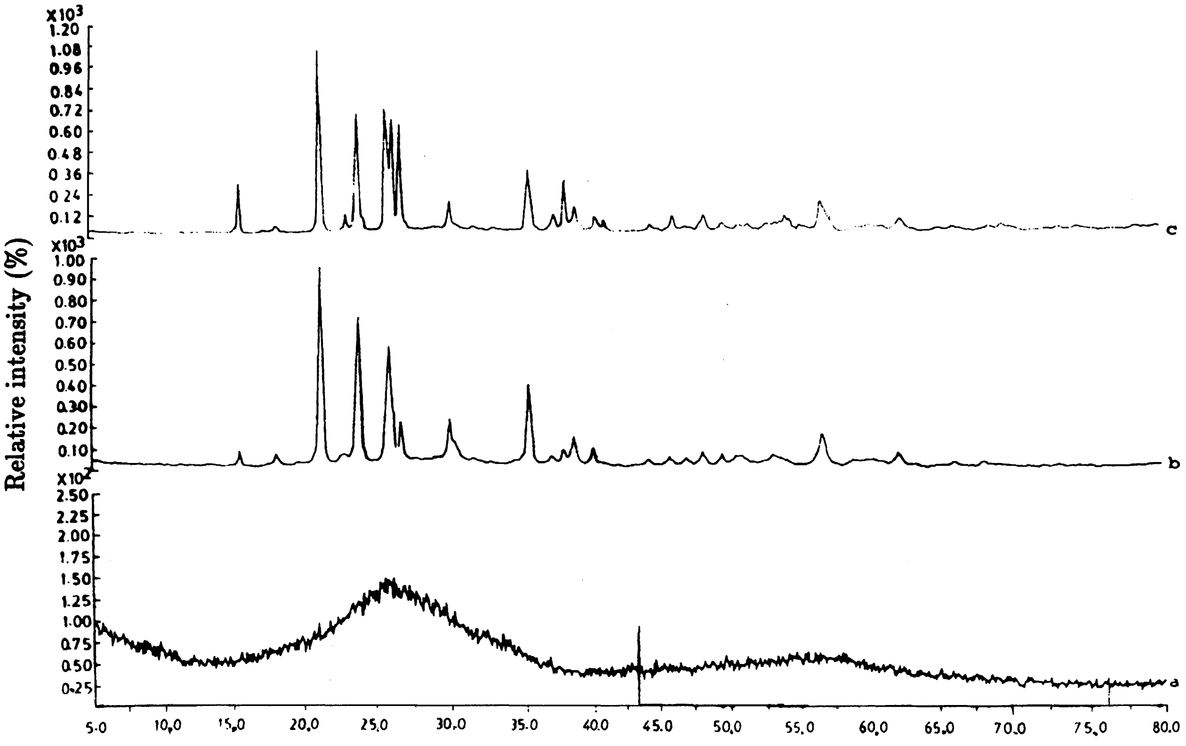

Fig. 2. X-Ray diffraction patterns of various samples of zirconium(IV) arsenate vanadate a=40°C, b=700°C, c=800°C.

Table 4. Distribution Coefficients of Metal Ions on Zirconium(IV) Arsenate Vanadate at 30 °C

Sl.	Metal ion	Ionic radius Å	Hydrated ionic radius Å	H_2O	0.1 M CH_3COOH	0.2 M CH_3COOH	0.4 M CH_3COOH	0.6 M CH_3COOH	0.1 M CH_3COOH : 1,4-dioxane 1 : 1	1 : 2	1 : 4
1.	Mg^{2+}	0.72	10.8	23	77	100	166	300	14	14	14
2.	Ca^{2+}	1.00	9.5	60	34	34	43	50	123	60	43
3.	Sr^{2+}	1.18	9.4	33	14	25	33	55	164	132	83
4.	Ba^{2+}	1.43	8.8	230	164	164	98	58	166	60	33
5.	VO^{2+}	0.79	—	14	14	17	19	35	6	40	44
6.	Cr^{3+}	0.80	—	300	263	166	166	166	77	60	33
7.	Mn^{2+}	0.83	6.8	173	134	310	720	1266	310	127	14
8.	Fe^{3+}	0.78	>8.0	92	680	387	290	129	116	56	56
9.	Co^{2+}	0.74	—	78	43	43	43	46	166	166	220
10.	Ni^{2+}	0.69	—	43	8	8	8	13	8	43	32
11.	Cu^{2+}	0.77	6.8	76	88	84	84	85	88	88	107
12.	Zn^{2+}	0.745	6.8	67	20	31	40	110	5	5	5
13.	Cd^{2+}	0.95	6.4	100	77	100	122	166	66	100	100
14.	Hg^{2+}	1.19	6.3	13	13	13	13	53	40	79	115
15.	Pb^{2+}	1.21	5.9	80	4	4	38	38	2	2	2
16.	Al^{3+}	0.535	>8.0	280	280	280	280	280	153	90	52
17.	Gd^{3+}	0.93	—	106	14	14	140	210	45	39	316
18.	$UO_2{}^{2+}$	0.89	—	100	700	700	700	220	400	45	45
19.	Zr^{4+}	0.72	—	29	387	387	7570	7850	460	95	11
20.	Ce^{4+}	1.01	—	39	39	80	137	177	38	39	316
21.	Th^{4+}	0.94	—	13	88	58	58	36	30	30	172

The trimeric species may be considered to be built up by the polymerization of $H_2VO_4{}^-$ ion, as evidenced from emf measurements at 4 °C in the acidic range, showing that the major species31) present are $V_3O_9{}^{3-}$ and $V_4O_{12}{}^{4-}$. On the basis of aqueous chemistry of arsenate, vanadate, the pH titration curve, the IR spec-

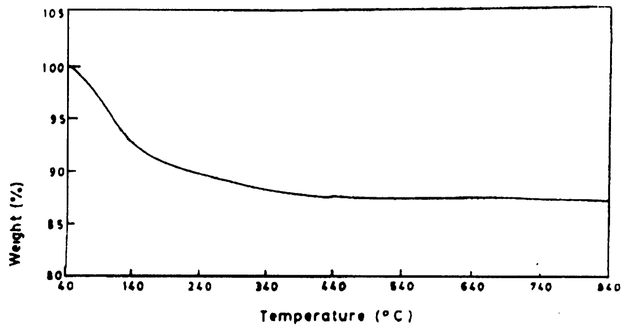

Fig. 3. Thermogram of zirconium(IV) arsenate vanadate.

trum and a thermogravimetric analysis, the following formula may be proposed for this exchanger:

$$[(ZrO)_9(HAsO_4)_6(V_3O_9)(OH)_3]_p{\cdot}nH_2O$$

The weight loss due to the presence of external water molecules in the gel was 8.0% of the total weight. Thus, the number of such water molecules per mole of the exchanger was determined on the basis of Alberti's equation,[32)]

$$18n = \frac{x(M+18n)}{100},$$

where x is the percent water content and $M+18n$ the molecular weight of the material. It gives a value of n for such water molecules as 10.39. If we assume that three hydrogen ions are exchanged at a pH of around 7, and that 6 hydrogen ions are exchanged at pH 11, the ion-exchange capacity calculated from the above formula is 1.29 and 2.58 meq g^{-1} for K^+ ion, respectively, which is in accordance with the experimental values (1.30 and 2.60 meq g^{-1} for K^+ ion).

The exchange characteristics of zirconium(IV) arsenate vanadate for a number of metal ions have been described (Table 4) in terms of the K_d values i.e. the distribution coefficients. It is clear that the distribution coefficients (K_d values) vary with the composition and nature of the contacting solution.

The affinity series for alkaline earth metal ions were found to be in the following order: $Ba^{2+}>Ca^{2+}>Sr^{2+}>Mg^{2+}$. In this series the most important factor is the hydrated ionic radii. Sorption studies on zirconium(IV) arsenate vanadate for different metal ions conclude that a number of important separations are possible.

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References

1) A. Clearfield, "Inorganic Ion-Exchange Materials," CRC Press, Inc., Boca Raton, Fl. (1982).

2) C. B. Amphlett, "Inorganic Ion-Exchanger," Elsevier, Amsterdam (1964).

3) Y. Inoue, *J. Inorg. Nucl. Chem.*, **26**, 2241 (1964).

4) S. Ahrland, A. Oskarsson, and A. Niklasson, *J. Inorg. Nucl. Chem.*, **32**, 2069 (1970).

5) G. Alberti, U. Costantino, and J. S. Gill, *J. Inorg. Nucl. Chem.*, **38**, 1733 (1976).

6) J. T. O'Connor, *Water Sewage Works*, **1974** (10), 72.

7) V. A. Shick O and E. S. Boichinova, *Zh. Prikl. Khim. (Leningrad)*, **41**, 526 (1968).

8) V. Vesley and V. Pekarek, *Talanta Rev.*, **19**, 224 (1972).

9) K. G. Varshney and A. A. Khan, *J. Inorg. Nucl. Chem.*, **41**, 241 (1979).

10) M. Qureshi and R. C. Kaushik, *Anal. Chem.*, **49**, 165 (1977).

11) M. Qureshi, R. Kumar, and R. C. Kaushik, *Sep. Sci. Technol.*, **13**, 185 (1978).

12) K. G. Varshney, R. Pal Singh, and S. Rani, *J. Indian Chem. Soc.*, **61**, 220 (1984).

13) T. Yonezawa and I. Tomita, *J. Inorg. Nucl. Chem.*, **39**, 1671 (1977).

14) P. S. Thind, S. S. Sandhu, and J. P. Rawat, *Chem. Anal. (Warsaw)*, **24**, 65 (1979).

15) S. A. Nabi, R. A. K. Rao, and W. A. Siddiqui, *J. Liq. Chromatogr.*, **6**, 777 (1983).

16) P. S. Thind and S. K. Mittal, *Synth. React. Inorg. Met. Org. Chem.*, **17**, 93 (1987).

17) S. Z. Qureshi and N. Rahman, *Bull. Chem. Soc. Jpn.*, **60**, 2627 (1987).

18) K. G. Varshney and U. Gupta, *Bull. Chem. Soc. Jpn.*, **63**, 1515 (1990).

19) S. K. Shakshooki and L. Szirtes, *J. Radioanal. Nucl. Chem.*, **137**(2), 159 (1989).

20) F. Sebesta and V. Stefula, *J. Radioanal. Nucl. Chem.*, **140**(1), 15 (1990).

21) Corcoran, W. Edward, Jr., and E. W. Vaughan David, "Solid State Ionics, 32-33 (Pt I)," 423-9 (1988), Pub. (1989).

22) S. Z. Qureshi and N. Rahman, *Bull. Soc. Chim. Fr.*, **1987**, 959.

23) F. J. Welcher, "The Analytical Uses of Ethylenediamine Tetraacetic Acid," D. Van Nostrand, Princeton, New Jersey (1958), p. 50.

24) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," D. Van. Nostrand, Princeton, New Jersey (1959), Vol. IIA, p. 389.

25) F. D. Snell and C. T. Snell, "Colorimetric Methods of Analysis," D. Van. Nostrand, Princeton, New Jersey (1959), Vol. IIA, p. 115.

26) N. E. Topp and K. W. Pepper, *J. Chem. Soc.*, **1949**, 3299.

27) F. C. Nachod and W. Wood, *J. Am. Chem. Soc.*, **66**, 1380 (1944).

28) S. R. Yogandrasimhan, *Indian J. Chem.*, **18**, 36 (1963).

29) F. A. Miller and C. H. Willkins, *Anal. Chem.*, **24**, 1253 (1952).

30) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, USA (1966), p. 803.

31) F. Brito, *Acta Chem. Scand.*, **21**, 968 (1967).

32) G. Alberti, E. Torracca, and A. Conte, *J. Inorg. Nucl. Chem.*, **28**, 607 (1966).