

The log k_1 and k_2 were evaluated by considering the degree of complex formation function (ϕ) and graphical extrapolation method of Leden. The stepwise formation constants were further verified by Yatsimirskii's method. The results are summarized in Table 1.

The results of application of the methods in synthetic mixture are presented in Table 2.

TABLE 2—RESULTS OF APPLICATION OF THE METHODS IN SYNTHETIC MIXTURE

Synthetic mixture	Pd ²⁺ found (mg)*	
	Reagent I	Reagent II
Pd ²⁺ = 0.1 mg, Pt ⁴⁺ = 1.0 mg, Ir ⁴⁺ = 1.0 mg, Rh ³⁺ = 1.0 mg, Ru ³⁺ = 1.0 mg, Os ³⁺ = 0.2 mg.	0.098	0.099

*Average of three determinations.

References

1. W. D. JACOBS, *Anal. Chem.*, 1961, 33, 1279.
2. W. D. JACOBS, C. M. WHEELER and W. H. WAGGONER, *Talanta*, 1962, 9, 243.
3. J. T. PYLE and W. D. JACOBS, *Talanta*, 1962, 9, 761.
4. J. H. YOE and L. G. OVERHOLSER, *J. Am. Chem. Soc.*, 1939, 61, 2058.
5. L. G. OVERHOLSER and J. H. YOE, *J. Am. Chem. Soc.*, 1941, 63, 3324.
6. M. L. HEIT and E. RYAN, *Anal. Chim. Acta*, 1966, 34, 407.
7. A. K. MAJUMDER and D. CHAKRABORTY, *Anal. Chim. Acta*, 1971, 53, 393.
8. H. S. GOWDA and B. KESHAVAN, *Indian J. Chem., Sect. A*, 1976, 14, 293.
9. W. D. JACOBS, *Anal. Chem.*, 1960, 32, 512.
10. B. SEN, *Anal. Chem.*, 1959, 31, 851.
11. M. AYASHI, *J. Chem. Soc. Jpn*, 1960, 81, 1703.
12. F. E. BEAMISH, *Talanta*, 1965, 12, 722.
13. I. LEDEN, *Z. Phys. Chem.*, 1941, 160, 188A.
14. K. V. YATSIMIRSKII, *J. Inorg. Chem.*, 1965, 10, 94.
15. K. V. YATSIMIRSKII, *J. Inorg. Chem.*, 1956, 1, 2306.
16. K. V. YATSIMIRSKII and T. I. FEDORVA, *Zh. Neorg. Khim.*, 1956, 1, 2301.
17. H. D. PORTER, *J. Am. Chem. Soc.*, 1954, 76, 127.
18. A. I. VOGEL, "Quantitative Inorganic Analysis", 3rd ed., Longmans Green and Co., London, 1961, p. 511.
19. A. RINGBOM, *Z. Anal. Chem.*, 1938-39, 115, 332.
20. G. H. AYRES, *Anal. Chem.*, 1949, 21, 652.
21. E. B. SANDELL, "Colorimetric Determination of Traces of Metals", Interscience, New York, 1956, p. 83.
22. P. JOB, *Compt. rend.*, 1925, 180, 928; *Ann. Chim. (Paris)*, 1928, 9, 113.
23. J. H. YOE and A. L. JONES, *Ind. Eng. Chem., Anal. Ed.*, 1944, 16, 111.
24. R. D. SAUERBRUNN and E. B. SANDELL, *Anal. Chim. Acta*, 1953, 9, 86.
25. A. E. HARVEY, JR. and D. L. MANNING, *J. Am. Chem. Soc.*, 1950, 72, 4488; 1952, 74, 4744.

Spectrophotometric Determination of Vanadium(V), Niobium(V) and Tantalum(V) in Presence of Each Other and in Presence of Other Ingredients Using 2,2'-Bipyridyl as Analytical Reagent

R. M. AWADALLAH, M. K. SHERIF and F. S. MOHAMED

Chemistry Department, Faculty of Science, Aswan,
A. R. Egypt

Manuscript received 18 September 1981, revised 24 December 1983, accepted 3 May 1984

THE microanalytical spectrophotometric determination of V⁵⁺, Nb⁵⁺ or Ta⁵⁺ in presence of each other, in presence of other ingredients or in admixture is of interest.

Niobium(V) and tantalum(V) in presence of each other, in presence of other ingredients and in rocks containing the elements were determined using oxine, alizarin red S and quinizarin-3-sulphonic acid, as chromogenic reagents. V⁵⁺, Nb⁵⁺, and Ta⁵⁺ were also studied spectrophotometrically using haematoxylin and murexide^{1,2}, 2,2'-bipyridyl³ and violuric acid⁴.

Experimental

Standard solutions of 10⁻³M V⁵⁺, Nb⁵⁺, and Ta⁵⁺; and 10⁻⁴M Fe³⁺, Fe²⁺, Co³⁺, Cr⁶⁺, Mo⁶⁺, W⁶⁺, Th⁴⁺, U⁶⁺, Ti⁴⁺, Zr⁴⁺, Ag⁺, Cu²⁺, Mg²⁺, Sr²⁺, Hg²⁺, Hg²⁺, In³⁺, Al³⁺, Sc³⁺, Y³⁺, La³⁺, Mn²⁺, Sn²⁺, Pb²⁺ and Bi³⁺ were prepared⁵ from the A. R. grades (Riedel de Hën, BDH or Merck, 99.9%) of V₂O₅, Nb₂O₅, Ta₂O₅, (NH₄)₂SO₄, FeSO₄·6H₂O, Fe₂O₃, CoCl₂·6H₂O, K₂Cr₂O₇, (NH₄)₂Mo₇O₂₄·4H₂O, Na₂WO₄·2H₂O, Th(NO₃)₄, UO₂(CH₃-COO)₂·2H₂O, TiO₂, ZrO(NO₃)₂, AgNO₃, CuSO₄·5H₂O, MgSO₄·7H₂O, SrCl₂·6H₂O, Hg₂(NO₃)₂·H₂O, HgCl₂, In₂(SO₄)₃·H₂O, AlCl₃, Sc(NO₃)₃·4H₂O, Y₂(SO₄)₃, La(NO₃)₃·6H₂O, MnSO₄·H₂O, SnCl₂·2H₂O, Pb(CH₃COO)₂, and Bi(NO₃)₃·5H₂O. 10⁻³M 2,2'-Bipyridyl (bipy) was prepared⁶ by dissolving the accurately weighted amount of bipy in ethanol. Buffer solutions of pH 3.90, 10.05 and 10.36 were prepared according to standard method⁷.

Pye Unicam SP 8000 Ultraviolet Recording spectrophotometer, silica cell, 1 cm light path, and Pye Unicam Model MK 2902 pH Meter were used to record the data.

The determination of V⁵⁺, Nb⁵⁺ or Ta⁵⁺ in presence of each other, in admixture or in presence of other metal ions was performed by measuring the spectral absorbances at 208, 210, 215, 220, 225, 230, 235, 240, 243, 250, 260, 265, 270, 272, 275 and 278 nm using constant [bipy] at 1×10⁻⁴M, equal concentration of V⁵⁺, Nb⁵⁺, Ta⁵⁺ and the other metal ions (Ag⁺, Cu²⁺) at 1×10⁻⁷M, and larger concentrations of the other elements at 1×10⁻⁶M and 1×10⁻⁹M in buffer solutions of pH 10.36 (in the case of the determination of V⁵⁺ in presence of Nb⁵⁺, Ta⁵⁺, (Nb⁵⁺ + Ta⁵⁺) or in presence of mixture of the other elements), 3.9 (ia

the case of the determination of Nb^{5+} in presence of V^{5+} , Ta^{5+} , ($\text{V}^{5+} + \text{Ta}^{5+}$) or in presence of mixture containing Ag^+ , Cu^{2+} , Mg^{2+} , Sr^{2+} , Hg_2^{2+} , Hg^{2+} , and 10.05 (in the case of the determination of Ta^{5+} in presence of V^{5+} , Nb^{5+} , ($\text{V}^{5+} + \text{Nb}^{5+}$) or in presence of the other ingredients) using blank solution containing the same [bipy] as in the test solution.

Results and Discussion

The results obtained reveal that V^{5+} can be determined spectrophotometrically at pH 10.36 in presence of Nb^{5+} , Ta^{5+} , Co^{2+} , Sn^{2+} and Fe^{2+} at 220 nm, Al^{3+} , Th^{4+} and Mo^{6+} at 225, and in presence of Al^{3+} and Th^{4+} at 250 nm without interference, whereas Mn^{2+} , Sc^{3+} , La^{3+} , Zr^{4+} and Cr^{6+} positively interfere.

Niobium can be determined in presence of equal or variable $[\text{V}^{5+}]$, $[\text{Ta}^{5+}]$, mixture of them or admixture of V^{5+} , Ta^{5+} , Fe^{2+} , Co^{2+} , Al^{3+} , Th^{4+} , Cr^{6+} , Mo^{6+} and W^{6+} at 230, 235 and 275 nm without interference, while Ag^+ , Cu^{2+} , Hg_2^{2+} , Mg^{2+} , Sr^{2+} , Sc^{3+} , Y^{3+} , La^{3+} , Sn^{2+} , Pb^{2+} , Ti^{4+} , In^{3+} , U^{6+} , Mn^{2+} and Fe^{3+} seriously interfere.

Tantalum can be assayed in presence of equal or variable $[\text{V}^{5+}]$, $[\text{Nb}^{5+}]$, mixture of them or admixture of Co^{2+} , Sn^{2+} (220, 225 and 250 nm), Th^{4+} and Mo^{6+} (225 nm), W^{6+} , Al^{3+} and Al^{3+} (210 nm) without interference. Ag^+ , Cu^{2+} , Hg_2^{2+} , Hg^{2+} , Mg^{2+} , Sr^{2+} , Sc^{3+} , Y^{3+} , La^{3+} , Ti^{4+} , Zr^{4+} , U^{6+} , Mn^{2+} , Bi^{3+} , Fe^{2+} and Fe^{3+} seriously interfere and underrate the determination of Ta. The method is simple, sensitive, accurate and useful for the determination of trace amounts (ppb ppm) of V^{5+} , Nb^{5+} and Ta^{5+} .

References

1. I. M. ISSA, R. M. ISSA and R. M. AWADALLAH, *Egypt. J. Chem.*, 1975, 18, 801.
2. M. K. SHERIF, R. M. AWADALLAH and F. S. MOHAMED, *Bull. Fac. Sci. Assiut Univ. Egypt*, 1978, 7, 461.
3. M. K. SHERIF, R. M. AWADALLAH and F. S. MOHAMED, *Bull. Fac. Sci. Assiut Univ. Egypt*, 1978, 7, 371.
4. R. M. AWADALLAH, *J. Indian Chem. Soc.*, 1980, 57, 685.
5. H. N. FURMAN, "Standard Methods of Chemical Analysis", 6th ed., Van Nostrand, 1966.
6. J. ROSIN, "Reagent Chemical and Standards", 5th ed., Van Nostrand, 1967.
7. H. T. S. BRITTON, "Hydrogen Ions", 4th ed. 1956.

Tris(2,2'-Dipyridyl) Iron(II) and Ethyl Orange as Indicators for the Titration of Vanadium(IV) with Cerium(IV) Sulphate

K. SRIRAMAM*, B. S. R. SARMA, M. S. JYOTI
and
K. UMA

Department of Chemistry, Nagarjuna University,
Nagarjunanagar-522 510

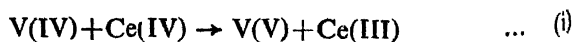
Manuscript received 20 November 1980, revised
12 September 1983, accepted 3 May 1984

THE reaction of vanadium(IV) with cerium(IV) in dilute sulphuric acid was considered slow in the light of the elevated temperature condition recommended for the potentiometric titration^{1,2}.

A recent study³, however, shows that the main reaction is fast, and that the difficulty is due to slow potential equilibration of vanadium system at the platinum electrode. It has been found that the titration can be done at room temperature to a potentiometric or visual end point, provided phosphoric acid is used as catalyst^{4,5}. The use of ferroin as internal indicator for this titration was investigated without success⁶. Later, ferroin indicator was successfully used⁷ by employing a titration medium of acetic acid and sulphuric acid mixture (7-8.5 M + 0.1-0.3 M). Other indicators^{8,9} are also used in such mixed acid medium, but none of them is superior to ferroin. The use of ferroin and some triphenylmethane dyes as indicators in 0.1-0.25 M sulphuric acid for this titration, employing hexacyanoferrate(III) as catalyst, has been reported¹⁰.

Tris (2,2'-dipyridyl) iron(II) is a metal complex of the ferroin type, but is much cheaper¹¹. Its redox potential is reported¹² to be 1.023 V. Despite the fact that the complex is much less stable in acid solutions than ferroin¹², it is successfully used as indicator in titrations of iron(II). We have investigated the use of this indicator in vanadium(IV)-cerium(IV) titration.

Methyl orange¹³ was used as indicator in the titration of vanadium(IV) with cerium(IV) sulphate using 0.5-1.0 M sulphuric acid as titration medium. We have observed that with the use of ethyl orange as indicator the working acid range is improved so much that vanadium(IV) in high acid solutions can be titrated without dilution. Ethyl orange like methyl orange is an irreversible indicator and evidently works in this titration owing to step (i) being faster than step (ii) :



Experimental

Vanadium(IV) solution in 0.25 M sulphuric acid was prepared and standardized by standard method³. Cerium(IV) sulphate solution in 0.25 M sulphuric acid was prepared from commercial cerium(IV) oxide and standardized against BDH AnalaR quality sodium oxalate. The strength of potassium hexacyanoferrate(III) solution was 1% and that of tris (2,2'-dipyridyl)iron(II) sulphate, 0.01 M. Ethyl orange (Chroma-Gesellschaft Schmid & Co.) was 0.5% solution in double distilled water. The indicator solutions have been found to be stable for more than six months.

Titration of vanadium(IV) :

Tris(2,2'-dipyridyl) iron(II) sulphate as indicator : 2.5-10.0 ml vanadium(IV) solution was treated with enough 1.0 M sulphuric acid to give an overall acidity of 0.1-0.25 M near the end point, and diluted to 45 ml. Then 0.5-1.0 ml of potassium