SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM AND OTHER COLOUR REACTIONS BY GALANGIN

By Mohan Katyal and R. P. Singh
(Department of Chemistry, University of Delhi, Delhi-6)

Received February 19, 1963

(Communicated by Prof. T. R. Seshadri, F.R.S., F.A.Sc.)

Not many organic reagents have been developed for trace analysis of zirconium by spectrophotometric methods. Alizarin[1-8] is considered as an important reagent for the colorimetric determination of zirconium. The colour reaction, however, is not ideal as it lacks high sensitivity. 3- and 5-hydroxy flavones have been found to be good chelating agents due to the presence of phenolic hydroxyl groups and a carbonyl group in them in suitable positions so as to form 5 or 6-membered chelate rings with cations. Some of them have been used for determination of zirconium. The use of flavonol[9] has been made for trace analysis of zirconium by fluorescence. Quercetin is another important reagent, introduced by Grimaldi and White, for colorimetric determination of zirconium.[10] The present communication deals with the use of galangin (3, 5, 7-trihydroxy flavone) for spectrophotometric determination of zirconium. The colour reaction of galangin with zirconium is highly sensitive and the complex is stable for several hours, in aqueous alcoholic medium, under ordinary conditions of temperature. Moreover, full colour development is instantaneous. The reagent blank is almost colourless in acidic medium in which zirconium can be estimated. The complex is quite stable over a wide range of acidity. The reagent can also be readily obtained in a pure form. The flavone has already been used by the authors for spectrophotometric determination of uranium[11] and thorium.[12]

On the addition of an alcoholic solution of galangin to the zirconium solution, an intense yellow colour is produced. The presence of alcohol was found to be necessary, in the reaction mixture, to prevent precipitation of the reagent. The complex obeys Beer's law over the concentration range of 1 to 6 p.p.m. of metal ion and thus small amounts of the latter can be conveniently estimated.

EXPERIMENTAL

Apparatus.—Spectrophotometric readings were taken with a Coleman spectrophotometer, model No. 14. A Metrohm pH-meter, type E-350, was used for pH measurements.

Reagents.—Standard solution of zirconium was prepared by dissolving zirconium nitrate (E. Merck) in water. Zirconium content of the solution was determined gravimetrically by oxine method. Galangin was obtained from the ether extract of the plant rhizomes of *Alpinia officinarum* Hance. An alcoholic solution of galangin containing 0·270 g./litre (M/1,000) was prepared. Other chemicals used were of reagent quality. Double distilled water was used throughout the work for preparing solutions.

Complex formation.—Zirconyl ions react with galangin forming a complex which is evident by the appearance of yellow colour and fall in pH.

Absorption spectra.—The maximum absorption by the complex was observed in the vicinity of 410 mμ while the absorption due to the flavone at this wavelength is very small. The spectra of the complex were taken varying the acidity from 0·5N HCl to pH 4·5. In all these cases there was no shift in absorption maximum showing thereby the formation of only one complex. The wavelength 410 mμ was consequently chosen for further investigations. The molar ratio of the flavone to zirconium was maintained at 10 while preparing solutions for spectral studies. One ml. of zirconium (M/1,000) was mixed with 10 ml. of the flavone solution (M/1,000) and the solution was diluted to 25·0 ml., maintaining 40% alcoholic medium. The flavone solution, under similar conditions, was used as blank.

Effect of Acidity on the Complex.—Figure 1 shows the effect of acid concentration on the complex. There is very slight increase in the optical density with increase in the acidity. However, 0·5N acidity was maintained in subsequent studies.

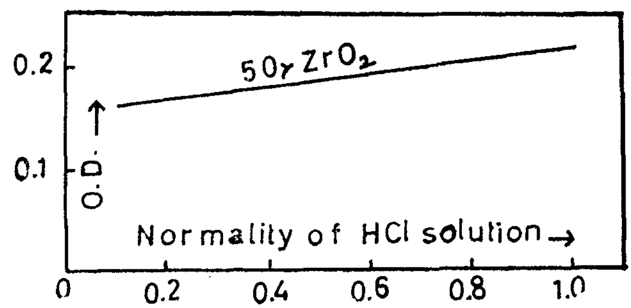


FIG. 1. Effect of acidity on the complex.

Some Properties of the Complex.—The yellow coloured complex of zirconium with galangin is soluble in aqueous alcohol and is not extractable by usual organic solvents like benzene, carbon tetrachloride and chloroform. In aqueous alcoholic medium, the complex is stable and thus suitable for spectrophotometric investigations. No appreciable change in colour was noticed even on keeping it for several hours in acidic medium. Acidic conditions (0·5 N-HCl) were maintained as the reagent solution is sufficiently coloured in absence of acid. Also it does not respond to a number of other cations, in acidic medium, thus increasing the selectivity. To maintain the acidity, hydrochloric acid was used because zirconium is more stable in this acidic solution.[13] Increase in the concentration of alcohol does not alter the optical density to any appreciable extent.

Minimum Amount of the Reagent Needed.—The optical densities of a series of solutions containing galangin and zirconium in the molar ratio of 1 : 1 to 10 : 1 were determined at 410 mμ, in 0·5 N-HCl concentration, maintaining 40% alcoholic medium. The results indicate that there is almost complete formation of the complex when five moles of the reagent are added to 1 mole of zirconium salt.

Beer's Law.—The solution of the complex has been found to obey Beer's law between the concentration range of 1 to 6 p.p.m. of metal ion in 0·5 N-HCl medium.

Composition of the complex.—The method of continuous variation[14, 15] was used for determination of composition of the complex. Optical densities of two series of solutions prepared by mixing (*a*) x ml. of 1×10^{-3} M galangin solution with $(10 - x)$ ml. of 1×10^{-3} M zirconium solution and finally diluting to 25·0 ml., maintaining 40% alcoholic medium and pH at 3·5, and (*b*) x ml. of 1×10^{-3} M galangin solution with $(10 - x)$ ml. of 1×10^{-3} M zirconium solution, and finally diluting to 50·0 ml., maintaining 40% alcoholic medium and pH at 2·5 (where x was varied from 1 to 9), were determined at wavelengths 410 mμ and 420 mμ. The peaks are obtained, in all cases, when the components are in molar ratio of 1 : 1 (Fig. 2).

The molar composition of the complex was also verified by the slope ratio method.[16] For this purpose, two series of solutions were prepared. In one series, zirconium concentration was varied maintaining that of galangin constant and in sufficient excess. In the other series, galangin concentration was varied maintaining that of zirconium constant and in sufficient excess. The optical densities of the solutions of both series were determined at 410 mμ and 420 mμ with aqueous alcohol, under similar

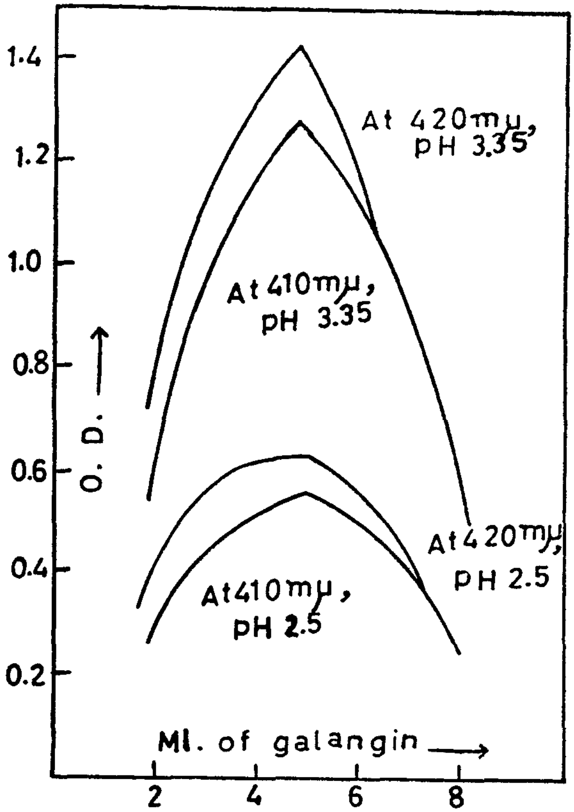
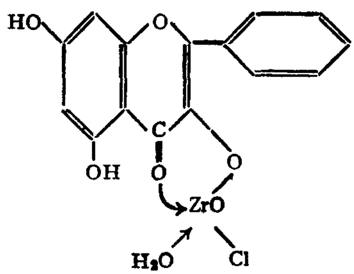


FIG. 2. Composition of the Complex by Job's Method.

conditions, as reference. Two curves were obtained at 410 mμ and another set of two, at 420 mμ. The curves were almost parallel showing thereby that the composition of the complex is 1 : 1.



As the complex contains one flavone radical per zirconium atom, a structure similar to zirconium quercetin complex[10] suggested by Grimaldi and White, may be assigned to zirconium galangin complex:

The formation of the zirconium complex by replacement of the hydrogen atom of the hydroxyl group on number 5 carbon atom is improbable as such complexes are much less stable than those formed by replacement of the hydrogen of the hydroxyl group on number 3 carbon atom.[17, 18]

Effect of Foreign ions of the Complex.—The effect of some of the foreign ions is recorded in Table I.

TABLE I

Conc. of zirconium = 0·00004 *M*, *Conc. of reagent* = 0·00032 *M*
Medium – 0·5 N HCl, 40% *ethanolic*

Foreign ion	Added as	Concentration of the added ion	Tolerance
UO_2^{++}	$UO_2(NO_3)_2$	200 p.p.m.	No interference
Th^{+IV}	$Th(NO_3)_4$	4 p.p.m.	No interference
Cu^{++}	$CuSO_4$	40 p.p.m.	No interference
Ni^{++}	$NiSO_4$	40 p.p.m.	No interference
Co^{++}	$CoSO_4$	40 p.p.m.	No interference
Ce^{+4}	$(NH_4)_2Ce(NO_3)_6$	6 p.p.m.	No interference
TeO_4^{--}	$(NH_4)_2TeO_4$	80 p.p.m.	No interference
	Succinic acid	170 γ	No interference
	Malonic acid	600 γ	Slight interference
	Sodium citrate	500 γ	Appreciable interference
WO_4^{--}	Na_2WO_4	10 p.p.m.	Serious interference

Other Colour Reactions of Galangin.—A qualitative investigation of the reactions of galangin with other cations has been made. For this purpose, solutions of cations were prepared taking their chlorides, sulphates or nitrates. The reagent solution was prepared in alcohol (M/1,000). Most of the ions like Cu^{++}, Pb^{++}, Cd^{++}, Hg^{++}, Mg^{++}, Zn^{++}, Mn^{++}, Co^{++}, Ni^{++}, Wo_4^{--} and MoO_4^{--} produce light yellow colour when the concentration of the cation, under-test, is of the order of 1×10^{-3} M. Ba^{++} ions, however, do not give any colouration even at much higher concentrations. Ce^{+4} ions give light brown colour while ferrous ions produce light yellow to light brown colour depending upon pH and concentrations of the components. This may be due to formation of more than one complex. Fe^{+3} ions give light green colour with galangin. Sodium and potassium ions are without effect even at concentrations of the order of 1M. VO^{++} ions do not seem to react with galangin even when the concentration of the former is 1×10^{-2} M. No change in colour was observed in this case. Intense yellow colour produced when galangin is added to titanium salt solution is under detailed spectrophotometric investigation.

SUMMARY

The spectrophotometric determination of zirconium is described, based on the formation of a yellow coloured complex between zirconium and galangin. Maximum absorption by the reaction product only at one specific wavelength (410 mμ) in the acidity range of 0·5 N-HCl to pH 4·5, suggests the formation of only one complex. The complex, not extractable by usual organic solvents, has been studied in 40% alcoholic medium. It obeys Beer's law from 1 to 6 p.p.m. of metal ion concentration and contains the two components in the molar ratio of 1 : 1. The effect of the reagent on other ions has been qualitatively studied. Also, the effect of foreign ions on the complex has been investigated.

ACKNOWLEDGEMENT

The authors thank Prof. T. R. Seshadri, F.R.S., for his encouragement during the work.

REFERENCES

1. DeBoer, J. H. .. *Rec. trav. Chim.*, 1925, **44**, 1071.
2. Flagg, J. F. *et al.* .. *J. Am. Chem. Soc.*, 1949, **71**, 3630.
3. Green, D. E. .. *Anal. Chem.*, 1948, **20**, 370.
4. Guenther, R. and Gale, R. H. *U.S. Atomic Energy Commission*, 1950, KAPL-305.
5. Liebhafsky, H. A. and Winslow, E. H. *J. Am. Chem. Soc.*, 1938, **60**, 1776.
6. Mayer, A. and Bradshaw, G. *Analyst*, 1952, **77**, 476.
7. Tananev, N. A. and Khovyakova, R. F. *Zhur. Obsh. Khim.*, 1951, **21**, 808.
8. Wengert, G. B. .. *Anal. Chem.*, 1952, **24**, 1449.
9. Alford, W. C. *et al.* .. *Ibid.*, 1951, **23**, 1149.
10. Grimaldi, F. S. and White, C. E. *Ibid.*, 1953, **25**, 1886.
11. Katyal, M. and Singh, R. P. *J. Ind. Chem. Soc.*, 1962, **39**, 585.
12. ——— .. *Ibid.*, 1963, **40**, 121.

13. Connick, R. E. and Reas, W. H. *U.S. Atomic Energy Commission*, 1949, AECD-2491.

14. Job, P. .. *Ann. Chim.*, 1928, **9**, 113.

15. Vosburgh, W. C. and Cooper, G. R. *J. Amer. Chem. Soc.*, 1941, **63**, 437.

16. Harvey, A. E. and Manning, D. L. *Ibid.*, 1950, **72**, 4488.

17. Horhammer, L. *et al.* .. *Naturwiss.*, 1954, **41**, 529.

18. ——— .. *Z. Anal. Chem.*, 1955, **148**, 251.