related compounds, Wiley Interscience, New York, 1981, p. 10.
3. Makrandi, J. K. and Grover, S. K., *Indian J. Chem.*, 1980, **B19**, 739.
4. Starks, C. M. and Liotta, C., *Phase transfer catalysis*, Academic Press, 1978, p. 91.
5. Singh, H., Jain, P. K, Makrandi, J. K. and Grover, S. K., *Indian J. Chem.*, 1982, **B21**, 547.
6. Jain, P. K., Makrandi, J. K. and Grover, S. K.,*Synthesis*, 1982, 221.
7. Kostanecki, S. V. and Feuerstein, W., *Ber.*, 1898, **31**, 715.
8. Bhide, G. V., Chandorkar, K. R., Pendse, H. K. and Limaye, S. D., *Rasayanam*, 1956, **2**, 135.
9. Ozawa, H., Okuda, T., Kawanishi, M. and Fujii, K., *J. Pharm. Soc. Jpn.*, 1951, **71**, 1178.
10. Goel, R. N., Jain, A. C. and Seshadri, T. R., *Proc. Indian Acad. Sci.*, 1958, **A48**, 180.
11. Narasimhachari, N. and Seshadri, T. R., *Proc. Indian Acad. Sci.*, 1948, **A27**, 223.
12. Kostanecki, S. V. and Courant, E., *Ber.*, 1906, **39**, 4033.
13. Kostanecki, S. V., Tambor, J. and Bonifazi, E., *Ber.*, 1906, **39**, 88.
14. Kostanecki, S. V., Tambor, J. and Bonifazi, E., *Ber.*, 1903, **36**, 4238.
15. Kostanecki, S. V. and Schreiber, B., *Ber.*, 1905, **38**, 2749.
16. Kostanecki, S. V. and Rudse, F., *Ber.*, 1905, **38**, 936.
17. Yusirokimura, *J. Pharm. Soc. Jpn.*, 1940, **60**, 151.
18. Kostanecki, S. V. and Tambor, J., *Ber.*, 1904, **37**, 79.
19. Reichel, L., Burkart, W. and Miller, K., *Ann.*, 1942, **550**, 146.

SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM AS MOLYBDOARSENO-ZIRCONIC ACID

T. V. RAMAKRISHNA AND M. S. SUBRAMANIAN
Department of Chemistry, Indian Institute of Technology, Madras 600 036, India.

SPECTROPHOTOMETRIC methods for the estimation of zirconium based on heteropolyacid formation have been described. Dehne and Mellon[1] utilised the reaction of zirconium with molybdate and sulphate to form the ternary heteropolyacids for the determination of zirconium after reduction to the heteropoly blue. Murata *et al*[2] have developed a method for zirconium based on the formation of molybdophosphozirconic acid. In this method, because of the very high absorbance of molybdophosphoric acid formed under the experimental conditions, prior extraction of the binary heteropoly acid into butylacetate is necessary before subjecting the aqueous phase for absorbance measurements. In the course of our investigations, it was found that replacement of phosphorus by the arsenic in the ternary system can render the method simple, as the molybdoarsenic acid formed if any, did not interfere with the determination of zirconium as molybdoarsenozirconic acid, and therefore eliminated the prior separation step. The details of investigations that led to the development of such a procedure are furnished in this communication.

Apparatus: All spectrophotometric measurements were made by using Carl-Zeiss spectrophotometer with 1 cm quartz cells. A Knick pH meter was used for measuring the pH. Analytical grade chemicals were used. Zirconium, 100 ppm—Suitable amounts of $ZrOCl_2.8H_2O$ dissolved in 1 : 1 hot sulphuric acid and the solution suitably diluted. Ammonium molybdate solution 0.05 M and sodium arsenate solution, 0.01 M were prepared by standard methods.

Procedure: Transfer an aliquot containing not more than 1000 μg of zirconium into a 100 ml beaker. Add 5 ml of ammonium molybdate and 2.5 ml of sodium arsenate and dilute to 50 ml. Adjust the pH of the solution to 1.5 using dilute sulphuric acid and ammonium hydroxide and heat the solution on a boiling water bath for about 20 min. Allow the solution to cool to room temperature and make up to 100 ml with distilled water. Measure the absorbance of the solution using 10 mm quartz cell at 340 nm, using blank as reference and establish the concentration by reference to a calibration graph prepared for 100 to 1000 μg following the above procedure.

Preliminary absorption spectra of the sample against the reagent blank showed that molybdoarsenozirconic acid absorb maximally at 323 nm. As the blank also absorbed considerably at this wavelength, it was decided to make measurements at 340 nm where the blank absorption was less. The absorbance remained constant in pH range 1.3-2.3 and therefore all further studies were made at 1.5.

The effect of ammonium molybdate and sodium arsenate concentration showed a constant and maximum absorbance when the aqueous phase contained at least 5 ml of 0.05 M ammonium molybdate and 2.5 ml of 0.01 M sodium arsenate. It was found that an optimum time of 20 min of heating over a boiling water bath was enough for maximum colour development. The system with a molar absorptivity of 7.63×10^3 l mole^{-1} cm^{-1} obeyed Beer's law upto 10 ppm of zirconium. The Sandell sensitivity was calculated to be 0.012 μg cm^{-2} when measurements were made at 340 nm.

The combining ratios of molybdenum, arsenic and

zirconium in the heteropolyacid was established to be 12:1:1 by the isomolar series method proposed by Babko[3].

Interference studies: The interfering effect of one milligram amount of several cations and anions in the determination of zirconium are shown in table 1. A deviation of more than ± 0.02 from the absorbance of the solution without any interefering ion was taken as a sign of interference.

TABLE 1

Interference studies (Zirconium 2 ppm).

Ions	Remarks
1. Ca, Mg, Cu(II), Co(II), Ni, Zn, Hg(II), Cd, Al, Be, Mn(II) NO_3^-, Cl^-, Br^-, I^-, SO_4^{2-}, ClO_4^-, acetate	No interference upto 1 mg level
2. Pb, Sr, Ba	Interfered by precipitation
3. Fe(III), Ce(IV), Ti(IV), Th, W(VI); V(V), Hf, U(VI), PO_4^{3-}, SiO_3^{2-}	Interfered by increasing the
4. Sn(II), F^-, citrate, tartrated, oxalate, EDTA	Interfered by decreasing the absorbance

The interference due to Ba, Pb and Sr was no longer noticed when the absorbance measurements were made after removing the precipitate by centrifugation. The interference of tin(II) was overcome by boiling with bromine water prior to the addition of ammonium molybdate and arsenate. Addition of 2 ml of 1% solution of beryllium sulphate prior to the addition of ammonium molybdate overcame the interference of fluoride. The interference due to phosphate, silicate and tungstate was removed by extraction of their heteropolymolybdates in 1:1 mixture of isobutylmethyl ketone and *n*-butanol at pH 1.0 in the absence of sodium arsenate. After extraction, colour was developed by reacting with sodium arsenate after adding a further quantity of 5 ml of ammonium molybdate and following the usual procedure. The interference due to titanium and uranium were overcome by coprecipitating zirconium with iron(III) hydroxide in the presence of one gram of ammonium chloride and 2 ml of 6% hydrogen peroxide at pH 4.0. The precipitate was repeatedly washed with dilute ammonium carbonate solution and then dissolved in 1:1 hydrochloric acid. After the removal of iron(III) by extraction with ether the aqueous layer was evaporated to dryness dissolved in 20 ml water and the estimation was carried out as described already.

7 April 1983; Revised 18 June 1983

1. Dehne, G. C. and Mellon, M. G., *Anal. Chem.*, 1963, **35**, 1382.
2. Murata, K., Yokoyama, Yu. and Ikeda, S., *Anal. Chim. Acta.*, 1969, **48**, 349.
3. Babko, A. K., *Complex components in solution, Moscow*, 1955, obtained from '*Photometric analysis*', Mir Publisher, Moscow 1971. p. 346.

CERIUM (IV) INDUCED ONE POT SYNTHESIS OF 2,4-DIHYDROXY-3-NITRO ACETOPHENONE—A MODEL FOR BIOMIMETIC AROMATIC HYDROXYLATIONS

H. MOHINDRA CHAWLA AND RAM S. MITTAL
Department of Chemistry, Indian Institute of Technology, New Delhi 110 015, India.

HYDROXYLATION of aromatic hydrocarbons is one of the most important reactions in biomimetic organic chemistry. Various attempts have been made to introduce a hydroxyl group into aromatic hydrocarbons by means of enzymes and using hydrophobic and hydrophilic catechols in the presence of ferric ions and hydrogen peroxide[1]. Such models achieved little practical success but nonetheless are important in establishing some of the enzymatic processes in the living cell[2]. Recently Barton and coworkers during their investigation on tetracycline synthesis, have hinted upon the plausible similarity between cerium dioxide (CeO_2) and hydrogen perioxide system to that involving singlet molecular oxygen[3] and since we were engaged in studies involving singlet molecular oxygen as a model for dioxygenases to mimic natural processes in polyphenols[4,5], we were interested in studying the efficacy of cerium compounds in biomimetic hydroxylations and developing simpler methods for obtaining difficultly accessible poly hydroxy benzenes.

One of the conventional ways of introducing hydroxyl group in benzene ring is *via* nitration, reduction and diazotisation. This process, though very much feasible has limitations because of the facile oxidation of phenols when treated with the nitrating agent instead of getting nitrated. Thus it seems imperative to develop methods for achieving chemoselective processes to get mononitrophenols which then can be converted to polyhydroxy benzenes by conventional methods. In our preliminary experiments, we have achieved a convenient synthesis of 2-nitro-1,3,4-trihydroxy benzene in good yields which can then be converted to 1,2,3,4-tetrahydroxy benzene. To get 2-