SHORT COMMUNICATIONS

EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF PLATINUM WITH CETYLTRIMETHYLAMMONIUM BROMIDE IN PRESENCE OF IODIDE

P. K. PARIA, T. K. THOKDAR and
S. K. MAJUMDAR
Department of Chemistry, North Bengal University, Darjeeling 734 430, India.

LITERATURE reveals the extraction of platinum (IV)[1] into nitrobenzene as an ion-association complex with Fe(phenanthroline)$_3^{2+}$. In presence of iodide or thiocyanate, platinum gets extracted into tributylphosphate[2]. In the process the metal has been separated from rhodium and iridium. In our laboratory it has been noted that platinum forms an ion-association complex with cetyltrimethylammonium bromide (CTA) in presence of potassium iodide. The green complex is extractable into ethyl acetate. This property of the platinum complex suggested that further studies of the system might lead to the development of a simple spectrophotometric method for the determination of platinum.

Spectral curves and analytical measurements were made with a Shimadzu PR1 model spectrophotometer equipped with stoppered quartz cells of 10 mm optical path length.

Chloroplatinic acid (Johnson & Matthey) (1 g) was dissolved in 100 ml of distilled water followed by its standardization[3]. Solution of lower concentration of the metal was prepared by appropriate dilution. Ethyl acetate and other solvents were distilled before use. Cetyltrimethylammonium bromide (0.1 M solution) and 0.05 M potassium iodide (BDH) were prepared in distilled water. All other reagents used for the purpose were of analytical grade. Standard solutions of diverse ions were prepared from their corresponding salts.

To an aliquot containing up to 30 μg of Pt(IV) were added 0.1 ml of 0.05 M potassium iodide and 0.1 ml of CTA (0.1 M) followed by adequate amount of hydrochloric acid and water to make the aqueous volume up to 10 ml and 0.5 M with respect to HCl. The mixture was then equilibrated with 10 ml of ethyl acetate for 30 sec. The separated organic layer was poured over anhydrous sodium sulphate to remove any retained water droplets. Finally the absorbance of the ethyl acetate extract was measured at 290 or 360 nm against a blank prepared under identical conditions. Amount of platinum was computed from a calibration curve. To test the effects of diverse ions, the respective foreign ions were added to the system before addition of the reagents.

When potassium iodide is added to a neutral or slightly acidic solution containing platinum (IV), a reddish-brown coloration due to the formation of $[PtI_6]^{2-}$ is formed. This complex anion is not extractable into acetate. On addition of an aqueous solution of CTA to this coloured solution, an ion-association complex, probably of the type, $[CTA^+]_2$ $[PtI_6]^{2-}$ is formed. This is extractable into ethyl acetate.

The absorbance spectrum of the Pt(IV)-I^--CTA complex in ethyl acetate, taken against a blank, shows absorption maxima at 290 and 360 nm. The reagent blank exhibits absorption at 250 nm and the absorption becomes insignificant beyond 290 nm. Wavelength of 290 or 360 nm may be selected for all analytical measurements.

The effect of acidity on the extractibility of Pt (IV) into ethyl acetate was examined in terms of absorbance of the complex. The complex exhibits constant and maximum absorbance when the extractions were carried out from 0.1 to 1 M hydrochloric acid medium. In a second consecutive operation within this acidity range, the organic extract virtually showed no obsorption. This indicated a quantitative extraction of platinum in a single extraction.

Apart from ethyl acetate, other solvents like benzene, chloroform and 1,2-dichloroethane were tested as the extracting solvents, but those offered no special advantages over ethyl acetate. The complex, however, is not extracted into carbon tetrachloride.

The absorbance of the platinum complex in ethyl acetate shows a linear response up to 3 ppm of platinum when measured at 290 or 360 nm. The molar absorptivities of the complex, based on platinum content, were found to be 5.36×10^4 and 3.08×10^4 l mol^{-1} cm^{-1} and sensitivities 0.0036 and 0.0063 μg/cm^2 at 290 and 360 nm, which classifies the colour reaction as one of the most sensitive for platinum. The colour is stable for at least 24 h.

With the variation of reagent concentrations, it

was noted that 0.1 ml of 0.05 M potassium iodide along with 0.1 ml of 0.1 M CTA was sufficient to extract up to 30 μg of platinum in a single extraction. Increased concentration of the reagents, however, did not bring about any significant change in the maximum value of absorbance. Order of adding the reagents had no effect on colour development.

To test the effects of diverse ions on the extraction behaviour, platinum (IV) was extracted and determined according to the recommended procedure in presence of the desired foreign ions. Extraction was carried out from 0.5 M hydrochloric acid medium. An ion was considered to interfere if the recovery of platinum differed by more than ±3% from the actual amount taken. Platinum (IV) (30 μg) could easily be determined without interference in presence of 100–200 fold excess of the following ions: Co (II), Ni (II), Cu (II), Pd (II), Fe (III), Cd (II), Zn (II), Mo (VI), V (V), Mn (II), U (VI), Zr (IV), Rh (III), Pb (II), Al (III), Ca (II), Ba (II), Sr (II), Be (II), Bi (III), Ce (III), Cr (III), La (III) and Mg (II). The system develops no colour in presence of mercury (II) and thorium (IV). In presence of silver, formation of some yellowish precipitate hampers the procedure.

Amongst the anions tested 200-fold excess of the followings do not interfere: borate, phosphate, tartrate, citrate, fluoride, phthalate, ascorbate, oxalate and EDTA. In presence of nitrate, high results are obtained. However, thiosulphate, thiocyanate and thiourea must be absent as these inhibit the colour development.

The precision and accuracy of the proposed method were tested by analysing solutions containing a known amount of platinum following the recommended procedure. The average of six determinations of 30 μg of Pt (IV) was 29.25 μg with a relative mean deviation of 2.84%. The process is very simple and rapid requiring only 10–15 min for each run.

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1. Yamamoto, Y., Tsubouchi, M., Okimura, I. and Takaki, T., *Nippon Kagaku Zasshi*, 1967, **88**, 745.
2. Berg, E. W. and Lau, E. Y., *Anal. Chim. Acta*, 1962, **27**, 248.
3. Vogel, A. I., *A textbook of quantitative inorganic analysis*, ELBS, London, 1978.

AZOTOBACTER POPULATION AS INFLUENCED BY SOIL PROPERTIES IN SOME SOILS OF NORTH KARNATAKA

H. T. CHANNAL, A. R. ALAGAWADI, T. D. BHARAMAGOUDAR, S. G. UDUPA, P. L. PATIL and I. M. MANNIKERI
Department of Soil Science, University of Agricultural Sciences, Dharwad 580 005, India.

AZOTOBACTER is a free living nitrogen fixing bacteria. Its population density varies from almost zero to several thousands per gram of soil depending upon soil type and its properties[1]. The organic carbon content, hydrogen ion concentration (pH), sodium salts and other elements may influence the growth and nitrogen fixation of Azotobacter. Hence a study was undertaken to investigate the relationship of some soil properties with Azotobacter population.

Surface soil samples, viz., acid soil (Sirsi), forest soil (Prabhunagar), red and black soils (Dharwad) and salt-affected soils (Hooli) were collected.

Azotobacter population in different soils was enumerated by dilution plate method using Norris nitrogen-free medium[2]. The chemical analysis of the soil samples was carried out by standard methods. Soil pH was determined by digital pH meter (model Elico, LI-122, in 1:2.5 soil water ratio), electrical conductivity was measured with the help of EC bridge (model Elico, CM 82T) and organic carbon[3], total nitrogen[4] and exchangeable cations[5], were ditermined by the methods reported earlier.

The results are presented in table 1. Azotobacter population is governed by some soil properties. The pH of these soils ranged from 5.6 to 8.1. Azotobacter requires almost neutral to slightly alkaline soil reaction for their growth[6,7].

The highest Azotobacter population (84×10^3/g) was observed in forest soil of Prabhunagar wherein it has the maximum amount of organic carbon (2.58%). The lowest population (6×10^3/g) was found in acid soil of Sirsi with 0.94% organic carbon. The trend is, with increase in organic carbon content in the soil the Azotobacter population has increased[8] ($r = 0.724^*$). Though organic carbon content is more in salt-affected soil of Hooli and acid soil of Sirsi than red soil of Dharwad, the Azotobacter population is less in those soils probably because of high exchangeable sodium in salt-affected soil of Hooli and low pH condition in acid soil of Sirsi.

Lack of organic matter in soil is a limiting factor in the proliferation of Azotobacter.