ESTIMATION OF OXALATE IONS AND
OXALIC ACID USING EDTA

The estimation of the oxalate anion and oxalic acid by the EDTA method\(^1\) involves the quantitative precipitation of the oxalate by adding a known excess of standard lead acetate solution and back titrating the excess lead acetate with EDTA. The method is simple and accurate. The precipitation merely involves mixing the cold solutions and the easily filterable precipitate shows practically no creep.

Discussion.—The method adopted is the reverse of the usual method for the estimation of lead\(^2\). It is found that under the conditions of precipitation with excess of lead acetate, oxalic acid and oxalate are both quantitatively precipitated and no distinct distinction in practical procedures is called for. The results both in the case of oxalic acid and oxalate show practically the same accuracy, \(\sim 0.5\%\). The presence of small quantities of oxidised impurities might pose a serious problem in the case of permanganometry, whereas the accuracy of EDTA method is not affected by such impurities.

Lead reacts with Erio T in ammoniacal medium. However, at this pH the lead is precipitated as hydroxide. To avoid precipitation, the addition of tartrate ion is necessary. The lead-tartrate complex is sufficiently stable to keep the lead in solution, but it is not sufficiently so to prevent its reaction with the indicator and with EDTA. The colour intensity of the lead-Erio T complex is somewhat dependent upon the concentration of the tartrate called "auxiliary complex-former" and too large an excess of the auxiliary complex-former should be avoided. The colour of the indicator before the end point is a bluish viole. However the disappearance of the last reddish tint is very abrupt and takes place within the range of a drop or part of a drop of titrant.

The following equation is relevant:

\[
Pb^{++} + H_2Y^- = 2H^+ + PbY^- \quad (H_2Y^- : \text{Anion of the disodium salt of EDTA})
\]

For comparing the EDTA method with the conventional method, the following procedure is adopted. Analar grade oxalic acid or sodium oxalate is used for preparing the solutions. A known excess of a standard solution of \(Pb^{++}\) ion is added to an aliquot of the oxalate solution, the precipitate is filtered off and the filtrate titrated against EDTA solution of known strength. The strength of the oxalate solution is then calculated and compared with its known value. Similarly a known excess of oxalate solution is added to a known volume of lead salt solution and after filtering off the lead oxalate, the solution is titrated against permanganate solution independently standardised. The known strengths of the permanganate and the lead salt solutions are then used to calculate the concentration of the oxalate solution. In the titration of \(Pb^{++}\) ion against EDTA, the pH is kept at 10 day buffering with tartrate-ammonia. Erio T is used as the indicator and the end point is the colour change from violet to blue. The results are excellent and the accuracy is usually better than 0.6%.

Department of Chemistry,  
G. Ramamurti,  
Madura College,  
K. Renganathan,  
Madurai 625011,  
L. R. Ganesan.  
(Tamil Nadu), December 30, 1974.


GROUP IB METAL BISTHIOSALICYLATO MERCURATES

Disodium bisthiosalicylato mercurate was prepared as reported earlier\(^3\). Copper and silver bisthiosalicylato mercurates were obtained by adding varying amounts of 0.01 M disodium bisthiosalicylato mercurate solution to fixed quantities of 0.01 M copper and silver sulphate solutions obtained from BDH (India) A.R. quality samples. Copper yielded a dark-green thick precipitate and a curdy light yellow precipitate was obtained in the case of silver bisthiosalicylato mercurate. The reaction mixtures were kept overnight at room temperature (25°C). The precipitates were filtered, washed with distilled water and dried in oven at 100°C for two hours. 0.01 M cold solution prepared from chloroauric acid obtained from Johnson Mathey Co., Ltd. (London), was standardized for its Au\(^{3+}\) content by the thiosalt method\(^4\). The pH of the solution was raised to 5.8. A fixed quantity of 0.01 M disodium bisthiosalicylato mercurate solution was treated with varying quantities of 0.01 M Au\(^{3+}\) solution. During the precipitation, the pH of the solutions goes on decreasing. Gold bisthiosalicylato mercurate when fresh is dark-yellow in colour but becomes black after drying in oven. Gold mercurate decomposes when dried at 100°C, whereas copper and silver bisthiosalicylato mercurates do not decompose at this temperature.

Copper and silver bisthiosalicylato mercurates were analysed for sulphur and mercury contents. Sulphur was estimated by fusing with fusion mixture and then completing estimation gravimetrically\(^5\) as
BaSO₄. Mercury was estimated quantitatively as HgS by thiosalt method. The method was slightly modified as the precipitates were filtered from the warm solution and washed thoroughly with ethanol to remove thiosalicylic acid which coprecipitates along with HgS. The experimental values of mercury and sulphur corresponded well with the theoretical values.

The infrared spectra of the solid metal bis-thiosalicylato mercurates were recorded between 600–4000 cm⁻¹ using nujol mulls on Perkin-Elmer 337 Spectrophotometer. The I.R. spectrum of thiosalicylic acid shows bands corresponding to —SH, C=O and C—S stretching frequencies appearing at 2250, 1700 and 755 cm⁻¹, respectively. The comparison with the nujol mull shows that bands corresponding to —SH frequencies disappear completely. But the bands corresponding to C=O stretching vibrations shift to lower frequency and are observed to split. C—S stretching vibrational bands also shift to a lower frequency. The disappearance of —SH frequency band and the lowering of C—S stretching frequency indicate the coordination through sulphur atom. The coordination through carboxyl oxygen and carboxylic group is indicated by lowering of C=O stretching frequencies. The splitting of the band may be due to coupling of some vibrations.

The author is indebted to Professor C. N. Kachru for providing the facilities and to Dr. K. P. Dubey for helpful supervision. My thanks are also due to CSIR, New Delhi, for the Senior Research Fellowship.

Chemistry Department, Maharaj K. Koul, University of Kashmir, Srinagar 190006, December 16, 1974.

1. Sachs, G. and Blessl, H., Ber., 1925, 58 B, 1493.

EXCYSTMENT OF SCHIZOPYRENUM RUSSELLI BY INDIVIDUAL AMINO ACIDS AND THEIR MIXTURES

SINGH, Mathew and Anand (1958) showed that aqueous extract of Aerobacter sp. and Escherichia coli caused nearly cent per cent excystment of cysts of Schizopyrenus russelli at a suitable pH. It was shown that part of the excystment inducing property of Aerobacter sp. extract was due to certain amino acids. Chemically pure amino acids also gave varying degrees of excystment. In general the excystment caused by individual amino acids was much lower than that caused by the bacterial extract. Drozanski (1961) also reported that aqueous extract of A. aerogenes and certain amino acids were able to cause excystment of cysts of soil amoeba belonging to the family Hartmannellidae. Jefferies (1962) found that amino acids could cause excystment of a ciliate, Pleurotricha lanceolata. Singh, Datta and Dutta showed that the percentage excystment of cysts of S. russelli with L-isoleucine, L-arginine monohydrachloride, L-alanine, L-serine and L-glutamic acids at 2-0% concentration in distilled water, pH about 6-5, was significantly higher than at 0-25% or 0-125%. When mixtures of all the amino acids at these concentrations were used, the percentage excystment was markedly increased. Singh, Datta and Dutta suggested that nearly cent per cent excystment of S. russelli obtained by E. coli extract may be due to a mixture of amino acids and other factors in the extract. Rastogi, Sagar and Agarwala (1973) observed that the excystment of S. russelli was quicker in a mixture of amino acids containing riboflavin than that obtained in the mixture of amino acids alone. The present communication deals with excystment of S. russelli by individual amino acids and their mixtures.

S. russelli was grown on non-nutrient agar plates supplied with E. coli. Eight to 10 days old cysts were harvested and freed from living and dead bacteria, and used for studying the excystment according to the method reported earlier. The chemically pure amino acids used were sterilized by autoclaving at 15 lb/sp. in. pressure for 15 min.

It has been found by Singh, Datta and Dutta that cysts of S. russelli, produced at different times with E. coli, gave somewhat varying degrees of excystment with L-isoleucine, L-arginine monohydrachloride, L-alanine, L-serine and L-glutamic acid. Therefore cysts prepared from the same batch were employed by them to show that mixture of the above amino acids gave higher percentage excystment than that obtained by individual amino acids. In these experiments the concentration of amino acids used in the mixture was five times more than that in the case of individual amino acids. In order to show the additive effect of mixture of the amino acids used by Singh, Datta and Dutta, cysts of S. russelli prepared from the same batch were used and the concentration of amino acids in the mixture was kept the same as in the case of individual amino acids. The results presented in Table I show that the percentage excystment with mixture of amino acids