# Oxidation of Low Valent Sulphur Compounds with Lead Tetraacetate: Part III—Determination of Tri- & Tetrathionates & the Redox Potential of Sulphate-Trithionate System

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The oxidation of tri- and tetrathionate solutions with lead tetraacetate is investigated. As little as 2 mg of Pb(IV) can be estimated by potentiometric titration in glacial acetic acid medium. The direct titration of the thionate solution with Pb(IV) acetate is also satisfactory and demonstrates the feasibility of determining amounts ranging from 0·27-123 mg and 0·5-12 mg of $S_3O_6^{2-}$ and $S_4O_6^{2-}$ respectively. The net reactions representing the oxidation of tri- and tetrathionates with Pb(IV) acetate are given. The titrations at the optimum conditions proceed fast and exhibit a large potential change at the end-point. The formal redox potential of the $SO_4^{2-}/S_3O_6^{2-}$ system has been determined at different $pH$ values. The $E_0$ value obtained by extrapolation to $pH = 0$ is 0·71 V.

PREVIOUSLY[1,2], we studied the reaction between lead tetraacetate and bisulphite, thiosulphate and metabisulphite. The quantitative course of the reactions were applied for the direct potentiometric determination of the lead(IV) reagent. The estimation of polythionates have been the subject of few titrimetric investigations[3-7]. In the present study, the reaction with lead tetraacetate has been applied for the determination of tri- and tetrathionates. The oxidation reactions of the two sulphur compounds are discussed. Attempts have also been made to evaluate the redox potential of the sulphate/trithionate system.

## Materials and Methods

Pb$^{2+}$-free solution of lead tetraacetate (0·05$M$) was prepared by a method similar to that of Berka *et al.*[8] and standardized potentiometrically against standard Fe(II) sulphate solution in 1$N$ sulphuric acid. Sodium tri- and tetrathionate solutions were prepared from analytical grade reagents and standardized, by reaction with mercuric chloride[5]. Concentrated solutions of $S_3O_6^{2-}$ or $S_4O_6^{2-}$ (>0·05$M$) were found unsatisfactory due to decomposition by atmospheric oxygen. The thionate content of diluted solutions did not alter appreciably when preserved in a well stoppered vessel. Testing of solutions having $\leqslant$0·04$M$ concentration gave no evidence for the production of $SO_2$ or sulphurous acid when allowed to stand for several days. Other reagents were prepared using the analar products and doubly distilled water.

The potentiometric set-up consisted of a titration half-cell and SCE as the reference. A platinum rod was used as indicator electrode. When the thionate solution was used as the titrant, the reference half-cell was connected to the cell with KCl (sat.) and NaOAc (sat.)-acetic acid (glacial) salt bridges. The e.m.f. of the titration cell was measured by a direct reading millivoltmeter of type radiometer (Mb 28).
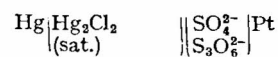
*Direct titration* — A measured volume of thionate solution was placed in the titration cell and mixed, if required, with the appropriate amount of 1$M$ $H_2SO_4$. The volume was made up to 100 ml with doubly distilled water, and then titrated with lead (IV) acetate at room temperature ($\sim$25°).

*Reverse titration* — A known volume of the lead (IV) reagent solution was placed in the titration cell and diluted to 50 ml with glacial acetic acid. The solution was then titrated with the thionate sample solution.

*Determination of the formal redox potential* — The cells of the types (A) and (B) were used for the determination of the formal redox potentials.

$$\text{Hg}\left|\begin{matrix}\text{Hg}_2\text{Cl}_2\\(\text{sat.})\end{matrix}\right.\quad\left\|\begin{matrix}\text{Pb(II)}\\\text{Pb(IV)}\end{matrix}\right|\text{Pt}$$

(A)

$$\text{Hg}\left|\begin{matrix}\text{Hg}_2\text{Cl}_2\\(\text{sat.})\end{matrix}\right.\quad\left\|\begin{matrix}SO_4^{2-}\\S_3O_6^{2-}\end{matrix}\right|\text{Pt}$$
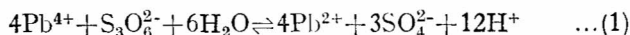
(B)

The potentials, $E_H$, of both Pb(IV)/Pb(II) and $SO_4^{2-}/S_3O_6^{2-}$ systems were measured at different $pH$ values. Systems having the composition 1:1 [Ox]/[Red] molar ratio were examined. The electrodes were immersed in the cell for sufficient time ($\sim$1 hr) before the $E_H$ measurements. The $E°$ values were obtained by extrapolation the $E_H$ vs $pH$ plots to $pH = 0$.
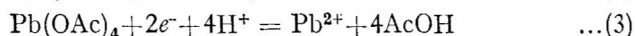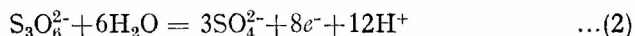
## Results and Discussion

### Determination of Trithionate

*Titration of trithionate with lead tetraacetate* — As shown in Fig. 1, the end point is characterized by a single large inflection ($\sim$100 mV/0·02 ml of

titrant). The volume of lead(IV) acetate consumed at the end-point indicate that the reaction proceeds in accordance with Eq. (1).

$$4Pb^{4+}+S_3O_6^{2-}+6H_2O \rightleftharpoons 4Pb^{2+}+3SO_4^{2-}+12H^+ \quad ...(1)$$

which is based on the two partial reactions (2 and 3)

$$S_3O_6^{2-}+6H_2O = 3SO_4^{2-}+8e^-+12H^+ \quad ...(2)$$

$$Pb(OAc)_4+2e^-+4H^+ = Pb^{2+}+4AcOH \quad ...(3)$$

The formal redox potential of the Pb(IV)/Pb(II) system have been thoroughly studied in acetic acid[9] as well as in dilute mineral acids[9,10]. On the other hand, the mechanism of the reaction

$$S_3O_6^{2-}+3H_2O = 3H_2SO_3+2e^- (E° = -0.3V)$$
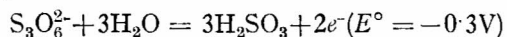
is no doubt complicated and the overall potential is probably not very significant[11]. Any oxidizing agent capable of oxidizing the trithionate will be sufficiently strong to oxidize the sulphurous acid to sulphate. This is apparently the case when trithionate is oxidized with Pb(IV) acetate. The

formation of sulphate is confirmed, however, by an absorption band at 310 nm.

The oxidation of trithionate with the lead(IV) reagent proceeds quantitatively in accordance with reaction (1) when the process is carried out at pH 3.5-5. It is, however, necessary for these titrations that the final pH (at the end-point) of the solution to be titrated should be $\geqslant 2.5$. Decomposition of trithionate to yield $SO_2$ does not take place under these conditions. This was confirmed experimentally by doing the titration in a closed system and testing the atmosphere above the titrated solution for $SO_2$, which was found to be absent. The titration proceeds rapidly at the start but as the end-point approaches the electrode equilibration becomes less rapid needing ~2 min after the addition of titrant. This is readily understandable from the liberation of $H^+$ ions according to reaction (1). At pH $\geqslant 5.5$ trithionate is slowly hydrolysed and the results obtained are not reliable. The method has proved successful for titrating amounts of $S_3O_6^{2-}$
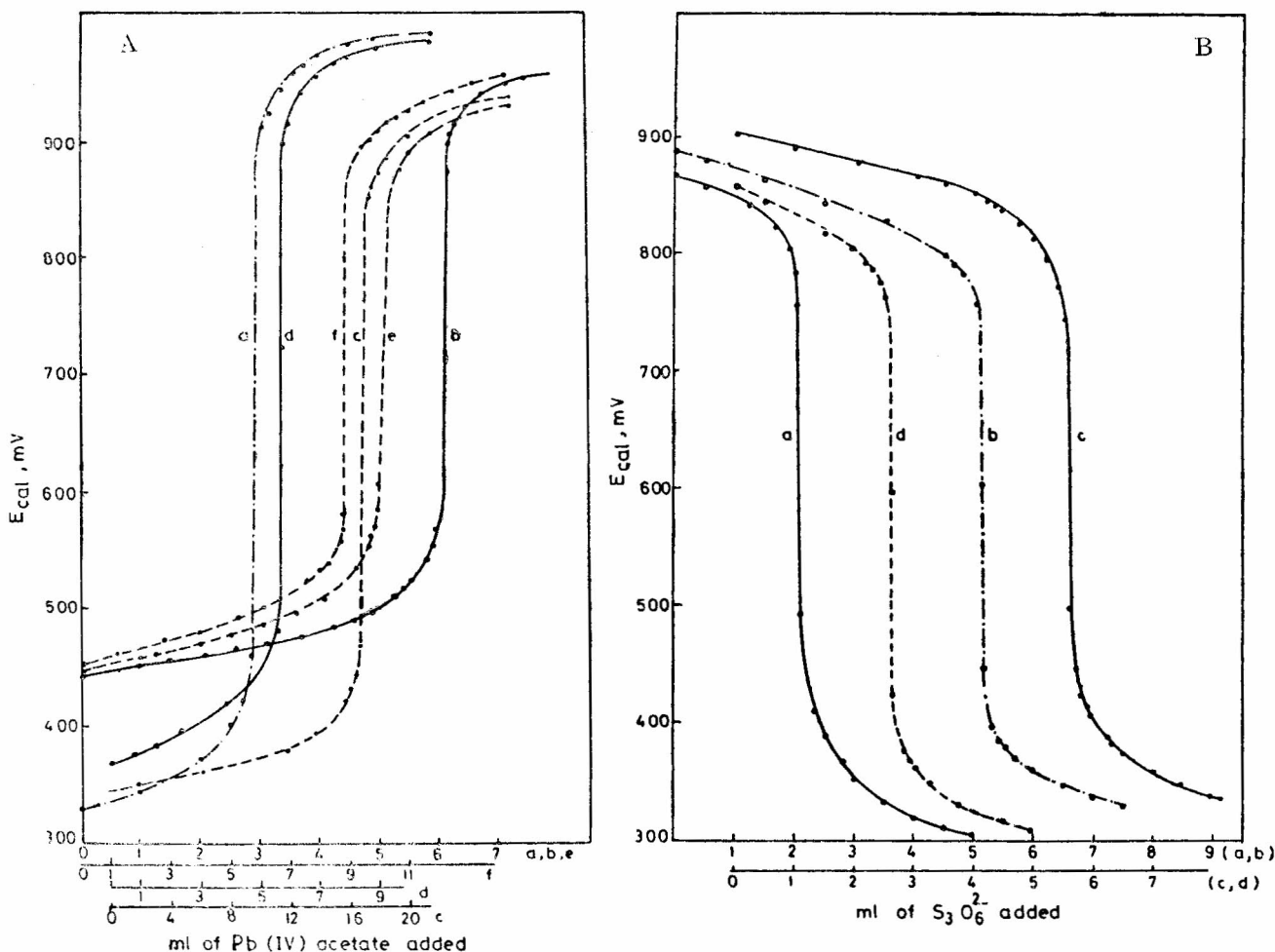


Fig. 1 — (A) Direct titration of trithionate with Pb(IV) acetate [Titration of (a) 1 ml of $2.5 \times 10^{-2}M$ $S_3O_6^{2-}$ with $0.070N$ Pb(OAc)$_4$ at pH 4.5; (b) 1 ml of $2.5 \times 10^{-2}M$ $S_3O_6^{2-}$ with $0.035N$ Pb(OAc)$_4$ at pH 4; (c) 2 ml of $6.2 \times 10^{-3}M$ $S_3O_6^{2-}$ with $0.0058N$ Pb(OAc)$_4$ at pH 4.5; (d) 2 ml of $2.1 \times 10^{-3}M$ $S_3O_6^{2-}$ with $0.0058N$ Pb(OAc)$_4$ at pH 4.8; (e) 1 ml of $2.1 \times 10^{-3}M$ $S_3O_6^{2-}$ with $0.0035N$ Pb(OAc)$_4$ at pH 3.5; and (f) 2 ml of $2.1 \times 10^{-3}M$ $S_3O_6^{2-}$ with $0.0035N$ Pb(OAc)$_4$ at pH 2.2]. (B) Reverse titration of Pb(IV) acetate with trithionate [Titration of (a) 2 ml $0.0175N$ Pb(OAc)$_4$ with $2.1 \times 10^{-3}M$ $S_3O_6^{2-}$; (b) 5 ml $0.0175N$ Pb(OAc)$_4$ with $2.1 \times 10^{-3}M$ $S_3O_6^{2-}$; (c) 5 ml $0.070N$ Pb(OAc)$_4$ with $6.2 \times 10^{-3}M$ $S_3O_6^{2-}$; and (d) 5 ml $0.0087N$ Pb(OAc)$_4$ with $2.1 \times 10^{-3}M$ $S_3O_6^{2-}$]

corresponding to 0·13-65 mg sulphur, the error being generally less than 0·5%.

*Formal redox potential of $SO_4^{2-}/S_3O_6^{2-}$ system* — The formal redox potentials were determined from potentials of the cells (A) and (B). The potentials were measured in the $p$H range 2-4·5. The values of $E°$ for the $SO_4^{2-}/S_3O_6^{2-}$ and $Pb^{4+}/Pb^{2+}$ two half-cells were determined from the Nernst equation (4), neglecting activity coefficients

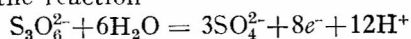$$E_H = E° + \frac{RT}{nF}\ln\frac{[Ox]^n}{[Red]^m} + \frac{RT}{nF}\ln[H^+]^x \quad …(4)$$

where $X$ represents the number of $H^+$ ions and $n$ and $m$ are the number of molecules of oxidant and reductant in the half-cell reactions

Hence, for the reaction

$$Pb^{4+} + 2e^- = Pb^{2+}$$
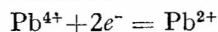
$$_IE_H = {_I}E° + \frac{0·0591}{2}\log\frac{[Pb^{4+}]}{[Pb^{2+}]} - \frac{0·0591}{2}X_I\,p\text{H} \quad …(5)$$

and for the reaction

$$S_3O_6^{2-} + 6H_2O = 3SO_4^{2-} + 8e^- + 12H^+$$

$$_{II}E_H = {_{II}}E° + \frac{0·0591}{8}\log\frac{[SO_4^{-2}]}{[S_3O_6^{-2}]} - \frac{0·0591}{8}X_{II}\,p\text{H} \quad …(6)$$

where $X_I$ and $X_{II}$ represent the numbers of $H^+$ ions involved in the two half-cell reactions.

Plots of $E_H$ vs $p$H are linear (Fig. 2A) with slopes of 0·115 and 0·075 for the $Pb^{4+}/Pb^{2+}$ and $SO_4^{2-}/S_3O_6^{2-}$ systems respectively. On extrapolation to $p$H = 0, the curves give $E_0$ values of 1·32 and 0·71 V respectively. The formal redox potential $(E_f)_x$, for the two systems at any required $p$H $(x)$, can be deduced from Eqs. (5) and (6) with the knowledge of $E_0$ value at $p$H = 0.

It is possible to calculate the values of the equilibrium constant $(K)$ and the extent of completion $(\alpha)$ for reaction (1) from a knowledge of the redox potentials of the systems under investigation for log $K$ is given by Eq. (7) where $Z$ is the number

$$\log K = \frac{(_IE - {_{II}}E)Z}{0·0591} \text{ and } \alpha = K^{1/n_1+n_2} \quad …(7)$$

of electrons involved in the overall reaction (8 in this case) and $n_1$ and $n_2$ are the oxidation-number changes for both systems. The results, obtained for $K$ and $\alpha$, show that the reaction is essentially quantitative at $p$H 2·5-4·5.

Since the slope of $E_H$ vs $p$H plot is equal to $0·0591X/n$, where $X$ is the number of $H^+$ ions participating in the reaction then, for the $Pb^{4+}/Pb^{2+}$ system $X_I$ is 4 and for the $SO_4^{2-}/S_3O_6^{2-}$ system $X_{II}$ is 12. Accordingly, the following equations (8 and 9) may be written to represent the reactions.

$$Pb(CH_3COO)_4 + 2e^- + 4H^+ = Pb^{2+} + 4CH_3COOH \quad …(8)$$

$$3SO_4^{2-} + 12H^+ + 8e^- = S_3O^{2-} + 6H_2O \quad …(9)$$
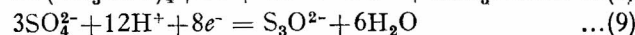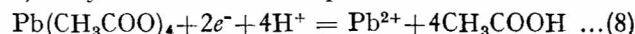
The overall reaction is in accordance with Eq. (1). The validity of the latter equation is verified by determining the slope of the $E_{cell}$ vs $p$H curve (Fig. 2B) for the overall cell reaction. According to Eqs. (5) and (6), when $Pb^{4+}/Pb^{2+} = SO_4^{2-}/S_3O_6^{2-} = 1$, then $E_{cell}$ is given by Eq. (10)

$$E_{cell} = E_0 + \frac{0·0591}{8}(2X_{II} - X_I)p\text{H} \quad …(10)$$

Substituting the values of $X_I = 4$ and $X_{II} = 12$ in Eq. (10), we get Eq. (11)

$$E_{cell} = E_0 + \frac{0·0591 \times 20}{8}p\text{H} = E_0 + 0·1477\,p\text{H} \quad …(11)$$

The slope found experimentally was 0·149, in excellent accordance with that expected (cf. Fig. 2).

*Titration of $Pb(IV)$ acetate with trithionate* — The reverse titration of $Pb(IV)$ acetate with $S_3O_6^{2-}$ is characterized by a single large inflection at which 8 equivalents of trithionate have been consumed
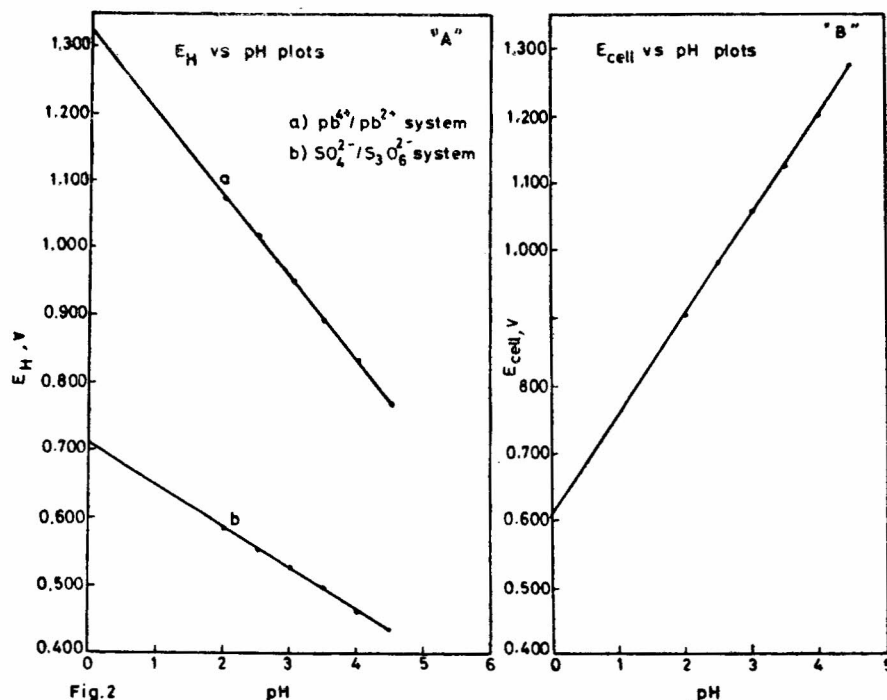
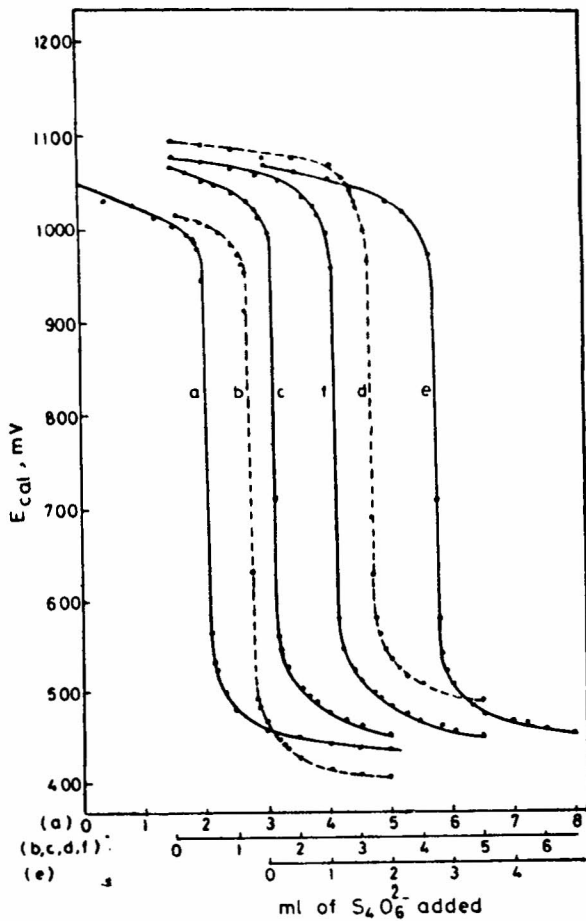

Fig. 2 — (A) $E_H$ vs $p$H plots and (B) $E_{cell}$ vs $p$H plots

Fig. 3 — Direct titration of Pb(IV) acetate with tetrathionate [Titration of (a) 25 ml $0.009N$ Pb(OAc)$_4$ with $1.13 \times 10^{-2}M$ S$_4$O$_6^{2-}$; (b) 15 ml $0.009N$ Pb(OAc)$_4$ with $1.13 \times 10^{-2}M$ S$_4$O$_6^{2-}$; (c) 10 ml $0.018N$ Pb(OAc)$_4$ with $1.13 \times 10^{-2}M$ S$_4$O$_6^{2-}$; (d) 15 ml $0.072N$ Pb(OAc)$_4$ with $3.39 \times 10^{-2}M$ S$_4$O$_6^{2-}$; (e) 2 ml $0.072N$ Pb(OAc)$_4$ with $5.70 \times 10^{-3}M$ S$_4$O$_6^{2-}$; and (f) 4 ml $0.072N$ Pb(OAc)$_4$ with $1.13 \times 10^{-2}M$ S$_4$O$_6^{2-}$

(Fig. 1B). The inflection at the end-point decreases as the concentration of Pb(OAc)$_4$ solution increases. The method can be applied successfully for titrating 2·2-40 mg of Pb (IV).
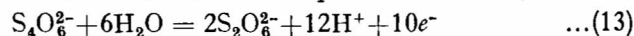
### Determination of Tetrathionate

*Direct titration of* S$_4$O$_6^{2-}$ *with* Pb(IV) *acetate* — The results obtained indicate that the reaction appears to proceed quantitatively in accordance with Eq. (12)

$$5Pb(OAc)_4 + S_4O_6^{2-} + 6H_2O \rightleftharpoons 5Pb(OAc)_2 + 2S_2O_6^{2-} + 10AcOH + 2H^+ \quad \dots(12)$$
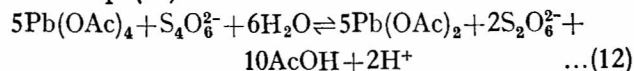
which is based on the two partial reactions (13 and 14)

$$S_4O_6^{2-} + 6H_2O = 2S_2O_6^{2-} + 12H^+ + 10e^- \quad \dots(13)$$

$$5Pb^{4+} + 10e^- = 5Pb^{2+} \quad \dots(14)$$

The titration curves show one reasonable inflection which amounts to 80 mV/0·02 ml titrant (Fig. 3). Amounts of tetrathionate solution containing as low as 0·28 mg of sulphur can be titrated successfully in this way provided that the final $p$H of solution (at the end-point) is between 2 and 4. The formation of dithionate as an oxidation product is confirmed by recording the absorption spectra of the titrated solution both prior to and at the equivalence point. The solution exhibits in each case an absorption band at 240 nm characterizing S$_2$O$_6^{2-}$. The formation of S$_2$O$_6^{2-}$ is verified by precipitating the Pb(II) formed, at the end-point, as PbSO$_4$ and estimation of S$_2$O$_6^{2-}$ in the filtrate by analysis by the method of Murthy[12].

*Indirect titration of Pb(IV) acetate with* S$_4$O$_6^{2-}$ — The results obtained on titrating Pb(IV) acetate corresponding to 0·9-75 mg of lead are in accordance with Eq. (12). The titration curves have a single sharp inflection at the end-point, the error being generally less than 1%.

### References

1. Issa, I. M., El-Meligy, M. S. & Idriss, K. A., *Indian J. Chem.*, **12** (1974), 877.
2. Idriss, K. A., Issa, I. M. & El-Meligy, M. S., *Indian J. Chem.*, **14A** (1976), 195.
3. Kurtenacker, A. & Bittner, K., *Z. anorg., allgem. Chem.*, **142** (1925), 119.
4. Lange, R. & Kurtenacher, A., *Z. anal. Chem.*, **123** (1942), 169.
5. Jay, R. R., *Analyt. Chem.*, **25** (1953), 288.
6. Kaushik, K. L. & Rugendra, P., *Indian J. Chem.*, **8** (1970), 462.
7. Idriss, K. A., Issa, I. M. & Mahmoud, M. R., *Can. J. Chem.* (in press).
8. Berka, A., Dvoràk, V., Nemec, I. & Zyka, J., *Anal. Chim. Acta*, **23** (1960), 830.
9. Tomicek, O. & Valcha, J., *Chem. Listy*, **44** (1950), 383.
10. Berka, A., Vulterin, J. & Zyka, J., *Newer redox titrants* (Pergamon Press, London), 1965, 79.
11. Latimer, W. M., *Oxidation potentials* (Prentice-Hall, New York), 1959, 78.
12. Murthy, A. R. V., *Curr. Sci.*, **22** (1953), 371.