Journal of Thermal Analysis, Vol. 37 (1991) 2713-2722

THERMOMETRIC TITRATIONS AT ELEVATED TEMPERATURES

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(Received October 24, 1990)

The oxidizing power of hexacyanoferrate(III) in alkaline conditions is wellknown. Unfortunately many if its oxidation reactions are too slow at room temperatures for direct titrimetric procedures.

A method has been developed for the determination of millimolar amounts of selenium(IV), arsenic(III), antimony(III), chromium(III), and thallium(I) using thermometric titrimetry at approximately 330 K. The reproducibility and accuracy of the method are approximately 1%.

Introduction

Although the oxidizing capacity of hexacyanoferrate(III) in alkaline media is high compared to those of other oxidants in these media, one of the reasons why it is not frequently used is that there are problems associated with the provision of suitable indicators, since the self-colour of the reaction mixture often obviates the use of an internal indicator. Under such circumstances thermometric titrimetry has well recognised advantages.

However, many of the reactions of hexacyanoferrate(III) are very slow under ordinary temperature conditions, even in the presence of a catalyst. For many reactions which are slow at or near the equivalence point, the method of continuous addition, commonly employed in thermometric titrimetry, is a distinct disadvantage, the thermograms obtained have pronounced curvature around the equivalence point and extrapolation procedures usually result in precisions which are not analytically acceptable.

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Akadémiai Kiadó, Budapest

Whilst in classical titrimetry, the use of indirect methods is possible for many 'slow' systems, the problem of internal indicators still remains for systems involving hexacyanoferrate(III). Although it is possible to use an indirect titration method in thermometric titrimetry, all indirect methods have the inherent disadvantage that a large amount of analyte results in a small 'back' titration and the errors become enhanced.

The use of elevated temperatures may increase the rate of many reactions to the extent that direct titrimetric procedures are possible. Elevated temperature conditions in thermometric titrimetry have been previously restricted to the titration of chlorides in an eutectic mixture of lithium nitrate and potassium nitrate [1].

This paper describes the design and use of an apparatus which enables the direct thermometric method to be used for any fixed temperature between 25° and 90°C. The apparatus has been tested using the reaction between oxalate (diethanoate) ions and permanganate [manganese(VII)] ions in an acidic medium. It has then be used for a series of redox reactions, none of which are feasible at ordinary ambient temperatures.

Experimental

(a) Thermometric bridge

The bridge previously described [2] was modified so that one of a series of thermistors could be chosen to give an appropriate resistance at the selected temperature. The resistance of the other arms of the Wheatstone type bridge were also made variable so that the bridge could have arms of equal resistance at the selected temperature and hence have maximum sensitivity at the time of measurement. (see Fig. 1)

The off-balance voltage of the bridge can be amplified by using a variable gain FET opamp which amplifies the d.c.voltage from 1–50 fold. This allows the use of a potentiometric recorder having a sensitivity of 1 mV for a full scale deflection.

(b) Elevated temperature titration cell and assembly

The titration cell and assembly are shown in Fig. 2. The cell consists of a thickwalled polyethylene vessel of a nominal capacity of 30 ml. The titration cell fits tightly into one of two wells cut into an aluminium block (Dimensions 12 cm×10 cm×8 cm.). A second well containing a similar thickwalled

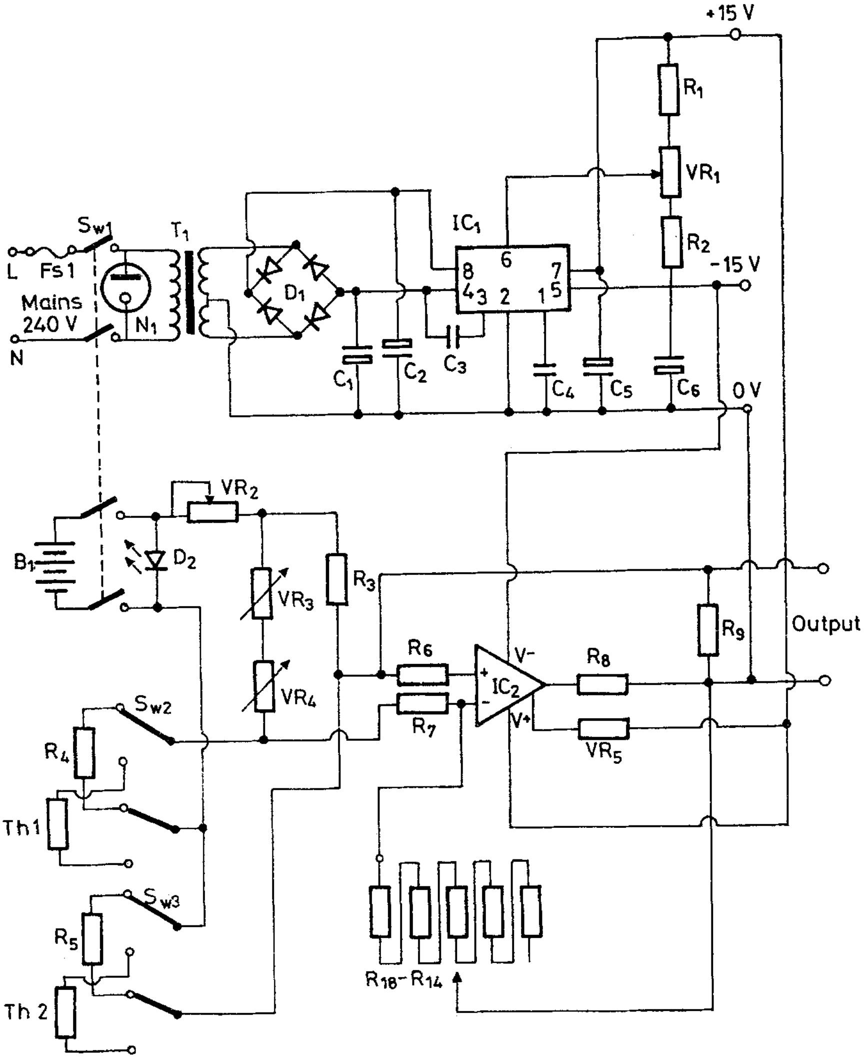

Fig. 1 Thermometric bridge with operational aplifier and associated power supplies.
Code: R_1=6.8 KΩ, R_2=6.8 KΩ, R_3=10 KΩ, R_4=10 KΩ, R_5=10 KW, R_6=10 KW, R_7=22 KΩ, R_8=1 KΩ, R_9=47 Ω, R_{10}=22 KΩ, R_{11}=22 KΩ, R_{12}=62 KΩ, R_{13}=100 KΩ R_{14}=200 KΩ; VR_1=10 KΩ Preset, VR_2=500 KΩ Preset, VR_3=2,5 KΩ Pot (10 turn), VR_4=10 KΩ Pot, VR_5=1 KW Preset; C_1=1000 μF 25 V, C_2=1000 μF 25 V, C_3=0.1 μF, C_4=0.1 μF, C_5=10 μF 25 V, C_6=10 μF 25 V; IC_1=Voltage Regulator IC ±15 V 100 mA, IC_2=Fet Input OPA, Th_1 and Th_2=10 KW Thermistors, SW_1=4 Pole DPTP Switch, D_1=1A Bridge Rectifier, D_2=L.E.D. (Gree or Red), FS_1=Mains Fuse 100 mA, T_1=15-0-15 Transformer

polyethylene vessel is filled with water and a length of neoprene tubing is coiled around inside the vessel, entering and exiting via small channels in the aluminium block. The tube connects the reservoir of the reagent solution and the titration sample via a peristaltic pump, which is between the reservoir and the heating block. This allows the pump to operate at the ambient temperature, and hence for calibration purposes, the viscosity of the solution is that of the solution at ambient temperature and the flow rate can be determined, gravimetrically, at the ambient temperature. The flow rate will remain constant irrespective of the actual temperature of the block.

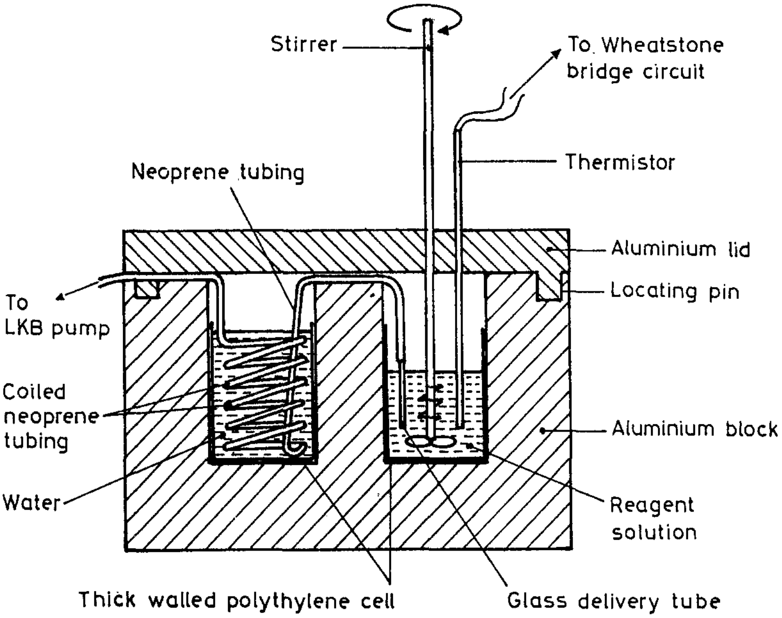

Fig. 2 Titration cell assembly in heated aluminium block

The block is covered with a precisely fitting lid, approximately 1 cm thick. Holes are drilled into the block to give precision fitting of a microstirrer, and the thermistors, which are used to measure the temperature of the block and to indicate changes in the temperature of the titration sample.

Aluminium was chosen as the material of construction of the elevated temperature system because of its high thermal conductivity, which ensures preciseness of the temperature control. Whilst it is recognised that the thickwalled polyethylene cells will have a slower attainment of thermal equilibrium between the aluminium block and the reaction system, they are used because they effectively insulate the heat changes during the course of a reaction against dissipation from the reaction system into the aluminium block.

The block is heated using relatively low wattage electrical heaters. The temperature of the aluminium block is controlled via a zero voltage switch by comparing the voltages at two points in the circuit. When both points are at the same temperature the heater is automatically switched off. The aluminium block is controlled to a precision of temperature of better than ±0.01°C by this proportional heat control method.

(c) Validation of the titration system using the reaction between oxalate and Mn(VII) in acidic conditions

It was considered that a comparison of the results obtained in the oxidation of oxalate ions by permanganate using classical methods and a thermometric method would serve as a suitable test for the validity of the thermometric method as a method of assay in a redox system at temperatures above ambient.

Potassium permanganate was purified by repeated recrystallization and filtration, air dried at 60°C for two days and then used as below.

Appropriate amounts of A.R. sodium oxalate (previously dried at 105°C, to constant weight) were dissolved in water and the solutions used as the standard samples.

The precision and the standard deviations of the two procedures were obtained by a ten fold repeat of each of the two procedures.

Thermometric method

The block was set at 60°C and sodium oxalate (2.00 ml of 0.1122 M) and sulphuric acid (10.0 ml of 4 M) were placed in the titration cell. A solution of Mn(II) (0.05 ml of approx 0.0001 M) was added as a catalyst. On attainment of thermal equilibrium, Mn(VII) was added as titrant via a previously calibrated peristaltic pump. The end point was sharp.

Results

(i) Thermometric titration of oxalate

Amount of oxalate taken in 2.00 ml of sample is 0.2244 mMoles.
Chart Distance in mm. 83.0 82.5 83.0 82.5 83.0 83.0 83.5 83.5 82.5 83.0
Mean Value is 82.85 mm. Standard deviation is 0.37

The Relative Standard Deviation is 0.00099 mMoles.

Determination of the Mn(VII) by classical methods

The Mn(VII), was standardised using sodium oxalate (25 ml; 0.5010 M) and sulphuric acid (100 ml; 2 M) at 60°C using the standard method [2].

(ii) Classical method

The amount of oxalate taken in 25.0 ml of sample is 1.253 mMoles.
Titrant (ml) 24.50 24.55 24.55 24.50 24.45 24.52 24.40 24.55 24.55 24.40.
Mean Value is 24.50 ml. Standard deviation is 0.053
The relative Standard Deviation is 0.00275 mMoles.

Purity of potassium permanganate

The following sequence of reactions were used for the assay of the transitional metal ions:

Antimony(III) and Arsenic(III)

Aliquots (25 ml containing 1–1.25 mMoles) of solutions of these ions were titrated directly with iodine in potassium iodide solution.

Starch solution was used to indicate the equivalence points in these reactions [2].

Determination of Arsenic(III)

Amount of sodium arsenite taken as sample = 1.233 mMoles
Amount of iodine delivered as titrant = 1.193 mMoles.
The R.M.D. = 0.005 mMoles.

Determination of antimony(III)

Amount of potassium antimonyl tartrate taken as sample = 1.283 mMoles.
Amount of iodine delivered as titrant = 1.273 mMoles.
The R.M.D. = 0.005 mMoles.

Chromium(III)

An aliquot (25 ml containing 0.05 mMoles) of chromium(III) chloride was boiled with 2 drops of 0.1 *M* silver nitrate solution and a known and excess amount (30 ml of 0.1 *M*) aqueous potassium peroxydisulphate solution until oxygen ceased to be evolved.

The potassium dichromate formed was then reacted with an excess of an acidified (sulphuric acid) solution of iron(II) ammonium sulphate. The excess of the iron(II) solution was determined by titration with standardized potassium dichromate solution. A mixture of diphenylamine sulphonic acid (2 drops of 0.2% w/v aqueous) and 3–5 ml of phosphoric acid was used as the indicator [2].

Determination of chromium

Amount of chromium chloride taken as sample = 0.0499 mMoles.

Amount of iron(II) ammonium sulphate delivered as titrant = 2.20 mMoles.

Amount of potassium dichromate delivered as titrant = 0.3361 mMoles.

The R.M.D. = 0.001 mMoles.

Selenium(IV)

An aliquot (25 ml) of the sodium selenite solution (containing approximately 1.0 mMoles) was treated with an excess amount of potassium iodide solution (20 ml of 10% w/v aqueous solution). The iodine liberated was titrated with standardized thiosulphate solution using a starch indicator for equivalence point detection [2].

The determination of selenium(IV)

Amount of sodium selenite taken as sample = 0.8898 mMoles.

Amount of sodium thiosulphate delivered as titrant = 3.549 mMoles.

The R.M.D. = 0.012 mMoles.

Thallium(I)

An aliquot (25 ml containing approximately 1.25 mMoles of thallium nitrate) was titrated with potassium iodate using the Andrews-Jamieson method [2].

Table 1 Thermometric titrimetry at elevated temperatures. In all the results below, the chart speed was 30.0 mm per minute and the flow rate was approximately 0.2 ml per minute. Both were determined each day and checked several times during the day.

Compound	(mMoles)	M.R.	Apparent purity (%)	R.M.D. (Therm)
Se(IV)	0.02544	2.01	100.5	0.0112
As(III)	0.0280	1.96	98.0	0.0115
Sb(III)	0.0187	1.97	98.5	0.0095
Cr(III)	0.01624	2.97	99.0	0.097
Co(II)	0.2392	0.999	99.9	0.098

M.R. = Molar Ratio calculated

R.M.D. is calculated from 10 replicates – refer to M.R.

Determination of thallium(I)

Amount of thallium(I) nitrate taken as sample = 12.53 mMoles.

Amount of potassium iodate delivered as titrant = 6.622 mMoles.

The R.M.D. = 0.003 mMoles.

The result of the above determinations are given in Table 1.

Calculated from thermometric procedure = 99.75%.

Calculated from classical method = 99.8%.

Reactions between potassium hexacyanoferrate(III) and some transitional metal ions

Approximately 0.6 *M* aqueous solutions of potassium hexacyanoferrate(III) were prepared by dissolving the appropriate amounts of the solid in water. Solutions were freshly prepared each day.

The following transitional metal ions were used: Selenium(IV) (as sodium selenite); arsenic(III (as sodium arsenite); antimony(III) (as potassium antimonyl tartrate); thallium(I) (as thallium(I) nitrate); and chromium(III) (as chromium(III) chloride).

An aliquot (2 ml) of the metal ion solution, sodium hydroxide solution (12.0 ml, 20% w/v); and osmium(VIII) solution (1 drop of approximately 0.5 mM osmium(VIII) oxide in 2 *M* NaOH) were placed in the titration cell. The block was heated to 60°C and potassium hexacyanoferrate(III) was added as titrant.

The equivalence points for all the titrations were acceptably sharp.

Precision and standard deviations were obtained from replicate analyses.

Titration of the transitional metals using 'classical' methods

(i) All amounts of analyte are calculated from the weights of solid taken to make the stock solutions.

(ii) All Relative Mean Deviations (R.M.D.) are calculated from 10 replicates.

Discussion

The apparatus described produced sharp equivalence points allowing for easy and accurate determination of the volumes of titrant used.

Although the enthalpograms had small and regular waves, in them, this did not impair the determination of the significant points. The regular and sinusoidal deviation from linearity caused by the switching of the fine control on the heater circuit, at temperatures in excess of 60°C the wavelength and the amplitude become less and at ca. 90°C the deviation from linearity is not discernable.

The results indicate that several inorganic species, which are usually determined titrimetrically by oxidation reactions that require an indirect method when ordinary ambient temperatures are used, may be determined rapidly and effectively by direct titration using oxidation with hexacyanoferrate(III) at temperatures of 60°C.

For example, although a direct method for the determination of arsenic(III) has been reported [3], it is only effective when the arsenic(III) sample is used as the titrant and the arsenic(III) must be added slowly when nearing the equivalence point. The use of an unknown as the titrant has obvious disadvantages especially if the sample (such as, for example, industrial fungicide or weedkiller) contains not only solids with low solubilities but substances such as polyelectrolytes to maintain these in suspension.

The results indicate that the classical and the thermometric method offer approximately the same precision and reproducibility, a precision of better than 1%. The thermometric method uses significantly smaller amounts of sample than do the classical methods, which is an advantage in some industrial situations in which large numbers of samples of a routine nature must be analysed.

The system offers the usual advantages of thermometric titrimetry over potentiometric methods in that not only does it avoid the use of salt bridges at elevated temperatures (which is, practically, inconvenient), but also surface active materials and suspended particles, which foul electrode surfaces causing spurious junction potentials, have no effect on the temperature sensor used in this system.

Coloured media and suspensions containing analytically inert material do not create any disadvantage. Thus it has been possible to use this system in commercial formulations which have an analyte of industrial importance, as in a pesticide or other toxic agrocidal preparation involving thallium or arsenic, a suspension agent and/or a wetting/spreading agent as well as coloured substances which are included for various industrial and commercial purposes.

References

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Zusammenfassung — Die Oxidationsfähigkeit von Hexacyanoferrat(III) unter alkalischen Bedingungen ist wohlbekannt. Viele seiner Oxidationsreaktionen sind bei Raumtemperatur leider viel zu langsam, um sie für direkte Titrationen zu verwenden.

Es wurde ein Verfahren entwickelt, um mittels thermometrischer Titration bei ungefähr 330 K Selen(IV), Arsen(III), Antimon(III), Chrom(III) und Thallium(I) im Millimolbereich zu bestimmen. Die Reproduzierbarkeit und Genauigkeit der Methode beträgt etwa 1%.