A NEW VOLUMETRIC METHOD OF CERIUM DETERMINATION BY THIOCYANATE

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Ceric sulphate is a valuable oxidant in quantitative analysis, because of its great stability[9, 10] and has almost supplanted permanganate and dichromate in certain analytical processes.[3, 4, 14]

Many quantitative analytical processes are based on the oxidation of thiourea and thiocyanates.[2, 12] In practically every case the sulphur atom of the anion is oxidized to sulphate, and in most cases the nitrogen escapes as hydrogen cyanide.[5]

Review of the literature showed that little data exist on the determination of cerium using thiocyanate. The addition of ammonium or potassium thiocyanate discharges the characteristic yellow colour of ceric sulphate, indicating its reduction to cerous condition. The possibility therefore, of using standard thiocyanate for the determination of cerium in a given ceric sulphate solution was studied.

Experimental

The ceric sulphate solution was prepared by digesting with concentrated sulphuric acid, a commercial sample containing about 40% ceric oxide as recommended by Willard and Young[11]; and standardised by titrating against ferrous ammonium sulphate of known strength, using *o*-phenanthroline ferrous complex or diphenylamine as the indicator.[7, 1] The thiocyanate solution was standardised by Volhard's method; and silver nitrate by the method of Mohr.

The end point in the titration of ceric sulphate against thiocyanate was found to depend on the way the thiocyanate was added. Whilst a rapid addition of thiocyanate entailed the possibility of overtitration, a slow dropwise addition took in a larger quantity of the reductant, leading to high results. Addition of the titre over a period ranging from 15 seconds to

30 minutes, offered no advantage, nor did the preheating of ceric sulphate solution. The following procedure was finally adopted:

A known excess (*a* ml.) of dilute thiocyanate solution was run in directly into (*b* ml.) of cold ceric sulphate solution with constant stirring till the yellow colour was discharged completely. This was followed by (*c* ml.) of silver nitrate (equivalent to *d* ml. of thiocyanate); the titration was finished by adding (*e* ml.) of thiocyanate, with ferric nitrate as the indicator.[8] The difference ($a + e - d$ ml.) was the thiocyanate required to reduce the ceric sulphate to cerous condition in terms of the equation

$$6\,Ce\,(SO_4)_2+KCNS+4\,H_2O \rightarrow 3\,Ce_2\,(SO_4)_3+KHSO_4+3\,H_2SO_4+HCN \quad (1)$$

Results of one representative series of experiments are returned in Table I.

TABLE I

Overall Acidity 2–3 *N* H_2SO_4

Expt. No.	Conc. of Ce $(SO_4)_2$	Normality of KCNS	Vol. of Ce $(SO_4)_2$ (*b* ml.)	Vol. of KCNS ($a+e-d$ ml.)	CeO_2 found gm.	CeO_2 Calcd. gm.	% Error
1	0·01840 N	0·01021	10	3	0·03163	0·03166	0·094
2	0·03572	0·01146	10	5·2	0·06153	0·06146	0·11
3	0·03793	0·01089	10	5·8	0·06523	0·06525	0·03
4	0·04592	0·01277	10	6·0	0·07889	0·07902	0·16
5	0·05500	0·01817	10	5·05	0·09473	0·09464	0·095
6	do.	do.	20	10·1	0·1894	0·18928	0·06
7	do.	do.	30	15·2	0·2852	0·28392	0·45
8	0·05792	0·01305	10	7·4	0·09968	0·09970	0·02
9	0·06219	0·01125	10	9·2	0·1069	0·1070	0·09
10	do.	do.	20	18·45	0·2142	0·2140	0·09
11	do.	do.	30	27·65	0·3211	0·3210	0·03
12	0·1111	0·01072	10	17·3	0·1914	0·1912	0·10
13	0·05500	0·01817	40	20·35	0·3819	0·37856	0·88
14	do.	do.	50	25·55	0·4793	0·4732	1·29
15	0·06219	0·01125	40	37·25	0·4325	0·4286	0·91
16	do.	do.	50	46·9	0·5448	0·5350	1·83

DISCUSSION

In the estimation of iron by thiocyanate, Peters and French[6] and Woods and Mellon[13] observed that $Ce^{\cdots}$, $(CN)'$ and SO_3'' ions did not interfere in the formation of ferric thiocyanate by more than 2%, when present in a concentration 250 times that of ferric ions.

In the present work, the detection of the end point and therefore, the accuracy of the result depends on the production of red ferric thiocyanate. It is suggested therefore, that the discrepancy between the observed and the calculated results in Expts. 13–16, Table I, may be ascribed to the influence of the large concentration of $Ce^{\cdots}$ and/or SO_4'' ions.

It follows from equation (1), that with the completion of the reaction, the total number of sulphate ions increases from twelve to thirteen. A quantitative estimation of sulphate in the ceric sulphate solution, with and without the addition of thiocyanate, should therefore serve as a further test of the suggested reaction mechanism.

To an aliquot portion of ceric sulphate a requisite amount of thiocyanate is added and the sulphate precipitated as usual. A blank estimation, without the addition of thiocyanate, is simultaneously carried out. From the knowledge of the actual amount of ceric sulphate present, the increase in the weight of precipitated $BaSO_4$ due to the addition of thiocyanate is calculated. Typical results in Table II show that the agreement between the calculated and the observed values lies within the limits of experimental error.

TABLE II

Expt. No.	Amount of $Ce(SO_4)_2$ in 10 ml. (gm.)	Wt. of $BaSO_4$ without KCNS (gm.)	Wt. of $BaSO_4$ with KCNS		Difference
			Obsd. (gm.)	Calcd. (gm.)	
1	0·1525	0·2141	0·2354	0·2352	+0·0002
2	0·1992	0·2699	0·2965	0·2963	+0·0002
3	0·2138	0·2898	0·3182	0·3179	+0·0003

Since the determination of cerium is based on the oxidation-reduction reaction, the presence of other trivalent rare earths—its almost invariable contaminants, does not affect the accuracy of the results.

A comparative study of the methods of estimation of thiocyanate by $KMnO_4$[12] and ceric sulphate shows that under identical experimental conditions one molecule of KCNS is equivalent to 6/5 and 6 molecules of permanganate and $Ce(SO_4)_2$ respectively; the utilisability of the latter in the determination of small quantities of thiocyanates is suggested. Experimental data given in Table I have been used in assessing the accuracy of the titration for the determination of thiocyanate, the ceric sulphate being assumed to be pure. It has been found that the method is quite accurate for the determination of thiocyanate. The above method indicates also an interesting possibility of silver estimation by ceric sulphate; this has already been confirmed by preliminary results of our investigation.

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SUMMARY

A new volumetric method for cerium determination, based on the reduction of ceric sulphate by potassium or ammonium thiocyanate added in excess and the determination of the excess by back-titration as in Volhard's method is developed. One molecule of KCNS reacts with six molecules of $Ce(SO_4)_2$; the sulphur atom of the thiocyanate is oxidized to sulphate. $Ce^{\cdots}$ and SO_4'' ions in moderate quantities and the usual rare earth impurities in ceric sulphate do not affect the accuracy of the method. The possibility of using ceric sulphate in the determination of small quantities of thiocyanate and in argentometric titration is suggested.

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