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Volumetric Method for the Estimation of Persulphate in Aqueous Solution

By

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During the kinetic study of oxidation of sodium thiosulphate by persulphate ion, it was observed by us that the reaction becomes very fast in the presence of a very small amount of copper sulphate¹. The great catalytic activity of copper sulphate on this reaction has been reported previously by KING and STEINBACH⁵ also. This suggested to us that the copper catalysed oxidation of sodium thiosulphate by persulphate ion may be used as a rapid method for the estimation of persulphate ion and this led to the present investigation.

The various methods used for the estimation of persulphate involved the catalytic oxidation of different reducing agents. Thus one¹⁰ of the earliest methods has been to reduce persulphate with excess of oxalic acid in presence of a small amount of silver sulphate and estimating the unreacted oxalic acid with standard potassium permanganate solution. Another method⁶ used is to add excess of ferrous ammonium sulphate to persulphate and after completing the reduction of persulphate in hot solution, the unreacted ferrous salt is estimated against standard potassium permanganate. BRIGHT and LARABEC² suggested the silver catalysed oxidation of manganous ion by persulphate ion to permanganate in hot acid solution as another method for this estimation. In this the permanganate thus formed is estimated against sodium arsenite. SANDELL, KOLTHOFF and LINGANE³ modified the method by suggesting the use of a mixture of sodium arsenite and sodium nitrite instead of sodium arsenite alone. In the above methods the time taken for the complete reduction of persulphate even in hot solution is about 30 minutes or so. Besides being time consuming, there is the possibility of slight self-decomposition of persulphate in hot solution.

One of the most suitable methods is the one first used by GOPALA RAO and coworkers⁷ and modified by SZABÓ, CSÁNYI and GALIBA⁹. In this method the persulphate is reduced by potassium iodide in presence of a mixture of copper sulphate and ferrous sulphate as catalyst and the liberated iodine is estimated against standardised sodium thiosulphate solution. In another method recently suggested by GUPTA and GHOSH⁴, the persulphate solution is run into a hot solution of a mixture of standard arsenious oxide, excess of potassium iodide and sodium bicarbonate, the iodine liberated from potassium iodide on oxidation being instantaneously consumed by the arsenite solution. The end point is indicated by the yellow colour due to liberated iodine when all arsenite has been used up. Here again, the estimation has to be carried out in hot solution (80° C). GUPTA³ has recently proposed yet another method for the estimation of persulphate in a 12.5N sulphuric acid solution by direct titration with permanganate. The results are satisfactory but great limitation of the method is the critical condition required.

In the present method, the persulphate solution to be estimated is added to an excess of sodium thiosulphate solution containing copper sulphate solution as catalyst. After allowing suitable time for the reduction of persulphate to be complete the remaining sodium thiosulphate is titrated against a standardised iodine solution. After making allowance for the added copper sulphate, the volume of sodium thiosulphate required for the reduction of persulphate is easily calculated and thereby the strength of persulphate solution.

Experimental

Reagents. Potassium persulphate G.R., E. Merck, and sodium thiosulphate, iodine, sodium persulphate, ammonium persulphate, arsenious oxide and copper sulphate all of A.R., B.D.H. quality have been used. Potassium iodide E.P., E. Merck has been used. All the salts used for seeing their influence on the accuracy of this method were also of A.R., B.D.H. quality.

Potassium persulphate solution was freshly prepared by direct weighing of the salt and dissolving in fresh conductivity water. Its strength was checked by iodometric method of SZABO and coworkers⁹. *Sodium thiosulphate solution* was prepared in freshly boiled conductivity water and was standardised against iodine solution which was standardised against arsenious oxide solution. The *iodine solution* was prepared in 0.1% solution of potassium iodide.

Preliminary experiments carried out showed that this small concentration of potassium iodide used did not liberate iodine from potassium persulphate solution at the concentration employed at room temperature. Further it was seen by us that the use of alcoholic solution of iodine did not in any way improve the accuracy of estimation, hence iodine solution prepared in 0.1% aqueous solution of potassium iodide was used throughout the course of the present investigation. Copper sulphate solution was prepared fresh daily in conductivity water.

Procedure. For carrying out the estimation 10 ml of potassium persulphate solution were taken in a 100 ml pyrex conical flask, 5 ml of copper sulphate solution of required concentration (0.01 M) were added and then 10 ml of sodium thiosulphate solution of required concentration (at least five times the concentration of persulphate taken) were added. The solution was allowed to stand for 10 to 15 minutes and then the excess of thiosulphate was titrated against a standardised iodine solution using starch as indicator. In order to determine the volume of iodine equivalent to 5 ml of copper sulphate added in each titration, 10 ml of thiosulphate solution were first titrated against iodine solution and then the mixture of 10 ml thiosulphate and 5 ml copper sulphate solution against the same iodine. The difference of these readings gave the value of iodine equivalent to copper sulphate added in each titration. This volume of iodine (equivalent to copper sulphate solution) added to volume of iodine obtained in each titration gave the volume of iodine required to oxidise the remaining thiosulphate in each case. Thus the volume of thiosulphate used by persulphate can be calculated and thereby the strength of persulphate. A number of titrations was carried out in each case and it was found that the results are generally concurrent.

In order to determine the suitable concentration of the catalyst copper sulphate and the reactant thiosulphate, estimations were carried

out at various concentrations of copper sulphate and sodium thio-sulphate, the results of which are summarised in Tables 1 and 2.

Table 1. *Effect of CuSO_4 Concentration*
Taken 10 ml $\text{K}_2\text{S}_2\text{O}_8$ solution (0.020196 N), 10 ml $\text{Na}_2\text{S}_2\text{O}_3$ solution (0.099 N)
 $\text{I}_2 = 0.096 \text{ N}$

Concentration of CuSO_4	Volume of I_2 equivalent to 5 ml of CuSO_4 added	Volume of I_2 in each titration	Volume of I_2 required to oxidise remaining $\text{Na}_2\text{S}_2\text{O}_3$	Calculated strength of $\text{K}_2\text{S}_2\text{O}_8$	Error
M	ml	ml	ml	N	%
0.010	0.50	7.71	8.21	0.020196	0
0.009	0.46	7.75	8.21	0.020196	0
0.008	0.40	7.81	8.21	0.020196	0
0.007	0.36	7.85	8.21	0.020196	0
0.006	0.30	7.86	8.16	0.020692	+ 2.48
0.005	0.26	7.88	8.14	0.020889	+ 3.46

It is seen from Table 1 that the suitable concentration of the catalyst copper sulphate is 0.007 M or more. Hence in subsequent titrations 5 ml of 0.01 M copper sulphate were used in each case.

Table 2. *Effect of $\text{Na}_2\text{S}_2\text{O}_3$ Concentration*
Taken 10 ml $\text{K}_2\text{S}_2\text{O}_8$ solution (0.0225 N), 5 ml CuSO_4 solution (0.01 M), $\text{I}_2 = 0.0956 \text{ N}$
Blank reading for 5 ml $\text{CuSO}_4 = 0.54 \text{ ml I}_2$ solution

Concentration of $\text{Na}_2\text{S}_2\text{O}_3$	Volume of I_2 (microburette reading)	Volume of I_2 required to oxidise the remaining $\text{Na}_2\text{S}_2\text{O}_3$	Calculated strength of $\text{K}_2\text{S}_2\text{O}_8$	Error
N	ml	ml	N	%
0.200	18.03	18.57	0.02244	- 0.28
0.175	15.40	15.94	0.02250	0
0.150	12.80	13.34	0.02250	0
0.125	10.19	10.73	0.02250	0
0.100	7.58	8.12	0.02240	- 0.44
0.050	3.16	3.70	0.01465	low value

A perusal of the results in Table 2 shows that the appropriate concentration of sodium thiosulphate for this estimation should be about five times or more than the concentration of potassium persulphate to be estimated.

Effect of $\text{K}_2\text{S}_2\text{O}_8$ Concentration. In order to test the accuracy of the method for various concentrations of persulphate the estimations were carried out for different concentrations of persulphate (upto about 0.001 N), the concentration of thiosulphate employed was correspondingly changed in each case as indicated in the results given in Table 3.

Table 3
Taken 5 ml CuSO_4 solution (0.01 M)

Concentration of $\text{K}_2\text{S}_2\text{O}_8$ 10 ml	Concentration of $\text{Na}_2\text{S}_2\text{O}_8$ 10 ml	Concentration of I_2	Vol. of I_2 (micro-burette reading)	Vol. of I_2 equivalent to 5 ml of CuSO_4 added	Calculated strength of $\text{K}_2\text{S}_2\text{O}_8$	Error
N	N	N	ml	ml	N	%
0.1005	0.5000	0.1709	23.14	0.26	0.1005	0
0.05025	0.2500	0.1709	11.43	0.26	0.05025	0
0.03934	0.2015	0.01993	78.82	2.54	0.03939	+ 0.11
0.02951	0.1513	0.01993	58.50	2.54	0.02959	+ 0.14
0.02010	0.1000	0.1709	4.415	0.26	0.02011	+ 0.25
0.01001	0.04901	0.02142	15.86	2.34	0.01005	+ 0.38
0.005004	0.02451	0.02142	6.82	2.34	0.004999	- 0.1
0.002002*	0.02000	0.01999	6.49	2.52	0.002000	- 0.09
0.001001*	0.01000	0.01999	1.981	2.52	0.001003	+ 0.21

* In the last two cases the solutions had to be kept for about 20 to 25 minutes to complete the reaction.

Hence it is seen that the method has reasonable accuracy up to even 0.001 N persulphate concentration provided sufficient time is allowed for the completion of the reaction.

Table 4. *Effect of Added Salts*

Taken 10 ml $\text{K}_2\text{S}_2\text{O}_8$ solution (0.01984 N), 10 ml $\text{Na}_2\text{S}_2\text{O}_8$ solution (0.0992 N), 5 ml CuSO_4 solution (0.01 N); $\text{I}_2 = 0.0393$ N; Blank reading for 5 ml of $\text{CuSO}_4 = 1.35$ ml of iodine. Volume of 0.1 N salt added = 10 ml

Salt	Volume of I_2 (microburette reading) ml	Volume of I_2 required to oxidise the remaining $\text{Na}_2\text{S}_2\text{O}_8$ ml	Calculated strength of $\text{K}_2\text{S}_2\text{O}_8$ N	Error %
NaCl	18.85	20.20	0.01984	0
KCl	18.85	20.20	0.01984	0
Na_2SO_4	18.85	20.20	0.01984	0
MnSO_4	18.85	20.20	0.01984	0
MgSO_4	18.85	20.20	0.01984	0
$\text{Al}_2(\text{SO}_4)_3$	18.85	20.20	0.01984	0

Effect of Foreign Ions. From the results in Table 4 it is seen that the salts sodium chloride, potassium chloride, sodium sulphate, manganese sulphate, magnesium sulphate and aluminium sulphate have no effect on this method of estimation of potassium persulphate.

Further the estimation of persulphate was carried out by using sodium persulphate and ammonium persulphate and it was seen that the results are of the same order of accuracy as with potassium persulphate as shown by the data in Table 5.

Table 5

Taken 10 ml $\text{Na}_2\text{S}_2\text{O}_8$ solution (0.0493 N), 5 ml CuSO_4 solution (0.01 M);
 $\text{I}_2 = 0.01798$ N; Blank reading for 5 ml $\text{CuSO}_4 = 2$ ml of I_2

Reactant 10 ml	Concentration of the reactant N	Volume of I_2 (microburette reading) ml	Volume of I_2 required to oxi- dise the remain- ing $\text{Na}_2\text{S}_2\text{O}_8$ ml	Calculated strength of the reactant N	Error %
$\text{Na}_2\text{S}_2\text{O}_8$	0.01004	19.79	21.79	0.0100672	+ 0.29
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	0.01003	19.79	21.79	0.0100672	+ 0.37

Conclusion. The above estimation results show that the percentage error in most cases is $\pm 0.4\%$ or less, the maximum obtainable by using a microburette reading up to 0.01 ml. Hence this method of estimation is very suitable for rapid estimation of persulphate in aqueous solution. Further the advantage of this method is that the estimation can be carried out at room temperature.

Summary

A rapid volumetric method for the estimation of persulphate using the persulphate-thiosulphate reaction catalysed by cupric ions has been proposed. The method consists in adding a known excess of standardised sodium thiosulphate solution to the persulphate solution containing 5 ml of 0.01 M copper sulphate solution and after the completion of the reduction of persulphate, titrating the remaining sodium thiosulphate against a standard solution of iodine.

Zusammenfassung

Die durch Kupfer(II)-ionen katalysierte Reaktion zwischen Persulfat und Thiosulfat wird zur raschen, volumetrischen Persulfatbestimmung benutzt. Bei dem Verfahren gibt man zur Persulfatlösung, die 5 ml 0,01 m Kupfersulfatlösung enthält, einen Überschuß an Thiosulfatlösung und titriert nach Beendigung der Reaktion mit Jodlösung zurück.

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Die polarographische Bestimmung kleiner Selenmengen

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Mit 8 Textabbildungen

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Das polarographische Verhalten des vierwertigen Selens wurde schon in einer ganzen Reihe von Grundlösungen untersucht^{1-4,6,8-11,13}. Außerdem finden sich in der Literatur Angaben über die Polarographie des zweiwertig negativen Selens⁷, eine indirekte Selenbestimmung⁵ und die polarographische Analyse des Natriumselenosulfates Na_2SSeO_3 ¹².

Ziel dieser Arbeit war es, die verschiedenen bekannten Grundlösungen hinsichtlich Empfindlichkeit und Genauigkeit der Selenbestimmung vergleichend zu untersuchen (mit Ausnahme der von DESHMUKH u. ASTHANA³ vorgeschlagenen Ammoniumacetatlösung, um nicht in laufende Untersuchungen dieser Autoren einzugreifen). Weiterhin sollten gegebenenfalls neue Grundlösungen gefunden werden, in denen sich insbesondere die Bestimmung sehr kleiner Selenmengen durchführen läßt. Von den verschiedenen Wertigkeiten des Selens wurde allein die Selenstufe in Betracht gezogen, da diese in wäßrigen Lösungen zuverlässig zu erhalten und bei Spurenanalysen allein von Bedeutung ist.

Die für die Versuche verwendeten Ausgangslösungen wurden durch Verdünnen von mäßig konzentrierten wäßrigen Selendioxid-Stammlösungen (etwa 70–130 mg SeO_2 /l) hergestellt. Sehr verdünnte SeO_2 -Lösungen nahmen beim Aufbewahren in Glasgefäßen mit der Zeit deutlich an Gehalt ab und wurden daher in Abständen von etwa einer Woche neu angesetzt.

Als Polarographen wurden das konventionelle Gerät PO3 der Fa. Radiometer (Kopenhagen) und der oszillographische Polarograph P576 der Fa. Kovo (Prag) verwendet. Die Messungen erfolgten im allgemeinen bei Raumtemperatur (ungefähr 22° C) gegen eine gesättigte Kalomelektrode. Die Lösungen wurden mit gereinigtem Stickstoff gespült, der zum Verhindern von Konzentrationsänderungen der Analysenlösungen vorher durch eine Waschflasche mit der gleichen Lösung geleitet worden war. Die pH-Messungen wurden mit dem pH-Meter Typ 4 der Fa. Radiometer durchgeführt (Glaselektrode).