DIRECT DETERMINATION OF SELENITE BY MEANS OF POTASSIUM FERRICYANIDE[1]

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A new method for the determination of selenite has been elaborated applying potassium ferricyanide as measuring solution. This method proved to be considerably simpler and more rapid than the iodometric and permanganometric determinations applied so far. It has been established that selenite-ferricyanide reaction proceeds even at a higher temperature and high base concentration, extraordinary slowly, but on adding a few drops of osmium tetroxide catalyst, it may become under suitable experimental conditions instantaneous. The effect of the different ions on the exactness of the determination has been submitted to a careful investigation.

A great part of the determinations of selenous acid is based on its reduction to selenium. Some of the procedures regard the gravimetric determination of selenium as a following step, while some of them carry on the analysis iodometrically. These latter determinations are to be found in the literature — owing to their sensitivity — in different forms, different reducing agents (sulphurdioxide, hydrazine, KJ, KBr, HCl, etc.), different methods in the back measuring of iodine, even different measuring solutions (arsenite, thiosulphate) are used [1].

SCHULEK and KŐRÖS [2] elaborated a new method for the determination of selenium. The sources of error resulting from the equilibrium reaction:

$$H_2SeO_3 + 4\ HJ = Se + 2\ J_2 + 3\ H_2O$$
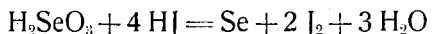
have been eliminated by the authors. Namely the determination was led back to that of BrCN after the hydroxilamine reaction through the oxidation of SeCN by Br_2. The conditions have also been examined in details under which the different side reactions can be eliminated.

The oxidation of selenous acid to selenic acid is a considerably slower process than the reduction of a metal to selenium. Potassium permanganate and potassium bromate have so far been used as oxidation measuring solutions. Since, however, the quantitative oxidation of the selenous acid takes in an acidic medium even 10—40 min. these measurements are rather long-winded. The oxidation of potassium permanganate in an acidic medium takes similarly a longer time. Although the rate of reaction may be considerably increased by increasing the temperature and the alkaline concentration, because

of the decomposition of potassium permanganate in an alkaline medium the results will not be exact as pointed out by a number of authors.

Recently I. M. Issa and his coworkers [3] have dealt with the potassium permanganometric measurement of selenite: at a high (70—80° C) temperature in a slightly alkaline, at room temperature in a strongly alkaline medium. In their indirect method — that is according to the authors a much more precise than the former ones — potassium permanganate was measured after 10—15 min. standing by formic acid.

The rapid and exact determination of selenous acid by this methods is very rare. The iodometric procedures involve of very many steps, they are, therefore, long-winded and very sensitive. The oxidation determinations are simpler, but exact results can be only indirectly achieved (10—40 min.).

The present determination is similarly an oxidations procedure. Since potassium permanganate, proved to be not suitable for rapid and exact determination another measuring solution was applied. In acidic media cer (IV) sulphate and bichromate could be used, these oxidize, however, selenous acid slower than bromate and potassium permanganate. In alkaline media hypohalogenites and ferricyanide could be used. The corresponding stability, ready treatment and the high redox potential achievable by increasing the alkaline concentration, point to the application of ferricyanide.

Examination of the ferricyanide—selenite reaction

Although the redox reactions of ferricyanide in acidic and alkaline media have already been studied in details by numerous authors and several analytical procedures have been elaborated applying ferricyanide, no reference is made in the literature on the ferricyanide-selenite reaction[2]

$$Na_3SeO_3 + 2 K_3Fe(CN)_6 + 2 KOH = Na_3SeO_4 + 2 K_4Fe(CN)_6 + H_2O.$$
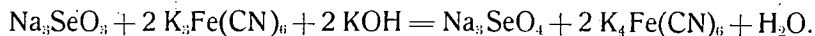
The redox potential of selenate/selenite is, in an alkaline medium, 0,05 mV, and that of ferricyanide/ferrocyanide 0,40 mV. On the basis of these two relatively similar values of potentials it would be expected that the reaction will proceed rather slowly. Thus in an 1—2 n alkaline medium there could be, either after a rather long time, no considerable change observed. It was mentioned, however, that the redox potential of ferricyanide steeply increases with the increasing alkaline concentration [4]. Accordingly, at a higher alkaline concentration the increase of the rate of the reaction would be expected. Such an increase was really observed, however, even at 5 n sodiumhydroxide concentration the reaction proceeds very slowly, so that the quantitative reaction requires at 1,5:1 ratio of ferricyanide-selenite about 18 hours. The rate of the reaction can be accelerated by heating in the presence of double quantity of ferricyanide, howewer, at 70° C, at 5 n alkaline concentration the reaction does not proceed, either in 15—20 min. quantitatively.

The rate of the reaction can be, accordingly, increased to a great extent, only by application of a suitable catalyst. The ferricyanide-arsenite reaction

was accelerated, as decribed in a recent paper of the author [5], by the application of a few drops of 0,01 Mol osmium tetroxide. The rate of the reaction ferricyanide-selenite could be similarly accelerated by osmium tetroxide. The effect of osmium tetroxide, alkaline concentration and temperature was in the above way examined in the reaction ferricyanide-arsenite in details.

To a known amount of selenite sodium hydroxide of different concentrations were added, the solution heated to the corresponding temperature and after adding a few drops of osmium tetroxide a smaller than the equivalent quantity of ferricyanide was introduced from the buret. (The $1-2°$ C decrease thus occured was taken into account.) Since we wished to establish, first of all, the conditions under which the reaction will be instantaneous we noticed to completing of the reaction only. The end point was most readily indicated electrometrically, with the most simple method, the dead-stop titration. Two Pt electrods were dipped into the solution which was polarized by 150—200 mV. The electrods were depolarized by the ferricyanide/ferrocyanide system and the current obtained measured by means of a microammeter. In the moment of the reaction of ferricyanide the current stops and the gauge shows the remaining current only. Accordingly, the time elapsed between the introduction of ferricyanide into the solution and the steps of the current were measured. The constant uniform stirring of the solution was secured by a magnetic stirrer. The measurements are summarized in Table I.

The data show that the ferricyanide-selenite reactions is greatly accelerated by osmium tetroxide. The effect of the alkaline concentration and of

Table I.

Taken 0,1 m $K_3Fe(CN)_6$ ml	Taken 0,1 n Na_2SeO_3 ml	NaOH concentration mol/l	Time of reaction sec	Temperature °C	Drops of OsO_4
3,00	3,40	1,25	660	25	1
3,00	3,40	2,50	300	25	1
3,00	3,40	5,00	90	25	1
3,00	3,40	1,25	170	25	3
3,00	3,40	2,50	112	25	3
3,00	3,40	5,00	25	25	3
3,00	3,40	1,25	85	45	3
3,00	3,40	2,50	25	45	3
3,00	3,40	5,00	8	45	3
3,00	3,40	1,25	52	75	3
3,00	3,40	2,50	10	75	3
3,00	3,40	5,00	2	75	3

the temperature can similarly be seen, according to which at a corresponding higher alkaline concentration and at a higher temperature the reaction rate is great which renders possible the direct titration of selenite.

According to our examinations in contrast with the other ferricyanide reactions, ferrocyanide formed in this process does not effect at all the rate of the oxidation of selenite.

For sake of completeness we studied the effect of the kind of alkali on the reaction rate. Namely the measurements of SCHOCH and FELSING [6] have shown that the redox potential of ferricyanide/ferrocyanide depends on the concentration of the potassium ions according to the following equation:

$$E = E_0 + 0,0591 \log \frac{[\text{Feic}] [\text{K}^+]^x}{[\text{Feoc}]} \qquad (x = 0,725 - 0,75).$$

Table II.

Taken 0,1 m K$_3$Fe(CN)$_6$ ml	Taken 0,1 m Na$_2$SeO$_3$ ml	KOH concentration mol/1	Time of reaction sec	Temperature °C	Drops of OsO$_4$
3,50	4,10	1,70	50	20	3
3,50	4,10	3,30	35	20	3
3,50	4,10	5,00	12	20	3
3,50	4,10	1,25	145	20	1
3,50	4,10	5,00	40	20	1
3,50	4,10	2,50	80	20	1
3,50	4,10	1,25	9	45	3
3,50	4,10	2,50	~2	45	3
3,50	4,10	1,25	~2	75	3
3,50	4,10	5,00	~2	77	3

Thus it could be expected that on using potassium hydroxide instead of sodium hydroxide the reaction rate will increase considerably. The data referring are enlisted in Table II. According to the measurements in a KOH solution of the same concentration as that of sodium hydroxide the rate of the reaction is really considerably greater.

Description of the procedure

With the knowledge of the optimum conditions of the reaction the following procedure is suggested for the direct determination of selenite with ferricyanide.

The reagents required: 0,1 Mol potassium ferricyanide

0,01 Mol osmium tetroxide

NaOH solution.

A sodium hydroxide solution of corresponding concentration is added to a solution containing 30—150 mg of selenite so that the potassium hydroxide concentration of the solution is 3,5—5 n. The suitable initial volume is 20—30 ml. The solution is heated to 55—65° C and after the addition of 3 drops of osmium tetroxide the solution is titrated by ferricyanide. The end point can be observed most readily by the dead-stop technique. In the end point owing to the depolarizing effect of the ferricyanide/ferrocyanide system a considerable current is obtained that may be well distinguished from the initial current. The current can be well measured with the aid of a sensitive ammeter. The determination takes a few minutes only, but care is to be taken that the alkaline concentration does not decrease in the end point below 2,5 n, and the temperature below 40° C. In case if the alkalisation is carried out by potassium hydroxide the measurement is similar to the above one but the alkaline concentration is sufficient to choose 2—3 n. Table III. illustrates the exactness of the determination. Our measurements were controlled by the classical method of SCHRENK and BROWING [7]. The selenite was oxidized by excess sodium permanganate in the presence of 12 g sodium hydrophosphate in a sulphuric acidic medium. After 40 min. standing the concentration of the selenic acid was calculated from the quantity unreacted of potassium permanganate. The error of determination is not more than 0,15—

Table III.

Taken 0,1 n Na_2SeO_3 ml	Found	Δ ml	NaOH concentration mol/l	Temperature °C	Drops of OsO_4
4,49	4,49	0,00	4,0	50	3
4,49	4,48	0,01	4,0	50	3
8,88	8,89	0,01	4,0	60	3
8,88	8,88	0,00	4,0	60	3
10,20	10,18	0,02	5,0	65	3
10,20	10,19	0,01	5,0	65	3
13,37	13,35	0,02	5,0	68	3
13,37	13,35	0,02	5,0	65	3
15,61	15,60	0,01	5,0	68	3
15,61	15,59	0,02	5,0	68	3

—0,2 %. 1 ml 0,1 n ferricyanide corresponds to 8,64 mg Na_2SeO_3. The end point may be indicated potentiometrically. The degree of the jump of the potential depends on the alkaline concentration.

The effect of interfering ions

The exactness of the determination has been submitted to careful examination in the presence of different ions. The substances of lower redox potential which may be oxidized by ferricyanide interfere, of course, the determination.

Besides, some complex forming substances interfere too, which during complex formation decrease the extent of catalysis or eliminate it practically. Such an interfering action is exerted by ammonia that can be present only at about a concentration of 0,02 n. Then, in the case if ferricyanide does not undergo a reaction, it is suitable to add another drop of osmium tetroxide thus controlling the reality of the end point. If the ammonia concentration of the solution is higher than the above one, ammonia is to be removed. The removal can be readily carried out in an alkaline medium by heating. A similar effect is exerted by the tellurite and tellurate compounds which act, already at low concentration, as to inactivate osmium tetroxide.

The mercuric and thallic ions do not interfere with the determination but in the presence of these substances the dead-stop end point indication cannot be applied. The end point may be indicated in these cases potentiometrically.

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References

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