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Argentometric Determination of Bromide with Nitroferroin as Redox Indicator

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The use of starch-iodine as redox indicator in connection with the argentometric determination of iodide has been known for many years (see *e.g.* Kolthoff and Stenger[1]). The principle of the method is as follows (see also Charlot and Bézier[2]):

The iodide solution is treated with starch and a very little free iodine (or a very small amount of the iodide present is oxidized to iodine). The solution is titrated with silver nitrate. The end-point of the titration is indicated by the disappearance of the blue colour of the starch-iodine complex. The oxidation potential of the liquid is:

$$E = E_0 + 0.03 \cdot \log \frac{[J_2]}{[J^-]^2}$$

During the titration, the starch-iodine complex acts as redox indicator with transition interval from blue to colourless when $E = ca.$ 0.90 volt is exceeded (corresponding to the absence in the solution of iodide ions necessary for the formation of the blue starch-iodine complex). When the blue colour has just disappeared, it is still possible to show the presence of free iodine in the solution; but if the titration is continued beyond the end-point, the free iodine may react as follows:

$$J_2 + 3\ H_2O \rightleftharpoons JO_3^- + 5\ J^- + 6\ H^+$$

which is equivalent to the equilibrium being forced to the right.

Crawford and Bishop[3] have used *o*-dianisidine as redox indicator instead of starch-iodine. Kolthoff[4] has investigated the titration potentiometrically.

In the present paper the same principle has been made the basis of a determination of bromide. As the normal potential, $2\ Br^-/Br_2$ (= 1.06 volt), is somewhat greater than the normal potential, $2\ J^{-}/J_2$ (= 0.53 volt), the redox indicator to be used must have a transition interval which is somewhat larger than that of starch-iodine. For the bromide/bromine system the following equation is valid:

$$E = 1.06 + 0.03 \cdot \log \frac{[Br_2]}{[Br^{-}]^2}$$

At the equivalence-point for the titration of Br^{-} with Ag^{+} (as the solubility product for silver bromide is $10^{-12.2}$) we get:

$$E = 1.06 + 0.03 \cdot \log[Br_2] + 0.37 = 1.43 + 0.03 \cdot \log\ [Br_2]$$

Therefore, the transition interval of the redox indicator should be about 1.30—1.35 volt (somewhat dependent on $[Br_2]$). Nitro-ferroin meets this requirement, as it can be used in the range at about 1.30 volt. The transition interval is, however, somewhat dependent on pH (a little smaller values for E in strongly acidic liquids — *cf.* Smith and Richter [5]).

In the following experiments solutions of potassium bromide and silver nitrate, which were made by weighing chemicals *p.a.*, were used. The potassium bromide used was 0.09988 M; the silver nitrate used was 0.09989 M.

EXPERIMENTAL

Method: To 20 ml water are added 5 ml 4 M nitric acid, 2 drops of 0.025 M nitro-ferroin and 2 drops (= 0.10 ml) of saturated bromine water. A few drops of 0.1 M potassium bromide are added, and then 0.1 M silver nitrate is added dropwise, until a transition takes place from red to nearly colourless (a faint violet). In order to ensure a correct fixation of the transition another drop of 0.1 M potassium bromide is added and then the small amount of 0.1 M silver nitrate which is now required for transition. The sample in which Br^{-} is to be determined, is added. Titration is now carried out with standard 0.1 M silver nitrate. The flask is held in slight rotation, and titration is continued until the red precipitate changes colour from red to yellow. A white porcelain plate is used as underlay. The transition from red to yellow is not denoted by a significant change of colour, and it is difficult to observe it in artificial light. However, the transition seems to be very sharp.

RESULTS

In Table 1 are given the results from a series of experiments, which show that the method yields results that are *ca.* 1 ‰ too high. In the experiments the same solutions as were used in the determination itself, were used for the fixation of the primary transition of the indicator; in principle, however, it is not necessary to know the exact concentration of the solutions that are used for the fixation of this transition of the indicator.

Table 1. Determination of Br^- *using nitro-ferroin as indicator. Calculated:* $M_{KBr} = 0.09988$. *Found as mean value (last column but one):* $M_{KBr} = 0.09997$. *Found as result of control determination No. 2 of the same solutions (last column):* $M_{KBr} = 0.10012$.

Expt. No.	Fixation of Indicator ml KBr	ml $AgNO_3$	Determination ml KBr	ml $AgNO_3$	Found M_{KBr}	Control No. 2
1	0.60	0.66	20.16	20.18	0.09999	0.10009
2	0.56	0.63	19.96	20.01	0.10014	0.10033
3	0.30	0.40	20.23	20.26	0.10004	0.10026
4	0.37	0.45	20.02	20.02	0.09989	0.09999
5	0.35	0.45	20.16	20.17	0.09994	0.10003
6	0.41	0.50	20.61	20.61	0.09989	0.10013
7	0.48	0.55	20.23	20.24	0.09994	0.10008
8	0.31	0.39	19.96	19.96	0.09989	0.10004
9	0.47	0.58	20.05	20.06	0.09994	0.09994
10	0.33	0.41	20.37	20.39	0.09999	0.10018

When the titrations were finished the following control of the results was carried out: A few drops (0.20—0.30 ml) of the standard 0.1 *M* potassium bromide were added and the solution was titrated with silver nitrate. This procedure was repeated, and the results from this control No. 2 are given in the last column of Table 1. It appears that on the whole the results are a further 1 ‰ too high. When control No. 3 was carried out in the same way, the transition was not usually sharp, presumably because the dissolved bromine gradually evaporates from the solution or possibly is oxidized. Consequently, it was not possible to show the presence of free bromine in the solution after the titration had been finished.

An attempt at following the titration potentiometrically was made. Approaching the equivalence-point the potential became constant rather quickly, but just before the equivalence-point the potential ($E =$ *ca.* 1.2 volt) became oscillatory and unstable, probably because of the evaporation of the free bromine due to the constant stirring.

During the determinations no iodide nor chloride must be present, which limits considerably the possibilities of the method in question. The method is mainly theoretically interesting.

By an argentometric method worked out by Uzel[6] for determination of bromide α-naphtoflavone is used as indicator. Although Uzel gives a different explanation of the mechanism, his method is presumably related to the method stated above.

SUMMARY

A new argentometric method for determination of bromide has been worked out. In this precipitation titration, nitro-ferroin is used as redox indicator, a small amount of free bromine having been added beforehand.

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