[CONTRIBUTION FROM THE PHARMACEUTICAL LABORATORY OF THE STATE UNIVERSITY OF UTRECHT]

THE USE OF POTASSIUM BI-IODATE AS A STANDARD SUBSTANCE IN ALKALIMETRIC AND IODIMETRIC TITRATIONS

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The use of potassium bi-iodate as a standard substance was first recommended by von Than.[1] According to his investigation, the salt is obtained in a pure state after two recrystallizations from water; its solution may be kept for years without changing its strength. Meineke[2] recommends potassium bi-iodate as a standard substance for both iodimetric and alkalimetric titrations. However, Wagner's[3] results with commercial products and his own preparations were not very favorable. Even with his own preparations he obtained a difference of 0.3% as compared to potassium dichromate as a standard substance. More recently, potassium bi-iodate has again been recommended by Shaffer and Hartmann[4] who give a method for its preparation. Koenig[5] prepares the acid salt from equivalent amounts of iodic acid and potassium iodate.

So far as we know, there is in the literature no thorough investigation as to whether potassium bi-iodate remains unchanged after recrystallizations from water, and whether it is a reliable standard substance. Meerburg[6] states that it may be recrystallized from water without changing its composition. For the standardization of alkali it has distinct advantages, as its equivalent weight is very high, and iodic acid is a strong acid which may be used with all indicators which show a color virage between dimethyl yellow and phenolphthalein. For the standardization of thiosulfate, however, the bi-iodate has no special advantage over potassium iodate.

Materials Used

Concerning the standardization of hydrochloric acid, using sodium thiosulfate and potassium iodate, and borax and potassium iodide, we refer to a previous investigation.[7]

Potassium Bi-iodate.—(1) Preparation supplied by Kahlbaum. (2) Preparation by a modification of the method of Koenig[5] in which the substance is crystallized from a mixture of potassium iodate and iodic acid solutions and concd. hydrochloric acid; the filtered and washed crystals

[1] von Than, *Math. Naturwiss. Ber. Ungarn*, **7**, 295 (1897).
[2] Meineke, *Chem.-Ztg.*, **19**, 2 (1896).
[3] Wagner, "Maassanalytische Studien," O. Leiner, Leipzig, **1898**, p. 60.
[4] Shaffer and Hartmann, *J. Biol. Chem.*, **45**, 376 (1920).
[5] Koenig, *Chimie et Industrie, Special No.*, 116 (Sept., 1925); *C. A.*, **20**, 348 (1926).
[6] Meerburg, *Chem. Weekblad.* **1**, 474 (1904).
[7] Kolthoff, THIS JOURNAL, **48**, 1447 (1926).

are recrystallized once from water, and part of them twice. (3) Preparation according to Shaffer and Hartmann;[4] potassium chlorate solution, concd. hydrochloric acid and powdered iodine are heated together and the solution is filtered giving, when cooled, crystals of bi-iodate which are recrystallized from water and dried; yield, about 70%.

According to Shaffer and Hartmann, the once-recrystallized salt is pure (100.00, 99.96, 99.95%); after a second recrystallization, 99.98 and 99.92%; after a third, 99.94 and 99.98%. We used a preparation that had been two, three and four times recrystallized and dried at 100°. It should not be dried at too high temperatures, as the iodic acid in the potassium bi-iodate loses its water of constitution and is transformed into the corresponding anhydride. When dried at 200°, this takes place quantitatively. A preparation dried in this way takes up the water again very slowly.

Experimental Part

In all experiments we used the same 100cc. buret as in earlier investigations.[7]

The strength of a 0.1 *N* sodium thiosulfate solution was determined with potassium iodate (Kahlbaum) as a standard substance, and the results were compared with those obtained with the different preparations of potassium bi-iodate.

The rational equivalent weight of potassium iodate is 35.66; that of potassium bi-iodate is 32.49.

The end-point was detected in the usual way with starch as an indicator.

Alkalimetric Experiments.—Two sets of experiments were performed. In the first, 1.9061 g. of borax (corresponding to 100 cc. of 0.1 *N* solution) was mixed with 3.9024 g. of potassium bi-iodate (corresponding to 100.1 cc. of 0.1 *N* solution) and 200 cc. of water. After solution of the crystals, 8 drops of 0.2% methyl red were added, and then 0.1 *N* borax solution from a microburet divided in 0.01 cc., until the color of the solution was the same as that of 8 drops of methyl red in 200 cc. of 0.1 *M* pure boric acid in water. The end-point may be detected with an accuracy of 0.01 cc. (=0.01%).

In another set of experiments 100 milli-equivalents of borax were mixed with 99.9 milli-equivalents of potassium bi-iodate and the titration completed with 0.1 *N* hydrochloric acid, added from a microburet.

It should be noted that the equivalent weight of potassium bi-iodate in these titrations is 389.85.

A small deviation from the normal composition is, therefore, detected much more accurately by the acidimetric than by the iodimetric titrations.

In Table I are given the results from the comparison between thiosulfate and bi-iodate, borax and bi-iodate. With Kahlbaum borax we found, within 0.01%, the same results as with a commercial preparation

recrystallized twice from water and subsequently dried to constant weight in a sodium bromide desiccator ($NaBr.2H_2O$ satd. soln.).

TABLE I

TITRATIONS

Standard substance	Description	With 0.1 N $Na_2S_2O_3$: No. of titr.	Av.[a]	Diff. from KIO_3, %	With borax: No. of titr.	Av.[a]	Diff. from borax, %
KIO_3	Ka.	4	100.00				
$KH(IO_3)_2$	Ka.	3	100.00	0.00	2	99.0	−0.10
$KH(IO_3)_2$	No. 2, once recr.	2	99.965	−0.03			
$KH(IO_3)_2$	No. 2, twice recr.	3	99.98	− .02	2	99.72	−0.28
$KH(IO_3)_2$	No. 3, twice recr.	2	99.95	− .05	2	99.97	− .03
$KH(IO_3)_2$	No. 3, thrice recr.	3	100.00	.00	4	99.97	− .03
$KH(IO_3)_2$	No. 3, 4 times recr.	3	100.00	.00	3	99.99	− .01

[a] The average variation from this average was ±0.01 cc.

Discussion of the Results

The potassium bi-iodate prepared according to Shaffer and Hartmann[4] gives a material that is very suitable as a standard substance, for thiosulfate as well as for alkali.

It is recommended to use the second or third recrystallization. From the results, it appears that potassium bi-iodate may be crystallized from water without changing its composition. Hence, the acid salt is in equilibrium with its saturated solution, even at temperatures as high as 60°.

Summary

1. Potassium bi-iodate may easily be prepared in a pure state according to the method of Shaffer and Hartmann.[4]

2. It is a good substance for the standardization of thiosulfate and alkali, particularly the latter because the equivalent weight is high and the iodic acid behaves as a very strong acid.

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