

Analysis of Small Amounts of Bromides in Presence of Large Amounts of Chlorides

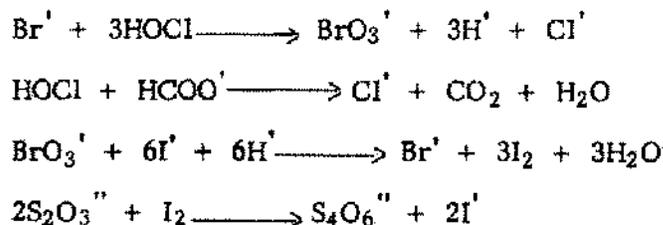
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ABSTRACT

This paper presents a description of Van der Meulen's method (1) improved by J. D'Ans and P. Hofer (2). All cited data are taken from the paper by D'Ans and Hofer (3).

Bromide is determined indirectly by its quantitative reaction (as bromate) with iodide to precipitate iodine. The liberated iodine is then titrated with sodium thiosulfate.

The reaction equations are as follows:



The bromide is first oxydized to bromate by hypochlorite. The excess of hypochlorite is reduced by formic acid or by a half saturated solution of sodium formate. The bromate is then reduced to bromide with potassium iodide in acidic solution liberating iodine which is titrated with a standard sodium thiosulfate solution.

The quantitative oxydation of bromide to bromate proceeds at a particular pH-value and in the presence of an excess of chlorides. D'Ans and Hofer do not state this pH-value, but give the quantities of alkaline phosphate buffer salts for accurate pH adjustment. These buffers vary with the dissolved ions in the solution to be analyzed.

If this solution is slightly acidic, disodium phosphate or a mixture of mono- and disodium-phosphate is used. For almost pure halites and sylvinites, monosodium phosphate is used as buffer. Magnesium salts do not interfere with the reactions. But if they are present in excess, a mixture of phosphates should be used. Diphosphates must be used if calcium chloride is present because monophosphates would precipitate di- and tricalcium phosphate, thus causing an acidic solution. Iron salts do not interfere in the presence of phosphates.

The quantitative oxydation of bromide into bromate takes place in 5 to 10 minutes at 90° C. The reduction of the excess hypochlorite by formate solution or formic acid (if diphosphates are present) must be done while the solution is hot.

D'Ans and Hoefler give the following recommendations:

The amount of bromine containing material used for the analysis should not be greater than the equivalent of 100 mls of a $\frac{N}{100}$ thiosulfate solution (1 ml of a $\frac{N}{100}$ thiosulfate solution is equal to 0.1332 mg bromine).

The thiosulfate solution should be standardized with potassium bromate. A known weight of air dried bromate is dissolved and the solution is made up to one liter. An aliquot part of the solution is taken for standardizing.

After adding of potassium iodide and 2N. hydrochloric acid, allow a few minutes for complete reduction of the bromate. Starch solution is used as an indicator for the titration of iodine. The solution turns white when all iodine is reduced to iodide.

Blank analyses must be made to determine the amount of bromine impurities in the reagents since they are most important causes of inaccurate results.

The following blank analysis (4) gives also the amounts of reagents which should be used for the adjustment of the right pH-value for the bromine analysis of relatively pure halite or sylvinit: 35 mls water, 3 gms monosodium phosphate, and 10 mls sodium hypochlorite solution (0.3-0.4 normal) are heated at 90° C. for 5 to 10 minutes. Then add 2 mls of a half saturated sodium formate solution. Cool the solution to room temperature, add 0.3 gm potassium iodide and 25 mls of a 2N. hydrochloric acid. The solution is then titrated with the $\frac{N}{100}$ sodium thiosulfate (using starch as indicator). The bromine impurities might be equivalent to approximately 0.2 mls in a typical blank.

Further blank analyses can be found in D'Ans and Hoefler (5).

I would like to thank E. L. Faulkner, University of Saskatchewan, for the thoughtful appraisal of the manuscript.

REFERENCES

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3. 4. 5. J. D'Ans and P. Hoefler, Untersuchungen an Brom: Angewandte Chemie. Jahrgang 47, no. 5, p. 73-74, 1934.