[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, COLLEGE OF THE CITY OF NEW YORK.]

# THE DETECTION OF BROMIDES IN THE PRESENCE OF THIOCYANATES, CYANIDES AND FERROCYANIDES.

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It was found some two years ago in this laboratory that the presence of thiocyanates interfered with the test for bromides by the chlorine-water method. While this investigation was in progress, Guareschi[1] published a method for overcoming this interference. His procedure, however, requires special apparatus and does not provide the means of roughly estimating the quantities of bromides present. It was, therefore, thought worth while to continue our work, the object of which was to determine the extent of this interference and to devise a simple and rapid method for overcoming this difficulty in the detection of bromides. Finding that cyanides and ferrocyanides also interfere, this investigation was extended to include these acid radicals. Ferricyanides do not interfere, it being possible to detect easily one milligram of bromine as potassium bromide in the presence of 500 mg. of ferricyanide by means of chlorine water.

**Determination of the Interference.**—Chlorine water saturated at room temperature was employed throughout this work and was kept in small glass-stoppered bottles of amber-colored glass. In making the tests, precautions were taken to maintain its strength by not allowing the bottle to stand open for any considerable length of time. In determining the amount to be used, it was found that with 3 drops of chlorine water, an excellent test was obtained with 1 mg. of Br as KBr, which was not appreciably improved by the further addition of a drop or two. It was also found that three drops of chlorine water gave a good test with 20 mg. of Br as KBr, although in this case all the bromine was not liberated. For the extraction of the liberated bromine, carbon disulfide was chosen as the solvent.

The general procedure was as follows: From a buret a definite volume of a standard potassium bromide solution was run out into a test tube. To this were added successively one drop of 10% hydrochloric acid, a definite volume of a standard solution of the potassium salt of the interfering acid, 0.5 cc. of carbon disulfide, and sufficient distilled water to make the volume up to 5 cc. Three drops of saturated chlorine water were then introduced and the mixture shaken. The results are shown in the tables.

All these tests were repeated with the same results. It is evident from an examination of the tables that thiocyanates offer the greatest and ferrocyanides the least interference.

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[1] *Atti. accad. sci. Torino*, 49, 15–21; *C. A.*, 8, 1938.

TABLE I.

*Interference of Thiocyanates.*

| 0.25 mg. CNS. | Test. | 0.20 mg. CNS. | Test. | 0.15 mg. CNS. | Test. |
|---|---|---|---|---|---|
| 1 mg. Br | Negative | 10.0 mg. Br | Faint | 1.0 mg. Br | Good |
| 5 mg. Br | Negative | 1.0 mg. Br | Faint | 0.5 mg. Br | Fair |
| 20 mg. Br | Negative | 0.5 mg. Br | Very faint (limit) | 0.3 mg. Br | Faint |
| | | | | 0.1 mg. Br | Very faint (limit) |
| | | | | 0.05 mg. Br | Negative |

TABLE II.

*Interference of Cyanides.*

| 1 mg. CN. | Test. | 0.8 mg. CN. | Test. | 0.3 mg. CN. | Test. | 0.1 mg. CN. | Test. |
|---|---|---|---|---|---|---|---|
| 1 mg. Br | Neg. | 1.0 mg. Br | Faint | 1.0 mg. Br | Good | 1.0 mg. Br | Excel. |
| 5 mg. Br | Neg. | 0.5 mg. Br | Very faint (limit) | 0.5 mg. Br | Fair | 0.5 mg. Br | Good |
| 10 mg. Br | Neg. | | | 0.4 mg. Br | Fair | 0.1 mg. Br | Faint |
| 20 mg. Br | Neg. | | | 0.2 mg. Br | Faint | 0.05 mg. Br | Limit |
| | | | | 0.1 mg. Br | Negative | | |

TABLE III.

*Interference of Ferrocyanides.*

| 4.0 mg. $Fe(CN)_6^{iv}$. | Test. | 3.5 mg. $Fe(CN)_6^{iv}$. | Test. | 3 mg. $Fe(CN)_6^{iv}$. | Test. | 2.0 mg. $Fe(CN)_6^{iv}$. | Test. |
|---|---|---|---|---|---|---|---|
| 1 mg. Br | Neg. | 1.0 mg. Br | Faint | 1.0 mg. Br | Fair | 1.0 mg. Br | Fair |
| 5 mg. Br | Neg. | 0.5 mg. Br | Faint | 0.5 mg. Br | Fair | 0.5 mg. Br | Fair |
| 10 mg. Br | Neg. | 0.4 mg. Br | Very faint | 0.4 mg. Br | Fair | 0.3 mg. Br | Faint |
| 20 mg. Br | Neg. | 0.3 mg. Br | Negative | 0.3 mg. Br | Faint | 0.1 mg. Br | Very faint (limit) |
| | | | | 0.2 mg. Br | Negative | | |

The above results may be accounted for on the supposition that the chlorine water exercises a selective action, oxidizing the interfering substance first before liberating the bromine from the bromide. Thus in Table I we see that the 3 drops of chlorine water added were sufficient to oxidize 0.15 mg. of CNS and still leave sufficient chlorine to liberate the bromine as indicated; while when 0.20 mg. CNS were present there was only a very small amount of chlorine left after the CNS had been oxidized, and hence the tests were faint. With 0.25 mg. CNS all the chlorine was consumed, and hence it was impossible to detect the bromine, however great it might be. If this theory be true, it should be possible by the continued addition of chlorine water to provide an excess over that required to oxidize the interfering substance and thus obtain a positive test in those cases where negative results were obtained with a limited amount of chlorine. This conjecture is confirmed only to a limited extent by the experimental evidence; for it was found that there is a limit in this case beyond which no amount of chlorine water will produce a positive result.

A determination of the limits was made by ascertaining in what amounts of interfering substances 1 mg. of bromine could be detected by the repeated additions of chlorine water, adding the latter 3 drops at a time and shaking after each addition.

TABLE IV.

*3–5 cc. Chlorine Water.*

| 1 mg. Br. | | 1 mg. Br. | | 1 mg. Br. | |
|---|---|---|---|---|---|
| 10 mg. CNS | Negative | 10 mg. CN | Negative | 40 mg. $Fe(CN)_6^{iv}$ | Negative |
| 4 mg. CNS | Negative | 5 mg. CN | Negative | 30 mg. $Fe(CN)_6^{iv}$ | Fair |
| 2 mg. CNS | Fair | 4 mg. CN | Faint | 20 mg. $Fe(CN)_6^{iv}$ | Good |
| 1 mg. CNS | Good | 2 mg. CN | Fair | 10 mg. $Fe(CN)_6^{iv}$ | Very good |
| | | 1 mg. CN | Good | | |

After much experimentation the following procedure was devised for the detection of bromides in the presence of thiocyanates, cyanides and ferrocyanides, based upon the precipitation of the respective radicals as cuprous salts in presence of sulfurous acid.

**Method.**—The solution to be tested, which should be neutral or slightly acid with sulfuric acid, is treated with 15 cc. of a saturated solution of $SO_2$ (this amount has been found by experiment to be sufficient to insure the precipitation of 500 mg. of CNS, CN or $Fe(CN)_6^{iv}$ as their cuprous salts). The solution is now heated just to boiling, and while hot it is treated with constant stirring with 2 *N* $CuSO_4$ solution, which should be slowly run out from a buret or dropping funnel. Enough $CuSO_4$ must be added to insure an excess, shown by the blue color of the supernatant liquid. (In the presence of CNS a green liquid indicates insufficient $H_2SO_3$ and more must be added until the solution becomes blue. This is important since the green solution still contains CNS which has not combined with the copper and which, therefore, will interfere with the subsequent test for bromine.) Filter while hot, wash twice with distilled water, adding the washings to the main filtrate contained in an Erlenmeyer flask. Boil down the filtrate to about 5–10 cc. (This removes the excess of $SO_2$ and reduces the volume so that the final test may be made in a test tube. A slight white precipitate may form during this operation but may be disregarded.) Cool the contents of the flask[1] and pour into a test tube. Rinse the flask with 3–4 cc. distilled water and add to the liquid in the test tube. Add 1 cc. of 3 *N* $H_2SO_4$, 1 cc. 1% $KMnO_4$, and shake.[2] Now add not more than 0.5 cc. $CS_2$ and shake. A yellow color in the $CS_2$ layer proves the presence of Br.

The acid and $KMnO_4$ are added and shaken first in order that the $CS_2$ may not be in contact with the $KMnO_4$ any longer than is necessary, since they react with the formation of a small amount of $MnO_2$ which with vigorous shaking may dissolve in the $CS_2$, yielding a color indistinguishable from that given by small amounts of Br. An excess of $CuSO_4$ is not ob-

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[1] This may be easily accomplished by holding the flask under the tap of running cold water.

[2] Dilute HCl and Cl water may be used instead of the $H_2SO_4$ and $KMnO_4$; but the former has the disadvantage that the solution cannot subsequently be tested for chlorides.

jectionable since $CuSO_4$ in the presence of $KMnO_4$ liberates all the Br from KBr.[1]

The following tests show the reliability of the method:

TABLE V.

| No. | Mg. Br. | Mg. CNS. | Mg. CN. | Mg. $Fe(CN)_6^{iv}$. | Results. |
|---|---|---|---|---|---|
| 1 | 0.0 | 250 | ... | ... | Absolutely no color |
| 2–5 | 1.0 | 250 | ... | ... | Negative |
| 6–7 | 1.5 | 250 | ... | ... | Fair |
| 8–16 | 2.0–3.0 | 250 | ... | ... | Good |
| 17–20 | 4.0–10.0 | 250 | ... | ... | Strong color |
| 21–25 | 2.0 | 500 | ... | ... | Good |
| 26 | 4.0 | 500 | ... | ... | Excellent |
| 27 | 1.0 | ... | 500 | ... | Negative |
| 28–30 | 2.0 | ... | 500 | ... | Excellent |
| 31 | 1.0 | ... | ... | 500 | Negative |
| 32–34 | 2.0 | ... | ... | 500 | Excellent |
| 35 | 2.0 | 200 | 150 | 150 | Good |
| 36 | 2.0 | 300 | 100 | 100 | Good |
| 37 | 2.0 | 100 | 200 | 200 | Good |
| 38 | 2.0 | 400 | 50 | 50 | Good |

The average time required for the completion of a test was 15 min.

## Summary.

1. Attention has been called to the interference of thiocyanates, cyanides and ferrocyanides in the detection of bromides by the ordinary methods.
2. The interference offered by each of these substances has been determined.
3. A rapid method has been devised which is capable of detecting 2 mg. of bromine in the presence of 500 mg. of each of the interfering substances.
4. Numerous test experiments show the method to be trustworthy.

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# ON FRACTIONAL DISTILLATION WITH REGULATED STILLHEADS.

[FIRST COMMUNICATION.]

## CASES IN WHICH THE BOILING-POINT CURVE PASSES THROUGH A MAXIMUM OR A MINIMUM.

BY M. A. ROSANOFF AND C. W. BACON.

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### Section 1. Introductory.

A recent joint communication[2] outlined a theory of fractional distillation based on a new relationship between the slopes of the total pressure curve and the relative compositions of the liquid mixtures and the corresponding vapors. In the mathematical treatment it was assumed that

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[1] Prescott and Johnson's "Qualitative Analysis," p. 346.

[2] Rosanoff, Bacon, and Schulze, THIS JOURNAL, 36, 1993 (1914).