

## ANALYTICAL NOTES

*From the Analytical Control Division of May and Baker, Limited*

### (I) THE OFFICIAL LIMIT TEST FOR CHLORIDE IN BROMIDES

BY L. W. CUMMING and MISS M. B. RHODES

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THE official method for the determination of chloride in bromides of ammonium, calcium, potassium and sodium and in hydrobromic acid is based on that evolved by Caven<sup>1</sup> who although concerned mostly with relatively large amounts of chloride, reported results of 0.085 and 0.081 per cent. of KCl in a determination on potassium bromide. Under routine control conditions high results of poor reproducibility have been obtained from time to time.

The official instructions are brief, no indication of the method of titrating the chloride, for example, being given. Caven filtered off the silver chloride but mentions direct titration in acid solution using the "shaking method"; in these laboratories Caldwell and Moyer's<sup>2</sup> modified Volhard method is used. The British Pharmacopœia specifies a rapid current of air both during the one minute boiling and whilst cooling, whereas Caven passed a gentle stream of air when heating to boiling and during actual ebullition, but increased the aspiration rate at the commencement of the cooling stage. The method is apparently misquoted in a standard reference book<sup>3</sup> in which it is not specified that a stream of air be passed whilst boiling, nor is a thermometer, as used by Caven, shown in the diagram.

*Effect of Omitting Aspiration of Air during the one minute Boiling Stage.* If air is not aspirated through the solution during ebullition, higher results are obtained. Thus, when air was passed whilst boiling and cooling 10 determinations yielded figures between 0.07 and 0.17 per cent. of Cl (mean 0.11 per cent.), whereas when air was passed only while cooling, the corresponding range was 0.11 to 0.21 per cent. of Cl (mean 0.16 per cent.). Reproducibility was poor in both series; this was not due to errors in the titration stage since direct Volhard titrations of comparable amounts of chloride alone gave a recovery of 100 to 102 per cent. of Cl. The discrepancy between the two series of results could be due either to loss of chloride when air was passed whilst boiling and cooling, or to incomplete removal of bromide when air was passed only whilst cooling. That the lower results of the first series were not due to loss of chloride was shown by applying the official procedure to chloride alone, when recoveries of 98 to 102 per cent. of Cl were obtained; hence it was inferred that the higher results of the second series were due to incomplete removal of bromide.

*Effect of Rate of Aspiration of Air and of Temperature.* With high aspiration rates throughout (greater than 1 cu. ft./hr.) it was impossible to maintain boiling, even with a full Bunsen flame, during the one minute specified, and high results were obtained (Table I). With low aspiration

## L. W. CUMMING AND MISS M. B. RHODES

TABLE I

EFFECT OF ASPIRATION RATE AND OF TEMPERATURE ON RECOVERY OF CHLORIDE\*  
ADDED TO POTASSIUM BROMIDE

Aspiration rate cu. ft./hr.		Temperature during 1 minute period ° C.	Recovery per cent.
1 minute boiling period	Cooling period		
1·2 to 3	1·2 to 3	104	101 101 102 102
1·2 to 3	1·2 to 3	103	135 129 125 127
1	2	105 to 106 (boiling)	99 99 99 101 100
Less than 1	Less than 1	106	120 220

\* 3·55 mg. of Cl added to 1 g. of potassium bromide containing 1·07 mg. of Cl.

rates throughout high results were again obtained but with aspiration rates of about 1 cu. ft./hr. during the boiling period and changing to a brisk current (about 2 cu. ft./hr.) at the commencement of the cooling period, correct results were obtained. To obtain reproducible and correct results it is therefore necessary to include a thermometer in the apparatus and to regulate the rate of air stream during the 1-minute boiling period in order to maintain a temperature of 105° to 106° C.

## PROPOSED METHOD

To 1 g. of bromide or 5 ml. of dilute hydrobromic acid, in a 500-ml. distillation flask, fitted with a rubber bung carrying a thermometer and tapered air inlet tube which will extend to the bottom of the flask, add 75 ml. of water (70 ml. of water in the case of dilute hydrobromic acid) and 25 ml. of nitric acid. Heat the solution and when it boils commence passing a gentle stream of air and continue boiling (105° to 106° C.) for 1 minute. Remove the source of heat and pass a brisk stream of air for 20 minutes. Add 5 ml. of 0·1N silver nitrate and 5 drops of nitrobenzene, shake and then titrate the excess of silver nitrate with 0·1N ammonium thiocyanate using ferric ammonium sulphate solution as indicator. 1 ml. of 0·1N silver nitrate is equivalent to 0·003546 g. Cl.

## SUMMARY

1. The effect of variation of conditions in the official limit test for chlorides in bromides has been determined.

2. Temperature and aspiration rate are particularly important. A temperature of 105° to 106° C. must be maintained during the 1-minute boiling period and an aspiration rate of not less than about 2 cu. ft./hr. is necessary during the cooling period.

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### REFERENCES

1. Caven, *J. Soc. chem. Ind.*, 1909, **28**, 505.
2. Caldwell and Moyer, *Industr. Engng. Chem., Anal. Ed.*, 1935, **7**, 38.
3. Bennett and Cocking, *Science and Practice of Pharmacy*, Vol. 2, Churchill, London, 1933, 97.

### (II) THE THIOCYANATE TITRATION OF MERCURY AND THE STANDARDISATION OF AMMONIUM THIOCYANATE SOLUTION

BY L. W. CUMMING and MISS S. SPICE

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IN the British Pharmacopœia and British Pharmaceutical Codex mercury in certain inorganic and organic compounds is determined ultimately by thiocyanate titration for which, however, conditions are given in outline only. No definite temperature is specified, acidity ranges from 0.4N to 5N in different monographs, and final volumes and titres also vary.

Although standardisation of thiocyanate against mercury was recommended<sup>1</sup> when the cause of low assays on mercuric oxide was discussed at the British Pharmaceutical Conference in 1933 the importance of the exact conditions of the titration was not mentioned.

The effect of varying conditions in the thiocyanate titration of mercury has been studied by several workers. As regards temperature, Karaoglanov<sup>2</sup> pointed out that at higher temperatures the end-point appears too soon owing to the ionisation of mercury thiocyanate. Kolthoff,<sup>3</sup> confirming Rupp's<sup>4</sup> observation that at lower temperatures acid concentration was less important, recommended a temperature of 15° C. Results obtained in these laboratories show that the end-point is less definite and that lower results of poor reproducibility are obtained at temperatures higher than 15° C. In the official assays for mercury in mercury ointment and in mercurochrome there is no instruction to cool the warm solutions before titrating, hence a temperature greater than 15° C. might easily arise.

Only at low temperatures are the results independent of acid concentration, as shown by Rupp and Kolthoff; the latter recommends a concentration of 0.6N, the advantage of a relatively low acid concentration being a lower sensitivity to temperature differences. The acid concentration in official assays, which varies between 0.4N and 5N, may with advantage be brought within a narrower range, that for mercuric oxide being increased to about 0.7N by using the same acid/water ratio as used for mercury. On the other hand, the acid concentrations for dilute mercuric nitrate ointment, mersalyl and mercurochrome should be reduced somewhat; in our experience 10 ml. of nitric acid is sufficient to dissolve the amalgam in these cases, the acidity at the end-point being 2N to 2.5N.

The amount of indicator does not appear to be so critical but Karaoglanov obtained low results with less than 1 ml. of 10 per cent. ferric nitrate whilst Kolthoff recommends the use of 2.5 ml. of 10 per cent. ferric alum solution