

## ANALYTICAL NOTES

### REFERENCES

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

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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

*Standardisation of Thiocyanate Solution.* The British Pharmacopœia does not specify standardisation methods, but the United States Pharmacopœia directs that ammonium thiocyanate solution shall be standardised against silver nitrate solution, which may be made from reagent pure silver nitrate or standardised in turn gravimetrically *via* silver chloride. Pure mercury, and not silver, was recommended by Jones<sup>1</sup> for the standardisation of ammonium thiocyanate solutions intended for use in mercury assays; no figures were given in support. It is clear from the previous discussion that this procedure would be of value only if identical conditions were adhered to in both standardisation and subsequent determinations. Kolthoff and van Berk<sup>5</sup> obtained identical factors using mercury and silver nitrate and concluded that mercury was an excellent primary standard for the standardisation of thiocyanate provided correct conditions were used. Table I, giving results obtained by the present authors, shows that thiocyanate may be standardised against mercury, silver or silver nitrate solution provided that any end-point correction<sup>3</sup> in the standardisation of the latter is taken into consideration.

TABLE I  
STANDARDISATION OF 0.1N THIOCYANATE

Method	Factor
Against silver nitrate standardised with sodium chloride by Mohr's method:—	
(a) With no end-point correction .. .. .	1.001
(b) With end-point correction .. .. .	1.003
Against silver nitrate standardised gravimetrically as AgCl .. .. .	1.004
Against silver wire by Volhard method .. .. .	1.004
Against mercury (redistilled in vacuo) .. .. .	1.004

Hence if silver nitrate solution standardised against sodium chloride by Mohr's method,<sup>6</sup> and used for the assay of sodium and potassium chlorides, is used for the standardisation of thiocyanate solutions, the end-point correction in the standardisation of the silver nitrate must not be overlooked.

#### REFERENCES

1. Jones, *Quart. J. Pharm. Pharmacol.*, 1933, **6**, 554.
2. Karaoglanov, *Z. Anal. Chem.*, 1943, **125**, 406.
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4. Rupp, *Arch. Pharm.*, 1903, **241**, 444; *Chem.-Ztg.*, 1908, **32**, 1077.
5. Kolthoff and van Berk, *Z. Anal. Chem.*, 1927, **71**, 339.
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### (III) THE DETERMINATION OF IODINE IN ORGANIC COMPOUNDS BY ALKALINE REDUCTION

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METHODS for the determination of iodine in organic compounds fall into three classes based on ignition,<sup>1,2,3</sup> oxidation<sup>4,5,6,7</sup> or reduction.<sup>6,8,9</sup> The ignition method is widely used in the British Pharmacopœia but has been