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[1] 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[5] 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[3] 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,[6] 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.

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(III) THE DETERMINATION OF IODINE IN ORGANIC COMPOUNDS BY ALKALINE REDUCTION

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Received January 8, 1952

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

criticised[3,5,10] and the United States Pharmacopœia has adopted an alkaline oxidation method. Reduction with zinc and acetic acid is used in the British Pharmacopœia for iodoxyl and iodised oil; zinc and nitric acid have been used,[11] whilst a method using zinc and sulphuric acid was devised by Powell and Taylor[13] and applied to injection of diodone, injection of iodoxyl, pheniodol and chiniofon. This method lacks precision (4 results for chiniofon in their Table II have a total spread of 1·7 per cent.), the titre is small (7 ml. for chiniofon), and it is not specific for iodine. Reduction with zinc and alkali, used in an identity test for pheniodol,[14] was suggested *inter alia* by members of a Pharmacopœia Sub-Committee as the basis of an assay; optimum conditions have been determined and the following method developed.

Method

Weigh accurately an amount of material containing about 0·5 g. of iodine into a 250-ml. conical flask and dissolve in a mixture of 12 ml. of solution of sodium hydroxide and 20 ml. of water, warming if necessary. Add 1 g. of zinc powder, attach a condenser and reflux gently for 30 minutes. Cool, add through the condenser 20 ml. of water, filter through cotton-wool, wash the flask with 2 quantities of water, each of 15 ml., and pass the washings through the filter. To the filtrate add 25 ml. of hydrochloric acid, cool to room temperature, add 10 ml. of solution of potassium cyanide and titrate with 0·05M potassium iodate until the dark brown solution which is formed becomes light brown; add 5 ml. of mucilage of starch and continue the titration until the solution is colourless. Each ml. of 0·05M potassium iodate is equivalent to 0·01269 g. of iodine.

From Table I, which gives results obtained by this and other methods on a range of substances, it is seen that the method is precise and accurate.

TABLE I

Iodine content by different methods of various iodocompounds

Iodocompound	Proposed alkaline zinc reduction	Ignition with sodium carbonate (B.P.)	Reduction with zinc and acetic acid (B.P.)	Reduction with zinc and sulphuric acid (Powell)	Alkaline oxidation with permanganate (U.S.P.)
Pheniodol* (Theory 51·37 per cent. of iodine)	51·35 51·3 51·37	51·05[a] 51·1[a] 51·0[b] 51·1[b]		49·7 51·1 51·3 50·8	
Mean	51·34	51·06		50·7	
Iodophthalein	55·42 55·46	55·14 55·03			
Iodoxyl	51·10 51·08	51·10 51·10	51·07 51·05		
Chiniofon	30·52 30·49 30·49 30·54	29·61 29·65		29·47[c] 29·68[c] 29·41[c]	29·83 29·2 29·53

* Specially synthesised and purified by recrystallisation.
a Using Meker burner.
b Using electric furnace at 700° C.
c Yellow colour still present after 3 hours.

Ignition with sodium carbonate gave slightly lower results except with chiniofon where the discrepancy was appreciable; Powell and Taylor also obtained low results in this case.

Notes on the Method

1. About 0·4 g. of zinc is consumed; for quantitative reduction not less than 10 ml. of sodium hydroxide solution and a reduction time of 20 minutes are required.

2. The reduction products of pheniodol, iodophthalein, iodoxyl and chiniofon, identified respectively as α-phenyl-β-(4-hydroxyphenyl)-propionic acid, phenolphthalein, N-methyl-4-pyridone-2:6-dicarboxylic acid and 8-hydroxyquinoline-5-sulphonic acid were found not to interfere with the iodate titration.

3. In the B.P. the end-point acid concentration for Lang's iodate titration[12] varies from the equivalent of 0·64N in the case of iodophthalein to 1·42N in the case of iodoxyl. For accurate results not lower than 1N was found necessary.

Summary

A method for the determination of iodine in iodophthalein, chiniofon, iodoxyl and pheniodol is described. The method is simple and rapid and is more accurate than the ignition method of the British Pharmacopœia.

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(IV) The Stability and Preservation of Litmus Solutions

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Received January 8, 1952

Litmus solution prepared as specified in the British Pharmacopœia is distinctly alkaline (*p*H 8) and rapidly undergoes fermentation, becoming acid and less sensitive. Prideaux[1] suggests phenol as a preservative but gives no details as to its use.

A quantity of litmus solution prepared according to the British Pharmacopœia was divided into 3 equal portions which were stored (*a*) in an amber glass-stoppered bottle, (*b*) in a clear glass-stoppered bottle, (*c*) in a clear glass-stoppered bottle after the addition of 0·5 g. of phenol per 100 ml.