XXX.—*On the Volumetric Estimation of Mercury.*

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IN the *Journal of the Chemical Society* for June, 1873 (vol. xxvi, p. 565), HANNAY described a method of estimating mercury volumetrically by means of ammonium hydrate and potassium cyanide; but as employed by him the process was restricted to the determination of the amount of metal in pure aqueous solutions of mercuric chloride. During the progress of an investigation instituted by the former of us, on the digestion (solubility) of calomel by pepsin and dilute hydrochloric acid (*The Lancet*, August 13th, 1870), it became necessary to make a considerable number of determinations of mercury in various mercuric and mercurous compounds, and we were consequently led to examine the different methods devised for this purpose. The process which seemed to offer the greatest facilities for rapid and yet accurate work, especially when the amount of mercury was small, was that invented by Hannay. Before, however, it could be considered capable of general application, it was found essential to subject the method to careful investigation. This task we have at all events partially accomplished, and we now beg to lay before the Society the results of our inquiry.

The method of estimating mercury by Hannay's process is very simple. A known volume of the mercury solution under examination is taken; a few drops of dilute ammonium hydrate are added; and the white precipitate which forms is dissolved by running in a standard solution of potassium cyanide until the last trace of opalescence disappears. Towards the end of the operation the solution is carefully stirred for about half a minute after each addition of potassium

cyanide. For the purpose of exactly ascertaining the vanishing point of the opalescence, the experiment should be performed in a beaker standing on some dull black material, such as a piece of black velvet. If the operation be properly conducted, and the potassium cyanide pure, the disappearance of the last trace of opalescence is easily observed, and the end of the process thereby sharply marked. The peculiar blue opalescence presented by the liquid when nearly the exact amount of potassium cyanide has been added, is so characteristic, that its disappearance can be readily seen, even in the presence of traces of the grey precipitate arising from impurities in the cyanide, with which the solution is sometimes contaminated.

The following are the standard solutions employed :—

Standard Solution of Mercuric Chloride.—13·55 grams of pure mercuric chloride are dissolved in 1 litre of water. 1 c.c. of this solution contains 0·01 gram of mercury.

Standard Solution of Potassium Cyanide.—17 grams of pure crystallised potassium cyanide are dissolved in 1 litre of water, and the solution thus produced is titrated with 10 c.c. of the standard solution of mercuric chloride. If x be the volume of cyanide requisite to remove the last trace of opalescence, then $10 - x$ c.c. of water must be added to every x c.c. of the remainder of potassium cyanide solution to standardise it.

When of proper strength, 1 c.c. is equal to 1 c.c. of the standard solution of mercuric chloride.

In addition to the foregoing, it is useful to have a solution of 1 part of strong ammonia in 10 parts of water, a solution of 5·36 grams of ammonium chloride in 1 litre of water, and a solution of 69 grams of potassium carbonate in 1 litre of water.

When the amount of mercury to be estimated is small, or great accuracy is required, a weaker solution of potassium cyanide than the one above referred to should be employed. It may be formed by diluting from 50 to 100 c.c. of the standard to 1 litre. The potassium cyanide solutions keep fairly well for several months, and when they have lost strength, fresh solutions can be easily prepared, or the old ones may be readily re-standardised.

The following experiments illustrate the process, and indicate the delicacy and accuracy of the results obtainable by it :—

α . 50 c.c. of a solution of mercuric chloride containing 0·1933 gram of the salt were taken, and the mercury estimated.

Potassium cyanide solution used, 14·25 c.c. = 0·19305 gram of HgCl_2 .

β . Another 50 c.c. of the same solution of mercuric chloride were divided into five quantities of 10 c.c., and the mercury estimated in each.

Potassium cyanide solution (*decinormal*) used, 28.65 c.c., 28.5 c.c., 28.52 c.c., 28.48 c.c., and 28.58 c.c.; total 142.73 c.c. = 0.19334 gram of HgCl_2 .

γ. 50 c.c. of a solution of mercuric chloride containing 0.02134 gram of the salt were taken, and the mercury estimated.

Potassium cyanide solution (*decinormal*) used, 15.78 c.c. = 0.02138 gram of HgCl_2 .

δ. Another 50 c.c. of the same solution of mercuric chloride as the last were divided into five quantities of 10 c.c., and the mercury estimated in each.

Potassium cyanide solution (*decinormal*, diluted with its own volume of water) used, 6.35 c.c., 6.25 c.c., 6.29 c.c., 6.38 c.c., and 6.33 c.c.; total 31.6 = 0.021385 gram of HgCl_2 .

ε. 50 c.c. of a solution of mercuric chloride, containing 0.00271 gram of the salt were taken, and the mercury estimated.

Potassium cyanide solution (*centinormal*) used, 19.8 c.c. = 0.002683 gram of HgCl_2 .

ζ. Another 50 c.c. of the same solution of mercuric chloride as the last were divided into five quantities of 10 c.c., and the mercury estimated in each.

Potassium cyanide solution (*centinormal*) used, 3.7 c.c., 3.95 c.c., 4.4 c.c., 3.7 c.c., and 4.2 c.c.; total 19.95 c.c. = 0.002703 gram of HgCl_2 .

It will now be seen that extremely small quantities of mercury may be accurately estimated by Hannay's method; in fact, a fraction of a milligram of this metal may be determined to within 2 or 3 per cent. of the actual amount present in a solution of pure mercuric chloride by a single experiment.

It, however, appeared to us probable that the presence of considerable quantities of ammonium salts would materially interfere with the applications of the process, and experiment at once proved such to be the case.

Influence of Ammonium Chloride.—In presence of large quantities of ammonium chloride, it was found that ammonium hydrate gave no precipitate with small quantities of mercuric chloride; and even with smaller amounts of ammonium chloride the precipitate that formed presented anomalies which rendered the process unreliable. Numerous experiments were made to determine what quantity of ammonium salt might be present without exerting a prejudicial effect. It was then found that any amount of ammonium chloride under 15 times the weight of mercury-compound present appeared to exert but little influence, but that a quantity of ammonium chloride exceeding 25 times that of the mercury salt materially interfered with the process.

Influence of Ammonium Nitrate.—Large quantities of this salt were

found to exert an influence similar to that produced by the chloride, *i.e.*, they prevented the formation of a mercury precipitate with ammonium hydrate. Repeated experiment showed that a quantity of ammonium nitrate equal to 25 times the weight of mercury salt entirely prevented the formation of any precipitate by ammonium hydrate, and that the quantity of ammonium salt necessary for this purpose was approximatively inversely as the concentration of the solution of the mercury salt. The amount of ammonium nitrate present should not exceed ten times the weight of the mercury salt; with smaller quantities of nitrate but little influence seemed to be exercised.

Influence of Ammonium Sulphate.—A long series of experiments was tried with this salt, and results were obtained which were very similar to those yielded with the chloride and nitrate. When the weight of ammonium sulphate was 25 times that of the mercury salt, no precipitate formed on the addition of ammonium hydrate. So long as the amount of ammonium sulphate did not exceed ten times that of the mercury salt, the accuracy of the method was not interfered with.

The explanation of the fact that a quantity of an ammonium salt equal to ten times the weight of mercury-compound may be present without affecting the process, whilst double this quantity of ammonium salt precludes its adoption, apparently exists in the circumstance that ammonium salts act entirely by preventing the formation of the precipitate by ammonium hydrate. For after this precipitate is formed, much larger quantities of ammonium salts than those above named are required to dissolve it, except after an inconvenient length of time.

Influence of Potassium and Sodium Salts.—The results obtained with ammonium salts were important, for we proposed to neutralise acid solutions containing mercury with ammonium hydrate as a preliminary to the application of Hannay's process.

It soon became evident, however, that unless the amount of mercury was known to be large, or the acidity of the solution very slight, this mode of neutralisation could not be adopted. Moreover, in separating certain other metals which might co-exist with the mercury, it would be necessary to introduce ammoniacal salts, and a prejudicial amount of them would be formed, in most cases where highly acid solutions had to be neutralised by ammonium hydrate.

It is likewise worthy of note that evaporation cannot be resorted to as a means of expelling any excess of acid that may exist in mercurial solutions, on account of the substantial loss of mercury to which it gives rise.

We next endeavoured to ascertain whether or not the sulphates, nitrates, chlorides, or acetates of potassium or sodium would interfere with the precipitation of mercury by ammonia, when it was found that

a quantity of either of these salts amounting to one thousand times the weight of the mercury salt was without influence on the process. It was, however noticed, that both potassium and sodium hydrate appear to impart a persistency to the precipitate, and to render the last traces of it difficultly soluble in potassium cyanide.

Potassium carbonate and sodium carbonate were without action. Accordingly an acid solution of mercury may be readily brought into a fit condition for the application of Hannay's process by neutralising it with potassium or sodium carbonate. If large quantities of ammonium salts be present, they can be easily removed by adding potassium hydrate, and gently boiling, until ammonia is no longer evolved. No loss of mercury occurs in this operation.

The general method employed by us for determining the amount of metal in any soluble salt of mercury was to add a small quantity of solution of ammonium chloride and then potassium carbonate, until an opalescent precipitate made its appearance. Standard solution of potassium cyanide was then run in, with constant stirring, until the precipitate dissolved, and the solution became perfectly clear. Compounds of mercury insoluble in water were dissolved in nitric, hydrochloric, or sulphuric acid, a small quantity of ammonium chloride solution added, and then solution of potassium carbonate, until the characteristic white opalescent precipitate formed. Mercury compounds insoluble in the above-named acids were dissolved in nitro-hydrochloric acid, and treated with ammonium chloride, &c., as before. The following analyses were performed in this manner:—

Mercuric Nitrate.—A solution of mercuric nitrate in nitric acid, and containing 1·62 gram of the salt per litre, was taken, and the following analyses conducted:—

Quantity of solution taken.	Potassium cyanide used.	Mercuric nitrate.	
		Found.	Used.
		Gram.	Gram.
5 c.c.	4·995 c.c.	0·008092	0·016289
5 "	5·070 "	0·008197	
25 "	25·030 "	0·040549	0·081130
25 "	25·050 "	0·040581	

Mercuric Sulphate.—A solution containing 1·48 gram of this salt per litre (in dilute sulphuric acid) was prepared, and the following analyses made:—

Quantity of solution taken.	Potassium cyanide used.	Mercuric sulphate.	
		Found.	Used.
		Gram.	Gram.
10 c.c.	9·96 c.c.	0·014741	0·044414
10 "	10·03 "	0·014844	
10 "	10·02 "	0·014829	
50 "	49·96 "	0·073940	0·222134
50 "	50·08 "	0·074120	
50 "	50·05 "	0·074074	

Mercuric Acetate.—A solution containing 3·18 grams of this salt per litre (in acetic acid) was prepared, and the following analyses made:—

Quantity of solution taken.	Potassium cyanide used.	Mercuric acetate.	
		Found.	Used.
		Gram.	Gram.
25 c.c.	25·25 c.c.	0·080295	0·160378
25 "	25·18 "	0·080083	

Mercuric Oxalate.—A solution containing 5·71 grams of this salt per litre (in hydrochloric acid) was prepared, and the following analyses made:—

Quantity of solution taken.	Potassium cyanide used.	Mercuric oxalate.	
		Found.	Used.
		Gram.	Gram.
5 c.c.	20·01 c.c.	0·028637	0·090884
5 "	19·78 "	0·028015	
6 "	23·92 "	0·034232	
26·5 "	20·08 "	0·143682	0·430114
26·5 "	19·95 "	0·143322	
26·5 "	20·00 "	0·143110	

Mercuric Sebate.—A solution containing 4 grams of this salt per litre (in hydrochloric acid) was prepared, and the following analyses made:—

Quantity of solution taken.	Potassium cyanide used.	Mercuric sebate.	
		Found.	Used.
		Gram.	Gram.
25 c.c.	20·08 c.c.	0·10040	0·30065
25 „	20·10 „	0·10050	
25 „	19·95 „	0·09975	
			0·3

Mercuric Citrate (Tribasic).—A solution containing 2·7284 grams of this salt per litre (in hydrochloric acid) was prepared, and the following analyses made:—

Quantity of solution taken.	Potassium cyanide used.	Mercuric citrate.	
		Found.	Used.
		Gram.	Gram.
10 c.c.	8·25 c.c.	0·026572	0·082152
10 „	8·46 „	0·027611	
10 „	8·38 „	0·027282	
25 „	21·03 „	0·069072	0·068660

Another solution of the same salt, containing 3·26 grams per litre, gave the following results:—

Quantity of solution taken.	Potassium cyanide used.	Mercuric citrate.	
		Found.	Used.
		Gram.	Gram.
5 c.c.	5·06 c.c.	0·016495	0·0978
10 „	10·02 „	0·032730	
15 „	15·08 „	0·049161	
			6·098386

Mercuric Cyanide.—A solution containing 2·18 grams of this salt per litre (in hydrochloric acid), was prepared, and the following analyses made:—

Quantity of solution taken.	Potassium cyanide used.	Mercuric cyanide.	
		Found.	Used.
		Gram.	Gram.
5 c.c.	17.50 c.c.	0.011019	0.032729
5 "	17.20 "	0.010830	
5 "	17.28 "	0.010880	
30 "	26.00 "	0.065500	0.131272
30 "	26.10 "	0.065772	
			0.1308

The foregoing mercury compounds have also been estimated when mixed with different amounts of other substances, such as the nitrates, sulphates, oxalates, citrates, acetates, butyrates, chlorides, &c., of potassium, sodium, and (in different quantities) of the corresponding salts of calcium and magnesium.

Neither these substances, nor various organic bodies, interfere in any way with the applicability of the process.

It may be mentioned that the sixth decimal figure in the above statements of analytical results is valueless, except so far as it points out the variations of which the process admits; in other words its degree of accuracy. Fewer figures would not so well have shown the differences between the repetitions of the same analyses.

The results above recorded indicate very clearly—

1st. That Hannay's process may be safely applied to the estimation of mercury, not only in pure solutions of HgCl_2 , but likewise in every salt of that metal.

2nd. That while the presence of ammoniacal salts radically interferes with the application of Hannay's method, still, if the precautions we suggest be carried out, the presence of such "foreign material" does not interfere with the trustworthiness of the results.

3rd. That, so far as we have yet gone, organic matters are of no moment.

This latter point, however, still remains to be investigated, when it is hoped that results will be obtained which will furnish us with a mode of rapidly and accurately estimating small quantities of mercury in chemico-physiological and chemico-toxicological inquiries.

XXXI.—*Note on the Discovery of Diamyl.*

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of the Owen's College.

IN my paper read before this Society, and published in the September number of the Society's *Journal* (1877, ii, 260), the discovery of diamyl is, through an oversight, attributed to Wurtz (in 1855). The priority, however, rests with Dr. Frankland, who first prepared it (in 1851) by heating zinc-amalgam with amyl iodide in sealed tubes (*Chem. Soc. J.*, iii, 30). The resulting diamyl was found to boil at 155°, under a pressure of 728 mm., and had a sp. gr. of 0·7704 at 11°.