#### 565

### XXIII.—On New Processes for Mercury Estimation, with some Observations on Mercury Salts.

## By J. B. HANNAY.

WHILE engaged in the analysis of some mercury ores, I had occasion to test most of the processes now in use, and found, by experience, that they were either very tedious or deficient in accuracy. I therefore set about devising a process which might be speedy, and at the same time accurate. A volumetric process, could I devise a satisfactory one, seemed most likely to afford these qualifications. The idea of estimating mercury by voltaic electricity seemed good, and all that was required was to show that it would work well in practice. I therefore took some pains to devise and perfect both methods. I will first describe the volumetric process; the method for estimation by the battery will be given further on.

Of the various chemical reagents tried, potassium cyanide seemed to be the least affected by the presence of other substances, and at the same time the conversion of mercury into cyanide was in every case quite I tried at first to ascertain when the reaction was complete complete. by bringing a drop of solution of potassium hydrate in contact with a drop of the mercury solution, when, if the conversion is complete, it should give no precipitate. It was found, however, that this test did not work well, as it very often gave a slight dimness after the mercury was completely saturated, probably owing to the presence of potassium carbonate. Another objection was that a drop had always to be taken out, and when working with small quantities of mercury, this seriously diminishes the accuracy of the process. It was found that by adding two or three drops of dilute ammonia to a solution of mercuric chloride, a white precipitate was formed, which was completely redissolved when the conversion into cyanide was complete. The point of saturation can be determined with great accuracy, as both the mercury and cyanide solutions are colourless, so that it is easy to detect the slightest dim-Before the last drop of cyanide is added, the precipitate is so ness. fine, that the liquid appears just as if fluorescent. When, however, the last drop is added, the fluorescence disappears instantaneously, and the liquid is perfectly clear. In making the following determinations. the exact point of saturation was determined by a method similar to that used by Professor Stas in his process for silver estimation by chloride of sodium. A lens, formed of a small glass bulb filled with water. was placed close to the outside of the beaker, so that its focus was inside the liquid. When there was no sunlight, a gas jet was placed near the beaker. As long as there was the slightest dimness, there

# 566 HANNAY ON NEW PROCESSES FOR MERCURY ESTIMATION,

appeared a brilliant streak in the liquid, caused by the light striking against the floating particles, but whenever enough cyanide was added to dissolve the precipitate, the lines (caused by the convergence of the rays) entirely disappeared. The point of saturation is thus very easily and accurately determined. For ordinary determinations the lens may be dispensed with, as the eye can detect a very slight dimness, but where great exactness is required this method should be used. To test this process, the following experiments were made :—

Potassium cyanide was dissolved in water, to form a dilute solution. 4:3424 grams of mercuric chloride were dissolved in 250 c.c. of water. A known volume of this solution was poured into a beaker, diluted with water, and a few drops (generally six) of dilute ammonia added. The cyanide solution was then poured in, until the liquid, after stirring, became perfectly clear. In all these experiments a Mohr's burette (with an Erdmann's float) graduated to tenths of a cubic centimeter, was used. The cyanide solution was run in from this burette, until the liquid was nearly clear, then the last few drops were added from a very fine burette, graduated to hundredths of a cubic centimeter; the length occupied by one cubic centimeter being about 150 millimeters. The following are the results :—

Mercuric chloride.	Potassium eyanide solu- tion used.	Therefore 1 c.c. of cyanide solution equals in mercury.
gram.	cubic centimeters.	gram.
Ŏ`0694	4.22	0.01213
0.1406	8.56	0.01212
0.1042	6.33	0.01214
0.0868	5.26	0.01216
0.1042	6.33	0.01214
0.1042	6.32	0.01216
0.2084	12.66	0.01214
0.1042	6 ·34	0.01213
0.1042	6.32	0.01216
0.8684	52 .85	0.01213
	Mercuric chloride. gram. 0 0694 0 1406 0 1042 0 1042 0 1042 0 1042 0 2084 0 1042 0 1042 0 1042 0 1042 0 1042 0 1042	$\begin{array}{c c} \mbox{Mercuric}\\ \mbox{chloride.} \end{array} \  \  \begin{array}{c} \mbox{Potassium eyanide solution used.} \\ \hline \mbox{gram.} \\ 0.0694 \\ 0.1406 \\ 0.1042 \\ 0.1042 \\ 0.1042 \\ 0.1042 \\ 0.33 \\ 0.1042 \\ 0.2084 \\ 12.66 \\ 0.1042 \\ 0.2084 \\ 12.66 \\ 0.1042 \\ 0.32 \\ 0.2084 \\ 0.1042 \\ 0.32 \\ 0.8684 \\ 0.285 \\ \end{array}$

The average of all these experiments is 0.01214 gram. As the same amount of ammonia had been added to each portion in the foregoing experiments, I wished to ascertain if more or less ammonia would affect the results.

Ammonia added.	$\mathrm{HgCl}_2$ solution used.	HgCl <sub>2</sub> .	KCN solution used.	1 c.c. equals in Hg.	
3 drops dilute 50 """ Large excess.	cub. cent. 6 6 6 6	gram. 0 ·1042 0 ·1042 0 ·1042	cub. cent. 6 · 34 6 · 33 6 · 34	gram. 0 ·01213 0 ·01214 0 ·01213	

### WITH SOME OBSERVATIONS ON MERCURY SALTS. 567

These results show that it does not matter what proportion of ammonia is added. It was found, however, that when the solution is very dilute (less than one part of mercuric chloride in a thousand of water) if a little less cyanide be added than is required for complete saturation, and the liquid agitated for five or ten minutes, it ultimately grows quite clear. This seldom or never makes a difference of more than 0.2 per cent. It shows, however, that the liquid should not be very dilute. The state of dilution, beyond a certain point, does not affect the results in the least, and even when it is very dilute, if the cyanide is run in quickly, and the liquid not stirred very long (not more than one minute at a time), the results are perfectly accurate, as the following experiment shows:—

0.0694 gram of mercuric chloride, dissolved in 200 c.c. of water, took 4.22 c.c. of the standard cyanide solution, which equals 0.0694 gram of mercuric chloride, showing that the results are perfectly accurate, even when the mercuric chloride solution contains only 1 part in 3,000 of water. Concentrated solutions of mercuric chloride also give good results. Take for instance the following experiment: -1.9879 gram of mercuric chloride was dissolved in 50 c.c. of water, giving a solution containing about 1 part in 25 of water, or nearly saturated at 15° C. This solution took 120.83 c.c. of cyanide solution, which equals in mercury 1.4668 gram, the calculated amount being 1.4667 gram. The mercury solution must not be hot, as in that case it invariably gives results a little too low, and if it is boiled after the addition of ammonia, insoluble compounds are generally formed, so that the cyanide solution seldom renders the mercury solution perfectly clear. The temperature does not affect the results, if kept between 8° and 20°.

As it was necessary that the mercury should be in the state of chloride, I set about to find the best way to obtain the metal in this state. so as to be in a fit state for estimation by cyanide. It was found that on dissolving the sulphide in aqua regia, the whole of the mercury existed as chloride (no sulphate being formed), so that, when mercury is mixed with other metals, it is only necessary to precipitate as sulphides with hydrogen sulphide, and separate the arsenic, copper, &c., by ammonium sulphide and nitric acid, or any process that may be applicable, so as to leave the mercury as sulphide. The sulphide thus obtained is dissolved in a small quantity of aqua regia, diluted and filtered from sulphur, neutralised with potassium hydrate, and after the addition of a few drops of ammonia, the mercury is estimated by standard cyanide. The following are the results of two estimations done after separation of the mercury from mixed solutions :--0.4342 gram of mercuric chloride mixed with cupric and ferric chlorides, after separation, took 26.38 c.c. cyanide solution, which equals in mercuric chloride, 0.4341 gram. Another portion, weighing 0.1736 gram, mixed with antimony, cadmium, and cupric chlorides, took, after separation,

10.55 c.c. cyanide solution, which equals 0.1734 gram of mercuric chloride. It will be seen from these experiments that this process is very satisfactory, being speedy, accurate, and simple.

The battery estimations were conducted as follows :---The apparatus employed is shown in the accompanying figure. A shows the battery in action, as used in performing an experiment. B is a section of the



support for the basin. It consists of a turned copper basin in a wooden support, the copper basin serving as a conductor, on which I place the platinum basin. A piece of platinum wire, coiled horizontally (the outer coil being a little less in diameter than the platinum basin) is used as the positive pole, being connected by a binding screw with the carbon of the battery. The copper basin in which the platinum basin rests is connected with the zinc of the battery. The following are some determinations made by the battery:—

0.4275 gram of mercury was heated with strong sulphuric acid, till the whole was converted into sulphate. This was transferred to the platinum basin, and the connections with the battery completed. The current was allowed to act for about six hours, when it was found that the solution gave no precipitate with stannous chloride, and the mercury was all in the fluid state on the surface of the basin. The basin was filled up with water, and, without disconnecting the battery, the solution was nearly all drawn off with a pipette. This was repeated several times, and the basin finally removed and washed with distilled water, absolute alcohol, and lastly with ether. It was then placed under a bell-jar, in which the pressure was reduced by the air-pump to about 160 mm. It was kept at this pressure for about two minutes, air was then admitted, and the jar again exhausted. This treatment was repeated, and the basin then weighed, when the mercury was found to weigh 0.4276 gram. This gives an excess of one-tenth of a milligram, and so is as accurate as any ordinary balance will weigh.

In the second experiment, 0.5610 gram of mercurous nitrate was converted into mercuric sulphate by treatment with strong sulphuric acid, and treated exactly as above, as far as the precipitation goes; only, instead of washing with ether, it was only washed with absolute alcohol, and dried in a current of air, at about 38°, and weighed when perfectly dry. It gave of mercury 0.3998, the calculated amount being 0.4007, showing a loss of nearly a milligram, or about two-tenths per cent.

0.5200 gram of mercurous nitrate was dissolved in water acidified with nitric acid, reduced directly, without conversion into sulphate, and dried exactly as the foregoing. It gave 0.3702 gram of mercury, the calculated amount being 0.3714, showing a loss of 1.2 milligram, or three-tenths per cent.

0.7359 gram of mercurous nitrate, acidified with nitric acid, and reduced directly as in the foregoing case, but washed with ether and dried *in vacuo*, gave 0.5257 grm. of mercury, the calculated amount being 0.5256 gram. In this case, as in the first experiment, there is an excess of weight only to the small extent of one-tenth of a milligram. The basin and mercury were heated to about  $60^{\circ}$ , a slow current of air drawn over them for about 6 minutes, and the weight again noted. The mercury weighed 0.5195, showing a loss of 6.2milligrams from the former weighing, or rather over 1 per cent.

0.5193 gram of mercurous nitrate was reduced as in the foregoing experiment, and the mercury washed with alcohol and dried in a current of air at 100°. After being kept at this temperature for about ten minutes, the mercury weighed 0.3610 gram, the calculated amount being 0.3709, showing a loss of 9.9 milligrams, or over 2.6 per cent.

0.8318 gram of mercurous nitrate treated as before, only washed with absolute alcohol and dried *in vacuo*, gave 0.6090 grm. of mercury. It was then washed with ether and dried *in vacuo*, when it weighed 0.5940. The calculated amount is 0.5940 gram. The first weighing showed an excess of 0.015 gram, or 2.5 per cent. of mercury.

Mercuric chloride is not reduced entirely to the metallic state, as a large portion gets reduced to mercurous chloride, and is not further acted upon, as the following experiment shows: 0.4555 gram of mercuric chloride was dissolved in water, and acidified with dilute sulphuric acid. It was then placed in the battery circuit, and treated exactly as in other cases, that is, dried with ether *in vacuo*. At first it was seen that a good quantity of a white powder was formed, which refused to be reduced even when the power of the battery was augmented. The contents of the basin weighed 0.3829 grm., the calculated amount being 0.3361, showing an excess of 0.0468 gram, or nearly 14 per cent.

#### 570 HANNAY ON NEW PROCESSES FOR MERCURY ESTIMATION,

It occurred to me that, if the chloride were first converted into cyanide, as in the volumetric process, it might suffer complete reduction.

0.3624 grm. of mercuric chloride was therefore weighed out, and treated with cyanide. It took for saturation 22.03 c.c. of cyanide solution, which equals in mercury 0.2674 gram. The solution after being reduced in bulk by evaporation, was placed in the basin, and the circuit with the battery completed. After being allowed to stand for six hours, it was treated with distilled water, alcohol, and ether, and dried *in vacuo*. It weighed 0.9671 gram. The calculated number and the cyanide determination, both gave 0.9674 gram: there is therefore a loss of only three-tenths of a milligram.

As the sulphate is completely reduced by the battery, I tried to convert the chloride into sulphate by heating with strong sulphuric acid. It was found that, as long as the acid was dilute, no action took place, and when the acid became so concentrated that its boiling point was raised to the temperature at which mercuric chloride volatilises, salt sublimed unchanged. After the excess of salt had been expelled by heat, the sulphuric acid was allowed to cool, and the salt which crystallised out (the solution becoming almost solid), was poured with sulphuric acid on an asbestos filter, and allowed to drain for three days, the moisture taken up by the sulphuric acid serving to carry the excess of acid through the filter. The salt was then washed with very small quantities of cold water, and dried between the folds of bibulous paper, then allowed to dry over sulphuric acid for two days. The salt which sublimed was purified in the same way. Both were analysed, and yielded as follows :---

Mercury, Hg Chlorine, Cl <sub>2</sub>	Sublimed. 73·820 27·177	Crystallised. 73·799 26·280	Calculated. 73.801 26.199
	100.997	100.079	100.000

This clearly shows that mercuric chloride dissolves without decomposition in strong sulphuric acid. The acid seemed to dissolve nearly half its own weight.

The mercury was estimated by cyanide solution and the chlorine as silver chloride. It is thus seen that mercury has a stronger affinity for chlorine than for sulphuric acid. This is also seen when mercuric sulphate is heated with hydrochloric acid, mercuric chloride and free sulphuric acid being formed. It was found that when mercury is heated with strong sulphuric acid, the resulting sulphate (although decanted from the unoxidised metal), on treatment with hydrochloric acid, gave from one-third to one-fourth of its weight of mercurous

#### WITH SOME OBSERVATIONS ON MERCURY SALTS. 571

chloride, showing that mercurous sulphate was formed at the same time as the mercuric salt. When, however, the whole of the mercury was converted into sulphate and the solution heated for a minute or so after, the resulting salt dissolved entirely in hydrochloric acid as mercuric chloride, showing that it existed entirely as mercuric sulphate. The formation of mercurous sulphate is due to the action of the sulphur dioxide evolved, as this substance in solution reduces at once both mercurous and mercuric sulphates and nitrates, partly to the metallic state, and partly to lower salts. By the aid of heat, however, they may generally be all reduced to the metallic state. Sulphurous acid does not at once reduce mercuric chloride, but after a little a white precipitate of mercurous chloride is formed. It was found, however, that, even after long standing and with a large excess of sulphurous acid, the reduction was never quite complete. Mercuric cyanide is not reduced at all by sulphurous acid.

It was noticed in the volumetric process, when only one or two drops of dilute ammonia were added to the mercury solution, that on adding the cyanide solution, the precipitate caused by the ammonia steadily increased, till about half the required amount was added, and from that point it was slowly dissolved by the further addition of cyanide. It was also noticed, that when a large quantity of ammonia was added, the precipitate began to dissolve from the first addition of cyanide, but if the two solutions be compared when about half the required amount of cyanide has been added, they will be found to be of nearly the same degree of opacity, provided of course, they are of the same degree of dilution. It was thought that the precipitates might be nearly the same in composition, so the following experiments were made to ascertain this.

14 c.c. of mercury solution (of the strength mentioned in the first part of this paper) were taken in each case, and diluted with 150 c.c. of water. To one portion five drops of dilute ammonia were added, to the other a large excess. 7 c.c. of the cyanide solution were run into each, that amount being about half the quantity required for saturation. The precipitate was allowed to settle, collected on a weighed filter, and dried over strong sulphuric acid for four days, then weighed. The precipitate in the portion with only five drops of ammonia weighed 0.0689 gram, and contained 16.5 per cent. of mercury, while the precipitate in the one with excess of ammonia weighed 0.1070 gram, and contained 78.5 per cent. of mercury, showing that the two precipitates have entirely different compositions.

It is well known that when a solution of mercuric chloride is evaporated, a portion of the salt is volatilised with the aqueous vapour. I have found that this takes place when a solution containing as little as one part in 500 of water is boiled, but when the solution is more dilute, no mercury could be detected in the distillate. I have also

## 572 HANNAY ON NEW PROCESSES FOR MERCURY ESTIMATION,

found that a solution of mercuric chloride, containing as much as one part in 20 of water, can be boiled without loss of mercury, provided it be acidified with dilute hydrochloric acid. When, however, the hydrochloric acid begins itself to be volatilised, considerable quantities of mercury may be detected in the distillate. In dissolving mercuric sulphide, it was found that, if the aqua regia was not very strong and was not boiled after the mercury sulphide was dissolved, no mercuric chloride could be detected in the washings of the gases evolved. Sulphuric acid has no effect either in retarding or accelerating the volatilisation of mercuric chloride. To show how much loss is caused by evaporating a solution of mercuric chloride, the following experiment may be taken. 0.4306 gram of mercuric chloride dissolved in 25 c.c. of water and evaporated to dryness on a steam-bath, left a residue of 0.4057, showing a loss of 5.76 per cent. I may mention, in connection with this subject, that when solutions of mercuric chloride are evaporated or boiled in a room, even when well ventilated, the salt which is thus thrown into the atmosphere is very injurious to the human system; in fact, all the symptoms of mercury poisoning are strongly manifested.

When it was seen that mercuric chloride was so volatile, experiments were made to find the best process by which metallic mercury might be converted into chloride for estimation, and at the same time to dispense with a condensing apparatus. It was found that, on dissolving mercury in aqua regia, considerable quantities of mercury were found in the distillate. When mercury was dissolved in hot nitric acid without actual boiling, no mercury could be detected in the washings of the evolved gases, so that mercury can be converted into chloride by dissolving in hot nitric acid and then gently heating with hydrochloric acid. By numerous experiments, I have found that by this method no loss of mercury is sustained. On converting mercury into sulphate by heating with strong sulphuric acid, no mercury was found in the washings of the evolved sulphur dioxide.

Mercuric cyanide when boiled evolves traces of hydrocyanic acid, but no mercury, even when concentrated. When, however, the point of saturation is reached, small quantities of mercury can be detected in the distillate; but if the evaporation to dryness is carried on without ebullition, as on a steam-bath, no mercury is volatilised. It will be seen from this, that, after estimating mercury by potassium cyanide, it may be evaporated to small bulk for estimation by the battery, without any loss whatever.

Experiments were made to find if mercurous or mercuric nitrate were volatile. Neither salt, when in dilute, or even moderately concentrated solutions, gives any mercury when distilled. When, however, the mercurous nitrate solution becomes concentrated, the distillate is sometimes of a slightly grey tinge.

When two or three drops of this solution are examined by the microscope, the grey substance is seen to consist of a flocculent matter like alumina, some very small shining pearly plates, and a few minute globules of metallic mercury. When dilute nitric acid is added to a solution of mercurous nitrate, and the mixture boiled, there is no mercury carried over, until the acid becomes sufficiently concentrated to oxidise the mercurous salt.

Whenever the evolution of the lower oxides of nitrogen begins, mercury can be detected in the distillate in sufficient quantity to give a black, nearly opaque liquid with stannous chloride. Whenever the oxidation ceases, no more mercury is found in the distillate, or only very faint traces in a concentrated acid solution. It is curious that on oxidising metallic mercury with nitric acid, no mercury comes over, although far more nitrous fumes are evolved than on oxidising a mercurous salt.

On finding how volatile mercuric chloride was, I thought it might be useful to determine the amounts of salt dissolved at different temperatures, as previous determinations had, in all probability, been made by evaporating a measured portion of the liquid to dryness. I also undertook the work as a test of the new volumetric process. In making the determinations, water kept at the desired temperature was digested on an excess of the carefully crystallised salt for at least half an hour, a portion was then drawn off with a bulb pipette kept at the same temperature, whose contents at 0° had been accurately determined. At 0° the amount dissolved was determined in two ways-first a solution saturated at about 15° was cooled down to 0° and allowed to stand at that temperature for an hour or so; the amount dissolved was then determined. The second method was to cool down water to 0° and then add an excess of the crystallised salt. The two methods gave closely agreeing results, the former being generally a little higher than the latter. When a saturated solution, from 97.5° upwards, is sucked up into a bulb, the salt invariably crystallises and blocks up the capillary point whenever the bulb is removed from the solution, so that, in determining the amount dissolved from 97.5° to 100.8° (the boilingpoint of a saturated solution of mercuric chloride), the following process was employed :- The small dry bulb (whose contents at  $0^{\circ}$ were known) was plunged under the solution, and allowed to remain there till the liquid rose to the mark on the neck. The upper tube was then sealed, the bulb removed from the solution, and the outside wiped quite clean. The capillary tubes were then broken off at each end, the bulb broken in a beaker, and the salt dissolved in cold water. The small tubes were then ground in an agate mortar, and the mixture of glass and salt washed into the beaker. The whole of the salt being in solution in the beaker, it was only necessary to add a few drops of VOL. XXVI.

2 s

#### 574 HANNAY ON NEW PROCESSES FOR MERCURY ESTIMATION.

ammonia, and estimate by standard cyanide solution. The following table gives the results of amounts dissolved and densities. The determinations were made almost without exception at each rise of 5°, and at each end, some intermediate ones were made. The densities were determined in the usual way, with a fine blown bulb, whose contents at 0° were accurately known.

Tempera- ture.	Per cent. dissolved.	Specific gravity.	Tempera- ture.	Per cent. dissolved.	Specific gravity.
$\begin{array}{c} 0 \cdot 0^{\circ} \\ 2 \cdot 2^{\circ} \\ 4^{\circ} \\ 5^{\circ} \\ 10^{\circ} \\ 15^{\circ} \\ 20^{\circ} \\ 25^{\circ} \\ 30^{\circ} \\ 35^{\circ} \\ 40^{\circ} \\ 45^{\circ} \end{array}$	$\begin{array}{c} 4 \cdot 09 \\ 4 \cdot 35 \\ 4 \cdot 61 \\ 4 \cdot 78 \\ 4 \cdot 85 \\ 5 \cdot 59 \\ 5 \cdot 93 \\ 6 \cdot 68 \\ 7 \cdot 17 \\ 8 \cdot 86 \\ 9 \cdot 72 \\ 10 \cdot 61 \end{array}$	$\begin{array}{c} 1 \cdot 039 \\ 1 \cdot 039 \\ 1 \cdot 039 \\ 1 \cdot 041 \\ 1 \cdot 042 \\ 1 \cdot 042 \\ 1 \cdot 045 \\ 1 \cdot 049 \\ 1 \cdot 056 \\ 1 \cdot 060 \\ 1 \cdot 067 \\ 1 \cdot 076 \\ 1 \cdot 083 \end{array}$	60° 65° 70' 75° 80' 85° 90' 95' 96.5° 97.5° 99°	$\begin{array}{c} 16 \cdot 23 \\ 18 \cdot 42 \\ 20 \cdot 81 \\ 22 \cdot 70 \\ 26 \cdot 52 \\ 28 \cdot 74 \\ 32 \cdot 30 \\ 36 \cdot 71 \\ 37 \cdot 82 \\ 41 \cdot 56 \\ 52 \cdot 51 \\ 55 \cdot 73 \end{array}$	$\begin{array}{c} 1 \cdot 116 \\ 1 \cdot 124 \\ 1 \cdot 146 \\ 1 \cdot 165 \\ 1 \cdot 181 \\ 1 \cdot 203 \\ 1 \cdot 225 \\ 1 \cdot 272 \\ 1 \cdot 287 \\ 1 \cdot 310 \\ 1 \cdot 346 \\ 1 \cdot 354 \end{array}$
50°	12.37	1 089	100.8°	56.02	1.357

The curves in the accompanying illustration are constructed from the above numbers, the continuous line referring to the amount dissolved, and the dotted line to the densities. The lateral numbers refer to the temperature, the upper to the percentage of salt dissolved, and the lower to the specific gravity.

In conclusion, I may mention that of the two processes the volumetric one is both more accurate and easier of application. It might be expected that the platinum basin used in the battery estimations would be seriously acted upon, but on dissolving off the mercury by nitric acid, the surface of the basin remains bright and clear, showing that the amalgamation is extremely superficial. The basin lost 8 milligrams in ten estimations, showing a loss of eight-tenths of a milligram for each estimation, which is not much more than would be caused by cleaning it. The loss depends entirely on the nature of the basin, some specimens of platinum being much more easily amalgamated than others.

