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THE DETERMINATION OF THE ACID RADICAL AND ITS RELATION TO THE CONSTITUTION OF COMMERCIAL BISMUTH SUBNITRATE.

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THE importance of the rôle which the subnitrate plays among the bismuth compounds so largely used in the practice of medical science has led to many attempts to determine its probable constitution. There has been little agreement, however, in the results obtained ; especially has this been the case with relation to the figures given for the acid-radical content.

It is not my intention to discuss at length here the determination of the percentage of bismuth. F. A. U. Smith (ANALYST, 1901, **26**, 73) has pointed out that the sulphide method of determination is reliable only when suitable precautions are taken to prevent the formation of free sulphur during precipitation and oxidation while drying. He recommends the oxide method, either by direct ignition in a porcelain dish, preferably by means of a muffle furnace, or by first precipitating the bismuth with ammonium carbonate, and finally igniting the dried precipitate. This procedure is, of course, combined with a qualitative examination to insure the absence of other inorganic impurities.

No method, so far as I am aware, has yet been published for the *direct* determination of the nitric acid radical in subnitrate of bismuth, although an indirect method has been described by F. A. U. Smith (*loc. cit.*).

Before trying the method of decomposition at the temperature of the waterbath, Smith worked at Thoms' method, which is carried out at the ordinary temperature. In this 2 grms. of the salt are shaken with a few c.c. of water in a 100 c.c. flask, mixed with 10 c.c. of $\frac{N}{1}$ potash, and shaken for five minutes. The solution is made up to 100 c.c. with water, and a portion titrated with $\frac{N}{1}$ hydrochloric acid solution, using litmus or phenolphthaleïn as indicator.

It is of interest to record here the results Smith obtained by the hot and cold process respectively.

TABLE I.

Percentages of N_2O_5.

B.P., 1898 formula $BiO.NO_3.H_2O = 17\cdot72$ per cent. N_2O_5.

				Hot Method.	Cold Method.
Sample A	...	...	...	19·45	15·59
,,　　B	...	...	...	17·78	14·19
,,　　C	...	...	...	18·01	14·11
,,　　D	...	...	...	18·56	13·43

It will be seen that the average difference in the results obtained by the two methods is about 4 per cent. One source of error obtaining by decomposition in the cold was that no correction was made for the volume occupied by the moist precipitate. Smith overcame this difficulty by filtering, but he apparently took no

steps to confirm his results by a different method of procedure. Although he finally decided on the hot process of decomposition. he seems to have had still some doubt as to which process gave the more accurate results. After giving Smith's process a fair trial, I found it was not possible to obtain concordant results working with the same sample ; and not being satisfied with the fact that the hot method gave different results from that carried out in the cold, I decided further to investigate the matter.

That higher results were obtained by heating pointed either to the incompleteness of the reaction in the cold or to the fact that another acid was being estimated by the procedure adopted. The former theory appeared more probable, but, mindful that phenolphthaleïn is very susceptible to the influence of weak acids, the possibility occurred that atmospheric carbonic acid was being absorbed by the excess of soda during the process of heating and stirring. The explanation of the difference in results was shown by the following experiment to be supported by the latter hypothesis.

Two grms. of the bismuth salt with 20 c.c. water and 10 c.c. $\frac{N}{1}$ caustic soda solution were introduced into each of three wide-mouthed carbonic acid flasks, two of which were closed by corks carrying Bunsen-valves, the other being left open to the influence of the air. All three were then heated on the water-bath for half an hour and treated in the manner described by Smith, excepting that the contents of one of the flasks carrying a Bunsen-valve was titrated without filtering. The following were the results obtained :

Open Flask.—The filtrate required 31·25 c.c. $\frac{N}{10}$ hydrochloric acid for neutralisation, corresponding to 18·6 per cent. N_2O_5.

Closed Flask No. I.—The filtrate required 38·35 c.c. $\frac{N}{10}$ hydrochloric acid, corresponding to 16·7 per cent. N_2O_5.

Closed Flask No. II.—The *unfiltered* contents required 40·7 c.c. $\frac{N}{10}$ hydrochloric acid, corresponding to 16·1 per cent. N_2O_5.

When using the nitrometer for a direct method of estimation, I found that the subnitrate was not easy to introduce into the instrument; also, in the process of decomposition, insoluble bismuth sulphate is formed, which aggregates into lumps and tends to envelop some of the subnitrate, so that even after long and vigorous shaking some uncertainty is felt as to the completeness of the reaction.

I therefore decided to first remove the bismuth by Smith's method, and to determine the amount of sodium nitrate in the filtrate. The latter, however, contains in addition traces of sodium carbonate, which must first be decomposed before introducing into the nitrometer. The procedure I adopt is as follows :

About 2 grms. of the bismuth subnitrate are mixed with 20 c.c. water and 10 c.c. $\frac{N}{1}$ caustic soda solution. The whole is brought to the boiling-point with stirring, and allowed to digest for about a quarter of an hour on a water-bath, until the oxide of bismuth formed has assumed a uniform lemon-yellow colour, showing that the process of decomposition is complete. The supernatant liquid having been poured through a filter, the oxide of bismuth is washed with hot water two or three times by decantation, finally on the filter, and the cooled filtrate made up to 100 c.c. To 25 c.c. of the solution thus obtained are added 0·5 c.c. in excess of the quantity of

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normal sulphuric acid required for neutralisation, using methyl orange as indicator. This is then carefully evaporated down to about 2 or 3 c.c., whereby the carbonic acid is driven off, allowed to cool, and finally decomposed in the nitrometer in the usual way.

Since the above process was elaborated, another method has been described by E. J. Brown (*Pharm. J.*, 1908, **26**, 378), which depends on the fact that bismuth subnitrate, when boiled with a solution of sodium chloride, is converted into insoluble oxychloride, permitting the filtrate to be used for the determination of the nitric radical. Brown states that the subnitrate is quantitatively converted into BiOCl, a point to which I shall refer later, and estimates the nitric acid present indirectly by first determining the amount of unused sodium chloride by titration with $\frac{N}{10}$ silver nitrate solution in an aliquot portion of the filtrate. Another fraction is then evaporated down with excess of strong hydrochloric acid, thus converting the sodium nitrate present into sodium chloride. By estimating the increase of the sodium chloride contents, the amount of anhydrous nitric acid present in the original bismuth salt can be calculated.

For the determination of the nitric acid, this method, if carefully carried out, gives results in good agreement with those obtained by means of the nitrometer. Its only advantage over the nitrometer method is that it entails no elaborate apparatus. Its chief disadvantages compared with the nitrometer process are—

I. The liability to spurting at the end of the reaction.

II. Two determinations are necessary, thus introducing two chances of error against one by the nitrometer method.

III. The number of c.c. of $\frac{N}{10}$ silver nitrate used is less than half the number of c.c. of nitric oxide obtained from the same quantity of bismuth salt.

I have obtained further confirmation of the results by the above two methods by means of the "nitron" process (ANALYST, 1907, **32**, 349), using the filtrate obtained by the decomposition of the bismuth salt with hot caustic soda solution. The precipitate was washed with ice-cold water, and a correction made for the solubility of the nitron nitrate.

In Table II. are collected the results obtained by the three methods on samples of bismuth subnitrate obtained from different manufacturers. Although the "nitron" method cannot perhaps be seriously entertained from an economic standpoint, there can be very little doubt that the nitric acid radical can be accurately estimated by any of the three methods.

The chief source of error in Smith's method was undoubtedly due, as I have already shown, to the absorption of carbonic acid by the caustic soda solution, and on comparing the results here given with those taken from his paper, it will be seen that the hot process results are much too high on this account; while those obtained by the cold method are lower than the average figure for the percentages of nitric acid recorded. The density figures given in this table are only roughly approximate, and were determined in each case by loosely filling a graduated tube, shaking down one hundred times, and reading off the volume occupied by the bismuth salt.

TABLE II.

Sample.		Percentage of Bi_2O_3.		Percentage of N_2O_5.			Percentage of H_2O (by Difference).	Relative Density expressed as Kilograms per Litre.
		Direct Ignition Method.	Ammon. Carb. Method.	Nitrometer Method.	Nitron Method.	Sodium Chloride Method.		
English manufacture	A 1	80·3	—	15·47	—	15·35	4·23	1·533
	A 2	80·5	—	15·47	—	—	4·03	1·502
	B 1	80·2	—	15·52	—	—	4·28	1·886
	B 2	79·8	—	15·66	—	—	4·54	1·382
	C 1	79·7	—	15·81	15·70	15·72	4·49	2·186
	C 2	80·0	79·9	15·52	—	—	4·48	1·826
	D 1	78·8	—	15·43	—	15·47	5·77	2·276
	D 2	79·8	—	15·62	—	15·47	4·58	1·836
	E	80 0	—	15·57	—	—	4·43	1·634
French manufacture	F	80·0	—	15·52	15·46	—	4·48	1·798
German manufacture	G	80·0	79·9	15·72	15·72	15·81	4·28	1·570

H. Rose (*Pogg. Ann.*, 1859, **110**, 411) has shown that oxychloride of bismuth is insoluble in dilute hydrochloric acid, and takes advantage of this to estimate bismuth by adding slight excess of hydrochloric acid to the solution of the bismuth salt, and diluting largely with water. He states, however, that the precipitate is liable to loose a little chlorine by prolonged washing. Brown (*loc. cit.*) adopts a modification of this, and states that when bismuth subnitrate is boiled with solution of sodium chloride it is converted into BiOCl. This I cannot confirm; the compound formed with all the samples I have tried has approximately the more complex formula $Bi_{12}O_{13}Cl_{10}$—an oxychloride which I believe has not hitherto been described. The following experiments are given in support of the composition of this body, which, as I shall afterwards show, has an important bearing on the composition of commercial subnitrate of bismuth :

Two grms. of sample G boiled for fifteen minutes with a solution containing 1·503 grms. pure sodium chloride yielded 1·769 grms. of precipitate when dried at 100° C. This precipitate, considered as BiOCl, corresponds to 79·08 per cent. Bi_2O_3, while if it possesses the more complex formula it corresponds to 80·45 per cent. Bi_2O_3. On titrating the filtrate, it was found that 0·34 grm. NaCl had been used up in the decomposition, this amount being equivalent to 1·778 grm. $Bi_{12}O_{13}Cl_{10}$, or only 1·508 grm. BiOCl. The amount of chlorine present in the precipitate was found to be 11·5 per cent. The compound $Bi_{12}O_{13}Cl_{10}$ contains 11·63 per cent. chlorine, while if the precipitate has the formula BiOCl, 13·68 per cent. chlorine should have been found. The amount of precipitate obtained by similar treatment of sample C 1 indicated 78·7 per cent. Bi_2O_3 if considered as BiOCl, or 80·2 per cent. Bi_2O_3

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reckoned as $Bi_{12}O_{13}Cl_{10}$. On estimating the amount of chlorine, 11·31 per cent. was found. This figure is somewhat lower than that obtained in the previous experiment, owing to very considerable washing of the precipitate—a fact which confirms Rose's observation on this point. The loss of chlorine experienced by washing the precipitate makes it somewhat difficult to judge when the excess of sodium chloride has been removed, and this, in my opinion, is one of the chief objections to this method of determining bismuth.

Turning to the question of the chemical constitution of commercial subnitrate of bismuth, the following table records the various formulæ and percentage compositions that have been put forward for this substance by different authorities :

TABLE III.

Authority.	Formula.	Percentage Composition.
British Pharmacopœia, 1898 ... French Pharmacopœia, 1908 ...	$\{$ $BiO.NO_3.H_2O$ $\}$ Corresponding to	76·3 per cent. Bi_2O_3. 17·7 per cent. N_2O_5. 6·0 per cent. H_2O.
German Pharmacopœia, 4th Edn., 1900.	None given	"Evolves yellowish-red vapours on heating, and finally leaves 79 to 82 per cent. bismuth oxide."
American Pharmacopœia, 1905...	None given	"Heated to redness, bismuth subnitrate evolves nitrous vapours, leaving not less than 80 per cent. of its weight of a yellow residue."
British Pharmaceutical Codex ...	$BiO.NO_3.\frac{1}{2}H_2O$	See light variety below.
National Dispensatory	—	"The product . . . is not likely to be of definite composition."
F. A. U. Smith	—	80 per cent. Bi_2O_3. 17·5 to 19·5 per cent. N_2O_5.
E. J. Brown	$\{$ $BiO.NO_3.H_2O$ (heavy variety) $\}$ $BiO.NO_3.\frac{1}{2}H_2O$ (light variety) $\}$	76·3 per cent. Bi_2O_3. 17·7 per cent. N_2O_5. 6·0 per cent. H_2O. 78·6 per cent. Bi_2O_3. 18·2 per cent. N_2O_5. 3·2 per cent. H_2O.

David Howard (*Chemist and Druggist*, 1898, **1**, 674), criticising the sulphide method of determining bismuth as prescribed in the British Pharmacopœia, stated that "the amount of sulphide which the British Pharmacopœia prescribes is founded on theory alone, and is unattainable in practice, corresponding to only 76·5 per cent. of oxide."

It is also of interest to record that a sample of subnitrate of bismuth, prepared according to the exact instructions given by the French Pharmacopœia, yielded on ignition 79·5 per cent. Bi_2O_3. The N_2O_5 figures given by Smith are based

on the hot caustic soda method of determination, which, as I have shown, gives erroneous results. Serious consideration cannot, therefore, be given to his conclusions on this point.

Brown devotes a considerable portion of his paper to showing theoretically that the light and heavy varieties of subnitrate are not chemically identical, and that the basicity of the salt is regulated by the amount of water used in the precipitation of the solution of bismuth nitrate. He supports his theory of the two varieties on the strength of one analysis of the heavy and two analyses of the light—at least, these are all he publishes—and on this rather meagre evidence recommends that the light variety, with its corresponding formula, should be officially adopted in the next edition of the British Pharmacopœia. If the percentage compositions based on Brown's formulæ are compared with the table of analyses, it will be seen that the amount of oxide yielded by sample D 1, which has the greatest density of the eleven samples recorded, is in excess of that calculated from the formula of the light variety. This sample is exceptional from a commercial standpoint, and is the only sample in my experience which has yielded less than 79 per cent. residue on ignition. The remaining ten samples, whether of British or foreign manufacture, contain on an average about 80 per cent. Bi_2O_3. This figure fulfils the requirements of the American and German Pharmacopœias, and is also supported by Smith's analyses. Referring to the same table, it is seen that the percentage of N_2O_5 never exceeds 16·0; and although my results testify to the efficacy of the sodium chloride method for the determination of the acid radical, I can only conclude, from the low percentages of bismuth oxide and the high N_2O_5 figures given by Brown, that the samples he analysed were exceptional, and not average commercial samples.

The various compositions that have been ascribed from time to time to commercial subnitrate of bismuth might lead to the conclusion either that there are many basic nitrates of bismuth, or that the salt of commerce is not a true compound. The analyses of the samples here considered, representing seven of the leading bismuth manufacturers in England and on the Continent, show, however, that the composition of this substance is approximately constant. In the following table the proportion $x : y : z$ in the general formula x Bi_2O_3, y N_2O_5, z H_2O, has been calculated for each sample—the y value being taken as the unit of reference—using the figures expressing percentages of N_2O_5, which were determined by use of the nitrometer.

TABLE IV.

	D		A		B		C		E	F	G
	1	2	1	2	1	2	1	2			
x -	1·19	1·19	1·21	1·21	1·20	1·18	1·17	1·20	1·19	1·20	1·19
y -	1·00	1·00	1·00	1·00	1·00	1·00	1·00	1·00	1·00	1·00	1·00
z -	2·26	1·77	1·63	1·55	1·66	1·72	1·71	1·74	1·69	1·74	1·64

The chief point to be noted is that practically in every case the ratio $x : y = 6 : 5$, which is in agreement with the formula $Bi_{12}O_{13}Cl_{10}$ for the oxychloride produced by the action of sodium chloride on the subnitrate. The z value for " D 1 " is considerably in excess of the mean of the corresponding values for the other samples, so that this must be considered an exceptional sample from a commercial standpoint. Working out the average proportion for the remaining ten, I find that $x : y : z = 1\cdot19 : 1\cdot00 : 1\cdot69$; so that $6Bi_2O_3$, $5N_2O_5$, $8\frac{1}{2}H_2O$, corresponding to the composition $80\cdot1$ per cent. Bi_2O_3, $15\cdot5$ per cent. N_2O_5, $4\cdot4$ per cent. H_2O, represents the simplest constitutional formula for commercial bismuth subnitrate.

In conclusion, I desire to thank Messrs. Howards and Sons, Ltd., in whose laboratory this investigation was carried out, for permission to publish the results contained in this paper.

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