BISMUTH—A COMPARISON OF THE METHODS FOR ITS ESTIMATION.

By THOS. B. STILLMAN, M. Sc.

BISMUTH has of late years assumed considerable importance in the arts, and the technical chemist is frequently called upon to examine alloys, medicinal and pharmaceutical preparations, toilet articles, paints, pigments, etc., containing it as an essential constituent or as an adulteration. With a view to determine the relative accuracy of the different methods for its estimation, as well as the chances of error as applied to commercial work, I have recently made a critical comparison of the same, and present a brief below.

The methods, as suggested by Fresenius, are as follows:

- a, as oxide, by precipitation as carbonate.
- b, as oxide, by ignition.
- c, as oxide, by evaporation.
- d, as sulphide.
- e, as arsenate.
- f, as chromate.
- g, as metallic bismuth.
- h, as iodate of bismuth (volumetric).

In each of the following determinations 50 c.c. of a solution of 25 grammes of bismuth nitrate in 2 liters of water were used, and, to insure greater accuracy, were weighed:

a. Determination as Oxide, by precipitation as carbonate: The solutions of bismuth were mixed with carbonate of ammonia in slight excess, warmed sometime nearly to boiling, filtered, dried, and ignited in porcelain crucibles, the process of ignition converting the carbonate into the oxide.

I. 51.4432 grammes of solution gave 0.3032 gramme $\text{Bi}_2\text{O}_3 = 0.5283$ per cent. Bi.

II. 51.3459 grammes of solution gave 0.2708 gramme $\text{Bi}_2\text{O}_3 = 0.5275$ per cent. Bi.

III. 51.6004 grammes of solution gave 0.3040 gramme $\text{Bi}_2\text{O}_3 = 0.5282$ per cent. Bi.

Average per cent. Bi = 0.5280.

b. By Ignition:

Three samples were evaporated and then ignited in porcelain crucibles until the weights remained constant, with the following results:

I. 51.2672 grms. solution gave 0.3014 gm. $\text{Bi}_2\text{O}_3 = 0.5273$ per cent. Bismuth.

II. 51.3568 grms. solution gave 0.3019 gm. $\text{Bi}_2\text{O}_3 = 0.5270$ per cent. Bismuth.

III. 51.0667 grms. solution gave 0.3000 gm. $\text{Bi}_2\text{O}_3 = 0.5267$ per cent. Bismuth.

Average = 0.5270 per cent. Bismuth.

c. By Evaporation.—Method given by J. Löwe (*Journ. f. Prakt. Chemie*, lxxiv., 344):

The solution of the nitrate was evaporated in a porcelain capsule on the water-bath till the neutral salt remained in a syrupy solution; added water, loosened the white crust that formed with a glass rod from the sides, evaporated again on the water-bath, and repeated the whole operation four times.

After the dry mass on the water-bath had ceased to smell of nitric acid it was allowed to cool thoroughly, and then treated with cold water containing a little nitrate of ammonia (1 in 500); after the residue and fluid had been a short time together, filtered, washed with weak solution of nitrate of ammonia, dried, ignited, and weighed as oxide.

I. 50.9808 grms. sol. gave 0.2995 gm. $\text{Bi}_2\text{O}_3 = 0.5266$ per cent. Bi.

II. 51.1758 grms. sol. gave 0.3011 gm. $\text{Bi}_2\text{O}_3 = 0.5275$ per cent. Bi.

III. 51.0738 grms. sol. gave 0.3004 gm. $\text{Bi}_2\text{O}_3 = 0.5272$ per cent. Bi.

Average = 0.5271 per cent. Bi.

d. Determination as Sulphide:

The solution was diluted with water, slightly acidified with acetic acid (to prevent the precipitation of a basic salt), and the bismuth precipitated with hydrogen sulphide.

The precipitate was collected upon a weighed filter, dried at 100° C., and weighed. The weighing required caution, as at first the precipitate loses weight by the evaporation of water; then it gains weight from the absorption of oxygen. Hence the weighings were made every half hour and the lowest weight taken as the correct one.

I. 51.4666 grms. sol. gave 0.3341 gm. $\text{Bi}_2\text{S}_3 = 0.5271$ per cent. Bi.

II. 51.7088 grms. sol. gave 0.3350 gm. $\text{Bi}_2\text{S}_3 = 0.5260$ per cent. Bi.

III. 51.9848 grms. sol. gave 0.3371 gm. $\text{Bi}_2\text{S}_3 = 0.5266$ per cent. Bi.

Average = 0.5265 per cent. Bi.

e. Determination as Arsenate:

H. Salkowski (*Zeitsch. f. Analytische Chemie*, viii., 205) recommends, since arsenate of bismuth is insoluble in nitric acid, that bismuth be thus estimated. Arsenic acid was added in slight excess, with constant stirring, so that the crystalline precipitate formed would not attach itself to the sides of the beaker; allowed to stand for one hour without warming, filtered upon a weighed filter, washed with water until the filtrate showed signs of turbidity, dried at 120° C. and weighed.

I. 51.5350 grms. sol. gave 0.4627 gm. bismuth arsenate = 0.5289 per cent. Bi.

II. 51.6382 grms. sol. gave 0.4668 gm. bismuth arsenate = 0.5273 per cent. Bi.

III. 51.4218 grms. sol. gave 0.4636 gm. bismuth arsenate = 0.5266 per cent. Bi.

Average = 0.5276 per cent. Bi.

f. Determination as Chromate (*Journ. f. Prakt. Chem.*, lxxvii., 464):

The solution of bismuth was poured into a warm solution of bichromate of potassa in a porcelain capsule, stirred, taking care to leave the alkaline chromate slightly in excess. The precipitate was orange yellow and dense throughout; boiled the contents of the dish for ten minutes, with stirring; then washed the precipitate, first by repeated boiling with water, and decantation on a weighed filter, at last thoroughly on the filter with boiling water; dried at 120° C., and weighed.

I. 51.3451 grms. sol. gave 0.4307 gm. bismuth chromate = 0.5247 per cent. Bi.

II. 51.3400 grms. sol. gave 0.4312 gm. bismuth chromate = 0.5261 per cent. Bi.

Average per cent. Bi = 0.5254.

g. Determination as Metallic Bismuth.—Method of H. Rose (*Pogg. Annal.*, xc., 104, cx., 136):

The excess of nitric acid was nearly neutralized with ammonia chloride of sodium added and then a rather large quantity of water. After allowing to stand for some time,

tested whether a portion of the clear supernatant fluid was rendered turbid by a further addition of water; after filtering, washed completely with cold water and dried.

The precipitate was carefully removed from the filter, the filter incinerated in a porcelain crucible, allowed to cool, the precipitate added thereto and reduced to metallic bismuth by fusion with cyanide of potassium.

In this fusion it sometimes happens that the crucible is attacked, and particles of porcelain are found mixed with the metallic bismuth. This was prevented from injuring the analysis by weighing the crucible together with a small filter before the experiment, collecting the metal on the filter, drying and weighing the crucible again with the filter and bismuth.

I. 51.6808 grms. sol. gave 0.2682 gm. Bi = 0.5189 per cent. Bi.

II. 51.4238 grms. sol. gave 0.2669 gm. Bi = 0.5188 per cent. Bi.

III. 51.3038 grms. sol. gave 0.2630 gm. Bi = 0.5130 per cent. Bi.

Average per cent. Bi = 0.5169.

h. Volumetric Determination of Bismuth (Buisson & Ferray, *Moniteur Scientifique* [third series], iii., 90):

This method is based upon the insolubility of iodate of bismuth in acetic acid. Briefly stated, the process is as follows:

0.500 gramme nitrate of bismuth is dissolved in a small quantity of water containing free nitric acid; bicarbonate of soda is added, in powder, until a permanent precipitate is formed. This is dissolved by the addition of acetic acid. The clear solution is transferred to a $\frac{1}{4}$ liter flask, 25 cubic centimeters iodic acid solution added, and water up to 250 c.c. After shaking well it is filtered through a dry filter into a dry flask; 100 c.c. of the filtrate are taken, potassic iodide and sulphuric acid added, and titrated with hyposulphite of soda solution. The excess of iodic acid used is thus found for 250 c.c. This excess, subtracted from the 25 c.c., gives the amount combined with the bismuth. The standard solution of iodic acid was formed by dissolving 30 grammes of the crystallized salt in a liter of water. The hyposulphite solution was such that 93.05 c.c. corresponded to 25 c.c. of the iodic acid solution. The solutions were standardized by means of two samples of C. P. Bismuth, each sample weighing 0.250 gramme.

I. 0.250 grammes bismuth treated as above directed; 25 c.c. of iodic acid used. 100 c.c. filtrate from iodate of bismuth required 13.17 c.c. of the hyposulphite solution; 250 c.c., or entire filtrate, required 32.95 c.c. hyposulphite solution. From this we find 60.10 c.c. of the hyposulphite solution corresponds to 0.250 gramme bismuth.

II. In the same manner 0.250 gramme Bi required 60.09 c.c. of the hyposulphite solution.

Three samples of the original solution of bismuth nitrate were treated in the same manner, with the following results:

I. Gave 0.5290 per cent. of bismuth.

II. Gave 0.5267 per cent. of bismuth.

III. Gave 0.5265 per cent. of bismuth.

Average, 0.5274 per cent. of bismuth.

It is recommended in this process not to use starch solution to indicate the end of the titration, as the solution becomes instantly colorless when the reaction is finished.

I found, however, that at times the solution would not become entirely colorless; that a strong yellow tint remained, upon which excess of hyposulphite solution had not the slightest effect. Starch solution was added, therefore, and, when the blue color disappeared, showed the end of the reaction, even if a yellow color remained.

Résumé:

a. 0.5280 per cent. Bi.

b. 0.5270 per cent. Bi.

c. 0.5271 per cent. Bi.

d. 0.5265 per cent. Bi.

e. 0.5276 per cent. Bi.

f. 0.5254 per cent. Bi.

g. 0.5169 per cent. Bi.

h. 0.5274 per cent. Bi.

It will be seen by a comparison of the above that the different methods give nearly identical results, with the exception of g (determination as metal), which gives a much lower percentage than any of the others. This is partially, if not entirely, due to the fact that the filter upon which the chloride of bismuth was dried, previous to its reduction with cyanide of potassium, burned with the bismuth flame. Although carefully executed, all the chloride of bismuth could not be removed from the filter before its incineration. Chloride of bismuth being volatile at a low heat, the loss by this method is thus explained.

THE MICROSCOPE IN CHEMISTRY.

By H. C. SORBY, F.R.S.*

Lines and circles have long been looked at through doubly refracting media, such as Iceland spar, but until lately no one seems to have systematically studied the appearances which present themselves when appropriate objects are observed with a microscope through various crystalline substances. These appearances are quite different, because the object-glass of the microscope collects the diverging rays, and we have new conditions. Dr. Royston Pigott described, in 1876, his refractometer. The principle made use of in this instrument was the increase of the focal length of the object-glass of a microscope caused by looking through media of different refracting power. Dr. Royston Pigott measured this displacement by means of a micrometer screw fixed under the stage in such a manner that it became unsuitable for its ordinary use. The author has succeeded in contriving an arrangement which, while it gives sufficient accuracy of measurement, allows the microscope to be used for general purposes. Practically, the application of this method is very simple. If an object be placed on the stage of a microscope and the fans adjusted accurately, on placing over the object a plate of some highly refracting substance the object will be invisible, and to bring it into focus the body of the microscope must be moved further out. If this distance be "d," and the thickness of the plate be T, Royston Pigott has shown that

$$u, \text{ the index of refraction,} = \frac{T}{T-d}$$

Now, this distance can be measured either by means of a scale and vernier attached to the body of the microscope, or by having the head of the screw which works the fine adjustment graduated. To take an example: Suppose we wish to determine the refractive index of water. A small piece cut

from a barometer tube is cemented to a glass slide, and the cell thus formed filled with water; the cell is then covered with a cover-glass (which must be larger than the tube, and the surface of the cover-glass must be parallel with that of the glass slide). Suppose the thickness of water, or

$$T, = 0.2360 \text{ in.}, \text{ while } d = 0.0790 \text{ in.}; \text{ then } u = \frac{0.2360}{0.2360 - 0.0790} = 1.335;$$

a second determination gave 1.334.

In order to determine "T" and "d" we proceed as follows: First, to get T, we focus to the upper surface (any dust or scratches will do for focusing) of the glass slide, and read off the position of the body of the microscope, then focus to the under surface of the cover-glass and read off; the difference between these two readings evidently gives us the thickness of the stratum of liquid, i.e., T. Secondly, to obtain "d," the image of a grating or circle is formed under the cell by means of a condenser under the stage, and the microscope focused to it; the cover-glass cell and slide are now placed on the stage so that the observer looks through the cover-glass and slide but not through the cell; the image is again focused; the difference between this reading and the first gives the displacement due to the slide and cover-glass. The cell is now pushed over the image and the latter focused; the difference between this reading and the second gives the displacement due to the stratum of liquid, i.e., "d."

A $\frac{3}{4}$ -inch objective and No. 2 eye-piece are usually employed to obtain accurate measurements. Many precautions are necessary, but, with care, "T" and "d" can be determined to $\frac{1}{1000}$ th of an inch. Red light is employed. For small quantities of liquid the ordinary live box is not convenient. The author has determined the refractive index of water with a film $\frac{1}{1000}$ th of an inch in thickness, and obtained the number 1.338. In a similar way the refractive indices of solids can be determined, the only conditions being that suitable slices be cut, which are transparent more or less, and whose surfaces are flat and parallel. If we look at the image of a grating, i.e., two systems of lines at right angles to each other, through a plate with flat parallel surfaces of glass, or any transparent mineral which has no double refraction, both systems of lines are seen at once. The image thus formed is said to be unifocal, and the index of refraction thus determined is that of an ordinary ray. If, however, the mineral possesses double refraction, the phenomena presented may be totally different; the ordinary ray has the same properties, and is strictly unifocal; but the characters of the extraordinary ray differ according as the section is cut, perpendicular, oblique, or parallel to the principal axis. Let us take calcite as an example: If we examine the image of the grating through a section parallel to the axis when the extraordinary ray is alone transmitted, the ordinary ray being cut off by a Nicol's prism, it will be found that there are two points separated from one another by an interval somewhat more than $\frac{1}{2}$ of the thickness of the section, at each of which only one system of lines can be seen at once, i.e., at one focus only the lines, say, from right to left are visible, at the other only those from top to bottom can be distinguished. The image is thus truly bifocal. If we examine a circular hole, furnished by an iris diaphragm, through a unifocal and a bifocal crystal respectively, in the first case the image is seen undistorted and well defined at one focus, whereas in the bifocal image there is no focal point at which the hole can be seen of its true size and shape; it is either drawn out into a long vertical band with curved ends, or a horizontal band, or forms a large circle without any definition. Crystals like aragonite, which have two optic axes, have no ordinary ray and no permanently unifocal images, but two bifocal images. With such a crystal a circular hole is drawn out into crosses. The lecturer then showed in what direction such crystals must be cut in order to obtain their true indices of refraction. The forms taken by gratings and circles were illustrated by models, and by means of the latter it was demonstrated how it was possible to tell at a glance in what direction a mineral had been cut in order to furnish the section under observation. The lecturer then proceeded to explain the application of this method of observation to rock section, and showed how valuable and simple the process was for identifying minerals. Even with sections $\frac{1}{1000}$ th inch in thickness and $\frac{1}{1000}$ th diameter, good results have been obtained. The sections must be flat and have parallel sides; they can be examined loose or mounted in Canada balsam, the method of observation being very similar to that described above, in the case of liquids. * Thus, in the meteoric irons of Krasnojarsk and Rittersgrün, a clear mineral was proved to be Olwine, and the three indices were found to be:

Krasnojarsk.....	1.71	1.68	1.63
Rittersgrün.....	1.70	1.68	1.66
Olwine.....	1.70	1.68	1.66

In some cases it is better to compare the index of refraction of the unknown mineral with that of a known mineral, e.g., quartz, which is lying close to it. With very black hornblendes good results can be obtained by using very thin sections, although the mineral is, in moderately thin sections, quite opaque. As an instance of the marvellously delicate nature of the method, the lecturer gave the examination of a section of a dolerite from near Glasgow, $\frac{1}{1000}$ th of an inch thick. In this extremely thin section a zeolite, probably analcime, labradorite, calcite and augite were identified with almost absolute certainty. In a similar way, in sections of shells of *Pinna*, $\frac{1}{1000}$ th of an inch thick, calcite was recognized, while in a section of the shell of *Nalotia tuberculata*, aragonite was identified. In conclusion, the lecturer referred to the connection between the indices of refraction and chemical composition. The subject is beset with difficulties principally from defective data, but some points come out clearly. The fluorides have low indices of refraction, all the zeolites have indices less than that of quartz. All the earthy carbonates, sulphates and birates have indices between those of quartz and corundum. All minerals with an index greater than that of corundum are metallic or metalloidal sulphur, and sulphides have indices above 2.000 and the arsenides above 2.500. A mineral containing calcium instead of the alkalies has a higher index, e.g., adularia, 1.52; labradorite, 1.61. Again, a mineral containing iron has a higher index than one in which calcium is substituted for that metal. Thus, in the lime garnet, $n = 1.74$; in the precious garnet, $n = 1.79$. The lecturer finished by stating that much information might be obtained in a very short time by a qualitative examination of a mineral, e.g., whether it was unifocal or bifocal, etc.

SOLUBILITY OF MAGNESIA, BARYTA, AND SULPHATE OF LIME IN SOLUTION OF SUGAR.—H. PELLET.—Magnesia is not quite insoluble in saccharine liquids; baryta is more soluble than in water. At ordinary pressure the solubility of calcium sulphate in water is little affected by the pressure of sugar.

* LECTURE delivered to the Chemical Society, April 4th, 1878.