

# **Universitäts- und Landesbibliothek Tirol**

## **A handbook of chemical manipulation**

**Williams, Charles Greville**

**London, 1857**

Section XXI. On Volumetric Manipulation

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## SECTION XXI.

## ON VOLUMETRIC MANIPULATION.

420. By volumetric analysis is understood the use of measured bulks of test-liquids containing known quantities by weight of certain substances, capable of producing with a solution of the assay sufficiently marked effects to show with precision the complete conversion of the substance sought to be estimated, into a compound the nature of which is perfectly known. The quantity of the matter sought is ascertained by observing the number of measures of test-liquid used. This method of research has become of almost universal application for the estimation of certain substances, the names of which are given below, and several others which are not necessary to be specified, as they are more usually determined in other ways.

421. The objection has been raised to all methods of volumetric analysis, that it is impossible to measure with accuracy; and this has been sought to be proved by the difficulty of so filling a measure with any liquid twice that it shall each time weigh exactly the same. But it is unnecessary, in reply to this, to do more than say, that the solutions are used in so dilute a state, that not only does any error of admeasurement become too small to have any influence whatever upon the results, but that accurate estimations may by this means be effected on quantities so small as to render it impossible to make use of the balance. This might, if necessary, be instanced by numerous cases; but it will be sufficient to allude to the paper of Bunsen "On a method of volumetric analysis of very general applicability\*," to show the really wonderful accuracy of which the method is susceptible.

422. There are one or two advantages of a general kind to be gained from the use of *measured*, which do not apply to *weighed*,

\* Liebig's Annalen, lxxxvi. p. 265.

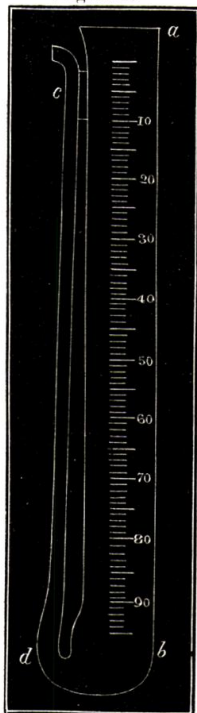
quantities. In the first place, the results are invariably obtained with far greater rapidity, all the operations of quantitative analysis which cause delay, as, for example, the washing, drying, and weighing of precipitates, being dispensed with. There is also another advantage which is peculiarly a feature in volumetrical estimations, namely, that when two experiments are made, the second is, if the solutions are properly prepared, almost absolutely correct. This feature will be more particularly dwelt upon further on.

423. The instruments most commonly used for the purpose are the burettes, figs. 211, 212, 214 and 215, test-mixers, and calibrated pipettes.

Guy Lussac's burette, fig. 211, is tolerably convenient, from the facility with which minute additions of liquid can be made, by gently inclining the instrument, the end, *a*, being closed during the process by the pressure of the thumb, which is relaxed when necessary, to allow of the atmospheric pressure upon the liquid in the tube, *a b*, so as to permit its exit by the aperture, *c*. The chief objection to this instrument is its fragility, the tube, *c d*, being extremely liable to be broken off by the slightest carelessness. If, however, a small piece of cork is inserted between the two tubes at *c*, and a string is bound round them both, the danger of breakage is so far lessened that in careful hands a burette of this kind will last in every-day use for years.

424. *Mohr's alkalimeter*.—This form of burette consists of a graduated tube open at both ends, *a b*, fig. 212, and fitted with a compression stopcock made of vulcanized india-rubber. It is fixed upon a vertical support,

Fig. 211.



and when it is intended that the liquid shall flow, pressure is applied to the two knobs, *c d*, which causes them to open. The

clasp is represented on a larger scale, and slightly open, in fig. 213. The instrument is sometimes made with a stopcock of glass, as in fig. 214; this, however, adds greatly to the expense, without increasing its efficiency.

An apparatus of this kind, but ungraduated, is, however, in some researches invaluable as a separator, where very volatile and rare fluids are to be removed from water, acid, or alkaline solutions, &c.

425. Binks' alkalimeter, fig. 215, is the most convenient of all the forms of burette; its construction is simpler than either of the others, and it is far less liable to injury. Strange to say, Dr. Mohr, of Coblenz, entirely misunderstanding its mode of use, describes it as incapable of being used without danger of spilling its contents. If made to hold 50 cubic centimetres, and of a length of 2 feet, very open divisions will be obtained, which will enable the operator to obtain extremely accurate results with considerable rapidity. It is generally the custom to

graduate these instruments in such a manner that it becomes necessary to hold it in the right hand during the operation of adding the test-liquid; it is much better, however, to reverse this, as a little practice will enable the operator to use the left

Fig. 213.

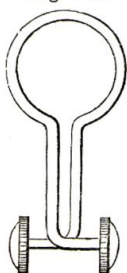
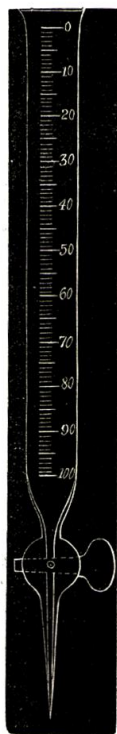


Fig. 212.

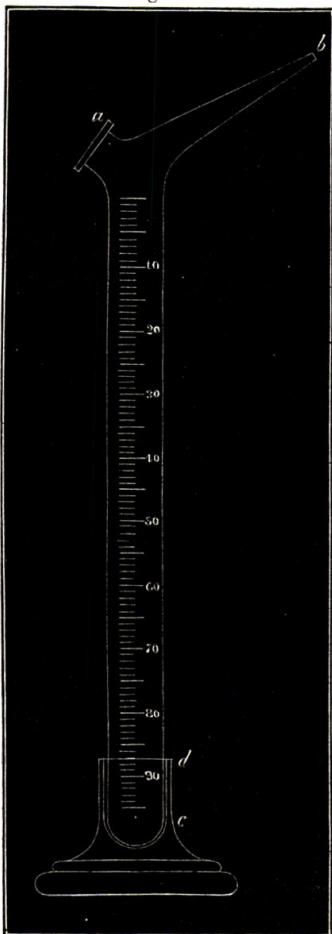


Fig. 214.



hand with equal facility, and then the right is at liberty, so that it may be used to stir the liquid, direct the course of the test-liquid with the glass rod, apply test-papers, regulate the gas-flame when heat is required, &c. If Binks' alkalimeter, full of test-liquid, is held in the left hand, in such a manner that the thumb closes the aperture, *a*, while *b* becomes the lowest part of the tube, the end, *a*, being elevated at an angle of  $20^{\circ}$  or  $30^{\circ}$ , no fluid will escape, but upon relaxing the pressure of the thumb, and allowing air to enter, it will rise in a succession of bubbles through the liquid, which latter escapes by the orifice; in this manner the rapidity of the flow may be regulated with the utmost nicety. When the effect sought has been obtained, and it becomes evident that the test-fluid has been added in sufficient quantity, the burette is placed in a vertical position in the stand, *d*, and allowed to remain until all the fluid has drained from the sides, and the liquid in the burette ceases to rise from this cause. After the operation has been concluded, it is invariably found that a small quantity of liquid remains in the spout, *b*, being retained by capillary attraction; it is necessary to make this unite with the rest of the fluid, by applying a mo-

Fig. 215.





mentary suction with the lips to *a*, before putting the instrument aside to drain.

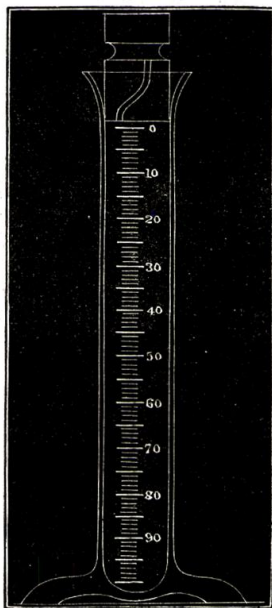
426. It is a matter of indifference what part of the curve formed by the water in the tube is employed as the line to read off from, if the same portion is taken invariably in the preparation of the standard liquid, and when using it. It is most common, however, to read from the lowest part of the curve.

427. Many contrivances have been adopted to render the readings extremely accurate, and lessen the errors of observation; and even tables have been constructed to correct for the influence of variations of temperature in altering the volume of the liquid; but it is better, as a general rule, to use tubes of small calibre and very dilute solutions, so as to reduce the error of observation to a point so far below the unavoidable errors of experiment as to be inappreciable; and it is more easy to do this than is generally supposed. Further on, experiments will be detailed to show the amount of accuracy attainable in several kinds of testing.

428. The alkalimeter on a foot, fig. 216, is, when made narrower than those usually sold, a convenient instrument for delivering test-liquids; the rapidity of flow is determined by the position of the grooves in the stopper; its use requires no particular precautions.

The volumetric method of estimation has been applied to the determination of the per-centage values of a great number of substances; it will be unnecessary, however, to describe them all, the manipulation with a few being

Fig. 216.



understood, will render it easy to acquire facility with the others described in works on analysis.

429. *Volumetric determination of acids.*—The volumetric method, as applied to acids, almost invariably depends upon the amount of an alkali required to neutralize them, and, with a little care, most persons will be able to estimate their strength with a degree of accuracy leaving nothing to be desired. It is usual to employ a different alkali in the case of hydrochloric and acetic acids to that used with the sulphuric, because with the former it becomes impossible to heat the solution to drive off the carbonic acid, the presence of which interferes with the reaction. But as it is inconvenient to have several alkaline test-liquids in the laboratory, I have been in the habit of using the same for all, it being equally applicable to the determination of fixed and volatile acids. The liquid alluded to is the solution of lime in sugar-water, recommended by Peligot in his modification of the nitrogen process of Will and Varrentrap, described in a subsequent part of this volume.

Lime is well adapted for the neutralization of acids, the only impediment to the use of lime-water being the small percentage of earthy base. But if, instead of using pure water, a tolerably strong syrup is substituted, the portion dissolved becomes much greater; and the fluid is extremely convenient for the estimation of the strength of acids, from the fact, that, being free from carbonic acid, it is unnecessary to employ heat. This will be adverted to at greater length under the head of Alkalimetry.

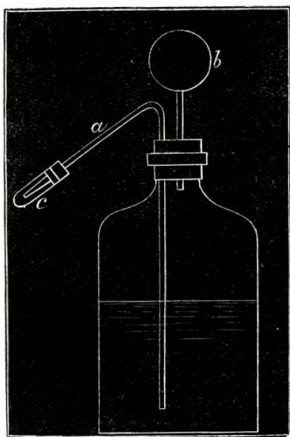
The solution of lime in syrup, if very concentrated, has a yellowish colour, but the equivalent of lime being low, it will bear considerable dilution. A solution of caustic soda is also a very convenient standard alkali. As the solution is intended to be used for all the acids, it becomes a question which to select to prepare it from, and no hesitation need be had in adopting sulphuric acid for the purpose. As it is necessary in every laboratory to have a standard sulphuric acid, it being required not only for estimating the value of the carbonates of potash and soda, but also for nitrogen determinations, it will be selected as the starting-

point for the other acidimetical and alkalimetical solutions. The preparation of this acid will be found described at p. 269.

The strength I am in the habit of employing is such that 50 cubic centimetres, equalling 100 divisions of the burette, are exactly equal to 20 grains of carbonate of potash; each division, therefore, is equivalent to  $\cdot 2$  grain of carbonate of potash, and as the instrument has very open divisions, it is perfectly easy to read off to half a division, equal in value to  $\cdot 1$  grain. If preferred, any other strength may be employed. As all caustic alkalies in solution are altered in value by keeping with a rapidity proportional to the amount of exposure, no good can result from making a very large quantity of the lime-syrup or caustic soda up to any exact standard, as it is necessary every few weeks to determine its saturating power. This does not deteriorate the value of the method, because the process of ascertaining the strength of the alkaline solution does not occupy five minutes.

430. The apparatus depicted in fig. 217 is admirably adapted for keeping the solutions of caustic soda and lime-syrup, and enabling the burettes to be filled with little exposure of them to the air. It is, I believe, the contrivance of Dr. Price. A glass bottle is fitted with a sound cork, through which pass two tubes, *a* and *b*. One of these reaches to the bottom of the fluid, and, when not in use, is closed by a small tube and cork, *c*. The other fits into a hole in one of the hollow vulcanized india-rubber balls used as a toy.

Fig. 217.



On applying pressure to the ball, the solution rushes up the tube *a*, and is forced into the burette or other vessel used to receive it. On removing the hand, the ball resumes its original shape, and a volume of air equal to the fluid expelled enters by *a*. The fact



that the volume of air entering is never greater than that of the liquid ejected, is one of the great merits of the instrument, because the quantity of carbonic acid in such a small bulk is so inconsiderable, that the solutions keep a long time unaltered.

If we find the number of divisions of lime-syrup required to neutralize the burette full of standard acid, we have the data for ascertaining the quantity of all other acids which the burette full of syrup is equivalent to. Suppose, for example, that the 100 divisions of the burette of lime-syrup or soda are just sufficient to neutralize 100 divisions of the sulphuric acid, it is evident, that as the 100 divisions of sulphuric acid are equivalent to 20 grains of carbonate of potash, that the 100 divisions of lime-syrup are also equal in saturating power to 20 grains of carbonate of potash; and to ascertain how much of each of the acids the 100 divisions of lime-syrup are capable of neutralizing, it is only necessary to calculate how much of each acid is equivalent to 20 grains of carbonate of potash.

The following equations give the values sought:—

$$\begin{array}{ccccccc}
 \text{KOCO}^2 & & \text{SO}^3 & & \text{KOCO}^2 & & \text{SO}^3 \\
 69 & : & 40 & :: & 20 & : & 11\cdot594 \\
 \\ 
 \text{KOCO}^2 & & \text{NO}^5 & & \text{KOCO}^2 & & \text{NO}^5 \\
 69 & : & 54 & :: & 20 & : & 15\cdot652 \\
 \\ 
 \text{KOCO}^2 & & \bar{\text{A}} & & \text{KOCO}^2 & & \bar{\text{A}} \\
 69 & : & 51 & :: & 20 & : & 14\cdot782
 \end{array}$$

The 100 divisions of lime-syrup are equal, therefore, to 11·594 dry sulphuric, 15·652 dry nitric, and 14·782 dry acetic acids. The quantities of the other acids may be calculated in the same manner, by substituting their equivalents for the second term in an equation like those given above.

431. To perform the analysis, 50 grains of the acid are weighed in a small capsule or flask, the quantity being adjusted by means of a pipette; the contents of the capsule are then washed out into a small basin; a little tincture of litmus, sufficient to give a brilliant scarlet to the fluid, is added, and the lime-syrup is slowly poured in until the colour begins to change; when this takes

place, the addition is made more slowly still, the fluid being kept constantly stirred. A point is at last reached when one drop more syrup is capable of turning the liquid from red to blue; the operation is then finished, and the small quantity of liquid remaining in the beak of the alkalimeter is made to join the rest by suction applied at *a*, fig. 215, and when the fluid has all run down, the volume remaining is read off.

432. It is proper in all cases where great accuracy is desired, to repeat the operation, care being taken to add the test-liquid very slowly when the point attained in the first experiment is nearly reached.

In order to calculate the result, it is merely necessary to consider that, as 100 divisions of the burette are equal to a certain amount of dry acid (which amount has been found by an equation similar to those on the previous page), so the number of divisions used in the experiment indicate the number of grains of dry acid in the specimen. Therefore, calling the amount of dry acid equal to the 100 divisions of the burette, *a*, and the number of divisions used, *b*, we have

$$\frac{a \times b}{100} = x.$$

*x* = the number of grains of dry acid in the quantity analysed, from which the per-centage can immediately be deduced.

433. *Volumetric determination of alkalies.*—There are many ways of ascertaining the quantity of caustic and carbonated alkalies in any given specimen, and the methods of manipulation will be found in their proper places in this volume. The mode of determining the quantity of alkali in carbonates by the weight of carbonic acid evolved on heating the sample with an acid, will be described in the section on Gas Manipulation.

434. The volumetric process, while susceptible of equal, if not greater precision than that last mentioned, is less troublesome, and occupies not half the time. It is, however, necessary in the first place to prepare a test-acid, and as this latter is also the standard from which the lime-syrup previously alluded to is made, great care should be taken that it is of exactly the proper strength.

To prepare it, concentrated sulphuric acid is diluted, say with twenty times its bulk of water; 20 grains of pure anhydrous carbonate of potash\* are then weighed out, dissolved in water in a porcelain basin, and some tincture of litmus added; the whole is then supported over a lamp and heated nearly to ebullition: a burette being filled to 0° with the acid, the latter is to be slowly added until the colour of the litmus changes to a red; if the operation has been carefully performed, it will be found that this red is only due to the liberated carbonic acid acting on the litmus, and if the solution is briskly boiled for a very short time, the blue colour which the litmus had before the addition of the acid will return; by thus adding the acid carefully, and boiling the solution, a point is at last reached when the smallest further addition of the acid will convert the solution from a distinct blue to a brilliant scarlet, which indicates the conclusion of the process. A little practice will enable any person to perform this with success. The operation is to be repeated, the test-acid being added with very great care as the point first obtained is approached; the second result is to be taken as the true one. The number of divisions used, of course indicates the quantity of the diluted acid equivalent to the 20 grains of carbonate of potash; and to make the standard acid from this, it is merely necessary to dilute the solution until the quantity thus obtained is made up to 100 parts. Thus, supposing 60 divisions of the burette to have been required, it is evident that to obtain the standard fluid, 60 volumes of the diluted acid are to have 40 volumes of water added. For this last operation any tall cylindrical jar will answer, if it is accurately graduated into 100 parts. It is better, after this has been done, to again make an experiment on 20, or any other number of grains of carbonate of potash, to ascertain whether the dilutions have been accurately made. If the liquid is still a little too strong, it may be again diluted on the same principle, but if too weak, more sulphuric acid must be added, and this involves a repetition of the whole process.

\* For precautions necessary in weighing deliquescent substances, see §§ 84, 91, 278.

435. If the above operations have been skilfully performed, results almost absolutely accurate may easily be obtained with the test acid. It is essential that the carbonate of potash used in this process should be carefully examined as to its purity. It is not sufficient to merely establish the absence of sulphates, chlorides, silica, &c.: its freedom from soda must be carefully ascertained, as it has been found that specimens of carbonate of potash considered as absolutely pure, have contained sufficient soda to cause serious errors to creep into analyses made with a standard acid, the strength of which has been determined by it.

A standard acid is also used in Peligot's modification of the process of Will and Varrentrap for estimating nitrogen.

436. *Volumetric methods in general.*—The volumetric method has been applied successfully to the determination of a great number of substances besides those enumerated, including, among others, baryta, bromine, chlorine, copper, manganese, tin, uranium, silver, iron, indigo, prussic acid, urea, and chloride of sodium in urine, &c. Baryta may be determined by the standard sulphuric acid; the process is, however, not so generally applicable as the conversion of it into a known weight of sulphate of baryta and weighing. Bromine may be very exactly determined, even when in presence of hydrobromic and hydrochloric acids, by means of a standard solution of pure oil of turpentine in alcohol\*, turpentine having the property of combining with bromine into a colourless oil, when present in the proportions of 34 of the former to 80 of the latter, being in the ratio of single equivalents, supposing the formula of turpentine to be  $C^5 H^4$ †. What-

\* Chemical Gazette, vol. xii. p. 432.

† Although 34 parts of turpentine decolorize 80 parts of bromine in presence of water, it is not necessary to assume  $C^5 H^4 = 34$  as the formula and atomic weight of turpentine; in fact  $C^{20} H^{16}$  appears to be the formula of the oil; for if we multiply 136 (which is the atomic weight; supposing  $C^{20} H^{16}$  to be the formula) by .0346, we obtain 4.7056 as the vapour-density for four volumes, and 4.76 has been obtained by experiment. The fact that the atomic weight of any organic substance, if multiplied by half the density of hydrogen, gives its vapour-density for four volumes, becomes obvious on a little reflection, and has already been mentioned in the section on Vapour Densities (§ 127).



ever the real formula of turpentine may be, the fact that 34 parts of pure turpentine are capable of decolorizing 80 parts of bromine (when the reaction takes place under the conditions given in the paper alluded to), is quite sufficient for all the purposes of the quantitative estimation of free bromine.

Chlorine, as it exists in chloride of lime, is capable of being volumetrically determined in several ways, the manipulation connected with which will be found in analytical treatises. Copper is determined by a solution of sulphuret of sodium, a preliminary assay being always made upon a known weight of pure metal, the solution of the sulphuret being prepared fresh each time by dissolving the crystals in distilled water; the method is, however, but little practised.

437. Uranium may be estimated by a solution of a phosphate of known constitution, the process being based upon the insolubility of the uranic phosphate.

438. Urea is determined by the new process lately introduced by Liebig, and which is founded upon its tendency to form definite compounds with corrosive sublimate.

439. The quantitative determination of silver by a solution of chloride of sodium is susceptible of the greatest precision. A standard solution of common salt is made of such a strength that 100 divisions of the burette are equal to 10 grains of silver, each division being equivalent to 0.1 grain, and a second solution is also made ten times more diluted, so that one division is only equal to 0.01 grain. The first assay is made with the strong solution, and is repeated, the process being stopped when the point is nearly reached, and the estimation is finished with the weak solution. The solution of the silver in nitric acid is placed in a rather capacious stoppered flask, which is briskly shaken after each addition of the test-liquid. As long as silver still remains in solution, the latter is milky, even after considerable agitation; but when the operation is finished the solution becomes clear. The milkiness alluded to is a great assistance in the process, as it enables the operator to know that sufficient test-solution has not been added, and fortunately it is not opaque enough to prevent



the cloudiness caused by each addition of the normal fluid from being seen.

440. In the French Mint very elaborate precautions are taken to ensure perfect accuracy in the measurements, tables of correction for the influence of temperature upon the bulk of the solution being used; such modifications are, however, merely useful where a great number of operations have to be performed daily, and are never adopted in scientific research, the silver in the latter case being almost invariably weighed as chloride.

441. *Test-papers, &c.*—There are several substances used in qualitative and quantitative experiments to determine the presence of excess of alkalies or acids, by the changes of colour produced in them. The most common of these, and perhaps the most generally useful, is litmus, which appears to be prepared from two or three species of lichen by a process which is by no means thoroughly known. As it appears in commerce, it consists of small square pieces about  $\frac{1}{4}$  of an inch long by  $\frac{1}{8}$  broad; these fragments, besides litmus, contain a great many substances, among which may be found ferric oxide, alumina, sulphate of lime, silica, and some others. Upon digesting this mixture with distilled water at a gentle heat, a blue solution is obtained of considerable intensity; this solution must have about a quarter of its bulk of alcohol added to it to prevent decomposition, which would otherwise take place on keeping. If pieces of white filtering-paper are saturated with the fluid thus prepared, and hung upon clean strings in a place free from dust and vapours, what are termed litmus-papers will be obtained; they should be cut into strips about  $\frac{1}{2}$  an inch broad and 3 or 4 inches long, which may be kept in small test-tubes, corked, for almost any length of time without injury. These papers are so valuable, and of such constant use in the laboratory, that no trouble should be spared to obtain them of the best quality. If the litmus, as sometimes happens, contains an excess of alkali, it is less sensitive as a test for acids, a portion of that present being expended in its neutralization before the remainder can act upon the colouring matter. This difficulty may be got over by adding a very dilute acid to the solution before

dipping in the paper, and when the fluid has begun to show the acid reaction, bringing the blue colour back with a little carbonate of potash.

*Litmus-papers* are preferred by some to the tincture in alkali-metrical experiments; the solution to be tested is applied to the paper with a glass rod, and if a red coloration is observed, the paper is gently warmed until dry, in order that if the reddening is caused by carbonic acid the latter may be dissipated by the heat, and the blue colour restored. When litmus-paper is intended to be used as a test for alkalies, it should be previously reddened by holding it in a moderately damp state over the vapour of acetic acid until of a distinct red, but not longer; the blue is readily restored by even very diluted alkaline fluids or the vapour of ammonia. The neutral-tint paper, sometimes prepared as a test for both acids and alkalies, is an unnecessary addition to the collection of test-papers.

442. *Turmeric-paper* is best prepared by macerating ground turmeric root with moderately strong spirits of wine, filtering off the bright liquid and saturating white filtering-paper with it; in consequence of the volatility of the spirit, the papers soon dry, and may then be preserved like those coloured with litmus. Turmeric-paper thus prepared, is of a brilliant yellow colour, which is turned to a reddish-brown or intense red by alkalies, according as they are more or less strong. The dilute alcohol is by far a better menstruum for the colouring matter of the turmeric than water, especially if the papers are intended for use at lectures, where it is desired to make the change of colour evident at a distance. Turmeric paper is much used to detect ammonia, but for this purpose it should be slightly moistened, in order that the volatile alkali may be absorbed and thus more effectually act upon the colouring matter.

443. *Lead-paper*, used for detecting the presence of sulphuretted hydrogen, is made by saturating filtering-paper with solution of acetate of lead, and, after drying, may be preserved in the same manner as the others. It is blackened by very minute traces of sulphur. If lead-paper be held over a bottle of sulphide of

ammonium until black, it becomes an excellent test of ozone in essential oils; for if a little turpentine, or other oil which has been exposed to the air until ozonized, is dropped upon the paper so blackened, and the latter be held over the furnace-plate or other source of heat until the turpentine begins to volatilize, the black stain disappears in the places where the ozonized oil has been, and the original appearance of the paper is restored. This change is due to the conversion of the black sulphuret into the white sulphate by the oxidizing tendency of the ozone.

444. *Logwood*.—The colouring matter of this substance is preferred by some to litmus for detecting the presence of excess of alkalis, an acid aqueous solution of the colouring matter being turned from red to blackish purple by small excess of alkali. It is especially used in neutralizing the sulphuric acid in Peligot's nitrogen process.

445. *Slips of fir-wood*, moistened with hydrochloric acid, are much used as a test in experiments on the volatile organic bases. The method of testing for pyrrol has been mentioned before, p. 236. A great number of volatile bases, when quite free from pyrrol, have the property of giving a bright yellow stain to fir and hydrochloric acid; the reaction is therefore not distinctive of any specific substance.

Carbolic acid is recognized by its property of giving a deep blue tint to slips of fir, moistened with moderately strong nitric acid; the blue colour soon passes, however, into a brown. It also gives a blue with fir-wood and hydrochloric acid.

446. Paper saturated with tincture of guaiacum assumes a blue tint when exposed to most oxidizing vapours, such as chlorine, bromine, nitric acid, ozone, &c.

#### EXPERIMENTS SHOWING THE ACCURACY OF THE METHODS GIVEN.

447. *Alkalimetry*.—A test-acid having been prepared, 100 divisions of the burette being equivalent to 20 grains of carbonate of potash, a little of the latter, which was ascertained by careful analysis to be chemically pure, was heated to redness in a platinum crucible, and on being weighed with the lid on, to

prevent moisture from being absorbed during the operation, was found to be equal to 10·8 grains. The contents of the crucible were washed into a porcelain basin, some tincture of litmus and a little more water being added, to make up about 2 ounces: the fluid was now heated nearly to ebullition, the test-acid being slowly dropped in, with constant stirring; after a time the solution became distinctly red, but on boiling for a few minutes the blue was restored; at last a point was reached when a single drop converted the boiling solution from a blue to an intense scarlet, which was not altered by prolonged ebullition. The burette was then replaced on its stand, the drop of fluid remaining by capillary attraction in the beak, sucked in so that it joined the rest of the fluid, and, after a few minutes being allowed for the sides to drain, the volume was read off, when 46 divisions still remained in the burette, and  $100 - 46 = 54$ , the number of divisions used to neutralize the 10·8 of carbonate, and

$$100 : 20 :: 54 : 10\cdot8.$$

In another experiment, 7·4 grains carbonate of potash required 37 divisions:—

$$100 : 20 :: 37 : 7\cdot4.$$

448. *Estimation of silver by standard solution of common salt.*—The burette, which was divided into 100 parts, held 50 cub. cent., and the jar for making the test-solutions held just ten times that quantity.

Now, to ascertain how much chloride of sodium is to be dissolved in 50 cub. cent. of water to make a standard solution, 100 divisions of which shall be equal to 10 grains of silver, we say—

$$\begin{array}{cccc} \text{Ag} & \text{Na Cl} & \text{Ag} & \text{Na Cl} \\ 108 : 58\cdot5 :: 10 : 5\cdot41. \end{array}$$

The latter is therefore the quantity of common salt to be added to 50 cub. cent. of water to make the standard solution, but to make ten times the quantity as a stock, 54·1 would be necessary. In order to allow for impurities in the salt, 64 grains were dissolved in the jar of water. To determine the strength of this solution two experiments were made.



I. 10 grains pure silver took 81 divisions.

II. 10       "       "       81       "

The 81 divisions were therefore made up to 100 with water.

I. 5 grains of pure silver took 51 divisions.

II. 10       "       "       100       "

III. 10       "       "       100       "

Per cent.		
I.	II.	III.
102	100	100

In the first experiment an excess of one division was added, which, although only equal to 0.10 grain when calculated to 100 parts, gave an excess of 2 per cent. The other experiments are exact, and with moderate care may be obtained equally correct every time. It must be mentioned that the experiments above quoted are taken at random from the laboratory note-book.

*Estimation of free bromine by oil of turpentine* (weighed quantities being used).—47.7 cub. cent. of bromine-water, treated with solution of turpentine in alcohol (containing 10 per cent. of the oil) until the colour of the bromine had disappeared, gave in eight experiments—

I. 4.16 of bromine.	V. 4.23 of bromine.
II. 4.16       "	VI. 4.23       "
III. 4.35       "	VII. 4.16       "
IV. 4.35       "	VIII. 4.16       "

Six estimations as bromide of silver gave—

I. 4.15	IV. 4.25
II. 4.15	V. 4.35
III. 4.26	VI. 4.14
Mean six estimations by turpentine.	Mean six estimations as bromide of silver.
4.225	4.216



Almost the same results were obtained in presence of hydrobromic and hydrochloric acids\*.

449. To show the necessity of carefully examining the carbonate of potash used for determining the strength of the test-acid, to ascertain its freedom from soda, the following analysis, made upon a specimen of carbonate of potash, sold as absolutely pure at an extravagant price, may be quoted:—

Carbonate of potash	. . . . .	91·35
„ soda	. . . . .	7·80
Loss	. . . . .	·85
		<hr/>
		100·00

A specimen of salt of tartar of commerce gave—

Carbonate of potash	. . . . .	75·7
„ soda	. . . . .	3·4
Sulphate of potash	. . . . .	3·2
Chloride of potassium	. . . . .	1·5
Water	. . . . .	15·9
		<hr/>
		99·7

450. The best method of ascertaining the existence of small quantities of soda in the presence of a great excess of a salt of potash, is to heat a fragment of the suspected mixture in the blue flame of the blowpipe, and see if the yellow flame, characteristic of soda, is obtained. A mere trace of soda may be detected in this manner, as it quite overpowers the peach-blossom flame produced by pure potash salts.

\* Chemical Gazette, vol. xii. p. 433.