This method, so far as the writer has been able to investigate it, applies to all organic combinations of sulphur, the halogens and phosphorus, but the amount taken must be limited to take only a moderate final weight of barium sulphate or silver halide, such as 0.1000 to 0.2500 gram.

RESULTS OF ANALYSES.

Sample.	Carius.	Inner cone crucible.
1. Texas crude oil	1.70	1.709
2. Texas gas oil	0.40	0.39-0.41
3. Ohio crude oil	0.99	1.03-1.05
4. Ohio gas oil	0.36	0.32-0.32
5. Kansas crude oil	0.62	0.57-0.59

The writer has made a number of analyses of organic combinations of sulphur, chlorine and bromine, but owing to the incomplete character of the results at this time, he prefers to reserve the work of investigating the use of the crucible for halogen compounds for a later publication.

The author wishes to express his indebtedness to J. Bishop & Company for kindness in making four different sets of crucibles for this work.

LABORATORY OF SAMUEL P. SADTLER AND SON,
PHILADELPHIA, PA.

A SIMPLE COLORIMETER FOR GENERAL USE, WITH REMARKS ON COLORIMETRIC METHODS AND APPARATUS.[1]

BY OSWALD SCHREINER.

Received June 22, 1905.

THE USE of colorimetric methods for the estimation of small amounts of materials has been on the increase in the past few years, not only in technical analysis but also in other lines of investigation. The applications of colorimetry to the determination of ammonia, nitric and nitrous acids, has been of long standing and these tests are familiar to every chemist. They have been used by the sanitary chemist for some time, and to these has lately been added the colorimetric determination of phosphates for detecting polluted waters. The mineralogical chemist has likewise recognized in the colorimetric tests for certain metallic elements the best, and in some cases the only, method for deter-

---

[1] Published by permission of the Secretary of Agriculture.

mining small quantities of these substances. The industrial chemist has used colorimetric methods as a ready and accurate means of valuation in the most varied industries, and the food analyst is also using them for detecting and estimating the extent of adulteration in foods and beverages, and injurious products in whiskies. The physiologist and the pharmacologist have found the application of these methods useful in the problems with which he has to deal, and the physical chemist and agricultural chemist have also applied them in the course of their studies on the solubility of glass, minerals and other difficultly soluble substances and in the study of the phenomena of adsorption.

How general the use of colorimetric methods has become in recent years, not only in their application to inorganic compounds, but also to the principal classes of organic compounds, may be illustrated by the following brief and therefore very incomplete presentation. In inorganic chemistry colorimetric methods have been worked out or suggested; for metals (such as alkalies,[1] chromium,[2] copper,[3] iron,[4] manganese,[5] magnesium,[6] potassium,[7] titanium,[8] tungsten,[9] etc.); for non-metals (such as carbon,[10] sulphur as sulphide[11] and sulphuric acid,[12] oxygen[13] as element and as hydrogen peroxide,[14] arsenic as arsenious acid,[15] phosphorus as phosphoric acid,[16] nitrogen as nitrous and nitric acids and as ammonia,[17] boron as boric acid,[18] etc.).

The use of photometric and nephelometric methods still further increases the list of metals and non-metals of which small amounts

---

[1] Mylius and Förster: *Z. anal. Chem.*, **31**, 250 (1892).

[2] See Hillebrand: "Some Principles and Methods of Rock Analysis," Bull. 176, U. S. Geol. Survey, p. 80.

[3] See Sutton's "Volumetric Analysis," and other texts.

[4] See Pulsifer: This Journal, **26**, 974 (1904).

[5] Marshall: *Chem. News*, **83**, 76 (1901); Clennell: *Eng. Min. J.*, **78**, 827 (1904). See also Blair's "The Chemical Analysis of Iron," and other texts.

[6] Schreiner and Ferris: This Journal, **26**, 961 (1904).

[7] Hill: This Journal, **25**, 991; Cameron and Failyer: *Ibid.*, **25**, 1063 (1903).

[8] See Hillebrand: *Loc. cit.*, pp. 67 and 73.

[9] Frabot: *Ann. Chim. Anal.*, **9**, 371 (1904).

[10] See Blair: "The Chemical Analysis of Iron," and other standard works.

[11] Winkler: *Z. anal. Ckem.*, **40**, 772 (1901); Lindlay: *School of Mines Quarterly*, **23**, 24 (1901).

[12] Winkler: *Z. anal. Chem.*, **40**, 465 (1901).

[13] Ramsay and Honefray: *J. Soc. Chem. Ind.*, **20**, 1071 (1901).

[14] Richardson: *J. Chem. Soc.*, **63**, 1109 (1893); Planes: *J. Pharm. Chim.* [6], **20**, 538 (1904).

[15] Peck: *Trans. Brit. Pharm. Conf.*, p. 452 (1901); Mai: *Z. anal. Chem.*, **41**, 362 (1902).

[16] See Schreiner and Brown: This Journal, **26**, 1463 (1904); Hewitt: *Ibid.*, **27**, 121 (1905).

[17] See Wiley's "Agricultural Analysis," and other standard texts.

[18] Hebebrand: *Z. Nahr. Genussm.*, **5**, 55 (1902); Cassal and Gerranz: *Chem. News*, **87**, 27 (1903).

can be quite accurately determined (such are, calcium,[1] sulphur as sulphates,[2] chlorine,[3] silver,[3] mercury,[4] etc.). In the field of organic chemistry, colorimetric methods have received wide application. The large number of color reactions shown by nearly all classes of organic compounds make the application of the principles of colorimetry especially fruitful in this field. They have been used in the determination of alcohols (ethyl alcohol,[5] etc.); of aldehydes (acetic aldehyde,[6] vanillin,[7] etc.); of acids (salicylic,[8] tannic,[9] etc.); of esters (ethyl nitrite[10]); of phenols (phenol,[11] cresol[12]); of carbohydrates (sugar,[13] glucose,[14] starch,[15] etc.); of alkaloids (morphine,[16] caffeine[17]); of haemoglobin,[18] chloroform,[19] etc. The photometric and nephelometric methods have also found application for determining small amounts of organic compounds (such as albumen,[20] citric acid,[21] etc.). It is needless to add that the principles of colorimetry are employed in the investigation of the artificial as well as natural dyes, as for instance in the valuation of indigo,[22] saffron,[23] the various dye woods, the aniline dyes as well as the dye content in technical dye liquors.

In devising colorimetric methods there have been two main objects throughout, namely, speed and the ability to estimate small amounts, both of which are common to many of the methods,

---

[1] Hinds: This Journal, **18**, 661 (1896); *Ibid.*, **22**, 269 (1900).

[2] Hinds: *Loc. cit.*; Jackson: This Journal, **23**, 779 (1901).

[3] Richards and Wells: *Am. Chem. J.*, **31**, 235 (1904).

[4] Eschbaum: *Pharm. Ztg.*, **47**, 260 (1902).

[5] Argenson: *Bull. Soc. Chim.*, **27**, 1000 (1902).

[6] Paul: *Z. anal. Chem.*, **35**, 647 (1896); Francois: *J. Pharm. Chim.* [6], **5**, 521 (1897); Argenson: *Loc. cit.*

[7] Dietrich: *Z. anal. Chem.*, **37**, 453 (1898).

[8] Langkoff: *Pharm. Centralhalle*, **41**, 335 (1900); Conrady: *Apoth. Ztg.*, **15**, 412 (1900); Harvey: *Analyst*, **28**, 2 (1903).

[9] Hinsdale: *Chem. News*, **64**, 51 (1891).

[10] Cowley and Catford: *Pharm. J.*, **63**, 471 (1899).

[11] Carré: *C. R.*, **113**, 139 (1891).

[12] Schneider: *Rep. Soc. Germ. Nat. and Phys.*, Sept., 1895; *Amer. Drugg.*, **28**, 252 (1895).

[13] Neitzel: *Z. Spiritusindustrie*, **20**, 165 (1896).

[14] Ruini; *Gazz.*, **31**, 445 (1901); Lyons: *Pharm. Rev.*, **20**, 155 (1902).

[15] Dennstedt and Voigtländer: *Forschungsb. ü. Lebensmittel*, **2**, 173 (1896); Ambuhl: *Chem. Ztg.*, **19**, 1508 (1895).

[16] Palmer: *Merck's Report*, **11**, 191 (1902).

[17] Archetti: *Apoth. Ztg.*, **15**, 110 (1900).

[18] Hoppe-Seyler: *Z. physiol. Chem.*, **16**, 505 (1892); Zangemeister: *Z. Biol.*, **33**, 72 (1896); Haldave: *J. Physiol.*, **26**, 497 (1901).

[19] Seyda: *Z. öffentl. Chem.*, **3**, 333 (1897).

[20] Riegler: *Pharm. Centralhalle*, **38**, 349 (1897); Guerin: *Apoth. Ztg.*, **14**, 726 (1899).

[21] Deniges: *C. R. Soc. Biol.*, **54**, 197 (1902).

[22] Koppeschaar: *Z. anal. Chem.*, **38**, 1 (1899).

[23] Vinassa: *Arch. Pharm.*, **231**, 353 (1892).

but not necessarily so. A colorimetric method may have speed and yet not be capable of estimating very small amounts. Speed is, through necessity perhaps, of the greatest importance to the works chemist and to the busy analyst. The ability to estimate very small amounts of material, however, is of the greatest importance to the modern investigator in the field of pure and applied sciences, and to him speed is of only secondary importance if indeed he values it at all. Some of the more recently devised colorimetric methods are for this very reason fully as laborious and perhaps even more tedious than the gravimetric methods, and their one virtue lies in the fact that they can be used in determining amounts so small that gravimetric methods fail, and hence they present a means of attacking problems which hitherto had been impossible of investigation.

The choice whether a gravimetric[1] or a colorimetric method should be used in a given case lies therefore almost wholly within that class of colorimetric methods which have been devised for speed, and the question in this case is usually only one of comparative accuracy as balanced by the gain in time. This gain in time may, however, be of the utmost importance, not only in a works laboratory, but also in a scientific investigation where it is necessary to know the amount of a substance present at any given time in the course of an experiment. In the second type of colorimetric methods, no choice between a gravimetric and a colorimetric method exists, when small amounts are involved. When larger quantities are available, the choice should always be in favor of the gravimetric method, providing, of course, that a reliable gravimetric method exists for the particular substance under investigation. When speed is also a consideration in the method this will somewhat complicate the choice between a gravimetric and a colorimetric method, and the needs of the immediate problem under consideration must guide the analyst.

As to the accuracy of the colorimetric methods no general statement can be made. Some colorimetric estimations have been brought to such a degree of perfection that they far surpass gravimetric determinations in accuracy. On the other hand, many of the colorimetric estimations are only gross approximations, but even these serve a purpose, for in such cases we usually have no other means of estimating the substance. It is, however, between

[1] These remarks apply to volumetric methods as well.

these two extremes that the majority of the methods lie. Folkard,[1] Krüss[2] and many others have pointed out the extreme degree of accuracy which is attainable with such methods when carried out with care, and there is little doubt that their accuracy is more frequently underestimated than overestimated. This is due to a number of causes, chief among which are the inability on the part of many persons to judge colors accurately, contamination while making the tests, the use of impure reagents, and the employment of faulty apparatus. Practice will do a great deal to enable one to make good comparisons, but it can never make up for a dulled or imperfect susceptibility to color. Great attention should be given to this point and the operator should test himself thoroughly by matching a standard against itself in several degrees of intensity. If no concordant results can be reached by practice in this way it is useless to go further with this color, but it may, nevertheless, be possible for him to read accurately some other color. Several cases of this kind have come under the author's observation while training assistants in these methods, and a man who cannot use one method with accuracy is frequently able to use another method with great precision. The use of impure reagents and contamination while carrying out the test are, of course, inexcusable, yet they have led to disparaging remarks concerning the application of colorimetric methods. One criticism frequently made is that merely diluting the standard solution to one-half its strength caused the unknown solution to be found only one-third as strong as had been found when measured against the full standard. It is obvious that had the half standard been measured against the full standard it would have been found that this was of much greater intensity than it should have been. This result could only have been obtained by gross contamination, which with the substance in question was very probable, even with distilled water as usually prepared in laboratories. It is, of course, possible that in this case the ability to judge the particular color was at fault.

The apparatus used in colorimetry is worth consideration from the point of view of accuracy, but at the same time the importance of speed must not be overlooked. A large number of colorimeters have been devised, but it would be impracticable to

---

[1] *Chem. News*, **75**, 73 (1897).

[2] "Kolorimetrie u. Quantitative Spektralanalyse" (1891).

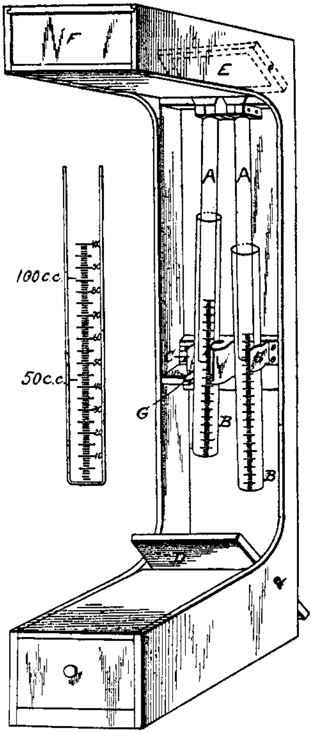
discuss the various forms here, and it must therefore suffice to outline briefly the three types of apparatus and procedures in most common use. In one of these the comparison vessels consist of a pair of parallel walled cells into which the standard and unknown solutions are put and then diluted until both are of equal intensity. In this type then, the length of column viewed by the observer remains constant and the equality of color is regulated wholly by dilution. The comparison is made in a suitably constructed camera. This general procedure is accurate but quite tedious.

A second type of procedure, and the one usually followed, has many objections and is likewise quite tedious if very accurate results are desired, as it involves a great many separate tests and comparisons. It consists in developing the color in equal volumes of the unknown solution and solutions of known strength, selecting the ones which come nearest to it in intensity and then repeating, this time within narrower limits, until a strength of known solution is found which exactly corresponds with that of the unknown. The apparatus used for making the comparisons consists of glass cylinders, preferably with polished glass bottoms, on which have been etched capacity marks, such as 25, 50 or 100 cc. Such tubes as are found on the American market are very faulty in their construction and only too often are made of very poor and tinted glass. The bottoms are exceedingly irregular and the capacity marks vary greatly in their height from the bottom of the tubes, so that it is highly essential that only well "matched" pairs of cylinders be used in making tests. Moreover, the tubes are usually quite tapering so that the lower 50 cc. will occupy an entirely different height from the upper 50 cc. This difference in height amounts to as much as 10 per cent. in tubes obtained from the most reliable American firms. It is, of course, the length of the column of liquid and not the volume which determines the intensity of the image viewed, and in such cases the operator is therefore always dependent upon the coincidence of both volume and height in the tubes used; in other words he must have a pair of well "matched" tubes.

In the third procedure the height of the standard column is changed until the intensity is the same as that in the unknown solution. This is by far the most speedy and when the proper conditions are observed it is also the most accurate of the procedures mentioned. This change in the heights of the solution has been accomplished in a variety of ways; by dropping from a burette into one of the above tubes, by providing such a tube with a stop-cock at the bottom, by connecting by means of a side tube at the bottom with a reservoir which allows moving the liquid up or down at will, and by changing the height by means of an immersion prism or tube. Curiously enough, the graduation into cubic centimeters has been carried over to the cylinders used in many of these instruments when it is perfectly obvious that it is the height of the standard liquid which determines the strength of the unknown solution. In these forms of apparatus the above-mentioned irregularity in the bore of the tubes becomes a vital defect when a cubic centimeter scale is used. The following conditions must therefore be complied with in graduating such a pair of tubes if they are to be used for accurate work: One of the cylinders must be uniform throughout its bore, a condition not easily met. On this are etched 50 and 100 cc. marks. The height of the 100 cc. mark is laid off on the comparison cylinder, which is to contain the known standard, and is provided with the outlet at the bottom. The distance from this mark to the bottom of the tube is divided into 100 equal divisions. In other words, the scale on the standard solution tube is really the scale which reads cubic centimeters in the unknown solution tube. If, therefore, the latter should be broken, the graduated tube has lost its value, for it would be difficult to find another tube which would correspond to this scale. The use of the cubic centimeter scale in graduating such colorimetric apparatus is entirely wrong in principle and should be abandoned. A rational graduation into scale divisions independent of capacity and therefore of the size or uniformity of the bore of the tube, is used in the instrument described below.

For some years this Bureau has been carrying on a series of studies in which the estimation of small amounts of mineral plant food constituents was of the utmost importance. Known colorimetric methods were adopted or new ones devised for this purpose, and as speed and ready manipulation, so far as the handling of the apparatus was concerned, were also of great importance in order to make possible the large number of determinations necessary in order to accomplish the work, especial attention was paid to constructing a simple, accurate and speedy apparatus for making colorimetric readings. The writer is under obligations to Prof. F. H. King for many practical suggestions and help in constructing the colorimeter. This instrument is the one used throughout the work described in Bulletin No. 26 of this Bureau, and has been found so useful in other colorimetric work during the last two years that it was thought of sufficient interest to bring it to the attention of chemists generally.

The working parts of the instrument, that is, those parts which come in contact with the solutions, are entirely of glass, mounted in a suitable camera of wood, as shown in the accompanying figure.



In its simplest form the colorimeter consists essentially of graduated glass tubes containing the standard and unknown colorimetric solution, the column of liquid in both tubes being changed by means of two smaller immersion tubes, also of glass. The immersion tubes *A* are 26 cm. in length and about 2 cm. in diameter and resemble the narrow Nessler tubes, the bottoms being well ground and polished. The upper ends of the tubes are mounted in blocks of wood which fit into grooves on the body of the colorimeter. This permits the ready removal of the tubes from the colorimeter for cleaning when the liquids are changed. The graduated tubes *B* have well-ground bottoms and are likewise 26 cm. in length, but have a diameter of about 3 cm. The scale divisions are 2 mm. apart. On the reverse side of the tube there are 50 cc. and 100 cc. marks for making the solutions up to definite volume. These tubes are supported by a block of wood about midway of the camera and are held in place by brass springs or clamps *C*, the tension of which can be regulated to suit the diameter of the tube, so as to allow it to be moved freely up or down by hand and yet be firmly held in position when the setting is made. It will be noticed from the figure that the glass tubes diverge slightly. This has been found of advantage, as it allows the operator to look down the center of both immersion tubes, as well as to bring the upper parts of the tubes, and consequently the images closer together. The openings to the immersion tubes can be covered by means of a microscope slide to prevent dust from falling into the tubes. The tubes are illuminated from the reflector *D* below, which carries a sheet of white cardboard or opal glass, and after passing through the tubes the light is reflected by a mirror *E* in the upper part of the instrument to the eye of the observer at *F*. The mirror *E* should, as far as practicable, be of colorless glass, as the greenish color of ordinary glass has a tendency to change the quality of the light and interfere in the estimation of weak solutions. This is especially true of the yellowish green color of the phosphomolybdate solutions obtained in the estimation of phosphates. The dimensions of the camera are about 70x32x16 cm.

To make the comparison the standard colorimetric solution is poured into one of the graduated tubes and put into place in the camera together with the immersion tube. The unknown colorimetric solution, made up to definite volume, is put into the other graduated tube and similarly placed in the instrument. The tube containing the solution of unknown strength is set at a convenient height, say fifty scale divisions, and the other tube containing the standard moved up or down, the operator watching the effect on the images in the mirror through the opening at the front of the camera. By moving the standard tube so that the image is alternately weaker or stronger than that of the unknown solution the setting can be accurately and quickly made. When both images show the same intensity of color, the setting is read by noting the division mark on the graduated tube opposite the ground bottom of the immersion tube. This reading will give the height of column of the standard which exactly corresponds with the intensity of color of the column of the unknown solution. It follows that the strengths of these two colorimetric solutions are inversely as the heights of the columns, that is, as the readings on the two tubes. If R is the reading of the standard solution of strength S, and r the reading of the colorimetric solution of unknown strength s, then

$$s = \frac{R}{r} S.$$

The same formula, of course, applies when the standard is fixed and the unknown solution moved up or down until the images are of equal intensity.

Standard glass slides may be inserted at G below one of the immersion tubes in place of the tube containing the standard solution, the immersion tubes being retained so as to give similar images when viewed from above. The Lovibond slides have been used for this purpose, the constant C for the slide being obtained by the formula

$$C = RS,$$

where R is the reading of the standard of strength S when the two images are of equal intensity. The simple colors can be used in some cases, such as the yellow for the nitrate method, but usually a combination of colors will be required to match the color of the solutions and this complicates the use of the slides considerably. A series of slides, of different intensities, but bearing a simple relation to each other, are necessary in order to measure both strong and weak solutions. The strength s of the unknown colorimetric solution, when measured against such a slide, is found by the formula

$$s = \frac{C}{r},$$

where C is the above-mentioned constant for the slide used and r the reading of the unknown solution. These slides are especially serviceable as a control for checking the standard solutions from day to day where the use of the latter is preferred.

In carrying out accurate tests it is highly essential that the standard solutions be carefully prepared and protected from any contamination, such as with the ammonia and nitrite standards, the phosphate standard where contamination by silica is very apt to take place, and many others. In many cases deterioration of the standard itself must be carefully guarded against, such as the aldehyde standard, where aldehyde ammonia is used. The solutions must be perfectly clear with no suspended particles whatever. They should both be at the same temperature, as the absorption spectrum of colored compounds and consequently the color of the solution changes with the temperature. The solvent itself has an absorption effect on the light and hence it is always advisable not to have the concentration of the unknown solution vary widely from that of the standard. It is better in this case to dilute the standard to a similar order of intensity with freshly distilled water. By this procedure the colors are likewise better compared as the absorption spectrum and consequently the transmitted color of many of the dyes is quite different in concentrated solution from what it is in more dilute solutions.

The glass parts of the colorimeter have been made for this Bureau according to the following specifications: The measuring colorimeter tubes are to be 26 cm. long, with *inside* diameter as nearly as practicable 27 mm.; in no case less than 25 mm., and not greater than 29 mm. The glass is to be colorless and the bottoms well ground and polished, with the internal surfaces of the bottoms plane, in no case appreciably convex or concave ; the bottoms to be ground down sufficiently so as to make the ground surfaces a little larger than the internal diameters of the tubes, each of the tubes to be provided with an etched scale of 100 two-millimeter divisions. The scale is to begin at the level of the inner surface at the bottom, the length of the marks being 6 mm., and every fifth mark 12 mm., numbering every tenth mark, on the right side, 10, 20, 30, etc., beginning at the bottom. On the reverse side of each measuring tube there are to be etched two capacity marks, one for 50 cc., and the other for 100 cc. The smaller tubes are likewise 26 cm. long, with *outside* diameter not greater than 20 mm., and not less than 18 mm., with the thickness of the glass the same in all the tubes. The bottoms of these tubes are to be carefully ground and polished and the inside of the bottom never sensibly convex or concave. They must be of colorless glass with the bottoms so ground that the diameter of the ground portion exceeds the internal diameter of the tube. These tubes are to be provided with neither scale nor capacity marks.

The tubes furnished by the makers of glass apparatus leave much to be desired. The bottoms of the tubes can, according to the statements of these makers, be ground and polished only on the outside, and this leaves the inner surface uneven, and slightly concave. For very accurate work, tubes with plates of plane glass cemented on the bottom are strongly recommended as the images obtained in this case are perfectly bright and free from all the objectionable features introduced by light passing through the uneven and somewhat concave bottoms of the ordinary tubes, which act as plano-concave lenses. The objectionable feature is the cement, which, with continued use of the alkaline or acid media of many of the colorimetric solutions, is rapidly disintegrated, and the tube will have to be replaced by another until repaired. When a colorimeter is in almost continued use, this loosening of the cement is very troublesome and the more faulty tubes with permanent glass bottoms above described have been found on the whole to be the most satisfactory for routine work in the laboratory and especially so for the field work, reserving the more perfect tubes with cemented bottoms for use in occasional research problems in the laboratory.

BUREAU OF SOILS,
U. S. DEPARTMENT OF AGRICULTURE,
WASHINGTON, D. C.

NOTES.

Note on the Gravimetric Determination of Sulphur in Iron and Steel.—In the gravimetric method for the determination of sulphur in iron and steel, the well-known danger of escape of unoxidized sulphur during the period of the violent action of the solvent nitric acid on the drillings may be obviated by the following method of solution.

Five grams of drillings are placed in a liter flask fitted with a doubly perforated cork. In one perforation is fitted a funnel-tube with a stop-cock. In the other is fitted a piece of quarter-inch glass tubing which extends about eighteen inches above the flask and is drawn to a point at the end out of the flask. The stop-cock being closed, introduce about 50 cc. strong nitric acid into the funnel tube. Open the stop-cock so that the acid runs into the flask at a rate not greater than two drops per second. When all the acid has passed into the flask, shut the stop-cock and heat the flask gently until solution is complete. The solution is then transferred to a dish. It is advisable to char the cork on its smaller end to prevent the oxides of nitrogen from acting on it.