COLORIMETRIC
ANALYSIS

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PREFACE

It has been the endeavor of the author so far as is possible to avoid needless repetition of material in this work. Therefore all the fine points as to theory, apparatus and its use and the figuring of results which will apply to practically every test given, have been gathered together into three chapters at the beginning of the book. From this it will be seen that a knowledge of these chapters, particularly Chapters Two and Three, is necessary to the success of anyone except an experienced operator, in the use of the methods of determination given on the succeeding pages. It has been the endeavor of the author to mention that a particular type of test was not applicable to those cases where the choice of methods is more limited than usual.

This book is, in essence, an attempt to combine in one volume for ready reference, all the colorimetric tests which experience has shown to be at all practical. Much material will be found here which has never been in print outside of the scientific magazines as well as the standard tests which may be found by reference to any complete work on chemical analysis. In going over the material, it has been evident to the author that little has been done with regard to the determination of the range of greatest accuracy of many of the tests. Whenever such information is available it has been incorporated, so that the operator may know what degree of accuracy he may expect from a sample after he knows the approximate amount of test substance contained in the sample.

It is hoped that this book will furnish a source to which students may refer for a knowledge of the colorimetric methods practical for use and a source to which practical workers may refer for information as to the methods of performing the particular tests with which they are occupied. In all cases, weights of substances to be dissolved as standard have been given to four places, altho that by no means implies that absolute accuracy is necessary in the last two places, since the dilution will minimize any error made there. The giving of these accurate weights will, however, show the operator the direction in which the weight should tend in these last two places and thus can assist to greater accuracy without increasing the labor of weighing to any great extent.

The author wishes to particularly acknowledge the splendid assistance rendered him by the Library of the University of the State of New York in placing at his disposal their files of magazines and reference works. Acknowledgement is also made of the courtesy of Eimer & Amend, C. J. Tagliabue Co. and Arthur H. Thomas Co. in the furnishing of cuts. Acknowledgment is made of the services of C. A. Tyler and W. H. Pearce in the reading of proof.

All factors have been figured by the 1918 table of atomic weights.

F. D. S.

New York, N. Y.
July, 1921.

CONTENTS

COLORIMETRIC ANALYSIS

CHAPTER ONE.

CONDITIONS OF USE OF COLORIMETRIC METHODS.

COLORIMETRIC methods of analysis consist of treating a solution of the substance to be tested with a reagent, in such a way as to produce a color which is proportional in intensity to the amount of the substance being tested for, present in the solution. The methods are not only applicable to the determination of many metals but also to acid radicals and compound radicals to a limited extent. The unknown is therefore spoken of in this general discussion as the test substance. The color having been produced, the solution containing an unknown amount of test substance is then estimated by comparison with a standard solution by one of the following four methods:

1. The sample diluted to a definite volume may be compared with a series of standards of the same volume, previously prepared, the amount of test substance in which is known and the value of the unknown then taken to be that of the standard to which it conforms most nearly. In this way the amount of test substance present is obtained without figuring since, if the volume and color of the unknown and the standard are the same, their contents of test substance will also be identical.

2. The standard and sample may be placed in similar graduated tubes and the darker diluted until its color when observed horizontally thru the tube is the same as that of the other. When this point is reached then each

c.c. of one solution must contain exactly the same amount of test substance as each c.c. of the other and the amount in the unknown is to the amount in the known directly as their volumes. This is the method of dilution.

3. A definite sample of unknown may be placed in one flat bottom graduated tube and amounts of the standard poured into another similar tube until their colors, when observed vertically thru the length of the columns of liquid, are identical. The amount of test substance in each tube will then be the same and since the amount per c.c. in the standard is known the total amount in the standard may be computed, which amount is identical with the total amount in the sample. To state it more briefly, their concentrations are inversely proportional to their depths. This is the method of balancing.

4. The sample may be made up to a definite volume and nearly that volume of water in a similar container be treated with the same reagents for bringing out the color of the solution as were used with the sample. A concentrated solution of standard is then run into the blank from a burette, adding it drop by drop when the end point is near. The volume of the blank may be brought up by the addition of more water until the two colors and volumes are identical. The amount of standard used in the making of the duplicate is then a measure of the amount of test substance in the sample. This is the method of duplication.

In order for the colorimetric test to be accurate the color produced by the action of the given reagent on the test substance must be the only color present in the solution. Therefore a colorimetric test is not possible if the original solution is colored before the test is begun, unless that color is produced by the test substance or will be removed by the reagent used. In some particular instances a slight contamination of one color may be allowed and equalized by contaminating the sample and standard equally. Neither is a colorimetric test possible if the solution to be tested contains anything other than the test substance which will give a precipitate or color with the given reagent. It is essential for the success of colorimetric methods that the color produced be reasonably permanent and that the conditions under which it was produced be such that they can be duplicated without great difficulty. Under certain conditions tests are made with colors which fade after short exposure to the light.

Colorimetric tests may be classified into two classes according to the reason for their use. Some find their popularity because they are fast, and the accuracy of the test is sacrificed for speed in obtaining the final result. The second class find use because they furnish a method of determination of small amounts of substances with greater accuracy than is possible by gravimetric or volumetric methods. The first class may all be made in a short time but it may often happen that the method of preparation of the second class of tests may take hours to insure the accuracy desired.

In spite of the limitations placed on its use by the previous requirements the colorimeter is coming into use more and more every day because of its answer to the demand in nearly every laboratory for speed. Colorimetric methods, used because of their speed, give results in five minutes to one hour from the time the test is begun which is in all cases less than half the time similar tests could be made by other methods. A leading brass manufactory of the country obtains an analysis of its brass from the laboratory within forty-five minutes after the delivery of the sample. Of the five constituents determined, four are determined by colorimetric methods.

Thus the main thing to be said for colorimetry is that its methods are rapid and reasonably accurate.

A broad field of usefulness of colorimetry is the analysis of salts or substances easily soluble in water or acid for the amounts of various impurities present. The methods are very delicate and accurate, some being so delicate as to detect one part in one hundred million parts of water, but they are seldom such as to permit of the determination of quantities greater than one per cent without resorting to aliquot parts and using a portion of the solution of the sample instead of the whole. The methods of accurate dilution are discussed in the next chapter; the only drawback to their use is that the use of a factor for determining the final result multiplies the error made in the comparison, often as much as a thousand times.

CHAPTER TWO.

APPARATUS USED AND METHODS OF USING IT.

As previously outlined there are four types of determinations made by colorimetric methods, each of which uses a more or less specialized form of apparatus.

In cases where a series of permanent standards are made up these are usually placed in either round or square glass bottles. Such a series of standards should be placed in a row on a shelf, with sufficient space between each two for setting in a similar bottle. The sample should be treated in a similar bottle and, after making up to the same volume as that of the standards, it may be set into various of the gaps between the standards until the place is found where one standard is higher than the sample and the one on the other side lower, as estimated from the intensities of their colors. The position of the sample relative to these two known quantities can then be estimated. In some cases when permanent standards are used one bottle may be made to serve as two standards. This is accomplished by the use of a rectangular bottle, twice as long as it is broad. The sample is then compared in a similar bottle and results are as follows: If the long way of the sample bottle compares with the long way of the standard the amounts of test substance in the two are the same. If the narrow way of the sample compares with the long way of the standard the sample contains twice as much test substance as the standard. If the long way of the sample compares with the narrow way of the standard the sample contains half as much test substance as the standard. Altho no further specific reference will be made to their use, this use of these special bottles is applicable in all cases where permanent standards are to be made up, except those where the actual color rather than the depth of color changes with the concentration. Care should be taken to see that the bottles used in all cases are clear in color and free from flaws.

In many cases the color produced by a reaction fades in a short time in the light. In such a case either a standard must be prepared at the same time as the sample and test made by one of the other methods or permanent artificial standards must be prepared. These are conveniently prepared from solutions of inorganic salts, combining the colors in such a way as to give the desired color. The solutions which find the greatest favor for this purpose are half normal solutions of the nitrates or chlorides of cobalt, iron and copper.[1] These three solutions may be combined in such a way as to form any color desired except the deep blues and reds. To remedy this it has been found that some of the missing colors can be obtained by using a solution of potassium dichromate instead of the iron solution and the remaining colors are obtained by combinations of potassium dichromate and potassium permanganate. As an example it is found that a mixture of the first series suggested, cobalt three parts, to iron nine parts, diluted with water, corresponds to the color given by Nessler's reagent in reaction with ammonia. Varied dilutions of this may be used for a series of standards, making each standard to correspond to the result obtained by the use of that known amount of ammonia treated with the reagents necessary to bring out the color. In a similar manner permanent standards may be prepared for any

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[1] J. Franklin Institute, *180*, 200.

test, keeping in mind the fact that every standard must be tested against a known amount of the test substance to make sure of its accuracy.

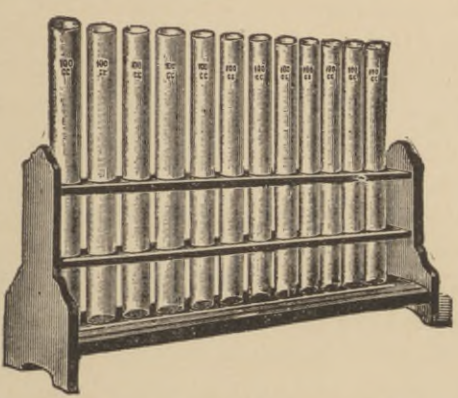

FIG. 1. Rack of Straight Graduated Tubes.

For the production of nonpermanent standards plain test tubes are ordinarily used. The solution may be quickly and conveniently emptied from these and the loss in case of breakage is not so great as from the use of graduated tubes such as Nessler tubes or from the use of bottles.

The apparatus for tests by the dilution method consists essentially of a pair of graduated tubes. There is, however, a very convenient device (Fig. 14) manufactured for use with this method known as the colorimetric camera. This is a light-proof box, painted black inside, with holders for the two tubes near one end. The end near the tubes is fitted with a ground glass screen; the other end is fitted to the face of the observer so that no side light may enter. By the use of this a more accurate judgment as to the colors of the two tubes may be made than if they are compared out in the open. One advantage of this apparatus is that it does not tire the eyes of the operator so quickly as do some of the types of colorimeter used for the balancing method. In all cases possible a colorimeter should allow the use of both eyes for making the comparison so as to eliminate fatigue. Sometimes the comparison of the two tubes is made by holding them in the hand and looking at them against a sheet of white paper.

Whether or not the camera is used for the comparison the operation of the dilution method is always the same. The standard and sample are in two graduated tubes or in two Nessler tubes. The former are used when the camera is used for the comparison, the latter are useful when no further apparatus is used. The colors of the two solutions should be nearly alike to begin with. The experienced operator soon learns to choose his sample so that the resultant color will be nearly the same as that of the standard which he is using. Water is then added to the solution of the darker, carefully mixing after each addition, until the colors of the two solutions when observed horizontally thru the tubes appear to be identical. When this point is reached the concentration of the test substance in each solution must be the same and their contents are then to each other as the volumes. Since the amount of test substance in the amount of standard used is definitely known, it is easy to figure the test substance in the sample by a direct proportion. Care should be taken that the tubes used are clear and free from flaws and that their thickness of glass, internal diameter and graduations are identical. A special type of tube (Fig. 13) manufactured for carbon determinations is applicable to all dilution tests. This has a bend about two inches from the top so that the tube may be lightly shaken to mix the water added without danger of the contents being spilled. Note that the standard may as well be diluted to match the sample as the sample to match the standard, provided only that the original volume of the standard is recorded and that the final colors are not too deep or too light to allow of accurate measurement.

Determinations by the method of duplication are usually carried out in graduated Nessler tubes. The sample is first diluted to some convenient, definite volume. The same reagents as were added to the sample are then added to a volume of water amounting to about half the volume of the sample, this will usually be specified for the particular experiment since the amount of water used for the blank varies according to the concentration of the standard to be used. To the blank containing the same reagents as those used for the sample there is now added a standard solution, carefully mixing after each addition, until the color of the sample is duplicated by that produced in the blank by the addition of the standard. The color of the blank having been made to balance that of the sample they will still differ in volume. It is simple enuf to figure at this point by proportion the amount of standard that would be necessary if the volumes were equal but, to eliminate any chance of error in that, it is best to duplicate the volume as well as the color of the standard. This is accomplished by the addition of water and standard alternately until the two solutions are identical in both color and volume. As said, a little simple mathematics will tell an operator of comparatively little experience the exact amounts of standard and water to be added after the colors have once been duplicated. The same cautions apply to this test as to the previous one insofar as apparatus is concerned; the tubes used must be of the same size, thickness of glass and internal diameter and the graduations on the outside must correspond in height. That is, the ten c.c. mark on each must be at the same distance from the bottom, otherwise the contents are not the same or the tubes are not accurately marked.

The apparatus for the balancing method is the most elaborate of all and the use of it, the simplest. The various instruments used include Hehner cylinders, Lovibond Tintometer and various types of colorimeters. The Campbell-Hurley, Duboscq, Schreiner, Stammer, Saybolt, and White types are described. Other specialized forms are used in some special applications but their use is mostly in physiological chemistry.

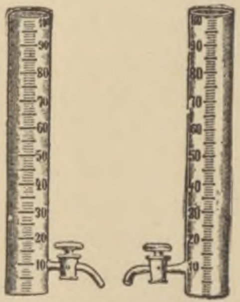

FIG. 2. Hehner Cylinders.

The Hehner cylinders are the simplest of the instruments for this use. They consist of two glass tubes with flat bottoms and each has a side tube with stop-cock, about three inches from the bottom. For the carrying out of a determination the solution of the sample is placed in one tube and the other tube is partially filled with the standard so that the depth of color seen by looking vertically downward thru the length of the column of liquid is deeper than that seen by similarly looking down thru the sample. An amount of standard is then drawn off, such that the colors of the two tubes when observed in this way are the same. The tubes are then said to be balanced and the readings of the volumes taken. The amount of standard used and its content of the test substance per c.c. is known. The test substance in the sample is then inversely proportional to the volume if the content per c.c. is desired, or the total amount of test

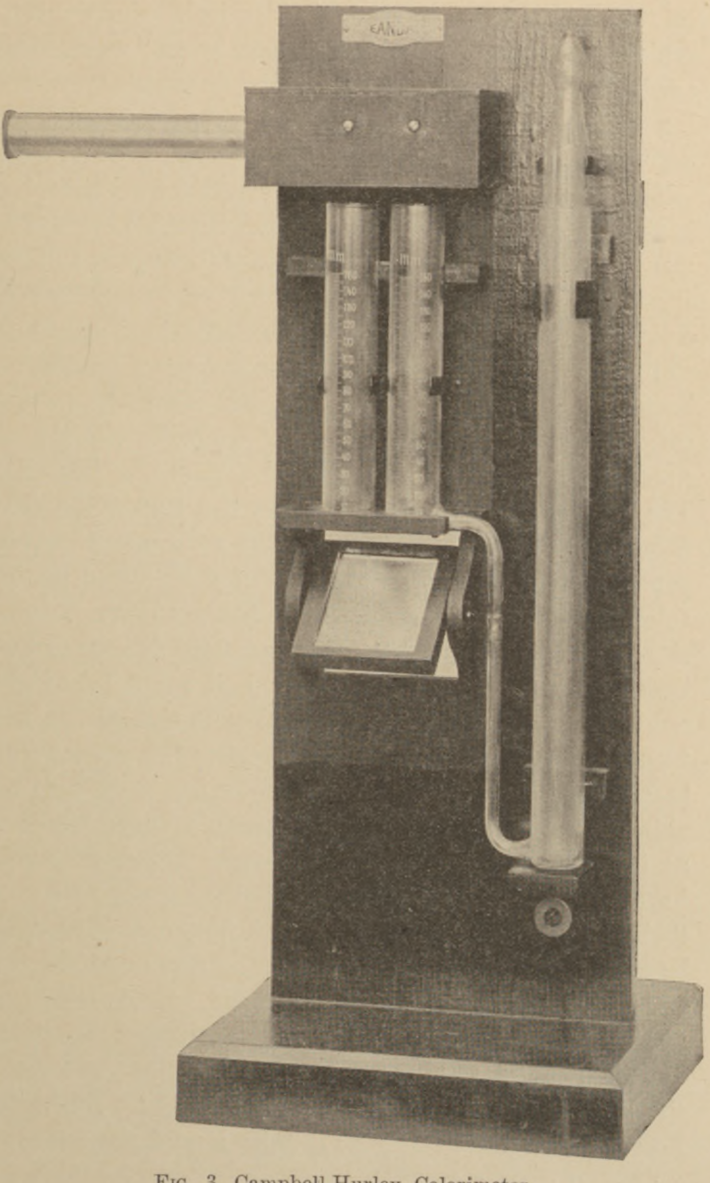

Fig. 3. Campbell-Hurley Colorimeter.

substance in the two solutions is identical. For the convenient balancing of the two liquids several mechanical appliances have been devised for the purpose of increasing the speed of the determination or of increasing its accuracy.

The Çampbell-Hurley type of colorimeter illustrated is the common form of such an instrument. This instrument[1] is a modification of the Kennicott-Sargent type of apparatus and is sometimes known as the Kennicott colorimeter. The following is the method of operation as illustrated by the diagram. The unknown solution to be tested is placed in the tube *A* and, since the volume can be readily governed so as to come to some even graduation, these are only placed at five c.c. intervals. The standard solution is placed in the right-hand tube *B* which, because of the fact that the accuracy of the test depends upon the careful reading of the volume in this tube, is graduated to single c.c. The readings of tubes *A* and *B* have been given as in c.c. but, for such readings to be accurate, tubes *A* and *B* must be of the same identical bore. The same effect is obtained in less accurately made instruments by having the graduations to cm. rather than c.c. The proportion may then be obtained between the heights of the two columns, the same as tho the units used were c.c., since the columns will have colors proportional to the depths regardless of their amplitude. The method used for graduation must be taken into account in figuring the results of the test and will be discussed under that head. Tube *B* is permanently connected by a glass tube with the reservoir *C* in which the glass plunger *D* works, so that the level of the liquid in *B* may be readily controlled by raising or lowering the plunger. As the tube *B* and the reservoir

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[1] J. A. C. S., *33*, 1112.

C are made in one piece the standard comes in contact with glass only, thus preventing the possibility of chemical change due to coming into contact with the container. The plunger *D* is sometimes provided with a rubber collar *E* to prevent it from coming into contact with the

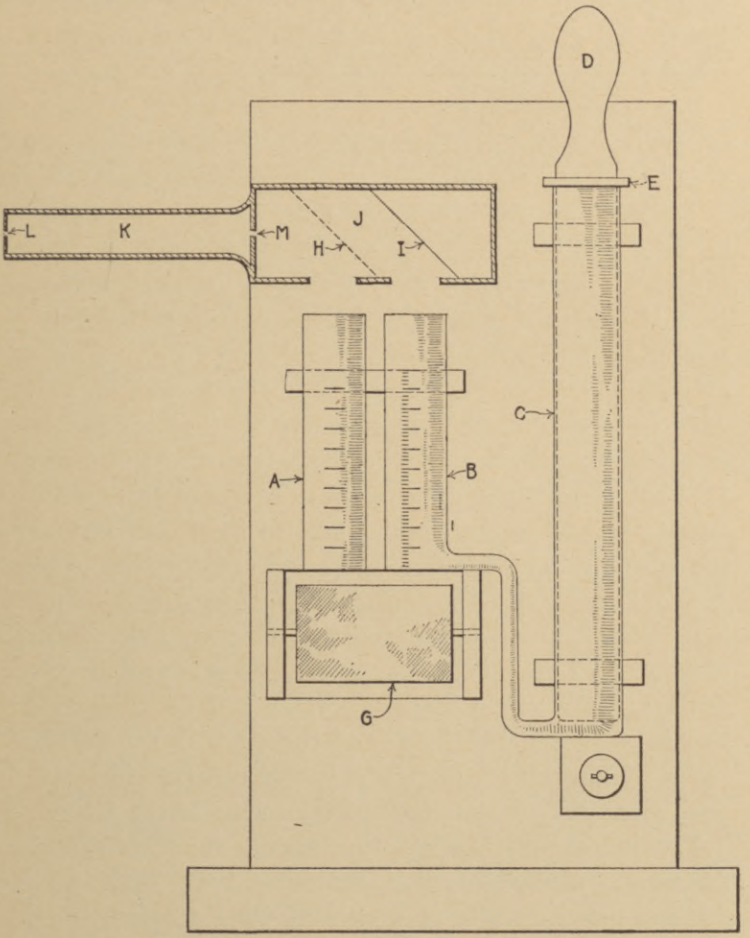

Fig. 4. Campbell-Hurley Colorimeter.

bottom of the reservoir and the resultant breakage possible. The tubes *A* and *B* and reservoir *C* rest on wooden supports with holes under *A* and *B* for the passage of light. All glass parts are held in place by spring clips which allow for the easy removal of the parts for cleaning.

For operation the colorimeter is turned with the back toward a window, preferably a north one, and the mirror *G* is so adjusted as to reflect skylight upward thru tubes *A* and *B*. By this arrangement the back of the colorimeter serves as a screen to cut off all light except that reflected upward from *G*. The light, passing upward thru the tubes *A* and *B*, impinges on the two mirrors *H* and *I* cemented to brass plates sliding in grooves cut at an angle of 45° in the sides of the wooden box *J*. This box has a loosely fitted cover so that it may be removed for the cleaning of the mirrors. The mirror *H* is cut vertically and cemented in such a position as to reflect one half of the circular field of light coming thru the tube *A*. The light, passing upward thru *B*, is reflected horizontally by the mirror *I* thru a hole in the brass plate supporting the mirror *H*. One half of the circular field of light from the tube *B* is cut off by the mirror *H*, the vertical edge of which acts as a dividing line between the two halves of the circular field. The image of one half of the tube *B* is then observed in juxtaposition to the opposite half of the image of the tube *A*.

The juxtaposed images are observed thru a tube *K*, 2.5 cm. in diameter and 16 cm. long, lined with black felt and provided with an eyepiece having a hole 1.5 mm. in diameter. At the point *M* in the tube *K* is placed a diaphragm having an aperture 8 mm. in diameter. All parts inside the box *J* except the mirrors are painted black so that no light except that coming thru the tubes *A* and *B* passes thru the tube *K*. By having the apertures in the eyepiece and the diaphragm properly proportioned only the images of the bottoms of tubes *A* and *B* can be seen, thus preventing the interference of side light from the vertical sides of the tubes.

A person looking thru the eyepiece observes a single circular field divided vertically by an almost imperceptible line when the two solutions are of the same intensity. By manipulating the plunger *D* the level of the liquid in *B* can be easily raised or lowered, thus causing the right half to assume a darker or lighter shade at will. In matching colors with an ascending column in *B*, that is, gradually deepening the color of the right half of the field, the usual tendency is to stop a little below the true reading, while in comparison with a descending column the opposite is the case. At first the operator should take a reading in each direction until after a little practice this tendency to error has been overcome.

In tests on a large number of titanium solutions by oxidation with hydrogen peroxide, using all concentrations from a very dilute (light yellow) to a fairly concentrated (deep orange) solution, the average percent of error was found to be less than one percent and the median error less than one half percent.

In some cases the depth of the column of liquid observed cannot be used as a measure of the test substance present as the concentration changes not only the depth of the color but the color itself. In cases where that is so, it will be mentioned in connection with the directions for the particular test.

A modified form of balancing instrument has a mirror directly over the tubes *A* and *B* reflecting forward the two circles of light which come to it. The mirror is encased in a lightproof box painted black on the inside

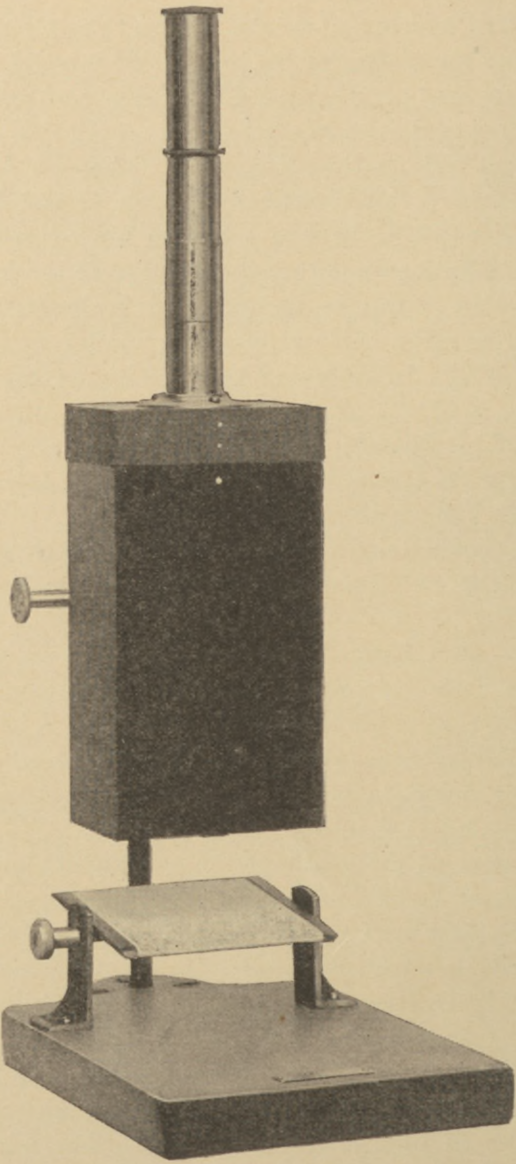

FIG. 5. Lovibond Tintometer.

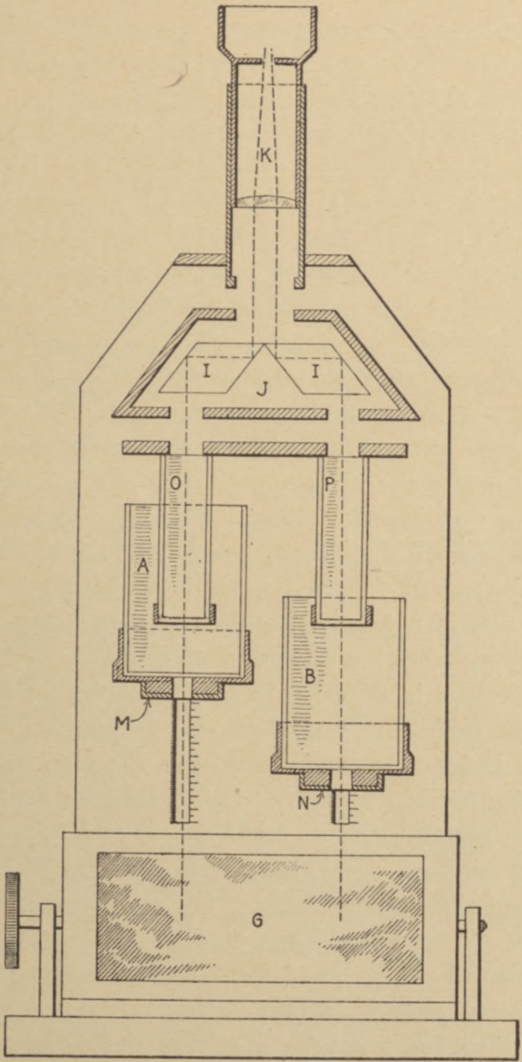

FIG. 6. Duboscq Colorimeter.

and about eight inches long. This is fitted to the eyes of the operator at the forward extremity so that side light cannot enter. The arrangement of the tubes *A*, *B* and *C* and plunger *D* is the same as in the previous instrument. By making the holes under the tubes *A* and *B* so small that they do not extend to the side walls of the tubes side light is largely eliminated and accurate results secured. In this case the alteration is made in the color of the right hand circle of light as compared with a circle of similar size appearing beside it.

The Lovibond Tintometer is another type of instrument, one which we shall not describe here at any length on account of the limited use that it finds. The instrument is expensive and so is comparatively rare. The comparison is made by graduating a liquid to match a glass of a certain color, thus doing away with the use of a liquid standard. Since a permanent liquid standard may be prepared for this use and so eliminate large expense this is not recommended. Glasses may be obtained for determining carbon in steel and color of water, petroleum, etc., in addition to which by combinations of glasses the color of any solution may be matched.

In the Duboscq type of instrument the same result as in the Campbell-Hurley type is obtained by a different method. The two independent tubes, *A* and *B*, are of the same size and are for holding the solutions of the unknown and the standard. Each is mounted in a wooden holder, *M*, *N*, which slides up and down in a slit cut in the backboard of the instrument and which is fastened at the chosen place by a thumbscrew. Light is reflected upward thru the tubes by a mirror *G*. Directly over tubes *A* and *B* which contain the solutions to be tested are two glass plungers, *O*, *P*, of a diameter equal to about half that of *A* and *B*. The bottoms of these plungers are finely ground and in the best instruments are fused on. In the cheaper instruments the bottoms are fastened with some sort of adhesive.

The telescope, *K*, for observation of the colors is perpendicular to the base so that the operator looks downward into the instrument. The light reflected upward thru the solutions in *A* and *B* is so reflected by the prisms, *I*, *I*, in the box *J* that two fields appear side by side, one from *A* and one from *B*. The arrangement of the prisms is such that the images observed in the field of the telescope are those of the bottoms of the plungers, *O*, *P*, rather than of the entire depth of liquid in *A* and *B*. By suitable cutting down of the aperture by screens all reflection from the sides of the tubes is cut off.

For use, the instrument is set to face a source of light and mirror *G* is set at the proper angle to reflect skylight upward thru *A* and *B*. The cylinder having the lighter color is then moved upward by sliding its holder in the slit in the backboard until the plunger just touches the surface of the liquid. The other container is then moved upward observing its movement thru the telescope until the image of the base of the plunger in that liquid appears to be of the same intensity as that observed from the other field. The instrument is then said to be balanced and the depths of liquid underneath the plungers have the same relation to each other as the total depths of liquid in *A* and *B* when the Campbell-Hurley instrument is balanced. The slits cut in the backboard in which the holders of *A* and *B* move are graduated so that the depths of liquid may be read off directly from these and possible errors in reading depths of liquid in glass due to the meniscus are eliminated.

The laws relating to the depths of liquid when the instrument is balanced are as follows. The concentration per c.c. of the sample is to that of the standard inversely as the depths of their liquids. Diameter of the containing vessels being the same, the sample solution of the depth indicated by *A* contains identically the same amount of test substance as a standard column of the depth indicated by *B*. The figuring of results from this data is taken up in the next chapter. The nephelometer is a modification of this type of instrument. For further information regarding that use see Chapter Twenty.

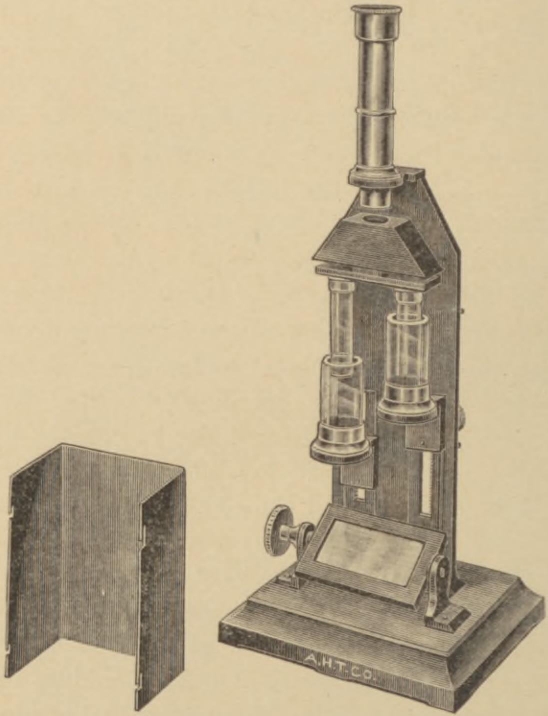

FIG. 7. Large Duboscq Colorimeter.

The Schreiner colorimeter is a simple modification of the Duboscq instrument, eliminating many of the more expensive features. The prisms are omitted and two round fields near each other are observed. The holders for *A* and *B* are two brass clips and the reading is taken by graduations on the glass of these tubes. The application of this instrument is recommended by the manufacturers for soil analysis.

The Stammer colorimeter is also a modified form of the Duboscq, and is particularly used for determination of the color of sugar solutions and of oils. The colors of the fields are transmitted to the telescope, *K*, by prisms, *I*, *I*, as in the Duboscq type. The alteration is in the character of the fields. Instead of two movable containers and two fixed pistons as in the other instrument the containers are fixed and one movable piston, *P*, is provided for the variation of the column in *B*. A false piston, *O*, is provided so that the light thru *A* will have to pass thru a similar thickness of glass. The column in *A* remains absolutely permanent, no variation in that being possible. Light is reflected upward by a mirror at *G* as in previous instruments.

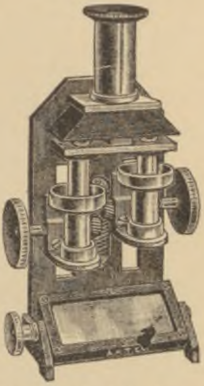

FIG. 8. Small Duboscq Colorimeter

Recently a new type of instrument has been evolved from the combination of the Lovibond Tintometer and the Stammer Colorimeter, known as the Saybolt Chromometer. This instrument is intended solely for the evaluation of the colors of lighting oils. This is similar to the Stammer instrument in that two tubes are provided, but the left-hand tube, *A*, is modified to an empty tube in which the color is obtained by the addition of one or more carefully prepared glass disks. The sample in *B* is drawn off until only such an amount is left as will duplicate the color of the disk used. From the graduations on the glass of *B* and the directions of the makers the oil may then be graded as so many degrees above or

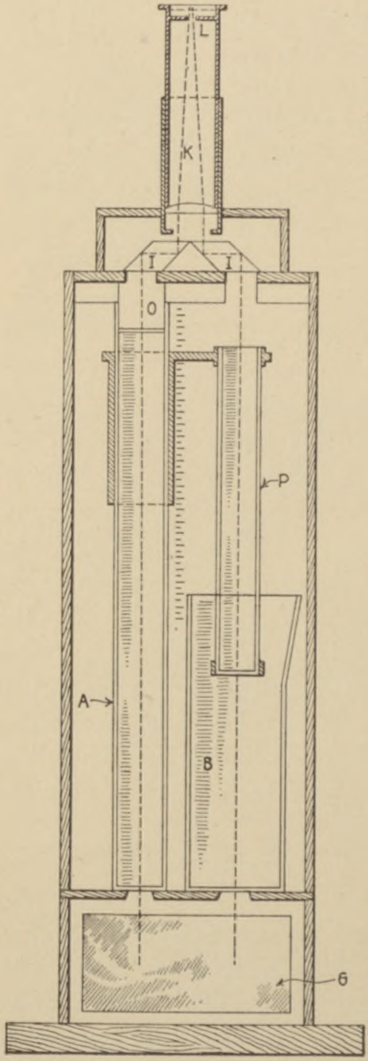

FIG. 9. Stammer Colorimeter.

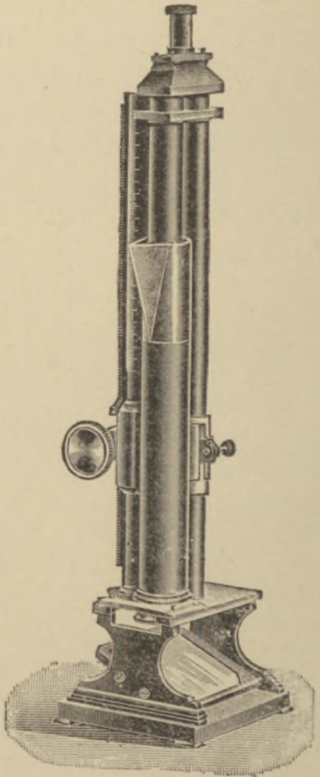

FIG. 10. Stammer Colorimeter.

below the standard colors for lighting oils (see Chapter Nineteen), depending on the disk used.

One other type, White's colorimeter,[1] shows promise of great importance because of its ease of operation. In this the thickness of two glass prisms observed is the variable. The apparatus consists essentially of two wedge-shaped hollow glass prisms of exactly equal dimensions, open at the large end for the introduction of the solutions to be tested. The wedges are held in vertical position side by side in a camera and may be raised or lowered by rack and pinion actuated by thumb-screws. The wedges are screened from view on the side of the operator, except for a narrow horizontal slit across the middle of the camera thru which the solutions are observed when a test is being made. The carriers are graduated to correspond to the length of the wedges, the zero of the scale being opposite the indicator when the sharp edge of the wedge is opposite the narrow opening in the screen thru which the color is observed. The screens are adjustable so that the opening may be altered to suit the operator. The ground glass shutter at the forward end of the camera, for diffusing the light, is hinged in the manner of a door to facilitate the transfer of the wedges to and from the camera. To carry out a determination by this method equal quantities of the standard and of the material to be tested are diluted to equal volumes and convenient amounts of the solutions transferred to the wedges. The wedge containing the solution of unknown strength is set at the graduation representing the percentage, or a multiple of it, of the coloring matter in the standard. The wedge containing the standard is then adjusted so that the two fields seen thru the camera appear identical. The percentage of

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[1] J. A. C. S., *34*, 659.

coloring matter in the unknown is then indicated by the reading of the scale on the carrier containing the standard. If the depths of color compared at first are too deep for accurate comparison the results may be checked without changing the solutions by setting the wedge containing the unknown at a new point on the scale and again adjusting the other wedge until equality is reached. The maximum error reported on a long series of experiments with this instrument was .6 percent.

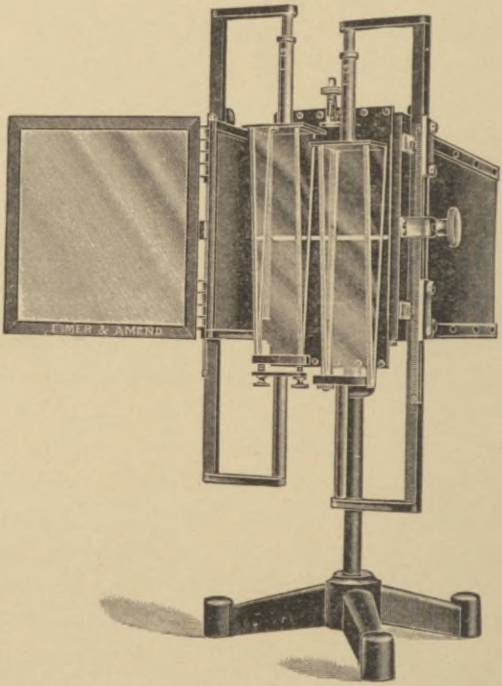

FIG. 11. White's Colorimeter.

The figuring of results obtained by these balancing methods is discussed in the next chapter.

In some cases it may be impossible to choose a sample having as small a content of the test substance as specified in the method, particularly if the substance being analysed is an ore or alloy containing a fairly large percentage of the test substance. In that case the sample may be taken containing somewhat more of the test substance than specified for the test and dissolved as directed. This solution may then be accurately diluted and an aliquot part taken. If, for example, the method specifies that a sample must be under .001 gram of the test substance and the smallest sample of the substance being analysed which can conveniently be weighed out will contain nearly one tenth gram of the test substance, this may be dissolved as specified and diluted to one liter in a volumetric. Ten c.c. of this may then be analysed as directed and the weight of test substance found in that amount of solution multiplied by 100 will give the amount in the original sample. In case it is necessary to use such a method the final result cannot be expected to be as accurate in regard to the amount of test substance by weight as shown in the result but the results are identically as accurate so far as the percentage of error is concerned. To illustrate, while accuracy to .6 percent in the case of a weight of substance showing .001 gram test substance would allow an error of only .000006 gram test substance, if the sample showed .5 gram test substance (an amount greater than would ordinarily be present in a weight of sample used), the maximum error then possible would be .003 gram of the test substance.

The rapidity with which colorimetric tests may be made often admits of the attainment of considerably greater accuracy than the theoretical by rapidly doing several tests and then averaging the results obtained.

The intensity of the color of the two solutions is an important factor, so results may be expected to be more accurate if the standard and sample have nearly the same color before a test is carried out by dilution or balancing methods than if the colors differ greatly. The intensity should also not be too great or too dilute; in either case errors will be greater than if the color produced was intermediate between the two extremes.

CHAPTER THREE.

FIGURING OF RESULTS.

In case a series of standards is used the weight of test substance in the unknown may be told at once by looking at the amount in the standard to which it corresponds. The percentage is then readily figured from this by dividing by the weight of sample used, thus:

Weight of sample, 5 grams.

Weight of test substance present, .0004 gram.

Sample therefore contains $.0004 \div 5 = .00008$ gram test substance per gram sample $= .008$ percent.

The figuring of results when the dilution method is used is somewhat more complex. In that case the darker of the two solutions is diluted until the colors of the two are identical when observed horizontally thru the tubes, at which point the content of test substance per c.c. is the same and the content of test substance of one is to that of the other directly as their volumes. To illustrate:

Weight of standard used, .2 gram.

Weight of unknown used, .2 gram.

Standard contains .32 percent test substance.

Readings, standard 38 c.c., unknown 45 c.c.

The weights of the sample and standard being the same in this problem we may eliminate the figuring of the weight of test substance in the sample and proceed directly to estimate by proportion the percentage. This is estimated thus:

Percent in standard : Percent in unknown = Volume of standard : Volume of unknown :

$$.32 : X = 38 : 45$$
$$X = .379$$

Therefore we find that the sample being tested contains .38 percent test substance.

The figuring of dilution method results does not always resolve itself into a mere comparison of percents as usually a definite volume of a standard solution whose content of test substance per c.c. is known is used as the standard. In that case the weight of test substance in the standard must be figured and from that the similar weight in the sample and then the percentage present in the sample. The method follows:

Weight of sample used, 2 grams.

Standard used, 20 c.c. of a solution containing .00002 gram test substance per c.c.

Readings, standard 20 c.c., unknown 48 c.c.

From the readings above it will be seen that in this case the color of the sample was darker than that of the standard and therefore the sample was diluted. There would be no change in the method had the standard been diluted.

Weight of T. S. in standard : Weight of T. S. in unknown = Volume of standard : Volume of unknown.

Weight of test substance in standard is 20 × .00002 = .0004 gram.

$$.0004 : X = 20 : 48;$$
$$X = .00096.$$

Therefore the two grams of sample used contained .00096 gram of test substance and the percentage in the sample was .048 percent.

Results by the method of duplication are easily obtained. A standard solution is added to a blank containing the same reagents as the sample until the color of the sample is matched. Water and standard are then cautiously added, alternately, until the volume as well as the color of the two solutions is identical. The result as to how much test substance is present in the sample is given by the amount necessary to form an identical standard. The percentage in the sample is then figured, thus:

Weight of sample, 5 grams.

Standard used contains .0002 gram test substance per c.c.

Standard used for duplication 2.3 c.c.

Then the total test substance used was $2.3 \times .0002 = .00046$ gram.

Therefore the sample contained $.00046 \div 5$ gram test substance per gram of sample or .000092, which is .0092 percent.

Results obtained by the balancing method are somewhat more complicated to obtain, especially if the apparatus used is graduated to cm. instead of cc.

To take, first, a case when the apparatus is graduated to c.c. and tubes *A* and *B* are identical, whether they be the Hehner cylinders or Campbell-Hurley apparatus or some other type of instrument,

Standard used contains .00002 gram test substance per c.c.

Volume of standard used to balance colors, 44 c.c.

Sample used, 4 grams.

The amounts of test substance in sample and standard are the same when the colors are balanced, that is the volumes differ but the total content is the same. Therefore the amount of test substance in the sample being the same as in the standard is

$$44 \times .00002 = .00088 \text{ gram.}$$

Since the sample used was 4 grams it was therefore .022 percent test substance.

To take the other case of cylinders graduated to centimeters, the results obtained with a cheaper instrument are accurate but more calculation is involved, thus:

Weight of sample 2 grams.

Volume of sample after solution before addition to tube $A = 50$ c.c.

Height of sample in tube $A = 7.3$ cm.

Height of standard in B to balance $= 8.4$ cm.

Content of standard per c.c. $= .00001$ gram test substance.

When the colors of A and B are balanced the concentrations of the contained solutions are inversely proportional to the volumes used, thus:

$$\text{T. S. per c.c. in } A : \text{T. S. per c.c. in } B = \text{Depth of liquid in } B : \text{Depth of liquid in } A;$$

$$X : .00001 = 8.4 : 7.3.$$

$X = .0000115$ gram test substance per c.c. in sample solution.

Then the total test substance in the sample is

$$50 \times .0000115 = .000575 \text{ gram.}$$

This is .0002875 gram per gram of sample and the sample is therefore .02875 percent test substance.

CHAPTER FOUR.

DETERMINATION OF IRON.

The determination of iron is one of the important applications of colorimetry both because of the widespread distribution of the metal and because of the inadequacy of gravimetric or volumetric methods to measure small amounts of the substance, especially in the presence of the other third group metals. Lunge recommends that some colorimetric method be used for the determination of small amounts of iron in preference to other methods.

There are seven methods for the colorimetric determination of iron, details of which follow.

Method A—Iron by Potassium Sulfocyanate.

The sulfocyanate method for the determination of iron depends upon the oxidation of all iron present to the ferric condition after which the reaction between ferric iron and potassium sulfocyanate is used to produce a red color proportional to the amount of iron present. It is a very rapid method and is delicate enuf for the detection of one part of iron in fifty million parts of water, especially in the presence of free mineral acid.[1] Use is therefore made of the method for the determination of traces of iron in water supplies and of iron in small content iron solutions such as solutions of salts and minerals known or suspected to contain a small amount of iron. It also furnishes a rough and ready method for the approximation of the iron content of minerals

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[1] C. N., *51*, 259.

which contain considerable amounts of the metal, even up to 30 percent, when accuracy within one percent is required rather than the greater accuracy of the slow analyses. This latter determination of course calls for the methods of accurate dilution given in Chapter Two.

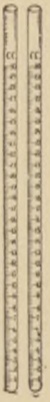
FIG. 12. Straight Graduated Tubes

Fluorides, phosphates, arsenates, oxalates, citrates, tartrates and iodates interfere, also acetates to a lesser degree.[2] It is therefore necessary that these substances be absent from the solution. Since the presence of a small amount of mineral acid has been found to make the test more delicate the determination is carried out in a solution slightly acidified with sulfuric acid. The amount of the iron ionized is dependent upon the concentration of the acid solution, so it is advisable to have the acid content of sample and standard uniform for the attainment of the correct results.

The amount of the sample must be so chosen that the final solution contains between .000001 and .0002 gram iron per c.c., of which solution ten c.c. is taken for the analysis. If the test is being made of a solid dissolved in water the sample may be so chosen as to conform to these limits, if the test is of a water for the iron content the water may be concentrated. In some special cases where great accuracy is not required it may be found possible to use twenty or even forty c.c. of a solution somewhat more dilute than the limit as a sample. To this solution add ten c.c. of concentrated sulfuric

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[2] J. A. C. S., *29*, 409.

acid and oxidise with potassium permanganate until a faint permanent blush appears. Then run in about five c.c. of a solution of potassium sulfocyanate, 97 grams to the liter, and dilute to fifty c.c. with pure water. The color to be tested appears at once and ranges from a faint pink to a deep red according to the amount of iron present. The test may be made by duplication or by balancing but the dilution and series of standards methods are not satisfactory in this test. The amount of ionization changes with the acid concentration of the solution and therefore the color would change with the addition of water independent of the amount of iron in the solution. A series of standards is not satisfactory as they fade out in light so soon. The addition of a small amount of potassium persulfate to a solution made up will keep the iron oxidised for some time longer if it is desired to preserve a sample or standard for several days.

The standards to be used in this test are made up as follows, if the result is to be stated as Fe weigh out .1405 gram of ferrous ammonium sulfate [$FeSO_4(NH_4)_2SO_4$, $6H_2O$], if the result is to be stated as Fe_2O_3 the weight of salt taken is .1473 gram. The weights given above are dissolved in water with the addition of a little dilute sulfuric acid. Ten c.c. of concentrated sulfuric acid are then added to this and potassium permanaganate run in until the iron has all been oxidised to the ferric state. Twenty c.c. of the sulfocyanate solution are then added and the beaker carefully washed out into a liter volumetric flask and the flask filled to the line. The addition of the sulfocyanate to the iron solution before washing it into the volumetric enables one to see that the beaker in which the oxidation was carried on is thoroughly washed out and all the iron transferred to the flask.

This standard solution contains .00002 gram Fe or .00003 gram Fe_2O_3 according to which weight was used. The use of the appropriate weight thus allows for the figuring of results more readily. It is well to add one tenth of a gram of potassium persulfate to the standard before dilution so that the color may remain clear for a longer time. The standard should then be kept in the dark and renewed at least once a week if used often.

This standard solution is to be added to thirty c.c. of water, and ten c.c. of concentrated sulfuric acid, measuring the amount of standard used accurately with a burette. Not only the color but also the volume of the standard must be identical with those of the sample before the end point of this method has been reached. The amount of iron in the sample is then measured by that necessary to make up the duplicate. If the test is to be made by the Campbell-Hurley apparatus or other type of balancing apparatus the standard mentioned above may be diluted to one tenth its present strength (ten c.c. diluted to one hundred) unless the color of the sample being tested is very deep.

It is often desirable to make a test of filter papers for iron as impurity. Such tests may be made on the original filter paper qualitatively by working the paper to a pulp in concentrated hydrochloric or nitric acid but the quantitative determination is made by dissolving the ash in acid, oxidation of the iron with permanganate, and testing this sample as a whole by the method already given.

For the determination of iron in lead and similar substances[1] soluble in acid a sample of ten to thirty grams, dependent on the iron content, is dissolved in nitric acid, thirty c.c. of sulfuric acid added, the precipitate allowed to settle and filtered. The filter is well washed with warm

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[1] J. Ind. Eng. Chem., 7, 1035, 1915.

water, small amounts at a time, and the filtrate rendered slightly alkaline by the addition of ammonia. This solution is boiled for a minute and the precipitate filtered out and well washed with warm water to remove traces of lead. Redissolve this precipitate which contains the iron as the hydroxide in dilute hydrochloric acid and test by the method given. If the amount of iron is too great to test as a single sample dilute to 100 c.c. and use ten or twenty c.c. of this solution for testing. For the oxidation of the iron in this latter test it is possible to add a slight excess of hydrogen peroxide to the iron solution to be oxidised and thus save the trouble of assuring oxidation with permanganate.

Method B. Iron as the Chloride in Concentrated Acid.

The yellow color of ferric chloride has been adapted to the analysis of samples containing iron for their iron content. The sample[1] is dissolved in hydrochloric acid or, if that is impossible, in aqua regia or nitric acid and the nitric acid expelled by heating until all nitric fumes are gone. The amount of iron present must be less than .0001 gram per c.c. and less than half this concentration is better. The color concentration of ferric chloride reaches its maximum when there is present 28 percent hydrochloric acid, so it is only necessary to make our solution more concentrated than that to have the uniformity of color desired. The presence of free chlorine will not interefere but nitric acid or its oxides will and for that reason it is necessary to remove every trace of nitrate if nitric acid was used in the dissolving of the sample. If copper is present it must be removed by hydrogen

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[1] Z. Anorg. Chem., *86*, 341.

sulfid as its chloride, when water of crystallization is not present, has the same color as iron. Manganese does not interfere and the method is therefore applicable to the analysis of iron in the presence of that substance and to the testing of manganese precipitates for iron. In such a dilute solution any small amount of cobalt or nickle will not produce sufficient color to cover up the results. If other substances with a red or yellow color are present the metals which will precipitate with ammonia may be separated by the addition of a slight excess of that reagent. The precipitate of hydroxides may then be dissolved in concentrated hydrochloric acid and tested as the sample.

The iron standard is best made up by dissolving one gram pure iron wire or such a weight of an impure iron that it is known to contain exactly one gram of pure metal. This is dissolved in nitric acid, hydrochloric acid added, and taken to dryness three times. In that way all trace of nitrate will be removed. The residue after these ignitions is made up to one hundred c.c. with concentrated hydrochloric acid. Ten c.c. of this solution is made up to one liter with concentrated hydrochloric acid and furnishes the standard for comparison. This standard contains .0001 gram Fe per c.c. The results may be obtained either by the dilution method, using concentrated hydrochloric acid for the dilution, or by the balancing method. On account of the cost of hydrochloric acid if a considerable number of tests are being run it is best to adopt the latter method.

METHOD C. IRON BY POTASSIUM FERROCYANIDE.

Lunge[1] recommends that for some cases the blue color produced by the action on ferric iron of potassium ferro-

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[1] Technical Methods of Chemical Analysis, Lunge.

cyanide is the most convenient method of analysis for iron. This method may be used to determine the ferric iron in the presence of ferrous or it may be used to determine the entire iron content. In the latter case the solution must first be oxidised with permanganate to bring all iron present to the ferric condition. Owing to the intensity of the color developed this method is only applicable to the determination of traces of iron as, for example, in water.

The solution to be tested should be suitably concentrated or diluted so that the iron content will approximate .000002 gram iron per c.c. The standards used are the same as those for method A. Ferrous ammonium sulfate [$FeSO_4(NH_4)_2SO_4$, $6H_2O$], .1473 gram if the result is to be determined as Fe_2O_3 or .1405 gram if the result is to be determined as Fe. In either case the salt is dissolved in water, five c.c. concentrated sulfuric acid added, and the solution oxidised to the ferric condition by permanganate. The solution is then diluted to one liter. Ten c.c. of this are pipetted out, ten c.c. potassium ferrocyanide [$K_4Fe(CN)_6$] added and the whole diluted to 100 c.c. This standard now shows the characteristic color reaction and contains .000002 gram Fe or .000003 gram Fe_2O_3 according to the weight taken.

For the test five c.c. of potassium ferrocyanide are added to fifty c.c. of the solution to be tested and this sample then compared with the standard mentioned above by dilution or by balancing. These methods are more applicable to the particular conditions of this experiment than are the other two.

METHOD D. IRON BY SALICYLIC ACID.

Ferric iron in reaction with salicylic acid produces an amethyst coloration, but ferrous iron produces no color.

This reaction[1] is therefore applicable to the determination of ferric iron in the presence of ferrous when the sample can be so chosen as to come within the limits of test by this method. The color will be too intense for satisfactory work if the sample contains more than .0002 gram of iron, the color may be detected if as little as .00001 gram of ferric iron is present. The method is applicable to the analysis of salts for impurity except in the presence of the following, which interfere with the test: phosphates, fluorides, thiosulphates, sulphites and bisulphites. The presence of free mineral acid also interferes with the test and it is therefore necessary that such be absent, preferably by the solution of the original sample in water, if that is not possible then by the neutralization of the acid by ammonium hydroxide after solution is complete.

The sample, if possible, is dissolved in twenty c.c. of pure water and any turbidity, the cause of which is known to contain no iron, is filtered out. If it is necessary to dissolve the sample in acid as dilute hydrochloric acid as possible is used, and the free acid after solution is complete, is neutralized with ammonia, taking care that an excess of the ammonia is not added as that would precipitate the iron. There should not be more than twenty c.c. of the solution after neutralization. If the sample to be tested contains organic matter it may be necessary to heat to dryness with nitric acid and ignite to remove such organic matter. If all the iron content is desired the sample is next oxidised with permanganate so that all iron is in the ferric condition. For this it may be necessary to slightly acidify the solution with sulfuric acid and later bring it back to neutrality after the oxidation. If only the ferric iron is to be determined this step of oxidation is omitted. Five c.c. of salicylic acid solution

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[1] Adapted from Method of W. S. Allen as given by W. W. Scott.

are now added and comparison made. Because of the fading of the color by exposure to light[1] it is not advisable to make up a series of standards but rather the test should be made by dilution or balancing. The use of the duplication method is also inadvisable since for the carrying out of it considerable time is required and fading may occur during that time.

A convenient standard is made by dissolving in water .0864 gram pure ferric ammonium alum [$Fe_2(SO_4)_3$ $(NH_4)_2SO_4$, $24H_2O$] with the addition of two c.c. of concentrated sulfuric acid and diluting accurately to one liter. This solution contains .00001 gram Fe per c.c. or .000014 gram Fe_2O_3. For the use of this standard twenty c.c. or other suitable quantity may be accurately measured out from a burette and five c.c. salicylic acid added just before it is used.

Method E. Iron as the Sulfid.

The determination of iron as the sulfid in alkaline solution is particularly applicable to the testing of drinking water but may be adapted to any test for ferrous iron in the presence of ferric, or to the analysis for the total iron content of a solution by the reduction of the iron content to the ferrous condition. If the test is to be made of water it is best made immediately after taking the sample. If the test[2] is not to be made at once it is necessary to add a few drops of hydrochloric acid and ten c.c. hydrogen sulfid water to a sample of not over one half liter and cork the bottle tightly at once. By the use of these preservatives the oxidation of ferrous to ferric iron may be prevented. The sample should have an iron content between .0015 and .0003 gram per liter.

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[1] Schreiner and Ferris, J. A. C. S., *26*, 961.

[2] Technical Methods of Chemical Analysis, Lunge.

If the amount of ferrous iron exceeds this the solution may be diluted, if the iron content is less than the prescribed limits the results may be attained by the use of a larger volume of solution than specified for the test.

For the determination of the entire iron content of a sample of water or of some solid substance dissolved in water or acid, the solution is evaporated to dryness with a small amount of hydrochloric acid and potassium chlorate. The residue is dissolved in warm water with the addition of a few c.c. of hydrochloric acid and five c.c. of hydrogen sulfide water. This solution is first filtered to free from sulfur clots and then diluted to 100 c.c. This is then treated the same as the entire solution would have been if analysis was being made for ferrous iron only.

A standard is made up by the solution in a liter of water saturated with hydrogen sulfide of .7022 gram of ferrous ammonium sulfate $[FeSO_4(NH_4)_2SO_4,\ 6\,H_2O]$ with the addition of one c.c. of sulfuric acid. This solution must be kept well corked and, if the gas gets free to such an extent that the bottle no longer smells of it, the liquid must be recharged. This standard contains .0001 gram ferrous iron per c.c.

The comparisons are made in plain glass cylinders by the method of duplication. The sample is 100 c.c. of the solution to be tested, a blank is run of 95 c.c. of distilled water. To each, sample and blank, is added five c.c. of an aqueous solution of hydrogen sulfid and two drops of ammonia. The standard solution is then added to the blank drop by drop until the colors of the two solutions are approximately equal. The color of the standard will show more of a brown hue than that shown by the sample and it is therefore necessary to decolorize the standard with a few drops of hydrochloric acid and then renew the color by the addition of a few drops of ammonia. The color which comes back will be the same sort of a brown as that shown by the sample. More standard can then be added to the blank if necessary in order to bring it to the point where the colors of the sample and standard are identical.

If extreme accuracy is desired the standard may again be decolorized and should come back by the addition of a few drops of ammonia to identically the same color as the sample.

Method F. Iron by Acetylacetone.

The principal objection to the tests for ferric iron with salicylic acid and potassium sulfocyanate already given is that they fade in the bright light necessary for the comparison of colors. This test has as its merit the nonfading of the results. The color produced[1] varies with the amount of free acid present and therefore the solution should not contain any appreciable amount of free acid. The solution to be tested, whether a sample of water or some substance in solution, is evaporated to dryness on the water bath and a few drops of sulfuric and nitric acids added to the residue to remove any organic matter present. If much iron is present the dilution will be carried to a considerable degree and the amount of acid used will not matter but if only a very slight amount of iron is present it may be necessary to heat and drive off most of the acid before adding water, in order that the acid may not be too strong. The range of greatest accuracy is between .0006 gram and .00005 gram; the sample should therefore be so diluted that fifty c.c. will contain an amount of iron somewhere between these limits. The

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[1] Pulsifer, J. A. C. S., *28*, 967.

dilution should be to 100 c.c., 500 c.c., or 1000 c.c., in order that the results may then be figured by aliquot parts.

The sample used is fifty c.c. of the solution above, to which there are added two c.c. of acetylacetone solution. The best method of completing the analysis is by the addition of a standard to a blank of 45 c.c. of distilled water and two c.c. of acetylacetone solution. The standard should consist of .1405 gram ferrous ammonium sulfate [$FeSO_4(NH_4)_2SO_4$, $6H_2O$] dissolved in water, oxidised with potassium permanganate to the ferric condition and made up to one liter. This standard contains .00002 gram of iron per c.c. The method of balancing is not applicable to this test as the color produced does not conform to the necessary laws. If a considerable number of tests are to be made it may be well to make up a series of standards from the standard solution already mentioned, using two to thirty c.c. of the solution at two c.c. intervals. For the determination of a few tests or for experimentation as to its applicability to a given use the method of dilution is easiest to arrange. The standard previously mentioned is further diluted by the dilution of ten c.c. to fifty with the addition of two c.c. of acetylacetone. This new standard for the dilution method contains .000004 gram iron per c.c.

METHOD G. IRON BY DIMETHYLGLYOXIME.

The red coloration produced by this reaction is very distinctive and permits of the estimation of the iron within an accuracy of one half percent of the metal present in the solution. The iron present[1] in the solution for this test should be between .00001 and .00006 gram per c.c. The presence of large amounts of aluminum and zinc must be avoided.

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[1] Z. Anorg. Chem., *89*, 401.

To the sample of fifty c.c. of the solution to be tested there is added one gram of hydrazine sulfate [$N_2H_4H_2SO_4$] and five c.c. of a saturated solution of dimethylglyoxime in ethyl alcohol and the solution heated to boiling. Add ten c.c. of a 25 percent ammonia solution and continue the boiling for one half minute. Cool the solution rapidly and dilute to 100 c.c. for comparison. The comparison is carried out by any of the usual methods.

As a standard the one prepared for methods A and C is satisfactory. This consists of .1473 gram of ferrous ammonium sulfate dissolved in water, five c.c. concentrated sulfuric acid added, oxidised with permanganate and made up to one liter. This solution contains .00003 grams Fe_2O_3 per c.c. For the method of duplication this standard is added to seventy-five c.c. of pure water in a tube similar to that containing the sample, after the dimethylglyoxime has been added to the blank in the same proportions as to the sample. The amount of standard necessary to bring the blank to the same color as the sample when it is of the same volume is the measure of the iron present in the sample. For a series of standards varying amounts of the standard are used and, after the addition of the same reagents as to the sample, each is made up to 100 c.c. For the method of dilution ten c.c. of the above standard are made up to 100 c.c. with the addition of the above reagents and tested as usual. As a standard for the balancing method it will be necessary to dilute a greater quantity of the standard, 25 c.c. diluted to 250 c.c. will be ample. The latter two standards after dilution contain .000003 gram Fe_2O_3 per c.c.

CHAPTER FIVE.

DETERMINATION OF COPPER.

ALTHO not so widely distributed a metal as iron a great deal of work has been done on the determination of copper to afford methods both rapid and accurate taking into account the many interferences apt to occur. The seven methods now in use follow.

METHOD A. COPPER BY AMMONIA.

The copper salt of nitric or sulfuric acid dissolves in ammonia giving an intense blue color which is proportional in intensity to the amount of copper present in the solution.[1] This method is particularly applicable to the determination of traces of copper in ores and slags soluble in nitric acid but is also useful in the analysis of salts containing a trace of copper as impurity. Nickel, cobalt, and manganese[2] interfere with the test so that in their presence the solution requires special treatment. In the presence of this interference the metals of the first two groups are precipitated by hydrogen sulfid in acid solution and filtered out. This precipitate of sulfids is washed and redissolved in nitric acid and this solution treated as tho it were the original. In the absence of fourth group metals the precipitation mentioned above is omitted.

The sample is chosen of from one tenth to ten grams according to the approximate copper content, the sample being so chosen as to include between .001 and .01 gram

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[1] Sutton, Volumetric Anal.

[2] Lunge, Tech. Meth. of Chem. Anal.

of copper. The sample is dissolved in nitric acid or, if it dissolves readily in water, the solution is strongly acidified with nitric acid, and placed in a bottle or comparison cylinder. Twenty c.c. of ammonia are then added and the solution diluted to 100 c.c. If the solution should be so strong that it was not neutralized by the twenty c.c. of ammonia mentioned a greater amount should be used until the ammonia has redissolved the precipitate first formed on its addition. Comparison is now made by one of the methods given in Chapter Two.

A standard solution is prepared by dissolving in nitric acid, .5 gram pure copper and diluting the solution to 500 c.c. If it is desired to prepare a series of standards these are made up by using from one to ten c.c. of this solution. The standards should each have twenty c.c. of ammonia added and be made up to 100 c.c. in bottles similar to the one in which the comparison is made. For the method of duplication seventy c.c. of water and twenty c.c. of ammonia furnishes the blank to which is added the standard specified above. This standard contains .001 gram copper per c.c. If a series of standards are used it will be necessary to renew them once a month as, altho they do not fade in the light, the ammonia present forms a flocculent precipitate with the glass after a time. A standard for the dilution or balancing methods is made up by diluting ten c.c. of the solution above to one liter with fifty c.c. ammonia and 940 c.c. water. This standard contains .00001 gram copper per c.c.

Experiment has shown that the greatest delicacy of test is given when the solution contains .00001274 gram copper per c.c. and that the addition of .000000016 gram copper can be detected at that concentration. It is with this experiment that the greatest amount of study as to the delicacy of given reactions has been made.

In some cases it may be found desirable to use the sulfate rather than the nitrate for the foregoing procedure. In case sulfuric acid is used for acidifying the sample the standard solution used must also have been acidified with sulfuric acid since, tho both the nitrate and sulfate of copper dissolve in ammonia with a deep blue color, the colors of the two for the same amount of copper are not the same.

METHOD B. COPPER AS THE CHLORIDE IN CONCENTRATED ACID.

If no other metals whose chlorides are also deeply colored are present the concentration of a copper solution may be told, if over thirty percent hydrochloric acid, by the intensity of the yellow color produced.[1] The actual intensity of the color reaches its maximum at an acid concentration of 28 percent and after that remains constant but in order to assure the full depth of color the concentrated acid is used. Free chlorine does not interfere but nitric acid or the presence of any of the nitrous oxides does and these must therefore be removed. Cobalt or nickel will have very little color in the concentrated acid solution unless the amount of them is very great. Manganese does not interfere. If nickel, cobalt or iron are present in quantities great enuf to color the solution the sulfid may be precipitated in acid solution and redissolved, thus getting rid of the disturbing factors quoted. Second group sulfids have no effect except those of the noble metals. Minute amounts of organic matter may produce a yellow color and if present must be burned out before dissolving in acid. Iron has a yellow coloration which is to that of copper as nine to five.

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[1] Huttner, Z. Anorg. Chem., *86*, 341.

For the test a sample is selected such that it contains about .1 gram or .01 gram copper. This sample is dissolved in hydrochloric acid directly if possible but such a solution is not usually possible. In case the sample does not dissolve in hydrochloric acid readily it is dissolved in nitric acid or aqua regia and hydrochloric acid added to the solution. This is evaporated to dryness, more hydrochloric acid added and the process repeated. After repeating the drying a third time the dilution is made with concentrated hydrochloric acid. If the sample was of one tenth gram of copper the sample is diluted to one liter, if the sample was of .01 gram copper it is diluted to 100 c.c. A standard is similarly prepared by the solution of .5 gram pure copper in nitric acid and subsequent expulsion of the nitric acid by the use of hydrochloric acid, as directed for the sample. This standard is finally taken up with dilute hydrochloric acid and diluted to 500 c.c. with concentrated hydrochloric acid. This standard contains .001 gram copper per c.c. Because of the concentrated acid used it is not advisable to try to keep permanent standards. The test may be made by dilution or balancing, if by dilution concentrated hydrochloric acid is used for the dilution.

This method is as accurate as the ammonia method and is much easier to apply in some cases. Fifty c.c. of the diluted sample is usually convenient for analysis by the dilution or balancing methods.

METHOD C. COPPER BY SALICYLIC ACID.

The color produced by copper with salicylic acid may be used for the quantitative determination of the copper present altho the color produced is not permanent. The presence[1] of free mineral acids, citric and tartaric acids,

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[1] Zeitsch. Untersuch. Nahr. Genussm., *22*, 727.

and more than a trace of iron, prevent the use of this test. An amount as small as .00001 gram of copper may be detected and estimated by this method.

The comparisons are always made against a series of temporary standards made up at the time of the experiment. A standard copper solution is made up by solution of .3928 gram of copper sulfate ($CuSO_4$, $5H_2O$) in water and making up to one liter. Of this standard amounts varying from one tenth to one c.c. are placed in plain test tubes and the sample in solution in about ten c.c. of water is placed in a similar plain test tube. The standards are each diluted to the volume of the sample, ten c.c., or if convenient a five c.c. sample may be used and dilution made to five c.c. There is then added to each of the tubes five drops of a two percent solution of potassium nitrate and five drops of ten percent acetic acid, then three c.c. of a one half percent solution of salicylic acid in dilute alcohol. The tubes are next heated to boiling in a water bath for three quarters of an hour. The reading of the sample is taken to be that of the standard to which it most nearly conforms. The standard solution for making the series of standards contains .0001 gram copper per c.c.

Method D. Copper by Potassium Ferrocyanide.

The amount of copper[1] in dilute solutions may be determined by the intensity of the purple-brown color produced in reaction with potassium ferrocyanide. The test is rendered more delicate by the addition of ammonium nitrate, ammonium chloride or potassium nitrate to the solution. In the presence of these salts the test will show one part in 2,500,000. Lead forms a white precipitate

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[1] Sutton, Volumetric Analysis.

with the ferrocyanide but unless the lead is in greater excess than it might be expected to be in such a solution the small amount of precipitate will be negligible. The solution in which the test is to be made must be exactly neutral; if it is acid the color produced will turn to an earthy brown, if alkaline the color will be partly dissolved and removed by the alkali. In the presence of large amounts of iron the solution may be rendered alkaline with ammonia and the iron filtered out for use in the determination of iron if one is to be made.[1] If the iron hydroxide is of large volume it may be well to dissolve in acid and reprecipitate to recover copper carried down with the precipitate the first time.

The sample is so chosen as to contain between .005 and .00005 gram copper.[2] If the sample is a solid, difficulty soluble, it is dissolved in nitric acid and the solution boiled until the excess of acid has been expelled. Five c.c. of sulfuric acid are then added and the solution boiled again. Filter, wash the precipitate with warm water and take the combined filtrate and wash water for the test. The sample, if acid, is rendered slightly alkaline with ammonia and the solution then boiled until the excess has been removed. Five drops of a 1:35 solution of potassium ferrocyanide are then added to the sample and the test made by duplication or dilution.

The standard is made up by the solution of .3928 gram of pure copper sulfate ($CuSO_4$, $5H_2O$) in water and dilution to one liter. This standard contains .0001 gram copper per c.c. For use with the method of duplication the sample is diluted to 50 or 100 c.c. If the latter is the case it may be advisable to divide the solution into two parts and use one for testing. The blank is prepared

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[1] Jour. Ind. Eng. Chem., *7*, 1035.

[2] Mining Sci. Press, *114*, 624.

by adding five drops of ferrocyanide solution to thirty-five c.c. of pure water and five c.c. of ammonium chloride solution in a tube similar to that containing the sample. The standard mentioned above is then run in until the color of the sample is duplicated and the volumes cautiously equalized as described for this method of determination. The color produced is not satisfactory for the balancing method and fades too soon to make the use of a series of standards practicable. For the method of dilution ten c.c. of the standard are diluted with twenty-five c.c. of water, five c.c. of ammonium chloride and five drops of ferrocyanide and made up to fifty c.c. The standard if darker in color is now diluted until the colors match, and the results figured.

In some cases for the purpose of concentrating the solution the copper may be precipitated with aluminum foil and the precipitate gathered and dissolved in nitric acid after which the procedure is carried on as before.[1]

METHOD E. COPPER AS THE SULFID.

A trace of copper in solution may be determined by the formation of the colloidal sulfid and the estimation of the color of the resultant brown solution by the use of a standard solution similarly prepared. The amount of copper must not be more than .00025 gram and less than half that amount is better.[2] The method is not applicable in the presence of lead but the ferrocyanide method can be used in that case and the lead determined from the same solution without separating the copper. The addition of ammonium chloride to the solution doubles the delicacy.

To the sample in solution are added a few c.c. sodium

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[1] Jour. Ind. Eng. Chem., 7, 1035.

[2] Sutton, Volumetric Analysis.

acetate, five c.c. saturated ammonium chloride solution and three c.c. concentrated nitric acid. The addition of two c.c. of hydrogen sulfid water will then produce the brown coloration. If the precipitate shows a tendency to gather in clots and settle another sample must be prepared and to this, in addition to the reagents mentioned, add five c.c. of a clear syrup, half sugar and half water. This will effectually prevent the settling of the precipitate.

The standard copper solution consists of .3928 gram copper sulfate ($CuSO_4$, $5H_2O$) dissolved in a liter of water. This contains .0001 gram copper per c.c. The tests are made by any method except that of a series of standards. The preparation of such a series even of the artificial standards is not satisfactory. For duplication the sample is diluted to fifty c.c., 25 c.c. of water are treated with the reagents for the sample and the above standard added a drop at a time. For dilution or balancing ten c.c. of the standard above are treated with the reagents specified for the sample with the exception that the amount of hydrogen sulfid water is increased to six c.c. This is then diluted to 100 c.c. and every c.c. contains .00001 gram of copper.

METHOD F. COPPER BY POTASSIUM ETHYL XANTHATE.

Small amounts of copper in solution react with potassium ethyl xanthate to produce a yellow color suitable for colorimetric examination.[1] If more than .001 gram copper is present in the sample the solution will be too strong and instead of the desired color there will be formed a bright yellow precipitate of copper xanthate. In that case the original sample chosen must be smaller and the experiment repeated. The presence of small amounts of

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[1] Scott, Standard Methods of Chemical Analysis, p. 165.

iron, lead, nickel, cobalt, zinc or manganese does not interfere. The test is one well adapted to the testing of salts for copper present as impurity.

The sample graduated in size according to the copper content is dissolved in water and diluted to 90 c.c. Ten c.c. of a solution of potassium ethyl xanthate, one gram to the liter, are then added. The yellow color appears at once. It is not advisable to make up a series of standards for the final test as after a time the copper shows a tendency to precipitate out. A standard copper solution is made up by dissolving .3928 gram of pure copper sulfate ($CuSO_4$, $5H_2O$) in water and diluting to one liter. Ten c.c. of this solution are then diluted to 100 c.c. so that it now contains .00001 gram copper per c.c. and serves for the examination by duplication. The blank contains sixty c.c. water and ten c.c. potassium ethyl xanthate solution into which the above standard is run until the colors match after which the colors and volumes are cautiously balanced at the same time. For determining the results by dilution or balancing another amount of standard must be diluted. Ten c.c. of the standard are diluted to five hundred c.c. with the addition of ten c.c. of the reagent to produce the color. This solution then contains .000002 gram copper per c.c. and is suitable for the determinations by these other two methods mentioned.

This method is applicable to the testing of substances insoluble in water by treating them with nitric acid to render them soluble. If that method is used the nitric acid must all be removed before completing the test. This is accomplished by adding hydrochloric acid and evaporating to dryness. The residue is then extracted with water and the copper will be present in the solution. If organic matter is to be removed by this ignition a few c.c. of sodium hydroxide and a similar amount of sodium or potassium nitrate are added to the solution before evaporation. The residue is then to be ignited until no more fumes are given off. Water must now be added, then hydrochloric acid and the residue again taken to dryness to remove all trace of nitrate. Since the examination is to be made in neutral or slightly acid solution the presence of any considerable amount of acid in the test solution must be avoided.

METHOD G. COPPER AS THE BROMIDE.

This method[1] is suitable for the determination of small amounts of copper present as sulfates, nitrates or chlorides. If the copper to be tested is present as some complex compound it will first be necessary to treat with concentrated acid to decompose the complex compound. The solution for the test is treated with a reagent made up as follows, 100 grams of potassium bromide are added to 150 c.c. of boiled water and the solution well shaken. This is then transferred to a 200 c.c. volumetric and diluted to the line with warm water. After cooling again bring up to the mark with cold water.

Five c.c. of the solution to be tested are used. If the sample requires more than that amount of acid or water to dissolve it, the above amount is taken from the total and the result figured by aliquot parts. For use twenty c.c. of the reagent above are precipitated by the careful addition with cooling of ten c.c. of concentrated sulfuric acid and the resultant potassium sulfate filtered off. Five c.c. of this solution are then added to the sample with two c.c. of concentrated sulfuric acid. For comparison several standards are made up by the use of a solution of .3928 gram of pure copper sulfate ($CuSO_4$, $5H_2O$) in a liter of water. The standard contains .0001 gram copper

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[1] Bull. Soc. Phar. Bordeaux, Aug.–Dec., 1915.

per c.c. These standards are reasonably permanent and so may be kept for some time. The ease with which the production of new standards may be carried out renders their use, after there is any doubt of their accuracy, unnecessary.

The reagent used is unstable and must be kept in brown glass and in a dark place. Renewal not less than twice a month is advisable, making up smaller amounts at a time if desirable.

CHAPTER SIX.

CARBON IN STEEL.

This is one of the best worked out and most used methods of colorimetric analysis, finding use as ordinary procedure for rapid determination of the carbon content of steels in most works laboratories. The basic principle assumed for the test is that a sample of steel when dissolved in nitric acid shows a brown color which is proportional in intensity to the amount of carbon present in the sample. The errors that enter into the determination of carbon by this method are these; only the carbon present in the form of carbide is transformed to this brown color, the composition of the brown coloration is not constant, presence of many impurities will cause colors which interfere. The carbon present in the steel as graphite, as it is apt to occur in high carbon steels, is not acted on by acids at all. In that case the flakes of carbon will be visible in the solution so that one may know that there is graphitic carbon present and therefore carry out a determination by the combustion method. It is sometimes assumed that in steels treated by the same identical process the proportion of graphitic carbon to carbide carbon will be the same and comparison therefore made, even of steels which do contain graphitic carbon. These results are not as accurate as those obtained by the usual colorimetric tests on steel.

Manganese, if present, lowers the apparent carbon content but may be disregarded if the amount is less than one percent. Nickel has a similar but much greater effect. If much nickel is present a green color is produced which is difficult of comparison. Over one percent of silica also produces a green color which is difficult of comparison. In cases where the presence of these substances is known, a standard should be taken which has the same content of the interfering substance as that in the sample. Comparison may then usually be made. Copper, cobalt and chromium also interfere.

From the foregoing it follows that the standard used should be as nearly as possible of the same composition as the sample. The following conditions should be met,[1]

1. Sample and standard should be made by same process.

2. Sample and standard should have same physical condition so far as this can be secured by mechanical means.

3. Sample and standard should not differ greatly in percentage of carbon.

4. Solutions of standard and sample should be made at the same time under the same identical conditions.

5. The standard used must be one whose composition is accurately known.

The tints resulting from different forms of steel are different, and cannot therefore be matched against each other, so as specified above, Bessemer steel must be tested against Bessemer steel and open hearth steel against open hearth steel. The results obtained are more accurate for mild steels than for hard steels.

Two methods are commonly used in steel works laboratories, the dilution method and the method by a series of standards. In the latter case the standards are artificially prepared from the cobalt, iron and copper solutions described in Chapter Two. In the operation of the dilution method the samples and standards are weighed

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[1] Steel Works Analysis, Arnold and Ibbotson, p. 50.

out alternately into test tubes, using .2 gram of each. To the tubes there is then added somewhat more than one c.c. of nitric acid (1:1) for every tenth of a percent of carbon supposed to be present in the steel. The color produced will be darker than it should be if too little of the reagent is used but an excess of acid may be added without causing any considerable change in the color. The test tubes are then placed in a special rack in the water bath. If the carbon content of the sample is under one percent it should go into solution in less than half an hour. A paraffine bath at 120 to 150 degrees may be used to hasten solution. Johnson[1] suggests a sand bath at 190 degrees and recommends that the tubes be grouped in bunches of six and each bunch covered with a beaker to prevent too rapid evaporation of the acid. If a temperature greater than 100 degrees is to be used it is advisable to allow for it by the addition of excess acid. Tubes should never be immersed in the heated medium below the level of the top of the liquid as a deposit of iron oxide will form. It is always best to add a hollow glass bead to each test tube after putting in the acid. This will float on the surface of the liquid and prevent the formation of a film of iron oxide.

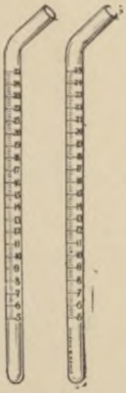

FIG. 13. Bent Graduated Tubes

For convenience in keeping the samples separated it is well to have a number scratched on the outside of each test tube ordinarily used for this work. The number of the test tube used for the sample may then be recorded beside the weight when samples are weighed out. This

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[1] Chemical Analysis of Special Steels, Steel-making Alloys and Graphites, Johnson.

is somewhat more satisfactory than gummed labels as the later are apt to be steamed off. The samples are removed from the heating medium as soon as it is seen that everything has been dissolved, and cooled by plunging in cold water. If solution is made by heating on a water bath no harm is done by allowing the sample to stay in the bath two or three minutes after the solid matter is all dissolved.


FIG. 14. Color Camera

The solution now shows a brown coloration which is diluted by the addition of two volumes of water to the cooled solution. This coloration is considered to be due to some variable organic compound which at first is to be seen as a precipitate in the solution and is dissolved by heating.[1] Another experimenter finds that as much as .03 percent of the carbon may be present as CO and CO_2 and therefore not show in the results.

If the sample is to be tested by dilution this is usually carried out by use of the camera described under apparatus. Since the weights of sample and standard used are identical the results are easily figured. The solutions[2] must be cooled below fifty degrees for this comparison, otherwise the iron will show color enuf to hide the results. The use of ferric nitrate for dilution is sometimes advised since the solutions are of that salt. Scott and Johnson recommend the use of tubes bent at the top, for the comparison, so that the water can be added to the sample or standard to be diluted and mixed by a gentle

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[1] Levy, Analyst, *37*, 392.

[2] Ann. Chim. Anal., *22*, 193 and 225.

rocking motion without danger of spilling. The manufacturers furnish both straight and bent graduated tubes for this purpose. The sample is carefully washed from the original test tube into one of these tubes and the standard into another and comparison made.

Experiments with the balancing instruments seem to show that because of the nonpermanence of the color obtained by this method the use of that type of instrument is not advisable. The duplication method is of course impossible. Standards and samples should be protected from light at all times as far as possible, as they fade with exposure. Phosphoric acid is sometimes added to the sample before dilution.

For convenience in dilution several little helps have been worked out. The standard may be diluted to a volume depending upon its carbon content, such as 6 c.c. for .6 percent carbon and the sample when diluted to an equal color will then give its carbon content by direct reading from the scale. When this is not done it is common to find an operator adding water, two tenths of a c.c. at a time, until the solution being diluted either equals the one which was lighter or has become lighter than the other solution. If the two colors are identical of course that reading is taken but if the solution has now been diluted to less than the color of the other the reading is taken as one tenth c.c. less than that shown by the scale, or what would have been the reading if the last addition had been of one tenth instead of two tenths c.c.

Samples for comparison with a series of standards are similarly prepared and washed into containers the same as those containing the standards.

CHAPTER SEVEN.

LEAD, BISMUTH AND ARSENIC.

THE presence of these substances is important particularly in food products because all are poisons. Lead is apt to occur as an impurity in many places, notably in water supplies not properly taken care of. Bismuth and arsenic are not so apt to be found as natural contaminations but the determination of small amounts of either is a problem often apt to arise thru their use as drugs.

LEAD AS THE SULFID.

A small amount of lead in solution on the addition of hydrogen sulfid will not precipitate but produces a brown coloration due to the presence of the colloidal sulfid in the solution.[1] If nitric acid is present the color will not appear unless sodium acetate is added to the solution. In a solution containing hydrochloric acid, sodium acetate must be added before the hydrogen sulfid or the solution will become turbid on the addition of the latter. The amount of lead in the sample must be between .00025 gram and .000005 gram. If the test is for a contamination in water the sample may be suitably concentrated or diluted; if the test is of an ore or an alloy for the lead content the operator may be governed in his choice of a weight of sample by the above conditions.

The sample, if a solid, is dissolved in twenty c.c. of nitric acid, the excess of acid boiled off and the solution made up to fifty c.c. If the sample is of water fifty c.c.

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[1] J. Chem. Soc., 97, 841.

are taken. Add a few drops of sodium acetate solution and, if the solution is not already strongly acid, acidify with two or three c.c. of nitric acid. The color will appear upon the addition of two c.c. of a solution of hydrogen sulfid. Comparison is then made with a standard. If the color produced shows a tendency to fade due to the presence of particles of precipitate the operation must be repeated on a new sample adding in addition to the above reagents, ten c.c. of a strong sugar syrup, which must be fresh and clear. This will prevent the formation and deposition of the precipitate.

Since the color of the sufid fades in the light the use of the natural series of standards is not satisfactory. The directions already given for artificial standards admit of the production of such standards where numerous tests are to be made by this method. The dilution and balancing methods are also applicable. As a standard dissolve .1598 gram of pure lead nitrate [$Pb(NO_3)_2$] in water and dilute to one liter. This standard contains .0001 gram lead per c.c. Amounts from one tenth to ten c.c. of this may be used to make up permanent standards by mixing the cobalt, iron and copper solutions specified so as to duplicate the color produced. If it is desired to use the duplication method this solution is run a drop at a time into 45 c.c. of water containing the same reagents as were specified for the sample. A standard for the dilution and balancing methods is made by adding to ten c.c. of the above solution, 900 c.c. of water, five c.c. sodium acetate solution, ten c.c. concentrated nitric acid and five c.c. of hydrogen sulfid water. This is then made up to one liter, so that the lead content will be exactly .000001 gram per c.c.

This test[1] is hindered by the presence of any consider-

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[1] J. Soc. Chem. Ind., *28*, 636.

able amount of iron. This cannot be precipitated by rendering the solution alkaline and filtering off the resultant precipitate since the ferric hydroxide will carry down with it the lead present in the solution. The obstruction caused by the iron may be overcome by adding sodium thiosulphate to reduce the iron and then a few c.c. of sodium or potassium cyanide. A colorless compound of the ferrous iron with the cyanide is formed and the lead may then be treated with sodium acetate and ammonium or hydrogen sulfid without rendering the solution acid.

It is often desirable to determine lead in the same solution in which copper is determined. This is accomplished by determining the copper by the potassium ferrocyanide method, then adding a few drops of potassium cyanide, which will remove the red color leaving the solution a light green, and determining the lead as the sulfid in the alkaline solution by the method given above. In case of the use of the latter procedure it is advisable to use the dilution or balancing methods and to prepare a special standard for the test, adding to it approximately the same amount of copper per c.c. as is present in the sample and treating it in the same way.

BISMUTH AS THE IODIDE.

A solution of bismuth in dilute nitric or sulfuric acid when acted on by potassium iodide assumes a yellow color due to the formation of bismuth iodide, which color is proportional to the bismuth content and therefore suitable for colorimetric examination. The solution must be free from large amounts of lead, copper, tin, antimony, gold and silver.[1] This is accomplished by precipitation.

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[1] J. Soc. Chem. Ind., *27*, 102.

Arsenic, copper and iron cause the results to be too high if they are present. The presence of hydrochloric acid and ammonium chloride is also to be avoided for the opposite reason. The weight of sample chosen must not contain more than .00015 gram bismuth.[1] This method is suitable for the estimation of bismuth present anywhere in small quantities as, for example, in impure copper.

The sample is dissolved in a small quantity of nitric acid and the bismuth precipitated by the addition of an excess of sodium carbonate. This will precipitate not only the bismuth but also a considerable volume of precipitate of other metals. This precipitate is filtered off and a qualitative test made on the filtrate to find out if the bismuth has all been removed. If not it must be allowed further time to precipitate. In exceptional cases it may take as long as five hours for this first precipitation to be complete. This may be somewhat hastened by stirring or shaking. The precipitate is well washed and redissolved in nitric acid. Five c.c. of lead nitrate are added, the solution nearly neutralized by the addition of ammonia and ammonium carbonate added to slight excess. The subnitrate of bismuth will be precipitated reasonably free from other metals. If this seems too impure on first precipitation it may be redissolved in nitric acid and reprecipitated. This purified precipitate is finally carefully dissolved in nitric acid, washing all parts of the paper with dilute acid. If the solution from which this last precipitation was made shows a high color due to copper a few c.c. of potassium cyanide are added before precipitation, to decolorize the solution. If the volume of the solution of the final precipitate in nitric acid is greater than 25 c.c. it is concentrated to approximately that volume. Ten drops of sulfurous acid are now added

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[1] Eng. Mining J., *104*, 1091.

and five c.c. of a solution of potassium iodide, 17 grams to the liter. The color is then tested as desired.

The color produced is permanent and a series of standards may be produced. A standard may be made up by dissolving .2327 gram bismuth nitrate, $[Bi(NO_3)_3, 5H_2O]$, in dilute nitric acid and making up to one liter. A similar standard may be made up by dissolving .1 gram of pure bismuth in nitric acid and diluting to one liter. Sufficient acid must be added to this solution in diluting it so that the bismuth does not precipitate out as the subnitrate. These standards will each contain .0001 gram bismuth per c.c. This standard may be used for making up the permanent standards or it may be added to 18 c.c. water and five c.c. nitric acid, treated with sulfurous acid and potassium iodide, and the result obtained by the duplication method. For dilution or balancing it is necessary that the standard be further diluted. For this purpose fifty c.c. of the standard are treated with ten c.c. concentrated nitric acid, 800 c.c. water, 25 c.c. potassium iodide solution and five c.c. sulfurous acid and diluted to one liter. This standard then contains .000005 gram bismuth per c.c.

METHOD A. ARSENIC BY THE STAIN PRODUCED ON MERCURIC BROMIDE PAPER BY ARSIN.

In the determination of arsenic by this method the arsenic is reduced to arsenious acid and then, by treatment in a hydrogen generator, to arsin. The arsin is led over paper treated with mercuric chloride or better with mercuric bromide[1] and the stain produced compared with stains produced by standard amounts of arsenic. Sulfid, phosphoric acid and antimony compounds interfere. The first two may be removed by oxidation with nitric acid. When antimony is present the arsenic may be

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[1] U. S. Dept. of Agriculture, Bureau of Chem., Bull. No. 102.

removed from the solution by precipitation with magnesium phosphate and filtration, but this method is not to be recommended. If results show that antimony is present it is advisable to concentrate a large amount of substance and carry out the determination by gravimetric methods.

Iron is necessary for the success of the experiment so if the sample is iron-free this is added in the ferrous condition before reduction of the arsenic.[1] This reduction is accomplished by heating near boiling in a 10 percent hydrochloric acid solution with potassium iodide and a few c.c. of stannous chloride. The stannous chloride is to take up any iodine freed. It is possible to reduce arsenates to arsenious acid by the action of the nascent hydrogen in the hydrogen generator but this is very difficult and the reduction previous to their introduction to the generator is recommended.

The generator consists of a one or two ounce wide mouthed bottle. An upright tube fifteen centimeters in length is attached to this, which tube is divided into two chambers. The upper chamber is filled with cotton moistened with a five percent solution of lead acetate, the lower chamber is filled with strips of lead acetate paper. To the top of this tube is attached a capillary tube 3 mm. in diameter and 12 cm. long. The lead acetate is for removing hydrogen sulfid, which would also stain the paper used. The sample chosen for analysis, which must contain less than .00004 gram of arsenic is dissolved in acid and reduced as previously mentioned. This is then introduced into the generator after it has run blank for one hour with 40 c.c. one : four sulfuric acid and four or five drops of stannous chloride dissolved in hydrochloric acid and approximately ten grams of arsenic-free zinc.

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[1] Orig. Com. 8th Inter. Cong. App. Sci., *1*, 9.

The arsin evolved produces a characteristic stain on the prepared paper suspended in the capillary tube, a deep orange stain of varying length shading sharply to a light yellow and then to the untouched paper.

For this paper the U. S. Dept. of Agriculture bulletin previously quoted recommends that mercuric bromide be used, since it does not require that it be developed if the results are to be preserved. Other authorities recommend the use of mercuric chloride. Strips of heavy drafting paper, 2.5 mm. by 12 cm., are used. These are soaked in a five percent solution of the salt for an hour, the excess of solution squeezed out and then hung up to dry.

A standard is prepared by dissolving .1320 g. arsenious oxide (As_2O_3) in sodium hydroxide, partially diluting to one liter, acidifying with hydrochloric acid, and completing the dilution to one liter. This is too strong and ten c.c. of this solution are now to be diluted to 250 c.c. This solution will then contain .000004 gram arsenic per c.c. Standards are to be prepared at intervals from .000001 to .00005 gram arsenic. These are prepared in identically the same manner as that specified for the sample and are suitable for keeping for six months if the bromide is used but will fade after a week or ten days if the chloride is used. The different amounts of arsenic present are shown by the differing lengths of the orange stain. If the stain produced has been contaminated with antimony it will be longer and lighter in color than the standard. This may be confirmed by exposing the stain to the fumes of hydrochloric acid. A stain from antimony will fade on exposure while an arsenic stain will be intensified.[1] It has been recommended that instead of zinc in the generator, arsenic-free iron be used for the production of hydrogen. This will produce[2] the

[1] Disc. 8th Inter. Cong. App. Sci., *27*, 4.

[2] Svensk, Farm, Tiskrift, *17*, 468, 491.

desired arsine (AsH_3) but not the undesirable stibine (SbH_3) or phosphine (PH_3). The use of a small amount of stannous chloride in the generator serves to sensitize the zinc. The generator must be so standardized that the production of hydrogen is uniform, both while producing the sample stain and the standard stains. If the sample contains organic materials it must be so treated that these will not interfere with the production of hydrogen at the desired rate. More than a trace of fluorine must be eliminated from the sample before testing.

METHOD B. ARSENIC BY SILVER NITRATE.

In this modification[1] of the previous method the arsenic is treated as before and passed thru the tubes with lead acetate paper but instead of the use of mercuric bromide paper the gas is then passed thru a tube containing a few crystals of silver nitrate. The black stain produced by the arsenic on these crystals is to be compared with stains produced by known amounts of arsenic in a similar way. The standards after production may be sealed in the tubes in which they were produced and kept indefinitely.

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[1] Compt. Rend., *158*, 869.

CHAPTER EIGHT.

ALUMINUM AND CHROMIUM.

Of the members of the third group of metals, iron was worthy of a chapter by itself, leaving us the remaining two for discussion here. Aluminum, besides its occurrence in rocks and minerals, is determined in cements and plasters. Chromium occurs in minerals to some extent but the big field of usefulness of this test for chromium is the analysis of chromesteel for the chromium content.

Aluminum by Alizarin-S.

The sodium salt of alizarin monosulfonic acid is a commercial indicator which shows purple with alkalies and yellow with acids. The coloration produced in acid solution[1] may be adapted to the determination of aluminum, the test being delicate enough for the detection of one part of aluminum in ten million parts of water. Small amounts of chromium and iron do not interfere, in the presence of large amounts of these metals it is necessary to add citric acid or a citrate to prevent them from showing. It is not advisable to render the solution alkaline with ammonia for the precipitation of the hydroxides from other substances present, as the reagents used are almost certain to contain traces of aluminum. The presence of phosphates or of moderate amounts of calcium, magnesium or zinc salts has no effect on the results. If cobalt is present the solution must never become alkaline. The sample should be chosen to contain between .00005 gram and .000005 gram of Al_2O_3.

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[1] J. Soc. Chem. Ind., *34*, 936.

The sample taken is to be dissolved in ten to twenty c.c. as dilute acid as possible or, if the sample taken exceeds the above limits, in a larger amount and an aliquot part taken. If the acid is very concentrated it should be partially neutralized so as to leave the final solution acid but not too strongly so. If the solution is made in water it is acidified. The use of nitric acid is to be avoided as far as possible since it tends to cause the color to fade more than do the other acids, altho all cause a slow fading of the color produced. Ten c.c. of glycerine are next added to the solution to counteract the tendency of the aluminum to precipitate and lastly five c.c. of a one percent solution of the reagent. The solution must stand for five minutes after which it is acidified with dilute acetic acid until no further change in color occurs, diluted to fifty c.c. and compared with a standard.

Because of the lack of permanency of the color a set of natural standards is not satisfactory and, because the solution is apt to fade more or less before the comparison is made, the use of artificial standards is not advised. The method of duplication is out of the question because it takes some time for the color to be produced after the standard comes into contact with the reagent. It is therefore better to use only the dilution method for this test, since to place the standard in the balancing apparatus for each determination would be a useless waste of time. A standard is prepared at the same time as the sample and subjected to the same conditions of temperature, etc. Any fading will then be about the same in each. As a solution for preparing the standard dissolve .9286 gram common alum [K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$] in water and dilute to one liter. Ten c.c. of this solution are then to be pipetted out and again diluted to one liter. The resultant solution contains .000001 gram Al_2O_3 per c.c. Five to twenty-five c.c. of this may be taken as necessary for the sample used and prepared as previously directed.

METHOD A. CHROMIUM AS THE CHROMATE.

Small amounts of chromium may be determined by the oxidation of the chromium to the form of a chromate. This method is particularly designed for the analysis of minerals but is also adaptable to steel analysis. The sample chosen must contain not less than .002 gram chromium as experiment shows that the error is too great in the oxidation of a lesser amount. The color may later be lessened by dilution and test of an aliquot part.

The sample is dissolved in as dilute sulfuric acid as possible and if the acid is very strong it is nearly neutralized by the addition of sodium carbonate. Concentrated sodium thiosulfate is now added to the solution, which precipitates chromium and manganese together with some other metals which will not interfere with the test. This precipitate is filtered off and dissolved in nitric acid. A few c.c. of silver nitrate are added as a catlyzer and then sodium persulfate which oxidises the chromium present to the form of the chromate. If there was manganese present in the original sample this will have been carried thru and will now be present as the permanganate. Since the color of the permanganate will cover up the yellow of the chromate it is necessary to remove the former, which is accomplished by adding ammonia and heating the solution for a short time.[1] The permanganate will be precipitated as the hydroxide and the silver as the oxide but the chromate will remain unchanged. Hillebrand recommends the addition of methyl or ethyl

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[1] Z. Anorg. Chem., *80*, 171.

alcohol to the solution to destroy the color of the permanganate.[1]

The precipitate is filtered off and if iron is present sodium phosphate is added to prevent interference from that source. The sample is then tested against a standard solution of potassium chromate (K_2CrO_4). This is made up by dissolving .2555 gram of the pure salt in water and diluting to one liter. The standard then contains .0001 gram Cr_2O_3 per c.c. The preparation of a series of standards is possible as the standard is permanent, or the sample may be duplicated by running a few c.c. of the above solution into a blank of water. The use of the above solution for dilution and balancing methods is possible or, if the sample is such that it seems to require it, 50 c.c. may be diluted to 250 c.c. and will then contain .00002 gram Cr_2O_3 per c.c.

METHOD B. CHROMIUM BY DISODIUM 1.8 DIHYDROXYNAPHTHALENE 3.6 DISULFONATE.

The analysis of steel for chromium has been simplified by the adaption of the above reagent to the use. The resultant color is pink and is so delicate that .0000008 gram of chromium can be detected. If a considerable quantity of vanadium[2] is present this produces a brown color which is apt to obscure the results. If the vanadium present is less than the chromium a correction may be introduced. Subtract from the percentage of chromium shown, one third of the percentage of vanadium as shown by a separate analysis in order to obtain the true percentage of chromium present. If the ratio of chromium to vanadium is high the error may be negligible and so can be disregarded. A correction may be introduced by using a similar amount of vanadium in the standard.

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[1] U. S. Geol. Surv., Bull. 176, p. 80.

[2] J. Ind. Eng. Chem., *5*, 298.

The sample of .2 gram is dissolved in ten c.c. dilute sulfuric acid, one half c.c. nitric acid added to oxidise the iron and evaporated to fumes. This is then cooled, slightly diluted with water, fifty c.c. of a ten percent solution of sodium hydroxide and one gram sodium peroxide added. After boiling for five minutes to destroy the excess of hydrogen peroxide the solution is cooled, diluted to 200 c.c., and filtered. Use as a sample 100 c.c. of this to which are added 2 c.c. of 85 percent phosphoric acid and two c.c. of König's reagent. The later is a one percent solution of the reagent for the test, disodium 1.8 dihydroxynaphthalene 3.6 disulphonate. The color will at once appear. For a steel low in chromium (under .15 percent), so that the color does not show up as very deep, it may be well to repeat the experiment using a .4 gram sample.

The examination may be made by the dilution method only, because of the peculiar character of the color developed and the danger of interference. The standard selected is a steel of known chromium content. The standard is treated by the same identical method as the sample.

CHAPTER NINE.

NICKEL, COBALT, MANGANESE AND ZINC.

Of the members of this group, two are commonly used in the form of alloys with steel and therefore their determination assumes vital importance in the steel industry. The other two, zinc and cobalt, are of such frequent occurrence in inorganic salts that even the occasions of their detection as impurity affords a considerable use of the methods here given.

Method A. Nickel by Potassium Thio-carbonate.

When nickel in ammoniacal solution[1] is acted on by potassium thio-carbonate a rose red to brown red is produced, suitable for colorimetric examination. Metals of the second group interfere but may be removed by precipitation with hydrogen sulfid. Manganese and iron are precipitated from the solution free from hydrogen sulfid, by bromine or hydrogen peroxide and ammonia. At the same time any cobalt present as cobaltous compounds is oxidised to the cobaltic state in which it does not interfere. Zinc forms a white precipitate with the reagent which is, however, so fine as not apt to obscure the test unless a considerable amount is present. If there is any doubt as to whether the zinc interferes a similar amount may be added to the standard. The sample should be so chosen as to contain between .0025 gram and .0004 gram of nickel.

The sample is dissolved in nitric, hydrochloric or sulfuric acid as is most convenient, altho nitric is recom-

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[1] Z. Anal. Chem., *53*, 165.

mended as ordinarily the quickest. If the sample is a salt soluble in water the solution is slightly acidified. The solution is then almost neutralized with ammonia and a solution of potassium thio-carbonate added (five c.c. is sufficient) and ammonia in excess. Comparison is made by dilution as the color is not permanent.

The standard is made up by dissolving .6730 gram of nickel ammonium sulfate [$NiSO_4$, $(NH_4)_2SO_4$, $6H_2O$] in water and diluting to one liter. This solution contains .0001 gram nickel per c.c. From one to twenty-five c.c. of this solution are treated in the same way as the solution of the sample and comparison then made by dilution. A series of standards is not permanent enuf. The solution may also be added to a blank containing the reagents, for the making up of a duplicate.

METHOD B. NICKEL AS THE CHLORIDE IN CONCENTRATED ACID.

Comparatively large quantities of nickel may be estimated by the intensity of the yellow color of the pure chloride in concentrated hydrochloric acid solution. The maximum color[1] is reached with the solution about thirty percent hydrochloric acid after which the color is constant regardless of the concentration of the acid above that point. The sample, if the ore or alloy to be examined contains from .1 percent to 10 percent nickel, is .2 gram. If the nickel content is greater than that, .1 gram will do, if less, the sample may be increased. Iron and copper must be removed. Copper is precipitated with hydrogen sulfid after which iron is oxidised to the ferric condition and precipitated as the basic acetate. There must be no nitric acid or free chlorine present, the presence of sodium chloride has no effect.

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[1] Z. Anorg. Chem., *86*, 341.

The sample of .2 gram or other weight as specified is dissolved in concentrated hydrochloric acid if possible. This will not usually be possible and the solution must then be made in nitric acid. In the latter case hydrochloric acid is added to the solution and it is taken to dryness after which more hydrochloric acid is added and the process repeated, likewise a third time. The residue is taken up with concentrated hydrochloric acid, transferred to a colorimetric tube and diluted with concentrated hydrochloric acid to fifty or 100 c.c. as is most convenient, taking into consideration the depth of color present.

Cobalt produces a color so that the correction for its presence is introduced by the use of a standard solution. The process also furnishes an estimate of the amount of cobalt present. The standards made up are 4.9556 grams of pure nickel nitrate [$Ni(NO_3)_2$, $6H_2O$] and 4.9361 grams of pure cobalt nitrate [$Co(NO_3)_2$, $6H_2O$]. These weights of the salts are dissolved in concentrated hydrochloric acid and each evaporated nearly to dryness. More concentrated hydrochloric acid is now added to each solution and the evaporation repeated, making sure that all nitric acid is expelled. The residues are taken up with hydrochloric acid and diluted to 500 c.c. each with concentrated hydrochloric acid, content .002 gram nickel or cobalt per c.c.

The determination of the nickel present in the sample, if it contains no cobalt, may be carried out by the balancing method. The making up of a series of standards is not advisable as this determination usually has two variables, the amount of cobalt solution added to the nickel solution and the amount of nickel solution which is used with pure acid. The dilution method is carried out by diluting the nickel solution with concentrated hydrochloric acid. If the sample solution shows a more or less green tinge the same tint is produced in the standard by the addition of the standard cobalt solution. The amount of this used is then a measure of the cobalt present in the sample. When the colors of the two solutions are identical the results may then be figured and by the usual proportions the weight and percentages in the sample obtained.

Caution, the nickel must always be in concentrated acid or the yellow will turn to green and similarly the cobalt must always be in concentrated acid or the blue color will turn to pink.

METHOD A. COBALT AS THE CHLORIDE IN CONCENTRATED ACID.

This method for the determination of cobalt is identical with the determination of nickel[1] which just precedes. The sample of .2 gram is dissolved in the same way and in the absence of nickel, iron and copper having been removed according to instructions given there, the test is made by dilution, using the cobalt standard as directed and diluting with concentrated acid. If nickel is present sufficient is added of the standard solution to duplicate the tint in the standard, after which dilution is carried out as usual.

METHOD B. COBALT BY A-NITROSO-B-NAPHTHOL.

The red color produced by cobalt in reaction with a-nitroso-b-naphthol may be used for the quantitative determination[2] of small amounts of the metal. If more than a trace of copper is present it must be removed by precipitation with hydrogen sulfid in acid solution.

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[1] Z. Anorg. Chem., *86*, 341.

[2] Analyst, *43*, 317.

Nickel, if present, is removed by precipitation with dimethylglyoxime, after which the excess of dimethylglyoxime must be removed by evaporation to dryness and treatment of the residue with aqua regia. The aqua regia having been driven off by heating, the residue may be dissolved in hydrochloric acid and the process continued. If the amount of manganese present is in excess it must be removed by the addition of an equal amount of nitric acid to the solution and a small amount of sodium bismuthate and boiling. If the manganese is not in excess of the cobalt it may be ignored. The manganese will be precipitated by the sodium bismuthate and should then be filtered off. Organic matter is removed by the evaporation of the solution to dryness and taking up with aqua regia, evaporating to dryness again and igniting, after which it is dissolved in concentrated hydrochloric acid and diluted for analysis. The addition of ammonium citrate prevents the interference of metals other than those mentioned above. The sample should be so chosen as to contain .002 gram to .00005 gram cobalt.

The sample chosen according to the above limits is dissolved in concentrated hydrochloric acid, the total volume of solution being about 25 c.c. Any of the interfering metals whose removal is necessary are removed, and the solution is then ready for treatment with the reagent. The pure solution of the reagent does not keep satisfactorily but by conversion to the sodium salt it becames permanent. This is accomplished by boiling .1 gram a-nitroso-b-naphthol with one c.c. caustic soda and diluting to 200 c.c. Before the addition of this to the sample the solution is nearly neutralized with ammonia and five c.c. of a solution of 500 grams citric acid in 250 c.c. of water and 500 c.c. of ammonia, added. This should have an excess of ammonia so that on addition of it the solution will become alkaline. If the solution is not slightly alkaline a small amount of ammonia is added to render it so and then diluted to nearly 100 c.c. Five c.c. of the reagent are then added and dilution to 100 c.c. completed.

A standard is prepared by dissolving .4936 gram of cobalt nitrate [$Co(NO_3)_2$, $6H_2O$] in water and diluting to one liter. This solution contains .0001 gram cobalt per c.c. One to twenty c.c. according to the estimated size of the cobalt content of the sample are taken as a standard, treated with the reagents and comparison made by the dilution method. A duplicate may be made up by running this solution into a blank of 75 c.c. of water with the same reagents added to it as to the sample. A series of standards cannot well be made up as the cobalt comes down after a short time as a red precipitate. For the balancing method fifty c.c. of the standard solution should be treated with double the quantities of reagents specified for the sample and then diluted to 500 c.c. This will then show the characteristic color and may be used at once but after a time will precipitate out. The latter solution contains .00001 gram cobalt per c.c.

METHOD A. MANGANESE AS PERMANGANATE OXIDATION BY PERSULFATE.

The red color of manganese after it has been oxidised to the permanganate[1] is used as a means of estimation of the manganese content of an ore or an alloy. Practically no metal interferes except chromium and that not unless it is in considerable excess of the amount of permanganate. If a large amount of iron is present as in the analysis of a steel for the manganese content, phosphoric acid is added to prevent the precipitation of the iron or a yellow color from that source. The samples should be

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[1] Z. Anorg. Chem., *80*, 171.

chosen as follows, .02 percent to .25 percent manganese take .5 gram, up to 4 percent use .25 gram. Above that limit .1 gram is to be used or the sample diluted and an aliquot part taken.

The sample is dissolved in dilute sulfuric or nitric acid and any residue of silica filtered off. Ten c.c. of fifth normal silver nitrate solution are then added as a catalyzer. If free chlorine or hydrochloric acid have entered into the solution in any way it may be necessary to add a considerable volume of silver nitrate to precipitate these before the catalyzer can be added.[1] Potassium persulfate is then added in sufficient quantity to oxidise all the manganese present to the condition of permanganate. The color will at once appear. If there is not too much chromium present the solution is now ready for testing, otherwise a further step must be gone thru.

In case too much chromium is present ammonia is now added and the solution heated. The manganese will be precipitated as manganese hydroxide and silver and a few other metals present will come down also. The chromium will, however, remain in the solution as the chromate unchanged. This is the same method that is used to purify the chromate solution for the obtaining of the chromium content. The precipitate containing the manganese is filtered off, dissolved in nitric acid and a further quantity of potassium persulfate sufficient to again oxidise the manganese is added. The permanganate color will reappear and the solution is ready for testing.

An old standard permanganate solution which has been used for iron analysis so that the iron factor is known, is best used as the standard. In that case the changes which occur in the solution when first made up are not to be reckoned with. In such a case multiply the iron

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[1] C. N., *83*, 76.

factor of the solution by .2952 to get the manganese factor. If a new standard must be made up .1439 gram potassium permanganate is dissolved in 100 c.c. of water. The water for this solution or for the dilution of the old solution, if it is to be diluted, must be boiled and cooled before it is ready for use. This 100 c.c. of solution is then diluted to one liter with the addition of ten c.c. of nitric acid. The latter standard contains .00005 gram manganese per c.c.

The making up of a series of permanent standards is not to be relied on. A blank may be prepared of twenty-five c.c. of water and the sample diluted to fifty c.c. after which the blank is made up as a duplicate by the addition of the above standard. The above standard may be further diluted, 100 c.c. diluted to 500 c.c. if thought desirable for the use of the dilution or balancing methods. Water to be used in carrying out the dilution method should have been boiled and cooled shortly before using.

METHOD B. MANGANESE AS PERMANGANATE, OXIDATION BY PERIODATE.

Instead of the use of a persulfate which involves the use of a catlyzer the oxidation may be carried out by the addition of sodium periodate to the solution.[1] It is necessary that there be an excess of free mineral acid in the solution, otherwise the manganese will precipitate out as manganese periodate or some oxide of manganese. The presence of much iron is taken care of by the addition of a few c.c. of strong phosphoric acid, which prevents the yellow color due to the iron as well as a possible precipitation. Other metals do not interfere unless they produce a colored solution in which case they must be removed.

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[1] J. A. C. S., *39*, 2366.

The sample is chosen as in the preceding method and dissolved in a mineral acid. The presence of hydrochloric acid or free chlorine will not interfere with this method. The concentration of the acid used is best, 15 c.c. concentrated sulfuric or 20 c.c. nitric acid or 10 c.c. strong phosphoric acid per 100 c.c. of solution. Any reducing substances may be removed by adding nitric acid and heating. .4 gram sodium periodate is added to the sample and the solution boiled for one minute, kept hot for ten minutes, cooled and diluted. The comparison is made with standards as specified in the previous method.

Zinc by Resorcinol.

Zinc is acted on by resorcinol in alkaline solution to produce a blue color.[1] The character of this alters somewhat on exposure to the air. The addition of hydrochloric acid turns the solution red and this color is not altered. Other metals do not interfere unless they have a colored solution before the addition of the reagent. In that case the metal causing the color must be removed. A sample suitable for examination by this method must contain between .003 and .000005 gram zinc.

The sample is dissolved in acid, diluted to 75 c.c. and neutralized by the addition of ammonia. The solution is diluted to 100 c.c. Two c.c. of ammonia are then added and two c.c. of a five percent solution of resorcinol, which will produce the characteristic color.

A standard is prepared by the solution of .1 gram of pure zinc in nitric acid and dilution to one liter. A suitable amount of this is treated the same as the sample. The standard so prepared must be very close to the color of the sample as the dilution method does not hold thru any considerable range in this case. The other methods

[1] Anales. Soc. Espan. Fis. Quim., *11*, 98.

are impracticable except the duplication method. For that the blank should contain 70 c.c. of water. After results have been obtained by the dilution method in alkaline solution a slight excess of hydrochloric acid may be added and the test checked by comparing the red color produced in acid solution.

CHAPTER TEN.

POTASSIUM AND MAGNESIUM.

The determination of potassium is of considerable importance in the examination of soils and drainage waters as well as the determination of traces of the metal in analysis of minerals and substances of all sorts when an accurate analysis is made. Magnesium occurs in minerals and as one of the dissolved substances in natural waters.

METHOD A. POTASSIUM BY DETERMINATION OF THE POTASSIUM PLATINO CHLORIDE BY REDUCTION WITH STANNOUS CHLORIDE.

This method for the determination of potassium depends on the precipitation and separation of potassium as the platino chloride, the solution of this amount of platinochloride and reduction with stannous chloride. The color produced[1] is a yellow proportional to the amount of platinum present which is in turn proportional to the amount of potassium present. Since the standard is a similar salt the proportion may be taken as directly resultant from the potassium without consideration of the fact that the color is due to the platinum rather than to the metal being tested for. This method admits of estimation of amount so small that they could hardly be detected by the usual gravimetric procedure. The amount of sample should be so chosen that the potassium content is between .00005 and .000005 gram per c.c. in a solution of 25 c.c.

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[1] J. A. C. S., *25*, 991.

The sample, if a solid, is dissolved, in water if so soluble, in hydrochloric or nitric acid if necessary. If the test is being made on a solution it may be necessary to concentrate in order to come within the limits. The sample solution is then evaporated to dryness with the addition of one c.c. of concentrated sulfuric acid. The residue is strongly ignited and dissolved in hot water, acidified with hydrochloric acid and an excess of chlorplatinic acid added. The solution is washed out of the dish onto a filter with alcohol (80 percent concentration or more) and washed with several successive small portions of alcohol. The precipitate is now dissolved in boiling water, cooled and made up to a definite volume. This should be 50 c.c. if the potassium content is low or 100 c.c. if the potassium content is high. In the latter case the solution is divided into two parts and one half used for the further procedure.

A stannous chloride solution is made up by boiling 75 grams of powdered or granulated tin in an erlenmeyer flask with 400 c.c. of concentrated hydrochloric acid until all the tin has dissolved. Three c.c. of this solution are added to the solution of the sample and the yellow color will appear.

A standard is made up by dissolving .0516 gram of potassium chlorplatinate (K_2PtCl_6) in water and making up to one liter. This solution will contain .00001 gram K_2O per c.c. If a series of standards is to be prepared from one to twenty-five c.c. of this solution are used for the original standards, treated with stannous chloride and made up to 50 c.c. For the method of duplication the above standard is run into a blank of 25 c.c. of water treated with three c.c. of stannous chloride. A standard solution showing the color so that it may be used for comparison by the dilution or balancing methods is made by treatment of 200 c.c. of the solution with five c.c. of hydrochloric acid and ten c.c. stannous chloride and making up to 250 c.c. This solution will then contain .000008 gram potassium per c.c.

METHOD B. POTASSIUM AS THE CHLORPLATINATE BY POTASSIUM IODIDE.

This method is for uses similar to those of the preceding method but is more delicate. The sample should be smaller than those recommended for the preceding method. The sample is dissolved and treated similarly until the solution of potassium chlorplatinate in water is obtained. The washing[1] of the precipitate should be with stronger alcohol than in the preceding case and the last washing must be with absolute alcohol. This must be allowed to stand for a sufficient time for all of the alcohol to evaporate before solution is made, otherwise the alcohol in the final solution will cause an impediment to correct results.

The fifty c.c. of sample are then treated with five c.c. of a solution of potassium iodide, 86 grams to the liter. A red coloration is produced which is darker for the same amount of potassium than that produced by reduction of the chlorplatinate with stannous chloride. The standard used is more dilute, .1032 gram of potassium platino chloride (K_2PtCl_6) is dissolved in one liter of water. The standard for the series of standards or duplication methods is made by dilution of ten c.c. of this solution to 100 c.c. so that it then contains .000002 gram K_2O per c.c. For the dilution or balancing methods five c.c. of the standard solution are treated with five c.c. of potassium iodide solution and made up to 100 c.c. The content per c.c. of this is .000001 gram K_2O per c.c.

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[1] J. A. C. S., *25*, 1063.

MAGNESIUM BY DETERMINATION OF THE PHOSPHATE AS PHOSPHOMOLYBDATE.

For the determination of magnesium the magnesium is changed to the form of the ammonium phosphate.[1] This is then treated with a standard molybdate solution which will give a yellow color proportional to the amount of phosphate present, which is in turn proportional to the amount of magnesium present. The standard is a phosphate solution and the amount of magnesium represented by a gram of P_2O_5 is known so that the percentage is obtained by this factor. Calcium precipitates, if present, but the addition of a few drops of ammonium oxalate solution entirely prevents this interference. The sample is so chosen as to contain between .0001 and .00003 gram magnesium.

The sample, if a solid, is dissolved in as small an amount of nitric or hydrochloric acid as possible, evaporated to dryness to drive off the excess of acid and the residue dissolved in water. If some silica is present this may be filtered off before evaporation to dryness. If the sample is a liquid at the start such as, for example, a drinking water it may be necessary to concentrate. The sample should finally be concentrated to about five c.c. of solution and cooled.

The phosphate reagent is made up by dissolving 17.4 grams potassium hydrogen phosphate (K_2HPO_4) and 100 grams ammonium chloride in 900 c.c. water, adding fifty c.c. strong ammonia and diluting to one liter. The cheaper sodium salt is not satisfactory as it is too difficult to wash because of its lesser solubility.[2] To the sample as specified above is added one drop of ammonia and two or three drops of ammonium oxalate and the

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[1] J. A. C. S., *26*, 961.

[2] J. A. C. S., *26*, 1463.

whole evaporated to dryness on the water bath. One c.c. of the phosphate solution is added to this residue and the whole thoroly stirred with a glass rod and allowed to stand for two hours. The precipitate is washed out onto a small filter with ammonium hydroxide and washed with further quantities of ammonium hydroxide, five c.c. at a time, until a total of fifty c.c. has been used. The original dish is washed out with each addition before it is added to the filter. The dish is washed out with five c.c. of pure water and the filter also washed with this. A clean beaker is placed under the filter and the dish washed out with five c.c. of concentrated nitric acid. This same acid is carefully poured over the filter so as to dissolve all the precipitate present. The dish and filter are washed with hot water, five c.c. at a time, until nearly 45 c.c. have been used. The filtrate is cooled, four c.c. of ammonium molybdate solution added and diluted to fifty c.c. The yellow color now appears and is at its greatest intensity after twenty minutes. The solution must therefore be allowed to stand until that time before comparison.

A standard is made up by dissolving .5043 gram of pure sodium acid phosphate (Na_2HPO_4, $12H_2O$) in water, adding 100 c.c. of nitric acid and making up to one liter. This standard contains .0001 gram P_2O_5 per c.c. The test cannot conveniently be made by the production of a duplicate since an addition of the standard takes twenty minutes to reach its full intensity. The standard for use by the balancing or dilution methods is made up by adding to ten c.c. of the above solution, 70 c.c. of water, 9 c.c. nitric acid and 8 c.c. of ammonium molybdate solution and making this up to 100 c.c. accurately. After standing, this solution attains the color representing its content of .00001 gram P_2O_5 per c.c. or representing

.00000342 gram magnesium. That is, the amount of phosphorus present as P_2O_5 is multiplied by the factor .342 to give the amount of magnesium represented by this result. The result is in terms of Mg. The factor to represent the result in terms of MgO is .568.

CHAPTER ELEVEN.

GOLD.

THE quantitative estimation of gold in solution is one field left almost exclusively to colorimetry. Tests may be performed which are so delicate as to show the presence of one cent's worth of gold in a ton of water and by concentration of the solution being tested even greater delicacy may be secured. It is by these methods that the well known fact that every ton of sea water contains a few cents' worth of gold is proven.

Eight brief methods follow.

METHOD A. GOLD BY METHOD OF DOWSETT.

This method for the determination of dilute gold solutions does not require the making up of a series of standards but requires that the worker have sufficient knowledge of the colors after some use of the methods to be able to estimate the gold content from the depth of color produced. A solution containing gold up to a value of 8 cents per ton may be used. If the test is to be made of an ore this is dissolved in some manner. The most convenient method is usually by the extraction of the gold by a dilute cyanide solution.

A sample[1] of 500 c.c. of the solution to be tested is poured into a bottle which has very little shoulder, such as a large soft drink bottle, ten to fifteen c.c. of a saturated solution of sodium cyanide added and two or three drops of a saturated solution of lead nitrate. Two grams of fine zinc dust are then added and the bottle

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[1] Met. and Chem. Eng., *12*, 460.

corked and shaken until the precipitate formed settles quickly, usually for about two minutes. The bottle is then inverted into a casserole and the clear liquid decanted off. Nitric acid is added to the precipitate until the reaction ceases, a drop or two in excess added and the solution evaporated to one or two c.c. This small volume of solution is transferred to a small test tube and one c.c. of stannous chloride solution added to bring out the color. If the quantity of gold is small this may take two or three minutes; in case the color is faint it is more readily detected by looking down the tube.

The colors produced are:

2 cents per ton—Very slight color.
3 cents per ton—Slight yellow color.
4 cents per ton—Slight pinkish yellow color.
6 cents per ton—Strong pink color.
8 cents per ton—Purple of Cassius.

For the experimenter to learn this method a few tests on known solutions are advisable, to get the colors firmly fixed in mind. The smallest amount of lead possible should be used so that the precipitate to redissolve will be small. Excess nitric acid will cause the colors to differ from those specified, therefore the nitric acid should be added cautiously. Mercury if present will cause a dark color which will cover up the results of the test.

METHOD B. GOLD BY METHOD OF PRISTER.

A copper solution[1] for carrying out this test is made by boiling a solution of two parts salt to one part copper sulfate with ten parts water in the presence of scrap copper for ten minutes and adding a few drops of acetic acid to the solution on cooling.

A sample of 200 c.c. of solution is acidified with hydro-

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[1] Proc. Chem. Met. and Min. Soc. of So. Af., *IV*, 235.

chloric acid and boiled several minutes to decompose cyanide if present. A slight excess of the copper solution is then added and a few drops of sodium sulfid solution. After boiling this solution for five minutes the precipitate is allowed to settle and the liquid decanted onto a filter. The precipitate in the beaker and on the filter is dissolved in three c.c. of a five percent solution of potassium cyanide to which has been added a few drops of potassium hydroxide. Two grams of zinc dust are added to this solution and the mixture then heated to 45 degrees for a half hour. The liquid is separated by decanting thru a filter after which the excess of zinc is removed by treatment with hydrochloric acid. The residue is now treated several times with ten c.c. of aqua regia passing it thru the filter and washing out the beaker thoroly.

The color will be produced by diluting this solution to twenty c.c. with stannous chloride. As in the preceding case, tests must be made on solutions of known gold content to become familiar with the colors produced.

METHOD C. GOLD BY METHOD OF DORING.

This method is for the analysis of ores poor in gold. One hundred grams of ore are slightly but evenly moistened in a stoppered bottle with one or two c.c. of equal parts of bromine and ether. This is to be shaken at frequent intervals for two hours, during which time the interior of the bottle must be filled with bromine vapor. Fifty c.c. of water are added to the bottle and it is allowed to stand for two hours shaking occasionally. The solution is then filtered, the filtrate evaporated to one fifth of its former volume, a little bromine water added and the solution treated with stannous chloride in a test tube. Results are as follows:

.1 percent solution, deep brown color, opaque even in thin layers.
.01 percent solution, brown violet immediately, 14 cm. column opaque.
.001 percent solution, pale violet immediately, increases after a time.
.0001 percent solution, evaporated to one fifth former volume, and a drop of bromine water added shows a distinct rose tint in a 14 cm. column.
.00005 percent solution shows faint but recognizable pink in 14 cm. column, after undergoing the same treatment.

This method will show as little as one half gram per ton of ore. From the percent of the solution the gold content of the ore may be calculated.

METHOD D. GOLD BY METHOD OF ROSE.

This method is for detection of gold in substances which can be dissolved in water, such as a trace of gold in a salt, or similar tests. The sample[1] is dissolved in water, this solution heated to boiling and then poured into a solution of stannous chloride. There is formed a gelatinous precipitate which has the purple of Cassius if considerable gold is present and shows a faint pink for amounts as small as one part in one hundred millions. The operator is expected to familiarize himself with the colorations produced by known quantities of gold.

Rose suggests the making up of a standard by solution of .00003 gram of gold in three liters of water. This would be one part in one hundred millions and could be concentrated to give a standard of the desired concentration.

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[1] C. N., *66*, 271.

This test used with sea water as a sample gives a very distinct reaction.

Method E. Gold by Method of Cassal.

This method[1] is for treatment of a cyanide solution for determination of the gold content. To the sample of 50 c.c. of solution a small amount of potassium bromate is added and then concentrated sulfuric acid until effervescence starts. The action will continue without further addition of acid until the cyanide is completely decomposed. The bromine is then boiled off and stannous chloride added in excess which will produce the color desired. If the test is made quickly it is not necessary to boil off the bromine before addition of the stannous chloride but the color will not remain at its true intensity for more than a minute unless the bromine is so removed. The colors are determined from the memory of those caused by standard amounts of gold. This test will show a light color from the presence of as little as one cent a ton. The purple of Cassius appears when only four dwt. of gold per ton are present.

Method F. Gold by Decomposition of the Cyanide by Potassium Bromide and Sodium Peroxide.

This method[1] is similar to method E except that potassium bromide is added to the 50 c.c. of sample solution and then sodium or potassium peroxide in excess. Bromine will be freed and the cyanide will be decomposed. Sulfuric acid is then added to the solution until neutrality is reached after which it is acidified with hydrochloric acid, stannous chloride added and the determination made as in the previous method.

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[1] Eng. Min. Jour., *76*, 661.

METHOD G. GOLD BY DECOMPOSITION OF THE CYANIDE BY AMMONIA.

This method is similar to method E except in the manner of reduction of the cyanide. To the solution[1] to be reduced is added one third its bulk of concentrated ammonia. Concentrated sulfuric acid is then added until neutrality is reached after which the solution is acidified with hydrochloric acid and treated with stannous chloride for the production of the color.

METHOD H. GOLD BY METAPHENYLENEDIAMINE.

The solution of the gold as a cyanide is treated with concentrated hydrochloric acid to decompose the cyanide and change the gold to the form of the chloride.[2] Five c.c. of a solution of five grams metaphenylenediamine to the liter are then added. Upon the addition of sulfuric acid a yellow to dark brown color is formed, dependent on the strength of the gold solution. The color shown is due to the presence of colloidal metallic gold. A solution as dilute as .005 percent will show a color by this method.

The reagent may become pink on standing in the light but may be decolorized by animal charcoal.

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[1] Eng. Min. Jour., *76*, 661.

[2] Chem. Ztg., *36*, 934.

CHAPTER TWELVE.

TITANIUM, VANADIUM AND TUNGSTEN.

THESE comparatively rare metals are not very widely distributed but notwithstanding their scarcity are of great importance. Their principal use is in alloys with steel where the amount of the metal present would be small and well adapted to this type of procedure.

METHOD A. TITANIUM BY HYDROGEN PEROXIDE.

This method of analysis for titanium is ordinarily applied to the solution titrated for total iron, after the titration has been completed. For use as standard the titanium content of a standard ferrotitanium must be known. The presence[1] of less than half of one percent of nickel or chromium may be equalized by the addition of a similar amount to the standard, a greater amount than this must be removed by methods to be given later.

The sample, if weighed out, is of .5 gram, the solution titrated for iron is just as good and much more convenient. The standard is made up by weighing out an amount of ferrotitanium such that its titanium content is approximately that of the steel under examination and adding to this enuf steel containing no titanium to bring the weight up to .5 gram. This standard is then treated as specified for the sample. If the sample contains more than one half percent nickel or chromium they are removed as follows: Fuse the .5 gram sample with 5 grams sodium carbonate and one gram potassium nitrate. The

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[1] Chemical Analysis of Special Steels, Steel Making Alloys and Graphites, Johnson.

melt is heated with 30 c.c. of one-one hydrochloric acid in a porcelain casserole for thirty minutes, filtered and washed. Thirty c.c. of dilute sulfuric acid are then added, the solution evaporated to fumes, transferred to a test tube, five c.c. nitric acid added, the red fumes boiled off and proceeded with as the solution of the sample.

The standard, and the sample if it does not have to have nickel or chromium removed, is dissolved in ten c.c. dilute sulfuric acid, five c.c. concentrated nitric acid added and heated until red fumes cease to be given off. The standard, and the sample obtained in one of the ways mentioned, are then poured into Nessler tubes or other tubes suitable for comparison by dilution. Hildebrand[1] says that five percent of sulfuric acid is necessary in this solution to make sure that any metatitanic acid formed is reverted to the metal. If phosphoric acid is present a similar amount must be added to the standard.[2] Five c.c. of a solution of hydrogen peroxide are now added to each of the tubes and the comparison made by dilution. If hydrogen peroxide is not available it may be supplied by dissolving 3.5 grams of sodium peroxide in 125 c.c. of dilute sulfuric acid and diluting to 500 c.c.

Since the large amount of iron present is apt to cause a yellow color, a correction is sometimes introduced for this or the iron removed from the sample before addition of the peroxide. The correction for iron present is as follows, .1 gram $Fe_2O_3 = .0002$ gram TiO_2 or 10 grams $Fe_2O_3 = .02$ gram TiO_2.[1] For the removal of the iron the sample is fused with sodium peroxide.[2] This leaves the iron as the insoluble oxide when the melt is extracted. The solution is acidified with sulfuric acid, in which case no hydrogen peroxide need be added as the excess of

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[1] U. S. Geol. Surv. Bull., No. 176, p. 80.

[2] J. A. C. S., *29*, 481.

sodium peroxide in solution will form a sufficient quantity in reaction with the acid.

METHOD B. TITANIUM BY THYMOL.

This method admits of the determination of much smaller amounts of titanium, as the color produced by titanium in reaction with thymol is about twenty-five times as intense as the yellow to orange produced by the preceding method. This method produces a red coloration. The only substance apt to be present which would alter the color is tungstic acid.

The reagent[1] is prepared by dissolving one gram thymol in 5 c.c. dilute acetic acid and this is then added to 95 c.c. of concentrated sulfuric acid. The thymol if dissolved directly in the sulfuric acid would give the solution a yellow color which is not present if solution is made first in acetic acid as directed. The solution of the reagent must be kept from bright sunlight or it will darken in a few hours. The amount of thymol added should be such that the ratio of thymol to titanium is less than 100:1.

The sample is placed in solution as in the preceding method, using all the same precautions, and then poured into Nessler tubes as in that case. Two c.c. of the above thymol solution are then added to the sample and standard and dilution carried out.[2] If desired a series of standards may be prepared from a standard ferrotitanium for this method. For convenience in dissolving the original sample it may be desirable to fuse it with potassium acid sulfate.

METHOD A. VANADIUM BY HYDROGEN PEROXIDE.

This metal in alloys and ores is determined by solution in acid and oxidation with hydrogen peroxide. The

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[1] J. A. C. S., *35*, 138.

[2] Orig. Com. 8th Inter. Cong. App. Sci., *1*, 285.

resultant color is, in practice, always compared by dilution or duplication. If chromium is present an equal amount must be introduced into the standard under the same conditions of temperature, acid concentration, etc. The sample is two grams of a steel low in vanadium or one gram of a steel with a high vanadium content. If of a mineral the weight of sample may be judged by the probable vanadium content.

The sample is dissolved in 40 c.c. of concentrated nitric acid, one tenth gram permanganate added and the solution digested for two minutes. Ammonium bisulfite is then added to clarify and the solution boiled to expel sulfur dioxide. The solution is then cooled and made up to 50 c.c.[1] (A).

As an alternate method of solution and treatment of the sample it may be dissolved in ten c.c. of sulfuric acid (1:3), two c.c. of concentrated nitric acid added, heated until the solution clears and fumes disappear, cooled and made up to definite volume of 50 c.c.[2] (A).

If the original solution contained chromium the standard must also be made up to contain chromium. In that case a standard vanadium steel is dissolved in 40 c.c. sulfuric acid, an amount of chromium equal to the amount in the sample added as potassium dichromate, ten c.c. of nitric acid added and the solution heated for ten minutes to complete solution and clarify. This standard so prepared may then be made up to fifty c.c. and is ready for comparison by dilution.

In case chromium is absent and the results are to be obtained by dilution an amount of vanadium steel is weighed out which contains approximately the same weight of vanadium as the sample. This steel is treated

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[1] J. Ind. Eng. Chem., *5*, 736.

[2] Chem. World, *2*, 341.

identically the same as the sample and when it reaches the point (A) in the process should be diluted to fifty c.c. and have the same color as the sample. The color present at this point, if any, will be entirely that of some metal other than vanadium, if the color of the contamination of sample and standard differs the determination of results will be rendered incorrect. If the results are to be obtained by duplication a blank of 45 c.c. of water is prepared at this point in the process adding to it as part of the total volume the same amount of the same kind of acid as is supposed to be present in the sample. Note that if nitric acid was used for oxidation the greater part of it may have been boiled off as brown fumes before proceeding to the next process.

The solution for determination of the sample by duplication consists of .1784 gram of V_2O_5 dissolved in the smallest possible amount of sulfuric acid and diluted to one liter. Each c.c. of the solution will then contain .0001 gram vanadium.

To the sample diluted to fifty c.c. and to the standard diluted to equal volume or to the blank of 45 c.c. of water and acid there is now added one c.c. of the commercial 3 percent hydrogen peroxide. The color resultant from the vanadium present appears and the determination is carried out by the method chosen. If commercial hydrogen peroxide is not available it may be made by adding two grams of sodium peroxide to 100 c.c. dilute sulfuric acid.

This method of determination of vanadium is accurate to about .04 percent.[1]

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[1] Pickard, Chem. World, *2*, 341.

METHOD B. VANADIUM BY STRYCHNINE.

By this method the vanadium is separated from the solution containing the iron by precipitation with ammonium molybdate,[1] oxidised with potassium chlorate and sulfuric acid, treated with a solution of strychnine in concentrated sulfuric acid and the results obtained by dilution. Ten minutes is necessary for the full color to appear after the addition of the last reagent so that determination by duplication is impracticable. The preparation of the large amount of standard necessary for the method by balancing is not satisfactory and the color is not permanent enough for the use of a series of standards. The sample is chosen as one or two grams as in the preceding test.

The sample is dissolved in 45 c.c. nitric acid (1:2) and one c.c. dilute sodium acid phosphate solution added. The solution is then cooled and 14 c.c. strong ammonia added. Boil until all the ferric hydroxide has redissolved in the excess of the solution, remove from the flame, add thirty c.c. of ammonium molybdate and shake well. Filter and wash free of iron with two percent nitric acid and then with water. The precipitate is then washed into a large beaker, a small amount of potassium chlorate and 20 c.c. sulfuric acid added and evaporated until fumes of sulfuric acid begin to pass off. This is then cooled and twenty c.c. of a solution of strychnine, four grams to the liter, in concentrated sulfuric acid are added. After standing for ten minutes the color will appear in its full intensity.

The standard is made by solution of .1784 gram of V_2O_5 in as small an amount of sulfuric acid as possible and diluted with concentrated sulfuric acid to 100 c.c. Each c.c. contains .001 gram vanadium. An amount of this

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[1] Chem. World, *2*, 341.

standard equal to the amount of vanadium estimated to be present in the sample is treated with potassium chlorate and sulfuric acid, carried on from that point, and used for dilution.

TUNGSTEN AS THE OXIDE IN COLLOIDAL SUSPENSION.

The sample dissolved in acid is treated with titanium trichloride. This frees the blue oxide of tungsten which will remain in suspension about one half hour.[1] More than ten percent of hydrochloric acid in the solution weakens the color. The method may not be applied in the presence of vanadium, phosphorus and molybdenum without first removing these factors. The amount of tungsten in the sample must not be over .001 gram, otherwise the oxide will precipitate.

Solution of the sample is made in five c.c. of hydrochloric acid, the solution boiled down to small volume, two c.c. are practical, cooled and diluted to forty c.c. Five c.c. of $TiCl_3$ are then added to the solution and dilution to 50 c.c. carried out. This is compared with the standard by dilution.

The standard for use by this method is prepared by weighing out a standard tungsten steel, of which the tungsten content is known, to an amount estimated to be near the amount of tungsten contained in the sample and adding nontungsten steel until the total weight is equal to the weight of sample taken. In case the estimate is being made of a mineral rather than of a steel it is advisable to use a steel as high in tungsten as possible and not to add the additional nontungsten steel as there will be no iron in the mineral. This standard is dissolved and treated by the same method as the sample.

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[1] Compt. Rend., *166*, 416.

CHAPTER THIRTEEN.

FLUORINE, CHLORINE AND PERCHLORATES.

Of the members of the halogens these two, fluorine and chlorine, may be estimated by colorimetric methods and also the compounds of one as perchlorates. The many places in which traces of these occur need hardly be mentioned, from drinking water to minerals they may be found distributed thruout nature, and in synthetic products the occurrence of chlorine in particular is frequent.

Fluorine by Estimation of Its Bleaching Action on an Oxidised Titanium Solution.

Small amounts of fluorine may be estimated by their action on a titanium solution which has been oxidised by the addition of hydrogen peroxide.[1] The results are obtained by one of two methods. There may be a similar titanium solution containing a known amount of fluorine prepared, such that its color is the same, or the bleached solution may be examined for its apparent titanium content. By subtraction of the apparent content from the real content and multiplication by a factor, the fluorine which caused the bleaching may be estimated.

There are a large number of impediments to this process. The presence of alkaline sulfates causes a bleaching action similar to that of fluorine.[2] Heating or the presence of considerable free acid will serve to bring back part of the color thus bleached. The color bleached by fluorine as well as that by alkaline sulfates will be

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[1] Am. Jour. Sci. (4), *28*, 119.

[2] J. A. C. S., *30*, 219.

restored by a large amount of free acid. If a large amount of silica is present, as usually is the case in minerals containing fluorine, this must all be removed before the procedure is begun. The color is estimated to be increased 5 to 15 percent by raising the temperature 30 degrees. Phosphoric acid also bleaches the titanium solution and so must be absent. Aluminum also bleaches, so if present it is removed by precipitation with ammonium carbonate. Iron prevents the bleaching by fluorine and by its color confuses the test, therefore it must be removed. A suitable sample contains .01 to .00005 gram fluorine. This method is more accurate than gravimetric methods for amounts below two percent and will not only detect but estimate amounts so small as not to be detected by gravimetric methods.

The sample is fused with three to five grams sodium potassium carbonate fusion mixture and the fusion dissolved in hot water as far as possible. Two grams of ammonium carbonate are then added and the solution evaporated on the water bath to small bulk, the ammonium carbonate at the same time being decomposed. Iron, aluminum and silica are precipitated and may now be filtered out. A standard titanium solution is prepared by the solution of one gram TiO_2 in concentrated sulfuric acid and diluted to one liter.[1] This solution contains .001 gram titanium dioxide per c.c. Four c.c. of hy-

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[1] Scott gives a somewhat more elaborate method of solution. An intimate mixture of one gram of TiO_2 and three grams of ammonium persulfate is heated until the vigorous action has ceased and ammonium sulfate is expelled. The residue is treated with twenty c.c. strong sulfuric acid, heated to fuming and, when cold, poured into about 800 c.c. of cold water. When the suspended salt has dissolved, 57.5 c.c. of strong sulfuric acid are added, and the solution made up to 1000 c.c. Fifty c.c. or more of the solution should be analyzed for TiO_2.

drogen peroxide are added to the solution to be tested, followed by ten c.c. of the above titanium solution and five c.c. of sulfuric acid. The addition of the acid should render the solution slightly acid. If such is not the case a further amount of acid is added until the solution is very slightly acid. More acid is now added, dependent upon the estimated fluorine content of the solution. For the maximum sample, .01 gram, twelve c.c. of acid are used, for the minimum sample, .00005 gram, one c.c. will be sufficient. The amount used is graded according to the amount present between these two extremes. The solution is then diluted to 50 to 100 c.c. according to the intensity of color and the original amount of the solution before dilution.

A standard fluorine solution must be made up if the standard is also to be bleached. This consists of 1.2403 grams potassium zirconium fluoride (potassium fluozirconate, K_2ZrF_6) dissolved in water and diluted to one liter. This solution contains .0005 gram fluorine per c.c. For determination by this method the fluorine in the sample must be estimated, a similar amount added to ten c.c. of titanium solution treated with hydrogen peroxide and the agreement with the sample noted. If this does not agree it is only a matter of a short procedure to make up another which will more nearly approximate the sample.

The desired result may be obtained from the factor figured by Steiger[1] from a large number of experiments. The solution bleached with fluorine may be estimated by first determining the apparent titanium present and subtracting this from the actual weight of titanium known to be present. Results show that fluorine will bleach slightly more than twice its own weight of titanium,

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[1] Steiger, J. A. C. S., *30*, 219.

accurately 35:75. For general estimation the difference between the two titanium readings may therefore be divided by two and this taken, for accurate work the difference between the titanium readings is multiplied by .4667. Factors for allowing for the presence of acid and of alkali, etc., have been figured but the tables are too long for inclusion here. For those records reference should be made to Steiger as indicated. The errors due to the presence of alkaline sulfates and excess acid are so small that they may well be neglected.

CHLORINE BY O-TOLIDINE.

Free chlorine present may be estimated by the green color produced by it in reaction with o-tolidine. The method[1] is especially designed for water analysis but may be adapted to other determinations of free chlorine. The reagent is so delicate that it will detect .00000005 gram of chlorine per c.c. of water, or to phrase it in terms of water analysis, .005 part per million. The sample should be twenty-five c.c. of a water high in chlorine or fifty c.c. of one low in that constituent.

Five c.c. of a solution of one gram of the reagent in a liter of ten percent hydrochloric acid are added. The color appears at once. The use of a natural series of standards is not advisable as they will not keep from day to day but the use of artifical standards made from the copper-iron or copper-dichromate series is possible. Because of the nature of the test substance the method of duplication would be practically impossible to control. Dilution or balancing methods may be used, the standard should be another solution whose chlorine content has been determined, treated with the same proportional amount of the reagent as the sample.

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[1] J. Ind. Eng. Chem., *5*, 915.

Perchlorates by Methylene Blue.

The reaction of perchlorates with methylene blue may be used for the estimation of the amount of perchlorate present.[1] This method is used in the test of soluble substances such as salts for the presence of these compounds, with particular reference to the analysis of Chili saltpeter. The sample used is one gram except in rare cases. The method has a considerable range.

The sample is dissolved in water and diluted to 25 c.c. Two c.c. of a solution of one gram nitrosodimethylaniline in alcohol diluted to one liter with water are then added. The preparation of a series of standards for use with this is advisable, not permanent standards but temporary standards, easily replaced. A standard solution is made up of potassium chlorate by the solution of .1468 gram in water and dilution to one liter. For use ten c.c. of this are diluted to 100 c.c. and will then contain .00001 gram ClO_3 per c.c. The non-permanent standards for the test may be made up by use of one to ten c.c. of this solution. If the tests are all being made on the same basic substance as, for example, on Chili saltpeter it is well to add that substance in large amount to the standard solution before dilution to the line so that the standard may contain approximately the same amount as the sample solution. It is also possible to add the solution of the salt upon which work is being done to the non-permanent standards when diluting them to the same volume as the sample, before treatment with the reagent.

It is necessary that the sample and standards be allowed to stand for several hours to fully bring out the colors. The sample is then compared with the series of standards prepared at the same time and an estimation made of its perchlorate content.

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[1] Arch. Sci. Phys. Nat., *42*, 210.

CHAPTER FOURTEEN.

NITRIC AND NITROUS ACIDS, AND AMMONIA.

The occurrence of these nitrogen compounds is frequent and the determinations made of them are many. The test for ammonia with Nessler's reagent is one of the oldest of methods for this sort of work. The above substances have to be frequently determined in water supplies and sewage effluents. The presence of nitric acid in sulfuric acid supposed to be chemically pure is also often to be detected and estimated by these methods.

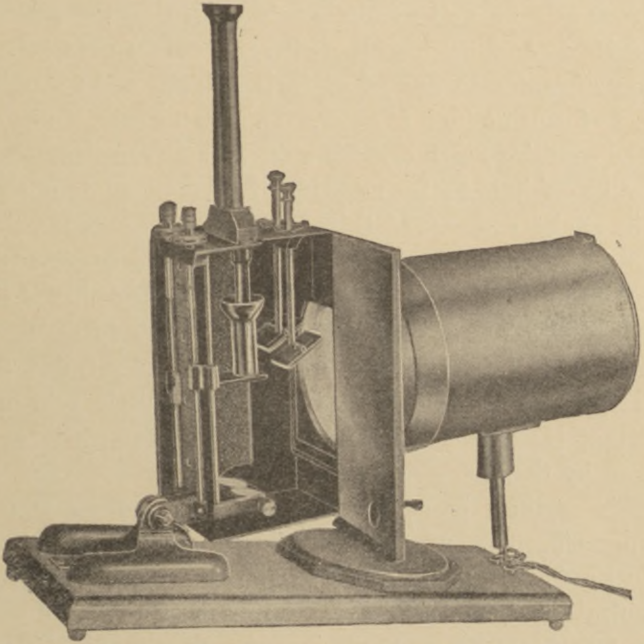

Fig. 15. Colorimeter with Lamp House Suitable for Night Work.

METHOD A. NITRIC ACID BY BRUCINE REACTION.

Nitric acid may be determined, colorimetrically, by its reaction with brucine in the presence of sulfuric acid, making the test by the sulfur yellow that follows the initial red coloration rather than by the original coloration which may not be relied on.[1] If nitrous acid is not to show in the final results there must be present two parts of sulfuric acid for every part of water. This method is given on the assumption that only nitric acid is to be determined. In case it is desired to determine nitrous acid as well as nitric acid, lessening the amount of sulfuric acid used, so that there would be present two parts of water to one of sulfuric acid, would have the effect of causing both to show. In case the solution being tested contains much organic matter or ferrous iron these must be oxidised by the addition of permanganate until it is in slight excess. If this oxidation is carried out it must be taken into account that nitrous acid present will be oxidised at the same time to nitric acid and that if the nitric acid in the presence of nitrous acid is to be determined it will be necessary to separately determine the nitrous acid, calculate it to the form of nitric acid and subtract the result obtained from the total nitric acid shown by the test.

This method is used for determinations on water, sewage effluents, and sulfuric acid, also for the analysis of salts for traces of nitric acid not removed in their purification. The sample chosen for the test should contain .00001 to .0002 gram nitric acid. If a liquid, a quantity to fall within those limits may be chosen.

The sample, if a solid, is dissolved in water and diluted to not over twenty c.c. The sample, if of a liquid, must be under that volume and is diluted to approximately

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[1] Chem. Zeit., *23*, 454; *25*, 586.

twenty c.c. The determinations are best made in Nessler tubes or some type of graduated tubes. One c.c. of a concentrated solution of brucine is added to the sample and then 30 c.c. of concentrated sulfuric acid. If the test is being made on sulfuric acid for nitric acid as impurity, ten c.c. of water and ten c.c. of acid are substituted for this addition of acid, leaving the volume somewhat smaller than in the other case. Care must be used in the addition of this sulfuric acid as it must be carefully poured down the side of the tube without causing the water to boil. If care is not used the water will boil and loss of nitric acid will result.

The most convenient method for making the test is by duplication. The blank of fifteen c.c. of water and five c.c. of sulfuric acid is treated as specified for the sample. The blank should show no color at this point, if it does the solution must be rejected unless it is known that the sulfuric acid used contained a small amount of impurity in the form of nitrate. In that case the contamination of sample and blank may be assumed to be the same and may be disregarded. The standard solution for addition to the blank is made by dissolving .1872 gram KNO_3 in water and diluting to one liter. This standard then contains .0001 gram N_2O_5 or .000115 gram NO_3 or .00002594 gram N_2 per c.c. The standard is run in and the sample duplicated in the usual manner.

The sample shows first an orange yellow changing to light yellow, on the addition of the sulfuric acid. Similarly the color of the blank will show first orange changing to yellow. If the carrying out of the test is delayed the solutions may become cooled in which case the change of color will be slowed down. In that case it is best to heat the solutions over a flame, to have them at sufficient heat to show proper color reactions.

METHOD B. NITRIC ACID BY DIPHENYLBENZIDINE.

The test for nitrates with diphenylamine is not absolutely satisfactory as some elements of the test do not seem possible to control.[1] It has been found by experiment that diphenylbenzidine is formed in the solution from the diphenylamine and that the use of this as the original substance gives more satisfactory results. In case diphenylbenzidine is not available diphenylamine may be used as a substitute following the same directions as those given for the former reagent. The sample chosen is to be five c.c. of solution which should contain between .000001 and .0000001 gram nitrogen per c.c. The best way of handling the test is to make up simultaneously a series of nonpermanent standards.[2]

A standard solution may be made up by dissolving .3608 gram potassium nitrate in water and making up to one liter. Ten c.c. of this solution made up to 100 c.c. will then contain .000005 gram nitrogen per c.c. From this solution standards are to be made up with .1, .2, .3, c.c., etc., of the standard solution diluting each to five c.c., similar to the volume of the sample.

To each of the standards and to the five c.c. sample solution twelve c.c. of concentrated sulfuric acid are added and the solutions set in water to cool. The reagent used is .1 gram diphenylbenzidine in 100 c.c. concentrated sulfuric acid. The tubes having been cooled, three c.c. of this are added to each of the test tubes and the color of the sample compared with that of the standards, after ten minutes have been allowed for the color to show. If it is desired to obtain the total nitrogen, nitrites may be oxidised to nitrates by adding permanganate before proceeding with the determination. For the determination of

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[1] Z. Anal. Chem., *56*, 28.

[2] Jour. Chem. Soc., *105*, 1157.

nitrites the total nitrogen and the nitrates may be determined and the nitrites present are then represented by the difference in the two nitrogen determinations.

The mixing of the reagent with the solution is accomplished by lightly stirring. Shaking is to be avoided as it lessens the color produced.

METHOD C. NITRIC ACID BY PHENOLSULFONIC ACID.

The yellow color produced by nitrates is reaction with phenolsulfonic acid is found to be a satisfactory method of determining the nitrates present in a solution such as, for example, drinking water. The phenolsulfonic acid for use is prepared[1] by heating ten grams of phenol on the water bath for two hours with 60 grams concentrated sulfuric acid and 30 grams fuming sulfuric acid, or four hours with 150 grams concentrated sulfuric acid. The sample, if colored, must first be decolorized by the addition of aluminum hydroxide, as is usual in water purification. The sample of water or solution selected should contain less than .0001 gram nitrogen, preferably less than half that amount.

The sample is evaporated nearly to dryness on the water bath and the last few drops of solution then allowed to evaporate at room temperature in a place sheltered from dust. One c.c. of phenolsulfonic acid is then added to the residue and thoroly rubbed over it with a glass rod. Ten c.c. of distilled water are now added and stirred until all is dissolved. Ammonium or potassium hydroxide is then added until the solution is alkaline after which it is poured into the tube or bottle in which comparison is to be made.

The standard is made up by dissolving .7217 gram of pure potassium nitrate in water and diluting to one liter.

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[1] American Committee on Standard Methods of Water Analysis.

Ten c.c. of this solution are then evaporated the same as was specified for the sample, moistened with two c.c. of phenolsulfonic acid and diluted to one liter for use as a standard. Each c.c. contains .000001 gram nitrogen. This standard is suitable for making up a series of standards or for the method of duplication.

For duplication the sample mentioned above is poured into a Nessler tube and diluted to 50 c.c. The standard is then run into a blank of 25 c.c. and colors and volumes equalized. For the preparation of a series of standards the following volumes of the dilute standard solution are used. The amount of nitrogen represented by each is shown opposite. The sample should be diluted to 100 c.c. for this method, as should also each of the standards. Five c.c. of concentrated ammonia are to be added to the solution of standard before it is made up to the final volume.

Vol. of Dil. Stan. Sol. Used.	Nitrogen Represented in Grams.
.0	.000000
1.0	.000001
3.0	.000003
5.0	.000005
7.0	.000007
10.0	.000010
15.0	.000015
20.0	.000020
25.0	.000025
30.0	.000030
35.0	.000035
40.0	.000040

In case chlorides are present add two c.c. of the reagent to the solution and 1.5 c.c. concentrated sulfuric acid before evaporation to small volume.[1] The evaporation to small volume may then be carried out on the steam bath,

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[1] J. Ind. Eng. Chem., 9, 585.

completing evaporation to the final small volume on a water bath at not over 70 degrees, after which the method is followed out. Chlorides are thus removed without serious loss of nitrates.

METHOD D. NITRIC ACID BY PYROGALLOL.

This method is more suited to confirmation of another estimate or to quick guesses at the approximate nitrogen contents of a sewage effluent or of water than to other use.

Ten c.c. of the sample are placed in a test tube and approximately .2 gram pyrogallol added and thoroly mixed with the sample.[1] A pipette partially filled with sulfuric acid is then inserted, the acid being held in the pipette by keeping the finger over the upper end until inserted, and two c.c. of sulfuric acid allowed to flow out as a seperate layer at the bottom of the tube, the pipette being again removed with the finger over the aperture. Upon the addition of .1 gram of dry powdered sodium chloride an effervescence is set up at the point where the two layers join and a purple ring proportional in size and intensity to the amount of nitrate present, is formed.

A standard solution is made up by dissolving .1872 gram potassium nitrate in water and diluting to one liter. This solution contains .0001 gram N_2O_5 per c.c. or .000115 gram NO_3. The eye of the operator using this test soon becomes so used to the estimation that he can tell pretty accurately from the first glance the amount of nitrate present. For confirmation of this he may take that amount of standard and another sample and, by carrying the two tests thru at once, see if they appear to be identical.

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[1] Report of the Royal Commission on Sewage Disposal, Vol. IV, Part V, p. 23.

METHOD A. NITROUS ACID BY SULFANILIC ACID AND A-NAPHTHYLAMINE.

The red coloration which appears after a time when acetic acid solutions of sulfanilic acid and a-naphthylamine are acted on by nitrous acid may be used for the determination of the amount of nitrous acid present. In the process[1] the sulfanilic acid is converted by the nitrous acid into the corresponding diazo compound and the latter reacts with the a-naphthylamine to form a red azo dye. The full color which will result does not appear for several hours, often not for days, but if the temperature and other conditions of the standard and sample are identical the color will appear at the same rate and after only a very short time the estimation may be made.

The standard solution of nitrite is made by preparing nitrosyl sulfuric acid. .0493 gram pure sodium nitrite is dissolved in 100 c.c. water, and ten c.c. of this solution added to 90 c.c. concentrated sulfuric acid. This solution contains .00001 gram nitrogen per c.c. in the form of nitrite. The solution of sulfanilic acid is prepared by warming one gram with 14.7 grams glacial acetic acid and 15 c.c. water. A further 270 c.c. of water are then added, the solution being kept stirred. Similarly the a-naphthylamine is prepared by dissolving .2 gram in 14.7 grams glacial acetic acid and 25 c.c. water, after which 300 c.c. of water are added. The solutions are mixed for use but only small quantities should be so prepared at a time.

For the analysis twenty c.c. of the sample are placed in one color comparison tube and eighteen c.c. of pure water in the other. Two or three c.c. of a mixture of the above reagents are added to each and an amount of the standard

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[1] Fowler, Sewage Works Analyses, p. 64.

added to the blank equal to the amount of nitrite estimated to be present. The colors will be dark enuf after five minutes for the operator to see how well they compare. If they are not identical an experienced operator can tell the variation in the amount of nitrous acid between the two solutions and may confirm his view by adding that amount of standard to a blank and running that with a new amount of sample, comparing these after five minutes.

METHOD B. NITROUS ACID BY METAPHENYLENEDIAMINE REACTION.

Metaphenylenediamine reacts with nitrous acid in solution to produce triaminoazobenzene (bismark brown), a substance of pronounced color.[1] Ferric compounds are apt to cause trouble but will interfere less if a considerable excess of sulfuric acid is present. The presence of organic matter has no effect. The color produced ranges from yellow to a yellowish brown.

The reagent is prepared by dissolving 5 grams of metaphenylenediamine in water, adding sulfuric acid at once until the liquid is distinctly acid and diluting to one liter. If the solution so made up shows color it may be decolorized with animal charcoal. The standard solution is the same as in the preceding test, .0493 gram pure sodium nitrite dissolved in 100 c.c. water and ten c.c. of this solution diluted to 100 c.c. with concentrated sulfuric acid. The standard contains .00001 gram nitrogen per c.c.

The comparison is made on 100 c.c. of the solution to be tested, acidified with two c.c. dilute sulfuric acid, to which is added one c.c. of the reagent. A series of standards may be prepared, using the nitrosyl sulfuric acid pre-

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[1] Ber., *11*, 624.

pared above and diluting the amount used to 100 c.c. before the addition of the reagent. The color appears quickly so that a duplicate may conveniently be prepared from 75 c.c. of water. A standard for dilution and balancing methods is prepared by treating ten c.c. of the nitrosyl sulfuric acid with two c.c. of the reagent and diluting to 100 c.c. The resultant standard contains .000001 gram nitrogen per c.c.

METHOD C. NITROUS ACID BY ZINC IODIDE STARCH SOLUTION.

The blue color produced by nitrous acid in reaction with zinc iodide starch solution is the basis for this determination. The test has been estimated to be twenty times as delicate[1] as the metaphenylenediamine reaction (method B). A color will show in seven minutes if .00000025 gram nitrous acid is present.

The starch solution is prepared by boiling five grams of starch and 20 grams stannous chloride in 100 c.c. distilled water for some hours until the starch has almost entirely disappeared. The water is replaced as it evaporates. To this solution add two grams zinc iodide (ZnI_2) and dilute to one liter. This solution should be allowed to settle for several weeks, decanting the clear solution as needed. For the determination add four c.c. of this solution to fifty c.c. of the sample acidified with two c.c. sulfuric acid. The blue color develops most rapidly in the light. A standard solution of sodium nitrite is made up by dissolving .4925 gram pure sodium nitrite in water and making it up to one liter. Ten c.c. of this solution are then accurately pipetted out and made up to one liter giving a standard solution containing .000001 gram nitro-

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[1] Analyst, *39*, 350.

gen or .000003285 gram NO_2 or .000004426 gram NO_3 per c.c. For making up a series of standards this standard is used in varying amounts. Because of the fact that the color takes some time to appear the use of the duplication method is not advisable. The balancing method and dilution method are carried out by using the same standard but before the last dilution to one liter fifteen c.c. of the reagent are added. This will then show the characteristic color and have the same value as the standard above.

METHOD D. NITROUS ACID BY A-NAPHTHYLAMINE HYDROCHLORIDE.

A very delicate nitrous acid test is obtained by use of a-naphthylamine hydrochloride with tartaric acid. The reagent may be made up in such a form that it will keep indefinitely. The content of nitrous acid of the water must be very small, not over .00015 gram per liter or the addition of the reagent will cause a precipitate.[1] The sample may be diluted if the content is too high.

The reagent for the test consists of one part a-naphthalamine hydrochloride to ten parts sulfuric acid and 89 parts tartaric acid. A fifty c.c. sample is treated with one c.c. of this reagent and the results will show at once. If the sample is very dilute it may be well to use 100 c.c. A standard nitrite solution is made up by dissolving .4925 gram pure sodium nitrite in a liter of water. A series of standards is not to be recommended for as delicate a test as this. For duplication the above standard is diluted, ten c.c. to 100, and will then contain .00001 gram nitrogen per c.c., as nitrite. For factor as nitrate see preceding test. As blank for the duplication method use 48 c.c. water and one c.c. of the reagent. A standard for

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[1] Chem. Weekblad, *11*, 1115.

the use of dilution or balancing methods is made by addition of one c.c. of the above standard to 800 c.c. of water, adding one c.c. of the reagent and making up to one liter. This solution will show the color representing .0000001 gram nitrogen as nitrite per c.c. Dilute as this is, it is nearly to the upper limit that may be tested by this method so from this some idea of the delicacy of the test may be gained.

METHOD A. AMMONIA BY NESSLER'S REAGENT.

In reaction with ammonia Nessler's reagent produces a yellow to brown color which is a very accurate indicator of the amount of ammonia present in the solution. The presence of calcium or magnesium is undesirable as those are precipitated with the reagent and the presence of the precipitate obscures the results. Rather than precipitate and filter it is usual to hold them in solution by adding a few c.c. of a solution of 50 grams Rochelle salt in 100 c.c. of water. For the preservation of this solution five c.c. of Nessler's reagent should be added to it at the time of preparation.

Nessler's reagent, by a recent and highly approved formula is prepared as follows,[1] dissolve 2.5 grams KI in three grams water, add 3.5 grams HgI_2 and, when this is all dissolved, add 100 grams of a 15 percent solution of KOH. Allow this to stand and settle and decant. If it is necessary to use the reagent at once it should be mixed with a little talc, and filtered thru sand if possible. The sample used may be of drinking water or sewage effluent, or a solution of some substance containing ammonia as impurity.

To 100 c.c. of the sample solution add two or three c.c. of the Rochelle salt solution followed by the same

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[1] Apoth. Ztg., *29*, 972.

quantity of Nessler's reagent. The color appears at once. The color is fairly permanent and a series of standards may satisfactorily be produced. For this a standard solution is prepared by dissolving .3140 gram ammonium chloride in water and diluting to one liter. The standard then contains .0001 gram ammonia per c.c. For the duplication method the blank should be 95 c.c. of water. A standard for the dilution or balancing methods is made up by adding to 100 c.c. of the above standard, twenty c.c. of the Rochelle salt solution and twenty c.c. of Nessler's reagent and diluting to one liter. This latter standard then contains .00001 gram ammonia per c.c. For some uses it may be necessary to again dilute this latter standard to one tenth of its strength.

METHOD B. AMMONIA BY PHENOL.

The reaction of ammonia with phenol[1] gives a method of estimation of ammonia more rapid than the test with Nessler's reagent and just as delicate but not one admitting of as great accuracy. For careful work its accuracy is not to be depended on. The time for a complete determination should not exceed four minutes. The method is applicable to all cases where ammonia is to be determined. Calcium is not affected by the test but the presence of a considerable amount of free acid spoils the test.

To five c.c. of the solution to be tested add one c.c. of a dilute solution of sodium hypochlorite ($NaOCl$) and one c.c. of a 4 percent solution of phenol. This is then diluted to ten c.c. The full intensity of the color shows on heating in boiling water for two minutes.

Comparison may be made with a series of standards. For their preparation an ammonium chloride solution

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[1] Gas World (Coking Section), *64*, No. 1654, 10.

containing .3140 gram to the liter is prepared. Ten c.c. of this solution are diluted to 100 c.c. thus containing .00001 gram ammonia per c.c. This standard is also suitable for determination of results by the duplication method, using a blank of five c.c. of water but diluting to only nine c.c. instead of ten before the addition of the standard. The application of the duplication method is not very satisfactory. Ten c.c. of the original ammonium chloride solution treated with five c.c. hypochlorite solution and five c.c. 4 percent phenol solution are diluted to one liter and will then on heating show the color. The content of this standard is .000001 gram ammonia per c.c., an amount suitable for dilution or balancing methods. The method is delicate enuf to detect .0000001 gram ammonia in the five c.c. sample.

CHAPTER FIFTEEN.

PHOSPHORUS, SILICA AND BORON.

THESE three substances, found occurring naturally in the earth, are conveniently determined by colorimetric methods in small amounts, somewhat more accurately than by gravimetric methods. The first two conflict when determined in the same solution so that it has been found advisable to work out a new method whereby, by introduction of the proper corrections, both may be determined in the same solution, each in the presence of the other. Boron is to be determined in the form of boric acid in which form it occurs to some extent as a preservative in food.

METHOD A. PHOSPHORUS AS THE PHOSPHOMOLYBDATE.

Since the gravimetric method of analysis for phosphorus by precipitation of the phosphomolybdate is very inaccurate for small amounts of phosphorus, the solution of these small amounts of phosphomolybdate may be tested colorimetrically.[1] Silica must be removed or the results will be too high, for which removal a method is given here. The silica forms a silicomolybdate which has a color similar to that of the phosphomolybdate. A method has also been worked out for the determination of the two in the presence of each other. For further details of that method see Silica, this same chapter.

Ten to 100 c.c. of solution which must contain less than .0005 gram phosphorus are evaporated to dryness. When the solution is partially dry add three c.c. nitric acid.

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[1] J. A. C. S., *26*, 975.

The residue is then heated at 100 degrees for two hours. If the substance being tested is such that it contains no silica this dehydration may be omitted. The residue after dehydration is dissolved in water. It will not be necessary to filter as the loss due to filtration would be greater than that possible due to the presence of a small amount of precipitate of silica in the solution. Two c.c. of nitric acid are added and four c.c. of a solution of 50 grams of ammonium molybdate in a liter of water. After three minutes the color is suitable for comparison.

As a standard dissolve .5043 gram of pure crystallized sodium acid phosphate (Na_2HPO_4, $12H_2O$) in water, add 100 c.c. nitric acid and dilute to one liter. This solution contains .0001 gram P_2O_5 per c.c. A series of standards prepared from this must be replaced daily as the darker solutions precipitate out after a time and the lighter solutions fade. The fact that the color is not complete for some minutes renders duplication inconvenient. For use with the dilution or balancing methods ten c.c. of the standard are diluted with 75 c.c. of water, five c.c. of the molybdate solution added and the solution made up to 100 c.c. This standard will contain .00001 gram P_2O_5 per c.c.

METHOD B. PHOSPHORUS, SEPARATED BY PRECIPITATION AS MAGNESIUM PHOSPHATE.

This method is similar to that given for magnesium. The phosphate[1] is precipitated as magnesium phosphate by the addition of an excess of magnesium chloride, the precipitate is filtered off, dissolved in nitric acid and tested colorimetrically by the addition of a solution of ammonium molybdate. The advantages of this method are that all silica is removed from the solution being

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[1] J. A. C. S., *26*, 1463.

tested, thus preventing errors due to the silicomolybdate, and that the organic matter is removed from the final solution. The interference of calcium is prevented as in the magnesium test by the addition of ammonium oxalate. Experiments have shown that satisfactory samples should range between .004 and .0005 gram phosphorus. Results obtained in the presence of various disturbing factors were uniformly satisfactory.

One drop of ammonia and two or three drops of ammonium oxalate are added to the sample solution after which it is evaporated to dryness on the water bath. A solution is made up of 13 grams magnesium chloride and twenty grams ammonium chloride in a liter of water which includes fifty c.c. strong ammonia. One c.c. of this solution is added to the dried precipitate and the two well mixed with a glass rod. The precipitate is then washed out onto the filter with five c.c. dilute ammonia and the dish and filter washed with further successive portions until the volume of the filtrate reaches 50 c.c. The dish and filter are next washed with five c.c. pure water and a new beaker substituted to catch further washings. Five c.c. of concentrated nitric acid are used to dissolve any precipitate remaining on the dish and the precipitate on the filter carefully dissolved with this same acid. Dish and filter are washed with successive five c.c. portions of hot water until the filtrate amounts to 45 c.c. Four c.c. of a solution of 50 grams ammonium molybdate in a liter of water are then added and the comparison made after twenty minutes.

The standard is made up by solution of .5043 grams sodium acid phosphate (Na_2HPO_4, $12H_2O$) in water with the addition of 100 c.c. nitric acid, and dilution to one liter. A series of standards may be prepared from this solution, which contains .0001 gram P_2O_5 per cc.c. A duplicate cannot well be made up since the color is so long in coming. A standard for dilution or balancing methods is made up by adding to ten c.c. of the above standard, 70 c.c. water, 9 c.c. nitric acid and 8 c.c. ammonium molybdate solution and making up to 100 c.c. This standard which contains .00001 gram P_2O_5 (per c.c.) must stand for twenty minutes before use in order to bring out the color.

SILICA BY AMMONIUM MOLYBDATE IN THE PRESENCE OF PHOSPHORUS.

In reaction with ammonium molybdate silica produces a compound, ammonium silicomolybdate, which has a color similar to that of ammonium phosphomolybdate, a greenish yellow. When silica is to be tested for in the solution and it is known that no phosphorus is present the test is carried out identically the same as in the test for phosphorus, Method A. The color caused by the silica differs from that caused by the phosphorus in that it reaches its full intensity only after some hours, whereas phosphorus shows its full color after twenty minutes. Another property of the silica coloration, upon which this test is based is that its intensity at the end of an hour and twenty minutes is twice that at the end of twenty minutes.[1]

The samples are treated as in the preceding Method A up to the addition of the ammonium molybdate. Two samples of the same substance or solution to be tested must be so prepared at the same time. Also a standard must be available which contains only phosphorus. One sample and the standard are acidified and allowed to stand for twenty minutes and tested against each other. At the time these are acidified and the ammonium molybdate added a similar amount of ammonium molybdate is

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[1] J. A. C. S., *26*, 975.

added to the other sample but no nitric acid. After one hour has elapsed this second sample is acidified with nitric acid and allowed to stand for twenty minutes. It is then tested against the same standard as the other sample. The reading of the first sample is called the A reading and the reading of the second sample the B reading. From the law given above the phosphorus can then be figured.

If B reading is twice A reading there is no phosphorus present but only silica. If B reading is not twice A reading the difference between them is subtracted from A reading and the remainder is phosphorus. To repeat, the silica reading at the end of one hour and twenty minutes from the time the ammonium molybdate as added and the end of twenty minutes from the time the nitric acid was added to it represents the same amount of phosphorus as the reading at the end of twenty minutes by the first sample and in addition a reading for silica twice that given at the end of twenty minutes by the first sample.

The phosphorus having been determined by this method the silica may be determined by the same method taking no account of the phosphorus and making the test against a standard containing only silica. This silica determination may then be corrected by allowing for the phosphorus previously determined. This silica standard may be prepared at the same time as the original samples and the same solution used, as the first sample may be kept for four to five hours and tested against a standard prepared a similar time before. The test is by dilution only.

If a solution of known silica content is available it is best to use that. If such is not available .3657 gram potassium silico fluoride (potassium fluosilicate K_2SiF_6)

is dissolved in hydrochloric acid using as little acid as posible, and diluted to one liter. This standard contains .0001 gram SiO_2 per c.c. Such quantities of it may be used as are estimated to be necessary to counterbalance the contents of the solution being tested.

METHOD A. BORIC ACID BY CURCUMIN.

The red coloration produced by boric acid when treated with oxalic acid and curcumin is especially adapted to the estimation of the quantity of boric acid present in food as in adulterant. The advantage is not in the speed but in the greater accuracy of the method over the gravimetric method. The weight of B_2O_3 present may be as much as .002 gram.

The sample[1] placed in a platinum or porcelain casserol is made strongly alkaline and evaporated to dryness. The residue is acidified with hydrochloric acid and extracted with several successive portions of hot water. The extracts are filtered and the filter transferred to a dish, made alkaline with barium hydroxide and burned to ash. This ash is dissolved in hydrochloric acid and added to the original filtrate, and the volume of the filtrate made up to 100 c.c. Ten c.c. of this solution are then mixed with ten to fifteen grams purified sand in a porcelain dish and made alkaline with barium hydroxide. Evaporate to dryness on a paraffine bath, add enough dilute hydrochloric acid to make the contents of the dish acid, two c.c. saturated solution of oxalic acid and two c.c. of an alcoholic solution of curcumin, one gram to the liter. Mix the contents of the dish well and cover with a glass funnel whose stem is connected to a set of potash bulbs containing barium hydroxide. The other end of the set of potash bulbs is connected to an aspirator, the dish placed on a paraffine bath, the potash bulbs set in water

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[1] C. N., *87*, 27.

and air passed thru by suction until the mass is dry. One c.c. of the curcumin solution is added to the dish and it is again dried.

Extract the contents of the dish with several portions of alcohol and add the contents of the bulbs to the residue in the dish. This is dried, made acid with hydrochloric acid, treated further with reagents as was the original substance, and dried. The alcoholic extract from this is added to the previous extract and the color is thus obtained.

A standard solution of boric acid is made up by solution of .2886 gram sodium tetraborate (borax $Na_2B_4O_7$, $10H_2O$) and contains .0001 gram B_2O_3 per c.c. Ten c.c. of this solution are treated in the same manner as the sample and analysis made by dilution with alcohol. It is obvious that the series of standards or duplication methods would be out of the question. If one tube apparently has more of an orange tint than the other that is due to the presence of an excess of curcumin and a drop or two should be added to the other tube until the colorations are similar, after which dilution may be more accurately carried out.

Method B. Boric Acid by Turmeric Paper.

The amount of boric acid in a sample may be estimated by treatment with methyl alcohol, distillation of the resultant methyl borate into alkali and, after further treatment, comparing the stain made on a standard turmeric paper with those made by known quantities of boric acid. The sample is chosen according to the amount of boric acid suspected. If the matter is of animal origin ten grams are ordinarily used, if of vegetable origin one gram is usually sufficient.

The sample[1] is heated in platinum until the organic

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[1] Compt. Rend., *157*, 1433.

matter is all removed. Then treat the ash with five to ten c.c. of phosphoric acid and rinse into a flask. Wash out the dish with twenty c.c. methyl alcohol and add to the solution in the flask. Distill on the steam bath receiving the distillate in a platinum crucible containing a few drops of normal sodium carbonate solution. Add ten c.c. more of methyl alcohol to the flask and distill this over into the original distillate. This should carry over with it the last traces of methyl borate. Evaporate the distillate to dryness, cool and add four drops hydrochloric acid and one half c.c. of water. Wash this into a small vial and dilute to one and a half c.c.

A turmeric paper is made by soaking in a solution of turmeric and drying, after squeezing out the excess of the solution. It is essential that the papers be of uniform thickness, width and saturation with the reagent. A good grade of drafting paper is very satisfactory. The width may be made such that it readily admits of their introduction into the vial used for the determination. A strip of this paper is immersed in the vial to a depth of 15 mm. and the vial exposed to a heat of 35 degrees for three hours. If time is not a consideration the vials may be allowed to stand at room temperature for 24 hours after which the results will be the same as by heating. The intensity of the red coloration produced on the paper is a measure of the amount of boric acid present in the sample.

The same standard as in the previous test, .2886 gram sodium tetraborate (borax, $Na_2B_4O_7$, $10H_2O$) to a liter of water, is used for the preparation of the standards. This standard contains .0001 gram B_2O_3 per c.c. The color of the standard papers so prepared is permanent and by protecting them from dust they may be kept several months.

CHAPTER SIXTEEN.

OXYGEN AND HYDROGEN PEROXIDE.

THE determination of the dissolved oxygen in drinking water and in sewage effluents is of vital importance as it is also in the preliminary examination of streams proposed as sources of sewage disposal. The use of hydrogen peroxide as an antiseptic and as a reagent requires that its strength be known.

METHOD A. OXYGEN BY CUPROUS CHLORIDE.

The properties of the copper chlorides in ammoniacal solution, cuprous chloride being colorless and cupric chloride a deep blue, may be made use of for the determination of oxygen in a solution.[1] The addition of cuprous chloride to the water will result in a blue color due to its oxidation to cupric chloride which color will be proportional to the amount of available oxygen in the solution tested. If the sample contained much calcium this would become turbid on the addition of the ammonia to make the solution alkaline, therefore two or three c.c. of hot saturated solution of ammonium chloride are added to the sample before the addition of the other reagents. If the test is being made on a sewage effluent or other solution which is slightly colored, a similar yellow may be added to the standard in the form of some yellow dye such as paranitrophenol. The error which will be introduced by the original solution being slightly yellow is not great.

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[1] J. Soc. Chem. Ind., *20*, 1071.

The sample is gathered in a bottle and the bottle tightly corked, taking care that there is not an air bubble left below the cork. A special apparatus is used to transfer this to the tube in which the test is to be made. A double-hole stopper is prepared to fit the sample bottle, with two tubes, one of which runs to the bottom of the bottle and one of which only enters the cork. A rubber tube is attached to the shorter tube. For the transfer of a sample from the bottle to the tube in which it is to be tested the rubber tube, which should be about a foot long, is filled half full with kerosene oil. The size of tubing used should not be over five to eight mm. internal diameter. The double hole stopper is then carefully fitted to the bottle of sample without introducing air. The liquids are next allowed to flow out the rubber tube. The oil will flow ahead if the tube is carefully managed and thus sweep out all air and prevent contact of the sample with the air. In the tube in which comparison is to be made the oil will rise to the surface and the sample then be run in under the layer of oil. The long tube added to the bottle serves as an air inlet, that the contents may run out. A small amount of the oil will always be introduced into the bottle in the process of fitting the stopper, which will rise to the upper surface of the liquid. The bottle is to be inverted as soon as satisfactory connections have been made and the oil will then form a layer at the upper, formerly the bottom, part of the bottle. The long tube used will let in air above this layer so that the sample has no chance to absorb oxygen from it.

The reagent for the test is prepared by warming a solution of cupric chloride with some scrap copper and pouring into water. The white precipitate which forms is filtered and washed, first with hot water, then with alcohol and then with ether. The powder is then dried and must be pure white. For use a small amount of the powder is dissolved in concentrated hydrochloric acid. This is added to the sample by placing the solution of the reagent in a tap funnel and inserting the tip of the tap funnel in the oil layer before the reagent is allowed to run into the solution. In that way the introduction of air is prevented.

The test is performed by dilution. A standard water for use is made by shaking pure water in a bottle until the air bubbles remain in the liquid and then allowing this to stand until the air bubbles vanish. A table may then be consulted to find the amount of oxygen necessary for saturation of a water solution at the given temperature.[1]

Temp.	Soluble in One Liter.
5.2°	8.856 c.c.
5.65°	8.744 c.c.
14.78°	7.080 c.c.
24.80°	5.762 c.c.
30.00°	2.610 c.c.

As a standard one part of this is to be used to three parts of boiled water which has shown no oxygen under test. The mixing is to be done in the colorimetric tube in which the test is to be made and under oil. To each, sample and standard, there are added a few c.c. of the solution of cuprous chloride dissolved in hydrochloric acid and immediately after that a few c.c. of ammonia. The white precipitate which appeared on the addition of the cuprous chloride must entirely disappear, otherwise too much of the copper solution has been added and a yellow interference will result. The ammonia brings out the blue colors of the solutions. The boiled water contain-

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[1] For further solubilities see Seidell, Solubilities of Organic and Inorganic Compounds.

ing no oxygen is then used for dilution of the darker until results are identical. The readings taken are those at the top of the aqueous solution, below the level of the oil. Since oil will transmit oxygen after a few hours it is necessary that this test be carried along to completion in a reasonable length of time.

If it is desired to make up permanent standards this is accomplished by dissolving three grams of copper wire in hydrochloric acid and evaporating to dryness. More acid is added and this repeated several times. The white residue is now dissolved in water, ammonia and hydrochloric acid added until the solution shows a deep blue color and the solution smells strongly of ammonia, and dilution to one liter carried out. Permanent standards may be made by addition to 100 c.c. of water of the following amounts of the standard made up.

Standard per 100 c.c.	Represents in c.c. Oxygen per Liter.
.36	1
.72	2
1.08	3
1.44	4
1.80	5
2.16	6
2.52	7
2.88	8
3.24	9

METHOD B. OXYGEN BY ADUROL.

The reagent for this test is adurol with ammonium chloride or a mixture of dry powdered borax and adurol. The method is not so accurate as the preceding because, from the conditions of the method, as great care as to accuracy cannot be used.

The sample of 50 or 100 c.c. water and the standard, prepared by saturation of a volume of water, are placed in bottles.[1] A pinch of adurol is added to each and .5

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[1] Z. Angew. Chem., *24*, 341.

c.c. ammonia containing about 20 percent ammonium chloride in solution. This solution sinks to the bottom. The standard may be varied by the use of varying amounts of boiled water with the saturated aqueous solution. To prevent the absorption of oxygen from the air in the bottle, before shaking at this point, it is well to allow carbon dioxide to flow into the bottles and thus displace the air which is present over the liquids. The bottles are then corked and shaken. The standard must be very nearly the same in color as the sample so that a guess may be made as to the content from the experience of the operator. Dilution is not satisfactory.

Borax heated for some hours at 50 degrees and mixed six parts of borax, one part adurol and three parts Rochelle salt furnishes a convenient reagent.[1] This is added instead of the adurol at the point in the test. The function of the Rochelle salt is to prevent the precipitation of calcium.

HYDROGEN PEROXIDE BY ITS OXIDISING ACTION ON FERROUS IRON.

For the analysis of a solution of hydrogen peroxide the sample solution is allowed to act on a solution of ferrous iron and the amount of the iron oxidised is tested by the addition of potassium sulfocyanate as in the iron test. The comparison may be made by any method.

Ten grams of ferrous ammonium sulfate [$FeSO_4$ $(NH_4)_2SO_4$, $6H_2O$] are dissolved in 100 c.c. of water. A test should be made on this with potassium sulfocyanate to make sure that all iron is in the ferrous condition. If not it must be reduced with hydrogen sulfid or by acidifying with sulfuric acid and adding zinc. This reagent must finally be available in a freshly reduced condition

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[1] *Ibid.*, *26*, 134.

free from reducing agents. If not already acidified it must be made acid for use. The test is made by the addition of one c.c. of this solution to a sample of ten c.c. of the solution to be tested and then the addition of one c.c. of a dilute solution of potassium sulfocyanate. The color produced may be compared with a series of standards. For these a solution of ferric iron and potassium sulfocyanate is made up and diluted with water until it is of the desired concentration for the varying standards. These fade after a time and must be renewed. A blank of nine c.c. of water may be used and hydrogen peroxide from a known solution added to it. The difficulty with that method is the obtaining of a definitely known solution. The commercial solution is approximately 3 percent when fresh. Similarly a standard for the dilution or balancing methods is made up by the addition of ferrous iron and potassium sulfocyanate to 25 c.c. of a solution of known peroxide content and suitable dilution.

CHAPTER SEVENTEEN.

SULFUR, HYDROGEN SULFID AND SELENIOUS ACID.

The methods for the determination of sulfur given here are those for the determination of sulfur in iron and steel and in similar substances from which it is possible to release it as hydrogen sulfid by the action of an acid. The method for hydrogen sulfid is for the analysis of a liquid containing dissolved hydrogen sulfid, as for example natural waters in some localities. A method is also given for the analysis for selenious acid, an acid of the rare element selenium which occurs in the presence of sulfur and has properties similar to those of sulfur.

METHOD A. SULFUR BY PARAPHENYLENEDIMETHYLDIAMINE.

The sulfur in iron may be determined by the intense blue color produced by its reaction with paraphenylenedimethyldiamine[1] (unsymmetrical). The color is so intense that it is necessary to dilute the sample to a considerable extent or to use a very small sample. The former method is more satisfactory.

A convenient sample is two grams. This is treated with hydrochloric acid and the resultant hydrogen sulfid absorbed in caustic soda, drawing the air from the flask where decomposition is carried on thru a potash bulb, by suction. This caustic soda solution is then diluted to 100 c.c. and ten c.c. pipetted out as a sample. To the sample add 1.5 c.c. dilute sulfuric acid and dilute to 50 c.c.

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[1] Columbia University, School of Mines Quarterly, *23*, 24.

To this 50 c.c. of solution add .1 c.c. of a two percent solution of the reagent above and finally a drop of a five percent solution of ferric chloride. The color results immediately on the mixing of these reagents and comparison of the color may then be made by any of the standard means.

As a standard dissolve .2435 gram sodium sulfid (Na_2S) in a liter of water. For making up a series of standards five c.c. of this solution are to be diluted to 100 c.c., at which concentration the sulfur content will be .000005 gram per c.c. A series of standards from a solution of this concentration would use one to 25 c.c. for the varying concentrations. As a basis for duplication use the same standard and a blank of twenty-five c.c. of water to which have been added the same reagents as to the sample. Standards do not keep very well. For dilution or balancing treat five c.c. of the standard solution first proposed with double the quantities of reagents specified for the sample and dilute to 500 c.c. The standard will then contain .000001 gram sulfur per c.c.

The dilution and aliquot parts of the sample specified allow for the testing of one tenth of the sample chosen. Simple multiplication of the result obtained, by ten, will then give the weight of sulfur in the sample and division of the weight of sulfur by the weight of sample will give the percent of sulfur. Others of the diamines may be used for this reaction as for example p-phenylenediamine.

Method B. Sulfur by the Action of Hydrogen Sulfid on Arsenious Oxide Paper.

The comparison of stains made by known amounts of sulfur on arsenious oxide paper with those made by a sample of steel or similar substance furnishes a method for the rapid estimation of the sulfur content of a sample.[1] The standards do not keep well and it is therefore necessary to prepare temporary standards at the time the test is made.

The prepared paper is made up by soaking a good grade of drafting paper in a solution of 10 grams As_2O_3 in 30 c.c. hydrochloric acid and 970 c.c. water. The paper is soaked, the excess of the reagent removed and the paper carefully dried. It is then to be cut into squares ten cm. on a side. The sample is placed in a glass tumbler and the varying standard amounts of a steel of known sulfur content are placed in other tumblers of the same size. Each tumbler is covered with a piece of the prepared paper, a piece of felt and a weight to hold the paper tightly to the top of the tumbler. To each tumbler there are then added, 10 c.c. benzine, sp. gr. .710, and 50 c.c. hydrochloric acid sp. gr. 1.1. The stain on the prepared paper produced by the sample may then be compared with that produced by the standard amounts and from that, estimation made. For the analysis of several samples at one time it is possible to run them simultaneously and compare with the same standards.

HYDROGEN SULFID BY METHYLENE BLUE.

This method is an adaptation of Method A for sulfur in iron and steel to the analysis of natural waters and other solutions containing a trace of hydrogen sulfid.[2] As the color produced is very permanent, standards may be prepared and kept several weeks before renewal. The addition of the reagents in the order specified is imperative as the order in which they are added will make a difference in the tint of the solution produced. Satisfactory

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[1] Iron Age, *93*, 1253.

[2] Z. Anorg. Chem., *86*, 143.

results may be obtained from solutions containing as little as .00001 gram hydrogen sulfid per liter.

The sample is five hundred c.c. of the solution. For contents of more than .001 gram hydrogen sulfid per liter add ten c.c. concentrated hydrochloric acid, .025 gram p-phenylenedimethyldiaminesulfate and 2.5 c.c. tenth normal ferric chloride in hydrochloric acid solution. If the content of the sample is less than .001 gram per liter add ten c.c. hydrochloric acid, .01 gram of the diaminesulfate and one c.c. tenth normal ferric chloride. The solutions must stand several hours before comparison is made.

For the preparation of the standard a solution of hydrogen sulfid in water must be determined by the usual iodometric method or some other similar way. Known quantities of this may then be treated as the samples were for their production of color.

SELENIUM AS SELENIOUS ACID BY POTASSIUM IODIDE.

The amount of selenious acid present in a solution may be estimated from the intensity of the coloration produced in reaction with potassium iodide. The method is delicate enuf to show .000001 gram per c.c.[1]

The sample, if fairly concentrated, is five c.c. If the sample is very dilute, more may be used. The sample is diluted to 70 c.c., one drop gum arabic solution and five drops 5 percent hydrochloric acid added, the whole mixed and diluted to 99 c.c. Add one c.c. potassium iodide solution, allow to stand for five minutes and compare with a standard by dilution. The potassium iodide solution must be colorless.

A standard is prepared by the solution of .1632 gram crystalline selenious acid (H_2SeO_3) in water and dilution

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[1] Z. Anal. Chem., *53*, 29

to one liter. This standard contains .0001 gram selenium per c.c. as selenious acid. If it is desired to obtain the results in terms of selenious acid the standard should be made by solution of .1 gram selenious acid when the same weight per c.c. would be present of selenious acid instead of selenium. One c.c. of this standard is diluted, treated with the same reagents as the sample and results obtained by dilution.

CHAPTER EIGHTEEN.

SALICYLIC ACID AND CYANIDES.

These two substances are of very infrequent occurrence. The first, salicylic acid, finds a limited use as an antiseptic and is used as a cheap wintergreen flavor. The method given for cyanides was developed for the determination of the cyanides present in poisonous plants suspected to derive their poisonous nature from that source but is applicable to all determinations of small amounts of the simple cyanides.

Salicylic Acid by Fehling's Solution.

This method is the opposite application of Method C for copper.[1] In this method the salicylic acid solution is treated with Fehling's solution and compared with a series of standards prepared at the same time. The determination is prevented by the presence of free mineral acid, citric and tartaric acids and any considerable amount of iron. The presence of .000001 gram per c.c. may be detected in a ten c.c. sample and correspondingly smaller amounts by suitable concentration. The sample may contain up to .0001 gram in a ten c.c. sample but if its content is over .00001 gram per c.c. the sample solution of ten c.c. should be diluted to 100 c.c. and ten c.c. taken for analysis.

A standard salicylic acid solution is made up by solution of .1 gram of the substance in water and made up to one liter. By the solution of .1160 gram sodium sali-

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[1] Zeit. Untersuch Nahr. Genussm., *22*, 727.

cylate the same strength solution as above may be obtained. Each contains .0001 gram salicylic acid per c.c. Temporary standards are prepared by the use of 0, .2, .4, .6, .8, and 1.0 c.c. of this solution in plain test tubes. The use of graduated tubes for the sample and standards is not necessary in this case. The sample is concentrated to two or three c.c. and placed in a similar tube. To each tube of standard and to the sample there are now added two c.c. of a solution of one part Fehling's solution to ten parts water, five drops of two percent potassium nitrate solution, five drops ten percent acetic acid and enough water to bring the volume of each up to about five c.c. The volumes must be the same of each. The tubes are then heated in boiling water for 45 minutes and are ready for comparison. The results must be obtained by inspection of the temporary standards only, as dilution of the samples does not prove satisfactory.

Fehling's solution is made by mixture of equal volumes of the following two reagents just before using, 34.64 grams pure copper sulfate in 500 c.c. of water, and 60 grams caustic soda and 173 grams Rochelle salt (sodium potassium tartrate, $NaKC_4H_4O_6$, $4H_2O$) in 500 c.c. water. The reagents keep perfectly unmixed but the solution must be used immediately after mixing.

Cyanides by Changing to Sulfocyanates and Coloring with Iron.

If the solution is an inorganic one it is only necessary to render the solution slightly alkaline with caustic soda. In the solution of a salt or solid substance to be analysed for cyanides the solution should be kept alkaline to prevent loss. The preparation of a solution of an organic nature is somewhat more complicated.[1] The

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[1] J. A. C. S., *35*, 1624.

substance to be tested is macerated and digested with 100 c.c. of water for some time. The extract is then filtered off and the solid residue washed with another 100 c.c. of water. This solution is to be placed in a flask, acidified with hydrochloric acid and three fourths of the volume distilled over into fifty c.c. of potassium hydroxide. This solution is then diluted to a convenient volume and fifty c.c. taken for the test.

To the sample of 50 c.c. of solution is added one c.c. of ammonium sulfid and the whole evaporated to dryness on the water bath. The residue is taken up with ten to fifteen c.c. hot water and slightly acidified with hydrochloric acid. Filter off the sulfur, add one half c.c. hydrochloric acid and boil for five minutes. The sulfur is now filtered off and the operation repeated, until the final solution comes clear. An alternate method is to use five c.c. of a solution of 40 grams potassium sulfid in one liter of water, instead of the one c.c. of ammonium sulfid. Less trouble will be experienced with sulfur if this is used. The clear solution from the previous operation is diluted to fifty c.c. and fifteen drops of a five percent ferric chloride solution added.

If the iron is precipitated on addition of this ferric solution it indicates that the solution was alkaline and must be acidified more. A lemon yellow rather than a red color indicates that the solution is too strongly acid. The red color produced is a result of the cyanide which has been changed to the form of the sulfocyanate. The standard is prepared directly from the sulfocyanate since the relation between the two compounds is known. A standard solution is made up by solution of 1.4923 grams potassium sulfocyanate in water and dilution to one liter. Each c.c. of this solution contains .001 gram KCN in which terms the results of this test will be stated. Permanent standards may be made up but possess the same properties as the results of the iron-sulfocyanate reaction always do, that they fade in the light after a time. Duplication is possible by the addition of this standard to a blank of 40 c.c. of water containing the ferric solution. For dilution ten c.c. of this solution may be diluted to fifty c.c., treated with fifteen drops of ferric chloride and the sample or standard diluted for obtaining the result. The amount used here may be suitably varied from ten c.c. if the solution so made is too strong or too weak. As a standard for balancing add two c.c. of ferric chloride to twenty-five c.c. of the standard and dilute to 250 c.c. This latter standard for balancing will then contain .0001 gram KCN per c.c.

CHAPTER NINETEEN.

COLOR OF WATER, OILS AND DYES.

The color of water is one of the things determined in water analysis in comparison with a standard solution officially specified. Oil is graded according to its color. The preliminary examination of dyes by colorimetric methods is possible in some cases.

Color of Water.

The color of water is graded by comparison with a standard platinum and cobalt solution made up as follows, dissolve .1426 gram platinic chloride and .1 gram cobaltous chloride in water, add ten c.c. concentrated hydrochloric acid and make up to 500 c.c.[1] The usual method is to make up a series of standards of 100 c.c. volume. These should be at five point intervals up to 40 c.c. and at ten point intervals from that point to 70 c.c. Grading is never made higher than 70. The number of c.c. used, of the solution above specified, is the measure of the number of the grade indicated by that standard.

For the preparation of a standard to be used by the balancing method the above 500 c.c. of standard may be diluted to one liter. The color value of this solution will then be 50 and, after balancing the instrument, the color value of the sample will be to that of the standard inversely as the volume of the two used. For rapid work in the field permanent glasses are made having the various standard colors as given by the official solution above specified.

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[1] Olsen, Quan. Chem. Anal.

COLOR OF OILS.

All oil is graded by color, both the refined grades and the lubricants and crude oils. The instrument in ordinary use for this purpose is the Stammer form of colorimeter. Lovibond's Tintometer is also used with a special series of glasses for oils. The grading of kerosene is into four classes, water white, superfine white, prime white and standard white. These grades all turn yellow on exposure to light but that has no effect on their burning qualities. The grading of oils other than lighting oil is too lengthy a subject for discussion here.

Recently there has appeared on the market a new instrument, the Saybolt Chromometer which combines the Lovibond Tintometer and the Stammer Colorimeter. This is treated at greater length under Apparatus, Chapter Two.

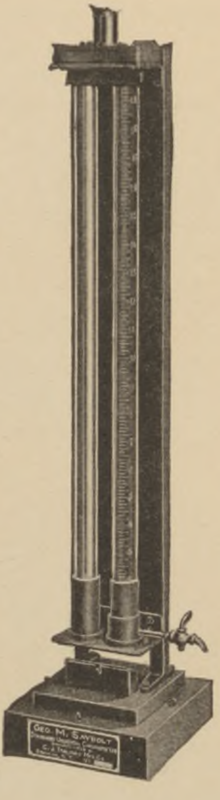

FIG. 16. Saybolt Chromometer.

COLOR OF DYESTUFFS.

The use of the colorimeter for determination of the strength of solutions of dyestuffs is very limited in extent, inasmuch as it is not reasonably accurate in practice in a majority of cases. It is however useful as a method of preliminary classification and may then be followed by the longer and more accurate test necessary after this preliminary has given a clue to the concentration to be expected.

Any of the four methods of colorimetric analysis are applicable to this use under the proper conditions. Lovibond's Tintometer finds some use in this field. It is of course necessary to dilute the sample to be used as commercial solutions of dyes are ordinarily so concentrated that the eye cannot penetrate the solution.

CHAPTER TWENTY.

NEPHELOMETRY.

In closing a word about the methods of nephelometric measurement may not be amiss. The tests given are entirely those depending upon colorimetry, the measurement of the intensity of light of a given color transmitted thru a solution. The methods of nephelometry measure the amount of a finely divided precipitate suspended in a solution. This was first tried by a method similar to that of colorimetric determination, passing a ray of light thru the solution and estimating the amount of precipitate present from the interference with light caused by its presence. Experiment has shown that the measurement of such a precipitate is made many times more delicate by measuring the amount of light reflected from it rather than the interference of the precipitate with light.

The instrument used for such determinations is a modified form of the Duboscq colorimeter with an opaque bottom to the cup. Precipitates suitable for such examination are those of silver chloride and barium sulfate in dilute solutions where the precipitate is described as an opalescence. Many applications to bacteriological and physiological work have been found. For more complete information on this subject see Journal Industrial and Engineering Chemistry, Vol. 10, No. 7, P. A. Kober.

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