REVIEWS.

REPORT OF THE INTERNATIONAL COMMITTEE ON ANALYSIS TO THE SIXTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY AT ROME, 1906.[1]

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The International Committee on Analysis appointed by the Fifth International Congress of Applied Chemistry (Berlin, 1903) and subsequently enlarged by the addition of new members selected by the original committee, was composed of 43 members representing 18 different countries. This committee was divided into 11 sub-committees, to which 14 questions were assigned as follows:

(I) (1) Uniform methods for the determination of lead, copper, silver, antimony and zinc.

(II) (2) Uniform materials for use as standards in volumetric analysis, and directions for purifying them and preparing them for weighing.

(3) Uniform manufacture of reagents.

(III) (4) Uniform principles relating to the adjustment and calibration of chemical measuring apparatus.

(8) Uniform principles concerning the adjustment and calibration of instruments for density and percentage determinations.

(9) Adjustment and legalization of balances and weights for chemical purposes.

(IV) (5) Methods of sampling materials for analysis.

(V) (6) Accurate statement of results obtained in fuel investigation.

(VI) (7) Uniform presentation of analytical results.

(VII) (10) Determination of arsenic in wall papers, fabrics, etc.

(VIII) (11) Determination of boric acid, benzoic acid, salicylic acid and other substances employed in the preservation of foods.

(IX) (12) Determination of sulphur in pyrites, blendes, etc.

(X) (13) Is it necessary to calculate the percentage of manganese in a permanganate solution the strength of which with respect to iron is known, by means of a coefficient different from that indicated by the equation?

(XI) (14) Methods of analyzing materials containing tartaric acid.

The statement is made by Dr. G. Lunge, chairman of the committee and editor of the report, that the work upon questions 2, 12 and 13 may be considered complete, or nearly complete;

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[1] Edited by Dr. G. Lunge. Pages iv+421. Zurich, 1906. Zürcher & Furrer.

that the work upon questions 1, 4, 5, 6, 7, 8, 9, 10 and 11 has led to the accumulation of much valuable material, but has not yet culminated in the establishment of uniform methods; that one member of the committee only has in each case reported upon questions 5 and 8, and that question 3 has received no attention whatever.

Sub-Committee I. Question 1. Uniform Methods for the Determination of Lead, Copper, Silver, Antimony and Zinc. (Pages 16–70.)—The work in this field has by no means led to the establishment of uniform methods. Considerable progress toward this goal has, however, been made in the study of methods for the determination, respectively, of zinc and of copper. The report embraces (A) a brief general discussion (by G. Chesneau, chairman of the first sub-committee) of the methods usually employed for rapid work in industrial laboratories, or for accurate work in scientific laboratories, together with a brief resumé of the experimental work performed by members of the sub-committee; (B) a discussion, both historical and experimental (by H. Nissenson and W. Kettembeil) of the methods employed in the determination of zinc; (C) an article (by Nissenson) on the importance of uniform, international methods of analysis; (D) a study of the electrolytic method for determination of copper (by A. Menozzi); and (E) a communication (by Nissenson) concerning the methods of assaying employed in the Central Laboratory of the Stock Company at Stolberg. A brief statement of some results obtained in the work upon the determination of zinc and copper should be of general interest.

On the Determination of Zinc.—Two volumetric methods are commonly employed in technical laboratories: titration with sodium sulphide solution, and titration with potassium ferrocyanide solution. The authors propose a slight modification of the latter method as employed by de Koninck and Prost (*Z. angew. Ch.* 1896, 460–468; 564–572). Instead of adding an excess of potassium ferrocyanide at the outset, and then titrating back the cold solution with a standard zinc solution, the authors titrate directly, heating the solutions in order to hasten the reaction. They employ a 1 per cent. solution of uranium nitrate as indicator, but find that a solution of ammonium molybdate containing 9 grams to the liter serves as a satisfactory indicator, reacting more rapidly than the uranium solution, and to certain observers offering a sharper end-point. A comparison of the results obtained by the use of the sodium sulphide method and the ferrocyanide method respectively, shows them to be remarkably concordant. Both methods are also shown to give results agreeing very closely with results obtained both with the gravimetric (precipitation with hydrogen sulphide) method and with Nissenson's (*Z. Elektrochem.* **9**, 761 (1903); *Chem. Ztg.* **27**, 659

(1903)) electrolytic method. Sufficient practical work has not yet been performed to warrant the selection for international use of either method in preference to the other.

The determination of zinc in scientific laboratories is in general accomplished by precipitating the zinc with hydrogen sulphide, preferably from a warm solution acidified with acetic or formic acid. The final treatment of the zinc sulphide obtained is subject to considerable variation in different laboratories. The remarkable agreement obtained by Nissenson between the results from the gravimetric and the electrolytic methods respectively, seems to point toward the latter as the standard method of the future.

For the complete analysis of metallic zinc several different methods have been in use. The method recommended by Nissenson is briefly as follows: 100 grams of the metal are placed in a 750 cc. Erlenmeyer flask provided with a safety tube, and are treated with about 200 cc. of water. Sufficient sulphuric acid is gradually added to maintain a slow evolution of gas. This gas is led into a small Erlenmeyer holding 10 cc. of a solution that contains 7 grams of bromine and 7 grams of sodium hydroxide per liter. When the zinc has almost entirely dissolved, the remaining spongy material is filtered off, and washed until all sulphuric acid has been removed. The amount of iron in the filtrate is determined by titration with permanganate. The spongy material is dissolved in nitric acid. A precipitate at this point may be caused by tin or by large amounts of antimony. If no precipitate appears, the solution is treated with 12 cc. of dilute sulphuric acid, and evaporated until white fumes appear. After the separation and determination of the lead, the filtrate is warmed and treated with hydrogen sulphide. The precipitate is filtered off, allowed to stand in a cold solution of sodium sulphide for some time, and is filtered. In the filtrate antimony is precipitated with sulphuric acid, allowed to subside, filtered off, and dissolved in concentrated hydrochloric acid. The solution is boiled until all hydrogen sulphide is expelled, treated with from 15 to 20 cc. of dilute hydrochloric acid, and is titrated while boiling hot with potassium bromate, indigo being used as indicator (*Berg. hüttenmänn. Ztg.* **62**, 421 (1903)). The residue left after the above-mentioned treatment with sodium sulphide is dissolved in nitric acid. The solution is almost neutralized with ammonium hydroxide, and is treated with ammonium carbonate until it reacts alkaline. After it has been standing (warm) for several hours the bismuth carbonate is filtered off and is dissolved in a few drops of sulphuric acid. The solution is evaporated until white fumes appear in order to remove the last traces of lead. The bismuth is once more precipitated, and is finally determined as Bi_2O_3. If copper is present in the filtrate from the first bismuth precipitate, this solution is decolorized with potassium cyanide.

Cadmium is precipitated with sodium sulphide, is filtered off and is weighed as CdO, while from the filtrate copper sulphide is precipitated by cautious addition of acid. The filtrate from the hydrogen sulphide precipitate is boiled to expel hydrogen sulphide, is oxidized and is treated with ammonium hydroxide. Iron is determined after a second precipitation. The filtrate from the first iron precipitate is acidified, and is treated (hot) with a few drops of barium chloride solution. The barium sulphate is removed by filtration. The barium remaining in the filtrate is precipitated with sulphuric acid, and is filtered off. The hot solution is treated with hydrogen sulphide. The arsenious sulphide is filtered off, and if it still contains antimony is treated with cold ammonium carbonate. The solution is again filtered. The arsenic in the filtrate is precipitated with dilute sulphuric acid, is filtered off, and after being dissolved in hydrochloric acid, to which some potassium chlorate has been added, is precipitated with magnesia mixture. This method is commendable in that a single 100-gram sample suffices for the determination of all ordinary impurities and in that provision is made for the determination of bismuth, an operation that has been neglected by authors of previously published methods. Nissenson believes that the percentage of zinc itself is best determined by difference. Chesneau, however, cautions chemists against the extension of this indirect method to other cases, however applicable it may in the case of zinc. He is of the opinion that the percentage of each impurity and the percentage of the metal itself should in each case be directly determined.

On the Electrolytic Determination of Copper.—This subject is discussed by A. Menozzi who has made an experimental study of the various conditions governing the deposition of copper for analytical purposes. The negative electrodes employed in the work comprised two platinum dishes with a capacity of from 100 to 150 cc., with an inside surface of from 100 to 125 sq. cm., and weighing from 60 to 62 grams; two cones with a working surface of 160 sq. cm., and weighing from 22 to 29 grams; a cylinder with a total surface of 260 sq. cm., weighing a little over 54 grams, and a cylinder of platinum gauze, with a surface of about 145 sq. cm., weighing 12 grams. Platinum spirals, discs and gauzes served as positive electrodes. Especial emphasis is laid upon the desirability of employing the rotating anode. For this work the electrodes of Classen are well adapted, while the gauze electrodes of Winkler are unsatisfactory. The stirring apparatus of Fischer and Boddaert was employed. The author's results may be summarized as follows: (A) Deposition from acid solution. A nitric or sulphuric acid solution should be employed. The amount of copper deposited should not exceed 1 gram in weight. From 2 to 5 volumes of concentrated nitric acid or from 3 to 5 volumes of sulphuric acid are added to 100 volumes of the electrolyte. The mean tension of the current for ordinary electrolysis should be from 1 to 3 volts; for electrolysis with rotating electrode, from 3 to 4 volts. The amount of current for ordinary electrolysis is from 0.1 to 0.5 ampere; for electrolysis with rotating electrode, from 4 to 5 amperes. The presence of an excess of nitric acid, or of chlorides, organic acids, arsenic, antimony, bismuth, mercury, silver or tin, is detrimental. Agitation of the liquid (by rotating electrode) remarkably facilitates the deposition of the copper. Heating the electrolyte favors the deposition of copper, but if the temperature is raised too high, removal of the last traces of copper becomes almost impossible. The deposit must be rinsed with water, alcohol, and alcohol and ether, without interrupting the current. The deposition requires from three to twelve hours when the ordinary method is employed; with the rotating electrode it requires about one hour. The end-point may be determined by testing the electrolytic solution for copper by the usual chemical methods, or by means of an auxiliary electrode. Copper may be separated by the electrolytic method from alkali and alkaline earth metals, from zinc, cadmium, nickel, cobalt, aluminum, chromium, iron (if present in small quantities) and from lead and manganese (in presence of an excess of nitric acid). One of the principal difficulties connected with the electrolytic precipitation of copper is to obtain, in acid solution, a complete deposition of the last traces of the metal. Some laboratories overcome the difficulty by concentrating the solution toward the end. Menozzi prefers to determine the residual copper colorimetrically, after treating the solution with ammonium hydroxide. (B) Deposition from alkaline solution. A nitrate, sulphate or chloride solution should be employed. The amount of copper deposited should not exceed 1 gram in weight. Sufficient ammonium hydroxide is added to redissolve the precipitate at first formed. Then more ammonium hydroxide (0.96) is added, from 20 to 25 cc. for a solution containing 0.5 gram of copper, and from 30 to 35 cc. for a solution containing 1 gram of copper. From 3 to 4 grams of ammonium nitrate are also added. The mean tension of the current for ordinary electroylsis is from 2 to 4 volts; with rotating electrode it is from 3 to 5 volts. The amount of current for ordinary electrolysis is from 0.1 to 0.5 amperes; with rotating electrode it is from 4 to 5 amperes. The presence of lead, bismuth, mercury, cadmium and nickel is detrimental. Agitation of the liquid (by rotating electrode) accelerates the deposition of copper. Heating is to be avoided. The deposited metal should be washed without interrupting the current. Precipitation requires from four to twelve hours by the ordinary method; with the rotating electrode it requires from one to two hours. The action may be considered complete when the solution has completely lost its color.

Sub-Committee II. Question 2. Uniform Materials for Use as

Standards in Volumetric Analysis, and Directions for Purifying Them and Preparing Them for Weighing. (Pages 71–153.)—The report of work accomplished in this field embraces a general statement by W. Fresenius (chairman of the second sub-committee), and two articles of considerable length already published elsewhere ("Beiträge zur chemisch-technischen Analyse," *Z. angew. Ch.* **17**, 195–203; 225–236; 265–270 (1904). *Centrbl.* 1904, I, 1036. "Zur Frage der Einstellung von Normalsäuren für Massanalyse," *Z. angew. Ch.* **18**, 1520 (1905); *Chem. Centr.* 1905, II, 1284) by G. Lunge. Other articles published ("Zur Frage über einheitliche Titersubstanzen (Urtitersubstanzen)," S. P. L. Sörensen, *Z. anal. Ch.* **44**, 141 (1905); "Uber die Anwendung von Natriumkarbonat und Natriumoxalat in der Acidimetrie," S. P. L. Sörensen und A. C. Anderson, *Z. anal. Ch.* **44**, 156 (1905), **45**, 217 (1906); "Zur Frage der Titerstellung von Normalsäuren," J. Sebelien, *Chem. Ztg.* **29**, 638 (1905)) by members of this sub-committee have been briefly reviewed in the chairman's report. In the opinion of W. Fresenius it may now be regarded as an established fact that either sodium carbonate (when prepared according to Lunge's directions) or sodium oxalate (ignited either over an alcohol flame, or a gas flame so applied that the products of combustion cannot come into contact with the salt) may be employed as standard materials for use in acidimetry, even in work requiring a high degree of accuracy.

Preparation of Sodium Carbonate for Use in Standardizing Acid Solutions.—The material selected should be of a pure white color, and should dissolve in water forming a perfectly clear solution. In quantities of from 1 to 2 grams it should give no reaction for sulphates, and with silver nitrate should give no more than the faintest opalescence. By heating, it is possible to insure the removal of water, and of any excess of carbon dioxide that may be present. If the temperature is too high, Na_2O may be formed. The fortunate circumstance that there is a considerable range of temperature through which the material may be heated without danger, gives to sodium carbonate the preference (according to Lunge) over all other substances hitherto suggested as the basis for standardization of acids. A platinum dish half filled with the material is so placed upon a sand-bath that the sand surrounds it to the height of the sodium carbonate within. The heating should be rapid until the temperature of 270° is reached, when it should be continued more slowly for one-half hour, during which time the temperature should not be permitted to rise above 300°. During this process the substance should be frequently stirred with a platinum spatula or with a flattened glass rod.

Preparation of Sodium Oxalate for Use in Standardizing Acid Solutions.—According to Sörensen's directions, the material is first precipitated with alcohol and dried at 240°. The sodium oxalate employed in the experiments of Lunge was obtained from

Kahlbaum, who had prepared it in this way. In order to obtain the greatest accuracy it is advisable to dry the salt in a water-bath drying-closet for some time before weighing. Lunge dried the salt for two and one-half hours, and then allowed it to cool in a desiccator for two hours. About 0.5 gram of the sodium oxalate is now weighed out into a platinum crucible provided with a cover, and is heated until complete transformation to sodium carbonate takes place. In one-fourth to one-half hour, according to Lunge, the change is complete, but the crucible should then be heated to a higher temperature in order to oxidize the small quantity of carbon liberated during the process. During this last operation the crucible should be left partly uncovered. As source of heat should be employed either an alcohol flame or a gas flame so applied that the products of combustion cannot come into contact with the salt. According to Lunge, the crucible should be set upon an asbestos plate through which a hole of proper size has been cut. If this precaution is not taken, the sulphur compounds in the illuminating gas will react with the sodium carbonate, introducing an appreciable error in the final result. After the ignition has been completed, the sodium carbonate is moistened with water and is then treated with the acid to be standardized.

The use of methyl orange as indicator is recommended in all cases except those in which a weak acid is involved. Phenolphthalein gives a sharper end-point, but necessitates a more complicated procedure. The nitrophenols and ferric salicylate show no superiority over methyl orange.

Pure iodine is still recommended as the basis of iodometric titrations. Potassium biiodate of constant composition may not be readily prepared. For the standardization of potassium permanganate Lunge has found that with certain precautions any one of the four following substances may be employed: (1) oxalic acid, (2) iron wire, (3) sodium oxalate and (4) hydrogen peroxide (by the nitrometer method).

Sub-committee III. Question 4. Uniform Principles Relating to the Adjustment and Calibration of Chemical Measuring Apparatus.—The report upon this subject consists in a series of regulations (stated in German, French and English) classified as follows:

International regulations concerning chemical measuring apparatus.

I. Measuring Vessels for Volumetric Analysis.
    A. General Rules.
    B. Shape and Calibration.
    C. Particular Rules.
    D. Limits of Error.
II. Measuring Apparatus for Gas Analysis.
    A. General Rules.

B. Shape and Calibration.
C. Limits of Error.

Question 8. Uniform Principles Concerning the Adjustment and Calibration of Instruments for Density and Percentage Determinations.—Under this head is given (in German, French and English) a series of regulations classified as follows:

International Regulations Concerning Hydrometers.

A. General Rules.
B. Shape and Calibration.
C. Special Hydrometers.
D. Limits of Error.

Question 9. Adjustment and Legalization of Balances and Weights for Chemical Purposes.—The report upon this subject presented by H. W. Wiley contains an account, both historical and descriptive, of the United States standards of weight and measure, together with a brief statement concerning the purpose of the Bureau of Standards. Reference is made to the method of T. W. Richards (this Journal, **22**, 144 (1900)) for standardizing weights.

Sub-committee IV. Question 5. Methods of Sampling Materials for Analysis. (Pages 190–220.)—The chairman of the fourth sub-committee, Dr. H. W. Wiley, has presented a report containing a detailed discussion of the topics mentioned in the following summary:

Part I. General Principles of Sampling.—(Applied to the sampling of gases, liquids and solids.)

Part II. Sampling Special Classes of Materials.

Soils.—General principles. General directions for sampling. Sampling with an auger. Sampling for moisture determination. Sampling to determine the permeability of soil to water or air. *Treatment of sample.* Air-drying.

Fertilizers.

Minerals Containing Fertilizing Materials.

Mixed Fertilizers. Barn-yard Manures.

Materials used for Road Building.

Food Products.—Dairy products (butter, milk and cheese). Sugars and molasses. Cattle foods. Insecticides. Foods. Drugs and chemicals (including (1) gummy substances, (2) powders, (3) crude vegetable drugs, (4) liquids, (5) goods solid at ordinary temperatures, but liquefied on warming, and (6) articles that congeal in part or as a whole at low temperatures.)

Sub-committee V. Question 6. Accurate Statement of Results Obtained in Fuel Investigation. (Pages 221–225.)—A brief and incomplete discussion of several questions bearing upon the analysis and testing of fuels. Among these questions may be mentioned the following: In what way may the results of a fuel examination be most intelligibly expressed? For example, should the higher or the lower heating value be reported; should the percentages of hydrogen and oxygen be directly reported, or should they be calculated as available hydrogen and chemically combined water? In what way should the percentage of sulphur found by analysis of the coal be reported? Should the amount of water formed by combustion of the coal be determined directly from combustion in the bomb, or should it be calculated from the ultimate analysis? What directions should be given with respect to the degree of comminution of the coal, the method of sampling, etc.? What directions should be given with respect to technical fuel tests and other methods for the determination of calorific value aside from the bomb-calorimeter method?

Sub-committee VI. Question 7. Uniform Presentation of Analytical Results. (Pages 226–279.)—The report upon this subject contains a discussion of various methods for expressing the results of analysis, to be used in the following lines of work:

I. For purely scientific analysis.
  (1) The establishment of chemical composition.
  (2) Determination of formulae.
  (3) Gas analysis.
  (4) Inorganic salts and the salts of metals with organic acids.
  (5) Double salts and complex compounds.
  (6) Mixtures, pigments, glass, cement, gunpowder, etc.
  (7) Minerals and rocks.
  (8) Organic substances.
II. Analysis of materials used in the trades and industries.
  (1) Products of the chemical industries.
  (2) Metals, ores and minerals.
  (3) Inorganic and organic dye-stuffs.
  (4) Medicines and pharmaceutical products.
  (5) Foods, beverages, perfumes and photographic materials.
III. Analysis of solutions.
  (1) Natural and artificial mineral waters.
  (2) Drinking water.
  (3) Solutions in general.
  (4) Urine analysis.

Sub-committee VII. Question 10. Determination of Arsenic in Wall-paper, Fabrics, Etc. (Pages 280–318.)—The report embraces articles upon the following subjects: (1) Electrolytic Method for the Estimation of Arsenic in Wall-paper, Fabrics and Similar Materials, by Chairman T. E. Thorpe; (2) Experiments on the Determination of Small Amounts of Arsenic Acid by Iodometric Acidimetry, by P. Klason and J. Köhler; (3) Quantitative Method for the Determination of Small Amounts of Arsenic in Commercial Articles, by J. Köhler; (4) Report of Estimation of Arsenic in Wall-papers, Tissues, etc., by H. W. Wiley.

(1) This method involves the use of an apparatus already described by the author (*J. Chem. Soc.* **83**, 974 (1903)). A weighed portion of the sample to be analyzed (usually about 2 grams) is treated in a platinum dish first with a little hot water, then with 20 cc. of arsenic-free lime-water and 0.5 gram of calcined magnesia. The material is next heated until the organic matter is thoroughly charred, when the dish is placed in a muffle furnace and heated until the carbon has been burned off. When cold the ash is moistened with water and is treated with 20 cc. of dilute sulphuric acid. After it has been warmed the material is transferred to a flask of about 120 cc. capacity. Half a gram of potassium meta-bisulphite is added, and the solution is boiled until free from sulphurous acid. The solution is now cooled, and is diluted to 50 cc. An aliquot portion is then taken for use in the apparatus. In order to admit of convenient comparison with standard deposits of arsenic, the deposit from the solution under consideration should contain not less than 0.005 mg. nor more than 0.0125 mg. of arsenic. Further details concerning the manipulation of the apparatus and the preparation of the standard deposits are given in the article.

(2) The work upon this subject embraces experiments upon (*a*) the direct titration of arsenic acid with $n/2$KOH; (*b* and *c*) the titration of arsenic acid by iodometric acidimetry; (*d*) the temperature to which small amounts of arsenic acid may be heated without loss; (*e*) the oxidation of arsenious to arsenic acid; (*f*) the titration of arsenic acid after distillation of the arsenic as trichloride; (*g*) the determination of small amounts of arsenic in paper; (*h*) the determination of arsenic in wool; (*i*) the stability of very dilute ($n/1000$ to $n/500$) hyposulphite solutions; (*j*) the stability of $n/500$ iodine solution. The principal points of interest in the experiments may be briefly stated as follows: (*a*) This method was found to give only approximately correct results, (*b* and *c*). This method is based upon the addition to the acid of a solution containing 1 equivalent of potassium iodate and 5 equivalents of potassium iodide. The amount of iodine liberated is determined by means of a hyposulphite solution. With proper precautions accurate results were obtained by the authors with a series of solutions containing from 0.067 mg. to 203.01 mg. of arsenic. The method is to be recommended provided organic substances are absent. (*d*) It was found that small amounts of arsenic acid (0.676 mg.) could not be heated to a temperature above 100° for a long time (several hours) without loss, probably due to reduction effected by dust particles in the air. (*e*) Nitric acid alone will not completely oxidize arsenious to arsenic acid, but will do so in presence of hydrochloric acid. (*f*) The temperature must be raised rapidly in order to prevent loss of hydrochloric acid before the temperature is reached at which distillation of the arsenic trichloride commences. (*i*) After ten days the loss

undergone by the $n/500$ solution was 3.9 per cent.; after seventeen days the loss in the case of the $n/1000$ solution was 12.7 per cent. (*j*) After thirty-two days the loss was 1.14 per cent.

(3) In this article is described a series of experiments intended to supplement the work of Klason and Köhler, with a view to eliminating the difficulties arising when organic matter is present. The procedure is essentially as follows. The arsenic is either converted into the trichloride by distillation with hydrochloric acid and then into arsenic acid by nitric acid, or it is precipitated as arsenious sulphide and then oxidized by nitric acid. After it has been evaporated to dryness the arsenic acid is treated with potassium permanganate (2 cc. 5 per cent. solution, with 1 cc. 30 per cent. sulphuric acid) in order to eliminate organic matter. It is then heated over a water-bath ten to fifteen minutes, and is reduced with sulphurous acid (10 cc. 7 per cent. solution). The sulphurous acid is removed by heating for thirty minutes to a temperature of 50–70°, and then to 100°. This treatment is repeated with 5 cc. of sulphurous acid, and the solution is again evaporated until complete removal of the sulphurous acid has been effected. If the liquid is not perfectly clear after the first treatment, oxidation with permanganate should be repeated. The residue is dissolved in 15 cc. of water, is neutralized with sodium bicarbonate, and is titrated with $n/500$ iodine solution. Starch is added, and the solution is vigorously shaken during the titration. The bicarbonate solution alone requires about 2 drops of the iodine solution before the blue color appears. The color remains but a few seconds. The method has been tested by seven different chemists with satisfactory results.

(4) This article contains a description of the method employed in the Miscellaneous Laboratory of the Bureau of Chemistry for the determination of arsenic in wall papers and fabrics. A full account of this method, which is essentially a modification of the method of Sanger (*Pr. Am. Acad.* N. S. **18**, 24 (1891)) has already been published. (Bulletin 86, Bureau of Chem. U. S. Dept. Agr. (1904)). Some use has been made of the electrolytic method of Thorpe (described above) in the Bureau of Chemistry. Most excellent results were obtained.

Sub-committee VIII. Question 11. Determination of Boric Acid, Benzoic Acid, Salicylic Acid and Other Substances Used in the Preservation of Foods. (Pages 319–343.)—The report includes two articles (1) by M. L. Lindet, chairman of the sub-committee, and (2) by H. W. Wiley.

(1) A general discussion is given in this article of the methods employed in the determination of the following substances: salicylic acid, benzoic acid, boric acid, borax, fluoborates, fluorides, alkaline fluoborates, alkaline fluosilicates and formaldehyde.

(2) In this paper is given a detailed description of the methods now used in the Bureau of Chemistry for the detection and deter-

mination of the following substances: formaldehyde, sulphurous acid, salicylic acid, saccharin, benzoic acid, boric acid and the borates, fluorides, borofluorides and silicofluorides. An account is also given of the methods used in the detection of coloring-matter in foods, in the determination of annatto in butter or other fat, and in the detection of coloring-matter in milk.

Sub-committee IX. Question 12. Determination of Sulphur in Pyrites, Blendes, Etc. (Pages 344–399.)—This report consists in the main of two articles, both of which have already been published elsewhere: (1) Determination of Combined Sulphuric Acid by the Methods of Lunge and of Silberberger, by G. Lunge (*Z. angew. Ch.* **18**, 449 (1905)). (2) On the Determination of Sulphuric Acid by Precipitation with Barium Chloride in Presence of Interfering Substances, by G. Lunge and R. Stierlin (*Z. angew. Chem.* **18**, 1921 (1905)). By referring to the following additional articles (Silberberger, *Ber.* **36**, 2755 (1903); Lunge, *Ibid.* p. 3387; Silberberger, *Ibid.* p. 4259; Lunge, *Z. angew. Ch.* **17**, 913 and 949 (1904); Küster, *Ibid.* p. 1180; Lunge, *Ibid.* p. 1180; Pattinson, *J. Chem. Ind.* **24**, 7 (1905); Hintz and Weber, *Z. anal. Chem.* **45**, 31 (1906); Dennstedt and Hassler, *Z. angew. Ch.* **18**, 1562 (1905); Lunge, *Ibid.* p. 1656; v. Knorre, *J. Chem. Ind.* **28**, 2 (1905)), more complete information concerning the method of Lunge may be obtained. This method is recommended by the ninth sub-committee for international use in the determination of sulphur in pyrites, blendes, etc.

Sub-committee X. Question 13. Is it Necessary to Calculate the Percentage of Manganese in a Permanganate Solution, the Strength of which with Respect to Iron is Known, by Means of a Coefficient Different from that Indicated by the Equation? (Pages 400–418.)—As a result of the experimental work performed by himself and his coworkers, chairman L. L. de Koninck draws the conclusion that it is possible, under conditions easily established, to obtain a sharp reaction between potassium permanganate and manganese salts, in the ratio $3MnCl_2 : 2KMnO_4$. It is therefore unnecessary to employ an arbitrary coefficient in calculating the strength of a permanganate solution from the analytical results obtained by a suitable modification of the Guyard method. The procedure adopted by de Koninck in proving his contention is essentially as follows: A measured volume of permanganate solution is reduced by heating with hydrochloric acid. The moderately acid manganous solution thus obtained, to which pure ferric chloride has been added, is treated at a slightly elevated temperature with zinc oxide suspended in water, until the point is reached at which further addition of the oxide effects a rather sudden coagulation of the precipitate. The supernatant liquid after it has been shaken (and warmed, if necessary) is completely clear and colorless, or at least only slightly milky. After diluting to about 300 cc. and adding in the majority of cases 20 grams of zinc sulphate the author titrates the solution at about 100° with the permanganate solution (of which a portion was reduced at the outset) until a pink color is obtained which persists even after the solution is boiled. The volume of permanganate solution required was in every case almost exactly two-thirds that of the permanganate solution reduced. This is obviously in accord with the ratio $3MnCl_2 : 2KMnO_4$. The author recommends for actual work a procedure somewhat as follows: A sample of manganiferous iron ore (for example) is dissolved in hydrochloric acid; the filtered solution, moderately acid, is diluted to 500 cc. Two samples of 100 cc. each are taken from this solution. To one of these samples is added the manganese chloride obtained by reduction of a measured volume of the permanganate solution with hydrochloric acid. After the iron has been removed from both samples by the addition of zinc oxide, the solutions are titrated with permanganate. From the difference the strength of the permanganate solution may be calculated, while from the lower result may be obtained the percentage of manganese in the sample.

The report upon this question contains also an article by G. Chesneau which has been published elsewhere (*Annales des Mines*, Feb. (1906)). This piece of work contains some experimental evidence corroborating the conclusions of de Koninck.

Sub-committee XI. Question 14. Methods of Analyzing Materials Containing Tartaric Acid. (Pages 419–421.)—For the determination of bitartrates it is proposed to abandon the method of direct titration without filtration. The approved method is briefly as follows: In a 500 cc. flask is placed 2.35 grams of the fine material, with 400 cc. of distilled water. The liquid is boiled for five minutes. Water is added, and the liquid is cooled, shaken, and is filtered upon a folded filter-paper. Of the filtrate 250 cc. are boiled in a porcelain dish, and titrated (neutral litmus-paper as indicator) with N/4 potash that has been standardized under the same conditions with a pure bitartrate. For the analysis of total tartaric acid the method of Goldenberg-Géromont (*Z. anal. Ch.* **37**, 312 (1898)) is usually employed. This method has been studied in detail by the committee. A brief statement is also made concerning the correction to be introduced for the volume of solid material—a subject to be considered in greater detail in a future report.

RECENT WORK IN AGRICULTURAL CHEMISTRY.

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As usual, numerous experiments have been made for the purpose of determining the relative value of different materials for supplying the essential elements, phosphoric acid, nitrogen and potash.