REVIEW OF PAPERS ON ANALYTICAL CHEMISTRY (INORGANIC) WHICH HAVE APPEARED DURING THE YEAR 1882.

By E. Waller, Ph. D.

A modification of the apparatus for the absolute DETERMINATION OF NITROGEN, invented by S. W. Johnson and E. H. Jenkins, is described by *T. S. Gladding* (*Am. Chem. Jour.*, IV., 42).

According to *A. Guyard* (*Chem. News*, XLV. 159), ALL ACIDS AND OXIDES OF NITROGEN are converted into ammonia by combustion with marsh gas and soda lime. The mixture is made in the proportion of 75 grs. of sodium acetate with 1½ oz. of soda lime, and the combustion conducted in the ordinary manner. The tube is charged first with about one-quarter of the above mixture, then the remainder mixed with 5 to 7 grms. of the substance to be examined is added, and finally pure soda lime.

The accuracy of the results thus obtained is disputed by *J. Ruffle*, (*Chem. News*, XLV., 186).

In experimenting on methods for the DETERMINATION OF NITROUS OXIDE, *W. Hempel* (*Ber. D. Chem. Ges.*, XV., 903 *et seq.*) finds it extremely difficult to obtain absolutely pure N_2O. The purest gas obtained contained 98.8%. He finds the best method of estimating the gas to be by explosion with hydrogen in an apparatus specially designed for the purpose, which is carefully described.

100 vols. N_2O with 460 vols. H was not explosive, while 100 N_2O with 116 vols. H caused such a violent explosion as to shatter the apparatus. The mixture therefore must be made within these limits.

Alkaline solutions of potassium permanganates or of chromic acid are recommended by *C. Boehmer* (*Fres. Zeits. Anal. Chem.*, XXI., 212,) as ABSORBENTS FOR N_2O_2 in analytical processes.

To determine the amounts of sodium SULPHIDE, SULPHITE AND THIOSULPHATE in the same solution, *G. E. Davis* (*Jour. Soc. Chem. Ind.*, I., 89), determines, 1. The amount of iodine absorbed by a measured quantity of the solution, by converting the alkalies present into bicarbonates with carbonic acid water and titrating with iodine solution. 2. The amount of sulphide and thiosulphate present; by adding $SrCl_2$ in excess, digesting for about half an hour at 65° to 70° C., filtering off the strontium sulphite, washing with air free from water, adding carbonic acid water to the filtrate, and titrating with iodine solution. 3. The amount of thiosulphate present; by separating the sulphite as in 2, and then separating the sulphide by digestion for half an hour with $CdCO_3$, filtering and titrating the filtrate with the same precautions as before. A correction must be applied to the results before calculating from the data obtained. It has been found that 100 cc. of a solution of $SrSO_3$ saturated at 65 to 70° C., consumes 0.3 cc. decinormal iodine, and the same bulk saturated at 12.7° C. consumes 0.16 cc. decinormal iodine solution. The bulk and temperature of the filtrates must therefore be taken.

To obtain the SULPHUR IN PYRITES in a form for estimation as sulphate, *Fr. Bockmann* (*Fres. Zeits. Anal. Chem*, XXI. 90), fuses 0.5 gms. with 25 gms. of a mixture containing 6 parts Na_2CO_3 to 1 part $KClO_3$.

In estimating CHLORINE GRAVIMETRICALLY, *D. Lindo* (*Chem. News*, XIV., 193) filters the Ag Cl through a Gooch filter and dries for half an hour at 140 to 150° C.

In the indirect estimation of CHLORINE AND BROMINE, *L. P. Kinnicutt* (*Am. Chem. Jour.*, IV., 22), after weighing the mixed silver salts in a platinum crucible, reduces to metallic silver by a battery, the crucible being made the positive electrode of the circuit.

The sanitary EXAMINATION OF GASES ESCAPING FROM CHEMICAL WORKS forms the subject of a paper by *W. J. Lovett* (*Jour. Soc. Chem. Ind.*, I., 210). For *nitrous compounds* the gases are brought into contact (by agitation) with hydrogen peroxide and water, the solution neutralized with pure soda solution (free from nitrates) evaporated to very small bulk, and after removing carbonic acid by a drop of sulphuric acid, using a Davis nitrometer tube with conc. H_2SO_4 and mercury, the volume of N_2O_2 being measured. For *sulphurous acid* the gases may be passed through a standard solution of potassium permanganate. For *oxygen*, the gas is caught in a U tube, one limb of which is sealed and graduated so as to form an eudiometer, and oxygen is absorbed by potassic hydrate and pyrogallic acid. For *sulphuretted hydrogen* the gas may be passed through $Pb(NO_3)_2$, and the precipitate converted into sulphate and weighed, or the excess of lead remaining in the solution titrated with potassium dichromate. For *chlorine* the gases are passed through KI solution, and the iodine set free titrated with sodium thiosulphate. To distinguish between the amounts of *free and combined chlorine* in such escapes, *G. E. Davis* (loc. cit. p. 214) passes the gases through H_2S water. The solution thus obtained is halved. One half is neutralized with $MgCO_3$, and then titrated with $AgNO_3$, giving total chlorine ; the other half evaporated to neutrality without any addition and titrated, giving combined chlorine.

To determine the amount of OZONE IN THE AIR, *D. Tommasi* (*Les Mondes*, I. [3] 123), draws a measured quantity through a tube having two branches. The air passing through one branch is drawn directly through a standard solution of sodium arsenite ; that passing through the other branch is first passed over red-hot platinum sponge before passing into a solution of sodium arsenite. The solutions are then titrated with potassium permanganate, and the difference of the results in the two solutions serves as a basis for the calculation of the ozone present, as in the second solution the ozone has been destroyed by the ignited platinum sponge.

Experiments on potassium permanganate in relation to its application for the EXAMINATION OF POTABLE WATERS, have been made by *A. Dupre* (*Analyst* VII. 1). Water acidified with sulphuric acid when absolutely pure, does not decompose permanganate in a closed flask at 80° F. In standardizing the permanganate for Tidy's test the operation should be performed in a closed flask. With waters for domestic use which are comparatively free from organic matter, the degree of temperature and the length of time for the action of the permanganate as well as the qantity of permanganate, make but little difference in the results obtained. With less pure waters the differences between the 3 hour and 4 hour test were very decided. On using phosphoric acid instead of sulphuric in Tidy's test, results much lower were obtained. The addition of sulphuric acid and boiling before adding permanganate, increases the amounts of oxygen absorbed. This increase was very marked when the test was tried on pure water, to which cane sugar, starch, or urine had been added, but was much less marked when gelatine or egg albumen was used. *C. W. Marsh* (*Am. Chem. Jour.* IV. 188) finds that in many waters examined, the distillate obtained by distilling with sodium carbonate, affords more ammonia (determined by the Nessler) on redistilling with alkaline potassium permanganate than if the Nessler test is directly applied to it.

The ORGANIC NITROGEN in waters, beer, etc., is estimated by *W. Bettel* (*Chem. News*, XLV. 38), in one operation by distilling from a copper flask in a current of hydrogen with pure soda (from sodium). The use of the copper flask admits of distillation to complete dryness, and ignition of the residue. At the close of the operation to break up cyanides, &c., which may have formed, a little potassium permanganate is added, and heat again applied. Nitrates, if present, are previously converted into ammonia by the action of the zinc-copper couple. The distillate contains all the nitrogen in the form of ammonia.

To convert NITRATES AND NITRITES IN WATER into ammonia, *F. P. Perkins* (*Analyst* VII. 66,) proposes the use of metallic magnesium aided perhaps by the addition of some Na Cl. *J. B. Kinnear* (*Chem. News*, XLVI. 33) finds that zinc with a dilute acid will effect the reduction in about ten minutes, provided that there are about 5,000 parts of liquid present for every part of nitric nitrogen. The rapidity of the reduction depends somewhat upon the amount of surface of zinc exposed.

Among delicate TESTS FOR NITRITES in water, *A. Jorissen* (*Fres. Zeits Anal. Chem.* XXI. 210) proposes a solution containing 0.01 gm. fuchsin in 100cc. of glacial acetic acid, which gives a change of color, passing through blue and green to reddish yellow. (Noted by Vogel *Jour. Prakt. Chem.* XCIV. 457), while *E. W. Davy* (*Chem News* XLVI. 1) recommends for the same purpose acidifying the solution, adding a few cc. of gallic acid and boiling. The presence of nitrites at once gives a tint to the water similar to that of the Nessler test with ammonia. The reaction is stated to be :

$$C_7 H_6O_5 + 2 H N O_2 = C_6 H_4 O_3 + C O_2 + 2 N O + 2 H_2 O$$

tanno-melanic acid being formed.

The COLOR METER FOR WATERS used by Messrs. *Crookes, Odling, and Tidy* in their examination of the London water (*Report to Local Government Board for* 1881) is described (*Chem. News* XLV. 170). The two-foot tube is used. For comparison colors, two wedges, one brown, the other blue, are used, which are slid over one another until a tint corresponding to that in the water is obtained. The solutions contain respectively :

Brown, 0.7 gm. metallic iron as ferric chloride
0.3 " " cobalt as chloride,

and a slight excess of free acid per litre.

Blue, 5 gms. pure crystallized cupric acid sulphate per litre. The results are recorded in figures representing the thickness in millimetres of the solutions required to simulate the color of the water thus : Brown : Blue, 20 : 10.

Regarding the examination of fertilizers for REVERTED OR RETROGRADE PHOSPHATES, *C. Richardson* (*Am. Chem. Jour.* IV. 183) finds that the use of ammonium oxalate for their extraction gives variable results depending upon the time and temperature of digestion, the degree of concentration of the solution, &c. In this connection see also results of *T. S. Gladding* (this *Journal*, p 113). *F. J. Lloyd* (*Jour. Lond. Chem. Soc.* XLI. 306) triturates 0.5 gm. of the fertilizer with 50cc. of a solution containing 30 per cent. citric acid, and enough ammonia to render it strongly alkaline. The mixture is made up to 100cc. and allowed to stand over night at the temperature of the laboratory. In 50cc. of the clear solution the lime is separated by acidifying with acetic acid and adding ammonium oxalate, and in the filtrate the phosphoric acid is determined by the use of magnesia mixture.

As to VOLUMETRIC processes for PHOSPHORIC ACID, *C. Mohr* (*Fres. Zeits. Anal. Chem.* XXI. 216) shows by a series of experiments that even small amounts of ammonia salts have a marked effect on the results obtained by the uranium titration, while *H. Pemberton* (*Jour. Franklin Inst.* CXIII. 184). proposes the use of a solution of neutral ammonium molybdate containing 89.543 gms. of the salt per litre (1cc=0.003 gm. P_2 O_2). For titration 100 to 125cc. of the solution is taken [which should not contain over 0.1 gm. P_2 O_5] 10 gms of ammonium nitrate, and 2cc. of nitric acid [sp. Gr. 1.14] are added and the solution is heated to 140° F. or over. The end reaction is the absence of further precipitation. Toward the close of the titration portions of the solution have to be filtered to give opportunity to observe the end reaction. If the titration is overrun, a measured quantity of Na_2 H PO_4 solution of known strength is added and the titration resumed. From the burette reading 0.5cc. is to be deducted for the effect of the nitric acid added. Silica and organic matter cause erroneous results when present, while chlorides, iron [to the extent of 0.1 to 0.3 gm.] &c., do not.

In the EXAMINATION OF TITANIFEROUS IRON ORES, *T. M. Drown and P. W. Shimer* (*Am. Chem. Jour.* IV. 1), treat the ore (2 to 5 grms.) with 50cc. of H Cl. (Sp. Gr. 1.12) evaporate to dryness and heat in the air bath for an hour, add 50cc more H Cl., heat and filter; turbidity in the washings is prevented by the use of ammonium nitrate. The phosphoric acid is extracted from the residue by fusion with sodium carbonate, extracting with water, evaporating to dryness with nitric acid to remove silica, &c. Molybdate mixture may then be added to the solution. In the first solution (obtained by H Cl.) the H Cl. is removed by evaporation with nitric acid, when after partially neutralizing, molybdate solution is added. This last molybdate precipitate requires purifying by dissolving in ammonia, treating the undissolved residue with nitric acid and precipitating that solution with more molybdate. After obtaining all the ammoniacal solutions of the phospho molybdate free from silica, titanic acid, &c., they are united and precipitated as usual with magnesia mixture.

For TITANIC ACID these gentlemen decompose the ore by fusion with K HSO_4 and after neutralizing and reducing with SO_2 precipitate by boiling as usual. *P. T. Austen* and *F. A. Wilber* (*Am. Chem. Jour.* IV, 211) find that the addition of 50 to 60cc. of acetic acid aid materially in the precipitation of the titanic acid, giving good results on boiling, even when chlorides are present. The last named decompose the ore by fusion with alkaline carbonates and treating with HCl, evaporating, &c.

For the *determination* of CARBON AND SILICON IN IRON, STEEL, etc., *F. Watts* (*Chem. News*, XLV., 279) gives the preference to a modification of Wohler's method.—Volatilization of the iron in a stream of Cl gas and making a combustion of the carbon remaining. Two operations are required for each analysis. In the first after volatilizing the iron in a current of *dry* chlorine free from oxygen, the residue is submitted to combustion, and the *total carbon* is thus determined. In the second the residue (after volatilizing iron) is weighed, giving *total carbon and slag*, while the gases from this operation are passed into water, where the Si Cl_4 is decomposed, and by boiling, evaporating to dryness, etc., the Si O_2 corresponding to *combined* silicon is obtained.

SODA COMPOUNDS may be estimated in potassium carbonate, according to *A. Van Hasselt* (*Jour. Soc. Chem. Ind.* I, 203), by treating a weighed quantity (converted into chloride) with H Cl. (Sp. Gr. 1.189) saturated with Na Cl.

To estimate CAUSTIC ALKALI IN PRESENCE OF CARBONATE, *R. B. Warder*, (*Sci. Proc. Ohio Mech. Inst.* I, 45) uses a process based upon the fact that phenolphthalein is colorless in the presence of alkaline bicarbonates. On titrating a very dilute solution of the sample (cold) until the phenol pthalein which has been added imparts no color to the solution, all the caustic and half of the carbonated alkali is neutralized, giving a result A. Then by boiling and titrating the remainder of the alkali is neutralized; result B. A+B measures total alkalinity, and A—B measures caustic alkali

To detect and separate ALKALIES IN ARGENTIC NITRATE. *M Stolba* (*Jour. de Pharm. et de Chim.*) uses hydrofluosilicic acid. By the use of phenol phthalein *M. Richter* (*Fres Zeits. Anal. Chem.*, XXI, 205) determines acidimetrically the CHROMIC ACID IN

POTASSIC DICHROMATE. Many other indicators cannot be used on account of the oxidizing action of the chromic acid upon them.

By fusing hydrorufigallic acid with potassa A NEW INDICATOR for alkalimetric titration is made by *J. Oser and W. Kalmann* (*Monatshefte f Chemie*, II, 50). It dissolves in alkalies with an olivegreen tint—a slight excess of alkali gives carmine red, changed to yellow by free mineral acids. It is unaffected by CO_2.

To DETERMINE ZINC in its ores, *A. Millot* (*Bull Soc. Chim.*, XXXVII, 339) recommends dissolving with HCl and $KClO_3$ evaporating, adding ammonia and ammonium carbonate, diluting the filtrate therefrom, and in an aliquot portion of this filtrate, adding a little K Cy and precipitating by the battery. The addition of ammonium acetate prevents the corrosion of the electrodes

In TITRATING ZINC by Fahlberg's method manganese must be first separated to obtain correct results. *R. W. Mahon* (*Am. Chem. Jour*, IV, 53). In titrating with Na_2S, the use of paper soaked in thallium solution is recommended by *M. Schröder* (*Berg. u Huttenmann, Zeit.* 1882, p. 4) as an indicator. If a slight excess of ammonia is present the thallium salt is unaffected by Zn S.

To separate NICKEL FROM COBALT *G. Delvaux* (*Comptes Rendus*) dissolves in aqua regia with excess of H Cl—adds ammonia in excess, then potassium permanganate until the rose color holds for some time. Solution of pure KHO will then precipitate nickel (with manganese if present), leaving cobalt in solution. In case small amounts of nickel and large amounts of cobalt are present *A. Jorissen* (*Fres. Zeits. Anal. Chem.*, XXI, 208) precipitates with NaHO, adds bromine, then a few cc. of K Cy, and agitates in the cold. The cobalt is dissolved while the nickel remains in the precipitate.

A. Carnot (*Bull. Soc. Chim.*, XXXVII, 482) ESTIMATES CHROMIUM (as base) by adding sodium acetate to the solution slightly acidified, adding an alkaline phosphate and boiling. The presence of oxalates must be avoided. The precipitate dried at 100° contains 6 H_2O. Ignited it consists of $Cr_2(PO_4)_2$, containing 51.86 per cent. Cr_2O_3.

In the examination of iron ores, etc., containing chromium error may be caused, according to *B. Reinitzer* (*Monatshefte f. Chem.*, 1882, p. 249), by the chromium preventing the precipitation of some of the iron and alumina on boiling the solution after neutralizing and adding sodium acetate.

For the detection of IMPURITIES IN COPPER several chemists communicate their methods—

For ARSENIC *J. Pattinson* (*Newcastle-on-Tyne Chem. Soc.*, Feb. 1882) dissolves in nitric acid; then by adding sufficient soda solution to a little more than neutralize the free acid present, the arsenic is precipitated as copper arsenate; after standing for half an hour with frequent stirring the precipitate is filtered and washed cold. The arsenic is thus concentrated in the precipitate. *A. H. Sexton* (*Chem. News*, XLV, 255) prefers to precipitate the arsenic from the nitric acid solution (by adding ferric nitrate, neutralizing, adding sodium acetate and boiling) as basic acetate. The precipitate is dissolved in acid, precipitated by H_2S, oxidized to arsenic acid, and determined as the magnesia compound.

For CADMIUM *A. Orlowski* (*Fres. Zeits. Anal. Chem.*, XXI, 214) first removes Bi if present, acidifies with HCl, decolorizes by $SnCl_2$, adds milk of sulphur and heats to boiling. This precipitates the copper as Cu_2S. From the filtrate the tin is removed by ammonia, leaving the cadmium to be detected in the solution. Another method by the same author is proposed, in which sodium thiosulphate is substituted for $Sn\,Cl_2$ and milk of sulphur. In other respects it is the same.

The same author (loc. cit.) proposes to detect CUPROUS COMPOUNDS IN PRESENCE OF CUPRIC by acidifying with HCl and boiling with milk of sulphur. As above, cuprous sulphide will precipitate, while the cupric compounds are unaffected. An elaborate scheme for the EXAMINATION OF COMMERCIAL COPPER for gold, silver, lead, bismuth, antimony, tin, arsenic, iron, cobalt, nickel, zinc, sulphur and phosphorous is given by *R. Fresenius* (*Fres. Zeits. Anal. Chem.*, XXI, 229).

M. M. P. Muir (*Jour. Lond. Chem. Soc.*, XLI, 1) determines BISMUTH VOLUMETRICALLY by separating it from other metals, as oxychloride, converting this compound into chloride, dissolving in glacial acetic acid and precipitating by excess of standardized solution of $K_2C_2O_4$. The precipitate is $K_2C_2O_4$, $Bi_2\,(C_2O_4)_3$ The excess of oxalate is titarted with permanganate.

For the VOLUMETRIC DETERMINATION OF ANTIMONY *E. T. Herroun* (*Chem. News*, XLV, 101) converts the antimony into $Sb\,Cl_5$ by treatment with HCl and $KClO_3$, boiling gently to expel excess of chlorine, cooling and adding an excess of KI. The iodine freed by the action of the $Sb\,Cl_5$ is then titrated with a standardized solution of sodium hyposulphite.

M. M. P. Muir (*Chem. News*, XLV, 69) detects TIN IN THE PRESENCE OF ANTIMONY by boiling the HCl solution for 10 minutes with copper turnings which reduces it to stannous form and permits of its being detected by $HgCl_2$.

To detect SMALL AMOUNTS OF SILVER IN LEAD (reduced from galena, etc.) *J. Krutwig* (*Ber. D. Chem. Ges.* xv, 307) dissolves in nitric acid and precipitates with large excess of NaHO. Silver plumbate remains insoluble. By extracting with ammonia, evaporating to dryness, dissolving in nitric acid and separating the lead by H_2SO_4, a solution is obtained in which the silver may be detected with HCl.

To SEPARATE GALLIUM from zinc and ferrous oxide *L. de Boisbaudran* (*Comptes Rendus*, 1882, *No.* 17) uses cupric hydrate instead of barium or calcium carbonate. The copper may afterward be separated by dissolving and adding H_2S.

ABSTRACTS.

Abstracts from *Journal of the Chemical Society*, London, by Arthur H. Elliott, Ph. B., F. C. S.

On some Higher Oxides of Manganese and their Hydrates.

(Part II., Vol. XL., p. 56). BY V. H. VELEY, B. A., F. I. C.

The higher oxides of manganese, when heated in dry nitrogen at temperatures ranging from 60°—200°C., are simply dehydrated without loss of available oxygen; the dehydrated oxide formed readily absorbs oxygen. The oxides, when heated in dry hydrogen, are simultaneously dehydrated and reduced; a hydrate of the red oxide is formed which readily absorbs oxygen. The quantity of water retained by the peroxides when heated to 200°C. in dry hydrogen, is greater than that retained by the same oxide at the same heat in air, oxygen, or nitrogen.

On a New Alkaloid from Cinchona Bark.

(Vol. XL., p. 66) BY DAVID HOWARD AND JOHN HODGKIN.

The alkaloid is obtained from *China Cuprea* of Dr. Fluckiger. Its specific rotary power is very near that of quinine: 100 cc. of ether free from alcohol dissolves 0.57 of it at 12°C. Ether containing 8 per cent. of alcohol dissolves 2.27. Alcohol of 90 per cent. at 12°C. dissolves 7.64 per 100 cc. When impure or mixed with