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

BY E. WALLER, PH. D.

MILK ANALYSIS.—To determine WATER, *Marpmann* (*Biedermann's Centrlb. fur Agrikult. Chem XI., pt. 2*) proposes to fill a calcium chloride tube with cotton wool, then to saturate the cotton with the milk, and to dry by drawing a stream of hot dry air through the tube. The FAT may also be determined in the same sample by extraction with benzol or ether.

O. Hehner gives the results of experiments on the methods for milk analysis adopted by the Soc. of Pub. Anal. (*Analyst,* VII., 60). In determining WATER the operation was more rapid on the water bath than in an oven. After drying for three hours an amount varying from 0.06 to 0.29 % may be driven out by further heating. A temperature above 100° C. apparently causes decomposition and loss of solids not fat. For BUTTER FAT the Soxhlet apparatus removes about 0.2 % more than boiling out with three or more successive quantities of ether. Nothing is gained by granulating the milk residue, by allowing the ether to act for a long time, or by adding 10 % absolute alcohol to it. Portions of the ASH are volatile at red heat.

A. Mayer states that the oil from ARTIFICIAL BUTTER has a much lower specific, gravity than that from natural butter. (*Fuehling's Landw. Ztg.* XXXI., 92)

The amount of COPPER NORMALLY PRESENT IN WHEAT is stated by *J. van D. Berghe* as 0.008 to 0.01 % (*Les Mondes*, I., [3] 209).

TO TEST BREAD FOR THE PRESENCE OF ALUM, *A. W. Blyth* (*Analyst,* VII., 16) proposes the use of slips of gelatine. The bread is crumbled into a vessel, a couple of slips of dry commercial gelatine placed with it, and distilled water added sufficient to cover the materials. On standing over night, the alum concentrates in the gelatine, and when dipped in fresh tincture of logwood, to which an equal bulk of 10 % solution of ammonium carbonate has been added the slips will dye blue if alum was present. When alum is not present, the slip becomes reddish brown, the tint being removable by soaking in glycerin. Experiments upon alumed bread seemed to show that much of the alum added remains as such after baking. Nearly all, if not quite all, of the alumina added as alum may be removed from the bread by soaking it in a 5 % HCl. solution.

In EXAMINING TEA, *J. Carter Bell* (*Analyst*, VII., 7) gives the results of the examination of 58 samples. The variations were as follows :

Per cent. of ash	5.64 to 8.58
Per cent. of ash soluble in water	32.70 to 67.41
Per cent. alkalinity of ash (=K_2O)	14.24 to 30.57

In EXAMINING ROASTED COFFEE, *A. Smetham* (*Analyst*, VII., 73) concludes from the examination of seven genuine samples, first, that moisture (loss at 100° C.) should always be first determined. The per cent. of "crude fibre" is the best guide where chicory is the adulterant. The determination of oil, cellulose, ash (soluble and insoluble), nitrogen, and sp. gr. of the 10 % infusion, are principally of service as checks on the work.

The crude fibre was found to vary between 73.71 and 75.7 %, referred to the dry samples. It was determined by boiling 2 gms. of the samples with three successive lots of water (100 cc. each), and finally washing on a tared filter until the washings were colorless.

For COLORIMETRIC ESTIMATION OF SALICYLIC ACID in articles of food, urine, &c., *MM. Pellet and De Grobert* (*Revue des Industries*, No. 53, 1882) propose ferric chloride solution (sp. gr. 1.005 to 1.008) containing 0.5 gms. free acid per 100 cc. In testing butter by this method, 25 gms. are shaken with 5 or 6 drops sulphuric acid (of 30° B.) and 75 cc. benzol. The total volume is then made up to some convenient bulk (100 cc.) It is then filtered, and 5 or 10 cc. mixed with the same bulk of water, and a few drops of the ferric chloride solution added. The mixture is gently shaken, the production of an emulsion being avoided, and the tint compared with that obtained in a standard solution.

EXAMINATION OF WINES. General methods are given by *J. Nessler and M. Barth* (*Fres. Zeitz. Anal. Chem.* XXI., 43) and *L. Roesler* (*Chem. Zeit.*, VI., 306).

For EXTRACT, the first named authors find that evaporation at 100° C. for three hours does not remove the glycerin. Some loss by decomposition of non-volatile acids will be experienced, unless a known bulk of $Ba(HO)_2$ solution is added. For genuine wines, the extract less acids is rarely under 10 %. *Roesler* asserts that evaporation at temperatures above 80° causes both loss of glycerin and decomposition of the residue. He recommends evaporation at 60° C. in partial vacuum.

For added SUGAR *Nessler and Barth* prefer a modification of Neubauer's polariscope test. Cane sugar if present is partially or wholly inverted by the acids of the wine on evaporating. Caramel has no optical effect. *Roesler* decolorizes with bone black and uses the Fehling test.

For FREE TARTARIC ACID *Nessler and Barth* evaporate a portion, add alcohol until no further precipitation ensues, filter, evaporate off the alcohol, add water, clarify by bone black, and then add one or two cc. of 20% solution of calcium acetate.' The amount of free tartaric acid should not be over one-sixth the amount of the non-volatile acids.

Roesler first determines tartar by adding 50 cc. ether to 10 cc. of wine, allowing to stand 24 hours, washing with ether, dissolving in boiling water and titrating. Then 10 cc. of the wine is neutralized with standard KOH solution, 40 cc. of the wine added, and 10 cc. of the mixture treated as above. The excess of the acidity in the second case is due to free tartaric acid.

Nessler and Barth also state that the ASH should be at most 1.4%. In some cases the wines may have been fraudulently diluted and the percentage of ash increased by use of SALT. In such a case the ash does not readily burn white. To detect this fraud, the wine is decolorized by bone black and Volhard's method used. The usual amount of Cl in wines is under 0.002%, the maximum 0.005%.

The last named authors also state that the maximum amount of CITRIC ACID in genuine wines is 0.002 to 0.003 per cent., but that acid is frequently added as such or in tamarinds (which contain 13.5%.

To determine it, 100 cc. of the wine are evaporated to 7 cc., cooled, the soluble portion extracted by alcohol (of 80%) the residue diluted to 20 cc., *partly* neutralized with milk of lime, (for red wines bone black is also added at this point) filtered, diluted to 100 cc., and the citric and tartaric acids separated by about one cc of neutral lead acetate. From this combination the lead is separated by agitation with H_2S water, and filtering. After removing the H_2S, lime is added to render the solution alkaline, and after filtering it is made slightly acid with acetic acid and allowed to stand to separate the calcium tartrate. In the filtrate the acetic acid is expelled by heat and the solution is finally boiled until the calcium citrate separates in crystalline form when it is filtered and weighed. *Roesler* determines the GRAVITY preferably by Sprengel's pyknometer; ALCOHOL by distilling off two-thirds, making the distillate up to the original volume and taking the gravity ; TANNIC ACID by distilling off the alcohol, making up to the original volume, agitating with bone black, filtering, and applying Neubauer's modification of Lœwenthal's method, (permanganate and indigo carmine); ACETIC ACID by adding baryta hydrate, distilling off alcohol, and then distilling with phosphoric acid (Kessel-Neubauer's method); GLYCERIN by evaporating (100 cc.) down to one-third, rendering slightly alkaline with slaked lime, evaporating to dryness, extracting with alcohol, evaporating this again to dryness and extracting the glycerin from the residue by a mixture of alcohol and ether, (Neubauer-Reich ardt's method); and NITROGENOUS CONSTITUENTS by evaporating 10 to 20 cc. in a thin glass vessel, pulverizing residue glass and all, and making a combustion as usual.

For TANNIN AND ŒNOGALLIC ACID, *F. Jean* (*Comtes Rend.* XCIV. No. 11) evaporates 50 to 100 cc. down to small bulk—adds dry precipitated silica, dries at 60 to 70°C., extracts with ether containing a little hydrochloric acid, evaporates the ethereal solution, and dissolves in water, up to the original bulk. In 10 cc. of this solution the combined acids are determined by titrating with iodine, and in the remainder the œnogallic acid is determined (after shaking with rasped hide to remove tannin) by titration again with iodine.

For GLYCERINE in sweet wines *E. Borgmann* (*Fres. Zeits. Anal. Chem.*, XXI, 239) evaporates 100 cc. to a syrup, extracts the residue with 100 cc. of absolute alcohol, and then adds 150 cc. of ether. The sugar settles to the bottom, leaving the glycerine in solution.

For RED COLORING MATTERS *J. De Groot* (*Repert der Analyt. Chem*, II, 95) adds to a wine or other liquid to be tested, one volume chloroform and three volumes absolute alcohol, and agitates briskly; three volumes of distilled water are then carefully added without shaking. Many coloring matters separate at the point where the two liquids are in contact. A few, as, for instance, fuchsin, pass into the chloroform. By the manner of separation or the coloration imparted to one or both liquids, many of the coloring matters may be identified. To detect BORDEAUX RED IN WINES *C. Thomas* (*Chem. Zeit.*, VI, 244) precipitates the wine with barium hydrate—filters—removes the excess of barium by ammonium carbonate, and in the filtrate by evaporation, ignition, etc.; tests for the presence of sulphuric acid arising from the presence of a sulpho compound. *M. Guichard* (*Journ. de Pharm. et de Chim.*, May 1882) tests for the same coloring matter by dyeing silk with the wine. The natural coloring matter gives only a violet or lilac shade, which turns greenish with ammonia, while the Bordeaux red dyes the silk a garnet shade, turning darker with ammonia; also a drop of genuine wine let fall on a lump of chalk moistened with alum solution gives a violet gray spot; whereas, if Bordeaux red is present, a red stain appears.

F. Musculus and *C. Amthor* (*Repert. Analyt. Chem.*, II, 142) find that the natural WINES OF A BAD YEAR contain but little alcohol and much acid, but contain more ash, extractive and phosphoric acid than even the best wines of a good year.

For SULPHUROUS ACID IN WINES *B. Haas* (*Ber. D. Chem. Ges.*, XV, 154) distils off about half of a measured quantity in a current of CO_2 into a bulb tube containing iodine solution, when the sulphuric acid formed may be determined by $BaCl_2$. *L. Lieberman* (*Ber. D. Chem. Ges.*, XV, 439) distils in a similar manner, oxidizing by the use of HNO_3. The last-named author makes a qualitative test upon the distillate by using iodic acid and chloroform. A small amount of SO_2 gives the violet coloration to the chloroform; larger amounts a yellowish brown.

OILS, &c.—To distinguish between OLIVE AND COTTON SEED OIL *M. Zecchini* (*Les Mondes*, May 13, 1882) agitates 5 cc. of the oil with 10 cc. of colorless nitric acid (sp. gr. 1.4), and then allows it to stand for five or six minutes. Pure olive oil will then appear a light ash gray color, with a slight yellow reflex; after some time only it becomes dark colored. Cottonseed oil becomes golden yellow, soon turning coffee brown. Mixtures of the two give intermediate shades.

To detect ROSIN OR PARAFFIN OIL IN LARD, TALLOW, ETC., *W. Rodiger* (*Chem. Zeit.*, 1882, 118) saponifies and then extracts with benzine. If much soda lye is necessary to cause the separation of the soap from its solution in water, palm or cocoanut oil is probably present.

To determine ROSIN IN FATS, *T. S. Gladding* (*Am. Chem. Jour.*, III, 416), dissolves about 0.5 gm. in 20 cc. alcohol (95 %) and saponifies by alcoholic potash solution, the addition being controlled by the indication of a drop of phenol phthalein in the solution. A slight excess of potash is used. After insuring saponification by heating, the solution is cooled, and then transferred to a 100 cc. cylinder by the use of ether, enough being used to bring the volume up to 100 cc. After thorough mixture by agitation, 1 gm. pure pulverized $Ag\,NO_3$ is added, and the mixture again well agitated for 10 or 15 minutes. The silver resinate goes into solution in the ether. An aliquot portion of the clear ether solution is then siphoned off into another cylinder, and agitated with 20cc. of HCl. (1:2 by vol.) to set the rosin free. On evaporating a measured amount of the last ether solution the rosin is left behind, together with a little oleic acid (0.00235 gm. to every 10 cc. of ether solution taken.)

Ulex tests for FOREIGN SEEDS IN RAPE-SEED CAKE (*Repert. Anal. Chem.*, 1882, p. 3,) by distilling with water, and testing for sulphur in the distillate by oxidation with bromine and precipitation with barium salt, 233 parts $BaSO_4 = 99$ parts oil of mustard. Rape-seed cake contains only 0.0238 % of that oil.

ALKALOIDS.—A solution of 1 gm. melted zinc chloride in 30 cc. of water is proposed by *Czumpelitz* (*Monit. Sci.* Feb. 1882). The substance to be examined is first dried, then moistened with the reagent and dried again. The colors produced are:

Strychnine,	Scarlet,	Quinine,	Pale Yellow,
Thebaine,	Yellow,	Digitaline,	Maroon,
Narceine,	Olive green,	Salicine,	Violet red,
Delphinine,	Red brown,	Santonine,	Violet blue,
Berberine,	Yellow,	Cubebine,	Purple,
Veratrine,	Red.		

When both strychnine and brucine are present the color obtained is a dirty yellow.

R. C. Woodcock (*Chem. News* XLV, 79) proposes TO SEPARATE ALKALOIDS from articles of food, &c., by the use of cubes of jelly prepared from a 6 % solution of gelatine. (Applied by *Dupre Analyst*, I, 186, to separate certain adulterants of wines.) In an experiment with strychnine, one part was satisfactorily separated from a million parts of substance.

H. Beckhurst (*Chem. Centr. bl.* XIII, 258) finds that the reduction of ferric compounds is not characteristic for the PTOMAINES.
To extract alkaloids from CINCHONA BARK *J. E. De Vrij*, (*Jour. Pharm. Chim.*, May, 1882) recommends Prollius's mixture consisting of:

Ether	88 parts.
Ammonia	4 parts.
Alcohol (92 to 96 %)	8 parts.

For the extraction and determination of the alkaloids in the above barks, methods are also given by *M. Fluckiger* (*Jour. Pharm. Chim.* Feb. 1882) and *E. R. Squibb* (*Ephemeris* I, 76 and 105). The first named boils the powdered bark with four times its weight of water and then adds milk of lime, after which the mixture is evaporated to dryness. The dry mass is exhausted with ether, and after the addition of a little hydrochloric acid (36 cc. of $\frac{1}{10}$ normal HCl. to the extract from 20 gms. of bark), the ether is distilled off. The solution is then acidified with HCl. and filtered. The cold solution is partly neutralized by $\frac{1}{10}$ normal NaHO solution 40 cc., allowed to stand until it clears, decanted or filtered if necessary, and soda lye (of sp. gr. 1.3) added to complete precipitation of the bases. The precipitate is dried between filter paper, then over sulphuric acid, and finally in an air bath at 100° C. before weighing. To separate the quinine the precipitate is boiled with thirty times its weight of water for an hour, and filtered boiling. On cooling, the quinine hydrate is deposited. If pure, the dry alkaloid is soluble in twenty times its weight of ether. *E. R. Squibb* takes 1.25 gm. quick lime, adds 30 cc. hot water, and as soon as it is slaked stirs in 5 gms. pulverized bark, and allows it to digest for some time. After drying over a water bath, the powder is digested in a closed flask over a water bath with 25 cc. amylic alcohol for four hours; 60 cc. of ether are then added and the digestion continued for an hour more with frequent shaking. It is filtered and washed with a mixture of 10 vols. amylic alcohol to 40 of ether. The ether is then boiled off, and the residue transferred to a small flask by the use of amylic alcohol. The solution and washings should not be over 10 cc. Then 6 cc. water and 4 cc. normal oxalic acid solution are added, and the mixture shaken. The aqueous solution is then filtered off and the amylic alcohol washed repeatedly with diluted oxalic acid solution. The solution is evaporated to about 15 cc., 20 cc. pure chloroform added, and a slight excess of normal soda solution. The alkaloids are thus separated, and are taken up by the chloroform, which, after washing, may be evaporated, leaving the alkaloids pure.

By shaking the alkaloids thus obtained with 5 gms. ground glass and 5 cc. ether, and pouring the mixture upon a filter wetted with ether, rinsing the adherent particles on to the filter until 10 cc. have passed through, and then washing with ether until a second 10 cc. (caught separately) have passed through, and evaporating these portions of ether separately, a basis for the estimation of the quinia is obtained. The first 10 cc. contains quinia plus some other alkaloids, the second 10 cc. approximately the same amount of alkaloids, not quinia, as the first. The difference between the weights of the residues left is therefore quinia.

E. R. SQUIBB also gives a process for the ASSAY OF OPIUM (Ephemeris I, 14), a modification of Fluckiger's process. Careful sampling and the determination of moisture are both indispensable. 10 gms. of the sample are first digested with 100 cc. water with frequent shaking for several hours. It is then filtered and percolated with water until the filtrate has a bulk of 120 cc. The residue is again shaken with more water and the percolation repeated, the filtrate being kept separate, and evaporated down to about 20 cc. before adding the stronger solution (of 120 cc.) ,the object being to avoid the effect of prolonged heat upon the major part of the alkaloids. The residue should be dried at 100° C. and weighed. The entire extract is finally evaporated to 20 cc.—cooled—5 cc. of alcohol added and well stirred in, then transferred to a tared flask, being mixed in with about 5 cc. water, 5 cc. more alcohol is added and after thorough admixture 40 cc. of ether. After vigorous shaking 4 cc. of ammonia (sp. gr. 0.96) is added, and the shaking is repeated until the crystals of morphia begin to separate, when the flask must be put aside for 12 hours. The ether solution is then decanted off through a filter wetted with ether, 20 cc. of ether is added to the flask and rinsed around without shaking and decanted through the filter. The funnel should be kept covered as much as possible while the ether is filtering through. Finally pour the aqueous solution on to the filter, rinse with a little water. Dry the filter and contents first with bibulous paper, afterward in the air bath (at 100°C) weigh, and deduct weight of filter. Invert the flask, dry and weigh it to get the weight of the morphia crystals which may adhere. The crystals of morphia are light brown or a loss has been sustained. 0.1 gm. of the precipitate when pulverized should dissolve completely on shaking in a corked test tube with 10 cc. of lime water (absence of narcotine). A description and criticism of the various methods for determining NICOTINE IN TOBACCO are given by *R. Kissling* (*Fres. Zeits. Anal. Chem.*, XXI, 64). The conclusion reached is that only Schloesing and Dragendorff's methods are at all satisfactory. The results of a number of experiments are detailed, and a list of analyses of 36 tobaccos given.

For the ESTIMATION OF TANNIN *F. Simand* (*Dingl. Jour.*, CCXLIV., 391) proposes a modification of Lœwenthal's method. In extracting, paper saturated with a solution containing ferrous chloride and sodium acetate is used to determine when the extraction is complete. 10 cc. of the extract should not require over 12 cc. of the permanganate solution. The permanganate solution should be one gm. per litre, 1 cc.=0.00135 tannin, 20 cc. of the indigo solution should be equivalent to 18 to 20 cc. of permanganate. 20 cc. of the solution is used for each determination. The gelatine solution is of the strength, &c., prescribed by Lœwenthal. To obtain satisfactory results close attention must be paid to the degree of dilution and the amount of acid used.

To DETERMINE GLYCERINE in dilutions thereof, it is proposed, (*Jour. Soc. Chem. Ind.*, I, 75), to moisten 5 to 60 gms. PbO_2 with 2 to 3 gms. of the dilution, and to dry the mixture for six hours in a desiccator, then one hour at 100° C. and finally one hour at 120° C. when it is cooled and weighed. $C_3H_6O_3$ Pb forms. The gain in weight multiplied by 1.3429 gives the weight of glycerine actually present.

To DETERMINE PHENOL *P Diacosa* (*Repert. Anal Chem.*, II., 137), proposes a reversal of the usual volumetric methods, viz., 20 cc. of bromine water the strength of which has been determined by the use of a standard solution of phenol, receives the addition of the solution containing phenol until the clear solution no longer acts upon iodized starch paper.

Jorissen's REACTION FOR FUSEL OIL.—A red coloration with anilin and H.Cl. is stated by *K. Forster* (*Ber. D. Chem. Ges.*, XV, 230), to be due to the presence of furfurol and not to that of amyl alcohol.

To determine ACETON IN WOOD SPIRIT *M. Kramer* (*Monit. Sci.*, Jan., 1882), adds 1 cc. of the sample, first 10 cc. of binormal solution of soda, then 5 cc. of binormal solution of iodine and agitates. The precipitate of iodoform is dissolved in 10 cc. of ether, and 5 cc. are evaporated on a weighed watch glass. From this the proportion of acetone is calculated. If the wood spirit is to be used in the manufacture of coal tar colors, not over 1 per cent. of aceton should be present.

To TEST ASPHALTUM, *D. Claye* (*Jour. Soc. Chem. Ind.* I., 203), dissolves in CS_2, filters, and evaporates off the solvent. The residue is then pulverized, and 0. 1gm. is treated with 5 cc. fuming sulphuric acid for 24 hours, and then poured slowly into 10 cc. of water with continuous stirring. Pure asphalt gives a clear light yellow solution, while the adulterants—pitch, coal tar, etc.—give a dark color.

URINE EXAMINATIONS—FOR UREA, *J. R. Duggan* (*Am. Chem. Jour.*, IV, 47), obtains the best results by first mixing the urea and soda solutions and then adding the bromine. The results of *T. G. Wormley's* experiments with Apjohn's apparatus (*Chem. News*, XXI, 37), are given as follows (*Chem. News*, XLV, 27): To insure the elimination of the whole of the nitrogen—1. The reagent must be freshly prepared. 2. The urea solution should be wholly added to the reagent, none of the latter being allowed to mix with the urea solution in the containing tube. 3. The amount of urea operated upon should not exceed one part to 1200 of the diluted reagent.

The volumetric uranium solution for PHOSPHORIC ACID cannot, according to *G. Guerin* (*Jour. Pharm. Chem.*, Feb., 1882), be successfully applied to urine examinations. According to this author, the uranium solution only gives accurate results when standardized in the presence of the same kind of salts as those existing in the substance to be analyzed.

List of books published on analysis during 1882 :

THE LABORATORY GUIDE: A Manual of Practical Chemistry, etc. By *A. H. Church.* Fifth Edition. London: J. Van Voorst.

TABLES FOR QUALITATIVE CHEMICAL ANALYSIS. *H. Will.* Third American Edition. Edited by *C. F. Himes.* Philadelphia : H. C. Baird & Co.

HANDBOOK OF VOLUMETRIC ANALYSIS. *F. Sutton.* Fourth Edition. London: J. and A. Churchill.

COMMERCIAL ORGANIC ANALYSIS. Vol. II. *A. H. Allen.* London : J. and A. Churchill.

QUANTITATIVE ANALYSE AUF ELEKTROLYTISCHEM WEGE. *Dr. Alexander Classen.* Aachen : J. A. Mayer.

ANALYSE VON PFLANZEN UND PFLANZEN-THEILEN. *Dr. Georg Dragendorff.* Gottingen : Vandenhoeck & Ruprecht.

FOODS : THEIR COMPOSITION AND ANALYSIS. *A. W Blyth.* London : Charles Griffin & Co.

MANUAL OF SUGAR ANALYSIS. *J. H. Tucker.* New York : D. Van Nostrand.

HANDBOOK OF THE POLARISCOPE. From the German of Landolt. By *D. C. Robb* and *V. H. Veley.* London : MacMillan & Co.