NOTES ON QUANTITATIVE ANALYSIS.

By L. H. Friedburg, Ph. D.

The following chapters make but little claim to originality, and treat only of well known facts. But as every chemist during a long period of analytical occupation developes for himself a particular *modus operandi,* based upon results obtained, it is proper to recommend what he deems to be valuable. In this sense I offer the descriptions given below, omitting all reference to literature or authorship of the different methods; premising only that not *one* is described that I have not myself frequently used.

A. ACIDIMETRY AND ALKALIMETRY.

The test liquids used are hydrochloric acid and ammonium hydrate. It is customary to prepare normal or deci-normal solutions. With solids, provided they are pure, this may be arrived at to a degree of accuracy practically sufficient. With solutions of gases such as $H\,Cl$ or NH_3 the preparation of a normal solution, even if performed with the greatest care and the best, standardized measuring vessels or specific gravity apparatus, we cannot omit quantitative determination of at least *one* of the liquids prepared. The following figures will show that in trying to prepare normal solutions of the aforesaid liquids a difference of 0.1957 per cent. of $H\,Cl$ and of 0.0740 per cent. of nitrogen were quantitatively determined. For very accurate work such determination ought to be made and no attempt to normalize afterwards by dilution or concentration is necessary or desirable. The measuring of new quantities of liquids is a source of new errors at best. The sacrifice of the advantage of rapid final calculation of results with such solutions is well balanced by greater accuracy obtained.

900 c. c. hydrochloric acid *puriss.,* Sp. Gr. 1.20, were mixed with about 8000 c. c. of distilled water, while 450 c. c. of the commercially pure, strong ammonium hydrate were added to about 6400 c. c. of dist. water. The mixtures were allowed to

stand for a week. Then it was ascertained how these two liquids would neutralize each other by volume. The whole length of the burettes was used, and in the last determination they were filled up again. It was found, using cochineal as an indicator, that :

a. 20 c. c. H Cl were neutralized by 25 c. c. $N H_4 O H$.
b. 20 c. c. H Cl were neutralized by 25 c. c. $N H_4 O H$.
c. 20 c. c. H Cl were neutralized by 24,95 c. c. $N H_4 O H$.
20 c. c. H Cl therefore corresponded to 25 c. c. $N H_4 O H$.

Next, three different weighed quantities of H Cl were taken and neutralized (using the same indicator) with ammonia. The results were:

a. 19.7861 grms. H Cl required 24,30 c. c. $N H_4 O H$,
consequently 1 grm. H Cl required 1,228 c. c. $N H_4 O H$.
b. 5.8800 grms. H Cl required 7,20 c. c. $N H_4 O H$
therefore 1 grm. H Cl required 1,224 c. c. $N H_4 O H$.
c. 15.4551 grms. H Cl required 19,00 c. c. $N H_4 O H$,
or, 1 grm. H Cl required 1,229 c. c. $N H_4 O H$.
1 grm. H Cl, therefore, was neutralized by 1.23 c. c. $N H_4 O H$.

Finally, three chlorine determinations were made. The silver chloride was dried as usual, but only that part of it which would spontaneously leave the filter when emptied into the porcelain crucible was determined as horn silver, the filter and the remaining amount were burned in a weighed platinum spiral until the silver was reduced to a metallic state, adhering as a little knob to the wire, which was again weighed. Following are the results:

a. 9,9710 grms. H Cl gave 1.66603 grms. Ag Cl equal to 0.42362 H Cl.
b. 1,8240 grms. H Cl gave 0.3023 grms. Ag Cl equal to 0.0769 H Cl.
c. 7,8802 grms. H Cl gave 1.31663 grms. Ag Cl equal to 0.33478 H Cl.

From these analyses the following amounts of H Cl in one grm. of the liquid were calculated:

a. 1 grm. H Cl contains 0.04249 grm. H Cl gas.
b. 1 grm. H Cl contains 0.04218 grm. H Cl gas.
c. 1 grm. H Cl contains 0.042485 grm. H Cl gas.

A noticeable loss having occurred in the determination *b*, the average of *a* and *c* was taken; 1 grm. H Cl contains 04249 gaseous H Cl. The difference between the average taken from all three determinations, and of that from the two mentioned, however, is only 0.0001 grm.

From all the above it follows that:

1 grm. H Cl solution is neutralized by=1.23 c.c. NH_4OH solution.
1 grm. H Cl solution contains=0.04249 gr. H Cl gas.
1 c.c. NH_4OH solution contains=0.013264 grm. nitrogen.
1 c.c. NH_4OH solution is neutralized by=0.8 c.c. H Cl solution.
1 c.c. H Cl solution contains=0.034543 grm. H Cl gas.
or=0.033596 grm. chlorine.

These solutions were prepared in February, 1888. The H Cl solution was kept in a large flask with doubly perforated rubber stopper, one hole of which allowed the escape of the liquid by means of a syphon (or self feeding burette) while the second opening was connected with a small flask containing a few c. c. of the same liquid as the large one. The ammonia bottle was closed with a doubly perforated *cork*. A small flask, containing a little liquid of the same strength, a second small flask which is kept empty and finally a cylinder, containing cotton, solid KOH and again cotton, are attached, in the above sequence, to one opening, the other serving for the outlet of the liquid.

These liquids are kept standing in the laboratory, not exposed to direct sunlight, but subject to the natural variations of temperature during the year. Nevertheless, they have not changed during these last *two years* under the given conditions. To-day, as two years ago, 20 c.c. of the H Cl solution is saturated by 25 c. c. of the ammonia solution, while both solutions, when used in a nitrogen determination of urea which had been six times recrystallized and finally dried over sulphuric acid, then heated with soda lime, was shown to have retained the previously determined percentage, the urea analysis yielding figures of *absolute* correctness.

B. ANALYSIS OF INSOLUBLE SILICATES, MAINLY PORPHYRIES, ETC. *

A quantity sufficient for eight different assays is crushed, powdered and sifted through fine muslin. No pressure should be used while dusting, but the muslin which covers a jar and carries the powder is covered by a piece of chamois, and both pieces are tied around the neck of the dry jar. The chamois is then gently tapped with the fingers.

FIRST PORTION.

SiO_2 ; Fe ; Al ; (Mn) : Ca ; Mg.

The powder is mixed in a platinum crucible with eight times its weight of absolutely dry powdered sodium carbonate. The crucible is covered and then heated with the blast lamp. At the beginning of this operation the sleeve at the mouth of the blow pipe is drawn so far forward that an agitated, blue flame results. The effect is, that the entire crucible (cover and all), become at once red hot, thus avoiding any decrepitation inside. After a time the sleeve is pushed back, allowing the ordinary flame to play. This is continued for about fifteen minutes, until the mass flows without bubbles. Then the crucible is suddenly cooled by turning off the gas and blowing the cold air from the bellows against it. The cake will subsequently fall out easily, without the necessity of pressing or distorting the crucible. If the fused mass looks merely greenish, this indicates only traces of sodium manganate, but if more intense coloration is visible the presence of manganese must be taken into account in the course of the analysis. The cake is put into a separate beaker, containing a little water, the crucible and cover are put into another beaker. Both beakers receive a gradual addition of H Cl and are gently heated. After all is dissolved, except gelatinous SiO_2, the heating is continued until no more CO_2 is present. The combined liquids from the two beakers are then transferred to a platinum dish and evaporated to dryness on the water bath. The lumps of gelatinous SiO_2 must be frequently crushed so that they cannot enclose soluble silicic acid. The residue is moistened with a few drops of conc. HCl, then diluted with

---

* This process with few changes was commonly used in Bunsen's laboratory. L. H. F.

water and filtered with the pump. The filter with SiO_2 is (after complete washing) put while moist into a platinum crucible, heated and weighed until the weight is constant. The silicic acid is then treated with HF (free from all residue), and a few drops of H_2SO_4 upon the water bath, until all volatile matter is driven off; the residual H_2SO_4 is expelled over a free flame, the residue, if any, is heated to redness and weighed. The treatment with HF and $H_2 SO_4$ may be repeated if necessary. In case the residue should be considerable it must be quantitatively tested for Al, Fe, Ca and Mg, otherwise a qualitative test is sufficient.

The *filtrate* from the SiO_2 determination is heated and oxidized by a few drops of HNO_3, after which Fe and Al are precipitated with a very slight excess of NH_4OH, and the unavoidable excess of this latter is boiled off immediately. Care should be taken not to expose this liquid too long to the air. It would attract CO_2 and precipitate Ca. If an interruption is unavoidable, the .beaker must be placed upon a dish containing a layer of NH_4OH and a larger beaker must be inverted over the smaller one, its edge immersed in the layer. The precipitate consists of Fe_2O_3 and Al_2O_3, with small traces of SiO_2, Ca and Mg.

This precipitate may be treated in two different ways, according as it is smaller or larger, especially as regards the quantity of iron present.

I.—*For small quantities of iron.* The precipitate is heated and weighed, then fluxed with potassium bisulphate in a closed crucible at low temperature, so as just to make the mass flow, cooled, dissolved in water, the iron is reduced with zinc and the solution titrated with permanganate. In case HCl was used to dissolve the reduced iron, H_2SO_4 is added before titration, in excess, because the sulphate solution is lighter in color than the chloride, and also because strong dilution is desirable.

II.—*The precipitate is abundant and much iron is present.* Dissolve in HCl and digest for half an hour in a platinum dish with an excess of KOH upon the water bath. The details of manipulation are as follows: The precipitate being washed thoroughly, is, for the greatest part, brought into the platinum dish by means of a platinum spatula. The remaining portions on the filter are dissolved in a hot mixture of equal parts of conc. HCl and H_2O by means of a pipette. The solution is allowed to run into the main precipitate in the platinum dish. The filter is washed with water, this filtrate running into a beaker. The mass in the platinum dish is then cautiously treated with KOH solution, a few pieces of solid KOH are added, digestion for half an hour upon the water bath follows, and the mass is then diluted with the wash filtrate which was collected separately in the beaker and filtered through the aforesaid filter. This filtrate contains the Al_2O_3. Acidulate with HCl, so that solution just takes place after the first precipitation, and precipitate with freshly prepared ammonium sulphide. This latter is used in preference to ammonium hydrate, because Al_2O_3 is less soluble in the former; the $(NH_4)_2S$ must be freshly prepared in order to avoid polythionic salts as well as ammonia resulting from decomposition by age.

The previously mentioned precipitate containing Fe_2O_3 (and traces of CaO, MgO and SiO_2) is heated and weighed. Of course, the crucible during this heating must remain open, in order to avoid reduction by gases from the flame. Dissolve in conc. HCl, filter from SiO_2, reprecipitate iron with NH_4OH and add the filtrate to the liquid containing these substances. SiO_2 and Fe_2O_3 are to be treated as described before, and weighed separately.

Should the remaining filtrate now be too abundant it must be concentrated after acidulation with HCl. A little NH_4OH is added to precipitate remaining Al_2O_3 and, if this is still present, the ammonia is driven off and the precipitate filtered, added to the first precipitate, heated and weighed as Al_2O_3.

The combined filtrates, concentrated as above, contain Mn, Ca and Mg for determination. If enough Mn were present this must first be precipitated by means of ammonium sulphide. Wash with water containing some $(NH_4)_2S$, redissolve in HCl, boil the solution to separate sulphur and filter. Concentrate the filtrate, precipitate with Na_2CO_3, boil in order to destroy manganese carbonate which might have formed, wash with boiling water, heat and weigh as Mn_3O_4.

Before precipitating Ca, the filtrate must be acidulated with

HCl, thus separating sulphur and then filtered. Render slightly alkaline with NH_4OH and add ammonium oxalate, boiling Filter after twelve hours. Put the moist, well washed filter, with precipitate, into a platinum crucible, heat strongly for fifteen minutes before the blast lamp and weigh as CaO. This weight must be controlled. Redissolve the CaO in HCl, reprecipitate as above, and add the filtrate to the liquid containing Mg. Heat the CaO to constancy before the blast lamp. Test it with the spectroscope for Ba and Sr.

Before precipitating Mg (particularly if this is present in small quantity only) drive off the ammonium salts as thoroughly as possible. Dissolve in a little HCl until the liquid is slightly acid, add sodium phosphate, then ammonium hydrate until a turbidity sets in, then a quantity of ammonium hydrate equal to one-third of the volume of the liquid ; filter after four hours and wash with a mixture of one part of NH_4OH and three parts of water. Formerly, a period of twenty-four hours was deemed necessary for this precipitation, but, generally, four hours are fully sufficient. The precipitate is washed until no more chlorine is present. Now, either dry the filter with precipitate and incinerate separately, or better, especially if the pump was used for washing, bring the moist precipitate and filter into a platinum crucible. Heat gently at first, finally before the blast lamp energetically. Should the pyrophosphate prove to contain a little carbon, moisten with a few drops of HNO_3, evaporate cautiously to dryness and heat again, as above.

If the spectroscopic research proved the presence of sufficient Ba and Sr, the CaO precipitate has to be further treated. Transfer from the platinum crucible into a small, thin well tempered flask of 5 to 10 c. c. capacity. Wash the residue from the crucible with HNO_3 into the flask and add more HNO_3 to this latter, until all Ca is transformed into nitrate. The solution may be turbid from filter ash or from Ba or Sr salts. Evaporate over a small, direct flame to dryness, blow out the residual HNO_3 vapor by means of a glass pipe, and add not more alcohol than is necessary to obtain on heating a syrupy solution of calcium nitrate. Allow to stand for twenty-four hours, filter from barium and strontium nitrate, wash with absolute alcohol. If a sufficient quantity now remains upon the filter, dissolve this in hot water and allow the solution to run into a weighed platinum crucible. Evaporate to dryness and heat before the blast to constant weight. (BaO and SrO.) Now dissolve in conc. HCl, evaporate in the same little flask as previously used to dryness, separate $SrCl_2$, soluble in absolute alcohol by means of this. Precipitate $BaCl_2$ as sulphate and weigh. Sr is found by difference. In case no weighable amount of $Ba\,Cl_2$ should have remained after the $Sr\,Cl_2$ was dissolved in absolute alcohol, allow the syrup of $SrCl_2$ to be taken up by a strip of filter paper, wind around this a thin platinum wire, incinerate in an open flame, heat until the sodium flame has disappeared and then use the spectroscope, dipping the platinum wire frequently into HCl. Mere traces of Ba will only become visible after almost perfect evaporation of $SrCl_2$.

SECOND PORTION.

DETERMINATION OF THE ALKALIES.

The powder is put into a platinum crucible, moistened with a few drops of conc. H_2SO_4 and then digested three or four times with conc. HF upon the water bath. This done, the small crucible is put upright inside of and near the bottom of a large platinum crucible lying horizontally. A small flame is applied underneath the side nearest the mouth of the large crucible and the burner is gradually pushed towards the middle and near the end. The H_2SO_4 and hydrofluorsilicic acid are thus expelled. This expulsion must be performed thoroughly so that afterwards no glass vessel may be attacked by remaining HF. The small platinum crucible is not allowed to become red hot in order that alkalies may not be lost. Should the mineral not have been fully decomposed, the resulting mass must again be treated with HF on the water bath and afterwards heated, as described. Now, while the large crucible is put vertically and the small one inserted into the same, enough conc. HCl is added to dissolve all $CaSO_4$, and the large crucible containing the small one standing within is heated upon the water bath. Generally it is found that a residue is left. The liquid must then be decanted and the residue treated as before. After perfect solution, the contents of the small crucible are emptied into the large one, washing carefully. Then $BaCl_2$ and (without filtering) NH_4OH and $(NH_4)_2CO_3$ are added and the precipitate is filtered and washed and the united filtrates are evaporated to dryness. The ammonia salts are expelled by very cautious heating, so that no decrepitation may take place. The residue is dissolved in water, NH_4OH and $(NH_4)_2CO_3$ are again added, filtration, evaporation and expulsion of ammonia salts is repeated again and again, until no further precipitate is formed by addition of these reagents. It is advisable to use for every new filtration a smaller platinum dish, so as not to get too much filtrate. The final solution must be absolutely free from ammonium salts.

A small quantity of pure, red HgO is added in order to transform $MgCl_2$ into MgO while HgO is transformed into volatile $HgCl_2$. The platinum dish is covered with a watch glass and digested (so that the mass is just kept moist) for two hours. An excess of water has to be avoided or else the reaction does not take place. After this dry for 1 to 2 hours on the water bath, and finally drive off the $HgCl_2$ by heating, but not to redness. Dissolve in a minimum of water, filter into a weighed platinum crucible, add a drop of HCl, evaporate to dryness, heat so as to keep the mass just in a fused state in the *covered* crucible and then weigh. In order to obtain thus the sum of the alkaline chlorides, this heating and weighing has to be repeated to constancy. After the first weighings a new addition of HCl is advisable since (owing to organic substance from the filter) carbonates may have formed in heating.

Now dissolve in a few drops of water and add an excess of platinic chloride. (The preparation of c. p. platinic chloride will be given at the end of this chapter.) Care has to be taken that all $NaCl$ is transformed into the double salt; no white cubes must remain visible in the precipitate, since these would be insoluble in alcohol. Evaporate to dryness on the water bath and in a *porcelain* dish. This is easily understood. In the first place the mixed chlorides of alkalies are generally dissolved and filtered after weighing, since an unavoidable residue of Fe may be present, which must be considered ; secondly, the platinic chloride must not be evaporated in a platinum dish, as it would dissolve platinum as subchloride, which is insoluble in alcohol and would result together with potassium-platinic chloride. Allow to cool, add a few drops of water in order to dissolve the sodium double salt and throw on a filter previously washed with alcohol, dried at 105° C. and weighed. Then wash the potassium double salt first with a mixture of 1 part alcohol and 1 part water, then with 1 part water and 2 parts alcohol, finally with absolute alcohol until the filtrate runs colorless. Then wash with a mixture of 4 parts alcohol and 1 part ether. The filtrates must be preserved for the following reason : In case the determination of MgO in the filtrate should not be necessary, but that the precipitate of K_2PtCl_6 should be lost, the $PtCl_4$ would have to be reduced to metallic platinum, as described below, in order to obtain NaCl.

The precipitate is dried at 105° C. and weighed to constancy.

The filtrate is diluted with water, heated to drive off ether and alcohol and then put into a little flask with doubly perforated stopper, which carries two rectangularly bent tubes. One of these latter nearly reaches the surface of the liquid, the other ends in the neck of the flask. This second one is connected with a hydrogen apparatus. The flask is heated gently and, while still hot, the longer rectangular tube is closed outside by means of a rubber tube with glass rod. The hydrogen apparatus is now set to work, the flask cools and the hydrogen absorbed by reduction is thus replaced spontaneously. The liquid becomes colorless and platinum is dendritically separated, generally floating for some time upon the liquid, which is now filtered. If some FeO should still be present, a drop of HNO_3 is added and then NH_4OH. The precipitate, if any, is filtered. Then MgO is determined and deducted as $MgCl_2$ from the above found sum of the combined alkaline chlorides.

PREPARATION OF C. P. PLATINIC CHLORIDE.

The platinic chloride used in the above determination is prepared, according to Bunsen, in the following manner, which involves the separation of platinum from iridium, rhodium and palladium :

Dissolve platinum in aqua regia, taking 4 pts. HCl and 1 pt. HNO_3, adding this latter very gradually while the flask stands on the water bath. After complete solution has taken place evaporate, also on the water bath, to a syrup, add water and evaporate again as before, repeating this process until upon renewed addition of a drop of water to the syrup no odor of nitrous acid is perceptible.

Now dissolve in water and filter into a porcelain dish. Add sodium hydrate solution, until strongly alkaline, while the liquid is kept boiling and continue to boil after the addition for a few seconds, during which time a drop or two of alcohol are added. At first the oxides of all the metals are thus formed, but after a while the excess of NaOH transforms Ir, Rh and Pd into the sesquioxides while platinum remains as oxide. Sodium hypochlorite is formed at the same time but this is destroyed by the addition of a little alcohol.

If now HCl be added and the heating continued a yellow precipitate is first formed, while the HCl and the excess of NaOH have just neutralized each other. Heating is continued and more HCl is added until the yellow precipitate is redissolved.

Platinic chloride and the sesquichlorides of Ir, Pd and Rh are formed.

All of these are soluble but only the platinic chloride is precipitated by potassium chloride. To the clear filtrate is added a hot, saturated solution of KCl, until no more precipitate is formed. After cooling, the canary yellow precipitate of K_2PtCl_6 is filtered, washed with a solution of KCl saturated in the cold, dried very thoroughly and reduced in a long, absolutely dry Bohemian glass tube by means of hydrogen at a very low temperature. The tube is put in an ordinary combustion furnace and the flames are kept very low.

After all of the double salt has become uniformly black, the mass is allowed to cool in the hydrogen current. The contents of the tube are then transferred to a porcelain dish, boiled with water and decanted, or filtered by decantation. This boiling is repeated until all KCl is dissolved and the wash water does not show the chlorine reaction. The pure platinum obtained is now dissolved in aqua regia, as described above for the impure metal and the syrup is treated with water until no further escape of nitrous acid takes place.

THIRD PORTION.

Hygroscopic Water.—Heat the substance (powdered as described), at 105° C. to constant weight. *Water of Combination.*—Heat the material for 15–20 minutes to redness in a Bohemian bulb tube and collect H_2O in a weighed $CaCl_2$ tube. Allow to cool in a current of cold, dried air. In case the silicate should contain FeO, the heating has to be performed in a current of CO_2, since it is desirable to weigh the bulb tube also for control.

FOURTH PORTION.

Take a well dried Bohemian glass tube, 1 foot long, closed at one end and put into it, by means of a long weighing tube, about 1 grm. of substance. With the aid of a long capillary funnel tube moisten the mass uniformly with some drops of water. Prepare a mixture of 6 pts. conc. H_2SO_4 and 2 pts. H_2O, allow it to cool and pour it through the same funnel tube upon the substance, until it occupies 8 to 10 times the volume of the latter. Reduce the diameter of the tube greatly at about two inches from its open end and replace the air above the liquid with carbon dioxide. Seal before the blast lamp. After cooling shake the tube vigorously in order to avoid caking. Heat the sealed tube for 4 to 5 hours in a thermostat to 200° or 220° C. When quite cold open the tube, transfer its contents, without filtering, into a high beaker, wash rapidly and titrate with permanganate solution, the titre of which has been determined immediately before use. It is evident that in presence of organic matter in the silicate this determination cannot be performed.

FIFTH PORTION.

For the determination of phosphoric acid fuse with Na_2CO_3 as directed for first portion, but dissolve in HNO_3 instead of using HCl. Reduce the silicic acid to a sandy powder, filter and acidulate with nitric acid. Prepare a solution of ammonium molybdate in the following manner: 100 grms. molybdic acid suspended in 240 grms. distilled water, of a temperature of about 50° C., are mixed with 160 grms. of NH_4OH of Sp. Gr. 0.91. If necessary, filter and allow *this* solution to run gradually *into* 1250 c. c. HNO_3 of Sp. Gr. 1.20. Shake at intervals and allow the clear solution to rest for five or six days in a moderately warm, dark place. Decant or syphon, if necessary, from yellow precipitate and add H_2O to make 2 litres. Preserve this reagent in the dark.

In case the amount of phosphoric acid in the sample does not amount to more than one decigramme, and provided the volume of the liquid to be tested does not exceed 150 c. c., add an excess of the above solution of ammonium molybdate and put the beaker into a water bath containing boiling water. Allow the beaker to remain for ten minutes in the boiling water and *all* phosphoric acid will be precipitated.

If the mineral is richer in phosphoric acid it must be treated with an excess of ammonium molybdate in a warm place for fully twenty-four hours.

In either case the precipitate is filtered, washed at first with the molybdate solution used for precipitation, finally with a solution of one-third that strength, obtained by dilution with H_2O. The united filtrates are allowed to stand for a while in order to see if an additional precipitate is formed.

The yellow precipitate on the filter is quantitatively dissolved in NH_4OH.

Magnesium mixture is now prepared in the following manner: Magnesium chloride is dissolved in conc. HCl in the proportion of 5 grms. $MgCl_2$ to 30 c. c. HCl. Dilute with water and supersaturate with strong NH_4OH. If the liquid should not remain clear, but precipitate magnesia, enough NH_4Cl must be added to redissolve this.

Of a solution thus prepared, take a certain volume and divide into halves. One-half is added to the ammoniacal solution of phospho-ammonium molybdate, after this has been nearly neutralized with HCl. Finally add strong NH_4OH, amounting to one-third of the entire volume of the liquid. Allow this to stand three to four hours.

Fill up the other half of the magnesium mixture taken, with the same quantity of NH_4OH used in forming the precipitate just described, and then with H_2O to obtain the same volume. A precipitate of magnesia formed here, should be deducted from the previously described one.

The filtration, washing and heating until magnesium pyrophosphate is obtained, takes place according to the description given, I.

SIXTH PORTION.

Fluorine is quite frequently found in silicates containing phosphoric acid. To determine F fuse the silicate, duly prepared, with Na_2CO_3 as previously described. Boil the cake with H_2O and a little NH_4OH in order to expel CO_2, thus preventing solution of either SiO_2 or alumina. Filter, add HCl until the liquid is almost neutral. (Avoid acidity since HF might escape.) Digest for some time with NH_4Cl in order to separate all SiO_2 and Al_2O_3, filter if necessary, add $CaCl_2$ solution and filter the precipitate consisting of calcium fluoride, calcium phosphate and calcium carbonate. Heat the precipitate to redness in a porcelain crucible. Now, after cooling, add acetic acid and evaporate the mass again to dryness. Continue this treatment with acetic acid, alternating with washing with water and decanting, until the weight of the residue remains constant. In this manner calcium acetate and phosphate are extracted and calcium fluoride remains.

SEVENTH PORTION.

In order to determine titanic acid, the mineral is fused with potassium bisulphate, using six to eight times the quantity of this latter. Dissolve the fused mass in a little cold water, dilute strongly and boil slowly in a round flask. From time to time add water, since titanic acid is only precipitated from very dilute solutions. In order to prevent precipitate of Fe add either sulphur dioxide, sodium hyposulphite or H_2S to the liquid, thus reducing Fe_2O_3 or avoiding the oxidation of FeO. The precipitate of titanic acid is heated and weighed. If not quite colorless repeat the operation.

EIGHTH PORTION.

For the determination of soluble silicic acid treat the mineral in a platinum crucible with conc. KOH solution upon the water bath for one-quarter to one-half hour. Avoid too great concentration of the liquid, as the silicic acid dissolved would be reprecipitated. If it be suspected that the mineral decomposes, heat only for a short time. The contents of the crucible are transferred to a beaker, diluted strongly, washed by decantation with boiling water until no further reaction of KOH is obtained. The residue is heated and weighed; the operation is repeated until the weight is constant.

If, upon decantation, the precipitate should not settle or should run turbid through the filter, a slight acidulation of the wash water will frequently serve. In case free quartz was present, this would become partly soluble on heating. In such case the mineral is treated several times with KOH solution, decanted each time, as described, but only heated and weighed once, which weight must then suffice.

COLLEGE OF THE CITY OF NEW YORK, May, 1890.

A CONTRIBUTION TO THE QUESTION OF ASSIMILATION OF ATMOSPHERIC NITROGEN.[1]

BY PROF. A. PETERMANN, Ph. D., Gembloux (Belgium).

Translated by L. H. FRIEDBURG, Ph. D.

The question of the intervention of atmospheric nitrogen in the nutrition of plants is certainly one of the greatest importance for the chemist as well as for the physiologist.

Almost forty years ago Boussingault and Ville published the

---

[1] Mémoires couronnés et autres Mémoires publiés par l'Académie royale de Belgique, 1889. Tome XLIV.

Bulletin de la station agronomique de l' état a Gembloux, No. 47; Mars, 1890.