

**A CRITICAL STUDY OF THE PRESENT STANDARD
METHODS OF ANALYSIS OF FELDSPARS**

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I INTRODUCTION

In the progress of chemistry new methods and reagents for qualitative detection and quantitative separation and estimation are gradually being devised and discovered. The belief that some well-established methods were adequate was shown to be unwarranted; some had to be discarded altogether; others were still utilizable after modification. Thus it has become possible to explain many hitherto incomprehensible variations in the composition of some rock species or types, as shown in earlier analysis. In many cases they failed to report one or more of the elements present. Thus most of these older analyses were incomplete. Feldspars have a large number of constituents making the analysis very complex, requiring considerable time and materials.

A search through the present literature on the subject has been made and it has been found that much work has been done on feldspars, but the results of the various analysts do not check. This was acknowledged to be true. No attempt was made to explain the cause of these variations. The amounts of sodium and potassium carbonate used in the fusions of the feldspars was widely varied to find out what effect, if any, this would have on the results. The feldspars used were those which were formerly analyzed for Professor J.W. Whittemore with varying results.

There is no specific procedure given for the analysis of feldspars. It is one of the purposes of this thesis to work out a definite procedure from the general procedure given for silicates, which will give accurate and dependable results for feldspars. The general procedure requires a long time and is often inaccurate. In this thesis the various and new methods of analysis for the elements found in feldspars have been tried and from these a procedure has been worked out.

II HISTORICAL

Feldspars are not decomposed by acids, hence a flux must be used. The most common of these are, hydroxides, peroxides, carbonates, borates, of the alkali metals, and acid fluorides. In addition to these common fluxes, lead oxide and carbonate(1), and bismuth nitrate are occasionally used. All these fluxes have their advantages and disadvantages, but for feldspars sodium carbonate is generally the best, because it can be obtained purer than most of the others.

Holthoff (2) has recommended sodium bicarbonate for the fusion. He says that there is less spattering onto the lid of the crucible than when the normal salt is used, however about 12 to 15 parts of it to 1 part of feldspar must be used instead of the customary 4 to 8 parts of the normal salt. Whether the normal salt or the bicarbonate is used the fusion must be made in platinum vessels.

Feldspars may also be decomposed by hydrofluoric and sulfuric acids (1). This is the best method to use for the analysis of the material for certain metals such as titanium and manganese, because there is no bulky salts to deal with.

The silica is usually determined by dehydrating several times with hydrochloric acid. The dehydrated silica is taken up with dilute hydrochloric acid and filtered off.

H.H. Willard and W.E. Calk (17) recommend perchloric acid as a dehydrating agent for silica on the ground that the silica obtained is purer than when hydrochloric acid is used, the time required is much less, and the salts formed

are all wholly and quickly soluble. The tests made by them upon silicates compared most favorably with those obtained by the usual methods.

The silicia obtained must be volatilized by hydrofluoric and sulfuric acids and the residue left analyzed for various impurities. Hillebrand (1) made special tests and occasionally found magnesium, but not in excess of 0.3 mg. of MgO. The statement that sodium chloride is one cause of persistent small losses of weight, when the silicia is ignited is directly opposite to the observations of Lenher and Truog (4).

F.W.Meier (7) used 8-hydroxyquinoline acetate in the rational analysis of feldspars, with small Fe content, which greatly shortens the time of the determination of aluminum and iron. The method depends upon the common precipitation of Al and Fe in acetic acid solution in the presence of sodium acetate, with an excess of "Oxine acetate" (8-hydroxyquinoline acetate) solution, and brometric titration of the excess oxine. In one part of the weak AcOH solution containing AcONa, Fe and Al are jointly precipitated by a precise quantity of oxine in excess, and the excess is brometrically determined. In the aliquote part, the Fe is determined iodometrically. By converting the Fe values found into cubic centimeters of oxine acetate solution, the number of cubic centimeters which corresponds to the quantity of Al is ascertained by the brometrical method of W.Manhot and Oberhauser (5), which shows the final end point of the titration through the change of an indicator by the uncombined Br. The certainty

and reliability of the method ^{is} ~~are~~ guaranteed even for very dilute solutions.

The most common method used for the precipitation of Al and Fe is by NH_4OH in a solution containing NH_4Cl . The Fe is first oxidized by bromine water or KClO_3 . In this method some Mn will be precipitated if it is present to any extent.

The basic acetate method may also be used if much Mn is present, but ordinary feldspars contain very small amounts of Mn, and to a person not experienced in precipitation by the basic acetate method, the precipitate is often not complete. The Mn content in feldspars is generally so small that it will cause no considerable error if it is precipitated along with the other elements.

There are various other methods by which Fe, Al, P_2O_5 , and Ti may be precipitated, but since they either do not work satisfactory or require a long time they are not mentioned here.

The Fe, Al, P_2O_5 , and Ti precipitate is ignited and the elements may be separated by various methods. Scott (9) dissolves the precipitate in HCl and adds Na_2O_2 until the precipitate first formed clears, the solution being cold and nearly neutral. It is then diluted and boiled for 10-15 minutes to precipitate the Fe. The Fe is filtered off and washed. He redissolves his $\text{Fe}(\text{OH})_3$ in HCl and reprecipitates it with NH_4OH .

Treadwell and Hall (15) uses practically the same method except they use KOH instead of Na_2O_2 . The Al remains in solution as the aluminate, which is soluble. The Fe is precipitated as $\text{Fe}(\text{OH})_3$. The Al is recovered from the filtrate by acidifying with HNO_3 and then adding NH_4OH .

The method used by Hillebrand and Lundell (1) consists of fusing the ignited precipitate of Al, Fe, Ti, and P_2O_5 with a small amount of Na_2CO_3 and extracting the Al with water, the Fe is extracted with HCl. The TiO_2 remains insoluble along with the residual silica.

There are several methods of determining the residual silica in the joint precipitate of Al, Fe, etc. One method is by the fusion as described above, the other methods are used when the recovery of the residual silica is not required. The procedure of Trautman (14) for removing it from Al is serviceable, especially for small amounts of the oxides. He recommends the evaporation of HF and H_2SO_4 in the platinum crucible containing the precipitate, after which the Fe and Al is again ignited and weighed. Selch (11) maintains that there is no danger of sensible loss of Al by volatilization as the fluoride when this procedure is followed.

Calcium is usually precipitated as the oxalate and if much magnesium is present a double or triple precipitation is used. When an extremely accurate determination of very little calcium is desired, especially in presence of much magnesium, direct precipitation as the oxalate is not satis-

factory. Of the available methods suitable for feldspars, which have been attacked by alkali fusion, that of C. Stolberg (1) as modified by O. Kallauner and I. Preller (3) and the E. Murmann method (14) are the best. One involves the use of lithium sulphate, the other presupposes knowledge of the amount of calcium present. Hillebrand (1) has devised a much more satisfactory method in which he precipitates the calcium along with the magnesium as the pyrophosphate, the oxalate precipitation being omitted. He separates the calcium by means of H_2SO_4 and alcohol.

After the excess ammonium salts have been removed, the magnesium is precipitated as the pyrophosphate. A great deal of uncertainty exists concerning the proper conditions for determining Mg as the phosphate (1) in spite of the enormous amount of work that has been done on it. Mg may also be determined by the mercuric oxide method, ammonium carbonate method, amyl alcohol method, alcohol-ether method or the 8-hydroxyquinoline method (16). Of these the 8-hydroxyquinoline method is probably the most accurate for small amounts of magnesium.

In recent years Titanium has received a great deal of attention. When titanium is unaccompanied by other elements that would be precipitated, it is best to throw it out of solution by NH_4OH . In feldspars the Al and Fe would interfere, hence the colorimetric method (9) must be used. Under favorable conditions the colorimetric method for Ti gives

results that are fully equal to those attained by the best gravimetric methods and in much less time, for such percentages as are found in rocks, clays, and soils (usually under 1%, but occasionally rising to 2 or even 3%). Normally the error should not exceed 2 per cent over a wide range of concentrations (17). In the case of feldspars they are decomposed by HF and H_2SO_4 , and the Ti oxidized by H_2O_2 . The Fe and Al do not interfere in the determination.

The Ba can be run on the same sample as the Ti. It is determined as $BaSO_4$, according to the method given by Hillebrand (1). If there is any strontium present it will be precipitated along with the Ba as the sulphate. Even when no attempt is made to separate contaminating traces of Sr and Ba from one another, the error is usually of no great consequence, for an absolute error of even 25 per cent in a substance constituting only 0.1 or 0.2 per cent of a rock is ordinary of small moment compared with the ability to certify to its presence with approximate correctness. Mar's method (6) for the separation of barium from calcium and magnesium by the solvent action of concentrated HCl mixed with 10% of ether could be used, but it is doubtful if it would give satisfactory results because of the small Ba content in feldspars.

Sodium and potassium is generally determined by the J. Lawrence Smith method(12). After the Na and K has been extracted by the chlorides or nitrates, they can be determined by several methods. The best method is that of G. Fredrick

Smith and A.C. Shead (11) using perchloric acid. The Na and K are changed to the perchlorates and the K is separated by using chloroplatinic acid, which forms K_2PtCl_6 and is insoluble in 95% alcohol. The sodium salt is soluble and can be separated by filtration. This method gives accurate results according to the authors. It has also the advantages that the Pt can be easily recovered, the perchlorates are stable at $350^{\circ}C$ and can be accurately weighed. The alcoholic solution does not have to be as strong as it did in the older methods. W.F. Hillebrand (1) used HF instead of the J. Lawrence Smith method for decomposition, but the results did not check as well as when the other method was used.

The manganese in feldspars can only be determined successfully by the periodate method. The use of KIO_4 for colorimetric determination of Mn in steel, ores, and minerals was first described by Willard and Greathouse (20). This method, both by virtue of chemical principles and working advantages, stands far ahead of the other existing methods. Where other methods are deficient and erratic the periodate method was successful and precise. Other methods are accepted and tolerated because of their priority and as a result of factors of conservatism not common alone among analytic chemists. The ammonium persulfate method for the colorimetric determination of Mn is older by approximately ten years than the periodate method and has fewer advantages. The periodate method depends upon the oxidation in an acid solution of

manganous salts to permanganate by means of periodate.

Phosphorous is almost always determined on a separate sample. It is usually determined by the molybdate method (1). This method has been used on feldspars and found that it gave very good results.

III PROCEDURE

A. LOSS ON IGNITION

Samples of feldspars, weighing approximately 0.5 gr., were weighed out accurately in platinum crucibles. The crucibles containing the samples were placed in an electric furnace at a temperature of 900°C. The samples were taken out after 8 minutes, cooled in a dessicator, and weighed. They were put back in the furnace and left for another 8 minutes, and again taken out, cooled, and weighed. They were then put in the furnace and left for five hours. At the end of that time they were again weighed. From the loss in weight the loss on ignition was calculated. This loss on ignition included the water, CO₂, and organic matter in the sample.

B. FUSION WITH Na₂CO₃, K₂CO₃, AND A MIXTURE OF Na₂CO₃ AND K₂CO₃.

Samples of feldspar weighing approximately 1 gram, were weighed out accurately, and mixed thoroughly with 3 to 8 grams of Na₂CO₃. In some cases 4 to 8 grams of K₂CO₃ or a mixture of the two salts were used instead of Na₂CO₃. The mixture of feldspar and Na₂CO₃ was placed in a platinum crucible of 20 to 30 ml. capacity. The crucible was placed, covered at first, over a moderately low flame of a blast lamp. The flame was gradually increased to a maximum (approx.) at 1000°C. and maintained there till the mass was quiescent.

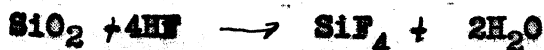
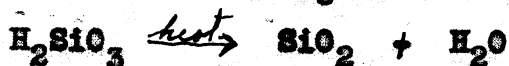
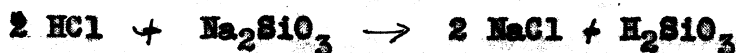
There should be no violent action. The contents of the crucible appeared as a viscous liquid, occasionally clear, but usually more or less turbid. When no further efferecence occurred the crucible was removed from the flame and the melt was gently swirled just as it was cooling and then thoroughly cooled. About 5 ml. of hot water was then added to the crucible and it was gently heated over a burner. The melt dissolved to some extent in the water. The solution in the crucible was poured into a beaker, and more hot water was added to the crucible, this process was continued until all the melt was dissolved out of the crucible. A little dilute HCl was added to the crucible and this poured into the main solution. Concentrated HCl was then added to the solution until it was acid.

C. SEPARATION AND DETERMINATION OF SILICA

The acid solution of the fusion was covered with a watch glass and evaporated to dryness on an electric hot plate. The residue left was taken up in dilute HCl and again evaporated to dryness, this process was continued until the silica had been dehydrated four times. After the last dehydration, 10 ml. of concentrated HCl was cautiously added to the beaker, and after 2 or 3 minutes 50 ml. of hot water was added. The solution was filtered bringing the silica upon the filter paper. The silica was washed with hot water and placed in a weighed Pt crucible, and dried. The filtrate was again evaporated to dryness, the residue taken up with 5 ml. of

HCl and 25 ml. of hot water and heated for about 10 minutes. The solution was filtered while still hot, the silica washed with cool dilute HCl (1:99), and finally with hot water. The filter paper, containing the silica, was placed in the same crucible with the first one. The combined silica was dried, the filter paper burned off without blazing, and ignited at 900°C. in an electric furnace for 3 hours. The crucible was then taken out, cooled in a dessicator, and weighed. The true silica was determined by moistening the ignited silica with a few drops of water, adding 1 or 2 ml. of concentrated H_2SO_4 and 10 ml. of HF. The crucible was placed on an electric hot plate and the silica volatilized off by the HF. Sometimes it was necessary to make several evaporations with HF to completely remove the silica. The H_2SO_4 was then carefully evaporated off and the crucible again ignited and weighed. The loss in weight gave the true silica in the sample. The residue left was dissolved by fusing with a little Na_2CO_3 and added to the main solution.

Reactions

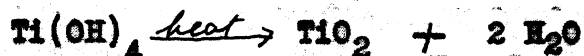
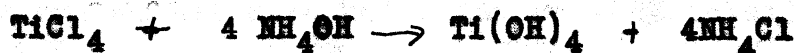
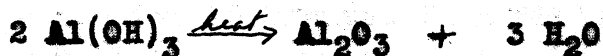
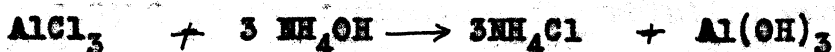
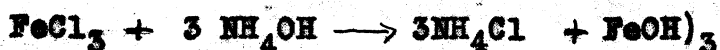


D. THE JOINT PRECIPITATION OF AL, Fe, Ti, AND PHOSPHOROUS

To the HCl filtrate from the silica determination, about 5 ml. of bromine water was added to completely oxidize the

Fe. The solution was boiled to expell the excess bromine, and about 5 grams of NH_4Cl was added to the solution. Then a few drops of methyl red was added and the solution heated just to boiling. Dilute ammonium hydroxide (1:1) was now carefully added until the color of the solution was changed to a distinct yellow. The solution was set on a hot plate for about 15 minutes. If the color of the solution changed to red more ammonium hydroxide was added. The solution was filtered at once and the precipitate thoroughly washed with hot water. The filter paper containing the precipitate was placed in a weighed crucible and ignited wet. When the filter paper had been burned off, the crucible was placed in a furnace at 900°C . for about 2 hours. It was then taken out and weighed as the oxides of the metals.

Reactions



E. DETERMINATION OF AL, FE, TI, AND RESIDUAL SILICA IN THE JOINT PRECIPITATE

The oxides in the platinum crucible were fused with a small amount of Na_2CO_3 and a few crystals of KNO_3 as described before. The melt was dissolved in water in a beaker. The

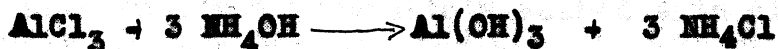
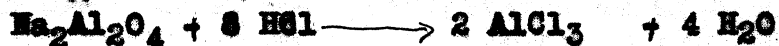
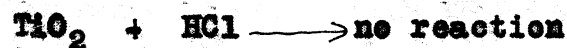
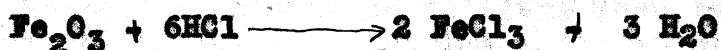
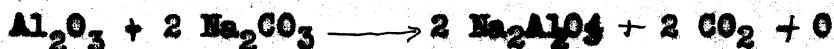
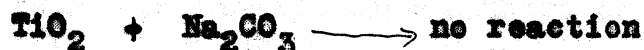
solution was heated to boiling and if any large particles existed they were broken up. The solution was filtered and the Al, which was in the form of sodium aluminate, was soluble and passed into the filtrate. The residue left on the filter paper was washed several times with hot water. The beaker containing the Al was removed and the residue was treated with hot dilute HCl and the filtrate caught in another beaker. After all the red particles of Fe_2O_3 were dissolved, the filter paper was washed with hot water until the last trace of the yellow color was removed. The washings were caught in the same beaker as the acid filtrate. The filter paper was placed in a weighed crucible, ignited, and weighed. The weight of the residue was the TiO_2 and the residual silica. The TiO_2 was determined by another method and subtracted from this weight, giving the residual silica.

The water solution containing the aluminate was made acid with HCl, heated, then alkaline with NH_4OH . The aluminum was precipitated as the hydroxide. The solution was set on the hot plate for 15 minutes then filtered at once. The precipitate was washed with hot water or a 2% solution of NH_4Cl . The filter paper, containing the precipitate, was placed in a weighed crucible, the paper burned off, ignited at 900°C ., and weighed as Al_2O_3 . If the sample contained any phosphoreous it will be precipitated along with the Al. The phosphoreous can best be determined on another sample and subtracted from this precipitate giving the true Al_2O_3 in the sample.

The acid solution, containing the FeCl_3 was treated with a little bromine water and boiled. The solution was then made alkaline with NH_4OH and set on the hot plate for 15 minutes. The solution was filtered hot and the precipitate washed thoroughly with hot water. The filter paper, containing the precipitate, was placed in a weighed crucible, ignited at 900°C , and weighed as Fe_2O_3 .

The Fe in the joint precipitate was also determined colorimetrically by dissolving it in dilute H_2SO_4 , adding NH_4SCN , and comparing with a known standard solution. The Fe and Al was also determined by using Na_2O_2 for the separation.

Reactions

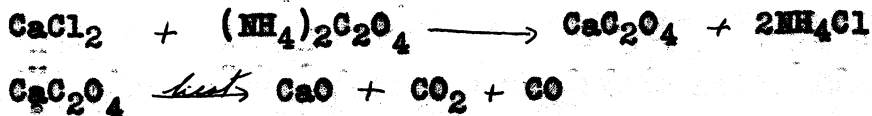


F. DETERMINATION OF CALCIUM

The filtrate from the joint precipitation was made acid with HCl and heated. Then about 15 ml. of a saturated solution of ammonium oxalate was added. The solution was heated to nearly boiling, made barely alkaline with NH_4OH , and allowed to cool. The solution was allowed to stand for 3 hours then

filtered and the precipitate washed cold water. The filter paper, containing the precipitate was placed in a weighed crucible, dried, ignited at 900°C , and weighed. the calcium was weighed as CaO .

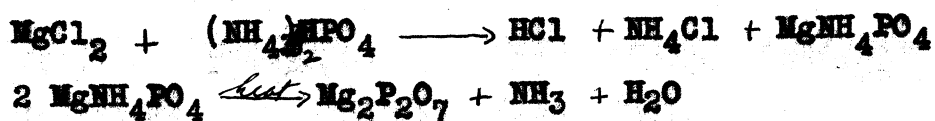
Reactions



G. DETERMINATION OF MAGNESIUM

To the filtrate from the oxalate precipitation, about 30 ml. of concentrated HNO_3 was added to get rid of the excess ammonium salts. The solution was evaporated to dryness, the residue taken up in the smallest amount of dilute HCl possible, and filtered. About 15 ml. of a saturated solution of diammonium phosphate was added to the solution, which was heated to just below boiling. When the solution was cool it was made alkaline with NH_4OH and let stand for about 12 hours. The Mg was precipitated as MgNH_4PO_4 . The solution was filtered, the precipitate washed with diluted NH_4OH (5:95) and finally with a 10% solution of ammonium nitrate, to aid in the ignition of the precipitate. The precipitate was placed in a crucible, dried, the filter paper carefully burned off, and ignited for several hours at 850°C . The crucible was taken out of the furnace cooled, and weighed. The Mg was weighed as the $\text{Mg}_2\text{P}_2\text{O}_7$ from which the MgO was calculated. The heating was repeated until the weight remained constant.

Reactions

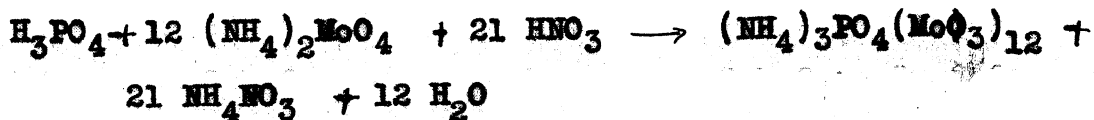


H. DETERMINATION OF PHOSPHOROUS

Phosphorous was determined on a separate sample. A one gram sample was fused with sodium carbonate. The silica separated by a single evaporation with nitric acid. The ignited silica was treated with HF and HNO₃, evaporated to expell the HF. This operation was repeated three times, then the small residue was brought into solution by boiling with HNO₃, and added to the main solution.

5 grams of ammonium nitrate, 1 to 2 grams of boric acid, and molybdate solution was added to the solution obtained above. The solution was allowed to stand at a temperature not over 40°C for 12 hours, then the precipitate was filtered off and washed with water containing 5% NH₄NO₃ and 1% HNO₃; After which it was transferred by a jet of water to a small beaker, which was then placed under the funnel containing the filter paper. The paper was washed with dilute NH₄OH then with water. Sufficient NH₄OH was then added to the beaker to dissolve the yellow precipitate. The insoluble matter was filtered off, the ammoniacal solution treated with magnesia mixture, and proceeded to the weighing of the phosphorous as Mg₂P₂O₇ as described under magnesium. From the weight of Mg₂P₂O₇ the amount of P₂O₅ was calculated.

Reactions



I. DETERMINATION OF BARIUM

A 2 gram sample of feldspar was treated with HF and H_2SO_4 . After several treatments to be sure that all the silica was removed, the excess flourine was expelled and the residue brought into solution as far as possible with warm dilute H_2SO_4 (1:10). The solution was filtered, the residue ignited, fused with Na_2CO_3 , and dissolved in HCl. To this acid solution a little H_2SO_4 was added to precipitate the barium as BaSO_4 . The BaSO_4 was filtered off, washed with water, ignited at 850°C , and weighed.

Barium was also run on other samples by fusing them with Na_2CO_3 , removing the silica by the general method as already described. After the silica had been volatilized with HF, the residue was fused with a little Na_2CO_3 , and added to the main solution. A little H_2SO_4 was added and the solution kept warm for 15 minutes to precipitate the BaSO_4 , which was filtered off and treated as described above.

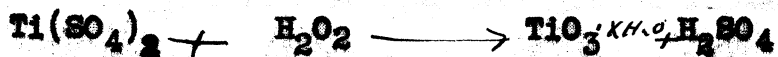
Reactions

K. DETERMINATION OF TiO_2

The filtrate obtained from the Ba determination, in which the sample was treated with HF and H_2SO_4 , was evaporated down to about 10 ml., making sure all the flourine and HCl had been driven off. This solution was diluted up to about

40 ml. A standard TiO_2 solution was made up by fusing 0.5 gram of TiO_2 with twenty times its weight of $KHSO_4$ in a platinum dish, keeping it at the fusion point until the oxide had dissolved. The fusion was dissolved in 5% H_2SO_4 , and made up to a volume of 500 ml. with 5% H_2SO_4 . This solution was standardized by precipitating the Ti from a known volume of the solution with NH_4OH , igniting, it was changed to TiO_2 , and weighed. The sulfuric acid solution of the sample was poured into a 50 ml. Nessler tube, 2 ml. of H_2O_2 (30% sol.) was added and the volume made up to exactly 50 ml. with 5% H_2SO_4 . The standard was prepared by pouring 40 ml. of 5% H_2SO_4 into a second 50 ml. Nessler tube, adding 2 ml. of H_2O_2 , followed by a sufficient amount of the standard titanium solution to exactly match the sample, and the volume made up to exactly 50 ml. with 5% H_2SO_4 . The titanium solution was added from a burette, noting the exact volume required. From the amount of standard titanium solution required, the amount of TiO_2 in the sample was calculated.

Reactions

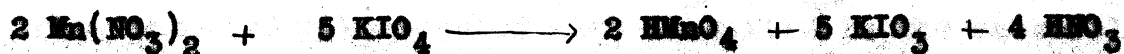


L. DETERMINATION OF MnO

The method used was that of Willard and Greathouse. The solution from the titanium determination was evaporated to about 15 ml., diluted up to about 60 ml., and 20 ml. of HNO_3 , 15 ml. of H_2SO_4 were added. By evaporation of the titanium

solution all the chlorides were gotten rid of. 0.2 to 0.4 gram of KIO_4 was added to the solution, which was boiled for a minute and kept hot for 5 to 10 minutes then cooled. This solution was compared with a standard of known Mn content, similarly prepared. The standard manganese solution was a solution of manganese sulfate, which was standardized by other methods. The two solutions to be compared were poured into two 100 ml. graduated cylinders, and 50 ml. of each solution were poured into two 50 ml. Nessler tubes, respectively. And their colors compared. If one was darker than the other, they were poured back into their respective cylinders, and the darker one was diluted until their colors matched. Then the solutions were poured back into their cylinders and their volumes read. From this the per cent of MnO in the sample was calculated.

Reactions



M. DETERMINATION OF SODIUM AND POTASSIUM

The J. Lawrence Smith method (12) was used for decomposing the feldspar for the determination of Na and K. 0.5 gram of the finely ground feldspar was ground intimately with an equal quantity of pure NH_4Cl in an agate mortar. 3 grams of precipitated $CaCO_3$ was added and mixed thoroughly with the former. The mixture was transferred to a J. Lawrence Smith crucible. The mortar was rinsed with 1 gram of $CaCO_3$, which was added to the contents of the crucible. The covered crucible

was placed in a slightly inclined position with the top protected from the heat of the flame. This was done by placing the crucible in a hole in a large sand crucible, which was inverted. The crucible was gradually heated over a small flame until no more ammonia was evolved, but sufficient heating to cause the evolution of NH_4Cl was avoided. This driving off of the ammonia required about 15 minutes. Then the temperature was raised until finally the lower three-fourths of the crucible was brought to a red heat, which was maintained for 1 hour. At the end of that time the crucible was allowed to cool, and the slintered cake removed by gently tapping the inverted crucible. When it was not possible to remove the cake by this method, the mass was digested a few minutes with water to soften it, then it was washed out into a casserole. The covered casserole was heated with 50 to 75 ml. of water for half an hour. The large particles were reduced to a fine powder by rubbing with a pestle in the casserole. The clear solution was decanted through a filter. The residue was washed eight times by boiling with 25 ml. of water and decanting the solution through the filter, finally the residue was transferred to the filter and washed with hot water until a few cubic centimeters of the washings gave only a slight turbidity with AgNO_3 . The aqueous extract obtained in the above operations contained the chlorides of calcium and the alkalies.

To remove the Ca, the solution was treated with ammonia and ammonium carbonate, heated to boiling, filtered, and the residue washed. As this precipitate invariably retains some of the alkali salts, it was dissolved in HCl and reprecipitated, filtered, and washed, the filtrate being added to the main filtrate. This solution was evaporated down to about 100 cubic centimeters, and a few drops of ammonia and ammonium oxalate were added to remove the last traces of calcium. After standing for several hours the calcium oxalate was filtered off.

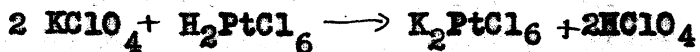
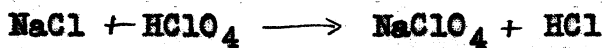
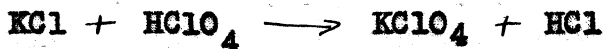
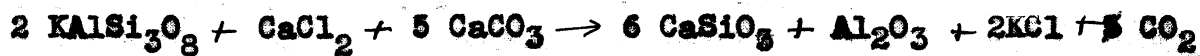
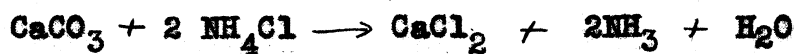
To the filtrate in a small beaker about 30 cubic centimeters of HNO_3 was added to expell the ammonium salts. The solution was evaporated to dryness. This operation was repeated several times. The residue contained the Na and K as the nitrates. The residue was taken up with HCl and evaporated to dryness. This operation was carried out several times in order to convert the nitrates to the chlorides. The combined chlorides were dissolved in water, and if any insoluble residue remained it was filtered off. The solution was poured into a platinum dish and evaporated to dryness, dried at 105°C for 1 hour and weighed as the chlorides.

From this point on there are several methods by which the Na and K may be determined, but the perchlorate-chloroplatinate method by G. Frederick Smith (11) and A.C. Shead is the best. The mixture of potassium and sodium chlorides obtained above were converted to the perchlorates by evap-

orating to dryness in a platinum dish with an excess of 70 to 72% perchloric acid. The mixture of the perchlorates was dissolved by heating with a few cubic centimeters of water. The solution was again evaporated to dryness, and heated for 15 to 30 minutes at 350°C, cooled, and weighed.

From this point the mixture of potassium and sodium perchlorates were again dissolved in 5 cubic centimeters of hot water and 5 cubic centimeters of 95% ethanol was added and the solution was heated to just below the boiling point. Small portions of a 10% solution of chloroplatinic acid dissolved in ethanol were added until potassium chloroplatinate began to precipitate. After digesting for a minute at just below the boiling point, the slow addition of the precipitant was continued until all the potassium present was precipitated, and the supernatant liquid was colored slightly yellow. Enough ethanol was added to make an 80 - 85% concentration of alcohol. The solution was digested for 5 minutes on an electric hot plate with stirring at just below the boiling point. The precipitate and the solution were cooled to room temperature, filtered through a Gouch crucible, washed with 85% or stronger alcohol. The filtering crucible and precipitate were dried for 5 minutes at 100 - 130 °C to remove the alcohol and finally for fifteen minutes at 350°C, cooled, and weighed. The K_2O was calculated from the weight of K_2PtCl_6 . The sodium was run by difference.

Reactions



Sample numbers $\frac{1}{2}$ -	@ 10	@ 11	12	13	14	15	16	17	18	19
Impure silica - - -	87.16%	87.21%	86.37%	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -
Residual silica - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -
Silica by HF - - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -
R ₂ O ₃ - - - - -	8.818%	8.796%	- - - -	- - - -	-v-	- - - -	- - - -	- - - -	- - - -	- - - -
Fe ₂ O ₃ by Na ₂ CO ₃ - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -
Al ₂ O ₃ by Na ₂ CO ₃ - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -
Fe ₂ O ₃ colormetric -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -
Ca O - - - - -	0.350%	0.422%	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -
MgO - - - - -	0.6724%	0.6489%	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -
TiO ₂ colormetric -	- - - -	- - - -	- - - -	0.0307%	0.0306%	0.0307%	0.0306%	0.0307%	- - - -	- - - -
MnO - colormetric - -	- - - -	- - - -	- - - -	0.02086%	0.02085%	0.02085%	0.02089%	0.02085%	- - - -	- - - -
P ₂ O ₅ - - - - -	- - - -	- - - -	0.000%	0.000%	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -
BaO - - - - -	- - - -	0.000%	0.00%	0.00%	0.000%	- - - -	- - - -	- - - -	- - - -	- - - -
Na ₂ O - - - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	3.634%	3.489%
K ₂ O - - - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	0.4539%	0.4352%
Loss on ignition - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -	- - - -

The samples @ were dehydrated five times instead of four times.

Sample number	20	21	22	23	Av.
Impure silica - - -	- - -	- - -	- - -	- - -	86.828
Silica by HF - - -	- - -	- - -	- - -	- - -	85.657
Residue silica - -	- - -	- - -	- - -	- - -	0.206
R ₂ O ₃ - - - - -	- - -	- - -	- - -	- - -	8.7664
Fe ₂ O ₃ by-Na ₂ CO ₃ sep.	- - -	- - -	- - -	- - -	1.49
Al ₂ O ₃ by Na ₂ CO ₃ sep.	- - -	- - -	- - -	- - -	6.499
Fe ₂ O ₃ colormetric -	- - -	- - -	- - -	- - -	- - -
CaO - - - - -	- - -	- - -	- - -	- - -	0.3665
MgO - - - - -	- - -	- - -	- - -	- - -	0.6910
TiO ₂ - - - - -	- - -	- - -	- - -	- - -	0.0307
MnO colormetric - -	- - -	- - -	- - -	- - -	0.0208
P ₂ O ₅ - - - - -	- - -	- - -	- - -	- - -	0.00
BaO - - - - -	- - -	- - -	- - -	- - -	0.00
Na ₂ O - - - - -	3.572%	3.591%	3.527%	- - -	3.563
K ₂ O - - - - -	0.4539%	0.4350%	0.4424%	- - -	0.44409
Loss on ignition	- - -	- - -	- - -	1.0979%	1.0979

Total. 100.065347

LOSS ON IGNITION

Sample	8 min. at 900°C	16 min. at 900°C	5 hours at 900°C
1	1.1445%	1.1445%	1.1051%
2	1.1334%	1.1334%	1.1135%
3	1.0751%	1.0751%	1.0751%

V. DISCUSSION OF RESULTS

The feldspar analyzed was not an ordinary one, as is shown by the results. It was too high in silica. The ordinary feldspars usually run around 66% silica, while this one ran 86%.

The loss on ignition showed some variations when heated for a short time. When they were heated for several hours they checked fairly well. This variation may be explained by the fact that some of the ferrous iron in the sample may not have been oxidized to the ferric state. Some of the samples actually gained weight when they were put in the furnace, after they had been burned for a short time, and left for several hours.

The variation of the amount of Na_2CO_3 had no effect on the results, except when less than 4 grams were used the feldspar would not go completely into solution. If more than 7 grams were used the excess salts made the determinations hard to run, especially, when the solution was evaporated to dryness. When K_2CO_3 was used the reaction was too volatile and could not be fused without loss by spattering or boiling over. The same thing occurred when a mixture of Na_2CO_3 and K_2CO_3 (1:1) was used.

The silica checked fairly well considering the percentages. There was some difference in the silica, depending on the number of times it was dehydrated. The residual silica vari-

ed considerable and a considerable error could be caused by not running the residual silica and adding it in with the main silica. One of the drawbacks to the volatilizing the silica with HF and H₂SO₄ is that the impurities are converted to the sulfates which cannot all be ignited to the oxides, causing the silica to be too small.

The R₂O₃ or joint precipitate of Al, Fe, Ti, showed fairly good checks, most of them were within the experimental error. It is in the separation of this precipitate that the greatest variations come in, depending on the method used.

In the separation of the R₂O₃ precipitate by fusion with Na₂CO₃ and a few crystals of KNO₃ was very complete. Tests were made on the separations and they showed that the Fe and Al were completely separated. Tests were also run for Mn and they showed that the Mn was not precipitated with either metal, because the concentration of the Mn in the solution was below that required to reach the solubility product for MnO(OH)₂.

In the colorimetric determination of Mn all the Cl must be expelled or it will break down the KIO₄ as shown by the equation.



When this determination is carefully followed it gives very good results. Colorimetric Fe can not be determined on the same sample as the Mn because the excess KIO₄ breaks down the NH₄SCN and gives a yellow color instead of a reddish

brown. Also CaC_2O_4 cannot be precipitated from the same sample, therefore they must be determined on a different sample.

The results showed that the CaO and the MgO checked fairly well. It was shown from the results that when the CaO was low the MgO was high and vice versa. It would be reasonable to expect when the CaO was high that some of the Mg had been precipitated along with the Ca . If an insufficient amount of ammonium salts are present some of the Mg will be precipitated with the Ca . The results showed that in some cases that there was incomplete separation of the two metals.

Colorimetric iron was run on several samples but the results did not check within a reasonable error. This method was discarded because it was impossible to be absolute sure that all the iron was in the ferric state.

The colorimetric TiO_2 checked very well and this is about the only method ^{for TiO_2} that can be successfully used. The other metals present in the feldspar would interfere with the other methods for determining TiO_2 .

The Na_2O and K_2O showed very good checks for the small amounts of them present. This is the best method for determining the sodium and potassium in feldspars.

Several tests were run for Ba and P_2O_5 , but in each case the test failed to show any trace of either of the elements.

VI. CONCLUSIONS

It was found that the variation in the amount of Na_2CO_3 used in the fusions had no effect on the results, except when an insufficient amount was used. A large excess is to be avoided, because it makes some of the determinations hard to run due to the large amount of salts present. The best amount of Na_2CO_3 to use for the particular feldspar was found to be 5 grams.

The procedure given will give the best results for feldspars, if followed carefully. It will take a person from three to five days to run a complete analysis by this procedure, depending on the experience he has had in this kind of work.

The variations of the various analysts seem to lie in the fact that they used different methods for determining the various elements in feldspars. Also it is almost impossible to secure absolutely pure chemicals. These impurities will sometimes cause considerable errors in the results when the elements are present in very minute quantities.

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