ON THE DETERMINATION OF ALKALIES IN ROCKS AND MINERALS

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In mineralogical analysis, and to a lesser extent, in rock analysis, the average laboratory worker is seldom in a position to undertake extensive researches into the field of devising new or unique methods for the determination of any particular constituent. He does, however, owing to paucity of available sample, have to display in many cases, considerable ingenuity in combining standard methods in such a way as to determine a large number of constituents on the same very small portion of material. The care with which these involved combinations must be used is emphasized by the fact that, in many instances, no second portion of the sample can be obtained in case of accident or error.

Whatever method is used in the determination of alkalies: whether by the usual J. Lawrence Smith method, by direct decomposition with acids, or determined after every thing else is removed from solution by volatile reagents, the final process usually consists in weighing them as the mixed chlorides of sodium and potassium with subsequent separation of the chloroplatinates by solution in alcohol. By this method the potassium is obtained in the form of chloroplatinate, insoluble in alcohol, whereas the sodium salt of the same acid is soluble. By weighing the mixed chlorides and calculating the potassium chloroplatinate back to potassium chloride the sodium is arrived at by difference. Any error in the determination of potassium results in a corresponding error in the results for sodium.

The simplest method, after obtaining a clear solution of the mixed chlorides, is to add a considerable excess of platinic chloride and evaporate to approximate dryness on the water bath. The residue is then covered with a large excess of alcohol. At present it is difficult to procure ethyl alcohol of satisfactory purity or freedom from denaturants. Alcohol of unknown quality is unsatisfactory as it tends to reduce the excess platinic chloride to platinum or to some insoluble compound or to deposit some gummy substance. Methyl alcohol, on the other hand, is just as satisfactory if not better than ethyl alcohol and can be purchased anywhere in relatively pure form without question and at a fairly low price.

For some years it has been the practice of the writer to filter the platinic potassium chloride on a small tared gooch crucible and to weigh it after drying at 120°C. This method gives excellent results provided that certain precautions are observed. The ordinary potassium salt is anhydrous, relatively stable, and represented by the formula K_2PtCl_6 or $2KCl \cdot PtCl_4$. This crystallizes in the isometric system, is yellow in color and practically insoluble in alcohol although easily soluble in hot water. Sodium forms no analogous salt and under the same treatment enters into a hydrated salt, represented by the formula $Na_2PtCl_6 \cdot 6H_2O$. This crystallizes in the triclinic system and is easily soluble in alcohol of almost any type or strength. The difference in behaviour of these alkalies provides the accepted easy method for their separation.

Despite all the precautions suggested by the foregoing it has been found recently that errors could and did enter into ordinary alkali determinations, particularly those which had been required to stand for some time in the laboratory atmosphere at that stage following the addition of the platinic chloride reagent. Although potassium and sodium are not isomorphous in the formation of the chloroplatinates, ammonium and potassium both form anhydrous chloroplatinates crystallizing in the isometric system. The ammonium salt is less soluble, both in hot water and in alcohol than the corresponding potassium salt. Ammonium chloride or other ammonium vapors are generally present in the laboratory atmosphere. This is easily demonstrated by the coating which forms on well washed glassware in a few days. In the laboratory of the writer, which is large, well ventilated, and accomodates only two workers, the glassware fogs promptly and the distilled water, dripping through several inches of air space, gives a distinct reaction for chlorine. Where the workers are busy and crowded the fumes are much more concentrated. It would appear that the ammonia vapors are quickly absorbed by the neutral chloroplatinate solution with the formation of ammonium chloroplatinate. With this factor left out of consideration the ammonium salt would be disregarded and weighed as potassium yielding an abnormally high result for this constituent with a correspondingly low result for sodium. This error is naturally magnified if, for any reason, the determination is delayed at this stage.

In consideration of the foregoing it is obvious that, unless a determination is carried to completion without the slightest delay

the results will be more or less in error if the weight of the potassium chloroplatinate is taken as final. Fortunately it is easy to overcome this handicap. Where it has been necessary to allow a determination to stand the weight of the potassium chloroplatinate should not be relied upon. This salt should be dissolved in hot water, the solution passing into a porcelain crucible. It is then slightly acidified with hydrochloric acid, a few drops of pure mercury are added and the whole evaporated to dryness on the steam bath and gently ignited. The residue in the crucible is the platinum from both potassium and ammonium chloroplatinates and potassium chloride, the ammonium salt having been volatilized. Simple leaching with hot water will remove the potassium chloride which can either be weighed directly after evaporation in a platinum dish or determined by difference after weighing the ignited filter and separated platinum in the original crucible.

It seems best to have the original platinic chloride reagent in solution in alcohol rather than in water and to filter it before use to avoid adding ammonium salts with the reagent.

The prejudice of many chemists against the use of platinum chloride prepared from laboratory scrap platinum appears to have no reasonable basis. The iridium content of ware made in recent years is very small since the price of iridium has been higher than that of platinum. Even where the iridium content of the solution is considerable it would appear to have little effect. The atomic weight of platinum (195.23) and iridium (193.10) are very similar. The two form analogous compounds with the alkalies which do not differ appreciably in solubilities in alcohols and water. Potassium chloriridate forms black octahedral crystals which serve to indicate the presence of iridium in the solution.

NOTES AND NEWS

STUDIES IN THE MICA GROUP (A DISCUSSION). A. F. HALLIMOND.

In a recent contribution to the *American Mineralogist* Dr. A. N.Winchell has included a very interesting comparison between a revision of his theory of the micas and the theory I ventured to suggest some time ago in the *Mineralogical Magazine.* The two theories yield in general very similar values for the composition of the principal minerals concerned, but Winchell's present assumption that Al_2O_3 is replaced by $MgO \cdot SiO_2$ necessitates a steady diminution in the ratio $K_2O:SiO_2$ as the MgO increases, while my own suggestion that Al_2O_3 is replaced by MgO leaves this ratio unaltered. Dealing with the composition of muscovite, he remarks that a