DETERMINATION OF ALKALI METALS IN INSOLUBLE COMPOUNDS BY REDUCTION WITH CALCIUM HYDRIDE

by

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Typed by Sue Bingham
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<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td></td>
</tr>
<tr>
<td>Methods of Analyzing for Alkali Metals</td>
<td>1</td>
</tr>
<tr>
<td>Methods of Solublizing Samples</td>
<td>6</td>
</tr>
<tr>
<td>HISTORICAL</td>
<td></td>
</tr>
<tr>
<td>Concept of Idea</td>
<td>9</td>
</tr>
<tr>
<td>Previous Methods and Apparatus</td>
<td>10</td>
</tr>
<tr>
<td>DISCUSSION OF RESULTS</td>
<td></td>
</tr>
<tr>
<td>Types of Compounds Analyzed</td>
<td>17</td>
</tr>
<tr>
<td>Various Apparatus Tried</td>
<td>19</td>
</tr>
<tr>
<td>EXPERIMENTAL RESULTS AND PROCEDURE</td>
<td></td>
</tr>
<tr>
<td>General Equipment and Chemicals</td>
<td>27</td>
</tr>
<tr>
<td>Special Apparatus</td>
<td>34</td>
</tr>
<tr>
<td>Experimental Procedure</td>
<td>36</td>
</tr>
<tr>
<td>Results</td>
<td>37</td>
</tr>
<tr>
<td>SUMMARY AND CONCLUSIONS</td>
<td>39</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>43</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>FIGURE</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Detail of Water Cooled Steel Crucible</td>
<td>12</td>
</tr>
<tr>
<td>2.</td>
<td>Sectional Drawing of Water Cooled Steel Crucible</td>
<td>13</td>
</tr>
<tr>
<td>3.</td>
<td>Schematic Diagram of Model 52-C Flame Photometer</td>
<td>23</td>
</tr>
<tr>
<td>4.</td>
<td>Calibration Curve for Direct Na⁺ and K⁺ analysis</td>
<td>30</td>
</tr>
<tr>
<td>5.</td>
<td>Calibration Curve for Na⁺ and K⁺ using 800 ppm Lithium as an Internal Standard</td>
<td>31</td>
</tr>
<tr>
<td>6.</td>
<td>Sectional Diagram of Nitrogen Swept apparatus</td>
<td>35</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>RESULTS OF ORTHOCLASITE AND FELDSPAR DETERMINATIONS USING WATER COOLED STEEL CRUCIBLE AND TITRATION WITH STANDARD ACID</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Results of Orthoclase and Feldspar Determinations using Water Cooled Steel Crucible and Titration with Standard Acid</td>
<td>21</td>
</tr>
<tr>
<td>II</td>
<td>Results of Lead Barium Glass and Opal Glass Determinations using Closed End Ignition Tube and the Perkin-Elmer Model 52-C Flame Photometer</td>
<td>23</td>
</tr>
<tr>
<td>III</td>
<td>Results of Lead Barium Glass Determinations using Gas Sweep Apparatus, Helium Gas and the Perkin-Elmer Model 52-C Flame Photometer</td>
<td>25</td>
</tr>
<tr>
<td>IV</td>
<td>Results of National Bureau of Standards Sample Determinations using Nitrogen Swept Apparatus and the Perkin-Elmer Flame Photometer</td>
<td>38</td>
</tr>
</tbody>
</table>
DETERMINATION OF ALKALI METAL IN INSOLUBLE COMPOUNDS BY REDUCTION WITH CALCIUM HYDRIDE

INTRODUCTION

Methods of Analyzing for Alkali Metals

The quantitative determination of the alkali metals which occur in insoluble materials can be resolved into two phases. The first of these is the solubilization phase, with which this thesis is primarily concerned. The second step is that of actually determining the amount of alkali metal in the sample by weighing some insoluble salt of the alkali metal, or comparing the sample with standards as in the flame photometric method, or some other convenient method.

Gravimetric Methods

a) Sodium: Sodium is often weighed as NaCl when it is already present as such or after conversion of other forms into the chloride. The conversion is usually effected by repeated evaporation of hydrochloric acid solutions to dryness until only the chloride remains. The procedure is similar when sodium is to be weighed as the sulfate, the only difference being the use of sulfuric acid in the latter case. (20, p. 878)

Small amounts of sodium in the presence of moderate amounts of potassium, ammonium, magnesium, calcium and
barium and in the absence of phosphates, silicates, oxalates and tartrates can be determined as sodium zinc uranyl acetate, $(\text{NaZn(UO}_2\text{)}_3(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6\text{H}_2\text{O})$. The method is complicated by the necessity of using a constant temperature bath of 20°C. $(\pm.0^\circ)$ during precipitation, and by the fact that the precipitate must be washed 5 to 10 times with 2 ml. portions of the zinc uranyl acetate reagent and about 5 times with 2 ml. portions of 95% ethyl alcohol saturated with sodium zinc uranyl acetate at 20°C. At best the method requires several hours to complete an analysis. (1, p. 1625)

Sodium in the presence of the chlorides of potassium, ammonium, calcium, magnesium, barium, strontium, iron, aluminum and chromium, can be precipitated as sodium magnesium uranyl acetate $(\text{NaC}_2\text{H}_3\text{O}_2 \cdot \text{Mg(C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 6\text{H}_2\text{O})$, dried and weighed. The procedure is much the same as that for the zinc uranyl acetate method and requires several hours for completion. (2, p. 3233)

b) Potassium: Potassium may be weighed as the chloride or sulfate after separating all other constituents. The procedure is the same as that for sodium. The principle disadvantage in both cases being the very complicated and time consuming process of separating the two metals from all others which tend to interfere.

The chloroplatinate method is applicable in the presence of chlorides of sodium, lithium, magnesium, calcium,
and strontium. The method is based on the fact that potassium chloroplatinate is practically insoluble in strong alcohol while the other chloroplatinates are readily soluble. The final precipitate is dried in an oven at 110°C, and weighed as K₂PtCl₆. Several modifications of this method are known and used.

In the presence of chlorides, phosphates and nitrates of barium, calcium, magnesium and the alkali metals, potassium may be determined by the perchlorate method. The separation depends on the insolubility of potassium perchlorate and the solubility of sodium and other perchlorates in 97% alcohol. (20, p. 871-872)

Two less common methods are the chloronitroololune-sulfonate method, (11, p. 2976) and the naphthol yellow-S method. (9, p. 209)

c) Lithium, Rubidium, Cesium: These metals are comparatively rare, but, methods for their determination are known. All of them can be separated as the chlorides or sulfates, dried and weighed. Lithium chloride differs from the other alkali metal chlorides by being soluble in amyl alcohol. Advantage is taken of this fact to effect separation. Rubidium and cesium can be determined by first precipitating them as the phosphomolybdates (or as sodium bismuth nitrites) and then converting them to the chloroplatinates. This procedure is used in the presence of
sodium and potassium and effectively separates rubidium and cesium from them. The procedure is to add special 9-phosphomolybdic acid reagent to a hot, acidic solution of the alkali metals. The molybdenum is removed from the precipitate by dissolving the latter in a 5% sodium hydroxide solution and saturating this with hydrogen sulfide. After removal of the molybdenum, the alkalis are converted to the chloroplatinate by addition of chloroplatinic acid. (13, p. 107-111)

After separating rubidium and cesium from the other alkali metals, they can be separated from each other, if they happen to occur together, by the silico tungstic acid method (15, p. 109), or the antimony trichloride-ferric chloride method. (17, p. 185) In both cases cesium is precipitated and rubidium is obtained by difference.

Flame Photometric Method

All gravimetric methods discussed so far suffer from being very time consuming. It is of definite advantage then, when a method is developed which greatly shortens the time and work involved in a given determination. Thus can the recent developments in flame spectrophotometry be termed definite advantages in the realm of alkali metal determinations.

The flame Photometer is an instrument for the rapid
determination of sodium, potassium and other metals in solution. It is designed to measure quantitatively the light emitted by various metal ions when they are atomized from solution, led to a burner and excited to spectral emission in a flame. Since the intensity of the light emitted by each element depends primarily on the concentration of its ions in the flame at any given instant, a measurement of the light intensity produced by a given element makes possible the quantitative determination of that element.

The flame photometric method does have some disadvantages. The cost of the instrument is often prohibitive in some laboratories; furthermore, the instrument must be calibrated each time it is used, and as with all the methods for the determination of alkali metals thus far mentioned, the sample must be in solution before a determination can be made.

Other Methods

Gravimetric and flame photometric methods are by no means the only ways of quantitatively detecting alkali metals. Others include a colorimetric method for potassium, (8, p. 1063) and a polarographic (using sodium tetraphenyl boron) (15, p. 635-641) method also for potassium. Spectroscopic and spectrographic determinations for
both sodium and potassium in rocks and minerals are also known and sometimes used. (13, p. 443), 4, p. 333-334, 10, p. 3) and 22, p. 627-633) An attempt at determining potassium and sodium in feldspars by activation analysis has recently been made. (5, p. 165-172) Objections to the above methods are lack of simplicity, expensive instrumentation in some cases and limited applicability in some cases.

**Methods of Solublizing Samples**

There are two methods commonly accepted by which alkali metal containing insoluble compounds are solublized. They are the Berzelius method (3, p. 169) and the J. Lawrence Smith method. (21, p. 269) The Berzelius method is much the older and has several disadvantages not encountered in the Smith method, however, it is very commonly used. The method begins by attacking the silicate with hydrofluoric and sulfuric acids. The sample is usually digested an hour or so on a steam bath in the presence of both acids, then heated strongly to sulfuric acid fumes several times to expel the excess HF and to convert the fluorides to sulfates. It is often necessary to repeat the hydrofluoric digestion several times to thoroughly decompose a sample, and some minerals such as andalusite, topaz and some varieties of tourmaline cannot be completely
decomposed by HF. The disadvantages of this method are obvious. First, since HF attacks glass it must be contained in platinum ware, which is both expensive and not always available. Secondly, the method is very time consuming, often requiring several hours for just the solubilizing step. Finally, as was mentioned, there are minerals which are not affected by hydrofluoric acid. (14, p. 930-932)

Some modifications of the Berzelius method are known. They include the use of perchloric acid instead of sulfuric in the initial digestion mixture, (24, p. 234) the use of hydrofluoric acid only, and various methods of digesting and fuming.

The J. Lawrence Smith method requires the grinding of 0.5 g. of sample with an equal weight of ammonium chloride in an agate mortar, and the intimate mixing of this mass with 4 g. of calcium carbonate. The mixture thus obtained is placed in a special platinum crucible and heated. The heating is slow at first, but is gradually raised to 1100°C. in the course of 20 to 30 minutes and there maintained for another 90 minutes. The fusion mixture is then leached and digested until thoroughly disintegrated. It is then filtered and any insoluble portions dissolved in hydrochloric acid.

The method suffers from several disadvantages. It is less time consuming than the Berzelius method, but
still requires about 2\frac{1}{2} to 3 hours to complete the solubilization step. It further requires the use of platinum crucibles, and if properly done, the use of a special J. Lawrence Smith platinum crucible, which is both costly, and of little use in any other ordinary laboratory work. However, despite these few disadvantages the method is reasonably satisfactory and is superior in most cases to the Berzelius method.

The above discussion of methods of solubilizing and determining alkali metals in insoluble compounds tends to point out the need for a simple, fast method for such analysis. It is well known that the above methods are very precise and capable of great accuracy, depending on the care taken during the course of a determination. Therefore no attempt is made in this work to improve on the accuracy obtainable by the older methods. The work of this thesis, as well as a great deal of work previous to it, was done in view of the need for an improved solubilization technique, one which would be fast, simple, and capable of being carried out in most laboratories.
Concept of Idea

Ebler and Herrdegen, (12, p. 2264-2267) in 1913, showed that sulfates could be completely reduced to sulfides with calcium hydride according to the equation

\[ \text{MSO}_4 + 4\text{CaH}_2 \rightarrow \text{MS} + 4\text{CaO} + 4\text{H}_2 \]

Caldwell and Krauskopf, (6, p. 2936-2942) and 7, p. 3655-3659) in 1929, enlarging on Ebler's work, developed a method for the quantitative determination of sulfur in insoluble sulfates and other sulfur compounds. It was during the course of this work that the investigators observed alkali metal being liberated and deposited on the crucible lid when the charge mixture containing alkali metal sulfates and calcium hydride was heated. This observation led to the proposal that an analytical method might be developed that would take advantage of the fact that alkali metals occurring in compounds can be replaced with calcium from calcium hydride at high temperatures, according to the reaction

\[ \text{M}_2\text{SiO}_3 + \text{CaH}_2 \rightarrow \text{CaSiO}_3 + 2\text{M} + \text{H}_2 \]

Calcium hydride is a grey solid which is stable at room temperature in the absence of moisture and air, but decomposes to the elements at 675°C. It is above this temperature that any replacement of alkali metals from
their compounds must take place.

Because of the results obtained by Ebler and by Caldwell and Krauskopf, it was strongly believed from the outset of this present phase of the work that a calcium hydride-alkali metal compound reaction at high temperature would be quantitative. The problem then, was resolved to determining if the reaction is quantitative, and if so, is quantitative in every case including such compounds as feldspars, silicates, glasses, ceramics and other similar, highly insoluble alkali metal containing compounds, and to devise a suitable apparatus and procedure where-by the liberated alkali metal could effectively be collected and analyzed, and consistent results be obtained.

**Previous Methods and Apparatus**

Several apparatus had been tried with varying degrees of success by Leonard et al. (16, p. 9-13) prior to the beginning of the work of this thesis.

Test tube: Probably the simplest of the types tried was the test tube apparatus. It consisted of a test tube into which was placed the charge. The end was then constricted to nearly capillary size at a point just above the charge. The charge was then heated with a Fisher burner and the liberated alkali metal was to pass through the constriction and condense on the upper portion of the tube. The alkali metal then could be dissolved in water.
and titrated with standard acid. This apparatus proved to be unsatisfactory since it was impossible to get all of the alkali metal into the upper portion of the tube, and also the calcium hydride had a marked tendency to replace the alkali metals from the pyrex test tube at high temperatures.

Whitton apparatus: The Whitton (23, p. 35-39) mercury apparatus was used for several runs. It consists of a steel crucible in which the charge mixture was placed, and a silver plate held over the crucible mouth by means of a clamp fastening onto a cup used for water cooling. It was found that not all of the liberated alkali metal deposited on the cooled silver plate, but that some of it also deposited on the walls of the crucible. This was unsatisfactory.

Quartz combustion tube: This apparatus was composed of a quartz tube fitted with a nitrogen source at one end and a water filled receiver flask at the other. The charge was contained in an alundum boat which was placed in the tube and heated strongly. Nitrogen gas was introduced at slight pressure at one end of the tube in order to sweep the alkali metal vapor away from the charge and into the water filled container. A Fisher burner was used as a heat source. The method was never successful, probably because the excess calcium forms calcium nitride which decomposes at a temperature well above the boiling
point of sodium and potassium and thus would tend to
blanket or occlude the metals and prevent them from being
swept into the receiver.

Iron crucible: An apparatus designed by Robert S.
Shoemaker¹ and capable of recovering 93 to 96 percent of
the theoretical sodium from sodium carbonate, consisted of
an iron crucible with a steel plate used as a cover. The
plate had a circular groove cut into it and was seated on
the crucible by being ground with valve grinding compound.

Water cooled crucible: The fifth apparatus is illus-
trated in figures 1 and 2. It consists of a stainless
steel crucible and collector sleeve and a copper cooling
wafer held onto the sleeve and crucible by means of a
threaded steel cap. The charge is placed in the crucible,
the sleeve inserted and the apparatus assembled. Cooling
water is passed through the copper wafer at a rate of one
liter per minute while the crucible is heated, first 15
minutes with two Fisher burners, then 5 more minutes with
a compressed air blast lamp. Alkali metal which has
collected on the cooled sleeve is dissolved and titrated
with standard acid.

It was with this apparatus that Leonard, (16, p. 17-19)
in 1955, showed that the calcium hydride-alkali metal

¹ Shoemaker, Robert S. Personal letter to Dr. William E.
Figure 1. Detail of apparatus (actual size)
Figure 2. Sectional drawing of assembled apparatus (twice actual size)
compound reaction is quantitative with materials such as NaCl, KCl, K₂CO₃ etc. Results obtained by Leonard and duplicated by this author show a percent deviation of from ±0.1 to ±2.8 in the materials mentioned above. Leonard further reported good agreement on samples of Orthoclase and Albite. This author was unable to duplicate those results with this particular apparatus and procedure. It was because of this failure, and the failure of others, also, to obtain good results on highly insoluble compounds that the present work was instigated.

A method which provides for the analysis of already soluble compounds by decomposing them and then titrating the liberated metal does not seem to have the merits or the demand that would warrant a specially constructed, expensive apparatus. If the compound is soluble, then it can be analyzed on the flame photometer or by one of the volumetric or gravimetric methods discussed above. However, in the case of highly insoluble compounds, where more than half of the total analyzing time could, and often is, taken up in the solubilizing step, an apparatus of special construction and a specific method is no doubt warranted and of great practical value to those involved in work of this nature.

To design a special apparatus, to devise a specific method, and to markedly reduce the total time involved in analyses of highly insoluble compounds was the basis and
the objective of the work of this thesis.
DISCUSSION OF RESULTS

Types of Compounds Analyzed

The decomposition temperature of calcium hydride is 875°C. It was necessary to attain temperatures above 675°C. to decompose alkali metal compounds and replace the metal with calcium. It was found that in the case of the alkali halides, where the lattice structure is such as to make the metal ions readily available for replacement, temperatures only slightly above the decomposition of CaH2 were required. With NaCl about 800°C. was sufficient to decompose the salt and 950°C. would distill the metal (boiling point 880°C.) onto a cooled surface. KCl was comparable to NaCl with slightly lower temperatures being sufficient for both decomposition and distillation. K2CO3 was slightly more difficult to decompose than the halide.

On the other hand, compounds such as silicates in the form of feldspars, which have definite crystalline configurations, and glasses, which are fused non-crystalline mixtures of basic oxides and silicon dioxide, were very difficult to decompose. The explanation lies in the structure of these glasses and silicate minerals. In the case of the glass the structure is not definite, but is in general similar to that of silicate minerals.

The tetrahedron of oxygen atoms with a silicon at the
center, which occurs in silica, is a general characteristic of all silicate minerals. In the orthosilicates such as zircon, \( \text{ZrSiO}_4 \), and olivine, \((\text{Mg,Fe})_2\text{SiO}_4\), the crystal is a lattice of \( \text{SiO}_4 \) tetrahedra and the positive ions; and the same is true of the orthodisilicates, the negative ion, \( \text{Si}_2\text{O}_7^{-6} \), consisting of two tetrahedra linked by a corner. The metasilicates (\( \text{SiO}_3 \) radical) may complete the tetrahedron of oxygen atoms by forming rings in which two corners of each tetrahedron are shared. In the pyroxenes, e.g., jadeite, \( \text{NaAl(3SiO}_3)_2 \) which are also meta silicates, the \( \text{SiO}_3 \) groups form infinite chains instead of rings, and the positive ions, that is \( \text{Na} \) and \( \text{Al} \), serve to bind the chains together.

Silicates containing the \( \text{Si}_4\text{O}_10^{-4} \) group (or \( \text{AlSi}_3\text{O}_10^{-5} \) if one \( \text{Si} \) is replaced by \( \text{Al} \)) form infinite sheets of silicon oxygen tetrahedra. Such sheets held together by positive ions are found in the clay minerals. Double sheets with the vertices of the tetrahedra pointing toward each other occur in the mica minerals such as muscovite, \((\text{OH})_2\text{KAl}_2\text{Si}_3\text{AlO}_10\). In the clay minerals the sheets are held together by alkali or alkaline earth ions, but the latter contain no intermediate atoms. This would seem to indicate that clays would be more easily decomposed by the calcium hydride technique, than would the mica minerals, and this was found to be the case.
It would seem that there are several positions occupied by the alkali metal ions in the various minerals, and that in these positions they would vary as to the difficulty or ease with which they are replaced by calcium. Steric factors then, would seem to be responsible for the difficulty with which the metals are released, and would serve as an explanation for the fact that in order to decompose plastic clay a rather low temperature of about 1000° to 1100°C. was required whereas for opal glass a temperature of at least 1300°C. was required. The feldspars and the soda-lime glasses which were solublized, were intermediate in ease of decomposition between clay and the opal glass. They required a temperature of something around 1250°C.

**Various Apparatus Tried**

The principle disadvantages of the water cooled, steel crucible used by Leonard was that it failed to selectively collect the alkali metals on the water cooled surface when extremely insoluble materials such as glasses and minerals were being determined. It was found that because these materials required such high temperatures for quantitative reduction, calcium from the calcium hydride was volatilized and deposited along with the alkali metals. Further, it was noted that the inner steel shell-crucible seal was
not entirely gas tight at those elevated temperatures, where the CaH₂ is completely decomposed and large volumes of H₂ are evolved, and that often considerable quantities of potassium and sodium would be lost. Table I illustrates the results of these two conditions; high results due to calcium being volatilized and ultimately titrated with standard acid, and low results due to either insufficient heat or loss of alkali metal through leakage. A combination of these factors, that is if alkali metal leaked from the apparatus at high temperatures and at the same time calcium was vaporized and deposited along with the alkali metal, would tend to nullify these errors and results would not indicate the true situation as regards the accuracy or dependability of the method.

Because of these disadvantages an apparatus was designed and constructed to eliminate any pressures developed in the charge area and to thus prevent pressure leaks. This apparatus consisted of a five inch length of one-half inch stainless steel pipe with a machined cap pressed onto one end and a water-cooled stainless steel one-quarter inch tube threaded onto the other by means of an adapter. The procedure was to place the charge in the tube and tap it down to the closed end, screw on the water cooled tube and heat. The alkali metal was to then be collected in the water cooled tube. This was found to work unsatisfactorily
TABLE I

Results of Orthoclase and Feldspar Determinations Using Water Cooled Steel Crucible and Titration with Standard Acid

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Metal Theoretical</th>
<th>% Metal Calculated</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaAlSi₃O₈</td>
<td>8.78</td>
<td>8.05</td>
<td>- 8.35</td>
</tr>
<tr>
<td>NaAlSi₃O₈</td>
<td>8.78</td>
<td>9.43</td>
<td>+ 7.4</td>
</tr>
<tr>
<td>KAlSi₃O₈</td>
<td>14.04</td>
<td>12.04</td>
<td>- 14.02</td>
</tr>
<tr>
<td>KAlSi₃O₈</td>
<td>14.04</td>
<td>22.03</td>
<td>+ 57.0</td>
</tr>
</tbody>
</table>
since the alkali metal would not condense entirely within the tube, but would pass on through and ignite at the end. To overcome this difficulty an extension of pyrex tubing was placed on the steel tube and this was plugged with pyrex wool. The alkali metals collected on the pyrex wool and on the condenser walls could then be dissolved and an analysis conducted. The results obtained from this apparatus (Table II) were more consistent, but were otherwise no better than those obtained with the water-cooled steel crucible. It was found that all of the alkali metal could not be driven out of the charge area with heat alone, and that also the excess calcium hydride, as in the other apparatus, was completely decomposed and the calcium difficult to remove from the walls of the ignition tube. Some calcium was distilled from the ignition tube and deposited in the water cooled condenser, but only alkali metal was apparent on the pyrex wool.

To overcome the fact that heat was not enough to drive the alkali metals from the charge area, the apparatus shown in figure 6 was constructed. It was intended that with this apparatus the metal vapors could be swept from the charge area with inert gas, and collected on the condenser walls and pyrex wool plug.

Nitrogen was the first gas to be tried as a sweep. It was introduced at a slight pressure (less than one pound)
TABLE II

Results of Lead Barium Glass and Opal Glass Determinations Using Closed End Ignition Tube and the Perkin-Elmer Model 52-C Flame Photometer

<table>
<thead>
<tr>
<th>Sample #</th>
<th>% K₂O Theory</th>
<th>% K₂O Found</th>
<th>% Error</th>
<th>% Na₂O Theory</th>
<th>% Na₂O Found</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>89</td>
<td>8.32</td>
<td>2.72</td>
<td>67.3</td>
<td>5.69</td>
<td>2.02</td>
<td>64.5</td>
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<td></td>
<td>3.01</td>
<td>63.8</td>
<td>5.69</td>
<td>2.19</td>
<td>61.6</td>
<td></td>
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<td>91</td>
<td>3.25</td>
<td>1.94</td>
<td>40.3</td>
<td>8.48</td>
<td>3.87</td>
<td>54.3</td>
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<td></td>
<td>2.06</td>
<td>36.6</td>
<td>8.48</td>
<td>4.12</td>
<td>51.4</td>
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and allowed to flow at rates varying from one to two liters per minute. It was found, after several runs, that at the elevated temperatures being used, (1200° to 1300°C.) the calcium was combining with the nitrogen sweep gas to form calcium nitride which in turn seemed to blanket the charge and prevent the alkali metals from being driven off.

Helium gas seemed to be the answer to the problem and was used in the same manner as the nitrogen. The results obtained (table III) indicate that almost the entire alkali metal content of the samples was being collected at the pyrex wool and along the walls of the condenser, but that also a great deal of vapor phase calcium from the decomposed calcium hydride was deposited along with it. This is understandable, since calcium has a boiling point of 1240°C., and at least this temperature is required for solublizing some samples. The vapor phase calcium proved to be pyrophoric and difficult to handle. In order to insure that none of the material was ignited and lost as oxide smoke, it was necessary to slowly oxidize it by allowing an air-nitrogen mixture to flow through the tube for several hours. In view of this length of time required, and also again the difficulty of cleaning the charge tube, the method was abandoned.

From the results obtained with the above apparatus it became apparent that a method using essentially the same
TABLE III

Results of Lead Barium Glass Determinations
Using Gas Sweep Apparatus, Helium Gas and
the Perkin-Elmer Model 52-C Flame Photometer

<table>
<thead>
<tr>
<th>Sample</th>
<th>% K₂O</th>
<th>% K₂O</th>
<th>% K₂O</th>
<th>% Na₂O</th>
<th>% Na₂O</th>
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apparatus, but requiring solublization of distillation products and also extraction of the alkali metals from the charge residue, would be required. The successful method encompassing these features is described under Experimental Results and Procedure.
EXPERIMENTAL RESULTS AND PROCEDURE

General Equipment and Chemicals

The Flame Photometer

Figure 3 shows a cut-away drawing of a model 52-C Perkin-Elmer Flame Photometer. This instrument was used extensively throughout the course of this work, and is considered an invaluable aid in the determination of the alkali metals by the method developed in this thesis, however, it is not indispensible, since the gravimetric methods mentioned at the beginning of the paper can be used after the sample has been solublized.

In using the flame photometer, the sample is poured into the inlet funnel and atomized by compressed air. The fine fog is separated from the spray in the glass atomizer chamber and blown into the base of the burner. When mixed with gas and burned, it colors the flame with characteristic spectra of the salts it contains.

The entrance slit of a two-prism monochromator looks directly at the center of the flame just above the top of the burner. Light from the flame is dispersed into a spectrum and divided by a beam splitting mirror so that part falls on a fixed exit slit and part on a moveable one. Each slit has its own photoelectric cell and amplifier.
Figure 3. Schematic Diagram of Model 52-C Flame Photometer
with independent gain controls for each. As a direct reading photometer, the gain control on the internal standard amplifier is set at zero. For use as a ratio photometer to compare the light falling on the internal standard cell with that falling on the other, the gain control on the internal standard amplifier is adjusted until its signal exactly balances that of the unknown.

In operation the flame photometer must always be calibrated with solutions containing known amounts of the elements to be measured. For more accuracy than is possible with direct intensity readings, lithium is added to the samples and used as an internal standard for the determination of the unknown. The effect of extraneous variables and interfering elements may be still further reduced by using standards with compositions similar to those of the samples to be analyzed.

Typical calibration curves for sodium and potassium are shown in figure 4 for direct intensity readings, and figure 5 illustrates calibration curves for sodium and potassium for readings on samples containing 800 parts per million (ppm) of lithium as added internal standard. (24, p. 1-25)

**Fisher Multiflame Burner**

Several types of burners and heat sources were used
FIGURE 4.

CALIBRATION CURVE FOR DIRECT NA$^+$ AND K$^+$ ANALYSIS
FIGURE 5.
CALIBRATION CURVE FOR $\text{Na}^+$ AND $\text{K}^+$ USING 800 PPM LITHIUM AS AN INTERNAL STANDARD
in the various methods of solublizing that were tried. The one that ultimately proved to be the best and was used exclusively in the latter phases of the work was the Fisher Multiflame Burner.

This burner, designed and sold by the Fisher Scientific Company, can be adjusted to give four principle flame types. Small or large annealing and small or large sealing flames. The design permits an almost unlimited flame size range. The flames used in this procedure were generally large brush type flames using oxygen.

The burner can operate on any gas from 500 B.T.U. per cubic foot to propane or butane from 2300 B.T.U. per cubic foot. It operates on ordinary city or natural gas pressures.

Oxygen

Oxygen for burner operation was ordinary commercial compressed gas, contained in 240 cubic foot capacity cylinders. It was obtained from National Cylinder Gas Company.

Nitrogen

The nitrogen used for sweeping and for maintaining positive pressure at one end of the apparatus was common commercial grade oil pumped nitrogen, also obtained from
National Cylinder Gas Company. Prior to use, the nitrogen was dried through a CaCl₂ drying tube and passed over phosphoric anhydride to insure the absence of water vapor.

Calcium Hydride

The calcium hydride used during all of this work was obtained from Metal Hydrides Incorporated, Beverly, Mass. It was distilled, reagent grade hydride, size four mesh. The material was kept in a tightly capped bottle. A quantity sufficient for one run was ground in a Sillimanite mortar just prior to mixing with the sample and igniting.

Hydrochloric Acid

Reagent grade, tested purity hydrochloric acid obtained from Eimer and Amend, New York, was used for all washing and neutralizing.

Samples

Samples of NaCl, KCl and K₂CO₃ used in proving the quantitativeness of the reduction reaction were reagent grade chemicals obtained from the J. T. Baker Chemical Company, Phillipsburg, N. J. Samples of glasses and minerals were obtained from the United States National Bureau of Standards, Washington, D. C. These samples were
accompanied by a certificate of analysis for each sample. The samples used were: # 70, feldspar; 80, soda-lime glass; 89, lead barium glass; 91, opal glass; 93, borosilicate glass; 98, plastic clay; 99, soda feldspar; 128, soda-lime glass.

These National Bureau of Standards samples are of the highest purity. The certificate of analysis on each indicates the various analysts who have analyzed the samples for the Bureau of Standards, and their results. These results are then averaged and a recommended percentage for each constituent appears on the certificate. All analyses are based on samples dried for one hour at 105°C to 110°C. The samples are -150 mesh as obtained from the Bureau of Standards and require no further subdivision.

Special Apparatus

Figure 6 illustrates the apparatus with which the best results were obtained. It consists of an ignition, or charge tube of \( \frac{1}{2} \) inch, type 430 stainless steel pipe, six inches in length. The pipe is threaded on each end with standard pipe threads to a distance of one inch. On the inlet end of the charge tube is screwed a stainless steel cap into the end of which a hole has been bored and tapped with standard pipe threads to receive a \( \frac{1}{4} \) inch stainless steel tube, 10 inches in length. Around this tube is
Figure 6. Sectional Diagram of Assembled Apparatus
fitted a glass water condenser about 7 inches long and held in place by rubber stoppers as indicated in the diagram. The outlet end of the charge tube is fitted with another \( \frac{1}{4} \) inch condenser tube which has a large shoulder at one end and is held onto the charge tube by means of a threaded nut, which, when screwed onto the ignition tube presses against the shoulder. Both the shoulder face and the ignition tube end are faced on a metal lathe to insure a gas tight seal when the nut is securely fastened. This tube is also covered with a water jacket constructed of electrical conduit, with the outlets silver soldered in place. Connected to the end of the outlet tube by means of a piece of pressure tubing is a pyrex tube 12 mm. in diameter and 8 inches long. During a run this tube contains a pyrex wool plug about 1 to 1\( \frac{1}{2} \) inches in length and of a density sufficient to allow none of the vaporized metal to pass through.

Nitrogen is dried through a 12 inch column of technical anhydrous CaCl\(_2\) contained in a 35 mm. pyrex tube and then over phosphoric anhydride contained in a 125 ml. Erlenmeyer flask before being passed into the inlet tube to insure complete absence of water vapor.

**Experimental Procedure**

The optimum procedure then was as follows: 0.2 to 0.4 grams of sample, ground to minus 150 mesh and dried at
least one hour at 110°C., was intimately mixed with 1 gram of freshly ground calcium hydride (minus 80 mesh). This was transferred immediately to the center portion of the charge tube by means of a spoon-type spatula (scoopula) and the apparatus assembled, care being taken not to disperse the charge mixture. Dried nitrogen gas was passed through the tube at a rate of about 1 liter per minute while the charge tube was being heated to a dull red (about 900°C.). Heating was continued at this temperature for about 5 minutes, after which time the tube was heated along its length to a bright orange (about 1300°C.) for another 15 minutes. The apparatus was allowed to cool, then disassembled and the charge residue and pyrex wool deposit dissolved in water. The inside of the charge tube, condenser and glass tube were washed with dilute HCl and distilled water, the washings being added to the dissolved residue and deposit. The solution was neutralized with HCl, filtered and analyzed on the flame photometer, using the internal standard method.

Results

Table IV shows the results obtained with the eight Bureau of Standards samples when moderate care was taken and the optimum procedure used.
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SUMMARY AND CONCLUSIONS

A rapid method for the solublization of alkali metals occurring in glasses, silicates, minerals, and clays has been developed. The solublization step, combined with an analysis using a flame photometer provides an easy, quick, complete alkali metal determination. The method is much faster than presently popular methods and compares favorably in most cases with their accuracy.

The simplicity of the method, which consists of grinding and mixing a weighed sample with powdered CaH₂, then igniting it in a stainless steel tube in a stream of nitrogen gas, dissolving the resultant charge mass and collected alkali metal in water and finally determining the metal content with a flame photometer, would seem to give it a decided advantage over existing methods and perhaps be the factor which would persuade many analysts in its favor.

The total time for the solublization step can be made as low as 1 hour and the flame photometer analysis takes from 15 to 30 minutes, depending on the number of alkali metals in the sample. Two complete alkali metal determinations have been made in three hours with a single apparatus, the results of which compared favorably with those obtained by more conventional means (see Table IV). With two apparatus it is estimated that 5 or 6 runs could be completed in 4
hours.

In some of the determinations made by this method the alkali metal oxide percentage found was as much as 0.3 percent lower than the known value (see Table IV). In most runs the results were only slightly lower than known values. These are attributed to possible small leaks in the joints of the apparatus and could be rectified by constructing a precision apparatus.

The solublization step prepares the analytical sample for ultimate analysis by use of the flame photometer. A method such that the alkali metal could be separated from calcium, reacted with water and titrated with standard acid, would be advantageous in a laboratory in which a flame photometer is not available. Such a method is possible in the case of simple salts as was demonstrated by Leonard. However, from a consideration of reaction temperatures necessary for solublization of more complex materials (1200° to 1350°C.), and the volatility of calcium at these temperatures (boiling point of calcium is 1240°C.), such a separation appears to be unfeasible for these materials. Further, if it were possible, then a gravimetric separation of sodium from potassium would need to be made, since most mineral samples and glasses contain both (see Table IV), and a titration would only indicate total alkali metal.
A gravimetric method for calcium, which would be used after determining total alkalinity due to calcium, sodium and potassium combined by titration with acid also has its weak points. In many minerals and glasses the total alkali metal content is as low as 3.0 percent. If a .200 g. sample were taken for analysis it would contain only 6 mg. of total alkali metal. After ignition with calcium hydride and distillation of metals to a collection point, the 6 mg. would be contaminated with about 500 mg. of calcium metal, the total would then be reacted with water and titrated. An extremely accurate titration would have to be made in order to account for the small amount of alkali metal present. Even if this were possible, the oxalate method for calcium, which is the most common and most accurate, would not be accurate enough to determine as much as 500 mg. to within .25 mg., which would be necessary to compare favorably with the flame photometer method and other methods for the alkali metals. The situation is further complicated by the fact that in the oxalate method for calcium the worst contaminants are the alkali metals, and from two to three reprecipitations of the oxalate under rather exacting conditions are necessary to free them.

A separation based on fractional distillation of sodium and calcium metals, or potassium and calcium metals might
serve this purpose but would probably be more involved than the gravimetric and colorimetric methods available for the determination of alkali metals.

For the above reasons the solubilization of alkali-metal compounds by reaction with calcium hydride will be most generally applicable and advantageous when ultimate analysis is carried out by means of the flame photometer.
BIBLIOGRAPHY


