A RAPID DETERMINATION OF THE ALKALI METALS

by

LAWRENCE STUART LEONARD

A THESIS

submitted to

OREGON STATE COLLEGE

in partial fulfillment of
the requirements for the
degree of

MASTER OF SCIENCE

June 1955

APPROVED:

Professor of Chemistry

In Charge of Major

Chairman of Department of Chemistry

Chairman of School Graduate Committee

Dean of Graduate School

Date thesis is presented_____7-3-54_____

Typed by Evelyn Kanzelmeyer

ACKNOWLEDGMENT

I wish to express my thanks to Dr. William E. Caldwell for his advice and encouragement during the course of the work described in this thesis.

TABLE OF CONTENTS

A RAPID DETERMINATION OF THE ALKALI METALS

INTRODUCTION

It is the purpose of this thesis to present a
different approach to the quantitative determination of
certain alkali metals in soluble or insoluble compounds.
The basis of this new determinative method is the vola-
tilization of the alkali metal from a decomposing mixture,
condensation of the alkali metal vapor on a cool selective
surface, immersion of the free alkali metal in water for
formation of a basic solution, and subsequent titration.

A review of the literature concerning the quanti-
tative determination of sodium reveals that the more
popular methods can be placed into two major categories:
(a) those that depend on the formation of an insoluble
salt, and (b) those that depend on the element's spectra.
Each of the above-mentioned categories will now be dis-
cussed:

INSOLUBLE SALT METHODS. One of the best methods
in this category is the "triple acetate method" which
depends on the formation of the slightly soluble NaM^{++}
$(UO_2)_3(C_2H_3O_2)_9 \cdot 6H_2O$; where M is either Zn (2 and 3) or
Mg (6). The conditions for precipitation are rather rigid
in that both the precipitating reagent and the alcohol
wash solution must be previously saturated with sodium
magnesium (or zinc) uranyl acetate and all solutions must
be prepared and used within 1° of 20^oC. During

precipitation the solution must be stirred vigorously for
45-60 minutes. The precipitate is then filtered, dried,
and weighed as the hydrate, or for small amounts of sodium,
redissolved and determined colorimetrically (7).

If the sample to be determined happens to be an
insoluble silicate, the additional steps of decomposition
and preparation of a water soluble alkali metal solution
with no other deleterious metal ions are required.

This method for the determination of sodium by
precipitation is obviously time consuming and troublesome
particularly if the sample is an insoluble silicate.

Much the same can be said of other precipitation
methods such as those involving formation of Na_2SiF_6 or
$Na_2H_2Sb_2O_7 \cdot 6H_2O$.

SPECTRAL METHODS. In recent years a great variety
of spectrographs, spectrometers, and photometers have
appeared in research laboratories and certain commercial
laboratories as an aid to the analyst. These instruments
have certainly become important analytical tools but their
cost is prohibitive to many laboratories. One of the less
expensive instruments in this category is the flame
photometer, which is especially suited for sodium (and
potassium) analyses. Aside from its initial cost, this
instrument has two other disadvantages -- the necessity
of day to day calibration and of having to solubilize the

sample.

Having briefly discussed the more popular analyti-
cal methods for sodium, a similar treatment of quantita-
tive determinations for other alkali metals will now be
presented.

POTASSIUM DETERMINATIONS. Probably the most
accurate means for the estimation of this element is the
chloroplatinate method which depends on the formation of
highly insoluble potassium chloroplatinate in strong
alcohol with subsequent filtering, drying, and weighing
as K_2PtCl_6. A modification of this method exists (9) in
which the K_2PtCl_6 is redissolved and reduced with mag-
nesium and hydrochloric acid yielding a flocculent pre-
cipitate of metallic platinum which is ignited and weighed.

Another gravimetric determination for potassium
involves the formation of potassium perchlorate which is
dried and weighed as such. The perchlorates of sodium and
potassium are both slightly soluble in water but can be
separated due to the relative solubility of the sodium
salt in ethyl acetate (15,p.255).

Many other determinative methods for potassium are
available which depend upon the formation of an insoluble
salt. Any gravimetric determination is inherently time
consuming and should therefore be replaced by another
method whenever possible. Other inconveniences encountered

in this type of analysis are co-precipitation and per-
nicious ion interference. Also, it is to be remembered
that before the above-mentioned methods can be employed,
the sample must be solubilized. The problem of decom-
posing siliceous material preparatory to the determination
of the alkalis will be discussed later in this section.

RUBIDIUM AND CESIUM DETERMINATIONS. Since the
determination of these rare elements is seldom called for,
literature concerning the subject is accordingly sparse.
A satisfactory method for the purpose is available, how-
ever, which involves the precipitation of rubidium and
cesium as phosphomolybdates (or as sodium bismuth
nitrites) and then converting these to chloroplatinates.
This procedure effectively separates rubidium and cesium
from potassium and sodium which would otherwise interfere.
The phosphomolybdates are formed by addition of special
9-phosphomolybdic acid reagent (12,p.108) 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 hydro-
gen sulfide. After removal of the molybdenum, the
alkalis are converted to the chloroplatinates by addition
of chloroplatinic acid. The sodium bismuth nitrite method
(1) is very similar in procedure to the 9-phosphomolybdic
acid method. The precipitating reagent is prepared from

sodium nitrite and bismuth nitrate.

Inasmuch as the above methods only serve to separate rubidium and cesium from the other alkali metals, it now remains to separate rubidium and cesium from each other. Unfortunately, this problem has not been satisfactorily solved. Two of the available approximate methods for this separation are the silico tungstic acid method (12,p.109) which precipitates cesium, and the antimony trichloride-ferric chloride method (11) which also precipitates cesium; rubidium being obtained by difference. Insofar as rubidium and cesium seldom occur together in appreciable amounts, these separatory methods are not often required.

Consider now the determination of the alkali metals in insoluble silicates. Since this determination is one of the major advantages of the method proposed in this paper, it is worthwhile to briefly discuss the present methods.

There are two attacks to the problem of decomposing insoluble silicates. One involves a basic fusion, while the other employs hydrofluoric acid. The fusion method is the most widely used of the two. Named after its perpetrator, the J. Lawrence Smith Method (13) involves heating the sample with a mixture of ammonium chloride and calcium carbonate. During the ignition, alkali chlorides are

formed which are easily extracted with water. It is necessary to run blanks for both potassium and sodium on the same amount of the fusion mixture due to the traces of alkali metals in the reagents and the small amounts taken up from the glassware and porcelainware used. The method is lengthy and involves tedious extractions and evaporations. After applying this method, one has to then resort to one of the methods outlined above to conclude the determination.

When hydrofluoric acid is used to decompose the silicate, the problem of removing the excess acid arises. If sulfuric acid is used, the sulfate must be removed as it interferes in the potassium determination. If perchloric acid is used, the glassware is attacked somewhat making a sodium determination impossible. Other procedures have similar disadvantages. Again, after dissolving the silicate, the determination has to be concluded by one of the above methods.

An obvious improvement over the methods mentioned would be the elimination of the necessity of solubilizing the sample.

Recognizing the various shortcomings of existing methods for the quantitative determinations of the alkali metals, a new approach to the problem was devised based on the following general considerations.

7

GENERAL CONSIDERATIONS

CALCIUM HYDRIDE. Calcium hydride is a grayish-white powder which decomposes at 675°C. to the elements. It is quite stable at ordinary temperatures if kept in a stoppered bottle away from moist air, and therefore poses no storage problem. The reducing power of this compound has been known for some time. In 1913, Ebler (8) demonstrated the complete reduction of sulfates to sulfides according to the reaction

$$MSO_4 + 4CaH_2 \longrightarrow MS + 4CaO + 4H_2 .$$

In 1929, Caldwell and Krauskopf (4 and 5) utilized Ebler's work to develop an analytical method for the rapid determination of sulfur in insoluble sulfates and other sulfur compounds. While investigating the alkali metal sulfates in heatings with calcium hydride, the authors noted the liberation of metallic sodium and potassium from the ignition mixture and their deposition onto the crucible lid. This last discovery is the basis for the proposed determination presented in this thesis; that is, the quantitative replacement and volatilization of certain alkali metals from their compounds in a high temperature reaction with calcium hydride, followed by dissolving the collected free metal in water, with subsequent acid titration.

THE ALKALI METALS. For convenience in the ensuing discussion, the melting points and boiling points of the stable alkali metals are tabulated below (10,p.819):

Element	Melting point, $^\circ$C.	Boiling point, $^\circ$C.
Lithium	179	1336
Sodium	97.9	882.9
Potassium	63.5	757.5
Rubidium	39.0	700
Cesium	28.45	670

Whereas temperatures of 600-900°C. are easily attained in the laboratory without special equipment, the high boiling point of lithium causes this element to be unamenable to the proposed procedure and therefore it will not be considered further.

With reference to the above tabulation, it can be seen that a high temperature reaction is necessary in order to completely volatilize the metals after they are freed from their salts. On the other hand, it is required that the condensing surface be either apart from the reaction or water cooled due to the low melting points of the metals. With this in mind, a suitable apparatus had to be fabricated. The choice of this equipment, including the problems encountered, will be described in the following section of this paper.

EXPERIMENTAL

SELECTION OF EQUIPMENT. Since the determination of
sodium would require the most vigorous ignition, the
selection of the most suitable apparatus was based on the
requirements for the complete recovery of sodium from a
sample of pure sodium carbonate mixed with an excess of
calcium hydride. Five varieties of apparatus were inves-
tigated.

Test tube. Perhaps the most simple in design, this
apparatus consisted of nothing more than a six inch Pyrex
test tube, which, after loading it with the charge, was
constricted to nearly capillary size at a point just above
the charge. With a Fisher burner as a heat source, it was
presumed that the liberated sodium vapors should pass
through the constriction and condense on the upper portion
of the tube. After completion of the reaction, the tube
could be broken at the constriction and the upper portion
containing the condensed sodium metal merely dropped into
a beaker of water and titrated with standard acid. Unfor-
tunately, it was impossible to remove all the sodium vapor
from the charge area. There were other disadvantages of
this method which forced its abandonment.

Whitton apparatus. Several trial runs were made
using the Whitton (14) mercury apparatus. The main diffi-
culty in using this apparatus was the inability to prohibit

the sodium vapor from condensing on the crucible walls.

Combustion tube. This assembly included a quartz combustion tube equipped with a nitrogen source at one end and a water-filled receiver flask at the other. The charge was placed in an alundum boat which in turn was placed in the combustion tube. A slight pressure of nitrogen was maintained to remove the sodium vapor from the vicinity of the charge. A Fisher burner served as a heat source. Upon conclusion of the reduction, the boat was removed and any condensed sodium could be swept into the receiver flask by washing the tube with water. This particular assembly was unsatisfactory. Instead of remodeling it to a more suitable form, however, the device was abandoned.

Iron crucible. Previous to the work mentioned in this paper, an apparatus designed by Robert S. Shoemaker[1] was investigated for its suitability in sodium determinations by the calcium hydride method. The apparatus was constructed by making a circular groove in a steel plate which fitted onto an iron crucible. The rim of the crucible was ground into the steel plate with the aid of valve grinding compound to obtain a tight joint. No provision was made for water-cooling. Shoemaker reported results varying from 93% to 96% of the theoretical percentage of

---

[1] Shoemaker, Robert S. Personal letter to Dr. William E. Caldwell. Madison, Wisconsin. December 8, 1951.

sodium in sodium carbonate. Although the simplicity of
his apparatus is desirable, it was thought that in order
to approach complete recovery of the alkali metals, this
simplicity would have to be sacrificed.

Water-cooled crucible. From the experience gained
by observation of previous equipment, it was now possible
to design a fifth type of apparatus which would employ the
advantages and exclude any disadvantages of the other four.
Drawings of this apparatus appear as Figures 1 and 2 on
the following pages. The machining and construction of
the several parts were performed by the Physics Department
at Oregon State College. Satisfactory results were
obtained with this equipment and it is suggested that
future determinations be made with equipment of similar
construction.

Several design features should be pointed out such
as: (a) the length of the condensing receptacle to pre-
vent condensation on the crucible walls, (b) the threaded
cap, which, in conjunction with the machined rim of the
receptacle, provides a good seal for the reaction chamber,
(c) the copper cooling chamber which insures complete
condensation of the alkali metal vapors, and (d) the tapped
hole on the receptacle to facilitate removal after com-
pletion of the reduction.

Steel cap

Copper cooling chamber

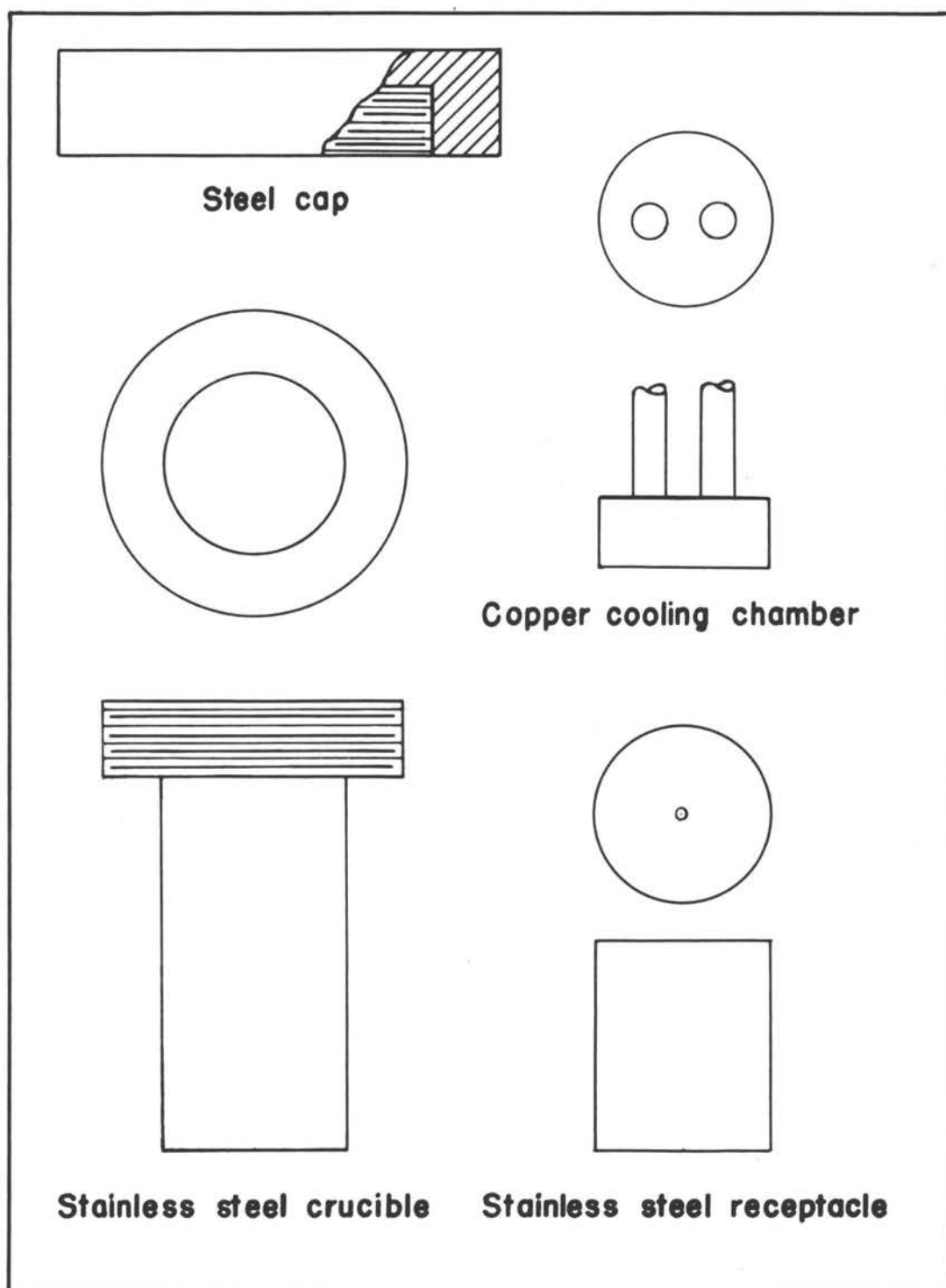**Stainless steel crucible   Stainless steel receptacle**

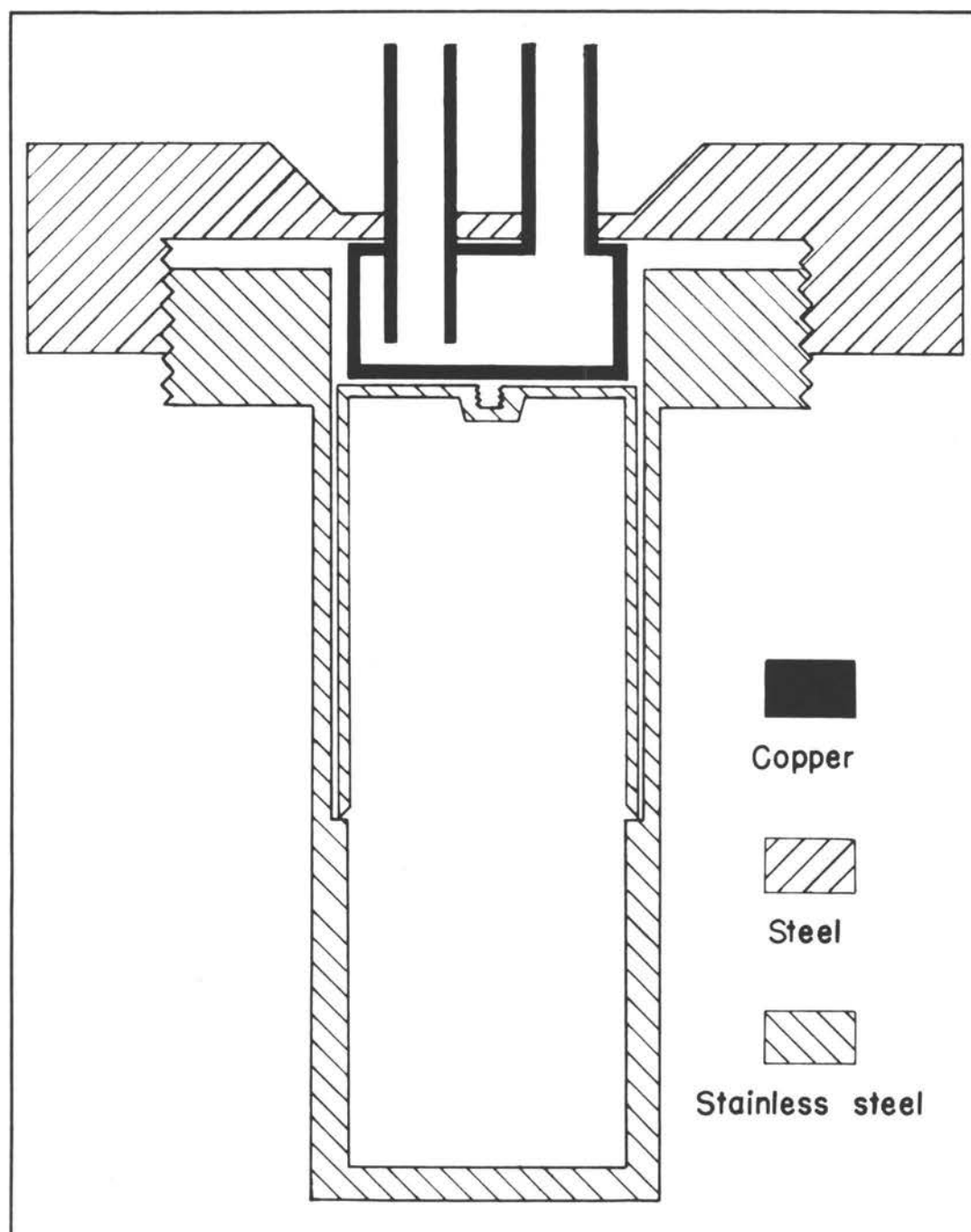Figure I.   Detail of apparatus (actual size)

Figure 2. Sectional drawing of assembled
apparatus (twice actual size)

REAGENTS. <u>Calcium hydride</u>. Distilled calcium hydride was obtained from Metal Hydrides Incorporated, Beverly, Massachusetts. This material was ground in a mortar and stored in a desiccator.

<u>Rubidium and cesium salts</u>. These compounds were obtained from A. D. Mackay, Inc., 198 Broadway, New York 38, New York. They were advertised as being 99% pure.

<u>Mineral samples</u>. These samples were taken from a collection of crystalline minerals prepared for display purposes by Eimer and Amend, New York.

<u>Other reagents</u>. All the other reagents which are mentioned in this thesis are of the best grade obtainable.

<u>Standard solutions</u>. Five liters of approximately 0.1 N NaOH was prepared and standardized with potassium biphthalate using phenolphthalein as the indicator. Five liters of approximately 0.1 N HCl was prepared and standardized with the above NaOH solution.

<u>Sample preparation</u>. All samples that were to be ignited with the calcium hydride were ground in a mortar until they passed through a 100 mesh screen and then dried for one hour in an oven at $110^{\circ}C$.

PROCEDURE. The procedure that was found most satisfactory will now be described in detail.

Having the sample and reagents prepared as described above, the ignition mixture was prepared. This was

accomplished by weighing out a 0.1 g sample of the alkali
metal salt and 2 g of CaH_2. The CaH_2 was weighed on a
trip balance. The weighed materials were then transferred
to the crucible. After these were mixed thoroughly, the
apparatus was assembled and connected to the cooling water
supply. To prevent the small amount of water which con-
denses on the copper tubing from entering the reaction
vessel during the heating period, a wad of cotton was
placed directly above the copper chamber. A satisfactory
support for the apparatus was made by resting five asbes-
tos pads on a four inch ring. A hole just large enough
for the lower section of the crucible body was conveniently
made by the use of a cork borer. After adjusting the flow
of cooling water to about one liter per minute, the
crucible was heated for twenty minutes. It was found that
two Fisher burners is a sufficient heat source for potas-
sium, rubidium, and cesium determinations, but for sodium
the use of a blast lamp provided with compressed air was
required to completely volatilize the metal. The procedure
used for heating sodium determinations was the combination
of a 15 minute period using two Fisher burners and a 5
minute period using a blast lamp. Following the heating
period, the crucible was allowed to cool while maintaining
the flow of cooling water.

When the crucible had cooled enough to be handled, the apparatus was disassembled and the cap containing the condensed alkali metal was placed in a 250 ml. beaker. The metal was then dissolved by the careful addition of distilled water. To conclude the determination, an excess of standard HCl was added and back-titrated with standard NaOH, using phenolphthalein as the indicator.

RESULTS. The results from the various salts investigated by this procedure are tabulated on the following pages. Since the "charge" in each case consists of 2.0 g of CaH_2 plus 0.1 g of the salt, it is only necessary to mention the name of the salt in this column.

Some of the materials investigated were of doubtful composition regarding their alkali metal concentration. The recovery of the metals by the calcium hydride method were then based on values obtained from submitting these materials to flame photometric determinations.

The two unknowns listed in Table I were provided by Dr. W. E. Caldwell. After reporting the percentage of sodium found in each of these materials by the calcium hydride method, the actual composition was revealed in order to calculate the percent deviation. Unknown #1 was a sample of crystalline cryolite (Na_3AlF_6) and unknown #2 proved to be sodium oxalate.

TABLE I

RECOVERY OF SODIUM

Run Number	Charge	% Sodium		Deviation %
		Theoretical	Found	
92	NaCl	39.3	38.7	-1.5
93			38.7	-1.5
94	NaNO$_3$	27.1	27.0	-0.4
95			27.1	0.0
90	Na$_2$CO$_3$	43.4	42.6	-1.8
91			42.6	-1.8
96	Albite	7.11*	6.95	-2.2
97	(Na$_2$O·Al$_2$O$_3$·6SiO$_2$)		6.92	-2.3
100	Unknown #1	32.9**	32.8	-0.3
101			33.1	+0.6
98	Unknown #2	34.3**	34.0	-0.9
99			33.9	-1.2

Ave. = 1.2

---

* Based on values obtained from Perkin-Elmer flame photometer Model 52-C using 800 ppm Li as an internal standard.

** See page 16.

TABLE II

RECOVERY OF POTASSIUM

Run Number	Charge	% Potassium Theoretical	Found	Deviation %
46	KNO$_3$	38.7	39.7	+2.6
47			39.8	+2.8
48	KCl	52.4	53.1	+1.3
49			53.2	+1.5
43	K$_2$CO$_3$	56.6	57.2	+1.1
44			57.1	+0.9
64	K$_3$PO$_4$	55.3	55.7	+0.7
65			55.7	+0.7
68	Kainite	14.3*	14.3	0.0
69	(KCl·MgSO$_4$·3H$_2$O)		14.4	+0.7
66	Orthoclase	14.1*	14.0	-0.7
67	(K$_2$O·Al$_2$O$_3$·6SiO$_2$)		13.8	-2.1

Ave. = 1.3

* Based on values obtained from Perkin-Elmer flame photometer Model 52-C using 800 ppm Li as an internal standard.

TABLE III

RECOVERY OF RUBIDIUM

Run Number	Charge	% Rubidium		Deviation %
		Theoretical	Found	
72	RbBr	51.7	50.9	-1.5
73			51.3	-0.8
78	$RbNO_3$	58.0	58.8	+1.4
79			58.6	+1.0
50	RbCl	70.7*	70.7	0.0
51			70.8	+0.1
74	Rb_2CO_3	74.0	73.9	-0.1
75			73.5	-0.7
76	Rb_2SO_4	64.0	64.0	0.0
77			63.4	+0.9

Ave. = 0.7

TABLE IV

RECOVERY OF CESIUM

Run Number	Charge	% Cesium		Deviation %
		Theoretical	Found	
80	CsCl	78.9	79.2	+0.4
81			79.2	+0.4
88	CsBr	62.5	61.6	-1.4
89			61.3	-1.9
84	$CsNO_3$	68.2	68.6	+0.6
85			69.2	+1.5
82	Cs_2SO_4	73.5	74.1	+0.8
83			74.6	+1.5

Ave. = 1.1

---

* Based on values obtained from Perkin-Elmer flame photometer Model 52-C using 800 ppm Li as an internal standard.

DISCUSSION OF RESULTS

Inasmuch as the overall deviation of the experimental results from the theoretical values was found to be only about 1%, which can be attributed for the most part, if not entirely, to experimental errors, there can be little doubt that the reduction itself was quantitative. Also, it is evident from the results that reasonably good precision is obtainable. For a more precise determination by this method, a crucible that could employ a larger charge would be required.

The major source of error (and also the disadvantage) of this method is in the determination of a sample which contains more than one of the alkali metals.

A major advantage of the calcium hydride method is the rapidity of analysis. A determination can be completed within 45 minutes, and, with a battery of four apparatuses, it is estimated that four complete determinations can be made within an hour. This advantage was especially evident when the writer was called upon to determine the alkali metal concentration in insoluble silicates by flame photometry to verify results obtained by the calcium hydride method.

During the course of the experimental work various deviations from the above procedure were investigated and should be mentioned here.

CALCIUM HYDRIDE TO SAMPLE RATIO. The minimum amount of calcium hydride to use would depend on the amount of alkali metal present and the completeness of the reactions. These quantities are, of course, impossible to predict. A considerable excess of calcium hydride is then required for a given amount of sample. On the other extreme, it was found that the use of over about 2-1/2 grams of hydride gave low results due to inefficient heat conduction. The prescribed 2 grams, then, was a satisfactory compromise.

LENGTH OF HEATING PERIOD. Since the conduction of heat through the charge is slow and relatively high temperature reactions are involved, a 20 minute heating period is necessary. Unless the prescribed heat sources are employed, accurate results are unobtainable due to insufficient heating.

COOLING WATER. By reference to the table of melting points on page 8, it is seen that cooling water is necessary for complete collection of the liberated alkali metal. Although the use of warm water for cooling purposes would eliminate the problem of water condensation on the copper tubing, it was found that best results were obtained by using cold tap water.

PARTICLE SIZE. It is important that the sample be ground to minus 100 mesh and the hydride to minus 60 mesh.

SUMMARY

A method has been presented for the rapid determina-
tion of sodium, potassium, rubidium, or cesium in their
salts and minerals. In view of the fact that the pro-
cedure eliminates the heretofore necessary (and at times
laborious) step of solubilizing the sample preparatory to
the actual determination, it can be applied to salts of the
alkali metals, regardless of their solubility, with equal
facility.

The proposed analysis consists of a high temperature
fusion with calcium hydride in a specially designed water-
cooled crucible. Calcium hydride serves to reduce the
alkali metal to the free element which is immediately
volatilized and collected in a removable receptacle in the
cooler portion of the apparatus. After completion of the
reaction, the receptacle containing the condensed alkali is
washed with water to dissolve the deposit. The determina-
tion is concluded by subjecting the resulting basic solu-
tion to an acid titration.

The amenability of various salts and minerals of
these alkali metals to this procedure was investigated.
Results indicate that the reaction is quantitative and that
the method can be applied to any salt or mineral containing
no more than one of the above-mentioned alkali metals.

A determination can be completed within 45 minutes, or, by the use of a battery of equipment, it was estimated that four determinations could be completed within an hour.

SUGGESTIONS FOR FUTURE WORK

It would be worthwhile to consider redesigning the apparatus to these ends:

1. To be able to determine any two alkali metals simultaneously.

2. To employ a larger charge which would increase the accuracy of the determination.

3. To construct the apparatus at a lower cost.

After discovering the best possible apparatus to use, an experimental program should be launched on a firm statistical basis to determine the relative accuracy of this method.

BIBLIOGRAPHY

1. Ball, Walter Craven. A new method for the detection of sodium, caesium, and rubidium. Journal of the chemical society 95:2126-2130. 1909.

2. Barber, H. H. and I. M. Kolthoff. A specific reagent for the rapid gravimetric determination of sodium. The journal of the American chemical society 50: 1625-1631. 1928.

3. Barber, H. H. and I. M. Kolthoff. Gravimetric determination of sodium by the uranyl zinc acetate method. II. Application in the presence of rubidium, cesium, potassium, lithium, phosphate or arsenate. The journal of the American chemical society 51:3233-3237. 1929.

4. Caldwell, William E. and Francis C. Krauskopf. Reduction reactions with calcium hydride. I. Rapid determination of sulfur in insoluble sulfates. The journal of the American chemical society 50:2936-2942. 1929.

5. Caldwell, William E. and Francis C. Krauskopf. Reduction reactions with calcium hydride. II. Determination of sulfur in sulfur oils and rubber. The journal of the American chemical society 52: 3655-3659. 1930.

6. Caley, Earle R. and C. W. Foulk. A gravimetric and colorimetric method for the direct determination of sodium. The journal of the American chemical society 51:1664-1674. 1929.

7. Darnell, Jr., M. C. and B. S. Walker. Determination of sodium in biological fluids. Industrial and engineering chemistry, analytical edition 12:242-244. 1940.

8. Ebler, E. and K. Herrdegen. Über die Einwirkung von Calciumhydrid auf Sulfate. Berichte der deutschen chemischen Gesellschaft 46:2264-2267. 1913.

9. Hicks, W. B. A rapid modified chloroplatinate method for the estimation of potassium. The journal of industrial and engineering chemistry 5:650-653. 1913.

10. Moeller, Therald. Inorganic chemistry. New York, Wiley, 1952. 966p.

11. Moser, Ludwig and Erich Ritschel. Über die quantitative Analyse des Rubidiums und Caesiums. Zeitschrift für analytische Chemie 70:184-189. 1927.

12. O'Leary, William J. and Jacob Papish. Analytical reactions of rubidium and cesium. Industrial and engineering chemistry, analytical edition 6:107-111. 1934.

13. Smith, J. Lawrence. On the determination of the alkalis in silicates by ignition with carbonate of lime and sal-ammoniac. The American journal of science and arts 101:269-275. 1871.

14. Whitton, W. W. The determination of mercury in ores. California journal of technology 4:35-39. 1904.

15. Willard, Hobart H. and Harvey Diehl. Advanced quantitative analysis. New York, Van Nostrand, 1943. 457p.