THE RADIOACTIVITY OF THE RUBIDIUM EXTRACTED FROM THE LEPIDOLITE AND ZINNWALDITE OF JAPAN.

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Nothing is known about the radioactive serial genesis of potassium and rubidium, and there remain several important subjects still for decision. It has often been considered that the feebleness of their radioactivity might be ascribed to their inferior isotopes admixed, viz. K^{41} and Rb^{87}: According to this supposition the activity of these elements might not be always the same when the mineral source of the elements are different. A number of preparations of potassium salt of different origins were ever examined for the activity, and it was pointed out that a fixed result was consistently obtained(1); but on rubidium no study of this line has yet been made. In the present work, it was undertaken, therefore, to prepare the pure rubidium preparations from some Japanese lithia micas and to compare their activities with that of the Kahlbaum's preparation which is probably derived from the Stassfurt deposits.

Method of Separating the Rare Alkalies. The separation of the rare alkalies was effected by adopting a special procedure improved by the authors. The method was based upon the sparing solubility of caesium antimony chloride(2) and rubidium stannic chloride(3) in concentrated hydrochloric acid. On treating the dried solid mixture of alkali chlorides with concentrated hydrochloric acid (sp. gr., 1.185), the most part of sodium chloride, which is least soluble in hydrochloric acid, is first removed, and subsequently caesium and rubidium are precipitated in presence of potassium and lithium from the filtrate, one after another by adding suitable quantities of hydrochloric acid solutions of antimony chloride and stannic chloride respectively. After removal of the tin and antimony as sulphides, the final filtrate is evaporated up to dryness, and the residue which contains the chlorides of whole lithium and potassium as well as a trifling remainder of sodium, is now put together with the first residue of sodium chloride and used for the estimation of lithium, sodium and potassium which are quite readily separable by the usual method. In carrying out this process, the volume of solutions, in which the precipitations occur, is very important and notably influences every precipitations, especially that of caesium antimony chloride. The solubilities of all the alkali chlorides and double chlorides in concentrated hydrochloric acid (1.185), which are given in Table 1 and Table 2,

TABLE 1.

Approx. Solubility of Alkali Chlorides in Hydrochloric Acid (sp. gr., 1·185) at 16∼17°C.

Chlorides.	Gr. chloride which are dissolved in 100 c.c. HCl.	C.c. HCl, in which 1gr. chloride dissolves
CsCl	55.3	1.8
RbCl	16.1	6.2
LiCl	31.3	3.2
KCl	1.1	90.0
NaCl	0.1	1000.0

TABLE 2.

Solubility of Double Chlorides in HCl (sp. gr., 1·185) at 20°C.

Double chlorides	Gr. double chloride which exists dissolved in 100 c.c. HCl solution.
$3CsCl \cdot 2SbCl_3$	0.4599 (=0.2416 CsCl or 0.2021 Cs_2O)
Rb_2SnCl_6	0.0194 (=0.0093 RbCl or 0.0072 Rb_2O)
K_2SnCl_6	0.1892 (=0.0689 KCl or 0.0435 K_2O)

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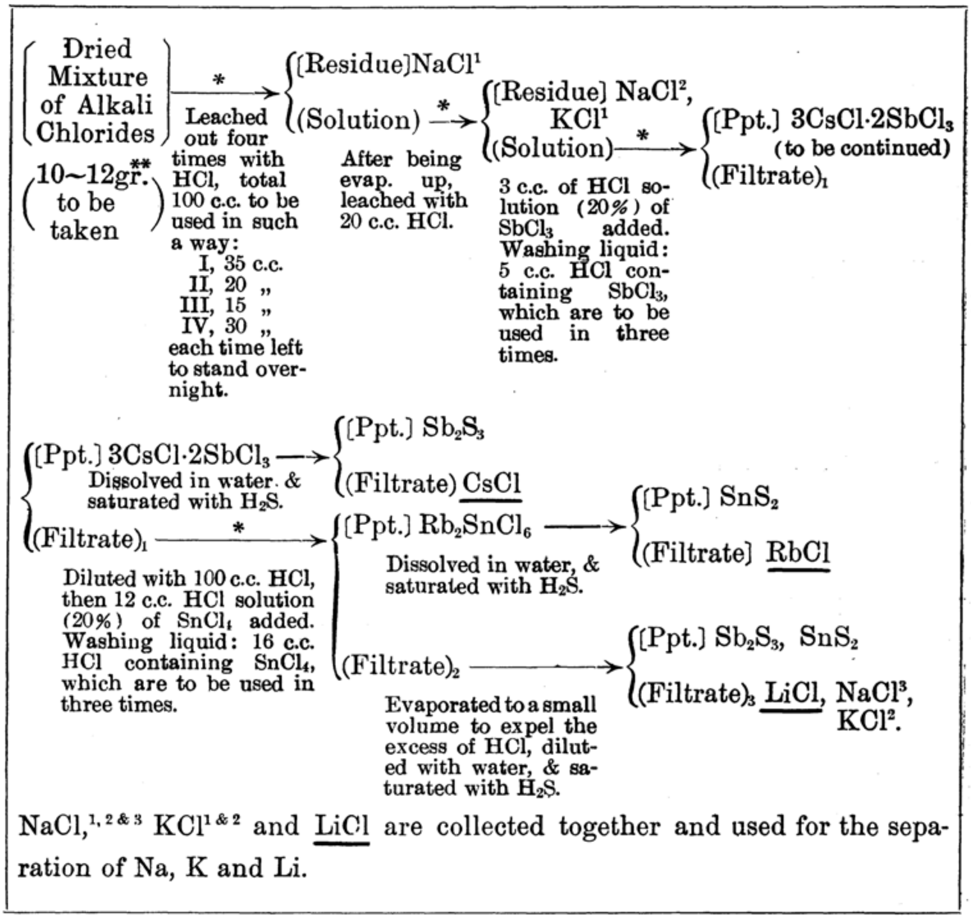
(1) N. R. Campbell, *Proc. Cambridge Phil. Soc.*, **14** (1908), 15.
W. Biltz & E. Marcus, *Z. anorg. Chem.*, **81** (1913), 369.

(2) R. Godeffroy, *Ber.*, **7** (1874), 376; *Liebig's Ann. Chem.*, **181** (1876), 176.

(3) S. P. Sharples, *Am. J. Sci.*, (2), **97** (1869), 178.

as well as the mutual effects upon solubilities were therefore determined, and a scheme of procedure was established. Table 3 illustrates the outline of the scheme. The vessels to be employed for the separation must strictly be avoided from moisture, consequently the asbestos filters, extracting flasks, etc. were used to kept in a large desicator. The process proved to give a quite satisfactory result.

TABLE 3.



Dried Mixture of Alkali Chlorides (10~12gr.** to be taken) →* Leached out four times with HCl, total 100 c.c. to be used in such a way:
I, 35 c.c.
II, 20 „
III, 15 „
IV, 30 „
each time left to stand overnight.

- [Residue]$NaCl^1$
- (Solution) →* After being evap. up, leached with 20 c.c. HCl.
  - [Residue] $NaCl^2$, KCl^1
  - (Solution) →* 3 c.c. of HCl solution (20%) of $SbCl_3$ added. Washing liquid: 5 c.c. HCl containing $SbCl_3$, which are to be used in three times.
    - [Ppt.] $3CsCl{\cdot}2SbCl_3$ (to be continued)
    - $(Filtrate)_1$

[Ppt.] $3CsCl{\cdot}2SbCl_3$ → Dissolved in water & saturated with H_2S.
- [Ppt.] Sb_2S_3
- (Filtrate) $\underline{CsCl}$

$(Filtrate)_1$ →* Diluted with 100 c.c. HCl, then 12 c.c. HCl solution (20%) of $SnCl_4$ added. Washing liquid: 16 c.c. HCl containing $SnCl_4$, which are to be used in three times.
- [Ppt.] Rb_2SnCl_6 → Dissolved in water, & saturated with H_2S.
  - [Ppt.] SnS_2
  - (Filtrate] $\underline{RbCl}$
- $(Filtrate)_2$ → Evaporated to a small volume to expel the excess of HCl, diluted with water, & saturated with H_2S.
  - [Ppt.] Sb_2S_3, SnS_2
  - $(Filtrate)_3$ $\underline{LiCl}$, $NaCl^3$, KCl^2.

$NaCl,^{1,2\&3}$ $KCl^{1\&2}$ and $\underline{LiCl}$ are collected together and used for the separation of Na, K and Li.

* Asbestos filter is to be employed for the filtration.

** Limiting amounts (gr.) of chlorides to be taken for separation:—
CsCl: 0·5, RbCl: 1·5, NaCl: 2·0, LiCl: 5·0 and KCl: 5·0, viz. total: 14·0 gr.

The Rubidium Content of the Lithia Micas of Japan. Since the rubidium usually occurs associated with lithium, all available specimens of

Japanese lithia and lithia iron micas were preliminary analyzed for alkalies by the ordinary method of J. Lawrence Smith with the result shown in Table 4.

TABLE 4.

Micas analyzed		Li_2O(%)	Na_2O(%)	K_2O(%)
Tanokami zinnwaldite	{large crystals, transparent with purple shade.}	4.24	5.00	7.89
〃 〃	{largec rystals, transparent with brown shade.}	3.66	2.18	7.52
Naegi zinnwaldite	{large crystals, transparent with brown shade.}	2.31	5.82	8.35
Nagatori lepidolite	{congregated mass of quartz and scaly mica.}	2.49	3.20	9.13
〃 〃	{ 〃 〃 , a diff. lump. }	1.94	2.70	6.71

For the extraction of rubidium the Tanokami zinnwaldite and Nagatori lepidolite were dealt with, and the separation was carried out according to the above mentioned method. The results obtained were as follows :

TABLE 5.

Micas	Amount taken (gr.)	Rb_2SO_4 yielded (gr.)	Rb_2O %
Tanokami zinnwaldite (1st sample):	60.11	0.6916	0.81
〃 〃 (2nd sample):	60.43	0.8538	0.98
Nagatori lepidolite :	60.05	0.8214	0.96

It has been proved spectrographically that all of these sulphate preparations contained no impurity but very small amount of caesium which could not be thrown down by antimony chloride in the course of separation. This amount of caesium contained in the preparations was so ascertained from the scale of procedure that it never exceeds 0.08% at most referred to to the sample.

The Radioactivity of the Rubidium Sulphate Preparations. The β-ray activity of these preparations was measured by means of a sensitive alpha-ray electroscope and compared with that of the Kahlbaum's preparation. The results obtained are set out in Table 6.

TABLE 6.

Sample	Thickness of layer(gr./cm.^{2})	Activity (div./hr.)	Comparison of activity
The β-ray standard (U_3O_8)	—	1425*	100
Rubidium sulphate preparation of Kahlbaum	0.0294	3.5 per gr.	0.246
Rubidium sulphate prep. from Tanokami zinnwaldite	0.0116	3.4 „	0.239
Rubidium sulphate prep. from Nagatori lepidolite	0.0256	3.6 „	0.253

* This is the limiting activity of the β-ray from the uranium oxide employed as the standard, corrected for the absorption by the aluminium foil of 0.05 mm. thickness used to cover the standard.

It will be seen that no marked difference in the activity of these preparations could be detected, the activities expressed per gr. in those layer thicknesses indicated in the above table having been directly compared with the limiting β-ray activity of the uranium oxide as the absorption coefficient of the prepatation for the β-ray from rubidium is unknown. Thus, it may be concluded that the activity of rubidium so far studied in the present work does not depend upon the mineral, from which the element has been extracted.

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