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# An Isotopic Analysis of Potassium and Rubidium Using a Thermal Ionization Source

# Analiza izotopowa potasu i rubidu przy zastosowaniu źródła jonów pracującego na zasadzie termoemisji jonowej

# Изотопический анализ калия и рубидия с применением термоионного источника

## INTRODUCTION

Natural potassium is composed of three isotopes: two stable isotopes of mass 39 and 41, and one radioactive of mass 40.

In the natural element the abundance of the stable isotopes is ca. 93 and 7 per cent, respectively. The radioactive isotope occurs in trace amounts and its quality does not exceed 0.01 per cent.

The first measurements of the isotopic composition of potassium established the abundance of the radioactive isotope $K^{40}$ and were based upon the determination of the relative activity of the element. In numerous papers it was shown that the relative activity, and thus the percentage amount of the $K^{40}$ isotope, remains constant [1, 2, 3]. The results obtained show agreement up to ca. 0.5 per cent within the experimental error. From the experimental data it may be judged that the isotopes of potassium do not separate in natural conditions, or that such a process could be detected only by more precise methods of measurements [4]. The measurements of the relative abundance of the stable isotopes $K^{39}$ and $K^{41}$ give diverging results. In spite of the easy separation of the two peaks, resulting from the marked difference of mass and from the advantageous value of the isotope ratio, the reported data vary considerably and the divergences exceed markedly the limits of the experimental error defined in the papers. Therefore, some of the authors suggested the possibility of a spontaneous resolution of the potassium isotopes 39 and 41 occurring in nature.

In order to investigate the process of spontaneous separation of the two isotopes, the isotopic composition of potassium samples from minerals and plants was determined, particularly that of seaweeds, and also the isotopic constitution of potassium isolated from sea water. A comparison was also made of the results obtained for minerals from different geological ages [5, 6, 7, 8, 9]. Depending upon the origin of the sample the isotopic ratic $K^{39} : K^{41}$ varied from 13.69 to 14.30 that is, deviations amounting to 4.5 per cent of the lower value.

Similar measurements of the isotopic constitution of the element were published by Cook [10], for samples of potassium from seaweeds and rocks of different geological ages. They found that the ratio $K^{39} : K^{41}$ remains constant within the experimental error and is equal to 14.12 ± 0,28. Cook explains the observed divergencies in the isotopic compositions as the isotopic effect occurring at the anode of the source of ions. Cook's investigations, and more recent works of other authors, suggest a critical consideration of the data published in earlier papers [11]. However, the more recent data continue to vary markedly. Thus for samples of unspecified origin White and Cameron [12] (1948) found the value 13.66 ± 0.1 for the ratio $K^{39} : K^{41}$, whereas Nier [13] (1950) reported a mean value 13.48 ± 0.7. The relative difference of the two values is 1.34 per cent and exceeds the experimental error.

Systematic measurements of the isotopic composition of potassium were carried out by Reuterswärd [14] (1956), who also discussed the possible sources of errors. Depending upon the source of the sample the values of the isotopic ratio have been found in the range 13.67 ± 0.08 to 14.20. The difference of these average values is 0.39, which is 2.8 per cent of the lower value. On the other hand, the error for a single measurement in a series does not exceed 0.4—1 per cent.

The author explains the observed divergence of results by the fractionation effect occurring during the thermoemission of ions from the anode of the spectrometer. This explanation is confirmed by the fact that for rubidium, which also has two isotopes, but of much heavier mass numbers amounting to 85 and 87, smaller divergences are observed.

The earliest measurements of the isotopic composition of rubidium are those of Brewer, who found the value of the ratio $Rb^{85} : Rb^{87}$ equal to 2.57—2.61 [15].

The results of more recent measurements do not differ much from this value; thus according to Paul [16] it is equal to 2.64 ± 0.03 and according to Nier 2.59 ± 0.03 [17].

## APPARATUS

Isotopic analysis was carried out by using a 60° mass spectrometer of the symmetrical type. The chamber of the spectrometer was made from a suitably bent and a flattened copper tube. The sections containing the source of ions, the collector, and the connections for two diffusion pumps were welded with silver. This permitted to heat the spectrometer tube by means of suitable spirals connected to a variable power source [18].

The spectrometer was supplied with easily exchangeable sources, one gaseous with electron ionisation and another working on the ion thermoemission principle.

A diagramatic presentation of the latter source employed in this work is given in Fig. 1.

The anode was a 0.1 mm tungsten wire coiled into a spiral 1 mm in diameter. The samples of potassium and rubidium were introduced to the anode in the form of aqueous solutions of KBr and RbBr. The anode was placed inside the slit $S_1$ of the screen 3 mm wide, which was connected electrically with the anode.

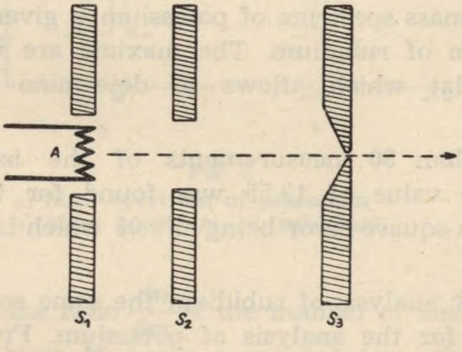

Fig. 1. Diagram of the source of ions: A — tungsten anode, $s_1$ — 3 mm, $s_2$ — 4 mm, $s_3$ — 0.05 to 0.2 mm

The slit $S_2$, 4 mm wide, was an intermediate potential between the anode potential and the ground potential, and its aim was to focus the beam of ions on the exit slit $S_3$, 0.05 mm wide. Another slit was placed in front of the magnetic field, which limited the angle of the beam entering the field to 1.5°. In the magnetic field the central ray of the beam was bent. The radius of the curvature amounted to 23 cm, and then the beam was focused on the slit (1—2 mm wide) of the collector of the spectrometer.

Under these conditions a resolving power of the order of 200 was obtained.

## PREPARATION OF SAMPLES AND METHOD OF MEASUREMENTS

Commercial KBr or RbBr was dissolved in water and the solution was applied to the anode. After careful heating of the anode it was dried and then mounted inside the spectrometer together with the whole source. After two-hour pumping-out and heating of both the source of ions and the whole tube of the spectrometer, the pressure inside the apparatus dropped to ca. $10^{-6}$ mm Hg, which allowed to start the measurements.

Ion currents were determined by means of a vibration electrometer. The mass spectra were determined by varying the current in the electromagnet coil and by simultaneous automatic recording of the ion current. Most measurements were carried out at anode potential of + 1500 V, and focusing slit potential + 1350 V. At the same time the exit slit of the source was kept at ground potential.

## RESULTS OF EXPERIMENTS

In Fig. 2a the mass spectrum of potassium is given, and in Fig. 2b — a typical spectrum of rubidium. The maxima are well separated and the peaks are flat which allows to determine the isotopic ratio accurately.

From more than 50 measurements of the isotopic composition of potassium, the value of 13.55 was found for the ratio of peaks $K^{39} : K^{41}$, the mean square error being ± 0.03 which is 0.2 per cent of the value measured.

For the isotopic analysis of rubidium the same source and technique was employed as for the analysis of potassium. From more than 100 measurements, the ratio of peak heights $Rb^{58} : Rb^{87}$ equal to $2.61 \pm 0.01$, was obtained.

## DISCUSSION OF RESULTS

The measurement of peak heights in a mass spectrum permits to determine the isotopic composition of the ion beam. If no discrimination of mass occurs in the spectrometer, the ratio of peak heights simulta-

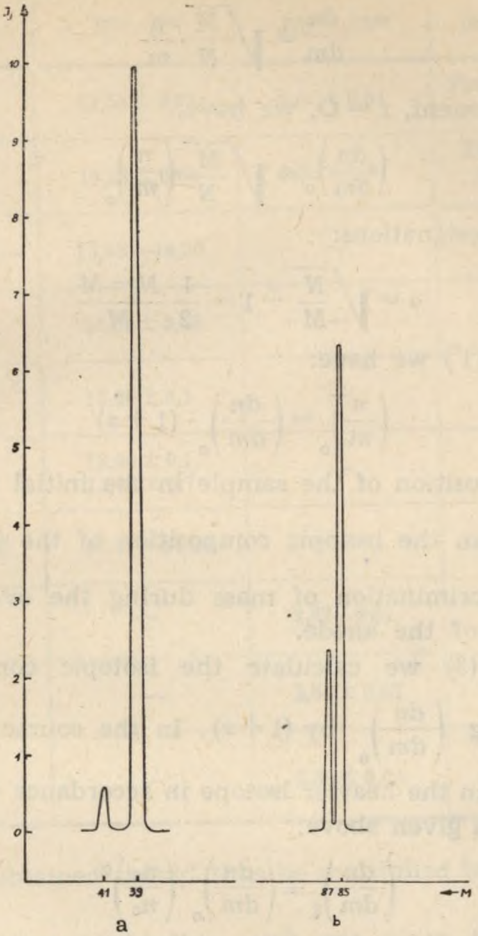

Fig. 2

a) Mass spectrum of potassium
b) Mass spectrum of rubidium

neously determines the ratio $\frac{dn}{dm}$ of the number of ions of mass $N$ to the number of ions of mass $M$, both evaporated from the anode in a unit of time.

As in the case of molecular outflow of gases, also in the ion thermoemission phenomenon a discrimination mass takes place due to the fact that the intensities of ion current emitted are inversely proportional to the square root of mass. If by $n$ and $m$ we denote the numbers of ions of mass $N$ and $M$ in the sample, assuming a homogeneous composition of the sample, we may write:

$$\frac{dn}{dm}=\sqrt{\frac{M}{N}}\cdot\frac{n}{m} \tag{1}$$

For the initial moment, $t = 0$, we have:

$$\left(\frac{dn}{dm}\right)_o=\sqrt{\frac{M}{N}}\left(\frac{n}{m}\right)_o \tag{1'}$$

Introducing the designations:

$$\alpha=\sqrt{\frac{N}{M}}-1\approx\frac{1}{2}\,\frac{N-M}{M} \tag{2}$$

from dependence (1′) we have:

$$\left(\frac{n}{m}\right)_o=\left(\frac{dn}{dm}\right)_o\cdot(1+\alpha) \tag{3}$$

The isotopic composition of the sample in the initial moment can thus be determined from the isotopic composition of the ion beam $\left(\frac{dn}{dm}\right)_o$ and from the discrimination of mass during the evaporation of ions from the surface of the anode.

According to (3) we calculate the isotopic composition of the sample multiplying $\left(\frac{dn}{dm}\right)_o$ by $(1+\alpha)$. In the course of operation the anode is enriched in the heavier isotope in accordance with the relations from the equations given above:

$$\left(\frac{dn}{dm}\right)_t=\left(\frac{dn}{dm}\right)_o\cdot\left(\frac{n_o}{n_t}\right)^{\alpha}$$

For potassium, for the ratio of isotopes $K^{39} : K^{41}$, we obtain

$$\sqrt{\frac{M}{N}}=\sqrt{\frac{41}{39}}=1.0253,\ \text{and}\ 1+\alpha=\sqrt{\frac{39}{41}}=0.9753$$

The isotopic ratio for rubidium is obtained in the same way. The ratio

$$\sqrt{\frac{M}{N}}=\sqrt{\frac{87}{85}}=1.009$$

$\alpha$ is negative, $(1+\alpha)$ being $\sqrt{\frac{85}{87}}=0.98845$

Assuming that the time of work of the anode of the source of ions is not too long and that the isotopic composition of the sample did not change markedly, formulae (1) and (3) may be employed.

In order to calculate the isotopic ratio of the sample, the ratios

| Publication | $K^{39} : K^{41}$ | $Rb^{85} : Rb^{87}$ | Remarks, references |
|---|---|---|---|
| Present work | 13,55 ± 0,03 | 2,61 ± 0,01 | From the ratio of peak heights |
| Present work | 13,22 ± 0,03 | 2,58 ± 0,01 | Taking into account discrimination of masses |
| Brewer A. K.,<br>Brewer A. K. — Bandisch O. | 13,68—14,30 | — | [5, 6, 7, 8] |
| Cook K. L. | 14,12 ± 0,28 | — | [10] |
| White J. R. | 13,66 ± 0,1 | — | [12] |
| Nier A. O. | 13,96 ± 0,1<br>13,48 ± 0,7 | — | [13] |
| Reuterswärd C. | 13,67—14,20 | — | [14]<br>depending on the sample |
| Brewer A. K. | — | 2,57—2,61 | [15] |
| Paul W. | — | 2,64 ± 0,03 | [16] |
| Nier A. O. | — | 2,59 ± 0,03 | [17] |

of peak heights obtained should thus be multiplied by $(1 + \alpha)$ according to eq. (3).

The results obtained in this work are given in the table, along with those reported in earlier works.

For the isotopic ratio of rubidium the data are in very good agreement, while for potassium larger divergencies occur. It seems that introducing a correction excessively decreases the isotopic ratio of potassium obtained in this study.

This effect can be observed in the case when the emitting surface loses excessively the light isotope with sufficient speed so that the assumptions of eq. (3) concerning the initial moment, $t = 0$ are no longer valid.

Additional information concerning the discrimination of masses occurring on the anode of the source might be obtained from a comparison of results acquired from a thermoemission source with data from a gas or vapour source of the electron ionization type [17].

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## STRESZCZENIE

Skład izotopowy potasu i rubidu badano używając termoemisyjnego źródła jonów. Próbki w postaci związków KBr i RbBr były niewiadomego pochodzenia. Bezpośrednio z pomiarów dla potasu znaleziono $K^{39} : K^{41}$ równe 13,55 ± 0,03 i dla rubidu $Rb^{85} : Rb^{87}$ równe 2,61 ± 0,01, co odpowiada składowi izotopowemu potau 93,12% i 6,87% oraz rubidu 72,3% i 27,7%.

Po wprowadzeniu poprawki na wyróżnienie mas w procesie emisji z anody wartości te zmieniają się odpowiednio, dla potasu na 13,22 ± 0,03 oraz 92,96% i 7,03%, zaś dla rubidu 2,58 ± 0,01 oraz 72,1% i 27,9%.

## РЕЗЮМЕ

Применяя термоэмиссионный источник ионов исследован изотопный состав калия и рубидия. Образцы KBr и RbBr были неизвестного происхождения. Неисправленные измерения дали отношение $K^{39} : K^{41} = 13{,}55 \pm 0{,}03$ и $Rb^{85} : Rb^{87} = 2{,}61 \pm 0{,}01$, что отвечает изотопному составу калия 93,12% и 6,87% а рубидия 72,3% и 27,7%. Вводя коррекцию по отличению масс в процессе эмиссии получаем соответственно: для калия 13,22 ± 0,03; 92,96% и 7,03%, для рубидия 2,58 ± 0,01; 72,1% и 27,9%.

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