the fact that potassium is necessary to sustain life while sodium is not. Correspondingly, the 12% preference it exhibits for K^{41} over K^{39} may be taken to indicate that the K^{41} is more closely related to the life processes going on within the cells.

In conclusion it should be mentioned that the results presented in this paper do not conflict with the atomic weight determinations of the various investigators who failed to detect any abnormality for potassium from various plant ashes. In the experiments of Baxter and MacNevin on hard wood ash the uncertainty factor in the atomic weight was about ±0.001; this corresponds to an uncertainty in the abundance ratio of ±0.11. Table III shows maple ash to give the normal ratio while oak ash exhibits an equivalent atomic weight divergence of only 0.0003 which could not have been detected chemically. Hönigschmid and Sachtleben in failing to detect a definite abnormality for potassium from hop flower had an uncertainty factor of about ±0.002 corresponding to ±0.23 in the abundance ratio. The results obtained from most leaves show the deviations to be less than this amount. In the case of the other investigations on the subject it is doubtful if the uncertainty factor would have permitted the detection of any of the deviations presented in this paper.

The writer is indebted to Dr. J. W. Turrentine for his interest and for furnishing many of the samples tested, to Dr. F. C. Kracek of the Geophysical Laboratory, Washington, D. C., for several mineral specimens, and Dr. C. A. Ludwig for furnishing the fresh water algae.

Summary

1. A mass spectrographic technique is described which has made possible an accurate measurement of the relative abundance of the isotopes of potassium in most potassium containing materials.

2. Most minerals exhibit only small differences in the isotope content. The abundance ratio in general is near $K^{39}/K^{41} = 14.25$.

3. Plant ashes show marked variations in the abundance ratio, the K^{41} content differing between plants by as much as 15%. Kelp exhibits the most pronounced deviation from the general average.

4. The factors contributing to the variations in the abundance ratio are (1) the variety of plant, (2) age, (3) soil, (4) section of plant.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

A Mass-Spectrographic Determination of the Constancy of the Atomic Weight of Potassium in Ocean Water

BY A. KEITH BREWER

Aston[1] has shown that the atomic weights of a large number of elements estimated from mass-spectrographic measurements are in excellent agreement with the chemically determined weights accepted by the Committee on Atomic Weights. It is the purpose of the present paper to show that a similar agreement exists in the values obtained by the two methods for potassium, and also to demonstrate the use of the mass spectrograph in estimating the possible variations in the relative concentration of the isotopes of potassium found in ocean water.

The samples of ocean water used in these tests were furnished by Professor C. L. Utterback of the Oceanographic Laboratory of the University of Washington. They were procured in the straits around San Juan County, Washington, and in the Pacific Ocean off Cape Flattery.

The mass spectrograph and technique used in determining the abundance ratio have been described in a preceding article.[2] In determining the abundance ratio (K^{39}/K^{41}) for the isotopes of potassium the samples of sea water were first evaporated to dryness, the salt powdered, then moistened with distilled water and coated directly on the platinum disk used for the positive ion source. The results so obtained were unsatisfactory since the salt distilled off the disk too rapidly to serve as a constant ion source. To overcome this difficulty the potassium was concentrated and converted to an adhering form by digesting the salt with perchloric acid, evaporating to dryness, and

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(1) F. W. Aston, *J. Chem. Soc.*, 2888 (1932).

(2) A. Keith Brewer, THIS JOURNAL, **58**, 365 (1936).

extracting the sodium with alcohol. No precautions were taken to remove all the sodium since it did not interfere with the experiment. The possibility of the results being influenced by the perchloric acid was investigated by comparing the ash of certain animal tissues, which analyzed quite differently from ocean water, with and without the perchlorate treatment; the abundance ratios obtained showed no effect from the treatment received.

The results obtained are collected in Table I.

TABLE I

Sample	Location	Depth	K^{39}/K^{41}
1	Off Browns Island	Surface	14.20
2	Pole Pass between Crane Island and Deer Harbor	Surface	14.20
3	Peavine Pass off Blakley Island	Surface	14.20
4	East Sound off Olga	Surface	14.22
5	Haro Strait	Surface	14.20
6	Haro Strait	100 meters	14.20
7	Straight of Juan de Fuca 25 miles in from Cape Flattery	Surface	14.21
8	Same as 7	185 meters	14.20
9	120 miles west of Cape Flattery 48° 24′ N., 128°01′ W.	200 meters	14.20
10	West of Cape Flattery 47°54′ N., 126°33′	Surface	14.21
11	Same as 10	2000 meters	14.19
12	South and West of Cape Flattery 46°39′ N., 127°47′ W.	Surface	14.20
13	Same as 12	1000 meters	14.20
14	Same as 12	2500 meters	14.20
		Average	14.20 ± 0.0035

The abundance ratios given represent an arithmetical average of many separate measurements. The average deviations between the values obtained for each sample are usually considerably less than ±0.03, while the maximum deviations seldom exceed three times this value.

The closeness of the values given must be taken as indicating that the abundance ratio is the same in each instance, potassium at the surface analyzing the same to within the limits of experimental error as potassium at a depth of 2500 meters. It is not felt that any significance can be attributed to the small differences observed.

The abundance ratio being known it now becomes possible to compute the atomic weight of potassium from mass-spectrographic data without recourse to chemical analyses or purifications. The estimation of the atomic weight from the abundance ratio necessitates a knowledge of the packing fraction and of the conversion factor from the physical to the chemical scale. Unfortunately, the packing fraction for potassium has never been measured. Aston[3] has shown, however, that the value for the packing fraction of any element is very close to that of the elements with adjacent mass numbers. The packing fraction for argon has been measured with a high degree of precision; Aston obtained -7.2 for A^{40} and -6.6 for A^{36}, while Bainbridge[4] obtained -6.9 for A^{40}, the values given being expressed in parts per 10,000. The probable value for the packing fraction for potassium is, therefore, close to -7.0. The masses of the isotopes computed from this packing fraction are $K^{39} = 38.973$, and $K^{41} = 40.971$. The conversion factor used by Aston for transposing from the chemical to the physical scale is 1.00022. Recent measurements of the oxygen isotope abundance ratio made by W. Bleakney lead to 1.00027 as a more probable value.

The atomic weight of potassium in the sea water can now be computed directly from the above values by the following expression.

$$x(1.00027 \times 15.20) = (14.20 \times 38.973) + 40.971$$
$$x = 39.094$$

where x is the atomic weight. The presence of K^{40} is neglected in these calculations since its relative abundance is too small to have an appreciable effect.[5]

The principal source of error in the above calculation doubtless enters from the necessity of assuming a value for the packing fraction. It seems improbable, however, that the value for potassium would deviate from that of argon by more than ±1.0. Assuming the packing fractions to be either of the two extremes -6.0 or -8.0 the atomic weights come out to be 39.098 or 39.090, respectively.

The conversion factor for changing from the chemical to the physical scale may contain an error of some parts in one hundred thousand, due to the experimental error involved in measuring the abundance ratios of the isotopes of oxygen.

The uncertainties arising in the estimation of the abundance ratio are small. It will be observed in the table that while the average deviation between the individual values in a given sample is within ±0.03, the average deviation between the average values for the different samples is only ±0.0035. The errors introduced in calculating the atomic weight from uncertainties of this magnitude in the abundance ratio are negligible since a change of 0.03 in the abundance ratio is

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(3) F. W. Aston, "Mass Spectra and Isotopes."

(4) K. T. Bainbridge, *Phys. Rev.*, **43**, 424 (1933).

(5) A. Keith Brewer, *ibid.*, **48**, 640 (1935).

equivalent to a change of only 0.00026 in the atomic weight.

In summarizing the possible sources of error in computing the atomic weight from pure mass-spectrographic data it will be seen from the above discussion that the uncertainty in the packing fraction introduces a maximum possible error of ±0.004 in the atomic weight, the uncertainty in the conversion factor may introduce an error of ±0.002, and the error in measuring the abundance ratio introduces a possible discrepancy of 0.00026.

In determining the uniformity of the atomic weight of potassium in ocean water, the uncertainties in the values used for the packing fraction and the conversion factor are not involved, the abundance ratio being the only variable to enter the calculations. It will be seen in referring to the table that no variations were detected with respect to depth while the slight variations for different localities are probably within the limit of experimental error. On the basis that the abundance ratio can be determined to within ±0.03 the atomic weight of potassium in all the samples analyzed is constant to less than ± 0.00026.

The results just presented are significant in several respects. The mass spectrograph is shown to be a sensitive tool for comparing the atomic weight of potassium in different sources; it possesses a possible advantage over the chemical method by a factor of about ten. While no such accuracy can be claimed in the mass-spectrographic determination of the absolute value of the atomic weight, due to the uncertainty involved in some of the constants, it is interesting to note that the present value of 39.094 is in excellent agreement with the modern value of 39.096 accepted by the Committee on Atomic Weights.[6]

The fact that the atomic weight of potassium in ocean water is found to be extremely constant, the possible variation in the K^{41} content being considerably less than 0.15%, is of interest in that it offers a marked contrast to the potassium in minerals where variations of 3% were observed and to plant ashes where the variations amounted to as much as 15%.

The writer is especially indebted to Professor C. L. Utterback of the University of Washington for furnishing the samples of ocean water tested.

Summary

The abundance ratio for the isotopes of potassium in Pacific Ocean water has been measured and found to be $K^{39}/K^{41} = 14.20$. No appreciable variations were observed between samples procured at different localities or at points down to 2500 meters in depth.

Variations in the atomic weight of potassium between the samples computed directly from the abundance ratios are less than ±0.00026. The value for the atomic weight computed from the observed abundance ratio, using 1.00027 for the conversion factor from the chemical to the physical scale, and the packing fraction of argon for that of potassium, is close to 39.094. This value is in close agreement with the value accepted by the Committee on Atomic Weights.

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[6] Baxter, Curie, Hönigschmid, LeBeau and Meyer, THIS JOURNAL, **56**, 753 (1934).