cated in the table. The results indicate the average value obtained from a series of ten determinations. The variations in results demonstrate the inaccuracy of the method in its present form. Ten cubic centimeters of the reagent was used with the equivalent of 0.1 cc. of linolenic acid. The mixture was heated for one hour in a boiling water-bath. Comparison was made in a colorimeter with the standard.

Qualitative color tests for unsaturated fatty acids have not been reported previously. It is hoped that the introduction of this new type of reaction into fat analysis will lead to modifications of the tedious processes now necessary in qualitative analysis of fats and oils.

At the suggestion of G. S. Jamieson, of the United States Department of Agriculture, the above test was applied to oiticica and tung oils, which he supplied.[4] Tung oil contains elaeostearic acid, isomeric with linolenic acid, and oiticica oil contains a keto acid having three double bonds. The test was applied in a purely qualitative manner, with the result that the tung oil was found to give no reaction, while the oiticica reacted positively. The significance of this further observation cannot be interpreted at present, due to lack of knowledge of the structural formulas of the acids concerned. The suggestion was made by Dr. Jamieson, as he has demonstrated the presence in these oils of the three double bond fatty acids mentioned. Therefore, the conclusions are drawn more conservatively to state that the test is positive for linolenic acid and certain other three double bond fatty acids.

(4) This work was done following submission of the paper for publication, and is therefore not incorporated in the body of the paper.

BALTIMORE, MARYLAND RECEIVED JUNE 8, 1935

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

The Abundance Ratio of the Isotopes of Potassium in Mineral and Plant Sources

BY A. KEITH BREWER

Within the past few years differences in the physiological behavior of the isotope of hydrogen have been shown to exist. Further it has been shown that the abundance ratio is not necessarily constant, since H^2 is apparently concentrated in certain plants. In the case of other elements no physiological isotope effect has been established definitely although it has been suggested for oxygen and has been the subject of some investigation for potassium.

Stoklasa[1] has obtained evidence to support his idea that the radioactivity of potassium is responsible for its action in plant growth. Loring and Druce[2] found the atomic weight of potassium in potato vines to be 40.5 ± 0.1, the potassium chloride so extracted being more radioactive than the normal. In contrast Hönigschmid and Sachtleben[3] observed no definite variation in the atomic weight of potassium from hop flower ash and from potassium tartrate. Heller and Wagner[4] obtained the normal atomic weight for potassium extracted from the roots and leaves of potatoes and beets. Again Lowry[5] obtained 39.111 ± 0.013 and 39.091 ± 0.016 for the atomic weights from cotton ash and from wheat flour ash, respectively, and concluded that in these cases there was no isotope effect. Baxter and MacNevin[6] found no variation in the isotope composition of potassium assimilated by plants from an examination of wood ash. A definite isotope effect in plants for potassium is, therefore, still undetermined.

Potassium is now known to have three isotopes with mass numbers 39, 40 and 41.[7,8] Measurements of the abundance ratio of these isotopes are few. In the case of K^{39}/K^{41} Dempster[9] obtained a ratio of 18 while Bainbridge[10] finds the ratio to be near 12.5. Recently Bondy, Johannsen and Popper[11] obtained ratios varying between 13.9 and 20.7 with an average near 16. The first measurements made in this Laboratory showed the ratio to be about 13.9 ± 0.4[12] while recent improvements in the experimental technique have

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(1) J. Stoklasa, *Ernähr-Pflanze*, **30**, 299 (1934).

(2) H. F. Loring and J. G. F. Druce, *Chem. News*, **140**, 34 (1930).

(3) Hönigschmid and Sachtleben, *Z. anorg. allgem. Chem.*, **213**, 365 (1933).

(4) K. Heller and C. L. Wagner, *Z. anorg. allgem. Chem.*, **200**, 105 (1931); **206**, 152 (1932).

(5) H. H. Lowry, THIS JOURNAL, **52**, 4332 (1930).

(6) G. P. Baxter and W. M. MacNevin, *ibid.*, **55**, 3185 (1933).

(7) A. O. Nier, *Phys. Rev.*, **48**, 283 (1935).

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

(9) Dempster, *ibid.*, **18**, 415 (1921).

(10) K. T. Bainbridge, *J. Franklin Inst.*, **212**, 317 (1931).

(11) Bondy, Johannsen and Popper, *Z. Physik*, **95**, 46 (1935).

(12) Brewer and Kueck, *Phys. Rev.*, **46**, 894 (1934).

shown it to be very near 14.25.[8] The ratio for K^{39}/K^{40} is far more difficult to determine but is close to 8300.

In the present paper are presented the abundance ratios for the isotopes of potassium (K^{39}/K^{41}) as obtained from various mineral and plant sources. Abundance measurements of this type serve to show not only the degree of constancy of the isotope ratio of potassium as found in nature, but also may aid in detecting the conditions under which this ratio is changed by natural processes.

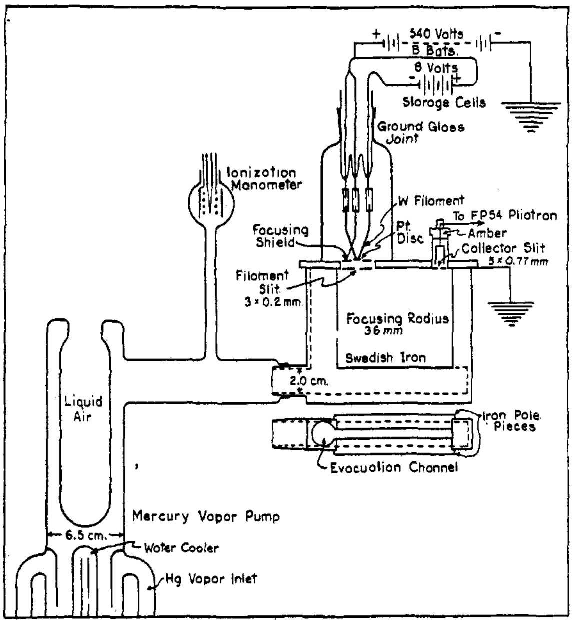

Fig. 1.—Mass spectrograph.

Apparatus

The problems involved in designing a mass spectrograph capable of giving a resolution sufficient for a complete separation of the isotopes of the various elements have received a vast amount of attention. The fundamental principles are well known. When a positive ion enters a magnetic field it is deflected by a force equal to Hev where H is the field strength, e the charge on the ion and v its velocity. This force is balanced by the centrifugal force of the ion mv^2/R where m is the mass and R the radius of curvature of the arc through which the ion is deflected. Thus

$$Hev = mv^2/R$$

and

$$R = mv/He$$

In order to obtain complete resolution in a mass spectrograph it is necessary that all the ions of a given kind come to a focus at the same point. It follows from the above equations that for the ions of a given mass to come to a focus (have the same radius), they must have the same initial velocity. The general theory of the spectrograph and the various means that have been used previously to obtain constant velocity sources or to correct for the inconstancy are discussed in detail by Aston[13] and by Bainbridge.[14]

An extremely simple means of obtaining a constant velocity source was employed in the present experiments. It possesses the advantage of permitting the entire primary ion beam to be focused on the entrance slit instead of a small fraction of the beam as obtained from the usual type of velocity filter. The system employed is illustrated in Fig. 1. The potassium ions were emitted from a platinum disk 2 mm. in diameter spot welded to a tungsten filament which was placed symmetrically above and from 6 to 8 mm. removed from the entrance slit. The disk was surrounded by a nickel washer type shield 12 mm. in diameter with a 4 mm. opening. The shield was placed about 0.5 mm. below the level of the disk, and was connected to the positive end of the filament. This arrangement enabled the ion beam to be deflected straight down, forming a spot on the slit usually not larger than the size of the disk. The filament and disk were maintained at 540 volts positive to the slit. The velocity of the ions emitted from such a source is given by the potential drop plus the contact potential variation over the surface of the disk; this latter quantity is usually negligible compared to the potential drop between the disk and slit.

The analyzing chamber was of the 180° focusing type developed by Dempster.[15] The various parts, as illustrated in Fig. 1, are drawn approximately to scale. The side walls were made of Swedish iron, thus serving as the pole pieces when placed between the poles of an electromagnet. The magnet was operated by heavy duty storage cells.

The chamber was designed for rapid and low pressure evacuation; this was accomplished by extending a large evacuation channel across one end and side. The mercury vapor pump was capable of a speed of 25 liters/sec. at 10^{-4} mm. The pressure was read with an ionization manometer and operated at about 3×10^{-6} mm.

The resolved ion current was measured with an FP54 Pliotron, using a balanced circuit hookup. The galvanometer deflections were regularly checked for non-linearity of response.

Materials

The minerals tested were pulverized, moistened with distilled water and coated lightly on the lower side of the platinum disk. The plant tissues were first washed in distilled water to remove any adhering mineral matter. They were then ashed in a platinum crucible which had been previously washed in hydrochloric acid and distilled water and ignited to bright redness. The ash was pulverized and coated as described. Any potassium-containing material so treated will serve as a source of potassium ions.

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(13) F. W. Aston, "Mass-spectra and Isotopes," Longmans, Green and Co., New York City.

(14) K. T. Bainbridge, *J. Franklin Inst.*, **215**, 509 (1933).

(15) A. J. Dempster, *Phys. Rev.*, **20**, 631 (1922).

Experimental Procedure

Commercial platinum contains an appreciable amount of dissolved potassium. This necessitated that before every determination the disk must be washed and glowed in place until no potassium ion emission could be detected. At a bright red heat the potassium was completely removed in less than half an hour. A primary positive ion current varying between 10^{-8} and 10^{-10} amp. was sufficient to give a resolved isotope current of the order of 10^{-12} amp. Positive ion currents of this magnitude are obtainable from most potassium containing materials at just visible temperature or at very dull red heat.

In measuring the resolved positive ion current due to K^{39} and K^{41} the magnet current was first set so that K^{39} was received by the collector. The filament head was then rotated until the center of the primary ion beam was focused on the slit, as shown by the resolved current being a maximum. The magnet current was then set on both sides and between the K^{39} and K^{41} peaks to see if the resolution was complete. With the apparatus in adjustment, the magnet current was set for a maximum deflection for K^{41} followed quickly for K^{39}, and then again for K^{41}, the process being repeated many times. This procedure was necessary to eliminate the danger of a drift in the primary ion current; if K^{47} was the same before and after K^{39}, it was assumed no change in the primary current had occurred.

After the abundance ratio was measured for the coated filament, the coating was carefully scraped off and the ratio determined for the contaminated platinum disk. During the time in which the disk was heated in contact with the ash sufficient potassium diffused from the ash into the platinum to cause the disk to become an excellent emitter of potassium ions. The results obtained with the scraped disk, while checking those from the ash, were in general the more constant due to the greater uniformity of the work function of the platinum.

Results

An accurate estimation of the abundance ratio is possible only when resolution is complete, the background between the peaks being inappreciable, and when the peaks are of such a nature that their relative heights can be measured with precision. Analysis curves for tripotassium phosphate are shown in Fig. 2 to illustrate the extent to which these demands are complied with.

The dotted curve A was obtained with wide slit widths; it will be observed that the peaks are flat topped, indicating that the ion beam is narrow with respect to the width of the collector slit. This slit arrangement was used in measuring the abundance ratios since the relative ion currents as represented by the height of the peaks can be measured with considerable accuracy. Curve B was obtained with narrow slits; while this arrangement is more sensitive in locating the position of the peaks it is not as suitable for accurate abundance ratio measurements. The magnified portion of the curve shows the comparative abundance of K^{40} and illustrates the relative size of the background.

The relative heights of the peaks as illustrated in Fig. 2, scatter slightly from run to run. The magnitude of the variations observed with coated and scraped filaments for Vesuvius lava is shown in Table I.

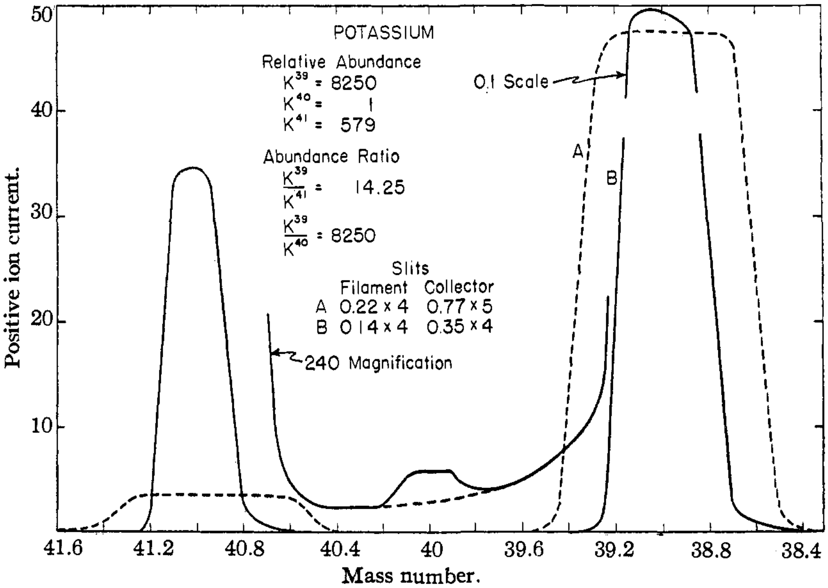

Fig. 2.

TABLE I

K^{39}/K^{41}

Coated	Scraped
14.3	14.25
14.3	14.22
14.3	14.3
14.3	14.27
14.25	14.3
14.28	Average 14.27 ± 0.03
14.2	
Average 14.27 ± 0.04	

The results obtained from several minerals are shown in Table II.

The ratio K^{39}/K^{41} is an average of series of runs of the type shown in Table I taken first with the platinum disk coated with the mineral in question,

TABLE II

THE ABUNDANCE RATIO OF POTASSIUM IN MINERAL SOURCES

Source	K^{39}/K^{41}	% K^{41}	% K^{41} deviation
Platinum	14.24 ± 0.05	6.56	0.3
$K_2O·Al_2O_3·2SiO_3$	14.32 ± .03	6.53	− .9
Cement dust	14.32 ± .03	6.53	− .9
Searles crude	14.25 ± .03	6.56	− .4
Wyomingite A	14.6 ± .05	6.40	−2.7
Wyomingite B	14.25 ± .03	6.56	− .4
Wyomingite KNO_3	14.2 ± .01	6.58	.0
Vesuvius lava	14.27 ± .03	6.55	− .5
Colorado granite	14.24 ± .03	6.56	− .3
K_3PO_4	14.24 ± .03	6.56	− .3
Hawaiian basalt	14.11 ± .03	6.62	.6
Wyoming shale	14.23 ± .03	6.57	− .2

and then with the mineral removed. Average deviations are given, although the maximum deviations may be as much as three to five times this amount. It will be seen, therefore, that the probable error in measuring the abundance ratio is small, being in general not more than 0.03% while the greatest possible error would seldom if ever exceed 1.0%.

Referring to Table II the ratio from the platinum source represents that obtained for potassium present as an impurity in commercial platinum. It is completely removed by glowing for a few minutes at white heat. The $K_2O·Al_2O_3·2SiO_2$ was a synthetic emitter made from commercial potassium nitrate. The cement dust was a concentrated cement flue dust containing about 35% potassium oxide. The Wyomingite (Wyoming lava) A was a small crystal broken from a large block of lava, while B was a sample obtained from several hundred pounds of pulverized and thoroughly mixed rock. The potassium nitrate was extracted from a sample similar to B.

The abundance ratio for potassium in various plant ashes is shown in Table III.

Special attention is called to the fact that the abundance ratio from various plant sources is not constant, but often shows marked variations from the normal, the concentration of K^{41} differing by almost 15%. In cases where the results showed any appreciable deviation from the normal ($K^{39}/K^{41} = 14.20$) tests were repeated with fresh samples to remove possible sources of error, many values being rechecked a month later.

TABLE III

THE ABUNDANCE RATIO OF POTASSIUM IN PLANT SOURCES

Source	K^{39}/K^{41}	% K^{41}	% K^{41} deviation
Maple	14.20 ± 0.03	6.58	0.0
Oak	14.15 ± .05	6.60	0.3
Corn	14.5 ± .03	6.45	−2.0
Beans	14.32 ± .02	6.52	−0.9
Poke	14.31 ± .02	6.53	− .76
Bran	14.15 ± .05	6.60	.3
Coconut shell	14.2 ± .05	6.58	.0
Rose leaf A	14.23 ± .02	6.57	.2
Rose leaf B	14.27 ± .02	6.55	− .5
Rose leaf C	13.70 ± .02	6.80	3.3
Distillery waste	14.4 ± .07	6.49	−1.4
Willow leaves	14.4 ± .02	6.49	−1.4
Rosin	14.2 ± .02	6.58	0.0
Water weed	14.3 ± .02	6.54	− .6
Potato skin	14.5 ± .05	6.45	−2.0
Potato pulp	14.3 ± .05	6.54	−0.6
Potato sprouts	14.6 ± .02	6.40	−2.7
Potato vine A	14.3 ± .02	6.54	−0.6
Potato vine B	13.77 ± .03	6.76	2.70
Potato vine C	13.77 ± .02	6.76	2.70
Potato vine C′	13.72 ± .02	6.78	3.10
Potato vine C″	14.1 ± .03	6.62	0.6
Sweet potato vine	14.2 ± .05	6.58	.0
Kelp (natural)	13.67 ± .03	6.81	3.5
Kelp, leached A	12.63 ± .20	7.33	11.4
Kelp, leached B	13.37 ± .03	6.96	5.8
Kelp KCl	13.54 ± .05	6.88	4.5
Agar agar	13.95 ± .03	6.69	1.7
Tobacco leaf	14.20 ± .05	6.58	0.0
Algae A	14.20 ± .03	6.58	.0
Algae B	14.20 ± .03	6.58	.0
Duck weed	14.22 ± .04	6.57	.1

It will be observed that kelp (Pacific) runs materially heavier in K^{41} than do most other plants. The natural kelp was made from dried kelp which had not been washed after drying. Leached kelp A was from the ash of the remaining fiber after the kelp had been boiled for some time in distilled water, while B was from a sample that had been washed in hot water. The kelp potassium chloride was the commercial salt. In comparison the water weed grown in fresh water is nearly normal, while agar is not as high in K^{41} as is kelp. Algae A and B are different fresh water varieties, and give the normal ratio.

In the case of the rose leaves sample A was obtained from a Washington hot house rose grown in an ideal fertilized soil, while B was grown under similar conditions but in a very poor clay soil. Sample C was a California hot house grown leaf. It will be observed that the California leaf runs considerably heavier than do the Washington leaves. No explanation of this peculiarity can be given unless it is due to a difference in the fertilizer.

The results obtained with potatoes are of interest in that they exhibit a trend with age. Potassium in the potatoes themselves trends to show a slightly high ratio. This is doubtless a general condition since it was evident in local, West Virginia and Idaho potatoes. The potato sprouts were cellar grown, from 8 to 15 cm. in length; they run appreciably high in K^{39}. Potato vine A was a young outside grown vine about 15 cm. high, the leaves and smaller stocks being ashed together. Vine B was an old but still green hothouse grown vine. Vine C was much the same as B only slightly older and partially dead. In obtaining C′, vine C was thoroughly washed and then boiled in distilled water. The pulp was filtered off, and the liquid evaporated to dryness and ignited. C″ was the ashed pulp filtered off from C′.

Discussion of Results

The principle source of error in the present results lies in the possibility that the observed ion ratios do not represent the actual atom ratio within the source. Such an error may enter in two ways, first by resolution occurring between the filament and the filament slit, and second by the presence of an isotope effect of free evaporation of the ions from the disk. The first difficulty was shown to be non-existent under the conditions of these experiments by rotating the filament head to expose a different section of the primary beam to the slit without producing a change in the ion ratio. Several potassium sources as well as contaminated platinum were tested for a change in the ion ratio during exhaustion of the alkali. The fact that no appreciable change was observed with potassium indicates that an isotope effect in the liberation of the ions is negligible, and that the ion ratio represents the true atom ratio.

The results presented in Tables II and III give the per cent. of K^{41} present and the per cent. deviation from that found in samples having an abundance ratio of 14.20. It will be observed that the K^{41} content exhibits a maximum variation of 15% between sources; this represents only a small change in the atomic weight of potassium, however, since a 1% change in the abundance ratio is equivalent to only a 0.003% change in the atomic weight.

The abundance ratios obtained for minerals show only minor deviations from the general average. Hawaiian basalt presents a small but distinct difference from the lava of Vesuvius and Wyoming. The crystal of Wyomingite A, presumably calcite, is a secondary formation. It is interesting to note that the calcite is low in K^{41} while the Hawaiian lava is high. The calcite is crystallized from a water extraction while the lava is a fraction remaining after exposure to water; a slightly greater solubility for K^{39} than for K^{41} will account for the observed difference in isotope content.

The results obtained with plant ashes are significant in that they demonstrate a distinct variation in the isotope ratio between different types of cells. It is interesting to note that plants have likewise been shown to exhibit a selectivity in the case of heavy hydrogen.[16]

A consideration of the results presented in Table III will reveal several of the factors giving rise to deviations in the relative concentrations of the isotopes. They are: (1) the specific nature of the plant. Kelp, for instance, is high in K^{41}, while willow leaves are low. (2) Age of the plant: young shoots containing 6.41% K^{41} grow from potatoes containing 6.54% K^{41}; this represents a decrease in K^{41} content of about 2%. As the vine matures the relative concentration of K^{41} increases, reaching 6.96% in old vines; this is an increase of 6.3% in K^{41} over that of the original pulp. These results confirm the findings of Druce and Loring[2] in that they show the heavy isotope to be concentrated in mature potato vines, although they fail to show anything like the concentration observed by these investigators. (3) The soil: this point is uncertain but it seems probable that the high concentration of K^{41} in the California rose leaves as compared to the Washington grown leaves is due to a difference in the soil or fertilizer. (4) Section of the plant: in the case of potato vines the leachings C′ contain 5% more K^{41} than does the leached pulp C″.

The basic cause underlying this selectivity is not obvious from the character of the results. The fact that kelp is extremely high in K^{41} is pertinent, however, since this is not a characteristic of all algae. Kelp, of all the plants listed, is grown under the nearest ideal conditions as to constancy of temperature and abundance of available potash; in consequence it is in the best position to exert a preference in its assimilation of mineral matter. Kelp does exhibit such a preference for potassium over sodium, an atom of the former being taken up about fifty times more readily than an atom of the latter. This preferentiality is generally assumed to have its basis in

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(16) Emeleus *et al.*, *J. Chem. Soc.*, 1207 (1934).

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.

WASHINGTON, D. C. RECEIVED AUGUST 19, 1935

[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).