POTASSIUM ANALYSIS OF SELECTED ROCKS
BY SOLID SOURCE MASS SPECTROMETRY

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Abstract

This work was undertaken with the hope of establishing a more convenient as well as reliable method for potassium analyses of Hawaiian rock and mineral samples.

A simple mass spectrometer employing a 4.6 cm radius of curvature and a fixed 3300 gauss magnetic field was built for potassium determinations by the isotope dilution technique. Thermal evaporation and ionization of the potassium was accomplished by passing a controlled current of up to 3 amperes through .008" diameter platinum filaments coated with the prepared sample. Ion currents were measured on a General Radio Type 1230A DC electrometer equipped with a recorder. Accelerating potential was made precisely variable by using a Spectrol Type 860 10-turn control and a General Radio Type 907-R-144 self-reversing dial drive mechanism.

Potassium contents were determined for seven Hawaiian rock samples analyzed previously by flame photometry. Comparison of results indicated a tendency toward increasing relative difference with decreasing potassium concentrations. The isotope dilution values were also found to be generally lower than those of flame photometry. Good agreement with the reported potassium concentrations in two standard samples seemed to indicate that the solid source isotope dilution method was reliable. This method is especially suited for the alkali metals and an extension of this procedure to rubidium analysis is theoretically feasible.

I. Introduction

A. Historical

Potassium was first isolated by Sir Humphrey Davy in 1807. It is considered to be one of the major elements. In fact, potassium is the seventh of twelve elements which together account for 99.4% of our environment. More than 4% of the earth's crust consists of this element. It is one of the indispensible constituents of animal and plant tissue.

Potassium, because of its radioactivity, is unique among the elements necessary to sustain life. Of the three naturally occurring isotopes of masses 39, 40, and 41, K^{40} was found to decay by beta emission to Ca^{40}. Beta activity is easily detected and was done as early as 1905. In 1937 Weizsäcker (1) suggested the possibility of another mode of decay for K^{40}. It was proposed that K^{40} decayed simultaneously to Ar^{40} by the process of K-capture. Evidence for K-capture was indeed established by Thompson and Rowlands (2) in 1943. Subsequently, Aldrich and Nier (3) in 1948 demonstrated that the principal content of argon in potassium minerals is associated with the decay of K^{40}. Because of the general occurrence of potassium and the favorable half-life associated with this decay scheme, they suggested the process as a potentially useful method for geochronometry.

In the potassium-argon dating method (4), two nuclear constants govern the rate of K^{40} accumulation. The first of these is λ_t, the total decay constant, which determines the rate at which K^{40} disappears. The second is the branching ratio R, which is the ratio

λ_K/λ_β. The decay constant λ_K is for the decay of K^{40} to Ar^{40} by electron capture and λ_β is the decay constant for the decay of K^{40} to Ca^{40} by electron emission (see Figure 1). The branching ratio R is therefore the ratio between Ar^{40} and Ca^{40} produced. If the branching ratio R and the total decay constant λ_t are known, the age of a sample can be calculated by determining the content of radiogenic argon and the amount of K^{40} present. The fundamental equation in calculating age by this method is:

$$t = \frac{1}{\lambda_t} \ln \left[1 + \frac{Ar^{40}}{K^{40}} \left[\frac{1 - R}{R} \right] \right].$$

The age t is in years and the Ar^{40} and K^{40} concentrations are in moles.

B. Background of Problem

Several laboratories undertook age determinations by this method and, although it proved feasible, significant variation was noted in the comparison of results reported for samples of supposedly identical age. Since radiogenic argon is present in microliter quantities or less per gram, this analysis was the first to come under suspicion. However, it soon became apparent that it was possible to analyze for Ar^{40} with greater precision and confidence than it was to analyze for potassium. This situation initiated a check of the various methods available for potassium analysis. In a study by Pinson (5) a homogeneous sample of biotite was sent to various laboratories for use

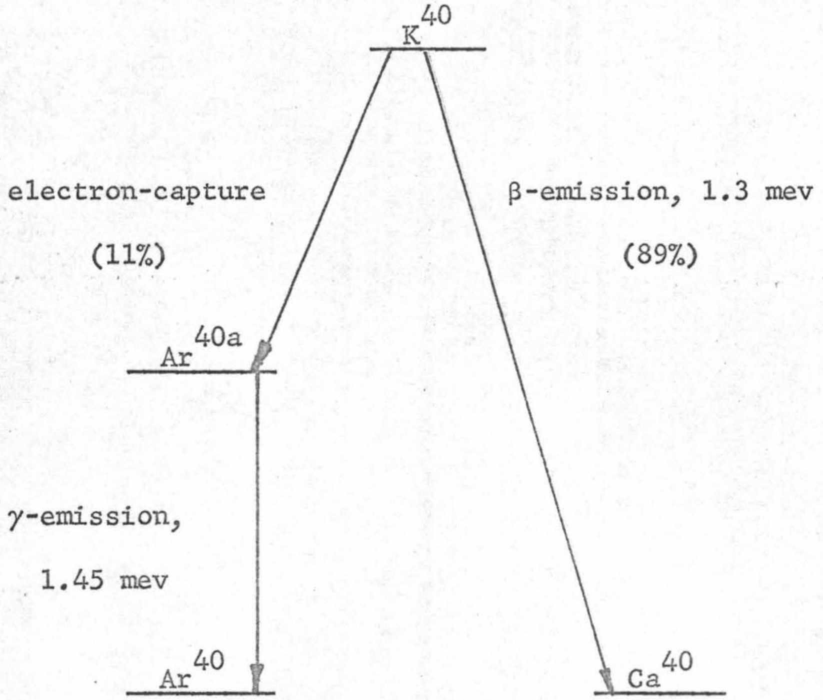

Figure 1. Decay Scheme of K^{40}.

as an interlaboratory standard. The results of that study are shown in Table 1. The significant part of that study was that the range of 7.4 to 7.8% amounts to a relative difference of approximately 6%, which is quite substantial.

An error of 5%, which is generally accepted for potassium analysis, is of no particular concern for most purposes. In age determinations, however, it becomes a problem. If, for example, we were to apply this error to an age determination involving rocks of the Silurian Period (405-435 x 10^6 yrs.) (6,7), the magnitude of the error would be greater than the length of the period itself. As more workers became interested in the potassium-argon method, a number of persons attempted to improve the source of greatest error, that of the analysis of potassium.

Wilson and Co-workers (8) tried direct radioactive counting of the gamma emission and reported a standard deviation of 0.28 when compared with gravimetric chemical analysis. The method was, however, of restricted applicability due to the widespread presence of other radioactive elements which emit gamma rays.

Beukenkamp and Rieman (9) and later Sweet, Rieman, and Beukenkamp (10) developed a method where the flame photometric analysis was preceded by separation of interfering ions by ion exchange chromatography. Results with an error of 5% were obtained but major difficulty was reported with the Dowex 50 ion exchange material used. Barnes (11) confirmed the difficulty with variation between different batches of Dowex 50 and modified the procedure with favorable

Table 1. Analysis of B-3203 [After Pinson (5)]

Potassium Content (%)	Method
7.80 ± 0.07	Neutron Activation
7.40	Flame Photometry
7.42	Gravimetric (K_2PtCl_6)
7.79	Flame Photometry
7.58 ± 0.03	Flame Photometry
7.40 ± 0.06	Gravimetric ($KClO_4$)
7.71 ± 0.07	Flame Photometry
7.68 ± 0.06	Gravimetric (K_2PtCl_6)
7.76	Flame Photometry
7.59, 7.60	Isotope Dilution
7.56	Flame Photometry

Average: 7.61

results by using a different ion exchange material.

Dean (12) reported the results of other workers who used the flame photometric technique and their attempts to avoid the interference effects. Edwards and Urey (13) separated the potassium by vacuum furnace distillation and then analyzed for potassium flame photometrically using a lithium internal standard. Adams (14) tried a set of very carefully prepared standards and reported good results on certain silicate glasses. Cooper (15) studied the effects of interference from other ions as a function of the burner, fuel, and actual concentration of the potassium used using both the Beckman DU flame photometer setup and the Perkin-Elmer 146. He obtained a precision of better than 1% but comparison of the results with those of the isotope dilution method showed a spread of several percent.

Attempts were also made to improve the classical Lawrence-Smith gravimetric analysis (7). Yankov (16) tried a gravimetric method which precipitated the potassium with tetraphenylboron. Ishimori and Takashima (17) tried a combined gravimetric-radioactive counting method in which the potassium is precipitated as potassium sodium cobaltinitrite where the cobalt used was radioactive. They reported good precision but poor accuracy.

Other methods such as isotope dilution mass spectrometry and neutron activation have been used. Some of the methods give excellent results for a specific type of sample but, in general, potassium analysis is limited to an accuracy of ±5% at the present time.

C. Object of Research

Dating of Hawaiian rock samples by the potassium-argon method was started at the University of Hawaii in July 1962. A method for potassium analysis had to be selected which was convenient and reliable. Since local samples have potassium contents in the range of only 0.02 to 3.5%, there is potentially an even greater error involved for Hawaiian rock samples than the Pinson study indicates for currently used methods. Gravimetric analysis, for example, is essentially an extraction method where the chlorides of sodium and potassium are separated and the potassium is precipitated as the chloroplatinate or perchlorate and weighed. This method gives systematically low results and a magnification of error would be expected for low concentrations. Flame photometry, while very rapid, is sensitive to contamination and interference from other ions. Neutron activation and conventional mass spectrometry were judged to be too expensive for serious consideration at that time. The method selected here was flame photometry preceded by ion exchange chromatography separation. A Beckman DU spectrophotometer with a Model 9200 flame photometer attachment was used.

The obvious advantages of mass spectrometric analysis, however, helped maintain interest in the method. This method was eventually proposed as an improvement over the flame photometric method in both reliability and convenience. The tedious ion exchange separation step could then be eliminated.

Mass spectrometry is not normally used for routine potassium analysis because of the great expense usually associated with setting up this type of apparatus. However, a unit was recently developed by Dewdney (18) which seemed to fit both our needs and our budget. This unit, while limited in application due to the fixed magnetic field and small radius of curvature, seemed to be suitable for potassium analysis and was simple enough to be fabricated in the average departmental shop. Accessories such as the DC power supply, oscilloscope, electrometer, and ion gauge power supply are not a permanent part of the system and could be removed very easily for other purposes when not in operation. The mass spectrometer was designed for qualitative demonstration but it seemed that this unit could be used for routine quantitative potassium analysis by isotope dilution technique. It was therefore decided that a unit similar to that of Dewdney would be built and a number of samples which had been analyzed repeatedly by other methods would be analyzed.

II. Experimental

A. Apparatus

1. Assembly

Since the assembled apparatus is not commercially available as a unit, the first project undertaken was construction of the mass spectrometer. The components of the basic chamber are made of brass and the permanently attached sections are soft-soldered together using 50-50 tin-lead alloy. The diameter of the circular plates used is 3 1/2 inches. Vacuum is provided by a Consolidated Vacuum Corporation Model MCF-60 oil diffusion pump using Dow Corning 704 pump fluid and backed by a Welch 1400B mechanical pump. The diffusion pump chamber is cooled by tap water flowing through coils of 1/4 inch copper tubing silver-soldered to the exterior of the chamber for efficient transfer of heat. Figure 2 (19) shows the general orientation of the parts. Electrical connections to the source and detector are made through kovar glass-to-metal seals which are soldered to the plates. Vacuum is measured with an RCA Model 1949 ionization gauge using a control circuit proposed by Lafferty (20). This unit was fabricated from parts commonly available from electronic supply shops. A power supply and control circuit was also fabricated for the source and the schematic diagram of it is shown in Figure 3. A Heathkit Model IP-32 DC power supply modified with a 10-turn potentiometer for the voltage control was used for accelerating and focusing potentials. On the four input terminals at the source plate two binding posts are attached for the mounting of platinum or tungsten filaments and two deflection plates are mounted for focusing control. These four pieces are held in place by set screws for easy removal when cleaning or replacing the terminals. On the single terminal at the detector plate a V-shaped brass collector is mounted. The main sections are held together by machine screws and O-rings are used to insure a good vacuum seal. An air release valve is soldered into the system for "breaking" the vacuum for disassembly between runs. Adjustable slits are installed in the source and

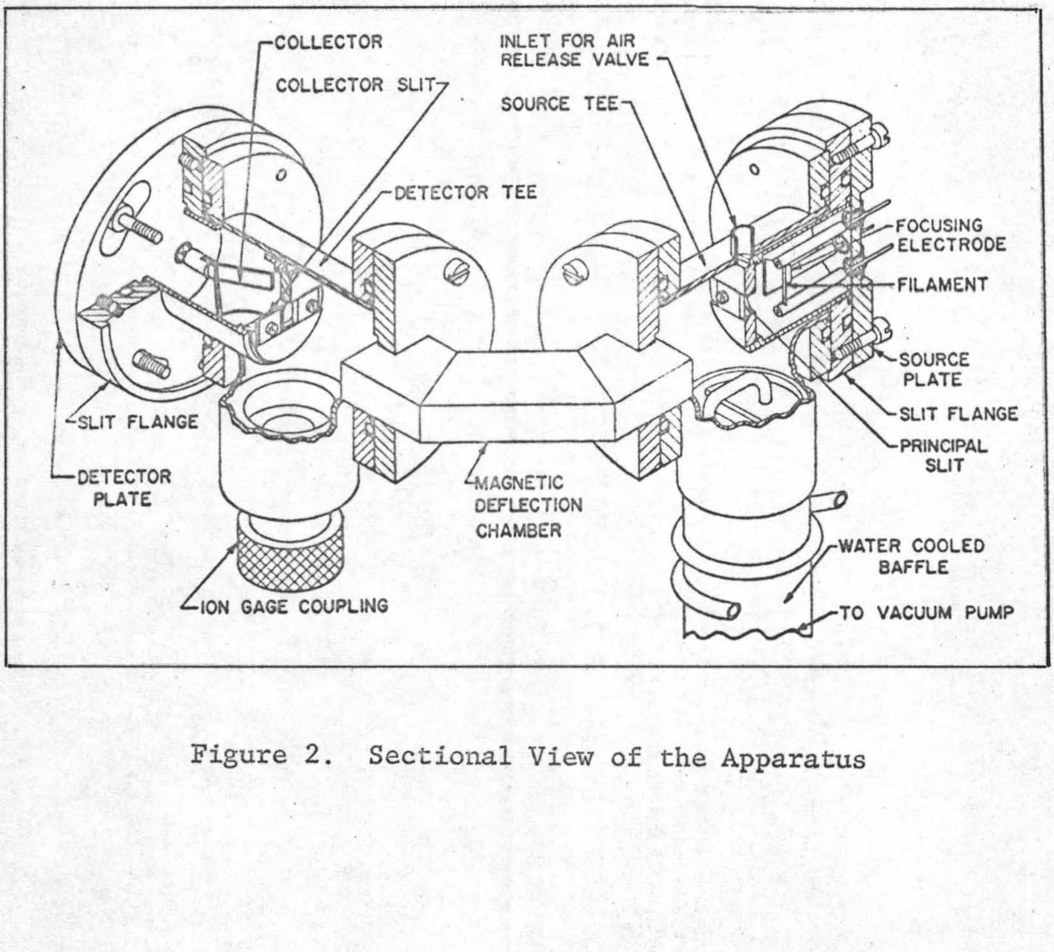

Figure 2. Sectional View of the Apparatus

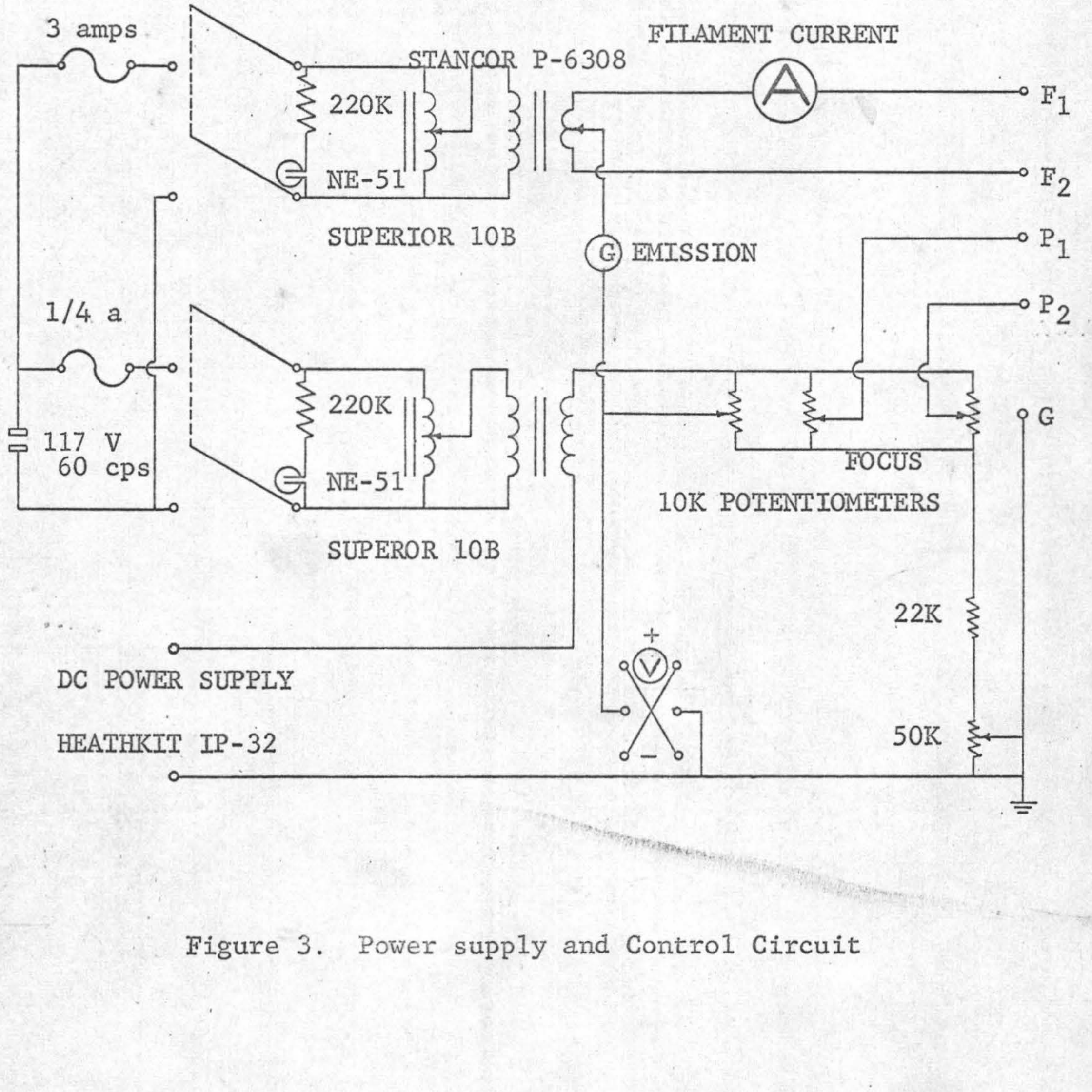

Figure 3. Power supply and Control Circuit

detector "tees." These "tees" can also be rotated about an angle of 10° without breaking the vacuum for fine focusing adjustments since silicon-greased O-rings are used between these sections. A permanent magnet was recovered from a surplus magnetron tube and mounted on a track which allowed three dimensional changes in position for focusing. Two inch square pole pieces were fitted to the magnet providing a 3300 gauss field in the 5/8 inch gap.

2. Theory of operation

Ions are produced with low kinetic energy by heating alkali salts on a metallic filament. They are electrically accelerated and then proceed from the source via a slit to a mass analyzer where they are acted upon by a transverse magnetic field. During acceleration through the electric field the ion acquires energy eV. If we assume that the energy gain is large compared to the initial energy of the ion,

$$eV = 1/2\ mv^2 \qquad [1]$$

where v is the velocity of the ion after acceleration. All ions carrying the same charge are accelerated to the same energy. If the magnetic induction in the analyzer is B, the ion experiences a force evB as it passes through the magnetic field. This is a centripetal force which is directed normal to the direction of the induction and to the direction of motion. The result is a circular orbit where the centripetal force is balanced by a centrifugal force and if r is the orbital radius, it follows that:

$$evB = \frac{mv^2}{r} \qquad [2]$$

Since both electric and magnetic fields are simultaneously present, a combined relationship can be obtained by eliminating v between equations [1] and [2]:

$$r = \left[\frac{2mV}{eB^2} \right]^{1/2} \qquad [3]$$

It is clear that ions are deflected according to the ratio m/e. For values of V and B satisfying equation [3], ions of a given m/e ratio are directed along a circular path of radius r to a slit. The ions pass through a collector slit to a collector plate of the Faraday-cup type and the collector current can be measured with an electrometer. The basic design is essentially the same as that for Dempster's original mass spectrometer (21) with the exception of the use of a 90° sector magnet instead of a 180° "dee." Since r and B are fixed in this apparatus, the particular m/e ratio brought into path r is a function of accelerating potential V. The ratio m/e is inversely proportional to V so the heavier isotopes would be expected to appear at lower accelerating potentials than the lighter ones. For example, K^{41} would be expected to appear before K^{39} when sweeping the accelerating potential toward higher potentials. In more versatile mass spectrometers both accelerating potential and magnetic field are variable, but this was not deemed necessary in this case.

3. Vacuum System

Before it was possible to do any adjusting it was first necessary to establish vacuum in the vicinity of 10^{-5} torr. The system was evacuated with the mechanical pump only and "baked" for 24 hours using heating tape wrapped around the exterior of the chamber and maintained at a temperature of 120°C. Higher temperatures would have been preferable, but the temperature range was limited by the use of soft solder in many of the joints. After all leaks were eliminated and vacuum was obtained in the vicinity of 10^{-3} torr, the diffusion pump was turned on. The diffusion pump oil was allowed to "degass" for a period of 24 hours before calibration of the ion gauge was attempted. The gauge was then calibrated against a Vacuum Equipment Company RG-75 vacuum gauge.

4. Alignment and focusing

Figure 4 is a schematic diagram of the geometry of the apparatus. If we imagine this to be a top view, the ion path shown would be that for theoretical first order focusing. If first order focusing were obtained, the apex of the magnet would lie on an imaginary line joining the two slits according to Barber's rule (22). However, due to the fringing field of the magnet, the experimentally obtained optimum lies about 1/2 inch behind the theoretical position. This position is shown in dotted lines in Figure 4. Focusing of this type is known as secondary directional focusing and is obtained by moving the magnet symmetrically toward the chamber in a horizontal direction while also optimizing the vertical position to give a maximum signal.

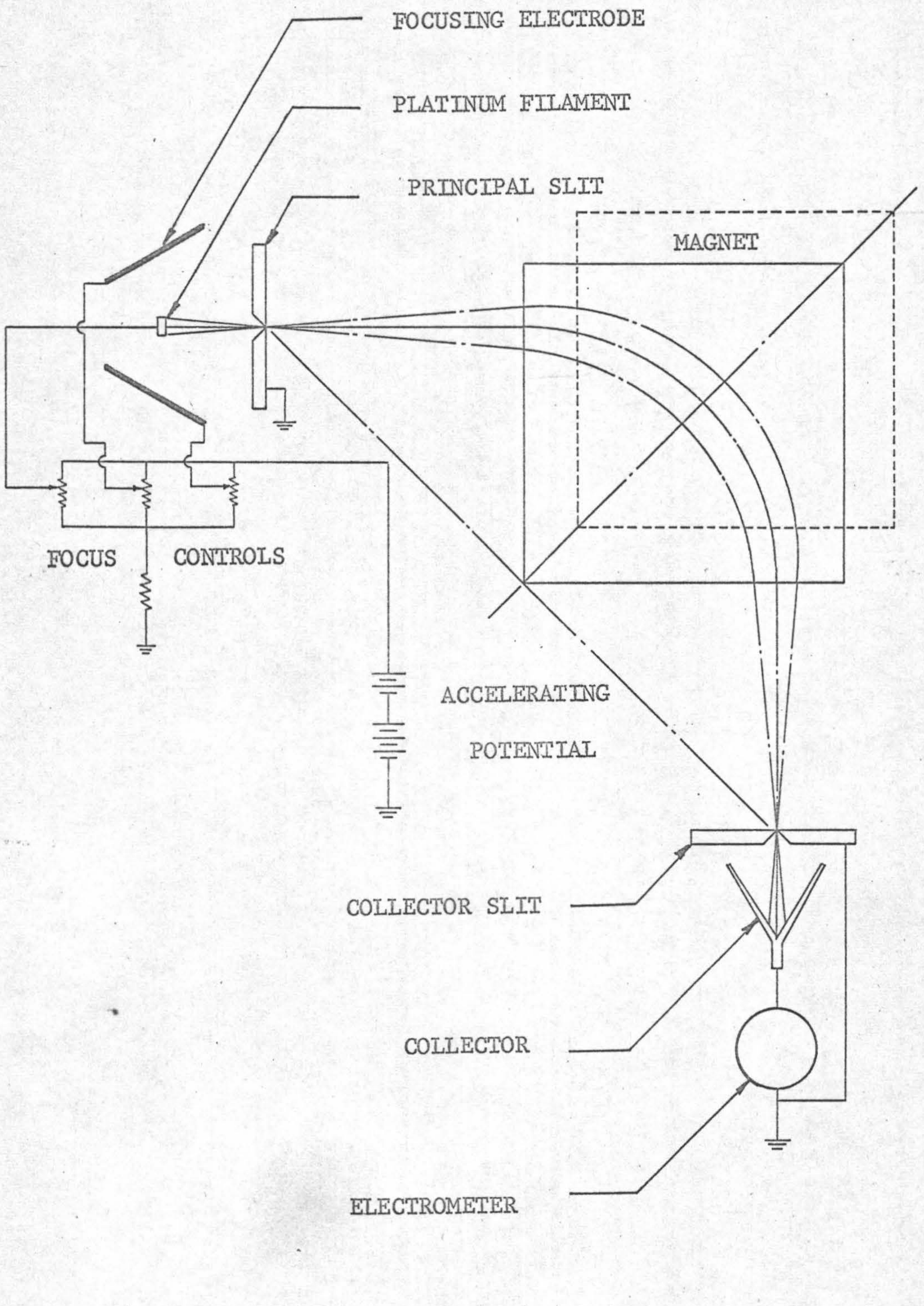

Figure 4. Schematic Diagram of the Apparatus.

Both slits were initially set at 0.4 mm using a Bausch and Lomb Model BV-73 stereomicroscope. A length of tungsten ribbon .001" thick and .003" wide was used for filament material and a crust of reagent grade potassium chloride was deposited on it by coating it with an aqueous solution of the salt and evaporating off the solvent. In operation, the evaporization and ionization of the potassium ions from the sample is accomplished by passing a controlled current through the filament.

Initial detection was achieved with a Tektronix Model 503 oscilloscope by "dropping" the ion current across a 72 megohm resistor into the vertical input terminals. Inspection of the power supply and control circuit diagram in Figure 3 will show that the secondary of one of the Superior 10B transformers is in series with the variable DC accelerating voltage. This allows 60 cycle modulation of an amplitude adjustable up to 25 volts to be superimposed over the DC accelerating voltage. If the horizontal sweep of the oscilloscope is made 60 cycle and properly phased, the resultant pattern is a display of ion current vs. accelerating potential. The slits were then narrowed to 0.2 mm and an Eico Model HF-32 high gain amplifier was installed between the detector and the oscilloscope to compensate for the reduced signal strength with narrow slits. Theoretically, resolution should be optimum with this slit setting for this apparatus. Fine adjustments on the focusing controls could then be made by watching the oscilloscope pattern for minimum distortion and maximum gain. An oscilloscope display at this point showing symmetrical peaks representing the two potassium isotopes K^{39} and K^{41} completely separated demonstrated that the instrument was functioning as desired.

B. Samples

1. Description

Seven rock samples were available which had been analyzed previously. Their source and general description are listed in Table 2. In addition, National Bureau of Standards sample No. 99 and Geological Society of America sample G-1 were available to serve as a check on accuracy. Some idea of the general composition of the samples used can be obtained from the complete analysis of a similar sample which is listed in Table 3. The notably high silica content of these samples makes it necessary to use a hydrofluoric acid treatment in the dissolving process.

2. Preparation

The samples were ground to a powder of 200 mesh or finer. The dissolving process is an acid digestion carried out in platinum evaporating dishes. The stepwise procedure used is listed in Table 4 and is the same procedure used for the flame photometric work. No further preparation was necessary for the samples. The final dilution is arbitrary and in this case was selected to match the tracer solution being used. It was necessary, however, to be extremely careful whenever handling the samples because of the sensitivity of the method to contamination.

Table 2. Hawaiian Rock Samples

Sample	Source	General Classification
HK-119	Waianae, Oahu	basalt
HK-120	Waianae, Oahu	hornblende-biotite rhyodacite
HK-121	Waianae, Oahu	hornblende-biotite rhyodacite
HK-122	Waianae, Oahu	olivine basalt
HK-123	Waianae, Oahu	theolitic olivine basalt
HK-124	Waianae, Oahu	alkalic olivine basalt
HK-125	Waianae, Oahu	alkalic olivine basalt

Table 3.

Analysis of a Hawaiian Rock

Al_2O_3	15.52%
CaO	2.78%
FeO	1.90%
Fe_2O_3	1.38%
K_2O	3.30%*
MgO	1.54%
MnO	.06%
Na_2O	4.39%
P_2O_5	0.50%
SiO_2	65.98%
TiO_2	0.68%

*2.74%K

Table 4.

Sample Dissolving Procedure

1. Heat an accurately weighed 200 mesh or finer rock sample in the range of 0.1 to 1.0 g to redness in a platinum evaporating dish.
2. Add 1.0 ml 6N H_2SO_4.
3. Add 5.0 ml HF and heat to SO_3 fumes.
4. Wash with 30 ml H_2O.
5. Add 5.0 ml concentrated HNO_3 and evaporate to dryness.
6. Add 30 ml 6N HCl and transfer to 500 ml volumetric flask. Dilute to volume with H_2O.

C. Quantitative Measurements

1. Equipment Modifications

Since actual measurement of the ion peaks was necessary for quantitative determinations, oscilloscope detection was judged to be inconvenient. The AC modulation was switched off and the oscilloscope was replaced with a General Radio Model 1230A DC electrometer. Maximum sensitivity for this instrument is 30 mv across 10^{11} ohms input resistance. Accelerating potential was made more precisely variable by using a General Radio Model 907-R-144 dial drive mechanism on the Spectrol Model 860 10-turn potentiometer installed on the DC power supply. This unit provides a speed of 144 degrees per minute and gives a corresponding voltage sweep rate of 20 volts per minute. A Nuclear Chicago Model R-1000 recorder was adapted to the output terminals provided on the electrometer. With the recorder speed set at its slowest rate, satisfactory tracings were obtained.

2. Isotope Dilution Technique

In the method of stable isotope dilution (23), the concentration of an element can be determined from the change produced in isotopic composition by the addition of a known amount of a stable isotope of that element. The relative abundances of the potassium isotopes found in naturally occurring potassium are 93.08% K^{39}, .0018% K^{40}, and 6.91% K^{41} (24). The potassium in the tracer obtained from the United States Atomic Energy Commission, Oak Ridge, Tennessee, was composed of 1.28% K^{39}, .01% K^{40}, and 98.72% K^{41}. If X atoms of normal potassium are mixed with Y atoms of the tracer and R is the ratio K^{39}/K^{41}, then X, Y, and R are related by the following equation:

$$R = \frac{93.08X + 1.28Y}{6.91X + 98.72Y} \qquad [4]$$

Hence,

$$X = Y\frac{98.72R - 1.28}{93.08 - 6.91R} \qquad [5]$$

If X and Y are replaced by x and y, the weights of normal and tracer potassium respectively, equation [5] must be modified to include the ratio of the different atomic weights of the two forms:

$$x = y\frac{98.72R - 1.28}{93.08 - 6.91R} \cdot \frac{\text{at. wt. normal K}}{\text{at. wt. tracer K}} \qquad [6]$$

Therefore,

$$x = y\frac{98.72R - 1.28}{93.08 - 6.91R} \cdot \frac{(6.91)(41) + (93.08)(39)}{(1.28)(39) + (98.72)(41)} \qquad [7]$$

The equation can be further rearranged in terms of R instead of percent abundances to the form used in making calculations:

$$x = 13.64\, y\frac{R - .013}{13.47 - R} \qquad [8]$$

Since y is known from direct weighing, all that is required to obtain x, the weight of potassium in the sample, is a measurement of the net relative ion currents of K^{39} and K^{41} in a mixture of tracer and sample.

3. Procedure

Approximately 10 mg of tracer in the form of KCl was available for the analysis. It was accurately weighed on a Mettler Model M-5 balance and diluted to a volume of 500 ml. If 1 ml of tracer were used for each run, the solution would be enough for 500 determinations. Sample sizes and dilution factors were selected to give potassium concentrations in the same range. To minimize measurement errors, it was judged desirable to have the ion currents of K^{39} and K^{41} at about the same intensity. The 1 ml "spike" of tracer was held constant but the sample sizes were adjusted to give the desired 1:1 ratio of the two isotopes. Slight adjustments were also made in the dissolving process to handle the larger samples with appropriate blank corrections for the changes in reagent volumes.

On the initial attempts at quantitative determinations the ion currents were detected in the expected accelerating voltage ranges but the ratios were in error by as much as 500%. It soon became evident that the tungsten filaments used in those determinations were contaminated with potassium. Repeated attempts were made to pre-treat the tungsten by air oxidation at high temperatures before applying the sample but, while improved accuracy was obtained, the results were generally unsatisfactory. The tungsten wire was replaced with platinum wire .008" in diameter which was "pre-burned" at twice the operating filament current for one hour before installing the sample. The use of platinum filaments eliminated the contamination problem and was continued for all subsequent work. It was later found, however, that a conditioning period of about thirty minutes or longer was also necessary at the beginning of each measurement before a signal stable enough for reproducible ratios was obtained. After this, if minimum filament current were used, emission remained relatively constant for a long period of time. For example, a 10^{-10} ampere signal was measured for a period of eleven hours with less than 10% reduction in signal level. Since the peaks for each ratio are recorded in less than one minute, any error due to changing signal strength between the measurement of the 39 and 41 isotopes is negligible.

Figure 5 is a recorder tracing of the K^{39}/K^{41} ratio in a sample of reagent grade potassium chloride. Figure 6 is a tracing of the ratio in a mixture of normal and tracer solutions where both solutions are in the concentration range of 1-10 ppm. Figure 6 also serves to illustrate the disadvantage of having the ion peaks very different in intensity. Measurement error would be ten times greater for K^{41} than for K^{39}. If one peak were less than 10 times smaller than the other it was possible to measure it on a more sensitive range on the electrometer, but in such a case a change in base line was usually encountered and it took several minutes for the electrometer to recover from the sudden disturbance. This was especially true in the highly sensitive ranges. It was more accurate and more convenient to adjust the sample size to give nearly equal peak heights. Each ratio reported in this study is an average of at least ten consecutive sweeps taken after the signal level was observed to be stable.

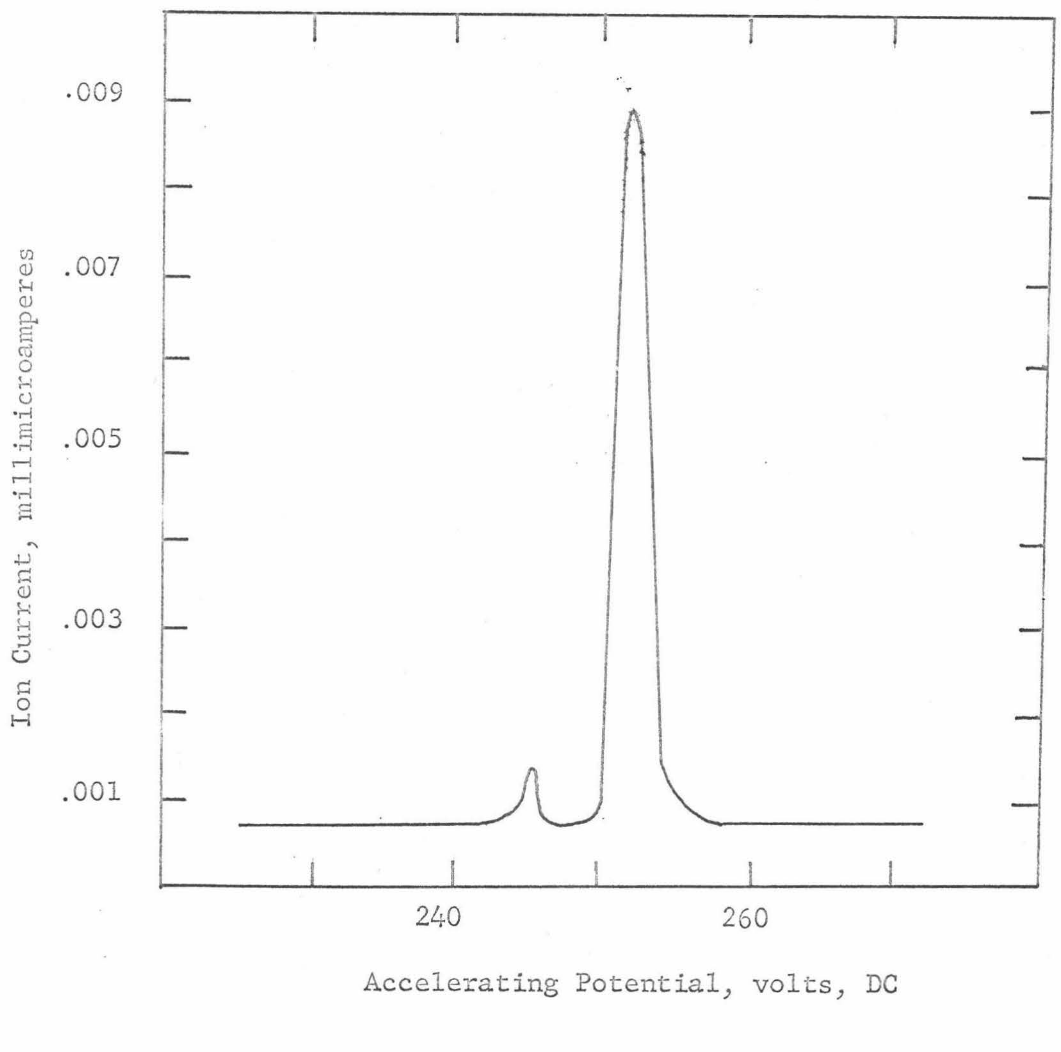

Figure 5. Recorder Tracing of Normal Potassium.

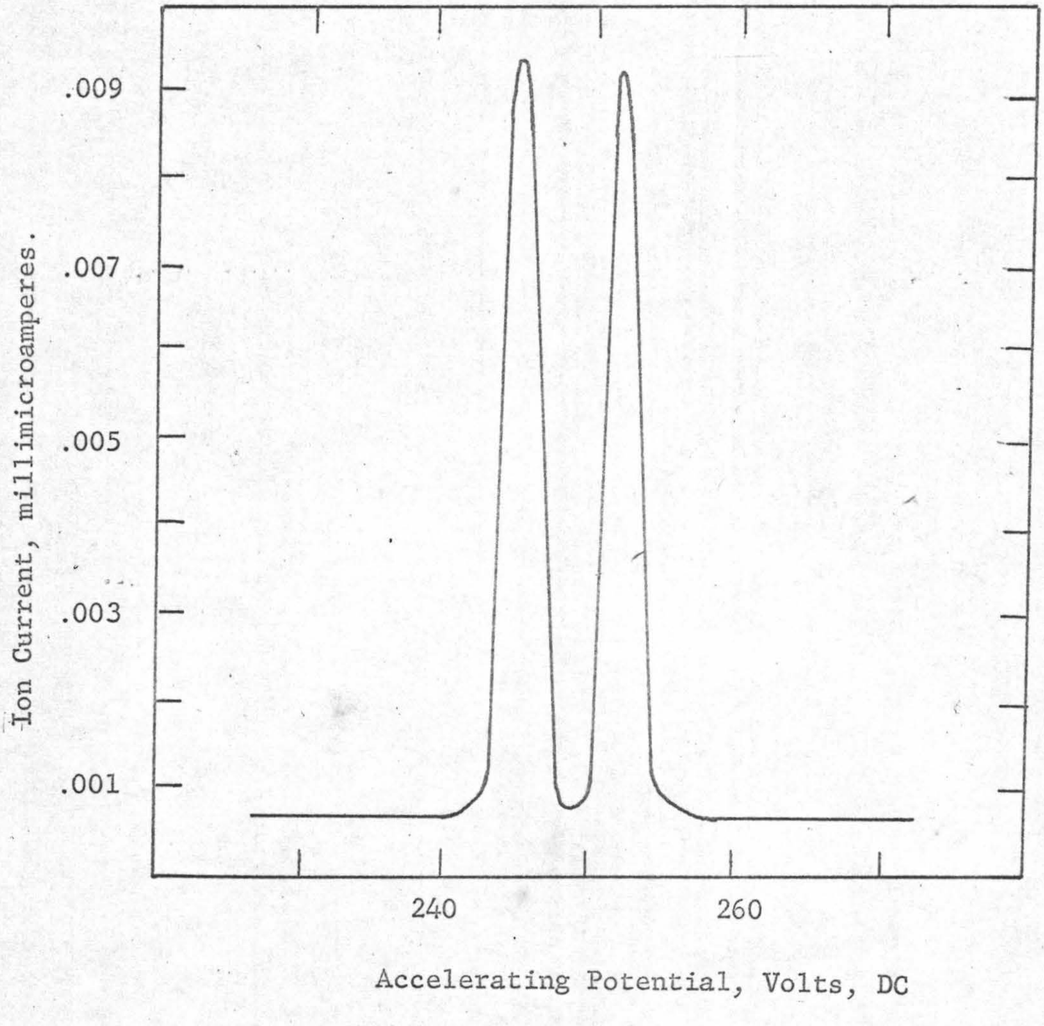

Figure 6. Recorder Tracing of a Mixture of Tracer and Sample

4. Calculations

Since the weight of tracer used is held constant for each run and is known to be .00490/500 g, equation [8] can be further simplified. Although 1 ml quantities of tracer and sample solutions are used, we are actually interested in the total potassium content of the entire sample so multiplication by a factor of 500 would be necessary. However, since both tracer and sample are diluted to 500 ml the results of a mixture of 1 ml of each solution are essentially the same as the results of a mixture of 500 ml of each and, for calculation purposes, using .00490 g for y would give x directly as the amount of potassium in the whole sample. The resulting working equation becomes:

$$x = (13.64)(.00490)\frac{R - .013}{13.47 - R} = .0668\frac{R - .013}{13.47 - R} \qquad [9]$$

If, for example, a sample weight of 0.3552 g were taken and the ratio K^{39}/K^{41} was found to be 1.04,

$$x = .0668\frac{1.04 - .013}{13.47 - 1.04} = .00552 \text{ g}$$

After making a blank correction of .00054 g we obtain the result:

$$\text{Net Potassium} = \frac{.00498}{.3552} = .0140 = 1.40\%$$

III. Results and Discussion

The experimental data obtained is tabulated in Table 5. The original samples were available from the flame photometric work so the results shown in Table 6 can serve as a direct comparison of the two methods. Unfortunately, the standard samples were not available at the time the flame photometric work was done.

It is interesting to note that the relative disagreement between the mean values reported for the flame photometric work in relation to that of the isotope dilution analysis amounts to 1.63 and 1.91% for HK-120 and HK-121 which have potassium contents over 3%, 4.20 and 3.40% for HK-119 and HK-125 which contain about 1.5% potassium, 6.49 and 9.96% for HK-122 and HK-124, which are a little under 1% potassium, and 30.3% for HK-123 which is less than 1/2 percent potassium. There seems to be a trend toward greater disagreement with lower concentrations of potassium. Moreover, the results in general are slightly lower for the isotope dilution analyses. The two standard samples selected for a check on accuracy span the range of the seven samples analyzed and the respective determinations, although single results, exhibited good agreement with the declared values. Although the flame photometric work employed ion-exchange separation of contaminating ions, there is a possibility that not all the interfering ions were eliminated. Potassium contamination may also have been introduced in the course of the ion-exchange elutions. Isotope dilution analysis, on the other hand, would be expected to give high instead of low results in the event of contamination since any

Table 5

Experimental Data

Sample	Weight(g)	Ratio	Net K	%K
HK-119A	0.3552	1.04	.00498	1.40
HK-119A	0.3552	1.07	.00515	1.45
HK-119B	0.3461	0.98	.00463	1.34
HK-119B	0.3461	1.07	.00515	1.49
HK-119C	0.3505	1.07	.00515	1.47
HK-119C	0.3505	1.04	.00498	1.42
HK-120A	0.1736	1.05	.00531	3.06
HK-120A	0.1736	1.09	.00557	3.21*
HK-120B	0.1696	1.04	.00525	3.10
HK-120B	0.1696	1.03	.00519	3.06
HK-120C	0.1753	1.06	.00537	3.06
HK-120C	0.1753	0.98	.00490	2.80*
HK-121A	0.1790	1.11	.00566	3.16
HK-121A	0.1790	1.12	.00572	3.20
HK-121A	0.1790	1.10	.00559	3.12
HK-121B	0.0908	0.582	.00268	2.95
HK-121C	0.3427	1.95	.01069	3.12
HK-121D	0.1434	0.90	.00444	3.10
HK-121E	0.1954	1.26	.00655	3.35

*Rejected values, Dean and Dixon (25)

Sample	Weight(g)	Ratio	Net K	%K
HK-122A	0.5915	1.03	.00465	0.786
HK-122A	0.5915	1.05	.00477	0.806
HK-122B	0.5997	0.98	.00436	0.727
HK-122B	0.5997	1.10	.00505	0.842
HK-122C	0.6050	1.11	.00512	0.846
HK-122C	0.6050	1.16	.00541	0.894
HK-123A	0.9561	0.90	.00336	0.351
HK-123A	0.9561	0.89	.00331	0.346
HK-123A	0.9561	0.90	.00336	0.351
HK-123B	0.9575	0.90	.00336	0.351
HK-123B	0.9575	0.91	.00342	0.357
HK-123C	0.9581	0.88	.00325	0.339
HK-123C	0.9581	0.91	.00342	0.357
HK-124A	0.5093	0.99	.00439	0.862
HK-124A	0.5093	1.08	.00494	0.970
HK-124B	0.5270	1.14	.00520	0.987
HK-124B	0.5270	1.08	.00494	0.937
HK-124C	0.5284	1.18	.00553	1.05
HK-124C	0.5284	1.12	.00518	0.980

Sample	Weight(g)	Ratio	Net K	%K
HK-125A	0.3468	1.07	.00515	1.49
HK-125A	0.3468	1.06	.00510	1.47
HK-125B	0.3507	1.07	.00515	1.47
HK-125B	0.3507	1.05	.00504	1.43
HK-125C	0.3515	1.12	.00545	1.55
HK-125C	0.3515	1.05	.00504	1.43
NBS-99	0.1951	1.33	.000671	0.343
G-1	0.0372	1.34	.00169	4.54

Table 6

Comparison of Results with Flame Photometry

Sample	Flame Photometric Analysis (%)	Isotope Dilution Analysis (%)
HK-119	1.49 ± .03	1.43 ± .05
HK-120	3.02 ± .03	3.07 ± .02
HK-121	3.20 ± .02	3.14 ± .18*
HK-122	0.870 ± .002	0.817 ± .058
HK-123	0.456 ± .004	0.350 ± .006
HK-124	1.06 ± .011	0.964 ± .061
HK-125	1.52 ± .004	1.47 ± .040
NBS-99 (.34%K)		0.343**
G-1 (4.58%K)		4.54**

* Manual scanning of accelerating potential used.

** Single analysis.

contamination would have been from natural potassium and would have resulted in an erroneously high K^{39}/K^{41} ratio. Suspiciously high results were not encountered in this study.

Precision was, however, somewhat erratic for the isotope dilution analysis. Relative standard deviations amounted to values of 3.49%, 0.65%, 5.73%, 7.09%, 1.71%, 6.32%, and 2.72%. There was no apparent correlation between potassium concentration and precision. This indicated that improvements were in order in handling technique. Results on individual determinations indicated that relative precision in the order of 2% can be obtained for this method. Erratic emission current may also have contributed to the lack of precision since accurate control was difficult throughout the study. Perhaps all that is necessary is a multi-turn control for the filament current adjustment, but a more elaborate system similar to those used on conventional mass spectrometers may be necessary.

IV. Conclusions

Both flame photometry and isotope dilution mass spectrometry appear to be satisfactory methods for potassium analysis of Hawaiian rock samples. This study seems to indicate, however, that the latter method may be more reliable for samples of very low potassium content. Both methods use the same sample dissolving procedure and require about the same length of time to obtain the final measurements, but the tedious ion-exchange chromatography separation step used in the best methods adopted for flame photometry is not necessary in the isotope dilution technique. Waiting times are necessary between runs to allow sufficient vacuum to develop, but the operator does not have to be constantly present during these periods. This isotope dilution mass spectrometric method, therefore, seems to offer a convenient and equally if not more reliable potassium analysis.

V. Suggestions for Further Work

Another system currently employed for geochronology involves the decay of Rb^{87} to Sr^{87}. The determination of rubidium and strontium on the same mass spectrometer is generally considered undesirable due to the large mutual interference caused by the similarity in mass. Rubidium has ionization properties similar to potassium and the simple instrument described here may possibly be suitable for the analysis of rubidium. This instrument has a resolving power of 75 and since the separation necessary for rubidium is one involving isotopes of masses 85 and 87, a difference of two mass numbers, this resolution is at least theoretically feasible.

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