FISSION PRODUCT CHAIN YIELDS FROM ISOTOPE ABUNDANCE MEASUREMENTS

by

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A Thesis

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Abstract

A 90° sector type mass spectrometer utilizing a heated relative abundances and yields of fission production isotopes of Cesium and Rubidium. The minimum sample requirements for analysis of alkali metals is of the order of .1 micrograms whereas at least 5 micrograms are necessary for alkaline earths such as Ba and Sr. Isotopic abundances are reported for stable Ea, Sr, Li, K, and Rb.

TABLE OF CONTENTS

I.	INTRODUCTI ON	****	1
II.	EXPERIMENTAL		• . 7
		Mass Spectrometry	7 9 12 13 14 15 15 16 19
III.	RESULTS		22
		Earium Cesium (radio-activo) Rubidium (radio-active) Lithium and Rubidium Potassium Strontium	22 23 28 30 32 35
IV.	SCOPE AND LIN	TTATIONS	34
₹.	SUMMARY		36
VI.	APPENDIX		37
VII.	BIBLIOGRAPHY		41

INTRODUCTION

Since the discovery of fission, a great deal of information has been accumulated about fission products. This information includes the nature of radiations, half-lives, mass numbers of fission product nuclides and accumulated fission yields of mass chains. This latter information is of considerable importance in understanding the fission process. All the early fission yield data was obtained by radio-chemical means, that is extracting the radio-active product, purifying it and by measuring its activity. The great bulk of this fission yield data falls on a smooth curve with two maxima in the neighborhood of mass 95 and 140 (see fig. 1). More recently, precise mass spectrometer methods have been applied to the accurate determination of the fission product isotopes of Kr and Xa. (1) This work has revealed for the first time fine structure in the smooth mass fission yield curve (see fig. 1). In extending this investigation the isotopes of Cs and Hb are of particular importance since the mass chains involved are adjacent to the chains already studies in the Xo and Kr mass ranges and a knowledge of their yields is essential in understanding the reason for fine structure in the mass yield curve. Mass spectrometric measurements of the abundances of these isotopes have been made and the results are reported in this thesis.

The fission process consists of a fissionable nucleus capturing a slow neutron (thermal) to form an excited compound nucleus when then splits assymetrically to form two primary fission products and on the avorage two neutrons. In the case of the fission of U235, the process

I



may be represented by the equation:

Ey virtue of the fact that the neutron to proton ratio of the fissioning nucleus is considerably higher than that corresponding to stability in the fission product region, the primary fission product is unstable towards the radio-active decay and achieves nuclear stability through a series of disintegrations (known as a fission chain.) The emission of a particle increases the nuclear charge or atomic number by one unit but does not change the mass number.

TABLE 1	Fission Product	Decay	Chains	Result	ting in	<u>Cs</u> 133,	135, and 137.
	Mass /Atomic No.(2) No.(A)	Sd 51	Te 52	I 53	ze 54	Cs 55	Ba 56
	133	(110mi	n.) -> (60m	22 <u>hr</u>	• 527d	→ stable
	134	(∠ 10m	a) → 4	ł3m. →	50.8m	> stabl	Le
	135		(< 2	20.) -	6.68h	≠ 15.3m.	2.1x10 ⁶ yr stable
	136				863 - e	stable -	13.7d →stable
	137				22.2s [/]	, instant 3.9m -	37y stable

It is impossible in practise to obtain a complete yield data for each momber of a chain because of the short half-lives encountered in the early members. The yields which are determined are generally those of the long-lived members of the chain and as such represent the cumulative yield of the decay chain.

If the mass yields are plotted as a function of mass number or the number of neutrons in the nucleus, (A-Z), it is readily seen that the

maxima correspond not only to the masses of 95 and 140 but also to the regions of 50 and 82 neutrons respectively. (see fig. 1). This has been proposed as further proof of the hypothesis that a certain number of protons and/or neutrons in the nucleus seem to be more stable. These so-called "magic numbers" which are indicative of stable nuclear shell are considered to be 2, 8, 20, 28, 50, 82 and 126.

The fine structure found in the smooth yield curve i.c. the abnormally high yields of Xe^{133} and Xe^{134} also occurs in the neighborhood of the 82 neutron shell. Each mass chain ending in stable Menon (except Xel31) has one member with 82 neutrons (see Table 1).

Glendenin⁽²⁾ has offered a qualitative explanation for these observations based on the extra stability of the nuclear shells of 50 and 82 neutrons. He has postulated that where a nuclei with 51 or 83 neutrons is formed as a primary fission fragment, the binding energy of the "extra" neutron is lower than normal and this neutron is emitted instantaneously instead of the usual particle thus giving rise to chain branching. An illustration of the proposed chain branching in the region of 82 neutrons is given in Table 2.

50 151 Sn	51 131 Sb 132	52 131 To 152	53 151 I 152	54 131 <u>Xe</u> 132	55	56
Sn	Sb	10	I	Xe		
153	133	133	133	133	133	
Sn	Sb	Te —	I —>	Xo —	Ca	
	134	134	134	134		
	Sb	Te	I>	Xe		
	1.55	135	135	135	135	135
	5b	10	I	Xe	Cs	Ba
	136	136	136	136		
	Sb	Te	I	Xo		
		137	137	137	137	137
		Te	I	Xe	Cs	Ba
		138	138	158 *	1138	138
		70	T ->	Xa	Ca	Ra

Of those chains having Cesium members (see Table 1) only three terminate in stable of long-lived members suitable for mass spectrometer measurement. These isotopes are the stable 133, the 10^6 year os $135^{(3)}$ and the 37 year Cs 137 ⁽⁴⁾. Inghrum et al ⁽⁵⁾ have made measurements on the abundances of these isotopes and have reported an abnormally high yield for the Cs 135. Since this abnormally high yield cannot be explained on the basis of the Glendenin mechanism and because Inghrom stated that he had not been absolutely correct for stable Cs 133 contamination in either his reagents or the original Uranium metal, it was proposed to repeat his work and extend it to include the isotopes of Eb.

4

TABLE

2 Chain Branching in the Region of the 82 Meutron Shell

In the mass spectrometer investigations of the rare gas fission products reported previously,⁽¹⁾ gas samples as small as 0.001 cc. at N.T.P. were found to be adequate for an analysis. These samples could be extracted from 20 grams discs of Uranium metal irradiated with thermal neutrons to produce 10^{17} fissions. Assuming the same number of fissions the amounts of other fission products can be estimated from the mass yield curve. These estimated yields for a number of other isotopes are given in Table 3.

		Partition and appropriate and the second	
Element	Mass Chains	s Total Yields 🖇	Weight 1x 10 ⁻⁶ gram
55 Cs	133,135, 137	16.6	3.7
37 Ed	85, 67	3.9	•55
56 Ba	138	6 . 2	1.4
38 Sr	88, 90	9.2	1.4
40 Zr	91, 92, 94 96, 93	30	4 . 7
42 No	95, 97, 98 100	24.6	4.0
41 Nb	93	6	.9
58 Ce	140, 142	11.9	2.8

Table 3. Cumulative Mass Yields Based on 1017 Fissions

Trilinear Chart of Muclear Species, by W.H. Sullivan

It is obvious that the problems are twofold, one to separate out the extremely minute samples and the second the spectrometer analysis. The problem of spearating and purifying the microgram fission product samples was handled by D.R. Wiles and is reported in detail elsewhere⁽⁶⁾. The spectrometer analysis of microgram samples has been solved in part by

the use of tungsten filements impregnated with the sample and then heated to give a thermionic source of ions.

Up to the present only Cs and Rb have been extracted from irradiated Uranium in sufficient quantities for analysis using a filament source. Preliminary analyses with stable Ba and Sr have been made to determine the minimum sample requirements. Li and K have been analyzed to investigate isotope fractionation effects from the filament surface. Li and Rb have been jointly analyzed as a test of the use of an internal standard for reference purposes.

EXPERIMENTAL

INSTRUMENTATION

Mass Spectrometry

The 90° sector type mass spectrometer used in this work has been described elsewhere (7). The spectrometer tube was modified to permit the introduction of samples into the source. This was done by means of attaching a 50/50 standard taper ground glass joint, the male portion being attached to the tube. The female section was used as support for the filament stem which was a 2 lead, 10 mm separation press seal.

The use of silicon grease on the 50/50 ground glass joint is not recommended as it became easily striated and had a tendency to "freeze" making it difficult to dismantle. Apiezon N was found to be satisfactory. When it was necessary to bake the tube, the ground glass joint was kept cool by means of a damp cotton scarf and a jet of air blowing around it. The scarf was maintained moist throughcapillary action from a attached vessel and a small compressor gave a convenient and reliable supply of compresses air.

An additional vacuum system consisting of a chamber with a $50/50 \text{ s}_T$ ground glass male joint, and duplicating the upper portion of the spectrometer tube, Macloed gauge, mercury diffusion pump, and a small vacuum pump. This auxillary line was used for sample preparation and the aging of filaments.

The electronic units consisting of stabilized high voltage unit current stabalizer and magnet filament current supplies, and the recorder were shared with another 90° mass spectrometer with the conventional gas type source. These units with the switching assembly and most recent revisions have been described by R.K. Wanless ⁽⁸⁾ and shall not be considered here. The D.C. amplifier was not shared with the other mass spectrometer and was mounted on the floor of the rack supporting "the tube.

The source assembly proper is a six plate arrangement (See fig. 2,3,4,) isimilar to the new Nier type (9) and is positioned on the analyzer tube by a guide dowel. The spent filament may be removed by means of the ground glass joint without disturbing the source assembly. If the source plates require cleaning, the electrical connections for the accelerating and focussing potentials may be removed and the complete assembly lifted out with long forceps. Details of the dimensions of the plates slit widths, and spacings are illustrated by the accompanying photographs and schematic diagram. (See fig. 2,3,4,)



TOP VIEW OF THE SOURCE ASSEMBLY

FIG. 3 SIDE VIEW OF THE SOURCE ASSEMBLY



SCHEMATIC DRAWING OF ION SOURCES

FULL SCALE

FIG 4



Filement Source:

Positive ions, as created from solids in mass spectrometerion sources are usually produced in either or both of two ways. First the material may be reduced to a molecular beam by vaporization from a simple furnace, filament or trough (10) after which ionization occurs through electron impact. The use of the furnace and several modifications has been described by previous workers (11, 12) in this laboratory. Their work dealt with the measurement of the Cu isotopes although the furnace has been used to better advantage on more refractory elements such as Ir, Mn, and Rh.

Second it has been known for many years that a large number of elements and their compounds emit positive ions directly on heating. The use of a filement in this respect as a source of positive ions in a mass spectrograph was pioneered by Dempster in 1918. Since then the use of coated or impregnated filements has been widespread in spectrographic work and in more recent years in spectrometers.

The advantages in their use are :

- (a) only a very minute sample is required (of the order of micrograms)
- (b) a high temperature is readily-attainable
- (c) the simplicity of sample preparation and operation. A list of elements which have been analyzed in this manner are to be found in table 4 and in the appendix.

The principal disadvantages of filement sources are the low efficiencies of ionization and the lack of doubly charged and dissociated ions. Investigations by Lewis, Carrison and Hayden⁽⁵⁾ have shown that the oxides of Ba, Sr, Fr, Sn, and Ce to be satisfactory ion emitters with an "overall loss factor" defined as the ratio of etoms consumed in the source to the number of ions received of the collector. This factor is governed by the efficiency of the ionization at the filement surface. Table 3 shows Hayden's ⁽⁶⁾ data on the efficiency of ionization of various salts.

Pable 5.	Ionization	Efficiencies	of	Salts	From	8	W	Filament

Salt	3 Efficiency	Salt 💈 🧏 Et	ficiency
Ba(no3)2	0.02	61(No3)2	•5
Sr(No ₃) ₂	•08	Sn(No3)2	,16
Y(No3)2	.025	Eu(Noz)2	.16
La(No3)3	16.0	Gd (No3) 3	.05
Сө (No ₃) з	.13	v₃o ₅	.008
Pr(Mog)3	12.0	RuCl ₃ , Ru (No3) 3	.01
Nd (No3)3	1.0	RhC13	.005

Discussions of the mechanism of positive ion emission from filament surfaces may be found in any reference pertaining to thermionic emission⁽¹³⁾ In general the criterion for emission is that the electron work function of the filament surface must exceed the ionization potential of the sample with which the filament is coated. The electron work function is defined as that work which has to be done in evaporating an electron from a surface at 0° C. This work is spent in overcoming the

Image forces and a force arising from polarization of the surface atoms due to the face that these atoms unlike those in the body of the metal have unbalanced forces acting on them. The nature and arrangement of the surface atoms determines the nature of the surface forces and hence the magnitude of the work function. The value for the work function of various metals and their oxides used in filaments are given in Table 6.

Table 6.	Thermionic	Work	Function	of	Filment	Motals	
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Letal	Ta	<u>n</u>	<u>11-0</u>	Pt	Cr	<u>N1</u>
Work function (0.v.)	4,52	4.48	9,2	5.9	4.6	5,24
Referance	17	17	18	19	20	19

Tantulum and Tungston are the most commonly used metals and tungsten-oxide offers the greatest attainable work function for a filament surface of any of the metals or oxides available to the present.

The filament to be coated consisted of Ta or W ribbon .040" wide, .010" thick and .59" in length. It was connected to the press seal mentioned above by means of .040" nickel sleeves. The procedure for fastening the ribbon to the sleevo is to crimp the nickel over the W and then spot weld both together. The correct length of ribbon between the sleeves is measured by use of a dummy filament.

The nickel sleeves slide over about 3/8" of the press seal lead and so allows leeway as to adjustment of the filament with regard to the vertical displacement above the first slit in the source assembly. The optimum position was as close as possible to the top slit, with allowance for sagging during the heating process. This was determined by trial and

error methods. To allow duplication of this positioning, a depth gauge was designed which measure the position of the filament from the base of the support. This gauge consisted of a brass rod 3/32" diameter with a brass disk 1" diameter positioned on it by a set screw.

The current for heating the filament was supplied by the output of a low voltage filament transformer (Hammond II54) fed from a 60 cycle Sorensen voltage regulator through a bank of four General Radio Variacs. Since the filament is held at the same potential as the source, the filament transformer must be able to withstand voltages of the order of 2000 volts.

Several determinations were made using direct current supplied from two wet cells in parallel to heat the filament. The use of a D.C. for heating the filament has been reported (22) but there is no apparent advantage over a well regulated A.C. supply.

Filement Pre-Treatment

The treatment of the filament before the sample is affixed greatly enhances the success of the analysis. The efficiency of ionization depends on the work function of the metal being used as a filament but this is in turn a function of the surface atoms of the metal. Hayden has reported () that filaments of W become more efficient in their ionizing action after they have been used several times. This improvement may be associated with an actual increase in the filament surface area being presented to the next sample. The phenomena of etching of W filament surfaces has been the object of several investigations (25,24,) and is not completely understood. As it is often not practical to re-use filaments, especially when dealing with radio -active materials, a period of heating in the auxiliary vacuum chamber prior to being impregnated, was substituted

Generally the ribbons were heated to a dull red for about 4 hours. Subsequent heating of the filament in air to insure an oxide layer was only necessary if the material to be ionized had a ionization potential for greater then 4.52 e.v., the maximum work function of tungston metal. The oxide layer effectively raises the work function of the W filament surface to a value of 9.2 e.v. (18)

Choice of compound

Generally the nitrate is the most convenient form in which to handle motallic element since they are soluble in water and decompose readily of form stable oxide. The oxides are in most instances good emitters of postive ions when heated on a filament. Extensive work of Bondy and (25,26)

his collaborators on hot filament ion sources indicated that chlorides and sulfates of the alkali metals (Li, K, and Rb) are not desirable ion emitters. These compounds volatilize too readily and (27) impoverish the filament source. However recent data obtained on the measurement of neutron deficient isotopes of Cs (cycltron produced, masses less than IS3) using a filament source in conjunction with a mass spectrograph indicates that the sulfate salt was most successful. By measuring the ratio of the amount of sample on the filament to that detected on the electrometer and designating a loss factor similar to that reported by Hayden (16) they found the following:

Table: 7	LOSS FACTORS	FOR	CS	COLPOUNDS	FROM .	AW	FILALENT
	Compounds				07e:	rall	Loss Factor
	CaNo 3				1.4	10	6
	CBC1				8.3	10	4
	Cs2(so4)				180		

In all the work to date nitrates have been used. However the data in Table 5 indicates that the Chlorides and sulphates would be much more efficient. In spite of this lower efficiency indicated for nitrates, samples of the order of .1 micrograms were analyzed successfully.

Filament Preparation

Microgram samples were prepared as aqueous solutions of concentrations approximating 1 microgram / .ool ml. A micropipette was used to pipette .002 ml. portions onto the filament surface. The solution was evaporated by means of a infra-red lamp and simultaneously passing a A.C. surrent of 2-3 amps through the filament.

When larger samples were available the filament was dipped into a slurry of the substance and then dried as above. If visible amounts of sample adhered to the filament a preliminary heating in the auxiliary vacuum chamber was advisable. This brought about a fusion of the sample to the filament and the excess could drop off harmlessly.

Sample Size

It was found that satisfactory ion currents could be obtained with extramely small samples. This was especially evident in the analysis of alkili mentals, where their characteristically low ionization potentials accounts for their high efficiency as thermionic emitters. Samples of the order of .1 micrograms of Cs and .01 micrograms of Rb were successfully analyzed . A recent report (28) on the mass assignment of neutron deficient isotopes of Cs (of masses less than of 153) has indicated that in a similar use of a W filament with samples of the order of .1 micrograms, a detectable reference line on a photographic plate was made. The alkaline earths such as Ba and Sr have a minimum sample requirement of the order of five micrograms.

24

Sample Fractionation

It is claimed by Inghram et $al^{(5)}$ that a fractionation of Cs isotopes of as much as five percent occurs at the filament during an analysis with their mass spectrometer. Extensive investigations with not only Cs but the other available alkali metals i.e. K, Rb and Li has indicated no such effect occuring during our analyses. In particular microgram samples of K and Rb were analyzed continuously for 6 hours and no fractionation was evident over this period. Even more conclusive is the fact that analysis of identical samples on two entirely different types of mass spectrometer gave the same results. The results as obtained from the double-focussing Shaw type crucible source mass spectrometer and the filament source 90° sector type mass spectrometer are reported in Table

Chemical Procedure

The procedure for the simultaneous isolation of carrier-free Cesium and Rubidium from irradiated uranium was as follows. The 20 gram disk was dissolved in 100 ml. of nitric acid (6N), and the solution was evaporated to crystals. The crystals were dissolved in diethyl either and the fission products separated from this solution by several extractions with small portions of 6N nitric acid. Ferric ion (1-2 mgs.) was added as scavenger to the aqueous portion and precipitated as the hydroxide with amonia gas, the supernatant liquid containing the Rb, Cs, Ba and Sr and devoid of all the hydroxide forming elements. To the supernatant liquid was added ammonium ion and the subsequent precipitation of the ammonium chloroplatinate carried down only the Cs and Rb. The excess ammonium salts were removed by an oxidation procedure outlined by Nyes

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and Bray⁽²⁹⁾. The chloroplatinate crystals were dissolved in hot water and the platinum was removed by reduction with formic acid. The carrier free Cs and Rb were then converted to the nitrate in which form they were satisfactory for mass spectrometer analysis.

In order to determine the amount of contamination of natural Cs and Rb a blank was prepared in the following manner. Two disks of equal weight were cut from a uranium rod and after irradiating one of them, both were dissolved in equal volumes of nitric acid. Helf of each of these samples were combined to make a synthetic sample having twice as much stable Rb and Cs contamination as the original active sample. The simultaneous separation of Rb and Cs was then carried through with both samples as in the procedure outlined above. The comparison of the abundances of the isotopes of the two samples makes possible the determinution of the contamination free isotopic abundances.

A Leeds and Northrup optical pyrometor was used in the measurement of the filament temperatures at various current inputs. A graph of the filament temperatures we filament currents is given in Fig. 5. Because of the variations of the resistance of different filaments, estimations of the temperature from the graph are accurate only to 50° C. By direct readings with the pyrometer and reference to the pyrometer calibration curve temperature measurements can be duplicated to ± 25 in the range of 800 - 1200° C.

Operational Procedure

After the final step in the preparation, the filament was transferred to the spectrometer tube and aligned in position. The maximum ion current was obtained when the filament was parallel to the slit system



there was only a slight decrease of the peak height. This indicated that the main positive ion current stemmed from the centre of the filement and that the transverse position of the filement is not too critical. It should be mentioned that the right angle of the filement has been reported ⁽²¹⁾ as advantageous. It supposedly gives more homogenous, mono-energetic ions and so contributes to better peak shape and resolution. In this work no such effect was detected, perhaps because of the focussing action of the Nier source.

If the sample to be analyzed has a molting point of 250° C or less it is advisable to bake the tube and usually 4-5 hours pumping will result in a vacuum which is satisfactory for the purpose of analysis, i.e. approximately 10^{-6} mm. of Hg. pressure.

The Nier source has an auxiliary filament as a source of electrons for ionizing gases by electron impact. Although this means of ionization has not been used effectively in conjunction with the thermionic emission in the analysis of a sample it is useful in obtaining test spectrograms of residual gases. These test spectrograms afford not only a means of locating the tube in its optimum position in the magnetic field in the original "setting up" but also a means of cetting the focussing potentials in the day to day analyses without depleting the solid sample. This is particularily valuable in microgram samples where the time of emission may be short.

The best results were obtained when the final temperature was reached slowly as the transition to a positive ion emitting state occurs quite abruptly. An ionization gauge attached to the spectrometer tube provided a convenience means for following the decomposition of the sample and the outgassing of the filament prior to reaching the state of

emission. When the pressure in the tube as indicated by the ionization gauge reached a steady state at a temperature only slightly lower than the required amount for emission, then the sample was considered ready for analysis.

· ·

EXPERTMENTAL

Discussion of Errors

The day to day variations of a particular analysis on the spectrometer are attributed to various sources of discrimination which cannot be completely eliminated. These discriminations may be of two types: mass discrimination in which the efficiency of production and collection of ions is different for different masses and peak height discrimination which is caused by varying sensitivity with intensity. Peak height discrimination is the least serious of the two and is caused mainly by the non-linear components in the current measuring equipment. The use of properly designed feed-back amplifier precludes the possibility of non-linearity from this source and the Speedomas recording system has been shown to have a linear relation between input voltage and recorder deflection. The grid leak in the pre-amplifier circuit is the source of most of the trouble. Inghram⁽³⁴⁾ has tested the linearity of 10¹¹ ohm resistors (I.R.C.) similar to those used in this laboratory. For a range of .001 to 10 volts he has found them to be satisfactory to 2% of their value. The grid leak of the solid source and the other spectrometers in this laboratory have been used with in this range. An indication of the linearity of these components is the consistent ratios obtained, independently of whether a high or low ion current is measured.

The factors which may possibly affect mass discrimination in the spectrometer analysis of solids are those concerned with the processes of ionization, acceleration and collection. Mass discriminations in the thermionic emission of positive ions from a filement surface may arise in

two ways. Theoretically if emission takes place from the liquid state in which there is perfect mixing at the surface, the lighter isotope (M_1) is favoured in the vapor state by a factor $(M_1/M_2)^{\frac{1}{2}}$ where M_1 and M_2 are the respective molecular weights. However if thermionic emission proceeds from the solid state where there is no such mixing the isotope effect is not detected. Secondly, differences in ionization potentials may be a source of discrimination. For example Hundley⁽³⁵⁾ found that discrepancies in the measured abundances of Li⁶ and Li⁷ could be accounted for on the basis of the differences in the ionization potentials. Both of these factors should decrease in the higher mass ranges.

The systematic discriminations in the ion source due to magnetic effects have been treated in mathematical detail by Jordan and Coggeshall,^(30,31) These effects are not important in the 90° sector type spectrometer where the source is considerably removed from the magnetic field. The most important criterion for an instrument free from mass discrimination in that the individual ion paths in the source should be the same for each mass under the conditions of collection. Varying the acceleration potential to permit collection of different masses (electrostatic scanning) has been recognized as leading to mass discrimination of soveral percent. This has been attributed to the fact that the lighter mass is collected under more efficient conditions, i.e. at a high accelerating potential. All the data obtained in this report was obtained by holding the accelerating potential constant and bringing the ion beams of different mass to focuss on the fixed collector by Varying the analyzer magnetic field.

In addition to these variations which are attributable to instrumental effects, the process of thermionic emission is inherently

unpredictable. Fluctuations in ion currents due to uneven heating of the filament and the sudden desorption of sample through outgassing or decomposition lead to further error in the isotopic analysis. These errors can be reduced to a minimum by rapid scanning back and forth over the two ion currents in question. Generally a minimum of ten complete spectrograms i.e. (a recording of the forward and reverse scanning of the ion currents) were measured to obtain the desired degree of reliability. In general where limits of error are presented the stundard deviation is used. A sample analysis is included in the appendix.

RESULTS

Barium

For the determination of the Emisstopes abundances, Em (No $_{3}$), was found to be the nost satisfactory compound as it decomposed readily to give BaO which emitted Ba. Attempts were made with Emile. But the ion currents were unsteady and no satisfactory analysis could be made. A temative explanation for the difference in the behaviors may be made if one considers their respective boiling points i.e. EmO cm 2000° c and Emilg at 1590°C. The filament temperature necessary to obtain positive ion emission with either salt, is of the order of 1450° C and hence the Emilg is likely to have a appreciable vapor pressure as compared to the Emil and thus effect the thermionic emission.

The results of the analyses of 5 microgram samples of Ba on a W filament are given in Table 8. The Ba isotopes of masses 150 and 152 which represent .25 of the total were not measured because the ion currents obtained with microgram samples were not sufficient to allow their detection. TABLE 8 ABUNDAMOUNT OF THE MORHAL BA ISOTOPES:

Investigator	hef.	Percentage relative abundance						
		134	135	135	137	153		
R.J. Horsley	(32)	2.33	6.47	7.70	11.03	72.1		
A.O.Nier	(33)	2.42	6.59	7.81	11.02	71.66		
This work		2.2	6.4	7.7	11.0	72.7		

The rapidity with which a sample of microgram proportions is lost from the filament surface is illustrated by figure 6 where the Ba 159 peak height is plotted as a function of the time in minutes.



While it is possible to do analyses of samples of 3-5 micrograms, there is a rapid depletion of the sample and the accuracy of the analysis suffers because of the small peaks. Very likely a more efficient ionization of the sample can be effected by using a combination of the thermionic emission and electron impact.

Cesium

The abundances reported in Table 9 are results of measurements made with entirely different types of mass spectrometer i.e. a Dempster type double focussing mass spectrometer using a modified Shaw crucible source and 90° sector type mass spectrometer utilizing a tungsten filament ion source.

The Cesium ratios become more meaningfull when correlated to the absolute yield of Xe 133 which was determined by McNamara et al to be 6.29%. However before this can be accomplished it is necessary to correct the Cs ratios for (a) stable isotopic contamination (b) the decay of Cs¹³⁷ (half life of 37 years) (c) possible fractionnation of the isotopes from the filement surface and (d) the thermal neutron capture of Xe¹³⁵.

The extent of stable isotopic Cs contamination was determined by analyzing a blank sample propared in the manner outlined in the chemical procedure. The results indicate (Table 9) that there is no detectable contamination.

To correct for the decay of Cs 137, we have used the 37 year value for the half-life. Thus knowing the time which has elapsed between the termination of irradiation and the date of analysis it is possible to re-determine to ratios to zero time. To illustrate consider the ratio of Cs 135/137 determined on sample A as 1.09, 4.58 years after irradiation.

$$N = N_{0} e^{-\frac{1}{t}}$$
where N = Cs 137 measured (=1)
N_{0} = Cs 137 at zero time
= decay constant i.e. .69
T1/2
t = elapsed time in years
1.00 = N_{0} e^{-\frac{.69 \times 4.58}{37}}
$$N_{0} = e^{.084}$$

or $N_0 = 1.09$ and therefore the Cs 135/137 ratio at "zero time" would

be 1.09/1.09 or = 1.00

No correction was made for the frationnation of isotopes from the filament during the analysis. Although this is contrary to the opinion of Inghram (5) the fact that analysis with two entirely different instruments have indicated no difference in the isotopic ratios from the beginning to the end of a large number of determinations appears to substantiate the assumption that under the conditions of our experiments little or no fractionnatio of Cs isotopes occurs.

The conflection for the thermal meutron capture by Xe 135 is best calculated from measurements on the Xe 134 / Xe 136 ratio on the same sample. This has been done for the Oak Ridge sample (designated as Sample A) where the Xe 134/136 ratio has a value of 1.16 (Fission Product note book p 28 1948). It has been found that samples shielded from thermal neutrons by Cadium show little or no increase in the Xe 136 due to the neutron coptine of Xe 135. These samples were found to have a ratio of 1.22. This indicates that in Sample A there was a loss of 5% on the Xe 135 and so the Cs 135/137 ratio would be low by an equivalent amount. The Cs 135/137 ratio of Sample A corrected for decay (see Table 10) should be also corrected upwards by a factor of 1.05 due to the Xe 135 loss.

In the case of sample C, irradiation data indicates that the flux was of the order of 5×10^{12} neutrons /cm² / sec. Previous samples determined for the Xe 134/136 ratio at analogous flux intensities have given the Xe 134/ 136 ratio as 1.05 i.e. of the order of 11.5% low. Correcting the Cs 135/137 ratio of sample B (.95) upwards for an equivalent 11.5% gives a ratio of 1.06 which when noramalized results in a absolute yield of approx. 6.1%.

Table 10 gives the Cesium ratios corrected for decay, neutron absorption and normalized to the 6.3% yield of Xe 133. A replica of a complete spectrogram (i.e. ion current recording Cesium isotopes extracted from sample A) is given in figure (7).

Table 9. MEASURED RELATIVE ABUNDANCES OF RADIOACTIVE CESIUM AND

RUBIDIUM IN THE THERMAL NEUTRON FISSION OF U235

(Uncorrected)

SAMPLE A. FROM URANIUM IRRADIATED AT OAK RIDGE (Dec. 3, 1945) Xe 134/136 1.16

Date	Anal	Lyzed	Sample No.	Instru- ment	Сэві <u>133/137</u>	um Ratio 135/137) H	dubidium 85/87
June	16,	1950	Composite Ul-U6	112	1.27 1.28	1.09 1.10	1.00 1.00	-
June	29,	1950	U-7	1 2	1.31±.01 1.29	1.09 1.08	1.00 1.00	
July	13,	1950	U-8	1 2	1.21 1.22	1.09 1.09	1.00 1.00	• 64 • 64
July	25,	195 0	U-9	1 2	1.21 1.22	1.09 1.11	1.00 1.00	• 60

SAMPLE B. URANIUM IRRADIATED AT CHALK RIVER, ONT. (July 11, 1948)

Date Analyzed		lyzed	Sample No.	Instru-	Cos	Rubidium			
				ment	133/137	135/137	137	65/87	
Aug.	16,	1950		1 2	1.12±.01 1.11±.01	L 1.045 L 1.040	1.00 1.00	•440 •442	.001
Aug.	18,	1950	Blank	1 2	1.12 1.12	1.040 1.040	1.00 1.00	•504 •510	.006

SAMPLE C. URANIUM IRRADIATED AT CHALK RIVER, OMT. (August 9, 1950)

Date Analyzed	Sample No.	Instru- ment	Cesium Ratio Rubidium 133/137 135/137 137 85/87
Jan. 2, 1951	Blank	1 2	1.11±01 .980±.01 1.00 1.10±.01 .950±.01 1.00

(1) Double focussing mass spectrometer, source of ions, cruicible heated by electron impact.

(2) 90° Sector type direction focussing mass spectrometer, in source heated filament.

SAMPLE A	Cesium	Mass Spectro- meter Results	Cs137 Decay	Normalized Yield	
	133 135 137	1.21 1.09 1.00	1.11 1.00 1.00	1.11 1.05 1.00	6.3 5.96 5.7
SAMPLE B	133 135 137	1.18 1.04 1.00	1.13 1.00 1.00	1.13	6.3 5.6
SAMPLE C	133 135 137	1.11 95 1.00	1.10 .95 1.00	1.10 1.06 1.00	6.3 6.1 5.7
INCRHAM(5)) 133 135 137		7	1.03 1.28 1.00	6.3 7.8 6.1

TABLE 10 CESIUM RATIOS CORRECTED FOR DECAY, NEUTRON ABSORPTION

AND NORMALIZED TO THE YIELD OF Xe133 AS 6.35



Fission Product Rubidium

Two long-lived Rubidium isotopes of masses 85 and 87 are formed in the fiesion process. Although their combines yields are only about one eighth of that for the Gesium isotopes, there is sufficient amount simultaneously extructed with Gesium to be readily analyzable. These isotopes are the result of the decay chains given in Table 11.

Table 11. Fission Product Chains Leading to Rb 85 and 87



The mass spectrometer results are to be found in Table 9 (sample B.). Corrections analogous to those for Cesium must be taken into account although in this case neutron absorption is a negligible factor.

Considerable contamination from some Rubidium other than that resulting from fission was evident in the analysis B. If we assume that this Rb contamination is of normal isotopic abundance (85/87 2.6) then we may correct for its presence by combining the ratios of the blank and the pure sample in the manner evolved by D.R. Wiles⁽¹⁶⁾.

For sample B the calculations are as follows:

Consider the ratio of the fission yields of 85/87 as 1/2 the amount of contamination of 87 as x, and the amount of Rb 85 contamination then is 2.6 x and the ratio of pure B may be represented as

$$\frac{1+2.6x}{a+x} = .422 \text{ (measured value)}$$

and the ratio of the blank as

$$\frac{1+5.2x}{a+2x} = .510 (\text{measured value})$$

hence eliminating x gives the net ratio of the Rb ficsion isotopes as .374.

It is also evident from Tablell that 25% of the mass 85 chain passes through the 9.4 yr. isomero of $K_{\rm T}$ 85 (). Thus it can be calculated in the case of Sample B which has docayed 2.1 years that 22% of the cumulative yield of Rb 65 is still blocked by Kr 85 isotopes, i.e. the value of .374 represents 70% of the yield and so 100% will be represented by a ratio of .475. The corrected results for sample B are given in Table 12 with the absolute yields computed on the assumption that the Rb 85 lies on the smooth fission yield curve.

Table 12. U²⁵⁵ Fiscion Yields of 2b Isotopes of masses 85 and 87

	Sample B Elank	Puro	Corrected for Contamination	for Kr 85 decay	Fission Yield
85	•506	•442	•374	•4 7 5	1.3%
87	1.00	1.00	1.00	1.00	8.75%

Sample spectrograms of stable Rubidium and fission product Rubidium are given in figures 8, and 9.



MASS



Lithium and Rubidium

Mahy determinations have been made of the ratio relative abundance of the natural occurring Li^6 and Li^7 isotopes. A tabulation of these investigations (See Table 13) (Appendix) illustrates the variations in the values for the Li 7/6 ratio. Differences would be expected because of the different methods used in the analyses yet the large variations cannot be completely explained on this basis. One is lead to suppose that there are relatively large variations of the isotopic abundances in nature, indeed fluctuations of 5% or more would be anticipated on the basis of comparison to recent measurements on the isotopic abundances of boron, (36) sulfur, (37) and carbon(38).

Whereas the aforementioned surveys were carried through on propared ongaseous samples and availed themselves of the high precision characteristic of the gas spectromenter a survey using a solid source spectromenter is complicated by the difficulty of obtaining a good reference standard. In the convential solid source spectrometer each separate analysis requires the dismantling of the assembly. The tube must let up to atmospheric pressure and the new sample on a fresh filement, re-positioned. To duplicate the conditions which had existed in the previous measurement is virtually impossible.

One solution to the problem of determining small variations in isotopic abundances with a solid source has been proposed by K.L. Cook (39) He applied a system of rotating Pt filaments whereby a new sample could positioned without bracking the vacuum.

Another method is to mix an internal standard of known abundances with each sample to be analyzed. The ideal standard, as concerned with the filement would be one that readily emits positive ions in the approximate mass range of the sample and whose ratio would indicate the day to day instrumental variations.

Preliminary experiments have been carried out using Rb as an internal standard in conjunction with the analysis of Li isotopes. The preparation of the filement was accomplished in the usual manner, solutions of Li No3 and EbCl being pipetted on to the filement and dried together under an infra-red larg. One microgram of Rb was ample but no lower limit was determined for Lithium.

In table 14 are the results of the analysis of the Li and Rb. Those analyses marked by an asterisk represent mixtures, the other determinations were carried out individually. The same source of Li and Rb was used for each sample and each value reported represents the average of at least seven double spectrograms.

Table 14. Results of Analyses of Pure and Mixed Samples of Li and Rb

Date 1950	Li 7/6 ratio	Hb 87/85 ratio	Li 7/6 ratio normalized to Rh 87/85 .382
May 22		.377	
30		.386	
June 18	12.26	.374	12.49
19	12.89		
20	18,63	.372	12.94
81		. 394	
28	12.77		
23	12.89	.383	12.82
30		.391	
July 5	12.69	.377	12.83
		.379	
Average	12.69	.381	12.77

Unfortunately only four analyses of Li-Rb mixtures were made however it appears that the day to day fluctuations in the Rb 87/Xb83 ratio has its counterpart in the Li⁷/Li⁶ variations. By comparing the standard deviation of the Li analyses of the mixtures normalized and unnormalized, there is some evidence of the smoothing out of the variations in the normalized values, i.e. standard deviation before normalizing was .13 and after wards .09.

The average value for the Ro ratio as determined in this work is compared to the values obtained by other investigators in Table 15.

Table 15. Rubidium Isotope Abundances

Investigator	Reference	Rb ⁸⁵ /Hb ⁶⁷ Ratio Valus		
This work		2.62		
Bondy, Vanicek	27	2.57		
Bondy, Johannsen,				
and Popper	26	2.68		
Brewer, Kaeck	40	2.58		
Nier	41	2.59 ± .003		

Potassium

Potassium is of widespread occurrence and is present as a contaminant in almost any sample that is investigated. The K isotope can therefore be used in checking the settings of the various focussing adjustments and could be used as an internal standard. The preferential om emission of the lighter isotope, effecting a change in the ratio during a long run has been reported⁽⁴⁶⁾ however this has not been substantiated either by previous experiments. The potassium essociated with a six microgram sample of Sr was measured over a period of 5 hours continuous emission and no change in the ratio could be detected.

Table 16. Potassium Isotopa Abundanca

Investigator	Reference	K ³⁹ /K ⁴¹ Ratio
This work		14.22 ±.06
Bainbridge	58	12.5
Bondy	25	14.1
Brewer	43	14_25
Brewer, Kueck	40	13.88 ± .4
Cook. K.L.	39	14.12 ± .3
Dempster	44	18.0
Manley, J.H.	45	$13.4 \pm .5$
Nier, A.O.	46	13.96 ± .1

Strontium

Strontium nitrate was analyzed, the proparation of the filament being accomplished in the usual mannor. The minimum amount of Strontium necessary for an analysis was found to be about 3-6 micrograms. This was larger than the yields of fission product strontium and so the filament source could not be employed. It is hoped that a joint use of electron impact ionization and thermionic emission will result in a ruch higher efficiency and thus allow the use of smaller samples.

Table 17. Strontium Isotope Abundance

Investigator	Reference	Sr Ratio	Sr Ratio
		01 80/01	01 00/00
This work		12.28	8.57
Horsely, R.J.	38	11.75	8.54 2.00
White, Cameron	58	11.89	8.49

SCOPE and LIMITATIONS

Problems have arisen during the past year for which the solid source is not applicable. There are limitations as to what elements will emit positive ions from a W filament. Those elements with an ionization potential of greater than 9.2 e.v. (the maximum work function for a W- filament cannot be ionized by thermionic means alone.

Sample size is also a limiting factor. This is important in the analysis of fission products where samples of the order of one to fivemicrograms are common. Higher icn efficiences are therefore essential. It is proposed to measure the ion efficiencies by means of radio-active tracers.

The present ion source contains an auxillary filement suitable for effecting ionization by electron impact. Results have been recently published⁽⁷⁵⁾ where similar equipment has been used to determine the abundances of the Vanadium isotopes. Certainly ionization by electron impact is a necessity in the instances where the ionization potential of the element excludes the possibility of thermionic emission. Further investigations concerning the use of the auxillary filements are planned.

The contamination with both stable and radio-active materials of the source assembly is a problem which is inherent in solid source mass spectrometry. Inevitably much of the sample becomes coated in the plates and spacers and eventually may effect a conducting surface resulting in electrical break down. A temporary expedient is to lower the accelerating voltage. However it is only a matter of time before the source must be removed and cleaned. It is interesting to note that despite a high degree

of contamination, in no instance was there any detectable memory effect from previous samples.

Two methods for preventing spacers from becoming conductors have been proposed. One is to machine furrows in the spacer, preventing the spattering from completing an overall contact; the other is to place guard plates which would shield the spacers. No modifications have yet been made.

Radioactive contamination is best removed by boiling the source assembly in a detergent solution. Dreft has been recommended, and trisodium phosphate is satisfactory. Contamination of the tube itself has not reached a point where it is considered to be a real hazard.

SULMARY

A 90° sector type mass spectrometer has been modified for use with solid substances. The use of impregnated, heated Tungsten filament (.010" x .040" x .38") has been shown to be an efficient source of positive ions, not only in regard to the amount of sample necessary for an analysis, but also in the ease of handling and general applicability.

Analyses of fission product samples of Cesium and Ro have been completed and the fission yields of their respective long-lived isotopes determined. Stable Ba and Sr have been analyzed and minimum sample requirements determined. in anticipation of the analysis of fission product Ba and Sr.

Preliminary determinations on mixtures of samples of Li and Rb indicate the feasability of the use of an internal standard in solid source spectrometry. The internal standard would be invaluable accessory in determinations of variations in abundances of natural occurring isotopes and in work such as in the rupturing of C-Li bonds of organo-lithium compounds as a reference point is important.

Extension of the work on fission product yields will include the elements Ba, Sr, Nb, Zr, Mo, and Ce. Further Cs and Rb analyses will be made in an effort to correlate Cs ratios and flux intensities of the N.R.X. pile at Chalk River.

APPRIDIX

Table 3 IONIZATION FOTENTIALS (75) (in electron volts) OF NON-GAJEOUS ELEMENTS parentheses contain references to the use of a compound of that element and a hot filazent as a ion source.

L1 5.37	Bo 9.30	B 8.28	0 11.24		N		0		F			
(21,29,40, 64)												
Na	Шg	Al	Si		P		S		C1			
5.09	7.63	5.94	8.14		10.43		10.42					
(26)	(21,64)	(21)										
K	Ca	Sc	Ti		V		Cr		<u>En</u>	Fe	Co	N1
4.32	6.09	6 . 7	6.8I		6.74		6.7		7.4I	7.83	7.8	7.6
(39,43)	(21,64,59)	(65)	(21)		(21,69)		(60)		(21)	(22)		(61)
Cu	Zn		Ga	Ge		As		Se	Br			
7.67	9.37		5.97	8.10		10.0	5	9.75				
		(2	22,56)									
Rb	Sr	Y	Zr		Mb		110		Te	Ru	Rh	Pā
419	5.68	6.6	6.92		6.9		7.2		7.I	7.5	7.7	8.3
(29,46)	(21,56,62)	(21)	(16)			~		677	-	(16)	(16)	
Ag	Ga		in	Sn		30		16	1			
7.58	ጸ •		5.76 (21,56,52)	Y . 04		8.00		Q•23				
Cs	Ba	La										
3.86	5.21	5.59										
(27,30)	(21,56,62)	(70)			-				-	•	-	574
		Lt	Hſ		19		W		Re	0s	lr	JT.
		7.3	7.6	701	7.0	734	7.0	De	7.8	8.7	8.8	8.8
An	Hg		TL	20 7 70		D1 17 95		F0 0 7	A6	1		
9.20	10.41	4	0 0 0	7,07	Do	7.20	TT	0.0	3.5	8		
rr a oa	Ka F OT	AC	57		57 .		57					
5.97	5•81 G-	0.0 D	J.r Na		D _a r '		Sm		En	Ga		
	6 5A	576	6.4		6.3		6.55		5.64	6,65		
	(70)	(16 71)) (16.71	}	(16)		(16.63	.72)	(16.67	.63)(16.	63.65.67	7)
	(10) mb	Dr	Ho		Er		Ta		Yb	,,		-
	6.74	6.82	6.9		6.9		6.9		7.06			
	(67)	(65.73)) (65)		(67,74)		(65,66)	(74)			
	•				-		-					

•

Spectrogram No.	Ratio Cs^{135}/Cs^{137}	â	d ²
, *	1 103	055	
1	7.101	•000	000003
2	1.050	.009	000002
<u>л</u>	1 048 T 02T	.005	000025
5	1.056	-002 010	000100
6	1.036	.010	.000100
7 +	1.019	.027	.000100
8	1.027	.019	-000361
9	1.040	-006	-000056
10	1.051	•005	000025
11	1.037	-011	-000121
12	1.052	-014	•000196
15	1.068	-022	000484
		•••••	••••
*	2		
Doubtful Result	g - d .113, d .	0015	
	areluding welues]	7 - 1.	046
OADTGIT WACLERD	Percinatus Astres 1	·,	0-20
Averace deviati	$m \leq d = 113 = 0$	10	
WADIAD GOATGAT	n 11		
Deviations of d	oubtful value #1.	055 - 2.5	may be rejected
avorage	deviation	010	
G			
Deviation of do	ubtful value #7	027 - 2.5	hence also
Avorago	deviation .	010	rejected.
		F 0	9 9
Standard deviat	ion of the mean	(đ,2	dg" dn")
		1	n
		0015	070 001
	5-	.0015	_ 004
	•	77	11
of reem enerran		- A	זנו
MOLEEO MEEN UU		2 m	
		n/n	11 52
Probable deviat	ion of the mean	67 1 12 8	, 2 2,
		···· / (a1	$u_2 = - d_1 = 0$
			n_1

.0024

SAMPLE OF STATISTICAL EVALUATION AND REJECTION OF RESULTS

TABLE 13

Previously	determined	values	for	137	11.16	ratio
TEATORDEA	descrimined	Varues	TOT	TTT .		TROTO

Investigator Re	eference	Method, Substance	Ratio Li7/Li6
Aston	47	Mass spectrograph, LiBr, Lit in graphite anode	11.00
Bainbridge	42	Mass spectrograph - heated spodumene	11.8
Bondy	27	Mass spectrograph - mixture of LioH, KoH, NooH and SiCz	12.0
Brewer	48	Mass 180 spectrograph, Pt disk	12.47 11.6
Brewer, Kueck	40	Mass spectrograph, W filament	12.144
Denspter	44	Mass spectrograph, metal anode election bombardment	4.8 37.
Harnwell, Bleakney	49	Mass spectrograph, W filament spodumene	8.4
Lu, Hoff	50	Amblygonite (Li,Al(F,OH)Fo4) in Pt cup	12.29
Anglerow, Hayden Hess	51	Mass spectrometer, W filament	12.53
McKellar, Jenkins	s 52	Optical method	8.57
Morond	53		14.9
Nakamura	54	Optical - absorption spectra of Li vapor	8.0
Ornstein, Nreeswijk, Walfad	55 olin	Optical	8.1 .4
Sampson, Bleakney	y 56	Mass spectrograph, W filament	11.66
Wijk, Koeueriage	57	Optical, intensity measurement of spectra	7.2
White, Cameron	58	Hass spectrometer, furnace LiAlCL/, vapor bombarded with 75 ei electro	ons 12.7 .07

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