

67
12
654

Robert M. Hayden

DETERMINATION OF URANIUM IN THE ASH
OF PLANTS, AND ITS PRECISION

By Claude Huffman, Jr., and Leonard B. Riley

Trace Elements Investigations Report 654

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY



UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
WASHINGTON 25, D. C.

March 29, 1957

AEC-414/7

Mr. Robert D. Nininger
Assistant Director for Exploration
Division of Raw Materials
U. S. Atomic Energy Commission
Washington 25, D. C.

Dear Bob:

Transmitted herewith are three copies of TEI-654, "Determination of uranium in the ash of plants and its precision," by Claude Huffman, Jr., and Leonard B. Riley, December 1956.

We plan to submit this report for publication in Analytical Chemistry.

Sincerely yours,

John H. Eric

for W. H. Bradley
Chief Geologist

JAN 25 2001

(200)
T672
no. 654

Chemistry

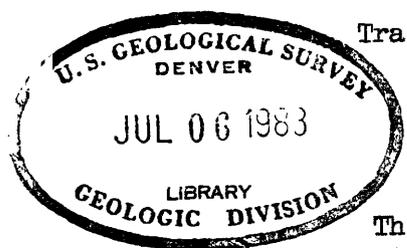
UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

DETERMINATION OF URANIUM IN THE ASH OF PLANTS
AND ITS PRECISION*

By

Claude Huffman, Jr., and Leonard B. Riley

December 1956



Trace Elements Investigations Report 654

This preliminary report is distributed without editorial and technical review for conformity with official standards and nomenclature. It is not for public inspection or quotation.

*This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

USGS - TEI-654

CHEMISTRY

<u>Distribution</u>	<u>No. of copies</u>
Argonne National Laboratory	1
Atomic Energy Commission, Washington	2
Division of Raw Materials, Albuquerque	1
Division of Raw Materials, Austin	1
Division of Raw Materials, Casper	1
Division of Raw Materials, Denver	1
Division of Raw Materials, Ishpeming	1
Division of Raw Materials, Phoenix	1
Division of Raw Materials, Rapid City	1
Division of Raw Materials, Salt Lake City	1
Division of Raw Materials, Spokane	1
Division of Raw Materials, Washington	3
Exploration Division, Grand Junction Operations Office	1
Grand Junction Operations Office	1
Technical Information Service Extension, Oak Ridge	6
Tennessee Valley Authority, Wilson Dam	1
U. S. Geological Survey:	
Fuels Branch, Washington	1
Geochemistry and Petrology Branch, Washington	25
Geophysics Branch, Washington	1
Mineral Deposits Branch, Washington	1
P. C. Bateman, Menlo Park	1
A. L. Brokaw, Grand Junction	1
N. M. Denson, Denver	1
L. R. Page, Washington	1
P. K. Sims, Denver	1
Q. D. Singewald, Beltsville,	1
F. N. Ward, Denver	1
A. E. Weissenborn, Spokane	1
TEPCO, Denver	2
TEPCO, RPS, Washington, (including master)	2

 64

CONTENTS

	Page
Abstract	4
Introduction	5
Acknowledgments	6
The fluorimetric method for uranium in plants	6
Preparation of the sample	6
Analysis of the ash	7
Study of precision	10
Conclusions	22
References	22

ILLUSTRATIONS

Figure 1. Example of working curves for uranium	9
2. Means and standard deviations from table 3 and their regression line	17

TABLES

Table 1. Duplicate determinations of uranium on plant ash	11
2. The range of uranium, arithmetic mean, variance and standard deviation for each plant species studied	15
3. Combined data for range, arithmetic mean, and standard deviation	16
4. Computation of regression line by least-squares method .	19
5. Observed and estimated average difference between pairs of determinations made on the ash of 24 aspen twig samples	21

DETERMINATION OF URANIUM IN THE ASH OF PLANTS
AND ITS PRECISION

By Claude Huffman, Jr., and Leonard B. Riley

ABSTRACT

In the routine fluorimetric procedure of the U. S. Geological Survey for the determination of uranium in the ash of plants, over 99 percent of the determinations during the past year fall in the range 0.4 to 50 ppm. The method uses a simple nitric acid leach for solution of the ashed sample. Elements that would interfere are eliminated by extracting uranium present with ethyl acetate after addition of aluminum nitrate as a salting agent. The extracted uranium is fused with a fluoride-carbonate flux, and the intensity of fluorescence produced in the cooled melt by ultraviolet light is measured in a transmission fluorimeter.

The precision of results in the range from 0.4 to 35 ppm uranium in plant ash is expressed by a simple equation (standard deviation = $0.063 U + 0.15$, where U is the observed uranium concentration in parts per million). This equation is based on 319 pairs of determinations, made during a period of about a year, on samples consisting of ash from sage brush, pinon pine, ponderosa pine, and juniper.

INTRODUCTION

Over the past five years the U. S. Geological Survey on behalf of the Division of Raw Materials of the Atomic Energy Commission has investigated the application of botanical methods to uranium prospecting on the Colorado Plateau (Cannon, 1954). These investigations included the determination, by the Survey's laboratory, of uranium in several thousand plant samples. About 90 percent of these samples have less than 6 parts uranium per million parts of plant ash ($< 6 \text{ ppm U}$). Values as low as 1.0 ppm U in ash have been considered as above background in some localities (Cannon and Starrett, 1956). Thus differences between results from samples containing very small absolute amounts of uranium are important to outlining mineralized areas. A description of the method of analysis and a study of its precision are given in this paper as an aid to the evaluation of these differences.

In the Survey's program for the season 1954-1955, many determinations of uranium in plant ash were made from two separate portions of ash from the same ashed sample. Samples so duplicated included, as a routine checking procedure, all those for which the first value obtained exceeded 1.0 ppm U and a considerable number, randomly selected, below this value. Thus these duplicate results were obtained as part of the routine procedure and not as a special precision investigation. A formula based on these results allows the precision of other routine determinations to be predicted with considerable assurance, if analyses are made by the described method.

Changes from the described method should not be expected to give the same precision; any altered method would need a separate precision study. For instance, it would be particularly dangerous to assume that the precision formula here given could be used for a direct fusion method, where plant ash and carbonate flux are fused with no preliminary extraction and separation.

Fluorimetric methods for determining uranium in many materials other than plants have been described by Grimaldi, May, Fletcher, and Titcomb (1954), and the method described here is essentially an adaptation of that developed by Grimaldi and his coworkers.

Acknowledgments

The assistance of Lewis F. Rader and Rollin E. Stevens during this study is gratefully acknowledged. Credit is due George T. Burrow, and Edward J. Fennelly and several summer assistants for making most of the uranium determinations.

THE FLUORIMETRIC METHOD FOR URANIUM IN PLANTS

Preparation of the sample

Dry the plant sample at 90° C for 24 hours. Grind the dried sample in a Wiley mill to pass a steel screen containing 1.5-mm circular openings. Weigh 10 g of the ground plant material in a porcelain crucible and place it in a muffle furnace. Gradually raise the temperature of the muffle to about 300° C and maintain this temperature until the sample is well charred. Then raise the temperature to 550° C and continue heating at

this temperature for about 2 hours. If the ash content is required, use a tared crucible in which to ash the sample, weigh the crucible and ash, and obtain the weight of the ash by difference. Mix the ash by stirring thoroughly and transfer to a 2-oz cardboard carton for storage.

Analysis of the ash

Weigh 50 mg of the plant ash and place it in a 30-ml glass-stoppered test tube. Add 6 ml of 15 + 85 HNO_3 to the sample. Bring the solution to a boil on a hot plate and gently boil the solution for 5 minutes; for multiple analyses a metal rack may be used. Add 9.5 g of recrystallized $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to the test tube and heat it again over the hot plate to dissolve the aluminum nitrate. Cool the tube to room temperature and add 10 ml of anhydrous ethyl acetate. Stopper the tube and shake it in a shaking machine for about 2 minutes. Centrifuge the solutions at 1000 to 1200 rpm for 5 minutes. Carefully filter the upper ethyl acetate layer by decanting it into a clean dry retentive filter paper held in the opening of a test tube, allowing the aqueous layer to remain behind. The ethyl acetate portion is filtered to obtain a more complete separation of the aqueous layer from the ethyl acetate layer and thus to remove traces of elements that quench the fluorescence of the carbonate fluoride phosphor. With a pipette measure a 2-ml aliquot of the ethyl acetate and place it in a 7-ml platinum dish, of the dimensions given by Grimaldi and others (1954). Place the dish in a shallow pan containing about 1/8 inch of water to keep the bottom of the dish cool. Ignite the ethyl acetate with a lighted taper and allow the ethyl acetate to burn completely. Evaporate the residue remaining in the platinum dish on a steam bath, then heat the

dish briefly over an open flame below a red heat to remove any remaining free nitric acid and organic matter. Add 2 g of flux 1/ to the dish and heat over a burner at a low temperature until the flux melts then heat for one additional minute keeping the flux a little above the melting point, swirling the flux to dissolve all the uranium and to obtain a uniform melt.

Set the dish on a level alundum plate to cool. Measure the fluorescence of the phosphor with a transmission fluorimeter such as that described by Kinser (1954). Determine the uranium in parts per million by reference to a standard curve. Standards containing 0.05 microgram of uranium per 2 g flux in the phosphors and reagent blanks are always run with each set of samples through all steps of the procedure starting with the addition of nitric acid to standardize the fluorimetric curve and to correct for small daily changes that may occur. An example of working curves covering two scales of a fluorimeter is shown in figure 1. About 14 determinations run in parallel, plus 2 standards and 2 blanks, can be made per man-day by this method.

After these data were obtained, a machine for multiple preparation of the phosphors (15 to 18 at one time) was developed in this laboratory (Stevens, Wood, Goetz, and Horr, 1956). Its use shortens the time of the preparation of each phosphor. The precision of the preparation by the machine closely duplicates that of the preparation by hand, when care is taken in the hand preparation.

1/ The flux used by the U. S. Geological Survey laboratories is a carbonate-fluoride mixture, described by Grimaldi and others (1954), containing 45.5 parts of sodium carbonate, 45.5 parts of potassium carbonate, and 9 parts by weight of sodium fluoride.

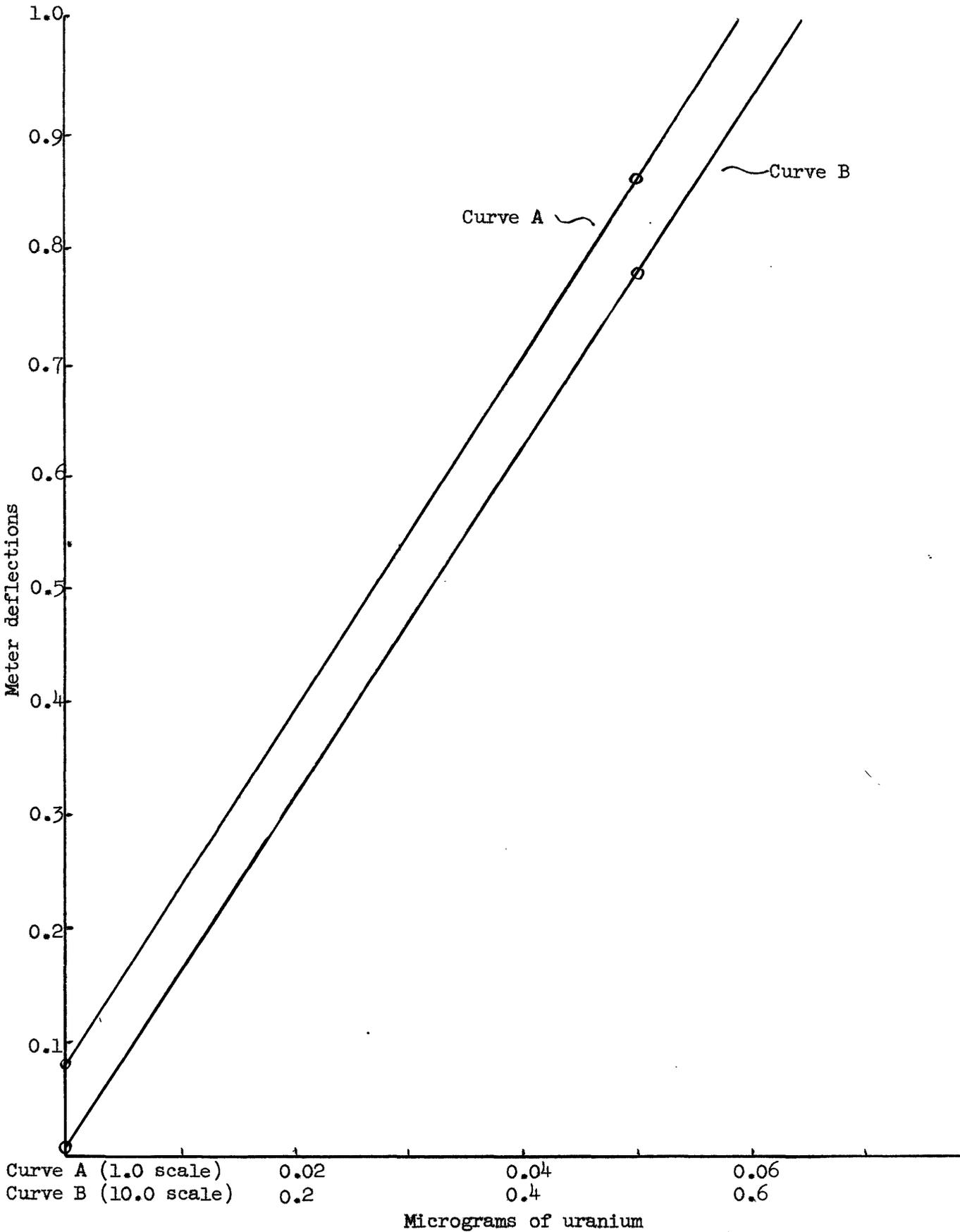


Figure 1.--Example of working curves for uranium.

Study of precision

The basic data for this study, consisting of the laboratory serial number, plant species, and the results of the duplicate determinations are given in table 1.

The possibility that the precision of the uranium determination might be different for different plant species was first studied. The four species of plants were: Artemisia sp? (sagebrush), Pinus edulis (pinon pine), Juniperus sp? (juniper), and Pinus ponderosa (ponderosa pine). The uranium range was subdivided into the classes shown and the arithmetic means, variances, and standard deviations calculated from the determinations in each class sub-range for each species, with the results shown in table 2. The formula used for calculating the variances (V) was:

$$V = \frac{d^2}{2n}$$

where d is the difference between the duplicate determinations for each sample and n is the number of paired determinations. This formula is essentially that given by Youden (1951, p. 16); it is easily derived from the general formulas for calculation of the standard deviation.

Inspection of the standard deviations in table 2 is sufficient to show that they are essentially independent of the species as compared to their dependence on the uranium content. Hence, table 3 was prepared to show the determinations combined without regard to species. When the standard deviations from this table are plotted against the corresponding arithmetic mean values, a close approximation to a straight line results (fig. 2). Using the same data, a formula for the regression line was

(Text continued on p. 18)

Table 1.--Duplicate determinations of uranium on plant ash.

Sample no.	U in ash (ppm)		Sample no.	U in ash (ppm)	
	(1) Run	(2) Run		(1) Run	(2) Run
	<u>Sagebrush</u>			<u>Sagebrush</u>	
220092	1.0	1.3	215953	4.5	5.5
106	1.4	1.8	954	4.8	3.9
109	1.1	1.3	957	5.1	4.3
112	1.1	1.2	972	3.3	4.1
126	0.8	0.8	216006	4.4	3.7
148	1.4	1.4	016	3.2	3.4
172	1.4	1.6	038	3.5	4.0
220084	2.2	2.5	043	3.1	3.4
088	1.9	1.6	220077	4.6	3.9
099	2.9	2.5	215813	11.0	11.0
105	3.6	2.8	864	8.5	9.0
127	2.0	2.0	899	8.7	9.2
128	2.2	2.0	220070	11.0	11.0
129	1.8	2.2	071	12.2	13.5
130	1.4	2.0	073	12.4	10.5
220158	1.9	1.9	074	11.8	11.0
220179	1.8	1.9	079	6.5	6.8
181	2.5	1.7	215938	6.5	7.7
189	2.0	3.1	216020	7.4	7.2
215943	2.5	3.1	215816	17.0	16.0
948	2.1	2.3	818	23.0	18.5
949	2.2	2.5	820	16.0	16.0
950	2.2	2.2	823	18.5	19.0
952	2.8	3.0	824	22.6	24.0
955	2.1	2.1	826	22.0	22.0
956	2.7	3.0	829	20.3	22.0
215962	2.7	2.8	832	16.0	18.5
967	3.0	3.3	215846	17.3	13.7
977	2.1	2.8	851	22.2	19.2
981	2.1	1.9	904	19.0	18.5
987	2.0	2.5	910	17.5	16.7
994	3.1	3.2	915	18.5	17.7
216001	2.4	2.6	920	23.0	21.0
025	3.0	3.1	922	15.4	15.8
030	2.5	1.9	220066	21.0	24.4
216043	3.1	3.4	067	13.6	16.0
220076	6.0	5.9	068	13.6	12.5
078	5.6	4.9	069	16.0	18.0
080	5.5	5.2	075	12.2	14.5
187	4.4	4.5	215838	31.0	24.5
215924	3.6	3.9	858	50.0	44.8
927	4.2	4.3	859	41.0	36.5
930	4.4	4.3	860	35.0	32.0
933	4.0	4.5	861	28.0	29.2
951	5.8	4.7	867	30.5	28.0

Table 1.--Duplicate determinations of uranium on plant ash--Continued.

Sample no.	U in ash (ppm)		Sample no.	U in ash (ppm)	
	(1) Run	(2) Run		(1) Run	(2) Run
<u>Sagebrush</u>			<u>Pinon pine</u>		
215868	29.0	28.5	218254	1.2	1.2
889	51.4	53.0	261	0.8	1.2
894	28.4	27.2	303	1.3	0.7
220064	38.4	37.5	342	1.5	0.9
220065	31.0	30.0	359	1.2	1.4
			373	0.8	1.1
			375	1.0	1.0
			394	1.0	0.9
			218405	1.1	0.8
214677	0.4	0.5	431	1.2	1.3
217998	0.5	0.6	436	1.4	1.2
218139	1.0	0.7	438	1.1	1.1
181	0.6	0.5	463	1.3	0.8
219194	0.7	0.7	218477	1.6	1.4
218196	0.7	0.7	486	1.1	1.1
318	0.7	0.7	222091	1.1	1.1
323	1.0	0.6	099	1.0	0.9
426	1.0	0.7	124	1.2	1.3
428	1.0	0.8	139	1.3	1.4
448	0.4	0.3	128	1.1	0.9
475	0.5	0.7	223529	1.3	1.4
222090	0.8	0.8	536	0.9	1.0
092	0.3	0.5	212112	2.6	2.7
144	0.5	0.6	218543	3.0	3.1
218554	1.3	1.3	552	2.4	2.6
559	1.0	1.1	557	3.2	3.0
214318	1.4	1.1	214408	2.0	3.7
319	1.5	1.4	630	1.8	1.8
386	1.3	1.1	218191	3.4	3.1
388	1.3	1.1	198	1.7	1.6
425	1.0	0.9	239	2.2	2.5
628	1.0	1.3	252	2.0	1.6
679	1.1	0.8	381	2.1	2.6
682	1.0	1.4	491	1.7	1.7
218054	1.0	0.9	222121	1.6	1.9
093	1.2	1.4	141	3.2	2.2
003	1.0	0.9	142	2.7	2.3
143	1.0	0.8	146	1.9	1.9
150	1.4	1.6	223510	1.9	2.1
188	1.0	0.8	520	2.0	2.2
193	1.0	1.2	524	2.7	2.2
197	1.0	1.1	530	1.6	1.7
211	1.0	0.8	533	3.0	2.9
238	1.0	1.0	535	1.9	1.8
241	1.1	1.0	208949	4.9	5.5
247	0.9	1.0	209045	4.6	4.5
251	1.5	1.8	218555	4.1	4.0
253	1.5	1.3			

Table 1.--Duplicate determinations of uranium on plant ash--Continued.

Sample no.	U in ash (ppm)		Sample no.	U in ash (ppm)	
	(1) Run	(2) Run		(1) Run	(2) Run
<u>Pinon pine</u>			<u>Juniper</u>		
214322	3.7	3.6	209975	1.0	1.0
632	5.0	4.8	957	1.3	0.5
218191	3.4	3.1	208971	1.0	0.5
441	5.8	6.0	209981	1.2	1.3
222135	4.2	3.7	983	1.2	1.2
136	4.9	3.3	991	1.3	1.2
140	3.9	4.3	210015	1.5	1.7
145	4.3	4.5	033	1.3	1.6
148	5.5	5.5	048	1.0	1.0
223509	4.8	4.5	214670	1.4	1.2
511	3.8	3.6	218183	1.2	1.5
<u>Juniper</u>			192	1.2	0.9
209012	0.2	0.3	256	0.7	1.2
027	0.5	0.4	462	1.1	0.8
031	0.4	0.4	496	1.1	1.3
037	0.7	0.3	223517	1.6	1.4
038	0.1	0.4	527	1.1	1.2
721	0.6	0.9	537	1.1	1.0
962	0.5	0.4	538	1.4	1.6
210048	0.3	0.5	209712	1.8	1.7
214678	1.0	0.6	719	1.8	2.4
865	0.8	0.5	982	1.8	2.0
866	0.5	0.4	210036	2.3	3.2
218123	0.2	0.2	218529	2.9	3.0
299	0.4	0.4	535	2.8	2.7
362	0.3	0.3	538	2.8	2.6
400	0.4	0.4	540	2.2	2.3
412	0.2	0.1	553	1.8	2.3
469	0.3	0.2	556	2.2	2.9
223504	0.2	0.2	221	2.2	2.4
531	0.8	0.7	222138	1.9	2.5
532	0.7	0.8	223514	2.1	1.9
540	0.7	0.6	516	2.5	2.4
218271	0.1	0.1	517	1.6	1.6
208945	1.1	1.2	528	1.6	1.9
209267	1.2	0.9	539	2.3	2.3
276	1.4	0.6	209713	5.7	6.2
303	1.4	1.3	980	4.9	4.0
676	1.4	1.7	210032	5.0	4.5
710	1.0	0.9	218533	5.4	4.5
718	1.3	1.5	539	3.1	3.5
720	1.2	1.7	541	5.0	4.8
968	1.8	1.2	542	3.7	3.8
972	0.9	0.9	558	3.4	3.5
973	0.8	1.2	223515	4.5	5.0
			534	3.5	3.5
			541	3.5	3.2

Table 1.--Duplicate determinations of uranium on plant ash--Continued.

Sample no.	U in ash (ppm)		Sample no.	U in ash (ppm)	
	(1) Run	(2) Run		(1) Run	(2) Run
<u>Juniper</u>			<u>Ponderosa pine</u>		
209714	10.5	9.1	213002	0.6	1.0
715	9.3	7.5	004	0.9	1.5
716	10.4	9.5	005	0.5	1.0
223513	7.0	7.0	212017	1.3	1.1
210037	14.0	13.0	019	1.3	1.2
027	9.0	8.0	042	1.3	1.3
222143	6.5	8.0	046	1.5	0.6
<u>Ponderosa pine</u>			051	0.8	0.9
218888	0.6	0.9	062	1.5	1.4
212900	0.4	0.4	223350	1.1	1.2
925	0.9	0.7	359	1.3	1.4
924	0.9	0.8	212832	1.7	1.7
041	0.3	0.8	853	2.0	2.0
223358	0.6	0.8	987	2.0	1.8
212830	1.3	0.5	998	2.0	2.7
834	1.0	1.1	223349	2.2	1.6
838	1.1	1.2	352	2.1	2.7
848	1.0	1.1	357	1.5	1.7
852	1.1	1.0	223360	1.7	2.3
877	0.9	1.0	361	2.7	2.7
913	1.4	1.2	362	2.0	1.7
930	1.0	1.0	213011	5.0	4.7
976	1.1	0.6	223346	3.4	3.4
989	1.0	0.9	347	4.2	5.5
991	1.3	1.1	348	6.5	6.5
997	1.3	1.5	353	3.9	4.0
			355	5.9	6.4
			356	5.8	5.9
			354	2.8	3.7

Table 2.--The range of uranium, arithmetic mean, variance, and standard deviation for each plant species studied.

Plant species	No. of pairs of samples	Range (in ppm)	Arithmetic mean (in ppm)	Variance (in ppm ²)	Standard deviation (in ppm)
Sagebrush	7	0.8 - 1.6	1.26	0.02429	0.16
Do.	29	1.6 - 3.2	2.43	0.09328	0.31
Do.	18	3.2 - 6.4	4.40	0.1839	0.43
Do.	10	6.4 - 12.8	9.64	0.4005	0.63
Do.	20	12.8 - 25.6	18.22	2.202	1.48
Do.	11	25.6 - 51.2	34.77	5.104	2.26
Pinon pine	15	0.0 - 0.8	0.65	0.01700	0.13
Do.	46	0.8 - 1.6	1.13	0.02717	0.16
Do.	22	1.6 - 3.2	2.31	0.1182	0.34
Do.	14	3.2 - 6.4	4.42	0.1321	0.36
Juniper	22	0.0 - 0.8	0.43	0.01636	0.13
Do.	30	0.8 - 1.6	1.19	0.05667	0.24
Do.	17	1.6 - 3.2	2.26	0.07559	0.27
Do.	11	3.2 - 6.4	4.28	0.1218	0.35
Do.	7	6.4 - 12.8	9.20	0.7329	0.86
Ponderosa pine	6	0.0 - 0.8	0.68	0.03583	0.19
Do.	23	0.8 - 1.6	1.10	0.05957	0.24
Do.	10	1.6 - 3.2	2.04	0.08700	0.29
Do.	8	3.2 - 6.4	4.85	0.1788	0.42

Table 3.--Combined data for range, arithmetic mean, and standard deviation.

No. of pairs of determinations	Range (ppm)	Arithmetic mean(x) (ppm)	Standard deviation(y) (ppm)
43	0.0 - 0.8	0.54	0.14
106	0.8 - 1.6	1.15	0.21
78	1.6 - 3.2	2.31	0.31
51	3.2 - 6.4	4.45	0.39
17	6.4 - 12.8	9.46	0.73
20	12.8 - 25.6	18.22	1.48
11	25.6 - 51.2	34.77	2.26

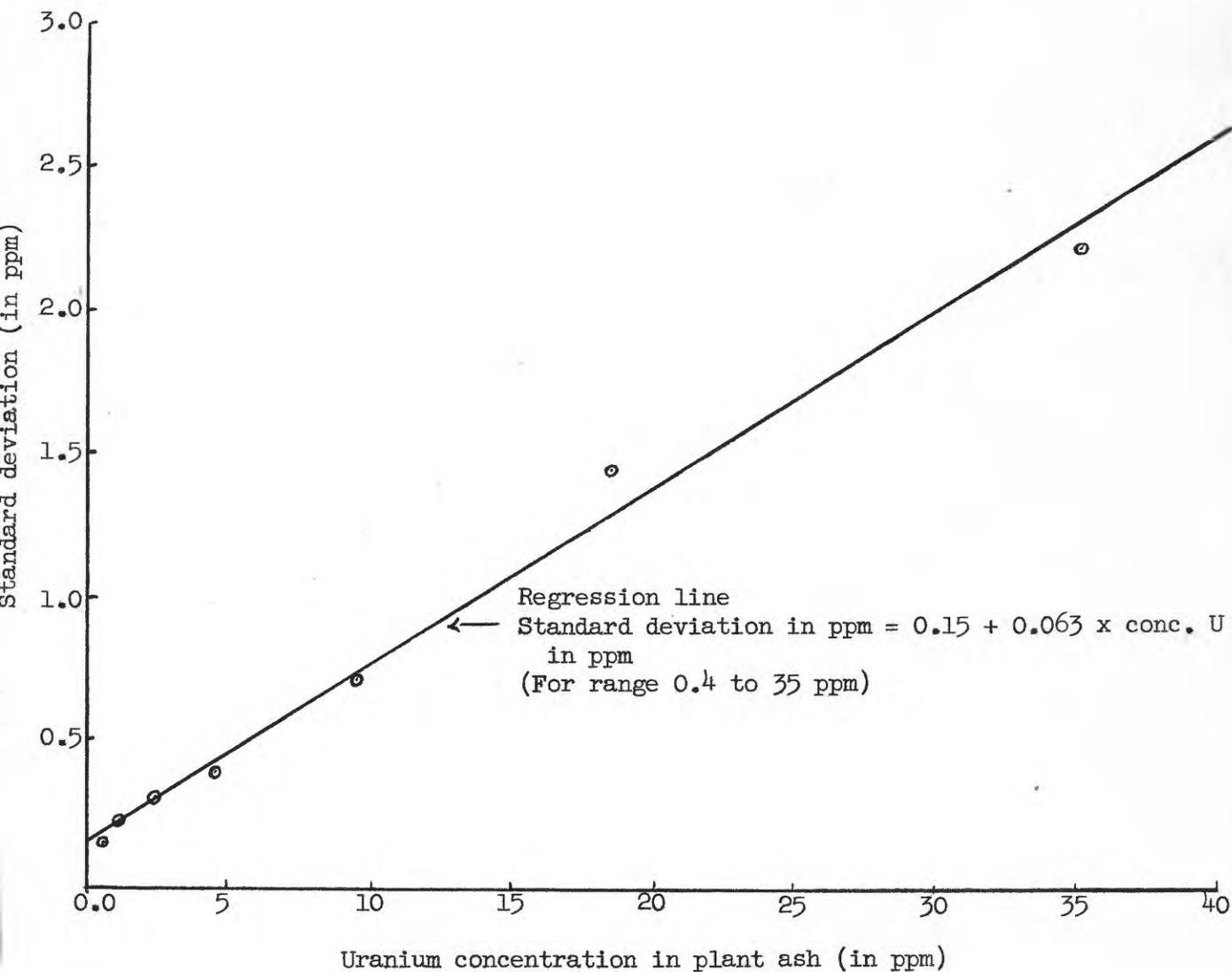


Figure 2.--Means and standard deviations from table 3 and their regression line.

obtained by the method of least squares (table 4). This formula, $y = 0.15 + 0.063x$, where y is the standard deviation and x is the uranium concentration in the ash, both in parts per million, allows a standard deviation to be estimated from a given uranium concentration. The range over which this regression formula is applicable is from about 0.4 to about 35 ppm uranium.

The following are examples of the use of this formula for estimating expected standard deviations:

- (1) Observed concentration of uranium in ash = 0.7 ppm. Then $x = 0.7$ and $y = 0.15 + (0.063)(0.7) = 0.19$ ppm or the expected standard deviation would be about 0.2 ppm, and the expected coefficient of variation would be about 27 percent after rounding.
- (2) Observed concentration of uranium in ash = 10.0 ppm. Then $y = 0.15 + (0.063)(10.0) = 0.78$ ppm or the expected standard deviation would be about 0.8 ppm, and the expected coefficient of variation would be 8 percent after rounding.

The above examples show one of the results of using a straight-line regression formula with two constants. Both the standard deviation and coefficient of variation change with changes in the observed uranium concentration. The change in the coefficient of variation at the lower levels of concentration is particularly desirable, as so many of the samples have low uranium contents.

For many purposes the formula could be rounded to $y = 0.2 + 0.06x$. If many solutions are needed, a graphical method may be helpful using a graph similar to figure 2.

Two precautions in the use of this formula should be noted. One is that the precision measured is for the analysis of uranium in a given sample of plant ash; the formula does not give the precision to be expected

Table 4.—Computation of regression line by least-squares method.

n	x	y	x^2	xy
1	0.54	0.14	0.2916	0.0756
2	1.15	0.21	1.3225	0.2415
3	2.31	0.31	5.3361	0.7161
4	4.45	0.39	19.8025	1.7355
5	9.46	0.73	89.4916	6.9058
6	18.22	1.48	331.9684	26.9656
7	34.77	2.26	1208.9529	78.5802
Summation	70.90	5.52	1657.1656	115.2203

Normal equations:

$$\text{I} \quad 5.52 = 7a + 70.90b$$

$$\text{II} \quad 115.2203 = 70.90a + 1657.1656b$$

Results: $a = 0.15, b = 0.063$

$$b = 0.15 + 0.063x$$

from two samples from the same tree. The other precaution is that the formula should not be overly extended (extrapolated) beyond the range of the samples used in its derivation (0.4 to 35 ppm U in ash).

It would, of course, be possible to subject these data to further statistical study and testing. However, a set of results not included in those used for the formula derivation is now available and a study of these results is thought to be a good test of the correctness of the formula. The results concerned are given in table 5. These are for uranium in ash from aspen twigs, and hence a different species from those used in deriving the standard deviation formula. The average difference between any set of duplicates may be derived from their standard deviation. The formula (after Youden, 1951, p. 16) is: $d = 1.128s$ where d is the difference and s the standard deviation. From this relation, the formula for the standard deviation previously given may be used to find the expected difference between duplicates of the same sample. Thus:
 $d = 0.169 + 0.071 U$, where d is the expected difference and U is the concentration of uranium in ash in ppm (in table 5 the uranium is based on the first run of each pair).

As an example, using sample no. 232367 in table 5, the first result was 0.1 ppm U; d , the expected difference, equals 0.169 plus 0.071×0.1 , or 0.18 ppm U after rounding. As the second result was 0.1 ppm U, the actual difference is 0.0.

Comparison of the averaged differences expected and found should give some confidence in the use of the original formula for estimating a standard deviation.

Table 5.--Observed and estimated average difference between pairs of determinations made on the ash of 24 aspen twig samples.

Serial no.	(1) Run	(2) Run	Absolute difference between pairs (ppm U)	
			Observed	Estimated
232367	0.1	0.1	0.0	0.18
377	0.1	0.1	0.0	0.18
397	0.1	0.1	0.0	0.18
414	0.1	0.2	0.1	0.18
425	0.1	0.1	0.0	0.18
349	0.2	0.2	0.0	0.18
339	0.3	0.5	0.2	0.19
344	0.3	0.7	0.4	0.19
410	0.3	0.2	0.1	0.19
	9 samples		Average = 0.09	Average = 0.18
232338	0.4	0.1	0.3	0.20
315	0.5	0.6	0.1	0.20
331	0.5	0.3	0.2	0.20
326	0.7	0.5	0.2	0.22
362	0.8	0.8	0.0	0.23
405	0.8	0.6	0.2	0.23
	6 samples		Average = 0.17	Average = 0.21
232310	0.8	1.0	0.2	0.23
269	1.0	1.2	0.2	0.24
320	1.2	0.9	0.3	0.25
274	2.0	1.8	0.2	0.31
295	2.2	2.5	0.3	0.33
300	4.4	3.5	0.9	0.48
285	5.1	4.5	0.6	0.53
290	7.8	6.3	1.5	0.72
279	11.0	11.0	0.0	0.95
	9 samples		Average = 0.47	Average = 0.45
	(Grand average for 24 samples)		0.25	0.29

A study of the accuracy of this method, as contrasted to its precision, has not been attempted. However, the use of blanks and of known solutions as standards, as described in the procedure, gives considerable assurance that there is no appreciable bias in the method.

CONCLUSIONS

1. The type of plant species (within the four species here studied) has little or no effect upon the precision. The standard deviation values were about equal for all four plant species. A few samples of ash from aspen indicate that these conclusions may be quite general for many species.

2. Over the range studied (0.4 to 35.0 ppm), a simple derived equation (standard deviation = $0.15 + 0.063 U$, where U is the observed uranium concentration in parts per million) is presented which gives a quick method for determining the expected standard deviation for a single uranium determination in plant ash. This should be useful in any interpretation of analytical results.

REFERENCES

- Cannon, H. L., 1954, Botanical methods of prospecting for uranium: Min. Eng., v. 6, p. 217-220.
- Cannon, H. L., and Starrett, W. H., 1956, Botanical prospecting for uranium on La Ventana Mesa, Sandoval County, N. Mex.: U. S. Geol. Survey Bull. 1009-M, p. 391-407.
- Grimaldi, F. S., May, Irving, Fletcher, M. H., and Titcomb, Jane, 1954, Collected papers on methods of analysis for uranium and thorium: U. S. Geol. Survey Bull. 1006, 184 p.

- Kinser, C. A., 1954, The Model VI transmission fluorimeter for the determination of uranium: U. S. Geol. Survey Circ. 330, 9 p.
- Stevens, R. E., Wood, W. H., Goetz, K. G., and Horr, C. A., 1956, Machine for preparing phosphors for the fluorimetric determination of uranium: U. S. Geol. Survey Trace Elements Inv. Rept. 578, 22 p.
- Youden, W. J., 1951, Statistical methods for chemists, New York, John Wiley and Sons, Inc., 126 p.