UM Libraries Depository

103314905024

This Thesis Has Been

MICROFILMED

Negative No. T- 1353

1952

Form 26

A COMPARISON OF METHODS OF DETERMINING THE AMOUNT
OF RADIUM IN ROCKS AND MINERALS.

BY

Oden Elbridge Sheppard, A.B.

Submitted in partial fulfillment of the
requirements for the degree of
Master of Arts
in the

GRADUATE SCHOOL

OF THE

University of Missouri.

1914

378.7M71
XSh49

A C K N O W L E D G E M E N T S .

The author wishes to thank Dr.W.G.Brown, Professor of Technical Chemistry in the University of Missouri, at whose suggestion this investigation was undertaken, for valuable assistance and encouragement in the pursuit thereof. He also wishes to thank Professor H.Schlundt for all specimens from the Yellowstone National Park and the carnotite concentrate specimen, and the City Clerk of Bradford, Pa. for the deep well sample from there.

TABLE OF CONTENTS.

I. Introduction.	page 1.
II. Electroscopes	" 3
III. Apparatus	" 5
A. Number 1.	" 5
B. Number 2	" 6
C. Number 3	" 7
IV. Some difficulties with and objections to the different forms of apparatus.	
A. Joly's furnace method	" 8
B. Solution in nitric acid apparatus.	" 10
C. Fusion apparatus	" 10
V. Standard used and calibrating the electroscope	
A. Apparatus 1.	" 12
B. Apparatus 2 and 3.	" 16
VI. Experimental results.	
A. With Joly's fusion method	" 19
B. With apparatus number 2.	" 21
C. With apparatus number 3 and comparison with number 2	" 27
VII. Summary and conclusions.	" 34

I N T R O D U C T I O N .

This paper is chiefly the outcome of a study of the radioactivity of the rock at different depths from the surface obtained during the drilling of the University deep well number 2. The first method described by J. Joly¹ for determining the quantity of radium in rocks and minerals was used. From the very beginning difficulty arose in getting results concordant enuf in calibrating the electroscope by this method. While I got calibration results that agreed as well among themselves as Joly's these did not seem sufficiently accurate for the work in hand. However about a hundred and twenty fusions were made in attempting to calibrate closer and in determining radium in various rock and mineral samples.

In addition to the rock from the deep well several of these samples were from the lot of Yellowstone National Park spring deposit specimens previously examined by Schlundt and Moore.² These samples yielded- varying with the samples- from 90% to several hundred per cent more emanation by the fusion method than by the solution method used by them.

Much trouble was experienced in regulating the rate of fusion etc.etc.³ which will be mentioned later and finally I undertook to replace the rubber bag of Joly with a carbon dioxide absorption train leading directly to the exhausted electroscope. Even this gave much trouble of regulation

1 Phil. Mag. vol.22,134.1911. 2 U.S.Geol.Survey,Bull.395.

3 Ebler - Zeit. für Elektrochemie. vol.18,532.1912.

on account of the shallowness of the mercury seal so that I tried substituting borax, and earlier bicarbonates¹, in the fusion in place of the sodium and potassium carbonates used by Joly. These results looked promising but here unfortunately the platinum resistance furnace gave way a second time. I then tried comparing the fusion method with a method by solution in nitric acid and immediate (without storing) determination of the emanation with other new features. Very promising results were obtained this way and the rest of my work on radium consists in comparing this method with a fusion method with carbonates in a hard glass test tube and a few determinations of radium in mineral and rock samples. The results of this comparison tend strongly, as will be shown, to prove an inherent error in Joly's method.

The electroscope made for the foregoing work was modified in some respects which make its use much more convenient. A method for mounting the gold leaf, simple and efficient, is described.

1. Bicarbonates were tried because C. Holthof claims that action between the silicate and carbonate takes place at a lower temperature than with the normal carbonates before fusion, and that for this reason there is almost no spattering onto the cover of the crucible.
Zeitschr. anal. Chemie, vol. 23, 1884, p. 499.

Fig. 1.

2a

ELECTROSCOPES.

The first electroscope used was that described by Randall¹ as his electroscope number 5. It was used only for a short time for qualitative work only and until the electroscope to be described could be completed. Randall's electroscope number 5 had too large an electrostatic capacity to be suitable for the work in hand i.e. was not sensitive enuf. The electroscope which was used was one designed by Dr. W.G. Brown and constructed by the University mechanician and myself. It consisted of a brass case (Fig. 1) $7\frac{1}{2} \times 12 \times 15\frac{1}{2}$ cm., two A. Pfeiffer brass stopcocks, a plate glass back and front mounted in picein, and the leaf system.

The leaf system is the distinguishing feature of the electroscope. It consists of the parts A, B, D, E, and F in Fig. 2. A consists of a brass rod X to which is attached a flat narrow brass plate M having attached to its upper part a short narrow brass plate N which makes a shoulder. To N is attached the narrow gold leaf O which extends just a trifle below M, by means of a drop of very dilute shellac varnish. B is a brass plate H having a central brass tube I tightly fitted. A is placed in B and held in place by sulphur around the rod X. This insulation seems almost perfect and caused very little trouble during the two years work. The close fitting lead washer D is placed on the tube I just below H and the whole placed in the threaded holder E so that the lead washer D is on top of E. Then the nut and cap holder F is screwed on making the electroscope air tight as regards the leaf

1 Trans. Am. Electrochemical Soc. vol. 21, 463. 1912.

Fig. 2.

3a

system. The rod X extends up as shown and the close fitting brass cap R may be placed on F after the electroscope is charged by touching ^{X with} the charging rod.

The gold leaf was cut by means of a razor blade - both the ordinary razor and the Gillette safety razor blades were used. The safety razor blades were found to be best. The gold ~~leaf~~ between two thin sheets of paper was placed on a piece of lead foil and a straight edge pressed firmly down on this and the razor blade drawn along the straight edge. This gave a leaf with an exceptionally good edge not the least bit ragged. By taking hold of the paper strips the leaf was gently shaken out on a piece of paper and by means of a clean dry knife blade brot in position and pressed gently against the shellac varnish on the plate N and the leaf cut to the proper length. It was found that the narrower ~~the~~ leaf was the more sensitive. The leaves varied from about 4 mm. in breadth to about 7 mm. and were about 3 1/2 cm. in length.

The inlets from the stopcocks are so arranged on the inside of the electroscope as to send the inrushing air to the side walls thus disturbing the leaf as little as possible. The entire electroscope was mounted on a wooden base and the telemicroscope made by Bausch and Lomb had a graduated scale and Ramsden eyepiece, magnification about 15 diameters, with a focal length of about 5 cm. and was mounted in front of the electroscope on a wooden block attached to this base. The electroscope has a capacity of about 1400 cc.

Apparatus Number 1.

Joly's Furnace and modifications.

The furnace used was an exact duplicate of Joly's first described furnace¹ (the one for use with a platinum crucible) except that instead of insulating the platinum resistance wire in powdered magnesia in a porcelain crucible the wire was enclosed in an alundum² cement cup which took the place of both the magnesia and the porcelain crucible.

From the furnace the gases first passed thru a U tube to condense steam and then thru two U tubes filled with soda lime to absorb the carbon dioxide and thence into a rubber football-bag. The manipulation of the furnace was the same as Joly describes. I found much difficulty in regulating a fusion so that the carbon dioxide was not given off faster than absorbed. This carbon dioxide would fill the rubber bag and the furnace would have to be stopped until the carbon dioxide was absorbed. Also there was always danger of a small leak in the rubber bag.³ For these reasons I later connected the furnace with two bottles containing strong potassium hydroxide solution, then a calcium chloride tube and thence directly into the electroscope. In making a determination I filled the entire apparatus with carbon dioxide from a cylinder⁴ and then exhausted the electroscope and apparatus except under the silica beaker. Then on starting heating I

1. Phil. Mag. vol. 22, 135. 1911. 2. Suggested by Dr. Brown.

3. In Zeit. für Elektrochemie vol. 18, 532. 1912, Ebler cites other objections.

4. I first tried using carbon dioxide generated from limestone in a Kipp generator but found that this showed decided radioactivity. The carbon dioxide from the cylinder showed no radioactivity.

controlled the reduced pressure under the beaker by means of the stopcock just outside the furnace using the mercury seal as an indicator.

Apparatus Number 2.

Apparatus for separating the emanation by means of nitric acid, heat, and carbon dioxide.

A small wide mouthed 200 cc. flask (Fig.3) with a three hole rubber stopper was used as a boiling vessel. Into this passed a tube from the carbon dioxide cylinder controlled by stopcock N. The acid was contained in the separatory funnel C and the gases and steam passed upward into the reflux coil condenser D thru the stopcock E and the condensing tube F (used to control the pressure in A.) thru the two potassium hydroxide solution bottles X and Y and the calcium chloride tube¹ and thence^{to} the exhausted electroscope. The potassium hydroxide solution was 20% by weight. To make a calibrating determination the uraninite was weighed into the dry flask A and the apparatus and electroscope exhausted to stopcock E. H was closed after mercury had reached height of U tube F. Then the stopcock I was closed and E opened gently and finally H. The nitric acid (diluted to 1:1 by volume) was then run in from C and heat applied to A, reduced pressure being constantly maintained in A by regulating the stopcock I.

1. It was found that at times the nitrogen oxides got this far in the apparatus and once even got into the electroscope and caused the leaf to stick to the plate M so that the leaf had to be discarded and so a little sodium peroxide was placed also in this tube to oxidize and absorb the last traces of them

Fig 3.

Finally when no other action occurred in A after boiling several minutes N was slowly opened to admit a slow stream of carbon dioxide to wash all emanation as far as X and finally the cylinder was detached from B and air swept thru to wash all emanation into the electroscope.

Apparatus Number 3.

Fusion Apparatus.

These fusions were carried on in hard glass test tubes 17 mm. x 25 cm. The apparatus just described was used except that in place of the flask and condenser a delivery tube from the inclined fusion tube was attached to E. For a calibration fusion 10 grams of mixed carbonates were mixed with 5 grams of powdered silica and a small known amount of uraninite. The apparatus was then exhausted to E and the reduced pressure in the fusion tube regulated to about 10 cm. of mercury by stopcock I. A blast lamp was used for the fusion. After the fusion was complete, liquid and homogeneous, a small crack was made in the fusion tube by touching it with a cold piece of metal. Air entered here to wash over all the emanation into the electroscope.

Some Difficulties with and objections to the
different forms of apparatus.

Joly's Furnace method.

Ebler¹ mentions the possibilities and probabilities for the colloidal rubber bag to absorb some of the emanation and also mentions other less probable objections. It is well known that there is danger of a small leak in a rubber bag and this causing loss of emanation and being a constant source of danger. Also as I have previously mentioned there is much difficulty in regulating the fusion so that the carbon dioxide is absorbed as fast as given off. Of course by adding more soda lime tubes the carbon dioxide could be absorbed rapidly enough but this would increase very largely the space that must be washed free from emanation into the rubber bag at the end of the fusion. Here is where the great difficulty and uncertainty of Joly's method is most noticeable i.e. in being sure of washing all the emanation from the apparatus into the limited capacity of the rubber bag² and then in being sure of getting all of this into the exhausted electroscope.

I think that the method as I have modified it as described under the apparatus overcomes all of these difficulties so far mentioned. Still another objection, however, must be offered to this method. This is that the platinum resistance wire after a time becomes brittle and finally actually

1. Zeit. für Elektrochemie vol. 18, 532. 1912.

2. The capacity of the bag I used was about 800 cc.

fuses. At points where there may be just the least stress the wire is drawn out a little and thus being diminished in diameter is here fused. This is very annoying and necessitates the taking out of all the platinum resistance wire and either welding it or sending it in as scrap platinum and getting new wire and then reforming the alundum around the wire. This fusing occurred four times during the some 120 fusions I made.

I also tried using Nichrome 2 - diameter 0.081 inches, resistance 104 ohms per 1000 ft. This is a special nickel-chromium wire put out by the Driver-Harris Wire Co. of Harrison, N.J. I tried to use some of this wire in the place of the platinum wire for the heating unit but found that this wire would not stand the heat nearly so long as the platinum wire and after a few fusions gave way.

Another difficulty is that the silica beaker soon becomes more or less etched on the inner top surface and is difficult to watch the progress of the fusion. This etching is probably due to the small amounts of fluorides in the substance fused.

Still another objection is the time required for the fusion. Using the same size charges and the same size platinum crucible as Joly I was almost never able to finish a fusion in less than three hours and keep the fused mass from boiling out over the top of the crucible though Joly seems to have taken only about an hour for a fusion.

I found this possible only a very few times when there was very little effervescence.

By using borax instead of the mixed carbonates this time-objection can be overcome and I found borax even more efficient than the mixed carbonates in getting off the emanation.

Solution in Nitric acid apparatus.

This apparatus offers no difficulties of manipulation and a little practice enables one to operate it perfectly. It also offers a very rapid method of getting off the emanation. In most cases tried from 15 minutes to a half hour was sufficient time to get the emanation from the dry finely ground substance into the electroscope.

The method has only two drawbacks that I can see. One is that boiling with nitric acid or for that matter with any of the common acids that can be used in glassware will not dissolve nor liberate all the emanation from all substances. The other is that this takes no account of the emanation given off in the cold from the substance as shown by Boltwood.¹ However as shown by my work all the emanation can be driven off from some substances e.g. carnotite by boiling with nitric acid even tho solution is not complete. Separate determinations must be made of the emanation given off in the cold.

1. Phil.Mag. vol.9,599.1905.

Fusion apparatus.

Care and practice are necessary to carry on the fusion

without breaking the fusion tube by letting drops of water condense and fall on its hot walls. Care and practice are also necessary in cracking the tube properly after the fusion is complete. The method by fusion in hard glass tubes under reduced pressure can only be used for small quantities -less than 10 grams - of a substance. Also from my limited work it seems to offer no advantage over the second method described and in fact is not nearly as efficient in getting the emanation from uraninite as the second method. In trying to replace the carbonates by borax I was unable to get a fusion without breaking the tube due largely to the amount of water given off.

Standard used and calibrating the electroscope
by the various methods.

The standard was the uraninite of unknown origin analysed by Randall¹ and used by him as a standard. It contains 53.03% of uranium when air dried and is ground to pass a sieve 120 meshes per inch (48 per cm.). The ratio of radium to uranium in old minerals was taken as 3.4×10^{-12} as given in Rutherford's book.²

There has been no work done with this uraninite to determine whether it gives off emanation in the cold. I stored a sample of it in a glass stoppered U tube and after a definite time washed out the air from the U tube into the exhausted electroscope shaking the uraninite during the passage of the air into the electroscope to prevent any occlusion of emanation. I made two determinations. on this point the data for which follow.

A sample of 1.3042 grams of uraninite was stored for four days and two hours (No.224) and for 4 days (No.231). Column 1 gives the determination number, column 2 the leaf value per scale division gain per hour $\times 10^{-12}$ grs radium, column 3 the gain in divisions per hour, column 4 the grams radium $\times 10^{-12}$ per gram uranium, and column 5 the per cent of the emanation given off in the cold.

1. Trans. Am. Electrochemical Soc. vol.21, 463. 1912.

2. Radioactive substances and their radiations. 1913.

1	2	3	4	5
224	3.84	771	7735	2.27
231	3.80	811	8686	2.55

The average is 2.41 % of the emanation given off in the cold. This correction must be applied to all of the work.

Apparatus Number 1.

Standardizing the electroscope by using Joly's furnace method.

For this purpose the charge consisted of a weighed amount of the uraninite mixed with 25 grams of the mixed carbonates of sodium and potassium (mixed in molecular weight ratio of 1:1) and 10 grams of a pure white saccharoidal sandstone from Crystal City, Mo. Below are tabulated some typical results.

Column 1 gives the determination number, column 2 the grams of uraninite, column 3 the air leak of the electroscope in scale divisions per hour, column 4 gives the maximum number of scale divisions fall per hour of the leaf, column 5 the gain in fall in scale divisions per hour, and column 6 the grams radium $\times 10^{-12}$ represented by a gain in the rate of fall of the leaf of 1 scale division per hour.

1	2	3	4	5	6
70	0.0283	16	703	687	7.75
71	0.0164	8	530	522	5.60
72	0.0045	14	128	114	7.11
73	0.0628	8	1742	1734	6.53
74	0.0058	16	193	177	5.71

The average is 6.54×10^{-12} and correcting for the emanation given off in the cold the value is 6.70×10^{-12} .

To test the carbonates and sand for radioactivity I made several blank determinations with 25 grams of the mixed carbonates and 10 grams of the sand. These resulted as follows. The column numbers have the same meaning as above.

1	23	4	45	6	7
77	8	8	0	0	-
78	7	8	1	0.26	
79	6	8	2	0.52	

The average is 0.25×10^{-12} which is within the experimental error. This shows that the sand and carbonates used were practically free from radioactivity and that there need be no correction made for them. However this was not the case with two samples of sand I had previously attempted to use for this purpose. One of these was of unknown origin and was not uniform in its radioactivity. The second one which was a sea sand was also not uniform in its radioactivity. The sand used finally was a saccharoidal sandstone from Crystal City, Mo. and is perfectly white and quite friable.

In reading the electroscope the readings were always taken between fixed points on the scale - between 80 and 20 - and timed by means of a stop watch. It was found that the maximum rate of fall of the leaf was reached at the end of three hours and that this maximum continued for about a half hour thereafter. Time was measured from time of admission into the electroscope. The time required to reach the maximum was found to be the same with all forms of apparatus ~~was~~ used.

After a lapse of several minutes between electroscope

readings it was almost invariably noted that the first reading showed a faster rate of fall of the leaf than any successive one. This is shown in the following table.

Time.	Time for leaf to pass over 60 scale divisions.
10:59	3 min. 22 sec.
11:04	3 min. 26 sec.
11:08	3 min. 32 sec.
11:14	3 min. 32 sec.
11:18	3 min. 32 sec.
12:06	3 min. 21 sec.
12:10	3 min. 32 sec.
12:14	3 min. 32 sec.

This is probably due to an accumulation of undischarged ions in the electroscope. It was found to be very persistent. The final constant values were always taken as this first reading was never a very constant value.

Many of the determinations by Joly's method had to be thrown out because of the evident failure to get all of the emanation despite the utmost precautions used. Several times in calibrating scarcely half as much emanation was obtained in the electroscope as at others tho as far as possible conditions had been identical in both cases.

Using borax in place of sand and carbonates with Joly's furnace the following results were obtained, the same leaf being used as in the preceding work. Column 1 is the determinative number, column 2 the grams uraninite, column 3 the grams borax, column 4 the air leak of the electroscope in scale divisions per hour and column 5 the maximum number of scale divisions fall per hour and column 6 the gain of scale divisions fall per hour and column 7 the value per scale division gain

per hour in grams radium $\times 10^{-12}$.

1	2	3	4	5	6	7
115	0.0202	2	8n	665	657	5.54
116	0.0000	2	7	8	1	-
117	0.0193	2	8	645	637	5.46
* 118	0.0153	2	10	470	460	5.99

The average is 5.66×10^{-12} and correcting for the emanation given off in the cold is 5.80×10^{-12} .

These results tend strongly to show that more emanation can be driven off from uraninite by fusing with borax than with mixed carbonates. It has been shown by Ebler¹ that as much emanation can be obtained from a Colorado carnotite by fusion with borax as by fusion with mixed carbonates. Later on in this paper will be shown that all the emanation was not gotten from uraninite by fusion with mixed carbonates. The percentage difference between fusing with carbonates and with borax in Joly's furnace is very close to the percentage difference between fusing with carbonates in ^ahard glass test tube and boiling off with nitric acid.

Calibration determinations were given for apparatus number 2 and 3 under description of the apparatus. The first calibration data by means of apparatus number 2 with the same leaf whose calibration by Joly's method and by substituting borax in the fusion resulted as follows. Column 1 gives the

* Electroscope leaked a little and some emanation lost.

1. Zeit fur Elektrochemie vol.18, 532.1912.

determination number, column 2 the grams uraninite, column 3 the air leak of the electroscope in scale divisions per hour, column 4 the maximum rate of fall of the leaf in scale divisions per hour, column 5 the gain in rate of fall of the leaf in scale divisions per hour, column 6 the value ~~for~~^{for a} gain of one scale division per hour in grams radium $\times 10^{-12}$.

1	2	3	4	5	6
120	0.0510	6	1624	.1618	5.68
123	0.0222	25	780	755	5.30
124	0.0204	30	752	702	5.23
125	0.0107	6	345	339	5.69
126	0.0081	6	257	251	5.81
127	0.0154	27	515	488	5.71
128	0.0129	8	418	410	5.67
172	0.00000	12	8	-4	-

The average is 5.57×10^{-12} and correcting for the emanation given off in the cold is 5.70×10^{-12} .

A water ^{Suction} pump was used in all cases to exhaust the electroscope and apparatus and after reading the maximum for each determination it was found necessary to keep a slow current of air going thru the apparatus for from three to four hours to wash out all the emanation and bring the electroscope back to its normal air leak. The air current had to be slow to prevent seriously disturbing the leaf. Alternately exhausting and filling the electroscope with air was found to be no more effective in lowering the leak than the ^{above} method. It was often found impractical

to bring the electroscope back to the normal air leak and the leak at that time was taken but in no case was this over 25 scale divisions above the normal air leak. After the leak gets down to this point it is rather persistent and reading it this way introduces only a very slight error - entirely negligible. By doing this it was often possible to make two determinations a day instead of one.

Experimental results.

By Joly's fusion method. (Apparatus number 1.).

The data for a comparison of the efficiency of fusing with normal carbonates and with bicarbonates by this method is of some interest and also shows something of the uncertainty of this method. Column 1 is the determination number, column 2 the grams uraninite, column 3 indicates that besides 10 grams of the sand 25 grams of the carbonates were used with the uraninite in the fusion, column 4 gives the air leak in scale divisions per hour, column 5 the maximum rate of fall of the leaf in scale divisions per hour, column 6 the gain in rate of fall in scale divisions per hour, and column 7 the value of each scale division gain per hour in grams radium $\times 10^{-12}$.

1	2	3	4	5	6	7
47	0.0080	$\left\{ \begin{array}{l} \text{Na}_2\text{CO}_3 \\ \text{K}_2\text{CO}_3 \end{array} \right.$	7	327	320	4.50
48	0.0164	"	5	466	461	6.41
49	0.0122	"	4	373	369	6.23
50	0.0156	"	6	520	514	5.47
51	0.0154	$\left\{ \begin{array}{l} \text{K}_2\text{CO}_3 \\ \text{NaHCO}_3 \end{array} \right.$	4	622	618	4.50
52	0.0071	"	4	240	230	5.28
53	0.0127	"	5	420	415	5.55

The average for the first four corrected for the emanation given off in the cold is 5.78×10^{-12} and for the last three is 5.24×10^{-12} . From these results it would seem that one was about as efficient as the other tho more consistent results were got with the bicarbonate. The carbonates were mixed in both cases in the molecular ratio of 1:1.

The following table contains a number of determinations.

Column 1 is the determination number, column 2 the grams of the sample, column 3 is the grams sand, column 4 is the grams of mixed normal carbonates, column 5 the air leak in scale divisions per hour, column 6, the maximum number of scale divisions per hour fall, column 7 is the gain per hour in scale divisions fall and column 8 is the grams radium $\times 10^{-12}$ per gram of the sample. 8a is the value using the first calibration, 8b using the second and 8c using the third.

1	2	3	4	5	6	7	8		
							a	b	c
80	10	10	25	12	6	-6	-	-	-
81	10	10	25	4	6	2	1.34	1.16	1.14
82	10	10	25	6	8	2	1.34	1.16	1.14
83	10	10	25	4	26	22	14.74	12.76	12.54
84	15	10	25	3	12	9	4.02	3.49	3.42
85	20	0	25	2	10	8	2.68	2.32	2.28
86	10	10	25	4	10	6	4.02	3.48	3.42
87	10	10	25	2	8	6	4.02	3.48	3.42
88	15	10	25	3	11	8	3.57	3.10	3.04
89	15	15	25	4	7	3	1.34	1.16	1.14
90	25	15	0	3	5	2	.53	.46	.45
92	5	4	25	3	14	11	14.74	12.76	12.54
93	10	0	25	2	42	40	26.8	23.20	22.80
94	10	0	25	4	44	40	26.80	23.20	22.80
97	5	0	25	3	960	957	1282.40	1110.	1091.

All the determinations in this table were made with the leaf whose calibration by three methods was given under calibrating and this affords a table for comparison of these values.

Number 80 is a barite of unknown origin. Nos. 81 to 87 inclusive were sand from a deep well boring near Bradford, Pa. The depth at which the sample was taken was 5690 feet. Nos. 88 to 90 inclusive were sample 17 - a limestone - from University of Missouri well number 2 on the campus. The depth at which this sample was taken was 85 feet. No. 92 is a spring deposit sample from the Artists Paint Pot, Gibbon Meadows Yellowstone National Park.¹ Nos. 93 and 94 is a sample from Forest Spring Canon Yellowstone National Park.¹ No. 97 is a spring deposit from Doughty springs Delta County western Colorado.

Determinations using apparatus number 2.

After determination number 128 was made the gold leaf was lost by nitrogen oxides getting over into the electroscope as has been mentioned above. Hence a new leaf had to be mounted and calibrated. Column 1 gives the determination number, column 2 the grams uraninite, column 3 the air leak in scale divisions per hour, column 4 the maximum number of scale divisions fall per hour, column 5 the gain in scale divisions fall per hour and column 6 the value of each scale division gain per hour in grams radium $\times 10^{-12}$.

I. Schlundt and Moore. U.S. Geol. Survey Bull. 395/
 Their values for these samples by the solution method are respectively 3.57×10^{-12} grams radium per gram and 1.45×10^{-12} grams radium per gram.

1	2	3	4	5	6
130	0.0151	8	484	476	5.71
131	0.0224	24	758	734	5.49
132	0.0185	12	661	649	5.14

The average is 5.44×10^{-12} and corrected is 5.57×10^{-12} .

Now come a series of results on a sample of a Colorado carnotite which had been thoroughly mixed and sampled and put thru a 120 mesh sieve. By using apparatus number 2 it is possible to make two determinations in a 14 hour day instead of one as with the first apparatus. The peculiar part about the following results is that nearly always a higher value was obtained from the morning determination than from the evening one. These samplese were taken from the same weighing bottle.

1	2	3	4	5	6	7
133	0.3432	evening	16	1069	1053	17121
134	0.2365	morning	8	864	856	20164
135	0.1363	evening	24	428	404	16523
136	0.2049	morning	9	742	733	19925
137	0.1982	evening	18	617	599	16833
138	0.1940	morning	8	Lost		
139	0.2064	evening	20	645	625	16866
140	0.2139	morning	8	655	647	16838
141	0.5104	evening	24	1687	1663	18146
142	0.3140	morning	20	1108	1088	19300
143*	0.2289	evening	15	691	676	16449
144	0.2000	morning	8	Lost		
145*	0.1474	morning	8	604	596	22521
146*	0.1590	evening	12	554	542	18986
147*	0.1226	morning	12	475	463	21028

In the above table column 1 gives the determination number, column 2 the grams of sample, column 3 the time of day, column 4 the air leak in scale divisions per hour, column 5 the maximum number of scale divisions fall per hour, column 6 the gain in divisions fall per hour, and column 7 the grams radium $\times 10^{-12}$ per gram sample. Those marked * were kept in cold storage several hours before the sample was weighed out.

At this point a leak in the electroscope caused the loss of the gold leaf and a new one was mounted and calibrated as follows. Column 1 gives the determination number, column 2 the grams uraninite, column 3 the air leak in scale divisions per hour, column 4 the maximum number of scale divisions fall per hour, column 5 the gain in scale divisions fall per hour, and column 6 the value of each scale division gain in grams radium $\times 10^{-12}$.

1	2	3	4	5	6
149	0.0090	12	457	445	3.64
150	0.0214	20	1054	1034	3.73
151	0.0139	12	694	682	3.67
152	0.0154	8	745	737	3.76

The average is 3.70×10^{-12} and corrected is 3.79×10^{-12} .

Further determinations on the carnotite sample gave the following results. The columns are numbered the same as in the second table preceding

1	2	3	4	5	6	7
148	0.1828	evening	9	837	828	17714
154	0.1948	morning	12	995	983	19358
155	0.2153	evening	24	1014	990	17427
156	0.2790	morning	15	1440	1425	19357
157	0.3233	evening	20	1543	1523	17853
158	0.2209	morning	8	973	965	16556
159	0.2628	evening	18	1186	1168	16844
160	0.1919	morning	9	Lost		
161	0.2336	evening	20	1096	1076	17457
162	0.1960	morning	10	978	968	18717
163	0.1992	evening	16	966	950	18072
164	0.1665	morning	8	822	814	18528
165	0.1714	evening	16	Lost		
166 *	0.2803	evening	24	1200	1176	15900
167	0.1308	evening	8	644	636	18428
168*	0.3340	morning	8	1588	1580	17929
169	0.2875	evening	12	1459	1447	19074
170	0.1593	morning	12	800	788	18747
172	0.0000	evening	12	8	-	-
176	0.1615	morning	8	Lost		

* Thoroughly mixed and shaken up before sampling.

The average of 29 determinations gives 18230×10^{-12} grams radium per gram.

During this time two determinations were made to find how much emanation was given off in the cold. For this purpose two grams of the carnotite was stored in a U tube having glass stopcocks controlling each arm. Cotton was put in the upper part of one of the arms. This side

was the one nearest the electroscope when introducing the emanation into the electroscope and kept any of the carnotite from being blown into the electroscope. The electroscope was exhausted and the U tube attached to its inlet.

A drying train consisting of a calcium chloride tube and a U tube partly filled with concentrated sulphuric acid was attached to the other arm of the storing tube. The air was first bubbled thru the concentrated sulphuric acid and then passed into the calcium chloride tube on thru the U tube into the electroscope. Column 1 gives the determination number, column 2 the size of sample in grams, column 3 the time stored in days, column 4 the air leak in scale divisions per hour, column 5 the maximum scale divisions fall per hour, column 6 the gain in scale divisions fall per hour, and column 7 the per cent of the maximum value for the emanation¹, and column 8 the grams radium X 10^{-12} per gram sample.

1	2	3	4	5	6	7	8
152	2	15.104	12	1963	1951	93.42	3957
171	2	8.90	20	1771	1751	79.90	4152

The average is 4054×10^{-12} then the total radium per gram of carnotite concentrate is 22284×10^{-12} grams per gram. I at first thot that there might be some connection between the temperature or pressure or both and the high and low values obtained for the carhotite, but tho I noted both temperature and pressure for quite a series of the above results there is absolutely no connection between them and the high and low values. Cold storage was tried

1. This value was taken from Makower and Geiger's
 "Practical Measurements in Radioactivity." 1912.

hoping by this means to get consistent results but without success. Thinking that a lower temperature might allow of more of the emanation being occluded if occlusion was the cause.

Next I thought that if this were true the stopper having been in the bottle all night more emanation would be occluded than during the day period where the weighings were only 6 hours apart. This would explain the higher results in the morning and the lower ones in the evening. To test this I thoroughly shook up the substance before weighing out the sample and left the stopper out of the weighing bottle between weighings. The results continued for the most part the same.

I next tried dividing the sample and putting half of it in one weighing bottle and the other half in another, weighing out of one bottle in the morning and out of the other in the evening. The results seem to be a little closer together but the high and low values continued. I then set the two weighing bottles aside for some time and on determining a sample from each bottle during the same day got uniformly high results. These two determinations were made by fusion in hard glass test tube. This fusion apparatus (No.3) showed the morning and evening effect likewise.

Number 174 below is a sample of the Doughty springs deposit mentioned under No.97 above. No.175 is the sample from the University well as mentioned under Nos.88 to 90 inclusive. Column 1 gives the determination number, column 2 the sample size in grams, column 3 the grams radium x 10⁻¹² per gram of sample.

<u>1</u>	<u>2</u>	<u>3</u>
174	5	162
175	25	0

Nitric acid does not dissolve either of these samples completely. From the spring deposit it is evident that the nitric acid liberates only a very small part of the total emanation. Number 175 shows that the carbonate and nitric acid soluble part of the University well sample shows no radioactivity. This has been confirmed in determination number 212.

With apparatus number 3 and comparison between it and apparatus number 2.

In the following three determinations the carnotite concentrate before mentioned was used and in each case the sample was mixed with 10 grams of normal carbonates and fused. In Number 177 the fusion tube was ^{not} evacuated before starting the fusion and in the other two it was. This means that in Number 177 the air from the fusion tube was collected in the electroscope while in ^{Sample} numbers 178 and 179 it was pumped away before beginning the fusion. Column 1 gives the determination number, column 2 sample ~~in~~ in grams, column 3 gain in scale divisions fall per hour, and column 4 the grams radium $\times 10^{-12}$ per gram of sample.

Value of leaf per scale division gain per hour = 3.79×10^{-12} ^{per} gram Ra

1	2	3	4
177	0.1410	673	18090
178	0.2155	865	15212
179	0.1702	651	14495

It is noticed that the second two give a value which is much lower than the first one and that the first one agrees very well with what I have *obtained* before with apparatus number 2. A probable explanation of this is that evacuating the fusion tube before starting the determination draws from the sample a part of its emanation. This is more probable ~~from~~ the fact that boiling with nitric acid seems to get all the emanation from carnotite concentrate tho it does not dissolve all of it. This shows that the emanation is not very firmly held by the carnotite. This fact too would seem to prove that pressure was at least partly responsible for the morning and evening differences tho the samll changes in barometer readings - never over 5 mm. during my work - did not make a noticeable difference when the determinations do not check better than within 3 or 4 per cent of each other.

At this point I lost the gold leaf. It became twisted and in trying to straighten it out I tore it. I mounted and worked with several leaves before I found another one satisfactory. Below are the calibration data for this leaf with apparatus 1 and 2. Column 1 gives the determination number, column 2 the apparatus number, column 3 the grams uraninite, column 4 the air leak in scale divisions per hour, column 5 the maximum rate of fall in scale divisions per hour, and column 7 the value of the gain of one scale

division per hour in grams radium $\times 10^{-12}$.

Since numbers 202 and 204 did not seem to get all the emanation from the uraninite in sample 208 and 209 I added to each fusion 5 grams of the white sand to see if the increased effervescence would not produce more of the emanation.

1	2	3	4	5	6	7
202	3	0.0245	14	968	954	4.63
204	3	0.0202	20	844	824	4.42
205	2	0.0355	15	1636	1621	3.94
206	2	0.0283	48	1414	1366	3.74
208	3	0.0261	24	1054	1030	4.56
209	3	0.0300	18	1180	1162	4.65

The average with apparatus number 3 is when corrected for emanation given off in the cold 4.67×10^{-12} and for apparatus number 2 when corrected 3.95×10^{-12} .

These results show that the fusion method with mixed carbonates and even with mixed carbonates and sand does not get all the emanation from uraninite. The determinations to follow show that the same amount of emanation can be obtained from the carnotite by the fusion method as by using nitric acid. In Joly's work he calibrates by fusing the uraninite with carbonates and silica and thus fails to get all the emanation off and gets too high a value for each scale division gain in his leaf fall. Then he determines a rock sample by the fusion method and if here he gets a high value for the sample it is probable that he does get all the emanation off from it and when he compares it with the uraninite which holds back some of its emanation the value appears high.

This assumption will serve to show how he could have gotten values from 20 to 30 per cent higher with the fusion method than the previous determinations made on these rock samples made by other methods. Since the percentage difference that I get between the two calibration methods is comparable with this.

It will be noted in determinations 177 and 179 that I have used the calibration values as determined by apparatus number 2. Also in the following table I have followed this plan because the amount of emanation - the gain in scale divisions fall per gram carnotite concentrate-is the same whether I use apparatus number 2 or 3.

1	2	3	4	5	6	7
212	25	2	28	16	-12	-
213	0.1504	3	8	718	710	18647
214	10.5	3	15	24	9	3.38
216	3	3	12	20	8	10.53
217	5	3	12	16	4	2.96
218	Blank	3	12	13	1	.40
220	5	3	27	1600	1573	1243
221	2	3	16	758	742	1465
222	1.8	3	20	722	702	1540
223	00.3010	3	8	1459	1451	19041

In the above table column 1 gives the determination number, column 2 the grams sample, column 3 the apparatus number, column 4 the air leak in scale divisions fall per hour, column 5 the maximum number of scale divisions fall per hour, column 6 the gain in scale divisions fall per hour, and column 7 the grams radium x 10^{-12} per gram.

Number 212 is the sample from the University deep well at a depth of 725 feet - sample 145 .

Number 214 is the residue from 212 after filtering and washing.

Numbers 213 and 223 are the same carnotite as before which had been stored in separate weighing bottles for about a month. Number 215 is another Yellowstone National Park sample labelled Terrace Springs #2 and its value from Schlundt and Moore's work by the solution method is 1.87×10^{-12} grams radium per gram. Number 216 is another of these labelled Ryolite, Golden gate whose solution method value is 1.51×10^{-12} grams radium per gram.

Number 217 is the deep well sample from near Bradford, Pa.

Number 218 is a blank with 10 grams of the carbonates.

Number 220, 221, and 222 are the Doughty springs deposit which is largely barium sulphate. The average of these three determinations gives 1416×10^{-12} grams radium per gram.

Another leaf was lost and a new one was mounted and calibrated as follows. Column 1 gives the determination number, column 2 the grams uraninite, column 3 the gain in scale divisions fall per hour, and column 4 the grams radium $\times 10^{-12}$ per gain of one scale division per hour.

1	2	3	4
225	0.0240	1129	3.83
226	0.0463	2213	3.77

The average when corrected gives 3.90×10^{-12} .

Samples of the Doughty springs deposit were then determined with apparatus number 2 but using 50 cc. of concentrated sulphuric acid instead of 30 cc. of dilute nitric acid. It was found that the deposit was soluble in concentrated sulphuric acid. .

Column 1 below gives the determination number, column 2 the grams sample, column 3 the gain in scale divisions per hour and column 4 the grams radium $\times 10^{-12}$ per gram.

1	2	3	4
227	2	1684	3233
228	2	542	1057
229	2	660	1287
230	2	714	1392

Number 227 is a very anomalous result and was probably due to a leak in the insulation as I noticed for the first time a leak in this leaf system insulation after this determination. On carefully brushing the dust from the insulation the leak disappeared. Number 228 is low probably due to the fact that it was not boiled so vigorously nor so long as the other two samples. The average for the other two results is 1345×10^{-12} grams radium per gram sample. This compares very favorably with the results by the fusion method. It looks as the solution in a liquid and boiling means complete liberation of the emanation and it is suggested that this would be the best way of making all determinations. Silicates might be decomposed by hydrofluoric acid in a platinum vessel.

To further try out this point of failing to get all the emanation from uraninite by fusing I made a fusion with a sample of uraninite the data of which are below. Column 1 gives the determination number, column 2 the grams of sample, column 3 the gain in scale divisions per hour.

1	2	3
232	0.0700	2755
233	-----	371
		<u>3126</u>

Calculating back from the known value per scale division gain in fall as determined by the second method the gain in scale divisions for this sample should be 3232. Considering the two determinations made to get this total value - the first by fusion with carbonates and the second by treating this fusion with nitric acid - 3 % is very good agreement. It at least shows that not all of the emanation is driven off from uraninite by fusion. The percentage of emanation by fusion agrees very well with the previous attempts at calibrating by the fusion method.

Summary and Conclusions.

1. All the emanation can not be obtained from uraninite by fusion with mixed carbonates. Solution in nitric acid does liberate all the emanation. This is true also of fusion with borax. The percentage of emanation that is liberated from the uraninite by fusion with carbonates is a constant, probably varying with each uraninite.

2. From the above it is evident that calibration cannot be made accurately by using the fusion method with uraninite as a standard and hence that Joly's

higher values for the radium in rocks by the fusion method is open to serious criticism.

3. From my work it seems that the fusion method does give much higher results for rock specimens than the solution and boiling off method.

4. The emanation is very loosely held by carnotite specimens. A large per cent - over 18 % in this case - being given off in the cold and the remainder given off either by fusion with borax or carbonates or boiling with nitric acid tho the sample does not completely dissolve in the nitric acid. From the morning and evening effect it is probable that the amount of emanation given off in the cold varies with the temperature, pressure, and whether the sample is open to air or not. Probably all three of these enter in to cause the effect noted.

5. Joly's apparatus, especially the rubber bag and the double transfer of the emanation, is open to serious criticism in the directions outlined in this paper.

6. Boiling off with nitric acid or with some other acid as necessity demands seems a very promising way to separate the emanation from rock and mineral samples. This method seems especially good for carnotite. Solution in an acid seems to liberate all the emanation so that it can be driven off by boiling.

7. Fusion with carbonates in a hard glass test tube as suggested by Dr. Schlundt seems a ~~possible~~ method for carnotite. It will not do for minerals or rocks with very low radium content where a large sample must be used.

UNIVERSITY OF MISSOURI
COLUMBIA

DEPARTMENT OF CHEMISTRY

The attached thesis of
Oden Elbridge Sheppard, A. B.
is "Approved" as to matter,
results and quality of the work.

The form is hardly suitable
for permanent preservation

N. G. Brown

15 May 1914

010-100950883

378.7M71

XSh 49

RECEIVED
OCT 6 1914
UNIV. OF MO.

This thesis is never to leave this room.

Neither is it to be checked out overnight.