UNCLASSIFIED

No. 38330

ISC-417

November 4, 1953

Contribution No. _____ from the Institute for Atomic Research and Department of Chemistry, Iowa State College, Ames, Iowa. Work was performed in the Ames Laboratory of the A.E.C.

ISC-417

THE DETERMINATION OF MESOTHORIUM IN THORIUM NITRATE

M. Allison, R. W. Moore, A. E. Richardson
D. T. Peterson and A. F. Voigt

ABSTRACT

A method is described for determining the amount of Ra^{228} (MsTh_1), the 6.7 year daughter of Th^{232} , present in thorium. The method is rapid, reproducible and accurate.

In connection with the processing of thorium for use in atomic energy or other applications, the behavior of the natural impurities in thorium, its daughter products, becomes of interest. The longest lived member of the chain of decay products is 6.7 year Ra^{228} or mesothorium-1 (MsTh_1) which has long been used as a component of luminous dial paint in place of Ra^{226} . It is the only non-thorium member of the chain with a half-life of more than a week. It has considerable commercial value and under certain circumstances may constitute a health hazard.

An estimate of its toxicity based on its chemical nature and half-life and the half-lives and energies of its alpha emitting daughter products shows it to be about as toxic as radium (Ra^{226}) if equal activities of the two are compared. Since its half-life is shorter than that of radium by a factor of 240, on a weight

UNCLASSIFIED

U

This report has been photostated to fill your request as our supply of copies was exhausted. If you should find that you do not need to retain this copy permanently in your files, we would greatly appreciate your returning it to TIS so that it may be used to fill future requests from other AEC installations.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

basis it is roughly 240 times as toxic as radium, making it one of the most toxic substances known. Fortunately this short half-life also establishes that its abundance is very small. At equilibrium 0.47 micrograms or 100 microcuries of Ra^{228} are present in each kilogram of thorium.

The decay and growth relationships in the thorium series are quite complicated (1). However, the amount of Ra^{228} , the first daughter product, follows the simple growth equation and in a period of 7 years after a separation of thorium and radium will be back to about half the above concentrations. The rate of growth in a freshly separated sample is close to 0.2 per cent of the maximum each week.

The separation of the Ra^{228} from a fairly old thorium sample and its collection and concentration in a small amount of material in chemical or metallurgical processing could create a health hazard. On the other hand the amount of Ra^{228} in a freshly separated sample would be so much smaller that the same operation could be done without hazard.

Consequently, it may be important either to know the history of the thorium being processed or to be able to analyse for its Ra^{228} content. Since this history includes the types of processes through which the thorium has been carried and the behavior of the Ra^{228} through these processes, it is not always determinable. An analytical method for Ra^{228} becomes the only answer in such a situation.

The complex decay chain of thorium (Fig. 1) makes the analytical problem difficult. Since Ra^{228} is a beta emitter, analysis by beta counting would appear feasible. However, its beta ray has a very low energy, 0.053 Mev, making it nearly impossible to measure.

Fig. 1 - Thorium Decay Chain.

The growth of its daughter, 6.1 hour Ac^{228} or mesothorium-2, would also complicate the analysis since it has a 1.55 Mev beta. The obvious answer, to let the daughter grow to equilibrium before making the measurement on the sample, is of no value since the other radium isotope in the chain, Ra^{224} or thorium-x, also gives rise to beta emitters which grow into the sample in about the same length of time. These are 10.6 hour Pb^{212} (ThB) followed by 60.5 minute Bi^{212} (ThC) and 3.1 minute Tl^{208} (ThC").

The two radium isotopes are present in thorium in very different amounts at various times after the preparation of pure thorium sample. As stated above, the growth of Ra^{228} is the simple growth of a daughter product, the first member of a chain, obeying the equation $(1 - e^{-\lambda t})$ in which λ is $0.693/6.7$ or 0.103 yr.^{-1} . The re-growth of Ra^{224} after a separation is much more rapid, of course, since in this case λ is 69.3 yr.^{-1} . However, once Ra^{224} reaches equilibrium it follows the behavior of its parent, the 1.9 year Th^{228} (RdTh). Because the chain has been broken by removal of Ra^{228} , the Th^{228} and Ra^{224} decrease in abundance with time for about 5 years at which time they are present to about 0.4 of their maximum abundance. They then gradually increase and are back near equilibrium in 20 years. Thus, a month after separation the Ra^{224} content would be near the value which it had before the separation while the Ra^{228} content would be less than a per cent of its pre-separation value. On the other hand, in thorium which has stood for about 6 years both radium isotopes would be near half their maximum concentration.

An analysis for total radium isotopes would have little meaning as far as the Ra^{228} content is concerned and a distinction

111

between the two radium isotopes must be made in order to determine the Ra^{228} . By reason of its shorter half-life, Ra^{224} is not a health hazard except at much higher concentrations than those for Ra^{228} . It is obviously of little value as an industrial source of alpha radiation. Its short life also means that it will decay out of a separated radium sample containing both isotopes so that the activity 3 to 4 weeks after the separation would be a measure of the Ra^{228} only. However, a delay of 3 weeks between the time of doing the analysis and obtaining the answer is certainly not desirable.

Examination of Figure 1 shows that Ac^{228} is the only isotope of actinium or of any rare earth-like element in the decay chain. Also, within two days after a separation the radioactivity due to Ac^{228} will be equal to that of Ra^{228} and will continue this way until another separation is made. Consequently, a determination of this unique isotope, Ac^{228} , can be used to measure the Ra^{228} content. The half-life is long enough to permit a fairly thorough separation and sufficiently different from other members of the chain that the purity of the precipitate can be checked by following the decay. Back extrapolation of this decay curve to the time of separation gives a number which measures the Ra^{228} content.

With the above ideas in mind a search for suitable separation methods was made. Outstanding among possibilities was the method developed by Hagemann (2) for the separation of actinium from other heavy elements using thenoyltrifluoroacetone (TTA). This method has been adapted to the problem and used to determine the Ra^{228} content of thorium and its compounds having a variety of ages. The remainder of the paper describes the method and the results obtained.

6115-1

EXPERIMENTAL

The method used for the determination of Ra^{228} in thorium samples is based on the separation of thorium and its radioactive decay products by extraction with thenoyltrifluoroacetone in benzene (2). In the presence of lanthanum and lead carriers, the thorium is removed by extraction at pH 2. The lanthanum, actinium and lead are removed by extraction at pH 6. Lead is removed by precipitating it as the sulfide. Lanthanum and actinium are then precipitated as oxalates, filtered and counted. The activity of this precipitate extrapolated back to the time of separation gives a value for the Ra^{228} activity of the original thorium sample which shows good constancy between runs and which agrees with the values obtained by separating the radium isotopes and waiting for the Ra^{224} to decay.

REAGENTS

The reagents used and their concentrations are listed below.

Thenoyltrifluoroacetone, TTA (Dow Chemical Co.) 0.25M in benzene

Ammonium hydroxide, 1 to 1

Sodium hydroxide, 1.0N

Nitric acid, 0.1N

Oxalic acid, 10 mg/ml

Lead nitrate, 10 mg of lead/ml

Lanthanum nitrate, 10 mg lanthanum/ml, 5.86 g La_2O_3
and 10 ml concentrated HNO_3 , diluted
to 500 ml

Fluoborate solution, 10 mg/ml, 1.9 g of NaF and 0.71 g of
boric acid diluted to 100 ml

Bromocresol green - chlorophenol red mixed indicator (3)

6175-6

APPARATUS

The radioactivity measurements were made with a Nuclear Instrument and Chemical Corporation Model 161 scaling unit and a Tracerlab Type TGC-1 Geiger tube with a 2.2 mg per sq. cm window.

PROCEDURE

The sample should contain no more than 0.85 grams of thorium. Thorium nitrate can be dissolved in water but thorium metal or thorium oxide should be dissolved in nitric acid plus about 5 drops of solution containing 10 mg per ml of fluoborate ion. The solution is diluted to 40 ml and 0.5 ml of lanthanum nitrate solution and 1 ml of lead nitrate solution are added as carriers.

The pH of the solution is raised with sodium hydroxide until thorium hydroxide just begins to precipitate. The thorium is extracted by shaking in a separatory funnel for 15 minutes with three successive 50 ml portions of TTA in benzene. The aqueous layer now contains the daughter products free of thorium.

If zinc is present in the sample, it should be removed at this point by means of a mercury cathode. The apparatus described by Melavan (4) is satisfactory. A current of 0.2 to 0.3 amperes for 45 minutes is sufficient to remove up to 0.100 grams of zinc.

The aqueous solution is adjusted to the color change of bromocresol green - chlorophenol red indicator (pH 6.1). The actinium, lanthanum, and lead are then extracted by shaking for fifteen minutes with 50 ml of TTA solution. The pH is readjusted to pH 6 every

five minutes during the extraction. A second extraction is made with 50 ml of fresh TTA and the two portions of TTA are combined. The time of the final extraction is noted and taken as the zero time in the extrapolation of the counting rate. The activity is stripped from the TTA solution by two successive extractions with 50 ml of 0.1N nitric acid.

The 0.1N nitric acid solution containing lanthanum, actinium, and lead is freed of benzene by boiling and then cooled before precipitating lead sulfide by bubbling H_2S through the solution. The lead sulfide is separated by centrifuging; the excess hydrogen sulfide removed from the centrifugate by boiling. Lanthanum and actinium oxalate are precipitated by adding 5 ml of oxalic acid solution and adjusting to pH 5 with dilute ammonium hydroxide. The precipitate is collected by filtering the solution through a filter stick. After drying at $110^{\circ}C$, the activity of the precipitate is measured by counting with the G-M counter. The activity of the sample is observed for twelve hours or more and the counting rate plotted against time. The purity of the precipitate is checked by observing the half-life and the decay curve is extrapolated back to the separation time to determine the amount of Ra^{228} in the samples.

RESULTS AND DISCUSSION

The reproducibility and accuracy of the method were checked by running a number of analyses of a selected sample of fairly old thorium nitrate which was taken as a standard (Table 1).

Table I
Results of Ra²²⁸ Analysis of Thorium Nitrate

Experiment	Activity cts/min/gmTh Individual Determinations	Average	Standard Deviation c/m/gm	%
Standard Extraction Method	1726*, 1870, 1905, 1965 1988, 2035, 2048	1969	65	3.3
LaF ₃ Precipitation	2035			
BF ₄ ⁻ Complex Ion Method	1881, 2012, 2025, 2048	1992	65	3.3
Zn ⁺⁺ Electrolytic Method	2025, 2080, 2116	2074	27	1.8
Equilibrium Thorium by Standard Extraction Method	9906, 10081, 10354	10110	180	1.8

* The steady increase in these results as the series progressed is quite good evidence that the technique was steadily being improved. The first measurement is sufficiently out of line with the others to be beyond the plausible limits of statistical fluctuations. Consequently, the average and standard deviation represent all values but the first. Averaging the reliable values from the various experiments using this solution gives a value of 2000 ± 72 . A weighting process eliminating some of the early low values gives 2034 ± 40 as the average.

In almost all cases the decay curve of the actinium sample showed only the 6 hour period of the Ac²²⁸ indicating that the samples were quite pure. If there was a slight amount of longer-lived material present it showed up as a low intensity tail to the decay curve (see Figure 2). After subtracting this component these decay curves had only the 6 hour component present. The principal uncertainty in the method is the completeness of recovery of the actinium. Since it is not isotopic with the carrier used

1195

10

Fig. 2 - Decay of Actinium-228 Samples.

for it, the customary procedure for determining a chemical yield and correcting the removed activity to 100 per cent chemical yield did not appear to be valid.

The completeness of recovery of actinium was checked by extracting the thorium from a sample, coprecipitating both radium isotopes with lanthanum fluoride, and counting this sample after the Ra^{224} and its daughters had decayed out. This value (Table 1, 2nd row) checked very well with the results obtained by the actinium separation procedure. Another check on this completeness is the agreement between different analyses on the same sample. This agreement is sufficiently close to indicate that accidental losses of actinium are small. A third check was obtained by the analysis of some equilibrium thorium nitrate. This material was Kahlbaum reagent thorium nitrate which is known to have been in the Chemistry Department for at least 35 years. The Ra^{228} content would thus be at least 97% of its equilibrium value. The analysis of this material by this procedure gave an average counting rate of 10110 ± 180 counts per minute per gram of thorium. The geometry of this position for the counter (second shelf) using a similarly mounted sample of standard P^{32} was found to be $3.8 \pm 0.3\%$. The use of P^{32} for geometry determination should be valid in this case since the P^{32} β -ray and that from Ac^{228} have similar energies, 1.71 and 1.55 Mev, respectively.

Using this geometry factor, $.038 \pm .003$, the disintegration rate of these samples becomes $(2.66 \pm 0.21) \times 10^5$ d/m/g Th. The calculated disintegration rate of Ra^{228} in equilibrium with thorium is 2.46×10^5 d/m/g Th.

6195

The complete dissolution of thorium metal and thorium oxide is extremely difficult unless a trace of fluoride ion is present as a catalyst. However, the concentration of fluoride ion must be very low to avoid precipitation of lanthanum fluoride and loss of some of the actinium. The hydrolysis of fluoborate ion was found to furnish sufficient fluoride ion to catalyze the dissolution of thorium samples and yet did not cause the precipitation of lanthanum. The results given in Table 1 show that addition of up to 2.5 mg of fluoborate ion did not affect the results of the Ra^{228} analysis.

Since thorium samples containing zinc were encountered in the application of the analytical method, a modification to eliminate the interference of zinc was developed. The interference of zinc results from the precipitation of zinc hydroxide when the pH of the solution is raised. Preventing this precipitation by complexing the zinc with sodium salt of ethylenediaminetetraacetic acid was unsatisfactory since this reagent also complexed lanthanum and prevented its extraction. Zinc was selectively complexed by 1,10-phenanthroline, but this reagent was extracted by the benzene permitting the zinc to precipitate.

Removing the zinc by use of a mercury cathode was found to be very satisfactory. Extraction of the thorium before using the mercury cathode improved the operation of the mercury cathode. Samples containing more than 0.1 grams of zinc were dissolved in hydrochloric acid since nitrate ion hindered the removal of larger amounts of zinc.

6195-100

CONCLUSIONS

The extraction of Ac^{228} with thenoyltrifluoroacetone provides a method for determining the amount of Ra^{228} , mesothorium-1, in thorium-containing materials. The method is reproducible and rapid. It gives results which agree with the calculated activity in thorium nitrate in equilibrium with its daughters and with the determination of Ra^{228} by the direct method which involves a delay of nearly a month before the answer is obtained.

BIBLIOGRAPHY

1. Fresco, J. Jetter, E. and Harley, J., "Radiometric Properties of the Thorium Series", *Nucleonics* 10, #8, 60 (1952).
2. Hagemann, F., "The Isolation of Actinium", *J. Am. Chem. Soc.* 172, p. 768-71 (1950).
3. Lange, Handbook of Chemistry, 8th Ed., Handbook Publisher, Inc., 1952, p. 944.
4. Melavan, A. D., "Electrolytic Cell for Use with the Mercury Cathode", *Ind. Eng. Chem., Anal. Ed.* 2, 180 (1930).