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THE DETERMINATION OF URANIUM ALPHA ACTIVITY

in

HUMAN URINE

F. W. Hurd, J. S. Fox

SECRET

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A B S T R A C T

A method for the determination of uranium in human urine by means of the alpha activity of the uranium is described. Using this method it is possible to detect the alpha radiation from 0.01 mg. of normal uranium per 100 ml. of urine or a concentration of 100 parts per billion. It is also possible to detect the alpha radiation from 0.01 micrograms of uranium 233 per 100 ml. of urine or a concentration of 0.1 part per billion. Amounts of uranium whose alpha activity lies between normal and pure uranium 233 can be determined in quantities which are inversely proportioned to their alpha activities.

The following method is used: A 100 ml. sample of urine is boiled with hydrochloric acid, aluminum nitrate is added and the pH of the solution raised to 6.5 with ammonium hydroxide. After centrifuging, the precipitate is dissolved and reprecipitated. This precipitate is redissolved in hydrochloric acid. The hydrochloric acid solution is evaporated slowly on silver disks and the disks are alpha counted in a low background alpha counter. Results are reported as alpha counts per minute per 100 ml. of urine.

THE DETERMINATION OF URANIUM ALPHA ACTIVITY

in

HUMAN URINE

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THE DETERMINATION OF URANIUM ALPHA ACTIVITY IN HUMAN URINE

A fluorometric method has been used to date for the routine determination of uranium in urine. By this method, ten parts per billion of uranium in urine can be determined; however, no estimate of the alpha activity of the uranium is possible by this method. Since the primary danger from uranium poisoning lies in its alpha activity, a method was necessary to determine the radioactivity of the uranium as well as the quantitative amount present in urine. This paper describes a method for the determination of the uranium alpha activity in urine.

Although a counting method has been reported for the determination of micro quantities of plutonium in urine (1) (2), no method of this type has been reported for the determination of uranium in urine. The methods for the determination of plutonium involve a chemical separation of plutonium from 1500 ml. of urine using a carrier. The plutonium is then separated from the carrier, mounted on a disk and alpha counted.

A summary of the contents of normal urine is given in Table I. Since urine contains 55 to 70 grams of dissolved solids per liter, a simple evaporation of the urine onto a silver plate, followed by alpha counting, is impractical, due to the absorption of the alpha particles in the urine solids. After attempts to electroplate the uranium from the urine directly to a nickel disk failed, it was obvious that the uranium would have to be separated from the urine chemically before it could be alpha counted.

Early work showed that aluminum hydroxide was an excellent carrier for ammonium diuranate if the urine was first boiled with hydrochloric acid for fifteen minutes to remove the urea. The removal of the uranium from the

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carrier was then undertaken. Attempts to extract the uranium from a nitric acid solution of the carrier with penta ether, hexone, or diethyl ether gave erratic results. The cause for this was the amount of sulfate and phosphate present in urine. These salts were occluded on the precipitate and prevented the uranium passing into the organic solvent. Since other methods were giving more promising results, work with solvent extractions was discontinued.

Attempts to extract the uranium from the aluminum hydroxide carrier using ammonium carbonate were more successful. The results of these experiments are summarized in Table II. It will be noted that from one third to one half of the uranium which was added was recovered in these experiments, when the uranium solution was evaporated onto silver disks. Attempts to plate the uranium on nickel disks were unsatisfactory.

Experiments then showed that it was possible to count the uranium present without removal from the carrier, if the amount of carrier was properly controlled, and the film correctly distributed on the silver disks.

EXPERIMENTAL

Apparatus and Reagents

Alpha Counter: An alpha counter especially designed for this work having a low background of approximately 0.5 counts per minute was used. This background was about 5 times lower than the background of routine alpha counters which are used in the Works Laboratory at K-25. This counter made it possible to count residues of uranium which had only 3 alpha counts per minute.

For 0.1 parts per billion or more of uranium 233, the alpha counters used for the routine determination of uranium 234 were used.

Silver Disks: The residues were evaporated on silver disks 0.002 inches thick. For determinations on the low background counter, disks 2 1/4 inches in diameter were used, but for use with routine counters, the disk diameter was 3 1/4 inches.

Urine: The urine which was used in this work was obtained from the K-25 Dispensary and came from patients who were not in contact with uranium.

Uranium: Solutions of uranium materials having various alpha activities were made by weighing out the uranium as urano-uranic oxide, dissolving in nitric acid and diluting to the desired concentration. A known volume of each solution was evaporated on a silver disk and alpha counted. By adding a definite volume of a standard uranium solution to 100 ml. of urine, the quantity of uranium and the number of counts added to the urine sample were known. Solutions of the following alpha activities were used in this work.

Solution A. 750 alpha disintegrations per minute per milligram of uranium metal per half solid angle (normal uranium).

Solution B. 75,000 alpha disintegrations per minute per milligram of uranium metal per half solid angle.

Solution C. 8×10^6 alpha disintegrations per minute per milligram of uranium metal per half solid angle (uranium 233)

Other Reagents: Other reagents which were used were A.C.S. analytical reagent grade checked for uranium contamination on the low background alpha counter.

Procedure

To 100 ml. of urine, 10 ml. of concentrated hydrochloric acid were added and the acidified solution was boiled gently for 15 minutes. Two ml. of a solution of aluminum nitrate (14 g. of $Al(NO_3)_3\ 9H_2O$ per liter) were added

and the solution was cooled in a stoppered flask. After cooling, the pH of the solution was raised to 6.5 by the addition of 1:1 ammonium hydroxide. The mixture was centrifuged at 1700 R.P.M. for two minutes and the supernatant liquid decanted and discarded. The precipitate was then dissolved in 5 ml. of concentrated hydrochloric acid, diluted to 100 ml. with distilled water, and reprecipitated with 1:1 ammonium hydroxide, again at a pH of 6.5. The material was centrifuged and the supernatant liquid discarded. Ten ml. of concentrated hydrochloric acid were added to the residue and this mixture was added dropwise to the silver disks and evaporated to dryness. If the residue on the disk was loose, it was moistened and redried to insure adherence. The disk was then counted in the low background alpha counter until the desired counting accuracy was obtained. The results were reported as counts per minute per 100 ml. of urine.

DATA AND DISCUSSION

To determine the effect of the absorption of alpha particles by the aluminum carrier, a series of experiments was carried out in which the same amounts of uranium and aluminum solution were evaporated on from one to four disks, thus testing various film thicknesses. The results of this experiment are summarized in Table III. It will be noted that the number of counts recovered from the solution decreased with a decrease in the number of disks which were used for the evaporation. With four disks of 2 1/4 inches in diameter, approximately 85% of the counts were recovered from the solution. With two disks, approximately 70% was recovered, and with one disk, only 30% was recovered. From these data it was decided either to use larger disks or to evaporate the residue on several small disks. Since only small disks could be used in the low background counter, the

material should be put on several disks for all routine determinations.

Table IV summarizes the results of an experiment to determine the smallest amount of normal uranium which could be detected using the low background alpha counter. This table shows that if 100 parts per billion of normal uranium were added to a sample of urine the counts from this urine sample were significantly different from the counts from a urine sample to which no uranium had been added. In these experiments, the solution was evaporated on two small disks, and the material was counted in the low background counter. These experiments showed an average recovery of around 70%.

Table V summarizes a series of determination which were run using both uranium solution B and uranium solution C. Solution C was counted on the routine alpha counter and solution B counted on the low background counter. The results of these experiments show that by alpha counting between 60 and 90% of the material which is added to the urine can be detected above the 1 part per billion level. Since it is not expected that any uranium of as high alpha count as solution C will be encountered, it would be necessary to count any samples which were analyzed by this method on the low background counter rather than on the routine counter. Routine counters were used to determine the feasibility of using larger disks which the low background counter could not accomodate. No corrections for self-absorption were applied in calculating any of the reported results.

CONCLUSIONS

A simple method for the determination of the alpha activity of uranium in urine has been demonstrated. Using this method it is possible to detect the alpha radiation from 0.01 mg. of normal uranium per 100 ml. of urine

or a concentration of 100 parts per billion. It is also possible to detect the alpha radiation from 0.01 micrograms of uranium 233 per 100 ml. of urine or a concentration of 0.1 part per billion. Amounts of uranium whose alpha activity lies between normal and pure uranium 233 can be determined in quantities which are inversely proportioned to their alpha activities.

Using a low background amplifier, it has been possible to determine the uranium alpha activity in about one tenth the volume used by previous workers.

The manipulation of the method is simple and can be carried out by a careful operator with no former chemical training. At least twelve determinations per day per operator are possible using this procedure.

ACKNOWLEDGEMENT

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TABLE I

COMPOSITION OF NORMAL URINE (3)

	Grams in 24 hours	Average Grams
Water	1000-1500	1200
Total Solids in Solution	55-70	60
Inorganic substances	20-30	25
Chloride chiefly NaCl	10-15	12.5
Phosphates estimated as H_3PO_4	2.5 - 3.5	3
(a) Alkaline earth (1/3 of total)		
(b) Alkali (2/3 of total)		
Sulphate estimated as H_2SO_4	1.5 - 3.0	2.5
Ammonia	0.5 - 1	0.7
Organic substances	30-40	35
Urea	25-35	30
Uric Acid	0.4 - 1.0	0.7

Traces of:

Inorganic	Organic
Iron	Creatinine
Carbonates	Hippuric Acid
Nitrates	Purine
Silicates	Oxalic Acid and Volatile Fatty Acid
Fluorides	Pigments
	Acetone

TABLE II

REMOVAL OF URANIUM FROM CARRIER USING AMMONIUM CARBONATE

(a) Residue Evaporated and Counted on Silver Plates

Sample Number	Micrograms U^{233} added to 100 ml. urine	Parts per billion added	Counts per minute added	Counts per minute Recovered Extraction I	Counts per minute Recovered Extraction II	Counts per minute Recovered Extraction III	Counts per minute Recovered Total	Total parts per billion	Percent Recovered
1	0.1	1.0	840	92	180	81	353	0.42	42
2	0.2	2.0	1680	360	252	82	694	0.82	41
3	0.5	5.0	4200	1567	469	200	2236	2.7	53
4	1.0	10	8400	1843	922	456	3221	3.8	38

(b) Uranium Electroplated on Electropolished Nickel Disks

Sample Number	Micrograms U^{233} added to 100 ml. Urine	Parts per billion added	Counts per minute added	Total Counts per minute Recovered	Parts per billion Recovered	Percent Recovered
5	0.1	1	840	75	0.01	9
6	0.2	2	1680	159	0.02	9
7	0.5	5	4200	2117	2.5	50
8	1.0	10	8400	2003	2.4	24

TABLE III

EFFECT OF THE NUMBER OF RESIDUE DISKS ON COUNTING RESULTS

Sample Number	Micro-grams per 100 ml. urine added	Counts per Minute	Parts per billion added	mg. of $Al(OH)_3$ used	Residue			Filtrate		
					No. of Disks Used	Parts per billion Recovered	Percent Recovered	pH	Parts per billion Recovered	Percent Recovered
1	0.09	700	0.9	6	4	0.8	85	8.1	0.1	11
2	0.09	700	0.9	6	4	0.8	95	6.6	0.05	6
3	0.09	700	0.9	6	4	0.7	82	-	-	-
4	0.09	700	0.9	6	2	0.7	80	7.1	-	-
5	0.09	700	0.9	3	2	0.6	65	7.8	0.0	1
6	0.09	700	0.9	6	1	0.3	28	-	-	-
7	0.09	700	0 9	6	1	0.4	44	7.8	0.04	4

TABLE IV

DETERMINATION OF COUNTS FROM NORMAL URANIUM

Sample Number	Parts per billion normal U per 100 ml. urine	Background of clean silver disks counts per minute			Urine precipitate and silver disks counts per minute			Urine Ppt. corrected Total(B-A)	Recovered by counting method		Recovered by fluorometric method	
		Disk (1)	Disk (2)	Total A	Disk (1)	Disk (2)	Total B	counts/min	p.p.b.	%	p.p.b.	%
1	0	0.5	0.1	0.6	0.4	0.2	0.6	0	-	-	-	-
2	0	0.3	0.8	1.1	0.4	0.4	0.8	-0.3	-	-	-	-
3	0	0.4	0.4	0.8	0.9	0.3	1.2	0.4	-	-	-	-
4	0	0.6	0.4	1.0	0.4	0.6	1.0	0.0	-	-	-	-
5	85	0.5	0.4	0.9	1.7	3.5	5.2	4.3	64	75	68	80
6	85	0.4	0.6	1.0	2.0	3.3	5.3	4.3	64	75	-	-
7	85	0.6	0.4	1.0	2.5	1.5	4.0	3.0	45	53	51	60
8	85	0.1	0.5	0.6	1.6	3.1	4.7	4.1	61	72	51	60

Table V

RECOVERY OF URANIUM FROM URINE SAMPLES

Using the Proposed Method *

Sample Number	Parts per billion added (100 ml. urine)	Type of Material	Counts per minute added	No. of disks used	Diameter of disks inches	Parts per billion Recovered	Counts per minute Recovered	Percent Recovered
1	1.0	C	800	1	3 1/4	0.86	691	86
2	1.0	C	800	1	3 1/4	0.86	685	86
3	1.0	C	800	1	3 1/4	0.76	608	76
4	0.1	C	80	1	3 1/4	0.06	47	59
5	0.1	C	80	1	3 1/4	0.05	43	51
6	0.02	C	14	2 *	2 1/4	0.01	7	50
7	0.85	B	6.4	2 *	2 1/4	0.71	5.4	84
8	0.85	B	6.4	2 *	2 1/4	0.76	5.7	89
9	8.5	B	64	2 *	2 1/4	6.2	47	73
10	8.5	B	64	2 *	2 1/4	5.4	40	63
11	8.5	B	64	2 *	2 1/4	7.2	54	84

* Two small disks were used in these cases because large disks could not fit in the chamber of the low background alpha amplifier.

Where the large disks 3 1/4" in diameter were employed the regular amplifiers in the Counting Section were used since a higher background on two or three counts would not seriously affect results.