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A METHOD OF CLEANING PLUTONIUM METAL SAMPLES FOR ANALYSIS

by

PUBLICLY RELEASABLE 11-8-95

William G. Smiley Per J. Brown, FSS-16 Date: ~~11-8-95~~

By Jonyak/DB, CIC-14 Date: 11-15-95

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TECHNOLOGY--PLUTONIUM (SPECIAL DISTRIBUTION)

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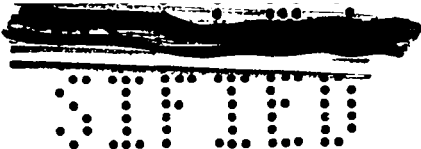
TECHNOLOGY--PLUTONIUM (SPECIAL DISTRIBUTION)

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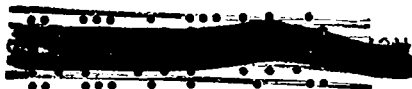
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ABSTRACT

The usual method of removing surface oxide from plutonium metal samples, by electrolytic cleaning in a mixture of ethylene glycol and phosphoric acid, is not satisfactory for preparing samples for oxygen determination. Samples prepared in this way give erratic oxygen values. This report describes a new method of electrolytic cleaning, using a 20 % aqueous potassium carbonate solution as the electrolyte. The sample is placed in a rotating tantalum cup which is made the anode. Electrolysis for two minutes at 4.5 volts is usually sufficient. Samples cleaned by the new method give lower and more consistent oxygen results than those prepared in the old way. The new method is also neater and more convenient.

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INTRODUCTION

Because of the relatively rapid corrosion of plutonium metal in ordinary atmospheres, analytical samples (usually lathe turnings) often have an oxide scale which it is desirable to remove, especially if oxygen is to be determined. The small size and irregular shape of the turnings would make mechanical cleaning very difficult, and all attempts at acid pickling of plutonium so far have been ineffective, resulting only in heavy blackening of the metal. The usual method of cleaning has been by electrolysis in a solution of phosphoric acid and ethylene glycol^(1, 2), in which the plutonium sample is made the anode. The sample is placed in a tungsten basket, whose high oxygen overvoltage causes almost all the current to flow through the plutonium. Frequent agitation is necessary to renew contact between the plutonium and the tungsten, which is broken probably by the formation of gas.

Although this method is fairly satisfactory for many purposes, it was found to be quite inadequate for preparing samples for oxygen determination. The oxygen values obtained were irregular and usually high, often higher than a fresh untreated sample (cf. Table I). The difficulty of rinsing off the viscous solution may be responsible, but it is also possible that a surface layer of oxide (metallic in appearance) was formed.

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This report describes a new method for removing the surface oxide layer from plutonium metal, using an alkaline instead of an acid solution. A carbonate is used to form a soluble complex of the plutonium, thereby preventing precipitation from the alkaline solution. Another feature of the method is the use of a rotating tantalum cup in place of the tungsten cup agitated by hand. This method appears quite satisfactory for preparing plutonium samples for oxygen determination, and has other advantages as well.

APPARATUS AND PROCEDURE

Figure 1 shows the apparatus in operation, and Figure 2 as it appears when opened to remove the sample. The whole apparatus is tilted at 30° to the horizontal, and the sample-cup is rotated at 12 r. p. m. by a small motor and gear reduction unit. The sample-cup (anode) is made of 0.004-inch tantalum foil, pierced so that it drains quickly, and is hung loosely on its shaft of tantalum wire so that it can be inverted to remove the sample. Tantalum is easier to fabricate than tungsten, and its oxygen overvoltage is sufficiently high. The cathode is a platinum wire, and the bath is contained in a 20 x 150 mm. test tube. The electrolyte is a 20 % aqueous solution of potassium carbonate. This was the first solution tried, and proved so satisfactory that no experiments were made with other salts or concentrations. The power supply consists of three dry cells in series (4.5 volts); no rheostat is needed.

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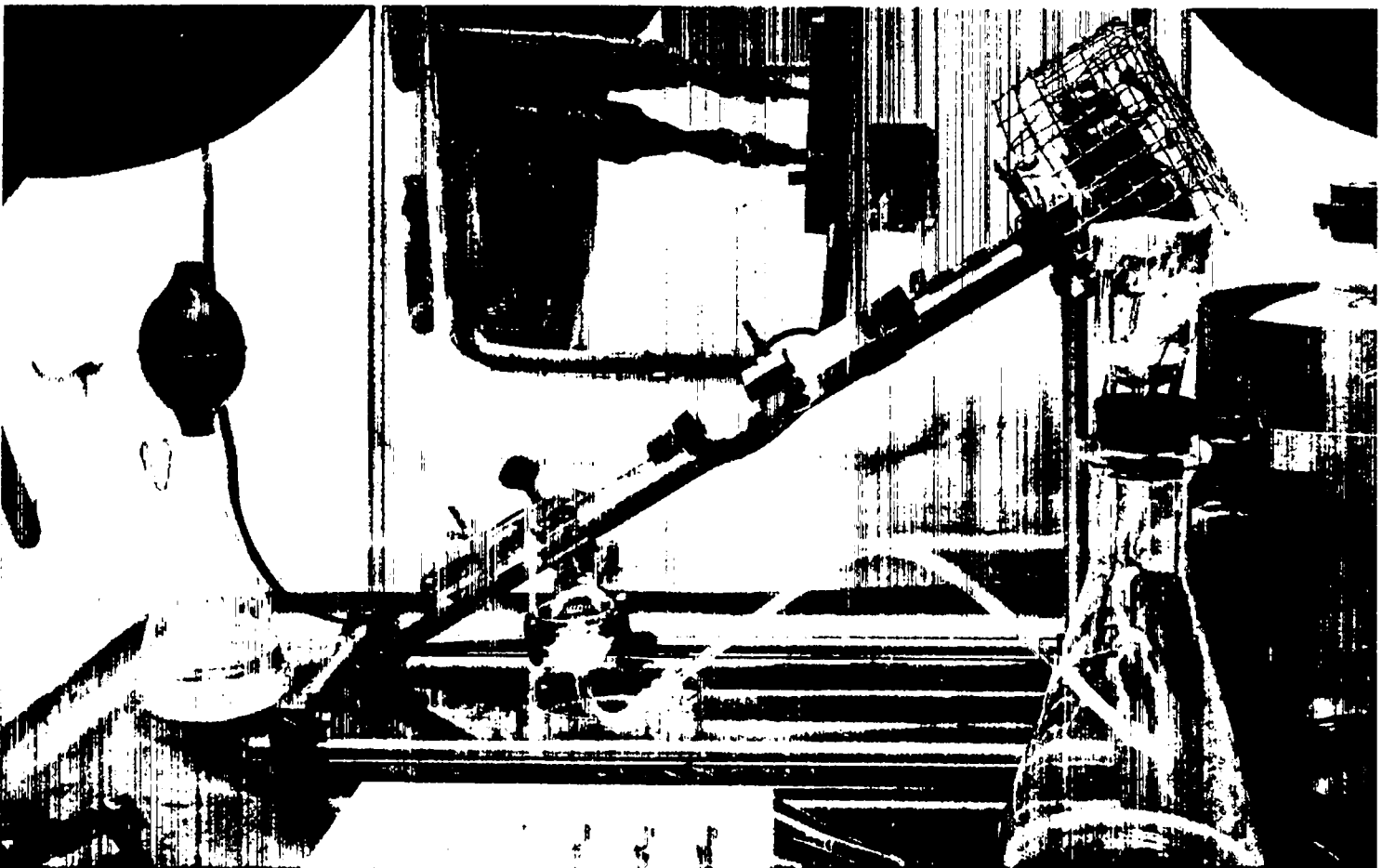


Figure 1

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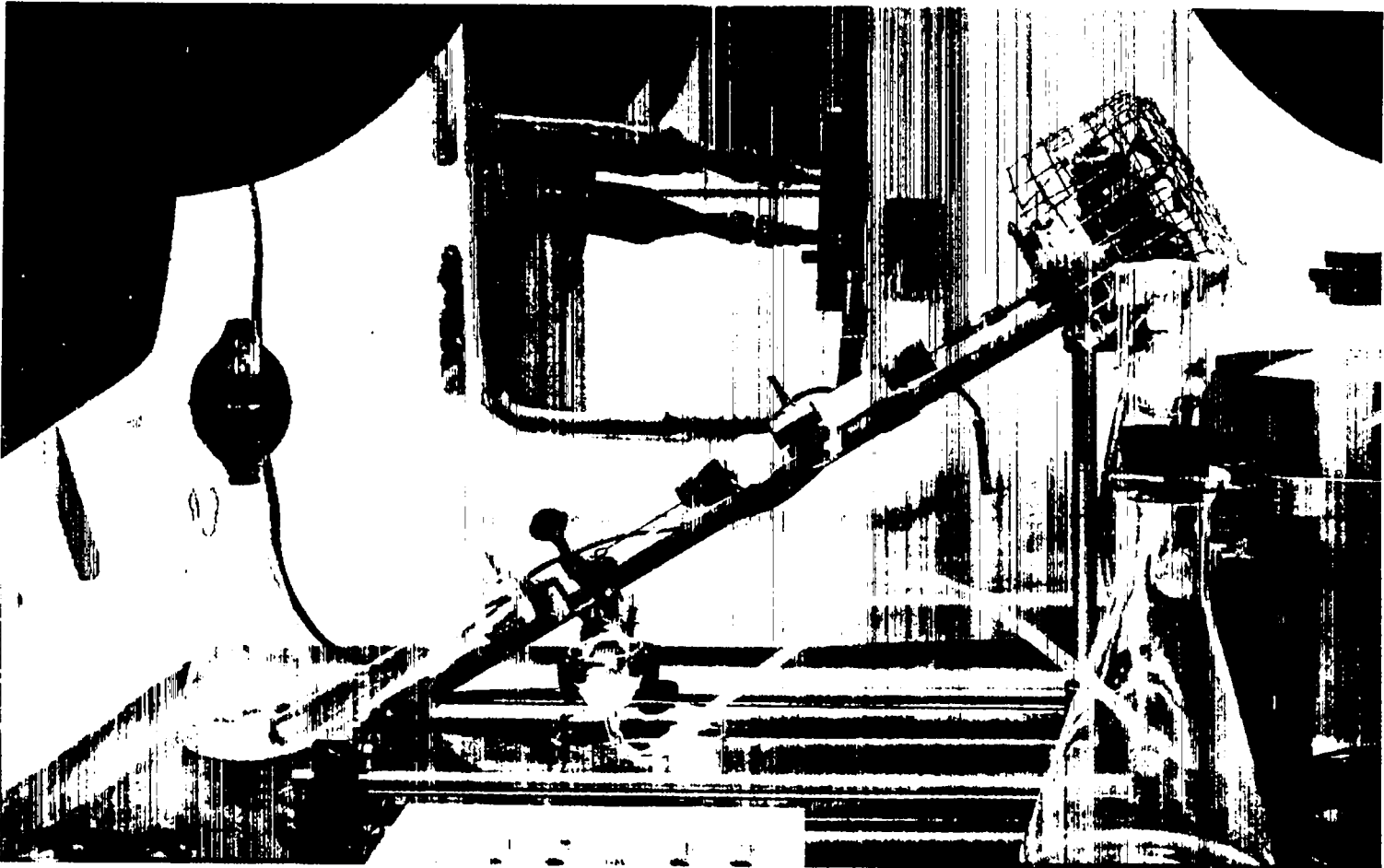


Figure 2

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The sample, which may consist of one or several pieces of plutonium, is dropped into the cup, the test tube is slipped over it and the stopper seated as shown in Figure 1. Rotation is started, and the electrode circuit is completed by connecting a battery clip to the tantalum shaft. The current fluctuates between zero and 100 milliamperes or more, depending on the size and condition of the sample. It is not necessary to use a milliammeter, since the action can be observed by the evolution of hydrogen at the cathode. The plutonium removed from the sample forms a clear green solution. The oxide does not dissolve and ultimately forms a fine sediment, but the total quantity is very small even after many samples have been cleaned.

Two minutes are usually ample for complete cleaning, but a considerably longer time may be needed for very heavily oxidized samples, which make poor contact at first. After two minutes of vigorous action, rotation is stopped and the sample is transferred to the sintered glass filter below the cup (it is usually necessary to tap the cup to dislodge the sample). It is then transferred to a platinum gauze cup, placed over another sintered glass filter, and thoroughly washed with water and acetone.

The filters retain any oxide particles, while the gauze allows them to be separated from the sample. The cleaned metal appears grey rather than bright. If any dark spots remain the treatment should be repeated.

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The operation is conveniently carried out in a dry-box adjoining the one in which the sample is to be analyzed. The loss in weight is less than one percent, so for oxygen determination the sample need not be reweighed.

DISCUSSION

Table I gives the frequency of occurrence of various oxygen values on a single plutonium sample both as received and after electrolytic cleaning by the old and by the new method. It is seen that the results after alkaline electrolytic cleaning were lower and more consistent than those obtained on the untreated sample or by electrolytic cleaning with the acid bath. While two of the samples cleaned in the acid electrolyte gave very low results, the median value was actually higher than that of the uncleaned samples. The cause of this erratic behavior is not known. All samples were treated as nearly alike as possible and all appeared bright and clean. The samples cleaned in the acid electrolyte were rinsed with ethanol and acetone, because ethanol removes the glycol and phosphoric acid mixture much more rapidly than water. All analyses were made within fifteen minutes after cleaning, usually within five minutes.

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Table I

Distribution of Oxygen Values on a Plutonium Sample

p.p.m. of Oxygen (to nearest 10 p.p.m.)

<u>Treatment</u>	<u>10</u>	<u>20</u>	<u>30</u>	<u>40</u>	<u>50</u>	<u>60</u>	<u>70</u>	<u>80</u>	<u>90</u>	<u>100</u>	<u>> 100</u>
As received			1	2	3		2				2
Cleaned in H_3PO_4 + glycol	2			2			2			2	1
Cleaned in aqueous K_2CO_3	4	4	1	1							

Note: The numbers in the table represent the number of determinations which gave the oxygen value at the head of the column.

Further evidence of the effectiveness of cleaning in the alkaline electrolyte was obtained on forty-seven routine samples, one duplicate of each sample being analyzed as received, and the other after electrolytic cleaning in potassium carbonate solution. The results are given in Table II. The average apparent decrease in oxygen content due to cleaning was 45 p.p.m., and only three out of forty-seven samples showed a small apparent increase. It is also interesting that only two samples gave results over 100 p.p.m. after cleaning, and both of these were over 500 p.p.m. before cleaning.

All of these results were obtained on delta phase plutonium (one percent gallium alloy). There has been relatively little experience with the alpha phase, but in some cases at least it appears to be more difficult

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to clean. The formation of black corroded spots, perhaps caused by cracks in the metal, is more frequent with the alpha phase.

The low viscosity and surface tension of the alkaline solution make it more convenient to use than the glycol and phosphoric acid mixture. Very little solution is transferred out of the bath with the cup, so that it needs refilling less often. The sample can be dumped out of the cup and rinsed by itself, while with the acid mixture the entire cup must usually be rinsed to remove the sample. Also, the acid solution is objectionable for use in a dry-box, since it tends to get on the gloves and various metal objects, causing corrosion.

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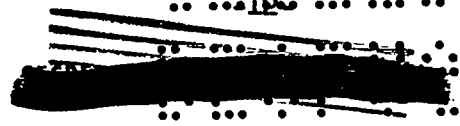
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Table II

Oxygen Values Obtained on Routine Plutonium Samples

(Results expressed as p.p.m., rounded to nearest 5 p.p.m.)

<u>Cleaned</u>	<u>Uncleaned</u>	<u>Difference</u>	<u>Cleaned</u>	<u>Uncleaned</u>	<u>Difference</u>
15	50	35	20	35	15
20	45	25	45	115	70
20	35	15	40	85	45
35	50	15	35	85	50
20	35	15	20	85	65
10	50	40	20	55	35
10	40	30	10	40	30
15	55	40	25	30	5
15	40	25	25	220	195
15	50	35	20	95	75
30	40	10	60	40	- 20
25	55	30	15	100	85
25	40	15	50	80	30
30	90	60	30	60	30
35	50	15	35	70	35
55	40	- 15	25	75	50
385	570	185	15	65	50
15	55	40	25	45	20
25	105	80	25	155	130
615	655	40	30	85	55
15	45	30	60	110	50
70	50	- 20	30	110	80
20	40	20	20	60	40
25	75	50			



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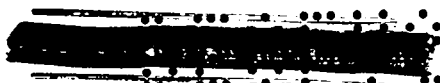
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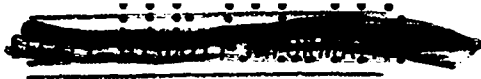
The rotary cup, besides being more convenient than one agitated by hand, gives much better results when the sample consists of more than one piece. Such pieces tend to protect each other, resulting in uncleaned spots, but in the rotary cup all surfaces are exposed and two or three pieces can be cleaned as easily as one.

The oxygen determinations were made by the capillary trap method⁽³⁾.

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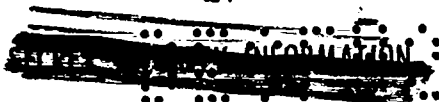
REFERENCES

- (1) LA-416, p. 5 (1945); LA-1100, p. 305 (1950).

Note: The signs on the electrodes in the figure are the reverse of those used in practice; the text is confused on this point.

- (2) Bergstresser, LA-1106 (1950).
- (3) Smiley, LA-1350 (1953).

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