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THE DETERMINATION OF OXYGEN IN PLUTONIUM

BY THE CAPILLARY TRAP METHOD

by

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ABSTRACT

A new method for the determination of oxygen in metals is described.
The sample is dropped into molten platinum in a graphite crucible. The
oxide in the sample reacts with carbon to form carbon monoxide, which
is swept out by a stream of argon at atmospheric pressure. The carbon
monoxide is oxidized to carbon dioxide, which is condensed in a capil-
lary trap and measured with a capillary manometer. The apparatus is
sensitive to 0.3 microgram of oxygen, and routine 50-milligram plutonium
samples give a standard deviation of 7 p.p.m. or 0.35 microgram.
Plutonium samples with added oxygen gave a standard deviation of 1.5
microgram or 2 % of the total oxygen, with no significant bias. The
apparatus is simple and rugged, permitting replacement of parts without
glassblowing. The speed is superior to vacuum fusion methods, most
samples requiring only twelve minutes for analysis.

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INTRODUCTION

Oxygen in metals is usually determined by the so-called vacuum fusion method. This involves the reaction of the sample with carbon, often in a flux of molten metal, collection of the evolved gas by a fast diffusion pump, oxidation of carbon monoxide to carbon dioxide, and separation of the carbon dioxide either by chemical absorption or by condensation. Templeton and Watters[1] discuss the advantages of both methods; condensation appears preferable. The final measurement is usually made with a McLeod gauge. At Los Alamos, a chemical absorption method was formerly used[2]; it proved unsatisfactory because of the excessive time required and the frequent failures of the complicated apparatus.

A method not involving vacuum was developed by Singer[3], who swept out the carbon monoxide in a stream of nitrogen, and, after oxidation to carbon dioxide, determined the latter gravimetrically.

This report describes a method which eliminates high vacuum, yet retains the high sensitivity inherent in measuring small volumes of gases. As in Singer's method, an inert gas (argon) is used as a carrier, but the carbon dioxide is condensed out in a capillary trap and measured with a capillary manometer. The small volume of the trap permits sensitivity in the microgram range without the use of a McLeod gauge. Only a mechanical pump is used, and only the trap is evacuated. A similar

method has been applied to carbon in plutonium[4].

As applied to oxygen in plutonium, the procedure may be summarized as follows. The sample is dropped into a graphite crucible containing molten platinum at about 1800° C. The carbon monoxide produced is swept by a stream of argon through a modified form[5] of Schütze's reagent[6], which converts it quantitatively to carbon dioxide. The carbon dioxide is frozen out in the capillary trap, chilled with liquid nitrogen. The trap is evacuated, then warmed, and the pressure is measured with the capillary manometer.

As compared to vacuum fusion, the capillary trap method has the advantages of considerably increased speed and a relatively simple apparatus, making it more suitable for routine work. It has been used for the routine determination of oxygen in plutonium at Los Alamos since December, 1951.

APPARATUS

Figure 1 is a schematic diagram of the apparatus, with the parts rearranged for the sake of clarity. The sample dumper (D) and furnace (F) are enclosed in a dry-box, as shown in Figure 2; Figure 3 shows the rest of the apparatus, mounted on a rack adjacent to the dry-box. The parts are connected by 1/4-inch copper tubing; Neoprene tubing is used for glass-to-metal joints, but in future apparatus it is planned to use brass spherical joints for this purpose. Brass bellows-type valves are
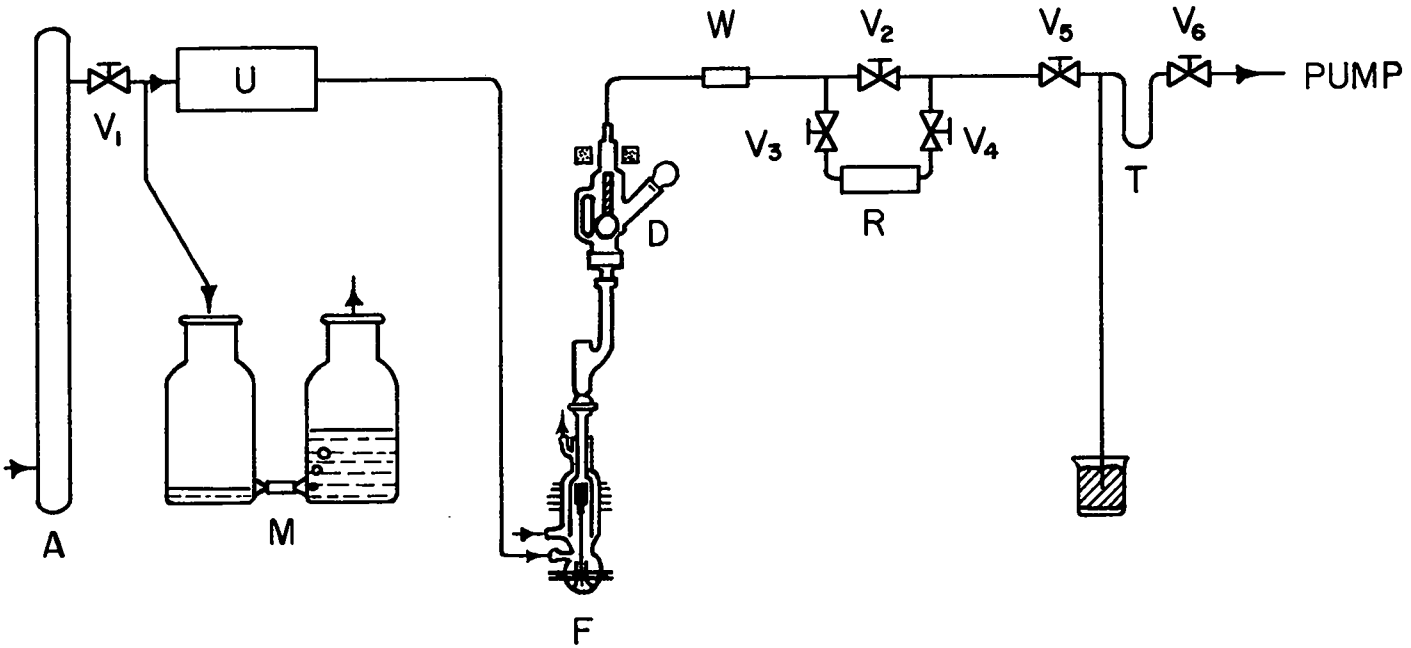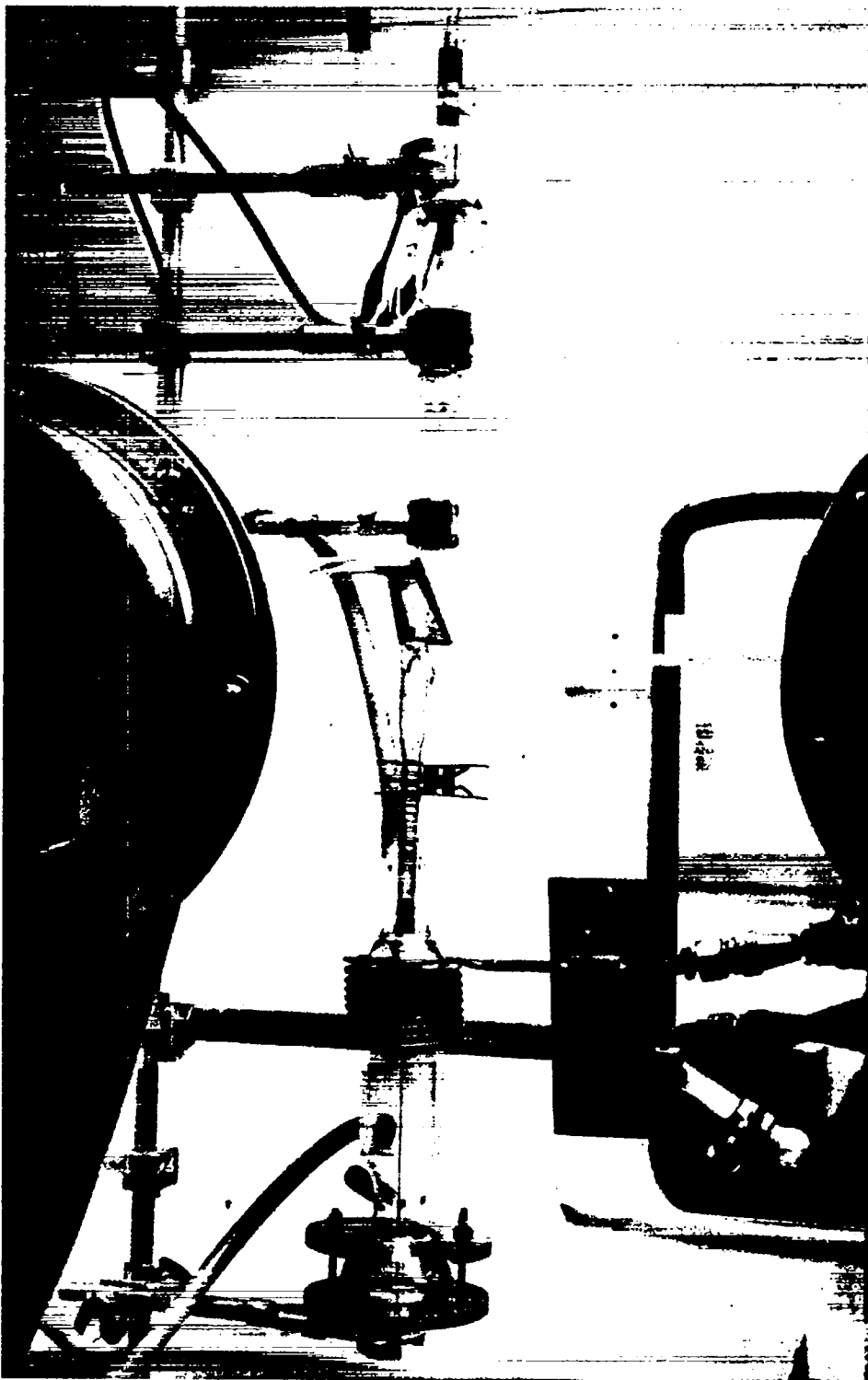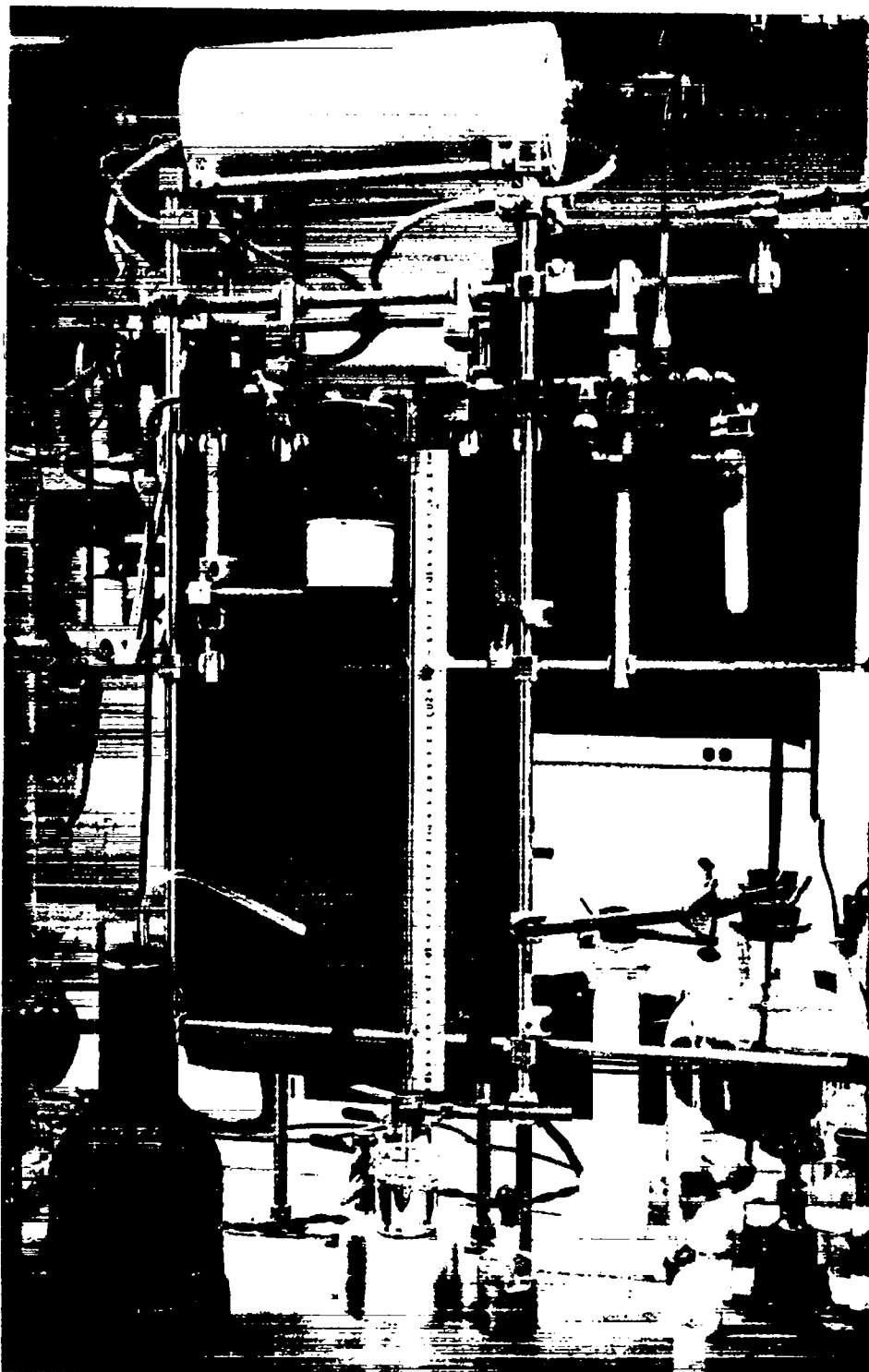
Figure 1

Figure 2

Figure 3

used rather than stopcocks. They permit better flow control and on the whole are more reliable, but they do occasionally develop leaks, and therefore are mounted so as to be easily replaced. All parts of the apparatus can be replaced without glassblowing; spare parts are kept on hand for this purpose. Several parts are interchangeable with those of the carbon apparatus.[4]

The entire apparatus up to valve (V_5) (Figure 1) is filled with argon at slightly more than atmospheric pressure. The manostat (M), made from two four-liter aspirator bottles and filled with Silicone oil, serves to maintain this pressure when the apparatus is not in use; its large volume compensates for barometric changes or slow leaks. During use of the apparatus, valve (V_1) is adjusted so that argon bubbles out slowly through (M). Welding grade argon is used; after reduction to less than one p.s.i., it passes through the tube (A), containing Ascarite and magnesium perchlorate. This tube is perhaps unnecessary; it is intended to remove moisture and conserve the uranium which is the principal purifying agent. The uranium furnace (U) (seen at the top of Figure 3) consists of a 1-inch nickel tube, packed with uranium turnings, and heated over 12 inches of its length by a Nichrome winding. The temperature at the center is about 625° C; higher temperatures have been tried without any improvement in the blank.

From the uranium furnace, the argon passes upward through the induction furnace (F) and sample holder (D). This direction of flow is opposite

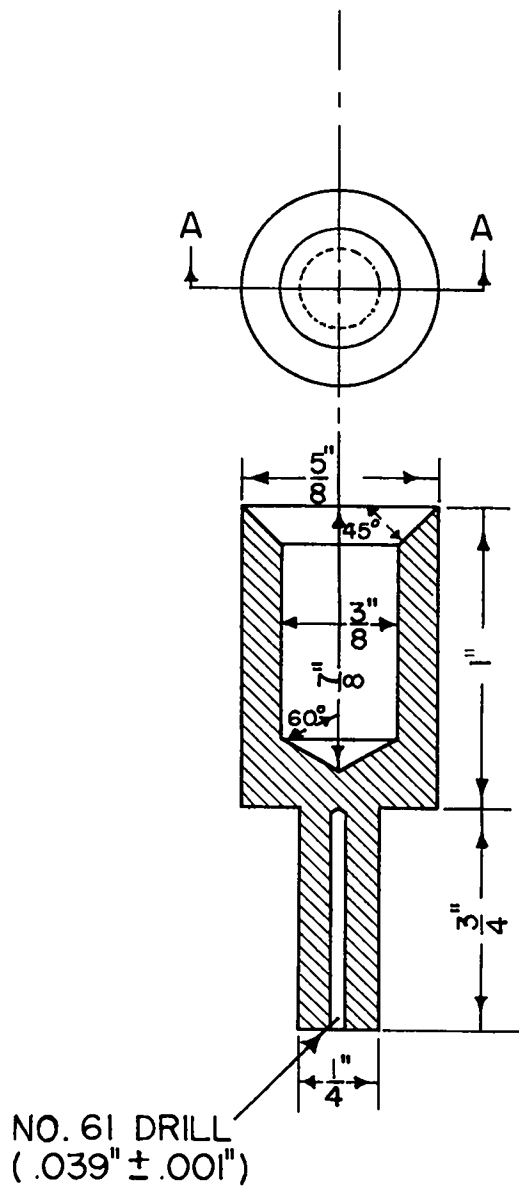to that used in the carbon apparatus[4] and is important because it prevents any oxygen that enters the sample holder from reaching the crucible. The tube carrying argon to the furnace is made of glass rather than metal, because it passes close to the heating coil.

The induction furnace (Figure 2) is made of vitreous silica ("fused quartz") and is water-jacketed, including the constricted part which guides samples into the crucible. The crucible is mounted on a 0.040" tungsten rod, which is supported by a capillary sealed into a spherical joint at the base of the furnace, large enough to pass the crucible. The crucible can thus be replaced without dismounting the furnace. The purpose of the spherical joint was to permit centering the crucible, but in practice this is a tedious process, and future furnaces will be made with standard taper joints. The bottom joint becomes quite hot and is lubricated with Silicone grease. It is held by a Bakelite clamp.

Figure 4 shows the dimensions of the graphite crucible. There has been one experiment with a larger crucible, which cracked. None of the small crucibles has ever cracked, though heated and cooled many times. Impurities in the graphite may affect the blank. Crucibles now in use were made by the United Carbon Products Co., Inc., of Bay City, Michigan, and were purified in the same way as spectroscopic electrodes. The crucible contains 5-6 grams of platinum as a flux. A new crucible is heated for about half an hour below the melting point of platinum, in order to remove all oxygen and thus avoid evaporation of the platinum.

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NO. 61 DRILL
(.039" ± .001")

SECTION A-A

Figure 4 -- Graphite crucible

In use, the crucible is operated just above the melting point of platinum, or about 1800° C. An optical pyrometer may be used to check the temperature, but soon loses its usefulness because of darkening of the window. The usual practice is to observe the setting of the induction heater at which the platinum melts, and operate at a slightly higher setting.

The induction heater is a "Thermonic" 10-kw. generator, with the addition of a gang of three 20-ampere Variacs in parallel, to control the input to the plate transformer. The platinum usually melts at a setting of 165 volts and the generator is normally operated at 172 volts. The heating coil consists of ten turns of flattened copper tubing, and is about 2 inches high and 2 inches in inside diameter. The leads are brought into the dry-box through a Lucite panel.

The sample holder is connected to the furnace through an adaptor ($ 19/38 at top, spherical 18/9 at bottom), which also contains a window to permit seeing the inside of the crucible. Samples are introduced into the holder through the side arm, whose ground joint is not greased. Both joints of the adaptor are greased with Apiezon N. Samples are dropped into the crucible by applying 110 volts D. C. to a coil (made for an H-B mercury relay) which lifts the iron-cored glass plunger. A 250-ohm rheostat is used in the coil circuit to permit lifting and lowering the plunger gently. The control knob is conveniently located outside the dry-box (at the right of Figure 3).

From the sample dumper the argon stream passes through a tube (W)
(Figure 1), containing magnesium perchlorate and glass wool. This tube
removes a small amount of moisture, probably diffusing in through the
sample dumper, which otherwise contributes to the blank. It also
filters out plutonium contamination and soot from the crucible. This
tube may be seen at the upper right-hand corner of Figure 3.

Next, the argon flows through the oxidizing reagent (R) (Figure 1).
Valves (V_2), (V_3) and (V_4) permit by-passing the reagent, which is
desirable when flushing the system after it has been out of use, or
during the first heating of a new crucible. These valves and the
reagent tube are below the right end of the uranium furnace in Figure 3.

The oxidizing reagent is prepared as follows[5]: Dissolve 5 grams of
iodine pentoxide (or the equivalent amount of iodic acid) in 25 ml. of
water. Mix the solution with 50 grams of coarse (6-16 mesh) silica gel.
Dry at 150° C for 1-2 hours. Mix in 10 ml. of concentrated sulfuric
acid and store the mixture overnight in a closed container. Pack the
mixture into the middle of a glass combustion tube, using glass wool
pads; fill the ends of the tube with silica gel. Evacuate the tube and
draw a slow stream of air through it. Heat the reaction mixture at
220° for about 4 hours, or until it is a uniform golden color. The
product resembles yellow sand. It must be kept hermetically sealed, as
it is very sensitive to moisture. It oxidizes carbon monoxide instantly
to carbon dioxide, with formation of free iodine, which appears as a

brown stain. The exhaustion of the reagent can be followed by the growth of the dark zone (at the top of the tube in Figure 3). A single batch of reagent should last for many months.

Valve (V_5) (Figure 1) is adjusted to control the flow rate, while (V_6) is open to the vacuum pump except during a measurement. These valves and the capillary trap (T) are seen at the center of Figure 3, below the uranium furnace. The trap and manometer are of Pyrex capillary, the trap being 1-millimeter bore and the manometer 1.5 millimeter. The U-shaped trap fits into a 250-ml. Dewar flask (shown in place in Figure 3). The dimensions of the trap and manometer are shown in Figure 5; however, the length of the manometer depends on the barometric pressure, and will in general be longer than that shown, which is suitable for the barometric pressure of 575-595 mm. prevailing at Los Alamos. The lower end of the manometer is immersed in a beaker of mercury, as shown in Figure 3, and the level is adjusted, by adding or removing mercury with a medicine dropper, to bring the column in the manometer to the zero mark when the system is evacuated. A millimeter scale is mounted by the manometer, reading downward from the zero mark. The trap is so arranged that the manometer is at the end at which the argon enters, so that the trap and manometer also serve as a flowmeter. The ends of the trap are sealed into the valves with Apiezon W. It is important to orient the valves so that the side with small volume (away from the bellows) is next to the trap.
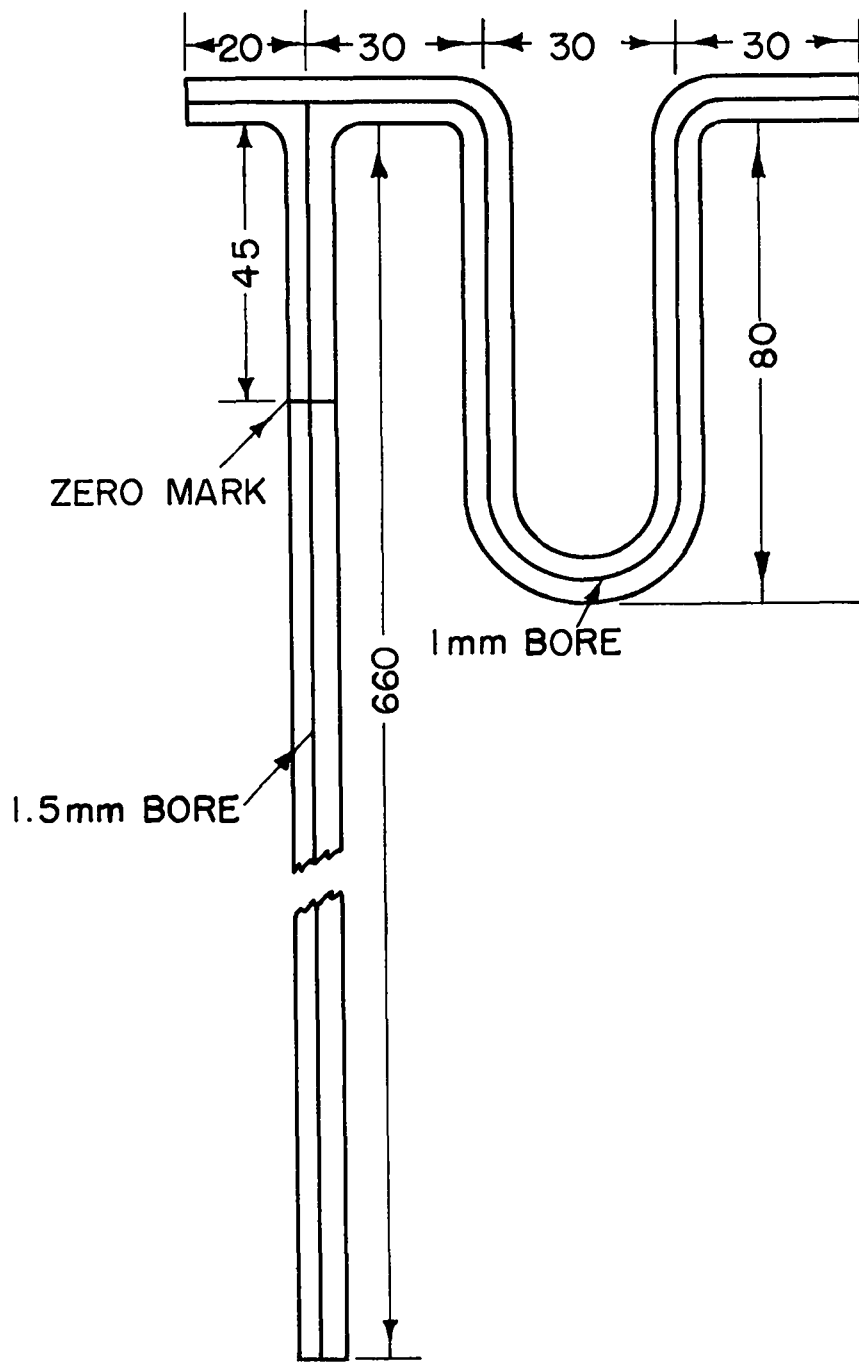
Figure 5 — Pyrex capillary trap and manometer (dimensions in millimeters).

CALIBRATION

Calibration of the apparatus involves determining the volume of the capillary trap. Since the volume increases as the mercury level in the manometer falls, the calibration is non-linear.

Let x = manometer reading = pressure in mm. of Hg.

   v = volume of capillary trap, including manometer, in mm^3.

   W = micrograms of oxygen.

Then by the ideal gas law,

$$xv = \frac{W}{16} RT \tag{1}$$

The formula weight of 16 is used because only one atom of oxygen per molecule of carbon dioxide comes from the sample. The proper value of R is 62.37 liter mm. $mole^{-1}$ $deg.^{-1}$ (since micrograms/$mm.^3$ = g./liter). The temperature is taken as 24° C or 297° K (a 3° change in temperature produces a 1 % error). Substituting and solving for W,

$$W = \frac{16xv}{62.37 \cdot 297} = 0.8637 \cdot 10^{-3}xv \tag{2}$$

If v_0 is the volume of the trap above the zero mark in $mm.^3$ and a is the cross-section area of the capillary bore in $mm.^2$,

$$v = v_0 + ax \tag{3}$$

Substituting in (2),

$$W = 0.8637 \cdot 10^{-3} (v_0 x + ax^2) \tag{4}$$

Let us define two calibration constants:

$$A = 0.8637 \cdot 10^{-3} v_o \qquad (5)$$

$$B = 0.8637 \cdot 10^{-3} a \qquad (6)$$

Then the calibration equation is:

$$W = Ax + Bx^2 \qquad (7)$$

B is determined as follows: Draw into the manometer sufficient mercury to extend a desired length, $\underline{x}$. Remove the beaker of mercury. By careful manipulation of the valves, adjust the upper meniscus to the zero mark. Read the position, $\underline{x}$, of the lower meniscus, to the nearest 0.5 mm. Expel the mercury into a tared container and weigh. If the weight of mercury in milligrams is M, the average cross-section, $\underline{a}$, is given by

$$a = 0.07388 \, \frac{M}{x} , \qquad (8)$$

where 0.07388 is the specific volume of mercury at 24° C. Combining (6) and (8),

$$B = 0.8637 \cdot 10^{-3} \cdot 0.07388 \, \frac{M}{x} = 0.638 \cdot 10^{-4} \, \frac{M}{x} \qquad (9)$$

In practice, the capillary is usually somewhat tapered so that B is not quite constant. The above measurement is therefore repeated for various values of $\underline{x}$ and B is plotted as a function of $\underline{x}$. The correct value of B to use in equation (7) is then read from this curve.

The volume $v_{\underline{o}}$, and therefore the constant A, cannot easily be measured directly because of the brass valves. The constant A is therefore

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determined from B, by the following procedure. Attach to the bottom of the manometer a rubber tube connected to a leveling bulb. Fill the bulb with mercury, taking care to eliminate bubbles which might enter the capillary. Open some connection so that valve (V_6) can be opened directly to the atmosphere. With this valve open, raise the mercury to the zero mark, close the valve, and read the barometric pressure, $\underline{h}$. Lower the leveling bulb to a point near the bottom of the manometer scale, and read the mercury level, $\underline{x}$. Open valve (V_6) to the atmosphere and read the new level, $\underline{x}'$. Repeat the process several times.

The pressure at the upper position of the leveling bulb was $\underline{h}$, the volume was proportional to A. On expanding to a volume proportional to A + B$\underline{x}$, the pressure was reduced by an amount $\underline{x}' - \underline{x}$. Therefore the final pressure was $\underline{h} - \underline{x}' + \underline{x}$. Then, by Boyle's law,

$$Ah = (A + Bx)(h - x' + x) \qquad (10)$$

Solving for A,

$$A = \frac{Bx(h - x' + x)}{x' - x} \qquad (11)$$

Four determinations of A usually fall within a range of one percent of its value.

Values of W can now be calculated from equation (7) and the curve of B vs. $\underline{x}$. For routine analysis, it is convenient to calculate a table giving W as a function of $\underline{x}$. For values of $\underline{x}$ below 100, in which the great majority of samples fall, values should be calculated for every half millimeter. It is necessary to use equation (7) only at 10-mm.

intervals, other values being obtained by interpolation. Values of W are rounded to 0.1 microgram.

The actual value of A is about 0.64 micrograms/mm., and of B, 0.0014 micrograms/mm^2. The length of the scale (Figure 3) is 510 mm. Readings are made to the nearest 0.5 mm. Therefore, the capacity of the apparatus is about 700 micrograms, and the precision of reading the scale varies from 0.32 microgram near the top to about twice this value at full capacity. The calibration is probably accurate to about one percent. Certain corrections (e. g., correcting the mercury column to 0° C), which amount to a fraction of one percent, have been neglected.

PROCEDURE

Note: The hands should never be placed in the dry-box while the induction heater is turned on.

Sample Preparation

Plutonium samples as received are usually lathe turnings or drillings. For oxygen determination, it is desirable to select pieces as compact as possible. Thin pieces have a high ratio of surface to volume, increasing the effect of any surface contamination, and they also tend to fall erratically and miss the crucible. For the same reasons, the sample should consist of not more than two or three pieces. The sample size depends on the precision desired. For most routine analyses 50-milligram samples are used.

Unless the sample is very fresh, it will have an oxide layer which must
be removed for accurate results. This is best accomplished by electro-
lytic cleaning in a 20 % solution of potassium carbonate in water[7],
followed by rinsing with water and acetone. To minimize corrosion, the
cleaning should be done immediately before the analysis.

Since most routine plutonium samples give very low oxygen values, even
without cleaning (usually less than 100 p.p.m.), the increased accuracy
obtained by cleaning has little practical significance for such samples.
On forty-seven samples analyzed with and without cleaning, the average
decrease due to cleaning was only 45 p.p.m.[7]. The current practice
at Los Alamos is to analyze routine samples in duplicate as received.
If either duplicate gives results over 500 p.p.m., two more analyses are
made, with electrolytic cleaning. In such cases, the oxygen content
after cleaning is always high also, at least 200 p.p.m.

Flushing

Whenever the apparatus has been idle for more than a few hours, it must
be flushed to reduce the blank. This is done as follows: Turn on the
argon and adjust valve (V_1), (Figure 1) so that argon bubbles out
through the manostat(M). Start the vacuum pump, open valve (V_6), and
adjust the mercury column to the zero mark by adding or removing
mercury, tapping the manometer to free the meniscus. Open (V_2), leaving
(V_3) and (V_4) closed, and adjust (V_5) to give a manometer reading of
50 mm. This corresponds to a flow rate of about 100 ml. per minute.

Be sure argon is still bubbling slowly through (M); adjust (V_1) if necessary. Turn on the cooling water to the furnace, and begin heating the crucible at the normal rate (about 1800°). After thirty minutes, open (V_3) and (V_4) and close (V_2), thus passing the gas stream through the reagent. Continue flushing for ten minutes, then make a trial blank run.

Blank

Close (V_5) and check the zero adjustment. Adjust (V_5) to give a manometer reading of 50 mm. Place a Dewar flask full of liquid nitrogen over the trap, and set a timer for ten minutes. After ten minutes, close (V_5), wait a few seconds, and close (V_6). Remove the liquid nitrogen and replace it with a Dewar flask of warm water. Remove the water when all ice is melted, and dry the trap with a cloth. Tap the manometer and read to the nearest 0.5 mm. Open (V_6) and check the zero, if it seems necessary.

Except on days of rapid barometric change, it is usually not desirable to change the initial zero adjustment. Any gradual zero shift will affect the blanks and the samples alike, and so cancel out. The zero should not be adjusted while the trap is chilled, as the mercury tends to stop below the zero mark at that time, reaching its true level only slowly. Some capillary effect is probably responsible.

Blank determinations should be repeated until two successive blanks agree within 0.5 mm. or less, before attempting to analyze a sample. Additional blank runs are made after every six samples, and always after the last sample. An extra blank determination must be made after a high sample (over 200 p.p.m.), as such a sample may not be completed in one ten-minute period.

Sample

With (V_5) closed and (V_6) open, <u>turn off the induction heater</u>, remove the stopper of the sample holder, drop in the sample, and replace the stopper with a slight twist to seat it firmly. Turn on the heater, adjust (V_5) to give a manometer reading of 50 mm., chill the trap with liquid nitrogen, and set the timer for 10 minutes. Operate the rheostat to drop the sample. After ten minutes, close (V_5), then (V_6), warm the trap and read the manometer as described above. The fall of the sample may be observed by looking (through a dark glass) into the mirror above the adaptor window (Figure 2). The reaction makes a distinct flash, visible even against the background of molten platinum.

Calculations

The x values for blanks and samples are converted into W by equation (7), or by use of a calibration table (see above, Calibration). The W value for each sample is then corrected by subtracting the W corresponding to the blank. If the blank shows a uniform trend, the correction for each sample is obtained by interpolation between the last

blank and the next. If there is no trend, the average value of the blank is used. Then the oxygen content in parts per million is given by:
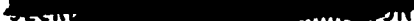
$$\text{p.p.m. oxygen} = \frac{W(\text{sample}) - W(\text{blank})}{\text{Wt. of sample (mg.)}} \times 1000 \qquad (12)$$

The actual value of the blank may be as low as 2-3 mm. or as high as 12 mm. or even more, depending on the history of the apparatus. The blank improves when the apparatus is in constant use and becomes worse when it is not used. The uncertainty in the blank correction is usually not more than 0.5 mm. (0.32 microgram).

An abnormally high blank after a high sample is counted as part of the sample, after correction for the normal blank.

Crucible Change

As explained later, the crucible must be replaced when the amount of plutonium reaches about 3 grams (for 5 grams of platinum). With a sample size of 50 mg., it must be changed after about 60 samples. The change is made as follows: Have the new crucible ready, containing 5-6 grams of platinum scrap or wire, and mounted on a tungsten stem. The length of the assembly should be that previously determined to bring the crucible just under the constricted part of the furnace. Start the vacuum pump and open valves (V_6) and (V_2) (others should be closed). Open (V_1) to bubble argon rapidly through (M). Remove the base of the furnace, replace the old crucible with the new, and replace the base as quickly as possible (it is usually not necessary to renew

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the grease). Adjust (V_5) to the standard flow rate (50 mm.) and adjust (V_1) so that argon bubbles slowly. Continue flushing without heating for about half an hour. If the base of the furnace has a spherical joint, the crucible may be centered during this time. Then begin heating at reduced power. The exact heating schedule is not important, provided that the crucible is heated and flushed for some time before the platinum is melted. With the present arrangement, in which the platinum melts at a setting of about 165 volts, the usual schedule is:

Flush 10 minutes at 120 v.

Flush 10 minutes at 140 v.

Flush 10 minutes at 160 v.

Raise voltage slowly and observe melting of platinum.

Flush 30 minutes at 172 v.

Change valves to introduce reagent.

Flush 10 minutes at 172 v.

Run blank.

One or two hours of flushing may be needed to obtain a satisfactory blank (successive values agreeing within 0.5 mm.).

Replacing the furnace, either by a new one or one that has been cleaned, always results in a high blank which is reduced only slowly. It is therefore better to avoid changing the furnace as long as possible. Heavy blackening of the furnace has not been observed to cause any difficulties.

The melting of the platinum is best observed with an optical pyrometer or an equivalent telescope and filter.

RESULTS AND DISCUSSION

The necessary conditions for accurate results in the oxygen determination are:

(1) Complete reaction of oxygen in the sample to form carbon monoxide.

(2) Complete conversion of carbon monoxide to carbon dioxide.

(3) No loss of carbon monoxide or dioxide (as by leakage).

(4) Complete separation of carbon dioxide in the trap.

(5) Accurate calibration.

The last four of these conditions were checked by analysis of a known compound, cuprous oxide. The compound was prepared by heating copper wire in air at 1000° C. Its purity was proved by its transparency under the microscope. Four small samples (1-2 mg.) were analyzed in the empty crucible (without a flux) at about 1400° C. The results were: Theory: 11.2 % oxygen. Analysis: 11.0, 11.1, 11.1, 11.0 %. About 99 % of the total was obtained in the first ten minutes and 1 % in the second ten minutes. These results compare well with vacuum fusion methods and indicate an accuracy quite satisfactory for trace analysis purposes.

Condition (1), above, must be verified separately for each new type of sample. The best way of doing this is to add measured amounts of oxygen to a metal sample of uniform (preferably low) oxygen content, and analyze. For example, Walter[8] showed in this way that a flux is needed for the complete recovery of oxygen from titanium. In general, a flux is likely to be necessary with any metal which, like uranium and plutonium, forms a stable carbide. When such metals react directly with carbon, the carbide "cinder" entraps some oxide which reacts slowly if at all[9].

The apparatus shown in Figure 6 was used to add measured amounts of oxygen to plutonium samples. It consisted of a small McLeod gauge, a "fused quartz" tube for heating the sample, and valves to admit oxygen and to evacuate the system. The sensitivity was about the same as that of the analytical apparatus. The procedure was to place a sample in the tube, evacuate, admit oxygen, read the McLeod gauge, heat for ten minutes, cool the tube with water, and break the vacuum. The temperature was 740° C measured in the furnace, but samples were not noticeably distorted, so their temperature may not have reached the melting point. The metal used for this experiment was fresh and had a pale golden color; it was not cleaned. After the oxygen addition, the color was metallic grey (PuO?). Three samples were analyzed as received and three after oxygen addition. A platinum flux was used. The results appear in Table I.
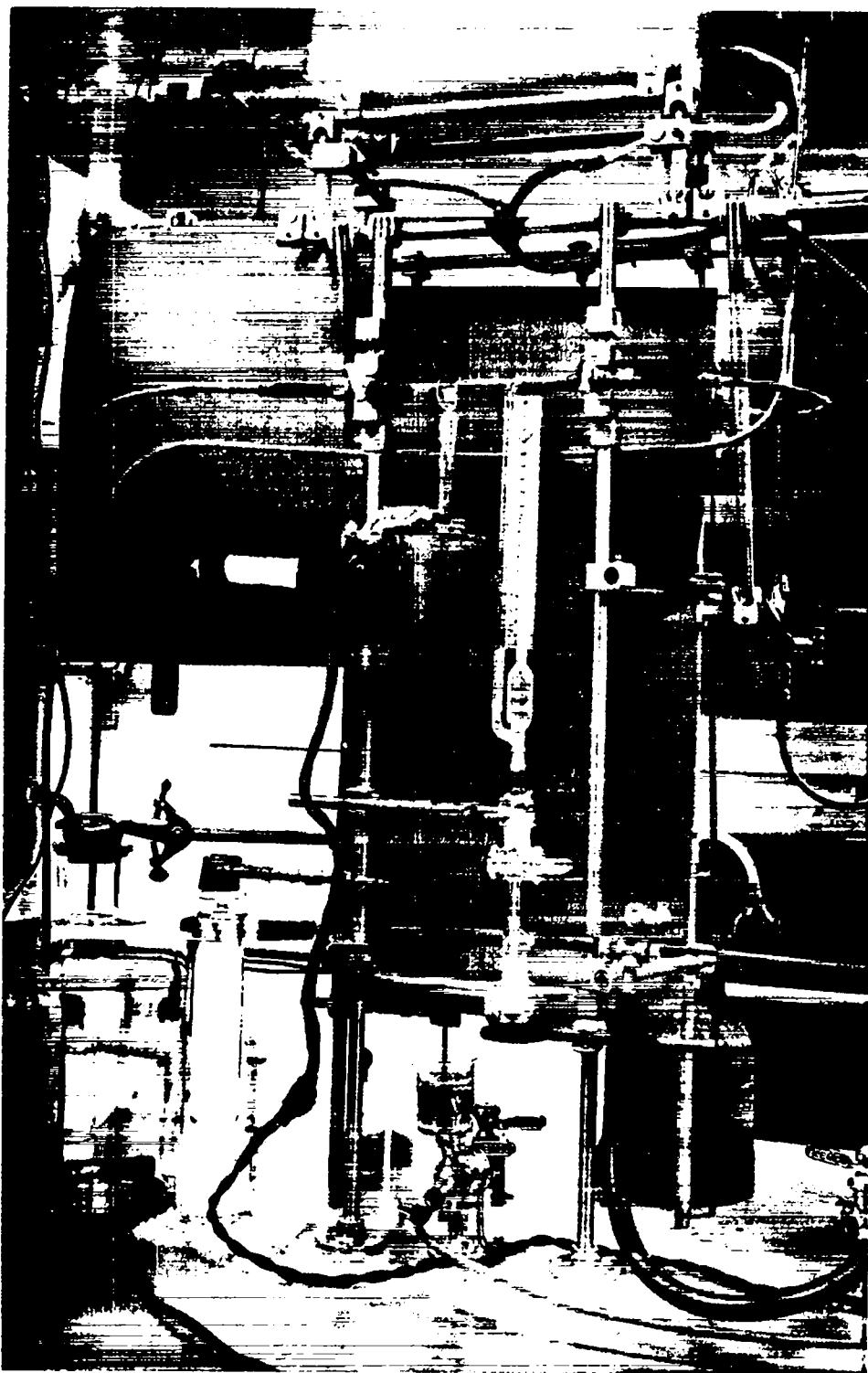
Figure 6

Table I

Oxygen Results on a Plutonium Sample with Added Oxygen

Wt. of sample, mg.	77.7	85.5	87.4	92.0	96.1	98.0
Oxygen added, micrograms	59.9	70.2	57.5	0.0	0.0	0.0
Oxygen found, micrograms	63.0	75.3	64.2	5.1	5.4	4.8
Initial oxygen, micrograms	3.1	5.1	6.7	5.1	5.4	4.8
Initial oxygen, p.p.m.	40	60	77	55	56	49
Average, p.p.m.		59			53	
Standard Deviation, p.p.m.		18.5			3.8	

Table I compares the initial oxygen content of the metal as given by direct analysis (right half of the table) with that obtained by subtracting the added oxygen from the total oxygen found (left half of the table). The difference of the two averages, 6 p.p.m., is far below even the 50 % level of significance. Also, it is in the wrong direction to be caused by any loss in analysis. Therefore, it may be concluded that, within the observed precision, recovery of added oxygen is complete, and that all five of the conditions set forth above are satisfied.

The standard deviation of 18.5 p.p.m. for the samples with added oxygen corresponds to about 1.5 micrograms or 2 % of the total oxygen. Since the results include any error in the oxygen addition as well as those of the analysis, the precision of the analysis itself may be somewhat

better. It is not possible to confirm this precision with untreated
plutonium samples, since plutonium of such high oxygen content is not
homogeneous, and replicates show wide variations in oxygen content.

Most actual plutonium samples have a low oxygen content, comparable
with the untreated samples in Table I. In this case, the sensitivity
of the manometer appears to be the limiting factor in the precision of
the results. The three samples in Table I gave an average and standard
deviation of 53 ± 3.8 p.p.m. Four samples of the same metal, of similar
size, were analyzed a few days earlier, giving 44 ± 3.4 p.p.m. The
difference is significant at about the 15 % level, and might be due to
corrosion. The standard deviation corresponds to about 7 % of the total
oxygen, or about 0.35 microgram. Since the manometer is read only to
the nearest 0.32 microgram, and any variation in the blank also affects
the results, the precision is about as good as can be expected. The
precision might be improved by using larger samples. Actually, since
there is little practical interest in such high precision in routine
analysis of plutonium, smaller samples (50 mg.) are used.

The precision obtained with routine 50-milligram samples is indicated
in Table II, which gives the first thirty oxygen values on samples of
this size (fifteen samples in duplicate). Two samples whose duplicates
differ by more than five times the average difference undoubtedly show
segregation and are excluded from the calculations. The other thirteen
pairs of duplicates give an average difference of 7.4 p.p.m. The

standard deviation calculated from the sum of the squares of the differences is 6.9 p.p.m., while that estimated by multiplying the average difference by $\sqrt{\pi}/2$ is 6.5 p.p.m. A standard deviation of 7 p.p.m. corresponds to 0.35 microgram, again showing that the precision is about as good as the sensitivity of the manometer permits.

Table II

Routine Analyses for Oxygen in Plutonium

(Average sample weight: 51.9 mg.   Unpolished Samples)

Duplicate Results, p.p.m.		Difference, p.p.m.
66	59	7
143	130	13
55	54	1
56	58	2
78	92	14
61	61	0
57	51	6
71	69	2
84	181	97 ⎫ Not included in the
38	73	35 ⎭ average
49	46	3
69	85	16
74	53	21
51	49	2
99	90	9

Average difference: 7.4

Standard deviation: 6.9 from sum of squares

6.5 from average difference

The importance of using a flux for oxygen in plutonium was demonstrated by an experiment in which eight samples were analyzed with and without the flux. The reaction without the flux was slower, requiring at least two ten-minute periods, and on all but the first two samples the value obtained without the flux was lower, the difference running as high as 70 p.p.m. The flux is therefore necessary for both speed and accuracy.

The choice of platinum as a flux was based on its low vapor pressure. Other metals having comparable vapor pressures[10] either have excessively high melting points or form stable carbides. Iron is often used as a flux; when saturated with carbon, it has a fairly low vapor pressure. Attempts to use iron as a flux in the present method have been disappointing. Although the amount of iron evaporated was moderate, it caused high and erratic blanks. Platinum does not evaporate to any appreciable extent provided the crucible is heated to remove oxygen before melting the platinum. The only objection to platinum is its high price. In recovering the plutonium from used crucibles, it might be practical to recover the platinum in a form in which it could be re-used.

Experience has shown that the flux becomes ineffective when the ratio of plutonium to platinum exceeds about 0.6 (with 50-mg. samples and 5 grams of platinum, not more than 60 samples should be analyzed). The exhaustion of the flux makes the reaction slower (increased blank after a sample). Also, dark spots can be seen on the surface of the hot

platinum, presumably carbide from incompletely assimilated samples.

Most of the advantages of the capillary trap method, as compared with vacuum fusion, arise from the use of a gas atmosphere in place of high vacuum. The collection of carbon monoxide by a stream of gas is faster than can be accomplished by a diffusion pump. The blank reaches a stable value more quickly (though the blank is not as low as can sometimes be achieved in vacuum fusion). The apparatus is simpler and more rugged--the elimination of glassblowing repairs is especially valuable with radioactive samples. An important effect of the gas atmosphere is that only carbon monoxide is formed. In vacuum fusion, there is often some carbon dioxide as well, which must be determined separately since both atoms of oxygen come from the sample. Evidently the argon atmosphere prevents carbon dioxide from escaping before it is reduced. This was shown by the accurate results on samples with added oxygen; if an appreciable amount of carbon dioxide had been formed, the results would have been low. In one experiment with cuprous oxide, the oxidizing reagent was by-passed; no carbon dioxide was obtained.

In vacuum fusion methods, the time required for a sample varies greatly, but is often an hour or more. In the capillary trap method, most samples require only twelve minutes. With all necessary flushing and blank runs, twenty-two samples have been analyzed in an eight-hour day.

One disadvantage of the capillary trap method is that, unlike vacuum fusion, it cannot readily be adapted to the determination of hydrogen and nitrogen.

CONCLUSIONS

(1) The capillary trap method is suitable for the routine determination of oxygen in plutonium.

(2) Plutonium samples with added oxygen gave a standard deviation of 1.5 microgram or 2 % of the total oxygen, with no significant bias.

(3) Routine 50-mg. samples give a standard deviation of 7 p.p.m. or 0.35 microgram, which is about the best precision to be expected from the sensitivity of the apparatus.

(4) The method is superior in speed and convenience to vacuum fusion.

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