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A NEW MICRO COMBUSTION METHOD FOR CARBON IN PLUTONIUM

William G. Smiley

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ABSTRACT

The new method differs from previous ones in using neither high vacuum nor induction heating. Samples are burned in a stream of oxygen at atmospheric pressure, and the carbon dioxide is condensed in a capillary trap and measured with a capillary manometer. About thirty-two determinations can be made in an eight-hour day. Precision is about 3 ppm on a 100-mg sample, and uniform plutonium samples give consistent results with an average deviation of 3-4 ppm. The method is useful also for carbon in nickel foil, uranium and steel. The capillary trap can be applied to oxygen determinations by using argon as a carrier gas.

INTRODUCTION

For the determination of carbon in plutonium, the microgasometric (low pressure combustion) method has been preferred because of high sensitivity, small sample size, and relative safety. Such methods customarily involve the combustion of the sample in an induction-heated platinum crucible, in oxygen at low pressure (a few cm). The carbon dioxide produced may be separated and determined by chemical absorption(1,2), or by condensation with liquid nitrogen and measurement with a McLeod gauge(3-7). The advantages of the condensation method have been discussed by Templeton and Watters(8). Experience at this laboratory has confirmed their conclusions. The chemical absorption method described by Cady and Rice(2) proved to be too slow and complicated for successful routine use (see Figure 1). Shutdowns for repairs and conditioning were frequent and prolonged.

In June 1948, a condensation apparatus was set up, based largely on the work of Naughton and Uhlig(6). The multiple sample dumper was retained from the old apparatus(2), and stopcocks were replaced by mercury cutoffs, except that brass bellows-type valves were used for admitting the oxygen, which was purified by distilling from a liquid nitrogen trap. Figure 2 shows the relative simplicity of this apparatus, which was in continuous routine use for almost two years. Speed and precision were fairly satisfactory. A half-hour was required for each sample, but because of the necessity of outgassing the system after reloading, a day's run was usually limited to eight samples, the capacity of the multiple dumper. The reproducibility

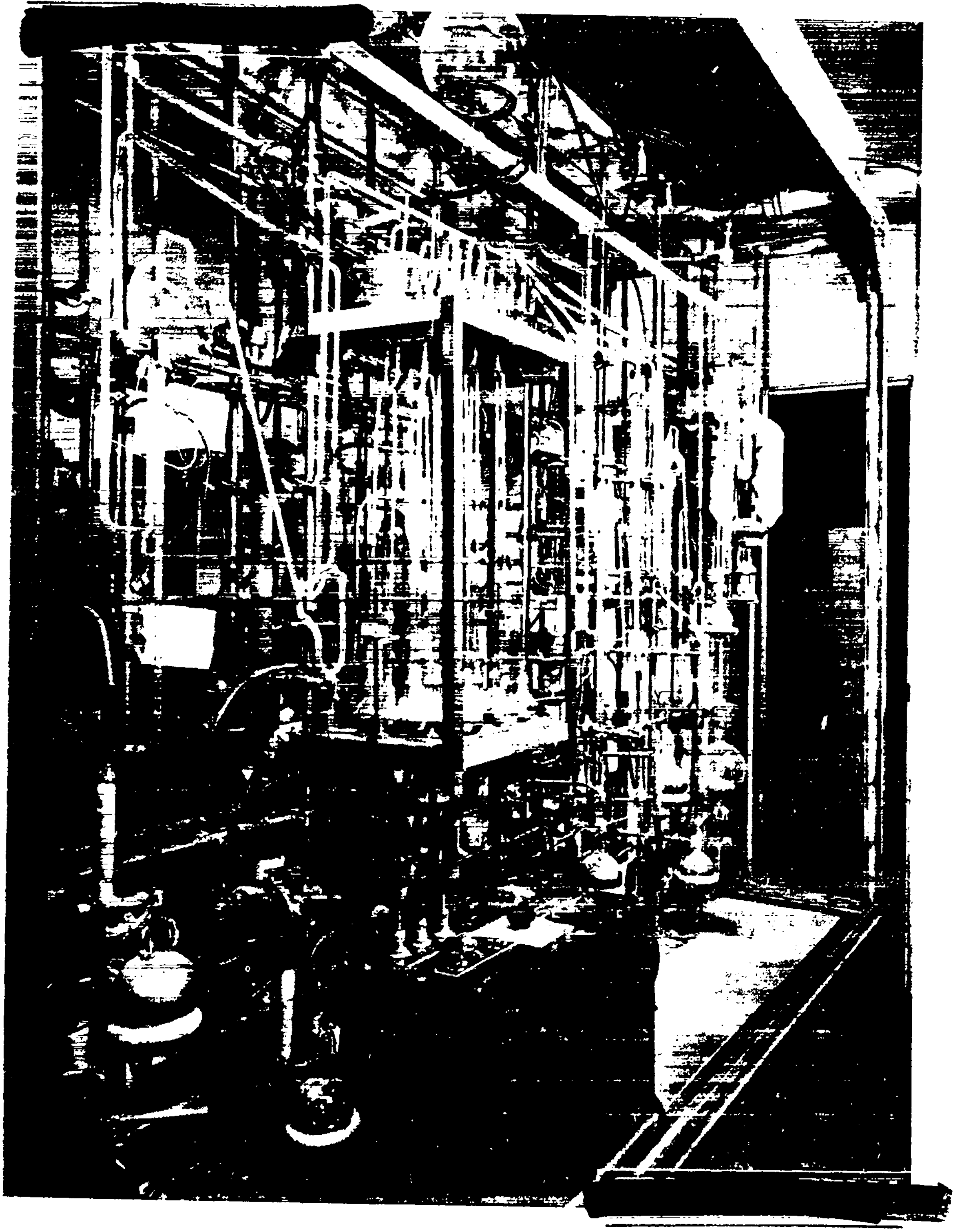

Figure 1

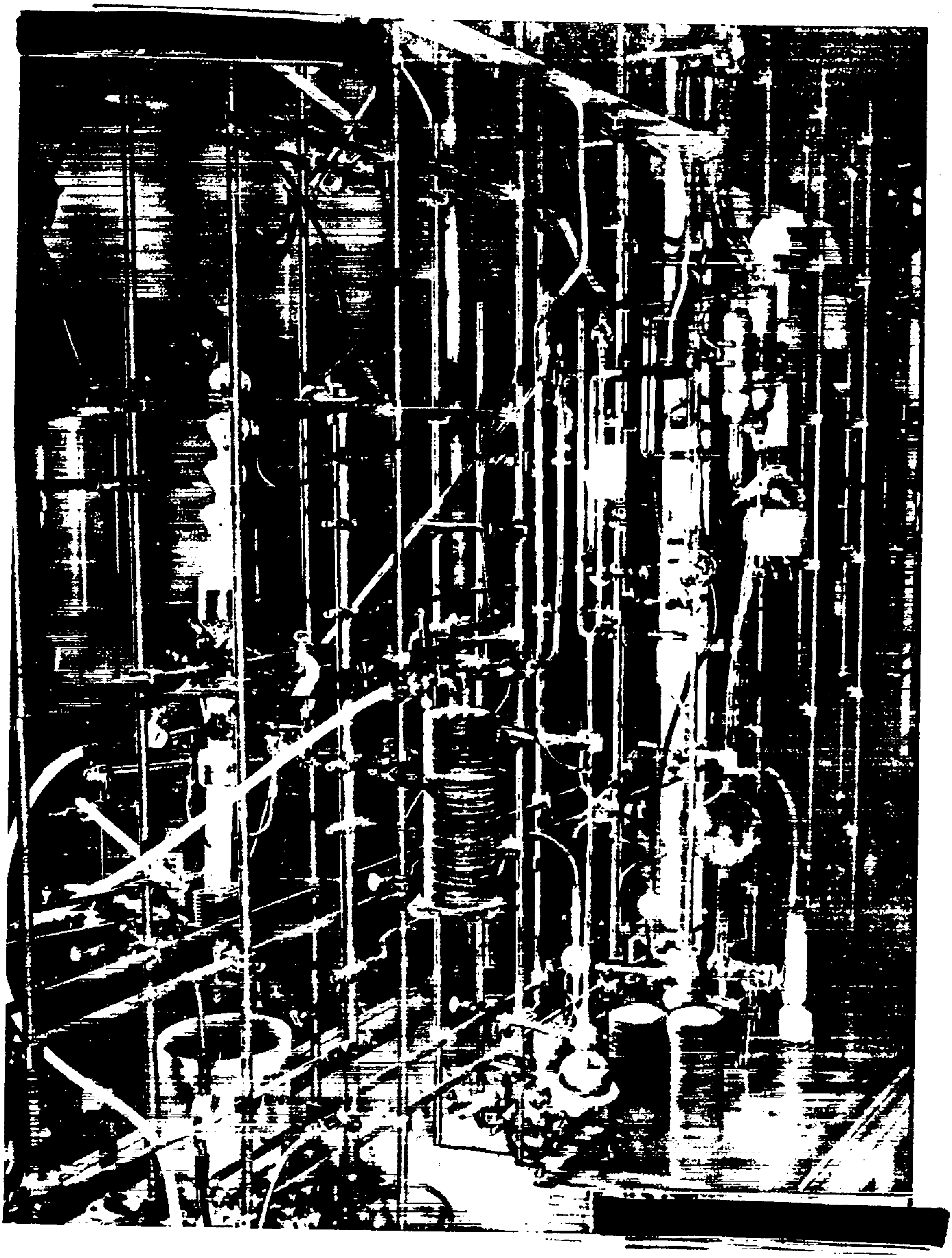

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Figure 2

of readings on the McLeod gauge was about 1/4 microgram of carbon, or 5-10 ppm on the sample sizes used. Duplicates usually agreed within 10-30 ppm, but certain samples gave large variations which were attributed to segregation of carbon in the metal.

Although this method was suitable for routine use, there were many respects in which improvement was desirable. The method of loading samples not only limited the number of samples per day, but also placed restrictions on the size and shape of the metal pieces used. A considerable increase in speed appeared possible, as is explained in the next section. The operation was hazardous in several ways; a construction which would permit all contaminated materials to be handled in a drybox was much to be desired. The use of platinum crucibles complicated the recovery problem and caused delays due to crucible failure. There were accidents due to leakage of mercury through joints and throwing of mercury when the vacuum was broken by power failures.

The new method described in this report has eliminated all of these difficulties and permits fast, safe, convenient operation with a minimum of maintenance. The precision is somewhat better than that of the old method, and it is believed that the results are more accurate in some cases. The advantages of the new method come chiefly from three major changes - - the use of a capillary trap, making high vacuum unnecessary, substituting a resistance furnace for induction heating and use of oxygen at atmospheric pressure instead of low pressure combustion.

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THE CAPILLARY TRAP METHOD

The previous microgasometric methods have had in common the use of a diffusion pump, with all the associated difficulties of high vacuum technique. It is to be noted that a fairly good vacuum is needed only because of the method of measurement in which a large volume of gas is compressed into a capillary (by a Töpler pump in the chemical absorption method, a McLeod gauge in the condensation method). A relatively short period of pumping is sufficient to remove carbon dioxide from the combustion zone(5), and the same result can be accomplished more simply by sweeping with a stream of gas, as in gravimetric combustion methods. Most of the troubles encountered with the condensation method here were directly or indirectly due to the use of high vacuum; half of the time spent on a sample was consumed in pumping down to a low enough pressure to permit the McLeod gauge to be used. Therefore, it was decided to use a method of measurement that would make the diffusion pump unnecessary.

This is accomplished by passing the stream of oxygen from the combustion tube through a U-shaped trap made of glass capillary tubing and immersed in liquid nitrogen. The trap is then closed off and warmed, and the pressure of carbon dioxide is read on a capillary manometer. Adequate sensitivity is thus obtained by small volume rather than low pressure. Only a mechanical pump is needed, and the small volume of the trap is evacuated almost instantly, eliminating the pumping period.

In some early experiments the capillary trap was combined with a low pressure combustion, but it was soon realized that there would be substantial advantages in using a flowing stream of oxygen at atmospheric

[redacted]

pressure (Naughton and Uhlig(6) successfully combined a similar technique with a high-vacuum condensation method). This procedure, in which only the capillary trap is evacuated, permits simple and rugged construction, including a ceramic combustion tube and a sample dumper of the desired speed and capacity. A wire-wound furnace is used in place of induction heating, eliminating the platinum crucible and the bulky high-frequency unit.

APPARATUS

Figure 3 is a photograph of the apparatus in its present form, while Figure 4 is a schematic diagram with the parts rearranged for clarity. Oxygen flows through the system from the gasometer G, passing through the preheater tube T_1, purifying tubes T_2 and T_3, the sample dumper D, the combustion tube T_4, purifying tubes T_5 and T_6, and through the capillary trap T_7 to the pump. V_1, V_2 and V_3 are 1/4-inch brass bellows-type valves. V_1 is opened only to refill the gasometer with oxygen, V_2 controls the flow rate, while V_3 is open except when measuring carbon dioxide.

The gasomometer, made from two four-liter aspirator bottles, serves to measure the oxygen and also to maintain a pressure slightly above atmospheric in all the apparatus up to valve V_2. Its operation is semi-automatic; in filling, any excess oxygen bubbles out through the open bottle, and when one liter has been delivered, an electrical contact rings a buzzer. The gasometer fluid is a potassium sulfate solution, to provide the necessary conductivity for buzzer operation.

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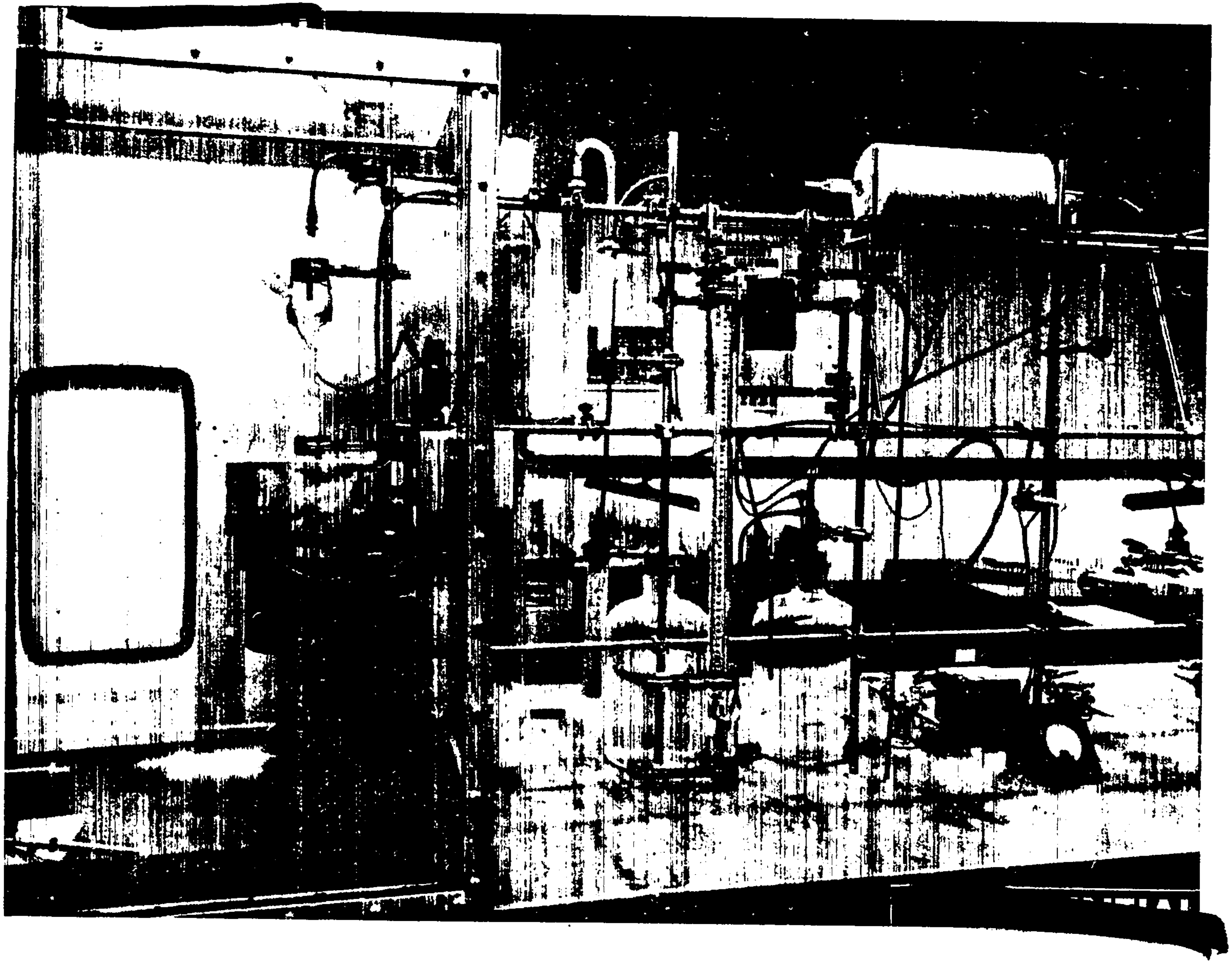

Figure 3

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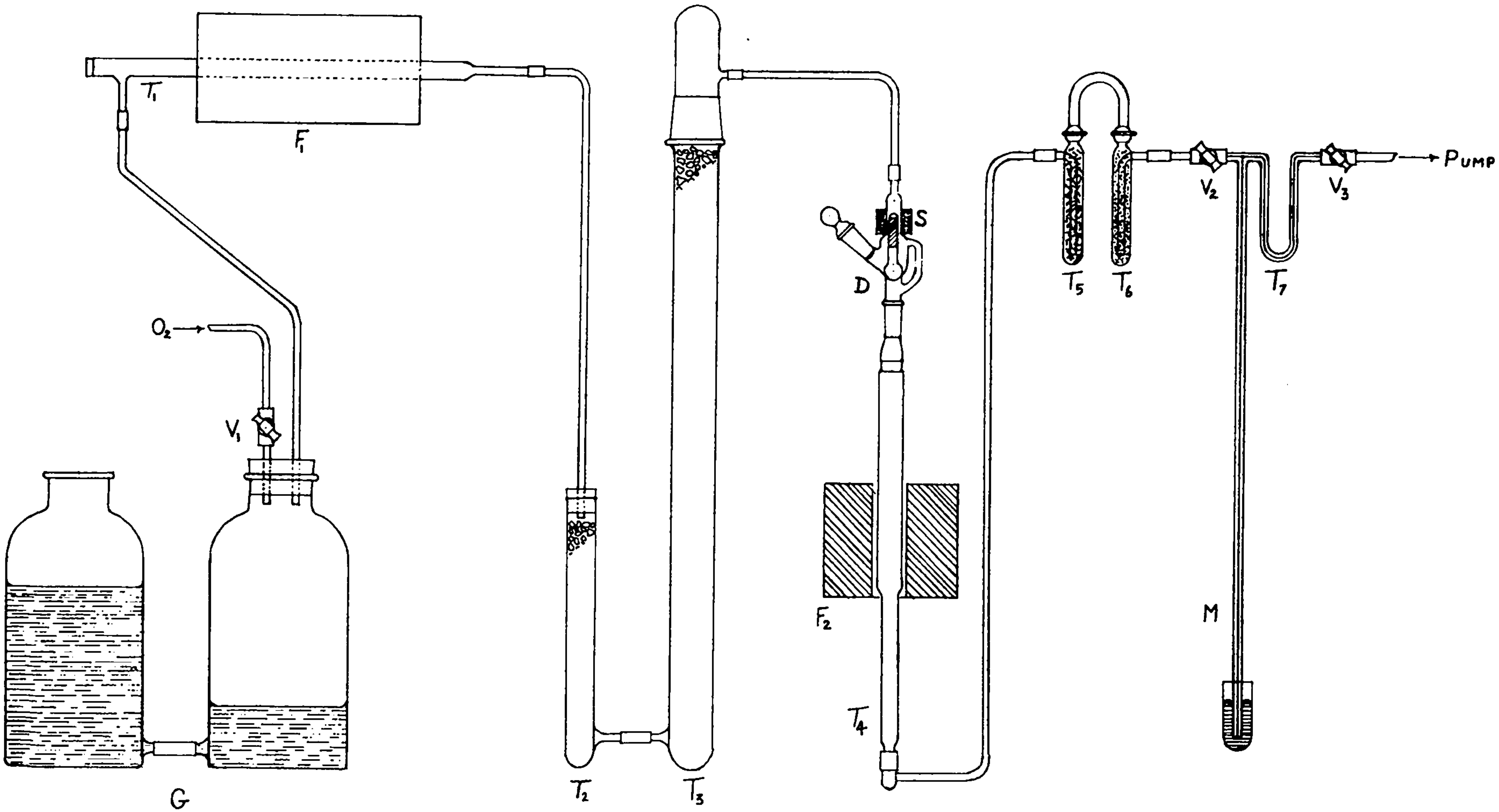

Figure 4

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The preheater tube, heated to 900° C by furnace F_1 is of quartz and contains a roll of platinum gauze as a catalyst (probably unnecessary, as is explained later). The bulk of the moisture from the gasometer is removed by silica gel in tube T_2, while Ascarite and silica gel in tube T_3 complete the purification of the oxygen. T_5 contains amalgamated copper turnings to remove a trace of some material which attacks mercury, and which made it necessary to clean the manometer almost daily before this tube was installed. Magnesium perchlorate in T_6 removes the last traces of moisture; silica gel was less satisfactory in this position because it apparently caused a slight lag in carbon dioxide collection, no doubt due to adsorption.

The combustion tube T_4 is made from a McDanel 1 1/4-inch clay tube, cut to a length of 45 cm and with a standard taper ground into the large end. It is mounted vertically, about 10 cm of its length being heated by furnace F_2. This furnace is platinum-wound and has been operated as high as 1300° C, but 1000° C has been found to be sufficient and the furnace is now kept continuously at this temperature. No crucible is used, the samples being burned on a packing of loose solid material which fills the lower part of the tube. At present, this bed consists of quartz chips, covered by a layer 2-3 cm deep of copper oxide (wire form), the latter thus being confined to the hot zone. The purpose of the copper oxide will be discussed later. The lower end of the tube is plugged with glass wool to retain any contaminated dust.

[redacted]

The glass sample dumper D is connected to the combustion tube through a standard taper adapter which is cemented with sodium silicate into the ground end of the tube. Samples are introduced through a side arm closed by a plain ground stopper, without grease or mercury seal. This is made possible by using atmospheric pressure rather than vacuum. The solenoid S (the coil of an H-B mercury relay) lifts the plunger to drop the sample into the combustion tube. A rheostat control is used to pick up and set down the plunger as gently as possible. The clearance is ample for the size and shapes of metal shavings usually encountered, without special selection or cutting as was necessary with the old multiple dumper.

The manometer M and trap T are made of glass capillary tubing, the manometer of 1.5 mm and the trap of 1 mm bore. The trap is designed to fit in a 250 ml Dewar flask. Its ends are sealed with Apiezon W into the two valves, which are oriented so that the side with small volume is that included in the trap-manometer system. Although these valves are in general much more satisfactory than stopcocks, especially in permitting gradual change of flow rate, they do occasionally develop leaks, and are therefore mounted so as to be easily replaced. The manometer is read by a millimeter scale extending downward from a zero mark etched on the tube 5 cm below the T-joint (to allow room for overshooting). The mercury well at the base of the manometer has a screw adjustment to correct the zero for changes in atmospheric pressure. A closed-arm manometer would avoid this adjustment, but the open construction is preferred because it permits cleaning the manometer by drawing chromic acid up into the capillary. By placing the manometer before the capillary trap, it is made

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to serve as a flowmeter, as will appear later.

The various parts of the apparatus are connected by 1/4-inch copper tubing; glass-to-metal connections are made with Neoprene tubing or stoppers. All parts can be readily removed and replaced. This construction, made possible by using atmospheric pressure, was very useful in experimental development; by keeping spare parts on hand, it also facilitates repairs or setting up new apparatus. Only at the upper connection to the sample dumper, where the Neoprene became quite hot, did it contribute to the blank; it was replaced by a flare fitting sealed to the glass with Apiezon W.

The combustion tube, furnace and sample dumper are mounted in a drybox, thus confining all contamination. All other parts, including the dumper rheostat, are outside for convenient operation. In Figure 3, the drybox gloves are removed for better visibility.

CALIBRATION

Since the volume of the capillary trap increases as the mercury falls in the manometer, the scale is non-linear. If the bore of the capillary were uniform, one would expect the calibration to follow the equation:

$$W = Ax + Bx^2,$$

where W is the weight of carbon, x the depression of the mercury, A is proportional to the volume of the trap with the mercury at zero, and B is proportional to the cross-section of the manometer bore. In practice the capillary is usually tapered, which adds a small cubic term to this

[redacted]

equation. B is determined by weighing mercury slugs whose length has been measured in various parts of the capillary. For W in micrograms, x in millimeters, and a temperature of 24° C,

$$B = 0.478 \cdot 10^{-4} \cdot \frac{\text{mg Hg}}{\text{mm}}$$

Since the volume of the trap includes that of the brass valves, A cannot be easily measured directly; it is determined from B by applying Boyle's law. A leveling bulb full of mercury is attached to the bottom of the manometer by a flexible tube. With the trap open to the atmosphere, the bulb is adjusted to set the mercury column at zero, and the valves V_2 and V_3 are then closed. The bulb is lowered to a point near the bottom of the scale, and the reading x is taken. Without moving the bulb, the trap is again opened to the air and x' is read. It follows from Boyle's law that:

$$A = \frac{Bx\,(h + x - x')}{x' - x}, \text{ where } h = \text{barometric pressure.}$$

If B is variable (the capillary tapered), one substitutes for Bx an expression giving volume correctly as a function of length, usually $B_1x + B_2x^2$ (a linear taper).

The complete calibration equation is then

$$W = Ax + B_1x^2 + B_2x^3.$$

For routine use it is convenient to calculate a table of W as a function of x. The calibration is reproducible within 2 parts per thousand.

The actual value of A is about 0.5 and of B, 0.001. The usable length of the manometer at this altitude (allowing room for a clamp and for the mercury well) is about 520 mm. Therefore, the capacity of the apparatus is

[redacted]

over 0.5 mg and the sensitivity per mm is 0.5 microgram at the lower readings, becoming 1.5 microgram at full scale. If the manometer is kept reasonably clean it can easily be read to 1/2 mm, giving a precision of about 0.3 microgram.

PROCEDURE

Plutonium samples of 100-150 mg are ordinarily used. The size and shape of the pieces is not particularly critical. With the gasometer filled with oxygen, the stopper of the sample dumper is removed, the sample dropped in, and the stopper replaced with a slight twist to seat it firmly. During the loading, oxygen flows out through the dumper, excluding all air. The gasometer is then refilled, and with valve V_3 open to the pump, V_2 is adjusted to give a manometer reading (about 50 mm) which corresponds to a flow rate of 1 liter in 10 minutes. The trap is immediately chilled with liquid nitrogen; the Dewar flask should be kept full. As soon as violent boiling stops, the sample is dumped, noting that all pieces have fallen. A bright flash occurs. When the buzzer rings indicating that one liter has passed, V_2 is closed, the gasometer is refilled, and V_3 is closed. The liquid nitrogen is removed and the trap warmed with hot water and wiped dry. The manometer is read to the nearest 1/2 mm, tapping with a rubber tube to free the meniscus. V_3 is then opened and the next sample loaded.

A blank is run in the same way, omitting the loading and dumping of the sample. Blanks must be run whenever the apparatus has been left unused for more than a few minutes. Running a stream of oxygen through the system

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when not in use will keep the blank down. Running oxygen at the usual rate for a half hour in the morning will reduce the blank to its operating value (0.5 microgram or less). The blank remains constant after running plutonium samples; this fact should be checked occasionally.

The zero should be checked and adjusted as often as necessary, tapping to free the meniscus. On days of unsettled weather it may be necessary to do so on every sample. This may be done before warming the trap or after discarding the carbon dioxide. If the meniscus sticks above the zero mark it should be moved downward by admitting a little oxygen, as it will not move downward freely under vacuum. It may then be adjusted from below upward. When the meniscus becomes too sluggish to adjust the zero properly, the manometer must be cleaned with chromic acid. This can be done overnight with little loss of time. The capillary is then rinsed three times with water and dried by passing a few liters of oxygen out through it (which simultaneously reduces the blank to its operating value).

The manometer reading is converted to micrograms of carbon with the calibration table and corrected by subtracting the blank (usually about 0.5 microgram):

$$\text{ppm carbon} = \frac{1000\ (W - \text{blank})}{\text{mg sample}}$$

Sometimes the blank is so small that it can be neglected entirely.

[redacted]

RESULTS

Much experimental work was done before the method was perfected in its present form. Though the results of this early work are now believed erroneous, some of them are worth considering in order to explain how the present procedure was developed.

Interpretation of the early runs was complicated by a high blank, about 5-6 micrograms. A copper oxide preheater at 600° C had no effect, and it was only at a much later stage of the work that it was discovered that a preheater containing quartz chips at 900° C would reduce the blank to less than one microgram. The platinum catalyst was added to the preheater because of a misinterpretation of later increases in the blank, and very probably it is not necessary. The preheater is completely ineffective below 800° C.

In the first experiments, the combustion tube was packed with broken pieces of ceramic combustion boats. This bedding material was abandoned when it was found that a calcite crystal, used as a carbon standard, gave very low results and slow recovery of carbon dioxide, no doubt because of adsorption. The effect was much less marked with steel and plutonium, data for which are given in Table I. Probably, because of the low carbon content of the plutonium and the slow combustion of the steel, the concentration of carbon dioxide did not become high enough to cause much adsorption. The irregularities in the plutonium results are believed to be due to another cause, as will appear shortly. The speed of recovery of carbon dioxide appeared to be satisfactory, and in fact it was during this period that the ten-minute running time was adopted as standard.

[redacted]

Table I

Ceramic Tube with Ceramic Chips, 1250° C

Sample	No. of Detns.	Carbon (Average and Average Deviation) Expected	Found
N.B.S. Steel 12e	4	0.371 ± 0.003 %	0.360 ± 0.014 %
Pu metal sample	9[a]	168 ± 3 ppm[b]	152 ± 24 ppm[a]

a Omitting 3 very low values
b Four determinations by old condensation method

Next, the ceramic chips were replaced by chips of broken quartz tubing. With this packing, excellent results were obtained on calcite: 11.86, 12.05, and 11.88 % carbon (theory: 12.00 %). The deviations were within the uncertainty in the high blank which still prevailed at that time. A series of plutonium metal samples was run, comparing the results with the high vacuum condensation method. Table II gives some representative data from these runs. In some cases, results by both methods are rather irregular, with fairly good agreement between the two, but in others, notably sample B, low values appear by the new method which have no counterpart in the old.

Table II

Pu in Ceramic Tube with Quartz Chips, 1250° and 1090° C

(All Results Rounded to Nearest 5 ppm)

Sample	ppm by Old Method	ppm by New Method
A	185, 255, 235, 255	190, 175, 225, 210
B	200, 180, 180, 185	195, 95, 55, 175, 195, 80, 185
C	215, 240, 210, 200	145, 170, 245, 230
D	125, 135, 120, 140	100, 130, 165, 165
E	140, 165, 155, 145	125, 170, 175, 140
F	185, 165	180, 185, 210, 185, 205, 195, 125

It was at this point that the problem of the blank was solved. Simultaneously, a quartz combustion tube with quartz chips was installed, and gave some rather encouraging results on uranium, which will be discussed later. Results with plutonium were no better than with the preceding tubes. However, a phenomenon now became apparent which had previously been obscured by the high blank. The blank increased slightly (about a microgram) after certain samples, and decreased again only slowly. At first this happened on every sample, later with decreasing frequency. As shown in Table III, the samples on which this occurred gave distinctly lower results, though the others also were quite irregular.

This effect can be explained by a theory which is now believed to account for most of the irregularities in the early plutonium runs. Under certain conditions, plutonium becomes so hot in burning that the oxide is fused into a hard mass, enclosing some carbide grains, which are then oxidized slowly if at all. There are two possible reasons why the effect is not observed with the high vacuum method. The sample burns while the crucible is still comparatively cool, and therefore may not reach such a high temperature; also, vacuum may aid in releasing carbon dioxide from the oxide lumps. The slow improvement with time is thought to be due to the building up of a layer of oxide with which the metal fuses to form a relatively porous mass. Therefore, it was hoped that providing a bed of a suitable oxide would be helpful. Copper oxide wire was chosen primarily because of its convenient physical form, insuring free passage of gas.

Whether this theory is correct or not, the effect of the copper oxide was even better than had been anticipated. The blank has remained very low and

[redacted]

nearly constant ever since the tube with copper oxide was installed, although hundreds of samples have been run. Table III shows the great improvement in consistency. A sample which had previously appeared quite inhomogeneous is now seen to be very uniform, the deviations being about equal to the precision of reading the manometer. Also, the results obtained without copper oxide, it now appears, were low even when no change in blank occurred. Assuming that the average of the copper oxide results is correct, 29 of the earlier results were low and only 4 were high. An occasional high result could be explained by a piece of metal happening to burn in contact with an oxide lump containing unburned carbide.

Table III

Plutonium Sample G

Description	No. of Detns.	Average ppm	Average Deviation
(In Quartz Tube with Quartz Chips, 1100° C:)			
Constant blank	17	194	34
Rising blank	16	131	36
(In Ceramic Tube with CuO Bed, 1000° C:)			
Electropolished	5	208	3
Unpolished	7	221	4

Table III also shows the effect of electropolishing the metal just before the analysis. There is a small but significant difference of 13 ppm. Since many less uniform samples show larger variations than this, it has not been thought worthwhile to electropolish samples routinely.

[redacted]

At one time it was thought that the early low results might be due to carbon monoxide formation. A tube containing modified Schütze reagent(9) was inserted in the position of T_6, Figure 4. After many runs there was still no color change such as the reagent would show if carbon monoxide were present. It was concluded that no carbon monoxide is formed, and the reagent was removed.

The speed of this method is much better than that of high vacuum techniques. An analysis takes about 12 or 13 minutes, and with the necessary blanks about 32 samples are run in an eight-hour day. About 150 samples were analyzed in duplicate in a two-week period, together with re-runs on any that failed to agree within 30 ppm.

Usually, when re-runs were made, three of the four runs agreed. Some samples, however appear to be highly segregated and give four different results. In this respect, experience has been much the same as with the old apparatus. Only the more uniform samples, such as the one shown in Table III, permit one to utilize the full precision of 3 ppm on a 100-mg sample (assuming the manometer reading is accurate to 1/2 mm). However, most samples give agreement of duplicates within 15 or 20 ppm. Results are customarily rounded to the nearest 5 ppm, instead of 10 ppm as was usual with the old method.

There is some reason to believe that the old method involved errors due to adsorption on the walls of the tube. This was suspected because the first samples run after pumping overnight tended to be low. Table IV gives a comparison between the old method and the new for a set of samples run in order on one day. It is seen that the first sample was decidedly lower by the old method, the difference decreasing as more samples were run, until fair agreement was obtained on the last. This could be explained by "saturation" of the adsorbent, building up a layer of carbon dioxide which would require prolonged pumping to remove. Such errors have been shown(6) to be due primarily to the layer of platinum deposited on the walls of the tube. Because of the pressure of routine work, and the fact that no increase in the blank was observed, this platinum film was allowed to become much heavier than is customary.

Table IV also shows that electropolishing had no significant effect on these samples, although they were four months old and covered with oxide scale.

Table IV

Comparison of Old and New Methods

(Results Rounded to Nearest 5 ppm)

Sample	Old Method	New Method Electropolished	New Method Unpolished
H	160, 160	220, 205	200, 140, 205, 200
I	180, 175	205, 195	205, 200
J	130, 125	150, 145	155, 150
K	135, 140	150, 145	140, 145

[redacted]

OTHER APPLICATIONS

In addition to its use for plutonium, an important application of the old condensation apparatus was the analysis of thin nickel foil for carbon. This method was indicated because of the small amount of sample available as well as its contamination. Rather surprisingly, it was found that although nickel was only superficially oxidized under the conditions used, the carbon was completely recovered. This conclusion was based on the facts that reasonable values were obtained and that the blank did not increase. It has now been found that the new method also can be used for this type of sample. The procedure is exactly the same as for plutonium. The blank does not increase, apparently indicating complete removal of carbon. Of course, this does not preclude the possibility that some carbon might be bound in such a way that it is completely unaffected. The success of the method undoubtedly depends on the nickel having a large surface to volume ratio; the procedure would not be expected to work for bulk nickel.

It seems very likely that the new method will be as effective for uranium as for plutonium. No uranium has been analyzed since the copper oxide was added, but a uranium Quality Control sample, previously analyzed by the standard macro combustion method, was run on both the old condensation apparatus and the new apparatus using a quartz tube and quartz chips at 1100° C. The results of the three methods are compared in Table V. Uranium seemed to behave somewhat better than plutonium, the blank increasing only on a few of the early runs, but the large fluctuations shown in Table V are probably due to a milder form of the same incomplete combustion found with plutonium. Presumably a copper oxide bed would give much better consistency. It is obvious from Table V that uranium, unlike plutonium, picks up carbon dioxide from the air and must be cleaned (by nitric acid, water, ethanol and ether) just before analyzing.

Table V

Uranium Quality Control Sample

Method	No. of Detns.	Average ppm	Average Deviation
Macro combustion	32	109	7
Old Method			
Cleaned day before	8	92	6
Freshly cleaned	15	76	9
New Method			
Cleaned weeks before	10	164	34
Freshly cleaned	10	99	17

The fair results obtained with a steel sample in the tube with ceramic chips (Table I), and some better data from an early all-quartz apparatus, indicate that the method is suitable for the less refractory steels. For this purpose the ceramic tube with quartz chips should be used, at 1200° C or higher. Even at 1250° C, a longer combustion time is required than for plutonium.

The small sample size and resulting reduction in heat generation would recommend the method for such metals as calcium and magnesium. The recovery of carbon from calcium is difficult by macro combustion methods(10); it would be interesting to see if copper oxide would solve this problem as in the case of plutonium.

[redacted]

The principle of the capillary trap is also applicable to the determination of oxygen. In fact, the first experiments with the method were for this purpose. The sample was fused in a graphite crucible in an atmosphere of argon, which was then pumped through modified Schütze reagent(9), to convert carbon monoxide to carbon dioxide, and through a capillary trap. Results on cuprous oxide were good, and work on the method is being resumed. Much of the apparatus is identical with that used for carbon.

CONCLUSIONS

(1) The use of a capillary trap in combination with combustion in a stream of oxygen at atmospheric pressure gives a fast, safe, and convenient method for carbon in plutonium. About thirty-two determinations can be made in an eight-hour day.

(2) A copper oxide bed in the combustion tube is an essential feature to secure complete recovery of carbon and a permanently low blank.

(3) There is a substance in the oxygen supply which contributes 5-6 micrograms of carbon per liter, and is oxidized only above 800° C.

(4) A uniform plutonium sample analyzed by the new method gives a standard deviation of 3-4 ppm, which is about the limit set by the sensitivity of the apparatus for a 100-mg sample.

(5) There is evidence that an adsorption error occurs with the low-pressure combustion method, and is eliminated by the new method.

(6) The new method can be used also for thin nickel sheet, uranium and steel.

[redacted]

(7) Electropolishing plutonium has little effect on the carbon content, but uranium appears to pick up carbon dioxide from the air and must be cleaned before analyzing.

(8) By using an inert gas as a carrier, the capillary trap can be used for oxygen determination.

ACKNOWLEDGMENT

Mr. C. G. Warren cut and weighed the plutonium samples and made many of the analyses.

[redacted]

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