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# **THE USE OF CALORIMETRY IN NUCLEAR MATERIALS MANAGEMENT**

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THE USE OF CALORIMETRY IN NUCLEAR  
MATERIALS MANAGEMENT

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U.S. Government Contract No. AT-33-1-GEN-53

A calorimeter is a device to measure evolved or adsorbed heat. For our purposes, the heat measured is that associated with radioactive decay and the unit of measurement is the watt. Each time an atom decays, energy is released and absorbed by the surroundings and heat generated. For each isotope, this heat is a constant related to the energy of the decay particles and the half-life of the isotope.

A point which is often overlooked is that calorimetry is one of the oldest techniques known for measuring radioactivity. In 1903, Pierre Curie and A. Laborde used a twin microcalorimeter to determine that one gram of radium generates about 100 calories per hour. Several months later, Curie and Dewar used liquid oxygen and hydrogen to show that the amount of energy developed by radium and other radioactive elements did not depend on temperature. At that time, this observation was extremely important. It indicated that the nature of radioactivity is entirely different and cannot be compared with any known phenomena. In all other thermal processes known in physics and chemistry, the rate at which heat is developed changes with temperature.

In 1942, Monsanto was asked by General Leslie Groves, Head of the Manhattan Project, to accept the responsibility for the chemistry and metallurgy of radioactive polonium. Late in 1943, two Monsanto scientists began a study of the half-life of polonium-210 using calorimetry.

Since 1943, over 100 manyears of experience in calorimetry has been accumulated at Mound and over 130 calorimeters built. Of these there are about 60-70 different designs of four basic types. Each of these works on the same basic principles. Each calorimeter is a heat flow type and consists of three essential

elements: a sample chamber; a temperature sensor and an electrical heater (Figure 1).

The sample chamber is separated from its environment by a constant thermal resistance. For most calorimeters, the environment is a constant temperature water bath. When a sample is placed in the calorimeter, the temperature of the sample chamber rises until the heat generated by the sample is equal to the heat lost to the environment through the thermal gradient. By maintaining the thermal gradient constant, the temperature rise is directly proportional to the power being dissipated in the calorimeter. This temperature is then measured ( $\Delta T_s$ ) and the calorimeter is calibrated using a four terminal electrical heater. This is done in one of two ways. In the replacement method the sample is removed and electrical power ( $W_H$ ) is added to give the same temperature rise ( $\Delta T_H$ ) in the calorimeter. The sample power is then compared to the heater power.

$$W_s = W_H \frac{\Delta T_s}{\Delta T_H}$$

In the differential method a twin calorimeter is used which has two identical sample chambers. In this case, the temperature rise in the sample chamber is balanced by electrical heat in the reference chamber. The power of the sample ( $W_s$ ) is then equal to power in the heater ( $W_H$ ) plus a small correction for the fact it is impossible to make both sides identical ( $\Delta T_s \times \text{sensitivity}$ ).

$$W_s = W_H + (\Delta T_s \times \text{sensitivity})$$

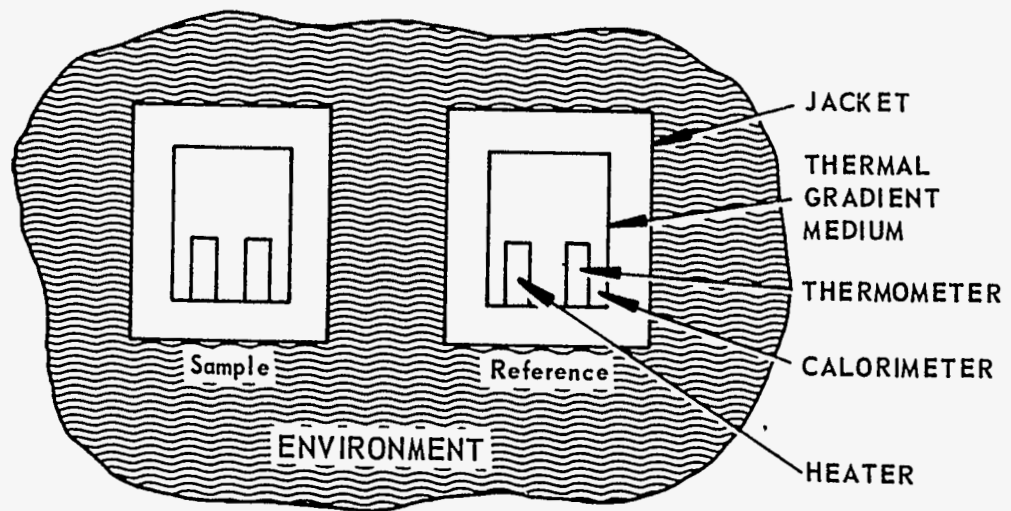


Figure 1: Heat Flow Calorimeter

One advantage of the heat flow type calorimeter is that it is not necessary to return to the zero power level after each run. Thus many samples of approximately the same size can be run using a single calibration. Another advantage is that the thermal resistance between the sample chamber and the environment can be tailored to fit the accuracy and time requirements of the sample. The time required for a calorimeter to reach equilibrium is a function of this thermal resistance and the heat capacity of the calorimeter and sample. The thermal response is exactly like the electrical response of an RC filter network (See Figure 2). Here "R" is the thermal resistance and "C" the heat capacity. Thus there is a direct relationship between accuracy and time/assay. The more accuracy needed, the more time it takes to reach equilibrium. Thus each calorimeter must be engineered according to the accuracy and time required.

When both high accuracy and fast equilibrium times are required, the calorimeter can be speeded up by automating. Here the sample chamber is controlled at a constant temperature. The control power is measured ( $W_0$ ) and then a sample placed in the calorimeter. The control power ( $W$ ) is again measured with the decrease in control power being due to the heat generated by the sample ( $W_s$ ).

$$W_s = W_0 - W$$

In this method, the calorimeter is always at equilibrium and only the sample has to come to equilibrium. With this method the time/assay can be practically reduced by about one-half.

To use a calorimetric measurement to calculate the mass of a particular isotope, the following information is necessary: The percent fraction of each isotope present, usually from mass spectral data; and the power per gram of each isotope, which is a constant that may be calculated from the energies of the radioactive disintegrations and the atomic masses or determined by calorimetry.

# CALORIMETER RESPONSE

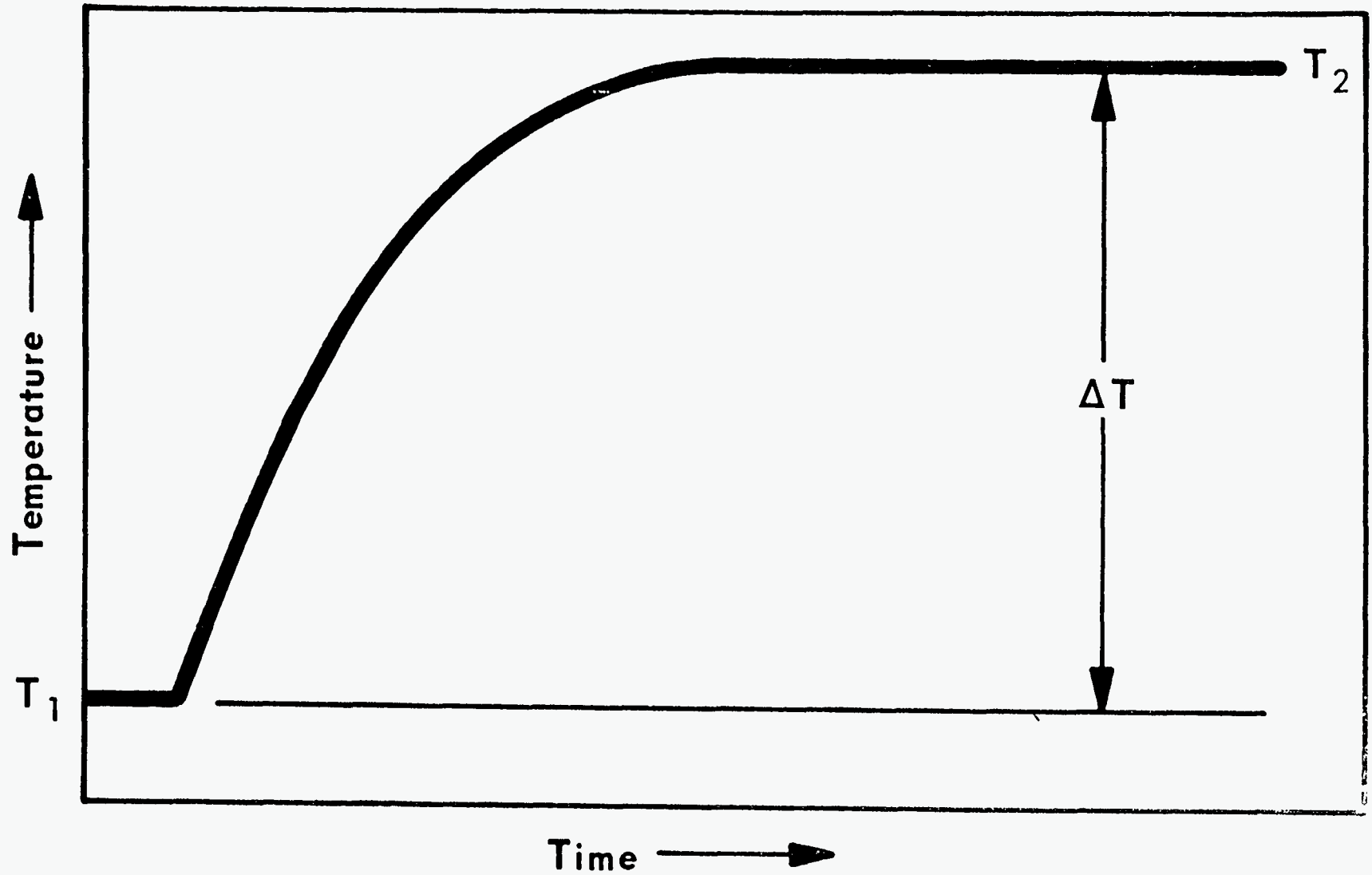


Figure 2: Thermal Response of a Heat Flow Type Calorimeter



The following equation can be derived to calculate the mass of a particular isotope in a sample:

$$m_1 = \frac{R_1 W}{R_1 F_1 + R_2 F_2 + \dots + R_n F_n}$$

where

- $m_1$  = the grams of the isotope
- $W$  = the total power of the sample observed by calorimetry
- $R_1$  = the fraction of isotope #1
- $R_2$  = the fraction of isotope #2
- $R_n$  = the fraction of the last isotope
- $F_1$  = the power per gram of isotope #1
- $F_2$  = the power per gram of isotope #2
- $F_n$  = the power per gram of the last isotope

The radioactive decay of any of the constituent isotopes of a sample has to be taken into account whenever the half-life of the isotopes and the time interval between the mass spectrometry determination and the calorimetric assay combine to produce a significant effect on the total power. Computer programs are employed at Mound to handle these cases and are available for general use.

Table I shows a calculation of a typical  $^{238}\text{PuO}_2$  shipment received at Mound. In this example, 99.9% of the measured heat comes from  $^{238}\text{Pu}$ ; and if no mass spectral data were available and the shipment was assumed to be only  $^{238}\text{Pu}$ , this analysis would be in error by 0.1%. With reasonable mass spec data, it is easily possible to reduce this error to 0.01%. From this, it is easy to see that for  $^{238}\text{Pu}$  this is indeed a powerful tool.

TABLE I

ANALYSIS OF A TYPICAL  $^{238}\text{PuO}_2$  SHIPMENT

<u>Isotope</u>	<u>Isotope Percent <math>R_1</math></u>	<u>Power Output (watts/gram) <math>F_1</math></u>	<u>Power/Isotope (watts/gram of metal) <math>R_1 \times F_1</math></u>
$^{238}\text{Pu}$	81.43	0.5664	0.461220
$^{239}\text{Pu}$	15.25	0.001924	0.000293
$^{240}\text{Pu}$	2.64	0.00709	0.000187
$^{241}\text{Pu}$	0.59	0.00450	0.000027
$^{242}\text{Pu}$	0.088	0.00014	0.000012
$^{241}\text{Am}$	<u>0.006</u>	0.1084	<u>0.000006</u>
	100.00		0.461745

Calorimetry value = 97.34 watts

$$\frac{97.34}{0.461745} = 210.8 \text{ grams Pu metal or } 171.7 \text{ grams } ^{238}\text{Pu}$$

As an example of how calorimetry is used at Mound, let us follow the fuel for the SNAP-27 heat source through the process lines.

A layout of our plutonium processing building is shown in Figure 3. Each box represents a calorimeter located at some strategic point in the process. Each of these calorimeters is operated from a master control station located in Room 105. The incoming material from the reactor site enters the building and is calorimetered in the shipping containers prior to being passed into the process lines. Figure 4 shows a technician loading a shipping container into a water-bath calorimeter.

About two and one-half years ago, the reactor site was provided with a calorimeter identical to the ones in use at Mound. Over the last two years, the total discrepancy in the shipper-receiver reports has been reduced to 0.0257%. This amounts to 8 grams out of 35,000.

Next, the material is passed into the process lines. Here we have two sizes of calorimeters. The larger ones, shown in Figure 5, have a sample chamber, 3.25 inches in diameter by 6.5 inches high, and handle from 5 to 175 grams of material. These are used to measure batches at each step of the process. This information is used to determine where the material is being lost and the efficiency of each step. All material is transferred between lines by a conveyor system operated by the material control group. All transfers are logged through this office.

The other calorimeters located in-line are smaller and are used for analytical samples. These have sample cans about 1" in diameter by 3" long. They are designed for 5 grams or less of accountable material. The accuracy of these in-line calorimeters varies from 0.1% to 0.3%. Each instrument normally handles from one to three samples a day.

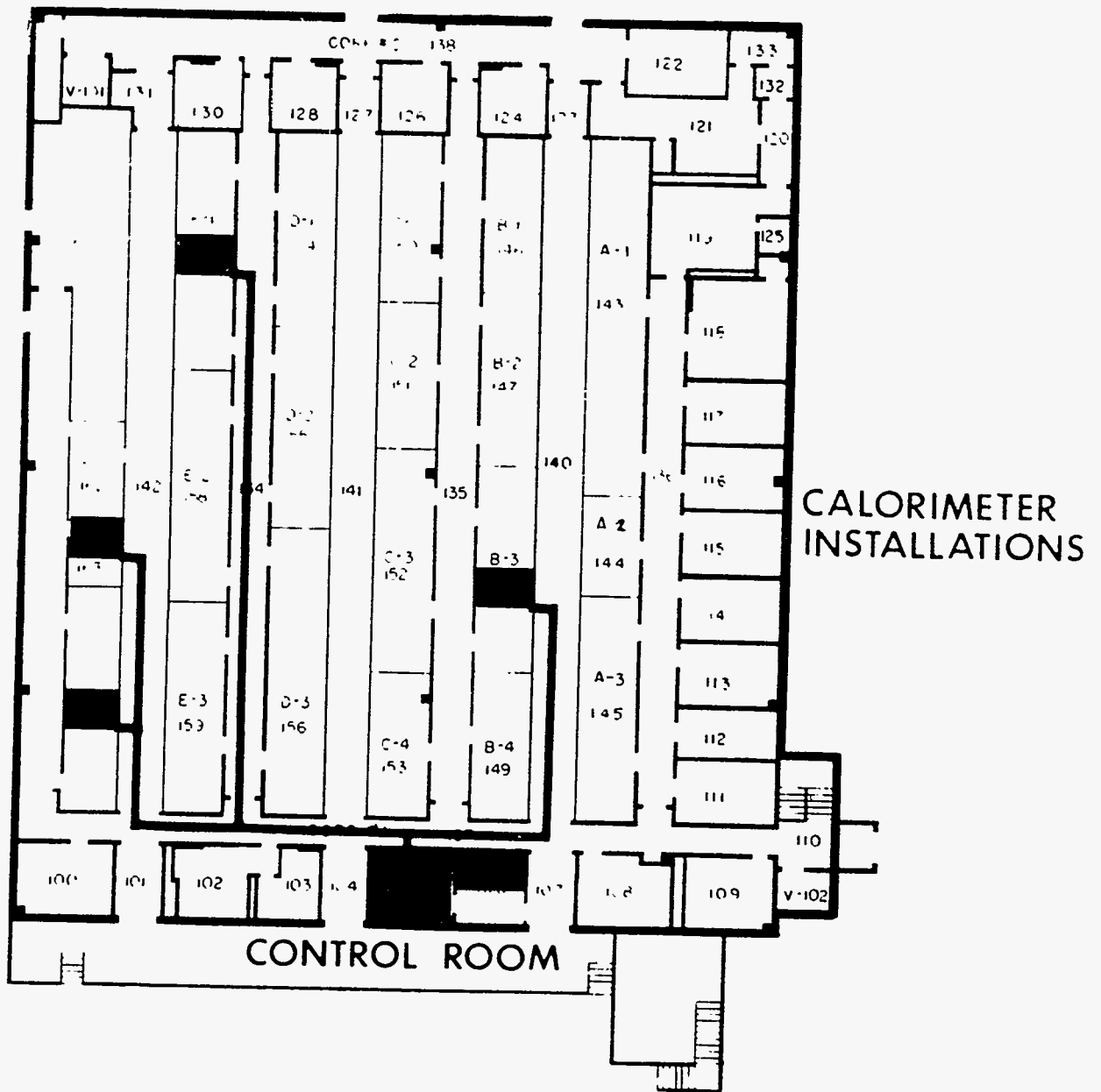


Figure 3: Layout of Plutonium Processing Building

Figure 4: Loading a Shipping Container into Calorimeter 92



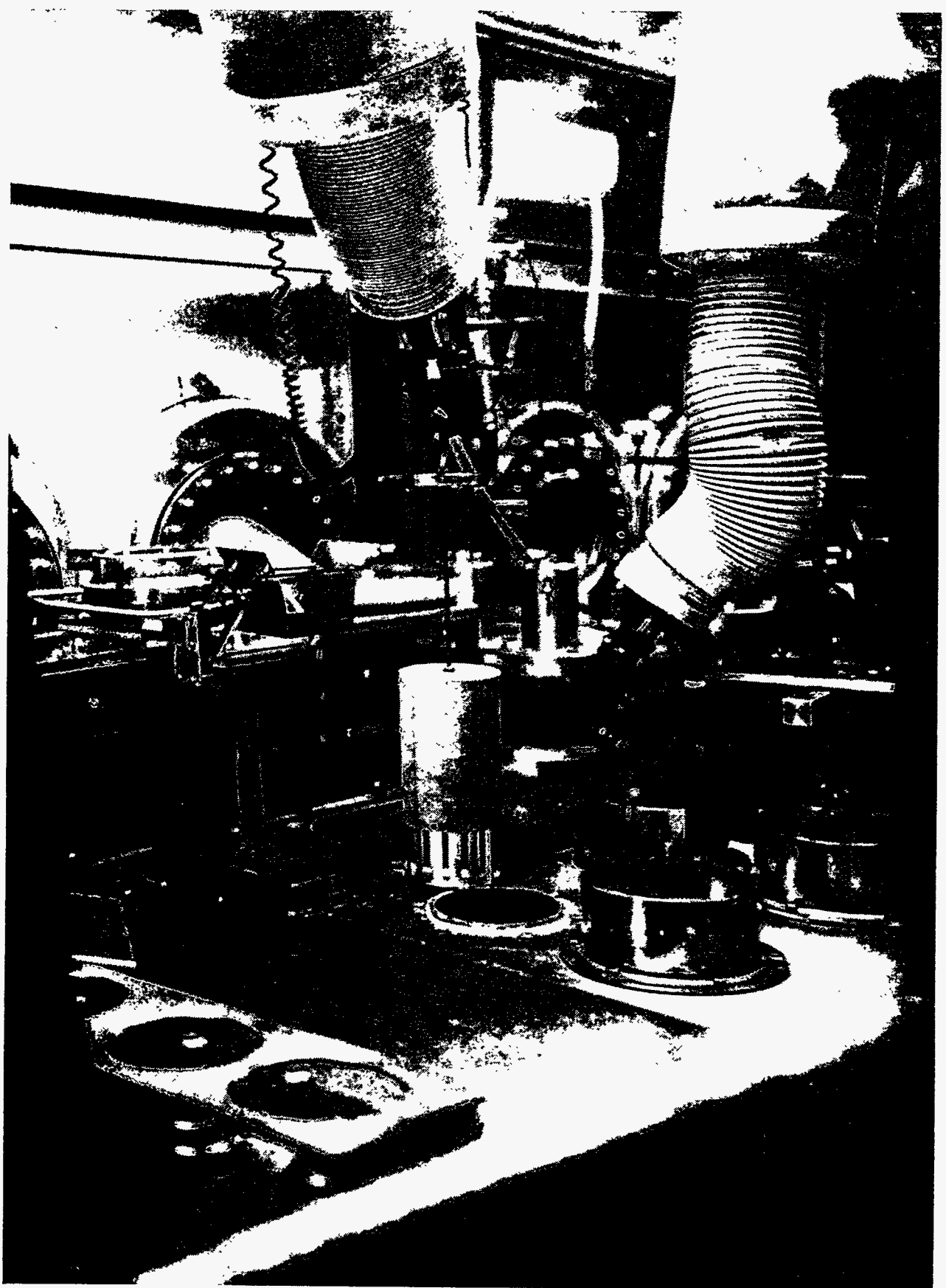


Figure 5: In-line Calorimeters

All five in-line calorimeters, the two water-bath calorimeters for shipments and an additional dry calorimeter are operated from a central facility by a single technician shown in Figure 6.

The final product of this process is plasma fired microspheres for the SNAP-27; 2,600 grams of Pu-238 were loaded into the final capsule with a total thermal output of 1,480 watts. The final capsule was measured in a special water-bath calorimeter.

This source powers a thermoelectric generator which supplies 70 watts of electricity to the Apollo Lunar Surface Experimental Package (ALSEP). The unit was placed on the moon by the crew of Apollo 12 and is still in operation (Figure 7).

In addition to the plutonium processing building, there are three other labs where routine assay work is done. In all, there are about 30 calorimeters in day to day operation. The measured accuracies vary from 0.001% to 0.5%. At the present time, the calorimeters in use at Mound range in size from 0.5 inch diameter by 0.5 inch long to 12 inches in diameter by 16 inches long. The minimum detectability is  $10^{-8}$  watts and the maximum sample size is 2 kilowatts, thus spanning a range of  $10^{11}$ . This compares with the distance from here to the moon and back to the diameter of an ordinary pencil.

The very best calorimeters are used for precise half-life measurements. Here the probable error of a single observation is less than 5 ppm and the detectability is 0.1 ppm. With this kind of sensitivity, it is possible to see the day by day decay of 1 gram of Pu-238 with its 87.8 year half-life.

As mentioned before, each calorimeter is engineered for a specific job. Ideally, we would like to have a universal calorimeter. Unfortunately, this is not possible. Such a calorimeter would be infinite in size and capable of measuring infinitely small samples. However, as size goes up, detectability goes down so a compromise must always be made.

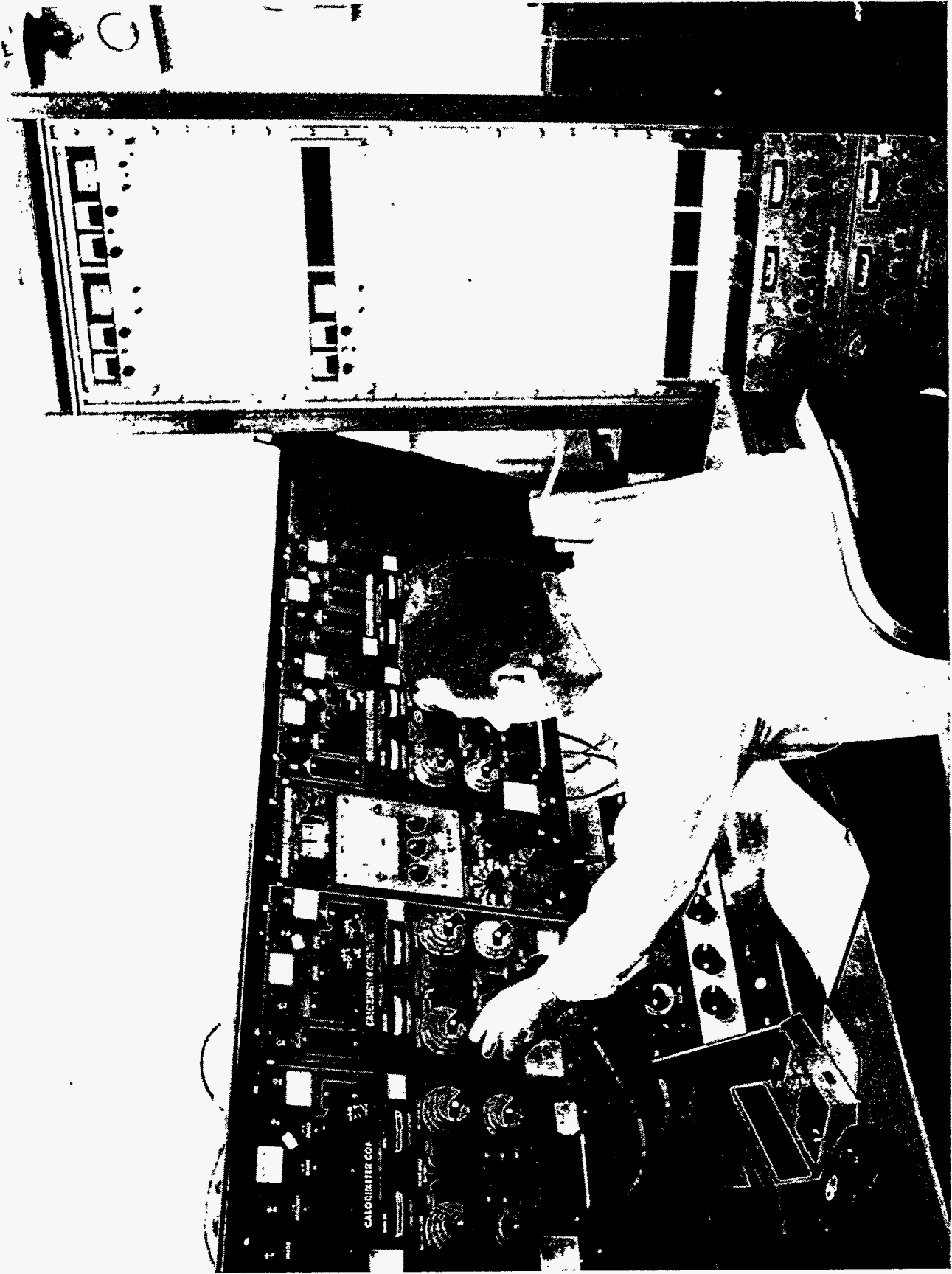


Figure 6: Master Control for all Calorimeters in the Plutonium Processing Building



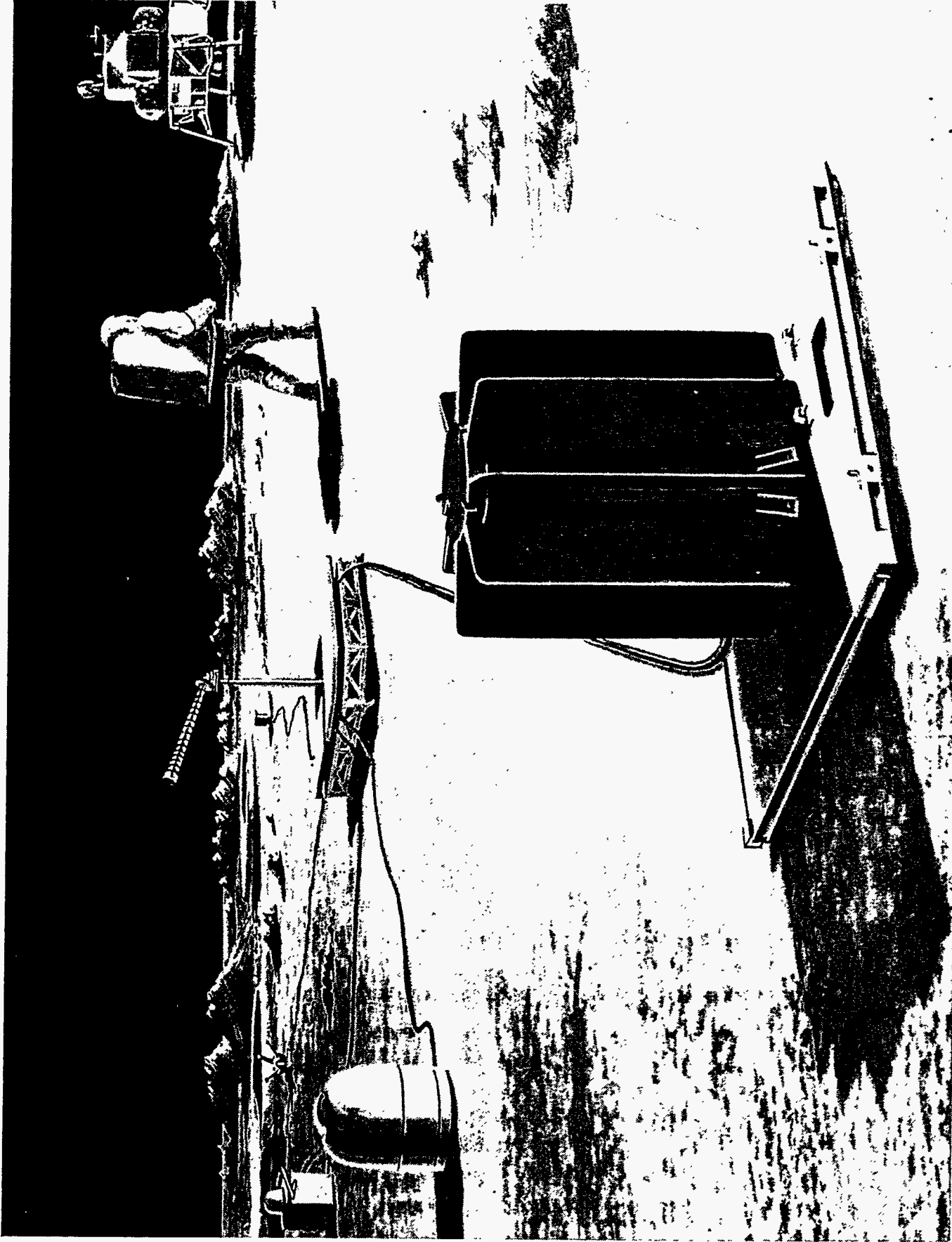


Figure 7: SNAP-27 Thermoelectric Package placed on the Moon by the Crew of Apollo 12

With this background in mind, let us consider calorimetry of reactor fuel material. The Office of Safeguards and Materials Management has provided us with funding to study the feasibility of applying calorimetric techniques to the safeguarding of reactor fuel material.

First, let us go through a similar analysis for a reactor fuel material shipment (Table II). In this case, power/unit mass is down by a factor of a hundred. Here the uncertainties in the isotopic ratios from mass spectral data limit the accuracy of the calorimetric assay of the Pu-239 content to about 0.3 to 0.5%. Thus an uncertainty of better than 0.1% in the calorimetric measurement would be unnecessary.

This kind of accuracy can be attained on 1 kg lots of  $^{239}\text{PuO}_2$ . For example, in our Model 102 Calorimeter which is 4.75 inches in diameter and 8.75 inches tall, the uncertainty at the 95% confidence level is 0.1%. This size calorimeter could also be used on plutonium nitrate solutions, hard scrap, mixed oxide batches and pellets. The uncertainties in Table III are based on measurements on standard heat sources in the 0.1 to 5 watt range.

In addition to being used to resolve shipper-receiver discrepancies, calorimetry can be used for in-plant material management and quality control purposes. For example, the uniformity of the blending process can easily be determined to 0.1% by comparing the heat outputs of a series of ten gram samples. Our automated low wattage assay calorimeter (ALWAC), shown in Figure 8, can measure a sample this size with a precision of 18 microwatts or about 0.06%. The calorimeter makes a measurement every 38 minutes and can be operated seven days a week, 24 hours a day.

The  $\text{PuO}_2$  content of individual fuel pellets, batches of fuel pellets and rods up to 3 ft. in length can be compared to 0.1% with existing calorimeters.

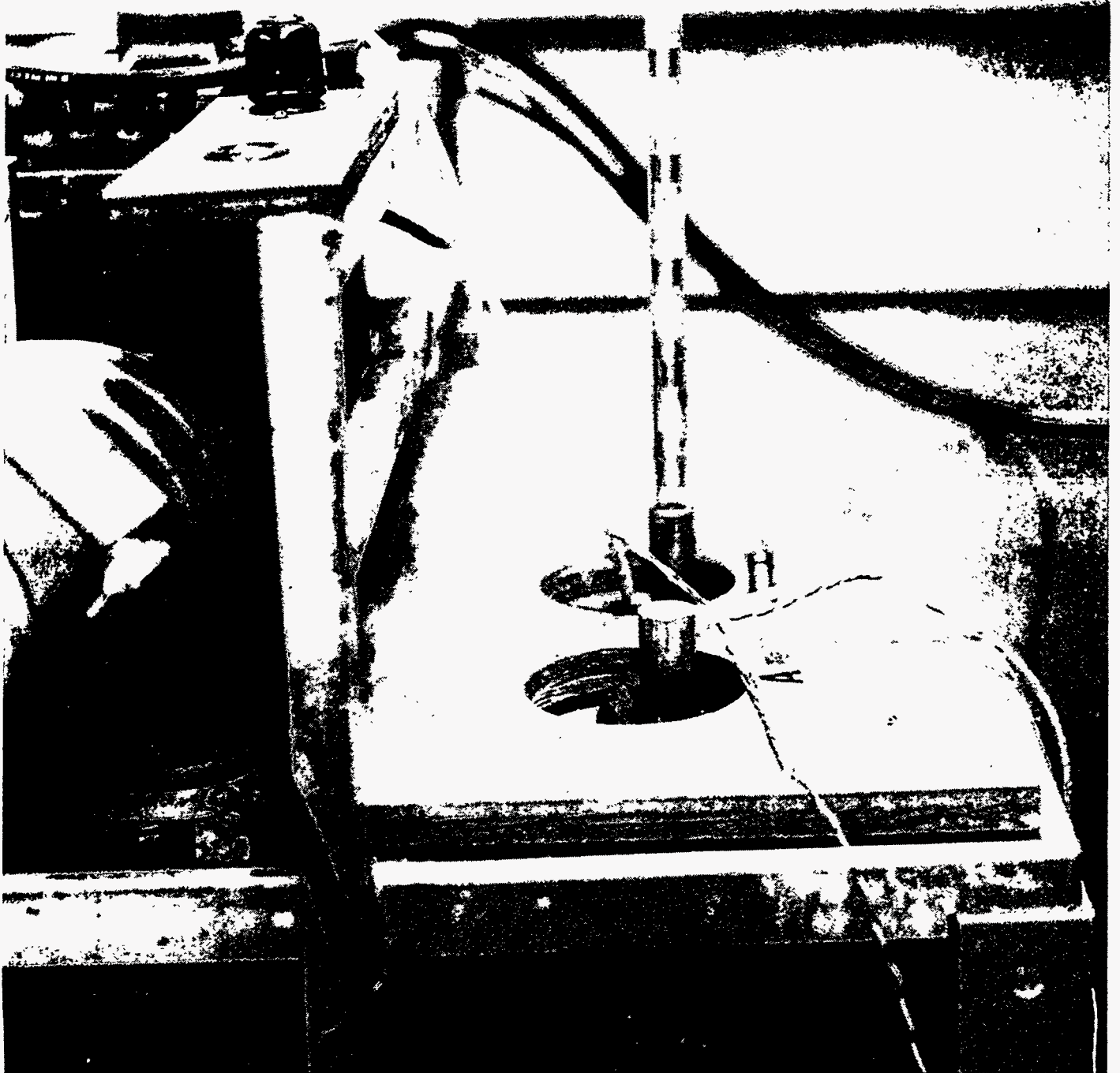


Figure 8: Automated Low Wattage Assay Calorimeter  
(ALWAC)

TABLE II

ANALYSIS OF A TYPICAL  $^{239}\text{PuO}_2$  SHIPMENT

<u>Isotope</u>	<u>Isotope Percent <math>R_i</math></u>	<u>Power Output (watts/gram) <math>F_i</math></u>	<u>Power/Isotope (watts/gram of metal) <math>R_i \times F_i</math></u>
$^{238}\text{Pu}$	0.236	0.5664	0.0013367
$^{239}\text{Pu}$	75.014	0.001924	0.0014433
$^{240}\text{Pu}$	18.424	0.00709	0.0013063
$^{241}\text{Pu}$	4.585	0.00450	0.0002063
$^{242}\text{Pu}$	1.108	0.00014	0.0000016
$^{241}\text{Am}$	<u>0.633</u>	0.1084	<u>0.0006866</u>
	100.000		0.0049808

Calorimetry value = 5.513 watts

1106.8 grams of Pu metal

830.3 grams of  $^{239}\text{Pu}$

TABLE III

**CALORIMETER PERFORMANCE  
CHARACTERISTICS<sup>a</sup>**

SAMPLE	AMOUNT OF <sup>239</sup> PuO <sub>2</sub> (Kg)	POWER OUTPUT (watts)	ACCURACY (0.95 confidence)
PuO <sub>2</sub> Feed Material	1.0	3.0	0.09
Mixed Oxides:			
2%	0.1	0.3	0.10
25%	1.0	3.0	0.09
Pu(NO <sub>3</sub> ) <sub>3</sub> Solutions <sup>b</sup>	0.4	1.2	0.09
Hard Scrap	0.5	1.5	0.09
Pellets	1.0	3.0	0.09

<sup>a</sup>Mound Calorimeter 104

<sup>b</sup>2 Liter Bottles (200 g/liter)

Thus combining mass spec data with calorimetry data, the absolute amount of Pu-239 can be determined to 0.3 to 0.5%. In addition, comparisons to 0.1% can be made at various stages in the fuel cycle.

In summary here are some of the advantages of calorimetry:

1. Calorimetry is nondestructive. It is not necessary to open the container the sample is in.
2. Calorimetry is simple. You don't need a Ph.D. or a computer to operate a calorimeter. A high school girl can start making measurements in a half an hour. Within two weeks, can perform with little or no supervision.
3. Calorimeters are rugged. We have calorimeters in use today that have been operated for 20 years. As a matter of fact, one check on a new calorimeter is to put the output on a recorder and once a straight line is established, rap it with a hammer. If it comes back to the same line, it is okay.
4. Calorimeters are accurate and precise. As a check, we have fabricated our own standard heat sources. As mentioned earlier, precisions of 3.5 ppm has been attained on these samples. In addition, internal agreement between various calorimeters at Mound is 20 ppm on our standards. On these same standards, our agreement with other AEC labs is 200 ppm. These standards are very useful for intersite comparisons.

## ACKNOWLEDGMENTS

I would like to thank the Office of Safeguards and Materials Management for their support in determining the feasibility of this approach for the assay of PuO<sub>2</sub> shipments. In addition, an in-plant test of this method will be conducted by the Vallecitos Plant of General Electric using Mound supplied instrumentation as a part of the Plant Instrumentation Program.

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