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Differential Thermal Analysis Apparatus
for Observation of
Refractory Plutonium Compounds

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UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG 36

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Printed in the United States of America. Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151

Price: Printed Copy \$3.00; Microfiche \$0.65

Written: January 20, 1969

Distributed: May 16, 1969

LA-4103
UC-37, INSTRUMENTS
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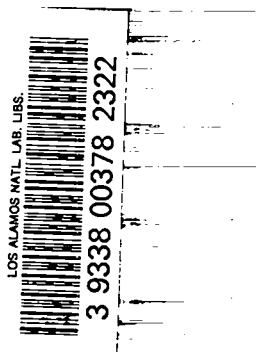
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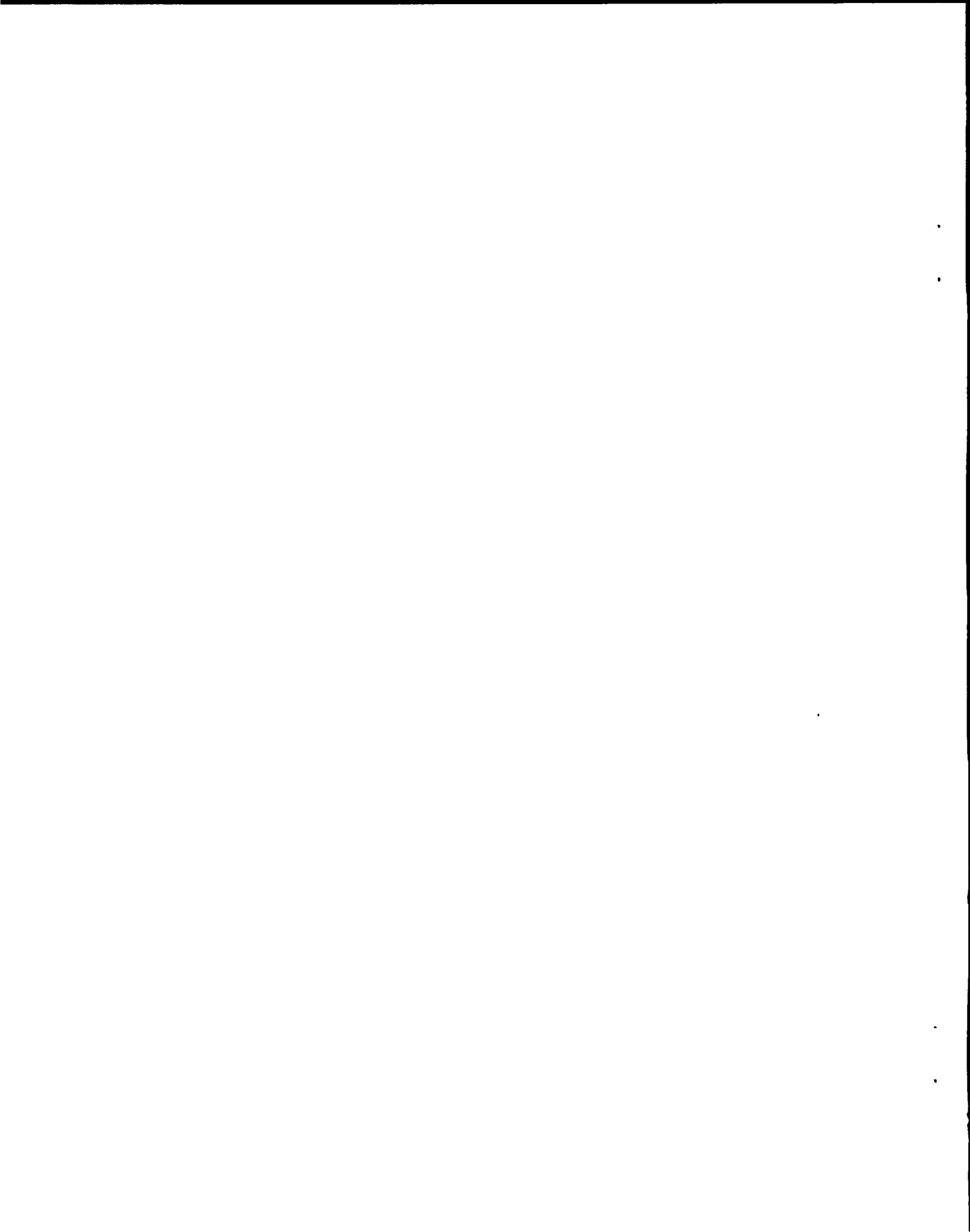
by

J. G. Reavis

J. F. Buchen

J. A. Leary





DIFFERENTIAL THERMAL ANALYSIS APPARATUS FOR
OBSERVATION OF REFRACTORY PLUTONIUM COMPOUNDS

by

J. G. Reavis, J. F. Buchen, and J. A. Leary

ABSTRACT

An apparatus has been constructed and used to measure melting points and temperatures of crystallographic transition of refractory compounds of Pu and other intense alpha emitters potentially useful as reactor fuels. The thermal analysis apparatus responds to light energy radiated by the sample and furnace, and temperatures are measured by optical pyrometry. The specialized nature of the equipment necessitated an intensive calibration study over the range 1000 to 2440°C.

INTRODUCTION

Measurement of the high temperature properties of refractory materials potentially useful as reactor fuels presents difficulties of containment so as to avoid unwanted chemical reactions at high temperatures. Observations of these materials are additionally complicated by the necessity of their near-absolute confinement in enclosures to protect laboratory personnel from the associated alpha activity. The differential thermal analysis apparatus described by Rupert¹ is excellent for observation of transition temperatures of refractory substances having little or no associated radioactivity, but extensive modification was necessary for use of the method for study of intense alpha-emitting refractories such as (U, Pu)C, (U, Pu)N, and UO₂-PuO₂. The major modification was enclosure of the furnace in an alpha-tight glove box. Other changes involved simplification of the optical system, improvement of the furnace to allow greater ease of assembly and reduction of thermal gradients, and addition of a motorized drive to the power control unit. A significant contribution to development of differential thermal analysis techniques applicable at high temperatures was

the selection and use of a series of reference materials for temperature calibration of the apparatus. This series was needed for periodic verification of accuracy of temperature measurements by optical pyrometry since a standard lamp could not be substituted for the furnace to measure absorption by the optical system.

APPARATUS

Figure 1 is a schematic view of the apparatus. Power to heat the furnace is supplied by a 25-kW, 0.45-MHz generator, the output of which is coupled to the furnace by an induction coil and current concentrator similar to that described by Rupert.² The generator output level is controlled by an electronic unit which can be adjusted manually or by a motorized drive. Controlled heating and cooling rates of 10 to 1000 deg/min can be attained; heating rates of greater than 2500 deg/min can be accomplished by manual power adjustment, but the furnace shown in Fig. 1 will not cool more rapidly than about 1000 deg/min.

The furnace assembly is enclosed by a stainless steel glove box which retains all radioactive particles. The furnace assembly consists of a Pyrex vacuum

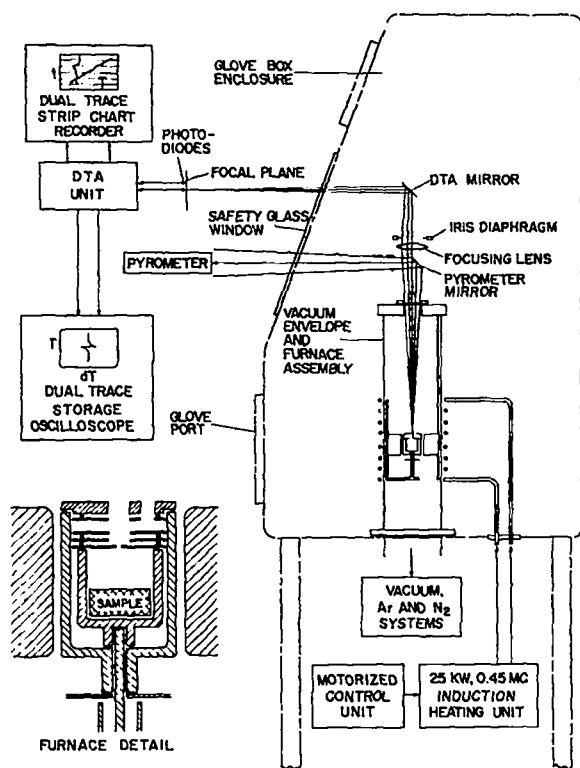


Fig. 1. Schematic drawing of the differential thermal analysis apparatus.

envelope (4 in. diam, 14 in. tall) which supports the water-cooled copper eddy-current concentrator which supports the furnace shown by the "furnace detail" inset of Fig. 1. The furnace consists of an outer susceptor (converter of electrical energy to heat) which has a lid penetrated by two 2-mm-diam holes, an inner crucible which has a lid penetrated by a 1-mm-diam hole, and several radiation reflectors. The reflectors and inner crucible reduce the magnitude of the thermal gradients that may occur in the susceptor. The furnace susceptor is 25-mm high and 19-mm diam. The construction materials are usually Ta, W, or graphite, chosen to minimize reaction with the sample to be heated. For observations of melting of noble metals, ThO_2 crucibles with ThO_2 lids are used as liners for Ta inner crucibles. Thin flakes of ThO_2 are placed on top of the highly reflecting metal samples to prevent direct reflection of the sight hole in the field viewed by the optical pyrometer.

The optical system which transmits radiant energy from the furnace to the optical pyrometer* is simple.

* Micro Optical Pyrometer, The Pyrometer Instrument Co., Inc., Bergenfield, N. J.

Approximately one-third of the diverging beam emerging through the window in the top of the current concentrator is intercepted by a mirror and reflected to the pyrometer for actual temperature measurement. The remaining two-thirds of the beam passes through a convex lens and an iris diaphragm and is reflected by a mirror to produce a magnified image of the top of the furnace in a vertical plane outside the glove box. One photoconducting diode* is positioned in this plane so that its active area is covered by the image of the hole in the crucible lid. A second diode is covered by the image of a small area of a radiation shield surface as seen through the second hole in the susceptor lid.

Signals from the diodes are amplified by a system very similar to that previously described.¹ Electrical outputs proportional to (1) the temperature, T , of the sample; (2) the difference between sample and radiation shield temperatures, ΔT ; and (3) the derivative of sample temperature with respect to time, dT/dt , are produced. T and ΔT signals are recorded simultaneously by a two-pen, strip-chart recorder, while a storage oscilloscope is used to record T as a function of dT/dt . For very fast thermal cycles, the oscilloscope is more useful in recording T and ΔT as a function of time. The recorder trace indicating temperature is calibrated by observing temperatures with the pyrometer during actual thermal cycling of samples.

CALIBRATION

Whenever an absorbing glass is placed between an optical pyrometer (disappearing filament type) and an incandescent object, the relationship between the true and observed temperatures (expressed in degrees Kelvin) is closely approximated by

$$\frac{1}{T_0} = \frac{1}{T} + A, \quad (1)$$

where T_0 is the observed temperature, T is the true temperature, and A is a constant for a given absorber.³ By use of a calibrated optical pyrometer and a tungsten strip lamp over the range 1000 to 1800°C, the value of

* Diode IN-2175, Texas Instruments, Inc., Dallas, Tex.

A was found to be $19 \times 10^{-6} \text{ deg}^{-1}$ for a mockup of windows and a mirror to be used in the assembled apparatus. The precision of the measurements used to calculate the value of A in Eq. (1) indicated uncertainties of $\pm 2^\circ$ at 1000° , increasing to $\pm 9^\circ$ at 3000°C , in the temperature correction for absorbance by the optical system.

Additional uncertainties in the value of A could arise from using a slightly different optical system geometry or from changes in the component absorbance (including the glove box window) with time. These considerations made it necessary to check the temperature measurement accuracy in the assembled apparatus periodically. Since a calibrated tungsten strip lamp could not be placed in the furnace position, the alternative, observing reference material transitions, was adopted for final apparatus calibration. This method produces a correction curve that accounts for optical absorption, pyrometer scale errors, and systematic errors in recording and interpreting differential thermal analysis curves. The materials chosen for reference are listed in Table I.

PERFORMANCE

The apparatus has operated satisfactorily during more than 2 years of observation of thermal effects in carbides, nitrides, and oxides of uranium and plutonium. Repeated observations of duplicate samples have shown that a single transition temperature measurement has an uncertainty limit of about $\pm 10^\circ$ if proper care is taken to exclude systematic errors such as those arising from reaction between sample and container, sample decomposition, or fogging of the current concentrator window by vaporization of the sample or furnace parts.

Table I. Reference Materials Used in Calibration of the DTA Apparatus

Material	Container	Transition	Transition Temp., $^\circ\text{C}$	
			Lit. (a)	Observed (b)
Cu	C	melting	1083	1081
Pt-C	C	eutectic	1734	1735
Pt	ThO ₂	melting	1770	1770
Rh	ThO ₂	melting	1960	1960
Al ₂ O ₃	W	melting	2050	2047
MoC _{0.2}	C	eutectic	2205	2205
Ir	ThO ₂	melting	2440	2440

(a) Literature values selected after study of References 4-9.
 (b) See text for discussion of accuracy.

Window fogging, which can be a serious problem during measurements in vacuo, was almost eliminated by filling the apparatus with an inert gas.

The reference materials listed in Table I were observed under Ar. Two or more samples of each reference material were observed. Transition temperatures observed during heating (melting) were more easily reproducible than those observed during cooling because of severe undercooling shown by almost all samples. Reversibility of the transition was shown in each case by slight reduction of furnace power to produce freezing before melting was completed.

Observed and literature⁴⁻⁹ values of transition temperatures of reference materials were used to calculate a value of A (Eq. 1) for each observation. These values were averaged to produce a new value of $20.5 \times 10^{-6} \text{ deg}^{-1}$ to replace the $19 \times 10^{-6} \text{ deg}^{-1}$ derived by use of the mockup and the W strip lamp. The new A-value was used to generate a smoothed correction curve for the range 1000 to 3000°C . Absorbance corrections from this smoothed curve were added to the uncorrected transition temperatures determined for the reference materials. These corrected values are listed as "Observed" transition temperatures in Table I. There were not enough transition temperature determinations for any given reference material to allow meaningful determination of standard deviations at each temperature. The standard deviation of individual observed transition temperatures from their respective literature values over all the series was $\pm 6^\circ$ after application of the smoothed correction curve. The averaged values of the transition temperatures listed in Table I show a standard deviation of $\pm 1.5^\circ$ from their respective literature values.

It appears that reference materials are necessary for highly accurate transition temperature measurements. The values listed in Table I are about 12° higher at 2440° and 3° higher at 1080° than those based on the A-value determined by use of the window mockup and the W strip lamp. Although this difference is about the same as the uncertainty of a single determination, the new correction curve significantly improves

the accuracy of transition temperatures based on multiple observations.

The validity of the correction curve has been rechecked periodically during several months of use by observation of reference materials selected from those listed in Table I. No significant change has been detected although many macro samples of intense alpha emitters have been observed. Greater changes may be expected, however, in systems in which windows are subjected to high levels of more penetrating radiations or to extremes of temperature.

ACKNOWLEDGMENTS

The authors are indebted to G. N. Rupert for helpful advice and to R. G. Sturgess for modification and construction of the amplifier system.

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