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A THERMOGRAVIMETRIC BALANCE FOR RADIOACTIVE SAMPLES
IN A HYDROGEN FLUORIDE ATMOSPHERE

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ABSTRACT

Requirements for and schematic of a custom built thermogravimetric balance are given. The equipment and innovations necessary to produce thermograms from reaction of radioactive samples with a hydrogen fluoride atmosphere are described. The method used for alignment of the balance sample pan with the reactor is outlined. Details are given concerning maintaining inert purge gas in the balance bell jar while hydrogen fluoride is passed through the reactor. The safety shut-down system is detailed. Typical performance curves are included.

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INTRODUCTION

In recent years, the development of automatic weighing and rapid continuous weight recording systems for analytical balances has given impetus to thermogravimetric analysis. In the Fall of 1962, the Rocky Flats Division of The Dow Chemical Company, a prime contractor of the U. S. Atomic Energy Commission¹, sought purchase of a thermogravimetric balance. Our purpose was to initiate thermogravimetric studies on the calcination and hydrofluorination of plutonium peroxide.

However, commercial equipment available at the time did not meet our needs. Thermogravimetric equipment with a reactor, which could handle a dynamic hydrogen fluoride atmosphere, was not on the market. The purpose of this paper is to describe the important features of a custom thermogravimetric balance designed to meet our needs.

REQUIREMENTS

Requirements are shown in Slide 1. A commercially available Ainsworth Type RVA -AU-2 Dual Sensitivity Automatic Recording Vacuum Balance more than met our weighing needs.

Reactor needs were satisfied by providing a short section of electrically heated 3" schedule 40 Inconel[®] pipe with flanged closure at each end.

The description which follows tells how we designed to meet the special requirements shown at the bottom of Slide 1.

¹U. S. Atomic Energy Commission Contract AT(29-1)-1106.

[®] A trademark of The International Nickel Co., Inc.

REQUIREMENTS FOR THE THERMOGRAVIMETRIC BALANCE PROJECT

Balance

Action	Automatic Recording
Max. Sample Weight	5 grams
Min. Sample Weight Change	1 %

Reactor

Gas Flow	Moist Hydrogen Fluoride
Max. Pressure	Atmospheric
Max. Vacuum	10 to 100 microns
Max. Temperature	800°C
Max. Rate of Temp. Rise	5°C per minute

Special

Locate reaction chamber in a glovebox designed for work with plutonium.

Provide a purge system to protect against moist HF.

Provide for automatic fail-safe action in case of power failure.

DESCRIPTION

Slide 2 is a general schematic showing how the reactor was installed in a suitable glovebox. Hydrogen fluoride gas enters at the back of the reactor and may leave at the front or the top depending on experiment requirements. The balance assembly was placed inside a stainless steel hood. The hood is equipped with a Plexiglas ^(R) front which moves vertically to permit access to the balance. The purpose of the hood is to prevent the spread of radioactive contamination in case an unexpected reaction would pressurize the system and lift the balance bell jar. However, it has also served to prevent contamination from external sources, and to protect the balance against accidental mechanical damage.

Also, note the following:

- a - Location of the adjustment plate assembly, and
- b - the sample pan suspension system with primary and secondary purge gas inlets.

A picture of the adjustment plate assembly is shown in Slide 3. It is a sandwich of two steel plates. The bottom plate is pinned to the bottom of the stainless steel hood. The top plate accepts the complete balance assembly. Via screw-stop adjustments, the top plate can be moved in any horizontal direction relative to the pinned bottom plate. This permits accurate positioning of the sample pan suspension chain in the suspension tube. The importance of this feature to the satisfactory function of the secondary purge system will be mentioned in a moment.

Since our design places the balance above the reactor, helium is used as purge gas because it is lighter than hydrogen fluoride

^(R) A trademark of Rohm and Hass Co.

Slide 2

Schematic of Thermogravimetric Balance

Slide 3

Suspension
Tube

Balance
Assembly

Top Base Plate

Stop

Bottom
Base Plate

Screw Adjustment

Screw
Adjustment

Stop

Stop

Bottom of Stainless
Steel Hood

555 146

and is inert. Referring to note "b" above concerning location of primary and secondary purge gas inlets, primary purge gas, which enters near the top of the suspension tube, supplies the balance chamber directly. Secondary purge gas, which enters just above the reactor, seldom permits reactor contents to escape via the upper portion of the suspension tube. Slide 4 shows why. The downflowing primary purge gas meets the secondary purge gas in the upper suspension tube chamber. The primary purge gas enters through the upper sample pan chain hole. The secondary purge gas meets it at right angles via the upper broached slot. All purge gas then enters the lower suspension tube chamber via the middle sample pan chain hole and the upper portion of the lower broached slot.

If a complete hydrogen fluoride atmosphere is required in the reactor, reactant gas is allowed to enter the lower suspension tube chamber via the lower sample pan chain hole and the lower portion of the lower broached slot. Then, all gases are withdrawn from the lower suspension tube chamber.

If experimental work permits dilution of hydrogen fluoride with purge gas, all gases are removed via the front of the reactor.

There have been no difficulties with excessive drag or noise on the sample pan chain or on the sample pan itself. Reasonable explanations for this are the short length of the three sample pan chain holes, and the lower of these holes being some distance above the balance pan.

Reaction chamber design is conventional. Note however, that a horizontal arrangement was selected. It was felt that this plan would create less draft problems and less noise. Experimental work to date seems to confirm this.

● PRIMARY PURGE GAS

Also, the high vacuum facility and off-gas systems are conventional design. The off-gas is fed to a common vacuum system via a manual control valve followed by a conventional pneumatic pressure control system.

Precautions were taken to avoid any low spots in the hydrogen fluoride feed system.

Reasonably good constant rate of temperature rise in the reaction chamber is obtained using manual heat control. At 5°C per minute rate of temperature rise precision is plus or minus 2°C.

The safety shut-down system permits operating personnel to evacuate the area without delay when a power failure occurs. Also, the system allows reentry to the area by anyone at any time, without the danger of an unanticipated release of radioactive sample.

Two pneumatic valves with on-off action are located as shown in Slide 5. The valve in the hydrogen fluoride line requires instrument air to open. The valve which is connected to the lower suspension tube chamber, requires instrument air to close; and it vents to the glovebox. Under normal conditions, full instrument air to these valve diaphragms keeps the hydrogen fluoride line open and emergency vent to the glovebox closed.

Upon power failure, the three-way solenoid valve in the instrument air line deactivates. This releases the air from the diaphragms on the pneumatic valves. Hydrogen fluoride feed is interrupted and the system vents to the glovebox, while purge gas continues uninterrupted. Thus, there is no gradual

Slide 5

Schematic of Safety Shut-down System

THERMOGRAVIMETRIC PLOT SHOWING DECOMPOSITION OF CALCIUM OXALATE MONOHYDRATE

THERMOGRAVIMETRIC PLOT SHOWING HYDROFLUORINATION OF PLUTONIUM PEROXIDE TO PLUTONIUM TETRAFLUORIDE

SAMPLE : 231 MILLIGRAMS OF PLUTONIUM PEROXIDE FROM ROCKY FLATS' PROCESS STREAM

ATMOSPHERES : DRY HELIUM FOR FIRST 102 MINUTES AT 176 STD. CC/MIN. THEN DRY HYDROGEN FLUORIDE SUPERIMPOSED AT 186 STD. CC/MIN.

SAMPLE PAN : DISHED PLATINUM, 3/4" DIAM., 1/16" DEEP

THERMOCOUPLE: LOCATED 1" HORIZONTALLY FROM CENTER OF SAMPLE PAN (HORIZONTAL FURNACE), AND SHEATHED IN INCONEL

PRODUCT : IDENTIFIED VIA X-RAY DIFFRACTION AND NEUTRON COUNT, SHOWING 22.2 W% F (24.0 W% F THEORETICAL).