After 5 minutes measure the absorption of this solution at 5150 A. against a reagent blank. Calculate the iron content from a standard calibration curve.

Uranium Recovery by Proposed Analytical Procedure. The recovery of uranium was tested by determining uranium in all solutions discarded in the recommended procedure.

Uranium loss due to incomplete extraction was determined by repeating the extraction of uranium from solution 1 and found to be less than 1%. Uranium loss due to washing of the organic extract was determined by re-extracting uranium from solution 2. Uranium remaining in the organic extract after sodium carbonate stripping (solution 4) was determined by repeating the alkaline washing. Uranium was finally determined polarographically. The amount of uranium found in solutions 2 and 4 was below 0.1%.

Table V. Reproducibility of Duplicate Determinations of U_3O_8 in Caldasite

(Over-all recovery of uranium. 5.086 mg. of U_3O_8 added)

Sample	U_3O_8 %[a]	U_3O_8 Found, Mg.[a]	% Recovery
1	0.336	5.12	100.7
	0.339		
2	0.317	5.11	100.5
	0.314	5.08	99.9
3	0.307	5.10	100.3
	0.304		
4	0.307	5.12	100.7
	0.306		
5	0.045	5.06	99.5
	0.046		
10	0.248	5.16	101.5
	0.246		
25–36	0.369	5.13	100.9
	0.370		

[a] Reagent blank and iron correction both taken into account.

An important loss of uranium would result on omitting the fluorization step. A significant adsorption of uranium on silica was found. Thus analyzing a sample of caldasite containing 0.35% of U_3O_8 we found that 0.11 mg. of U_3O_8 was adsorbed on silica, which corresponds to 1.5% of the uranium content.

In Table V the reproducibility of the proposed method for uranium determination is illustrated by typical results of duplicate analysis (column 2) of some caldasite samples.

The aqueous phase (solution 1) after the TBP extraction contains most of the original constituents of the analyzed ore. A known amount of uranium was added to this solution (see Table V) and thereafter determined according to the outlined procedure. Table V shows the over-all recovery of the added uranium (column 4), which constitutes a good measure of the accuracy attainable by the analytical process under discussion.

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Differential Thermal Analysis and Thermogravimetric Analysis of Fission Product Oxides and Nitrates to 1500° C.

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▶ Apparatus is described for differential thermal analysis (DTA) and thermogravimetric analysis (TGA) in air to 1500° C. This equipment was used to study the thermal stability of strontium oxide, strontium nitrate, cesium nitrate, zirconyl nitrate dihydrate, cerous nitrate hexahydrate, ruthenium dioxide, and mixtures of these materials with alumina. Evidence is presented for the formation of $CsAlO_2$ in the temperature range 940° to 1100° C., and the course of the thermal decomposition of RuO_2 is described.

THE CONVERSION of radioactive liquid wastes, resulting from the reprocessing of spent fuel elements, into a granular solid by a fluidized bed calcination process is under investigation by the Atomic Energy Commission (*7*). The product of this operation is a solid mixture of aluminum oxide and small amounts of radioactive fission product oxides and nitrates. The calcined material is then stored in underground, air-cooled vessels. Of concern in this processing scheme is the possibility of failure of the cooling system, resulting in a subsequent temperature rise to 1500° to 2000° C. Under these conditions the radioactive solids, which are normally stable at lower temperatures, might decompose or volatilize and escape to the surrounding area by rupturing the storage vessel.

This work was undertaken to investigate the seriousness of the problem by determining the thermal stability of selected fission product oxides and nitrates at temperatures to 1500° C. by DTA and TGA. Although there is considerable information in the literature on the design of DTA and TGA equipment for use up to 1200° C. (*6, 12*), only a few papers are available on the application of these techniques at higher temperatures (*9, 11*).

EXPERIMENTAL

Materials. Alcoa type A-2 alumina (low iron, −325 mesh, >99% Al_2O_3),

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C.P. silver sulfate (Fisher Scientific Co.), C.P. calcium oxalate (Matheson Coleman & Bell Div. of The Matheson Co., Inc.), C.P. zirconyl nitrate (Amend Drug and Chemical Co.), and C.P. cesium nitrate, cerous nitrate (A. D. Mackay Co.) were used without further purification.

Ruthenium dioxide, purchased from A. D. Mackay Co., was further purified by fusion in a KOH–KNO_3 mix to form the soluble ruthenate and perruthenate salts. The melt was dissolved in water and filtered, and acetone was added to the clear filtrate to reduce the ruthenates to the insoluble hydrated oxide. The hydrated oxide was then slurried with paper pulp, the slurry filtered, and the cake ignited in air to form the anhydrous oxide. The product analyzed 99.8% RuO_2 by hydrogen reduction. Prior to thermal analysis, the samples were pulverized, if necessary, to −100 mesh using a mortar and pestle. Approximately 0.5-gram samples were used for DTA and 0.2- to 0.3-gram samples for TGA.

DTA Apparatus. The DTA furnace was heated by eight Globar rods spaced around a 5-inch diameter circle, which were supported by Johns-Manville-3000 firebrick. The sample holder, contained within a Mullite tube, 3 inches in outer diameter × $2^3/_4$ inches in inner diameter was cast from Alundum 33 HD cement. The sample holder was $2^1/_2$ inches in diameter by $1^1/_{16}$ inches thick, and contained four symmetrically positioned cavities, $^1/_2$ inch in diameter by $^9/_{16}$ inch deep, in which were placed the alumina crucibles containing the samples and reference material. Differential temperatures and furnace temperatures were measured with Pt-Pt (13% Rh) thermocouples. The power input to the furnace was regulated by an 8-kw. powerstat, the heating rate was controlled by a Wheelco program controller, and furnace temperatures were indicated on a Brown recorder. Heating rates of 6.3° and 10° C. per minute were used in all runs. A Kintel Model 111-BF direct current amplifier was used to amplify the low level output of the differential thermocouple, and the output of the amplifier was traced on a modified Brown recorder.

At temperatures above 1200° C., stray currents from the heaters and electrical leakage resulting from the greatly increased conductivity of the refractories can cause fluctuations in the low level differential thermocouple circuit and lead to errors in the thermogram. The following precautions were taken to avoid this difficulty:

The thermocouple lead wire, recorder, and direct current amplifier were grounded to a common point; thus eliminating ground loops.

A Sola transformer was used to supply constant voltage to the direct current amplifier.

Thermocouples were shielded with grounded platinum foil.

A 15-mil thick platinum liner was used on the inside of the furnace. The liner and the control equipment were grounded to a common point. The platinum liner, also served to improve the heat distribution in the furnace and thus smoothed out the heating rate in the lower temperature range.

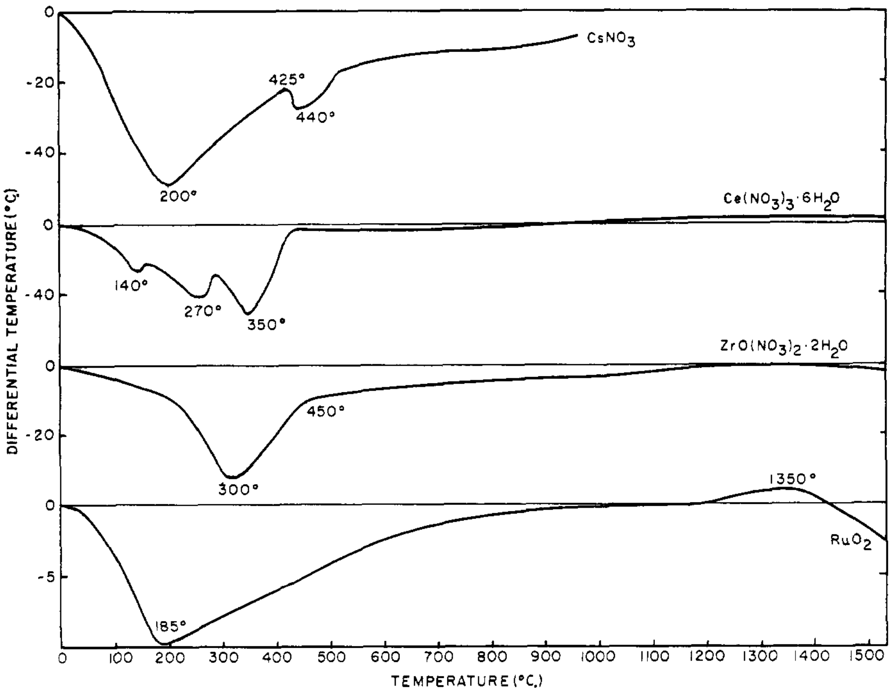

Figure 1. Thermograms of fission product oxides and nitrates

To check the accuracy of the DTA apparatus, thermograms were obtained on materials with known transition temperatures such as silver sulfate. The results obtained reproduced very well the transition and decomposition temperatures reported by Barshad (*1*).

TGA Apparatus. The apparatus used in the present study was adapted from those described by Campbell and Gordon (*3*) and Groot and Troutner (*8*). A conventional analytical balance was modified by the addition of an Atcotran Model 6208M linear variable differential transformer to one of the arms and a yoke, from which a refractory rod carrying a platinum crucible extended upwards through the balance case into a furnace, to the other arm. A differential transformer contains a movable magnetic armature which is centered within a transformer core. Motion of the armature (attached to the balance beam) is converted to an alternating current signal which is tapped off the secondary of the transformer, demodulated, and fed to a recorder. The measurable weight range is determined by the diameter of a nonmagnetic metal rod suspended beneath the armature, which dips into a liquid of known density. Under these conditions the weight range, W, is given by

$$W = \pi r^2 dh$$

where

r = radius of rod
d = density of liquid
h = vertical deflection of rod.

The maximum vertical deflection of the rod is fixed by the linear range of the transformer which, for the Model 6208M is ±0.5 cm. from the null position. In this study mineral oil was used as an immersion fluid (d = 0.85 gram per ml.) and the rod diameter was 1.27 cm., thereby providing a measurable range of ±0.538 gram. The sensitivity of the system was maximized by varying the input voltage to the transformer so as to obtain full scale deflection of a Brown recorder for a ±0.5-cm. motion of the armature. The weighing error, determined by the minimum detectable deflection of the recorder, was about 0.5% of the sample weight.

After calibration of the apparatus, preliminary runs were made with zinc sulfate and calcium oxalate. The results obtained were in agreement with published data (*4*), and work was, therefore, begun on the oxide and nitrate samples.

RESULTS AND DISCUSSIONS

Cesium Nitrate. The differential thermal analysis of cesium nitrate to 900° C. has been discussed by Campbell and Gordon (*2*) who report an endotherm at 145° to 164° C. due to a hexagonal to cubic crystalline transition, another at 404° to 415° C. due to fusion, and visually observed bubbling and thermal decomposition from 531° to 900° C., the highest temperature reached in their experiment.

Our results, shown in Figure 1, are in general agreement with those of Campbell and Gordon. Endotherms for the crystalline transition and fusion were observed in the range 150° to 200° C., and 425° to 440° C., respectively. The temperature for the onset of thermal decomposition is indicated in the TGA curve of Figure 2. The 0.3008-gram sample began to decompose with the evolution of brown fumes at 710° C., and the decomposition continued to 970° C., at which temperature the sample was completely volatilized.

The effect of alumina on the thermal stability of $CsNO_3$ is shown in the TGA curve of Figure 2. In this experiment a mixture of 0.1914 gram of $CsNO_3$ and 0 0957 gram of Al_2O_3 was heated at a constant rate of 6.9° C. per minute. As in the previous run with $CsNO_3$ alone, decomposition began at about 700° C. and continued to 940° C., at which temperature some 50% of the sample had volatilized. From 940° to 1100° C., however, a plateau in the weight loss curve was observed, indicating formation of a stable compound which then decomposed slowly from 1100° to 1525° C., the highest temperature reached in the experiment.

An attempt was made to identify the compound formed in the 940° to 1100° C. region by air quenching a 2:1 by weight mixture of $CsNO_3$ and Al_2O_3 from 1025° C. and analyzing the water-soluble residue. Some of the aluminum was solubilized and the molar ratio of soluble cesium to aluminum was 1:1.1, thus indicating the formation of $CsAlO_2$. X-ray diffraction analysis of an air-quenched sample of the powder, however, failed to confirm the presence of $CsAlO_2$. Some unidentified lines were found as well as lines due to alumina and platinum metal arising from attack on the crucible. Further work is required to identify the high temperature species.

Strontium Nitrate. The DTA of strontium nitrate has been reported by Campbell and Gordon who observed fusion at 618° C., evolution of nitrous fumes from 635° to 715° C. and vigorous bubbling commencing at 672° C. (*2*). Our DTA results are in close agreement and are not reproduced here.

The results of TGA of a 0.3687-gram sample of strontium nitrate are shown in Figure 2. The 50-mg. weight loss between 355° and 555° C. is ascribed to residual water of hydration. The actual thermal decomposition accompanied by evolution of nitrogen fumes began at 600° C. and was complete at 745° C. The observed weight loss of 0.1865 gram is 101.0% of theoretical for the decomposition of strontium nitrate to strontium oxide.

Cerous Nitrate Hexahydrate. DTA and TGA curves for cerous nitrate hexahydrate are shown in Figures 1 and 2. The DTA curve shows a series of endotherms at 140°, 270°, and 350° C., and no other thermal effects up to 1500° C. These endotherms are due to the stepwise dehydration and thermal decomposition of the compound. Evolution of nitrous fumes was observed to begin at approximately 200° C. The TGA curve of Figure 2 indicates a continuous weight loss of the 0.3732-gram sample up to 400° C., and no further changes to 1500° C. The observed weight loss of 0.2134 gram is 94.7% of theory for the reaction

$$Ce(NO_3)_3.6H_2O \rightarrow CeO_2 + 6H_2O + \text{nitrogen oxides}$$

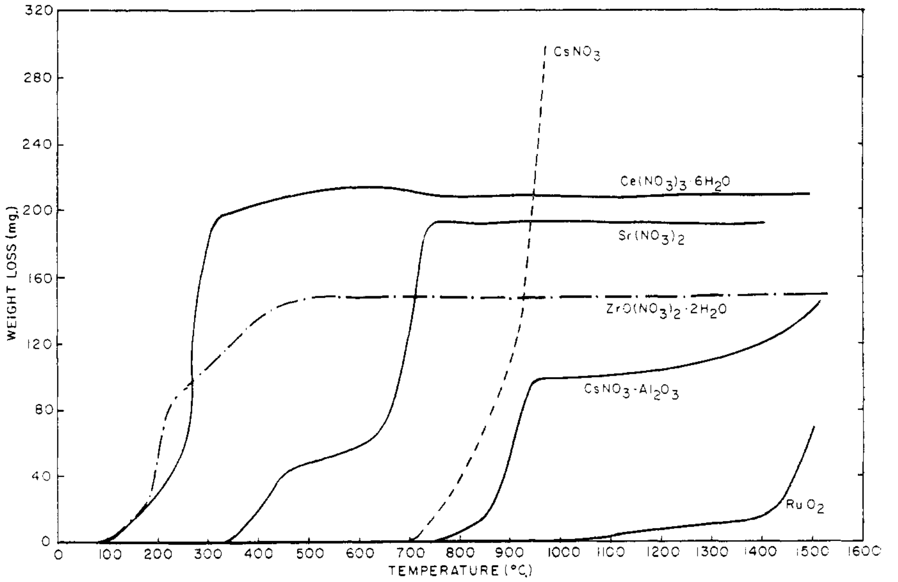

Figure 2. TGA of fission product oxides and nitrates

Zirconyl Nitrate Dihydrate. The results of TGA and DTA of zirconyl nitrate dihydrate are shown in Figures 1 and 2. The thermogram indicates a broad endotherm in the 60° to 450° C. temperature range with a minimum at 300° C. This endotherm is due to the dehydration and decomposition of the compound to ZrO_2. In TGA, a continuous weight loss was observed over the same temperature region, and no further changes were observed to 1500° C. The loss of 0.1489 gram from the 0.2726-gram sample was 101% of theoretical, assuming the over-all reaction to be

$$ZrO(NO_3)_2.2H_2O \rightarrow ZrO_2 + 2H_2O + \text{nitrogen oxides}$$

Ruthenium Dioxide. The thermogram of Figure 1 shows an endotherm at 185° C., an exotherm at 1350° C., and the beginning of a second endotherm at about 1450° C. The TGA curve of the 0.2122-gram sample indicates no weight loss up to 1025° C., a slow weight loss from 1025° to 1400° C., and a more rapid loss from 1400° to 1515° C., the highest temperature reached in the experiment.

We have no explanation for the low temperature endotherm since no weight loss occurs at this temperature and no crystalline transitions or phase transitions occur below 1000° C. (*10*). Based upon the thermodynamic data of Glassner (*5*), several reactions are possible at temperatures above 600° C. These are:

$$RuO_{2(s)} \xrightarrow{> 600° \text{ C.}} Ru_{(s,\ \alpha)} + O_{2(g)} \quad (1)$$

$$Ru_{(s,\ \alpha)} \xrightarrow{1035\ °\text{C.}} Ru_{(s,\ \beta)} \xrightarrow{1200° \text{ C.}} Ru_{(s,\ \gamma)} \xrightarrow{1500° \text{ C.}} Ru_{(s,\ \delta)} \quad (2)$$

$$RuO_{2(s)} + O_{2(g)} \xrightarrow{25° - 1500° \text{ C.}} RuO_{4(g)} \quad (3)$$

$$RuO_{4(g)} \xrightarrow{> 1425° \text{ C.}} Ru_{(s,\ \gamma,\ \delta)} + 2O_{2(g)} \quad (4)$$

Reaction 1 is spontaneous at temperatures above 600° C., and is probably responsible for the slow weight loss between 1025° and 1400° C. The theoretical weight loss for Reaction 1, however, is 0.051 gram as compared to the 0.070-gram weight loss observed. Oxidation of RuO_2 to RuO_4 vapor (Reaction 3) must, therefore, occur at a rapid rate at 1400° to 1500° C., accompanied by the gas phase decomposition of RuO_4 (Reaction 4) at temperatures above 1425° C. The mechanism proposed is supported by the x-ray diffraction analysis of samples which were rapidly quenched in air from 1400° C. An unidentified phase was found, together with a large amount of elemental ruthenium. When the samples were cooled slowly at the natural cooling rate of the furnace, ruthenium dioxide was recovered as well as the unidentified phase and a much smaller amount of ruthenium metal.

Finally, the endotherm which begins in the 1450° to 1500° C. region is ascribed to the γ to δ transition of ruthenium metal. The heat of transition for this reaction is reported to be 0.23 kcal. per gram atom (*5*).

ACKNOWLEDGMENT

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Automatic Direct-Reading X-Ray Spectrometry

Application to Determinations of Silver

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► **Commercially available preset counting and timing circuits have been added to a manual x-ray spectrometer to provide digital recording of direct analytical results over the linear calibration range. Semiautomatic correction for background is provided. Automatic sample-advancing equipment was built for use with samples in the form of thin sheets or films. Applications of the equipment to the determination of silver in photographic films are described, including the selection of optimum operating conditions.**

IN APPLICATIONS of x-ray spectrometry involving large numbers of similar samples, as in the routine determination of silver in photographic materials, automation of sample handling and the use of a direct-reading print-out device can save time and reduce calculation and transcription errors to a minimum. Although digital recording on punched cards or printed tape may be obtained with commercially available counters, and printed results are available from the Norelco Autrometer (*5*), from a special-purpose instrument made by Norelco for the Eastman Kodak Co., and from x-ray spectrometers made by other manufacturers, many instruments in the field do not have this feature. The print-out system described may be added to existing manual spectrometers. Through the use of commercially available circuits, it provides, at moderate cost, semiautomatic compensation for background and, over the range of linear calibration, printed analytical results in direct weight units of the element being determined. Automatic sample handling is provided by mechanical changes in the sample compartment.

APPARATUS

X-Ray Spectrometer. A Norelco x-ray spectrometer, Type 52157A, was used. The Phillips FA-60 x-ray tube was operated at 55 kv. with stabilized currents up to 40 ma. A 0.005-inch collimator, a lithium fluoride analyzing crystal, and a scintillation counter were also used. Originally, the Norelco pulse amplification system was used, but recently this has been replaced with feedback-stabilized pulse amplifiers, a pulse-height analyzer, and a 1-μsecond decade scaler supplied by Hamner Electronics Co., Inc., as Type N302S, plus a modified preamplifier. The output of this scaler drives the usual Norelco binary scale of 256.

Digital Print-Out Attachments. For reasons noted later, the "fixed-time" mode of operation was of greater interest than the more common "fixed-count" method, but the apparatus was designed to make either possible. Output pulses are taken from the Norelco scaler at the "scale-factor" switch and fed to a cathode follower rather than to the usual count register. Up to this point, the detecting and scaling circuits operate continuously. Beyond the cathode follower, the pulses are fed to gating circuits and then to a combination counter-timer which accumulates counts received in a specified time. At the end of each measurement, the number of counts is printed out automatically on adding-machine tape and the counter-timer is reset to its initial condition. A simplified functional block diagram is shown in Figure 1.

Because x-ray intensity measurements must be expressed in terms of a net counting rate above a background, it is desirable to subtract the background automatically from each measurement of gross counts. This is done by providing a selector switch on each decade counter, so that any given digit can be preset into that stage before the count begins. With a 5-decade counter, which can accumulate 99,999 counts before repeating, a background of N counts is thus set into the instrument as the complementary figure $(100{,}000 - N)$; the counter starts the count from this value and, after N counts have been received, the register indicates zero so that, at the end of the cycle, the read-out device prints the quantity (gross counts $-N$) directly. For ease in setting, the selector-switch dials are engraved in reverse sequence, so that when the index is at n, the complement $9 - n$ appears in the preset counter.

The timer used is also a 5-decade counter driven by the signal from a 1000-c.p.s. tuning fork. Presetting is provided in the same manner as for the pulse counter, so that time intervals may be selected in steps of 0.001 to 99.999 seconds. The electronic gates actuated by the timer pulses start and stop the counting without the delays inherent in mechanical clocks or relays. Since one bank of counters operates the start-stop gating, while the other accumulates counts which are printed out, it is possible to switch from fixed-time