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TABLE OF CONTENTS

INTRODUCTION	1
I. RADIOCHEMISTRY AND GAMMA RAY SPECTROSCOPY	2
1. Experimentally Determined n, γ Cross Section for ^{54}Mn in a Reactor Spectrum	2
2. Evaluation of Copper as a Dual Dosimeter	9
3. Development of Long-Term Thermal Neutron Flux Monitor	14
4. Peach Bottom End-of-Life Fuel Element Gamma Scan Data Reduction	16
5. Equipment Improvements in the Sigma II Computer - Analyzer Laboratory	19
II. X-RAY DIFFRACTION	20
1. Quantitative Analysis by X-Ray Diffraction	20
III. HTGR FUEL REPROCESSING SUPPORT	29
1. Determination of Thorium in Solvent Extraction Organic Phase Without Stripping	29
2. Uranium Separation from Thorium by Tri-(n-octyl) Phosphine Oxide	30
3. Free Acid Determination in Reprocessing Solutions by Enthal- pimetric Titration	32
4. Determination of Boron and Cadmium in Thorium-Cerium Thorex Solutions by Atomic Absorption Spectrophotometry	37
5. Boron as Fluoroborate Ion in Solutions by Atomic Absorption Spectrophotometry	37
6. Determination of Cadmium in Thorex Solutions by Atomic Absorp- tion Spectrophotometry	38

TABLE OF CONTENTS

7.	Determination of Calcium in Triso-Coated Fertile Particles by Atomic Absorption Spectrophotometry	38
8.	Chloride Determination in Nitric Acid Leach Solutions	39
9.	Determination of Dibutyl Phosphate in Reprocessing Solutions	41
10.	Fluoride Determination in Reprocessing Solutions by Fluoride Specific Electrode	43
11.	Gravimetric Determination of Formic Acid in Nitric Acid Solutions .	47
12.	Determination of Sodium in Silicon Carbide Hulls by Atomic Absorption Spectrophotometry	47
IV.	HTGR FUEL DEVELOPMENT SUPPORT	48
1.	Determination of Uranium and Silicon in Triso-Coated Weak-Acid Resin Kernels	48
2.	Nitrogen Determination in Weak-Acid Resin Kernels	48
3.	Determination of Oxygen in WAR Kernels Using High Oxygen Analyzer	49
4.	Free Carbon in Carbonized Resin Kernels	50
5.	Determination of Zirconium in Uranium Carbide-Zirconium Carbide Sintered Kernels	50
6.	Low-Level Boron in Uranium-Thorium Oxides by Atomic Absorption Spectrophotometry	51
7.	Hydrogen, Oxygen, and Nitrogen in TRISO-Coated Thorium Oxide Via Vacuum Fusion Analysis	51
V.	TRIGA FUEL FABRICATION SUPPORT	53
1.	TRIGA Fuel Analysis by X-Ray Fluorescence	53

TABLE OF CONTENTS

2.	Determination of Erbium in TRIGA Materials	56
3.	Hafnium in Zirconyl Nitrate Solution by Atomic Absorption Spectrophotometry	57
VI.	MISCELLANEOUS PROCEDURES	58
1.	Ammonia Determination in Oakenite Detergent	58
2.	Determination of Free Carbon in Cr_{23}C_6 Powder.	58
3.	Recovery of Boron in Solutions After Evaporation	59
4.	Lithium in Graphite and Boronated Graphite by Atomic Absorption Spectrophotometry	60
5.	Material Balance on Milligram Quantities of Uranium Oxide . .	64
6.	Phosphorus in Incoloy-800	65
7.	Sulfur in Anticorrosion Oil Via Sulfur Dioxide Ion Specific Electrode	65
8.	Determination of Titanium and Zirconium in Hydroxides and Oxalates of Thorium Containing Rare Earths	66
9.	Enhancement of Zirconium Signal on Atomic Absorption Spectrometer	67
10.	X-Ray Fluorescence Measurement of Uranium-Thorium Ratio . . .	69
VII.	ELECTRON MICROPROBE	70
VIII.	INFORMATION MEETINGS	
1.	Phase II HTGR Interlaboratory Program	73
2.	HTGR Recycle Information Meeting	75

INTRODUCTION

This report describes analytical methods developed or adopted for use by the Analytical Chemistry Department during 1975. The individual items in the report range from brief one paragraph descriptions of methods used to several page descriptions of some development programs. This year, we have included some detailed procedures.

The analysis of HTGR materials constitutes the major part of the development workload. As in 1974, the HTGR cold recycle pilot plant was the largest customer for analytical services.

The Department provides services to organizations throughout General Atomic Company. Support of research and development efforts in the overall HTGR fuel cycle program ranging from new fuel concepts to fuel recycle studies requires most of the department's efforts.

I. RADIOCHEMISTRY AND GAMMA RAY SPECTROSCOPY

Experimentally Determined n, γ Cross Section for ^{54}Mn in a Reactor Spectrum* T. B. Crockett and E. E. Anderson

One of the most useful and often used dosimeters to monitor the fast neutron flux and fluence in long-term reactor experiments is one using the nuclear reaction $^{54}\text{Fe}(n, p)^{54}\text{Mn}$. In order to evaluate the fast neutron flux and fluence from an iron dosimeter the following parameters must be known as accurately as possible:

1. Reactor power history
2. Primary nuclear reaction cross section of the dosimeter
3. Specific activity of ^{54}Mn /milligram of dosimeter
4. Percentage abundance of the ^{54}Fe nuclide in the dosimeter
5. Thermal neutron depletion cross section of ^{54}Fe target nuclide
6. Thermal neutron depletion cross section of ^{54}Mn product nuclide.

The literature values for the thermal neutron depletion cross section for ^{54}Fe (Item 5) seem to be fairly consistent, while those for ^{54}Mn (Item 6) range from <10 barns (Ref. 1) to 38 barns (Ref. 2). With the exception of Item 6, the remaining parameters are known quite accurately.

It is recognized that the effect of burnout in both ^{54}Fe and ^{54}Mn is dependent upon the magnitude of both the thermal neutron flux and the cross section. For example, if one assumes the worst case of 38 barns for ^{54}Mn depletion and a nominal thermal flux of $3 \times 10^{14} \text{ n/cm}^2/\text{sec}$, the depletion reaction rate constant would be:

$$\lambda' = \bar{\phi} \bar{\sigma}$$
$$\lambda' = 1.14 \times 10^{-8} \text{ sec}^{-1}$$

where:

$$\begin{aligned}\lambda' &= \text{depletion reaction rate constant (sec}^{-1}\text{)} \\ \bar{\phi} &= \text{effective thermal flux (n/cm}^2\text{/sec)} \\ \bar{\sigma} &= \text{effective cross section (cm}^2\text{)}\end{aligned}$$

*This work was supported by ERDA Contract No. E(04-3)-167, PA 17.

whereas the decay constant for ^{54}Mn is:

$$\begin{aligned}\lambda &= 0.693/t_{\frac{1}{2}} \\ \lambda &= 2.56 \times 10^{-8} \text{ sec}^{-1}\end{aligned}$$

where:

$$t_{\frac{1}{2}} = \text{half life of } ^{54}\text{Mn} \text{ (in seconds)}$$

During irradiation, the effective reaction rate for ^{54}Mn depletion is the sum of the two reaction rates:

$$\lambda = \lambda' + \lambda = 3.96 \times 10^{-8} \text{ sec}^{-1}$$

Therefore, when the reactor is at power, the effective half-life of ^{54}Mn is reduced to 213 days. Conversely, during reactor down periods, ^{54}Mn decays with a half-life of 313 days. There are three major implications to be drawn from this example:

1. Higher fluxes than the one used in the example would have a more serious impact.
2. An effective half-life of 213 days limits the useful life of an iron dosimeter to approximately 400 days.
3. Fast fluences calculated with incorrect or no depletion cross section would contain a serious error.

It is evident from the foregoing that a more precise knowledge of the depletion cross section from ^{54}Mn was required. To resolve the uncertainty of the depletion cross section, evaluation tests were made in capsule irradiation experiments P13R and P13S. For these tests iron-free manganese-54 was required. This iron-free manganese-54 activity was prepared from an irradiated iron wire which contained ^{54}Mn and ^{59}Fe activity.

The wire was dissolved and the solution was made 8M in HCl. This solution was extracted with isopropyl ether to remove the iron. After several extractions, the ether extract was checked for ^{59}Fe activity by gamma-ray spectrometry and was determined to contain 0.06% of original ^{59}Fe activity. A final extraction was performed and analysis revealed no detectable ^{59}Fe activity. The indigenous ^{59}Fe activity served as an excellent monitor of the ^{54}Mn purification.

Eight test specimens were prepared by encapsulating a few microcuries of iron-free ^{54}Mn (as the oxide) in quartz ampoules. The actual amount of ^{54}Mn in each specimen was unimportant in that a method of activity ratios was to be used. This method had the advantage that the radioactivity of each specimen did not have to be known quantitatively, and there was no need to know the exact half-life of ^{54}Mn .

Each sample was counted at a fixed distance from a GeLi detector until the count rate in the ^{54}Mn photopeak had a 1 sigma uncertainty of $\pm 0.2\%$. Following irradiation, the samples were again counted at the same fixed distance. This ensured that there were no errors due to differences in counting geometry.

Three test specimens were inserted in P13R and three test specimens were inserted in P13S. Each sample had a ^{59}Co dosimeter in close proximity to measure the thermal neutron exposure. The two remaining specimens were sealed and stored as unirradiated reference sources.

Theory

When the designated samples are irradiated in a comparatively high flux reactor, the effective half-life of ^{54}Mn will become smaller by an amount dependent on the n, λ reaction rate constant. This is defined as:

$$\bar{\lambda} = \lambda + \bar{\phi} \cdot \bar{\sigma}$$

where:

$\bar{\lambda}$ = effective decay constant (sec^{-1})

λ = decay constant of ^{54}Mn (sec^{-1}) (313 days, $t_{1/2}$)

$\bar{\phi}$ = effective thermal neutron flux ($\text{n/cm}^2/\text{sec}$)

$\bar{\sigma}$ = effective cross-section in barns (cm^2)

The above expression applies only during the time when the reactor is at power. During reactor down periods, then:

$$\bar{\lambda} = \lambda$$

If the effective cross section is very small ($< 1\text{b}$), then the n, γ reaction rate constant becomes insignificant compared to the natural decay constant of ^{54}Mn . If this were the case, the initial and final measured ratios would not change.

Conversely, if the effective cross-section is as large or larger than the highest quoted literature values, the final ratios should be considerably larger than the initial ratios. It follows then that the actually observed initial and final ratios are directly related to the effective n, γ cross-section of ^{54}Mn .

Treatment of Data

The two capsule irradiation experiments, P13R and S, which contained the ^{54}Mn test specimens, began irradiation in the General Electric Test Reactor (GETR) on 17 December 1973 beginning with cycle 154-4 and were removed on 31 October 1974 following cycle 163-2. The total residence time in the reactor was 318 calendar days and was at full reactor power of 50 megawatts for 261 days. There was a total of 24 reactor up periods and 23 reactor down periods.

Because of the comparatively large number of up and down periods, each of which must be considered in the calculation, a Fortran program called "MANG" was written to do the data reduction.

Program "MANG" required that the reactor power history to be read in first. The initial and final ratios are read in next, along with the thermal neutron fluence as determined by the adjacent ^{59}Co dosimeter. The fluence value is based on a 36.8b cross section for the $^{59}\text{Co}(n, \gamma)^{60}\text{Co}$ reaction. Using the reactor power history and the thermal neutron fluence, the thermal neutron flux is calculated for each reactor period.

The ratio of the unirradiated reference source to irradiated specimen both measured at the same time after irradiation is defined as R_f .

The initial ratio is considered to be made up of a numerator, which equals the ratio, and a denominator of 1. Variable name is assigned these values: Example $\text{VAR1} = \text{RATIO}$, $\text{VAR2} = 1$.

VAR1 is related to the unirradiated reference source, while VAR2 is being related to the irradiated specimen.

Both variables are evaluated for each reactor cycle by the following algorithm:

$$\begin{aligned}\text{VAR1} &= \text{VAR1} \times \text{EXP}(-\lambda \times t_f) \\ \text{VAR2} &= \text{VAR2} \times \text{EXP}(-\lambda + \phi \sigma) \times t_f\end{aligned}$$

where:

- λ = the natural decay constant for ^{54}Mn (sec^{-1})
- t_i = time in seconds of reactor interval i (sec)
- ϕ = thermal neutron flux ($\text{n/cm}^2\text{sec}$) for reactor interval i
- σ = cross section in barns (cm^2) for the $^{54}\text{Mn} (n,\gamma) ^{55}\text{Mn}$ reaction.

An initial guess of 1 barn for σ is used for the first time through the power history.

After one pass through the power history, a ratio is calculated by $R_c = \text{VAR1}/\text{VAR2}$. This value is compared to the final measured ratio, R_f , input to the program; if it does not agree to within $\pm 0.5\%$, the cross section σ is altered by multiplying σ by the factor R_f/R_c . At this point, the values VAR1 and VAR2 are reset to their original values and taken through the power history again, however, with a new σ . It can be seen that the adjustment factor R_f/R_c causes the calculated ratio R_c to converge on the value R_f . The iteration continues until the R_c agrees with R_f to within $\pm 0.5\%$ at which time the final σ is output. The program then returns for the next ratio set and thermal fluence values to be input. This process continues until all specimens are calculated. Table I shows an itemized list of the initial and final ratios and the calculated effective cross section $\bar{\sigma}$.

Since all of the irradiated samples belong to the same population, a simple average and a 1 sigma standard deviation is calculated for $\bar{\sigma}$. Thus the ^{54}Mn depletion cross section was established as 11.7 ± 2.4 barns.

TABLE 1

Sample Ident.	Thermal NVT x 10 ²¹	Mn-7/Mn-n		Mn-8/Mn-n		Calculated $\bar{\sigma}$	
		Initial	Final (R _f)	Initial	Final (R _f)	Mn-7	Mn-8
Mn-1	6.41	0.6061	0.6508	0.7188	0.7601	10.35	7.94
Mn-2	lost	-----	-----	-----	-----	-----	-----
Mn-3	5.97	0.8793	0.9665	1.043	1.129	15.04	12.48
Mn-4	5.72	0.7861	0.8429	0.9322	0.9843	11.38	8.67
Mn-5	5.58	0.8402	0.9127	0.9964	1.066	13.96	11.21
Mn-6	5.20	0.7115	0.7712	0.8437	0.9006	14.56	11.62

Mean $\bar{\sigma}$ = 11.7 ± 2.4 barns

REFERENCES

1. Neutron Cross Sections, BNL-325, Third Edition, Volume 1, June 1973.
2. J. D. Jenkins, "The Thermal-Neutron Cross Section for ^{54}Mn ", ANS, 14, 353-354 (1971).

Evaluation of Copper as a Dual Dosimeter, T. B. Crockett and D. M. Fleishman

The main interest in copper, initially, was the evaluation as a long-term fast neutron fluence monitor. Currently, iron dosimeters are used to measure fast neutron fluences associated with capsule irradiation experiments and these are restricted to ~600 days residence time in a reactor due to half-life (313 days) of ^{54}Mn . Furthermore, there was some uncertainty in the ^{54}Mn burnout correction⁽¹⁾ at the time of these planned irradiations. Correction could be made for the burnout of ^{54}Mn , however, with a 38 barns value and when irradiated at a thermal neutron flux of $3 \times 10^{14} \text{ n/cm}^2 \text{ sec}$, the useful residence time would be roughly 400 days. With this limitation, iron dosimeters would be inadequate for the longer residence times being planned for reactor irradiation experiments.

Copper has been used to measure thermal fluxes in short irradiations via measurement of the 12.8 hour ^{64}Cu activity. While the short-lived ^{64}Cu would be useless for long term irradiations, subsequent activation of the ^{64}Cu decay product, stable ^{64}Zn , does yield the longer lived activity, ^{65}Zn . In addition to ^{60}Co via (n, α) reaction, by also measuring this double activation product ^{65}Zn , copper affords an opportunity to obtain thermal and fast neutron data from a single dosimeter, thereby providing a convenient backup for both.

To evaluate the copper dosimetry, samples of copper wire were irradiated concurrently with cobalt and iron dosimeters during recent capsule irradiations in ORR (Oak Ridge Reactor) and GETR (General Electric Test Reactor). The capsule experiment OG-2 began irradiation in ORR on 19 July 1974 and was removed on 5 January 1975. The total residence time was 170 calendar days and 129 effective full power days. Capsule experiments P13R and S began irradiation in GETR on 17 December 1973 and were removed on 31 October 1974. Total residence time was 318 calendar days and 261 effective full power days.

⁽¹⁾ See section on the evaluation of the ^{54}Mn burnout correction in this report.

The thermal neutron fluence was determined by the adjacent ^{59}Co dosimeter and the fluence value is based on a 36.8 barn cross-section for the $^{59}\text{Co} (n, \gamma) ^{60}\text{Co}$ reaction. All cross-sections and half-lives used in these evaluations are listed in Table 1. The fast neutron fluence was determined by the adjacent ^{54}Fe dosimeter and the fluence value is based on a 45.6 millibarn cross-section for the $^{54}\text{Fe} (n, p) ^{54}\text{Mn}$ reaction for $E > 0.18$ MeV.

All dosimeter activities were measured on a GeLi detector and decayed back to end of irradiation. From these inputted activities per milligram of copper, reactor power history summaries and the reaction cross-sections, the DOSE-1 program computed the thermal and fast neutron fluences shown in Table 2 and 3 respectively. Shown for comparison are the DOSE-1 computed thermal and fast neutron fluences from cobalt and iron. Standard deviations calculated for each set of ratios shows good agreement between "copper" fluences and fluences measured by cobalt and iron dosimeters. This agreement verifies the feasibility of using the single dosimeter material as backup to cobalt and iron dosimeters. Furthermore, copper can extend fast neutron fluence monitoring over a period of years.

TABLE 1

<u>Dosimeter Reaction</u>	<u>Cross Section barns</u>	<u>Half-Life</u>	<u>Neutron Energy</u>	<u>Influence</u>
$^{59}\text{Co}(n,\gamma)^{60}\text{Co}$	36.8	5.27 yrs.	Thermal	Product
$^{60}\text{Co}(n,\gamma)^{61}\text{Co}$	2.0	n/a	"	A
$^{63}\text{Cu}(n,\gamma)^{64}\text{Cu}$	4.51	12.8 hrs.	"	Intermediate Product
$^{64}\text{Zn}(n,\gamma)^{65}\text{Zn}$	0.78	243.7 days	"	Final Product
$^{54}\text{Fe}(n,p)^{54}\text{Mn}$	0.0465	312.97 days	$E > 0.18\text{Mev}$	Product
$^{54}\text{Fe}(n,\gamma)^{55}\text{Fe}$	2.3	n/a	Thermal	B
$^{54}\text{Mn}(n,\gamma)^{55}\text{Mn}$	11.7	n/a	"	A
$^{63}\text{Cu}(n,\alpha)^{60}\text{Co}$	0.000320	5.27 yrs.	$E > 0.18\text{Mev}$	Product
$^{63}\text{Cu}(n,\gamma)^{64}\text{Cu}$	4.51	n/a	Thermal	B

where:

A = burnout of product nuclei

B = disappearance of target nuclei by competing reaction

n/a = not applicable

TABLE 2

Sample Ident.	Thermal Fluence (10^{21} n/cm ² sec)		Ratio <u>Cu Zn/CoCo</u>
	⁶³ Cu→ ⁶⁵ Zn	⁵⁹ Co(n,γ) ⁶⁰ Co	
ORR-1	1.13	1.10	1.027
-2	1.18	1.10	1.073
-3	1.55	1.58	.981
-4	1.80	1.86	.968
-5	1.81	1.86	.973
-6	1.54	1.56	.987
-7	0.60	0.60	1.000
-8	1.11	1.07	1.037
-9	1.12	1.09	1.027
-10	1.41	1.42	.993
-11	1.62	1.65	.982
-12	1.64	1.66	.988
-13	1.43	1.42	1.007
-14	0.65	0.65	1.000

Standard Deviation of Ratios = 2.9%

GETR-1R	6.19	6.38	.970
-2R	5.73	6.31	.908
-3R	4.53	4.73	.958
-4R	3.01	2.93	1.027
-5R	1.11	1.23	.902
-1S	6.14	5.83	1.053
-2S	5.73	5.63	1.018
-3S	4.58	4.50	1.018
-4S	Lost	Lost	-
-5S	Lost	Lost	-

Standard Deviation of Ratios = 5.4%

TABLE 3

Dosimeter Identification	Fast Fluence E > .18Mev		Ratio CuCo/FeMn
	$^{63}\text{Cu}(n,\alpha)^{60}\text{Co}$	$^{54}\text{Fe}(n,p)^{54}\text{Mn}$	
ORR-1	1.18	1.13	1.044
-2	1.76	1.84	.956
-3	2.69	2.81	.957
-4	3.20	3.32	.964
-5	3.33	3.40	.979
-6	2.75	2.82	.975
-7	1.25	1.29	.969
-8	1.10	1.08	1.018
-9	1.72	1.76	.977
-10	2.52	2.72	.926
-11	3.03	3.17	.956
-12	3.21	3.33	.964
-13	2.74	2.89	.948
-14	1.37	1.45	.945

Standard Deviation of Ratios = 4.0%

GETR-1R	1.27	1.25	1.016
-2R	1.40	1.39	1.007
-3R	1.11	1.14	.974
-4R	0.74	0.76	.974
-5R	0.28	0.29	.966
-1S	1.24	1.24	1.000
-2S	1.34	1.39	.964
-3S	1.14	1.16	.983
-4S	Lost	Lost	-
-5S	Lost	Lost	-

Standard Deviation of Ratios = 1.8%

Development of Long-term Thermal Neutron Flux Monitor

(T. B. Crockett and T. L. Williams)

Cobalt (cobalt-59) generally is selected when one desires to measure long-term thermal fluxes. Low-concentration cobalt alloys can be employed to monitor fluxes of 10^{13} n/cm²-sec, and these low concentration cobalt alloys can be utilized at still higher fluxes (10^{14} n/cm²-sec) by correcting for depletion of the Co-60 being formed. In an attempt to reduce the radiation level further, reduction of the cobalt concentration was not deemed advisable because of the difficulty in achieving a homogeneous alloy at the lower concentration. Because of the decision not to reduce the cobalt content, an alternate long-term, high thermal neutron flux monitor was sought.

High-purity vanadium appeared to be an excellent candidate for this purpose. The reaction product of interest is stable thus avoiding the radiation level problem. Also, the product (chromium) has a low depletion (activation) cross section, although this is not too important since the new product is also chromium. Finally, the levels of chromium expected could be easily analyzed by Atomic Absorption Spectrophotometry (AAS) for fluences exceeding 5×10^{20} nvt.

To evaluate the vanadium dosimetry, samples of vanadium were irradiated concurrently with cobalt dosimetry during Capsule Irradiation Experiments P13R & S. The chromium produced in the vanadium was measured by AAS, and the values were used to measure thermal fluence by the following formulation:

$$V = V_0 (1 - e^{-\phi\tau\sigma}) \quad (1)$$

Rearranged

$$\phi\tau = \ln \frac{1}{1 - V/V_0} \quad (2)$$

where

V = Chromium produced

V_0 = Vanadium initial

$\sigma = {}^{51}\text{V}(n,\gamma) {}^{52}\text{V} = 4.88 \times 10^{-24} \text{ cm}^2$

$\phi\tau$ = Fluence, nvt.

A comparison between thermal neutron fluences measured with vanadium and cobalt dosimetry is shown in Table 1. Modifications planned in AAS technique are expected to improve the comparison.

TABLE 1

CAPSULE	THERMAL NVT		RATIO
	V	Co	
P13R	2.62×10^{21}	2.91×10^{21}	.900
P13S	2.61×10^{21}		
P13R	4.28×10^{21}	4.69×10^{21}	.913
P13S	4.18×10^{21}	4.46×10^{21}	.937
P13R	5.61×10^{21}	6.26×10^{21}	.896
P13S	5.57×10^{21}	5.58×10^{21}	.998
P13R	6.04×10^{21}	6.33×10^{21}	.954
P13S	6.19×10^{21}	5.78×10^{21}	1.071

Peach Bottom End-of-Life Fuel Element Gamma Scan Data Reduction*

E. Anderson and D. Hill

1. Introduction

The Peach Bottom end-of-life fuel element gamma-scan data reduction was performed mostly by the Sigma-2 Computer-Analyzer. The Phase I short half-life isotope scans were computed using the basic spectrum integration routine (GULF) of the analyzer. However, the Phase II long half-life scans were of much poorer quality because of equipment problems at the Peach Bottom site. Thus a new integration subroutine was written to give more consistent results for these spectra.

2. Procedure

The original gamma-ray spectra were recorded on magnetic tape at the Peach Bottom site on equipment furnished by Intelcom Rad Tech. Each spectrum, which consists of 4096 words (16 binary bits), was recorded on magnetic tape as a single record. Since the Sigma-2 is not capable of reading a record of this length, a program was written on the Univac 1108 computer to convert the spectra to the Sigma-2 spectral format and add information regarding scan parameters to be used in computation. These parameters included a tag number for spectrum identification, the ADC live time, the total count time (real time), the date of the count, and the start and stop times of the count to the nearest second.

The spectra were taken in blocks at Peach Bottom. Each block represented a single fuel element and usually consisted of a calibration spectrum and a background followed by a series of spectra taken while the fuel element was moved slowly past a collimator in front of the detector. These were followed by several spectra taken with the fuel element stationary and finally another calibration spectrum.

For each block of spectra, the calibration spectra were read into the computer and the channel locations of the calibration peaks determined to the nearest hundredth using the GULF program. The gain (KeV [gamma energy]/channel) and intercept (KeV offset) of the spectra were calculated from these

*This work was supported by ERDA Contract No. E(04-3)-167, PA 56.

locations. These values and a set of characters identifying each spectrum were added to all the spectra by program CONVERT which transformed the Univac 1108 format into the complete GULF spectral format.

For Phase I of the gamma scans, these spectra were read into the computer, and the CPMs and the % one sigma errors in the CPMs were determined for all the peaks in each spectrum by the GULF program. This data along with the spectrum parameters were written out on magnetic tape for use by the data output program.

This process could not be used for the Phase II gamma scans because the gamma peaks had a very broad low-energy slope, and the GULF program could not consistently pick the correct low-energy baselines. A subroutine called INTEG was written to account for this broad slope on peaks which are known to be present in a spectrum. This subroutine was designed to read in spectra and compute the CPMs and % two sigma errors of predetermined peaks for direct use by the output programs.

Data was output in three different forms for each Phase utilizing six programs. Programs ERROR and ERROR2 were used for Phase I and Phase II, respectively, to print out the raw CPMs and % two sigma errors for the designated peaks in each spectrum. Programs PBGS2 and PBGSR used correction factors to correlate the decayed CPMs to the actual disintegrations per minute within the fuel. The factors included in these corrections were the intrinsic photopeak counting efficiency of the detector, the absolute intensity of the gamma line, the absorption factor for 1/2-in thick steel, and the relative internal absorption factor in the fuel bodies (Ref. 1). Various ratios of these CPMs and a few of the CPMs were printed out for each spectrum. The Phase I spectra were later rerun with the Phase II programs.

The spectra were printed out by fuel element blocks which consisted of a header explaining the data followed by a line of data for each spectrum. The data lines contained (1) the tag number, (2) the date, (3) the start time, (4) the real time, (5) the spectrum identification, (6) the median counting position, (7) the distance traveled during the count, (8) the distance

traveled during the recording of the spectrum, and (9) the CPM data. Items 6, 7, and 8 involved the distances the fuel element had traveled during the moving scans and were left blank for the stationary spectra.

Nine isotopes were printed out for Phase I spectra and seven isotopes for Phase II spectra. The isotopes are given below along with their half-lives, gamma energies, and which Phase they were printed out in.

<u>Isotope</u>	<u>Half-Life</u>	<u>Energy</u>	<u>Phase</u>
Ce-141	284.4 d	133	I, II
Ce-144	32.5 d	145	I
Pa-233	27.0 d	312	I, II
I-131	8.06 d	364	I
Ru-103	39.8 d	497	I, II
Ru-106	369.0 d	512	II
Cs-137	30.2 y	662	I, II
Zr-95	65.5 d	724	I, II
Cs-134	2.06 y	796	I, II
La-140 (Ba-140)*	12.8 d	1596	I

* La-140 and Ba-140 are in transient equilibrium giving an effective half-life of 12.8 days. For more detailed information, see Ref. 2.

3. Summary

There were 2555 spectra computed for Phase I of the Peach Bottom gamma scans and 3889 spectra for Phase II. This amounts to 120,085 data points for Phase I and 81,669 data points for Phase II, and a grand total of 201,754 data points computed for the Peach Bottom end-of-life fuel-element gamma scans.

4. References

1. Memo, E. Anderson to C. F. Wallroth, "Calculated Corrections to the Observed CPM Obtained from the Peach Bottom Gamma Scans of Fuel Elements," dated 2/6/75.
2. Report GA-D13477, E. Anderson, "Method of Data Reduction Used for Peach Bottom Gamma Scan," dated 5/15/75.

Equipment Improvements in the Sigma-2 Computer-Analyzer Laboratory

(E. Anderson, I. Guerrier, D. Hill, A. Bagierek)

1. High Geometry Lift Mechanism

A lift mechanism has been added to the laboratory in order to allow sources with relatively large amounts of gamma activity to be counted. Without the lift, the hottest samples that could be counted measured about 9 MR gamma at 1 ft. With the lift, samples as hot as 50 MR gamma at 1 ft have been counted. The lift consists of a sample stage attached to a long screw inside a slotted tube. Circular motion of the screw moves the stage up or down along the slot. This arrangement extends through the roof of the building to allow enough height and is covered by a metal cupola. The upper sample position is 300 cm from the detector. The limits of the stage movement are set by microswitches and are thus adjustable.

2. Automatic Sample Changer

An automatic sample changer has been implemented to count large groups of samples with similar activity. The changer can handle up to 100 samples at a time, but it is limited at present to small-size samples. Thus far it has proven useful for handling mullite fission-product collectors and gold flux-monitor wires for long-term evening and weekend runs.

II. X-RAY DIFFRACTION

Quantitative Analysis by X-ray Diffraction

P. K. Gantzel

Introduction

An X-ray diffraction pattern from a mixture of crystalline compounds can not only aid in their identification but may also indicate their relative proportions. Calibration of relative intensities is frequently done by blending relatively pure powders, or by use of a known mixture. This note will be concerned with an alternate method, whereby the relative scattering power is calculated from known atomic arrangements.

Formulas* and their Application to Chromium Carbide Coatings for Wear Protection of Steam Generator Tubes

The Bragg equation, $\lambda = 2 d \sin \theta$, relates the peak position on a film or the angle of a diffractometer scan to the distances within the crystal lattice. Through this equation, d-spacings in Ångstrom units may be compared with tabulations in the Powder File. While the National Bureau of Standards has provided many reliable, precisely measured X-ray diffraction patterns of a variety of compounds, Cr_7C_3 is not one of these.

The d-spacings of a crystal are the result of its periodicity, the distance between identical atomic environments. In three dimensions, this periodicity may be visualized as a "brick pile" of unit cells. For an orthorhombic unit cell with orthogonal axes a, b- and c, d-spacings may be computed with the formula

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} .$$

By ranging the Miller indices h, k, and l through integral values, only peak positions are calculated; however.

For CuK_α X-rays of 1.54 Å wavelength, the predominant scattering is from electrons, and the scattered X-ray intensity (I) from a powdered material is:

* A glossary of terms not defined in the text is given with the references.

$$I = G F_p^2 \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \quad (1)$$

The structure factor, F , expresses the cooperation (or lack of) between scattering from each region of a unit cell for a set of h , k , and l . For a centrosymmetric crystal (every atom at x , y , z has an equivalent at $-x$, $-y$, $-z$), the equation

$$F_{hkl} = \frac{1}{V} \sum_i T_i f_i \cos 2\pi (hx_i + ky_i + lz_i) \quad (2)$$

enables one to compute the total of scattering contributions from the i atoms, whose average positions within the unit cell are expressed by fractional coordinates x , y , z . Heavy metals such as tungsten give the highest F values (but only a small number of peaks) because of a large electron concentration per unit volume that scatters in phase.

The independent atomic positions and the space group symmetry combine to give the i atoms for Eq. (2), and substitution in Eq. (1) gives the scattered intensity per unit volume of a component in a mixture. Multiplication by the crystal density (ρ),

$$\rho = \frac{\sum_i m_i \text{ (g atoms/mole)}}{V \text{ (Å}^3\text{)} 10^{-24} \text{ (cm}^3\text{/Å}^3\text{)} 6.023 \times 10^{23} \text{ (atoms/mole)}} \quad (3)$$

changes it to per unit weight.

The results from these calculations for Cr_3C_2 , Cr_7C_3 , Cr_{23}C_6 , Cr , Cr_2O_3 , nichrome (20% Cr), AgCl and ThO_2 are given in Tables I and II. The relative scattering power for the strongest X-ray diffraction peak (except for AgCl and ThO_2) of each compound is given per unit weight in Table I; while Table II includes other strong peaks and has been scaled to make the strongest line the 100 conventional units.

The use of these two tables is illustrated in the following examples of film and diffractometer scans listed in Table III. Weak Cr_7C_3 peaks observed in Union Carbide's Lot #1 Cr_{23}C_6 powder may be used to obtain $\text{Cr}_7\text{C}_3:\text{Cr}_{23}\text{C}_6$ weight ratio by:

- (1) finding the calculated intensity ratios of Cr_7C_3 (210) and (102) peaks to Cr_{23}C_6 (420) and (422) from Table II,

$$\frac{(210)}{(420)} = \frac{33}{27} = 1.22 \quad \frac{(102)}{(422)} = \frac{46}{28} = 1.64$$

- (2) multiplying these ratios by the scale factors from Table I, 105 for Cr_7C_3 and 161 for Cr_{23}C_6 ,

$$\frac{(210)}{(420)} = 1.22 \cdot \frac{105}{161} = 0.80 \quad \frac{(102)}{(422)} = 1.64 \cdot \frac{105}{161} = 1.07$$

- (3) converting intensity ratios from the measurements listed in Table III to weight ratios,

$$\frac{\text{Cr}_7\text{C}_3(210)}{\text{Cr}_{23}\text{C}_6(420)} = \frac{10}{44} \cdot \frac{1}{0.8} = 0.28 \quad \frac{(102)}{(422)} = \frac{7}{58} \cdot \frac{1}{1.07} = 0.11$$

compared with Guinier camera film measurements

$$\frac{\text{Cr}_7\text{C}_3(210)}{\text{Cr}_{23}\text{C}_6(420)} = \frac{27}{202} \cdot \frac{1}{0.8} = 0.17 \quad \frac{(102)}{(422)} = \frac{29}{211} \cdot \frac{1}{1.07} = 0.13$$

- (4) By assuming less preferred orientation in the film method (because of transmission geometry rather than reflection used in the diffractometer measurements), the average ratio of $\text{Cr}_7\text{C}_3/\text{Cr}_{23}\text{C}_6 = 0.15$ indicates $0.15(100)/1.15 = 13$ weight % Cr_7C_3 if only these two components are present.

As a second example, the intensities of Cr_7C_3 (102), Cr_{23}C_6 (422), and ThO_2 (220) peaks may be used to compute weight percentages of M-3 (Table III) in the following manner.

			<u>% Made Up</u>
Cr_7C_3 (102)	$= \frac{27}{0.46(105)} = 0.56$	$56/1.47 = 38\%$	39
Cr_{23}C_6 (422)	$= \frac{24}{0.28(161)} = 0.53$	$53/1.47 = 36\%$	40
ThO_2 (220)	$= \frac{144}{376} = 0.38$	$38/1.47 = 26\%$	21
	1.47 (sum)	100%	

Discussion

The application of X-ray diffraction intensity formulas to quantitative analysis of powder mixtures has been outlined. With established crystal structure data (unit cell and atomic position parameters), calculations of peak positions and intensities give a basis for judging the quality and information content of X-ray diffraction measurements. This method circumvents the necessity of calibration with materials of known composition.

With proper equipment and technique, Chung⁽¹⁾ has achieved accuracies of about 5% relative error for powder pattern diffractometer measurements; thus, one might expect some improvement over the 15% discrepancies that seem prevalent in Table III. The AgCl and ThO₂ were used not only to illustrate a wide range of atomic number, but addition of one to a Cr₂₃C₆ sample enables one to measure Cr₂₃C₆ and Cr₇C₃ weight percentages without assuming that these constitute 100% of the sample. Application of this addition principle to M-3 would thus require 21% to be calculated for ThO₂ content rather than the 26% that is listed above (and in the table). Cr₂₃C₆ then becomes $36 \times 21/26 = 29\%$, Cr₇C₃ becomes 31%, and 19% of the material is unclassified (due to experimental error in this case).

In the practice of quantitative analysis by X-ray diffraction, a number of factors may introduce errors. Integration over peak profiles is less subject to crystallite size and perfection; transmission geometry usually avoids the large enhancement that reflection geometry may give to plate-like crystals; use of neighboring peaks mitigates any absorption effects that might have to be calculated for G factor in Eq. (1); identical X-ray absorption for components of a mixture may be attained by prolonged grinding or by similar composition of each granule.

Additional constraints that are peculiar to the use of Eqs. (1) and (2) come from the accuracy of the crystal structure determination and its applicability to the material at hand. For example, disorder⁽²⁾ in the atomic positions of Cr₇C₃ eliminates peaks at 2.287, 2.140, and 1.965 Å. By com-

binning the unresolved 2.287 and 2.295 Å peaks of the orthorhombic structure, one can see the uncertainty from 33 (disordered = hexagonal) vs 33 + 14 = 47 intensity units that arises where the Cr_7C_3 content is too low to detect the unresolved 2.140 or 1.965 Å peaks. Thus, the 2.120 Å Cr_7C_3 peak has been used to calculate percentages listed in Table III.

TABLE I

RELATIVE SCATTERED INTENSITY OF CuK_α X-RAYS FOR POWDER DIFFRACTION

COMPOUND	LATTICE PARAMETERS (Å)	DENSITY (gm/cm^3)	hkl	INTENSITY	
				Per Volume	Per Weight
Cr_{23}C_6	$a=10.650$	6.97	$\left. \begin{matrix} 511 \\ 333 \end{matrix} \right\}$	112	161
Cr_7C_3	$a=7.007, c=4.525$	6.90	211	73	105
Cr_3C_2	$a=5.533, b=11.472, c=2.829$	6.66	121	42	63
Cr_2O_3	$a=4.954, c=13.584$	5.24	104	40	76
Cr	$a=2.885$	7.19	110	260	362
Nichrome 20% Cr	$a=3.54$	8.58	111	218	254
AgCl	$a=5.556$	5.55	220	142	256
ThO_2	$a=5.584$	10.02	220	379	376

TABLE II
SELECTED (>10 INTENSITY AND $d > 1.5 \text{ \AA}$) X-RAY INTENSITIES
CALCULATED FOR $\text{CuK}\alpha$ X-RAYS

I_c	$d(\text{\AA})$	hkl	I_c	$d(\text{\AA})$	hkl
Cr_{23}C_6 $a = 10.650\text{\AA}$			Cr_2O_3 Trigonal $a = 4.954, c = 13.584$		
27	2.381	420	69	3.627	012
28	2.174	422	100	2.663	104
100	2.050	511, 333	93	2.477	110
20	1.883	440	29	2.173	113
25	1.800	531	39	1.814	024
14	1.775	442, 600	91	1.671	116
Cr_7C_3 Hexagonal $a = 7.01\text{\AA}, c = 4.526\text{\AA}$			$\text{Cr } a = 2.885$		
33	2.295	210	100	2.040	110
14	2.287	*	Nichrome $a = 3.54$ 20% Cr		
10	2.140	*			
46	2.120	102	100	2.044	111
100	2.047	211	47	1.770	200
12	2.024	300			
17	1.965	*			
11	1.847	301			
25	1.814	202			
15	1.753	220			
Cr_3C_2 Orthorhombic $a = 5.533\text{\AA}, b = 11.472\text{\AA}, c = 2.829\text{\AA}$					
18	2.747	011	45	1.949	211
23	2.546	140	32	1.912	060
13	2.492	220	32	1.893	141
100	2.306	121	45	1.870	221
59	2.241	230	28	1.821	310
18	2.119	150	25	1.782	051
24	1.991	240	23	1.696	151

* Additional lines for orthorhombic Cr_7C_3 .

TABLE III

OBSERVED INTEGRATED INTENSITIES, COMPOSITION AS MADE, AND PERCENTAGES CALCULATED FROM INTENSITIES

COMPOUND	hkl	UCAR	M-1	M-2	M-3	DENSITOMETER MEASURES OF GUINIER FILM		
		LOT #1				M-4	M-5	UCAR Lot #1
Intensities								
Cr ₂₃ C ₆	420	44	28	20	21	111	71	202
Cr ₇ C ₃	210	10	36	25	24	47	125	27
Cr ₂₃ C ₆	422	58	38	24	24	120	89	211
Cr ₇ C ₃	102	7	37	30	27	55	154	29
Cr ₂₃ C ₆	511,333	244	246	182	172			
Cr ₇ C ₃	211							
AgCl	220							
ThO ₂	220							
Weight % as made up								
Cr ₂₃ C ₆			51	35	40	71	34	
Cr ₇ C ₃			49	33	39	29	66	
AgCl				32				
ThO ₂					21			
Weight % calculated from above intensities								
Cr ₂₃ C ₆	(422)	90	52	32	36	70	38	89
Cr ₇ C ₃	(102)	10	48	37	38	30	62	11
AgCl	(220)			31				
ThO ₂	(220)				26			

GLOSSARY

- λ is the X-ray wave length, in units of 10^{-8} cm (Ångstroms)
- θ is one-half the angle between the incident and scattered X-ray beams.
- d is the interplanar spacing in a crystal, a quadratic function of the Miller indices h , k and ℓ .

$$\frac{1}{d^2} = h^2A + k^2B + \ell^2C + hkD + h\ell E + k\ell F$$

(most inorganic compounds can be described with fewer coefficients)

- h, k, ℓ are reciprocals of fractional intercepts of a plane with the unit cell axes a , b , and c .
- a, b, c are three non-coplanar vectors which define a unique volume in a crystal that is repeated throughout every adjacent parallelepiped.
- p is the number of combinations that a given h, k, ℓ triplet can have in the particular crystal system.
- G and T are equal to 1.0 for these calculations.
While G is considered to be a constant proportionality factor in this application, it is a function of θ for an asymmetric Guinier camera (from X-ray absorption and variation in sample to film distance) and becomes significant when lines of very different θ values are compared.

Atomic vibrations or other causes of average displacement from the atomic coordinates, x, y, z , generally cause little variation in T for d -spacings greater than $1.5\text{\AA}$.

f is the atomic scattering factor. It begins at approximately the atomic number and decreases with increasing $\sin \theta/\lambda$, lighter atoms more rapidly than heavier ones.

V is the unit cell volume

$$V = abc(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{1/2}$$

where angles between a, b, c axes are α , β , and γ .

m is an atomic weight.

REFERENCES

1. F. H. Chung, J. Appl. Cryst. 7, 519 (1974).
He gives precise measurements of ZnO, KCl, LiF etc. powder mixtures.
2. Rouault et al., Ann Chim. (Paris) 1970, 461. The atomic positions for Cr_7C_3 are given in this paper.
3. International Tables for X-ray Crystallography, Volumes I - III, Kynoch Press, Birmingham, England.

These volumes contain the symmetry information and scattering factor tables that are needed for equation (2).

4. Powder Diffraction File, published by the Joint Committee on Powder Diffraction Standards, Swarthmore, Pennsylvania.

III. HTGR FUEL REPROCESSING SUPPORT*

Determination of Thorium in Solvent Extraction Organic Phase Without Stripping

E. M. Knox

Thorium may be determined gravimetrically in solutions of tributyl phosphate-normal paraffin hydrocarbon after wet ashing to destroy the organic. The resulting phosphoric acid solution may be analyzed for thorium by precipitation with oxalic acid. Thorium oxalate is filtered, ignited, and weighed as thorium oxide.

An aliquot of solution containing approximately 100 mg thorium is transferred to a 250 ml beaker. Do not exceed a 10 ml aliquot. Five ml of concentrated HNO_3 and approximately 1 ml 70% HClO_4 are added to the sample solution. The sample is heated in a perchloric acid hood to dense fumes of HClO_4 . HNO_3 and HClO_4 are added until the organic is destroyed. When the organic is decomposed, the sample will not char when evaporated to near dryness, no fumes of NO_2 will be detected, and with the addition of more HNO_3 , the two phases will be gone. Concentrated NH_4OH is added to a pH between 8 and 9. The heavy metal hydroxides are filtered onto Whatman #541 filter paper and washed with 10% NH_4OH . The filtrate is discarded. The precipitate is dissolved through the filter paper into the original 250 ml beaker with 3N HCl . The final wash is with distilled water. The solution is re-precipitated with NH_4OH to ensure complete separation from the phosphate ion. This time the filtered thorium hydroxide is dissolved with 10 ml concentrated HCl using an eye dropper and water wash, through filter paper into the same beaker. The volume is adjusted to 200 ml with water (final concentration 5% HCl). Twenty-five ml of 10% oxalic acid are added. The precipitate is allowed to stand for at least 1 hr at a low temperature, then cooled to ambient. The thorium oxalate is filtered onto Whatman #42 filter paper containing filter pulp. The precipitate is washed three to four times with 2% oxalic acid - 1% HCl wash solution. The paper with precipitate is transferred to a tared platinum crucible, charred, and ignited at 900°C for 1 hr. The residue is weighed as ThO_2 .

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Uranium Separation from Thorium by Tri-(N-Octyl) Phosphine Oxide

R. G. Wilbourn

Uranium is quantitatively extracted from aqueous solution with tri-(n-octyl) phosphine oxide (TOPO) in kerosene. Thorium interference may be eliminated by treatment with disodium ethylenediaminetetra acetate (EDTA) at pH 2.5 to 3.0 prior to extraction.

Work has demonstrated a separation of 50 mg of Th from 50 μ g of U. Water may be used to back-wash, as U is tightly held in the extractant. Recoveries of >90% were observed at the 25- and 50- μ g U levels. Arsenazo III buffered with glacial acetic acid was used to strip the organic phase. Two successive treatments with buffered Arsenazo III solution are required to return extracted U to an aqueous phase. Direct colorimetry is employed to measure the U content of Arsenazo III strip solution.

Procedure

1. Reagents

- (1) U Standard, 5 μ g U/ml. Prepare standard in 1% nitric acid by appropriate dilution of a uranyl nitrate stock solution.
- (2) Sodium Nitrate Solution. Dissolve 42 g of NaNO_3 in distilled water and dilute to 100 ml.
- (3) Monochloroacetic Acid Buffer. Dissolve 18.9 g of ClCH_2COOH in 50 ml distilled water. Neutralize 25 ml of this solution with NaOH to phenolphthalein. Add to the remaining 25 ml of solution and dilute to 100 ml (pH 2.85).
- (4) EDTA Solution. Dissolve 5 g of disodium ethylenediaminetetraacetate in 100 ml distilled water.
- (5) TOPO Solution, 0.05 M. Dissolve 9.67 g of tri-(n-octyl) phosphine oxide in 500 ml of kerosene.
- (6) Acetic Acid Solution, pH 2.0. Adjust pH of 500 ml glacial acetic acid to 2.0 with 5% sodium hydroxide solution.
- (7) Arsenazo III, 0.05%. Dissolve 0.5 g of Arsenazo III in distilled water and dilute to 1000 ml.
- (8) Buffered Arsenazo III Solution. Dilute 200 ml Arsenazo III to ~500ml with distilled water. Add 400 ml of pH 2.0 acetic acid and dilute to 1000 ml.

2. Standard Curve

- (1) Pipet aliquots of uranium standard to contain 0, 10, 15, 25, 50, and 75 μg U into 50 ml volumetric flasks.
- (2) Add 20 ml of pH 2.0 acetic acid solution.
- (3) Dilute to approximately 35 ml with distilled water.
- (4) Add 10 ml of 0.05% Arsenazo III solution.
- (5) Dilute to volume, mix, and read absorbance in 5 cm cells at 660 nm.
- (6) Plot standard curve, μg U vs absorbance.

3. Sample analysis

The following steps permit the analysis of 0 to 50 μg U in presence of ≤ 50 mg of Th.

- (1) Transfer an aqueous sample aliquot (≤ 10 ml) to a 125 separatory funnel.
- (2) Adjust pH to 2 to 3 with nitric acid or sodium hydroxide solution.
- (3) Add 1 ml of NaNO_3 solution.
- (4) Add 10 ml of monochloroacetic acid buffer (pH 2.85).
- (5) Add 5 ml of EDTA solution.
- (6) Add 25 ml of 0.5M TOPO in kerosene.
- (7) Extract U by shaking for 2 min.
- (8) Allow phases to separate. Drain off aqueous layer.
- (9) Wash organic layer two times (15 sec) with 15 ml portions of water.
- (10) Return U to aqueous phase by stripping two times with buffered Arsenazo III solution (2 min each).
- (11) Combine the aqueous strip solutions (centrifuge if necessary to improve clarity) and measure absorbance in 5 cm cells 660 nm.
- (12) Determine U content from standard curve.

4. References

- (1) C. J. Rodden, "Analysis of Essential Nuclear Reactor Materials," US Government Printing Office, 1964, pp 53-59.
- (2) P. M. Palei, "Analytical Chemistry of the Elements - Uranium," Translated by N. Kaner, Ann Arbor-Humphrey Science Publishers, 1970, pp 43-45 and 287.

Free Acid Determination in Reprocessing Solutions by Enthalpimetric Titration

R. B. Hower with H. K. E. Janke1

A thermometric method of measuring free acid concentrations in reprocessing samples submitted by the cold recycle pilot plant was adopted. Samples typically contain thorium, uranium, aluminum, zirconium, normal paraffin hydrocarbons, tributyl and dibutyl phosphate, and fluoride in addition to nitric acid. The hydrolyzable ions (Th, U, Al, Zr) are complexed by potassium fluoride in order to prevent their interference during the titration of the acid. The end point is determined by a drop in the rate of rise in temperature (sensed by a thermistor) during the titration. The rise in temperature is due to the heat of reaction.

Since the analysis is temperature-sensitive, there are several critical factors involved such as placement of the thermistor relative to the point at which the sodium hydroxide titrant enters the solution, the rate of addition of base, and the rate of mixing of reactants. However, these can be pre-set when initially setting up the equipment.

In order to determine the accuracy and precision of the method, a series of titrations was carried out on various solutions. Table I shows the increase of relative error with decreasing acid content. The lower limit of acid content for sample aliquots was generally taken to be 0.5 milliequivalent because at lesser concentrations the error exceeds 2%.

To determine the acid recovery of the method for solutions containing a hydrolyzable ion, a solution of thorium nitrate and nitric acid was analyzed. The accuracy of the method is indicated by the agreement of the theoretical and experimental free acid values. See Table II.

In order to determine the accuracy of the analyses of reprocessing-type solutions, a synthetic matrix of acid, Th, U, Al, and fission products was prepared. Table II shows that the method yielded satisfactory results for solutions with this type of matrix.

The useful range of free acid concentration is approximately 0.05 M

through 14 M, depending upon aliquot size; acid-deficient solutions may be analyzed by adding an appropriate acid spike.

Equipment

1. Thermo-titrator, Alcan Model (Sanda, Inc.) modified to feed temperature signal directly to recorder through a 1:1000 voltage divider.
2. Thermistor, 2000-ohm resistance at 20°C.
3. Radiometer-Copenhagen ABV-12 Autoburette; 25 ml.
4. Magnetic stirrer with bar.
5. Beaker, tall form, 100 ml, with styrofoam container.
6. Chart recorder, linear instruments.

Reagents

1. HNO_3 , 0.2N - standardized by conventional methods.
2. NaOH, ~0.5N, determine constant as in sample procedure except pipet a 5 ml aliquot of standard 0.2N HNO_3 instead of sample in Step 3.

$$\text{Constant} = \frac{N \text{ HNO}_3 \times \text{ml aliquot}}{\text{titration distance, cm (with correction factor from Step 4.)}}$$

Distance is measured between breaks on titration curve.

4. Complexing Reagent, 5M KF. Dissolve 470 g of $\text{KF} \cdot 2\text{H}_2\text{O}$ in 1 liter de-ionized water. Add 3 ml of 0.1% ethanol solution of phenolphthalein. Let equilibrate for 24 hr before using.

Procedure

1. Turn on power of autoburette, thermo-titrator control, and recorder. Titration delivery speed set at "10" which is equal to 3.40 ml/min. Chart speed set at 2 in/min which is equal to 5.08 cm/min.
2. Flush titrator system to eliminate any air bubbles.
3. Pipet an aliquot of sample containing 0.5 to 3 milliequivalents of free acid into a tall 100 ml beaker with stirring bar.
4. Add 10 ml complexing reagent if hydrolyzable ions are present; dilute to about 50 ml.

NOTE: The complexing reagent may contribute some free acid to the solution; a correction factor can be determined by analyzing a known amount of acid with and without the 10 ml of complexing reagent.

5. Place beaker in styrofoam container on magnetic stirrer; place thermistor

- and titrator tubing into the solution; turn on the stirrer and set at "4."
6. With meter on "balance," adjust dual dial to get a reading of zero. This balances the Wheatstone bridge.
 7. Fill the automatic buret with NaOH.
 8. Switch meter to "Test-C."
 9. Press "start" button.
 10. Adjust zero knob on recorder to bring pen near zero; let it run a bit to get a good pre-titration line, ~1 in.
 11. Press "empty-buret" and let titration run.
 12. When curve levels off, let it run a few inches more; release the "empty-buret" button to stop addition of NaOH.
 13. Turn meter off by switching back to "balance"; this also turns off recorder.
 14. Measure the horizontal distance between the two inflection points of the curve.
 15. Calculations:

$$\text{moles H}^+ = \frac{(\text{titration distance sample, cm}^*)(\text{constant})}{\text{Sample aliquot, ml}}$$

*With correction factor from Step 4.

References

1. F. G. Bodewig, "Enthalpimetric Titration of Free Acid in Simulated Nuclear Fuel Solutions Containing Thorium and Other Hydrolyzable Ions," Anal. Chem., 46, 46 (1974).
2. E. Van Dalen and L. G. Ward, "Thermometric Titration Determination of Hydroxide and Alumina in Bayer Process Solutions," Anal. Chem., 45, 2248 (1973).

TABLE I EFFECT OF ACID CONCENTRATION ON STANDARD ERROR

Test Sample	Number of Test Samples	Mean	Relative Standard Deviation
1.98 meq HNO_3	8	1.98	1.0%
0.494 meq HNO_3	7	0.496	1.9%
0.199 meq HNO_3	8	0.202	6.9%

TABLE II FREE ACID ANALYSIS OF SOLUTIONS OF THORIUM NITRATE BY THERMOMETRIC TITRATION

Test Solutions:

10.0 ml of 0.239 N HNO_3 - 0.1 M $\text{Th}(\text{NO}_3)_4$
 10 ml of 5 M KF

Titrant:

0.508 N NaOH

Free Acid, Experimental

0.242 N
 0.238 N
 0.242 N
 0.241 N
 0.239 N
 0.233 N
 0.239 N
0.239 N

Mean = 0.239 N

Standard Deviation: ± 0.003

Relative Standard Deviation: $\pm 1.3\%$

TABLE III ACID RECOVERY BY THERMOMETRIC TITRATION FOR VARYING ACID CONCENTRATIONS

Test Solutions:

2.0 ml of Synthetic Matrix HNO_3 Solution

10 ml of 5 M KF

Titrant:

0.549 N NaOH

Meq. HNO_3 Added	Meq. HNO_3 Found	% Difference
1.34	1.34	0.0%
2.67	2.67	0.0%
4.00	4.01	0.3%
5.26	5.34	1.5%
6.64	6.68	0.6%

Determination of Boron and Cadmium in Thorium-Cerium Thorex Solutions by
Atomic Absorption Spectrophotometry

D. V. Matutina

Cadmium and boron may be determined in thorex solutions containing large amounts of thorium and cerium by atomic absorption.

The cadmium determination is very sensitive. A 0.03 ppm cadmium solution gives a 1% absorption at 228.6 nm in an air-acetylene flame system. Since most of the samples analyzed have been high in cadmium, a large sample dilution had to be made, thus eliminating any matrix effect.

The boron determination is not as sensitive. A 30 ppm solution of boron gives a 1% absorption at 249.4 nm in a nitrous oxide-acetylene flame system. Significant matrix effect has been noted, hence boron standards have to be spiked with the solution being analyzed.

Attempts were made to determine boron by flame emission, but the presence of interfering ions made the readings nonreproducible.

Boron as Fluoroborate Ion in Solutions by Atomic Absorption Spectrophotometry

D. V. Matutina

Questions were raised regarding the accuracy of the boron determination in Thorex solution by atomic absorption if most of the boron is present as BF_4^- . A suggestion was made that BF_4^- is highly stable and not easily decomposed at the high temperatures of the flame, therefore resulting in low absorbance readings. However, a literature reference⁽¹⁾ suggests the instability of BF_4^- in acidic or basic solutions.

To find out whether BF_4^- is not easily decomposed as suggested, boron standards were prepared using NaBF_4^* . The difference in absorbance of these

* NaBF_4 technical grade assumed to be 95% pure.

(1) Orion Fluoroborate Electrode Instruction Manual, 1968, p 9.

standards as compared to H_3BO_3 standards was found to be insignificant.

I. B ($\text{H}_3\text{BO}_3 + \text{HNO}_3 + \text{HF}$)*	ppm	Absorbance
	50	0.004
	100	0.008
	200	0.018
II. B ($\text{NaBF}_4 + \text{H}_2\text{O}$)	53	0.005
	106	0.010
	212	0.020

*10% HNO_3 , 1% HF

Determination of Cadmium in Thorex Solutions by Atomic Absorption Spectrophotometry

D. V. Matutina

Cadmium in Thorex solutions may be analyzed directly on an atomic absorption spectrophotometer using an air-acetylene flame system at 228.5 m. The range of the standard curve is 0.1 to 1.0 $\mu\text{g/ml}$ cadmium. No matrix effect was noted.

Determination of Calcium in Triso-Coated Fertile Particles by Atomic Absorption Spectrophotometry

D. V. Matutina

The Triso-coated beads are crushed in a tungsten carbide mortar under alcohol, then dried under a heat lamp. Approximately 1 g of powdered sample is weighed into a platinum crucible and fused with potassium pyrosulfate. The melt is leached in 5% hydrochloric acid and transferred to a 50 ml volumetric flask, diluted to volume with distilled water and stored in a polybottle. Any residue may be fused with sodium carbonate, combined with the above and analyzed for calcium by atomic absorption spectrophotometry at 422 nm using an air-acetylene flame system. An aliquot of each standard subsequently is spiked with the sample to correct for matrix effects in the flame. Reagent blanks are prepared. The method is sensitive to 1 $\mu\text{g Ca/g}$ sample.

Chloride Determination in Nitric Acid Leach Solutions

F. C. Rowlen

Total chloride can be determined in nitric acid leach solutions containing high concentrations of thorium, cerium, and uranium. In the samples tested, the nitric acid concentration was 10M. Interferences are removed by converting the sample solutions to a strongly basic medium with 50% NaOH, precipitating the interfering ions. Through a sequence of centrifuging and washing, the isolation of chloride is obtained. The chloride then may be measured using an Aminco-Cotlove Chloride Titrator.

1. Procedure

- (1) Transfer a suitable sample aliquot to a 50 ml centrifuge tube.
- (2) Slowly add an equal aliquot of 50% NaOH; mix.
- (3) Centrifuge for 3 to 5 min to settle precipitate. Decant supernatant into a 200 ml volumetric flask without disturbing the precipitate.
- (4) Wash the precipitate for residual chloride twice using 5 drops of 50% NaOH and ~30 ml deionized water with stirring. Centrifuge and treat as in Step 3.
- (5) Adjust pH of supernatant in a 200 ml volumetric flask to ~7 with concentrated nitric acid. Dilute to volume with deionized water.
- (6) Pipet a 1 to 20 ml aliquot from the above solution into a 25 ml volumetric flask.
- (7) Add 2 ml of an acetic acid - nitric acid buffering solution (15 ml conc. HNO_3 , 235 ml glacial acetic acid) and dilute to volume with deionized water.
- (8) Titrations are performed as outlined in instruction manual for the Aminco-Cotlove Chloride Titrator.

A data summary follows. Sample 9H yielded results for chloride concentration which had a mean variance of $\pm 2.4\%$. The variance for sample 70X was 7.6%. From these results one can conclude the procedure for removal of interfering ions is reproducible.

	A	B	C		D
<u>Sample</u>	<u>Original Volume, ml</u>	<u>1st Dilution</u>	<u>2nd Dilution</u>	<u>Titration Time (sec.)</u>	<u>Average Titration Time (sec.)</u>
9H - a	100	5/100	10/25	200.15, 199.1	199.6
9H - b	100	5/250	15/25	123.7, 123.5	123.6
7 Ox - a	100	5/100	10/25	13.2, 13.2	13.2
7 Ox - b	100	5/250	15/25	12.1, 12.15	12.1

	D	E	F	G	H	I
<u>Sample</u>	<u>Titration Time (sec)</u>	<u>Ave. Time 10 ppm Cl⁻</u>	<u>Ave. Time Blank</u>	<u>Concentration Cl⁻ ppm</u>	<u>Dilution Factor</u>	<u>Total Cl⁻</u>
9H - a	199.6	6 standards	9.0 sec.	32.18	5×10^3	161 mg
9H - b	123.6	Ave. Time =	(8.95, 9.0)	20.29	8.33×10^3	169 mg
7 Ox - a	13.2	64.5 sec.		0.72	5×10^3	3.6 mg
7 Ox - b	21.1			0.51	8.33×10^3	4.25 mg

Equations

$$\text{Dilution factor} = H = A / (B \times C)$$

$$\text{Concentration Cl}^- \text{ ppm} = G = (D - F) 10 \text{ ppm} / (E - F)$$

$$\text{Total Cl}^- = I = G \times H$$

Determination of Dibutyl Phosphate in Reprocessing Solutions

R. B. Hower and D. V. Matutina

Dibutyl phosphate (DBP) may be determined in solvent extraction process-stream samples by extraction, decomposition, and color development of the ortho phosphate ion. In the organic phase, DBP is separated from monobutyl phosphate and tributyl phosphate by extraction with carbon tetrachloride (CCl_4) followed by methyl isobutyl ketone (MIBK). In the aqueous phase, the CCl_4 extraction may be omitted. The MIBK extract is evaporated and fumed with perchloric acid to release the phosphate. The phosphate ion is analyzed spectrophotometrically as molybdenum blue.

Analysis of synthetic samples in a typical reprocessing solution matrix indicates the procedure is useful for aliquots of sample containing 20 to 200 μg of DBP; the accuracy is $\pm 10\%$.

Procedure

1. Organic Phase Samples

- (1) Pipet a sample aliquot containing 20 to 200 μg DBP into a 125 ml separatory funnel.
- (2) Dilute solution to ~25 ml with normal paraffin hydrocarbon.
- (3) Extract DBP into an aqueous phase with 15 ml of 1.0 M Na_2CO_3 - 0.1 M NaF solution, shaking for ~30 sec. Transfer the lower aqueous layer to another separatory funnel.
NOTE: Na_2CO_3 is preferred over NaOH since samples containing very high concentrations of Th result in heavy precipitation if NaOH is used.
- (4) Repeat Step 3, collecting the aqueous layer in the second separatory funnel. Discard the organic layer.
- (5) Scrub the aqueous solution with 10 ml CCl_4 to remove any TBP. Shake for ~30 sec; discard lower CCl_4 layer.
- (6) Repeat Step 5.
- (7) In a 250 ml beaker, add 20 ml 8M HCl. Add the aqueous solution from the separatory funnel to the beaker. Wash the separatory funnel with a minimum amount of water. Be careful in transferring

the CO₂ solution to the acid solution as the CO₂ effervescence could cause a loss of sample. Warm the solution for a few minutes (do not boil) to remove CO₂.

- (8) Transfer the solution to the original separatory funnel.
- (9) Add 10 ml MIBK and shake ~1 min. Discard aqueous layer.
- (10) Wash MIBK with ~10 ml 1M HCl. Discard aqueous layer.
- (11) Pipet an aliquot of the MIBK extract into a 50 ml Erlenmeyer flask.
- (12) Evaporate to dryness.
- (13) Add 10 drops conc. HNO₃ and 1 ml HClO₄.
- (14) Heat on hot plate to dense white fumes, cool.
- (15) Dilute solution to 25 ml with water.
- (16) Add 10 drops of 10 M NaOH to solution and 1 drop phenolphthalein. Add more 10M NaOH dropwise until solution turns pink.
- (17) Add 1:1 HNO₃ dropwise until solution turns colorless.
- (18) Add 2 ml ammonium molybdate solution (2.5% in 28% H₂SO₄).
- (19) Add 10 drops SnCl₂/glycerin solution (0.3 g SnCl₂·2H₂O in 25 ml glycerin).
- (20) Transfer solution to a 50 ml volumetric flask and dilute to volume with water.
- (21) Allow to stand 20 min after addition of SnCl₂ reagent.
- (22) Read absorbance at 690 nm using 1 cm cells.
- (23) Prepare reagent blank using 1 ml H₂O instead of DBP.

2. Aqueous Phase Samples

- (1) Pipet a sample aliquot containing 20 to 200 µg DBP into 125 ml separatory funnel.
- (2) Dilute to ~25 ml with water.
- (3) Add 6 ml conc. HCl and 1 ml 3M HF.
NOTE: Hydrochloric acid provides a strong acid medium necessary for the extraction of HDBP. The fluoride ion breaks up metal-DBP complexes such as Zr-DBP.
- (4) Proceed as in Steps (9) - (23) of Organic Phase Samples.

3. Calculations

$$\frac{\mu\text{g DBP (std curve)}}{\text{ml sample aliquot}} \times \frac{\text{ml MIBK Total}}{\text{ml MIBK aliquot}} = \text{PPM DBP}$$

References

1. C. J. Hardy and D. Scargill, "Studies of Mono- and Di-n-butylphosphoric Acids - I, " J. Inorg. Nucl. Chem., 10, 323-327 (1959).
2. "Spectrophotometric Determination of Dibutylphosphate Following Alumina Column Separation," Allied Chemical Analytical Methods Manual, Part 1, TID-4500, May 1970, DBP-Color 1.
3. W. W. Schultz, "Macroreticular Anion Exchange Resin Cleanup of TBP Solvents," Atlantic Richfield Hanford, May 15, 1972, ARH-SA-129, p 8.

Fluoride Determination in Reprocessing Solutions by Fluoride Specific Electrode

E. M. Knox

Total fluoride in the range of 0.001 to 1.0 M can be measured in solutions containing high concentrations of Th, U, Al, and Zr, such as 1.5 M Th, 0.15 M U, 0.1 M Al, and 0.02 M Zr, with an ion specific electrode. The samples are made highly concentrated in phosphate ion to complex the interfering metal ions, thus releasing fluoride. Phosphoric acid, 10N, also provides a nearly constant pH and ionic strength.

A method of standard addition is employed. Voltage measurements are made following addition of 1 ml quantities of fluoride solution, about 100 times more concentrated than the sample solution, to 100 ml of the sample. The voltage of each successive addition is plotted on volume-corrected Grans' Plot Paper. A straight line is drawn through the points and extrapolated to the horizontal axis. The original sample concentration or dilution thereof may be calculated from the intercept. The accuracy of method is within $\pm 3\%$.

Equipment

1. Meter, pH/mV, digital, Orion Research Model 701 or its equivalent, capable of measuring ± 0.1 mV.
2. Printer, digital, Orion Research Model 751 or its equivalent, interfaced with pH/mV meter.
3. Electrode, fluoride ion activity, Orion Model 94-09 or its equivalent.

4. Electrode, reference, single junction, Orion Model 90-01 with filling solution 90-00-01, or its equivalent.
5. Motor, stirring, with 1.9 cm Teflon stir bars.
6. Beakers, polyethylene, 50 ml and 250 ml.
7. Autopipet, Pipetman P5000, 0 - 5.00 ml or its equivalent.
8. Dispenser, capable of delivering 99 ml.
9. Electrode holder, Orion Model 92-00-01.
10. Silicon Oil Orion No. 94-09-03.
11. Balance, analytical; with the capability of weighing to the nearest 0.1 mg.
12. Grans' Plot Paper, 10% volume corrected, Orion No. 90-00-90.

Reagents

1. Fluoride Standard Solution 0.1 M. Weigh 4.199 g of reagent-grade sodium fluoride predried at 100°C. Dissolve in deionized water, transfer to 1000 ml volumetric flask, and dilute to volume with deionized water. Store in a polyethylene bottle. Orion Fluoride standard 94-09-06 may be substituted.
2. Fluoride Calibration Standard, 100 ppm, Orion No. 94-09-07.
3. Fluoride Calibration Standard, 10 ppm. Pipet 10 ml of 100 ppm standard from Item 2 into 100 ml volumetric flask. Dilute to volume with deionized water.
4. Phosphoric Acid, 10 N. Dilute 228 ml of concentrated H_3PO_4 to 1000 ml with deionized water.

Calibration

1. Check out pH/mV meter with shorting strap as per instruction manual.
2. Add filling solution to reference electrode daily as per instructions.
3. With an absorbent tissue, apply daily a small amount of silicone oil on fluoride electrode body and sensing element to minimize sample contamination due to solution carryover.
NOTE: Blot with oil, do not wipe since scratches will cause slow electrode response.
4. Assemble electrodes, pH/mV meter and digital printer as per manufacturer's instructions.

5. Rinse electrodes with deionized water and blot dry with absorbent, lint-free tissue.
6. Pour about 30 ml of 10 ppm fluoride calibration standard into a clean 50 ml polyethylene beaker. Add stir bar and immerse the electrodes.
7. Stir solution making certain no air bubbles form at the bottom of the fluoride electrode.
8. Switch the digital pH/mV meter to EXP on function switch.
9. Set TIME switch on digital printer to 0.5 min. Activate PRINT switch.
10. Leave the solution in contact with the electrodes until a constant reading is obtained.

NOTE: Solutions containing 1 to 20 ppm F^- may require 10 min to stabilize when going from a low to high potential.

11. Deactivate PRINT switch. Activate ADVANCE switch.
12. Record voltage.
13. Switch pH/mV meter to standby (STDBY).
14. Remove electrodes from solution. Rinse electrodes with deionized water and blot dry.
15. Repeat Steps 5 to 13 for 100 ppm fluoride calibration standard.
16. Subtract the voltages from the calibration standards to determine the change in potential (ΔE). Change at 20°C is 58.16, at 25°C it is 59.16. If ΔE at ambient is not 58 ± 1 mV, do not proceed to Procedure. Consult instruction manual for trouble shooting.

Procedure

1. Pipet 1 ml of sample solution into a 250 ml polyethylene beaker.
2. Add 99 ml 10 N H_3PO_3 to sample. Add stir bar.
3. Immerse electrodes in sample solution.
4. Stir solution, making certain no air bubbles form at bottom of fluoride electrode.
5. Switch the digital pH/mV meter to EXP on function switch.
6. Set TIME switch on digital printer to 0.5 min. Activate PRINT switch.
7. Leave solution in contact with electrodes until a constant reading is obtained. Record voltage.
8. Deactivate PRINT switch. Activate ADVANCE switch.
9. Pipet 1 ml of 0.1 M fluoride standard solution or an appropriate

dilution thereof into sample solution. Activate PRINT switch.

- (1) Sufficient ions should be present in a 1 ml addition to produce a 45° slope on the plot.
10. Leave solution in contact with electrodes until a constant reading is obtained. Record voltage.
11. Repeat Steps 9 and 10 two more times in succession, recording voltage each time.
12. Switch pH/mV meter to STDBY. Remove electrodes from solution. Rinse electrodes with deionized water and blot dry.
13. Plot voltages from 7, 10, and 11 on Grans' Plot Paper.
 - (1) Shift X axis to the right by three major divisions (1 major division = 1 ml). Reassign "0" ml on graph paper.
 - (2) On Y axis, plot mV scale every 5 mV. Decrease mV readings in ascending order.
 - (3) Draw a straight line through points, extrapolate to baseline.
14. Determine X value for sample solution as being the number of divisions in milliliters to the left of the zero addition, or $X = 0$.
15. Calculate molarity of fluoride ion in sample solution.

Calculation

$$MF^- = X \bar{C} \cdot D$$

where:

X = number of divisions to the left of zero addition, ml

$\bar{C}$ = number of moles fluoride added in one addition divided by total sample volume, 100 ml

D = dilution factor of sample, 100 ml.

References

1. Orion Research Instruction Manual Model 701, 1973.
2. Orion Research Instruction Manual Model 751, 1972.
3. Orion Research Instruction Manual Model 94-09, 1967.
4. "Determination of Total Fluoride in Concentrated Thorium, Uranium or Aluminum Samples by Fluoride Specific Ion Electrode," Purex Analytical Procedures (FSE-1B), 1973.

Gravimetric Determination of Formic Acid in Nitric Acid Solutions

D. V. Matutina, R. G. Wilbourn, E. M. Knox

Carbon monoxide is quantitatively liberated from formic acid solutions when treated with hot concentrated sulfuric acid. Nitrogen is the purge and carrier gas (~5 cc/sec). The carbon monoxide evolved is converted to carbon dioxide by passage through a catalyst furnace (LECO catalyst #507-019 or "hopcalite" Mine Safety Safety Appliances) at 300°C.

Carbon dioxide formed is measured by absorption in a bulb containing Ascarite (asbestos-supported NaOH) and magnesium perchlorate. The bulb is weighed before and after absorption to determine the weight of CO₂ produced from decomposition of a known volume of solution. The formic acid content of the sample may be calculated from the CO₂ weight data. Accuracy is ±4% based on commercially available formic acid solution, 88%.

Determination of Sodium in Silicon Carbide Hulls by Atomic Absorption Spectrophotometry

D. V. Matutina

Moist SiC hulls believed to contain >1% Na were submitted for analysis. The material was dried in an oven at 115°C for 2 hr, then crushed in a SiC mortar to obtain a more homogeneous sample. The crushed material was fused with potassium carbonate in a platinum crucible. Upon cooling, the melt was leached in 10% HCl, filtered through Whatman #541 paper to remove silica, washed with deionized water, and diluted to a suitable volume. A blank was prepared in the same manner.

The Na concentration, after making blank and dilution corrections, was determined by atomic absorption at 590 nm using an air-acetylene flame system. Sensitivity of the method is 0.015 ppm.

IV. HTGR FUEL DEVELOPMENT SUPPORT

Determination of Uranium and Silicon in Triso-Coated Weak Acid

Resin Kernels

D. V. Matutina

Weighed kernels are crushed (under alcohol) in a tungsten carbide mortar. The powder is transferred to a platinum crucible. The mortar is wiped with alcohol-soaked filter paper, and the wipes are added to the crucible with the sample. The material is charred and then ignited at 800°C for ~1 hr. Upon cooling, the powder is transferred to a Teflon beaker and leached with Thorex solution. The SiC is filtered off and washed. The filtrate is evaporated to <15 ml and analyzed for U via ferrous ion reduction method⁽¹⁾. The filter paper with the SiC is fired in a platinum crucible, then fused with sodium carbonate. The melt is leached in 5% HCl. Perchloric acid is added, and the solution is evaporated to dehydrate silica. The Si content may be determined gravimetrically as SiO₂.

(1) "Titrimetric Determination of Uranium in Product, Fuel and Scrap Materials After Ferrous Ion Reduction in Phosphoric Acid," New Brunswick Laboratory Report - 252, July 1970.

Nitrogen Determination in Weak Acid Resin Kernels

M. A. Hiatt

Resin kernels were submitted for Kjeldahl analyses for nitrogen. A modification of our procedure was employed. The dissolution was done in phosphoric acid which will dissolve all the nitrides of uranium. Studies have shown that hydrochloric acid, as used in our former procedure, will dissolve mononitrides, but not dinitrides and sesquinitrides. Sulfuric acid will not dissolve the sesquinitrides.⁽¹⁾

(1) "Determination of Nitrogen in Vanadium Nitrides and Uranium Nitride (UN)." D. H. Bollman and D. M. Mortimore, Anal. Chem., **43**, 154 (1974).

A sample of WAR kernels was ground under ~1:1 H_3PO_4 in a glass mortar and pestle (similar to a tissue grinder) with stirring motor. When completely ground, the kernels and solution were transferred to a beaker and allowed to digest on a hot plate. Upon dissolution, the solution was transferred to a steam distillation apparatus, made alkaline, and distilled. The ammonium ion in the distillate is measured using a Nessler colorimetric or an ammonia specific electrode procedure.

Determination of Oxygen in Weak Acid Resin Kernels Using High Oxygen Analyzer

D. M. Nolan

Oxygen may be determined in weak acid resin (WAR) kernels using a LECO RO-16H high oxygen analyzer. A blank is determined by outgassing carbon black in a covered graphite crucible. Nitrogen is used as the carrier gas. After the accelerator is outgassed, a tightly crimped tin capsule is placed in a nickel basket, then into the graphite crucible. The blank is determined. The blank reading is inversely proportional to the "sample weight compensator" setting. For the greatest precision, it is important that the proper blank be subtracted, especially for samples containing less than 0.50% oxygen. That is, after an average blank is recorded on the digital voltmeter (DVM), switch "sample weight compensator" to each weight setting to be used for samples being analyzed, thereby determining the correct reading to be subtracted from each sample weight. This must be done quickly since the DVM will tend to drift after a minute or so. Return the DVM to zero. Adjust "blank" dial until desired blank reading is obtained on the DVM. A sample or standard, the weight of which corresponds to the blank reading just set, may be run. A new blank setting is dialed in as necessary with successive samples.

NBS 950, a U_3O_8 , prefired, is used to standardize the equipment. Between 0.050 to 0.100 g U_3O_8 is placed in a tin capsule. The crimped capsule is placed in a nickel basket, then into an outgassed graphite crucible with carbon black. U_3O_8 contains 15.20% oxygen. The nominal value to set the "slope" is one-half this percent of oxygen. Set twice the sample weight being used on the "sample weight compensator" and adjust the "slope" dial so the DVM reads 7.60%.

Samples are analyzed in the same manner as for standardization of the instrument; however, coated resin kernels must be specially prepared prior to analysis. These samples will not decompose at 2600°C, the maximum temperature produced. It is necessary to crush the sample and encapsulate it (so that it is airtight) in an inert atmosphere (rapid hydrolysis of the carbide will occur in a normal atmosphere).

Uncoated kernels may be fired without crushing, however keeping them in an inert atmosphere and encapsulating them are desirable in the event of any pyrophoric tendencies.

The accuracy is $\pm 0.05\%$ or $\pm 2\%$ of the oxygen present, whichever is greater.

Free Carbon in Carbonized Resin Kernels

D. V. Matutina and E. M. Knox

Free carbon may be determined by dissolving the kernels in concentrated nitric acid. The nitric acid is boiled to assure complete decomposition of the carbides. The free carbon remains undissolved. The carbon is filtered onto a tared sintered porcelain crucible filled with Celite, dried in air at 100°C, cooled, and weighed.

Determination of Zirconium in Uranium Carbide - Zirconium Carbide Sintered Kernels

L. K. Alfonso and E. M. Knox

A weighed crushed sample is ignited to the oxide and then fused with potassium pyrosulfate. The melt is leached in dilute hydrochloric acid. A solution of 0.1 M p-bromo-mandelic acid is added with constant stirring, then allowed to digest for 20 min at 80 to 85°C, cooled to ambient temperature, and filtered. The precipitate, zirconium bromomandelate, is washed, charred, ignited, and weighed as zirconium oxide.

Low-Level Boron in Uranium-Thorium Oxides by Atomic Absorption Spectrophotometry

D. V. Matutina

Uranium-thorium oxide blend, in a ratio of 1U:4Th, was mixed with boric acid using a Wiggle-Bug. A weighed amount was dissolved in a minimum amount of Thorex solution (~15 ml) and diluted to ~100 ml. The solution was passed through an ion exchange column of Dowex 50⁽¹⁾, to remove the uranium and thorium. Boron goes through the column as effluent. (Column size: 1 in x 12 in length). The column was washed several times with distilled water. The effluent was transferred to a 200 ml volumetric flask, diluted to volume, and analyzed by atomic absorption spectrophotometry at 249.8 nm using a nitrous oxide-acetylene flame system. The recovery was low by 1.7%.

Since the absorbance reading for the sample was so low, a way of reducing the volume of the effluent without losing the boron was necessary, hence the addition of mannitol was initiated. Another sample of $\text{UThO}_2\text{-H}_3\text{BO}_3$ blend was taken through the above method; however, mannitol was added to complex the boron in the effluent. The effluent then was evaporated to less than 50 ml. The solution was transferred to 50 ml volumetric flask and diluted to volume. The recovery was high by 0.5%.

⁽¹⁾J. R. Martin and J. R. Hayes, Anal. Chem., 24, 182 (1952).

Hydrogen, Oxygen, and Nitrogen in Triso-Coated Thorium Oxide Via Vacuum Fusion Analysis

M. A. Hiatt

Since concentrations were too high for inert gas fusion, an attempt was made to shock the particles at 2800°C to crack the Triso coating in the vacuum fusion apparatus. However, while outgassing the system at that temperature, a corona was produced, requiring the use of a lower temperature.

The samples were dropped into the graphite crucible, no bath, and shocked at 0.35 amp (approximately 2600°C) for 1 min. The current then was

turned back to 0.25 amp (approximately 2100°C) for 10 min. The gas pressures were measured in the appropriate volumes.

It took 45 min for the hydrogen pressure to equilibrate. This is assumed to be the result of some hydrocarbon being evolved, then having to be decomposed at the palladium filament.

The content of hydrogen was found to be 8 ppm, nitrogen less than 5 ppm, and oxygen 30 ppm.

V. TRIGA FUEL FABRICATION SUPPORT

TRIGA Fuel Analysis by X-ray Fluorescence

C. L. Chaney

The X-ray fluorescence uranium assay method used for analysis of TRIGA fuel was modified several times to obtain a precision and an accuracy of $\pm 0.5\%$ relative error for a single sample analysis. Attempts to obtain the desired precision and accuracy are described below.

A quality assurance constraint that the entire uranium-zirconium TRIGA fuel alloy sample submitted be used in an assay method for uranium caused serious problems. Sample weights ranged from 0.5 to 4.0 g in the form of metal turnings. Previously, samples were dissolved in a nitric-hydrofluoric acid mixture and diluted with water to a fixed volume. The uranium content was determined by measuring its X-ray $L\alpha$ line intensity, ratioing it against a strontium $K\alpha$ X-ray line intensity, and then referencing the ratio to a standard calibration curve to determine the concentration of uranium. Strontium is added as an internal standard to the sample solutions to compensate for the wide range of X-ray absorption by the sample solutions. This method is referred to as the "constant volume" method. The effect of sample weight size on the final analytical results is shown in Table I.

TABLE I. EFFECT OF SAMPLE SIZE USING A FIXED SOLUTION VOLUME. (WITH STRONTIUM AS AN INTERNAL STANDARD.)

<u>Sample (g)</u>	<u>% U Present</u>	<u>% U Found</u>	<u>% Relative Error</u>
0.61	8.50	8.57	+0.8
1.24	8.50	8.55	+0.6
2.00	8.50	8.44	-0.7
2.45	8.50	8.44	-0.7
3.54	8.50	8.37	-1.5

The data in Table I shows that variations of sample weight do affect the relative percent error of the amount of uranium assayed or that the internal standard does not sufficiently correct for X-ray absorption of the sample solution.

The "constant volume" method described above was modified to make the final sample solutions equal to 100 times the metal sample weight, or a constant metal concentration of 1.0 g per 100 g of solution, which will be called the "constant weight" method. A top-loading balance served to check final dilutions on a weight basis. The results are shown in Table II.

TABLE II. EFFECT OF SAMPLE SIZE USING A FIXED SOLUTION WEIGHT EQUAL TO 100 TIMES THE SAMPLE METAL WEIGHT

<u>Sample (g)</u>	<u>% U Present</u>	<u>% U Found</u>	<u>% Relative Error</u>
0.25	8.50	8.49	-0.1
0.40	8.50	8.52	+0.2
1.00	8.50	8.56	+0.7
1.65	8.50	8.50	0.0
1.96	8.50	8.48	-0.2

Because no strontium internal standard was used, the zirconium $K\alpha$ X-ray line intensity was measured to help correct for solution X-ray absorption. The results in Table II show that this method is somewhat better than the constant volume method; however, it failed to give the overall precision and accuracy desired. Tests using strontium or an internal standard did not improve the relative error. The effect of nitric acid on the uranium assay is shown in Table III.

TABLE III. EFFECT OF NITRIC ACID ON THE ANALYSIS OF URANIUM

<u>Grams of HNO₃ in 100g of Solution (g)</u>	<u>% U Present</u>	<u>% U Found</u>	<u>% Relative Error</u>
6.0	8.50	8.50	0.0
12.5	8.50	8.54	+0.5
25.0	8.50	8.68	+2.1
47.5	8.50	8.99	+5.0

The effect of the nitric acid is to change the density of sample solution, which affects the measured X-ray line intensities.

An attempt was made to control the sample solution density by adjusting the amount of nitric acid used, so that it was a constant ratio to the quantity of sample dissolved but still employing the constant weight method. For most samples, the modified method yielded the desired precision and error value sought. However, for some samples it did not. Samples with high surface areas, oxide coatings, and samples in the range of 2 to 4 g caused problems; either by the loss of nitric acid during the dissolution process or because heating on a hot plate was necessary to complete the dissolution process.

Controlling the solution density via the quantity of nitric acid used and taking into consideration the stability of the X-ray intensity measurements, the best precision that can be obtained lies within the range of ± 0.40 to $\pm 0.49\%$ of the amount present. This compares favorably to precisions given by Baechmann⁽¹⁾ of $\pm 0.45\%$ and by Silverman⁽²⁾ of ± 0.42 to $\pm 0.48\%$. How one corrects for loss of nitric acid due to chemical reaction and evaporation during the dissolution of the sample is not clear at this time. If the reproducibility of these losses are constant, then, of course, the optimum relative percent error can be obtained. One can approach this if a fixed sample weight is used in the assay method.

References

1. A. von Baechmann, "Determination of Actinide Elements by X-ray Analysis," Anal. Chem. of Nucl. Fuel, Proceedings of a Panel, Vienna, International Atomic Energy Agency Vienna, 1972, pp 33-44.
2. L. Silverman, W. Hauk, and L. Moudy, "Determination of Uranium Dioxide in Stainless Steels by the X-Ray Fluorescence-Solution Method," Advances in X-Ray Analysis, 1, Plenum Press, N.Y., 1960, pp 271-281; and Analytical Chem. 29, 1762 (1957).

Determination of Erbium in TRIGA Materials (Revised)

D. V. Matutina

Erbium may be determined gravimetrically in turnings of TRIGA meats by precipitation of the oxalate. The erbium is separated from the uranium and zirconium by the formation of erbium fluoride. The fluoride precipitate is filtered off, washed, and wet ashed to remove the fluoride. The residue is dissolved in a minimum of hydrochloric acid and diluted with water. The pH of the solution is adjusted to 1.0 with ammonium hydroxide. A nearly saturated solution of oxalic acid is added to precipitate erbium oxalate which is fired to the oxide at 900°C. Typical precision gives a relative standard deviation of 1%.

Procedure

The turnings are degreased by washing with ether, followed with ethyl alcohol, dried in an oven at 110°C, and cooled to ambient temperature. A 1.0 g sample is weighed into a 250 ml Teflon beaker. Carefully, 10 ml water, 5 ml conc. HNO_3 and 15 ml 48% HF are added to the beaker and covered. To ensure complete dissolution of turnings and precipitation of the erbium fluoride, the solution is warmed. Upon cooling, it is filtered through Whatman #42 filter paper, containing a little filter pulp, and washed several times with water. The filtrate is discarded. The filter paper with precipitate is transferred to a 250 ml beaker. Ten ml of fuming nitric acid is added. The mixture is heated to high temperature on a hot plate, but it is not allowed to go dry as bumping will occur. Five ml of concentrated H_2SO_4 are added and heated to dense white fumes. If the solution turns black, a few drops of fuming nitric acid are added. The solution is heated until colorless. Then it is evaporated to near dryness and allowed to cool. The residue is dissolved in 5 ml conc. HCl, and the solution diluted to 100 ml with water. After adjusting the pH of the solution to 1.0 with NH_4OH , 25 ml of 10% oxalic acid is added. The precipitate is allowed to digest at a low temperature for 1 hr. The erbium oxalate precipitate is collected on Whatman #42 filter paper, containing a small amount of paper pulp, and washed with dilute oxalic acid (2% in 1% HCl). The filter paper with precipitate is transferred to a tared Pt crucible, charred, ignited at 900°C for 2 hr, and then cooled in a dessicator.

The erbium is weighed as Er_2O_3 .

Reference

1. E. M. Salkeld and M. A. Hiatt, "Erbium in TRIGA FLIP Materials," GA-A13536, October 27, 1975, pp 44.

Hafnium in Zirconyl Nitrate Solution by Atomic Absorption Spectrophotometry

D. V. Matutina

Hafnium is determined in zirconyl nitrate solutions by atomic absorption spectrophotometry. The hafnium concentration is determined in order to prepare TRIGA standards for uranium and zirconium analysis by X-ray fluorescence.

A hafnium stock solution is prepared by dissolving 1 g pure hafnium metal in 4 ml 48% HF and diluted to 100 ml. A standard matrix curve is prepared to contain 0.5% HF, 50% sample, and 20% varying concentrations of hafnium. The absorbance is measured at 287 nm in a nitrous oxide acetylene flame system. Sensitivity of this method is approximately 20 ppm hafnium.

VI. MISCELLANEOUS PROCEDURES

Ammonia Determination in Oakenite Detergent

M. A. Hiatt

Ammonia in detergent may be determined by NH_3 specific electrode following steam distillation. The method used for steam distillation was a modified Kjeldahl technique. A blank was distilled using dilute NaOH in place of the sample.

Twenty ml of detergent was placed in a three-necked distillation flask. Deionized water was added to bring the volume up to the steam vent. The system was assembled. Ten ml of 1% H_3BO_3 were added to the condensate trap. Forty ml of 50% NaOH were added to the sample solution. After opening the steam vent, ~80 ml of distillate were collected.

The distillate was made up to a 100 ml volume and transferred to a beaker. Before measurement, the samples as well as the standards were made basic with 1 ml of 25% NaOH. The response was measured by an NH_3 specific ion electrode and the concentration read from a standard curve prepared from NH_4Cl solutions.

Determination of Free Carbon in Cr_{23}C_6 Powder

D. V. Matutina

If material is pure Cr_{23}C_6 , it will dissolve readily in dilute sulfuric acid. If there is any Cr_7C_3 present, it will dissolve upon heating near boiling point. However, any insoluble material may be Cr_3C_2 which is very resistant to H_2SO_4 . Cr_3C_2 dissolves only in boiling perchloric acid. Therefore, to determine the amount of free carbon, an indirect method need be employed. Cr_3C_2 can be oxidized readily to Cr_2O_3 below 1050°C . From this weight of Cr_2O_3 , a back calculation for Cr_3C_2 and free carbon may be made.

The material is dissolved in 25 ml of 20% H_2SO_4 and heated to near boiling for 2 hr. Any insoluble material is filtered onto a tared porcelain crucible with Celite. The crucible and insoluble material are dried for 4 hr

in a drying oven at 115°C, cooled in a dessicator, and weighed as Cr_3C_2 + free C. Then the crucible is transferred to a muffle furnace at 900°C and fired for 2 hr, transferred to a dessicator to cool, and weighed as Cr_2O_3 . The free C may be calculated as follows:

$$\% \text{C}_{\text{free}} = \frac{(\text{Wt } \text{Cr}_3\text{C}_2 + \text{free C}) - \left(\text{Wt } \text{Cr}_2\text{O}_3 \times \frac{2 \text{ Cr}_3\text{C}_2}{3 \text{ Cr}_2\text{O}_3} \right)}{\text{Sample Weight}} \times 100$$

Recovery of Boron in Solutions After Evaporation

L. K. Alfonso and D. V. Matutina

Boric acid solutions may be evaporated to a very small volume without loss of boron if mannitol is present. This is particularly useful when working with low-level boron samples.

Mannitol has no effect on the atomic absorption of boron. However, in the colorimetric determination of boron with carminic acid, the presence of mannitol (1:1) causes a slight enhancement in absorbance. This can be corrected by preparing standards spiked with mannitol.

Colorimetric

<u>B (μg)</u>	<u>Absorbance W/O Mannitol</u>	<u>Absorbance With Mannitol</u>
0	0	0
20	0.514	0.530
40	0.902	0.987
60	1.352	1.404

Atomic Absorption ($\text{N}_2\text{O} - \text{C}_2\text{H}_2$ Flame)

<u>B (ppm)</u>	<u>Absorbance W/O Mannitol</u>	<u>Absorbance With Mannitol</u>
0	0	0
50	0.008	0.008
100	0.015	0.015
200	0.029	0.032

Lithium in Graphite and Boronated Graphite by Atomic Absorption Spectrophotometry

D. V. Matutina and E. M. Knox

Lithium in graphite and boronated graphite may be determined following the oxidation of the graphite with perchloric acid under reflux. The resultant solution is analyzed for lithium on an atomic absorption spectrophotometer at 670.2 nm in an air-acetylene flame system. A reagent blank is run in the same manner as the sample.

The method determines lithium as low as 10 ppb with an accuracy of $\pm 10\%$ relative. No interferences were encountered since reactor-grade graphite should be free of interferences.

Equipment

1. Dissolution Apparatus

1.1 Quartz Erlenmeyer reaction flask, 250 ml (for samples > 5 grams) 24/40.

1.2 Soxlet extractor, Pyrex, accommodation volume about 50 ml.

1.3 Air condenser, Pyrex, Vigreux type with standard taper joint (34/45). Total length 10 inches.

1.4 Hot plate, Corning RC 100, 12" x 12", with remote control.

1.5 Support stand and clamps.

2. Hood, perchloric acid with hanging safety glass and safety window.

3. Quartz beaker, 150 ml with speedy-vap.

4. Atomic absorption spectrophotometer, Perkin Elmer 503 or its equivalent.

5. Balance, analytical; either a single or double pan with capability of weighing to the nearest 0.1 mg.

Reagents

1. Stock lithium standard solution, 100 ppm Li, dissolve 0.9940 g LiNO_3 in deionized water and dilute to 1000 ml volume.
2. Lithium standard solution, 1 ppm Li, pipet 10 ml of the stock solution into a 1000 ml volumetric flask and dilute to volume with deionized water.
3. Perchloric acid, reagent grade, assay 70%.
4. Nitric acid, fuming reagent grade, assay 90%.

Precautions

1. Operator should not physically expose himself to dissolution apparatus while sample is being heated.
2. The addition of more acid should be made only after turning off the hot plate and cooling for 15 minutes.
3. Do not allow sample to go to dryness prior to complete dissolution.
4. No plastic or organic material should be in hood work area.

Procedure

1. Dissolution and Sample Preparation
 - 1.1 Weigh 10 grams of sample into a 250 ml Erlenmeyer flask.
 - 1.2 Add 10 ml fuming nitric acid and 100 ml perchloric acid.

- 1.3 Assemble dissolution apparatus and place assembly on hot plate securing to a support stand.
- 1.4 Set the hot plate dial to achieve 140 - 150°C. Increase the temperature after the first hour to maximum temperature of 180 - 190°C.
- 1.5 Add more (10-20 ml) perchloric acid as needed, along with an occasional drop of fuming nitric acid, until all graphite is destroyed. Oxidation of the graphite is complete when the solution is completely clear.
- 1.6 Turn off hot plate when the acid level in the extractor is approaching the top of the siphon arm.
- 1.7 When at ambient temperature, carefully remove extractor portion and discard acid. All Li remains in reaction flask.
- 1.8 Transfer contents of flask to 150 ml quartz beaker rinsing with de-ionized water. Cover with speedy-vap.
- 1.9 Run blank on all reagents.
- 1.10 Evaporate sample solution and blank solution down to near dryness.
- 1.11 Transfer with de-ionized water to 10 ml volumetric flask.

2. Preparation of Standards

- 2.1 Pipet 0, 1, 5, 10, 25 and 50 ml of lithium standard solution into 100 ml volumetric flasks and dilute to volume with de-ionized water. Concentrations are 0, 10, 50, 100, 250, and 500 ppb respectively.

3. Atomic Absorption

3.1 Instrumental Parameters

Wavelength	670.2 nm
Flame Type	Air-acetylene (lean-blue)

3.2 Aspirate standards, record absorbance readings and plot concentration, ppb vs. absorbance.

3.3 Aspirate blank and sample solution. Dilute sample solutions as necessary. Record absorbance readings.

3.4 Subtract blank absorbance readings from sample absorbance readings and determine concentration of lithium (ppb) in sample solution from standard curve.

Calculations

$$\text{ng/g (or ppb) Li} = \frac{(A) \cdot (B) \cdot (C)}{G}$$

A = volume of sample solution, ml

B = ppb or ng/ml, lithium conc. as read from standard curve.

C = dilution factor, if any, or 1

G = sample wt., grams

Material Balance of Milligram Quantities of Uranium Oxide

D. V. Matutina, H. K. E. Jankel, D. M. Nolan

The purpose of this experiment was to determine if a material balance within 10% on ~mg of U_3O_8 could be obtained. The sample was run for oxygen (LECO oxygen analyzer - Model R016H) first, then the uranium in the residue was dissolved and titrated using ferrous ion reduction method⁽¹⁾.

The original sample handling for oxygen analysis calls for encapsulating the material in a tin capsule and adding nickel as a flux. However, tin interferes in the uranium titration, while a small quantity of nickel does not. To solve the problem, the sample was placed in a capsule or envelope made out of 1/4 x 1/4 in. nickel foil. Preignited carbon black was the only accelerator used. The slope of the O_2 determinator was set at 1.52% using a 10 mg sample U_3O_8 . That is, setting weight at 0.1000 for 10 mg would give $10 \times 1.52\%$ or 15.2% oxygen content for U_3O_8 .

After the oxygen analysis, the residue + graphite crucible + carbon black were transferred to a quartz beaker and fired overnight in a muffle furnace at 900°C. The fired sample was dissolved in 15 ml conc. HNO_3 . The solution was evaporated to <5 ml and transferred to a 400 ml beaker carefully so the final solution, including the "washings," did not exceed 15 ml. The dichromate titration following ferrous ion reduction was done with a 5 ml semimicro buret because of the very low level of uranium present.

Experimental Data

% U found	=	84.04	% O found	=	15.2
		84.35			15.2
		<u>84.92</u>			<u>15.3</u>
$\bar{A}$		84.44	$\bar{A}$		15.23
% U in U_3O_8 pure	=	84.80	% O in U_3O_8 pure	=	15.23
% Error	=	0.4	% Error	=	<0.3
Material Balance:		U	84.44		
		O	<u>15.23</u>		
			99.67		

(1) "Titrimetric Determination of Uranium in Product, Fuel and Scrap Materials After Ferrous Ion Reduction in Phosphoric Acid," New Brunswick Lab Report 252, July 1970.

Phosphorus in Incoloy-800

L. K. Alfonso

A colorimetric procedure for the determination of phosphorous in steel has been successfully applied to Incoloy-800 samples. The determination is based on the formation of phosphovanadomolybdic acid which is soluble in iso-amyl alcohol. The yellow color, which is proportional to the amount of phosphorous present, is very stable and can be measured spectrophotometrically at 460 nm. The procedure is reproducible and involves a considerable saving in time as compared to phosphomolybdic acid to molybdenum blue. The yellow $\text{H}_3\text{PO}_4 \cdot \text{VO}_3 \cdot 11\text{MoO}_3$ complex obeys Beers Law and is of a definite composition as compared to molybdenum blue of nondefinite composition.

An NBS standard 1165 iron ingot, which contains 80 ppm phosphorous, was found to show an average result of 72 ppm.

Sulfur in Anticorrosion Oil Via Sulfur Dioxide Ion Specific Electrode

D. V. Matutina

This method is being adopted for the analysis of sulfur in oil. It involves the combustion of the anticorrosion oil in an oxygen flask fitted with a quartz cup sample carrier. The SO_2 is absorbed in an aqueous solution and measured by a gas detecting SO_2 ion specific electrode⁽¹⁾.

The sample is weighed into a small quartz dish, specially designed to fit the oxygen flask. A strip of low ash black filter paper is dipped in the sample such that one end extends above in order that it can be ignited by infrared ignition. The SO_2 is collected in 100 ml tetrachloromercurate solution⁽²⁾. After burning the material, the flask is cooled to ambient temperature. The solution is filtered through glass wool to remove most of the carbon soot. The flask is washed thoroughly with deionized water. The filtrate is collected in a 200 ml volumetric flask. Twenty ml of SO_2 buffer⁽²⁾ are added. Sulfamic acid, 0.5 g, to destroy any nitrogen oxide that may be present, is added to the same solution, then diluted to volume with deionized water. A reagent blank is prepared in the same manner, less the sample. The SO_2 is

determined using a SO_2 gas-sensing electrode. The "known addition method" is employed using Grans Plot paper with 10% volume correction. The potential (mV) is plotted against the volume (ml) of the standard solution added for 100 ml of original solution.⁽³⁾ The SO_2 concentration may be read directly from the Grans plot. The addition of 1 ml of 1000 ppm SO_2 standard to 100 ml of solution is equal to 10 ppm SO_2 . The potentials are plotted such that for a monovalent element, each major division on vertical axis is 5 mV; each minor division is 1 mV (assuming 58 mV slope). The horizontal axis is for ml SO_2 added. A line is drawn through points plotted and extrapolated to the horizontal axis. The original sample concentration or dilution thereof may be calculated from the intercept.

References

1. J. A. Kreuger, "Use of a Potentiometric Sulfur Dioxide Electrode for Lamp Sulfur Determinations," Anal. Chem., **46**, 1338-1341 (1974).
2. Sulfur Dioxide Instruction Manual - Orion Research Inc.
3. "Know-how on Known Addition," Orion Newsletter, July 1969.

Determination of Titanium and Zirconium in Hydroxides and Oxalates of Thorium Containing Rare Earths

D. V. Matutina and L. K. Alfonso

The presence of large quantities of rare earths in the samples makes dissolution with Thorex solution ineffective. The addition of concentrated sulfuric acid was found to work.

Approximately 0.5 g samples are weighed into a platinum crucible and allowed to digest in 10 ml 8N HNO_3 , 10 ml conc. H_2SO_4 , and 10 ml 48% HF. Upon dissolution, the solutions are fumed to dryness, and the residue dissolved in 30 ml 10N HCl and diluted to 50 ml in volumetric flasks. If necessary, titanium may be kept in solution with 3 to 5% H_2O_2 . Titanium may be analyzed employing an atomic absorption spectrophotometer at 365 nm in a nitrous oxide-acetylene flame system. Sensitivity is $\sim 1 \mu\text{g}$ titanium per gram sample.

Zirconium is analyzed spectrophotometrically⁽¹⁾ following solvent extraction of zirconium-BPHA (N-benzoylphenyl-hydroxylamine) chelate into chloroform. Thorium does not extract from 9M HCl. The extracted zirconium is measured

colorimetrically as the zirconium-Arsenazo III (1, 8 dihydroxynaphthalene - 3,6 - disulfonic acid - 2, 7 bis [(azo-2)-phenylarsonic acid] complex at 665 nm. Sensitivity is ~0.5 μg zirconium per gram sample.

(1)"Determination of Trace Elements in Uranium Compounds - Specification Analyses," Goodyear Atomic Corp., GAT-507 (Chemistry TID 4500).

Enhancement of Zirconium Signal on Atomic Absorption Spectrophotometer

D. V. Matutina

Zirconium absorption is enhanced by the presence of HF. Zirconium is a highly refractive element. The route to free atoms in the flame (nitrous oxide-acetylene) is probably through the oxide. The presence of fluoride ion inhibits the formation of the oxide, forming instead a stable complex fluoro-acid which is more easily decomposed at the high temperature of the flame. Slavin, et al.⁽¹⁾ however experienced zirconium enhancement in the presence of HCl and NH_4Cl . The ammonium ion most probably helps in the suppression of ionization in the flame. They did not explain how Cl^- enhances absorption, but it probably behaves in the same manner as does F^- .

Zirconium determinations in the past were done in solutions containing 0.4% to 2% HF. Standard solutions were prepared by dissolving zirconium metal in HF. The final dilution was such that the solutions were in 2% HF. Matrix curves for sample solutions were prepared by adding:

1 ml of 2% HF (as blank)

1 ml of desired standard solutions (all in 2% HF)

in 5 ml volumetric flasks and diluting to volume with solutions being analyzed for zirconium. Assuming that F^- is absent in the sample, the concentration of F^- would be ~0.4%.

Zirconium standard solutions in 4% NH_4Cl - 2% HF were prepared. There was a marked enhancement on absorption.

Zr, ppm	Absorbance (4% NH ₄ Cl - 2% HF)	Absorbance (2% HF)
40	0.020	0.015
100	0.050	0.037
200	0.100	0.080
300	0.150	0.129
400	0.190	0.168

However, for solutions which are high in Th, the presence of too much F⁻ results in the precipitation of ThF₄. The problem was to find a matrix solution which would enhance the sensitivity of the Zr absorption in the absence of F⁻. It was found that solutions containing 4% NH₄Cl exhibit almost the same magnitude of enhancement as those solutions with 4% NH₄Cl - HF. From a stock solution which contained 10,000 ppm Zr in 2% HF, dilute standards (50, 100, and 200 ppm Zr) were prepared. All dilutions were done in 4% NH₄Cl.

Zr, ppm	Absorbance (4% NH ₄ Cl)	Absorbance (4% NH ₄ Cl - 2% HF)
50	0.024	0.025
100	0.057	0.050
200	0.122	0.100

Limit of sensitivity = 10 ppm Zr equivalent to 1% absorption.

(1) Atomic Absorption Spectroscopy, Walter Slavin, 1968, p.p. 178, 180-188.

X-Ray Fluorescence Measurement of Uranium-Thorium Ratio

C. L. Chaney

A rapid X-ray fluorescence method was developed to determine the U-to-Th ratio in samples containing these mixed oxides. The method was used to assist in the spectrographic analysis of these mixed oxides.

Depending upon the U-to-Th ratio, one of three spectrographic procedures is employed to determine the impurity content of the mixed oxide samples.

Ratio: U/Th	Spectrographic Procedure
0.050 to 0.500	Analysis of impurities in ThO_2 - Method SQ-12
0.600 to 2.500	Analysis of impurities in 1:1 ThO_2 - U_3O_2 - Method SQ-10
3.0 to >60	Analysis of impurities in U_3O_8 - Method SQ-11

The ratio is determined by the following formula:

$$\text{U/Th} = \frac{(\text{U}) (0.132)}{(\text{Th})(0.151)}$$

where (U) equals uncorrected U $\text{L}\alpha$ 26.2° 2θ X-ray intensity, (Th) equals the uncorrected Th $\text{L}\alpha$ 27.44° 2θ X-ray intensity, 0.132 is the correction for the background contributions of Th on the U X-ray intensity, and 0.151 is the correction for the background contribution of U on the Th X-ray intensity.

VII. ELECTRON MICROPROBE

T. H. West Jr.

The electron microprobe laboratory provided analytical support to many programs at GAC during the year. Programs for which microprobe samples were analyzed included the Fort Saint Vrain reactor project, HTGR fuel development programs, the HTGR spent fuel reprocessing project TRIGA reactor fabrication, medical products, and miscellaneous metall

Brief summaries of some of the work in each area are given below.

Fort Saint Vrain Reactor

Plugging, corrosion, formation of deposits and metal to metal incompatibilities were studied with the probe on components such as capillary tubes from moisture monitors, Bourdon tubes from the pressure control system for reserve shutdown, and steam generator parts.

HTGR Fuel Development

Much work was done in support of the fuel particle program. The probe provided much needed insights into the doped fuel kernel fabrication and high temperature behavior of these fuel particles. In the alloyed pyrocarbon coating program alone, over sixty batches of particles were analyzed during the year.

Migration of fuel and chemical attack of fuel particle coatings were studied on fuel particles subjected to long term heating in a steep thermal gradient.

Twelve batches of irradiated fuel were studied. Some of the mounts analyzed in 1975 ran over 40 R/hr ($\beta + \gamma$) at 2 inches. Because most of the activity was from low energy β 's, it was possible to analyze these samples in our unshielded probe. The first irradiated resin kernel fuel was studied in 1975. Once again, valuable insights into particle behavior

during irradiation were provided, most of which are unobtainable by other methods of analysis.

HTGR Fuel Reprocessing

Problems with agglomeration of fuel particles in the burning step and in bench scale research experiments were investigated with the probe.

TRIGA Fuel Fabrication

Several problems associated with changes in fuel fabrication methods were studied. The probe provided information on problems with cracking of the fuel, erbium distribution, and formation of metallic blisters on the exterior of the fuel rods. Probe data was also used in the investigation of a problem occurring in an analysis of TRIGA fuel by another instrumental technique.

Fusion

Effects of ion bombardment (including hydrogen and helium ions) on materials was studied by means of the probe. Determinations of composition and thickness of very thin (several hundred to several thousand angstroms) coatings were made in an area bombarded by protons. Two thickness measurement techniques were combined to perform the measurement. Energy loss measurements of the impinging electron and X-rays from the substrate under the coatings were both used to provide the necessary range of depth measurement.

Miscellaneous

About sixty metallurgical specimens from in-house metallurgical testing and fabrication programs were analyzed. These came from such sources as the welding laboratory, corrosion experiments, diffusion experiments, and the plasma spray coating program. About forty pieces of Incoloy 800 were analyzed for sulfur distribution on a micro scale to

provide information used to solve a contamination problem incurred in the drilling of hundreds of holes in a steam generator tube support plate. Many of the corrosion experiment studies were micro analyses of the substructure of thin scales formed on the surfaces of metals.

Routine, as well as special problem, analyses were performed for the Medical Products Division. These analyses included silicon distribution in silicon alloyed pyrocarbon coated heart valve components.

Investigations of unusual events, usually from laboratory experiments, were conducted. These included identification of deposits formed in laboratory and pilot plant processes, and corrosion of printed circuit boards.

VIII. INFORMATION MEETINGS

Phase II HTGR Interlaboratory Comparison Program Information Meeting

The analysis of the HTGR fuel has proven to be a challenge to the analytical chemist. Failure to reach reasonable agreement between laboratories on the analysis of HTGR fuel led to the organization of a round-robin by the New Brunswick Laboratory. The results of the first round-robin on the analysis of TRISO-coated U-Th carbide fuel particles was reported in NBL-269, November 1973. A second round-robin was run on both BISO and TRISO-coated Th-U carbide particles over a period of 10 months.

An information meeting on this second round-robin was held at GAC November 3-4, 1975. An evaluation of this program has been published as NBL-279, June 1976. The agenda of the information meeting follows.

PHASE II HTGR INTERLABORATORY COMPARISON PROGRAM INFORMATION MEETING, NOVEMBER 3-4, 1975

General Atomic Company
La Jolla, California

AGENDA AND PROGRAM

Monday, November 3

0900 Welcome

General Atomic Company
ERDA, New Brunswick Laboratory (NBL), C. D. Bingham

0915 Introduction of Participants and Observers

0920 Review of Background of HTGR Interlaboratory Comparison Program

C. D. Bingham (NBL)

1000 Description of Sample Materials, Characterization of Reference Materials, and Sample Preparation for Interlaboratory Distribution

N. M. Trahey (NBL)

1030 Methodology for Sample Treatment and Analysis for Uranium (Note: Thorium measurement procedures may be discussed).

G. R. Waterbury (LASL)
D. A. Costanzo (INL)
H. Zibulsky (NBL)
D. V. Matutina (GAC - Chemistry)
E. C. Snooks (GAC - QC Laboratory)

1330 Nondestructive Assay for ^{235}U Content, Including Details of System Calibration

H. O. Menlove (LASL)

1430 Phase II Program Design and Presentation of Results

J. T. Bracey
C. D. Bingham

Tuesday, November 4

0900 Discussion of Results

Participants and Observers

1030 Future Needs, Problem Areas, Phase III

Participants and Observers

1130 Safeguards Implications of Phase II

ERDA/DSS
NRC
GAC

1330 Tour of GAC Facility

HTGR Recycle Information Meeting

An information meeting on the HTGR Recycle Program was held at GAC November 5-6, 1975. Individuals from ORNL, Allied Chemical-Idaho Falls, and GAC participated. The process being developed in the GAC recycle pilot plant was the main topic discussed on the first day. Analytical Chemistry was the subject of the second day's discussions. The agenda for the meeting follows:

HTGR RECYCLE INFORMATION MEETING - PROCESS

November 5, 1975

Glen Benedict, presiding

9:00 a.m.	Head-End Operations - Crushing	D. Emrick, GAC
9:30	Head-End Operations - Burning	W. Rickman, GAC
10:00	Aqueous Separations - Leaching SX Feed Preparation	G. E. Benedict, GAC
10:30	Coffee Break	
10:45	Aqueous Separation - Solvent Extraction	G. E. Benedict, GAC
11:15	Aqueous Separation - Waste Processing	D. T. Pence, GAC
11:45	Lunch	
1:00 p.m.	Inspection - Refabrication	D. A. Costanzo, ORNL
1:30	Discussion	Leader: G. E. Benedict, GAC
2:30	Tour, Recycle Area	

HTGR RECYCLE INFORMATION MEETING - ANALYTICAL

November 6, 1975

A. W. Mosen, presiding

9:00 a.m.	Thermometric Titration - Free Acid	R. Hower, GAC
9:30	HTGR Analytical Methods Development---A General Survey	J. R. Delmastro Allied Chemical
10:00	X-Ray Fluorescence Methods for HTGR	W. A. Ryder Allied Chemical
10:30	Coffee Break	
10:45	Overview of Analytical Work and Development	D. A. Costanzo ORNL
11:45	Lunch	
1:00 p.m.	Discussion of Current Analytical Problems	Discussion Leader: A. W. Mosen, GAC