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DIRECT ANALYSIS OF PLUTONIUM METAL FOR GALLIUM, IRON, AND NICKEL BY ENERGY DISPERSIVE X-RAY SPECTROMETRY *

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ABSTRACT

An x-ray secondary target method for routine determination of gallium, iron, and nickel in plutonium metal is described that has significant advantages over wet chemical analysis. Coupons requiring minimal preparation for analysis are produced as a breakaway tab on the plutonium ingot. All three elements are determined on the same coupon. Gallium is determined using an arsenic secondary target followed by iron and nickel using a zinc target. The analysis times are 5 minutes for gallium and 15 minutes for the combined iron and nickel. The method of analysis was evaluated in the range of from 0.5 to 1.5% gallium. Iron was investigated over the range of 67 to 3000 ppm and nickel from 64 to 110 ppm.

INTRODUCTION

The room temperature crystal structure of pure plutonium (Pu) metal is monoclinic. Since monoclinic metals are difficult to machine, one alternative used is to stabilize the high temperature face-centered cubic phase of plutonium by addition of gallium (Ga).

Historically, analysis of Ga at the Rocky Flats Plant has been done by two wet chemistry methods. The first analytical method, and also the one being used currently, is based upon spectrophotometric measurements. In this method which is the same as the one used at Los Alamos National Laboratory, the 8-hydroxyquinolate of Ga is prepared and extracted by $CHCl_3$. The

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solution is buffered with citric acid and the results calculated from optical densities measured on a spectrophotometer. For a time in the mid-1960's a volumetric determination based upon first separating the Pu from the Ga by ion exchange was used. An excess of EDTA was added to the Ga fraction and back titrated with $Th(NO_3)_4$. Due to the difficulty in determining the titration end point, the method was eventually discarded in favor of a return to spectrophotometric measurements.

The iron (Fe) and nickel (Ni) analyses likewise have been difficult over the years. At first wet chemical analysis and emission spectroscopy were used. Atomic absorption is being used at the present time.

Since the weighing of samples and subsequent wet chemistry must be done in gloveboxes using at least 25 mil thick lead gloves, the methods noted above are slow and require especially skilled personnel. Therefore, in recent times a considerable effort has been made to establish reliable XRF methods for determining these elements at the Rocky Flats Plant.

Historically, application of XRF to Ga analysis is not new.[1] Also, an EDS device for determination of Ga in bulk sized Pu parts was built by the authors of this paper. Both of these methods used an Yttrium (Y) secondary target.

TARGET SELECTION

The importance of choosing the proper secondary target cannot be over emphasized. The energy of the K_α lines from the secondary target <u>must</u> just barely exceed the K_{ab} edge of the element being analyzed. After discussion with Kevex Corporation personnel, a zinc (Zn) target was selected for Fe and Ni. An arsenic (As) target was selected for Ga. A comparison of counting efficiency showed that one hundred thousand counts could be accumulated in the Ga peak in five minutes using the As target while the Y target took twenty minutes for the same number of counts.

EQUIPMENT USED

A Kevex 810A secondary target system with computer control of the target and sample was used. A 3.5 Kw molybdenum target was chosen. A new type amplifier was selected for the lithium drifted silicon detector with the capability of discriminating against all radiation above and below the region of interest. All of the data in this paper was taken with a Tracor 880 Pulse Height Analyzer System using direct memory access for counting and containing a Digital Equipment Corporation 11/04 computer with 28 K words core. All spectral data was stored on floppy disks.

Appropriate software for sample changing and quantitative analysis was generated in-house by the authors.

GALLIUM

For production support, the samples for analysis are disks 1-1/4" in diameter and 1/8" thick which will be generated as a break away tab on the Pu ingot. For samples requiring only Ga analyses, minimal polishing is necessary before wrapping in mylar film to contain spread of Pu contamination. When Fe and Ni results are desired, polishing to about 600 grit is necessary. Due to the very high mass absorption coefficient of Pu it is necessary to achieve as high a through put of counts as possible since system dead time from radioactive decay alone may run 20%. This is accomplished by operating the tube at 30 Kv and 70 mA, using a large diameter collimator, inserting a 4 mil polyethylene post filter, and adjusting the amplifier window to the edges of the Ga Kα and Pu M lines. A count time of five minutes was used for all Ga data collection (See Figures 1 and 2).

A ratio of the counts in the Ga Kα lines to the counts in the Pu Mαβγ complex is plotted against known values of standards determined by wet analysis. The computer accomplishes this calibration using regression analysis. Results of typical calibration calculations are shown in Table 1. The high correlation coefficient proves that the calibration line is linear.

The standard deviation was determined (Table 2) and found to be comparable to wet analysis at the 1% Ga level. Since Pu oxidizes rapidly, a coupon was allowed to oxidize one week and compared with a freshly polished coupon from the same ingot. (See Table 3).

Clearly, oxide formation on a standard will not be a significant error if calibration coupons are polished on a weekly bais. Since a high and a low standard are counted with each tray of samples, daily polishing would result in a shorter useable lifetime for the expensive standards.

To test the sensitivity of the analysis to surface conditions, two coupons from the same ingot were polished with different size grits. The spread of the means between a 240 grit and a 600 grit polish demonstrates a low sensitivity to surface roughness. (See Table 3).

IRON AND NICKEL METHOD

Samples which also need Fe and Ni must be polished with the utmost care using a final step of 600 grit or finer. Polishing materials should be analyzed to find sources that are as low as

possible in Fe. Excessive pressure on the sample during polishing can cause embedding of Fe containing materials into the soft Pu surface.

A ratio of the counts in the Pu M-N doublet just above the Pu Mαβγ complex is plotted against known values of standards determined by atomic absorption analysis. Fifteen minutes counting time was used. The regression line (Table 1) is linear as shown by the correlation coefficient. Typical precision results (Table 2) are comparable to atomic absorption standard deviations for the range of interest.

Nickel standards were very difficult to find with a satisfactory range of values. However, a limited range curve which covers our current levels in samples was constructed (Table 1). The correlation coefficient indicates a satisfactory degree of linearity.

CONCLUSION

An x-ray spectrometrix method for analysis of Ga, Fe and Ni has been developed that has significant advantages over current practice. No wet chemistry steps are involved which means that the analysis can be done in a plutonium foundry area if desired. Weighing is not required and less skilled personnel are needed. Also less elapsed time per sample along with less actual work time per analysis is taken than with current wet chemistry methods.

REFERENCES

1. P. L. Wallace, P. K. Hosmer, J. C. Walden, and W. L. Haugen, "The Direct Measurement of Ga in Binary Pu-Ga Alloys Using X-Ray Spectrometric Techniques", X-Ray Spectrometry, Vol. 7, No. 4, pp. 212, 1978.

TABLE 1
Regression Analysis Data

	Ga		Fe		Ni	
	Ratio	Wt. %	Ratio	PPM	Ratio	PPM
1.	.27672	.544	.06629	67	.059709	64
2.	.53942	.998	.18983	267	.07308	81
3.	.82279	1.507	.36902	540	.092426	87
4.			.62983	1070	.098982	99
5.			1.7261	3000	.11987	110
(a)	.052676		-77.583		22.878	
(b)	1.7639		1781.8		735.50	
(c)	.99994		.99955		.97785	

(a) Y intercept
(b) Slope
(c) Corr. Coef.

Table 2

Standard deviations for ten repeditive analyses on the same coupon by EDS.

	WEIGHT PERCENT Ga	PPM Fe	PPM Fe
	.99800	243	504
	.99995	237	527
	1.00522	272	501
	1.00952	232	543
	1.00528	234	548
	1.01876	233	514
	1.00749	256	518
	1.00730	244	528
	1.00257	233	519
	1.00316	247	527
MEAN =	1.005725	243	523
STD. DEV. =	.005773	12.76	15.09
KNOWN VALUE -	.998		

Table 3

	OXIDATION TEST*		SURFACE TEXTURE TEST*	
	WITH OXIDE	CONTROL	240 GRIT	600 GRIT
	.55232	0.54401	.54378	.54400
	.53975	0.54642	.54748	.54165
	.55199	0.54285	.53768	.54355
	.54798	0.54729	.53934	.54439
	.54969	0.55652	.53615	.54248
	.54563	0.54744	.53074	.53817
	.54552	0.54508	.53548	.53774
	.56182	0.55336	.54267	.54500
	.54713	0.54794	.53754	.54353
	.54851	0.54089	.53995	.54127
MEAN =	.54903	0.54719	.53908	.54136
STD DEV. =	.0057599	.0047295	.004735	.002682
DIFFERENCE = (OF MEANS)	.001844		.003279	

*Results of 10 repeditive measurements on 2 coupons from the same ingot.

Corrected on PMT

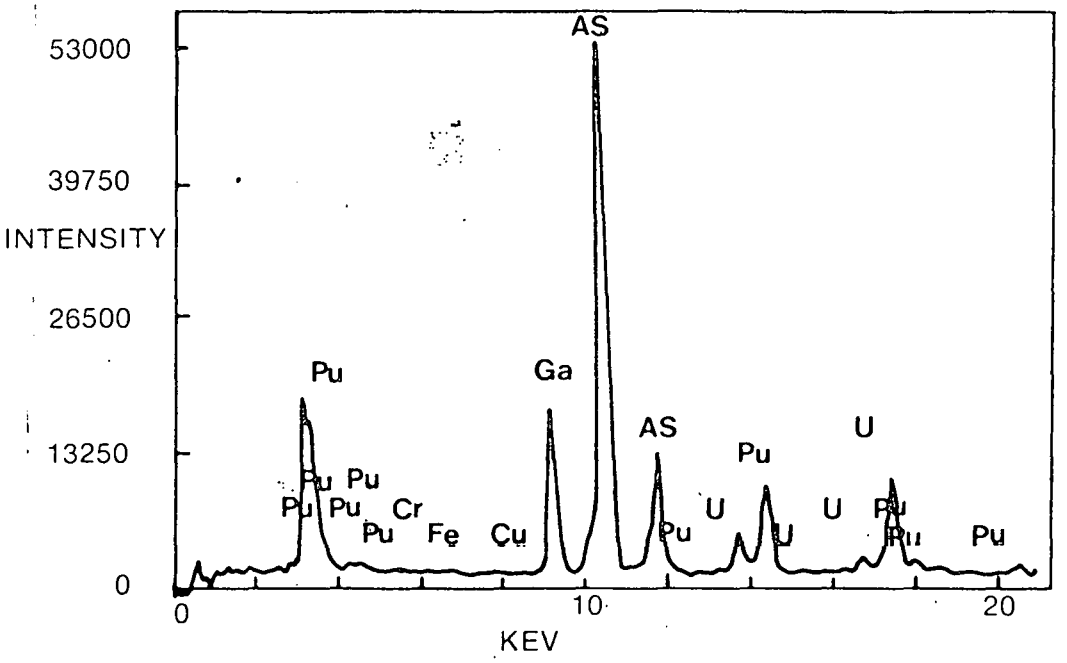

Figure 1. Before insertion of the post filter and amplifier window. (1% Ga in Pu using an As secondary target.)

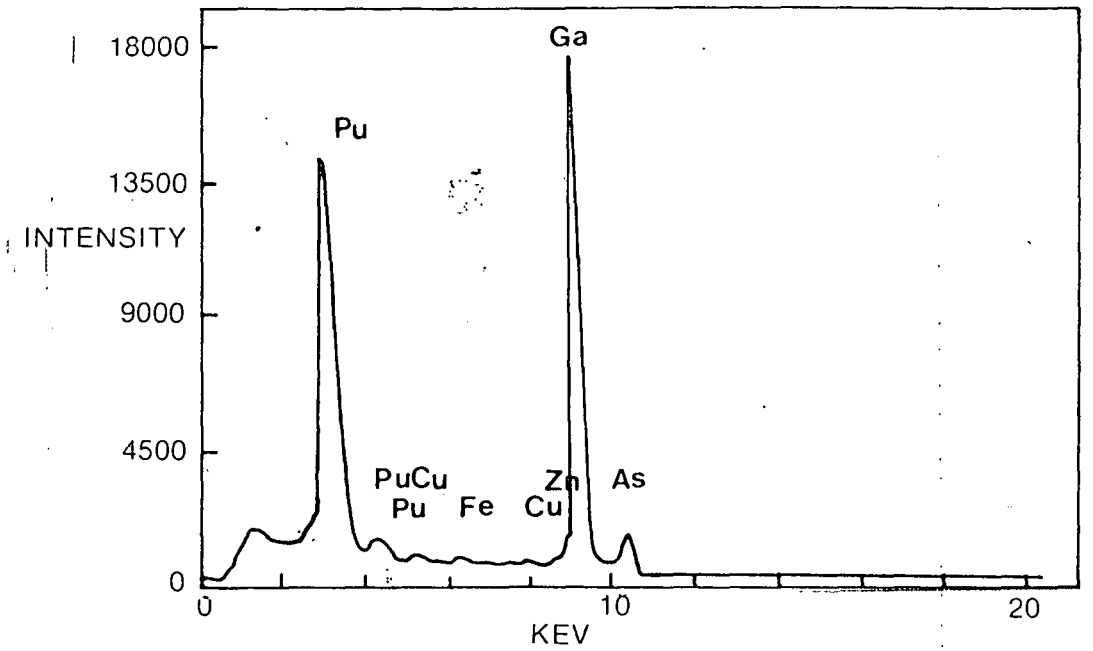

Figure 2. After insertion of the post filter and amplifier window.

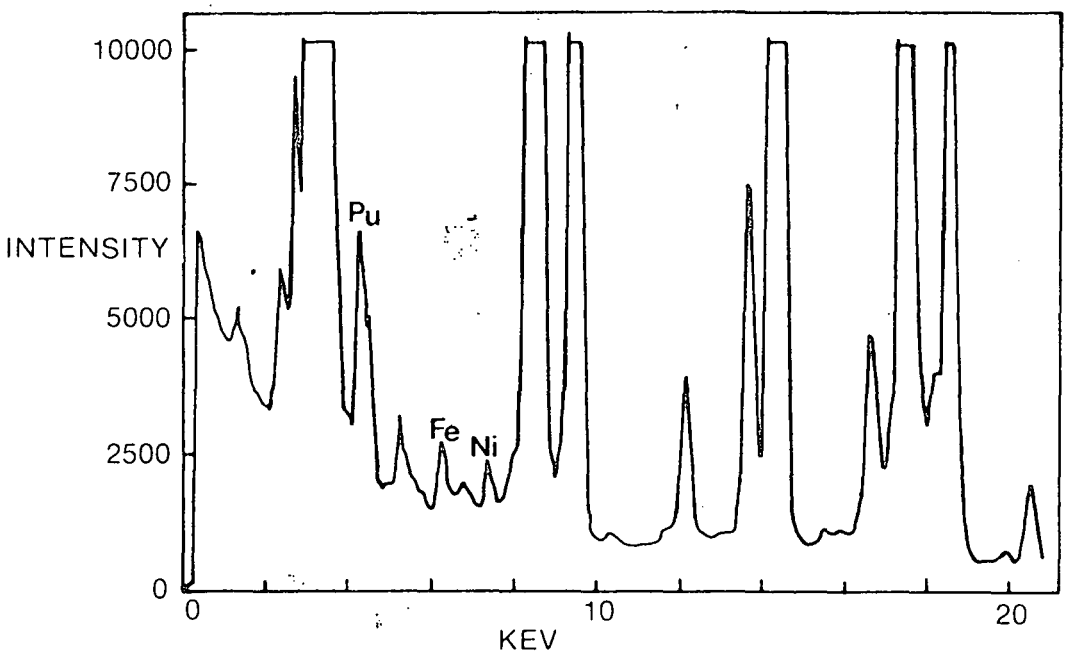

Figure 3. 110 ppm Ni and 205 ppm Fe in Pu metal.