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Sample Sampling of a Plutonium Metal Button

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MULTIPLE SAMPLING OF A PLUTONIUM METAL BUTTON

by

Lawrence A. Bruckner

ABSTRACT

Fifteen samples were taken from a plutonium metal button and submitted for chemical and isotopic analyses. The button was found to be quite homogeneous with respect to the isotopes and, if one sample was omitted, with respect to plutonium. There was some indication of americium segregation. The analytic techniques produced values whose variances were consistent with the currently used variance estimates for all the isotopes and for plutonium, but not for americium.

I. INTRODUCTION AND SUMMARY

A plutonium metal button was received as part of shipment HRA-AUA-147 (dated 9/24/81). Fifteen samples were taken from the button, blinded, and submitted for chemical and isotopic analyses. Except for ^{238}Pu, the isotopes were measured by mass spectrometry. The 238-isotope was measured by radiochemistry, and americium by radioanalysis.

The plutonium content was estimated by chemical analysis for each of the 15 samples. Also, a single wattage was obtained for the button by calorimetry. Then the isotopic and americium values were used with the wattage to provide another 15 estimates of the plutonium content. This data, which was taken from the memo of Wagner and Torres[1], is shown in Table I. (The americium values are in parts per million (ppm) and the isotopic values are given as percents.)

Sections I.A-C present some conclusions that can be drawn from the reported data.

A. Button Homogeneity

1. The button appears to be quite homogeneous with respect to the isotopes and with respect to plutonium concentration if the "skin" sample is removed (see Sec. I.B,3, below).

2. There is some indication of americium segregation. For example, pieces chiseled from the surface appear to have a lower americium concentration than pieces drilled from the interior.

B. Analytic Procedures

The analysis was performed on 15 distinct samples from one button. Hence, the following includes both sampling and analytic error.

1. The variances of the isotopic determinations were smaller than the estimates currently used. Except for ^{242}Pu, the differences were significant at the 5% level.

2. The variance of the americium determinations was significantly larger than the estimate currently used for analytic uncertainty alone. This may be due to americium segregation in the button or to greater-than-expected variations in the analytic procedures.

3. The variance of the chemical assay percents was smaller than the currently used estimate. One sample had a value which was a statistical outlier. This might be due to the presence of skin, but could be due to analytic procedures (see Sec. I.A,1).

4. The averaging of two cuts to get the isotopic percents reduced analytic error as it should. (This is not discussed in the text but the data is available on the chemical analysis report.)

TABLE I

RESULTS OF ISOTOPIC AND CHEMICAL ANALYSIS

I.D.	^{238}Pu (%)	^{239}Pu (%)	^{240}Pu (%)	^{241}Pu (%)	^{242}Pu (%)	Am (ppm)	Pu[a] (g)	PCT[b]	Pu[c] (g)
215	0.0080	94.085	5.685	0.2015	0.0215	1320	2140	98.81	2150
006	0.0082	94.095	5.675	0.1995	0.0200	1330	2139	98.68	2147
007	0.0081	94.080	5.690	0.2020	0.0195	1320	2139	98.63	2146
010	0.0082	94.080	5.690	0.2010	0.0205	1370	2134	98.68	2147
011	0.0085	94.090	5.680	0.2005	0.0200	1390	2131	98.68	2147
012	0.0083	94.090	5.680	0.2035	0.0205	1370	2134	98.71	2148
014	0.0083	94.080	5.690	0.2010	0.0200	1360	2135	98.68	2147
015	0.0083	94.090	5.680	0.1990	0.0195	1360	2134	98.70	2148
016	0.0083	94.085	5.685	0.2000	0.0205	1350	2134	98.13	2135
017	0.0084	94.100	5.670	0.2000	0.0200	1360	2135	98.71	2148
018	0.0086	94.090	5.685	0.1985	0.0200	1390	2135	98.70	2148
019	0.0079	94.085	5.685	0.2035	0.0215	1320	2141	98.65	2147
020	0.0088	94.095	5.680	0.1995	0.0190	1330	2136	98.66	2147
021	0.0081	94.090	5.680	0.1995	0.0200	1310	2141	98.49	2143
022	0.0079	94.085	5.680	0.2030	0.0220	1300	2143	98.80	2150
$\bar{x}$	0.00826	94.088	5.682	0.2008	0.0203	1345	2137	98.65	2147
s	0.00025	0.00592	0.0056	0.0016	0.0008	28.8	3.5	0.1604	3.6
$s/\bar{x}$	0.03028	0.00007	0.00099	0.0080	0.0404	0.021	0.002	0.0016	0.002
s_1[d]	0.0013	0.02	0.02	0.005	0.0011	10.00	10.5	0.2	4.5

[a] Pu as determined by calorimetry.

[b] PCT is the plutonium percent as determined by chemical assay.

[c] Pu as determined by chemical assay.

[d] Currently used estimate (reflects precision and accuracy).

C. Calorimetry vs Chemical Analysis

1. The plutonium values as estimated by these two methods appear statistically independent.

2. The data suggests that perhaps chemical assay gives higher plutonium values then calorimetry. Because only one wattage reading was obtained, bias cannot be further investigated.

These conclusions are based on the analysis of the 15 samples taken from one button. Whether or not these results will hold for other buttons or other plutonium materials is not known. The locations on the button from which the samples were taken are shown in Fig. 1. Each location is tagged with the sample I.D. number, depth from the surface, plutonium percent as determined by chemical assay and the Am value in parts per million.

The last rows of Table I give the mean ($\bar{x}$), standard deviation (s) and coefficient of variation ($s/\bar{x}$) of the sample data and the estimate (s_1) of the population standard deviation currently used in limit of error calculations. It should be noted that the calculated variances reflect sampling and analytic errors, including some short-time, day-to-day variation. The usual estimates include long-term variation and accuracy as well. Except for americium, the calculated variances are all smaller than the current estimates. The question of why the americium data has such large variability will be discussed in Sec. IV.

Statistical relationships among the variables will be explored in Sec. II and III. Analysis of the chemical assay results is presented in Sec. V and a comparison of the plutonium estimates from calorimetry and from chemical assay is given in Sec. VI. The final section, Sec. VII, contains some concluding remarks.

As indicated in Fig. 1, sample 016 includes skin. The data indicates that this sample is remarkable only in that its chemical assay value, 98.13% plutonium, is a statistical outlier. The isotopic and americium values are not unusual. Thus, in the following sections, unless otherwise noted, all 15 samples will be considered.

For ease of expression in equations, tables, and references to the data, the normal isotopic notation will be replaced by a same-line notation--thus, P239 will be used in place of ^{239}Pu. Also, Pu will be used for plutonium, and Am will be used for americium.

II. STATISTICAL RELATIONSHIPS AMONG VARIABLES

The correlations among the variables of Table I are presented in Table II. The Pu value as determined by chemistry was omitted because it is obtained directly from the net weight (2185 g) and the chemical assay percent, PCT. Thus, Pu refers to the plutonium content as determined by calorimetry.

Am is highly negatively correlated with Pu, and the variation in Am accounts for 84% of the variation in the Pu values. (Recall that the wattage is fixed.) P238 is also negatively correlated with Pu although P242 is positively correlated. Most of the isotopes are negatively correlated among themselves, which is expected as the isotope percentages sum to 100.

When sample 016 is excluded from consideration, the correlations change little except that the sample correlation coefficient between P242 and PCT rises to 0.51, and the correlation between PCT and Pu drops to - 0.03.

In order to determine which isotopes are the most influential in the estimation of the amount of plutonium in this button, multiple linear regression of Pu on the isotopes and Am was employed. If all 15 samples are considered,

$$Pu = 2254 - 0.10\ Am - 924\ P242 \qquad (r = 0.88,\ se = 1.31)$$

where r is the coefficient of determination and se is the standard error of the regression.

Without sample 016, this becomes

$$Pu = 2250 - 0.10\ Am - 1004\ P242 \qquad (r = 0.91,\ se = 1.14).$$

In both cases, the partial correlations of Pu on the remaining isotopes are not significantly different from zero. Plots of Pu vs Am and Pu vs P242 are shown in Figs. 2 and 3 respectively. The individual regression lines are also drawn.

It is interesting to note that P238, which contributes more to the wattage determination than P242, is not as useful as P242 in predicting the amount of plutonium present in this button once the Am is accounted for. This is explained by the relatively high positive correlation between Am and P238. Once Am is in the regression equation, most of the effect of P238 is also included. Hence, given the wattage, the plutonium content is almost completely determined by the Am value.

III. THE ISOTOPES ^{239}Pu AND ^{241}Pu

The US Department of Energy regulations require that the combined ^{239}Pu and ^{241}Pu weights be reported. Table I gives the mean and standard deviation of the individual isotopes. The mean of the sum is easily obtained as the sum of means, but the variance of the sum involves the covariance between the isotopes. Rather than compute the covariance, it is easier simply to add the P239 and P241 values and compute the variance of the summed values. This results in a value of 2.889×10^{-5} for the variance of the 15 sample values. As with the individual isotopes, this calculated value is much smaller than the current estimate of the variance, 0.0004.

TABLE II

CORRELATION MATRIX

	P238	P239	P240	P241	P242	Am	PCT	Pu
P238	1.0000							
P239	0.4972	1.0000						
P240	-0.2081	-0.9225	1.0000					
P241	-0.6234	-0.4563	0.2519	1.0000				
P242	-0.7388	-0.3463	0.1084	0.6568	1.0000			
Am	0.6277	0.1300	0.0279	-0.3297	-0.3608	1.0000		
PCT	-0.0847	0.1033	-0.1429	0.2491	0.1695	0.0018	1.0000	
Pu	-0.7119	-0.1494	-0.0024	0.3660	-0.5195	-0.9145	0.1819	1.0000

NOTE: For a sample size of 15 (14), a sample correlation coefficient is significantly different from zero at the 5% level if it exceeds 0.51 (0.53) in absolute value.

Frequently in treating shipments of plutonium-bearing material, the approximation: Fraction (P239 + P241) = 1 - Fraction (P240) is used. A plot of P239 vs P240 is displayed in Fig. 4. The regression line is

$$P239 = 99.60 - 0.97\ P240 \quad (r = 0.85,\ se = 0.0024).$$

As P241 is about 0.2%, this becomes

$$P239 + P241 = 99.8 - 0.97\ P240\ ,$$

which supports the above approximation.

IV. AMERICIUM

The americium values for the 15 samples range from 1300 to 1390 ppm with a mean of 1345.3 and standard deviation of 28.75 ppm (2.8×10^{-5}). The currently used estimate for this standard deviation is about 1.0×10^{-5}). The much larger value obtained in this experiment might be attributed to sampling error (americium segregation), or to analytic variation.

Figure 1 indicates that three of these samples were chiseled from the button; the others were drilled from the interior. The average Am value for the 3 chiseled pieces was 1313 ppm, but the average of the remaining 12 samples was 1353. The probability of this difference occurring if the average Am values were the same is less than 0.03. This suggests that the americium is segregated in this button. Also, if the points in Fig. 2 are labeled by the sample I.D. number, it is apparent that many of the Am values are clustered by drilling location.

Table III shows the Am values by date of analysis. The two values obtained on November 4, 1981, are low in comparison to the values obtained on November 2 and 3. It is possible that these two low values occurred on the same day (November 4) just by chance. But because this would happen less than 10% of the time, it seems reasonable to at least entertain the <u>possibility</u> of significant day-to-day variations in the determination of americium.

A random effects model was used to estimate the day-to-day variation, if any. The estimates for the between and within-day variances are given at the bottom of Table III. Unfortunately, the within-day variances are so large that one can not reject the hypothesis of no day-to-day variation. More data is needed to investigate this further.

Thus, although it is not feasible to attempt to separate the effects of segregation and of different-day analyses with this limited data, it does appear that there is a possible day-to-day effect as well as segregation.

TABLE III

AMERICIUM VALUES (ppm) BY DATE OF ANALYSIS

	Nov. 2	Nov. 3	Nov. 4
	1330	1320	1320
	1320	1370	1300[a]
	1370	1360	
	1390	1360	
		1350	
		1360	
		1390	
		1330[a]	
		1310[a]	
$\bar{x}$	1352.5	1350.0	1310.0
s	33.0	25.5	14.1
$s_{\bar{x}}$	16.5	8.5	10.0

Variance Estimates from Analysis of Variance--Random Effects Model.

Variance: Between days - 1.76×10^{-10}

Within days - 7.23×10^{-10}

Total - 8.99×10^{-10}

[a]Am values from chiseled pieces.

V. CHEMICAL ASSAY VALUES

The 15 samples give values of 98.13 to 98.81% for plutonium as determined by chemical assay. As mentioned earlier, the low value 98.13% is for the sample that included skin (016) and is a statistical outlier.* If this sample is removed, the remaining data have the following statistics:

Data Statistics Excluding Sample 016

minimum	98.49%
maximum	98.81%
average	98.68%
variance	5.66×10^{-3}
coefficient of variation	7.62×10^{-4}

When expressed as a fraction, the variance is 5.66×10^{-7}, which is significantly smaller than the current variance estimate[2] of 4.0×10^{6}. It is interesting to note that in past experiments to estimate the variance of the fraction that is plutonium, frequently an extreme value would occur as above. Thus, it is not clear if the value for sample 016 was due to the skin or due to the analysis.

VI. PLUTONIUM VALUES: CALORIMETRY vs CHEMICAL ASSAY

Only one wattage (5.182771 $\pm$ 0.00311) was obtained by calorimetry for this button. When the isotopic concentrations from the 15 samples were applied to this, the Pu values ranged from 2131 to 2143 g. As it is customary to use 1% of the element value as a limit of error (2 σ) for the element value, the calorimetry Pu values are all $\pm$ 21 g.

The chemical assay fraction is multiplied by the cleaned ingot weight (2175.0 g) and added to the plutonium in the oxide (0.7 g) to get the Pu value. The range of Pu values (including sample 016) is then 2135 to 2150 g. If sample 016 is excluded, the minimum becomes 2143 g. The limit of error for these is determined from the variance-of-a-product formula and would be about 9 g.

* This value is considered an outlier because it is more than 3 standard deviations below the mean of all 15 values.

The true plutonium value is unknown but the shipper reports that the button contains 2148 g plutonium. The shipper's limit of error is not available, but if 2148 is taken as the true value, all calorimetry-determined values and all chemical-assay-determined values, save for sample 016, are consistent with it. If 2148 is assigned an uncertainty comparable to Los Alamos' limit of error, the sample 016 value of 2135 is reconcilable with the shipper's value.

Table IV gives the Pu values for each sample as estimated by the two methods. For every sample, the chemical assay value is greater than the calorimetry value. It is interesting to note that for sample 016, the difference is only 1 g. Because the calorimetry values all depend on common wattage observation (wattage has a probability distribution) these values are statistically dependent. Ignoring sample 016, the estimates of the chemical assay mean and standard deviation are 2147.4 g and 1.7 g respectively. The average calorimetry value 2136.9 is more than 6 standard deviations away from the chemical assay mean.

It would have been very useful if more wattage observations had been obtained on this button. Then, the bias between the methods, if any, could have been estimated. As it is now, the observed difference between the methods could conceivably be entirely due to a low observed value of the wattage.

The sample correlation coefficient between the calorimetry and chemical assay values is 0.18 for all 15 samples and - 0.03 if sample 016 is ignored. This suggests that these determinations were independent.

TABLE IV

PLUTONIUM DETERMINATIONS

I.D.	Chemical Analysis (C) (g)	Calorimetry (CA) (g)	C - CA (g)
215	2150	2140	10
006	2147	2139	8
007	2146	2139	7
010	2147	2134	13
011	2147	2131	16
012	2148	2134	14
014	2147	2135	12
015	2148	2134	14
016	2135	2134	1
017	2148	2135	13
018	2148	2135	13
019	2147	2141	6
020	2147	2136	11
021	2143	2141	2
022	2150	2143	7
mean	2146.5 (2147.4)[a]	2136.7 (2136.9)	9.8 (10.4)
s.d.	3.6 (1.7)	3.5 (3.5)	4.5 (3.9)

[a]The numbers in parentheses give the relevant statistics for the data when sample 016 is omitted.

VII. CONCLUDING REMARKS

The multiple sampling of this button has provided very useful information about button homogeneity and analytic methods. The Am values raise questions concerning americium segregation and variation in analytic techniques. Because the americium content is a very important determination of the plutonium content by calorimetry, resolution of these questions is desirable.

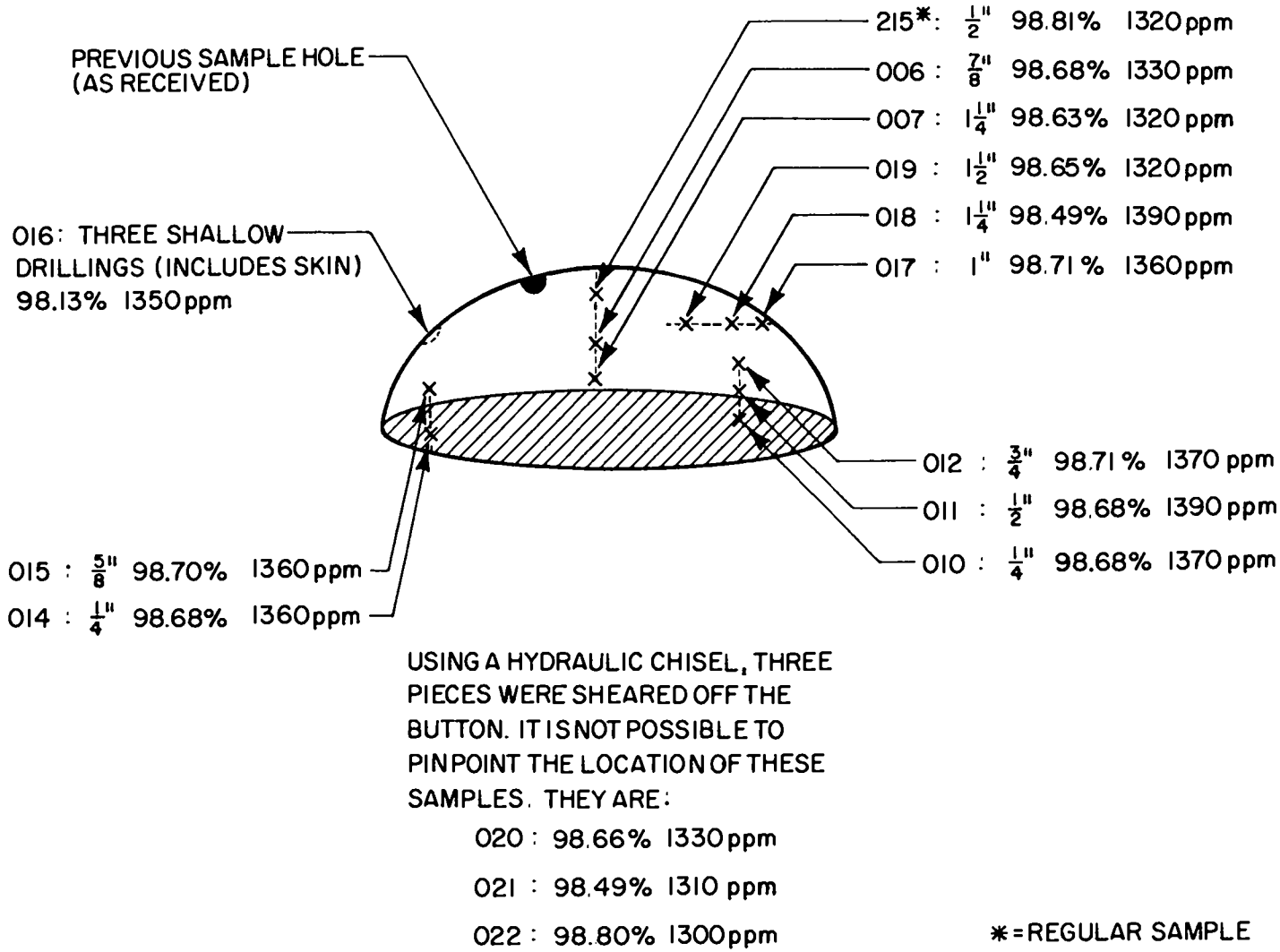

Fig. 1. Sample locations on button HRA147215.

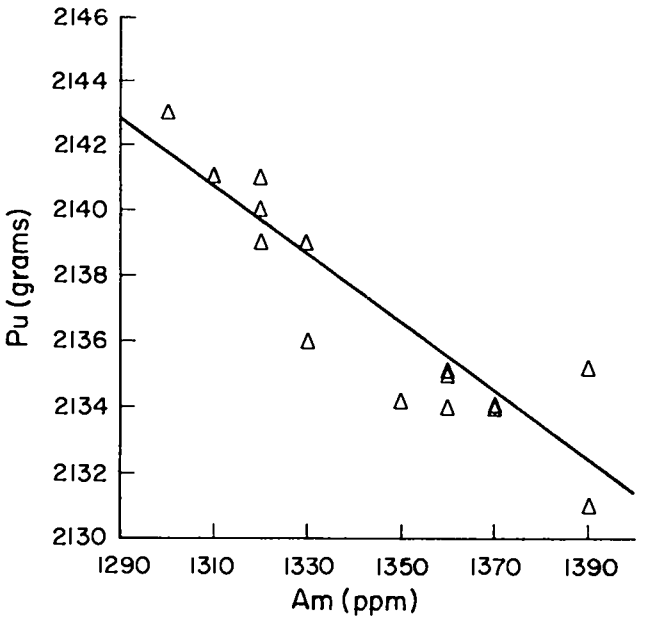

Fig. 2. Pu vs Am.

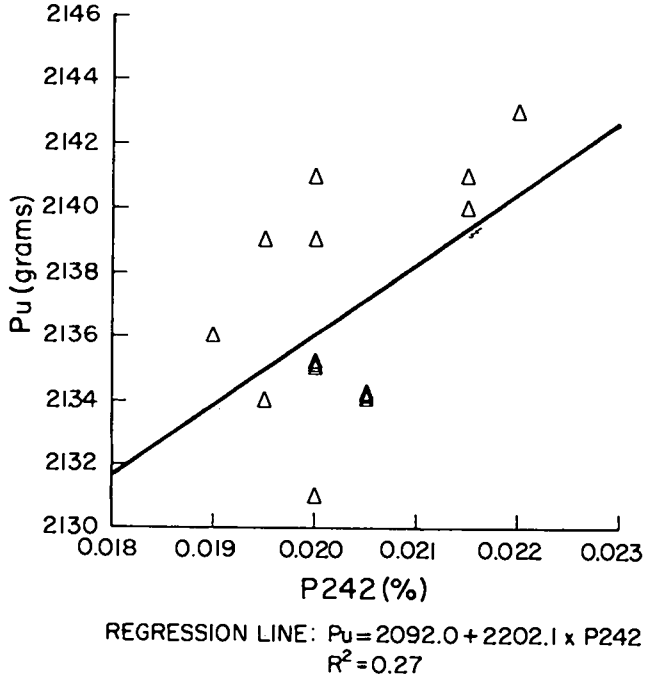

Fig. 3. Pu vs P242.

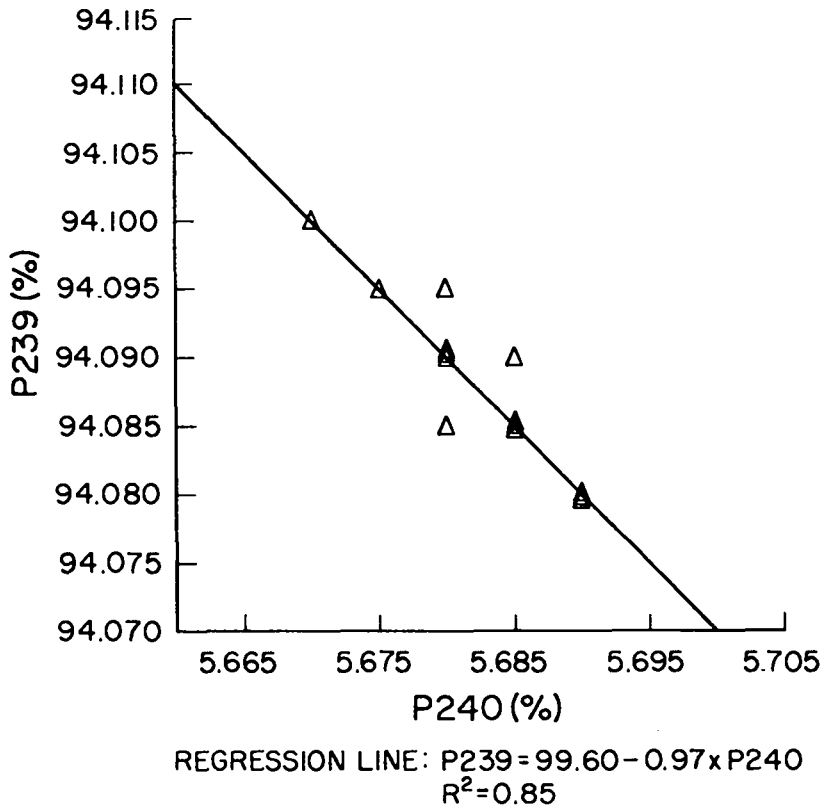

Fig. 4. P239 vs P240.

ACKNOWLEDGEMENT

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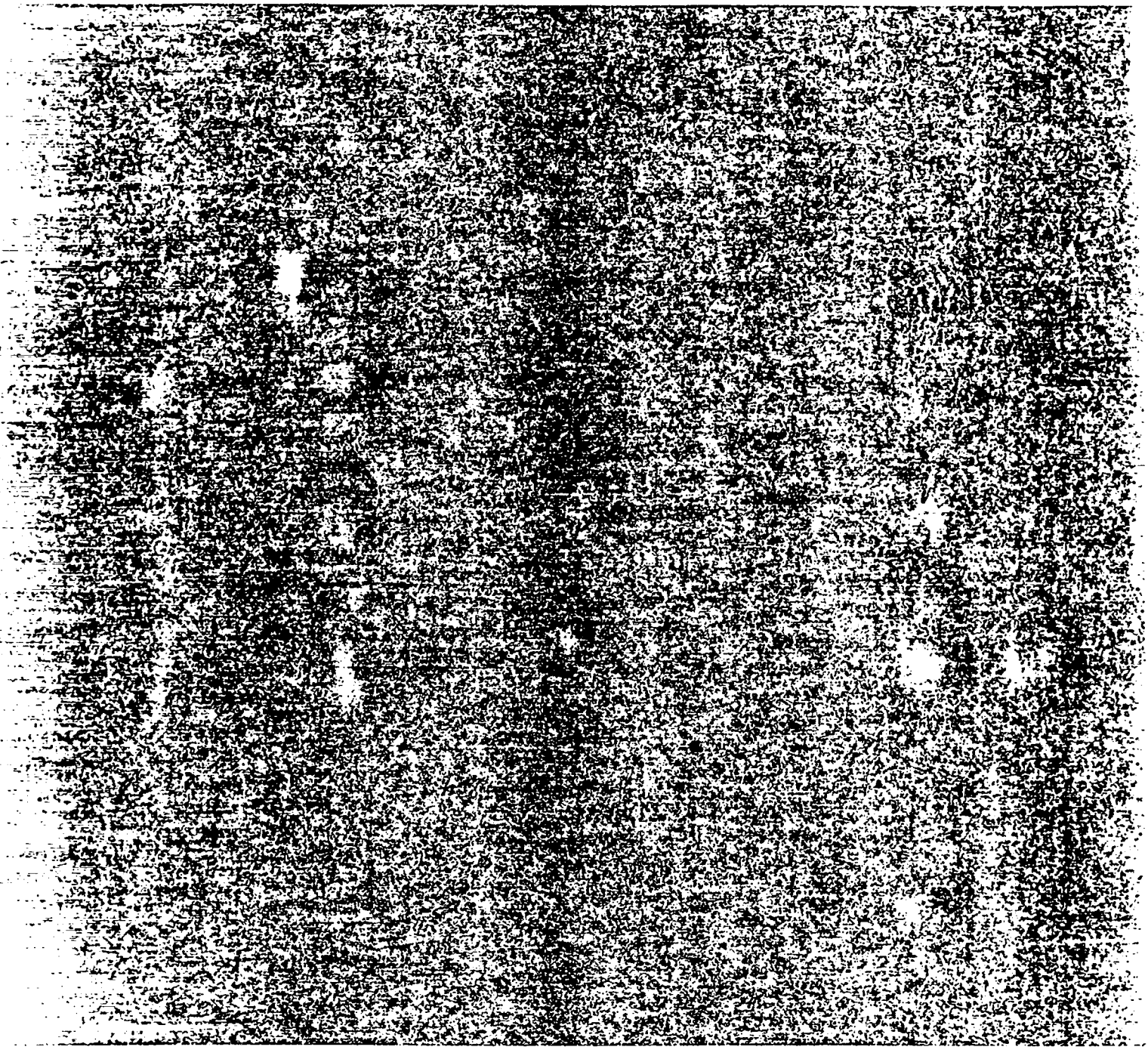

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