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MONITORING OF DIRECT CHEMICAL ASSAY
OF FABRICATED PARTS

AUTHOR

K. M. Harmon

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January 23, 1957

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MONITORING OF DIRECT CHEMICAL ASSAY
OF FABRICATED PARTS

INTRODUCTION

The specification for the plutonium content of fabricated parts (Specification P-10039) requires that for each three-months production a statistical estimate be made of process variance (variation in actual plutonium content from part to part). Prior to the fourth quarter of 1956, this requirement was met by the following indirect technique: 1) Chemical assay was made of at least one-half the parts produced; 2) by-difference analysis (subtraction of the measured impurities from 100 per cent) was made of all parts produced; and 3) the chemical assay and by-difference measurements were analyzed to permit partition of the observed, between-part variance in chemical assay results into process variance and analytical variance.

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DS Lewis 10/3/92

DG. Kuehn 12/1/92

J. E. Sluvely 12-11-90

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Starting in October, 1956, at the request of the Assistant Director of Production, Los Alamos Scientific Laboratory, the direct chemical assay was set up on a basis such as to permit calculation of the process variance by analysis of variance in the chemical assay data. Evaluation of the results obtained during the last quarter of 1956 has now been made and is presented in the following report of 1956 are summarized in Table I.

SUMMARY

TABLE I

The analysis of variance of chemical assay data made on groups taken at consecutive time intervals during the last quarter of 1956 showed a marked and consistent decrease in analytical variation. The improvement in analytical precision, however, was accompanied by an upward trend in process variance. This increase in the estimate of process variance was of sufficient magnitude to completely offset the decrease in analytical variation and resulted in a statistically demonstrated minimum plutonium content of only 0.06 percent above the specification requirement.

1st	25	0.06792	0.02108	0.0168	0.04383
2nd	45	0.02146	0.01006	0.00693	0.01273

In a comparison of the two methods for estimating process variance, the analysis of variance of chemical assay data gave an estimated value more than seven fold greater than that obtained from the co-variance of chemical assay and by difference measurements. An analysis of variance of the difference between the chemical assay and by difference measurements demonstrated a significant day-to-day variation of the same magnitude as the difference between the two estimates of process variance. Specific recommendations are made to minimize the effect of this day-to-day variation and to provide greater assurance that analyses of future production will demonstrate that the product meets the minimum plutonium content specification analytical variance, might be expected to be high due to changes in laboratory operation in -

RECOMMENDATIONS

1. The estimate of total variance of analytical and process variance should be maintained by routine calculations of process variance and process average should be maintained by direct chemical and by difference measurements. The latter has been programmed for the 702 computer and attempts are being made to decrease the same for the future. The estimate of the process variance provided by the computer is the prompt application of these calculations up to date will provide a basis for the prompt application of the estimated process variance measure completely nullified the gain in analytical precision but also resulted in the statistically demonstrated minimum plutonium content being near the specification.
2. Day-to-day variation in direct chemical analysis should be monitored and controlled through the use of plutonium standards and the comparison of direct chemical and by difference laboratory measurements near the end of the quarter, using all available data and the results are summarized in Table II.
3. The analyses of the dilutions prepared from each part should be spread over a three day period, to minimize the effects of day-to-day variation in direct chemical analysis.

VARIANCE COMPONENTS AND LIMITS USING TOTAL AVAILABLE DATA

DISCUSSION

Starting in October, 1956, the direct chemical assay for the measurement of the plutonium content of selected parts was expanded to provide the data required for the estimation of process variance. For each part analyzed, three accurately weighed cuttings of 500 mg. were each dissolved and diluted to 250 ml. The plutonium content of each dilution was determined by two analysts making independent dilutions with

	"200"	"200"	"250"	"250"
Process Average	98.88	98.871	98.908	98.856
Demonstrated Minimum Pu Content	98.56	98.558	98.518	98.543

The larger number of parts analyzed fortunately offset the increase in process variation so that the statistically demonstrated minimum plutonium content was above the specification value. The narrow margin of only 0.058 per cent for the "200" model and 0.043 per cent for the "250" model indicates that close monitoring of both the process average and the variance estimates will be required for assurance that analysis of future production will demonstrate that the product meets the minimum plutonium content specification. As a comparison with previous production, the process variance estimate was calculated by J. T. Merrill by the method used prior to October, 1956. The co-variance of the chemical assay and by-difference measurements on the "200" model parts gave an estimate of process variance which was less than one seventh that obtained by the analysis of variance of chemical assay data on the same parts.

Process Variance and Average on 130 Analyzed "200" Models

	<u>Chemical Assay</u>	<u>By-Difference</u>
Process Variance	0.017173	0.002349
Process Average	98.871	98.873

A possible source of the higher value of the process variance estimate made by analysis of variance is the lack of independence of the titration and dilution analytical data. This arises from the impracticality of completely random assignment of analytical work. When the laboratory is operating normally, most of the parts are analyzed on the same day they are sampled. Any day-to-day variation in the analytical results would inflate the estimate of process variance. Based on the difference between chemical assay and by-difference measurements on the same part, an analysis of variance showed a significant day-to-day variation for the data obtained on 87 parts during 24 consecutive operating days.

VARIANCE OF THE DIFFERENCE BETWEEN CHEMICAL ASSAY
AND BY-DIFFERENCE RESULTS

Variance between days	0.011354
Variance within days	0.011576
Total Variance	0.022529

This day-to-day variance is of the same magnitude as the difference between the two estimates of process variance. As a means of detecting the source of this day-to-day variance, standard plutonium solutions prepared from alpha metal are being analyzed each day by the 234-5 Control Laboratory personnel. While the use of plutonium standards and comparison of chemical assay and by-difference measurements will aid in the detection and eventual minimization of this day-to-day variance, the changing of the analytical schedule to minimize the inflation of the estimate of process variance would be of immediate benefit. Complete randomization of the titration and dilution steps is impractical; however, a major improvement would be realized if the dilution and titration steps for each part were distributed over a three day period rather than completed in one day. This would result in a minimum backlog of twelve dilutions at the present rate of four parts analyzed per day. The chemical assay data would not be available until at least the third day after the sample

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is received by the laboratory. While backlogging of dilutions and delay of analytical results are undesirable, the decrease in the process variance estimate which should result from minimizing the effect of this day-to-day variance in analytical data is needed to provide greater assurance of demonstration of required product purity.

The laboratory range limits, method of calculating part average, individual part limits for by-difference measurement, limits on spread between direct and by-difference assay, and statistical test for comparison of the two methods for estimating process variance were determined by J. T. Merrill based on data obtained during the last quarter of 1956 and are attached to this letter.

K. M. Harmon

Manager, Process Chemistry Operation
CHEMICAL PROCESSING DEPARTMENT

KM Harmon:DF Shepard/efg

Enclosure

Notes by J. T. Merrill

Range limits for two titrations:

$$s^2_{\text{titrations}} = .034508$$

$$s_{\text{titration}} = .1858$$

$$\text{Upper limit with 5\% above} = 0.515$$

Range limits for three titrations:

$$\text{Upper limit with 5\% above} = 0.619$$

Range limits for three dilutions: (each with two titrations)

$$s^2 = \frac{.055433}{2.0141} = .027522$$

$$s = .1659$$

$$\text{Upper limit with 1\% above} = .693$$

Range limits for two dilutions:

$$\text{Upper limit with 1\% above} = .611$$

Rules for part average - throw out significant outliers, add up all individual analytical results remaining, and divide by number of results remaining.

Limits on Individual BD

$$\text{Effective d.f. } n^1 = 43$$

$$s^2_{\text{BD(obs.)}} = .006096$$

$$s^2_{\text{BD Method}} = .003747$$

$$s_{\text{BD method}} = .0612$$

$$\overline{\text{BD}} = 98.873$$

Tolerance limits (1-0 = 97.5%, P = .95)

$$t_p = 2.411$$

$$\text{Lower limit} = 98.73$$

Looking at the problem the other way, how low can a BD result be and still have reasonable confidence that the result arose from a part having a true value above the nominal limit.

$$x = \bar{\bar{x}} = 98.648 \text{ or } \bar{\bar{x}} = 98.65$$

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Looking at the statistic (CA-BD) for individual parts:

$$\text{Var (CA-BD)} = .012949$$

$$\text{Effective degrees of freedom: } n^1 = 248$$

$$S_{\text{Diff}} = .1138$$

Assuming an expected value of zero

$$95\% \text{ confidence, } 95\% \text{ of population: } 0 \pm 2.125 (.1138) = -.242 \text{ to } + .242$$

Grouping the data by model and by day:

$$95\% \text{ confidence, } 95\% \text{ of population: assuming four parts analyzed per day} \\ 0 \pm 2.125 \left(\frac{.1138}{2} \right) = -.1209 \text{ to } +.1209$$

Two process variance estimates possible:

$$E \left(\frac{S_n^2}{S_o^2} \right) = 1.0 \quad \text{assuming they are estimating the same thing.}$$

Routinely, estimates can be obtained by both methods and the ratio can be tested using an F-table. A significantly large ratio would seem to indicate that S_N^2 is estimating a source of variation in addition to process variation (although S_o^2 could also be biased low). Just by the nature of the two systems, we know that S_N^2 will be affected by any biases that occur in the ceric method. In general, biases will affect the older system to a much lesser degree.

Comments on Graph

Too much variation in the observed points.

But, if anything, the precision of the ceric method is estimated on the low side !

Leads to the conclusion that the two methods are not estimating the same thing.

CHEMICAL ASSAY MINUS BY-DIFFERENCE

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