77.5 7-15-55

IDO-14345

OPERATIONS EVALUATION AT THE IDAHO CHEMICAL PROCESSING PLANT
OF THE U. S. ATOMIC ENERGY COMMISSION

Frank P. Vance
Fred H. Tingey

June 29, 1955

PHILLIPS PETROLEUM CO.
ATOMIC ENERGY DIVISION
(UNDER CONTRACT NO. AT (10-1)-205)
IDAHO OPERATIONS OFFICE
U. S. ATOMIC ENERGY COMMISSION

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

<u>Internal Distribution</u>	<u>Copies</u>
R. W. Thomas, Bartlesville	1
P. M. Arnold, Bartlesville	2
K. H. Hachmuth, Bartlesville	3
R. L. Doan	4
J. P. Lyon	5
J. R. Huffman	6
B. F. Boardman	7
F. H. Tingey	8
F. P. Vance	9
Technical Library	10 - 34 45

<u>External Distribution</u>	
J. B. Philipson, IDO	46 47
TIS, Oak Ridge	35 - 36
	37 - 39
	48 - 50

**DO NOT
PROTEST**

TABLE OF CONTENTS

	<u>Page</u>
Summary	4
I. Introduction	5
II. Procedure	6
III. Product Measurements	21
IV. Plant Waste Streams	22
V. Summation	24
Figure 1	25
Figure 2	26
Figure 3	27
Figure 4	28
Appendix A (Nomenclature)	29
References	30

SUMMARY

Application of the formal methods of statistical analysis to correlation (regression analysis) of plant-scale operating variates is described, citing examples from recovery of enriched uranium from spent reactor fuel at the Idaho Chemical Processing Plant of the AEC. The utility and strength of these mathematical tools in the solution of chemical processing problems is illustrated in detail.

The specific requirement of surveillance and apprehension of nuclear criticality in dissolution equipment containing enriched uranium was met by formulation of a dissolver operating line which complied with the definition of safe conditions. This was accomplished by a systematic procedure for identification and optimization of measurement errors, under a technique such that routine scrutiny of plant-scale process data afforded surveillance of measurements, and assurance at the necessary confidence level that operation was safe.

The optimization of measurement control effort with precision warranted close scrutiny at this Plant because of the high value of the material. The same principle will apply equally, however, whether the material being handled is uranium, butadiene, or polio vaccine.

Note: This paper has been prepared for consideration by the American Institute of Chemical Engineers, for presentation at the Annual Meeting, Detroit, Michigan, November 27-30, 1955.

OPERATIONS EVALUATION
AT THE
IDAHO CHEMICAL PROCESSING PLANT
OF THE
U. S. ATOMIC ENERGY COMMISSION

BY

Frank P. Vance
Fred H. Tingey

I. INTRODUCTION

The construction of plant material balances is one of the most fundamental chemical process calculations. At the Idaho Chemical Processing Plant, where the raw material is enriched uranium spent reactor fuel, material balances are of necessity given an uncommon emphasis. Virgin enriched uranium is fabricated into aluminum, zirconium and other alloys into the necessary shapes under AEC contracts, inserted into reactors operated by other Contractors, and transferred to the Idaho Chemical Processing Plant operated for the Commission by Phillips Petroleum Company when the desired level of U-235 burn-up has been attained. There the spent fuel is dissolved in nitric acid and fission products are separated from the uranium by liquid-liquid extraction. In this manner the uranium is ultimately returned to AEC channels. A host of unique problems of measurement and, consequently, construction of plant material balances is posed by the fact that the radioactivity level of the "slugs", of dissolver solution, and of the uranium-lean raffinate is of the order of many curies per cubic centimeter. Process losses must be kept at the low level dictated by the dollar value of the recovered uranium.

Vigorous surveillance must be maintained over the metal. This problem is rendered complex by factors such as the following: the slug fabricators must perforce assign "average" contents to some categories of slug, as no precise method is in use for measuring content after fabrication; uranium content of the hot slugs is not known exactly by the reactor operators, because each must estimate U-235 burn-up from the best information available regarding the integral of energy dissipated from the relevant area of the particular reactors occupied by particular slugs. Finally, when the product solution emerges from the ICPP extraction system, the level of radioactivity is sufficiently low that a gravimetric assay can be performed.

Thus, in order to maintain adequate safeguards on the metal, close scrutiny of measurements is imperative, and realistic limits of uncertainty must be derived and attached to material balance components in order to insure that costly investigations of apparent discrepancies can be avoided, and, more important, that actual discrepancies will not be disregarded.

II. PROCEDURE

As a first step it was absolutely essential that measurement reliability be evaluated. The processing of spent fuel at the Idaho Chemical Processing Plant commenced early in 1953. At the beginning of these operations, attempts were made to assess measurement error by a rather modest program of synthetic control samples. It was evident that this was inadequate by the time the present Contractor took charge in October, 1953. At about this time a short processing run was completed on Materials Testing Reactor-type fuel. The plant was clean at the beginning of the run, and was thoroughly cleaned out following the run as no material was immediately available for processing and a human-tolerance level of decontamination was required to facilitate a construction program which was beginning.

The quantity of material processed during this run was capable of estimation by four different--essentially independent--modes:

1. MTR estimate of burn-up, based upon gross reactor energy dissipated, apportioned to individual fuel elements;
2. burn-up estimate provided by the accurately measured isotopic distribution in the spent fuel, utilizing stoichiometric relationships described in following sections;
3. measurement of uranium solution content by,
 - (a) polarographic-U concentration, and
 - (b) isotopic dilution, a technique utilizing the mass spectrometer, and a procedure of "spiking" the sample with a measured quantity of another uranium isotope not occurring in the irradiated fuel.

Thus it was possible to study a large number of measurements between the limits, clean plant-to-clean plant, under the unique conditions of having had four different estimates of the same quantity. This led to an identification of sampling and analytical errors which in turn resulted in formalization of plant procedures for solution homogenization, sampling, and analytical techniques. It is apparent that, due to the extreme radioactivity of the material being handled and the solutions produced, manipulation of many plant streams must be performed remotely. Because of the high value of the material, however, great care must be exercised to insure that a ten-milliliter sample, say, drawn from a vessel containing, say, several hundred liters will accurately represent the average properties of the vessel contents.

To determine the precision which should be associated with each method of estimation referred to in connection with the MTR-run described in the preceding section, a statistical technique first described by Grubbs (1) was modified to apply to these data. The evaluation of the variability of a population which is defined by many parameters is performed by use of a tool of mathematics called "analysis of variance".

The "variance" of a population is the mean square deviation of its members from the population mean. In the usual case we lack complete knowledge of the entire population; hence, the properties must be deduced from those exhibited by samples. If care is taken to insure that the samples are chosen in a random manner, i.e., their selection is governed only by pure chance, it is reasonable to suppose that the properties of the sample accurately represent those of the population. This enables definition of the properties of the population at stated levels of confidence, i.e., probability of being correct. The variance has the useful property of additivity, and is expressed as follows:

$$\text{Var}(x) = \frac{\sum_{i=1}^n x_i^2 - \left[\sum_{i=1}^n x_i \right]^2 / n}{n - 1}$$

The square-root of the variance is defined as the "standard deviation", usually denoted by σ , and has the following physical significance:

This curve is a plot of the values shown by the members of a population, or sample from a population, versus the number of members having the given value. Thus, the peak of the curve occurs at the mean of the population, and the point of inflection occurs at one-sigma. When these values are so-called "normally" distributed, the area under the curve from $x - \sigma$ to $x + \sigma$ embraces 68.3 per cent of all values, and from $x - 2\sigma$ to $x + 2\sigma$ embraces 95.4 per cent.

When it is necessary to estimate the variance and standard deviation of a population based upon the properties of a sample, these limits are adjusted according to the size of the sample. Thus, limits will be computed as $\pm t \sigma$, where "t" denotes a function of the sample size and degree of confidence expressed. At the 95 per cent level, i.e., probability of 19:1 that the true value lies within the stated limits, values for t are tabulated below (2):

TABLE I

Sample Size	t
2	12.71
10	2.20
100	1.98
∞	1.96

Following the MTR run, as described in a preceding section, four sets of data were available for study. The cumulative total of these values differed in the following manner: estimates 1 and 2 agreed fairly well, and estimates 3(a) and 3(b) agreed fairly well, but 1 and 2 were apparently significantly different from both the methods 3. This indicated that the plant material balance was seriously in error, and that the imbalance represented considerable value. By formulation of a mathematical model fairly representative of the data behaviour, construction of the system of simultaneous equations i.e., analysis of variance can be performed readily.

We use the subscript i to denote the particular batch being measured, and the subscript j to denote the measurement method. We have then,

$$x_{ij} = \mu_i(1+b_j)(1+\epsilon_{ij}) \dots\dots\dots(1),$$

where μ_i is the true concentration,

b_j is the systematic error committed by method j, and

ϵ_{ij} is the measurement error peculiar to batch i by measurement method j, which is on the average assumed to be zero, the variance of which, average ϵ_{ij}^2 for given j we denote by σ_j^2 .

An expansion of equation (1) gives

$$x_{ij} = \mu_i + \epsilon_{ij}\mu_i + \mu_i b_j \dots\dots\dots(1A),$$

neglecting the second-order effect, $\mu_i b_j \epsilon_{ij}$.

The model illustrated by equations (1) and (1A) is based upon the assumption that for the type of measurements being performed, a constant relative error can most readily be assumed.

In order to formulate a truly representative mathematical model for the statistical properties to be computed, it is necessary to introduce certain assumptions--the validity of which can be verified--regarding the degree of independence of each mode of measurement. Thus, if we denote $\sigma(\epsilon_{i1}\epsilon_{i2})$

as the "covariance" between measurement modes "1" and "2" on batch "i", the following assumptions are believed valid:

$$\begin{aligned} \text{Average } (\epsilon_{i1}\epsilon_{i2}) &= \sigma(\epsilon_{i1}\epsilon_{i2}) = 0 \\ \text{and, similarly, et seq.*} \quad \sigma(\epsilon_{i1}\epsilon_{i3}) &= 0 \\ \sigma(\epsilon_{i1}\epsilon_{i4}) &= 0 \\ \sigma(\epsilon_{i2}\epsilon_{i3}) &= 0 \end{aligned}$$

However, since measurement methods "3" and "4" utilized the same sample in each case, it was conceivable that sampling error component of the total error was common to these two measurements; hence a positive correlation could be expected. Also in the case of measurement modes "2" and "4", the batch U-236 percentage on which method 2 was based was also a component in the corresponding values obtained by the isotopic dilution method of analysis; hence a correlation between measurements was possible.

It followed therefore, under the assumptions that the measurement errors ϵ_{ij} are on the average zero, and the covariance between these values is zero except for measurement methods 2 and 4, and 3 and 4, that the analysis is effected by

(1) observing that the natural logarithm of equation (1) is

$$\ln x_{ij} = \ln \mu_i + \ln(1+b_j) + \ln(1+\epsilon_{ij}) \dots \dots \dots (3)$$

which for convenience we write as,

$$x_{ij}^* = \mu_j^* + b_j^* + \epsilon_{ij}^* \dots \dots \dots (3A)$$

where the * indicates the $\log_e$ of the argument for x_{ij} and μ_i

and b_j^* and ϵ_{ij}^* indicates the $\log_e$ of "one plus the argument";

* We denote methods 3(a) and 3(b) as "3" and "4" for convenience.

- (2) that differencing the observed values by pairs corresponding to two different measurement modes results in expressions of the form,

$$\begin{aligned} d_{i12} = x_{i1}^* - x_{i2}^* &= (\mu_1^* + b_1^* + \epsilon_{i1}^*) - (\mu_1^* + b_2^* + \epsilon_{i2}^*) \dots \dots \dots (4) \\ &= (b_1^* - b_2^*) + (\epsilon_{i1}^* - \epsilon_{i2}^*) \dots \dots \dots (4A) \end{aligned}$$

in the case of methods 1 and 2, and similar equations for any of the other five pairs possible;

- (3) that the sample estimate of the variance of the d_{ijk} 's;

$$\frac{\sum_{i=1}^n (d_{ijk} - \bar{d}_{jk})^2}{n-1} \quad \text{estimates}$$

$$\sigma_{\epsilon_j^*}^2 + \sigma_{\epsilon_k^*}^2 - 2\sigma_{\epsilon_j^* \epsilon_k^*} \dots \dots \dots (5)$$

$$\text{where } \bar{d}_{jk} = \sum_{i=1}^n d_{ijk} / n$$

and n is the number of batches,

$$j \neq k = 1, 2, 3, 4,$$

and $\sigma_{\epsilon_j^* \epsilon_k^*}$ symbolically represents the covariance between the transformed measurement errors associated with the j and k'th measurement modes;

- (4) equations (5) result in a system of six simultaneous equations in the unknowns $\sigma_{\epsilon_j^*}^2$, $j = 1, 2, 3, 4$ and the two non-zero covariance

terms $\sigma_{\epsilon_3^* \epsilon_4^*}$ and $\sigma_{\epsilon_2^* \epsilon_4^*}$ a solution of which results in the estimates

of these values;

- (5) according to the propagation of errors formula,

$$\sigma_{\epsilon_j^*}^2 \approx \left(\frac{1}{1 + \text{Ave } \epsilon_{ij}} \right)^2 \sigma_{\epsilon_j}^2 \approx \sigma_{\epsilon_j}^2 \dots \dots \dots (6)$$

$$\begin{aligned} \sigma_{\epsilon_j^* \epsilon_k^*} &= \sigma_{\ln(1 + \epsilon_{ij}) \ln(1 + \epsilon_{ik})} \approx \left(\frac{1}{1 + \text{Ave } \epsilon_{ij}} \right) \left(\frac{1}{1 + \text{Ave } \epsilon_{ik}} \right) \sigma_{\epsilon_j \epsilon_k} \\ &\approx \sigma_{\epsilon_j \epsilon_k} \end{aligned}$$

- (6) therefore an analysis such as this results in plant estimates for the precision of each measurement method, and the correlation between the two chosen pairs.

With reference to the original model, equations (1) and (2), it is apparent that $(100)(\sigma_{\epsilon_j})$, $j = 1, 2, 3, 4$ gives the per cent error in the j 'th measurement method since the error term in the model is ϵ_{1j}/μ_1 . The following results were obtained for the processing run cited above, by this technique of data analysis:

TABLE II
EVALUATION OF MEASUREMENT ERRORS

<u>Variables</u>	<u>Value</u>
σ_{ϵ_1}	$\pm 2.51 \%$
σ_{ϵ_2}	$\pm 3.43 \%$
σ_{ϵ_3}	$\pm 15.64 \%$
σ_{ϵ_4}	$\pm 15.41 \%$
$\rho_{\epsilon_1 \epsilon_2}$	0.035
$\rho_{\epsilon_3 \epsilon_4}$	0.80

where σ_{ϵ_j} ($j = 1, 2, 3, 4$) denotes the standard deviation of the measurement, and $\rho_{\epsilon_j \epsilon_k}$ ($j \neq k = 1, 2, 3, 4$) denotes correlation coefficient which is computed from relevant covariances and standard deviations.

At this time the polarographic method of measuring uranium concentration was the accepted measurement for SS Accountability purposes. The isotopic dilution method of analysis was being investigated as a possible replacement of the polarographic. Needless to say, it was disconcerting to find that the uncertainty in a polarographic determination was of the order of $\pm 30\%$ and that this evaluation of measurement errors showed there was little choice between these two methods. At the time, the 95% confidence limit for the polarograph was being stated as $\pm 7\%$ and so used in plant material balance computations, while the isotopic dilution method was believed to be precise to within ± 3 per cent.

It was evident therefore, that certain weaknesses existed in the Quality Control program resulting in inaccurate estimates of the precision which should be associated with a given technique. This was primarily due to the fact that a synthetic sample quality control program alone cannot adequately and effectively yield realistic uncertainty limits where there is reason to believe that sampling and sample preparation error are of a significant magnitude. This is very likely the rule rather than the exception in any chemical processing plant. It is not at all surprising that this was found to be the case at the Idaho Chemical Processing Plant where ample opportunity exists for magnification of measurement errors by the remote nature of the operation and sampling, and additional steps such as decontamination which are required in many cases before analysis can be attempted.

An additional factor exists which made it imperative that an accurate evaluation of plant input uncertainties be available, entirely separate from the requirements of SS Accountability. Because of nuclear criticality limitations, the maximum allowable dissolver content of fissionable material must be reduced by an amount equal to the heel uncertainty. This limitation has a significant effect upon plant through-put since the amount of metal in the dissolver determines dissolution rate in large degree. The residual heel is equal to the cumulative shipper's charge figures, less the cumulative batch-wise measurement of dissolver solution uranium content in the unadjusted feed tanks. It is apparent that any systematic error in either of these figures could have disastrous consequences. Therefore a comprehensive evaluation of the uncertainties affecting the heel estimate was in order.

The investigation of input measurements began with the coarse-feed, or feed-adjustment tanks. Following the completion of the MTR fuel element processing described in preceding sections, and while the dissolver cells were decontaminated to human-tolerance level, several calibration runs were made on each tank. These consisted in introducing a known volume of water to the vessel at regular volume increments and calibrating this against readings on a liquid-level manometer, and a Taylor recording liquid-level instrument. It was apparent from the residual error associated with each fitted line (there are four such tanks) that negligible uncertainty would be introduced by using these calibration curves to determine tank volume in the overall computation.

In view of the anticipated sampling error associated with an increment of dissolver solution as suggested by the 30 per cent uncertainty previously found, a series of homogeneity tests was conducted in order to determine the minimum time necessary to bring a relatively heterogeneous uranyl nitrate-nitric acid-aluminum nitrate-fission product-water system to uniform composition throughout. In analysis of the data collected under this program indicated that 45 minutes was sufficient essentially to bring sampling error to an irreducible minimum as judged by the analytical method upon which plant input is based, isotopic dilution, or Spike-U. This accordingly became standard operating procedure. In addition, it was deemed wise to specify a minimum of 10 minutes of purging of the sample-draw line between collections in order to insure that samples were truly independent.

An integrated Quality Control Program was formulated with the following objectives in view:

1. Analysis of the resulting data would facilitate a resolution of the total variation into its relevant components; hence the Quality Control Supervisor would be enabled to trouble-shoot vulnerable steps in the overall measurement;
2. Realistic estimates of the precision for SS Accountability purposes and also for defining an operating line for dissolver chargings;

3. The direction in which to proceed to effect reductions in analytical effort without seriously impairing the overall precision;
4. Data would be collected in a manner to allow evaluation of the effects of the important operating variables, and other parameters of the system.
5. Estimation of the bias and precision to be associated with each analytical method and each process sample with a substantial reduction in the number of analyses (fifteen per cent of the laboratory total effort) being performed solely for the purpose of quality control.
6. Any shift in the bias and precision of a technique as applied to a given process sample would be immediately detected and steps taken to effect resolution.

With these objectives, the program was effected in two parts. First, a series of designed experiments using process samples to accomplish the objective with regard to precision, and secondly a vastly reduced and simplified synthetic control program augmented by bench-standard checks and regression analysis for bias estimation. In particular the sampling scheme used on all process solutions measured tank-wise, batch-wise, or sample bottle-wise, is known as the nested, hierarchial, or multi-stage grouping type. For example, the precision of an isotopic dilution analysis of a given coarse-feed tank batch is influenced by many sources of error; primarily the homogeneity of the solution is reflected by the degree to which the sample represents (or fails to represent) the average batch concentration; the sample preparation step involving remote pipetting of 500 lambda of the sample solution, the spiking of this sample with a measured volume of U-233 and the subsequent decontamination of the spiked solution; and the reproducibility of the mass spectrometer by which the isotopic distribution is measured, from which the sample concentration is finally computed.

A mathematical model relating these components to the observed value is,

$$x_{ijklm} = \mu + \alpha_i + \beta_j(i) + \gamma_{k(ij)} + \delta_{m(ijk)} \dots \dots \dots (7)$$

where x_{ijklm} denotes the m'th analysis on the k'th preparation of the j'th sample drawn from the i'th batch,

μ denotes the "true" average batch concentration,

α_i denotes that part of the deviation of x_{ijklm} from the overall mean, attributable to the particular batch sampled,

$\beta_j(i)$ denotes the deviation peculiar to the j'th sample drawn from the i'th batch,

$\gamma_{k(ij)}$ denotes the deviation attributable to the k'th preparation of the j'th sample from the i'th batch, and

(continued on next page)

$\delta_{m(ijk)}$ denotes that part of the total deviation due solely to analytical error, i.e., reproducibility of the mass spectrometer.

In the general case no restriction need be placed on the number of groups of the first-order corresponding to subscript i , the number of second-order groups corresponding to subscript j , the number of third-order groups corresponding to subscript k , nor the number of fourth-order groups carrying subscript m . Furthermore the number in any given sub-group need not be the same for all groups. The flexibility of this sampling plan and the ease of analysis make it ideal for surveillance of chemical plant material balance measurements.

The explicit scheme which is used at the Idaho Chemical Processing Plant to estimate variance components is as follows: Five process batches are randomly selected and designated as Quality Control batches. From each batch two samples are drawn, two aliquots from each of the duplicate samples are pipetted, spiked and decontaminated independently of the others, and from each of the resulting solutions two aliquots of the precipitate are collected on filaments for mass distribution analysis. Schematically the plan is as follows:

It is apparent from equation (7) that the variation in the α_i 's reflects the batch-to-batch variation. Similarly the variation in the $\beta_{j(i)}$'s for all i and j reflects the sample-to-sample variation. Furthermore if the $\gamma_{k(ij)}$'s were known, they could be used to estimate the variation between preparations of the same sample. Finally the average of the squares of the $\delta_{m(ijk)}$'s for all m, i, j , and k would provide an estimate for the analytical component. Clearly the individual deviations are not available; however by the method of analysis of variance the variance component estimates are easily derived.

In the general case, for n batches sampled according to the above scheme,
We let $T_{\cdot}(ijk)$ denote the total of the two observations on the k'th preparation
of the j'th sample from the i'th batch,

$T_{\cdot\cdot}(ij)$ = total of the four observations on the i'th batch and j'th
sample from the batch,

$T_{\cdot\cdot\cdot}(i)$ = total of 8 observations on the i'th batch,

$T_{\cdot\cdot\cdot\cdot}$ = total of all 8n observations,

where $i = 1, 2, \dots, n$; $j \neq k = 1, 2$.

Symbolically we represent the variance of the component deviations in equation (7)
by

σ_{α}^2 for the α_i 's

σ_{β}^2 for the $\beta_{j(i)}$'s

σ_{γ}^2 for the $\gamma_{k(ij)}$'s

σ_{δ}^2 for the $\delta_{m(ijk)}$'s

Then it can be shown (2) that

$$\sigma_{\delta}^2 \text{ is estimated by } \frac{\sum_{i,j,k,m} (x_{ijkm}^2) - \sum_{i,j,k} \frac{(T_{\cdot\cdot\cdot}^2)_{ijk}}{2}}{4n} \quad (8)$$

$$\sigma_{\delta}^2 + 2\sigma_{\gamma}^2 \text{ is estimated by } \frac{\sum_{i,j,k} \frac{(T_{\cdot\cdot\cdot}^2)_{ijk}}{2} - \sum_{i,j} \frac{(T_{\cdot\cdot\cdot}^2)_{ij}}{4}}{2n} \quad (9)$$

$$\sigma_{\delta}^2 + 2\sigma_{\gamma}^2 + 4\sigma_{\beta}^2 \text{ is estimated by } \frac{\sum_{i,j} \frac{(T_{\cdot\cdot\cdot}^2)_{ij}}{4} - \sum_i \frac{(T_{\cdot\cdot\cdot}^2)_{\cdot\cdot\cdot i}}{8}}{n} \quad (10)$$

$$\sigma_{\delta}^2 + 2\sigma_{\gamma}^2 + 4\sigma_{\beta}^2 + 8\sigma_{\alpha}^2 \text{ is estimated by } \frac{\sum_i \frac{(T_{\cdot\cdot\cdot}^2)_{\cdot\cdot\cdot i}}{8} - \frac{(T_{\cdot\cdot\cdot\cdot}^2)}{8n}}{n-1} \quad (11)$$

The individual component estimates are easily derived from this set of equations.
The usefulness of these components estimates is immediate. By a comparison of the
magnitude of these estimates it is apparent where effort should be exerted to re-
duce the variability. Furthermore the anticipated precision of any sampling-
sample preparation-analysis scheme can easily be derived. Thus, the estimated 95%
limits of uncertainty on a single analysis for a single preparation of a single
sample from a given batch is approximately equal to

$$\pm 2 \sqrt{\sigma_{\beta}^2 + \sigma_{\gamma}^2 + \sigma_{\delta}^2}$$

Similarly, if two analyses are to be performed on each batch, an examination of the
four variance components shows clearly where the doubled effort should be spent in
order to effect the greatest reduction in imprecision. Furthermore such an analysis
is a prerequisite to any optimum allocation study of number of samples and number
of analyses per sample to minimize any given loss function.

It is interesting to note that the first application of this design resulted in an over-all precision estimate to be associated with a single analysis on a single preparation of a single sample drawn from a given batch of about $\pm 20\%$; the sample preparation component being grossly larger than any other. Accordingly, a re-examination of this step in the measurement was made. It was found that a modified manipulation of the remote pipetter, and standardized technique in the sample decontamination step produced the necessary reproducibility. Thus, when the design was repeated, the over-all precision had evidently improved considerably, such that it was by then possible to attach a 95% limit of uncertainty to a single measurement as described above, of $\pm 5.4\%$. In addition, it is emphasized that this is expressed as tank concentration, uncertainty.

A program for control of systematic error associated with unadjusted feed samples was effected under the following plan. For several reasons a program based only on synthetic bias control samples was felt to be inadequate in the surveillance of systematic errors. In many cases in which there appeared to be a bias associated with the method, based on controls, it was found that the apparently true content of the synthetic was in error, or had shifted due to evaporation and the like. Furthermore, especially with regard to synthetic samples analyzed in replicate simultaneously or over a fairly narrow time interval--as in the case of gravimetric uranium--it was found that the day-to-day, or time effect on the samples greatly exceeded the variation between the replicates. Thus, the existence and magnitude of the bias depended to a large extent upon the time when the synthetics were submitted to the laboratory. We do not wish to imply that such a situation is peculiar to this laboratory alone.

To augment the program of synthetic control samples which, by the way, was reduced to bare minimum, three alternate methods were simultaneously put into effect. Previous to the analyses of any series of process samples, bench standards are run. These bench-standards are fabricated with extreme precision and are changed quite frequently. The reduction in routine quality control samples enabled the standards laboratory to exercise more care in preparation and handling of the bench standards and also in more frequent compounding. The synthetic solutions are then analyzed in replicate by the Special Analysis Group to establish the true level of the component measured and the precision that can be expected on these samples. Based on the established precision of the method as determined by the replicate analyses on the synthetic samples, re-run limits are provided the analysts for each technique-sample combination. The limits are determined by an application of the theory of statistical tolerance limits to the samples. Any significant deviation from the stated level is called to the attention of the shift supervisor who in turn attempts to determine the cause of the excessive deviation. Such a program results in a closer surveillance of the laboratory technicians by the shift supervisor, and tends to standardize the methods.

An additional method of maintaining surveillance of measurements which we have found to be extremely valuable is based upon a regression analysis (2) of the process variables of the system. Data collected during steady-state operations can be subjected to statistical analysis to identify those parameters whose effect is significant. All of these variables may well be significant between major changes in operating conditions, but day-to-day effects of minor changes in certain variables, or major changes in variables the effect of which is minor, can be ignored. The technique of regression analysis, i.e., evaluation of "best estimates" of the parameters provides an empirical equation relating the significant variables.

Thus, dissolver effluvia contain uranyl nitrate, nitric acid, mercuric nitrate, and fission product in solution. For the usual, batch-by batch, day-by-day cases, none of these parameters will change over a wide range. At a fairly constant level of burn-up, charging a constant number of slugs or fuel elements to each batch, starting with the same acid concentration, mercuric nitrate content, and so on, a system of measurement limits can be established, deviation from which provides a prompt signal that closer surveillance is required. In this manner, regression analysis of plant data provided a relationship between uranium concentration, solution specific gravity and acidity. This equation contains factors which provide the best estimate for the dependent variable, in this case, uranium concentration.

For laboratory reference, the equation was represented in nomograph form and, by computation of the relevant limits of uncertainty surrounding this "best estimate", an independent check of the laboratory measurement of uranium concentration was provided. Accordingly, when the "spike-U" measurement was found to differ by more than 0.09 concentration units from the value indicated by the nomograph from specific gravity and acidity, the analysis was re-run. Results have been extremely satisfactory. The nomograph is illustrated in Figure 1.

To provide an additional degree of process surveillance, control was effected on changes in process variables in sequential steps. For example, acidity and specific gravity are measured both in the dissolver and coarse-feed tank. The solution transfer is effected by steam-jet eductors, hence a slight decrease in each of these parameters can be anticipated. Analysis of plant data provided limits for control charts to show the expected change, dissolver to coarse-feed tank. As above, deviates signal possible trouble. Typical charts are illustrated in Figures 2 and 3.

A third method which proved most valuable is the estimation of burn-up and, thence, residual uranium content of spent fuel, by U-236 balance. To the degree that a stoichiometric relationship exists between the U-236 produced and the U-235 fissioned, we can write,

$$\text{Grams residual uranium} = \frac{(\text{Grams Cold-U})(\alpha)}{\alpha + z} \dots \dots \dots (12)$$

where z denotes atom fraction of U-236,

α denotes the capture-to-fission nuclear cross-section ratio for U-235 (3,4)

Grams cold-U is determined from shipper's and fabricator's data, and a local piece-count.

656 - 16

As mentioned in a preceding section, a valid input measurement with the associated limits of uncertainty is crucial to optimum dissolver operation under the nuclear-criticality limitations. Similarly, the validity of the stated residual U-235 content of the spent reactor fuel elements is just as important, since the residual fissionable material in a dissolver at any given time is equal to the cumulative amount charged as calculated from shipper's figures, less the cumulative amount dissolved as measured batch-wise by the isotopic-dilution method of analysis. The "operating line" for a dissolver, i.e., the cumulative allowable charge appropriate for each successive batch, reflects this heel calculation and the associated uncertainty in the calculations. The usual definition of the limits of uncertainty (5% and 1% risk of error) seem inadequate, in view of the possible consequences of an inaccurate estimate. For this reason the heel uncertainty was estimated with a 1:10,000 risk which was felt to be adequate since the dissolvers rarely run more than 80 consecutive batches before a complete cleanout is effected.

Little information is available from which the random errors associated with a given dissolver charge can be deduced. Usually all fuel elements of a given type have the same nominal uranium cold content and enrichment factor, and will have been apportioned reactor energy according to estimated distribution curves. Any systematic error, however, should be reflected in the accuracy with which the residual heel is estimated over various dissolver runs, assuming that the amount dissolved as determined by the isotopic dilution method, is in control.

Accordingly, a detailed examination of eight process dissolver sequences, clean dissolver-to-clean dissolver, of approximately 40 batches in each sequence showed that a consistent over-estimation of residual heel of about 2 per cent resulted from summation of batch-wise measurements by the isotopic dilution method described heretofore. This was particularly disturbing for two reasons: first, the systematic over-estimation of total dissolver charge resulted in a fallacious restriction on the apparent amount of metal which could be charged at a given batch. This causes a lower through-put since maximum dissolution rate is obtained when the dissolvers are charged to capacity within the criticality limitation. Secondly, it was uncomfortable to observe that if this discrepancy were the result of the random errors entering the measurements from which the heel was calculated, it could just as well be low as high, and of an order of magnitude not expected from an analysis of the quality control data on each measurement made!

In view of the extent of the quality control program on all measurements associated with the batch-wise measurements of the amounts dissolved, a rigorous examination was made of the shipper's stated residual content of the charges, by means of the U-236 balance. It was apparent that the shipper had been understating the burn-up in this fuel, by a small but systematic percentage.

Closer scrutiny revealed that part of this error was due to a minor clerical error which was readily resolved. The remainder was due to two factors, (a), apportionment of reactor energy integral, and (b) a slightly erroneous value for energy per fission. No means existed, of course, for evaluation of these two factors without plant-scale data from processing the fuel. When the indicated changes in calculations were made, material balance data on all lines was within 0.1 per cent.

As a corollary, values were computed (5) for "spectrum averages" for and energy per fission. A summation of these results is given in Table II.

TABLE III

<u>Material Type</u>	<u>α</u>	<u>Mev per Fission</u>
NP and MTR	0.185 $\pm$.005	195 $\pm$ 10

The equation relating the uncertainty in the estimated total charges to the dissolver of the "n'th" coarse feed-tank measurement contains the following terms:

- (1) uncertainty in the bias estimate associated with the analytical measurement of all dissolver batches,
- (2) uncertainty associated with the measured content of the i'th batch,
- (3) uncertainty associated with the estimated charge corresponding to the i'th batch.

Since the shipper's burn-up calculations had been corrected it was felt that these values were unbiased; hence no correction for bias in that estimate appears in the equation.

The bias associated with the analytical method of measurement, i.e., isotopic dilution, was isolated to the remote dilution-pipetting step of the sample preparation. A rigorous control is maintained over the operations, and bias estimates and associated limits are routinely computed. The uncertainty in the measured content of any given is determined from the routine application of the nested-type sampling program described in preceding sections.

In application of the equation for heel uncertainty calculations, the anticipated extreme in amount dissolved and in dissolver charge over a given run were in lieu of the actual values, as well as the extreme in the burn-up associated with a given batch. Thus the equation becomes a function primarily of "n", the batch number, and reduces to a form amenable to easy solution.

In the case of a particular type of fuel, where the number of fuel elements or slugs charged to each cycle is fixed, and information is available regarding the unirradiated and irradiated content of the material, the operating line equation would have the form,

$$D_n = A \left\{ (x_b B n)^2 + (x_r B \sqrt{n})^2 + [C(n')^{\frac{1}{2}}]^2 \right\}^{\frac{1}{2}} \dots \dots \dots (13)$$

where D_n denotes maximum allowable dissolver charge for batch n ,

x_r denotes the random uncertainty or imprecision of the measurement method,

A denotes maximum allowable dissolver charge when heel uncertainty is zero,

B denotes maximum amount of material dissolved per batch,

C denotes maximum average uncertainty in the estimate of burn-up attributed to the material by the shipper,

x_b denotes uncertainty in the estimated bias of the analytical method, and

n' denotes a modified function of n to adjust for variations in charging procedure at the beginning of a run.

In practice it has been found that the locus of dissolver charges intersects the operating line at about 60 batches. Safe operation is then effected either by reducing the heel by a dissolution cycle without a charge, or by reducing the charge size. An examination of the operating line beyond the point of intersection with the locus of dissolver charges indicates that the frequency of the need for heel reductions increases; thus throughput drops sharply. Similarly with regard to charge size reduction, this tends to reduce the amount dissolved, by reducing the total amount of metal in the dissolver; hence the net effect is similar. A flexible charge-size program is considered undesirable, as this introduces an additional opportunity for operator error, as affecting the hazard represented by a multiple, or erroneous dissolver charge. A schematic representation of dissolver operation is illustrated by Figure 4.

A decision must be made at this point, therefore, to suffer either a somewhat reduced overall dissolution rate, or a momentary gross reduction in dissolution rate by arresting charged altogether, and effecting complete dissolver clean-out. By cleaning out, the heel uncertainties are forced to zero, and the locus of dissolver charges can be restored to the high values allowable at the beginning of a run. A usual dissolver clean-out will comprise six to eight dissolutions, with no fresh material being charged. Knowing the average amount dissolved in each routine process batch, amortization of the accompanying loss of production can readily be shown.

III PRODUCT MEASUREMENTS

The problems associated with maintenance of rigid control over product measurements is not as complex as for feed. Plant product is in the form of concentrated uranyl nitrate solution, with fission product content reduced to the point where radioactivity is only a few times background. The solution streams from the final product evaporator and accumulates in harp-like banks of vertical storage cylinders in a geometric configuration such that nuclear criticality is impossible. Stainless steel flasks are filled from these banks and their contents assayed prior to shipment.

To formulate a sampling-analytical program which would provide the optimum combination of measurement effort and precision, an experiment was designed similar to that just described for input measurements. This was also an hierarchical, or nested scheme, exactly similar in design, but with different labels on the levels indicated with the diagram on page 14, namely, bank, bottle, sample, and analysis in lieu of batch, sample, preparation, and analysis.

Thus, α_i denotes the deviation attributable to the i'th bank;

$\beta_{j(i)}$ denotes the deviation attributable to the j'th bottle from the i'th bank;

$\gamma_{k(ij)}$ denotes the deviation peculiar to the k'th sample from the j'th bottle from the i'th bank; and

$\delta_{m(ijk)}$ denotes the deviation peculiar to the m'th analysis of the k'th sample from the j'th bottle from the i'th bank.

Following the experiment, which was conducted on actual plant data being collected routinely, each of the error components was evaluated, and the specific points at which measurement effort economy could be effected were clearly identified. Actually, the γ 's and δ 's were confounded in this study, as it had been established by previous calibration tests that both sample-to-sample, and analysis-to-analysis variations were essentially negligible. Accordingly, the following sampling-analytical scheme was adopted:

1. Uranium concentration is determined by the gravimetric method; the result reported on a given bottle being the average of one analysis each on two samples drawn from the bottle. One sample is drawn from the bottom and one from the top;
2. the U-235 percentage to be associated with all bottles drawn at a given time from a given bank is determined by the average of one analysis each on two different samples. The samples to be analyzed are selected in a random manner from the two for each bottle in the bank-time; the only restriction being that each sample must come from a different bottle;
3. spectrochemical analyses are performed on one of the two samples available from each product bottle. It was apparent that the bottle-to-bottle variation tended to mask the analytical-plus-sampling errors; hence little is to be gained by doing two analyses on each bottle. Furthermore, the increase in precision resulting from duplicate analyses on each bottle has negligible effect on the correction which is applied to the grav-U determinations;

4. specific gravity determinations were greatly reduced; instead of making this measurement on each of the two samples available from each bottle, a program similar to that for U-235 was adopted. Two samples, each from different bottles were randomly selected from all available from a given bank-time-draw combination. These samples were analyzed once and the average reported as the specific gravity of all bottles drawn from that bank.

In every case, re-run limits were provided on the basis of the above experiment. Similarly, for Material Accountability purposes and process control, limits of uncertainty were derived for each measurement according to the sampling scheme under which it was obtained. With regard to gravimetric-U and spectrochemical, these limits reflected only the variation between samples and analyses drawn from a bottle at a given time. For U-235 percentage and specific gravity, the re-run limits were an indication of the variation between samples and analyses from a given bottle, plus the variation between bottles from a given bank. In addition it was apparent that under steady-state conditions of the extraction system, a control on column performance could be effected by maintaining control charts on the ranges and mean results of measurements performed on "n" bottles, especially with regard to total impurities and uranium concentration. Control charts on individual values--the limits a reflection of the sampling scheme under which they were obtained--assisted laboratory personnel in detecting outliers either analysis-wise, sample-wise, or bottle-wise.

A natural consequence of such a program is a gross reduction in the number of measurements routinely being made. With regard to mass distribution and specific gravity, the number of analyses was reduced by a factor of three. Spectrochemical measurements were cut in half. The number of gravimetric uranium analyses routinely being performed remained the same, however. An analysis of the data indicated that little improvement in precision is realized by analyzing both samples from each bottle, but in view of the consequences of an undetected outlier (however remote this might be) producing an apparent shipper-receiver discrepancy, it was deemed wise to analyze both samples, this being about the least expensive analysis in the laboratory.

IV PLANT WASTE STREAMS

The plant waste streams consist of solutions of fission product bearing minuscule quantities of uranium. The usual method of analysis for uranium concentration in these solutions is by the fluorophotometric technique. Because of the low concentration and the fact that these solutions frequently bear particulate matter in suspension, tremendous analytical and sampling errors are experienced in many cases. It is, in fact, extremely difficult to establish precision or reproducibility for any measurement on these waste streams, since the errors have been found to depend to a large extent upon the particular solution being sampled. For this reason, any control program for precision on a given solution must utilize only the information available from

the analyses of samples from that solution. Over a period of several months solution turbidity and heterogeneity apparently extended over a wide range. Whenever possible, samples were obtained which conformed to a nested sampling scheme as described in preceding sections. In each case, estimates for the sampling and analytical errors were obtained. As anticipated, these estimates ranged from the sublime to the ridiculous indicating that to assume an overall analytical and sampling error was simply not justified. It was obvious therefore that some multiplicate sampling scheme for each solution must be put into effect. Because of the dilute nature of these solutions, high analytical precision was not justified on the basis of dollar value of the material. Accordingly, a sequential type of analytical and sampling program was adopted.

Initially a single sample is drawn and analyzed from the process waste tanks. If the result of this analysis, plus the uncertainty (deduced from the most pessimistic estimates of the sampling and analytical errors obtained previously by the nested sampling scheme) does not exceed the solution tolerance limits, only the single analysis is made.

By far the majority of waste batches fall in this category. If, however, the analytical result plus the limit exceeds the maximum permissible concentration, another sample and, in some cases, depending upon the precision required, several samples are taken and the average of the resulting analyses reported.

Bias control is effected by a system of synthetic samples routinely submitted to the laboratory. For the reasons just described, however, the imprecision usually associated with an analysis is so large that very little effort for bias control is warranted.

In addition to process stream samples, many other solutions are sampled and analyzed for specified components. These are mainly "cold" samples in which sampling errors are insignificant. Hence, the synthetic sample control program can serve to estimate both the bias and the precision to be associated with the particular solution and the particular method.

In every case, whether the sample is a process stream or cold sample, some component is being measured, or whether the technique of analysis is being tested, bench standards are run prior to any series of such samples; and whenever two or more analyses are made on a given solution, re-run limits reflecting the component errors are provided.

V SUMMATION

Application of the formal methods of statistical analysis to correlation (regression analysis) of plant-scale operating variates is described, citing examples from recovery of enriched uranium from spent reactor fuel at the Idaho Chemical Processing Plant of the AEC. The utility and strength of these mathematical tools in the solution of chemical processing problems is illustrated in detail.

The specific requirement of surveillance and apprehension of nuclear criticality in dissolution equipment containing enriched uranium was met by formulation of a dissolver operating line which complied with the definition of safe conditions. This was accomplished by a systematic procedure for identification and optimization of measurement errors, under a technique such that routine scrutiny of plant-scale process data afforded surveillance of measurements, and assurance at the necessary confidence level that operation was safe.

The optimization of measurement control effort with precision warranted close scrutiny at this Plant because of the high value of the material. The same principle will apply equally, however, whether the material being handled is uranium, butadiene, or polio vaccine.

26

FIG. 2 CHANGES IN SPECIFIC GRAVITY FROM DISSOLVER TO COARSE-FEED TANK, COMPARED WITH EXPECTED CHANGE

652-255-

FIG. 3 CHANGES IN ACID NORMALITY FROM DISSOLVER TO COARSE-FEED TANK, COMPARED WITH EXPECTED CHANGE

28

FIG.4 DISSOLVER CHARGE SEQUENCE EXPRESSED AS PER CENT OF ALLOWABLE AT ZERO HEEL UNCERTAINTY

656-27

NOMENCLATURE

μ

denotes "true" value of a population mean estimated from a sample of size "n".

Var(x)

denotes variance of the parameter x and is estimated by the mean square deviation of a sample from the population. This is expressed mathematically by

$$\text{Var}(x) = \frac{\sum_{i=1}^n x_i^2 - \left[\sum_{i=1}^n x_i \right]^2 / n}{n - 1}$$

σ_x

denotes the standard deviation of a population and is equal to the square root of the variance.

ρ

denotes correlation coefficient, and is expressed as

$$\rho = \frac{\sigma_{xy}}{\sigma_x \sigma_y}$$

σ_{xy}

denotes the co-variance of the parameters x and y, and is a statistical function which measures the degree of dependence of x and y upon each other.

b, α , β , γ , δ

denote sources of measurement error identified for specific examples in the text.

i, j, k, m

(pages 13, 14) are subscripts denoting process batch, sample, sample preparation, and analysis, respectively.

i, j, k, m

(page 21) are subscripts denoting product storage bank, bottle, sample, and analysis, respectively.

(pages 17, 19) denotes the nuclear cross-section ratio, capture-to-fission for U-235. As used here it is a stoichiometric relationship, atoms U-236 produced per atom U-235 fissioned.

C, G, N^A

denote uranium concentration, gm/liter; specific gravity; and acid normality, respectively, in the equation,

$$C = 10.93(G - 1.021) - 0.304N^A$$

REFERENCES

- (1) Grubbs, F. E., "On Estimating Precision of Measuring Instruments and Product Variability", J. Am. Stat. Assn. 43, No. 242 (June 1948)
- (2) Hald, A., "Statistical Theory with Engineering Applications", Jno. Wiley & Sons, Inc., New York, 1952
- (3) BNL-250, August 1, 1954 (AEC Classified Report)
- (4) BNL-276, January, 1954 (AEC Classified Report)
- (5) IDO-14332, April 12, 1955 (AEC Classified Report)