

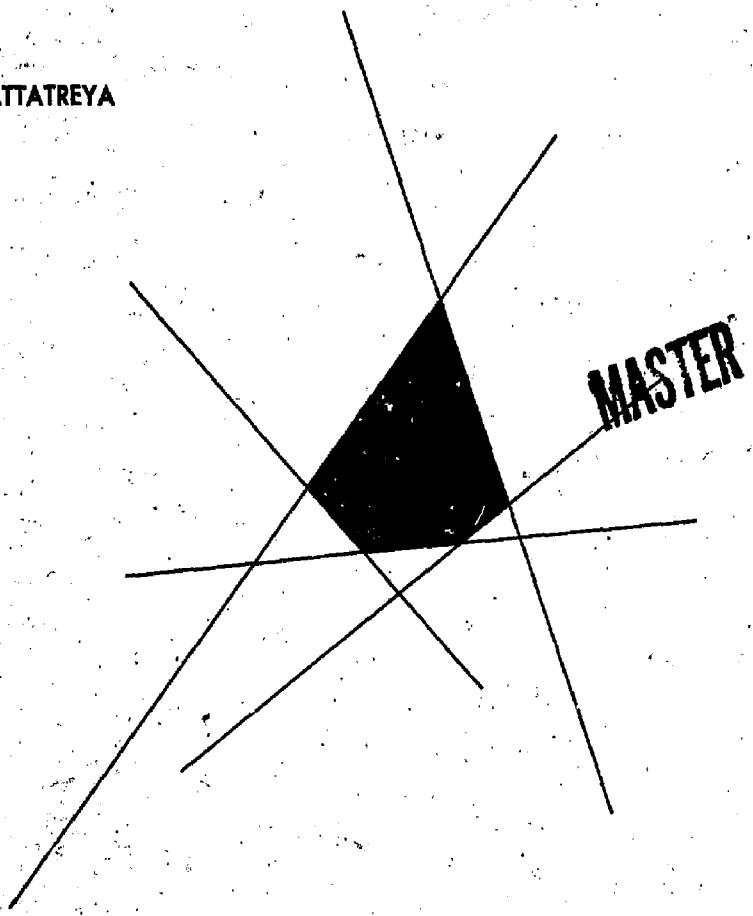
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MODELS AND ERROR ANALYSES OF MEASURING INSTRUMENTS IN ACCOUNTABILITY SYSTEMS IN SAFEGUARDS CONTROL

by
E. SUNDARARAJAN DATTATREYA



OPERATIONS RESEARCH CENTER

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ABSTRACT

Essentially three types of measuring instruments are used in plutonium accountability systems: (i) the bubblers, for measuring the total volume of liquid in the holding tanks, (ii) coulometers, titration apparatus and calorimeters, for measuring the concentration of plutonium; and (iii) spectrometers, for measuring isotopic composition. These three classes of instruments are modeled and analyzed. Finally, the uncertainty in the estimation of total plutonium in the holding tank is determined.

TABLE OF CONTENTS

	Page
CHAPTER 1: INTRODUCTION	2
CHAPTER 2: VOLUME AND MASS MEASUREMENTS	7
CHAPTER 3: CONCENTRATION MEASUREMENT	12
3A. Controlled Potential Coulometry	12
3B. Dry Calorimetry	25
3C. Amperometric Titration	33
CHAPTER 4: ISOTOPIC COMPOSITION	37
4A. A General Model	37
4B. Gamma Ray Spectrometer	41
4C. Mass Spectrometer - I	42
4D. Mass Spectrometer - II: Isotope Dilution Method	44
CHAPTER 5: ESTIMATION OF TOTAL PLUTONIUM	49
REFERENCES	51

Symbols Used in Section 1

a, b	Instrument error coefficients
C	Plutonium concentration in solution
$\bar{E}(\cdot)$	Expected value of argument
M	Mass of solution in accountability tank
Q	Mass of plutonium in the accountability tank
$\text{Var}(\cdot)$	Variance of argument
X	A measurement by an instrument
α	Composite atomic weight of plutonium corrected for isotopic composition
β, ν, θ	Error coefficients in model
ϵ_i	Error components
μ	Expected value of X

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1. INTRODUCTION

Estimation of total plutonium held in a reprocessing plant is of fundamental interest in plutonium accountability systems. The estimation procedure can be divided into three major steps:

- (i) Estimation of the total mass, M , of plutonium containing material, e.g., the acid solution in an accountability tank. Pressure-type devices [bubblers] are used for this purpose.
- (ii) Estimation of the concentration of plutonium, C , in the plutonium containing material. *Coulometers, calorimeters and titration apparatus* are used for this estimation.
- (iii) Estimation of the isotopic composition of plutonium, α . Gamma ray and mass spectrometers are used for this purpose.

If we denote the total mass of plutonium by Q , we can then write

$$(1.1) \quad Q = M \cdot C \cdot \alpha .$$

Thus, Q is not measured directly; it is estimated indirectly from estimation of M , C and α .

The quantities M , C and α , in turn, are derived from measurements by more basic measuring instruments such as balances, pressure gauges, voltmeters, etc.

The variance in the estimation of Q can be represented as a function of the variances of estimates of M , C and α using (1.1). The variances of estimates of M , C and α can be computed from the error variances of the basic instruments used by careful analysis of the actual measurement procedure.

In this report, we first develop expressions for the variances of estimates of M , C and α , in terms of the error variances of the basic instruments. These variance estimates can then be used to compute the error variance in the estimation of total plutonium.

Unless otherwise noted, we have assumed that the errors in the basic measurements are independent. We also make one other assumption about the relation between mean and variance of the measurements as discussed below.

Let \tilde{X} be the true value of a property, and X be the value as measured by an instrument. Let ϵ denote the instrument error. Then,

$$X = \tilde{X} + \epsilon .$$

Let

$$E(X) = \mu .$$

The error variable ϵ can be thought of as having three components, showing three kinds of behavior. Let

$$\epsilon = \epsilon_1 + \epsilon_2 + \epsilon_3$$

where the error components ϵ_1 , ϵ_2 and ϵ_3 are such that:

- (i) ϵ_1 has constant relative standard deviation, i.e., standard deviation of ϵ_1 is proportional to the magnitude of μ or variance of ϵ_1 is proportional to μ^2 :

$$\text{Var } \epsilon_1 = \theta \mu^2 .$$

θ is a constant of proportionality.

- (ii) ϵ_2 has constant relative variance, i.e., variance of ϵ_2 is proportional to the magnitude of μ :

$$\text{Var } \epsilon_2 = \beta |\mu| ,$$

β being a constant of proportionality.

- (iii) ϵ_3 has constant variance, i.e.,

$$\text{Var } \epsilon_3 = \lambda = \text{constant},$$

independent of the value of μ .

Assuming that the components are mutually independent, we can express the variance of ϵ in terms of component variances as:

$$\begin{aligned} \text{Var } \epsilon &= \text{Var } \epsilon_1 + \text{Var } \epsilon_2 + \text{Var } \epsilon_3 \\ &= \theta \mu^2 + \beta |\mu| + \lambda . \end{aligned}$$

In the case of certain instruments, some error components might dominate the others. For example, if $\theta = \beta = 0$ and $\lambda \neq 0$, then we have constant variance behavior for ϵ , etc.

Instrument errors are often expressed as (a % of full scale + b % of reading). Here we have

$$\theta = \left(\frac{b}{100}\right)^2$$

$$\beta = 0$$

$$\lambda = \left(\frac{a}{100} \times \text{full scale}\right)^2 .$$

We square the quantities on the right-hand side because the instrument errors are usually given as standard derivation components, and here we are computing variances, and

$$\text{variance} = (\text{standard derivation})^2 .$$

In this report, we have treated the error component with constant relative standard deviation as significant. Therefore, all final error computations are expressed in terms of relative standard deviations. However, these can easily be modified to include the other two kinds of error behavior.

Symbols Used in Section 2

A	Cross sectional area of tank
$E(\cdot)$	Expected value of argument
g	Acceleration due to gravity
H	Height of liquid in the tank
M	Mass of liquid in the tank
P	Pressure reading
V	Volume of liquid in the tank
Var (\cdot)	Variance of argument
X , Y	Random variables
Z	Heel or zero correction
ϕ	Slope of calibration curve = $\frac{A}{g}$
ψ	Intercept of calibration curve = $\frac{AZ}{g}$
ρ	Density of liquid in the tank

2. VOLUME AND MASS MEASUREMENTS

Principle:

The pressure at a point inside a liquid varies directly as the density of the liquid and the height of the liquid surface above that point. If we know the density of the liquid, the height can be determined by measuring the pressure at a point within the liquid. By a knowledge of the geometry of the tank or by means of calibration experiments, the volume and hence the mass of liquid in the tank can be determined.

Sources of Error:

1. Departure of the tank geometry from the assumed geometry due to temperature change, etc.
2. Uncertainty in the value of the zero correction Z .
3. Errors in measuring devices, i.e., pressure gauges.
4. Errors due to inadequate operator techniques.

Let

P = pressure reading from the pressure gauge

ρ = density of liquid in the tank

H = height of liquid in the tank [measured from the bottom of the tank]

Z = zero correction [heel]

A = cross sectional area of the tank

V = volume of liquid in the tank and

M = mass of liquid in the tank.

We need the zero correction Z because the point at which the pressure P is measured is not at the bottom of the tank. Thus, even when P is

zero, there could still be some liquid in the tank. Note that Z is the pressure that corresponds to the smallest quantity of liquid that can be measured.

We have

$$(Z + P) = \rho g H$$

$$V = A \cdot H$$

$$= A \cdot \frac{(Z + P)}{\rho g}$$

and

$$M = \rho \cdot V$$

$$= \frac{A}{g} [P + Z]$$

$$= \frac{A}{g} \cdot P + \frac{A}{g} Z = \phi P + \psi$$

where

$$\phi = \frac{A}{g} \text{ and } \psi = \frac{A}{g} \cdot Z .$$

ϕ is the slope of the calibration curve and ψ is the zero intercept.

Thus, given the pressure reading, the corresponding mass can either be computed as above or read off from the calibration curve.

The variance of M is now given by:^{*}

$$(2.1) \quad \text{Var } M = \phi^2 \text{Var } P + P^2 \text{Var } \phi + \text{Var } \psi ,$$

assuming the independence of ϕ , P and ψ .

* The following approximations [6] are frequently used in this report: If X and Y are two independent random variables, then,

$$\text{Var } (X \cdot Y) \cong E^2(X) \cdot \text{Var } (Y) + E^2(Y) \cdot \text{Var } (X)$$

$$\text{Var } \left(\frac{X}{Y} \right) \cong \frac{E^2(X)}{E^2(Y)} \left\{ \frac{\text{Var } (X)}{E^2(X)} + \frac{\text{Var } (Y)}{E^2(Y)} \right\} .$$

If X and Y are not independent, then,

$$\text{Var } \frac{X}{Y} \cong \frac{E^2(X)}{E^2(Y)} \left\{ \frac{\text{Var } X}{E^2(X)} + \frac{\text{Var } Y}{E^2(Y)} - \frac{2 \text{Cov } (X,Y)}{E(X)E(Y)} \right\} .$$

Example 1: Large Accountability Tank

The unprocessed fissionable materials are stored in acid solution in a large accountability tank.

Using typical values [5] for ϕ and P and relative standard derivations of .04% for measurement errors, we get:

$$\begin{aligned}
 P &= 4.68 \times 10^5 \text{ dynes/cm}^2 & \text{Var } P &= 3.5 \times 10^4 \\
 \phi &= 11.38 \text{ cm sec} & \text{Var } \phi &= 2.1 \times 10^{-5} \\
 \psi &= 5.2 \times 10^4 \text{ gms/sec} & \text{Var } \psi &= 4.3 \times 10^2 \text{ and} \\
 \text{Var } M &= 9.06 \times 10^6 .
 \end{aligned}$$

Setting $M = 10^6$ gms, we get the relative standard derivation of M to be .3%.

Example 2: Small Concentration Tank

Concentrated plutonium nitrate at the end of the process is stored in a small tank having a capacity of about 10 litres. Assuming proportional dimensions as in the case of the large tank, we have:

$$\begin{aligned}
 P &= 2.736 \times 10^4 \text{ dynes/cm}^2 & \text{Var } P &= 1.19 \times 10^2 \\
 \phi &= .653 \text{ cm. sec} & \text{Var } \phi &= 6.8 \times 10^{-8} \\
 \psi &= 3.04 \times 10^3 \text{ gms/sec} & \text{Var } \psi &= 1.47 \text{ and} \\
 \text{Var } M &= 1.0085 \times 10^2 \text{ gm}^2 .
 \end{aligned}$$

Setting $M = 2 \times 10^4$ gms we get the relative standard deviation of M to be .05%.

Relative errors can similarly be computed in other practical situations.

Symbols Used in Section 3A

A	Equivalent weight of plutonium
B_i	Background readings from integrator
D, S	Integrator readings
e	Equivalents of plutonium per gram of solution
E	Equivalents of plutonium in standard solution
$E(\cdot)$	Expected value of argument
F	Faraday constant
F_c	Chemical calibration factor
G	Atomic weight of plutonium
M	Grammolecular mass of plutonium
P	Concentration of plutonium
Q	Quantity of electricity
rsd (\cdot)	Relative standard deviation of argument
Var (\cdot)	Variance of argument
W_i	Mass of solution
X	Mass of sample solution
Z	Random variable
ϵ_i, θ_i	Error variables
σ_i^2	Variance of ϵ_i
π_i	rsd corresponding to ϵ_i

3. CONCENTRATION MEASUREMENT

3A. Controlled Potential Coulometry

Principle:

The sample to be analyzed is dissolved in an electrolyte and electrolyzed. From the quantity of electricity needed by the electrolysis, the mass of the substance being determined [i.e., Pu] can be computed using Faraday's Law or by using calibration runs with standards.

By carefully controlling the potential at the electrodes, unwanted electrode reactions are precluded and the required reaction [i.e., electrolysis of plutonium] is completed.

Procedure:

The following is a description of the procedure as detailed in Reference [1].

1. Standard: Dissolve a weighed amount of plutonium in 5ml of 6M HCl and dilute with 2M H_2SO_4 . Weigh the solution again and compute the equivalents of Pu/gm of solution.

$$\text{eq. of Pu/gm of solution} = e = \frac{\text{wt. of Pu standard}}{\text{wt. of solution} \times \text{at. wt. of Pu}}$$

2. Background: Fill the cell with the electrolyte, and carry out the electrolysis for the period of time normally required for plutonium samples. Record the integrator voltage as the background reading B_2 .
3. Calibration: Quantitatively transfer aliquot of plutonium standard solution containing 9 to 15 mg of plutonium into the

cell. Carry out the electrolysis till the transformation is complete. Record the integrator reading voltage as D .

4. Compute the chemical calibration factor F_c as follows:

$$F_c = \frac{E}{(D - B_2)}$$

where, E = equivalents of plutonium in aliquot of standard solution.

5. Sample solution: A solution of the sample to be analyzed is prepared in a way similar to the preparation of the standard plutonium solution.
6. Background: The background reading for the sample is taken as in step 2. Call this integrator voltage reading B_1 .
7. Electrolysis: Quantitatively transfer an aliquot of sample plutonium solution into the cell. Carry out the electrolysis to completion. Let the integrator reading voltage be S .
8. Compute: The plutonium assay of the sample is given as follows:

$$\text{gms of Pu/gm of sample} = \frac{(S - B_1)F_c \cdot A}{X}$$

Here:

X = mass of sample aliquot in gms and

A = equivalent weight of Pu adjusted for isotopic composition.

Notes:

- (A) Electrical calibration: Although chemical calibration as in (3) above is recommended for the determination of plutonium, periodic [once in 6 months] electrical calibration will serve to indicate

the proper and reliable performance of the integrator. For methods of pooling together results of chemical and electrical calibration, see References [2] and [3].

The quantity of plutonium present, W , is computed as follows:

$$W = \frac{1.0018}{F} \cdot MQ$$

where:

F = Faraday constant = 96,485 coulombs

per gm equivalent

M = grammolecular mass of plutonium adjusted for isotopic composition

Q = quantity of electricity in coulombs.

- (B) Maximum accuracy and precision are achieved with a quantity of plutonium of 5 to 15 mg per coulometric determination.
- (C) Analysis time: The time for one operator to carry out the analysis of one sample in triplicate is about 4-6 hours. This includes two calibration runs with standards.
- (D) Reliability of the method: A relative standard deviation of .04% has been obtained for this method in the replicate analysis of a single plutonium solution.

Sources of Error:

- (i) Calibration error due to uncertainty in the value of the standard used.

- (ii) Weighing errors due to accuracy uncertainty of the analytical balance (0.026%).
- (iii) Inadequate sparging of oxygen from cell prior to and during the electrochemical steps.
- (iv) Uncertainty in the integrator reading (0.03%).
- (v) Error can occur due to a malfunctioning reference electrode.
- (vi) Errors due to inadequate operator techniques.

The Model:

We have:

$$P = \frac{F_c A}{X} (S - B_1)$$

where

P = concentration of plutonium in the sample

F_c = calibration constant determined with the standard

A = equivalent weight of plutonium corrected for isotopic composition

X = mass of the sample

S = integrator reading for the sample

B_1 = background reading.

In the following analysis, each measurement random variable [e.g., X] is expressed as the sum of a constant \tilde{X} and an error variable $[\epsilon_j]$.

Each ϵ_i is assumed to have mean zero and variance σ_i^2 , and in addition independent of other error variables. Clearly, X is a good estimate of \tilde{X} and is used so here.

Now, let

$$S - B_1 = \tilde{S} + \epsilon_1$$

where S is the true value of the quantity being measured above background [a constant] and ϵ_1 is the total error in the estimate $(S - B_1)$ and has the following components:

$$\epsilon_1 = \epsilon_{11} + \epsilon_{12} + \epsilon_{13}$$

where

ϵ_{11} = error due to inadequate sparging of oxygen

ϵ_{12} = error due to malfunctioning of the reference electrode

ϵ_{13} = operator error.

Similarly we have:

$$F_c = \tilde{F} + \epsilon_2 ,$$

ϵ_2 is the error in the estimation F_c .

$$X = \tilde{X} + \epsilon_3 ,$$

ϵ_3 is the weighing error.

$$A = \tilde{A} + \epsilon_4 ,$$

ϵ_4 is the error in the value of A .

$$E = \tilde{E} + \epsilon_5$$

where E = equivalents of plutonium in an aliquot of standard solution,

and ϵ_5 is the error in its estimate. Recall that

$$F_c = \frac{E}{(D - B_2)} .$$

ϵ_5 is a combination of weighing errors. Also let

$$D - B_2 = \tilde{D} + \epsilon_6$$

where ϵ_6 has similar components as in ϵ_1 .

It is interesting to compare the variance of X and E , i.e., of ϵ_3 and ϵ_5 , since

$$\text{Var } X = \text{Var } (\tilde{X} + \tilde{\epsilon}_3) = \text{Var } (\epsilon_3)$$

and

$$\text{Var } E = \text{Var } (\tilde{E} + \epsilon_5) = \text{Var } \epsilon_5.$$

Let:

$$\text{Var } \epsilon_1 = \sigma_1^2,$$

and

W_1 = weight of plutonium dissolved to make the standard solution

W_2 = total weight of standard solution prepared

W_3 = weight of aliquot of the standard solution used in calibration

G = equivalent atomic weight.

Then,

$$E = \frac{W_1}{W_2} \cdot \frac{W_3}{G}.$$

The variance of E is now given by:

$$\text{Var (E)} = \frac{(W_1 \cdot W_3)^2}{W_2^2 G^2} \left[\frac{\text{Var (W}_1 \cdot W_3)}{(W_1 W_3)^2} + \frac{\text{Var } W_2}{W_2^2} \right]$$

Here, θ_i is the weighing error in W_i ,

$$W_i = \bar{W}_i + \theta_i$$

and we have used W_i as an estimate of \bar{W}_i and, as before, mean of θ_i is zero. Setting

$$\text{Var (W}_i) = \text{Var } (\theta_i) = \sigma_0^2, \quad i = 1, 2, 3$$

(since all errors are due to weighing), we get:

$$\text{Var (E)} = \frac{\sigma_0^2}{G^2} \left\{ \frac{W_1^2 + W_3^2}{W_2^2} + \frac{W_1^2 \cdot W_3^2}{W_2^4} \right\} = \sigma_5^2$$

Now,

$$\text{Var X} = \text{Var } (\varepsilon_3) = \sigma_3^2 \approx \sigma_0^2$$

(as both are weighing errors). But, since W_1 and W_3 are small compared to W_2 , we can expect σ_5^2 to be small compared to σ_3^2 .

Applying the expressions for variances of products and ratios of random variables to the relation for P, the concentration, we obtain,

$$\text{Var} (P) = \sigma^2$$

$$= \frac{\tilde{S}^2 \tilde{F}^2 \tilde{A}^2}{\tilde{X}^2} \left[\frac{\tilde{S}^2 \tilde{F}^2 \sigma_4^2 + \tilde{S}^2 \tilde{A}^2 \sigma_2^2 + \tilde{F}^2 \tilde{A}^2 \sigma_1^2}{\tilde{S}^2 \tilde{F}^2 \tilde{A}^2} + \frac{\sigma_3^2}{\tilde{X}^2} \right]$$

Define the relative standard derivation of a random variable Z to be

$$\text{rsd of } Z = \frac{\sqrt{\text{Var} (Z)}}{E(Z)}$$

(rsd of Z) \times 100 = rsd expressed as a percentage.

Let

$$\frac{\sigma_1}{\tilde{S}} = \pi_2 = \text{rsd of } (S - B_1)$$

$$\frac{\sigma_2}{\tilde{D}} = \pi_2 = \text{rsd of } F_c$$

$$\frac{\sigma_3}{\tilde{X}} = \pi_3 = \text{rsd of } X$$

$$\frac{\sigma_4}{\tilde{A}} = \pi_4 = \text{rsd of } A$$

$$\frac{\sigma}{P} = \pi \text{ rsd of } P .$$

Rewriting the expression for σ^2 in terms of the relative standard deviations, we have:

$$(3A.1) \quad \sigma^2 = \frac{\tilde{S}^2 \tilde{F}^2 \tilde{A}^2}{\tilde{X}^2} \left[\frac{\tilde{S}^2 \tilde{F}^2 \frac{\sigma_4^2}{A^2} \tilde{A}^2 + \tilde{S}^2 \tilde{A}^2 \frac{\sigma_2^2}{F^2} + \tilde{F}^2 \tilde{A}^2 \frac{\sigma_1^2}{S^2} \tilde{S}^2}{\tilde{S}^2 \tilde{F}^2 \tilde{A}^2} + \frac{\sigma_3^2}{\tilde{X}^2} \right]$$

$$= \frac{\tilde{S}^2 \tilde{F}^2 \tilde{A}^2}{\tilde{X}^2} \left[\pi_4^2 + \pi_2^2 + \pi_1^2 + \pi_3^2 \right]$$

or

$$(3A.2) \quad \pi = \frac{\sigma}{\tilde{P}} = \frac{\tilde{S} \tilde{F} \tilde{A}}{\tilde{P} \tilde{X}} \sqrt{\pi_1^2 + \pi_2^2 + \pi_3^2 + \pi_4^2}.$$

It is interesting to note that if the amount of plutonium used in calibration is nearly equal to the amount of plutonium in the sample, the multiplying constant $\frac{\tilde{S} \tilde{F} \tilde{A}}{\tilde{P} \tilde{X}} = \frac{\tilde{S} \tilde{A} \tilde{E}}{\tilde{P} \tilde{X} \tilde{D}}$ will be close to unity as follows:

$\tilde{A} \tilde{E}$ = amount of plutonium (in gms) used for calibration

$\tilde{X} \cdot \tilde{P}$ = mass of sample x concentration

= amount of plutonium in sample and

$\tilde{S} = \tilde{D}$ since the amounts of plutonium in the two cases are equal.

Thus,

$$\left(\frac{\tilde{S} \tilde{A} \tilde{E}}{\tilde{P} \tilde{X} \tilde{D}} \right) = \left(\frac{\tilde{A} \tilde{E}}{\tilde{P} \tilde{X}} \right) \left(\frac{\tilde{S}}{\tilde{D}} \right) = 1.$$

In this case,

$$(3A.3) \quad \pi = \sqrt{\pi_1^2 + \pi_2^2 + \pi_3^2 + \pi_4^2}.$$

If the π_i are expressed as percentages, π also will be in percentage.

Of course, the variance in the value of \tilde{P} can be reduced by replicated

Suppose we use two standards to calibrate the instrument and then use one sample to estimate the plutonium concentration.

Let E_1 and D_1 and E_2 and D_2 be the values obtained from standard experiments. We take

$$F_1 = \frac{E_1}{D_1} \quad \text{and} \quad F_2 = \frac{E_2}{D_2}$$

and

$$F_c = \frac{F_1 + F_2}{2}$$

where F_1 and F_2 are the calibration constants for the two experiments and F_c is their mean. Now,

$$P = \frac{S \cdot F_c \cdot A}{X}$$

(here we have dropped the \sim for notational convenience), and

$$\begin{aligned} \text{Var } F_c &= \frac{1}{4} (\text{Var } F_1 + \text{Var } F_2) \\ &= \frac{\sigma_2^2}{2} . \end{aligned}$$

Therefore,

$$(3A.4) \quad \pi = \frac{SF_c A}{PX} \sqrt{\pi_1^2 + \frac{\pi_2^2}{2} + \pi_3^2 + \pi_4^2} .$$

Suppose we use the same standard and calibration for measurement on two aliquots of the given sample, the expression of variance becomes:

$$P_1 = F_c A \frac{S_1}{X_1}$$

$$P_2 = F_c A \frac{S_2}{X_2}$$

$$P = \frac{P_1 + P_2}{2}$$

and

$$\begin{aligned} \text{Var } P &= \frac{\text{Var } P_1 + \text{Var } P_2}{4} + \frac{1}{2} \text{Cov } (P_1, P_2) \\ &= \frac{1}{4} \left\{ (F_c A)^2 \cdot \text{Var } \frac{S_1}{X_1} + \left(\frac{S_1}{X_1} \right)^2 \text{Var } (F_c A) \right. \\ &\quad \left. + (F_c A)^2 \cdot \text{Var } \frac{S_2}{X_2} + \left(\frac{S_2}{X_2} \right)^2 \cdot \text{Var } (F_c A) \right\} \\ &\quad + \frac{1}{2} \frac{S_1}{X_1} \frac{S_2}{X_2} \cdot \text{Var } (F_c A) . \end{aligned}$$

Assuming $S_1 \approx S_2 \approx S$ and $X_1 \approx X_2 \approx X$, we get:

$$\text{Var } P = \frac{1}{2} (F_c A)^2 \text{Var} \left(\frac{S}{X} \right) + \frac{1}{2} \left(\frac{S}{X} \right)^2 \text{Var} (F_c A) + \frac{1}{2} \frac{S^2}{X^2} \text{Var} (F_c A)$$

$$= \frac{1}{2} F_c^2 A^2 \text{Var} \left(\frac{S}{X} \right) + \frac{S^2}{X^2} \text{Var} (F_c A)$$

$$= \frac{1}{2} F_c^2 A^2 \frac{S^2}{X^2} \left(\frac{\sigma_1^2}{S^2} + \frac{\sigma_3^2}{X^2} \right)$$

$$+ \frac{S^2}{X^2} \left[F_c^2 \frac{\sigma_4^2}{A^2} A^2 + A^2 \frac{\sigma_2^2}{F_c^2} F_c^2 \right]$$

$$= \frac{F_c^2 A^2 S^2}{2 X^2} \left(\pi_1^2 + \pi_2^2 \right) + \frac{F_c^2 A^2 S^2}{X^2} \left(\pi_4^2 + \pi_2^2 \right)$$

$$\text{Var } P = \frac{F_c^2 A^2 S^2}{X^2} \left(\frac{\pi_1^2}{2} + \pi_2^2 + \frac{\pi_3^2}{2} + \pi_4^2 \right)$$

or

(3A.5)

$$\pi = \frac{F_c A S}{X P} \sqrt{\frac{\pi_1^2}{2} + \pi_2^2 + \frac{\pi_3^2}{2} + \pi_4^2}$$

Symbols used in Section 3B

A , B	Random variables
C	Weight percent of plutonium in fuel rod
Cov (•)	Covariance of argument
E_i	Voltage readings
$E(•)$	Expected value of argument
J_i	Weight percent of i^{th} isotope in fuel rod
K	Constant
K_i	Power factor of i^{th} isotope
M	Mass of fuel rod
N	Number of isotopes present
Q	Weight percent of americium in fuel rod
R	Power factor of americium
rsd (•)	Relative standard derivation of argument
T	Temperature for calorimeter
Var (•)	Variance of argument
W	Wattage produced by fuel
X , Y	Wattage readings
α , β	Intermediate computations
ϵ_i	Error variables
π_i	rsd corresponding to ϵ_i
σ_i^2	Variance of ϵ_i

3B. Dry Calorimetry

Principle:

Plutonium, as it undergoes radioactive decay, gives out a small quantity of heat. The rate at which heat is produced is proportional to the total amount of plutonium. Thus, an estimate of the amount of plutonium in a fuel rod can be obtained by measuring the heat given out.

Procedure:

The following is a description of the procedure as detailed in Reference [4].

The dry calorimeter is maintained at a constant temperature T (a few degrees above the ambient temperature) by heating it electrically. The wattage required, X , to maintain this temperature is noted. Now, the fuel rod is inserted into the calorimeter, and the temperature is brought back to T . The wattage required to maintain the calorimeter and the fuel rod at T , Y , is noted. Y will be smaller than X because when the fuel rod is in the calorimeter, the heat supplied by the electric coils is supplemented by the heat from the fuel.

Thus,

$$(\text{Watts produced by the fuel}) = W = X - Y .$$

But W is the sum of the watts produced by the different isotopes in the fuel rod.

Let:

M = mass of fuel rod in grams

J_1 = weight percent of each isotope in the fuel rod [plutonium 238,

239, 240, 241 and 242]

K_i = power factor for each isotope in watts/gram

C = weight percent of plutonium in the fuel rod

Q = weight percent of Americium in the fuel rod

K = power factor for Americium

N = number of isotopes present.

In the above, J_i are determined by using mass spectrographic methods. K_i are either computed from the energies of radioactive disintegrations or by separate coulometric measurements.

We now have:

Total mass of plutonium = MC

Mass of i^{th} isotope = MCJ_i

Watts produced by i^{th} isotope = $MCJ_i K_i$

Watts produced by Americium = MQR .

Therefore, the original relation becomes:

$$(\text{Watts produced by the fuel rod}) = W = \sum_{i=1}^N MCJ_i K_i + MQR$$

or

$$C = \left(\frac{W - MQR}{\sum MJ_i K_i} \right)$$

The Model:

In our simplified model, we will assume all errors to be independent. We will also require that J_i , K_i and Q and R be known sufficiently accurately, so that the errors in their values are small compared to errors in weighing etc. Determination of J_i is discussed in Section 4.

We then have

$$\text{Var } C = \text{Var} \left[\frac{W - \text{MQR}}{M \sum J_i K_i} \right].$$

Using the expression for the variance of a ratio, we get

$$\begin{aligned} \text{Var } C &= \frac{\text{Var } (W - \text{MQR})}{\left[M \sum J_i K_i \right]^2} + \frac{\left[\sum J_i K_i \right]^2 (\text{Var } M) (W - \text{MQR})^2}{\left[M \sum J_i K_i \right]^4} \\ &\quad - \frac{(W - \text{MQR})}{\left[M \sum J_i K_i \right]^3} \text{Cov} \left[(W - \text{MQR}), \left(M \sum J_i K_i \right) \right] \\ &= \frac{\text{Var } W + (\text{QR})^2 \text{Var } M}{\left[M \sum J_i K_i \right]^2} + \frac{(\text{Var } M) [W - \text{MQR}]^2}{M^4 \left[\sum J_i K_i \right]^2} \\ &\quad - \frac{W - \text{MQR}}{\left[M \sum J_i K_i \right]^3} \cdot \text{Cov} \left[(W - \text{MQR}), \left(M \sum J_i K_i \right) \right]. \end{aligned}$$

Now, let

$$W = \tilde{W} + \varepsilon_1,$$

where ε_1 is the error in the value of W .

$$M = \tilde{M} + \varepsilon_2,$$

where ε_2 is the weighing error.

Also, let

$$\text{Var } W = \text{Var} (\tilde{W} + \varepsilon_1) = \sigma_1^2$$

$$\text{Var } M = \text{Var} (\tilde{M} + \varepsilon_2) = \sigma_2^2$$

and

$$\text{Var } C = \sigma^2 .$$

To compute

$$\text{Cov} \left[(W - MQR) , \left(M \sum J_i K_i \right) \right]$$

consider

$$\text{Var} (A + B) = \text{Var } A + \text{Var } B + 2 \text{Cov} (A, B)$$

or:

$$\text{Cov} (A, B) = \frac{1}{2} [\text{Var} (A + B) - \text{Var } A - \text{Var } B]$$

where A and B are two random variables.

Thus:

$$\begin{aligned} & \text{Cov} \left[(W - MQR) , \left(M \sum J_i K_i \right) \right] \\ &= \frac{1}{2} \left\{ \text{Var} \left[W - MQR + M \sum J_i K_i \right] - \text{Var} (W - MQR) - \text{Var} \left(M \sum J_i K_i \right) \right\} \\ &= \frac{1}{2} \left\{ \text{Var } W + \text{Var } M \left[\sum J_i K_i - QR \right]^2 - [\text{Var } W + Q^2 R^2 \text{Var } M] - \left[\sum J_i K_i \right]^2 \text{Var } M \right\} \\ &= \frac{1}{2} \sigma_2^2 \left\{ \left[\sum J_i K_i - QR \right]^2 - Q^2 R^2 - \left[\sum J_i K_i \right]^2 \right\} \\ &= \frac{1}{2} \sigma_2^2 \left[- 2QR \sum J_i K_i \right] \\ &= - \sigma_2^2 QR \left[\sum J_i K_i \right]. \end{aligned}$$

The expression for the variance of C now becomes

$$\text{Var } C = \sigma^2 = \frac{\sigma_1^2 + (QR)^2 \sigma_2^2}{M^2 \left[\sum J_i K_i \right]^2} + \frac{\sigma_2^2 [W - MQR]^2}{M^4 \left[\sum J_i K_i \right]^2} - \frac{[W - MQR]}{M^3 \left[\sum J_i K_i \right]^3} \sigma_2^2 \left[\sum J_i K_i \right]$$

$$(3B.1) \quad \text{Var } C = \frac{1}{M^2 \left[\sum J_i K_i \right]^2} \left\{ \sigma_1^2 + (QR)^2 \sigma_2^2 + \frac{\sigma_2^2}{M^2} [W - MQR]^2 - \frac{[W - MQR]}{M} \sigma_2^2 \right\}.$$

Let $\frac{1}{M} (W - MQR) = \alpha$ and $\sum J_i K_i = \beta$. Then,

$$\text{Var } C = \sigma^2 = \sigma_1^2 + \frac{[(QR)^2 + \alpha^2 - \alpha]}{M^2 \beta^2} \sigma_2^2.$$

Let

$$\frac{\sigma_1}{W} = \pi_1 = \text{rsd of } W$$

and

$$\frac{\sigma_2}{M} = \pi_2 = \text{rsd of } M$$

$$\frac{\sigma}{C} = \pi = \text{rsd of } C.$$

Then,

$$(3B.2) \quad \pi = \frac{1}{MBC} \sqrt{W^2 \pi_1^2 + [(QR)^2 + \alpha^2 - \alpha] M^2 \pi_2^2}.$$

The error in the estimation of W can be further analyzed as follows:

$$W = X - Y$$

as before, but X and Y are of the form

$$X = KE_1^2$$

$$Y = KE_2^2$$

where K is a constant and E_1 and E_2 are the voltages measured across the heating coil of the calorimeter.

The value of K is estimated by an independent calibration experiment as

$$K = \frac{E_4}{E_3 R_2}$$

where E_3 is the voltage across the heating coil and E_4 is the voltage across a standard resistor R_2 connected in series with the coil.

Thus

$$W = \frac{E_4}{E_3 R_2} [E_1^2 - E_2^2]$$

Now, letting

$$E_3 = \tilde{E}_3 + \epsilon_3$$

$$E_4 = \tilde{E}_4 + \epsilon_4$$

$$E_1^2 = \tilde{E}_1^2 + \epsilon_5$$

$$E_2^2 = \tilde{E}_2^2 + \epsilon_6$$

and $\text{Var } \epsilon_i = \sigma_i^2$ we have:

$$\text{Var } W = \frac{E_1^4 \sigma_3^2 + E_4^2 \sigma_5^2 + E_2^4 \sigma_3^2 + E_4^2 \sigma_6^2}{E_3^2 R_2^2} + R_2^2 \sigma_4^2 \cdot \frac{E_4^2 [E_1^2 - E_2^2]^2}{E_3^4 R_2^4}$$

It should be observed here that $\sigma_3 \approx \sigma_4$ and $\sigma_5 \approx \sigma_6$, but σ_3 (or σ_4) may not be equal to σ_5 (or σ_6), since E_1^2 and E_2^2 are estimated using integration and time averages whereas E_3 and E_4 are read off on voltmeters.

Now, π_1 can be computed as

$$\pi_1 = \sqrt{\frac{\text{Var } W}{W}}$$

and this value can be substituted in (3B.2) to estimate π .

Symbols Used in Section 3C

A , B	Titration mass
C	Milliequivalent/gram of titrant
$E(\cdot)$	Expected value of argument
D	Milliequivalent mass of plutonium
P	Concentration of plutonium
Var (\cdot)	Variance of argument
X	Mass of sample
ϵ_i	Error variables
σ_i^2	Variances of ϵ_i
π_i	Relative standard derivation corresponding to ϵ_i

3C. Amperometric Titration

Summary of the Method: (see Reference [1])

Plutonium is oxidized to the hexavalent state in a sulfuric acid solution with argentic oxide. After the excess oxidant is destroyed by heating, the plutonium is titrated amperometrically with standard iron (II) sulfate. The endpoint is detected by measuring the current generated by excess titrant at a rotating platinum microelectrode versus a saturated mercurous sulfate reference electrode.

Sources of Error:

1. Calibration error due to uncertainty in the value of the standards used for titrant standardization and calibration.
2. Weighing errors.
3. Error due to change in standardization value of the iron titrant due to air oxidation.
4. Errors due to inadequate operator techniques.

The Model:

We have:

$$P = (A - B) \frac{CD}{X}$$

where

P = plutonium concentration in the sample

A - B = grams of titrant required by plutonium (for a method to compute (A - B) see Reference [1])

C = milliequivalent/gram of iron titrant

D = milliequivalent mass of plutonium adjusted for isotopic composition

X = mass of sample.

Let

$$A - B = \tilde{A} + \epsilon_1$$

where \tilde{A} is the true value of which $(A - B)$ is an estimate and ϵ_1 is the error in this estimate. Similarly

$$C = \tilde{C} + \epsilon_2$$

$$D = \tilde{D} + \epsilon_3$$

and

$$X = \tilde{X} + \epsilon_4$$

Let

$$\text{Var } \epsilon_i = \sigma_i^2$$

The variance of P is now given by

$$(3C.1) \quad \text{Var } P = \sigma^2 = \frac{\tilde{A}^2 \tilde{C}^2 \tilde{D}^2}{\tilde{X}^2} \left[\frac{\tilde{A}^2 \tilde{C}^2 \sigma_3^2 + \tilde{A}^2 \tilde{D}^2 \sigma_2^2 + \tilde{C}^2 \tilde{D}^2 \sigma_1^2}{\tilde{A}^2 \tilde{C}^2 \tilde{D}^2} + \frac{\sigma_4^2}{\tilde{X}^2} \right]$$

Expressing in terms of the relative standard deviations, we have

$$\text{Var } P = \frac{\tilde{A}^2 \tilde{C}^2 \tilde{D}^2}{\tilde{X}^2} \left[\pi_3^2 + \pi_2^2 + \pi_1^2 + \pi_4^2 \right]$$

$$\pi = \frac{\sigma}{\tilde{P}}$$

i.e.,

$$(3C.2) \quad \pi = \frac{\overline{ACD}}{\overline{XP}} \sqrt{\pi_1^2 + \pi_2^2 + \pi_3^2 + \pi_4^2} .$$

In the above $\pi_1 - \pi_4$ are the relative standard deviations of the quantities (A - B) , C , D and X .

Symbols Used in Section 4

A_i	Atomic weight of i^{th} isotope
$\text{Cov}(\cdot)$	Covariance of argument
$E(\cdot)$	Expected value of argument
i, j	Indexing variables
R	Total number of isotopes present
m_o	Mass of diluting isotope
P_i	Peak value corresponding to i^{th} isotope
$\text{Var}(\cdot)$	Variance of argument
X_i	Fractional content of i^{th} isotope
X, Y	Random variables
α	Composite atomic weight of plutonium corrected for isotopic composition
ϵ_i	Error in measurement of P_i
σ^2	Variance of ϵ_i
A, C, P, V_1, V_2	Intermediate results

4. ISOTOPIC COMPOSITION

Virtually every computation involving a quantity of plutonium needs the equivalent weight of plutonium, α , adjusted for isotopic composition. α is a linear combination of the equivalent weights of the different isotopes present.

Let

$$\alpha = \sum_{i=1}^R a_i X_i$$

where

a_i = atomic weight of i^{th} isotope

X_i = fractional content of i^{th} isotope, and

R = number of different isotopes present.

Clearly

$$(4.1) \quad \sum X_i = 1.$$

4A. A General Model

Here we assume that each isotope fraction is measured independently.

$$X_i = \tilde{X}_i + \epsilon_i$$

where \tilde{X}_i is the true value of the fraction of isotope i present, X_i is the measured value and ϵ_i is the error. The error variables ϵ_i are mutually independent.

From the values of X_i , $i = 1, \dots, R$ we can obtain two different estimates of each of the \tilde{X}_i as below:

$$X_{i1} = X_i$$

and

$$X_{i2} = 1 - \sum_{j \neq i} X_j$$

We can also take a weighted average of these two estimates according to their precisions. Let

$$\text{Var}(\epsilon_i) = \sigma^2$$

Then,

$$\text{Var} X_{i1} = \text{Var} X_i = \sigma^2$$

and

$$\text{Var}(X_{i2}) = (R-1)\sigma^2$$

Therefore, the composite estimate \hat{X}_i is:

$$\hat{X}_i = \frac{\frac{X_{i1}}{\text{Var} X_{i1}} + \frac{X_{i2}}{\text{Var} X_{i2}}}{\frac{1}{\text{Var} X_{i1}} + \frac{1}{\text{Var} X_{i2}}}$$

$$= \frac{\frac{X_{i1}}{\sigma^2} + \frac{X_{i2}}{(R-1)\sigma^2}}{\frac{1}{\sigma^2} + \frac{1}{(R-1)\sigma^2}}$$

$$= \frac{1}{\sigma^2} + \frac{1}{(R-1)\sigma^2}$$

$$= \frac{(R-1)}{R} X_{i1} + \frac{X_{i2}}{R}$$

i.e.,

$$\hat{X}_i = \frac{(R-1)}{R} X_i + \frac{1}{R} \left(1 - \sum_{j \neq i} X_j \right).$$

From this, an estimate of α is:

$$\hat{\alpha} = \sum_{i=1}^R a_i \hat{X}_i$$

and the variance of this estimate is:

$$(4A.1) \quad \text{Var } \hat{\alpha} = \sum_i a_i^2 \text{Var} (\hat{X}_i) + \sum_{i \neq j} \sum_j a_i a_j \text{Cov} [\hat{X}_i, \hat{X}_j].$$

Now

$$\begin{aligned} \text{Var } \hat{X}_i &= \text{Var} \left[\frac{R-1}{R} X_i + \frac{1}{R} \left(1 - \sum_{j \neq i} X_j \right) \right] \\ &= \frac{(R-1)^2}{R^2} \sigma^2 + \frac{1}{R^2} (R-1) \sigma^2 \\ &= \frac{\sigma^2}{R^2} [(R-1)^2 + (R-1)] \end{aligned}$$

or

$$(4A.2) \quad \text{Var } \hat{X}_i = \frac{(R-1)}{R} \sigma^2.$$

And for $i \neq j$,

$$\begin{aligned}
 \text{Cov} (\hat{X}_i, \hat{X}_j) &= \text{Cov} \left[\left[\frac{R-1}{R} X_i + \frac{1}{R} \left(1 - \sum_{n \neq i} X_n \right) \right]; \left[\frac{R-1}{R} X_j + \frac{1}{R} \left(1 - \sum_{n \neq j} X_n \right) \right] \right] \\
 &= -\frac{R-1}{R^2} \sigma^2 - \frac{R-1}{R^2} \sigma^2 + \frac{1}{R^2} (R-2) \sigma^2 \\
 &= \frac{\sigma^2}{R} [-(R-1) - (R-1) + (R-2)]
 \end{aligned}$$

or

$$(4A.3) \quad \text{Cov} (X_i, X_j) = -\frac{\sigma^2}{R}.$$

Substituting (4A.2) and (4A.3) in (4A.1) we have:

$$\begin{aligned}
 \text{Var} \hat{\alpha} &= \sum a_i^2 \frac{(R-1)}{R} \sigma^2 + \sum_{i \neq j} \sum a_i a_j \cdot \frac{(-\sigma^2)}{R} \\
 &= \left[\frac{R-1}{R} \sum a_i^2 - \frac{1}{R} \sum_{i \neq j} \sum a_i a_j \right] \sigma^2
 \end{aligned}$$

or

$$(4A.4) \quad \text{Var} \hat{\alpha} = \left[(R-1) \sum a_i^2 - \sum_{i \neq j} \sum a_i a_j \right] \frac{\sigma^2}{5}.$$

Consider a hypothetical case with $R = 5$, $a_1 = 238$, $a_2 = 239$,
 $a_3 = 240$, $a_4 = 241$ and $a_5 = 242$. We get

$$\begin{aligned}
 \text{Var} \hat{\alpha} &= [1152040 - 1151990] \frac{\sigma^2}{5} \\
 &= 10\sigma^2.
 \end{aligned}$$

4B. Gamma Ray Spectrometer

The isotope Pu^{242} does not emit gamma rays, while all other isotopes of plutonium do. The procedure is to estimate the proportions of all other isotopes X_2, \dots, X_R using the gamma ray spectrometer, and then use the equation (4.1) to compute X_1 , the proportion of Pu^{242} .

The model is:

$$X_1 = 1 - \sum_{i=2}^R X_i .$$

The variance of α is then:

$$\text{Var}(\alpha) = \sum a_i^2 \text{Var} X_i + \sum_{i \neq j} \text{Cov}(X_i, X_j) a_i a_j$$

i.e.,

$$(4B.1) \quad \text{Var}(\alpha) = \sum a_i^2 \text{Var} X_i - a_1 \sum_{j=2}^R a_j \text{Var}(X_j) .$$

Now, setting $a_1 = 242$, $a_2 = 238$, $a_3 = 239$, $a_4 = 240$, $a_5 = 241$, $R = 5$ and using the usual error model

$$X_i = \bar{X}_i + \epsilon_i$$

and $\text{Var} X_i = \text{Var} \epsilon_i = \sigma^2$, we have

$$\text{Var} \alpha = 56174\sigma^2 .$$

4C. Mass Spectrometer - I

A sample of the material to be analyzed is used to get a mass spectrogram, and the peak readings P_i corresponding to the isotopes $i = 1, \dots, R$ are measured. The P_i values include in them any conversion factors associated with the spectrometer. Then, an estimate of the fractional content of isotope i is obtained as

$$X_i = \frac{P_i}{\sum_{i=1}^R P_i}.$$

Thus,

$$\begin{aligned} \alpha &= \sum a_i X_i \\ &= \frac{\sum a_i P_i}{\sum P_i}. \end{aligned}$$

Now, if X and Y are two random variables which are not independent, then the variance of (X/Y) can be approximated [6] as:

$$\text{Var} \left(\frac{X}{Y} \right) \approx \left(\frac{E(X)}{E(Y)} \right)^2 \left(\frac{\text{Var } X}{E^2(X)} + \frac{\text{Var } Y}{E^2(Y)} - \frac{2 \text{Cov}(X, Y)}{E(X)E(Y)} \right).$$

Let

$$P_i = \tilde{P}_i + \varepsilon_i$$

where P_i is the measured value of the peak, \tilde{P}_i is the true value of the peak and ε_i is the measurement error.

Let

$$\text{Var } \epsilon_i = \sigma^2 \quad \text{for } i = 1, 2, \dots, k,$$

since the ϵ_i are all peak measurement errors. We will use P_i as an estimation of $E(P_i)$ for computing variances. We will also assume the error variables, ϵ_i , to be independent.

We have

$$\begin{aligned} \text{Var } \left[\sum a_i P_i \right] &= \sum a_i^2 \text{Var } P_i \\ &= \sum a_i^2 \sigma^2 \\ \text{Var } \left[\sum P_i \right] &= \sum \sigma^2 \\ &= R\sigma^2 \end{aligned}$$

since R is the number of isotopes.

$$\text{Cov} \left[\sum a_i P_i, \sum P_i \right] = \sum a_i \sigma^2.$$

Thus we have

$$(4C.1) \quad \text{Var } \alpha = \left[\frac{\sum a_i P_i}{\sum P_i} \right]^2 \left[\frac{\sum a_i^2 \sigma^2}{\left(\sum a_i P_i \right)^2} + \frac{R\sigma^2}{\left(\sum P_i \right)} - \frac{2 \sum a_i \sigma^2}{\left(\sum a_i P_i \right) \left(\sum P_i \right)} \right].$$

To restate the expression in a simple form, let

$$V_1 = \text{Var} \sum a_i P_i = \sum a_i^2 \sigma^2$$

$$V_2 = \text{Var} \sum P_i = R\sigma^2$$

$$C = \text{Cov} \left[\sum a_i P_i, \sum P_i \right] = \sum a_i \sigma^2$$

$$A = \sum a_i P_i$$

and

$$P = \sum P_i .$$

We then have:

$$(4C.2) \quad \text{Var} \propto \frac{A^2}{P^2} \left(\frac{V_1}{A^2} + \frac{V_2}{P^2} - \frac{2C}{AP} \right) .$$

4D. Mass Spectrometer - II: Isotope Dilution Method

(1) Diluting Isotope Not Already Present.

A measured quantity of an isotope which is not present in the sample is added to the sample and a mass spectrogram obtained. The peaks are measured. Let P_0 correspond to the peak for the new isotope, and P_i to the i^{th} isotope, $i = 1, \dots, R$. Let m_0 be the mass of the isotope added. Then, the fractional content of i^{th} isotope is given by

$$X_i = \frac{\frac{P_i}{P_0} m_0}{\sum_{j=1}^R \frac{P_j}{P_0} m_0}$$

or

$$\alpha = \sum a_i X_i$$

$$= \frac{\sum a_i \frac{P_i}{P_o} m_o}{\sum \frac{P_i}{P_o} m_o}$$

i.e.,

$$\alpha = \frac{\sum a_i P_i}{\sum P_i}$$

which is of the same form as in 4C. The variance of α can therefore be computed as in 4C. Thus, as far as α is concerned, the dilution method does not improve the precision over the direct method.

α can also be computed in a different manner:

$$X_i = \frac{P_i}{P_o} m_o$$

and

$$\alpha = \sum a_i X_i$$

so that,

$$\alpha = \frac{m_o}{P_o} \sum a_i P_i$$

$$\text{Var } \alpha = \text{Var } \frac{m_o}{P_o} \cdot \left(\sum a_i P_i \right)^2 + \left(\frac{m_o}{P_o} \right)^2 \cdot \text{Var} \left(\sum a_i P_i \right).$$

Let

$$\text{Var } P_i = \sigma^2 \quad i = 0, 1, \dots, R$$

$$\text{Var } m_o = \sigma_1^2$$

$$\text{Var } \frac{m_o}{P_o} = \left(\frac{m_o}{P_o} \right)^2 \left(\frac{\sigma_1^2}{m_o^2} + \frac{\sigma^2}{P_o^2} \right) = \frac{\sigma_1^2}{P_o^2} + \sigma^2 \cdot \frac{m_o^2}{P_o^4}$$

and

$$\text{Var } \sum a_i P_i = \sum a_i^2 \sigma^2.$$

Thus,

$$(4D.1) \quad \text{Var } \alpha = \left[\frac{\sigma_1^2}{P_o^2} + \frac{m_o^2}{P_o^4} \sigma^2 \right] \left(\sum a_i P_i \right)^2 + \left(\frac{m_o}{P_o} \right)^2 \left[\sum a_i^2 \sigma^2 \right].$$

(if) Diluting Isotope Already Present

First a mass spectrogram of the sample is obtained and the peaks are measured. Let the peak values be P_i . Now, a measured quantity m_o , of an isotope, say R^{th} isotope, is added and a new mass spectrogram obtained. Let the new peak values be Q_i . Then, the fractional contents of the isotopes are given by:

$$X_i = \left(\frac{P_i + Q_i}{2} \right) \frac{m_o}{(Q_R - P_R)}, \quad i = 1, \dots, R - 1$$

$$X_R = P_R \frac{m_o}{(Q_R - P_R)}$$

and

$$\begin{aligned} \alpha &= \sum a_i X_i \\ &= \frac{m_o}{2(Q_R - P_R)} \left[\sum_{i=1}^{R-1} a_i (P_i + Q_i) + 2P_R \right]. \end{aligned}$$

Let

$$\text{Var } P_i = \text{Var } Q_i = \sigma^2$$

and

$$\text{Var } m_o = \sigma_1^2.$$

Then,

$$(4D.2) \quad \text{Var } \alpha = \frac{m_o^2 G^2}{4(Q_R - P_R)^2} \left\{ \frac{2Rm_o^2 \sigma^2 + G^2 \sigma_1^2}{m_o^2 G^2} + \frac{2\sigma^2}{(Q_R - P_R)^2} + \frac{4\sigma^2}{m_o G(Q_R - P_R)} \right\}$$

where

$$G = \sum_{i=1}^{R-1} a_i (P_i + Q_i) + 2P_R.$$

Symbols Used in Section 5

C	Concentration of plutonium
$E(\cdot)$	Expected value of argument
M	Mass of solution
Q	Mass of plutonium
$\text{Var}(\cdot)$	Variance of argument
α	Equivalent weight of plutonium corrected for isotopic composition

5. ESTIMATION OF TOTAL PLUTONIUM

Variance of error in the estimation of the total plutonium content of two types of accountability [or "holding"] tanks are considered in this section. The first type of tank holds large quantities of plutonium solution but at very low concentrations. The second type holds small quantities of concentrated plutonium solutions. The examples are primarily intended to illustrate the application of the analysis in the previous sections.

Analysis:

The total quantity of plutonium in a tank is given by

$$Q = M \cdot C \cdot \alpha$$

where

M = total mass of liquid (solution) in the tank

C = concentration of plutonium in the liquid before isotopic correction in equivalents of plutonium per gram of solution and

α = equivalent weight of plutonium after correction for isotopic composition.

The total mass of liquid in the tank is estimated by means of a pressure type device.

The variance of M, as computed in Section 2 is 9.06×10^6 for the large tank and 1.0085×10^2 for the small tank.

The concentration can be determined [1] by using wet chemical methods to within .04%.

The large tank has a concentration of 0.1 gm/litre or 2×10^{-7} equivalents/gm. This gives the variance of C^* to be 6.4×10^{-21} .

* Note: $\text{Var } C = C^2 \cdot (\text{rsd of } C)^2$.

For the small tank, the concentration is 175 gms/litre or 1.45×10^{-3} equivalents/gm. This gives the variance of C as: 3.36×10^{-13} . And the variance of $\alpha[1]$ is 2.6×10^{-2} .

Finally, since

$$Q = M \cdot C \cdot \alpha ,$$

the variance of Q is:

$$(5.1) \quad \text{Var } Q = M^2 \alpha^2 \text{Var } \alpha + M^2 C^2 \text{Var } C + \alpha^2 C^2 \text{Var } M .$$

For the large tank ($M = 10^6$ gms; $C = .1$ gm/litre),

$$\text{Var } Q = 0.022$$

and $E(Q) = 50$ gms gives $\text{rsd of } Q = .0029$ or .29%. For the small tank ($M = 2 \times 10^4$ gms; $C = 1.75$ gm/litre),

$$\text{Var } Q = 30.94$$

and $E(Q) = 1750$ gms gives $\text{rsd of } Q = .00318$ or .318%.

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