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Statistical Design of Mass Spectrometry Calibration Procedures

Charles K. Bayne

UNITED STATES PROGRAM FOR TECHNICAL ASSISTANCE TO IAEA SAFEGUARDS

POTAS
DEPARTMENT OF STATE
DEPARTMENT OF ENERGY
ARMS CONTROL AND DISARMAMENT AGENCY
NUCLEAR REGULATORY COMMISSION

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Statistical Design of Mass Spectrometry Calibration Procedures

Charles K. Bayne

Computer Science and Mathematics Division
Oak Ridge National Laboratory, Oak Ridge, Tennessee

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This work was sponsored by the U.S. Program for Technical Assistance to IAEA Safeguards (POTAS) under Task D.198: "Statistical Design of Mass Spectrometry Calibration."

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EXECUTIVE SUMMARY

Task A.198 was sponsored by the United States Program for Technical Assistance to the International Atomic Energy Agency (IAEA) safeguards programs through the International Safeguards Projects Office (ISPO) for the Measurement Technology programs at the IAEA's Safeguards Analytical Laboratory (SAL), Seibersdorf, Austria.

The main objective of this task was to agree on calibration procedures to estimate the system parameters (i.e., dead-time correction, ion-counting conversion efficiency, and detector efficiency factors) for SAL's new Finnigan MAT-262 mass spectrometer. SAL will use this mass spectrometer in a clean-laboratory which was opened in December 1995 to measure uranium and plutonium isotopes on environmental samples. The Finnigan MAT-262 mass spectrometer has a multi-detector system with seven Faraday cup detectors and one ion-counter for the measurement of very small signals (e.g. 10^{-17} Ampere range).

ORNL has made preliminary estimates of the system parameters based on SAL's experimental data measured in late 1994 when the Finnigan instrument was relatively new. SAL generated additional data in 1995 to verify the calibration procedures for estimating the dead-time correction factor, the ion-counting conversion factor and the Faraday cup detector efficiency factors.

The system parameters estimated on the present data will have to be reestablished when the Finnigan MAT-262 is moved to the new clean-laboratory. Different methods will be used to analyzed environmental samples than the current measurement methods being used. For example, the environmental samples will be electroplated on a single filament rather than using the current two filament system. An outline of the calibration standard operating procedure (SOP) will include the following items.

A. Dead-Time Calibration
  1. Selection of the uranium reference material.
  2. Number of different samples that should be measured.
  3. Number of filaments/blocks/scans that should be measured. Levels of ion-intensities.
  4. Data validation criteria.
  5. Estimation procedure
     (a) First -- estimate the bias correction factor.
     (b) Second -- estimate dead-time.

B. Ion-counting and Faraday Cup Conversion Efficiency
  1. Selection of the uranium reference material.
  2. Selection of Faraday cups for measurements.
  3. Number of samples/filaments that should be measured.
  4. Procedure to estimated ion-counting conversion efficiency.
     (a) First -- estimate the bias correction factor on the Faraday cups.
     (b) Second -- estimate the ion-counting conversion efficiency.

C. Faraday Cup Efficiency Factors
   1. Selection of the uranium/plutonium reference material.
   2. Peak-jump calibration experiment.
   3. Data validation criteria.
   4. Estimation procedure -- regression analysis.

D. Acceptance Criteria for Calibration.
   1. Schedule for calibration
      (a) Fixed Schedule (e.g., every 6 months).
      (b) Recalibrate when QC samples are above out-of-control limits.
   2. Data acceptance based on accuracy and precision.
   3. Establish control limits for dead-time and ion-counting conversion factors.

Table 0.1 shows the estimated system parameters using SAL's experimental data.

Table 0.1. Estimated bias correction factors (BCFs), dead-time (DT), ion-counting conversion factor (K) and detector efficient factors (DEFs) from SAL's 1995 experimental data.

System Parameter	Estimated Value	Standard Deviation	Lower 95%Confidence Interval	Upper 95% Confidence Interval
DT BCF	0.001514	0.000102	0.001375	0.001653
Dead-Time	17.4 ns	0.75 ns	15.9 ns	18.9 ns
K BCF	0.001264	0.000506	0.001173	0.001355
K	52,592.4	1406.3	52,338.2	52,846.6
%K	84.1478%	2.2501%	83.7411%	84.5545%
DEF 2:5	1.002438	0.000125	1.002349	1.002527
DEF 3:5	1.001131	0.000173	1.000998	1.001264
DEF 4:5	0.995761	0.000056	0.995714	0.995808
DEF 6:5	0.983022	0.000136	0.982975	0.983069
DEF 7:5	0.994696	0.000186	0.994553	0.994839
DEF 8:5	0.995570	0.000117	0.995486	0.995654

1. INTRODUCTION

The Finnigan MAT-262 is the latest in a series of magnetic sector, thermal ionization, multi-detector mass spectrometers. This mass spectrometer has the option of precise isotopic measurements for isotopes with low abundance using an ion counting system. For higher abundance, isotopes are measured by Faraday cup detectors. Figure 1.1 shows the multi-detector configuration of the Finnigan MAT-262.

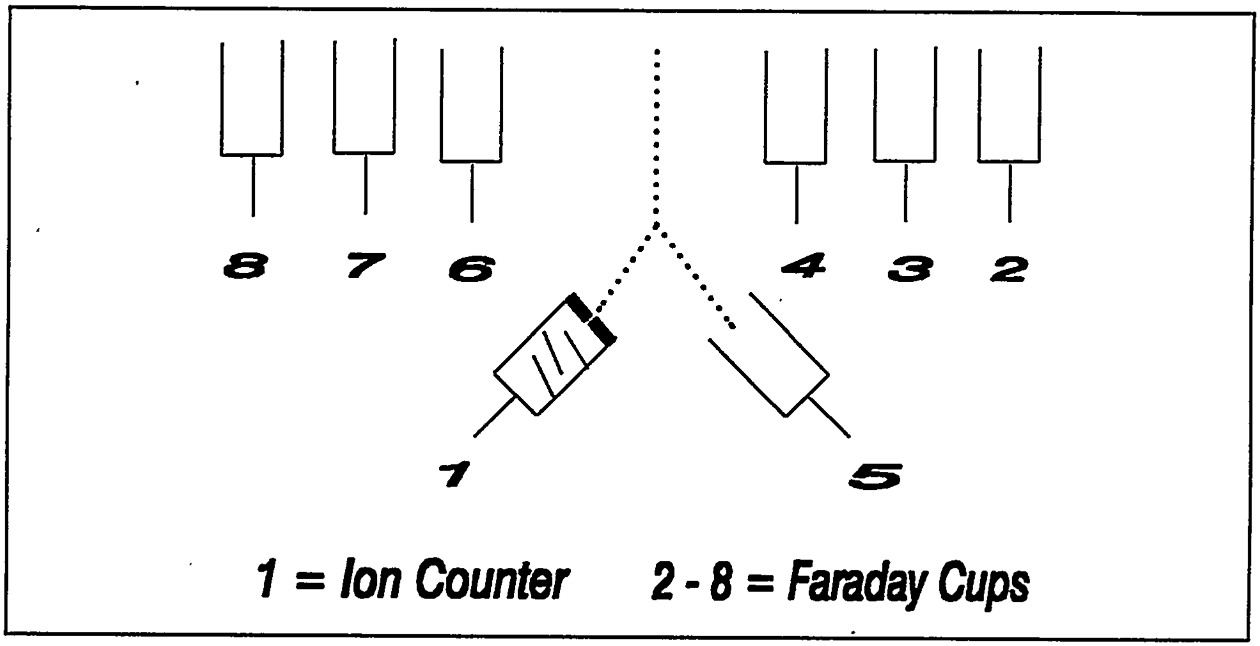

Fig. 1.1. Multi-collector configuration on the Finnigan MAT-262.

SAL uses three different calibration experiments to characterize the multi-detector system:

1. dead-time correction for the ion counter.
2. ion-counting conversion efficiency to convert ion count rates to equivalent millivolt measurements in a Faraday cup.
3. Faraday detector efficiency factors (DEFs) to correct for between cup biases among the Faraday cups.

For any ion-counting system consisting of a detector with its associated electronic equipment there exists a minimum time interval, τ (s/counts), by which two consecutive events must be separated for both to be recorded. Events arriving during this dead time are lost and the fraction of events lost increases with increasing counting rate [*1*]. Safeguards Analytical Laboratory (SAL) has run dead-time experiments using CBNM-072/08 standard uranium reference material. Oak Ridge National Laboratory (ORNL) used this data to estimate both the bias correction factor (BCF) and the dead-time correction for the ion-counting system.

The Finnigan MAT-262 measures low abundance isotopes as ion-count rates by an ion-counting system. Higher abundance isotopes are measured as millivolts by Faraday cup detectors. Isotopic ratios of low abundance isotopes relative to higher abundance isotopes require the conversion of ion-count rates to an equivalent millivolts. The ion-counting conversion factor (i.e., K counts/s/mv) is estimated by measuring a standard reference material with a low abundance isotope on the ion-counting system and a high abundance isotope in the Faraday cups. SAL conducted experiments using CBNM-072/08 standard uranium reference material and ORNL estimated both the associated BCF and ion-counting conversion factor. The ion-counting conversion factor was also expressed as relative percent (%K) when compared with the manufacturer's reported value of 62,500 counts/s/mv.

All thermal ionization mass spectrometers are sensitive to time dependent measurement parameters. Measurements on single detector systems require time-lag corrections because these systems sequentially measure the ion intensity of each isotope. The Finnigan MAT-262 has eliminated time-lag corrections because all ion-intensity measurements are made simultaneously with an array of Faraday cups. However, ion-intensity measurements may not be equivalent in different detectors because detectors may vary with respect to their geometry, construction, component materials, etc. These differences are corrected by estimating detector efficiency factors (DEFs) that relate the measurements in each Faraday cup to a selected reference detector. An adjusted ion-intensity measurement ($I_{adjusted}$) can be calculated for a Faraday cup relative to a reference Faraday cup by dividing by the gain factor and DEF.

SAL has made measurements on the Faraday cups with a series of peak-jump experiments using the ^{238}U isotope. Peak-jump experiments [*2*] measure the ion intensities of a single isotope in each Faraday detector relative to the selected reference Faraday detector cup No. 5. ORNL's statistical analysis of these peak-jump experiments show that the relative biases for the DEFs (i.e., $100\% \times |DEF - 1.0|/1.0$) range from 0.25% to 1.70%. These high relative biases are shown to depend on the gain factors. The maximum relative bias for the (Gain Factor × DEF) products in the denominators of $I_{adjusted}$ is 0.02% for Faraday cup 2, and the denominator products only increase the ion-intensity measurements by a maximum of 0.03%. The denominator products for Faraday cups 3, 6 and 7 are not significantly different than 1.00000 (5% significance level). DEF values and the gain factor values are highly negatively correlated (e.g., DEF values decrease with increasing gain factor values). This correlation can be used to approximate the adjustment to the measured ion-intensities without performing peak-jump experiments.

2. DEAD-TIME CORRECTION

For any ion-counting system consisting of a detector with its associated electronic equipment there exists a minimum time interval, τ (s/cts), by which two consecutive events must be separated for both to be recorded. Events arriving during this dead time are lost and the fraction of events lost increases with increasing counting rate [*1*]. In July 1995, Safeguards Analytical Laboratory (SAL) measured on the Finnigan MAT 262 the isotopic abundances of ^{233}U:^{235}U:^{238}U for CBNM-072/08 standard reference material (e.g., about a 1:100:100 ratio). ORNL used this data to estimate both the bias correction factor and the dead-time correction for the ion-counting system. ORNL made these estimations with the following procedure

1. Estimate the bias correction factor (BCF) from the measured ^{235}U/^{238}U isotopic ratios.

2. Estimate the dead-time [τ (s/cts)] from the measured ^{233}U/^{235}U isotopic ratios based on the BCFs in step 1.

The isotopic abundances of CBNM-072/08, the average BCF, and the dead-time estimates are given in Table 2.1.

Table 2.1. CBNM-072/08 isotopic abundances, the average BCF, and the dead-time correction.

CBNM 072/08	Atomic Isotope Ratio	System Parameter	Estimated Value	Estimated Standard Deviation	95% Confidence Interval
^{235}U/^{238}U	0.99319	BCF	0.001514	0.000102	± 0.000139
^{233}U/^{235}U	0.010165	Dead-Time	17.4 ns	0.75 ns	± 1.46 ns

2.1 Experimental Data

SAL measured 8 filaments (Identification: 3640, 3643, 3644, 3647, 3648, 3649, 3651, and 3652) of CBNM-072/8 uranium standard on the Finnigan MAT-262. Each filament was measured by the ion-counting system. Filament samples were measured in 5 time blocks and within each block the sample was scanned 7 times in the uranium isotopic sequence of (233,235,238,238,235,233). This dead-time experiment generated 1680 individual uranium isotopic intensity measurements.

$$1680 = \text{Filaments} \times \text{Blocks} \times \text{Scans} \times \text{Isotopes} \times \text{Replicates} = 8 \times 5 \times 7 \times 3 \times 2.$$

Figure 2.1 illustrates the measurements of the dead-time experiments.

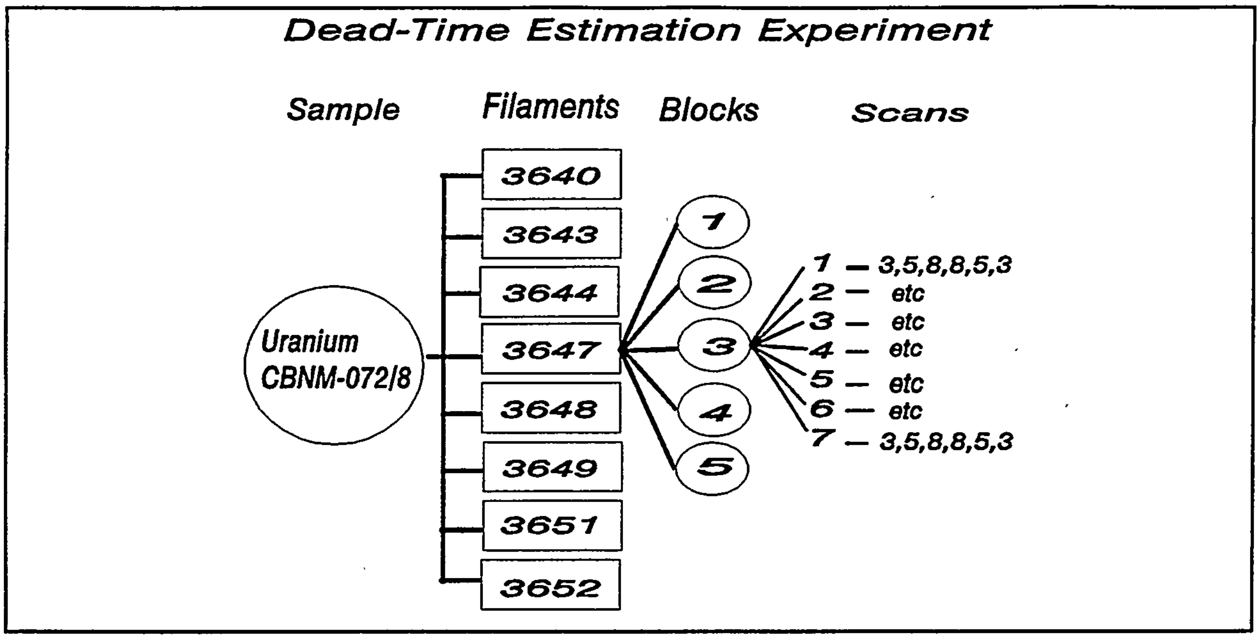

Fig. 2.1. Measurement sequence for the dead-time experiment.

Prior to evaluating the dead-time parameter, we statistically analyzed the data to see if there were any usual measurements that would be considered outliers. The outlier investigation used two methods of identification. First a statistical model was fitted to the data using Proc GLM in the SAS Programming Language [3]. Each residual (i.e., residual = observed value - predicted value) from the fitted model was then compared to its estimated standard deviation. Residuals greater or less than ±3 standard deviations were identified as possible outliers. The statistical model used for this outlier analysis is a nested model

$$(C_{adj})_{fbsit} = Mean + Fil_f + Blk_{b(f)} + Scn_{s(bf)} + Mass_i + Slope_{fbs} \times Time + \delta \qquad \textbf{(2.1)}$$

where C_{adj} = adjusted count rates for each isotope. The count rates are normalized for each isotope by dividing each count rate by the standard deviation of all count rates. This adjustment normalizes the standard deviation of C_{adj} for each isotope to one. The indices "fbsit" indicate filament, block, scan, isotope and time, respectively.

Fil_f = the f-th Filament (f = 1, 2, ..., 8),
$Blk_{b(f)}$ = the b-th Block within the f-th Filament (b = 1,2, ..., 5),
$Scn_{s(bf)}$ = the s-th Scan within the b-th Block within the f-th Filament (s = 1,2, ..., 7),
$Mass_i$ = the mass of the I-th isotope (I = 1, 2, 3),

Slope_{sbf} = the Slope for the s-th Scan within the b-th Block within the f-th Filament. Note this means that a line is fitted to each measurement scan.

Time = the time during a scan the measurement was made (sec = 4.0, 19.0, 32.0, 36.1, 49.1, 64.1), Note this means that a line is fitted to each measurement scan.

δ = represents the measurement error not accounted for by the fitted model.

The nested statistical model accounted for 99.8% (%R^2) variation in the data with a percent relative error of %RE = 0.64%. Table 2.2 shows 25 measurements that were identified as outliers. The identified outliers occurred in three filaments (3640, 3644, and 3651). Most of the identified outliers occurred in the last block (i.e., Block = 5) of the measurements. These patterns indicate that all measurement values in a single Scan may be treated as suspect.

A second statistical outlier analysis examined all 3 isotopic measurements in a Scan simultaneously using principal components analysis [PCA, *4*]. For each Scan, the replicate isotopic count rates were averaged. Hotelling's T^2 statistics were calculated from the principal components of the three isotopic averages using for all 280 Filament × Block × Scan combinations. An outlier "Scan" was identified if its Hotelling's T^2 statistic exceeded the upper 1% percentile value [i.e., $T^2(p,n,0.01) = 11.42$ where $p = 3$ principal components, $n = 280$ data points, 0.01 = upper percentile level]. Table 2.3 shows the identified outlier Scans based on the PCA.

Table 2.2. Outlier scans identified by principal components analysis.

No.	Filament	Block	Scan	Hotelling(a) T^2
1	3644	3	2	22.86
2	3644	5	3	55.10
3	3644	5	4	62.47
4	3644	5	5	51.57
5	3644	5	6	13.78
6	3644	5	7	45.82
7	3644	3	3	27.41

(a) The 1% percentile for this data set is T^2 (p,n,0.01) = 11.42.

Table 2.3. Count measurements identified as possible outliers.

No.	Filament	Block	Scan	Isotope	Time (s)	Standard Deviation of Residual
1	3640	1	1	233	4.0	-3.2
2	3640	1	7	233	64.1	-3.5
3	3644	3	2	233	4.0	-6.0
4		3	2	235	19.0	+4.4
5	3644	5	3	233	64.1	+5.8
6		5	3	235	19.0	+6.0
7		5	3	238	32.0	+9.2
8		5	3	238	36.1	-16.8
9	3644	5	4	233	4.0	+5.6
10		5	4	233	64.1	+6.9
11		5	4	238	32.0	-6.6
12		5	4	238	36.1	-4.5
13	3644	5	5	233	4.0	-6.7
14		5	5	233	64.1	-3.1
15		5	5	235	19.0	+5.5
16	3644	5	6	233	4.0	+5.2
17		5	6	235	19.0	-3.5
18		5	6	235	49.1	+3.9
19		5	6	238	32.0	-3.1
20	3644	5	7	233	4.0	-6.7
21		5	7	233	64.1	-5.7
22		5	7	238	32.0	+6.1
23	3651	3	3	233	4.0	+4.1
24		3	3	233	64.1	+6.6
25		3	3	235	49.1	-3.4

The PCA and the residual analysis for identifying outliers gave comparable results. All of the outlier Scans identified by PCA had been identified by the residual analyses to have individual outlier results. However, the combinations of (Filament,Block,Scan) = (3640,1,1) and (3640,1,7) did not show up in the PCA but did have measurement values identified as outliers by the residual analysis.

The set of measurement values set aside as suspected outliers were those in the Scans identified by PCA in Table 2.3 and those in the two Scans (3640,1,1) and (3640,1,7). A total of nine Scans were set aside leaving 271 Filament × Block × Scan combinations for estimating the dead time.

2.2 Bias Correction Factor:

The true values of isotopic ratios are estimated by multiplying the measured isotopic ratios by a bias correction factor (BCF). This BCF accounts for the effect that mass differences cause isotopes to be collected with slightly different efficiences. The BCF is estimated from the $^{235}U/^{238}U$ isotopic ratio measurements of the CBNM-072/8 uranium standard. This isotopic ratio was chosen for estimating the BCF because the count rates for ^{235}U and ^{238}U are about equal so any effect due to dead-time would be negligible. The statistical model [*5*] used to estimate the BCF is

$$R_M^{5/8} = \frac{R_{Ref}^{5/8}}{1 + BCF \times \Delta M^{5/8}} + \epsilon \qquad \textbf{(2.2)}$$

where

$R^{5/8}{}_M$ = measured $^{235}U/^{238}U$ isotopic ratios,
$R^{5/8}{}_{Ref}$ = CBNM-072/8 reference value ($^{235}U/^{238}U = 0.99319$),
BCF = Bias Correction Factor to be estimated,
$\Delta M^{5/8}$ = mass difference (e.g., $\Delta m^{5/8} = 235 - 238 = -3$ for $^{235}U/^{238}U$), and
ϵ = measurement errors assumed to be independent with a normal distribution having zero mean and constant variance (σ^2).

One method of estimating BCF is by the method of least squares [*6*]. This method finds a parameter "A" that minimizes the square of the measurement errors.

$$SSE = \sum \epsilon^2 = \sum (R_M - AR_{Ref})^2 \ . \qquad \textbf{(2.3)}$$

The value of BCF that minimizes this least-squares problem is

$$BCF = \frac{\left(\dfrac{N8 \times R_{Ref}^{5/8}}{N5} - 1 \right)}{\Delta M^{5/8}} \qquad \textbf{(2.4)}$$

where N5 and N8 are the average count rates from a Scan for ^{235}U and ^{238}U, respectively. Figure 2.2 shows the 271 calculated BCF values for dead-time experiment.

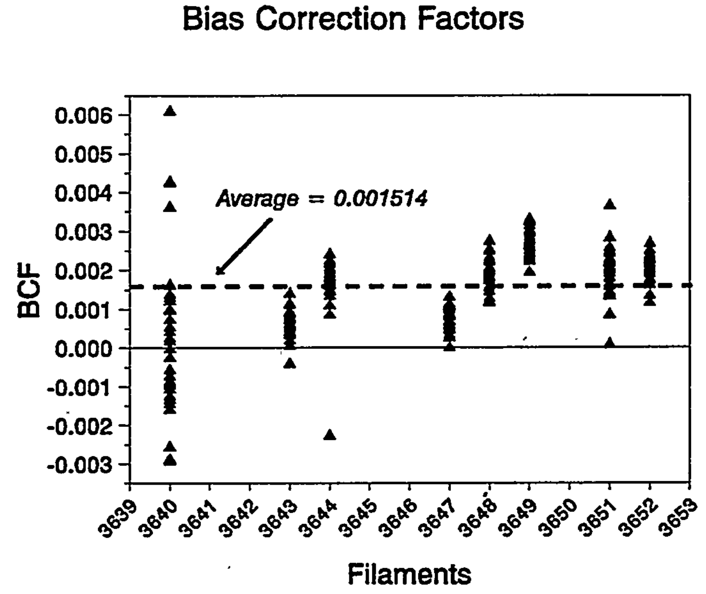

Fig. 2.2. Bias correction factors calculated for each scan.

Table 2.1 lists the average BCF, its standard deviation, and the 95% confidence interval. Figure 2.2 indicates that Filament 3640 has the most variation and the average BCF values for each Filament may show significant change. An analysis of variance [ANOVA, *7*] of the BCF values shows that the average BCF values among Filaments is highly significant (p-value < 0.0001) but average BCF values among blocks within Filaments are not significantly different (p-value = 0.47). Table 2.4 shows the BCF average values for each Filament. BCF variation due to different Filaments contributes about 51% to the total BCF variation for the 271 values. ORNL calculated the BCF values for each Scan to estimate the dead-time value to minimizes BCF variations among Filaments and Blocks.

Table 2.4. BCF summary statistics for each Filament arranged by increasing BCF averages.

Filament	3640	3643	3647	3644	3648	3651	3652	3649
Num	33	35	35	29	35	34	35	35
BCF Avg	0.000173	0.000701	0.000755	0.001632	0.001924	0.002050	0.002128	0.002710
BCF St Dev	0.000361	0.000057	0.000049	0.000151	0.000062	0.000101	0.000052	0.000057
(±) 95% C.I.	0.000735	0.000116	0.000100	0.000310	0.000127	0.000205	0.000106	0.000117

2.3 Dead-Time Correction

For any counting system consisting of a detector with its associated electronic equipment there exists a minimum time interval, τ, by which two consecutive counts must be separated for both to be recorded [*1*]. Counts arriving during this dead time are lost, and the fraction of counts lost increases with increasing counting rate. There are two types of detectors: (1) systems with extendable dead-times (or paralyzable, cumulative, or updating), and (2) systems with nonextendable dead-times (or nonparalyzable or noncumulative). The difference between these two systems depends on their response to counts arriving during a dead-time.

If the dead-time is increased by such input counts, so that a time interval of τ must elapse following the last input count before another output count can be produced, the system is called extendable. Equation 2.5 describes the expected output rate of an extendable system.

$$N_m = N_{corr} \exp[-N_{corr}\tau] \tag{2.5}$$

where N_m is the expected output count and N_{corr} is the correct or true mean rate of the input counts.

If the dead-time is not increased by input counts arriving while the system is dead, the system is called nonextendable. The theoretical formula relating the expected output counting rate, N_m, and the expected input counting rate, N_{corr}, is:

$$N_{corr} = \frac{N_m}{(1 - N_m\tau)} \ . \tag{2.6}$$

Dr. Johannes Schwieters [*8*] from Finnigan MAT GmbH describes the dead-time of the ion-counting system as the "effective dead-time." He says the effective dead-time of the system is not a simple number which can be deduced from basic principles. It is related to both:

- the electronic dead-time which can be measured exactly on the oscilloscope, and
- the dead-time of the Secondary Electron Multiplier (SEM) which, in a certain range, is an individual quantity for each SEM.

The latter is related to several system properties: the electric capacity of the SEM dynodes, the resistors in the resistor chain of the SEM, the surface chemistry of the individual SEM dynodes, the setting of the discriminator level of the pulse counting electronics and to the gain of the multiplier. This is why Finnigan MAT prefers to use the word "effective dead-time." The effective dead-time has to be determined by experiments for each individual electronic/SEM combination. This is the dead-time calibration of the system. The system can be called both extendable and nonextendable.

SAL and ORNL decided to base the estimated dead-time on the non-expandable correction formula Eq. 5. ORNL estimated from the 271 measurement values of $^{233}U/^{235}U$ isotopic ratio the CBNM-072/8 uranium standard. These isotopic ratios were correct by the BCF:

$$R_C^{3/5} = (1 + \Delta M^{3/5} \times BCF) \times \frac{N3}{N5} \ . \tag{2.7}$$

where $\Delta M^{3/5} = -2$, N3 and N5 are the average background corrected ^{233}U and ^{235}U count rates from each Scan.

$$\tau = \frac{R_C^{3/5} - R_{REF}^{3/5}}{N5 \times R_C^{3/5} - N3 \times R_{REF}^{3/5}} \ . \tag{2.8}$$

Table 2.1 lists the average dead-time (i.e., 17.4 ns), its standard deviation, and the 95% confidence interval. Figure 2.3 shows the 271 estimates for each Filament. This figure does not indicate any changes in the average dead-time for the different Filaments. An analysis of variance of the dead-time values shows no significant differences among Filaments (p-value = 0.16) or Blocks within Filaments (p-value = 0.77). This analysis indicates that the overall average dead-time may be used for samples measured on different Filaments.

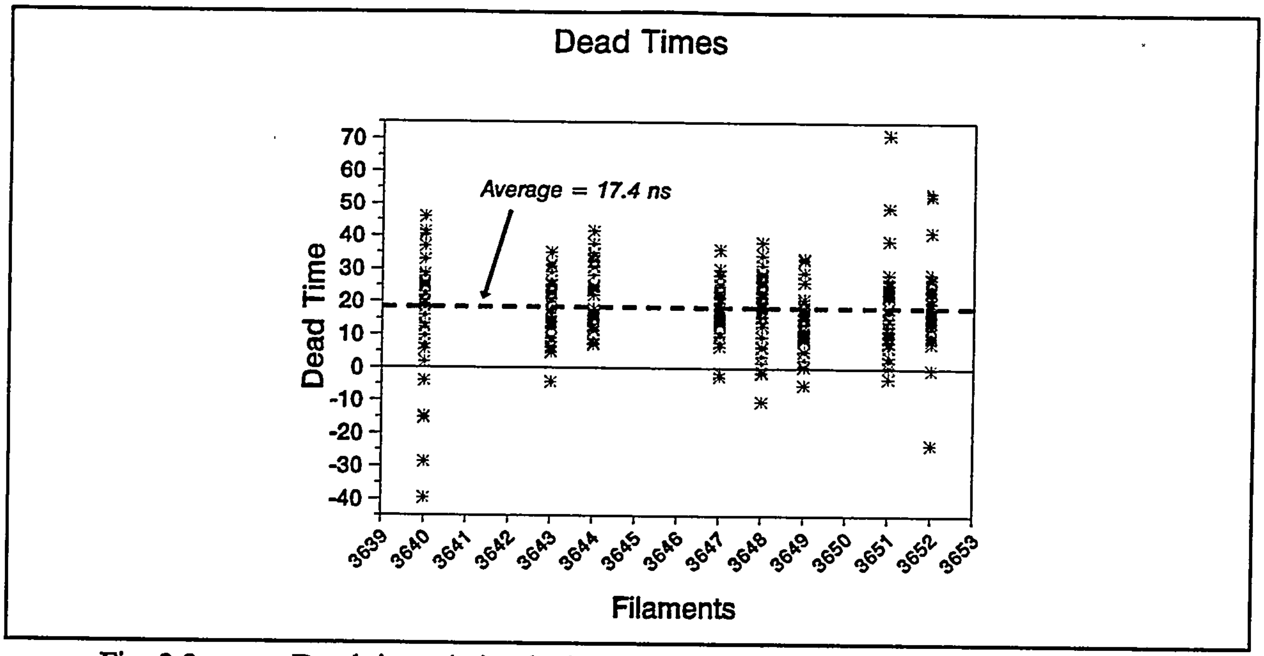

Fig. 2.3. Dead times (ns) calculated for each scan.

2.4 Dead-Time Calibration Procedure

ORNL and SAL developed the following operating procedure to be used for the dead-time calibration procedure. The dead-time calibration procedure is based on a uranium reference material with ^{233}U, ^{235}U, and ^{238}U isotopes (e.g., CBNM-072 series). Let N3, N5, and N8 represent corresponding average background-corrected ion-count rates in either a block or a scan. For example the calculations will be illustrated for the numerical values:

$N3 = 4{,}501$ $N5 = 438{,}237$ $N8 = 439{,}128$ $R^{5/8}_{REF} = 0.99319$ $R^{35}_{REF} = 0.010165$

1. Estimate a bias correction factor(BCF) for each block/scan from the measured $^{235}U/^{238}U$ isotopic ratios.

$$BCF = \frac{\left(\frac{N8 \times R_{REF}^{5/8}}{N5} - 1\right)}{\Delta M^{5/8}}$$

where $R^{5/8}_{REF}$ is the reference value for $^{235}U/^{238}U$ and $\Delta M^{5/8}$ is the difference between the atomic mass for the isotope in the numerator and the atomic mass for the isotope in the denominator (i.e., $\Delta M^{5/8} = 235 - 238 = -3$).

EXAMPLE

$$BCF = \frac{\left(\dfrac{439{,}128 \times 0.99319}{438{,}237} - 1 \right)}{-3} = 0.001597 \ .$$

2. Correct the measured $R^{3/5} = N3/N5$ for the bias correction factor.

$$R_C^{3/5} = (1 + \Delta M^{3/5} \times BCF) \times \frac{N3}{N5} \ .$$

where $\Delta M^{3/5} = -2$.

EXAMPLE

$$R_C^{3/5} = (1 + (-2) \times 0.001597) \times \frac{4{,}501}{438{,}237} = 0.010238 \ .$$

3. Estimate the dead-time from the non-expandable correction formula.

$$R_{REF}^{3/5} = R_C^{3/5} \times \frac{1 - N5 \times \tau}{1 - N3 \times \tau} \ ,$$

or

$$\tau = \frac{R_C^{3/5} - R_{REF}^{3/5}}{N5 \times R_C^{3/5} - N3 \times R_{REF}^{3/5}} \ .$$

EXAMPLE

$$\tau = \frac{0.010238 - 0.010165}{438{,}237 \times 0.010238 - 4{,}501 \times 0.010165} = 16.4ns \ .$$

4. Dead-times can be calculated either for (a) each scan and averaged to get an estimated dead-time for a block, or (b) use the average count rates for each block to calculate the block dead-time. The maximum difference between the two dead-time estimation procedures for the different blocks in the preliminary data was less than 0.8 ns. Calculating the dead-times for each scan will give a method to partition the dead-time variance into each component (e.g. filament, block, and scan) in the measurement process. Examination of these variance components will suggest the number of filaments, blocks, and scans to use for the dead-time calibration experiments.

3. ION-COUNTING CONVERSION FACTOR

The Finnigan MAT 262 measures low abundance isotopes as counts/s by an ion-counting system. This ion-counting system consist of the following components: (1) a secondary electron multiplier (SEM) system, (2) a discriminator (i.e., Finnigan design with a preset discrimination level of 1.2v to eliminate noise spikes and low level cosmic rays), and (3) a Philips counter. Higher abundance isotopes are measured as millivolts by Faraday cup detectors. Isotopic ratios of low abundance isotopes relative to higher abundance isotopes require the conversion of ion counts/s to an equivalent millivolts. The ion-counting conversion factor (i.e., K cts/s/mv) is estimated by measuring a standard reference material with a low abundance isotope on the ion-counting system and high abundance isotopes in the Faraday cups.

In July 1995, Safeguards Analytical Laboratory (SAL) measured the uranium standard CBNM-072/08 to estimate the ion-counting conversion factor (K). This standard has isotopic abundances of ^{233}U:^{235}U:^{238}U with about a 1:100:100 ratio. SAL measured the isotopic abundance of ^{233}U on the ion-counting system and the isotopic abundance of ^{235}U and ^{238}U on Faraday cup No. 3 and Faraday cup No. 2, respectively. ORNL used this data to estimate the ion-counting conversion factor by the following algorithm

1. Use the dead time (e.g., $\tau = 17.4$ns) from the dead-time calibration experiment.
2. Measure ^{233}U (N3, counts/s) on the ion-counting system and ^{235}U (MV5, millivolts) and ^{238}U (MV8, millivolts) on Faraday cups.
3. Adjust the background-corrected ^{233}U ion count rates by the dead-time

$$N3_{adj} = \frac{N3}{1 - N3 \times \tau} \quad . \tag{3.1}$$

4. Adjust the Faraday cup measurements (e.g., MV5 and MV8) for background and gain.

Adjust millivolts = 1000*(MV - Bkg)/Gain.

5. Calculate the bias correction factor (BCF) from $MV5_{adj}$ and $MV8_{adj}$ using the CBNM-072/08 reference value for $^{235}U/^{238}U$ (i.e., $R_{REF}{}^{5/8} = 0.993190$)

$$BCF = \frac{\dfrac{MV8_{adj} \times R_{REF}^{5/8}}{MV5_{adj}} - 1}{\Delta M^{5/8}} , \tag{3.2}$$

where $\Delta M^{5/8} = 235 - 238 = -3$ is the mass difference between the two isotopes.

6. Estimate the ion-counting conversion factor (K, counts/s/mv) using the BCF, $N3_{adj}$, $MV5_{adj}$, and the CBNM-072/08 reference value for $^{233}U/^{235}U$ (i.e., $R_{REF}{}^{3/5} = 0.010165$)

$$R_{REF}^{3/5} = \frac{(1 + \Delta M^{3/5} \times BCF) \times N3_{adj}}{K \times MV5_{adj}} , \tag{3.3}$$

or

$$K = \frac{(1 + \Delta M^{3/5} \times BCF) \times N3_{adj}}{MV5_{adj} \times R_{REF}^{3/5}} , \tag{3.4}$$

where $\Delta M^{3/5} = 233 - 235 = -2$ is the mass difference between the two isotopes. The ion-counting conversion factor will also be expressed as a percentage of the theoretical value (62,500 counts/s/mv) given in the literature (i.e., %K = 100% × K/62,500).

Table 3.1 gives the results of the statistical analyses for the July 1995 ion-counting conversion factor calibration.

Table 3.1. Estimated parameters from the July 1995 conversion calibration experiment.

Parameter	Number of Data points	Estimate Parameter	Standard Deviation	Lower 95% Confidence Interval	Upper 95% Confidence Interval
BCF	120	0.001264	0.000506	0.001173	0.001355
K	120	52,592.4	1406.3	52,338.2	52,846.6
%K	120	84.1478%	2.2501%	83.7411%	84.5545%

3.1 Experimental Data

SAL measured 6 filaments (Identification: 3625, 3627, 3628, 3630, 3631, and 3632) of CBNM-072/8 uranium standard on the Finnigan MAT-262. Filament samples were measured in 2 time blocks. Each block was scanned 10 times with ^{233}U ion counts/s being measured by the ion-counting system and ^{235}U and ^{238}U being measured by Faraday cup No. 3 and No 2, respectively. Figure 3.1 illustrates the measurement sequence of the conversion calibration experiment.

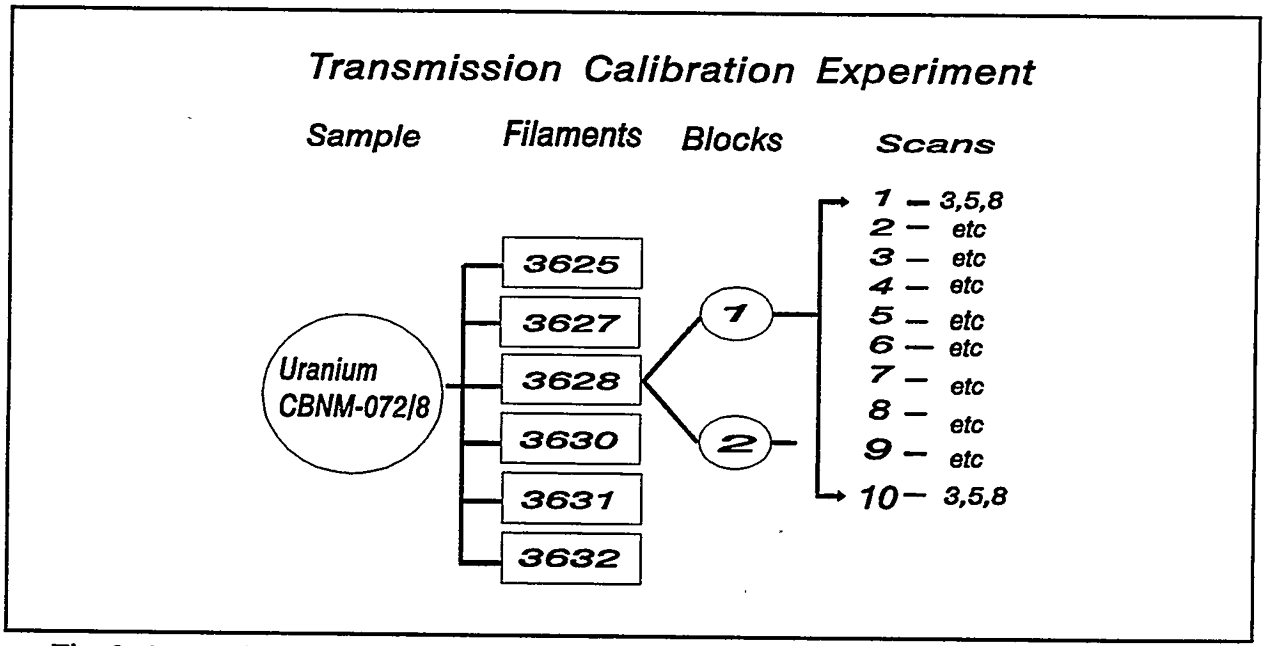

Fig. 3. 1. Measurement sequence for estimating the ion-counting conversion factor.

SAL measured 120 data points (Filaments × Blocks × Scans = 6 × 2 × 10 = 120) from the conversion calibration experiment. A principal component analysis [PCA, *4*] of the adjusted data (e.g., $N3_{adj}$, $MV5_{adj}$, and $MV8_{adj}$) was used to detect any unusual or outlier values. This PCA analysis didn't show any data points that would be considered outliers.

3.2 Bias Correction Factor

The average BCF values for the 6 Filament are significantly different (5% significance level). The comparisons were made using an estimated pooled measurement error from the within Scan BCF values for each Block. A partition of the total BCF variance for the 120 values shows that 96.2% is due to different Filaments, 1.4% is due to different Blocks within Filaments, and 2.4% is due to different Scan values with in Blocks. Table 3.2 gives the average BCF values for each Filament. The differences among the BCF averages for the Filaments are not correlated to either the magnitude of the counts/s or millivolts, or to the rate of change (slope) of the counts/s or millivolts with each Scan sequence. Figure 3.2 illustrates the BCF averages (ordered from largest to smallest magnitude) and their 95% confidence intervals.

Table 3.2. Average BCF (ordered in descending magnitude) for each Filament.

Filament	Number of Data Points	Average	Standard Deviation	Lower 95% Confidence Interval	Upper 95% Confidence Interval
3628	20	0.001966	0.000067	0.001935	0.001997
3627	20	0.001515	0.000102	0.001467	0.001563
3631	20	0.001357	0.000112	0.001305	0.001409
3632	20	0.001277	0.000114	0.001224	0.001330
3630	20	0.001149	0.000098	0.001103	0.001195
3625	20	0.000321	0.000088	0.000280	0.000362
All Filaments	120	0.001264	0.000506	0.001173	0.001355

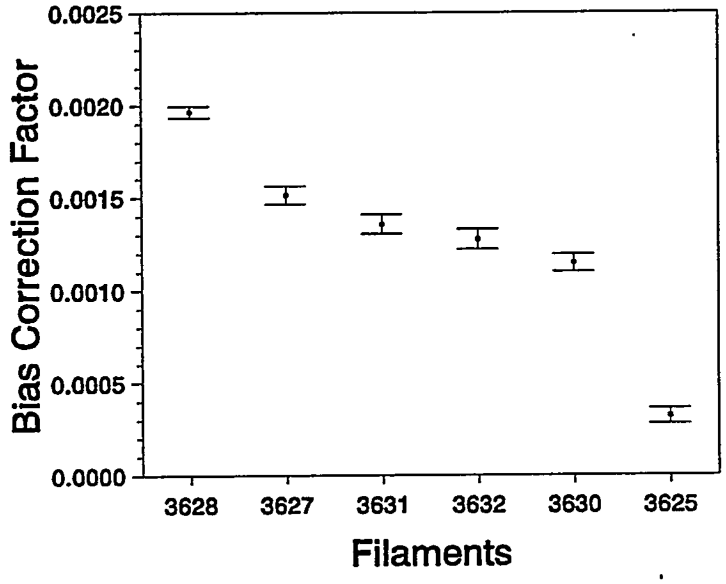

Fig. 3.2. Average BCF for each Filament with 95% confidence intervals.

3.3 Ion-Counting Conversion Factor

A nested analysis of variance [ANOVA, 7] was used to determine the major sources of variation and to examine the differences among ion-counting conversion factors for each Filament. The ANOVA model had Scans nested within Blocks, and Blocks nested within Filaments. This ANOVA shows that 99.5% of the total variation among K-factors is due to different Filaments. Only 0.1% of the total variation is due to differences between Blocks within Filaments and 0.4% of the total variation is due to differences among the K values for Scans within each Block. These variance components indicate that the conversion calibration experiment should use as many Filaments as possible, and that 2 Blocks and 10 Scans are sufficient for uncertainty estimates on the K-factor.

Table 3.3 shows the average value of the K-factors for each Filament. The average Filament K-factors are significantly different at the 5% significance level. The differences among the K-factor averages for the Filaments are not correlated to either the magnitude of the counts/s or millivolts, or to the rate of change (slope) of the counts/s or millivolts with each Scan sequence. Figure 3.3 illustrates the K-factor averages (ordered from largest to smallest magnitude) and their 95% confidence intervals.

Table 3.3 Average K-factors (ordered in descending magnitude) for each Filament.

Filament	Number of Data Points	Average	Standard Deviation	Lower 95% Confidence Interval	Upper 95% Confidence Interval
3627	20	55,195	133	55,133	55,257
3632	20	53,492	94	53,448	53,536
3625	20	52,189	104	52,140	52,238
3631	20	52,094	129	52,034	52,154
3628	20	51,700	85	51,660	51,740
3630	20	50,884	53	50,859	50,909
All Filaments	120	52,592	1406	52,338	52,847

The overall estimate of the ion-counting conversion factor (K) with 95% confidence intervals is

Est. K = 52,592.4 ion counts/s/mv ± 253.8 ion counts/s/mv ,

or

Est. %K = 84.1478% ± 0.4067% .

Therefore, low abundance isotopic ratios using both count data and millivolt data is estimated by

$$R_M = [1 + \Delta M \times (0.001264)] \times \frac{N_{adj.}}{52{,}592.4 \times MV_{adj}} \quad . \qquad \textbf{(3.5)}$$

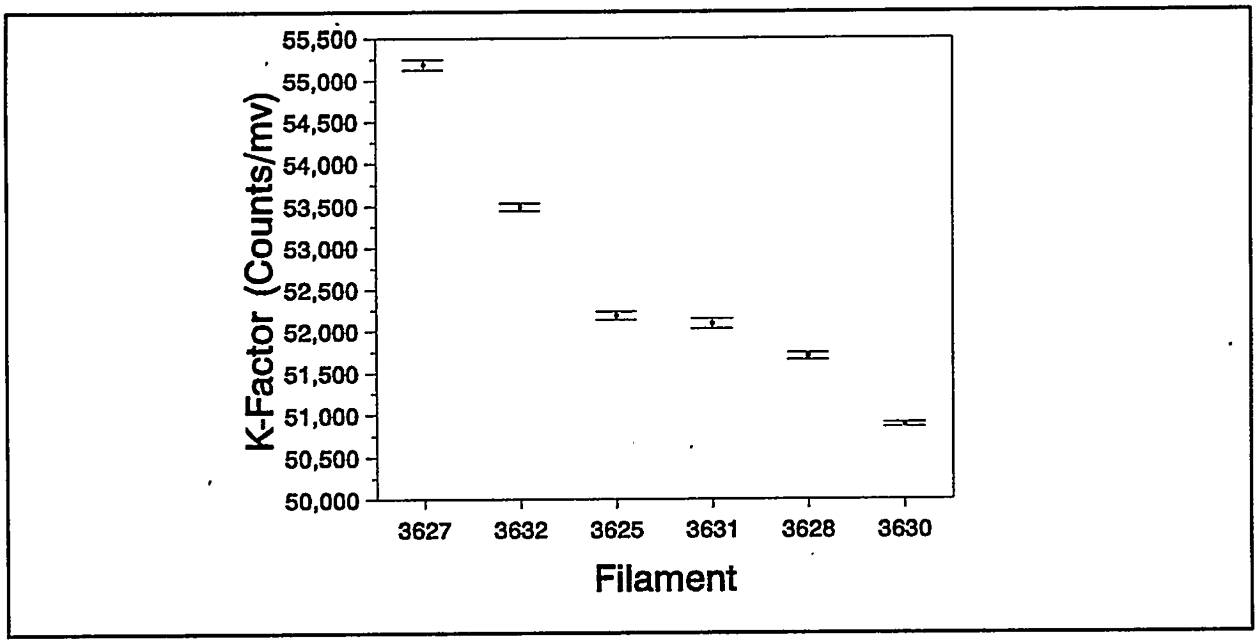

Fig. 3. 3. Average K-factor for each Filament with 95% confidence intervals.

3.4 Conversion Factor Procedure

The measurements for Filament = 3625, Block = 1, and Scan = 1 will be used to illustrate the calculations for the ion-counting conversion factor.

OBS	Filament	Block	Scan	N3	MV5	BKG235	MV8	BKG238	$N3_{adj}$	$MV5_{adj}$	$MV8_{adj}$
1	3625	1	1	104332.00	598.613	202.704	597.736	199.885	104521.75	197.115	198.314

Step 1. Use the dead time (e.g., $\tau = 17.4$ns) from the dead-time calibration experiment.

Step 2. Measure ^{233}U (N3, counts/s) on the ion-counting system and ^{235}U (MV5, millivolts) and ^{238}U (MV8, millivolts) on Faraday cups. Adjust N3 for multiplier background count rate (e.g, usually only 0 to 4 counts/s). The multiplier background count rate for this example was zero and therefore no adjustment was needed.

$$N3 = 104332.00,\ MV5 = 598.613, \text{ and } MV8 = 597.736.$$

Step 3. Adjust the ^{233}U ion counts/s by the dead-time by equation (3.1)

$$N3_{adj} = \frac{104{,}332}{1 - 104{,}332 \times 17.4 \times 10^{-9}} = 104{,}521.75\ .$$

Step 4. Adjust the Faraday cup measurements (e.g., MV5 and MV8) for background and gain.

$$MV5_{adj} = 1000 \times (598.613 - 202.704)/2008.51526 = 197.115, \text{ and}$$

$$MV8_{adj} = 1000 \times (597.736 - 199.885)/2006.16840 = 198.314.$$

Step 5. Calculate the bias correction factor (BCF) from $MV5_{adj}$ and $MV8_{adj}$ using the CBNM-072/08 reference value for $^{235}U/^{238}U$ (i.e., $R_{REF}^{5/8} = 0.993190$) by equation (3.2)

$$BCF = \frac{\dfrac{198.314 \times 0.993190}{197.115} - 1}{-3} = 0.000256\ .$$

Step 6. Estimate the ion-counting conversion factor (K, counts/s/mv) using the BCF, $N3_{adj}$, $MV5_{adj}$ and the CBNM-072/08 reference value for $^{233}U/^{235}U$ (i.e., $R_{REF}^{3/5} = 0.010165$) by equation (3.4)

$$K = \frac{(1 + (-2) \times 0.000256) \times 104{,}521.75}{197.115 \times 0.010165} = 52{,}138.32 \quad ,$$

or

$$\%K = 100\% \times \frac{52{,}138.32}{62{,}500} = 83.4213\% \quad .$$

4. DETECTOR EFFICIENCY FACTORS

4.1 Experimental Data

Prior to shipping, the Finnigan factory carefully tests the Faraday cup detectors to ensure that intercup bias is within 30ppm. Nevertheless, occasional deterioration does occur with use and is dependent on the number and type of ions impinging on the internal surfaces of the Faraday cups. To correct for Faraday cup changes, SAL uses a peak-jump experiments with a single elemental isotope (e.g. ^{238}U) to measure the ion intensities in each Faraday cup. These measurements are then compared to the ion intensities measured in a reference Faraday cup. Peak-jump experiments measure an ion beam in a reference Faraday cup and then switches the ion beam to a selected Faraday cup. This switching back and forth is repeated several times until another Faraday cup is selected. Figure 4.1 is an illustration of the peak-jump experiment for the Finnigan MAT-262 using Faraday Cup No. 5 as the reference Faraday cup.

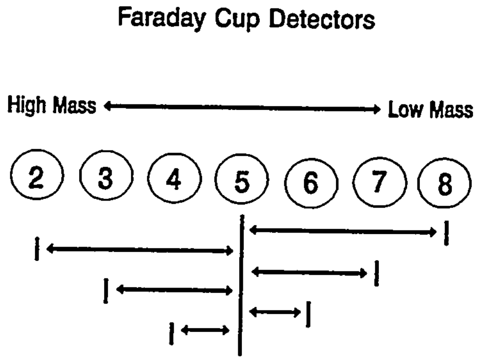

Fig. 4.1 Peak-jump experiment.

Each peak-jump run in a peak-jump experiment represents a comparison of the ion-intensity measurements in a selected Faraday cup detector with those in the reference Faraday cup detector No. 5. Figure 4.2 illustrates a peak-jump run for the data from peak-jump experiment No. 7 for the comparison of Faraday cup No. 2 with Faraday cup No. 5. For this peak-jump run, the measurement sequence (5-2-2-5-2-5-5-2) for the Faraday cups is repeated 3 times. The ion-beam is measured for 2 seconds in each Faraday cup. It takes 7 seconds to move the ion-beam between different Faraday cups and there is a 0.5 second pause between measurements in the same Faraday cup. The mid-point times for measurements made in the Faraday cups are used to estimate the detector efficiency factors (DEFs). For example, Fig. 4.2 shows that the measurement times for the first sequence are (1.0-10.0-12.5-21.5-30.5-39.5-42.0-51.0) seconds. Each peak-jump run is 167 seconds long with 24 measurements during the peak-jump run.

Figure 4.2 plots the logarithm (base e) of the adjusted voltage measurements versus time. The measured voltages are adjusted by subtracting the background (Bkg) and dividing by the gain factor (GF). This figure shows a linear increase in the measurement responses with time. The responses [e.g., log[(volt - Bkg)/GF)] may be either increasing or decreasing.

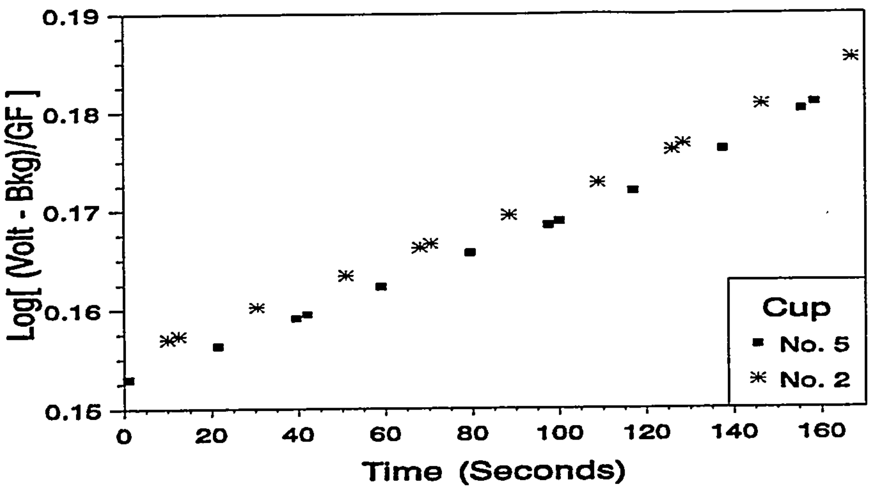

Fig. 4.2. Peak-jump run comparing Faraday cup No. 2 with Faraday cup No. 5.

SAL performed 10 peak-jump experiments each with 6 peak-jump runs for a total of 1,440 measurement values (e.g., total = experiments × runs × measurements = 10 × 6 × 24 = 1,440). Table 4.1 gives the final estimated detector efficiency factors (DEFs) relative to the reference Faraday cup. These DEFs along with the gain factors are used to adjust the ion-intensity measurements as if they had been measured on Faraday cup No. 5.

$$I_{Adjusted} = \frac{(\, I_{Measured} - Background \,)}{Gain\ Factor \times DEF} \quad . \qquad \textbf{(4.1)}$$

Figure 4.3 shows the estimated DEFs and their 95% confidence intervals for the Faraday cup detectors. The relative biases for the DEFs (i.e., 100% × |DEF - 1.0|/1.0) range from 0.25% to 1.70%. These high relative biases will be shown to depend on the gain factors in the denominator of $I_{adjusted}$. The maximum relative bias for the (Gain Factor × DEF) product is 0.02% for Faraday cup 2. The (Gain Factor × DEF) product for Faraday cups 3, 6 and 7 are not significantly different than 1.00000 (5% significance level). DEF values and the gain factor values are highly negatively correlated (e.g., DEF values decrease with increasing gain factor values).

Table 4.1. Estimated DEFs from the peak-jump experiment.

Faraday Cup	[a]Number of Data Sets	DEF Estimate	Standard Deviation	Lower 95% Confidence Interval	Upper 95% Confidence Interval
2:5	10	1.002438	0.000125	1.002349	1.002527
3:5	9	1.001131	0.000173	1.000998	1.001264
4:5	8	0.995761	0.000056	0.995714	0.995808
6:5	10	0.983022	0.000136	0.982975	0.983069
7:5	9	0.994696	0.000186	0.994553	0.994839
8:5	10	0.995570	0.000117	0.995486	0.995654

a) Adjusted for outlier values.

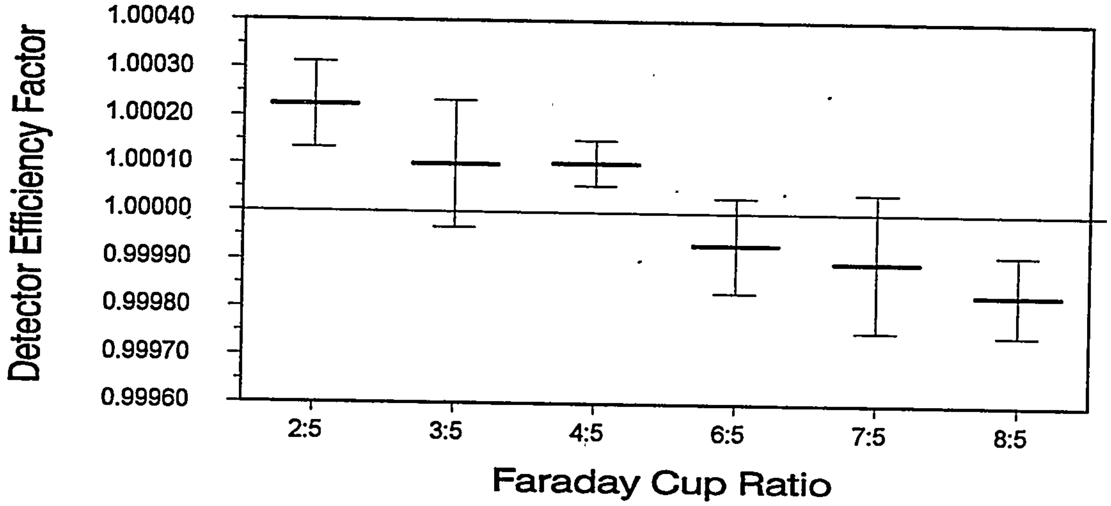

Fig. 4.3. Detector Efficiency Factors relative Faraday cup No. 5 with 95% confidence intervals.

4.2. Calibration Model

A peak-jump calibration model [2] was used to estimate the DEFs and statistically evaluate the data for outliers and unusual data values. Independent factors in the peak-jump calibration model account for the major sources of variation that influence the ion-intensity measurements. The peak-jump calibration model is expressed as the relation between $\log_e [(I_{measured} - Bkg)/\text{Gain Factor}]$ measurements and the effects of the Faraday cup detector and the peak-jump run time.

$$Ln(I_{dr}) = K + D_d + g(t_r) + error \quad . \tag{4.2}$$

where, $Ln(I_{dr})$ = logarithm (base e) of the r-th ion-intensity (voltage adjusted for background and gain factor) measured on the d-th Faraday cup detector during a peak-jump run.

K = model intercept,

D_d = the effect of d-th Faraday cup detector, d = 2, 3, ..., 8. The DEF for detector D_d relative to Faraday cup detector No. 5 is $\exp(D_d - D_5)$,

$g(t_r)$ = a continuous function of run time. Usually the decay function is assumed to be a linear function of the run time with the same slope for each Faraday cup (e.g., $g(t_r) = \beta\, t_r$) ,and

error = the experimental error. For establishing uncertainties on the estimated DEFs, the measurement errors are assumed to be independent and have an identical normal distribution with a zero mean and a constant variance (e.g., σ^2).

The method of least squares [6] was used to estimate the DEFs, σ^2's, and the uncertainties on the DEF's estimates. The peak-jump calibration model is fitted to 6 peak-jump runs in each peak-jump experiment (i.e., Faraday cups = 2, 3, 4, 6, 7, and 8). A good fit to a peak-jump run should have an estimated standard deviation less than 10×10^{-4}. Table 4.2 gives the four cases that showed high estimated standard deviations.

Table 4.2. Four cases of the peak-jump experiment with high estimated standard deviation for the measurement errors.

Data Set	7	9	4	1
DEF	3:5	4:5	7:5	4:5
Estimated Standard Deviation ($\times 10^4$)	26.38	28.55	30.47	38.01

The standard deviations of the DEFs are directly proportional to the standard deviations on the measurement errors

$$\textit{Std. Dev. of DEF} \approx 0.408 \times \sigma \quad . \tag{4.3}$$

Figures 4.4 a, b, c, and d show the peak-jump run plots for the four cases in Table 1. These four peak-jump runs were considered outlier runs and the data were not included in the final estimate of the DEFs. The large estimated standard deviations are due to sudden changes in the ion-intensity responses. These changes do not depend on which Faraday cup is being used for the measurement. This independence of the Faraday cup suggest that the voltage changes are related to either variations in sample chemistry or fluctuations in mass spectrometry parameters (e.g., ion-filament temperature, evaporation-filament temperature, ion-beam focus, or lens geometry). For example, the variation in filament temperature may cause small movements (warps) in the filament that changes focusing conditions.

The sudden changes in the responses in Fig. 4.4 a-d represent jumps of 10, 9, 17, and 12 millivolts for data sets 1, 4, 9, and 7, respectively. Although, the remaining 56 peak-jump runs had standard deviations less than of equal to 10×10^{-4}, some of these peak-jump runs also exhibited sudden changes in the measurement responses but not as large as those for the four cases in Fig. 4.4 a-d.

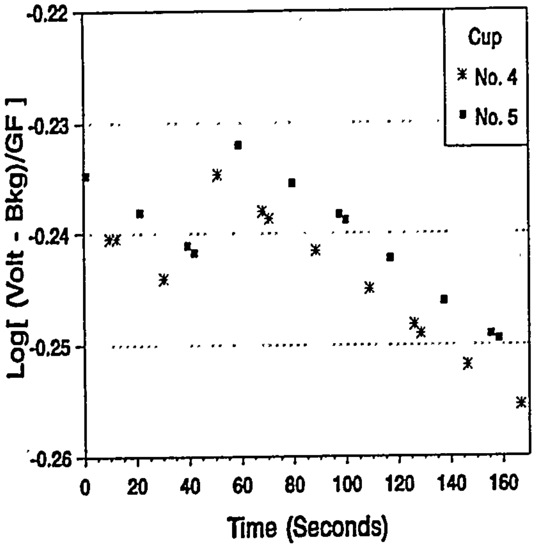

Fig. 4.4a. Peak-jump run with a measurement standard deviation of 38 × 10^{-4}.

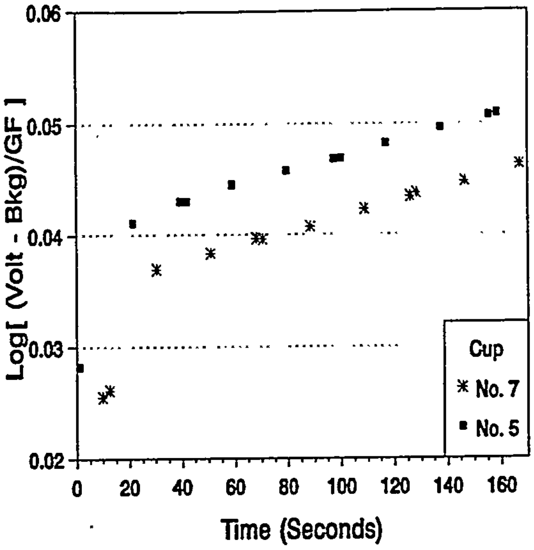

Fig. 4.4b. Peak-jump run with a measurement standard deviation of 30 × 10^{-4}.

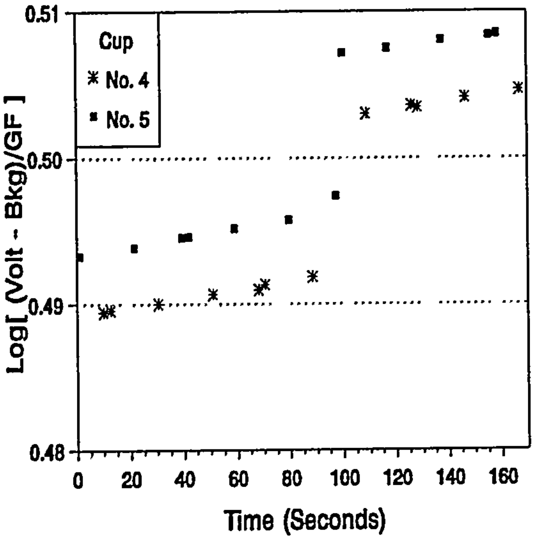

Fig. 4.4c. Peak-jump run with measurement standard deviation of 29 × 10^{-4}

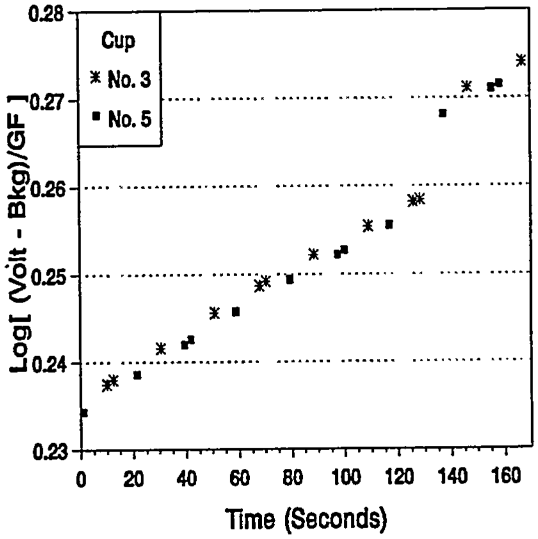

Fig. 4.4d. Peak-jump run with measurement standard deviation of 26 × 10^{-4}.

4.3 Gain Factors and Detector Efficiency Factors

Measured ion-intensities in equation 4.2 are adjusted for background intensities and gain factors prior to determining the DEFs. The gain factor for a Faraday cup is its gain voltage relative to the gain voltage for Faraday cup No. 5. Table 4.3 gives the gain factors for Faraday cups No. 2-8 that were measured over a 5 month period from 26 June 1995 to 23 November 1995.

Table 4.3 Gain factors relative to Faraday cup No. 5.

Date	Gain Factors						Gain Voltage No. 5
	2:5	3:5	4:5	6:5	7:5	8:5	
1 950626	0.997800	0.998967	1.004371	1.017202	1.005208	1.004273	2010.592
2 950703	0.997809	0.998970	1.004371	1.017207	1.005229	1.004276	2010.568
3 950706	0.997796	0.998965	1.004362	1.017190	1.005206	1.004259	2010.605
4 950804	0.997817	0.999018	1.004380	1.017214	1.005293	1.004302	2010.270
5 950804	0.997796	0.998997	1.004369	1.017211	1.005243	1.004282	2010.563
6 950807	0.997769	0.998961	1.004350	1.017216	1.005218	1.004284	2010.723
7 950810	0.997781	0.998924	1.004335	1.017202	1.005204	1.004270	2010.757
8 950814	0.997780	0.998944	1.004331	1.017218	1.005216	1.004282	2010.745
9 950818	0.997780	0.998958	1.004354	1.017219	1.005230	1.004283	2010.693
10 951114	0.997790	0.998986	1.004363	1.017179	1.005234	1.004276	2010.853
11 951123	0.997779	0.998980	1.004372	1.017178	1.005237	1.004294	2010.864
Avg	0.997791	0.998970	1.004360	1.017204	1.005229	1.004280	2010.657
Std	0.000014	0.000025	0.000016	0.000015	0.000025	0.001160	166.767

The DEFs have a strong negative correlation with the gain factor values. Figure 4.5 plots the DEFs versus the gain factors. A line is fitted to the data which accounts for 99.95% of the total variation. This fitted line indicates that low DEF values occur for high gain factor values and high DEF values occur for low gain factor (GF) values.

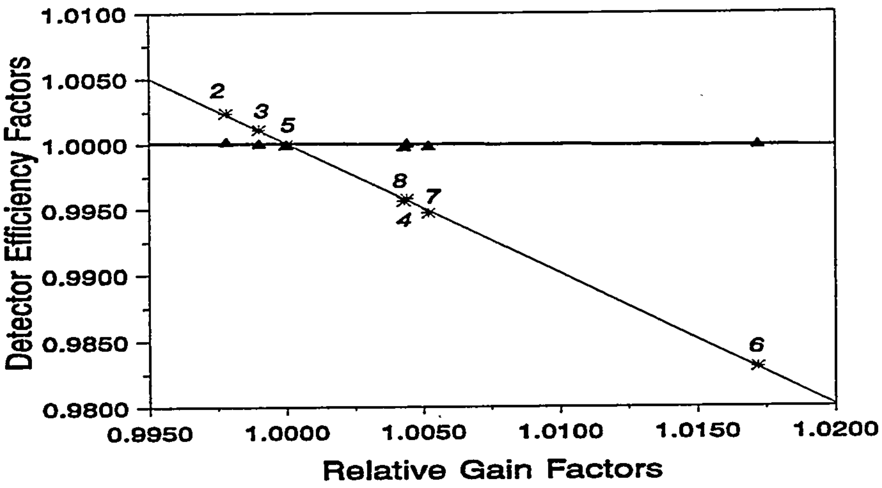

Fig. 4.5. DEF values (asterisks) as a function of gain factors. Triangles represent the product of DEF values and gain factors (DEF × Gain Factor).

The equation of the fitted line is

$$DEF = 1.9963 - 0.9962 \times GF \tag{4.4}$$

The intercept and slope standard deviations are 0.0099 and 0.0098, respectively. Considering the uncertainty on the intercept and slope suggests that a good approximation to the adjusted intensities would be

$$I_{Adjusted} = \frac{(\,I_{Measured} - Background\,)}{Gain\ Factor \times DEF} \approx \frac{(\,I_{Measured} - Background\,)}{GF \times (2 - GF)} \; . \tag{4.5}$$

The approximation in equation 4.5 would have a value of one in the denominator when GF = 1 .

4.4 Detector Efficiency Factor Procedure

DEFs are estimated for the 6 peak-jump runs in each peak-jump experiment by the following algorithm.

1. Perform K (e.g., K = 10) peak-jump experiments for each of the 6 Faraday cups relative to a selected reference Faraday cup (e.g., reference = Faraday cup No. 5). Adjust the voltage measurements by subtracting the background measurements and dividing by the gain factors.

2. Fit the peak-jump calibration model in equation 4.2 by the least-squares method. This fitting can be done either by SAS computer software [3] using PROC GLM or by Microsoft Excel [9] using the array function LINEST. Table 4.4 shows an example of an Excel worksheet for peak-jump experiment No. 7 for the comparison of Faraday cup No.2 with the reference cup No. 5 (see Fig. 4.2).

3. Check the estimated standard deviation of the responses (i.e., the root mean square error) with the value of 10×10^{-4}. Those peak-jump runs larger than this critical value should be examined and may be considered outlier peak-jump runs.

4. Estimate the DEF for Faraday cup "d" relative to reference Faraday cup "r" for each of the K peak-jump experiments.

   Define the following notation:

   N = 2 × Nd = 2 × Nr = the number of measurements in a peak-jump run (e.g. N = 24). Nd and Nr are the number of measurements for Faraday cup d and reference Faraday cup r, respectively.

   T = Td + Tr = the sum of the measurement times for a peak-jump run (e.g., T = 1008.00 + 1008.50 seconds for the peak-jump runs in this memo). Td and Tr are the measurement times for Faraday cup d and reference Faraday cup r, respectively.

SST = sum of the squared measurement times for a peak-jump run (e.g. SST = 229,827.25 for the peak-jump runs in this memo).

Z, Zr, and ZT = sum of log(volt) measurements in both Faraday cups d and r, sum of log(volt) measurements in just Faraday cup r, and the sum of [time × log(volt)] for both Faraday cups d and r, respectively.

Calculate the coefficients to estimate the DEF values:

$$A = \frac{Nr \times SST - Tr \times T}{\Delta}, \; B = \frac{T^2 - N \times SST}{\Delta}, \; and \; C = \frac{Nr \times (Tr - Td)}{\Delta} .$$

where $\Delta = Nr \times [\, Nr \times SST - Td^2 - Tr^2 \,]$.

For the peak-jump runs used in the experiments in this report, the coefficients have the following values:

$A = 0.083275$, $B = -0.166667$, and $C = 6.8985 \times 10^{-7}$.

The DEF for Faraday cup d relative to Faraday cup r is estimated by:

$$\mathbf{DEF} = \mathbf{exp\,(A \times Z + B \times Zr + C \times ZT)} .$$

The DEF for Faraday cup 2 relative to Faraday cup 5 in Table 4.4 is calculated by:

$DEF = \exp[\,(0.083275)(4.03491) + (-0.166667)(2.00265) + (6.8985 \times 10^{-7})(349.60615)]$

$DEF = \exp[0.002475] = 1.002478$

5. Calculate the final DEFs from the average of the individual DEFs for the K peak-jump experiments. The estimated standard deviation for the DEFs and their 95% confidence intervals can also be calculated using these DEFs and assuming a normal probability distribution.

Example: DEF for Faraday cup 2 relative to Faraday cup 5.

Peak-Jump Experiment	DEF (2:5)
1	1.002263
2	1.002559
3	1.002628
4	1.002431
5	1.002294
6	1.002274
7	1.002478
8	1.002490
9	1.002519
10	1.002445
Average	1.002438
Standard Deviation (S)	0.000125

95% Confidence Interval

$\text{Average} \pm t(0.975, 9) \times S/\sqrt{N}$

$1.002436 \pm (2.2622) \times (0.000125)/\sqrt{10}$

1.002438 ± 0.000089

where t(0.975, 9) is the 0.975 percentile point of the t-distribution with 9 degrees of freedom.

Table 4.4 Excel worksheet example for peak-jump experiment for the comparison of Faraday cup No. 2 with Faraday cup No.5.

Log(volt)	Cup_d	Cup_r	Time	Log(Volt) X Time	Log(Volt) X Cup_r	Cup_d X Time	Cup_r X Time	Time X Time
0.15298	0	1	1.0	0.15298	0.15298	0.0	1.0	1.00
0.15701	1	0	10.0	1.57010	0.00000	10.0	0.0	100.00
0.15735	1	0	12.5	1.96688	0.00000	12.5	0.0	156.25
0.15633	0	1	21.5	3.36110	0.15633	0.0	21.5	462.25
0.16026	1	0	30.5	4.88793	0.00000	30.5	0.0	930.25
0.15914	0	1	39.5	6.28603	0.15914	0.0	39.5	1560.25
0.15953	0	1	42.0	6.70026	0.15953	0.0	42.0	1764.00
0.16346	1	0	51.0	8.33646	0.00000	51.0	0.0	2601.00
0.16232	0	1	59.0	9.57688	0.16232	0.0	59.0	3481.00
0.16620	1	0	68.0	11.30160	0.00000	68.0	0.0	4624.00
0.16662	1	0	70.5	11.74671	0.00000	70.5	0.0	4970.25
0.16570	0	1	79.5	13.17315	0.16570	0.0	79.5	6320.25
0.16947	1	0	88.5	14.99810	0.00000	88.5	0.0	7832.25
0.16848	0	1	97.5	16.42680	0.16848	0.0	97.5	9506.25
0.16887	0	1	100.0	16.88700	0.16887	0.0	100.0	10000.00
0.17285	1	0	109.0	18.84065	0.00000	109.0	0.0	11881.00
0.17198	0	1	117.0	20.12166	0.17198	0.0	117.0	13689.00
0.17614	1	0	126.0	22.19364	0.00000	126.0	0.0	15876.00
0.17675	1	0	128.5	22.71238	0.00000	128.5	0.0	16512.25
0.17621	0	1	137.5	24.22888	0.17621	0.0	137.5	18906.25
0.18075	1	0	146.5	26.47988	0.00000	146.5	0.0	21462.25
0.18021	0	1	155.5	28.02266	0.18021	0.0	155.5	24180.25
0.18090	0	1	158.5	28.67265	0.18090	0.0	158.5	25122.25
0.18540	1	0	167.0	30.96180	0.00000	167.0	0.0	27889.00

Z	ND	NR	T	ZT	ZR	TD	TR	SST
4.03491	12	12	2016.5	349.60615	2.00265	1008.0	1008.5	229827.25

Linear Regression: Faraday cup No. 2 relative to Faraday cup No. 5: St. Dev. of Error = 0.00066353

0.000175	0.1521518	0.154627	0
2.7E-06	0.0002969	0.000297	#N/A
0.99514	0.0006635	#N/A	#N/A
1433.436	21	#N/A	#N/A
0.001893	9.246E-06	#N/A	#N/A

Calculate the coefficients for the DEF estimate.

Delta	A	B	C
8697489	0.0832754	-0.16667	6.89854E-07

Calculate detector efficiency factor:

DEF = 1.002478

5. CONCLUSIONS

This reports presents the calibration procedures for estimating the mass spectrometer parameters of dead-time, ion-counting conversion factors, and detector efficiency factors for the Finnigan MAT-262. These calibration procedures are used to estimate the mass spectrometer parameters from experimental data measured at IAEA's Safeguards Analytical Laboratory (SAL) in Seibersdorf, Austria. The estimated values are listed in the report (Table 0.1). At this time, we do not know how frequent the calibration procedures have to be performed. SAL will have to monitor these system parameters through their quality control program to determine the length of time that these values do not change. Additional investigation is recommended to verify the relationship between the detector efficiency factor and the gain factor in equations (4.4) and (4.5). If these equations are adequately verified, peak-jump experiments are not necessary for adjusting ion-intensities for different detector efficiency factors.

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