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Use of a Non-Linear Method for Including the Mass Uncertainty of Gravimetric Standards and System Measurement Errors in the Fitting of Calibration Curves for XRFA Freeze-Dried UNO_3 Standards.

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Use of a Non-Linear Method for Including the Mass Uncertainty of Gravimetric Standards and System Measurement Errors in the Fitting of Calibration Curves for XRFA with Freeze Dried UNO_3 Standards

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ABSTRACT

At LLL we have used a sophisticated non-linear multiparameter fitting program to produce a best fit calibration curve for the response of an x-ray fluorescence analyzer to uranium nitrate, freeze dried, 0.2% accurate, gravimetric standards. The program is based on unconstrained minimization subroutine, VA02A. The program considers the mass values of the gravimetric standards as parameters to be fit along with the normal calibration curve parameters. The fitting procedure weights with the system errors and the mass errors in a consistent way. The resulting best fit calibration curve parameters reflect the fact that the masses of the standard samples are measured quantities with a known error. Error estimates for the calibration curve parameters can be obtained from the curvature of the "Chi-Squared Matrix" or from error relaxation techniques. We have shown that non-dispersive XRFA of 0.1 to 1 mg freeze-dried UNO_3 can h ve an accuracy of 0.2% in 1000 sec.

KEYWORDS: Non-linear least squares, x-ray fluorescence analysis, uranium, two-dimensional calibration.

INTRODUCTION

The goal of the work described here was to be able to produce highly accurate (0.1 to 0.2%) calibration curves of non-destructive assay instruments where the accuracy of the standards available is the limiting factor, or at least a major source of calibration error.

In reaching the ultimate accuracies possible for a particular NDA measurement system, the instrument long-term precision is often not the limiting factor. The variability of sample preparation and the accuracy and applicability of the standards used for calibration of the instrument usually create the greatest source of uncertainty.[1]

We have developed a mathematical method of dealing with these types of errors in a statistically correct way. Our first test of this method was with standards accuracy for x-ray fluorescence analysis of freeze-dried[2] UNO_3. The method can also be used to evaluate the importance of sample variability errors. The type of computer code we have used in this method is commercially available from several sources[3,4] as a package which requires only a small amount of input-output user generated software.

METHOD

Our LLL XRFA system[5] has a repeatable precision which has been measured to be 0.1% (two standard deviations). In attempting to utilize this system for accountability measurements in the nuclear fuel cycle, we were continually frustrated by the lack of high accuracy solid samples in the mass range from 10 to 1000 μg. We were finally able to produce UNO_3 standards by a freeze-drying method with an NBS traceable accuracy of 0.2% (one standard deviation).[1] These samples were thought to have particle size absorption, but because of the uniform fibrous nature[1] of these freeze-dried samples it was expected that these absorption effects would be calculable to high accuracy. We have used 100 of these standards to calibrate our XRFA instrument.

Since the mass accuracy error of the standards was estimated to be twice as large as the instrument precision errors, we felt it was particularly important to include the mass

uncertainty in the calibration procedure. Our approach was to treat the mass values of the standards in *exactly the same way as we normally treat* the instrument's response to those standards. That is, the mass value of each standard is a gravimetrically measured quantity. The gravimetrical mass value, M_i, is not the "true mass" of the standard. It differs from the true mass in a normal way. The gravimetrically measured mass, M_i, has a 67% probability of deviating from the true mass value by less than 0.2%. We therefore created a set of parameters which represent the true mass values,

$$\{X_i\}$$

There is one X_i, or true mass, for each standard. It is now possible to use these new parameters in expressing the instrument response calibration curve equation, YFUN.

$$YFUN = G(A,B,C,a_1,a_2,X_i)$$

The true mass X_i of the standard is one of the variables in the calibration function instead of being a fixed constant. Consequently, the true mass, X_i, may be fit along with A,B,C, a_1 and a_2, the "usual" calibration curve fit parameters.

The result of this technique is to start from a set of gravimetrically measured standard mass values and measured XRFA instrument responses to those standards and arrive at both the most probable, or true mass, of the standard, *and the most probable system response values*. This is diagrammed schematically in Figure 1.

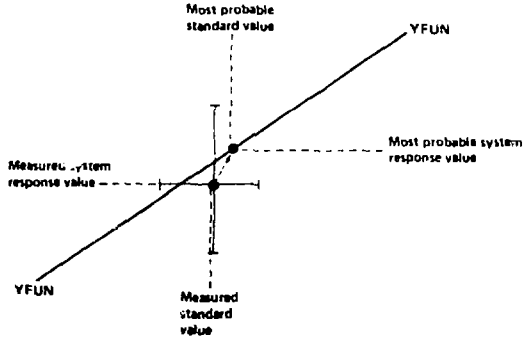


Figure 1. Overall result of non-linear least squares fitting is a most probable system response value and a most probable standard mass value.

The fitting procedure is accomplished by a commercially available,[2] non-linear, unconstrained minimization, computer program. The program minimizes the quantity chi-squared. Our chi-squared not only involves the deviations in the instrument response from the calibration curve as is usual, but must also include the deviations of the gravimetric mass values from the true mass. The value of chi-squared per degree of freedom is a measure of the "goodness" of fit of the calibration curve and true masses to all the experimental data. Our chi-squared is defined in Figure 2. The expression for chi-squared has two sums of weighted, squared deviations. The first of these terms is similar to the whole expression used for fitting programs in the past. It is different in that the true mass, X_i is used in place of the gravimetrically measured mass, M_i. The second term is new, and is the sum

TO CONSISTENTLY USE BOTH TYPES OF ERRORS CHISQUARED MUST INCLUDE THE STANDARDS MASS ERRORS

System response

$$Q = \sum_i \left[\frac{R_i - YFUN(A_1, B_2, \mu_1, \mu_2, C, \boxed{X_j})}{2\sigma_i} \right]^2 \quad \text{Almost normal CHISQUARED}$$

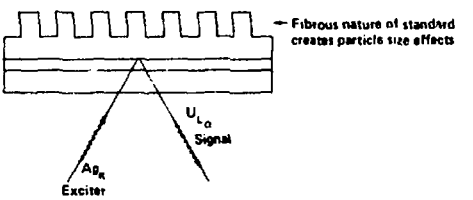
Standards variations

$$+ \sum_j \left[\frac{\boxed{X_j} - M_j}{2\sigma_j} \right]^2 \quad \text{New contribution to CHISQUARED}$$

Figure 2. New two-dimensional definition of chi-squared used in the non-linear fitting technique. Note the use of true rather than gravimetric mass.

of the squares of the deviations of the measured mass from the true mass, weighted by the gravimetric errors. The actual calibration curve function, YFUN, which we used in this work is shown in Figure 3. The function contains three terms; the first term is a constant, the second is a term that represents simple mass absorption, and the third term allows for absorption in the long thin fibers of UNO_3 oriented perpendicular to the plane of the sample. The fact that the free parameters in this function $A, B, C, \mu_1, \mu_2, X_j$ appear as products and that the expression for chi-squared contains X_j's which are free parameters, dictates the use of a non-linear fitting program.

FOR XRFA OF FREEZE DRIED UNO_3 STANDARDS WE CHOOSE A PHYSICALLY REALISTIC MODEL



$$YFUN \equiv A + B[1-e^{-\mu_1 m}] + C[1-e^{-\mu_2 m}]$$

Background — Normal mass absorption — Fibrous particle size absorption

- Thus the function becomes

$$YFUN = A + B[1-e^{-\mu_1 X_j}] + C[1-e^{-\mu_2 X_j}]$$

Figure 3. The actual calibration curve used in this work has a term for normal mass absorption and also a term for fibrous particle size absorption.

RESULTS

The final results of using this technique is a "best-fit" value for A,B,C,b_1,b_2 and all the X_f's as shown in Figure 4 numerically and Figure 5 graphically. As can be seen in Figure 5, 40% of the under response is due to simple mass absorption and 60% is due to particle size absorption.

THE FINAL RESULT OF THIS TECHNIQUE IS

- A set of most probable model parameters

$$YFUN = 1.02 \times 10^6 + 4.6 \times 10^5 \left[1-e^{-2.1 \times 10^{-4} X}\right] + 5.6 \times 10^5 \left[1-e^{-2.3 \times 10^{-4} X}\right]$$

Background — Normal mass absorbtion — Fibrous particle size absorbtion

- A set of most probable standard values

X DATA	X FIT	RES/SIGMA	SIGMA
4 .54E+00	4 .29E+00	1 .59E+00	1 .00E-01
4 .47E+00	4 .34E+00	1 .18E+00	1 .00E-01
9 .52E+00	9 .59E+00	-.7 .33E-01	1 .00E-01

Figure 4. Actual numerical results of our fitting method showing our best fit parameters.

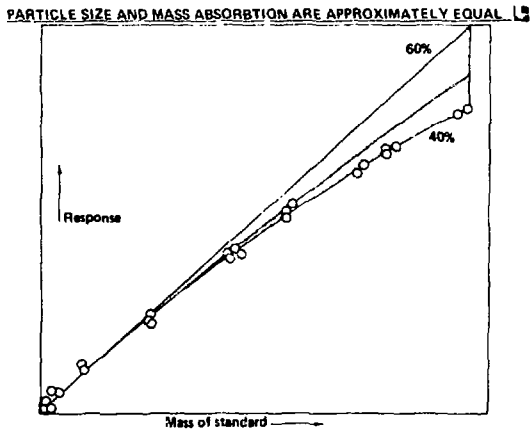


Figure 5. Graphical representation of our best fit calibration curve showing the normal mass absorption, 40%, and the fibrous particle size absorption, 60%, under responses from the linear.

ERRORS

A non-linear least squares fitting program does not use simple matrix inversion to obtain a unique best fit value for each free parameter and consequently does not produce a unique error matrix for the free parameters. However, estimates of the overall error is possible by two methods. In the first method, the curvature of chi-squared space near the best fit value of each parameter is an indication of the sensitivity of the fit to that parameter. The second and more useful method is to relax the errors on the gravimetric masses and/or the instrument response precision until a chi-squared per degree of freedom of approximately three is obtained. A chi-squared per degree of freedom of three means the probability that all the fit parameters are within one standard deviation of their "correct" value is 67%. We were able to obtain a chi-squared per degree of freedom of three by relaxing the instrument response errors to 0.2%. The conclusion we draw from this is we should accumulate counts on an unknown sample until the precision of the response is 0.1% and then the error we assign to the measurement of that sample will be 0.2% (1 sigma).

SUMMARY

We have found the non-linear fitting techniques as described here to be a powerful method of creating realistic calibration curves for an NDA instrument and a particular standards set. The method uses both the gravimetric mass errors and the instrument response errors in a statistically consistent way. It incorporates the independent gravimetric measurement of the standards in the calibration curve parameters thus extracting all the experimental information available for the instrument response and the standards set. It determines the actual most probable value of each standard mass. It allows sensitive selection among the calibration curve models. It eliminates the need to cross measure standards, and it allows a realistic appraisal of the overall accuracy error of an NDA instrument and it's standards.

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