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USE OF MULTIVARIATE CALIBRATION FOR PLUTONIUM QUANTITATION BY THE Pu(III) SPECTROPHOTOMETRIC METHOD

by

Lawrence E. Wangen, Marilyn V. Phillips, and Laurie F. Walker

ABSTRACT

Two new multivariate calibration methods for using all of the relevant spectral information are applied to the determination of plutonium. The analyte response signal originates from the absorbance spectrum of Pu(III) from 500-900 nm. Partial least squares (PLS) regression gives an average absolute error of 0.114 ± 0.108 mg when predicting plutonium content of standards containing 65-90 mg total plutonium. PLS uses all of the signal in the spectrum and is a more robust calibration procedure than a method based on absorbances at five wavelengths. Another calibration procedure involving least squares curve fitting (LSCF) fits either the entire spectrum or individual spectral intervals derived from standards to spectra of unknowns. In addition, an arbitrary linear base line can be included. The best LSCF option for the same calibration and test set as used for PLS was the full spectrum (522-900 nm) with a linear base-line option. The average absolute error when predicting with LSCF was 0.130 ± 0.092 mg plutonium. LSCF has an advantage over PLS in that the linear base line can account for certain types of interferences that have been observed for this plutonium assay procedure. An example is given.

INTRODUCTION

The Analytical Chemistry Group at Los Alamos has been using the doublet at 560 and 605 nm for routine quantitation of total plutonium in plutonium oxides for some time. These peaks result from absorption by Pu(III) complexes in acidic chloride solutions.

The Pu(III) absorption spectrum from 500 to 620 nm is shown in Fig. 1. Absorption intensities at the wavelengths labeled A, B, C, D, and E have been used quite successfully for calibration. Calibration using absorbance at these points provides four estimates of plutonium concentration that can be used for checking consistency when applied to unknowns. This procedure also compensates for certain kinds of base-line shifts. Using this calibration method, applied to spectra that are derived from relatively pure oxides, gives precisions on the order of 0.2% relative error. Standard errors, as determined for standards processed as unknowns, are also about 0.2% relative error.

In Fig. 1, it is apparent that only points labeled B, C, and D contain signal, whereas A and E are background. Clearly much more signal is available in this doublet than is contained in the three absorbance values used. The spectrum for the Pu(III) complex from 500-900 nm is shown in Fig. 2. Apparently there is additional structure in this spectrum, which should be useful for enhancing signal-to-background ratio and therefore providing a potential for increasing the precision of the procedure.

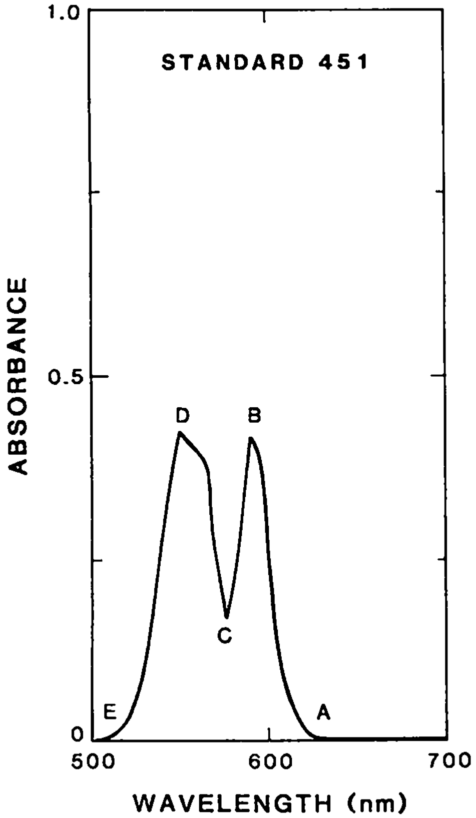

Fig. 1. Absorbance spectrum of a Pu(III) standard solution showing the parts of the spectrum used in the five-point calibration method.

Recent chemometric developments in multivariate calibration point out advantages of full spectrum methods for quantitation.[1,2] Such methods can provide enhanced signal-to-noise ratio, multicomponent analysis, interference detection, and outlier detection. Certain multivariate methods also enable determination of unknown chemical constituents, for example, two-component curve resolution.[3] Our interest in the use of multivariate procedures for plutonium quantitation by the Pu(III) spectrophotometric procedure was based on a desire to develop a more robust analytical procedure that could be applied to samples other than the relatively pure plutonium oxides. In addition, we were interested in possibly increasing procedure precision by using the full spectrum and in investigating the possibility of accounting for interferences with curve-fitting methods.

In this report, we present the results of using partial least squares (PLS)[1] regression and least squares curve fitting (LSCF)[2] for calibration of our Pu(III) spectrophotometric method.

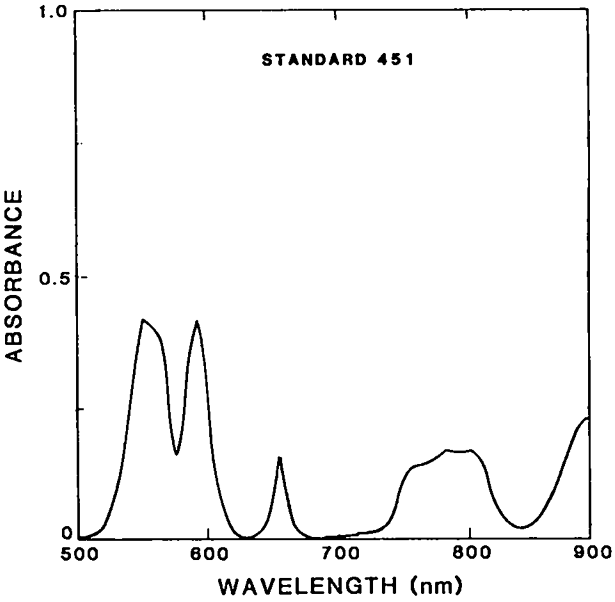

Fig. 2. Absorbance spectrum of a Pu(III) standard solution from 500-900 nm.

EXPERIMENTAL

The chemical procedure is documented in another report.[4] Samples were prepared by dissolving 100 mg of plutonium oxide in concentrated HCl with a trace of HNO_3 and HF and then transferring the solution to calibrated 25 mL volumetric flasks. Standards were prepared from high-purity, well-characterized metal, which was dissolved in HCl. Weighed aliquots of solution containing from 60 to 100 mg of plutonium standard were transferred to calibrated 25-mL volumetric flasks to which a small amount of HNO_3 and HF is added to simulate the dissolution medium for samples. The final concentration of HCl for samples and standards is ≈ 2 $\underline{M}$. Plutonium is reduced to Pu(III) by ascorbic acid in the presence of zirconyl chloride and aminoquanidine to counteract the effects of trace fluoride and to stabilize the ascorbic acid deterioration, respectively. The reduction by ascorbic acid is rapid. Spectra of samples and standards are measured with an HP-8450 diode array spectrometer within an hour of reduction to minimize any spectral drift or instability.

Precision on replicate readings of a single solution at a single wavelength shows the stability of the spectrophotometer to be ±0.0001 AU (or 0.02% for the

Pu(III) peaks at ≈0.5 AU). Relative precision for sample and standard weights is 0.03% and for the calibrated glassware 0.03%; thus, the combined error from these sources is ≈0.05%. This does not include possible errors in quantitative transfers of samples or standards.

Each spectrum was recorded at 2-nm intervals vs a reagent blank for 20 s. The digitized absorbance values were shipped to an IBM PC/XT for PLS regression and from the PC to a VAX 780 for the LSCF analysis. The spectra of 19 standards, taken over several weeks of routine application of the five-point procedure, were used as calibration and test sets. In addition, six unknowns from this same time period were selected to provide a means of comparing PLS and LSCF methods with the five-point method previously used. Two of these unknowns were problematic because of inconsistent predicted concentrations from the five-point calibration that were suggestive of base-line interferences.

RESULTS AND DISCUSSION

One recommended technique for testing a regression model is cross validation.[5] In cross validation, which is an iterative technique, we have a set of I samples for which plutonium concentrations and spectra are given. The regression model for calibration is developed by using a subset of the I samples and then by using this model to predict the concentrations of those samples *not* used to develop the regression model. This process is repeated until all I samples that were not used for model development have been used for prediction. The cross validation technique provides a more valid assessment of the calibration model than does the modeling error because it computes errors based on samples that were *not* used to develop the prediction equations. In contrast, methods for assessing model utility based on R^2 or residual errors are calculated for all samples used in development of the model and thus are not as powerful as cross validation methods. Of course, the best test of the model is in predicting the concentrations of future samples whose correct values are known by some independent method.

FIVE-POINT METHOD

Before presenting results for PLS and LSCF, the five-point procedure previously used will be briefly described and results will be given for comparison.

For each spectra, the four net absorbances corresponding to A-B, B-C, D-C, and D-E in Fig. 1 are calculated. With three to five standards, separate linear calibration lines are calculated for each of these four net absorbances. Parameters from these calculations are then used to make four separate estimates of plutonium content for each unknown.

With the five-point procedure, precision is better when standards run on separate days are not pooled (i.e., results for a given day are based only on standards run on that day). Thus, routine operation of the Pu(III) spectrophotometric method has entailed daily recalibration with the five-point method.

For comparison with PLS calibration, *all* 19 standards are used to develop four linear calibration lines. The average fits, together with the true values, are given in Table I. By using only the absorbance data corresponding to D-E, a better result is obtained. The average absolute error for the D-E method is 0.098 ± 0.067 mg. Because normal operation using the five-point method does not compare results over the period of more than 1 day and because the point of this study is analysis based on absorbances at only a few wavelengths vs analysis that uses all of the spectral information, it is logical to use the best method, i.e., the D-E method, for comparing standard data over the many day period with the PLS method.

The plutonium concentrations tabulated in Table II calculated using the five-point method were determined using daily calibration as described in the preceding paragraph.

PLS METHOD

To assess the utility of PLS regression for quantitation of total plutonium, we used cross validation, leaving one sample out of the model development step each time, with the 19 plutonium standards. These spectra were obtained over several weeks, so this serves as a test of using the same calibration over long instrument operation times. Results of this analysis are given in Table III. The second column contains the known concentrations; the third column contains the modeled values obtained when *all* 19 standards are included in development of the model equations; and the fifth column contains the cross validation prediction results. For prediction, the average absolute error of plutonium and its standard deviation are 0.090 ± 0.082 mg. For the model fit, the corresponding values are 0.067 ± 0.060 mg, which directly compares with the values of 0.181 ± 0.141 mg for the five-point method or 0.098 ± 0.067 mg for the D-E calibration shown in Table I. For prediction, only one of the standards deviates by greater than 0.20 from true value

TABLE I. Plutonium Concentrations

Day	Sample	True Value (mg)	Modeled Value (mg)	Absolute Error (mg)	Modeled Value (mg)	Absolute Error (mg)
			(Avg. of all four)[a]		(D-E alone)[b]	
1	Std. 580	66.09	65.67	0.42	65.90	0.19
	581	73.45	73.10	0.35	73.34	0.11
	582	66.58	66.23	0.35	66.46	0.12
2	506	85.49	85.53	0.04	85.52	0.03
	507	66.20	66.39	0.19	66.31	0.11
3	490	71.98	71.91	0.07	71.89	0.09
	491	74.59	74.57	0.02	74.54	0.05
	492	90.26	90.26	0.00	90.28	0.02
4	470	74.40	74.58	0.18	74.51	0.11
	471	85.56	85.57	0.01	85.50	0.06
	472	66.57	66.81	0.24	66.72	0.15
	450	78.48	78.79	0.31	78.64	0.16
	451	89.01	89.37	0.36	89.21	0.20
	452	63.69	63.90	0.26	63.73	0.09
	0	95.80	95.58	0.22	95.77	0.03
	1	65.80	65.82	0.02	65.79	0.01
	2	75.76	75.77	0.01	75.77	0.01
	3	89.27	89.01	0.26	89.03	0.24
	4	86.00	86.13	0.13	86.09	0.09
				Avg. = 0.181		Avg. = 0.098
				Std. Dev. = 0.141		Std. Dev. = 0.067

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[a] Concentration is an average based on all four of the estimates obtained by the five-point method (see text).
[b] Concentration is based on only the D-E spectral subtraction.

TABLE II. Comparison of Plutonium Mass (Milligrams of Plutonium in 25 mL Total Solution) of Six Unknowns Predicted by the Five-Point and PLS Calibration Methods

Sample	Five-Point Method	PLS Method
465	87.13	87.02
493	87.40	87.53
512	86.78	87.04
518	86.65	89.37
522	86.33	86.47
589	87.63	87.52

TABLE III. Plutonium Mass (Milligrams of Plutonium in 25 mL Total Solution) as Modeled and as Predicted Using Cross Validation

Sample	True Value	Modeled Value	Absolute Error	Predicted Value	Absolute Error
Std. 580	66.09	66.12	0.03	66.09	0.00
581	73.45	73.54	0.09	73.54	0.09
582	66.58	66.63	0.05	66.62	0.04
506	85.49	85.51	0.02	85.52	0.03
507	66.20	66.11	0.09	66.09	0.10
490	71.98	71.90	0.08	71.84	0.14
491	74.59	74.59	0.00	74.58	0.01
492	90.26	90.34	0.08	90.39	0.13
470	74.40	74.42	0.02	74.42	0.02
471	85.56	85.41	0.15	85.37	0.19
472	66.57	66.64	0.07	66.66	0.09
450	78.48	78.53	0.05	78.54	0.06
451	89.01	89.12	0.11	89.18	0.17
452	63.64	63.63	0.01	63.62	0.02
0	95.80	95.85	0.05	95.87	0.07
1	65.80	65.76	0.04	65.70	0.10
2	75.76	75.76	0.00	75.74	0.01
3	89.27	89.02	0.25	88.93	0.34
4	86.00	86.09	0.09	86.11	0.11
			Avg. = 0.067		Avg. = 0.090
			Std. Dev. = 0.060		Std. Dev. = 0.082

and six deviate by greater than 0.10. Thus 68% are predicted within 0.10 of the true value. Clearly PLS regression is a good full-spectrum method for calibrating this analytical procedure.

The PLS regression model developed was used to predict plutonium concentrations in the six unknowns that were previously determined with the five-point calibration procedure. Table II contains the values obtained by the two calibration methods. The five-point calibration estimate of Sample 518's concentration has been manually corrected for a shifted base line by assuming a linear base line from zero absorbance at 640 nm to the observed value at 520 nm. Measured values at points B, C, D, and E were adjusted before application of the calibration procedure (Sample 518's spectrum is shown in Fig. 3). The analyst was alerted to the necessity for doing something with this sample because of differences in the plutonium concentrations obtained by using different calibration points. The five-point calibration is a simple multivariate method and, for this sample, demonstrates the usefulness of multivariate methods for detecting abnormal sample spectra. Five-point calibration also indicated a problem with Sample 512.

PLS predictions for these samples are all quite close to those obtained from the five-point method, except for Sample 518 and perhaps Sample 512. The predicted values also are divided evenly between positive and negative differences. Thus, it appears that PLS predicts plutonium concentrations consistent with the five-point method. Furthermore, PLS can be used to detect outliers, such as Sample 518, by use of the spectral residuals predicted by the PLS method. Methods for detecting outliers are being incorporated into the PLS program.

LSCF METHOD[2]

If the observed spectral absorbances obey Beer's model, the total spectrum (or each individual peak) is a linear sum of the spectra of the pure chemical constituents contributing to it. In this case, if all chemical constituents are known, an unknown's spectrum can

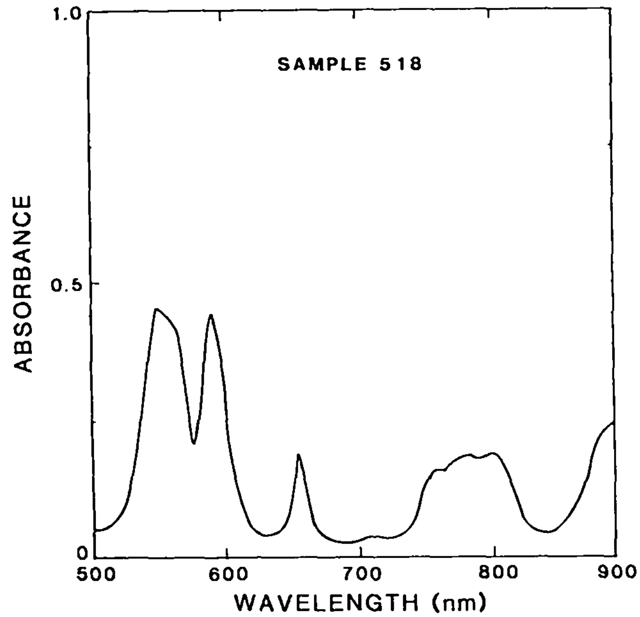

Fig. 3. Absorbance spectrum of a sample containing Pu(III) showing a shifted base line.

be fit, using least squares methods, by a linear combination of the standardized spectra of the known constituents. It is also possible to include a linear or quadratic base line to the least squares fit to account for a shifting or variable base line. The LSCF program developed at Sandia National Laboratories was used for this study.[6] The Sandia LSCF program has several options that were tested on this problem. These options are full-spectrum fits (500 to 900 nm) with either a linear or no base-line, a fit of the full spectrum's first derivative, and fits across each spectral region or peak including a linear base line. The 19 standards were split into a calibration set containing 10 standards and a prediction set of 9 standards. (The best average absolute model or fit error modeled for plutonium using all 19 standards was 0.129 ± 0.082 mg for the full spectrum with linear base-line fit.) The upper part of Table IV contains results of the LSCF model for the 10 calibration set standards, and the bottom part contains results for predicting the remaining 9 standards. Either use of the full spectrum with linear base line or of the 520- to 640-nm peak with linear base line gives the best results. Both of these fits have an average absolute error of 0.130 mg for prediction. Consideration of the signs of the errors from the data in Table IV suggests a bias toward over-prediction for the zero-base-line case, whereas the other methods are not biased significantly high or low. For these standards, the results indicate that we have accounted for all constituents and that including a variable linear base line is necessary for good fitting.

For a direct comparison of LSCF with PLS, a PLS model was developed using these same 10 standards and then was used to predict the concentrations of the 9 standards used as unknowns. Results of these predictions are given in the bottom part of Table IV (far right column). The results show an average absolute error of 0.114 mg.

LSCF results for the same six unknown samples used in the PLS calibration study (Table II) are found in Table V. All fitting options were tested. As in the above, the least squares, zero-base-line option gave a positive bias, compared with the five-point calibration. With the exception of the zero-base-line case, the concentrations estimated by the various least squares fitting methods overlap with each other within the 95% confidence intervals of the fit. Thus, all the fits give the same result, and any one or a combination of them can be used. We prefer to use all of them as a consistency check to alert us to unusual samples. Note that the LSCF method does a nice job of automatically compensating for large differences or changes in base line between standards and samples, as seen in the results for Samples 512 and 518. The base-line shift of Sample 518 is obvious by comparing Fig. 2 with Fig. 3. The linear base-line fit adequately corrects for this feature.

CONCLUSIONS AND SUMMARY

The average absolute error in PLS-predicted plutonium concentrations and in the corresponding standard deviation on nine samples, using the cross validation method, was 0.11 ± 0.11 mg. The average absolute prediction error for the best least squares procedure was 0.13 ± 0.09 mg. Thus, PLS gives a slightly better result for this data. PLS has the advantage that *not* all sample chemical constituents need be known to determine the desired constituent. However, all constituents that absorb light at the spectral wavelengths used for the determination *must* be present in the calibration samples if they are present in future unknowns. In contrast, *all chemical constituents* giving rise to spectral absorbance must be known for LSCF for adequate calibration. However, LSCF can compensate for major base-line shifts if the general shape is known, for example, Sample 518 in Tables II and V. LSCF can also detect outliers by lack of fit for the unknown, and indeed the residuals may give some indication of the identity of an interfering constituent. PLS also has the capability of detecting outliers and

TABLE IV. LSCF Results for the Ten Standards Used to Calibrate (Top) and the Nine Standards Used for Prediction (Bottom)

CALIBRATION

		Base-Line Treatment					
Sample	True Value	Zero	Linear Spectrum	Linear Across Peak			First Derivative
				520-640	660-702	740-900	
Std. 580	66.09	66.15	65.88	65.86	65.69	65.88	65.67
582	66.58	66.63	66.43	66.41	66.23	66.45	66.23
507	66.20	66.23	66.32	66.32	66.46	66.37	66.42
491	74.59	74.63	74.46	74.58	74.60	74.36	74.56
470	74.40	74.64	74.54	74.53	74.65	74.61	74.60
472	66.57	66.82	66.77	66.76	66.85	66.87	66.86
451	89.01	89.43	89.20	89.20	89.37	89.30	89.28
0	95.80	95.82	95.65	95.64	95.48	95.64	95.46
2	75.76	75.73	75.72	75.66	75.67	75.78	75.76
4	86.00	86.12	86.04	85.98	86.05	86.11	86.10
Average		0.126	0.137	0.132	0.237	0.183	0.222
Absolute Error		±0.134	±0.059	±0.072	±0.138	±0.084	±0.141

PREDICTION

		Base-Line Treatment						
Sample	True Value	Zero	Linear Spectrum	Linear Across Peak			First Derivative	PLS Value[a]
				520-640	660-702	740-900		
Std. 581	73.45	73.56	73.30	73.29	73.11	73.29	73.06	73.55
506	85.49	89.60	85.52	85.55	85.61	85.49	85.46	85.50
490	71.98	71.90	71.81	71.92	71.73	71.72	71.91	71.87
492	90.26	90.37	90.16	90.32	90.33	90.05	90.20	90.33
471	85.56	85.67	85.52	85.52	85.68	85.58	85.56	85.39
450	78.48	78.80	78.65	78.66	78.82	78.74	78.79	78.54
452	63.64	63.84	63.79	63.78	63.93	63.88	63.96	63.64
1	65.80	65.70	65.76	65.70	65.73	65.84	65.84	65.65
3	89.27	89.02	88.95	88.90	88.90	89.02	88.93	88.91
Average		0.599	0.130	0.130	0.197	0.160	0.171	0.114
Absolute Error		±1.319	±0.092	±0.103	±0.135	±0.110	±0.163	±0.108

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[a] For direct comparison, PLS prediction after calibration using the same 10 standards.

TABLE V. Plutonium Mass (Milligrams of Plutonium in 25 mL Total Solution) for Six Unknowns Obtained by LSCF Compared with the Five-Point Method

	Least Squares Values[a]						
				Linear Over Peaks			
Sample	Five Point	Zero	Linear Over Spectrum	520-640	660-702	740-900	First Derivative
Std. 465	87.13	87.94	87.20	87.18	87.29	87.30	87.30
493	87.40	88.04	87.35	87.44	87.36	87.28	87.40
512[b]	86.78	89.13	87.77	86.65	86.78	86.69	87.00
518[b]	86.65	102.70	86.87	86.30	86.44	86.36	86.37
522	86.33	87.55	86.33	86.30	86.38	86.31	86.34
589	87.63	88.26	87.22	87.26	86.90	87.05	86.90

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[a] Different columns refer to type of base-line fit used, except for first derivative.

[b] These two samples were corrected for a sloping base line before application of the five-point calibration.

of providing information about constituent identity by a consideration of residuals of the reproduced spectrum. PLS cannot compensate for base-line structure, different from that of the calibration set, in unknowns (PLS result for Sample 518 in Table II). However, a background or base-line subtraction could be performed on all spectra before calibration and prediction.[6] Both PLS and LSCF are more precise and robust than the five-point method. For example, the PLS average absolute model error for the 19 standards is 0.067 mg compared with 0.181 mg for the five-point method, 0.098 mg for the D-E calibration, and 0.129 mg for LSCF. PLS and LSCF results are based on using all standards over several days of operation, whereas the other two results are based on daily calibrations using just three to five standards. Results indicate that daily calibration is necessary using the five-point method, whereas it is not needed with the PLS and LSCF methods.

We are currently evaluating PLS calibration as a method for routine calibration and prediction of total plutonium concentration by the Pu(III) spectrophotometric method. PLS models are being developed for the entire spectrum, 520-900 nm, and separately for each spectral area. These, then, are used to provide consistency checks for unknowns as a kind of outlier detection technique.

REFERENCES

1. Avraham Lorber, Lawrence E. Wangen, and Bruce R. Kowalski, "A Theoretical Foundation for the PLS Algorithm," *Journal of Chemometrics* **1**, 19-31 (1987).

2. David M. Haaland and Robert G. Easterling, "Improved Sensitivity of Infrared Spectroscopy by the Application of Least Squares Methods," *Applied Spectroscopy* **34**, 539-548 (1980).

3. William H. Lawton and Edward A. Sylvestre, "Self-Modeling Curve Resolution," *Technometrics* **13**, 617-633 (1971).

4. Terry R. Hahn and Tom K. Marshall, "A Spectrophotometric Procedure for the Determination of Total Plutonium After Reduction to the Pu(III) State," Los Alamos National Laboratory, unpublished report.

5. Svante Wold, "Cross-Validatory Estimation of the Number of Components in Factor and Principal Components Models," *Technometrics* **20**, 397-405 (1978).

6. David M. Haaland, Robert G. Easterling, and David A. Vopicka, "Multivariate Least-Squares Methods Applied to the Quantitative Spectral Analysis of Multicomponent Samples," *Applied Spectroscopy* **39**, 73-84 (1985).

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