1.0

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A study of error propagation for multicomponent analysis in the presence of sample related interferences by the generalized standard addition method has been made. The results of the examination have lead to an alternate experimental design and optimal computation algorithms which are tested using a four component spectrophotometric analysis. Additionally, the theory describes fundamental constraints to multicomponent analysis in the presence of chemical, physical and spectral interferences.

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Error Propagation and Optimal

Performance in Multicomponent Analysis

by

Clemens Jochum, Peter Jochum,[1] Bruce R. Kowalski

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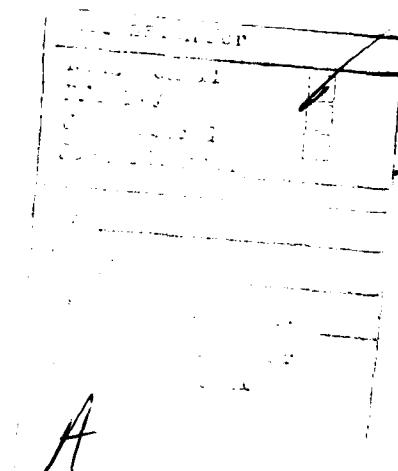
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Abstract

A study of error propagation for multicomponent analysis in the presence of sample related interferences by the generalized standard addition method has been made. The results of the examination have lead to an alternate experimental design and optimal computation algorithms which are tested using a four component spectrophotometric analysis. Additionally, the theory describes fundamental constraints to multicomponent analysis in the presence of chemical, physical and spectral interferences.

Since many methods of quantitative chemical analysis are not "fully selective" (1), or, in other words, not free from interferences, important goals of the analyst are to detect, characterize and, hopefully, eliminate interferences that arise during the course of an analysis. Interferences that do not arise from chemical species (e.g., electronic drift) in the sample clearly should be eliminated. However, interferences (i.e., chemical, physical or spectral) arising from chemical species in the sample can be regarded as "misplaced analytical signal" and it would be best to sort these interferences during a multianalyte analysis. For example, it is well known that when the 422.7 nm line is used for the atomic emission analysis of calcium, the presence of sodium in the sample will cause an overestimation for the quantity of analyte in the sample due to an interference. It is common practice to apply a correction to the calcium signal based on the strength of the sodium signal. However, this negative correction to the calcium signal ideally should be accompanied by a positive correction to the sodium signal. In this way, the influence of sodium on the calcium line would not be wasted but would be correctly sorted giving rise to a conservation of analytical signal and increased sensitivity.

Ideally, a method is clearly needed that can 1) detect interferences during a multianalyte analysis, 2) mathematically characterize these interferences, no matter how complex, and 3) sort all interference signals to allow the maximum utilization of all analytical signals. This method would not only provide more accurate multianalyte analyses but would also serve to characterize the selectivity of the analytical instrument and therefore be an important aid for analytical method development.

Recently, our laboratory developed the mathematical basis for just such a method. It is based on the preferred method of standard additions and is a generalization to include any number of analytes. Hence it is referred to as the Generalized Standard Addition Method (GSAM) (2) for simplicity. The GSAM is applicable to multicomponent analysis where interferences of any kind are a problem.

This paper deals with the limitations of the linear model GSAM and the development and testing of optimal computer algorithms and experimental designs for carrying out multicomponent analyses using the GSAM. During the course of the study, certain fundamental concepts and limitations to multicomponent analysis were discovered. These concepts allow the analyst to calculate, in advance, the penalty or cost of performing a multicomponent analysis when interanalyte interferences are present. This penalty takes the form of an amplification of the measurement error as it is propagated to the final results (initial analyte concentrations and/or response constants). This theory should be of considerable utility to the analytical chemist as it describes, quantitatively, the usefulness of an analytical system and can even be used to compare and select systems. This same theory has vastly improved our understanding of the characteristics of the GSAM and has provided direction for the optimization of its application.

In the remainder of this paper, the linear response GSAM is briefly reviewed, the theory mentioned above is described in detail, and the improvements given by the theory are tested on a four component spectrophotometric analysis.

BACKGROUND AND THEORY

The Generalized Standard Addition Method - A Brief Overview

As any analyst knows, the standard addition method requires the measurement of the analytical signal before and after addition of known quantities of the analyte (standard additions) have been added to a sample. The analyte concentration is found by extrapolating the regression line to the negative portion of the plot of signal vs. concentration added (Δc). The model assumes that the analytical signal, or more generally the response, R_ℓ is given by:

$$R_\ell = ck_\ell = (\Delta c + c_o) k_\ell \qquad \text{1)}$$

where Δc is the effective total concentration change of the analyte after any standard addition, c_o is the initial analyte concentration and k_ℓ is the linear response constant. Of course, if analytical signal, ℓ, is responsive, again in a

linear manner, to r components in the sample (interference effects), the true
response equation is:

$$R_\ell = \sum_{s=1}^{r} c_s k_{s\ell} \qquad \qquad 2)$$

where c_s is the concentration of the $s^{\underline{th}}$ component and $k_{s\ell}$ its response
constant. For later use, it is most important to note that R_ℓ can be expanded
as:

$$R_\ell = \sum_{s=1}^{r} \Delta c_s k_{s\ell} + \sum_{s=1}^{r} {}_\circ c_s k_{s\ell} \qquad \qquad 3)$$

which simply says that the total concentration is the sum of each initial concen-
tration plus its change in concentration brought about by standard additions.

Now, for r analytes, p analytical responses ($p \geq r$) must be measured. Each
response can depend on any combination of the r components provided that each of
the r components (hereafter referred to as analytes as all r concentrations will
be determined simultaneously) affects at least one of the p responses. The GSAM
requires that n multiple standard additions (MSA's) be made so as to span the
r-dimensional concentration space ($n \geq r$). Expressing the above in matrix form
gives,

$$\underline{R} = \underline{C}\,\underline{K} \qquad \qquad 4)$$

where $\underline{R}$ is the n x p matrix of measured responses to the n MSA's. $\underline{C}$ is the n x r
matrix with the total concentration ($\Delta c + c_\circ$) of the r analytes in each of the n
rows and $\underline{K}$ is the r x p matrix of constants relating the contribution of each of
the r analytes to the p responses. Note that many elements of $\underline{K}$ can be near zero
if interferences are not present.

The solution for $\underline{K}$ is given in
reference (2) to be,

$$\underline{K} = (\underline{\Delta C}^T\,\underline{\Delta C})^{-1}\,\underline{\Delta C}^T \underline{\Delta R}, \qquad \qquad 5)$$

where $\underline{\Delta C}$ is an n x r matrix of total concentration changes for r analytes

at each of n MSA's. Given $\underline{K}$, $\underline{c_o}$, the column vector of initial analyte concentrations, can be found by

$$\underline{c_o}^T = \underline{r_o}^T \underline{K}^{-1}, \quad \underline{r_o} = ({_oR_1}, \cdots, {_oR_r})^T \qquad 6)$$

It is very important to recognize that $\underline{\Delta C}$ in equation 5 is the matrix of effective total concentration changes for each analyte after the MSA's and, unless volume changes are negligible, $\underline{\Delta C}$ cannot be known since the initial concentrations are unknown. In practice, this is not a problem as simple volume corrections convert concentrations to absolute quantities (e.g., moles).

Equation 2 can be rewritten,

$$R_\ell = \sum_{s=1}^{r} \frac{N_s}{V} k_{s\ell} \qquad 7)$$

where N_s is the total number of moles of analyte s in a volume V. This leads to

$$Q_\ell \equiv VR_\ell = \sum_{s=1}^{r} N_s k_{s\ell} \qquad 8)$$

which can now be separated,

$$Q_\ell = \sum_{s=1}^{r} \Delta N_s k_{s\ell} + \sum_{s=1}^{r} {_oN_s} k_{s\ell} \qquad 9)$$

${_oN_s}$ is the initial number of moles for analyte s and ΔN_s in the total amount of analyte s added which is now known. Hence, for equation 4, if all responses at all MSA's are volume corrected, $\underline{C}$ is the matrix of amounts expressed in moles and the solution can proceed as in reference 2. The solution $\underline{K}$ of the overdetermined system

$$\underline{\Delta N}\ \underline{K} = \underline{\Delta Q} \qquad 10)$$

is now

$$\underline{K} = (\underline{\Delta N}^T \underline{\Delta N})^{-1} \underline{\Delta N}^T \underline{\Delta Q} \qquad 11)$$

with $\underline{\Delta N}$ expressed in total changes of quantitites and $\underline{\Delta Q}$ equal to the matrix of volume corrected response changes.

The GSAM requires that MSA's be made prior to each of the n measurement steps. One MSA may consist of the addition of one standard or several standards. The MSA's are attempts to span an r-dimensional concentration

space. If the linear model holds for the simple standard addition method (one analyte) the method of additions is clear (3). Unfortunately, this is not the case for the GSAM.

The goal in this study was to determine the optimal method of performing the multiple standard additions. "Optimal" meaning the lowest errors in the determination of K and n_o.

The accuracy of the determination of n_o, the vector of initial amounts of all the analytes, is dependent on at least five items.

1) The accuracy of each response is of paramount importance and represents a limiting condition as in any quantitative analysis.

2) With the GSAM, the multiple standard additions must be made without determinate error and with acceptable precision. Again, this is true of any analysis regardless if calibration or standard addition methods are used.

3) The third item deals with interferences which can be described using mathematical properties of the K matrix to be explained later.

4) The experimental design, as might be expected, can strongly influence the accuracy of K and hence n_o.

5) The mathematical algorithms selected for computation can effect the results due to round-off errors. This will be clear in the following.

The emphasis of this paper is item 4. However, in a search for better ways to implement the GSAM, much has been learned about all five items and a more fundamental understanding of multicomponent analysis has been the result. This paper describes the manner in which measurement accuracy (item 1), experimental manipulation involved with calibration (item 2) and interferences (item 3) influence chemical analyses, and how the way in which the analyses are performed (item 4) can alter these influences and the results calculated (item 5).

Error Propagation

After computation of the K matrix, the desired initial quantities (the components of n_o) are obtained by solving

$$K^T n_o = q_o \qquad\qquad 12)$$

If the $\underline{K}$ matrix is well conditioned (i.e., the analytical sensors are very selective) any linear equation solver may be applied to equation 12. If not (i.e., the columns of $\underline{K}$ are nearly linearly dependent), Househoulder's triangular decomposition (see Appendix) should be preferred in order to at least guarantee a minimum of numerical rounding errors (item 5 above). Nevertheless, the magnification of experimental errors may be crucial.

The experimental application of the GSAM is as subject to experimental errors as any measurement procedure. These errors may be propagated twice: first, in determining the $\underline{K}$ matrix by solving the least squares problem and, second, in solving the linear system 12 using the calculated $\underline{K}$ matrix. The sensitivity of the solution of a numerical problem with respect to errors (i.e., the size of the error magnification factor) is usually called the <u>condition</u> of the problem. Even in the linear case the relative data error may be magnified by a factor which can lead to completely unreasonable results. Hence, a very careful analysis should be applied to the sensitivity of the final result $\underline{n_o}$ with respect to instrumental and performance errors and, consequently, to the optimal design of the addition matrix $\underline{\Delta N}$.

Error amplification can be shown by a simple but illustrative example. Assume the following two by two system of linear equations, $\underline{A}\underline{x} = \underline{b}$, is to be solved,

$$\begin{pmatrix} 3.56 & -1.92 \\ -1.92 & 2.44 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \begin{pmatrix} -20.0 \\ 15.0 \end{pmatrix} \qquad 13)$$

The solution is $\underline{x} = (-4.0, 3.0)^T$ as is easily verified. Now suppose the right-hand side, $\underline{b}$ is perturbed by the error vector $\underline{\delta b} = (0.3, 0.4)^T$ which produces a relative error $\|\underline{\delta b}\| / \|\underline{b}\|$ of 2%. ($\| \cdot \| \equiv$ square root of sum of squares of vector elements.) The corresponding solution $\underline{\bar{x}} = \underline{x} + \underline{\delta x}$ to $\underline{\bar{b}} = \underline{b} + \underline{\delta b}$ is $\underline{\bar{x}} = (-3.7, 3.4)^T$ which corresponds to a relative solution error $\|\underline{\delta x}\| / \|\underline{x}\|$ of 10%. Thus an error amplification factor of 5 results. To put this result in a more general context the introduction of the norm of a matrix is required.

For a matrix $\underline{A} \in \mathbb{R}^{n,r}$, the number

$$\|\underline{A}\|_2 \equiv \text{lub}_{\underline{x} \in \mathbb{R}^r} \frac{\|\underline{Ax}\|_2}{\|\underline{x}\|_2} = \max_{\|\underline{x}\|_2=1} \|\underline{Ax}\|_2 \quad \text{(lub means \underline{l}owest \underline{u}pper \underline{b}ound)} \qquad 14)$$

will be called the <u>Euclidian</u> <u>norm</u> (or simply <u>norm</u>) of $\underline{A}$. The square roots of the eigenvalues of the positive definite matrix $\underline{A}^T\underline{A} \in \mathbb{R}^{r,r}$ are called <u>singular</u> <u>values</u> of $\underline{A}$. In the case where $n=r$ and $\underline{A}$ is <u>normal</u> (i.e., $\underline{A}^T\underline{A} = \underline{A}\underline{A}^T$) the singular values are the absolute eigenvalues of $\underline{A}$ (e.g., all symmetric matrices are normal). It is well known that the biggest and the reciprocal smallest singular values of $\underline{A}$ are equal to the norms of $\underline{A}$ and $\underline{A}^{-1}$, respectively (4).

$$\|\underline{A}\| = \sigma_1, \quad \|\underline{A}^{-1}\| = \sigma_n^{-1}. \qquad 15)$$

Using the same notation as before and starting with equation 12 where $\underline{K}$, the matrix of response constants, is assumed known <u>exactly</u> for now, and $\underline{q}_0$ is the vector of initial volume corrected responses, a useful result can be found. It is known that

$$\|\underline{q}_0\| \leq \|\underline{K}^T\| \cdot \|\underline{n}_0\| \qquad 16)$$

If $\underline{K}^{-1}$ exists, as it must in chemical analysis, then

$$\underline{n}_0 = (\underline{K}^T)^{-1} \underline{q}_0 \qquad 17)$$

Now, a small change in $\underline{q}_0$, represented by $\delta\underline{q}_0$, gives rise to an error $\delta\underline{n}_0$, which must be kept small in a chemical analysis. Since,

$$\delta\underline{n}_0 = (\underline{K}^T)^{-1} \delta\underline{q}_0, \qquad 18)$$

$$\|\delta\underline{n}_0\| \leq \|(\underline{K}^T)^{-1}\| \cdot \|\delta\underline{q}_0\| \qquad 19)$$

Combining 16 and 19 and using $\|(\underline{K}^T)^{-1}\| = \|\underline{K}^{-1}\|$ give

$$\frac{\|\delta\underline{n}_0\|}{\|\underline{n}_0\|} \leq \|\underline{K}\| \cdot \|\underline{K}^{-1}\| \cdot \frac{\|\delta\underline{q}_0\|}{\|\underline{q}_0\|} \qquad 20)$$

Defining the condition number of any nonsingular matrix $\underline{A}$ as

$$\text{cond} (\underline{A}) = \|\underline{A}\| \cdot \|\underline{A}^{-1}\| \qquad 21)$$

and using the fact that   cond $(\underline{A})$ = cond $(\underline{A}^T)$ the final result is

$$\frac{\|\,\underline{\delta n_o}\,\|}{\|\,\underline{n_o}\,\|} \leq \text{cond } (\underline{K}) \cdot \frac{\|\,\underline{\delta q_o}\,\|}{\|\,\underline{q_o}\,\|} \qquad \qquad 22)$$

The condition number can have different values depending upon the chosen norm. It is always greater than one and herein lies an important result. If $\underline{q_o}$ is the true response vector that gives rise to the true analyte vector $\underline{n_o}$, then 22 shows that a small error in response $\underline{\delta q_o}$ can be _magnified_ by cond $(\underline{K})$ in the worst case to produce a greater relative concentration error; error amplification.

All of the above relates to the third item mentioned in the introduction. The analyst selects a particular analytical method characterized by the matrix $\underline{K}$, the response constants of the method. Inequality 22 characterizes the "cost of inter- ferences" in the method. The cost is paid in increased relative uncertainty in the initial concentrations to be determined. The ideal case of fully selective sensors (no interferences) with equal sensitivity gives rise to a $\underline{K}$ matrix with a condition number of one and absolutely no error amplification.

During an actual application of the GSAM, the $\underline{K}$ matrix is determined as the solution of an overdetermined linear system and therefore is not known exactly. Hence, the propagation of errors due to the $\underline{K}$ matrix must be examined. The following similar error estimate taking matrix entry errors into account can be found in reference 4, p. 195:

$$\frac{\|\,\underline{\bar{x}} - \underline{x}\,\|}{\|\,\underline{x}\,\|} \leq \frac{\text{cond } (\underline{A}) \dfrac{\|\,\underline{E}\,\|}{\|\,\underline{A}\,\|}}{1 - \text{cond } (\underline{A}) \dfrac{\|\,\underline{E}\,\|}{\|\,\underline{A}\,\|}} \qquad \qquad 23)$$

where $\underline{\bar{x}}$ is the solution of the perturbed system $(\underline{A} + \underline{E})\underline{\bar{x}} = \underline{b}$, whose error matrix $\underline{E}$ has to be sufficiently small $(\|\,\underline{A}^{-1}\underline{E}\,\| < 1)$.

Using 23 and 22 (by a Taylor expansion neglecting higher order terms) the combined error estimate is obtained

$$\frac{\|\,\underline{\delta n_o}\,\|}{\|\,\underline{n_o}\,\|} \leq \text{cond } (\underline{K}) \left[\frac{\|\,\underline{\delta q_o}\,\|}{\|\,\underline{q_o}\,\|} + \frac{\|\,\underline{\delta K}\,\|}{\|\,\underline{K}\,\|} \right] \qquad \qquad 24)$$

Now, to estimate the second term in the brackets a sensitivity analysis of the generalized solution of equation 11 with respect to experimental error amplification must be done. It is considerably more complicated, whence only the final inequalities are cited here. For details the reader is referred to (4, 5, 8). The first estimate analogous to equation 22 (transcribed to this paper's notation) can be found in Reference 4, p. 221, to be,

$$\frac{\| \overline{k} - k \|}{\| k \|} \leq \text{cond } (\Delta N) \frac{\| \overline{\Delta q_1} - \Delta q_1 \|}{\| \Delta q_1 \|}. \tag{25}$$

where cond $(\Delta N) = \| \Delta N \| \, \| \Delta N^{\dagger} \|$ is now the _generalized condition number_ of ΔN and Δq_1 and $\overline{\Delta q_1}$ are the projections of Δq and $\overline{\Delta q}$ onto the range of ΔN. The generalized condition of the rectangular matrix ΔN may be computed by the formula

$$\text{cond } (\Delta N) = [\text{cond } (\Delta N^T \Delta N)]^{1/2}, \tag{26}$$

where the number in brackets denotes the usual (see equation 21) condition of the square matrix $\Delta N^T \Delta N$.

Further generalizations are not only beyond the scope of this paper but are actually unnecessary for achieving our goals. The analytical chemist is not usually interested in calculating upper bounds on the relative errors of initial concentration vectors. Actually, statistical error propagation, the subject of other work in our laboratory, is usually of greater interest. Rather, the forms of equations 24 and 25 are far more important as they show the dependence of analytical accuracy, δn_o, on measurement accuracy, δq_o, interferences, cond (K), and the experimental design, cond(ΔN). Functional dependence of item two is covered in the Appendix, its effect being a bit more complex. These dependences demand that measurement errors be small, interferences be few and small [cond (K) close to one], multiple standard additions be made as accurately as possible (Appendix) and that the experimental design lead to the smallest cond (ΔN) as possible. The first three demands are not unknown to the analytical chemist. But the final demand has guided this work to the experimental designs proposed in the following section.

Suggested Variants of the GSAM

The sensitivity of the initial quantities, n_o, is highly dependent on the condition of ΔN and, thus, on the experimental design of the GSAM. In order to minimize the error propagation factors two variants of the GSAM, as presented in the original paper, are now suggested for use.

The original GSAM method used the total difference calculation and does not differ in experimental design from the now suggested incremental difference calculation. Rather, the difference lies only in the definition of ΔN and, correspondingly, of ΔQ. The entries in the ΔN matrix for the total difference calculation are the accummulative amounts of standards added. For the incremental difference calculation, the entries are just the amounts added at any one MSA. Likewise, the ΔQ entries for the total difference computation are the total changes in response from q_o and only the stepwise incremental response changes for the incremental difference computation.

The second variant procedure, called the Partition GSAM, or PGSAM, amounts to a true change in experimental design. The sample is first split into as many partitions as there are analytes. (In practice, the analyst would begin with r aliquots of the sample.) Then, for each partition, all of the responses are measured before and after standard additions of only one standard per partition.

As will be seen in a later section, the condition of ΔN for the incremental difference computation GSAM and the PGSAM is unity amounting to no error amplification for either variant. (Actually, this is true only when identical quantities of each standard are added or ΔN is scaled in a manner to be described later.) The normal GSAM is performed in one vessel and the PGSAM requires multiple vessels. In most cases, the GSAM would be preferred but if, for example, additions of several different standards to a single sample leads to changes in the k_{sl}'s (equation 3), this model nonlinearity may be avoided by employing the PGSAM. Experimental considerations can now dictate which procedure to use and the sensitivity of the sensors can dictate the amount of each standard to use for any one MSA.

EXPERIMENTAL

Reagents:

Four aqueous solutions of 0.01 M $NiCl_2$, 0.01 M $CuCl_2$, 0.01 M $CoCl_2$, and 0.002 M $K_2Cr_2O_7$ (all A.C.S. Reagent Grade) were used to serve as standards for the additions and to prepare the "unknown" mixture consisting of 1.0 ml each of the $NiCl_2$, $CuCl_2$ and $CoCl_2$ standard solutions. Standard additions were made in units of one ml of the respective solutions or 1.0×10^{-5} mole of $NiCl_2$, $CuCl_2$, $CoCl_2$ and 2.0×10^{-6} mole $K_2Cr_2O_7$.

Apparatus:

A Cary 219 spectrophotometer was used for all measurements. The responses measured were the absorbances of every solution at five wavelengths. The wavelengths corresponded to absorbance peak maxima for each of the four analytes with a second peak maximum for nickel included. Wavelength were assigned as follows: $\lambda_1 = 351.0$ nm ($Cr_2O_7^{2-}$), $\lambda_2 = 394.5$ nm (Ni^{2+}), $\lambda_3 = 511.5$ (Co^{2+}), $\lambda_4 = 660.0$ nm (Ni^{2+}), $\lambda_5 = 820.0$ nm (Cu^{2+}).

Procedure:

A: (GSAM) 16 additions, 4 for each analyte, were added to the unknown mixture in the following order: 4 times 1 unit of $NiCl_2$; 4 times 2 units $CuCl_2$; 4 times 4 units of $CoCl_2$; and 4 times 8 units of $K_2Cr_2O_7$. After each addition the absorbances at all five wavelengths were recorded.

B: (PGSAM) Four equal aliquots of unknown mixture.

To the first aliquot 4 additions of 1 unit $NiCl_2$,

to the second aliquot 4 additions of 1 unit $CuCl_2$,

to the third aliquot 4 additions of 1 unit $CoCl_2$, and

to the fourth aliquot 4 additions of 1 unit $K_2Cr_2O_7$, were made.
After each addition the absorbances of the respective partition at all five wavelengths were recorded.

Computer Program:

All programs are written in Fortran IV and are available from Infometrix, Inc., P. O. Box 25888, Seattle, WA 98125.

RESULTS AND DISCUSSION

The experimental goal was to corroborate the theoretical considerations according to possible addition techniques. Hence, an experiment was selected that was easy to perform and that allowed the testing of different addition matrices on an instrument with a large and linear dynamic range. One experiment that meets these requirements is the determination of the concentrations of inorganic ions in a mixture by visible light spectrophotommetry. As described in the Experimental Section, two procedures were used to perform the experiment: the standard GSAM and the sample partition GSAM or PGSAM.

The results were calculated in two different ways; the total difference computation and the incremental difference computation (TDC and IDC). During the experiment the responses (absorbances) at 5 different wavelengths were measured although only four would have been necessary since an unknown mixture consisting of only four analytes was considered. This was done to obtain different K matrices using different combinations of selected wavelenths in order to compare results. Of course, a generalized inverse solution for the initial quantities starting with equation 12 can be used when $r > p$.

In a real analytical sample the analyst is faced with possible large differences among the initial analyte concentrations and varying sensitivities among the transducers used to obtain the analytical responses. Therefore, the concentration changes made for each analyte may be quite different in magnitude. This necessary element of the experimental design produces large differences in relative magnitudes among columns of ΔN leading to artificially increased condition numbers. To get the smallest possible condition number for a certain addition matrix ΔN and thus the smallest error estimate of the K matrix the addition and response matrices were scaled such that,

$$\sum_{j=1}^{r} (\Delta n_{ij})^2 = 1 \qquad\qquad i = 1,\ldots,n.$$

27)

Table I shows the addition matrix and the five volume corrected response columns of the TDC before scaling. Note that the additions are summed since the total change in the response was observed with respect to the initial response q_0. Since the additions are given in above defined units, the results are also given in the same units. Also, unequal amounts of each standard were used for the additions. Although this experimental design may not be ideal from the experimental or statistical point of view, it gives a smaller cond (ΔN) for the total difference GSAM than equal additions, a fact that easily can be verified by the reader.

Table II gives the data for the incremental difference computation. Note that the addition matrix now consists of only the additions made at one time and the response matrix consists of only the changes of the responses with respect to the response before each addition was made. The scaled $\Delta N^T \Delta N$ matrix is therefore a diagonal matrix with condition number one.

Likewise, Table III shows the results for the sample partition method, PGSAM. The addition matrix, ΔN, shows that amounts are again accumulative but only within a single sample partition per column. Besides the experimental advantage mentioned above, the use of the PGSAM has the additional advantage that the scaled $\Delta N^T \Delta N$ has a condition number of one. The major disadvantages of the PGSAM are the extra amount of sample required and the manipulation necessary when a sample is partitioned which can introduce additional experimental error. In the present experiments, the normal GSAM results were obtained using only one pair of cuvettes for the spectrophotometer. One reference cuvette and four sample cuvettes, one for each partition, were used for the PGSAM. Thus the errors associated with volume transfers and cuvette positioning in the instrument were compounded by the use of more experimental equipment.

Formally, the first calculation step in the GSAM is the determination of K. Since K results for the TDC-GSAM, IDC-GSAM, and the PGSAM were nearly identical, only the K matrix for the IDC-GSAM for each of the two selections of wavelengths is given. Table IV shows the experimentally determined K for the "most selective"

combination of wavelengths. Although none of the wavelengths are fully selective for any one element, only one wavelength (λ_2) represents a serious interference problem. The resulting error amplification limit [cond $(\underline{K})$] is slightly less than a factor of two. Table V shows the $\underline{K}$ for a less selective combination of wavelengths reflecting more serious interferences and a much larger error amplification factor [cond $(\underline{K})$].

Table VI gives the final results for the TDC-GSAM, IDC-GSAM, and the PGSAM for the most selective combination of wavelengths and only the IDC-GSAM for the less selective combination of wavelengths. The result for the second group of wavelengths paralleled the results of the first group and are not reported here for brevity. The eigenvalues and condition numbers are all as expected. The first three estimates of cond $(\underline{K})$ are essentially equivalent reflecting only experimental error of the estimates of the $\underline{K}$ matrices pointed out above. The last cond $(\underline{K})$ is larger and quantitatively estimates the potential cost of performing the chemical analysis with a less selective analytical system.

The interesting results for the analytical chemist come at the bottom of Table VI. The most accurate results using the first group of wavelengths is achieved with the application of the IDC-GSAM. Its average absolute % error of 1.33% is quite close to the precision limit (est. 1%) of the instrument used for the range of absorbances measured. This result also points out a strength of the GSAM that can be understood by a closer examination of Table II. Since the $\underline{\Delta q}$ values are volume corrected, a group of four values in a column corresponding to the addition of equal amounts of any one standard should, ideally, be equal. They are not equal because measurement and addition errors, in some cases, vary widely. Using as true values the averages of the four sets of values corresponding to the changes in the primary spectral peak for each of the four analytes, statistical standard error estimates of 4.3%, 2.6%, 7.1% and 3.5% are calculated. These standard error estimates are much greater than the standard error estimates in the final concentration values (bottom line of Table VI) which simply demonstrates the

statistical equilibration obtained by multiple measurement in the presence of random error.

The 1.3% result for the IDC is a significant improvement over the 3.3% average absolute error obtained using the same raw data but using the TDC. The most obvious explanation for the poorer result of the TDC is the error amplification suffered as a consequence of the higher condition number of ΔN with the TDC. A rationalization, untested by these experiments, is that the TDC uses q_o to calculate each row of ΔQ whereas the IDC uses each measurement to calculate no more than two rows of ΔQ. Since q_o in the present case contains values nearest the sensitivity limit of the instrument (lowest concentrations), they could contain the largest errors and have a compounded effect on the final results with the TDC.

The overall accuracy of the PGSAM lies intermediate between the TDC and the IDC. Its result is better than the TDC, most probably because of its lower error amplification factor [cond $(\Delta N) = 1.0$]. It is poorer than the IDC, most probably because of experimental considerations explained earlier.

The errors obtained by the IDC using the second group of wavelengths are surprisingly low considering the K obtained and its condition number (Table V). The same is true for other, even less selective, wavelength combinations that allowed concentrations to be calculated at the cost of analysis accuracy.

Finally, as a direct result of using the Househoulder method, a more detailed error analysis (see Appendix) was obtained and is given in Table VII. The presentation of these results (see estimate 45, Appendix) allows an understanding of how each source of error, standard addition error (ΔN) and measurement error (Δq), influences the determination of each row of K and hence the final concentrations. In each case, the generalized condition of ΔN dominates the coefficient of the err (ΔN) term to give that term a greater influence than the influence of the err (Δq) term. This is especially true of the TDC method. According to 45 (Appendix), Table VII indicates that the PGSAM has the predicted advantage over the normal GSAM even using the IDC. However, for reasons given earlier, use of the PGSAM may indeed

lead to higher values for err (Δq) and perhaps even err (ΔN) as was most certainly found to be true here.

CONCLUSION

In this paper the theoretical basis for the constraints on multianalyte analysis in the presence of sample related interferences has been investigated. The detailed error estimation afforded by the Househoulder method and exploitation of the properties of matrix and vector norms have lead to improvements to the GSAM as published in an earlier paper (2). These include:

1) A new definition of the problem to be solved (the IDC-GSAM) and a scaling method (equation 27) together yielding a vastly reduced error propagation for the determination of $\underline{K}$.

2) A new experimental design (the PGSAM) with desirable error propagation properties.

3) A single quantity, the cond (K), that can be used to, quantitatively, compare two analytical methods designed to perform the same multicomponent analysis.

Finally, a more quantitative understanding of the limitations faced by the analytical chemist has been achieved. Armed with a collection of "fully selective" sensors, the analyst can use the simple standard addition method to perform an analysis for several analytes on a complex sample with absolutely no amplification of the measurement uncertainty as it is propagated through the mathematical methods to the initial analyte concentrations. Using the appropriate variation of the Generalized Standard Addition Method the analyst can now perform the same analysis with "non-selective sensors" and also minimize the effect of error amplification in the determination of the linear response constants, $\underline{K}$, and the initial analyte amounts, $\underline{n}_o$, or concentrations, $\underline{c}_o$. Additionally, with an approximation (from analysis of a previous sample or standard) of the selectivity of the analytical system as expressed by $\underline{K}$, the analyst can determine, in advance, the cost of non-selectivity in units of error amplification limits. In some cases the cost

might be high enough to force the analyst to conclude that an analysis with a desired accuracy may be futile.

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APPENDIX

Improving Numerical Stability

Mathematically, equation 10 represents a system of n linear equations with r right-hand sides $\Delta q_1, \ldots, \Delta q_r$ (being the columns of $\underline{\Delta Q}$) corresponding to the r unknown colums $k_1, \ldots, k_r$ of $\underline{K}$. As the number of additions normally exceeds the number of analytes and sensors, this system, being overdetermined, will generally have no exact solutions since the right-hand sides, $\Delta q_1, \ldots, \Delta q_r$, involve randomly distributed measurement errors. Therefore, generalized solutions, k_j, yielding an optimal fit to equation 10, in a certain sense to be defined, must be found.

In the following, the column subscript j of k_j and q_j is suppressed fixing an arbitrary index $1 \leq j \leq r$ to give,

$$\underline{\Delta N} \underline{k} = \underline{\Delta q}, \quad \underline{\Delta N} \in \mathbb{R}^{n,r}, \quad \underline{k} \in \mathbb{R}^{r}, \quad \underline{\Delta q} \in \mathbb{R}^{n}. \tag{28}$$

For any vector $\underline{x} \in \mathbb{R}^{n}$, its <u>Euclidian</u> <u>norm</u>, $\|\underline{x}\|_2$, is defined by

$$\|\underline{x}\|_2 \equiv (\sum_{i=1}^{n} x_i^2)^{1/2} = (\underline{x}^T \underline{x})^{1/2}. \tag{29}$$

A vector $\underline{k}$ will be called a <u>generalized</u> (or <u>least</u> <u>squares</u>) solution, in numerical analysis jargon, of equation 28 if it minimizes the <u>defect</u> of equation 28, i.e., if

$$\|\underline{\Delta N} \underline{k} - \underline{\Delta q}\|_2 = \min_{\underline{x} \in \mathbb{R}^{r}} \|\underline{\Delta N} \underline{x} - \underline{\Delta q}\|_2 \tag{30}$$

Minimizing the defect of a linear system with respect to the Euclidian norm is well known as <u>linear</u> <u>regression</u> and leads to the so-called <u>normal</u> <u>equations</u>,

$$(\underline{\Delta N}^T \underline{\Delta N}) \underline{k} = \underline{\Delta N}^T \underline{\Delta q}, \tag{31}$$

which are   derived by partially differentiating the function

$$\underline{f(x)} = \|\underline{\Delta N} \underline{x} - \underline{\Delta q}\|_2^2 =$$
$$= \underline{x}^T \underline{\Delta N}^T \underline{\Delta N} \underline{x} - 2\underline{x}^T \underline{\Delta N}^T \underline{\Delta q} + \underline{\Delta q}^T \underline{\Delta q} \tag{32}$$

and by setting the partial derivatives to zero. The normal equations have a unique solution $\underline{k}$ if and only if $\underline{\Delta N}$ has full rank r in which case $\underline{k}$ is formally given by

$$\underline{k} = (\underline{\Delta N}^T \underline{\Delta N})^{-1} \underline{\Delta N}^T \underline{\Delta q}. \tag{33}$$

The matrix $(\underline{\Delta N}^T \underline{\Delta N})^{-1} \underline{\Delta N}^T$ is called the <u>generalized</u> (or <u>Moore-Penrose</u>) <u>inverse</u> of $\underline{\Delta N}$.

The reader should keep in mind that the definition of a generalized solution, $\underline{k}$, is based on the special choice of the Euclidian norm which is reasonable in the case of   <u>normally</u> <u>distributed</u>, random perturbations of the right-hand side entries $\underline{\Delta q_i}$ (6). In the case of   non-normally distributed errors, the L_1-norm

$$\|\underline{x}\|_1 \equiv \sum_{i=1}^{n} |x_i| \tag{34}$$

is an appropriate function to be minimized (7), i.e.,

$$\|\underline{\Delta N} \underline{k} - \underline{\Delta q}\|_1 = \min_{\underline{x} \in \mathbb{R}^{r}} \|\underline{\Delta N} \underline{x} - \underline{\Delta q}\|_1. \tag{35}$$

Equation 28 might also be poorly conditioned meaning heuristically that a small relative error of the right-hand side, $\underline{\Delta q}$, produces a large relative error of the solution vector $\underline{k}$. In that case there may appear large negative components of $\underline{k}$, which can be prevented by minimizing equation 32 under the regularizing conditions $k_{ij} \geq 0$ (non-negative least squares (ref. 8, Chap. 23). Also a combination of the L_1-norm and the non-negativity conditions might be reasonable.

In the following, consideration is restricted to the simpler problem (equation 30) which can be solved by a very effective numerical algorithm allowing a transparent and useful error analysis. Therefore, the subscript of the norm is suppressed writing $\|\underline{x}\|$ instead of $\|\underline{x}\|_2$.

At first sight, the most obvious way to compute the generalized solution of equation 30 is to solve the normal equation 31. In fact, if $\underline{\Delta N}$ has full rank, then $\underline{\Delta N}^T \underline{\Delta N}$ is positive definite, and almost any algorithm appropriate for positive definite linear systems (e.g., Cholesky's algorithm) may be applied. From the point of view of numerical stability, however, it is well known (4,8) that Househoulder's orthogonalization is highly preferable in most cases. In addition, Househoulder's procedure provides, as a by-product, some useful information for an a posteriori error estimate to be discussed in the next section. A short outline of the algorithm follows:

A square matrix $\underline{P} \varepsilon \mathbb{R}^{r,r}$ is called orthogonal, if its columns span an orthonormal basis of $\mathbb{R}^r$ (i.e., $\underline{P}^T \underline{P} = \underline{I}$). The product of orthogonal matrices is orthogonal. Multiplication of a vector $\underline{x} \varepsilon \mathbb{R}^r$ by an orthogonal matrix $\underline{P}$ does not change its Euclidian length. Therefore, solving the minimization problem (equation 30) is equivalent to solving

$$\| \underline{P \Delta N k} - \underline{P \Delta q} \| = \min_{\underline{x} \varepsilon \mathbb{R}^r} \| \underline{P \Delta N x} - \underline{P \Delta q} \|$$

(36)

for any orthogonal matrix $\underline{P}$. Now, a matrix $\underline{P}$ of the form

$$\underline{P} = \underline{I} - 2 \underline{w}\underline{w}^T, \quad \underline{w}^T\underline{w} = 1, \quad \underline{w}\in\mathbb{R}^r, \tag{37}$$

is easily shown to be orthogonal and symmetric. To a given vector $\underline{x}\in\mathbb{R}^r$, $\underline{w}$ can be chosen in a way that

$$\underline{P}\underline{x} = \lambda\underline{e}_1, \lambda\in\mathbb{R}, \quad \underline{e}_1 = (1,0,\ldots,0)^T\in\mathbb{R}^r. \tag{38}$$

Taking the first column of $\underline{\Delta N}$ for $\underline{x}$ in the first step and writing $\underline{P}_1$ for $\underline{P}$ the product $\underline{P}_1\underline{\Delta N}$ has the form

$$\underline{P}_1\underline{\Delta N} = \begin{pmatrix} \lambda & | & * & \cdots & * \\ \hline o & | & * & \cdots & * \\ \vdots & | & & & \vdots \\ \vdots & | & & S & \vdots \\ \vdots & | & & & \vdots \\ o & | & * & \cdots & * \end{pmatrix} \equiv \underline{\Delta N}^{(1)} \tag{39}$$

the stars denoting arbitrary entries. Applying the same procedure as indicated above (leaving the first column unaffected) to the submatrix, $\underline{S}$, produces, after $r-1$ multiplications by orthogonal matrices $\underline{P}_1,\ldots,\underline{P}_{r-1}$, a matrix of the form

$$\underline{P}_{r-1} \cdots \underline{P}_1\underline{\Delta N} = \begin{pmatrix} \underline{W} \\ \hline \underline{0} \end{pmatrix} \begin{matrix} \}r \\ \}n-r \end{matrix} \tag{40}$$

where $\underline{W}$ is upper triangular. Now equation 36 can be written as

$$\left\| \begin{pmatrix} \underline{W}\underline{k} \\ \hline \underline{0} \end{pmatrix} - \underline{P}\underline{\Delta q} \right\| = \min_{\underline{x}\in\mathbb{R}^r} \left\| \begin{pmatrix} \underline{W}\underline{x} \\ \hline \underline{0} \end{pmatrix} - \underline{P}\underline{\Delta q} \right\| \tag{41}$$

Partitioning the vector $\underline{P}\underline{\Delta q}$ analogously to $\underline{P}\underline{\Delta N}$ one obtains for equation 41

$$\left\| \begin{pmatrix} \underline{W}\underline{k} - \underline{h}_1 \\ \hline -\underline{h}_2 \end{pmatrix} \right\| = \min_{\underline{x}\in\mathbb{R}^r} \left\| \begin{pmatrix} \underline{W}\underline{x} - \underline{h}_1 \\ \hline -\underline{h}_1 \end{pmatrix} \right\| , \quad \begin{pmatrix} \underline{h}_1 \\ \hline \underline{h}_2 \end{pmatrix} = \underline{P}\underline{\Delta q} \tag{42}$$

the solution of which is

$$\underline{W}\underline{k} - \underline{h}_1 = \underline{0} \Longleftrightarrow \underline{W}\underline{k} = \underline{h}_1 \tag{43}$$

As $\underline{W}$ is triangular, $\underline{k}$ can be calculated explicitly from equation 43 provided $\underline{\Delta N}$ has full rank (in which case $\underline{W}$ is nonsingular). The minimal norm of the defect according to equation 42 is

$$\| \Delta N \, \underline{k} - \underline{\Delta q} \| = \| \underline{h}_2 \|.$$
<div align="right">44)</div>

Since equation 28 and respectively equation 30 must be solved for r right-hand

sides $\underline{\Delta q}_1, \ldots, \underline{\Delta q}_r$, the orthogonal transformations $\underline{P \Delta q}_1, \ldots, \underline{P \Delta q}_r$ should of course be

performed simultaneously with the transformation of ΔN.

Error Estimation

An informative error bound estimate is given by Reference 5, p. 177. It

considers matrix errors and is deduced by Taylor expansion neglecting higher order

terms:

$$\mathrm{err}(\underline{k}) \leq [\mathrm{cond}(\underline{W}) + \mathrm{cond}(\underline{W})^2 \, \frac{\| \underline{h}_2 \|}{\| \underline{\Delta N} \| \, \| \underline{k} \|}] \, \mathrm{err}(\underline{\Delta N}) +$$

$$\mathrm{cond}(\underline{W}) \, \frac{\| \underline{\Delta q} \|}{\| \underline{\Delta N} \| \, \| \underline{k} \|} \, \mathrm{err}(\underline{\Delta q}),$$
<div align="right">45)</div>

where the relative error of a quantity, $\underline{a}$, $\mathrm{err}(\underline{a}) = \dfrac{\| \underline{\bar{a}} - \underline{a} \|}{\| \underline{a} \|}$,

the bar indicating the perturbed values. $\underline{W}$ and h_2 are the terms appearing in the

Househoulder algorithm (see equations 43, 44). Since multiplication by an ortho-

gonal matrix leaves the norm of a vector invariant, the norm of $\underline{\Delta N}$ is easily

calculated in terms of $\underline{W}$:

$$\| \underline{\Delta N} \| = \max_{\| \underline{x} \| = 1} \| \underline{\Delta N x} \| = \max_{\| \underline{x} \| = 1} \| \underline{P \Delta N x} \| = \max_{\| \underline{x} \| = 1} \| \underline{W x} \| = \| \underline{W} \|$$
<div align="right">46)</div>

As $\underline{W}$ is a small triangular matrix the computation of its condition and its norm by

determining its singular values is easier. Very popular (but not always realistic)

estimates of $\| \underline{W} \|$ and cond $(\underline{W})$ are given by the following formulas:

$$\| \underline{W} \| \geq \max_{i,j = 1, \ldots, r} |w_{ij}| \, ; \qquad \mathrm{cond}(\underline{W}) \geq \frac{\max\limits_{i,j} |w_{ij}|}{\min\limits_{i} |w_{ii}|}$$
<div align="right">47)</div>

Thus using the Househoulder algorithm, the terms appearing on the right hand side

of 45 are obtained as an easily calculable byproduct allowing the determin-

ation of an upper bound for the error entering the columns $\underline{k}_1, \ldots, \underline{k}_r$ of the $\underline{K}$

matrix.

TABLE I

Experimental Design ($\underline{\Delta N}$) and
Responses ($\underline{\Delta Q}$) for the TDC-GSAM

Ni	Cu	Co	Cr_2O_7	$\Delta q(\lambda_1)$	$\Delta q(\lambda_2)$	$\Delta q(\lambda_3)$	$\Delta q(\lambda_4)$	$\Delta q(\lambda_5)$
1.00	0.00	0.00	0.00	0.0422	0.491	−0.010	0.174	0.058
2.00	0.00	0.00	0.00	0.0822	0.979	−0.012	0.345	0.093
3.00	0.00	0.00	0.00	0.0151	1.48	0.004	0.532	0.198
4.00	0.00	0.00	0.00	0.209	1.99	0.018	0.723	0.266
4.00	2.00	0.00	0.00	0.265	1.98	0.005	1.11	1.81
4.00	4.00	0.00	0.00	0.326	2.00	0.002	1.49	3.28
4.00	6.00	0.00	0.00	0.413	2.00	0.017	1.89	4.88
4.00	8.00	0.00	0.00	0.507	2.04	0.044	2.31	6.44
4.00	8.00	4.00	0.00	0.565	2.16	1.99	2.41	6.52
4.00	8.00	8.00	0.00	0.502	2.17	3.85	2.45	6.39
4.00	8.00	12.00	0.00	0.606	2.32	5.77	2.59	6.61
4.00	8.00	16.00	0.00	0.733	2.54	7.80	2.75	6.70
4.00	8.00	16.00	8.00	6.71	4.22	7.87	2.71	6.57
4.00	8.00	16.00	16.00	12.6	5.85	7.90	2.61	6.18
4.00	8.00	16.00	24.00	18.9	7.70	8.06	2.65	6.38
4.00	8.00	16.00	32.00	25.4	9.99	8.45	2.92	6.58

TABLE II

Experimental Design (ΔN) and
Responses (ΔQ) for the IDC-GSAM

Ni	Cu	Co	Cr_2O_7	$\Delta q(\lambda_1)$	$\Delta q(\lambda_2)$	$\Delta q(\lambda_3)$	$\Delta q(\lambda_4)$	$\Delta q(\lambda_5)$
1.00	0.00	0.00	0.00	0.042	0.491	-0.010	0.174	0.059
1.00	0.00	0.00	0.00	0.040	0.488	-0.001	0.172	0.035
1.00	0.00	0.00	0.00	0.069	0.497	0.016	0.186	0.105
1.00	0.00	0.00	0.00	0.058	0.516	0.013	0.191	0.068
0.00	2.00	0.00	0.00	0.056	-0.007	-0.012	0.382	1.54
0.00	2.00	0.00	0.00	0.060	0.018	-0.003	0.388	1.47
0.00	2.00	0.00	0.00	0.087	-0.008	0.015	0.399	1.60
0.00	2.00	0.00	0.00	0.094	0.048	0.027	0.419	1.56
0.00	0.00	4.00	0.00	0.058	0.115	1.95	0.103	0.079
0.00	0.00	4.00	0.00	-0.063	0.015	1.86	0.034	-0.129
0.00	0.00	4.00	0.00	0.104	0.152	1.92	0.144	0.223
0.00	0.00	4.00	0.00	0.128	0.218	2.03	0.154	0.089
0.00	0.00	0.00	8.00	5.98	1.67	0.075	-0.039	-0.125
0.00	0.00	0.00	8.00	5.93	1.63	0.026	-0.098	-0.389
0.00	0.00	0.00	8.00	6.27	1.85	0.165	0.036	0.192
0.00	0.00	0.00	8.00	6.50	2.30	0.389	0.275	0.202

TABLE III

Experimental Design (ΔN) and
Responses (ΔQ) for the PGSAM (TDC)

Ni	Cu	Co	Cr_2O_7	$\Delta q(\lambda_1)$	$\Delta q(\lambda_2)$	$\Delta q(\lambda_3)$	$\Delta q(\lambda_4)$	$\Delta q(\lambda_5)$
1.00	0.00	0.00	0.00	0.078	0.513	0.026	0.193	0.103
2.00	0.00	0.00	0.00	0.100	1.00	0.010	0.363	0.129
3.00	0.00	0.00	0.00	0.172	1.52	0.029	0.552	0.292
4.00	0.00	0.00	0.00	0.220	2.02	0.025	0.732	0.286
0.00	1.00	0.00	0.00	0.031	-0.006	0.001	0.200	0.799
0.00	2.00	0.00	0.00	0.072	0.013	0.010	0.393	1.52
0.00	3.00	0.00	0.00	0.108	0.021	0.019	0.596	2.31
0.00	4.00	0.00	0.00	0.166	0.039	0.028	0.803	3.09
0.00	0.00	1.00	0.00	0.010	0.023	0.495	0.028	0.035
0.00	0.00	2.00	0.00	0.036	0.050	0.962	0.047	0.019
0.00	0.00	3.00	0.00	0.020	0.080	1.45	0.078	0.058
0.00	0.00	4.00	0.00	0.019	0.104	1.94	0.100	0.066
0.00	0.00	0.00	1.00	0.718	0.197	0.011	-0.002	0.005
0.00	0.00	0.00	2.00	1.51	0.435	0.026	-0.004	-0.030
0.00	0.00	0.00	3.00	2.22	0.642	0.035	-0.003	-0.009
0.00	0.00	0.00	4.00	3.07	0.891	0.048	-0.005	-0.018

TABLE IV

K Calculated by IDC-GSAM Using Wavelengths

λ_1, λ_2, λ_3, λ_5.   Cond (K) = 1.93

	λ_1	λ_2	λ_3	λ_5
Cr	0.76	0.23	0.02	-0.01
Ni	0.05	0.49	0.00	0.06
Co	0.08	0.02	0.48	0.01
Cu	0.04	0.01	0.01	0.77

TABLE V

K Calculated by the IDC-GSAM Using Wavelengths
λ_1, λ_3, λ_4, λ_5.   Cond $\underline{(K)}$ = 5.24

	λ_1	λ_3	λ_4	λ_5
Cr	0.77	0.02	0.01	-0.01
Co	0.01	0.48	0.03	0.02
Ni	0.05	0.01	0.18	0.07
Cu	0.04	0.01	0.20	0.77

TABLE VI

Final Results

	λ_1, λ_2, λ_3, λ_5			λ_1, λ_3, λ_4, λ_5
	TDC–GSAM	IDC–GSAM	PGSAM	IDC–GSAM
Generalized Cond ($\underline{\Delta N}$)	3.42	1.0	1.0	1.0
Eigenvalues of $\underline{K}^T\underline{K}$ 1	0.701	0.723	0.700	0.666
2	0.586	0.585	0.579	0.582
3	0.231	0.235	0.236	0.234
4	0.195	0.194	0.198	0.024
Cond ($\underline{K}$)	1.90	1.93	1.88	5.24
Calculated Initial Units				
Ni (True = 1.0)	1.034	1.018	0.995	1.032
Cu (True = 1.0)	1.015	1.002	0.962	1.001
Co (True = 1.0)	1.032	1.014	0.989	1.014
Cr (True = 0.0)	0.018	0.006	0.015	0.005
Average Absolute % Error *	3.30	1.33	2.30	1.73
Standard Error Estimate **	3.0	1.4	2.5	2.0

* Average Absolute % Error $= 100.0 \times \dfrac{\Sigma|\text{True-Calculated}|}{\Sigma(\text{initial amounts})}$

** Standard Error Estimate $= \left[\dfrac{\Sigma(\text{True-Calculated})^2}{\Sigma(\text{initial amounts})^2}\right]^{1/2} \times 100.0$

TABLE VII

Error Analysis According to Equation 45

Method	Wavelengths	Coefficients of err (ΔN)*	Coefficients of err (Δq)**
TDC-GSAM	$\lambda_1, \lambda_2, \lambda_3, \lambda_5$	3.42, 3.42, 3.42, 3.42	0.54, 0.90, 0.70, 0.78
IDC-GSAM	$\lambda_1, \lambda_2, \lambda_3, \lambda_5$	1.02, 1.04, 1.03, 1.04	0.51, 0.51, 0.50, 0.51
PGSAM	$\lambda_1, \lambda_2, \lambda_3, \lambda_5$	1.0, 1.0, 1.0, 1.0	0.18, 0.18, 0.18, 0.18
IDC-GSAM	$\lambda_1, \lambda_3, \lambda_4, \lambda_5$	1.02, 1.03, 1.04, 1.04	0.50, 0.50, 0.50, 0.50

* $\left[\text{cond}(W) + \text{cond}(W)^2 \dfrac{\|h_2\|}{\|\Delta N\| \ \|k\|}\right]$

** $\left[\text{cond}(W) \dfrac{\|\Delta q\|}{\|\Delta N\| \ \|k\|}\right]$

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