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TENSORIAL RESOLUTION: A DIRECT TRILINEAR DECOMPOSITION

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SUMMARY

Modern instrumentation in chemistry routinely generates two-dimensional (second-order) arrays of data. Considering that most analyses need to compare several samples, the analyst ends up with a three-dimensional (third-order) array which is difficult to visualize or interpret with the conventional statistical tools.

Some of these data arrays follow the so-called *trilinear* model,

$$\mathbb{R}_{ijk} = \sum_{r=1}^{N} X_{ir} Y_{jr} Z_{kr} + \text{Error}_{ijk}$$

These trilinear arrays of data are known to have unique factor analysis decompositions which correspond to the true physical factors that form the data, i.e. given the array $\mathbb{R}$, a unique solution can be found in many cases for each order X, Y and Z. This is in contrast to the well-known second-order bilinear data factor analysis, where the abstract solutions obtained are not unique and at best cannot be easily compared with the underlying physical factors owing to a rotational ambiguity.

Trilinear decompositions have had the disadvantage, however, that a non-linear optimization with many parameters is necessary to reach a least-squares solution. This paper will introduce a method for reducing the problem to a rectangular generalized eigenvalue–eigenvector equation where the eigenvectors are the contravariant form (pseudo-inverse) of the actual factors. It is shown that the method works well when the factors are linearly independent in at least two orders (e.g. X_{ir} and Y_{jr} are full rank matrices).

Finally, it is shown how trilinear decompositions relate to multicomponent calibration, curve resolution and chemical analysis.

KEY WORDS Tensor Superdiagonalization GRAM Three-way Multilinear Trilinear PARAFAC

INTRODUCTION

Instruments that generate two-dimensional arrays of data are now commonplace in the analytical laboratory. Emission–excitation fluorescence, chromatography–spectroscopy combinations, MS–MS and 2D-NMR, are a few of the many so-called 'hypyhenated methods' that generate such data.[1,2] These instruments have become very important for the analyst mainly because of their higher selectivity and resolution of signals, allowing for analysis of mixtures. The main similarity between all these instruments is that each analyzed sample

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produces a two-dimensional array of data (second-order tensor). The amount of information produced by such instruments is overwhelming; ironically, for quantitative analysis, only a small portion of the data is actually used.

The situation is even more complicated when several samples have to be compared, because the accumulated data will form a three-dimensional array (third-order tensor). Why bother generating such data if it is obvious that when using the standard statistical tools (e.g. univariate linear regression) the chemist is seriously underprepared to analyze it? Even multivariate statistical techniques are hard pressed to analyze higher-order data, and in the best case they cannot always extract all the information available.

This paper will present a brief introduction to the available techniques for analysis of third-order tensor data and will focus on the interesting trilinear case for which unique decompositions into their physical conforming factors are possible on many occasions. A tensorial representation of the problem is presented, in consistency with the two previous papers of this series, that effectively integrate the analysis of first-, second- and third-order data arrays.[3,4] Finally, the primary contribution of this paper will be a closed-form solution for the trilinear decomposition that avoids the tedious non-linear optimizations previously used to solve the problem. This solution is restricted to the case where the intrinsic factors are linearly independent in at least two orders (e.g. X and Y), without identical intrinsic factors in the corresponding third order (Z).

Nomenclature

Boldface capital letters represent second-order tensors (matrices), e.g. $\mathbf{A}$. For a given matrix $\mathbf{A}$, the matrices $\mathbf{A}^{\mathrm{T}}$ and $\mathbf{A}^{+}$ stand for its transpose and pseudo-inverse respectively. Open-face capital letters represent third- and higher-order tensors, e.g. $\mathbb{R}$. In general, an alternative representation for any tensor is given by its tensor components, italicized, e.g. x_i, X_{ij}, M_{ijk}, $M_{ij\ldots n}$ for a first-, second-, third- and nth-order tensor respectively, either subscript or superscript. A first-order tensor is equivalent to a vector. Boldface lower-case letters represent first-order tensors and column vectors, $\mathbf{v}$, and their transpose for a row vector, $\mathbf{v}^{\mathrm{T}}$. A matrix, e.g. $\mathbf{V}$, and the set of its column vectors $\{\mathbf{v}_i\}$ are conveniently designated with the same letter, in upper-case and indexed lower-case respectively. The symbol $\otimes$ represents the tensor or outer product, e.g. $\mathbf{x} \otimes \mathbf{y} = \mathbf{x}\mathbf{y}^{\mathrm{T}}$. The conventional distinction between columns and rows will be extended with *tubes* to the third order. The term 'order' is borrowed from the tensorial literature (*order* of a tensor) as a synonym to 'ways' or 'modes',[5] and it is not to be confused with the order of a matrix as defined in numerical analysis.

SECOND- AND THIRD-ORDER FACTOR ANALYSIS

A matrix of data $\mathbf{R}$ simultaneously contains information from two vector spaces: the column and the row spaces. For example, if the data arise from emission–excitation fluorescence, each row is an emission spectrum and each column is an excitation scan. Theoretically, these row and column vectors are linear combinations of a few basic vectors corresponding to the actual physical factors that constitute the data. For multicomponent samples with overlapping spectra it would be desirable to decompose such a matrix into these intrinsic factors, i.e. the emission spectra of the individual analytes ($\mathbf{x}_r$) and the corresponding excitation spectra ($\mathbf{y}_r$). Many researchers have studied this problem in detail, and the broad classes of methods used to solve it are called *factor analysis*.[6]

If each column of $\mathbf{R}$ is a linear combination of N column-factors, each corresponding to a

different analyte, $\sum_{r=1}^{N} a_{ri}\mathbf{x}_r$, and each row is also a linear combination of corresponding row-factors, $\sum_{r=1}^{N} b_{rj}\mathbf{y}_r$, the combined equation for the data can be expressed as

$$\mathbf{R} \approx \mathbf{X}\mathbf{Y}^{\mathrm{T}} = \sum_{r=1}^{N} \mathbf{x}_r \otimes \mathbf{y}_r + \mathbf{E} \tag{1}$$

where $\otimes$ represents the tensor product (outer product), $\mathbf{x}_r \otimes \mathbf{y}_r$ is a dyad (equivalent to the matrix product $\mathbf{x}_r\mathbf{y}_r^{\mathrm{T}}$), $\mathbf{R}(I \times J)$ is the data matrix (second-order tensor or *dyadic*), $\mathbf{E}$ is the error of the model and $\mathbf{X}(I \times N)$ and $\mathbf{Y}(J \times N)$ are the matrices with columns $\{\mathbf{x}_r\}$ and $\{\mathbf{y}_r\}$, corresponding to the intrinsic physical factors in the column and row spaces, respectively. In the example above, the $\{\mathbf{x}_r\}$ are the fluorescence emission spectra and the $\{\mathbf{y}_r\}$ are the excitation spectra.

Lawton and Sylvestre were among the first to recognize that the possible vectors $\{\mathbf{x}_r\}$ and $\{\mathbf{y}_r\}$ which satisfy equation (1) are restricted to N-dimensional subspaces (note that N is the number of factors in the summation of equation (1), which in turn is the number of analytes with significant response), regardless of their original dimensionality. Unfortunately, there are an infinite number of possible decompositions of $\mathbf{R}$, and no unambiguous solution of the problem is possible without further information. For example, it is known that both fluorescence emission and excitation spectra are positive, therefore the problem can be presented as a linear programming equation,

$$\mathbf{R} \approx \mathbf{X}\mathbf{Y}^{\mathrm{T}}, \qquad X_{ir} \geqslant 0, \quad Y_{jr} \geqslant 0 \tag{2}$$

which may still have infinite solutions for $\mathbf{X}$ and $\mathbf{Y}$, though they are restricted to smaller subspaces, from which the analyst can sometimes make reasonable factor extractions (e.g. two-component curve resolution). Many other solutions for equation (1) have been published for specific cases such as chromatographic data, spectral monitoring of reaction kinetics, time relaxation phenomena, etc.[6]

Nevertheless, the factor analysis problem can be solved uniquely, without the use of additional information, by going one step above with *third*-order tensors. This was discovered in the early 1970s by researchers in psychology, who analyzed data from multi-order questionnaire data.[7,8] A necessary condition for unique decomposition is that the entries in the data matrix may be modeled with a *trilinear* model,

$$\mathbb{R} = \sum_{r=1}^{N} \mathbf{x}_r \otimes \mathbf{y}_r \otimes \mathbf{z}_r + \mathbb{E} \tag{3}$$

which is a natural extension of the bilinear model (equation (1)). Workers in multi-order data analysis, especially in psychology, have come to call this model the PARAFAC–CANDECOMP model on the basis of the algorithms used for the decomposition.

The methods for estimating $\{\mathbf{x}_r\}$, $\{\mathbf{y}_r\}$ and $\{\mathbf{z}_r\}$ are based on alternating least-squares (ALS), a non-linear optimization algorithm. ALS estimates $\{\mathbf{z}_r\}$ assuming $\{\mathbf{x}_r\}$ and $\{\mathbf{y}_r\}$, and then does the same thing for $\{\mathbf{x}_r\}$ and $\{\mathbf{z}_r\}$,[7] repeating the cycle over and over until convergence.

It has been shown earlier in this series[4] that for the particular case where there are only two 'slices' in one of the orders (e.g. Z) it is possible to reduce the trilinear decomposition to a generalized eigenvalue–eigenvector problem, eliminating the need for any optimization, under the condition that the vectors $\{\mathbf{x}_r\}$ and $\{\mathbf{y}_r\}$ are linearly independent and there are not two identical vectors $\{\mathbf{z}_r\}$. Naturally, if there are only two dimensions in the third order, the $\{\mathbf{z}_r\}$ vectors will all be linearly dependent when the number of factors is greater than two.

This paper will generalize the two-slice solution to the general case with three or more slices.

A non-iterative direct solution for $\{\mathbf{x}_r\}$, $\{\mathbf{y}_r\}$ and $\{\mathbf{z}_r\}$ will be introduced that reduces the problem to a rectangular generalized eigenvector–eigenvalue equation.

Other important third-order models will now be presented since they are useful in the development of the method.

Third-order factor analysis models

It is possible to model any third-order data array using equation (3) if enough terms are added, even if the intrinsic physical factors which form the data do not follow the trilinear model. In fact the multilinear model is used to define the rank of any Mth-order array: the rank of an Mth-order array is the minimum number of M-vectors (M-order vector outer products) into which that array can be decomposed.[9] This definition of rank nicely reduces to rank of a matrix for the special case $M = 2$.

A trilinear decomposition often yields non-orthogonal (oblique) vectors. However, it is sometimes useful to decompose a matrix into orthogonal vectors instead. The most general model for third-order data is the so-called *Tucker-3* model,[10] which is another generalization of the blinear decomposition:

$$\mathbb{R} = \sum_{p=1}^{Np} \sum_{q=1}^{Nq} \sum_{r=1}^{Nr} \mathbb{G}_{pqr} \mathbf{u}_p \otimes \mathbf{v}_q \otimes \mathbf{w}_r + \mathbb{E} \tag{4}$$

If the vectors $\{\mathbf{u}_r\}$, $\{\mathbf{v}_r\}$ and $\{\mathbf{w}_r\}$ are orthonormal, and chosen with the *core* array $\mathbb{G}$ so as to minimize the error term $\mathbb{E}$ in a least-squares sense, then this is one of the possible generalizations of the singular value decomposition to third order. A non-linear optimization is necessary to find the subspaces spanned by $\{\mathbf{u}_p\}$, $\{\mathbf{v}_q\}$ and $\{\mathbf{w}_r\}$ that will yield minimum residual. However, the choice of the vectors for the expansion is arbitrary, making this decomposition non-unique.

Comparing equation (4) with equation (3) it is obvious that the trilinear model is a special case of the Tucker-3 model, with $\mathbb{G}$ chosen superdiagonal ($\mathbb{G}_{pqr} \neq 0$ only for $p = q = r$). Other special cases are the Tucker-1 and Tucker-2 models.[11]

Tucker-1 finds a set of vectors $\{\mathbf{u}_p\}$ that span just *one* of the vectorial spaces which conform the third-order tensor (either the row, column or 'tube' space). For example, for the row space,

$$\mathbb{R} = \sum_{p=1}^{Np} \mathbf{S}_p \otimes \mathbf{u}_p + \mathbb{E} \tag{5}$$

where $\{\mathbf{S}_p\}$ is a set of matrices of size (J, K). Unfolding $\mathbb{R}$ into an $I \times JK$ matrix followed by a principal component decomposition is sufficient to generate $\{\mathbf{u}_p\}$ vectors as the loadings that will span the column space in the least-squares sense. In a similar way vectors $\{\mathbf{v}_q\}$ and $\{\mathbf{w}_r\}$ can be estimated for the other orders (row and tube spaces). The three sets of vectors can be combined into a Tucker-3 model (equation (4)), but it will not represent a least-squares decomposition.

Tucker-2 finds two sets of vectors, $\{\mathbf{u}_p\}$ and $\{\mathbf{v}_q\}$, that span *two* of the vectorial spaces which conform the third-order tensor (leaving out either the tube, row or column space). For example, decomposing the row and column space yields

$$\mathbb{R} = \sum_{p=1}^{Np} \sum_{q=1}^{Nq} \mathbf{s}_{pq} \otimes \mathbf{u}_p \otimes \mathbf{v}_q + \mathbb{E} \tag{6}$$

where $\{\mathbf{s}_{pq}\}$ is a set of vectors of size (K). The alternating least-squares algorithms are usually

used to generate orthogonal $\{\mathbf{u}_p\}$ and $\{\mathbf{v}_q\}$ such that the sum of squares of the elements of $\mathbb{E}$ is minimal.

In summary, a third-order tensor $\mathbb{R}$ simultaneously contains information from three vector spaces: the column, row and tube spaces. Models for these data can be built that approximate either one, two or three of the vectors spaces, namely the Tucker-1, Tucker-2 and Tucker-3 models. If these vectors are chosen such that the projection leaves least-squares residuals, the methods are respectively an unfolded principal components, TUCKALS-2 and TUCKALS-3.[12] The special Tucker-3 case with a superdiagonal core array is called the trilinear or PARAFAC–CANDECOMP model in the psychometrics literature. For further discussion of these models see e.g. Reference 11.

THIRD-ORDER ARRAYS IN CHEMISTRY

The interest in multi-order arrays is increasing, as evidenced by the recent MULTIWAY '88 conference in Rome, Italy. Chemistry, a latecomer in the third-order world, is perhaps much more suitable for third-order factor analysis than many other branches of science owing to the abundance of instruments that can automatically collect precise third-order data arrays in a short period of time.

The number of possible combinations of instruments in chemistry provides limitless possibilities for second-order instruments, many of which are already available in many laboratories. Examples of such instruments for GC/MS, LC/UV, emission–excitation fluorescence, MS–MS, etc. Hirschfeld provided a very complete table of all the feasible combinations[1] and it continues to expand with time.[2] It is estimated from Hirschfeld's table that about 60% of the techniques are bilinear, under certain conditions, and considering that analyzing several samples will generate a trilinear array, trilinear decomposition methods are applicable to many instruments in chemistry. This factor, combined with the uniqueness properties of these data, make trilinear models very attractive.

For example, consider the group of instruments that combine chromatography with spectroscopy. It is a fact that many bilinear methods can be classified in this group. In particular, if a data matrix $\mathbb{R}$ was generated from a liquid chromatograph with a diode array UV detector (LC/UV), applied to the analysis of several multicomponent samples, its trilinear model is

$$\mathbb{R} = \sum_{r=1}^{N} c_r \mathbf{x}_r \otimes \mathbf{y}_r \otimes \mathbf{z}_r + \mathbb{E} \tag{7}$$

where $\{\mathbf{x}_r\}$ is the set of chromatographic profiles for each pure analyte, $\{\mathbf{y}_r\}$ is the set of pure analyte UV spectra, $\{\mathbf{z}_r\}$ is the set of concentration profiles among samples and $\{c_r\}$ is the set of normalization constants (in equation (3), $c_r = 1$). (It is assumed that retention times do not change between runs for a given analyte.)

Florescence spectroscopy is another rich source of bilinear, trilinear and even quadrilinear data.[13] Many simultaneous combinations are possible with fluorescence, where emission, excitation and time relaxation can be monitored for different samples. The trilinearity of some fluorescence experiments, combined with the high sensitivity of the technique, make its application very desirable. The multi-order advantage of fluorescence for obtaining unique decompositions was recognized by Appellof and Davidson, who provided the first application of trilinear decompositions to chemistry using both simulated and real LC/emission/excitation fluorescence data.[14] They essentially divided the decomposition into two steps: a projection to latent structures using a Tucker-1-like algorithm in every order to reduce the number of parameters to optimize, and then an alternating least-squares optimization of the factor

matrices until convergence. Recently, Russell and Gouterman provided an application to time decay/emission/excitation fluorescence using the same algorithm.[15-17]

Other applications have been reported in chemistry. De Ligny *et al.* used iterative ALS trilinear decompositions to estimate the relationship between chromatographic column parameters and retention time.[18] Wold *et al.* have used a Tucker-1 model to build bilinear models of *M*th-order arrays and then used these reduced representations for calibration, score plots and pattern recognition in applying the method to a variety of chemical data.[19]

A significant amount of work has been done in chemistry on comparing two bilinear arrays that have factors in common. These two arrays can be interpreted as a third-order array with only two slices in the third order. Ho, Christian and Davidson presented what they called 'rank annihilation', an iterative scheme to extract one known factor (equation (7)) out of an array of several facors by monitoring the rank of the matrix until it reached a minimum. Lorber, and independently Kim, showed that it was possible to solve the problem in a non-iterative fashion:[20,21]

$$\mathbf{R}_1 = \mathbf{R} - \frac{\mathbf{x}\mathbf{y}^{\mathrm{T}}}{\mathbf{x}^{\mathrm{T}}\mathbf{R}^{\dagger}\mathbf{y}} \tag{8}$$

where if rank($\mathbf{R}$) = N then rank($\mathbf{R}_1$) = $N - 1$. In fact this is the classical problem of reducing the rank of a matrix by one unit using Lagrange's theorem,[22]

$$\mathbf{R}_1 = \mathbf{R} - \frac{\mathbf{R}\mathbf{v}\mathbf{u}^{\mathrm{T}}\mathbf{R}}{\mathbf{u}^{\mathrm{T}}\mathbf{R}\mathbf{v}} \tag{9}$$

and finding $\mathbf{u}$ and $\mathbf{v}$ such that $\mathbf{R}\mathbf{v} = \mathbf{x}$ and $\mathbf{u}^{\mathrm{T}}\mathbf{R} = \mathbf{y}^{\mathrm{T}}$.

Sanchez and Kowalski developed a method for trilinear decomposition of the 'two-slice' case, reducing the problem to a rectangular generalized eigenvalue–eigenvector problem.[23] They applied the method to LC/UV data for both single column[24] and parallel column chromatography.[25] The previous paper in this series described this method,[4] and this paper will extend the solution to the general case of more than two slices. A related method was developed by Sands and Young for preprocessing third-order data arrays for trilinear decomposition.[26]

DIRECT TRILINEAR DECOMPOSITION

The simplest third-order tensor is composed of two matrices of the same size, $\mathbf{R}_1$ and $\mathbf{R}_2$. Without loss of generality, assume the $\{\mathbf{z}_r\}$ vectors in equation (3) span the third order. For this particular case it is possible to write the trilinear model as

$$\begin{aligned} \mathbf{R}_1 &= \sum_{r=1}^{N} z_{r1}\mathbf{x}_r \otimes \mathbf{y}_r \\ \mathbf{R}_2 &= \sum_{r=1}^{N} z_{r2}\mathbf{x}_r \otimes \mathbf{y}_r \end{aligned} \tag{10}$$

where $\mathbf{z}_r = (z_{r1}, z_{r2})$. The problem of estimating $\{\mathbf{x}_r\}$ and $\{\mathbf{y}_r\}$ can be solved using the generalized rank annihilation method,[4] reducing equation to a simultaneous rectangular eigenvalue–eigenvector problem: if the $\{\mathbf{y}_r\}$ vectors are linearly independent, for every term in the summation (10) it is possible to find a vector $\mathbf{y}^r$ such that $\mathbf{y}^r \cdot \mathbf{y}_q = \delta_{rq}$ Kronecker delta $[r = q \rightarrow \delta_{rq} = 1]$, $[r \neq q \rightarrow \delta_{rq} = 0]$:

$$\begin{aligned} \mathbf{R}_1\mathbf{y}^r &= z_{r1}\mathbf{x}_r \\ \mathbf{R}_2\mathbf{y}^r &= z_{r2}\mathbf{x}_r \end{aligned} \tag{11}$$

The vector $\mathbf{y}^r$ is the rth contravariant vector for the $\{\mathbf{y}_r\}$ base. If $\mathbf{Y}$ is a matrix with columns $\{\mathbf{y}_r\}$, the matrix $\mathbf{Y}^+$ with rows $\{\mathbf{y}^r\}$ is a generalized inverse of $\mathbf{Y}$, $\mathbf{Y}^+\mathbf{Y} = \mathbf{I}$, where $\mathbf{I}$ is the identity matrix. Extracting $\mathbf{x}_r$ from both equations (11), we obtain the desired eigenvalue problem:

$$\mathbf{R}_1\mathbf{y}^r z_{r2} = \mathbf{R}_2\mathbf{y}^r z_{r1} \tag{12}$$

where the contravariant vectors $\{\mathbf{y}^r\}$ are eigenvectors. Equation (12) can be solved by projecting $\mathbf{R}_1$ and $\mathbf{R}_2$ to square matrices (see Appendix I) and then applying the QZ algorithm for simultaneous diagonalization.[27] Notice that such an unrestricted eigenvalue problem may contain imaginary solutions as conjugate pairs for eigenvalues. In practice this seems to occur for systems with significant deviations from bilinearity.

Notice that any vector $\mathbf{e}$ belonging to the null space of $\mathbf{R}_1$ and $\mathbf{R}_2$ will also be a valid eigenvector in equation (12), with arbitrary eigenvalues. Those vectors belonging to the null space can be easily detected using the property $\mathbf{R}_1\mathbf{e} = \mathbf{R}_2\mathbf{e} = \mathbf{0}$. For real data, some vectors will also correspond to the noise and will yield $\mathbf{R}_1\mathbf{e} = \mathbf{R}_2\mathbf{e} \approx \mathbf{0}$. It is possible to avoid these problems by reducing the original array to a simpler core array using a Tucker model with all the null space discarded and the noise contribution significantly reduced.

The $\{\mathbf{x}_r\}$ vectors can be similarly estimated from the *left* eigenvectors (eigenvectors of the transposed $\mathbf{R}$'s):

$$\mathbf{R}_1^{\mathrm{T}}\mathbf{x}^r z_{r2} = \mathbf{R}_2^{\mathrm{T}}\mathbf{x}^r z_{r1} \tag{13}$$

where the eigenvectors $\{\mathbf{x}^r\}$ are the contravariant form of the vectors $\{\mathbf{x}_r\}$. However, once the eigenvectors $\{\mathbf{y}^r\}$ from (11) are known, equation (13) can be avoided by estimating $\{\mathbf{x}_r\}$ directly from equation (11):

$$\mathbf{x}_r = \frac{\mathbf{R}_1\mathbf{y}^r}{\| \mathbf{R}_1\mathbf{y}^r \|} \tag{14}$$

(Note that the use of equation (14) with $\mathbf{R}_1$ is valid for $\mathbf{x}_r$ only if the corresponding coefficient z_{r1} in equation (10) is not negligible.) It follows that the uniqueness conditions for the solutions are:

(1) $\mathbf{R}_1$ and $\mathbf{R}_2$ must follow the bilinear model (equation (10)) with common factors $\{\mathbf{x}_r\}$ and $\{\mathbf{y}_r\}$.
(2) The vectors $\{\mathbf{x}_r\}$ and $\{\mathbf{y}_r\}$ must be linearly independent. This follows from the fact that in order to estimate the contravariant form $\{\mathbf{y}^r\}$ it is a requirement for $\{\mathbf{y}_r\}$ to be a basis and therefore linearly independent.
(3) No vector $\mathbf{z}_r = (z_{r1}, z_{r2})$ may be the null vector $(0, 0)$, and no other vector $\mathbf{z}_s = (z_{s1}, z_{s2})$ may point in the same direction as $\mathbf{z}_r$, i.e. $\mathbf{z}_r \cdot \mathbf{z}_s < |\mathbf{z}_r\| \mathbf{z}_s|$. If several eigenvectors violate the latter condition they will be degenerate and therefore the solutions will not be unique.

Three or more variables in third order

If there are three or more slices, there are several simultaneous bilinear models:

$$\begin{aligned}
\mathbf{R}_1 &= \sum_{r=1}^{N} z_{r1}\mathbf{x}_r \otimes \mathbf{y}_r \\
\mathbf{R}_2 &= \sum_{r=1}^{N} z_{r2}\mathbf{x}_r \otimes \mathbf{y}_r \\
&\vdots \\
\mathbf{R}_K &= \sum_{r=1}^{N} z_{rK}\mathbf{x}_r \otimes \mathbf{y}_r
\end{aligned} \tag{15}$$

where $\mathbf{z}_r = (z_{r1}, z_{r2}, \ldots, z_{rK})$. The problem can be presented as a simultaneous series of $K(K-1)/2$ eigenvalue–eigenvector problems:

$$\begin{aligned} &\mathbf{R}_1\mathbf{y}^r z_{r2} = \mathbf{R}_2\mathbf{y}^r z_{r1}, \\ &\mathbf{R}_1\mathbf{y}^r z_{r3} = \mathbf{R}_3\mathbf{y}^r z_{r1}, \quad \mathbf{R}_2\mathbf{y}^r z_{r3} = \mathbf{R}_3\mathbf{y}^r z_{r2} \\ &\qquad\vdots \qquad\qquad\qquad\vdots \\ &\mathbf{R}_1\mathbf{y}^r z_{rK} = \mathbf{R}_K\mathbf{y}^r z_{r1}, \quad \mathbf{R}_2\mathbf{y}^r z_{rK} = \mathbf{R}_K\mathbf{y}^r z_{r2}, \quad \ldots, \quad \mathbf{R}_{K-1}\mathbf{y}^r z_{rK} = \mathbf{R}_K\mathbf{y}^r z_{rK-1} \end{aligned} \tag{16}$$

In practice, owing to the presence of noise, there is not a single $\mathbf{y}^r$ that can simultaneously satisfy all these equations. But noise is not the only problem: some slices may not have significant contributions from all of the factors, so different pairs $(\mathbf{R}_p, \mathbf{R}_q)$ may have different solutions.

The problem may be solved by finding matrices $(\mathbf{S}_1, \mathbf{S}_2)$ that are representative of all the slices. Such a pair must contain all the dyads $(\mathbf{x}_r \otimes \mathbf{y}_r)$ and follow the necessary conditions outlined in the previous section in order to apply the generalized rank annihilation method.

A possible approach is to pick any pair of slices $(\mathbf{R}_p, \mathbf{R}_q)$, obtain estimates of $\{\mathbf{x}_r\}$ and $\{\mathbf{y}_r\}$ using GRAM and then use them to yield a least-squares estimate $\{\mathbf{z}_r\}$. However, there is no guarantee that the matrices $(\mathbf{R}_p, \mathbf{R}_q)$ contain all the dyads $(\mathbf{x}_r \otimes \mathbf{y}_r)$ or that the p/q dyadic ratios are different for all the dyads.

Instead of searching for two slices that are representative among the set $\{\mathbf{R}_k\}$, it is possible to find two linear combinations of the slices that follow the conditions necessary for uniqueness (last section). These two matrices may be generated using a two-component Tucker-1 model for $\mathbb{R}$ (equation (5)) for the $\{\mathbf{z}_r\}$ space:

$$\mathbb{R} = \sum_{p=1}^{2} \mathbf{S}_p \otimes \mathbf{w}_p + \mathbb{E}_{\mathbf{w}} \tag{17}$$

Here the $\{\mathbf{S}_p\}$ are (I, J)-size matrices and the orthogonal vectors $\{\mathbf{w}_p\}$ belong to the $\{\mathbf{z}_r\}$ space:

$$\mathbf{S}_p = \sum_{k=1}^{K} w_{pk}\mathbf{R}_k \tag{18}$$

A suitable choice for the two $\{\mathbf{w}_p\}$ vectors are the principal components of the unfolded $\mathbf{R}$ in the $\{\mathbf{z}_r\}$ space. Their corresponding matrices $\mathbf{S}_1$ and $\mathbf{S}_2$ are a sensible choice for the two matrices necessary to perform the decomposition, because they are 'scores' of the first and second principal components respectively. Therefore they are most likely to include contributions from all the dyads $\mathbf{x}_r \otimes \mathbf{y}_r$ (See Appendix II for further discussion on the choice of $\mathbf{S}_1$ and $\mathbf{S}_2$, and Appendix III for an algorithmic implementation of the direct trilinear decomposition.) The $\mathbf{S}_p$ can be expressed directly as a function of $\mathbf{x}_r \otimes \mathbf{y}_r$:

$$\mathbf{S}_p = \sum_{k=1}^{K} w_{pk} \sum_{r=1}^{N} z_{rk}\mathbf{x}_r \otimes \mathbf{y}_r = \sum_{r=1}^{N} (\mathbf{x}_r \otimes \mathbf{y}_r) \sum_{k=1}^{K} z_{rk} w_{pk} \tag{19}$$

Defining $a_{rp} \equiv \sum_{k=1}^{K} z_{rk} w_{pk} = \mathbf{z}_r \cdot \mathbf{w}_p$,

$$\mathbf{S}_p = \sum_{r=1}^{N} a_{rp}(\mathbf{x}_r \otimes \mathbf{y}_r) \tag{20}$$

For $\mathbf{S}_1$ and $\mathbf{S}_2$ we get (compare with equation (10))

$$\begin{aligned} \mathbf{S}_1 &= \sum_{r=1}^{N} a_{r1}\mathbf{x}_r \otimes \mathbf{y}_r \\ \mathbf{S}_2 &= \sum_{r=1}^{N} a_{r2}\mathbf{x}_r \otimes \mathbf{y}_r \end{aligned} \tag{21}$$

which we can solve for $\{\mathbf{x}_r\}$ and $\{\mathbf{y}_r\}$ just like we could solve equation (10). The vectors $\{\mathbf{z}_r\}$ can be estimated by least squares from $\{\mathbf{x}_r\}$ and $\{\mathbf{y}_r\}$:

$$\begin{aligned} \mathbf{P}: \quad & P_{kr} = \sum_{i=1}^{I} \sum_{j=1}^{J} R_{ijk} \hat{X}_{ir} \hat{Y}_{jr} \\ \mathbf{Q}: \quad & Q_{st} = \sum_{i=1}^{I} (\hat{X}_{is} \hat{X}_{it}) \sum_{j=1}^{J} (\hat{Y}_{js} \hat{Y}_{jt}) \\ & \hat{\mathbf{Z}} = \mathbf{P}\mathbf{Q}^{-1} \end{aligned} \tag{22}$$

where the r columns of $\hat{\mathbf{Z}}$ are estimates of the spectra $\{\mathbf{z}_r\}$.

In a similar approach, Sands and Young proposed to compare each slice $\{\mathbf{R}_k\}$ with the sum of all slices, $\sum_{k=1}^{K} \mathbf{R}_k$, or some other linear combination of the matrices, also reducing the problem to an eigenvalue–eigenvector equation.[26] They used the estimates of $\{\mathbf{x}_r\}$ and $\{\mathbf{y}_r\}$ as initial guesses in an ALS iteration to solve the trilinear decomposition in a least-squares sense.

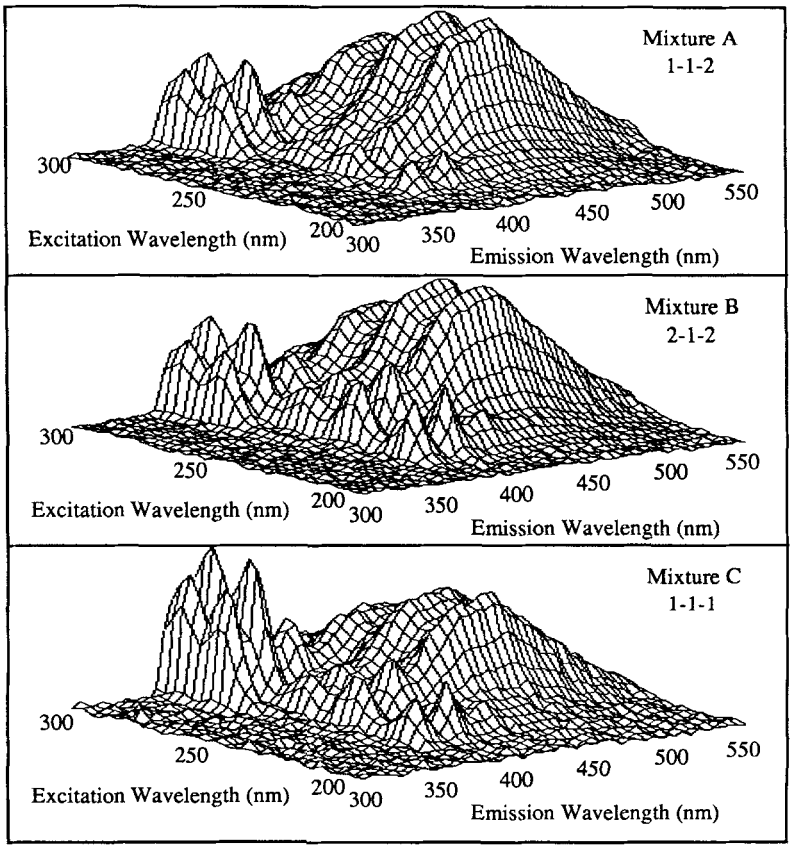

Figure 1. Synthetic emission–excitation fluorescence spectra for three mixtures of anthracene, chrysene and fluoranthene; 1% of maximum emission for mixture B added to all three mixtures. The numbers represent the relative anth–chry–fluo concentrations

An example

Figure 1 shows a representation of the simulated emission–excitation matrix (EEM) for three samples. Each sample contains contributions from anthracene, chrysene and fluoranthene. The spectra were synthesized as ternary integer linear combinations of actual EEMS of the pure analytes—[1, 1, 2], mixture A; [2, 1, 2], mixture B; [1, 1, 1], mixture C—where the bracketed amounts represent the coefficients for [anth, chry, fluo] respectively. These mixtures were designed such that two of the concentration ratios between any two samples would always be equal, e.g. A/B = [0·5, 1, 1]. Normally distributed noise with standard deviation equal to 1% of the maximum emission from B was added to all three EEMs.

Figure 2 shows the spectra estimated by direct trilinear decomposition, both emission and excitation for all three analytes, compared with the actual spectrum before noise was added.

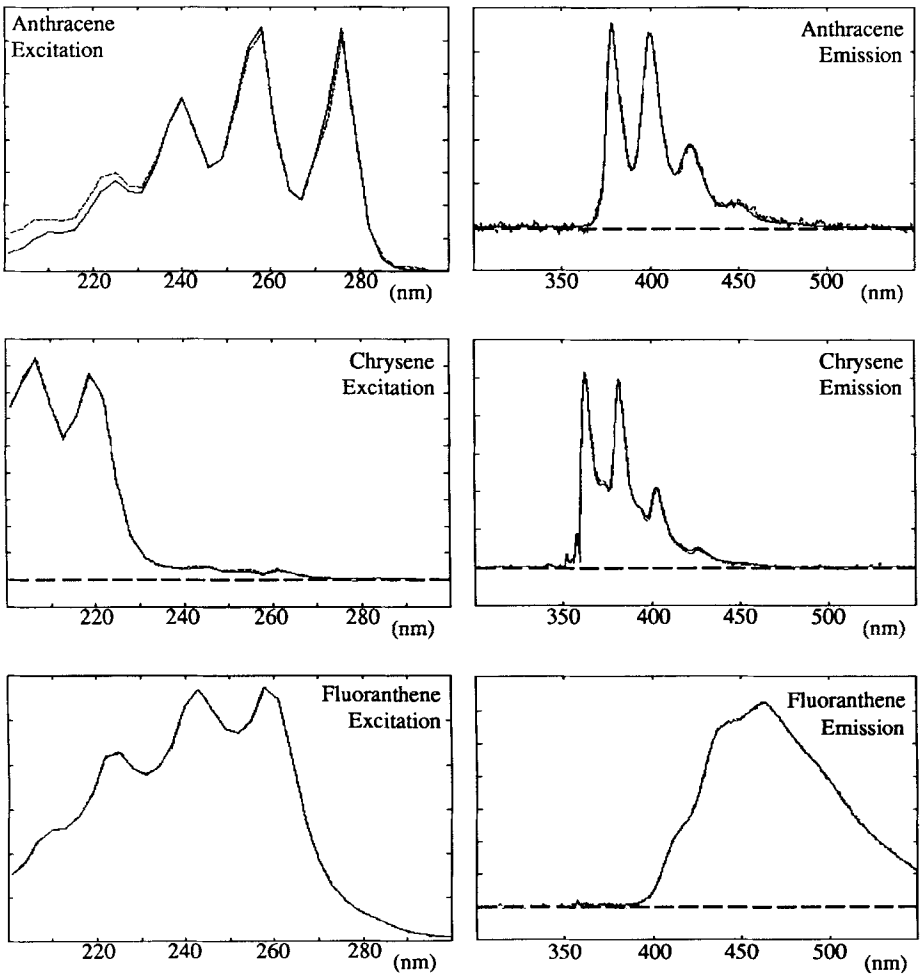

Figure 2. Direct trilinear decompositions of mixtures A, B and C. DTD-resolved emission and excitation spectra for all three analytes, showing notable agreement between estimated (...) and pure (—) spectra

Figure 3 shows the results using the generalized rank annihilation method when comparing mixtures A and B. Since the ratios A/B for chrysene and fluoranthene were chosen to be identical, their GRAM-estimated spectra are rather poor. In fact the other two possible combinations, A/C and B/C, also gave poor results for the corresponding analyte pair that had the same ratios (Table 1). The trilinear decomposition does not have that problem because it uses linear combinations of all three mixtures. Table 1 presents further details of this simulation, including the GRAM results for all possible pairs of mixtures. It is important to point out that direct trilinear decomposition treats the composition vector Z as just another order. The method would work equally well if the Z-order represented time or phase in an emission–excitation–time decay experiment on a single sample.[17]

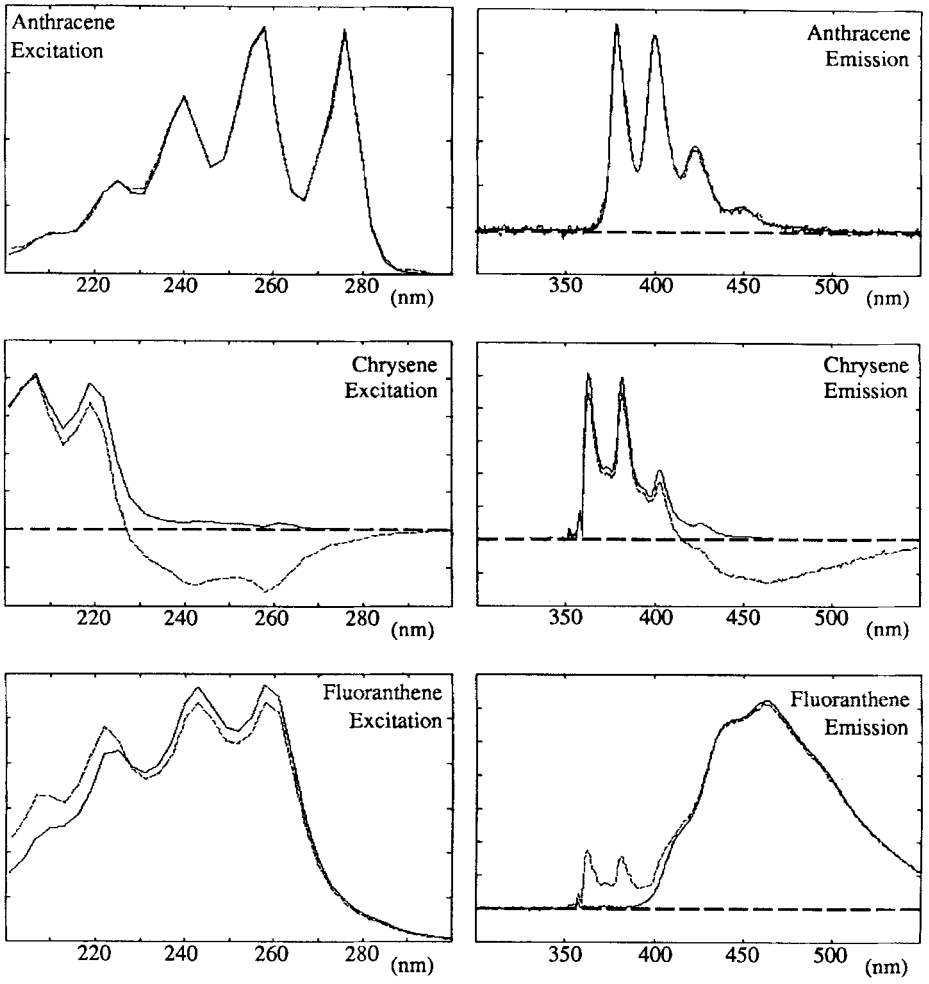

Figure 3. GRAM decompositions for the A/B pair. GRAM fails to resolve chrysene and fluoranthene because their ratios of concentration are the same; in fact the other combinations A/C and B/C were purposely simulated to have the same problem. Estimated (...) and pure (—) spectra

Table 1. Relative concentrations for the three mixtures and three analytes, comparing the true values with the values estimated using direct trilinear decomposition (DTD). Both the emission and excitation spectra correlations are presented between the estimated spectra and the pure spectrum (pure was estimated as the average of the pure EEM in either order), comparing the direct trilinear decomposition results with the generalized rank annihilation method (GRAM)

	Relative concentrations					
	Anthracene		Chrysene		Fluoranthene	
	True	Estimated	True	Estimated	True	Estimated
Mixture A	1·00	1·02	1·00	1·01	1·00	2·00
Mixture B	2·00	1·97	1·00	0·99	2·00	2·00
Mixture C	1·00	1·00	1·00	1·00	1·00	1·00
	Emission spectra correlations					
	Anthracene		Chrysene		Fluoranthene	
GRAM(A,B)	0·9985		0·9408		0·9863	
GRAM(A,C)	0·8660		0·7424		0·9999	
GRAM(B,C)	0·7567		0·9997		0·9964	
DTD(A,B,C)	0·9978		0·9991		0·9999	
	Excitation spectra correlations					
	Anthracene		Chrysene		Fluoranthene	
GRAM(A,B)	0·9995		0·9370		0·9780	
GRAM(A,C)	0·5929		0·9877		1·0000	
GRAM(B,C)	0·9801		0·9999		0·9803	
DTD(A,B,C)	0·9955		0·9998		1·0000	

DISCUSSION

In the context of analytical chemistry, any discussion of the relative merits of direct trilinear decomposition as opposed to ALS or other solutions should include both quality of the resolved spectra and accuracy of the ratios of concentration among samples (or any other third-order variable).

It is interesting to realize that for GRAM, accurate quantitation without identification is possible when ratios are equal or very similar. The degenerate eigenvectors will be abstract linear combinations of the pure spectra, hindering identification or library matching; however, the ratios will still be accurate, providing quantitative information.

The use of the first two 'score' matrices from an unfolding in the Z-order provides the best two matrices that represent all the data in a least-squares sense, making it a sensible choice likely to contain some of the variance from every component, hopefully in different ratios. However, there is no warranty that this will happen in every case, and the analyst should be careful to compare all the eigenvalues and study those that are very similar in value. Sands and Young compare the mean matrix with an arbitrarily chosen combination of the matrices, a valid approach for a good ALS starting value.

Owing to the multivariate nature of the method, it is advisable to have the response of all significant analytes within the same order of magnitude for accurate results. If one measures $A + B$ with error Δ, even if B is accurately known, if $A \sim \Delta \ll B$, the estimate of A will be $\hat{A} = (A + B \pm \Delta) - B = A \pm \Delta$; therefore the error would be $\sim 100\%$! This simple reasoning applies to any multicomponent method, either multivariate or multi-order in nature.

In the theory section it was assumed that the X- and Y-spaces should be spanned first, and then the Z-space should be shrunk to two score matrices. Since any third-order array can be transposed in six ways, there is no distinction between any of the orders. However, it is classically assumed when using second-order instruments and multiple samples that the Z-order represents the individual differences or the individual chemical samples. Certain three-dimensional arrays may have variables in all three orders, making this distinction somewhat artificial for a general theory of trilinear decomposition, i.e. emission–excitation–time decay fluorescence. In terms of fundamental 'analytical capacity', or degree of resolution for a particular order it is convenient to assign the order with the least analytical capacity to the Z-order in order to maximize the probability that the X and Y orders will stay linearly independent.

The selection of the number of components of the expansion of the tensorial space (N) is as elusive as it is for the factor analysis techniques. However, we have found that a slight overdetermination of N does not affect the resolved spectra as much as underestimation. Assume an array with a 'true' number of factors equal to N. If $N-1$ vectors are estimated instead of N they will all be linear combinations of the true spectra, as opposed to the estimation of $N+1$ vectors where N of them will be similar to the true spectra and the last vector will correspond to noise. In practice, owing to non-random deviations from the trilinear model, the problem is not as simple.

For the special problem of calibration with second-order instruments we have a set of $I \times J$ matrices $\{\mathbf{R}_k, c_k\}$ with their corresponding prediction properties (e.g. concentrations) and another set of matrices $\{\mathbf{R}_u\}$ with unknown properties. If the array R_{ijk} follows the trilinear model and the $\mathbf{c} = \{c_k\}$ are concentrations of an analyte present in the samples, one of the $\mathbf{z}_r$ vectors should be correlated with $\mathbf{c}$, and a standard linear or non-linear regression can be built to relate $\mathbf{z}_r$ with $\mathbf{c}$.

The tendency of direct trilinear decomposition to yield imaginary eigenvalues when significant deviations from the model occur is not a problem for ALS, where the iterations are forced to converge within the real domain. This would probably be useful for the analysis of multiple chromatograms with multichannel detection, where the lack of synchronization causes this kind of deviation. Furthermore, the direct trilinear decomposition requires linear independence for the sets of vectors $\{\mathbf{x}_r\}$ or $\{\mathbf{y}_r\}$, whereas ALS has the weaker condition that the dyadic sets $\{\mathbf{x}_r \otimes \mathbf{y}_r\}$, $\{\mathbf{y}_r \otimes \mathbf{z}_r\}$ and $\{\mathbf{z}_r \otimes \mathbf{x}_r\}$ be linearly independent. Finally, ALS will provide a least-squares solution to the problem if it converges to the true minimum. On the other hand, ALS, as with any iterative optimization technique, will not necessarily converge to the absolute minimum, depending on how good the initial estimates are. By combining a direct trilinear decomposition as an initial estimate with ALS for improvement, it is possible that better results would be obtained than by using them independently.

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APPENDIX I

The QZ algorithm for simultaneous diagonalization of two non-symmetric square matrices solves the generalized eigenvalue–eigenvector problem

$$\mathbf{A}\mathbf{x}\alpha = \mathbf{B}\mathbf{x}\beta \tag{23}$$

This algorithm can be easily extended to (I, J)-size rectangular matrices by projecting the rectangular data matrices to a subspace such that the resultant matrices are square. Furthermore, it is useful to reduce the number of variables in each order to the minimum possible without degradation of the $\mathbb{R}$ matrix in order to reduce the number of parameters to be estimated. This can be accomplished by singular value decomposition of the unfolded $\mathbb{R}$ matrix. There are three ways to unfold $\mathbb{R}$:

(1) as an IJ by K matrix with n_w singular vectors $\{\mathbf{w}_r\}$ in the $\{\mathbf{z}_r\}$ space
(2) as an IK by J matrix with n_v singular vectors $\{\mathbf{v}_r\}$ in the $\{\mathbf{y}_r\}$ space
(3) as a JK by I matrix with n_u singular vectors $\{\mathbf{u}_r\}$ in the $\{\mathbf{x}_r\}$ space.

The intention is to build three independent Tucker-1 models and then combine the resultant loadings into a Tucker-3 model. It is interesting to note that the number of components may be different in each order, in contrast with second-order tensors in which the rank is the same in both orders. Assume $n_u \geqslant n_v \geqslant n_w$ without loss of generality. Designating the projected matrix as $\underline{\mathbb{R}}$,

$$\underline{\mathbb{R}} = \sum_{r=1}^{N} c_r(\mathbf{U}\mathbf{U}^T\mathbf{x}_r) \otimes (\mathbf{V}\mathbf{V}^T\mathbf{y}_r) \otimes (\mathbf{W}\mathbf{W}^T\mathbf{z}_r) \tag{24}$$

the same tensor $\underline{\mathbb{R}}$ can be expressed in the **uvw** bases as

$$\underline{\mathbb{R}}_{uvw} = \sum_{r=1}^{N} c_r(\mathbf{U}^T\mathbf{x}_r) \otimes (\mathbf{V}^T\mathbf{y}_r) \otimes (\mathbf{W}^T\mathbf{z}_r) \tag{25}$$

$$\underline{\mathbb{R}}_{uvw} = \sum_{r=1}^{N} c_r\mathbf{a}_r \otimes \mathbf{b}_r \otimes \mathbf{c}_r \tag{26}$$

The tensors $\underline{\mathbb{R}}$ and $\underline{\mathbb{R}}_{uvw}$ represent the same mathematical object; they are equivalent. Therefore solving equation (26) for $\{\mathbf{a}_r\}$, $\{\mathbf{b}_r\}$ and $\{\mathbf{c}_r\}$ will be an equivalent problem to solving equation (24). By setting $n_u = n_v$, the matrices in the first and second order will be square, permitting the use of the QZ algorithm.

Many other methods for estimating the bases $\{\mathbf{u}_r\}$, $\{\mathbf{v}_r\}$ and $\{\mathbf{w}_r\}$ are conceivable, such as an alternating least-squares (ALS) decomposition. The usual problem of determining how many components are significant is faced for the three decompositions; in practice we have found that is better to overestimate the number of components in order to guarantee the presence of all the significant solutions. In fact it is possible to eliminate the projection step all together and still obtain valid solutions with the method proposed here; however, the set of eigenvectors will not only include valid solutions but also noise-related vectors if the **R** matrix was less than full rank.

APPENDIX II

Two matrices $\mathbf{S}_1$ and $\mathbf{S}_2$ must be found as linear combinations of the matrices $\{\mathbf{R}_k\}$ such that they represent the dyads $(\mathbf{x}_r \otimes \mathbf{y}_r)$ for all factors. Linear combinations of the K Z-slices in **R**

are given by

$$\mathbf{S}_p = \sum_{k=1}^{K} w_{pk}\mathbf{R}_k \tag{27}$$

Using the definition of $\mathbf{R}_k$ (equation (15)),

$$\mathbf{S}_p = \sum_{k=1}^{K} w_{pk} \sum_{r=1}^{N} z_{rk}\mathbf{x}_r \otimes \mathbf{y}_r = \sum_{r=1}^{N} (\mathbf{x}_r \otimes \mathbf{y}_r) \sum_{k=1}^{K} z_{rk} w_{pk} \tag{28}$$

Defining $a_{rp} \equiv \sum_{k=1}^{K} z_{rk} w_{pk} = \mathbf{z}_r \cdot \mathbf{w}_p$,

$$\mathbf{S}_p = \sum_{r=1}^{N} a_{rp}(\mathbf{x}_r \otimes \mathbf{y}_r) \tag{29}$$

Therefore a_{rp} must satisfy $a_{rp} \neq 0$ for every r in order to include every dyad in $\mathbf{S}_p$. In terms of the vector of weights $\mathbf{w}_p$, it must satisfy $\mathbf{w}_p \cdot \mathbf{z}_r \neq 0$ for every r, i.e. $\mathbf{w}_p$ must not be perpendicular to any factor $\{\mathbf{z}_r\}$ in the third order. Even though it is possible to conceive of a case in which the first and second principal components may be orthogonal to one or more of the $\{\mathbf{z}_r\}$ factors (e.g. by choosing all factors orthogonal), in general this will not be the case, making the principal components a sensible choice.

APPENDIX III: DIRECT TRILINEAR DECOMPOSITION ALGORITHM

The direct solution of the trilinear decomposition problem by reduction to an eigenvalue–eigenvector problem can be outlined in three steps: (1) Tucker-3 model of the $I \times J \times K$ matrix reduced to a $N \times N \times 2$ array (effectively, two $N \times N$ matrices); (2) solution of the simultaneous eigenvalue–eigenvector problem of the two matrices; (3) calculation of the intrinsic factor matrices $\mathbf{X}$, $\mathbf{Y}$ and $\mathbf{Z}$. The input of the algorithm is an $I \times J \times K$ array $\mathbb{R}$ and the number of factors of decomposition, N (note, however, that N is not necessarily known *a priori*). A more detailed description of the algorithm follows.

1. Tucker-3 model of the $I \times J \times K$ array $\mathbb{R}$ to compute an $N \times N \times 2$ core matrix $\mathbb{G}$.
   1.1. Singular value decomposition of the adjoined $\{\mathbf{R}_k\}$ matrices, where the $\mathbf{R}_k$ are $I \times J$ slices of $\mathbb{R}$, $\mathbf{R}_k = R_{ijk}$:

$$[\mathbf{R}_1 | \mathbf{R}_2 | \mathbf{R}_3 \ldots | \mathbf{R}_K] = \mathbf{U}_1\mathbf{S}_1\mathbf{V}_1^{\mathrm{T}}; \quad \text{define } \mathbf{U} = \mathbf{U}_1(I \times N) \quad \text{(first } N \text{ columns)}$$

   1.2. Singular value decomposition of the adjoined $\{\mathbf{R}_i\}$ matrices, where the $\mathbf{R}_i$ are $J \times K$ slices of $\mathbb{R}$, $\mathbf{R}_i = R_{ijk}$:

$$[\mathbf{R}_1 | \mathbf{R}_2 | \mathbf{R}_3 \ldots | \mathbf{R}_I] = \mathbf{U}_2\mathbf{S}_2\mathbf{V}_2^{\mathrm{T}}; \text{ define } \mathbf{V} = \mathbf{U}_2(J \times N) \quad \text{(first } N \text{ columns)}$$

   1.3 Singular value decomposition of the adjoined $\{\mathbf{R}_j\}$ matrices, where the $\mathbf{R}_j$ are $K \times I$ slices of $\mathbb{R}$, $\mathbf{R}_j = R_{ijk}$:

$$[\mathbf{R}_1 | \mathbf{R}_2 | \mathbf{R}_3 \ldots | \mathbf{R}_J] = \mathbf{U}_3\mathbf{S}_3\mathbf{V}_3^{\mathrm{T}}; \text{ define } \mathbf{W} = \mathbf{U}_3(K \times 2) \quad \text{(first two columns)}$$

   1.4 Project the $\mathbb{R}$ tensor down to the $(\mathbf{U}, \mathbf{V}, \mathbf{W})$ base sets. Because there are only two columns in $\mathbf{W}$, the projected tensor $\mathbb{G}$ will consist of two $N \times N$ matrices, $\mathbf{G}_1$ and $\mathbf{G}_2$:

$$\mathbf{G}_1 = \sum_{k=1}^{K} w_{k2}(\mathbf{U}^{\mathrm{T}}\mathbf{R}_k\mathbf{V}), \qquad \mathbf{G}_2 = \sum_{k=1}^{K} w_{k1}(\mathbf{U}^{\mathrm{T}}\mathbf{R}_k\mathbf{V})$$

   where $\mathbf{R}_k$ is the kth $I \times J$ slice of the $\mathbb{R}$ array.

2. Solve the eigenvalue–eigenvector equation.
   2.1 Using the QZ algorithm (e.g. EISPACK, IMSL) find eigenvectors $\tilde{\mathbf{x}}^r$ that satisfy the equation (similar to equation (12) but with $\mathbf{G}_1$ and $\mathbf{G}_2$)

$$\mathbf{G}_1\tilde{\mathbf{x}}^r\lambda_{2r} = \mathbf{G}_2\tilde{\mathbf{x}}^r\lambda_{1r}$$

   2.2. Compute the inverse of the matrix of eigenvectors $\{\tilde{\mathbf{x}}^r\}$; call it $\tilde{\mathbf{X}}$ (with columns $\{\tilde{\mathbf{x}}_r\}$).
   2.3. Using the QZ algorithm find eigenvectors $\tilde{\mathbf{y}}^r$ that satisfy the equation

$$\mathbf{G}_1^{\mathrm{T}}\tilde{\mathbf{y}}_r\lambda_{2r} = \mathbf{G}_2^{\mathrm{T}}\tilde{\mathbf{y}}^r\lambda_{1r}$$

   2.4. Compute the inverse of the matrix of eigenvectors $\{\tilde{\mathbf{y}}^r\}$; call it $\tilde{\mathbf{Y}}$ (with columns $\{\tilde{\mathbf{y}}_r\}$).
3. Calculation of the intrinsic factors.
   3.1. $\hat{\mathbf{X}} = \mathbf{U}\tilde{\mathbf{X}}$ where the N columns of $\hat{\mathbf{X}}$ are estimates of the spectra $\{\mathbf{x}_r\}$.
   3.2 $\hat{\mathbf{Y}} = \mathbf{V}\tilde{\mathbf{Y}}$ where the N columns of $\hat{\mathbf{Y}}$ are estimates of the spectra $\{\mathbf{y}_r\}$.
   3.3 Least-squares estimate of $\mathbf{Z}$, given $\hat{\mathbf{X}}$ and $\hat{\mathbf{Y}}$.
      3.3.1. $\mathbf{P}$: $P_{kr} = \sum_{i=1}^{I}\sum_{j=1}^{J}\mathbb{R}_{ijk}\hat{X}_{ir}\hat{Y}_{jr}$.
      3.3.2. $\mathbf{Q}$: $Q_{st} = \sum_{i=1}^{I}(\hat{X}_{is}\hat{X}_{it})\sum_{j=1}^{J}(\hat{Y}_{js}\hat{Y}_{jt})$.
      3.3.3. $\hat{\mathbf{Z}} = \mathbf{P}\mathbf{Q}^{-1}$ where the columns of $\hat{\mathbf{Z}}$ are estimates of the spectra $\{\mathbf{z}_r\}$.

An alternative version of the algorithm is possible if a least-squares Tucker-2 model is desired for the initial projection, by substituting the first step with the following.

1. Tucker-2 model of the $I \times J \times K$ array $\mathbb{R}$ to compute an $N \times N \times 2$ core matrix $\mathbb{G}$.
   1.1. Singular value decomposition of the adjoined $\{\mathbf{R}_k\}$ matrices, where the $\mathbf{R}_k$ are $I \times J$ slices of $\mathbb{R}$, $\mathbf{R}_k = R_{ijk}$:

$$[\mathbf{R}_1|\,\mathbf{R}_2|\,\mathbf{R}_3 \ldots |\,\mathbf{R}_K] = \mathbf{U}_1\mathbf{S}_1\mathbf{V}_1^{\mathrm{T}}; \quad \text{define } \mathbf{U} = \mathbf{U}_1(I \times N) \quad \text{(first } N \text{ columns)}$$

   Assign for every k: $\mathbf{R}_k^* = \mathbf{U}\mathbf{U}^{\mathrm{T}}\mathbf{R}_k$; $\mathbb{R}^* = \{\mathbf{R}_k^*\}$.
   1.2. Singular value decomposition of the adjoined $\{\mathbf{R}_i^*\}$ matrices, where the $\mathbf{R}_i^*$ are $J \times K$ slices of $\mathbb{R}^*$, $\mathbf{R}_i^* = R_{ijk}^*$:

$$[\mathbf{R}_1^*|\,\mathbf{R}_2^*|\,\mathbf{R}_3^* \ldots |\,\mathbf{R}_I^*] = \mathbf{U}_2\mathbf{S}_2\mathbf{V}_2; \quad \text{define } \mathbf{V} = \mathbf{U}_2(J \times N) \quad \text{(first } N \text{ columns)}$$

   Assign for every i: $\mathbf{R}_i^* = \mathbf{V}\mathbf{V}^{\mathrm{T}}\mathbf{R}_i$; $\mathbb{R}^* = \{\mathbf{R}_i^*\}$.
   1.3. Repeat 1.1 and 1.2 until convergence to obtain least-squares $\mathbf{U}$ and $\mathbf{V}$ matrices. When convergence has been achieved, project all the $I \times J$ slices $\{\mathbf{R}_k\}$ into the $\mathbf{U}$, $\mathbf{V}$ subspaces:

$$\mathbf{R}_k^* = \mathbf{U}\mathbf{U}^{\mathrm{T}}\mathbf{R}_k\mathbf{V}\mathbf{V}^{\mathrm{T}}, \qquad \mathbb{R}^* = \{\mathbf{R}_k^*\}$$

   1.4. Singular value decomposition of the adjoined $\{\mathbf{R}_j^*\}$ matrices, where the $\mathbf{R}_j^*$ are $K \times I$ slices of $\mathbb{R}^*$, $\mathbf{R}_j^* = R_{ijk}^*$:

$$[\mathbf{R}_1^*\,|\,\mathbf{R}_2^*\,|\,\mathbf{R}_3^* \ldots |\,\mathbf{R}_J^*] = \mathbf{U}_3\mathbf{S}_3\mathbf{V}_3^{\mathrm{T}}; \quad \text{define } \mathbf{W} = \mathbf{U}_3(K \times 2) \quad \text{(first two columns)}.$$

   1.5. Project the $\mathbb{R}$ tensor down to the $(\mathbf{U}, \mathbf{V}, \mathbf{W})$ base sets. Because there are only two columns in $\mathbf{W}$, the projected tensor $\mathbb{G}$ will consist of two $N \times N$ matrices, $\mathbf{G}_1$ and $\mathbf{G}_2$:

$$\mathbf{G}_1 = \sum_{k=1}^{K} w_{k1}(\mathbf{U}^{\mathrm{T}}\mathbf{R}_k\mathbf{V}), \qquad \mathbf{G}_2 = \sum_{k=1}^{K} w_{k2}(\mathbf{U}^{\mathrm{T}}\mathbf{R}_k\mathbf{V})$$

   where $\mathbf{R}_k$ is the kth $I \times J$ slice of the $\mathbb{R}$ array.

A version of the first algorithm has been implemented in MATLAB (Mitchell & Gauthier Associates, Concord, MA) and is available from the authors.

REFERENCES

1. T. Hirschfeld, *Anal Chem.* **52**, 297A (1980).
2. T. Hirschfeld, *Science*, **230** (1985).
3. E. Sanchez and B. R. Kowalski, *J. Chemometrics*, **2**, 247 (1988).
4. E. Sanchez and B. R. Kowalski, *J. Chemometrics*, **2**, 265 (1988).
5. B. Budiansky, 'Tensor', in *Handbook of Applied Mathematics*, ed. by C. E. Pearson, Chap. 4, p. 179, Van Nostrand Reinhold, New York (1974).
6. E. R. Malinowski and D. G. Howery, *Factor Analysis in Chemistry*, Wiley, New York (1980).
7. R. A. Harshman, *UCLA Working Papers in Phonetics* **16**, 1 (1970).
8. J. D. Carroll and J. J. Chang, *Psychometrika* **35**, 283 (1970).
9. J. B. Kruskal, *Psychometrika* **41**, 281 (1976).
10. L. R. Tucker, in *Contributions to Mathematical Psychology*, ed. by H. Gulliksen and N. Frederiksen, p. 110, Holt, Rinehart and Winston, New York (1964).
11. W. A. van der Kloot and P. M. Kroonenberg, *Psychometrika* **50**, 479 (1985).
12. P. M. Kroonenberg, *Three-mode Principal Component Analysis: Theory and Applications*, DSWO Press, Leiden (1983).
13. I. M. Warner, G. Patonay and M. P. Thomas, *Anal. Chem.* **57**, 463A (1985).
14. C. J. Appellof and E. R. Davidson, *Anal. Chem.* **53**, 2053–2056 (1981).
15. M. D. Russell and M. Gouterman, *Spectrochim. Acta* **44A**, 857 (1988).
16. M. D. Russell and M. Gouterman, *Spectrochim. Acta* **44A**, 863 (1988).
17. M. D. Russell, M. Gouterman and J. A. van Zee, *Spectrochim. Acta* **44A**, 873 (1988).
18. C. L. De Ligny, M. C. Spanjer, J. C. Van Houwelingen and H. M. Weesie, *J.* Chromatogr. **301**, 311 (1984).
19. S. Wold, P. Geladi, K. Esbensen and J. Öhman, *J. Chemometrics*, **1**, 41 (1987).
20. A. Lorber, *Anal. Chim. Acta* **164**, 293 (1984).
21. R. R. Kim, *Ph.D. Dissertation*, Massachusetts Institute of Technology, Cambridge, MA (1985).
22. C. R. Rao and S. K. Mitra, *Generalized Inverse of Matrices and Its Applications*, Wiley, New York (1971).
23. E. Sanchez and B. R. Kowalski, *Anal. Chem.* **58**, 496 (1986).
24. E. Sanchez, L. S. Ramos and B. R. Kowalski, *J. Chromatogr.* **385**, 151 (1987).
25. L. S. Ramos, E. Sanchez and B. R. Kowalski, *J. Chromatogr.* **385**, 165 (1987).
26. R. Sands and F. W. Young, *Psychometrika* **45**, 39 (1980).
27. B. E. Wilson, E. Sanchez and B. R. Kowalski, *J. Chemometrics*, **3**, 493 (1989).