

REASSESSING THE TRANSFORMATION STEP IN FACTOR THEORY. THE CASE FOR A NON-ORTHOGONAL TRANSFORMATION MATRIX

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Abstract

The existing factor rotational methods (an assortment of orthogonal, oblique and simplex techniques) are assessed for their potential to be generalized for use at higher dimensions (i.e. above threefold factor space). An answer is sought to the problem of why the application of an orthogonal rotation results in mathematical solutions (those containing negative entries) rather than all positive solutions having physical and chemical meaning. Such positive solutions will be within the limits of experimental error if non-perfect data is used. An evaluation of a methodological improvement to an algorithm on factor analysis based on the optimization of the $m(m - 1)$ independent variables of a transformation matrix T' of m factors is made, and a case is presented for its introduction as a realistic alternative to the established methods.

1. Introduction

Factor analysis is a popular but conceptually little understood technique of multivariate data analysis, used in chemistry to evaluate spectroscopic as well as other types of data. From its application, one can determine:

- (1) the number of primary components;
- (2) the nature of the primary components (i.e. their chemical identity); and
- (3) how much of each component is present in each of the mixtures (i.e. their relative concentrations).

The basic concepts of factor analysis, and its application to IR spectroscopy in particular, has already been fully discussed in earlier papers [1–3]. This study addresses only a specific area of the factor problem: namely, the ambiguity of rotational methods and the need to use a non-orthogonal transformation. Four principal objectives are defined:

- (1) Firstly, to review the existing factor rotational methods and assess their usefulness.
- (2) Improve understanding of the factor transformation step.

- (3) Give examples, using perfect data, of the type of solutions produced using \mathbf{T} and \mathbf{R} (\mathbf{T} represents a general (non-orthogonal) transformation matrix and \mathbf{R} an orthogonal rotation).
- (4) To evaluate the merits and potential of a new approach to factor theory which is dependent on the software-controlled optimization of a general (non-orthogonal) transformation matrix \mathbf{T}' .

Factor theory is a general term used in the broadest sense to describe the mathematical basis of factor analysis – the analytical technique. It involves two main processes: eigenanalysis and a transformation step. The latter term refers to that part of factor theory which requires some form of transformation to convert the intermediate solutions given by \mathbf{S}_m and \mathbf{V}_m into factor solutions which are equivalent to (for perfect data only) or closely approximate the true solutions.

The difficulty in finding a suitable transformation is a major hurdle to the advancement of factor analysis as a general analytical technique. Only by finding the correct transformation can the intermediate solutions be converted into factor solutions which closely approximate the true solutions. When applied to IR spectroscopy, the eigenspectra and pseudo concentration matrices must be transformed via application of an appropriate transformation into the primary component spectra and concentration matrices, respectively.

1.1. LIMITS OF ANALYTICAL TRACTABILITY

The separation and identification of individual components within a multi-component mixture is a major problem for the analytical chemist. It is both expensive and time-consuming, so tends to be avoided whenever possible. Although factor analysis showed great potential as an analytical technique, it was not until the 1980's, when the specific advantages of a computerized approach became apparent, that its popularity increased. Prior to this time, the technique was not suitable for routine use, being limited to problems involving a couple of factors. This was mainly due to the repetitive nature of the calculations involved. By adopting a computerized approach for which factor analysis is perfectly suited, the method has been transformed into a widely used analytical tool which is labour saving, efficient and relatively cheap to implement. New methods of tackling the reconstruction of the primary components (i.e. via optimization) have now become possible.

1.2. CHEMICAL APPLICATIONS

The introduction of factor analysis into chemistry, and particularly vibrational spectroscopy, began during the 1970's [4–7]. Kowalski et al. [8–10] and Gilbert [11] helped to popularize the method by extending its use into other areas of chemistry. In recent years, it has been extensively applied to problems encountered in science, medicine and technology. The main concern here, however, is with the application

of factor analysis to IR spectroscopy. The articles by Gemperline [12], Brown et al. [13], and Beebe et al. [14] provide numerous references on factor analysis and associated methods.

We shall begin with a critical assessment of the existing factor rotational methods.

2. Factor rotational methods

Factor rotational methods is the collective name given to a whole variety of techniques which are used to carry out the intermediate transformation step in factor theory. These methods are summarized in fig. 1. They include:

- (1) Orthogonal rotations which preserve the angles between the axes.
- (2) Non-orthogonal rotations (oblique rotations) which do not preserve the angles between the axes.

Sometimes, a further subdivision then occurs into:

- (1) Analytical rotations – those dependent on rules to "simplify" the solutions.
- (2) Empirical rotations – those relying on practical experience (i.e. experiment).

Confusion exists in the literature concerning the terminology used to describe the transformation step [15, p. 48]. There has been a general tendency to interchange the words transformation and rotation. In keeping with their graphical approach to solution hunting and the need to determine "axes of rotation", the early researchers were inclined to favour the word rotation.

To date, most of the work on factor theory has depended on traditional rotational methods. Such methods include analytical rotations, which can be orthogonal (varimax and quartimax) [16, 17] or oblique (oblimax, quartimin, etc.) [15, 18]. By far the most popular of the former group are varimax rotations [19]. These have been used in the majority of publications. Many authors have been quick to point out that standard transformations such as varimax rotations do not appear to be very satisfactory [20, 21] and [22, p. 37].

Empirical methods include target rotation (also known as least-squares rotation). Target factor analysis (TFA) provides a means of determining whether or not a particular component is present in the multicomponent mixture. Most articles on TFA do not specify the nature of the rotation [23–25]; a few refer to the use of an oblique [15, 21] or orthogonal rotation [17], while others refer to a transformation matrix [26, 27].

In summarizing TFA, we begin with the factor equations

$$\bar{\bar{S}} = S_m R \quad (1)$$

and

$$\bar{\bar{V}} = R^{-1} V_m. \quad (2)$$

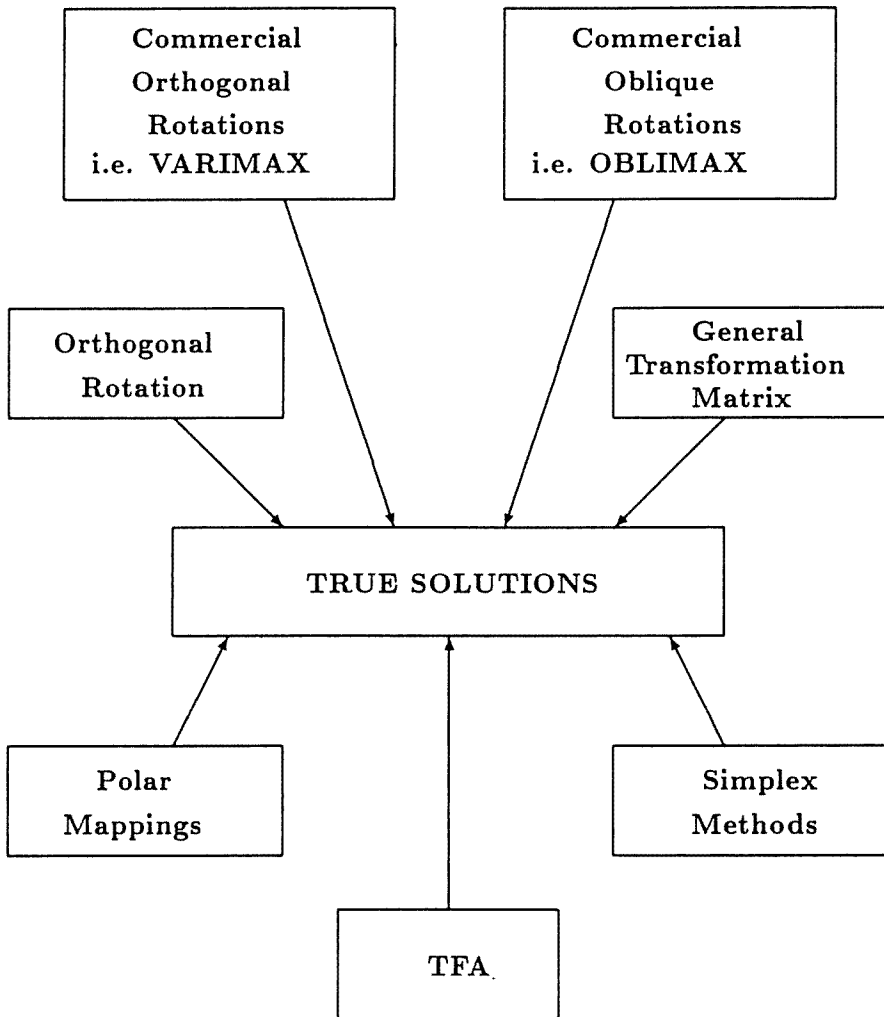


Fig. 1. Techniques used to carry out the transformation step in factor theory.

$\bar{\bar{S}}$ = software derived, spectral factor solutions,

$\bar{\bar{V}}$ = software derived, relative concentration matrix,

S_m = reduced eigenspectra matrix (m -fold factor space),

V_m = reduced pseudo concentration matrix (m -fold factor space).

m corresponds to the number of factors. On rearranging eq. (1), this leads to the TFA equation

$$\mathbf{R} = (\mathbf{S}_m^T \mathbf{S}_m)^{-1} \mathbf{S}_m^T \bar{\bar{S}}. \quad (3)$$

The major disadvantage of TFA is the need to know the identity of the primary components so that a suitable test vector can be chosen; otherwise, the prospect of matching the factor solution against possible components would be a daunting task. TFA requires that the test vector be prepared under conditions closely resembling, or indeed duplicating, those used to construct the multicomponent spectral absorbance data matrix \mathbf{D} [28,29]. The efficiency of this method depends on the ability of the analyst to accurately locate the correct test vector. When used in conjunction with a spectral reference library, the effectiveness of TFA is greatly increased [30–32]. Then a large number of "possible" primary components (i.e. library spectra) can be scanned, greatly simplifying the identification process.

Other factor rotational approaches include simplex-based methods which require a geometrical representation [33–35]. These become visually difficult to interpret at higher dimensions, thus severely limiting their general application to factor theory. Indeed, no example above three factors could be found which utilized simplex rotational methods. Quoting from Borgen and Kowalski [36, p. 24], "the practical generalization of the necessary algorithms is not a trivial problem" and that "the location of permitted regions will require very efficient programming in the multicomponent case".

Several groups have attempted to use polar transformations but, like simplex methods, they are only really suited to problems involving a few factors [37–39]. (Here, examples are mainly restricted to areas of chemistry other than IR spectroscopy.) If further advancement is therefore to be made toward a generalized factor analytical technique, it will be necessary to look for new approaches toward the transformation step rather than try to extend the existing rotational methods.

3. The factor transformation step

The non-uniqueness of the factor equations $\bar{\mathbf{S}} = \mathbf{S}_m \mathbf{T}$ and $\bar{\mathbf{V}} = \mathbf{T}^{-1} \mathbf{V}_m$ is well established [1]. However, provided $\bar{\mathbf{S}}$ and \mathbf{D} are known for a given data set, then there exists a unique general (non-orthogonal) transformation matrix \mathbf{T} which satisfies these equations. This implies that a unique orthogonal rotation \mathbf{R} cannot also exist which satisfies these equations. The application of \mathbf{R} results in intermediate matrices having only mathematical meaning.

From worked examples using perfect data, it will be shown that:

(1) A unique general transformation matrix \mathbf{T} exists that satisfies the factor equations

$$\mathbf{D} \equiv \mathbf{D}_m = \mathbf{S}_m \mathbf{T} \mathbf{T}^{-1} \mathbf{V}_m \quad (4)$$

$$\bar{\mathbf{S}} = \mathbf{S}_m \mathbf{T} \quad (5)$$

and

$$\bar{\bar{\mathbf{V}}} = \mathbf{T}^{-1} \mathbf{V}_m. \quad (6)$$

If

$$\bar{\bar{\mathbf{S}}} = \bar{\mathbf{S}}, \quad (7)$$

($\bar{\mathbf{S}}$ contains the spectra of the m primary components) and

$$\bar{\bar{\mathbf{V}}} = \bar{\mathbf{V}}, \quad (8)$$

($\bar{\mathbf{V}}$ is the relative concentration matrix of the m pure components), then

$$\mathbf{D} = \bar{\mathbf{S}} \bar{\mathbf{V}}. \quad (9)$$

Returning to the factor solutions,

$$\mathbf{D}_m = \bar{\bar{\mathbf{S}}} \bar{\bar{\mathbf{V}}}. \quad (10)$$

(2) On application of the unique \mathbf{T} , \mathbf{S}_m is directly transformed into the pure components $\bar{\mathbf{S}}$:

$$\mathbf{S}_m \xrightarrow{\mathbf{T}} \bar{\mathbf{S}}. \quad (11)$$

Likewise,

$$\mathbf{V}_m \xrightarrow{\mathbf{T}^{-1}} \bar{\mathbf{V}}. \quad (12)$$

(3) A unique \mathbf{R} cannot also exist which satisfies the same factor equations. Now

$$\mathbf{D} \equiv \mathbf{D}_m = \mathbf{S}_m \mathbf{R} \mathbf{R}^{-1} \mathbf{V}_m. \quad (13)$$

The factor solutions are given by eqs. (1) and (2). However,

$$\bar{\mathbf{S}} \neq \mathbf{S}_m \mathbf{R} \quad (14)$$

and

$$\bar{\mathbf{V}} \neq \mathbf{R}^{-1} \mathbf{V}_m. \quad (15)$$

Thus,

$$\bar{\bar{\mathbf{S}}} \neq \bar{\mathbf{S}} \quad (16)$$

and

$$\bar{\bar{\mathbf{V}}} \neq \bar{\mathbf{V}}, \quad (17)$$

hence,

$$\mathbf{D}_m \neq \bar{\bar{\mathbf{S}}} \bar{\bar{\mathbf{V}}}. \quad (18)$$

(4) Application of \mathbf{R} results in factor solutions $\bar{\bar{\mathbf{S}}}$ and $\bar{\bar{\mathbf{V}}}$, which are only mathematical solutions. These are solutions with negative entries.

$$\mathbf{S}_m \xrightarrow{\mathbf{R}} \bar{\bar{\mathbf{S}}} \xrightarrow{?} \bar{\mathbf{S}}. \tag{19}$$

Likewise,

$$\mathbf{V}_m \xrightarrow{\mathbf{R}^{-1}} \bar{\bar{\mathbf{V}}} \xrightarrow{?} \bar{\mathbf{V}}. \tag{20}$$

When these equations are applied to experimental data, slight modifications are required. For instance, eqs. (7) and (8) are no longer exact due to noise error; thus

$$\bar{\bar{\mathbf{S}}} \cong \bar{\mathbf{S}}$$

and

$$\bar{\bar{\mathbf{V}}} \cong \bar{\mathbf{V}}.$$

4. Orthogonal versus non-orthogonal transformation

The basic factor equations associated with the use of a rotation \mathbf{R} are given by

$$\bar{\mathbf{S}} = \mathbf{S}_m \mathbf{R} \tag{21}$$

and

$$\bar{\mathbf{V}} = \mathbf{R}^{-1} \mathbf{V}_m. \tag{22}$$

\mathbf{R} is an orthogonal matrix since

$$\mathbf{R}^T \mathbf{R} = \mathbf{I} \tag{23}$$

and therefore

$$\mathbf{R}^{-1} = \mathbf{R}^T.$$

Now, if we apply the analogue of the orthogonality condition for square matrices to rectangular matrices, then $\bar{\bar{\mathbf{S}}}$ is shown to be non-orthogonal since

$$\bar{\bar{\mathbf{S}}}^T \bar{\bar{\mathbf{S}}} \neq \mathbf{I}. \tag{24}$$

Likewise, for the true solutions

$$\bar{\mathbf{S}}^T \bar{\mathbf{S}} \neq \mathbf{I}. \tag{25}$$

On applying the orthogonality condition to the RHS of eq. (1)

$$(\mathbf{S}_m \mathbf{R})^T (\mathbf{S}_m \mathbf{R}) = \mathbf{R}^T \mathbf{S}_m^T \mathbf{S}_m \mathbf{R}$$

and making the substitution given by

$$\mathbf{\Lambda}_m = \mathbf{S}_m^T \mathbf{S}_m, \quad (26)$$

i.e.

$$\mathbf{S}_m^T \mathbf{S}_m \neq \mathbf{I}, \quad (27)$$

then

$$(\mathbf{S}_m \mathbf{R})^T (\mathbf{S}_m \mathbf{R}) = \mathbf{R}^T \mathbf{\Lambda}_m \mathbf{R} \neq \mathbf{I}.$$

By making use of eqs. (23)–(25) and (27) to demonstrate the orthogonality/non-orthogonality of each term in question, we can therefore show that eq. (1), i.e.

$$\text{Non-orthogonal } \bar{\bar{\mathbf{S}}} = \text{Non-orthogonal } \mathbf{S}_m \times \text{Orthogonal } \mathbf{R}$$

and eq. (21)

$$\text{Non-orthogonal } \bar{\mathbf{S}} = \text{Non-orthogonal } \mathbf{S}_m \times \text{Orthogonal } \mathbf{R}$$

hold. However,

$$\bar{\bar{\mathbf{S}}} \neq \bar{\mathbf{S}}.$$

Let \bar{s}_k be the k th column and \bar{s}_j the j th column of $\bar{\mathbf{S}}$, respectively; then

$$\bar{s}_k^T \bar{s}_j \neq 0, \quad k \neq j,$$

$$\bar{s}_j^T \bar{s}_j \neq 1.$$

Repeating this for s_k and s_j , the k th column and j th column of \mathbf{S}_m

$$s_k^T s_j = 0, \quad k \neq j,$$

$$s_j^T s_j \neq 1.$$

For the factor solutions, there are two possibilities:

Case 1

$$\bar{\bar{s}}_k^T \bar{\bar{s}}_j \neq 0, \quad k \neq j,$$

$$\bar{\bar{s}}_j^T \bar{\bar{s}}_j \neq 1$$

(see the example given in section 3, using rotation **R**), or

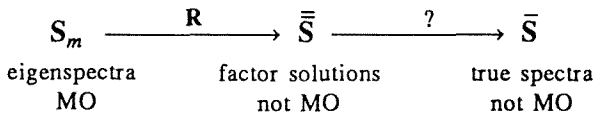
Case 2

$$\bar{\bar{s}}_k^T \bar{\bar{s}}_j = 0, \quad k \neq j,$$

$$\bar{\bar{s}}_j^T \bar{\bar{s}}_j \neq 1.$$

This situation would arise, for example, if the values assigned to the Euler angles for the general 3D rotation given by eq. (46) were $\phi = 90^\circ$, $\theta = 90^\circ$ and $\psi = 90^\circ$.

4.1. CASE 1



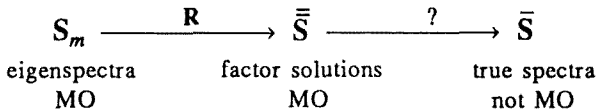
MO implies that the columns are mutually orthogonal.

In case 1, the factor solutions, like the true solutions, are not mutually orthogonal, although $\bar{\bar{\mathbf{S}}}$ and $\bar{\mathbf{S}}$ agree in this respect

$$\bar{\bar{\mathbf{S}}} \neq \bar{\mathbf{S}},$$

i.e. eq. (16) holds. $\bar{\bar{\mathbf{S}}}$ contains substantial negative entries, therefore it cannot represent the true solutions. The mutual orthogonality between the columns of \mathbf{S}_m has not been preserved by **R**.

4.2. CASE 2



The mutual orthogonality between the columns of \mathbf{S}_m and $\bar{\bar{\mathbf{S}}}$ has been preserved by **R**. The factor solutions and true solutions therefore differ with respect to the MO condition. Again, eq. (16) holds. Repeating the argument for the concentration matrix,

$$\bar{\bar{\mathbf{V}}}^T \bar{\bar{\mathbf{V}}} \neq \mathbf{I}. \tag{28}$$

Also,

$$\bar{\bar{\mathbf{V}}}^T \bar{\bar{\mathbf{V}}} \neq \mathbf{I}. \quad (29)$$

Applying the orthogonality condition to the RHS of eq. (2) leads to

$$\begin{aligned} (\mathbf{R}^T \mathbf{V}_m)^T (\mathbf{R}^T \mathbf{V}_m) &= \mathbf{V}_m^T \mathbf{R} \mathbf{R}^T \mathbf{V}_m \\ &= \mathbf{V}_m^T \mathbf{V}_m \\ &\neq \mathbf{I}. \end{aligned}$$

Now,

$$\mathbf{V}_m = \mathbf{Q}_m^T. \quad (30)$$

Here, \mathbf{Q}_m is a rectangular matrix representing the reduced set of eigenvectors in m -fold factor space, obtained from the covariance matrix \mathbf{Z} given by

$$\mathbf{Z} = \mathbf{D}^T \mathbf{D}.$$

Premultiplying eq. (30) by \mathbf{V}_m^T gives

$$\mathbf{V}_m^T \mathbf{V}_m = \mathbf{Q}_m \mathbf{Q}_m^T.$$

In the reduced factor space, $\mathbf{Q}_m \mathbf{Q}_m^T \neq \mathbf{I}$ but $\mathbf{Q}_m^T \mathbf{Q}_m = \mathbf{I}$. Hence,

$$\mathbf{V}_m^T \mathbf{V}_m \neq \mathbf{I}, \quad (31)$$

but

$$\mathbf{V}_m \mathbf{V}_m^T = \mathbf{I}. \quad (32)$$

Using eqs. (23), (28), (29) and (31) to likewise show the orthogonality/non-orthogonality of each term in eqs. (2) and (22), i.e.

$$\text{Non-orthogonal } \bar{\bar{\mathbf{V}}} = \text{Orthogonal } \mathbf{R}^{-1} \times \text{Non-orthogonal } \mathbf{V}_m$$

and

$$\text{Non-orthogonal } \bar{\bar{\mathbf{V}}} = \text{Orthogonal } \mathbf{R}^{-1} \times \text{Non-orthogonal } \mathbf{V}_m.$$

Once again, even though the fundamental equations (2) and (22) hold,

$$\bar{\bar{\mathbf{V}}} \neq \bar{\mathbf{V}}.$$

Note that if eq. (32) were used instead of eq. (31), then the RHS of eq. (2) gives

$$\begin{aligned}
\bar{\bar{\mathbf{V}}}\bar{\bar{\mathbf{V}}}^T &= (\mathbf{R}^T \mathbf{V}_m)(\mathbf{R}^T \mathbf{V}_m)^T \\
&= \mathbf{R}^T \mathbf{V}_m \mathbf{V}_m^T \mathbf{R} \\
&= \mathbf{R}^T \mathbf{R} \\
&= \mathbf{I}.
\end{aligned}$$

However,

$$\bar{\bar{\mathbf{V}}}\bar{\bar{\mathbf{V}}}^T \neq \mathbf{I}.$$

From a consideration of all these facts, it therefore seems inappropriate to use \mathbf{R} since this will not result in the true solutions.

5. Factor theory applied to perfect data ($m = 3$ case)

5.1. OBTAINING THE GENERAL (NON-ORTHOGONAL) TRANSFORMATION MATRIX

A brief account will now be given on how the general transformation matrix for a particular set of data is obtained. For the $m = 3$ case, $\bar{\mathbf{S}}$ consisted of three columns – the primary component spectra, constructed from perfect data (i.e. data that contain no noise). Six distinct multicomponent spectra d_k (where d_k is the k th multicomponent spectrum of \mathbf{D}) were then artificially generated from the linear sums of various combinations of \bar{s}_j (\bar{s}_j being the j th column of $\bar{\mathbf{S}}$, where $j = 1, \dots, m$) to form the spectral absorbance data matrix \mathbf{D} (eq. (36)). The six multicomponent spectra d_k are given by:

$$d_1 = \bar{s}_1 + \bar{s}_2, \tag{33}$$

$$d_2 = \bar{s}_1 + \bar{s}_3,$$

$$d_3 = \bar{s}_2 + \bar{s}_3,$$

$$d_4 = 0.5 \bar{s}_1 + 0.25 \bar{s}_2, \tag{34}$$

$$d_5 = 0.5 \bar{s}_1 + 0.25 \bar{s}_3,$$

$$d_6 = 0.5 \bar{s}_2 + 0.25 \bar{s}_3.$$

From a knowledge of the individual components and their amounts present in every column of \mathbf{D} , $\bar{\mathbf{V}}$ could therefore be constructed. The eigenspectra matrix \mathbf{S} contained m eigenspectra corresponding to the primary (true) eigenvectors. The remaining $n - m$ eigenspectra, where n is the number of multicomponent spectra in \mathbf{D} , contained

all zero entries (for perfect data only). These correspond to the secondary eigenvectors (or insignificant noise terms) produced by experimental data:

$$\begin{pmatrix} 1 & 1 & 1 \\ 2 & 1 & 1 \\ 3 & 2 & 2 \\ 4 & 2 & 4 \\ 5 & 3 & 4 \\ 6 & 4 & 9 \\ 5 & 7 & 6 \\ 4 & 5 & 5 \\ 3 & 6 & 4 \\ 2 & 3 & 3 \\ 1 & 2 & 2 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 1 & 1 & 0 & 0.50 & 0.50 & 0 \\ 1 & 0 & 1 & 0.25 & 0 & 0.50 \\ 0 & 1 & 1 & 0 & 0.25 & 0.25 \end{pmatrix} \quad (35)$$

$\bar{S} \qquad \qquad \bar{V}$

$$= \begin{pmatrix} 2.00 & 2.00 & 2.00 & 0.75 & 0.75 & 0.75 \\ 3.00 & 3.00 & 2.00 & 1.25 & 1.25 & 0.75 \\ 5.00 & 5.00 & 4.00 & 2.00 & 2.00 & 1.50 \\ 6.00 & 8.00 & 6.00 & 2.50 & 3.00 & 2.00 \\ 8.00 & 9.00 & 7.00 & 3.25 & 3.50 & 2.50 \\ 10.00 & 15.00 & 13.00 & 4.00 & 5.25 & 4.25 \\ 12.00 & 11.00 & 13.00 & 4.25 & 4.00 & 5.00 \\ 9.00 & 9.00 & 10.00 & 3.25 & 3.25 & 3.75 \\ 9.00 & 7.00 & 10.00 & 3.00 & 2.50 & 4.00 \\ 5.00 & 5.00 & 6.00 & 1.75 & 1.75 & 2.25 \\ 3.00 & 3.00 & 4.00 & 1.00 & 1.00 & 1.50 \\ 2.00 & 2.00 & 2.00 & 0.75 & 0.75 & 0.75 \end{pmatrix} \quad (36)$$

D

The covariance matrix

$$Z = D^T D = \begin{pmatrix} 582 & 622 & 634 & 216.75 & 226.75 & 232.75 \\ 622 & 697 & 685 & 234.75 & 253.5 & 247.5 \\ 634 & 685 & 703 & 235.5 & 248.25 & 257.25 \\ 216.75 & 234.75 & 235.5 & 81.1875 & 85.6875 & 86.0625 \\ 226.75 & 253.5 & 248.25 & 85.6875 & 92.375 & 89.75 \\ 232.75 & 247.5 & 257.25 & 86.0625 & 89.75 & 94.625 \end{pmatrix} \quad (37)$$

Now

$$S_m = DQ_m. \tag{38}$$

$$S_m = \begin{pmatrix} -3.69645 & -0.05013 & 0.14578 \\ -4.95704 & 0.47213 & 0.94462 \\ -8.65349 & 0.42200 & 1.09039 \\ -12.34785 & 1.61132 & 0.42917 \\ -14.82742 & 1.22766 & 1.30498 \\ -23.39140 & 2.51167 & -1.46939 \\ -22.13707 & -1.72893 & 0.15278 \\ -17.22165 & -0.77289 & -0.06996 \\ -15.96315 & -2.53459 & -0.06180 \\ -9.82875 & -0.67263 & -0.36152 \\ -6.13230 & -0.62251 & -0.50729 \\ -3.69645 & -0.05013 & 0.14578 \end{pmatrix} \tag{39}$$

and from eq. (30),

$$V_m = \begin{pmatrix} -0.50919 & -0.55529 & -0.56006 & -0.19035 & -0.20187 & -0.20426 \\ -0.36058 & 0.73809 & -0.40296 & 0.00741 & 0.28208 & -0.28845 \\ 0.68402 & -0.10698 & -0.62035 & 0.32068 & 0.12293 & -0.13375 \end{pmatrix}. \tag{40}$$

The transformation matrix T was obtained using the NAG-based routine F04AMF [40] to solve a series of m linear equations involving S_m and \bar{S} of the form

$$s_{i1} a_j + s_{i2} b_j + s_{i3} c_j = \bar{s}_{ij} \quad i = 1, \dots, nwave, \quad j = 1, \dots, m, \tag{41}$$

where a_j , b_j and c_j are constants giving the elements of T corresponding to t_{ij} , where $j = 1, \dots, m$.

$$\begin{pmatrix} s_{11} & s_{12} & s_{13} \\ s_{21} & s_{22} & s_{23} \\ \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots \\ s_{i1} & s_{i2} & s_{i3} \end{pmatrix} \begin{pmatrix} a_1 & a_2 & a_3 \\ b_1 & \cdot & \cdot \\ c_1 & \cdot & \cdot \end{pmatrix} = \begin{pmatrix} \bar{s}_{11} & \bar{s}_{12} & \bar{s}_{13} \\ \bar{s}_{21} & \bar{s}_{22} & \bar{s}_{23} \\ \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots \\ \bar{s}_{i1} & \bar{s}_{i2} & \bar{s}_{i3} \end{pmatrix}. \tag{41}$$

$S_m \qquad T \qquad \bar{S}$

The first column of \mathbf{T} would therefore be produced by

$$\begin{aligned} s_{11} a_1 + s_{12} b_1 + s_{13} c_1 &= \bar{s}_{11}, \\ s_{21} a_1 + s_{22} b_1 + s_{23} c_1 &= \bar{s}_{21}, \\ &\vdots \\ s_{i1} a_1 + s_{i2} b_1 + s_{i3} c_1 &= \bar{s}_{i1}, \quad i = 1, \dots, nwave. \end{aligned}$$

The unique transformation \mathbf{T} and its inverse \mathbf{T}^{-1} , derived from the NAG routine F01AAF and satisfying the factor equations, are given by

$$\mathbf{T} = \begin{pmatrix} -0.25221 & -0.25698 & -0.30308 \\ 0.39023 & -0.75082 & 0.34786 \\ 0.59869 & 0.08533 & -0.70568 \end{pmatrix} \quad (42)$$

and

$$\mathbf{T}^{-1} = \begin{pmatrix} -1.26060 & 0.52225 & 0.79885 \\ -1.21897 & -0.90592 & 0.07697 \\ -1.21688 & 0.33353 & -0.73003 \end{pmatrix}. \quad (43)$$

5.2. USING GENERAL TRANSFORMATION MATRIX \mathbf{T}

Using eq. (5)

$$\bar{\mathbf{S}} = \begin{pmatrix} 1 & 1 & 1 \\ 2 & 1 & 1 \\ 3 & 2 & 2 \\ 4 & 2 & 4 \\ 5 & 3 & 4 \\ 6 & 4 & 9 \\ 5 & 7 & 6 \\ 4 & 5 & 5 \\ 3 & 6 & 4 \\ 2 & 3 & 3 \\ 1 & 2 & 2 \\ 1 & 1 & 1 \end{pmatrix} \quad (44)$$

and from eq. (6)

$$\bar{\bar{\mathbf{V}}} = \begin{pmatrix} 1 & 1 & 0 & 0.50 & 0.50 & 0 \\ 1 & 0 & 1 & 0.25 & 0 & 0.50 \\ 0 & 1 & 1 & 0 & 0.25 & 0.25 \end{pmatrix}. \quad (45)$$

A comparison of eqs. (44) and (45) with (35) shows that, for perfect data, the factor solutions are equivalent to the true solutions. \mathbf{T} results in all positive entries for $\bar{\bar{\mathbf{S}}}$ and $\bar{\bar{\mathbf{V}}}$, i.e.

$$\bar{\bar{\mathbf{S}}} = \bar{\mathbf{S}}$$

and

$$\bar{\bar{\mathbf{V}}} = \bar{\mathbf{V}};$$

hence, eqs. (11) and (12) hold.

5.3. USING ROTATION \mathbf{R}

Since it has been established that a unique \mathbf{R} does not exist which satisfies eqs. (1) and (2), we must now consider what happens when a general 3D rotation is used where

$$\mathbf{R} = \begin{pmatrix} \cos \psi \cos \phi - \cos \theta \sin \phi \sin \psi & \cos \psi \sin \phi + \cos \theta \cos \phi \sin \psi & \sin \psi \sin \theta \\ -\sin \psi \cos \phi - \cos \theta \sin \phi \cos \psi & -\sin \psi \sin \phi + \cos \theta \cos \phi \cos \psi & \cos \psi \sin \theta \\ & \sin \theta \sin \phi & -\sin \theta \cos \phi & \cos \theta \end{pmatrix}. \quad (46)$$

The values assigned to the Euler angles ϕ , θ and ψ are completely arbitrary.

Example

Let $\phi = 45^\circ$, $\theta = 30^\circ$, $\psi = 45^\circ$.

$$\mathbf{R} = \begin{pmatrix} 0.06699 & 0.93302 & 0.35356 \\ -0.93302 & -0.06699 & 0.35356 \\ 0.35356 & -0.35356 & 0.86603 \end{pmatrix}. \quad (47)$$

Substituting eqs. (39) and (47) into eq. (1) gives

$$\bar{\mathbf{S}} = \begin{pmatrix} -0.14931 & -3.49705 & -1.19839 \\ -0.43860 & -4.99063 & -0.76762 \\ -0.58791 & -8.48767 & -1.96602 \\ -2.17884 & -11.78047 & -3.42433 \\ -1.67733 & -14.37791 & -3.67818 \\ -4.42995 & -21.47338 & -8.65477 \\ 0.18418 & -20.59252 & -8.30575 \\ -0.45729 & -15.99163 & -6.42274 \\ 1.27360 & -14.70230 & -6.59358 \\ -0.15867 & -8.99754 & -4.02596 \\ -0.00935 & -5.50050 & -2.82756 \\ -0.14931 & -3.49705 & -1.19839 \end{pmatrix}. \quad (48)$$

Now,

$$\mathbf{R}^{-1} = \begin{pmatrix} 0.06699 & -0.93300 & 0.35355 \\ 0.93300 & -0.06699 & -0.35355 \\ 0.35355 & 0.35355 & 0.86602 \end{pmatrix}. \quad (49)$$

Substituting eqs. (40) and (49) into eq. (2) gives

$$\bar{\mathbf{V}} = \begin{pmatrix} 0.54415 & -0.76366 & 0.11912 & 0.09371 & -0.23324 & 0.20815 \\ -0.69275 & -0.52971 & -0.27622 & -0.29147 & -0.25070 & -0.12396 \\ 0.28487 & -0.02802 & -0.87771 & 0.21304 & 0.13482 & -0.29003 \end{pmatrix}. \quad (50)$$

Other examples chosen were ($\phi = 30^\circ$, $\theta = 60^\circ$, $\psi = 60^\circ$) and ($\phi = 45^\circ$, $\theta = 60^\circ$, $\psi = 90^\circ$). On comparing the factor solutions given by eqs. (48) and (50) with eq. (35), it is immediately apparent that

$$\bar{\mathbf{S}} \neq \mathbf{S}_m \mathbf{R}$$

and

$$\bar{\mathbf{V}} \neq \mathbf{R}^{-1} \mathbf{V}_m.$$

The presence of substantial negative entries in $\bar{\mathbf{S}}$ and $\bar{\mathbf{V}}$ indicates that these are indeed not the true solutions. The latter have physical and chemical meaning and must therefore be positive. It follows that the use of \mathbf{R} in TFA will also result in solutions which do not resemble the true factors.

5.4. DEVELOPMENT OF NEW APPROACH

Muller and Steele [1,2] have successfully reduced the problem of finding a suitable transformation to one of software-controlled optimization of the $m(m-1)$ independent variables in a general transformation matrix \mathbf{T}' of m factors having the form

$$\mathbf{T}' = \mathbf{TK}, \quad (51)$$

with \mathbf{K} an arbitrary scaling matrix.

The approach of Muller and Steele can be more easily adapted for use at higher dimensions than previously possible using graphical representations. (See fig. 2. The symbol SFT indicates that the first stage of factor theory has been carried out, i.e. eigenanalysis and the determination of m factors.) The standard factor equations are given by

$$\bar{\mathbf{S}} = \mathbf{S}_m \mathbf{T}' \quad (52)$$

and

$$\bar{\mathbf{V}} = \mathbf{T}'^{-1} \mathbf{V}_m. \quad (53)$$

A full account of \mathbf{T}' and the constraints required to regenerate \mathbf{D} are given in refs. [1] and [2]. Additional background details on factor theory are to be found in an article by Muller [3].

5.5. MERITS OF NEW APPROACH

Let us now consider the advantages of such an approach.

- (1) Firstly, the computer-oriented nature of factor theory is reinforced since this method allows the intermediate transformation step to be carried out entirely under software control.
- (2) The input of the $m(m-1)$ variables of \mathbf{T}' is completely arbitrary (this is the *main* advantage). Optimization of these variables using the NAG-based routine E04FDF [40] is quick and efficient, and the resulting factor solutions, when chosen from the correct diagonal sign choices (see point (3) below), give good approximations to the true factors.
- (3) The arbitrary setting of the diagonal values of \mathbf{T}' to ± 1 provides a means of eliminating unsuitable solutions from the range of possible sign choices available, i.e. $(+++)$, $(++-)$, $(+--)$, etc. Unsuitable solutions are defined as those which contain large negative values (greater than experimental error), where $\text{FSUMSQ} \gg 0$. FSUMSQ is a measure of the success of the optimization process. Maximum optimization therefore occurs when FSUMSQ, which contains the sum of the squares of the negative terms

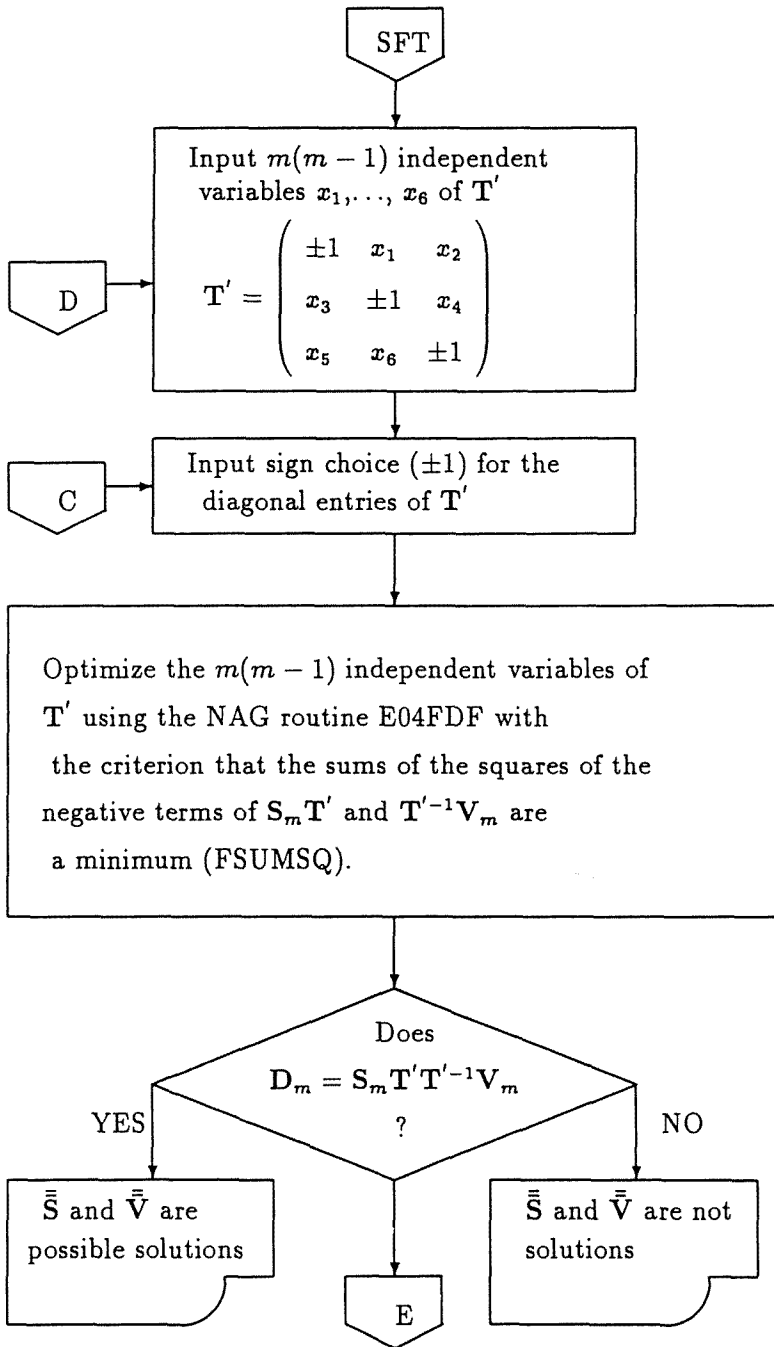


Fig. 2. (caption on next page).

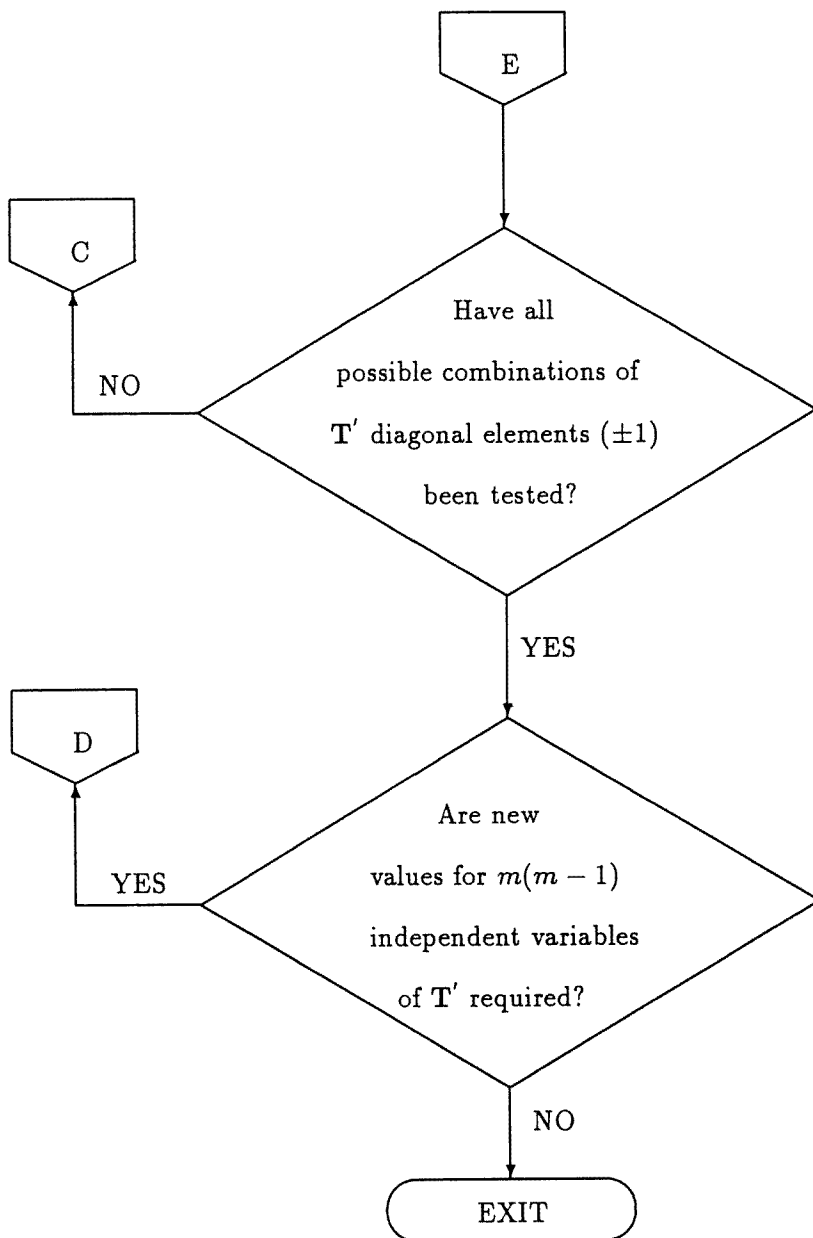


Fig. 2. Main steps in the recovery of the component spectra from the multicomponent experimental data matrix \mathbf{D} ($m = 3$ case).

in $S_m T'$ and $T'^{-1} V_m$, is a minimum. Now, the first primary eigenspectrum (by primary, one means the eigenspectra associated with the true components) will contain all positive or all negative values, depending on the sign on the first eigenvector. The factor solutions are to be found from among those whose sign for the first diagonal element corresponds to that for the first eigenspectrum. The best solution can then be determined from the value of FSUMSQ, i.e. the best solution is that closest to FSUMSQ = 0.

So far, no major disadvantages have been found.

6. Conclusion

Even from this very brief summary of the main factor rotational methods, it is at once apparent that many of the traditional approaches are extremely limited in their use. In practical terms, their generalization to higher factor space (above three) would not be feasible.

The use of an orthogonal rotation R in factor theory appears in general to be highly suspect. This is indeed born out in the literature by frequent references to unsatisfactory solutions. Perfect data (although not a good substitute for experimental data) provides a means of understanding the transformation step. It was concluded that under such circumstances, R results only in mathematical solutions.

Against this background, the application of a non-orthogonal transformation effected under computer control seems a very realistic alternative to the problem of finding a suitable transformation that will succeed in obtaining the primary components.

References

- [1] A. Muller and D. Steele, *Spectrochim. Acta* 46A(1990)817.
- [2] A. Muller and D. Steele, *Spectrochim. Acta* 46A(1990)1177.
- [3] A. Muller, to be published.
- [4] N. Ohta, *Anal. Chem.* 45(1973)553.
- [5] Z.Z. Hugus, Jr. and A.A. El-Awady, *J. Phys. Chem.* 75(1971)2954.
- [6] J.J. Kankare, *Anal. Chem.* 42(1970)1322.
- [7] P.C. Gillette, J.B. Lando and J.L. Koenig, *Anal. Chem.* 55(1983)630.
- [8] M.A. Sharaf and B.R. Kowalski, *Anal. Chem.* 53(1981)518.
- [9] M.A. Sharaf and B.R. Kowalski, *Anal. Chem.* 54(1982)1291.
- [10] D.W. Osten and B.R. Kowalski, *Anal. Chem.* 56(1984)991.
- [11] R.A. Gilbert, J.A. Llewellyn, W.E. Swartz and J.W. Palmer, *Appl. Spectrosc.* 36(1982)428.
- [12] P.J. Gemperline, *J. Chemometrics* 3(1989)549.
- [13] S.D. Brown, T.Q. Barber, R.J. Larivee, S.L. Monfre and H.R. Wilk, *Anal. Chem.* 60(1988)253R.
- [14] K.R. Beebe and B.R. Kowalski, *Anal. Chem.* 59(1987)1007A.
- [15] E.R. Malinowski and D.G. Howery, *Factor Analysis in Chemistry* (Wiley, UK, 1980).
- [16] B.F.J. Manly, *Multivariate Statistical Methods. A Primer* (Chapman and Hall, London, 1986).
- [17] R.W. Rozett and E.M. Petersen, *Anal. Chem.* 47(1975)1301.

- [18] F.J. Luk, *SIAM J. Sci. Stat. Comput.* 5(1984)764.
- [19] M. Forina, C. Armanino, S. Lanteri and R. Leardi, *J. Chemometrics* 3(1988)115.
- [20] C.G. Swain, H.E. Bryndza and M.S. Swain, *J. Chem. Inf. Comput. Sci.* 19(1979)19.
- [21] D.H. Lowenthal and K.A. Rahn, *Atm. Environ.* 21(1987)2005.
- [22] P.C. Gillette, J.B. Lando and J.L. Koenig, *Fourier Transform Infrared Spectroscopy (Application to Chemical Systems)*, Vol. 4, ed. J.R. Ferraro and L.J. Basile (Academic Press, New York, 1985).
- [23] P.H. Weiner, E.R. Malinowski and A.R. Levinstone, *J. Phys. Chem.* 74(1970)4537.
- [24] P.K. Hopke, D.J. Alpert and B.A. Roscoe, *Comput. Chem.* 7(1983)149.
- [25] B.A. Roscoe and P.K. Hopke, *Comput. Chem.* 5(1981)1.
- [26] E.R. Malinowski, *ASTM Special Technical Publication, Comp. Quant. IR Anal.* 934(1987)155.
- [27] E.R. Malinowski, *Anal. Chim. Acta* 103(1978)339.
- [28] M. McCue and E.R. Malinowski, *Appl. Spectrosc.* 37(1983)463.
- [29] E.R. Malinowski and M. McCue, *Anal. Chem.* 49(1977)284.
- [30] R.P. Gluch, *Amer. Lab (USA)* 14(1982)98.
- [31] C. Po Wang and T.L. Isenhour, *Appl. Spectrosc.* 41(1987)185.
- [32] M. Ruprecht and J.T. Clerc, *J. Chem. Inf. Comput. Sci.* 25(1985)241.
- [33] S.N. Deming and S.L. Morgan, *Anal. Chem.* 45(1973)278A.
- [34] H. Martens, *Anal. Chim. Acta* 112(1979)423.
- [35] D.J. Leggett, *Anal. Chem.* 49(1977)276.
- [36] O.S. Borgen and B.R. Kowalski, *Anal. Chim. Acta* 174(1985)1.
- [37] J. Chen and L. Hwang, *Anal. Chim. Acta* 133(1981)271.
- [38] B. Vandeginste, *Pure Appl. Chem.* 55(1983)2007.
- [39] B. Vandeginste, R. Essers, T. Bosman, J. Reijnen and G. Kateman, *Anal. Chem.* 57(1985)971.
- [40] Numerical Algorithms Group Ltd., Mayfield, 256 Banbury Road, Oxford OX2 7DE, UK.