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Spectral transformations for deconvolution methods applied on gas chromatography–mass spectrometry data

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Abstract

In hyphenated chromatography, overlapping chromatographic peaks can be resolved into pure spectra and pure chromatographic profiles by several multivariate deconvolution techniques. In general, these methods require bilinearity, which implies that the spectrum of each analyte is constant. The slow scan speeds normally used in gas chromatography–mass spectrometry (GC–MS) will destroy bilinearity and introduce systematic noise in the data because the concentration in the detector changes during the scan. This effect, described as the *scan effect*, may hinder successful resolution by multivariate deconvolution. In selected ion monitoring (SIM) GC–MS, the scan effect may be removed by simple transformations of the mass spectra. The effects of different transformations are demonstrated both on pure chromatographic peaks and on difficult resolution problems where there are small differences between the spectra of the analytes.

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1. Introduction

1.1. Basic theory

In the chromatographic analyses of complex samples complete resolution of all compounds can rarely be achieved. With the use of hyphenated chromatography, e.g. liquid chromatography with diode array detection (LC–DAD) and gas chromatography–mass spectrometry (GC–MS) several methods that use spectral information for resolution of overlapping chromatographic peaks have been developed. The basic idea of these methods is to decompose the raw data matrix X into matrices containing pure spectra, S^T , in row vectors and pure chromatographic profiles, C , in

column vectors.

$$X = CS^T + E \quad (1)$$

X has the dimension $N \times M$, C has the dimension $N \times A$ and S^T has the dimension $A \times M$.

N is the number of data points in the chromatographic profile (number of spectra measured) and M is the dimension of the spectra (number of wavelengths or masses). A is the number of analytes in the peak cluster and can be estimated by several methods described elsewhere [1–7]. E is the error matrix, which has the same dimension as X . Each analyte in the system is represented by a column vector c describing the chromatographic profile and a row vector s^T describing the spectrum, thus Eq. (1) can be rewritten as:

$$X = \sum_{a=1}^A c_a s_a^T + E \quad (2)$$

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Assuming that E is small enough to be neglected, estimates of C can be found from estimates of S by the following formula:

$$C = XS(S^T S)^{-1} \quad (3)$$

Similarly, estimates of S^T can be found from estimates of C :

$$S^T = (C^T C)^{-1} C^T X \quad (4)$$

The estimates of C and S^T can be achieved by several approaches, which roughly can be divided into direct and iterative methods. In the direct methods, the pattern of peak overlap is usually analysed by evolving factor analysis (EFA) [8,9] or modifications of EFA such as the fixed size moving window (FSMW–EFA) [10] or eigenstructure tracking analysis (ETA) [11]. Other methods such as latent projective graphs (LPG) [12] may also be applied. The overlap pattern reveals where pure spectra or chromatographic profiles can be found, and complete resolutions can often be achieved by the application of Eq. (3) or (4) or by using information from zero concentration windows to find estimates for C and S^T . This can be done by rotating the scores and loadings from principal component analysis (PCA) into estimates of C and S^T :

$$CS^T = TRR^{-1}P^T \quad (5)$$

R is a $A \times A$ rotation matrix, T is the PCA score values and has the same dimension as C . P^T is the PCA loading values with the same dimensions as S^T . Different procedures for finding R are described and compared elsewhere [8,9,12–14].

In the iterative methods, initial estimates of C or S^T are refined in a repetitive manner until a convergence criterion is met. The Eqs. (3)–(5) are usually involved in one or several steps in the procedure. Good initial estimates, which can be found by several methods [4,5,15–18], are critical. The initial estimates are refined by applying constraints on the estimates of C and S^T . Common constraints are positivity in C and S^T , and unimodality in C , *i.e.* each chromatographic peak in C has only one maximum. Common iterative procedures are alternating regression (AR) [19], also called alternating least squares (ALS), iterative target transformation analysis (ITTFA) [20] and GENTLE [21].

1.2. The scanning problem

The various methods mentioned earlier have one thing in common. They all depend on the validity of Eq. (1). As can be seen from Eq. (2), this implies that each analyte must be explained by a single chromatographic vector, c , and a single spectral vector, s^T . Any deviations from this attribute may severely limit the chances of successful resolution. A common source of deviations is non-linear detector response. Another source of error appear with scanning detectors, *i.e.* detectors where the signals (wavenumbers in DAD, masses in MS) in the spectrum are not recorded simultaneously. The concentration in the detector changes during a scan. The last signals recorded in the spectrum will therefore be overestimated relative to the first signals recorded when the detector concentration is increasing. Similarly the pattern is reversed in when the detector concentration is decreasing during the scan. This source of error will be referred to as the *scan effect* in the remainder of the article.

The problems caused by the scan effect have been thoroughly discussed by others, especially related to the assessment of peak purity in HPLC–DAD analyses [22–24]. The scan effect is usually much larger in GC–MS than in HPLC–DAD. Because the number of scans per peak is typically lower in GC–MS than in HPLC–DAD, the relative concentration change from scan to scan and is higher in GC–MS.

The *scan time* is defined as the time lag between the start of one scan and the start of the next scan. Typical scan times for HPLC–DAD are in the range 10–50 ms [22,24]. With typical peak widths of 30 s, at least several hundred spectra are recorded for each chromatographic peak. In GC–MS typical scan times are higher and the peak widths narrower. A typical scan rate for a quadrupole or magnetic sector instrument is 10–20 scans per peak. Although the scan rate can usually be increased, this may lead to a significant drop in signal-to-noise ratio (see Section 3). In this context, it should be mentioned that there are GC–MS detectors where the scan effect is absent, *i.e.* the time-of-flight mass spectrometers where all ions enters the flight zone simultaneously in pulses.

For the remainder of the article, spectra will generally be referred to as mass spectra, even though parts of the discussion is valid also for other kinds of hyphenated chromatography.

1.3. Corrections in the time domain

A principle for correction of the scan effect by transformations in the time domain has been proposed [22,25]. The difference in signal abundance, as a function of time for a specific ion in a spectrum, is calculated by interpolation with the signal in the next recorded spectrum. If the time lag between the detection of each ion in the spectrum is known, the signals may be corrected as if all ions were recorded simultaneously. Details are given in the references above.

This method has several possible drawbacks. One is that the shape of the concentration profile cannot be accurately modelled by linear interpolation. It has been proposed to use a second-order interpolation from three consecutive spectra to reduce this problem [23]. A second problem is that the correction procedure does not distinguish between differences caused by the scan effect and differences caused by the presence of a second eluent in the spectrum, consequently the procedure may correct for changes that are not caused by the scan effect.

A third problem is that details about the data acquisition that are not always available must be known. The time lag between the last ion in one scan and the first ion in the next scan (*inter-scan time lag*) is usually larger than the time lag between the ions within a scan (*inter-ion time lag*). If this difference is large it should be corrected for to achieve maximum accuracy.

1.4. Corrections in the spectral domain

Contrary to most other types of spectra, mass spectra are non-continuous, meaning that two consecutive masses are independent of each other. In this feature lies the key to corrections of the scan effect by transformations of the mass spectra. Two consecutive masses in the mass spectrum are measured almost simultaneously; the scan effect has therefore limited influence on the ratio of these masses. Since a mass spectrum is non-continuous, it can be expressed as ratios of consecutive masses without loss of information, but the scan effect is removed or significantly reduced. A similar transformation on a continuous spectrum would just remove most of the signal.

In this work, the effect of transformations to ratio spectra is investigated both on pure peaks and on resolution problems. The effect of the transformations is

demonstrated on resolution of overlapping peaks with very similar mass spectra.

2. Materials and methods

2.1. Analytical

cis isomers of methyl esters of 9-octadecenoic acid (9–18:1), 11-octadecenoic acid (11–18:1), 9,12,15-octadecatrienoic acid (9,12,15–18:3), 11,14,17-eicosatrienoic acid (11,14,17–20:3) and 5,8,11,14-eicosatetraenoic acid (5,8,11,14–20:4) >99% pure, were purchased from Nu-Chek Prep (Elysian, MN). *trans* isomers of 9,12,15–18:3 were produced as described elsewhere [26]. All samples were dissolved in isoocane (HPLC grade).

All analyses were performed on a 5890 series II gas chromatograph equipped with electronic pressure control and a 5972 mass spectrometer (Agilent Technologies, Palo Alto, CA). The system was controlled by the MS-Chemstation software G1034C. Helium, 99.996% pure, was used as carrier gas. All analyses were performed using selected ion monitoring (SIM), six ions were recorded. Different analytical conditions are described below as Programs 1–5.

Program 1: This was applied for studies of a pure compound. Analyses were performed on a HP-1 MS capillary column (Agilent Technologies), $L = 30$ m, i.d. = 0.25 mm, $d_f = 1$ μ m. Approximately 25 ng 11–18:1 FAME (0.5 μ l) were injected (splitless) at an oven temperature of 60 °C. After 3 min the temperature was increased by 50 °C/min to 250 °C, thereafter by 2 °C/min to 270 °C. Injection temperature was 290 °C, MS transfer line temperature was 280 °C. The column head pressure was increased with the oven temperature to give an estimated column flow of 29.4 cm/s. Masses of 55, 57, 69, 74, 81, and 84 amu were recorded. The *dwell time*, the time the mass spectrometer records a certain ion before it proceeds to the next ion, was varied from 25 to 100 ms.

The resolution problems was investigated using a BPX-70 column (Programs 2–5), $L = 60$ m, i.d. = 0.25 mm, $d_f = 0.25$ μ m (SGE, Ringwood, Australia). Injector and MS transfer line temperatures were 250 °C. Different programs were used.

Program 2: Samples (0.5 μ l) were injected (splitless) at an oven temperature of 60 °C. After 4 min the

temperature was increased by 30 °C/min to 190 °C, thereafter by 4 °C/min to 260 °C. The column head pressure was 92 kPa. Recorded ions were 55, 57, 69, 74, 81, and 84 amu. Dwell time was 50 ms.

Program 3: Samples (1 µl) were injected (splitless) at an oven temperature of 60 °C. After 4 min the temperature was increased by 30 °C/min to 230 °C, where the temperature was held for 20 min. Column flow was increased with oven temperature to give an estimated flow of 15.9 cm/s. MS parameters were identical to Program 2.

Program 4: Samples (0.5 µl) were injected (splitless) at an oven temperature of 60 °C. After 4 min the temperature was increased by 30 °C/min to 180 °C, thereafter by 3 °C/min to 240 °C. The column head pressure was 92 kPa. Recorded ions were 55, 67, 74, 79, 80, and 91 amu. Dwell time was 50 ms.

Program 5: GC parameters identical to Program 3. Recorded ions were 55, 67, 79, 80, 91, and 95 amu. Dwell time was 50 ms.

2.2. Determination of MS scan parameters

The time lag between the recording of each ion (*inter-ion time lag*) and between the last ion recorded in a scan and the first ion recorded in the next scan (*inter-scan time lag*) was determined by the following procedure: The scan time was measured for different SIM programs where the number of ions recorded was gradually reduced from eight to one. Every fifth ion from 50 to 85 amu was recorded. When the dwell times are known, the inter-ion time lag and inter-scan time lag can be estimated from the scan times by linear regression. The experiment was performed both with dwell times of 25 and 50 ms. In both cases, the inter-ion time lag and the inter-scan time lag were measured to 14 and 60 ms, respectively.

2.3. Transformations

The following transformations were applied on the mass spectra:

- Transformation A: The abundance of each ion was divided by the abundance of the ion recorded immediately after. The abundance of the last ion in a scan was set to 1 (equal to division by itself).
- Transformation B: The abundance of each ion was divided by the abundance of the ion recorded im-

mediately before. The abundance of the first ion in a scan was set to 1 (equal to division by itself).

- Transformation C: The abundance of each ion was divided by the abundance of the ion recorded immediately after. The abundance of the last ion in a scan was divided by the abundance of the first ion in the next scan.
- Transformation D: The abundance of each ion was divided by the abundance of the ion recorded immediately before. The abundance of the first ion in a scan was divided by the abundance of the last ion in the scan before.
- Transformation E: Transformation in the time domain using first-order interpolation according to reference [22].
- Transformation F: Transformation in the time domain using second-order interpolation according to reference [23].

In transformations A–D the new spectrum was normalised after the transformation to have the same sum of signal abundances as the untransformed spectrum.

2.4. Software

All transformations were performed in Matlab 5.3 (MathWorks, Natick, MA). PCA was performed in Unscrambler 7.5 (CAMO, Oslo, Norway), LPG and GENTLE was performed in Xtricator 2.0 (Pattern Recognition Systems, Bergen, Norway).

3. Results and discussion

3.1. Effects on a pure peak

The results of the scan effect on a pure compound (11–18:1) can be seen in Fig. 1, where the spectrum at the peak apex is compared to spectra recorded at increasing and decreasing detector concentration. The locations of these spectra are illustrated in Fig. 2. There is a significant difference between the spectra, especially for the first and last ions in the scan. From Fig. 1 it can be seen that the 5972 mass spectrometer scans from the highest to the lowest mass; of the three spectra m/z 55 is highest and m/z 84 is lowest in the spectrum recorded with increasing concentration in the detector.

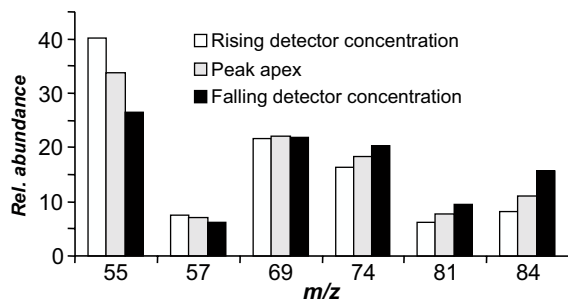


Fig. 1. SIM spectra of a pure peak (11–18:1 fatty acid methyl ester) recorded with a dwell time of 100 ms. Chromatographic conditions are described as Program 1 in Section 2. The sum of abundances is normalised to 100.

In theory, if PCA is performed on a pure peak free of noise the first principal component (PC1) should explain 100% of the variance. PCA on a pure peak may therefore be used to measure the noise in the system. The variance that is not explained by PC1 may be regarded as noise. The patterns of the scores and loading may reveal information about the type and source of noise. PCA was performed on the pure peak with the spectra collected at different retention times as objects and the different masses as variables. The dwell times were 100 ms. The score values of the three first principal components are given in Fig. 2.

PC1 describes the peak profile. The profile of PC2 looks like the first derivative of PC1. This is typical for the scan effect and has also been reported by others [24]. The spectra seen in Fig. 1 are collected at the retention times with the most extreme scores on PC2. It can be seen from the explained variance that PC2 explains 99% of the variance that is not explained by PC1. Thus, the scan effect is totally dominating as noise source in this system. PC3 looks like a second derivative of PC1. This is a pattern that can be caused by non-linearities in the detector response, but it may also be caused by other sources [24]. PC3 will show this pattern when PCA is performed on simulated data with the scan effect as the only source of noise, thus PC3 may also explain noise caused by the scan effect.

The effects of different dwell times and transformations are shown in Table 1. For the untransformed data, it can be seen that the unexplained variance after the extraction of PC1 is decreasing with decreasing dwell times. It can also be seen that PC2 explains most of the remaining variance. For all dwell times,

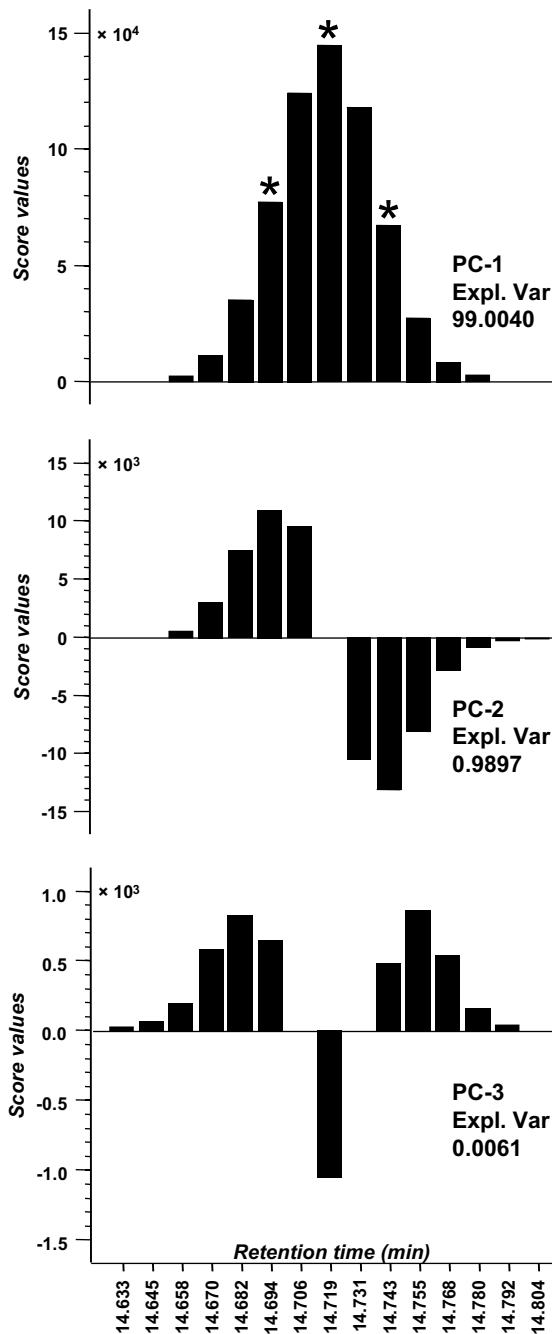


Fig. 2. PCA scores of a pure peak (11–18:1 fatty acid methyl ester) recorded with a dwell time of 100 ms. Chromatographic conditions are described as Program 1 in Section 2. The asterisks mark where the spectra in Fig. 1 were collected. Expl. var. is percent of total variance explained.

Table 1
PCA on datasets of a pure peak (11–18:1). Percent of total variation that is unexplained (residual variance) after extraction of one, two and three principal components (PC). Different dwell times and transformations are compared. The transformations are described in Section 2

PC number	Dwell time		
	100 ms	50 ms	25 ms
Untransformed			
1	0.9960	0.3366	0.1333
2	0.0063	0.0010	0.0006
3	0.0002	0.0002	0.0001
Transformation A			
1	0.0330	0.0127	0.0058
2	0.0019	0.0011	0.0011
3	0.0003	0.0002	0.0002
Transformation B			
1	0.0131	0.0050	0.0024
2	0.0008	0.0009	0.0006
3	0.0003	0.0003	0.0002
Transformation C			
1	0.0171	0.0161	0.0166
2	0.0013	0.0010	0.0009
3	0.0002	0.0001	0.0001
Transformation D			
1	0.0017	0.0016	0.0012
2	0.0006	0.0008	0.0006
3	0.0002	0.0002	0.0002
Transformation E			
1	0.2983	0.0491	0.0123
2	0.0041	0.0013	0.0005
3	0.0002	0.0003	0.0002
Transformation F			
1	0.2905	0.0456	0.0109
2	0.0016	0.0008	0.0004
3	0.0003	0.0002	0.0001

the scores of PC2 showed the same pattern as in Fig. 2, indicating that although the scan effect is significantly reduced by reduction of the dwell times, it is still the major source of noise in the data. For the dwell times of 50 and 25 ms PC3 did not show any clear pattern as seen for PC3 in Fig. 2. The importance of PC3 is also significantly lower at 50 and 25 ms.

The data in Table 1 indicate that the dwell time should be as short as possible. However, reduction of the dwell times gives significant reduction of the signal. The inter-ion and inter-scan time lags are independent of the dwell time. When six ions are monitored, the mass spectrometer is not acquiring signals for

130 ms per scan. With a dwell time of 10 ms the mass spectrometer is only acquiring data for 32% of the total scan time. With a dwell time of 100 ms this is increased to 82%.

The effects of the different transformations are also shown in Table 1. In transformations C and D, all ions are divided by the ion scanned immediately before or after. In theory, transformations C and D should be the ideal transformations if the inter-scan time lag is similar to the inter-ion time lags or small compared to the dwell times. If transformations C and D is performed on simulated data with the scan effect as the only source of noise, it removes the scan effect completely when the inter-scan time lag is equal to the inter-ion time lag. Increased inter-scan time lags leads to reduced performance of these transformations. Transformations A and B is always non-ideal, but may perform better than C and D with large inter-scan time lags or low dwell times.

By using the variance explained by PC1 as measure of performance, these effects can be seen by comparing transformations A and C. At 100 ms dwell time (high dwell time compared to inter-scan time lag) transformation C performs better than transformation A. The performance is approximately equal at 50 ms dwell time, and A is clearly better than C at 25 ms dwell time. Transformations B and D does not show the same pattern. D is always better than A, but the differences are small at the two shortest dwell times. After application of transformation D, the scan effect was no longer visible in the score plot patterns.

The reason why transformation D always perform better than transformation C, and transformation B always perform better than transformation A is possibly related to the directions of the transformations. Weak signals often have lower signal-to-noise ratios than strong signals. If a strong signal is divided by a weak noisy signal, the result is a strong signal with large amount of noise. The noise in the dataset may, therefore, be increased by these transformations. This may be a problem in full-scan spectra where all masses in a certain range are recorded. In full-scan spectra, there are usually a lot of masses that will only contain noise. Solutions for full-scan spectra may be to divide by a range of signals, *e.g.* the divisor in the transformation may be the sum of the 10 masses recorded before the dividend. Other solutions may be different weighting procedures or removal of ions with high residuals

after PCA. So far these issues has not been thoroughly pursued.

3.2. Application to curve resolution problems

The effect of the transformations can be investigated by use of LPG on two resolved peaks with sim-

ilar spectra. In theory, a pure chromatographic peak will produce a straight line in the LPG if no noise is present. Two monounsaturated FAMES, 11–18:1 and 9–18:1 are compared in Fig. 3. At the conditions applied (Program 2), the peaks are chromatographically separated (chromatographic resolution $R_s = 1.27$). The untransformed data are projected as two lobes

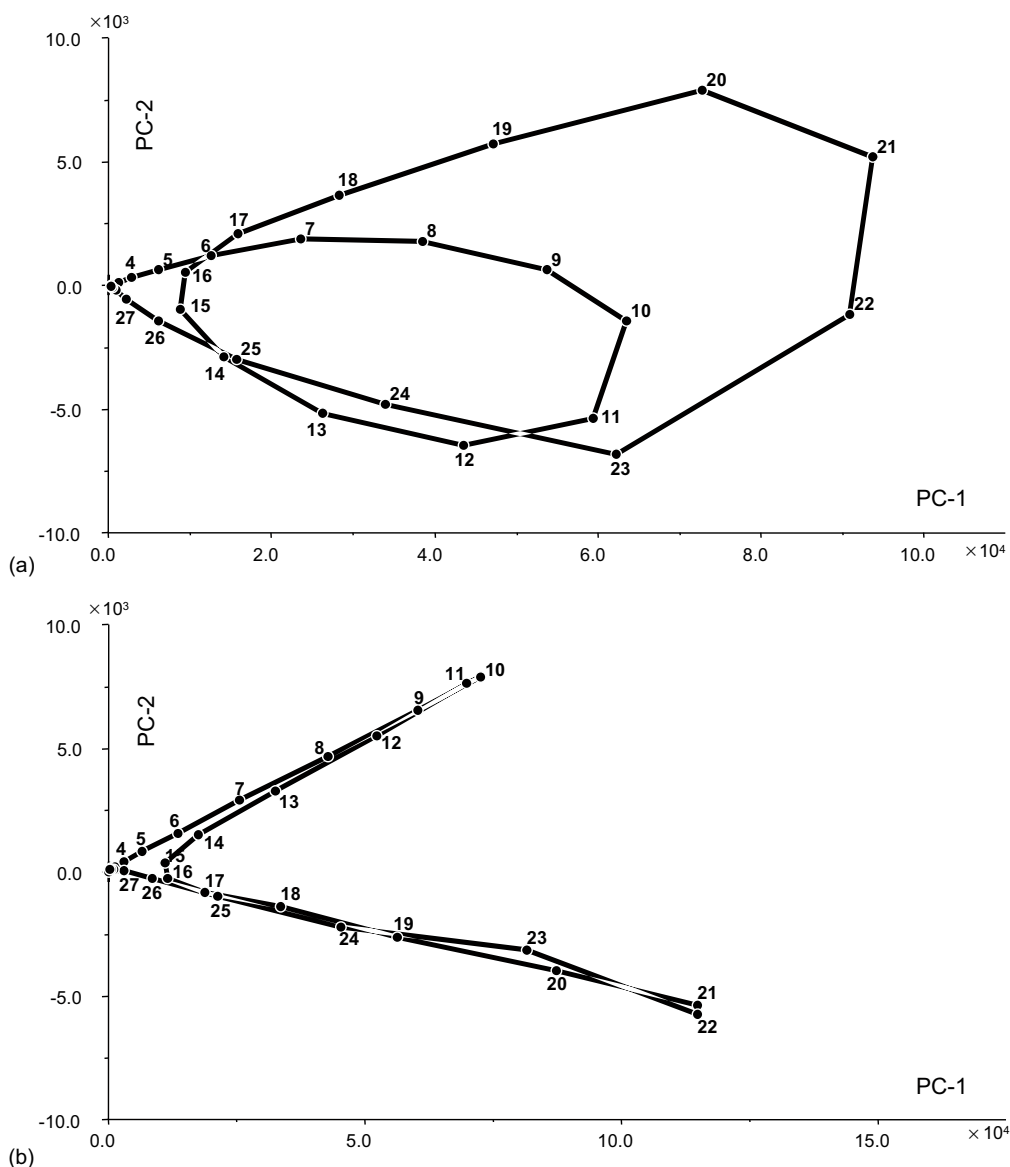


Fig. 3. LPG plots (time domain) of 9–18:1 and 11–18:1 fatty acid methyl esters. Resolution $R_s = 1.27$. Chromatographic conditions are described as Program 1 in Section 2. (a) Untransformed data, (b) data transformed with transformation D described in Section 2.

that are nearly completely overlapping (Fig. 3a). This shows that the scan effect is larger than the spectral difference between the analytes and that resolution of overlapping peaks would not be possible. After application of transformation D, the data are projected as two well separated straight lines (Fig. 3b) illustrating that the scan effect has been removed.

GENTLE was chosen as deconvolution method because it does not force unimodality on the chromatographic profiles [21]. In the presence of a strong scan

effect, unimodality constraints on the chromatographic profiles may produce solutions that looks good because each chromatographic peak have only one maximum. But the results are often inaccurate and the variance in the residual matrix E is often high because X cannot be properly explained under these constraints. With the application of GENTLE, it is easier to observe the influence of the scan effect from the deconvoluted profiles. The initial estimates of S^T were calculated by the simplified Borgen method [18].

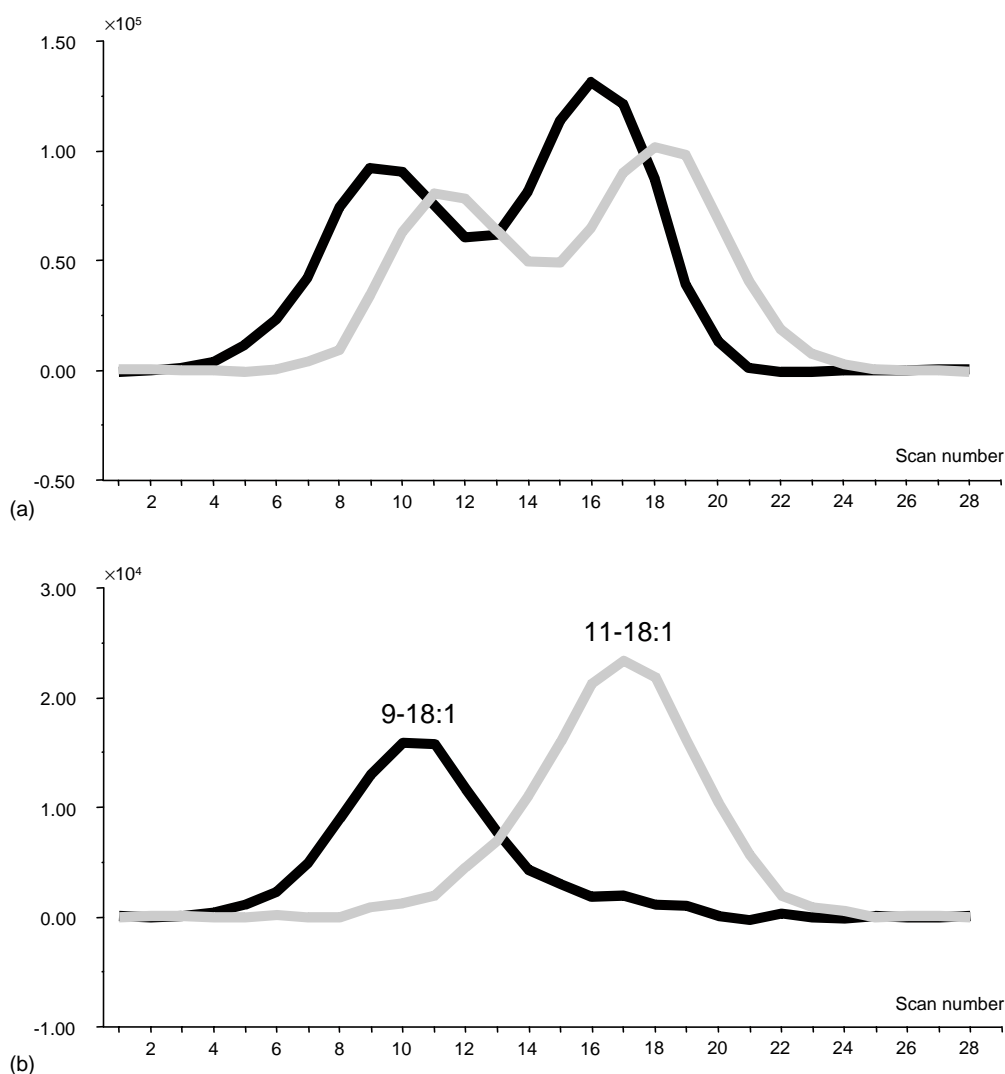


Fig. 4. The results of GENTLE applied to the resolution of 9-18:1 and 11-18:1 fatty acid methyl esters. (a) Untransformed data, (b) data transformed with transformation D described in Section 2; $R_s = 0.68$.

Since the deconvolutions were performed on reference mixtures with known composition, it was not necessary to estimate the number of analytes A .

The two monounsaturated FAMES 11–18:1 and 9–18:1 overlap more severely ($R_s = 0.68$) under the chromatographic conditions applied in Program 3 than in Program 2. The effect of transformation D on the resolution of the two peaks is shown in Fig. 4. The untransformed data are not resolved and the two chromatographic profiles explain the scan effect in-

stead of the differences between the two compounds. The transformed dataset is resolved into two Gaussian peaks. Integration of the two peaks gave areas of 41.4 and 58.5%. Integration of the two corresponding peaks analysed by Program 2 (chromatographic resolution) gave corresponding areas of 43.7 and 56.3%.

Another difficult resolution problem is illustrated in Fig. 5, where a small amount (20%) of 11,14,17–20:3 elutes under a larger amount (80%) 5,8,11,4–20:4. The isomers were analysed at conditions described as

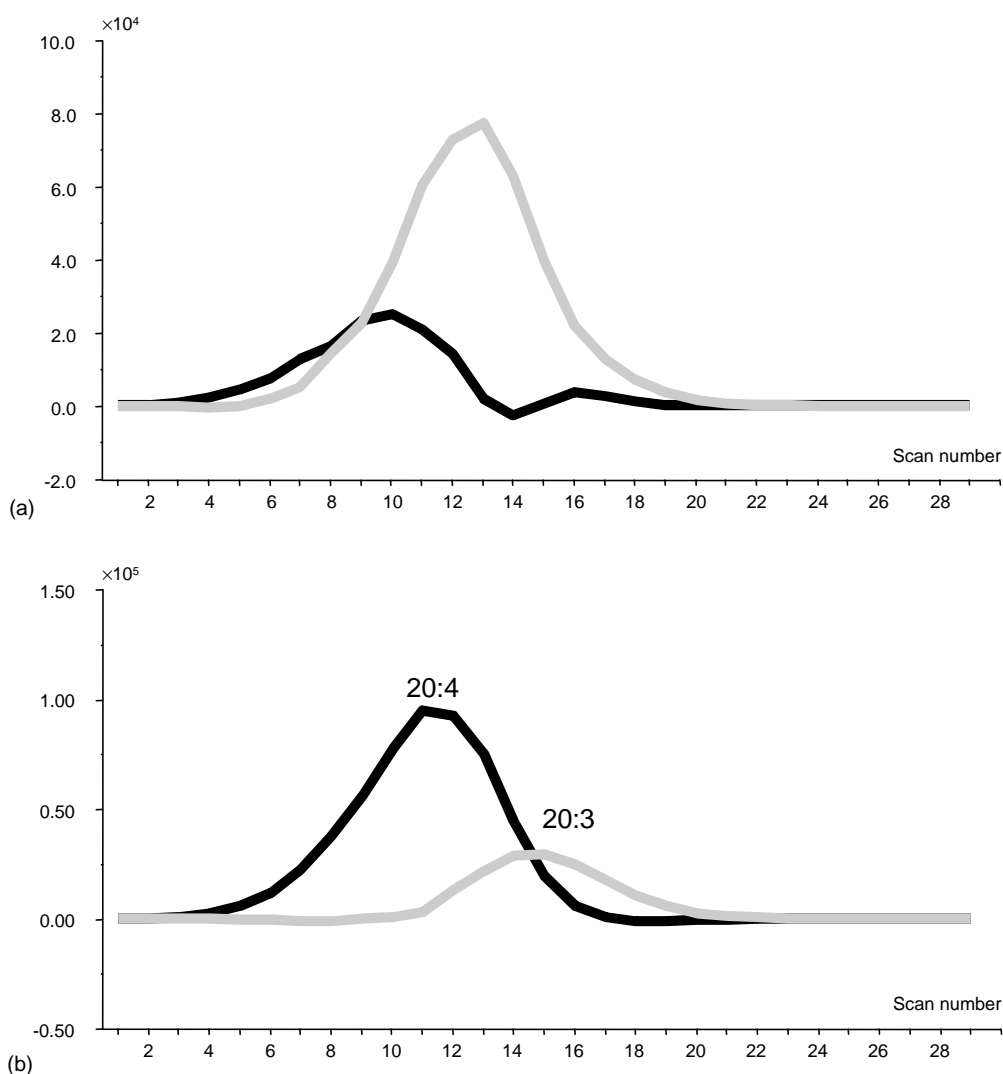


Fig. 5. The results of GENTLE applied to the resolution of 5,8,11,14–20:4 (80%) and 11,14,17–20:3 (20%) fatty acid methyl esters. (a) Untransformed data, (b) data transformed with transformation D described in Section 2; $R_s = 0.29$.

Program 4 in Section 2. The 20:3 isomer is the last eluting compound [26]. The difference between these two spectra is larger than the difference between the spectra in the previous example, but because there is a large difference in peak size, the variance introduced by the scan effect of the larger peak will dominate the dataset and hinder proper resolution. The result of GENTLE applied to the untransformed dataset is shown in Fig. 5a. GENTLE applied to the dataset after

transformation D is shown in Fig. 5b. The appearance of the smaller peak in front of the larger peak in Fig. 5a is an incorrect solution. The profile of the smaller peak is also bimodal. Resolution of the transformed data (Fig. 5b) shows the small peak at the expected position. Integration of the two peaks gave areas of 78 and 22%. Investigation of the spectra of the resolved profiles also confirmed that resolution in Fig. 5a fails because of the scan effect, while the spectra after the

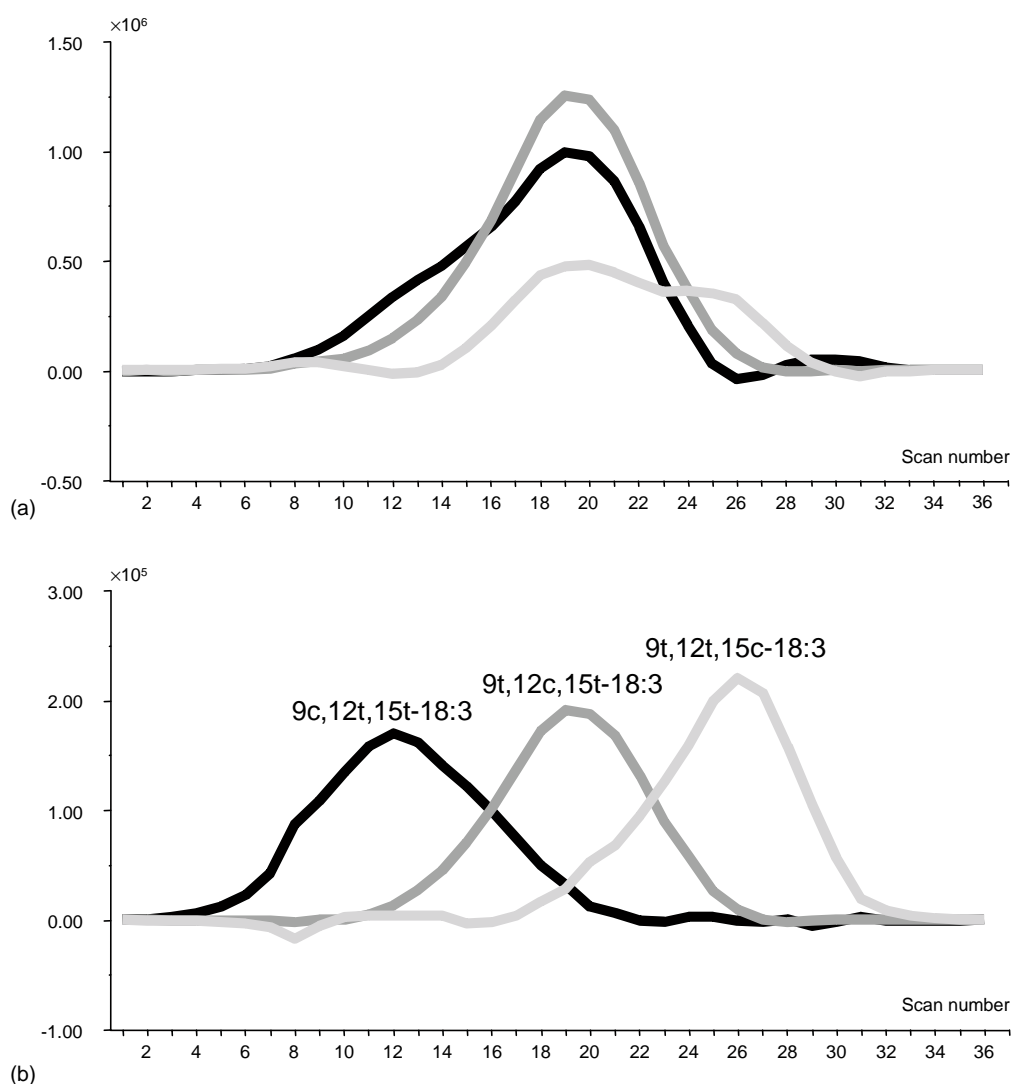


Fig. 6. The results of GENTLE applied to the resolution of *trans* isomers of 9,12,15–18:3 fatty acid methyl esters. (a) Untransformed data, (b) data transformed with transformation D described in Section 2. R_s (left/central peak) = 0.51, R_s (central/right peak) = 0.54.

resolution in Fig. 5b resemble the differences in the spectra of the pure peaks.

The last example is resolution problem with three analytes. The three isomers of 9,12,15–18:3 containing one *cis* and two *trans* double bonds were analysed at the conditions described as Program 5 in Section 2. The mixture was produced as described elsewhere [26]. The exact composition is not known, but since the double bond positions do not influence the isomerisation rate [27], the three isomers are expected to be present at approximately in equal amounts. These three isomers differ only by the geometries of the double bonds. Consequently, there are only small differences in the mass spectra, and especially the spectra of the 9-*cis* and 15-*cis* isomers are very similar [26]. Still resolution was possible after transformation of the data (Fig. 6b), while resolution of the untransformed data failed completely (Fig. 6a). In the case of the untransformed data, GENTLE could not converge to a solution without negative values in the spectra.

The two transformations in the time domain, transformations E and F, was also applied to the resolution problems described above. LPGs of the dataset applied in Fig. 3 indicated a significant improvement in the data structure, but the transformations were less efficient than the transformations in the spectral direction. The two peaks were still expressed as two lobes, but there was no overlap between the lobes as seen with untransformed data (Fig. 3a). None of the resolution problems in Figs. 4–6 could be resolved after application of transformation E or F.

4. Conclusions

With scanning mass spectrometers the slow scan speeds will introduce systematic noise in the data. This effect may hinder resolution of overlapping chromatographic peaks by methods frequently applied for deconvolution in hyphenated chromatography. With SIM GC–MS resolution of compounds with very similar spectra is possible after removal of the scan effect by simple spectral transformations. The proposed transformations are suitable for non-continuous spectra, e.g. mass spectra or signals from multi-detector instruments.

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