Talanta 85 (2011) 835–849

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Review

Recent trends in application of multivariate curve resolution approaches for improving gas chromatography–mass spectrometry analysis of essential oils

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ARTICLE INFO

Article history:
Received 6 March 2011
Received in revised form 15 May 2011
Accepted 18 May 2011
Available online 27 May 2011

Keywords:
Chemometrics
Multivariate curve resolution
Essential oil
Gas chromatography–mass spectrometry

ABSTRACT

Essential oils (EOs) are valuable natural products that are popular nowadays in the world due to their effects on the health conditions of human beings and their role in preventing and curing diseases. In addition, EOs have a broad range of applications in foods, perfumes, cosmetics and human nutrition. Among different techniques for analysis of EOs, gas chromatography–mass spectrometry (GC–MS) is the most important one in recent years. However, there are some fundamental problems in GC–MS analysis including baseline drift, spectral background, noise, low S/N (signal to noise) ratio, changes in the peak shapes and co-elution. Multivariate curve resolution (MCR) approaches cope with ongoing challenges and are able to handle these problems. This review focuses on the application of MCR techniques for improving GC–MS analysis of EOs published between January 2000 and December 2010. In the first part, the importance of EOs in human life and their relevance in analytical chemistry is discussed. In the second part, an insight into some basics needed to understand prospects and limitations of the MCR techniques are given. In the third part, the significance of the combination of the MCR approaches with GC–MS analysis of EOs is highlighted. Furthermore, the commonly used algorithms for preprocessing, chemical rank determination, local rank analysis and multivariate resolution in the field of EOs analysis are reviewed.

Contents

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doi:10.1016/j.talanta.2011.05.045

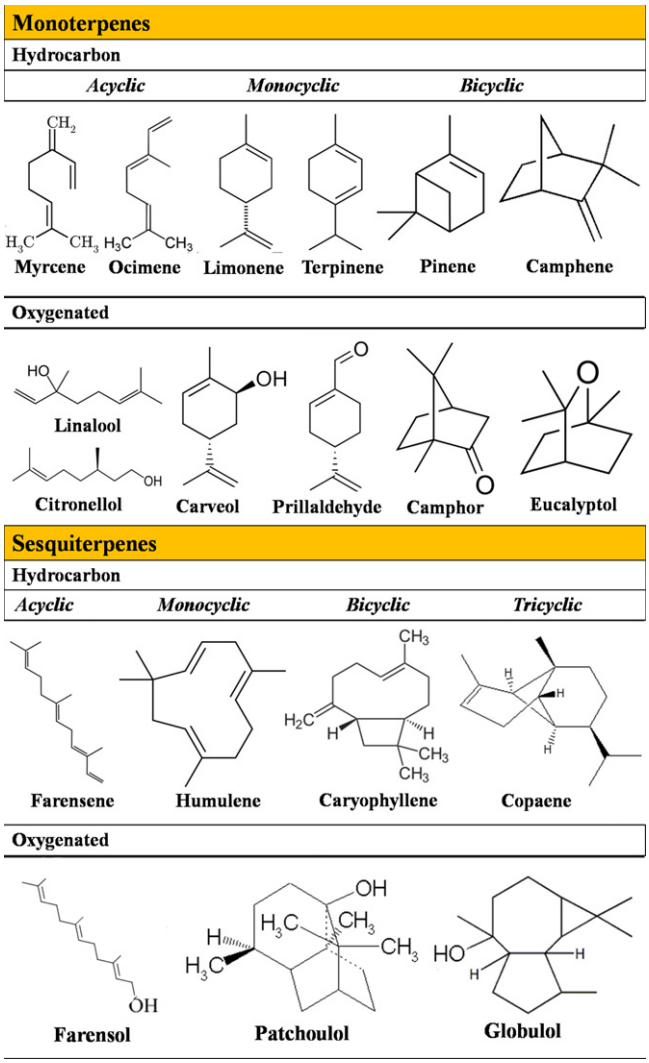

Fig. 1. Classification and chemical structure of some monoterpenes and sesquiterpenes.

1. Introduction

1.1. Composition and uses of essential oils

Essential oils (EOs) are natural, complex and multi-component mixtures of volatile organic compounds produced as secondary metabolites in plants. They can be obtained from different parts of plants including flowers, buds, seeds, leaves, twigs, bark, herbs, fruits and roots. It is believed that the term 'essential oil' is derived from the effective component of a drug "Quinta essentia" [1]. In general, the effective components of EOs can be classified into two groups. The first group is the volatile fraction of the oil and mainly composed of monoterpenes (hydrocarbons and oxygenated derivatives), sesquiterpenes (hydrocarbons and oxygenated derivatives), aliphatic aldehydes, alcohols and esters. The second group is the nonvolatile fraction and contains hydrocarbons, fatty acids, sterols, carotenoids, waxes, coumarins, psoralens and flavonoids [2]. It must be pointed out that the volatile compounds are the main fraction of the oil and composed the majority of it. Fig. 1 categorizes the volatile fraction of EOs and shows some examples for each category.

Up to now, approximately, 3000 EOs are identified, from which 10% are commercially important [1]. These valuable natural products can be used in many fields, including perfumes, cosmetics, foods, human nutrition, and pharmaceuticals. From the pharmaceutical point of view, it has been shown that EOs exhibit anticancer, antibacterial, antiviral, antitoxigenic, antiparasitic and antisecticidals properties [3]. Several excellent reviews have been published about the EOs and their biological activities [1,3–5].

The composition of EOs may vary considerably between plant species and varieties, and within the same variety but with different climates, seasonal and geographic conditions and harvest periods. In addition, the composition of EOs from different parts of the same plant can also vary widely. Considering all the aforementioned differences in EOs composition, it is clear that only a detailed knowledge of constitutes of an EO will lead to a proper application of its components. However, such a detailed knowledge can only be obtained by means of applying suitable extraction techniques and carefully performed chromatographic analysis.

1.2. Extraction and GC–MS analysis of EOs

Several techniques have been used to extract EOs from different parts of the aromatic plants. These techniques can be classified into three groups of discontinuous, continuous and hybrid approaches [2]. The discontinuous techniques include the use of either organic solvents or water. Extraction with organic solvents can be accelerated with ultrasounds [6]. In addition, steam distillation, hydrodistillation and vacuum distillation are among continuous methods. Some methods have been reported involving both continuous and discontinuous approaches, such as micro-simultaneous distillation extraction (MSDE) [7] and Soxhlet extraction [8]. Microwave-assisted extraction (MAE) [9] together with supercritical CO_2 extraction (SCE) [10], continuous supercritical water extraction (CSWE) [10], pressurized liquid extraction (PLE) [11] and microwave hydro-diffusion and gravity (MHG) [12] are considered as recent alternatives for the isolation of highly valuable volatile components of EOs. In addition, great attention has been paid in recent years on the application of different modes of micro-extraction techniques such as single-drop micro-extraction (SDME) [13], liquid-phase micro-extraction (LPME) [14] and solid-phase micro-extraction (SPME) [15] for the isolation of volatile components from the plant materials.

Chromatographic techniques have been the most frequent applied analytical techniques for EOs analysis. Gas chromatography (GC) has shown major contribution towards the determination of the volatile fraction of EOs [16]. Different detection systems can be coupled to GC for a better qualitative and quantitative analysis, such as flame ionization detector (FID), Fourier transform infrared (FT-IR), mass spectrometer (MS) and tandem mass spectrometer (MS/MS) [16,17]. Another interesting development of GC methods in EOs analysis is the application of the GC-olfactometry (GC-O) or GC-sniffing technique [18]. However, due to the complexity of EOs, there has been a high demand for sophisticated instruments to analyze them. The application of multi-dimensional GC (MDGC) or heart-cut GC is one of the most effective adopted technologies for EOs analysis [16]. In addition, in recent years, comprehensive two-dimensional GC (GC × GC) has attracted the attention of many scientists for the EOs analysis. This is due to the much higher resolving power as well as addressing the shortcomings of conventional MDGC [16]. Apart from the GC × GC, other types of comprehensive chromatographic techniques such as comprehensive GC–liquid chromatography (GC × LC) and supercritical fluid chromatography–GC (SFC × GC) are also proposed for the analysis of EOs [16]. On the other hand, the non-volatile fraction of EOs can generally be studied by high-performance liquid chromatography (HPLC) and in some cases with capillary electrophoresis (CE) combined with different detection systems such as diode array detector (DAD), nuclear magnetic resonance (NMR), MS and MS/MS [19]. Furthermore, like GC × GC, LC × LC has been proposed for the

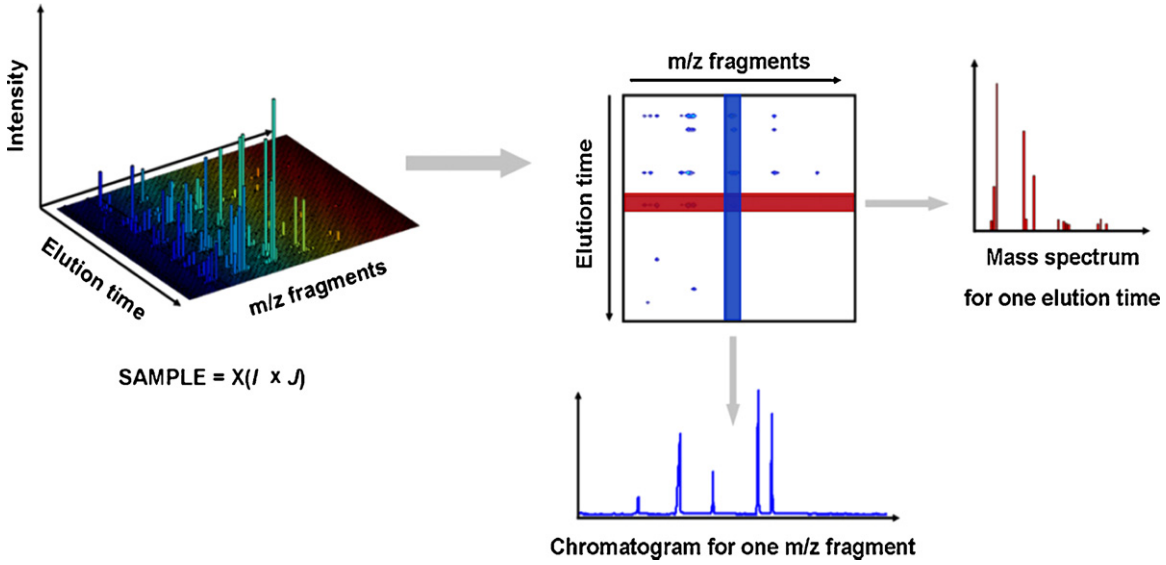

Fig. 2. Visualization of a chromatographic landscape for one sample [25].

comprehensive analysis of non-volatile components of complex mixtures, such as EOs [20].

Nowadays, GC–MS is one of the most important methods for the analysis of volatile compounds, finding a wide variety of applications in chemistry and biology. GC is a very powerful separation technique for multi-component mixtures of analytes such as EOs. The resolving power can be increased when MS is coupled to GC, since the MS dimension provides additional resolving power compared to traditional detection systems, such as FID. The main advantages of GC–MS are the potential of analyzing a great number of analytes, identifying the separated components by using mass spectra, the high sensitivity and the low limit of detection. These advantages make GC–MS one of the most widespread analytical techniques in many scientific fields. Several excellent reviews have recently been published showing the possibilities and the limitations of the GC–MS in the analysis of different samples [21–23].

1.3. Common problems in analysis of EOs using GC–MS

A GC–MS experiment includes the eluting of compounds through the GC column and entering into the MS ion source via interface. The m/z (mass to charge ratio) intensities can be recorded by MS in full scan or selected ion monitoring (SIM) modes [24]. Therefore, after a GC–MS analysis, a series of mass spectra taken at different elution times will be obtained that can be arranged in a two-way data matrix [25]. A typical GC–MS data in full scan mode is shown in Fig. 2.

A single column of the full scan GC–MS data matrix is called *mass chromatogram*. It represents the elution profile of a single m/z channel. Usually, the GC–MS data matrix is visualized as the sum of its mass chromatograms, which is called *total ion chromatogram* (TIC). A TIC is obtained by summing the GC–MS data matrix, **X**, along its columns [24].

Due to the complexity of EOs, there are different problems in their GC–MS analysis. As mentioned by Amigo et al. [25] and Bro et al. [21,26] these problems can be arisen from the common sources of variability of these systems such as chromatographic device, detection system and experimental conditions. The effect of these problems can be reflected in the signal and therefore, the final results of the GC–MS analysis will be affected. The fundamental problems in the GC–MS analysis of EOs are shown in Fig. 3 and are listed as follows:

(1) Baseline drift and spectral background.
(2) Different types of noise (homoscedastic and heteroscedastic).
(3) Changes in the peak shape (non-Gaussian peaks).
(4) Low S/N ratio.
(5) Co-elution (overlapped and/or embedded peaks).

Among these issues, co-elution is one of the most observed chromatographic problems. This is mainly due to complexity of samples, insufficient peak capacity and need to faster chromatographic analysis [25]. As pointed out by Bro et al. [26] there are two main strategies for solving the co-elution problem. The first strategy is the *a priori solution*, which tries to achieve perfect separation by improving the classical chromatographic parameters, such as stationary phase composition, temperature programs. The second strategy is the *a posteriori solution*, which relies on the chemometric modeling after chromatographic run. In this strategy, the co-eluted chromatographic peaks are decomposed into the contribution of the pure components. However, the first strategy is time consuming and it is usual to find that some co-eluted peaks still remain after re-programming the methods. In the meantime, the second strategy relies on the selective nature of the chromatographic profiles [25]. This means that for the co-eluted peaks with the lack of selective regions in the chromatographic dimension the chemometric modeling may fail. There is also a third alternative, which is to seek for the specific mass chromatograms. This is very useful when the co-eluted components have different mass spectra. Sometimes, however, two co-eluted components may have very similar mass spectra and, therefore, finding specific ions will not be an easy task.

Multivariate curve resolution (MCR) techniques have been applied in chromatographic studies during the last thirty years, offering robust and reliable data analysis alternatives to handle problems derived from the instability of the GC–MS systems, such as baseline drift/spectral background, noise problem, low S/N ratio, or even the co-elution problem.

2. Theoretical backgrounds

2.1. Multivariate curve resolution

The MCR of a multi-component chromatographic system is based on the description of the variation of the measurements as a

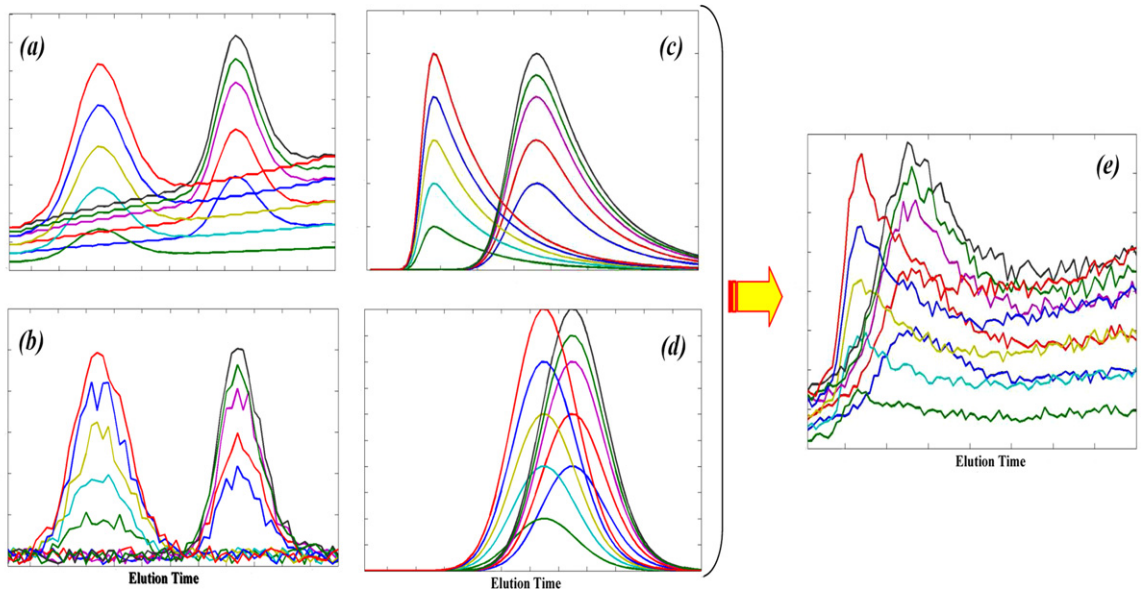

Fig. 3. Common problems in GC–MS: (a) baseline drift, (b) low S/N ratios, (c) changes in the peak shape (e.g. peak-tailing), (d) co-elution, and (e) combination of all problems [26].

linear model of the contributions of their pure components [27–30]. Therefore, relevant and sufficiently informative experimental data, such as those obtained from the analysis of EOs using GC–MS, is needed.

As it can be seen from Fig. 2, all the performed measurements can be organized in a data matrix, where one direction is related to the elution order (e.g. chromatograms) and the other direction refers to the variation in the detector response (e.g. mass spectra).

MCR methods are powerful approaches that do not require a lot of prior information, because neither the number nor the nature of the pure components in a system needs to be known beforehand. The bilinear structure of data set is the main prerequisite for the MCR approaches [30]. A MCR bilinear model allows for the decomposition of the data matrix **X** into the product of two data matrices of **C** and $\mathbf{S}^{\mathbf{T}}$ (where T means the transpose of the matrix, i.e. reflecting the matrix over its main diagonal). Each of **C** and $\mathbf{S}^{\mathbf{T}}$ matrices contains the pure response profiles of the n mixture components associated with the row and the column directions of the initial data matrix, respectively. Fig. 4 depicts the MCR procedure for a typical multi-component GC–MS data.

In matrix notation, the general model for the MCR is:

$$\mathbf{X} = \mathbf{C}\mathbf{S}^{\mathbf{T}} + \mathbf{E} \quad (1)$$

where **X** ($I \times J$) is the original GC–MS data matrix, **C** ($I \times n$) and **S** ($J \times n$) are the matrices containing the pure chromatograms and mass spectra, respectively. **E** ($I \times J$) is the error matrix. The variables I and J represent the number of rows and columns of the original data matrix **X**, respectively, and n is the number of chemical components in the matrix.

2.2. MCR methods

Lawton and Sylvestre [31] have developed the first algorithm for MCR, originally applied to binary mixtures. Indeed, their approach was also the first feasible region estimation appeared in the literature. After that, many other works with different mathematical

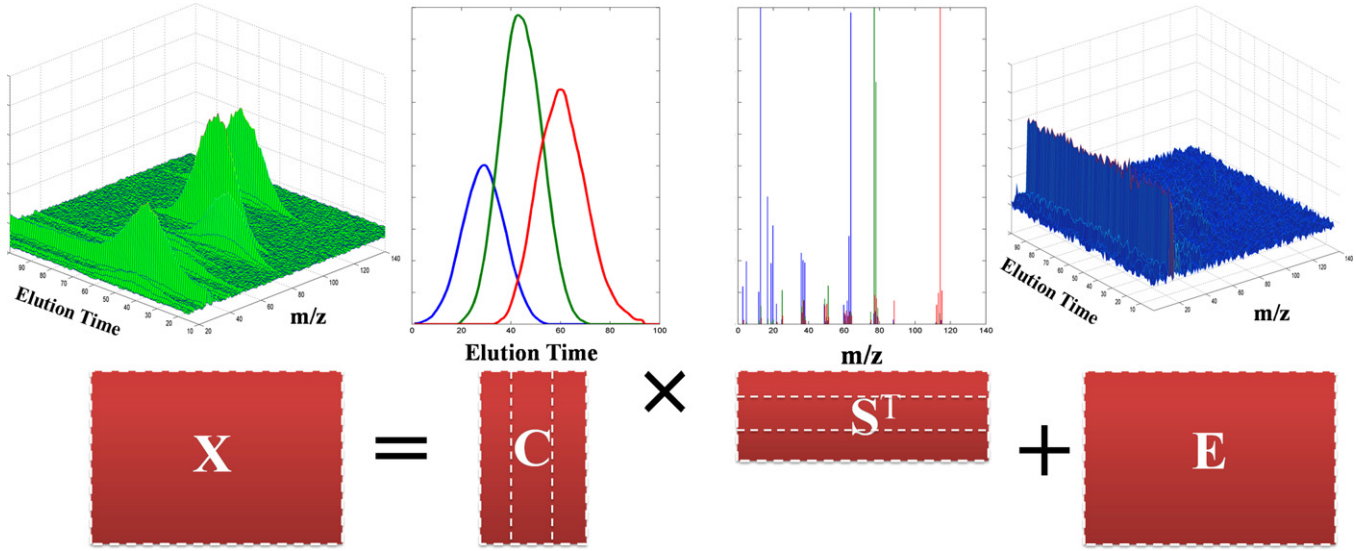

Fig. 4. Mathematical decomposition provided by MCR approaches and graphical representation of the information obtained for a GC–MS data set.

Table 1
Classification of the MCR methods.

Method	Year	Author(s)
Non-iterative		
Evolving factor analysis (EFA)	1987	Maeder [33]
Window factor analysis (WFA)	1992	Malinowski [34]
Heuristic evolving latent projection (HELP)	1992	Kvalheim and Liang [35]
Orthogonal projection resolution (OPR)	1994	Liang and Kvalheim [36]
Sub-window factor analysis (SFA)	1999	Manne et al. [37]
Evolving window orthogonal projection (EWOP)	1999	Liang et al. [38]
Parallel vector analysis (PVA)	2002	Jiang et al. [39]
Alternative moving window factor analysis (AMWFA)	2006	Liang and co-workers [40]
Iterative		
Iterative key set factor analysis (IKSFA)	1982	Malinowski [41]
Iterative target testing factor analysis (ITTFA)	1985	Vandeginste et al. [42]
Alternating regression (AR)	1989	Karjalainen [43]
Simple-to-use interactive self-modeling mixture analysis (SIMPLISMA)	1991	Windig and Guilment [44]
Multivariate curve resolution-alternating least square (MCR-ALS)	1993	Tauler et al. [45,46]
Orthogonal projection approach (OPA)	1996	Cuesta Sanchez et al. [47]
Positive matrix factorization (PMF)	1997	Paatero et al. [48]
Non-negative matrix factorization (NMF)	1999	Lee and Seung [49]
Elementary matrix transformation (Gentle)	2000	Manne and Grande [50]
Modified window target testing factor analysis (MWTTFA)	2000	Wentzell et al. [51]
Iterative orthogonal projection (IOP)	2001	Liang and co-workers [52]
Resolving factor analysis (RFA)	2001	Maeder and co-workers [53]
Simplex-based resolution method	2003	Jiang et al. [54]
Penalty function alternating least square (PALS)	2003	Gemperline and Cash [55]
Multivariate curve resolution-weighted alternating least square (MCR-WALS)	2006	Wentzell et al. [56]
Multivariate curve resolution-objective function minimization (MCR-FMIN)	2007	Tauler [57]
Higher-order statistics		
Adaptive immune algorithm (AIA)	2004	Shao et al. [58]
Mean-field independent component analysis (MF-ICA)	2006	Shao et al. [58]
Window independent component analysis (WICA)	2008	Shao et al. [59]
Non-negative immune algorithm (NNIA)	2009	Shao et al. [59]

backgrounds have been proposed taking the basic ideas provided by Lawton and Sylvestre.

In general, two-way MCR techniques can be divided into two classes of non-iterative and iterative methods. Table 1 summarizes the classification of the MCR methods and their historical evolution after the first paper of Lawton and Sylvestre. In general, non-iterative techniques aim at finding a unique solution, in which the pure variables are uniquely defined according to the mathematical principles involved. However, the non-iterative methods can give very biased 'unique' results if the pure components are not involved in the data matrix. In this case, only the purest variables can be extracted [32]. In contrast, iterative techniques attempt to find a rational solution, in which the pure variables do not violate the constraints such as non-negativity and/or unimodality [30]. Better comparison of non-iterative and iterative methods is presented in Section 3.4.

It is important to note that most of the mentioned MCR techniques are based on second-order statistics, which tries to maximize the variance explained in the data. However, there are some iterative techniques which are based on higher order (e.g. fourth order) statistics that can be used for the resolution of the multicomponent mixtures [58,59]. It is reported that in some situations the quality of the MCR results are better in the case of using higher order statistics [58,59]. Some of these techniques are presented in Table 1.

2.3. Uncertainty in MCR results

Although MCR techniques give astonishing results using only the raw experimental data, but there are some uncertainties in their solutions. Very often, rotational and intensity ambiguities may present in the MCR solutions. It means that, instead of a unique solution a range of feasible solutions that fit the data equally well may be obtained. These two kinds of ambiguities can be easily explained, as pointed out by de Juan and Tauler [27]. The general equation of MCR, $\mathbf{X} = \mathbf{CS}^{\mathrm{T}}$, can be transformed as follows:

$$\mathbf{X} = \mathbf{C}(\mathbf{T}\mathbf{T}^{-1})\mathbf{S}^{\mathbf{T}} \tag{2}$$

$$\mathbf{X} = (\mathbf{CT})(\mathbf{T}^{-1}\mathbf{S}^{\mathrm{T}}) \tag{3}$$

$$\mathbf{X} = \mathbf{C}_{\mathrm{new}}\mathbf{S}_{\mathrm{new}}^{\mathrm{T}} \tag{4}$$

where $\mathbf{C}_{\mathrm{new}}$ and $\mathbf{S}_{\mathrm{new}}^{\mathrm{T}}$ describe the $\mathbf{X}$ matrix as correctly as the true $\mathbf{C}$ and $\mathbf{S}^{\mathrm{T}}$ matrices do, though the $\mathbf{C}_{\mathrm{new}}$ and $\mathbf{S}_{\mathrm{new}}$ are not the required solutions. Therefore, there are different $\mathbf{T}$ matrices that can provide MCR solutions and all of them have the same fit values [27,29,30]. In the case of intensity ambiguity, the general MCR model can be shown as follows:

$$\mathbf{X} = \sum_{i=1}^{n} \left(\frac{1}{k_i} c_i\right) \left(\mathbf{k}_i \mathbf{s}_i^{T}\right) \tag{5}$$

where k_i are scalars. The chromatograms of the $\mathbf{C}_{\mathrm{new}}$ matrix would have the same shape as the real one, but being k_i times smaller, whereas the spectra of the new $\mathbf{S}_{\mathrm{new}}$ matrix would be shaped like the $\mathbf{S}$ spectra, though k_i times more intense.

The extent of ambiguity can be significantly reduced or even suppressed by the use of constraints. In principle, ambiguities produce a set of feasible solutions that do not violate the constraints incorporated in the iterations. Therefore, the estimation of the range of feasible solutions is of most significance for the evaluation of the MCR results. As mentioned before, the first method for the estimation of the extent of rotational ambiguity in MCR solutions was proposed by Lawton and Sylvestre [31]. After this work, several methods have been proposed to address the problem of finding the range of feasible solutions. Borgen and Kowalski [60] have proposed the simplex rotation algorithm to calculate the extent of rotational ambiguity for the three-component systems, as the generalization of Lawton and Sylvestre's method. Henry and Kim [61–63] have published some papers related to the solution for

finding the feasible regions for N-component systems using linear programming and unmix multivariate receptor model. Gemperline [64] and Tauler [65,66] have proposed two similar strategies based on minimization and maximization of relative component contribution (RCC) for feasible region estimation. Rajko and Istvan [67] have proposed a method based on Borgen plots to address the problem of finding the range of feasible solutions for the three-component systems. In addition, Maeder et al. [68] have introduced a method based on RFA and grid search for the calculation of the feasible regions. In recent years, great efforts have been put forward to improve the proposed methods and to develop new methods for more complex cases [69–71]. Jaumot and Tauler [72] have recently developed a user-friendly software, named MCR-BANDS, for the calculation of the extent of rotational ambiguity in an easy way based on maximization and minimization of RCC. The latest method for calculation of feasible region has been proposed by Maeder et al. [73] based on the area of feasible solution (AFS). This method is a proper way for feasible region estimation of noisy three-component systems and its extension to four-component systems.

3. Improvement the GC–MS analysis of EOs using MCR approaches

EOs are valuable natural products with very limited knowledge known about their chemical compositions. This is mainly due to the fact that they are multi-component systems with components mostly unknown. Application of the MCR approaches to the field of EOs offers particular advantages for solving certain problems encountered, e.g. varying baseline, spectral background, changes in the peak shapes and co-elution, more easily and successfully than is possible with other physical or physicochemical techniques. Fig. 5 shows the overall framework of the MCR approaches combined to the GC–MS analysis of EOs. The detail of each step is presented in the following.

The TICs of EOs are very complicated due to the large number of constituents of these mixtures. In addition, the efficiency of MCR techniques is increased when the number of chemical components and artifacts like baseline drift and noise remain under certain level in a data matrix. It means when more components included in the data matrix, the probability of the peak overlap (co-linearity) in chromatographic and spectrometric dimensions increases [74]. Therefore, usually the TIC of EOs is divided into desired number of parts according to the extent of complexity of the TIC. However, each part can be analyzed by an independent MCR procedure, as indicated in Fig. 5. It should be noted that the way by which the two-dimensional matrix is reasonably split is uncertain. The use of local rank analysis may be useful in dividing the TIC to smaller segments [74]. After splitting the TIC to a desired number of segments, each segment is converted to a data matrix (ASCII format) using instrument's software and then is transferred to a numerical computing environment such as MATLAB (MathWorks Inc., Natick, MA, USA) for further analysis.

3.1. Preprocessing strategies

Any GC–MS signal can be divided into three parts of analytical signal ($\mathbf{X}_{\text{signal}}$), background signal ($\mathbf{X}_{\text{background}}$) and noise ($\mathbf{X}_{\text{noise}}$). This can be formulated as:

$$\mathbf{X}_{\text{GC–MS}} = \mathbf{X}_{\text{signal}} + \mathbf{X}_{\text{background}} + \mathbf{X}_{\text{noise}} \quad (6)$$

Before the actual data analysis, fundamental problems such as noise, baseline drift and spectral background must be handled. In chemistry, noise can be considered as a high-frequency signal that arises from uncontrollable variables of the physical or chemical processes and experimental apparatus. The presence of noise makes chemical signals more complex. Various denoising and smoothing methods have been developed to reduce the effect of noise in signals. In general, denoising methods removes the small amplitude components of signals regardless of their frequency. On the other hand, the high frequency components of signals can be removed using smoothing methods regardless of the amplitude [74,75].

One of the most important methods for noise reduction is Fourier transform (FT). In FT a signal converts from one form to another form and simplifies the signals [74]. In spite of the existence of this method, there are other methods for noise reduction. One of them is Savitzky–Golay method, which is a convolution method based on least squares for smoothing and differentiating data [76]. In addition, the performance of wavelet transform [77] in denoising has been investigated by lots of researchers. Liang and co-workers [78] have introduced the roughness penalty approach to overcome white noise in the hyphenated chromatographic data. Wang et al. [79] and Shen et al. [80] have proposed methods based on the frequency difference between the signal and the noise to distinguish the signal and noise patterns in two-way data.

Another serious problem in GC–MS analysis is baseline drift during the chromatographic elution. In the presence of baselines more complicated analysis is required to resolve the data. Therefore, development of a theoretically perfect method to handle the baseline problem is a hard procedure. Conventionally, a straight line (first-order polynomial) is used to connect the two ends of a signal peak. In this method, the first-order polynomial is considered as baseline and subsequent calculations of peak area and peak height are based on it. Object-centering (row-centering) has been proposed to correct the baseline drift in chromatographic direction [74]. In addition, new approaches have been developed to make a better estimate of the baseline. Golotvin and Williams [81] have taken a two-step procedure to recognize and model the baseline in the data. Ruckstuhl et al. [82] have proposed a robust local regression to estimate the baseline. Some works have estimated the baseline by using the wavelet analysis. Shao et al. [83] have presented a baseline correction by finding an approximate baseline in the decomposition process. Ma and Zhang [84] have estimated the baseline by removal of the elements of analyte signal. Wang and Mo [85] have taken a special way using Mexican hat wavelet to handle the baseline problem. Gan et al. [86] have used iterative polynomial fitting to estimate the baseline based on the idea of automatic threshold.

A final problem that should be considered in two-way chromatographic data is the presence of a background in the spectral direction. Similar to the row-centering procedure to correct the baseline drift in chromatographic direction, it is possible to use variable centering (column-centering) for removing the spectral background in the spectral direction [87]. Furthermore, there are some methods that can deal with the problems of baseline drift and spectral background, simultaneously. For instance, double-centering procedure, which is the combination of row- and column-centering, has been proposed for simultaneous correction of the baseline drift and spectral background [87]. Liang et al. [87] have developed congruence analysis method and least-square fitting for correcting the baseline drift and spectral background. Gemperline et al. [88] have used a similar idea to that of Liang and coworkers and have automated the whole procedure. Eilers [89] has presented a method for the baseline correction using asymmetric least squares (AsLS). Also, Boelens et al. [90], for the correction of the spectral background, have developed a method called elimination of background spectrum (EBS) based on the polynomial fit. Generally speaking, fitting a certain curve (e.g. polynomial) is often the most widespread and often the simplest approach to implement for correction the baseline drift and spectral background.

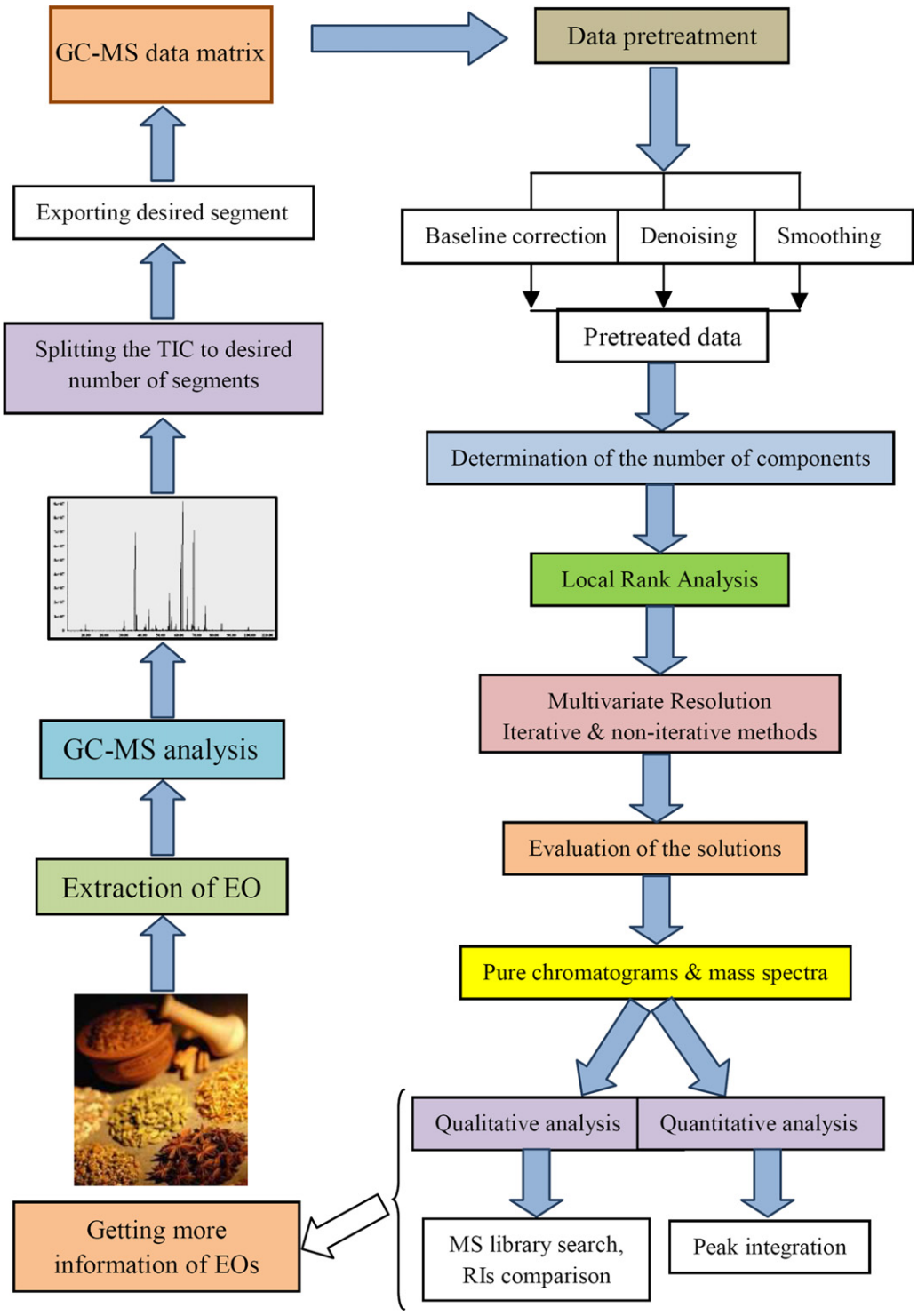

Fig. 5. Overall framework for the combination of MCR approaches with the GC–MS analysis of EOs.

3.2. Chemical rank determination

The rank of a data matrix (mathematical rank) can be defined as the minimum number of linear independent variables (rows or columns). From the analytical chemistry point of view, the rank (chemical rank) can be defined as the number of significant chemical components in a data matrix. For example, the chemical rank in a chromatographic data is ideally equal to the number of peaks. In an ideal and noise free data matrix, the chemical and mathematical ranks are equal. However, in most situations due to the presence of experimental noise, the chemical rank is much lower than the mathematical rank.

There are some issues in the experimental data that makes the chemical rank determination more difficult. These issues are: (1) the presence of the baseline drift and spectral background, (2) the presence of different types of noise, (3) heteroscedasticity of the noise, (4) low signal to noise ratios and (5) co-elution problem in the chromatographic data [28].

Table 2
Common methods for the determination of chemical rank.

Chemical rank determination technique	Ref.
Principal component analysis (PCA)	[91]
Eigenvalues	[91]
Logarithm of eigenvalues	[91]
Eigenvalues ratio	[91]
Error indicator function (INF)	[92]
Residual standard deviation (RSD)	[92]
Root mean square (RMS)	[92]
Residual sum of square plot (RSS)	[93]
Imbedded error (IE)	[94]
Reduced error (RE)	[92,94]
Reduced eigenvalues (REV)	[92,94]
Factor indicator function (IND)	[92,94]
Residual percent variance (RPV) (Scree test)	[95]
Exner function (ψ)	[96]
Ratio of derivatives of error indicator function (ROD)	[97]
Ratio of RSD (RSD Ratio)	[92]
F-test	[98]
Cross-validation	[99]
Morphological score	[80]
Orthogonal projection approach (OPA)	[47]
Simple-to-use interactive self-modeling mixture analysis (SIMPLISMA)	[44]
Correlation plots	[93]
Derivative plots	[92]
Evolving principal component analysis (EPCA)	
Evolving factor analysis (EFA)	[33]
Fixed-size moving window-evolving factor analysis (FSMW-EFA)	[100]
Evolving principal components innovation analysis (EPCIA)	[101]
Subspace comparison (SC)	[102]
Simplified Borgen method (SBM)	[103]

Therefore, determination of the number of chemical components (chemical rank) is a critical step in the GC–MS analysis of EOs. In addition, the subsequent qualitative and quantitative analyses are related to this step. Several methods exist for the chemical rank determination.

Some of them are based on principal component analysis (PCA) [91]. Malinowski [92] has presented several procedures for the determination of the chemical rank in different types of chemical data. Many of these techniques can also be used for the GC–MS data of EOs. Table 2 categorizes the most common methods for the chemical rank determination and key references. As it can be seen, different classes of methods can be used.

Elbergali et al. [97] and Meloun et al. [104] have divided these methods into two classes of precise and approximate methods. Precise methods are relied on the experimental errors of the data. The chemical rank in this class is determined by comparing a statistical index with the experimental error. Examples of these methods are RSD and RMS. In other words, approximate methods can be used when there is no prior knowledge about the experimental error in the data. This class of methods can approximate the number of significant chemical components and also the size of the error in the data. Eigenvalues, logarithm of eigenvalues, eigenvalues ratio, exner function, scree test, imbedded error, IND and *F*-test examples of approximate methods for the determination of the chemical rank.

There is also another type of categorization for the chemical rank determination techniques. Wasim and Brereton [105,106] have divided the methods into three groups according to the generated outputs. The first group contains only rank providing methods such as *F*-test, RE, REV, IND, scree test, exner function, cross validation, morphological score, EFA, FSMW-EFA and EPCIA. The second group involves only key variable providing methods such as SBM. The third group includes rank and key variable providing methods such as OPA, SIMPLISMA and SC.

3.3. Local rank analysis

A prior exploration of the chromatographic data can give useful information for subsequent resolution process. Chromatographic data exploration includes estimating the number of chemical components including target analytes and interferences (Section 3.2), knowing the elution sequence of the components in the chromatographic data, and defining the concentration and spectral windows of different components in a data set [29].

Three types of windows can be defined by the methods of the local rank analysis: (i) *zero-component region*; which is defined as region where no chemical component elute in chromatographic development. Such a region has, by definition, a chemical rank of zero and is of prime importance to establish the noise level of a data set, (ii) *one-component region (selective region)*; which is the region where only one chemical component elutes in chromatographic direction. The chemical rank is one in this region. This region can give some pure chromatographic and spectral information for the chemical components in a data set, and (iii) *mixture region (co-eluted region)*; which is the region where at least two chemical components elute in elution sequence. Therefore, the chemical rank is at least two in this region [32].

There are several chemometric methods, which are able to obtain the local rank map of co-eluted peaks such as EFA [33], FSMW-EFA [100], exhaustive evolving factor analysis (E-EFA) [107], eigenstructure-tracking analysis (ETA) [108], and evolving latent projective graphs (ELPGs) [35]. Among these methods, EFA, FSMW-EFA and ELPGs techniques, to some extents, have more extensive applications compared to the other methods.

Here, a simple example is utilized to illustrate how a local rank analysis can be performed on a two-way GC–MS data. Fig. 6a shows the 3D representation of two-component (A and B) simulated GC–MS data set and Fig. 6b depicts its chromatographic profile. In this figure the selective regions are shown by A and B and co-eluted region is illustrated by A + B. In addition, the zero-component regions for components A and B are demonstrated by blue and brown double arrows, respectively. The results of the local rank analysis methods of ELPGs, EFA and FSMW-EFA on this data set are shown in Fig. 6c–e. From these figures, one can see that the plots clearly reveal the locations of the zero-component regions, the selective regions (A and B), and the co-eluted region (A + B) with a rank of two. With this information at hand, one can easily guess how the chemical components are eluted.

3.4. Multivariate resolution methods

The ultimate aim for the analysis of two-way GC–MS data of EOs is to obtain qualitative and quantitative information about the eluted chemical components as hidden in the chromatographic data. This topic is discussed in detail with some examples, in this section.

Several resolution tools have been put forward to deal with the GC–MS data of EOs. To decide which methods have to be applied for a certain data set, requires some experiences.

Non-iterative resolution methods can be regarded as evolutionary. It means that local chromatographic sections of the data set should be combined to obtain the pure chromatograms and mass spectra of the components. These local chromatographic sections can be obtained by using the local rank analysis methods. After recovering the profiles in chromatographic or mass spectrometric dimension, a least-squares procedure is used to obtain the other matrix dimension (**S** or **C**, respectively). A common feature of non-iterative techniques is the use of the informative "windows", such as the selective information regions, zero-concentration regions and also the co-eluted regions [30]. Thus, the correct definition of the concentration and spectral windows based on the local

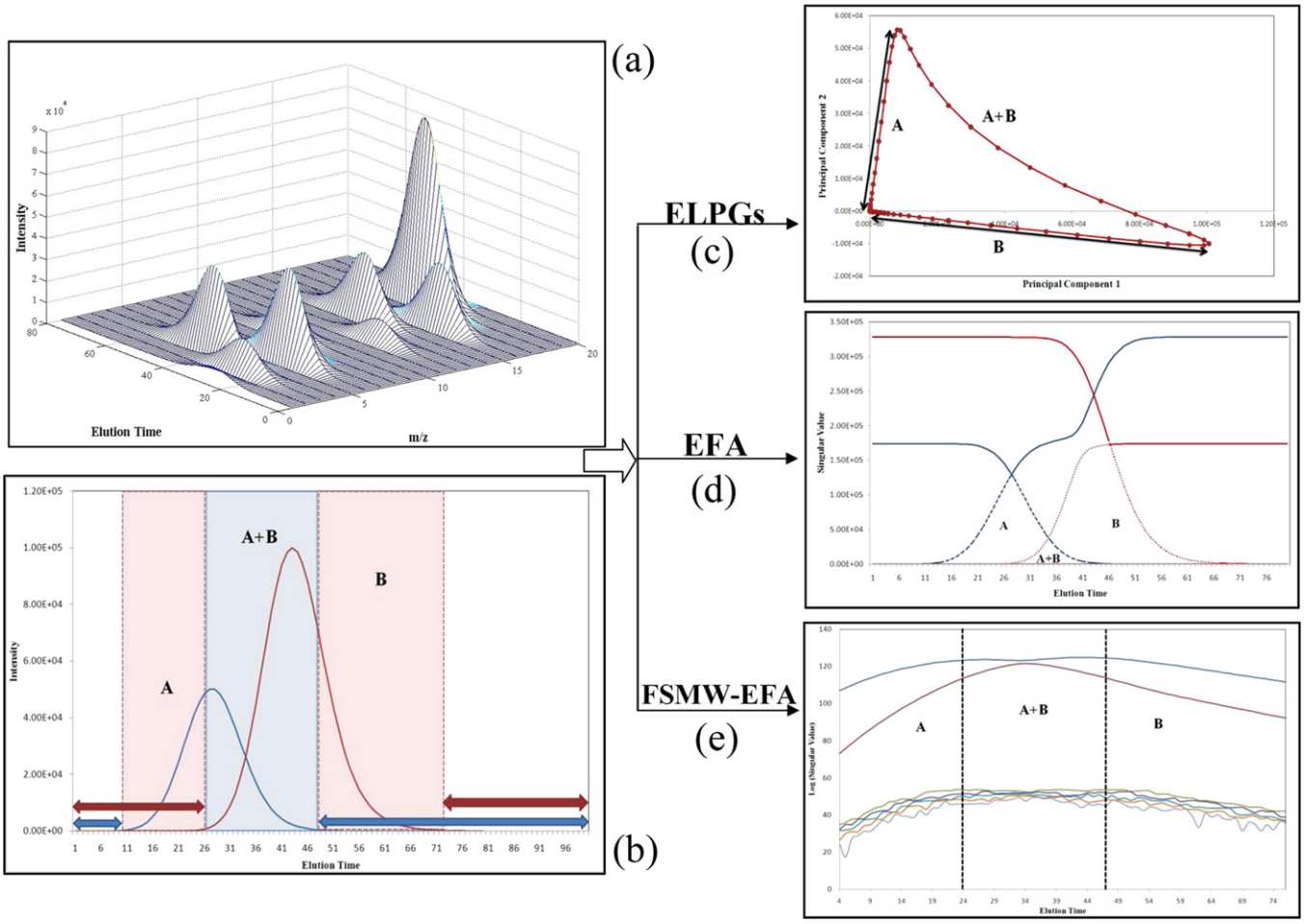

Fig. 6. (a) 3D representation of a two-component simulated GC–MS data, (b) pure chromatograms of the data set (a). A and B show the selective and A + B demonstrates the overlapped regions. In addition, double arrows show zero-component region for each component (blue for A and red for B). (c) ELPG plot, (d) forward and backward EFA plots, and (e) FSMW-EFA plot for simulated data set. Selective (A and B) and overlapped (A + B) regions are indicated in these plots. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

rank maps is crucial in obtaining the correct resolution results. In principle, the uniqueness property of the resolution results in non-iterative methods is related to the definition of these informative windows [28]. In addition, the one-at-a-time recovery of the chromatograms and mass spectra is another advantage of these methods that can make them useful when only partial information of a system is of interest [29]. However, non-iterative techniques have restricted applicability to the evolutionary systems. In other words, for embedded systems due to the absence of selective information for some components the correct resolution cannot be attained. However, some strategies, such as component stripping, have been proposed for resolving the embedded systems [35].

As an example, here, the resolution of a GC–MS peak cluster of the essential oil of lemon is presented. Fig. 7a and b shows its mass chromatograms and TIC, respectively. As it can be seen, the S/N ratio is low and a large contribution of baseline exists in this data. In addition, apparently there are two components in this signal. However, after noise reduction, baseline correction, chemical rank determination and local rank analysis, interesting results can be obtained using the HELP method and applying component stripping strategy. Fig. 7c and d depicts the resolved chromatograms and mass spectra, respectively, for the desired data. As it can be seen, despite the absence of selective information for components ***b***, ***d*** and ***e***, reasonable results have been obtained for this complex peak cluster.

Iterative resolution approaches are likely the most popular MCR methods due to their flexibility to cope with different types of data structures and chemical problems. In addition, this class of techniques has the ability to consider external information during the MCR procedure. Initial estimates of $\mathbf{C}_0$, $\mathbf{S}_0$, or $\mathbf{T}_0$ are the starting points for the optimization process depend on the type of algorithm. These initial values are modified iteratively under the application of proper constraints [30]. Constraints force the profiles in $\mathbf{C}$ and/or $\mathbf{S}^T$ to obey some predefined chemical or mathematical properties and they are the cornerstone of iterative methods. On the other hand, they serve as a way of introducing all available priori chemical or mathematical information to ensure the recovery of meaningful solutions. In other words, the correct selection and application of constraints either minimizes or eliminates the ambiguity linked to the resolution results. Non-negativity is the most common constraint applied to both chromatographic and mass spectrometric directions. However, it is possible to apply other constraints related to the peak shape or sequential elution pattern of compounds. Therefore, unimodality constraint can be applied to chromatograms to preserve only one maximum for each peak. Also, selectivity constraint can consider the information of local rank analysis, such as selective and zero-component regions for a better resolution of the profiles [29]. Fig. 8 demonstrates the effect of the most common constraints applied to the analysis of a GC–MS data.

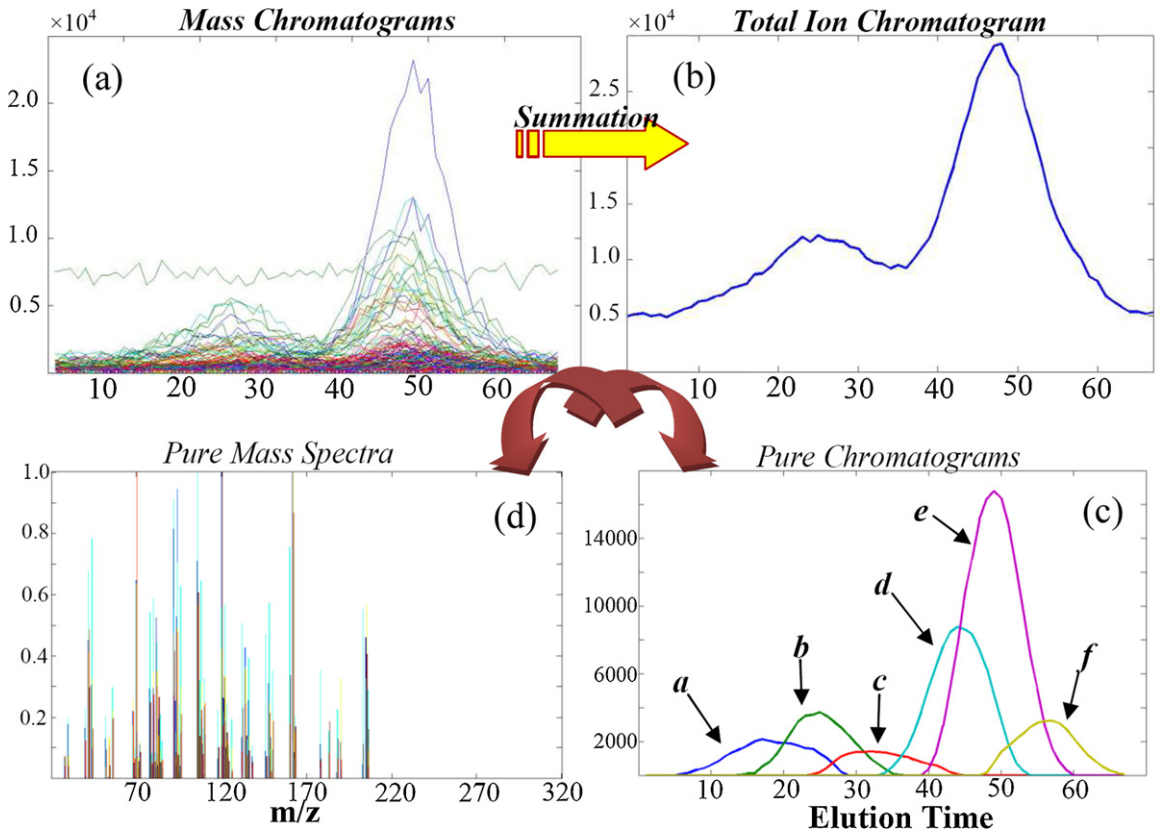

Fig. 7. Results of the resolution of the GC–MS peak cluster of lemon using non-iterative techniques (HELP method). (a) Mass chromatograms, (b) total ion chromatogram, (c) resolved chromatograms, and (d) resolved mass spectra.

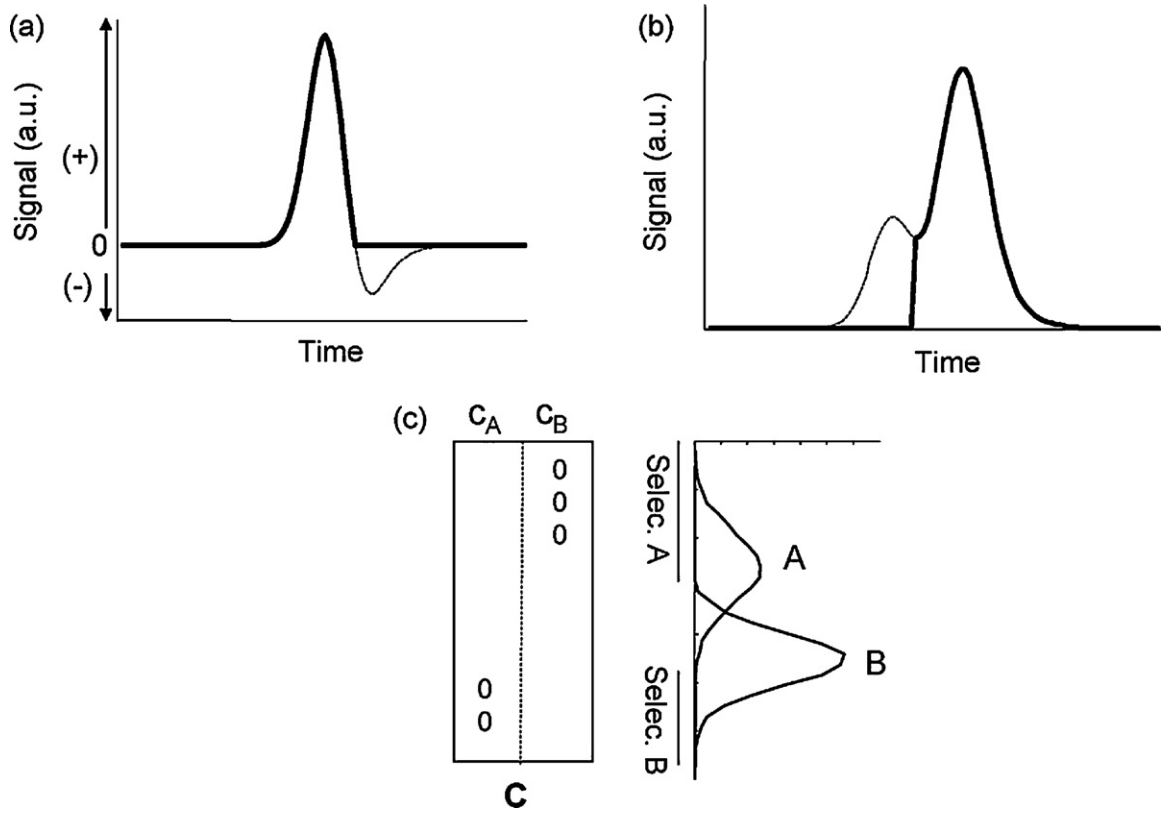

Fig. 8. Common constraints applied to a GC–MS data set. (a) non-negativity, (b) unimodality, and (c) selectivity, included a null concentration for the absent components [29].

Table 3
Features and limitations of the two-way MCR methods.

Class of method	Main features	Constraint(s)	Limitations
Non-iterative	-Fast algorithms -One-step calculation algorithms -One-at-a-time recovery of profiles -Use of single least square step -Use of local rank information -Applicable to systems with partial information -Unique solutions (*for components with selective regions*)	Non-negativity	-Correct definition of the concentration windows -Restricted applicability to systems with sequentially evolving components -Analysis of embedded systems *without selective information* -*Extension to multi-way data*
Iterative	-One-at-a-time or simultaneous refinement of the profiles at each cycle of optimization process -Flexibility to cope with many kind of data structures -Need to initial estimates -More versatile than non-iterative ones -Applicability to systems with partial selectivity or no selectivity (embedded) -Extension to multi-way data sets	Non-negativity, unimodality, selectivity, normalization	-Larger calculation times -Non-unique solutions -Dependence on initial estimates -Selectivity is needed in order to get correct results

The differences among the iterative methods can be related to the type of profiles that are iteratively optimized, the initial estimates used, the nature and application of the constraints, or the structure of data set to make the analysis feasible. In general, the use of nonrandom estimates shortens the iterative optimization process and helps to avoid convergence to a local optimum, which is different from the desired solution. It is better to use chemically meaningful estimates if we have a way to obtain them easily or if the necessary information is available [30]. There are several chemometric methods for calculating these initial estimates; some of them are particularly suitable when the data consists of evolutionary profiles of a process, such as EFA [33], whereas some other methods mathematically select the purest rows or columns of the data matrix as initial profiles, such as SIMPLISMA [44], OPA [47], SBM [103] and needle search [109]. Table 3 summarizes the main features and limitations of different MCR techniques in analysis of a chromatographic data.

Fig. 9 illustrates the application of the iterative MCR approaches in two cases. In the first one (Fig. 9a), a chromatographic segment is chosen from the TIC of rose oil. In this peak cluster there are two components with embedded nature. Indeed, this complex case cannot be resolved using the non-iterative techniques. However, by using the OPA-MCR-ALS as an iterative technique, it is possible to obtain reasonable results. The resolved chromatograms and mass spectra for this peak cluster are shown in Fig. 9c and d, respectively.

In the second case (Fig. 10), the problem is even more complicated, as there are a large number of components and great amount of noise and background contributions. In addition, there are some

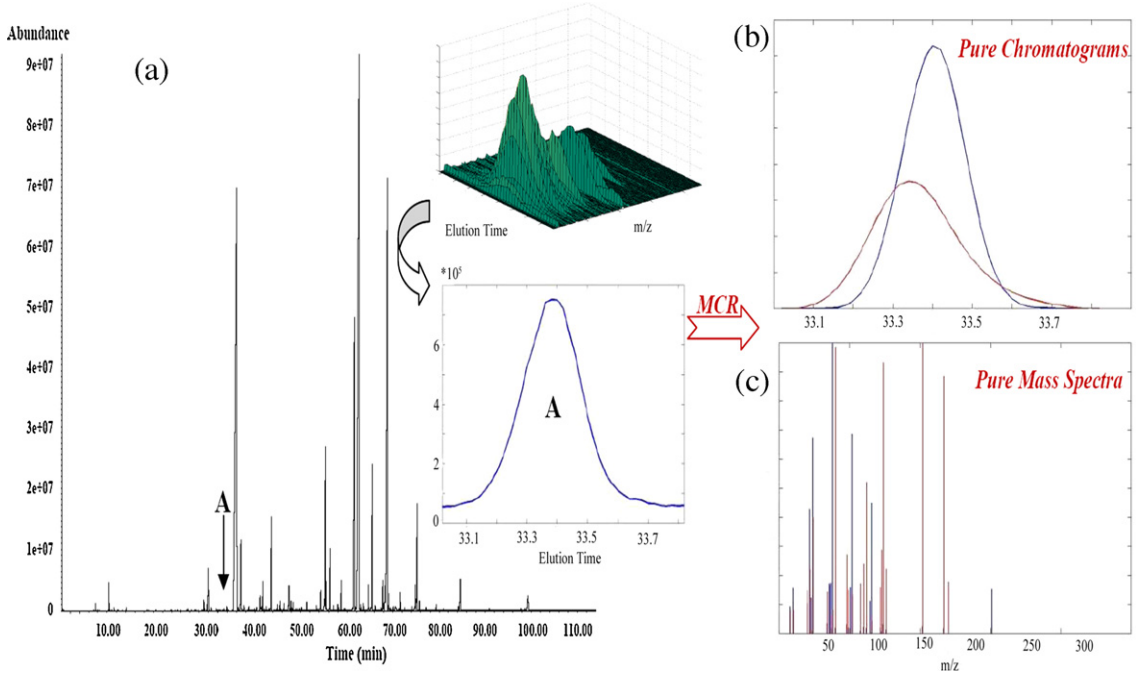

Fig. 9. Resolution results using iterative resolution methods (OPA-MCR-ALS). (a) TIC of the rose oil and the demonstrated embedded profile (A), (b) estimated chromatograms, and (c) estimated mass spectra for peak cluster A.

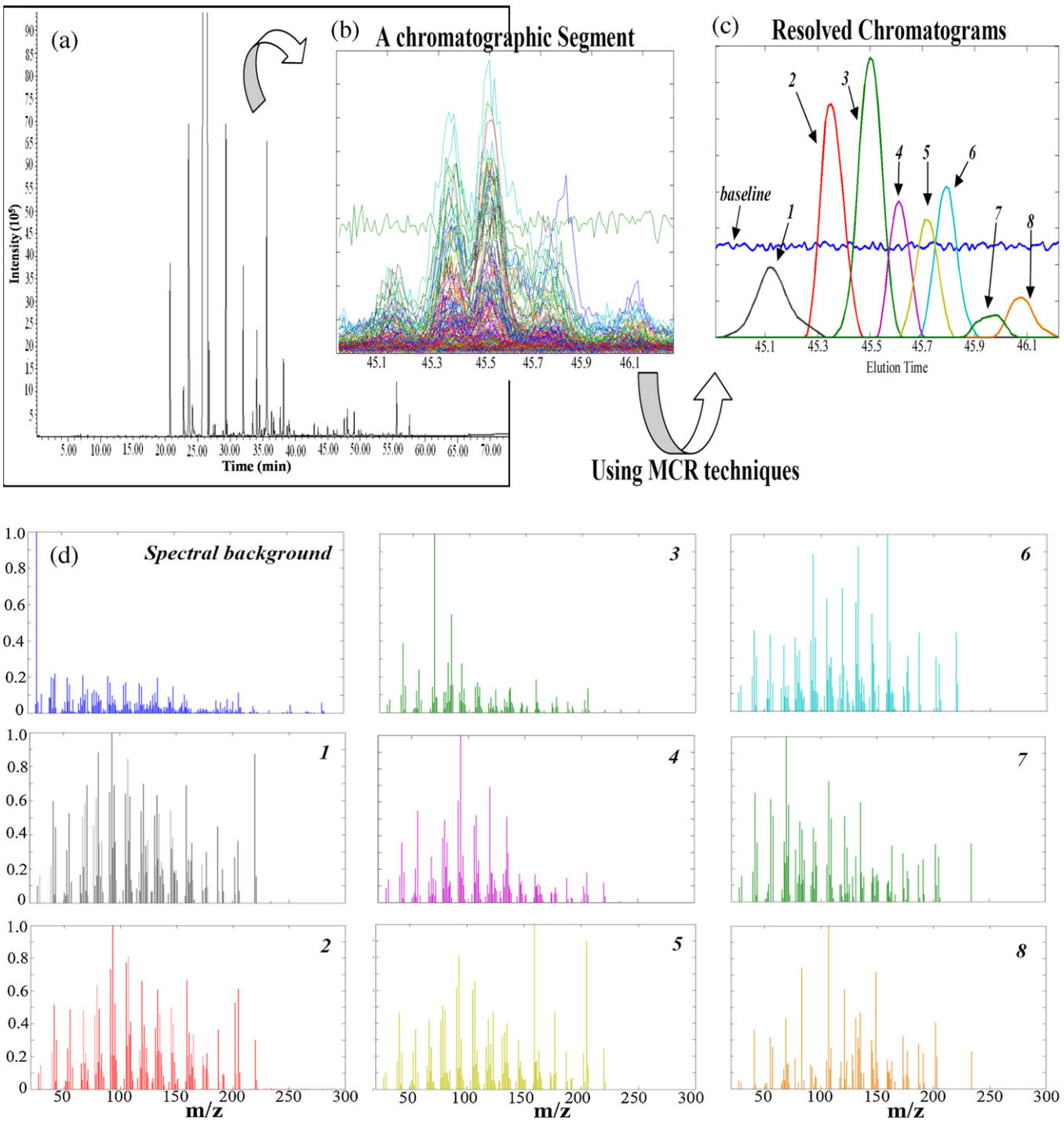

Fig. 10. (a) TIC of grapefruit essential oil, (b) mass chromatograms of a selected segment, (c) resolved chromatographic profiles (1–8) and baseline, and (d) resolved mass spectra of the chromatograms in (c).

isomers with practically similar mass spectra in this signal. In this situation, it is even more complicated to find specific ions. Actually, it is difficult to detect that there is an overlapping problem. Still, iterative methods (OPA-MF-ICA in this case) can solve the problem, and from the estimated mass spectra, the existence of the embedded isomers can easily be detected. In addition, by using this technique the baseline can be modeled instead of its removing. Fig. 10c demonstrates the resolved chromatograms together with the background signal. It can be realized that the background profile has been considered as an independent component, so it has also been resolved. Fig. 10d depicts the resolved mass spectra, which correspond to the resolved chromatograms in Fig. 10c. The match factors (MFs) between the resolved mass spectra and those of the standards in the library are greatly improved, which means that the quality of the resolution process is reasonable. It is important to note that without using the MCR techniques, only five components with very low MF values and ambiguous identities were obtained for this peak cluster.

Due to the great impact of the combination of the MCR approaches to the GC–MS analysis of EOs, various research groups in the world are working in this field. The fields of application of the MCR approaches on the GC–MS analysis of EOs are very diverse,

as evidenced in the nonexclusive list shown in Table 4. This table also highlights the type of the MCR approaches for each sample. As it can be seen, up to now, different classes of MCR techniques for different types of EOs have been used.

3.5. Evaluation of the MCR results

Evaluation of the MCR solutions is a very important step in the MCR analysis of analytical data, such as GC–MS. To the best of our knowledge, there are five different ways for evaluating the MCR solutions for a GC–MS data including: (1) chromatographic shape recovery that is an important aspect from the analytical chemistry point of view, (2) statistical parameters of variance explained (R^2), lack of fit (LOF) and standard deviation of residuals *vs*. experimental data (σ), (3) match factor (MF) and/or reverse match factor (RMF) for comparison of the resolved mass spectra with those of the standards in the MS database, (4) evaluation of the extent of rotational ambiguity according to the methods discussed in Section 2.3, based on relative component contribution (Gemperline-Tauler's approch) [64–66], Borgen plots (Borgen-Raijko's approach) [67], RFA and grid search (Maeder et al.) [68] and area of feasible solution (AFS) (Meader et al.) [73] and (5) injection of the standards of identified components at the same instrumental conditions and comparison of the retention indices (co-injection).

Among these methods, using chromatographic shape recovery, statistical parameters and MF or/and RMF are common for the evaluation of the resolved profiles by MCR in the GC–MS analysis of EOs. Estimation of the feasible regions for the evaluation of MCR results of real data is limited due to the application of the proposed approaches only for two- and three-component systems with a low amount of artifacts and, on the other side, the lack of user-friendly software to perform them. Co-injection is also a reliable method to confirm the MCR results, however, there are some limitations in the availability of the standards for the EOs components.

3.6. Qualitative and quantitative analysis

The final results of the multivariate resolution are a matrix containing the pure mass spectral profiles and a matrix containing the pure chromatographic profiles for each GC–MS signal.

The resolved mass spectra using MCR approaches are used for the qualitative analysis. In general, there are two common methods for identification of each component. The first one is based on the comparison of their GC retention indices (RIs), determined relative to the retention time of a series of n-alkanes with linear interpolation, with those of authentic compounds and literature data. The other is based on the comparison of their resolved mass spectral fragmentation patterns with those stored in the *Wiley MS library* and *NIST MS Spectral Search* program, built up using pure substances and the mass spectra from the literature. *NIST MS Spectral Search* program, distributed by *Standard Reference Program of NIST*, is the most widely used MS library for the identification of unknown mass spectra. The MF for the resolved mass spectrum is a weighted count describing how well the resolved spectrum matches the standard spectrum of a candidate in the library.

The overall volume integration (OVI) [124] is commonly used method for computing the amount of each component after resolving the chromatograms and mass spectra of EOs. The advantage of this quantitative method over the general peak-area integration is that all mass spectral intensities are taken into account. However, by using this technique only some information about the relative percent (composition) of each component in the whole TIC can be obtained. This strategy has been used in most of the works presented in Table 4. However, obtaining the exact quan-

Table 4
Application of MCR approaches combined with GC–MS for the analysis of EOs in the past 10 years.

No.	MCR Approach	EOs	Ref.
1	SFA	Ramulus cinnamomi	[110]
		Schisandra chinensis Baill	[111]
		Si-Wu decoction	[112]
		Radix Rehmanniae	[113]
		Artemisia capillaris	[114]
		Ginger	[115]
		Angelica sinensis	[116]
		Houttuynia cordata	[117]
		Rhizoma asarum	[118]
		Rododendron	[119]
		Cut tobacco	[120]
		Coffee	[121]
		Radix Angelicae Sinensis	[122]
		Dong quai	[123]
2	HELP	Ginger	[115]
		Rhizoma asarum	[118]
		Peptic powder	[124]
		Cortex cinnamomi	[125]
		Rhizoma liguistici chuanxiong-Radix paeoniae rubra (RLC-RPR)	[126]
		Syringa oblata Lindal (lilac)	[127]
		Geranium	[128]
		Cut tobacco	[129]
		Herba schizonepetae-ramulus cinnamomi (HS-RC)	[130]
		Damask rose	[131]
		Eucommiu ulmoides Oliver	[132]
		Cortex magnolia officinalis	[133]
		Magnolia biondii pamp	[134]
		Osmanthus fragrance	[135]
3	AMWFA	Rhizoma ligustici chuanxiong-Radix paeoniae rubra (RLC-RPR)	[40]
		Eucommiu ulmoides Oliver	[132]
		Clematis	[136]
		Pericarpium Citri Reticulata Viride-Pericarpium Citri Reticulata	[137]
		Ginseng	[138]
		Citrus Reticulata Blanco	[139]
		Herba schizonepetae-Radix saposhnikoviae (HS-RS)	[140]
4	OPR	Si-Wu decoction	[112]
		Ginger	[115]
		Cut tobacco	[130]
		Cumin and Caraway	[141]
5	EWOP	Ramulus cinnamomi	[110]
		Radix Rehmanniae	[113]
		Radix Angelicae Sinensis	[122]
		Notoptergium incium (NI)	[142]
		Artemisia capillaris herba	[143]
6	EFA	Ginger	[115]
		Rhizoma asarum	[118]
7	WFA	Rhizoma asarum	[118]
8	OPA	Notoptergium incium (NI)	[142]
9	IOP	Cortex cinnamomi	[52]
10	MWTTFA	Garlic-Houttuynia cordata Thunb	[144]
11	MCR-ALS	Damask rose	[131]
		Cumin	[141]
		Caraway	[141]
		Crocus sativus L. (saffron)	[145]
12	MCR-FMIN	Crocus sativus L. (saffron)	[145]
		Citrus Lemon	[146]
13	MF-ICA	Citrus lemon	[147]
		Citrus reticulata	[147]

Table 5
Available MCR softwares.

Software	Software available at:	Developed by:	Ref.
Commercial			
AMDIS	www.amdis.net	Standard Reference Program of NIST	–
AnalyzerPro	www.spectralworks.com/analyaerpro.asp	Spectralworks Ltd.	–
Xtricator	www.prs.no/Extricator/SirExtricate.html	O.M. Kvalheim et al.	–
MS-Resolver	www.prs.no/MS Resolver/MS Resolver.html	O.M. Kvalheim et al.	–
PLS Toolbox	www.eigenvector.com	Eigenvector Research Inc.	–
Unscrambler	www.camo.com	CAMO Software Inc.	–
Free			
MCRC Software	http://sharif.ir/~jalali/	M. Jalali-Heravi et al.	[154]
MCR-ALS Toolbox	www.ub.edu/mcr/web_mcr/welcome.htm	R. Tauler et al.	[155]
MCR-BANDs Toolbox	www.ub.edu/mcr/web_mcr/welcome.htm	R. Tauler et al.	[72]
ICA Toolbox	http://isp.imm.dtu.dk/toolbox/ica/	O. Winther et al.	[156]
GUIPRO	http://personal.ecu.edu/gemperlinep/	P. Gemperline et al.	[55]
N-way Toolbox	www.models.life.ku.dk/nwaytoolbox	R. Bro et al.	[157]

titative results needs to have the standards for each component and using multi-way resolution methods such as generalized rank annihilation method (GRAM) [148], matrix-augmented MCR-ALS (MA-MCR-ALS) [46], parallel factor analysis (PARAFAC) [149], and PARAFAC2 [150]. This topic is out of the scope of this review. There are some valuable books and reviews covering this subject [151–153].

4. Available softwares for MCR

In the recent years, extensive efforts have been done by many research groups for developing different softwares (commercial or freeware) for the implementation of MCR techniques. However, there are still some limitations for non-expert users. This is due to the need of some basic knowledge about the MCR methods and the problem under study as well as some user interactions. Table 5 summarizes some of the common softwares for the MCR techniques.

Some of these softwares are written in the popular environment of MATLAB. Some of the packages are freely available for the public download. The most recent software is the *MCRC software* developed by Jalali-Heravi et al. [154], which is freely available to public and is dedicated to chemometric analysis of GC–MS and HPLC-DAD data. Some methods previously mentioned for preprocessing, chemical rank determination, local rank analysis, multivariate resolution and peak integration are included in this software.

5. Conclusions and final remarks

Essential oils as valuable natural products have a broad range of applications in medicine, food, human nutrition, cosmetic and perfume. EOs are very complex mixtures and some of them consist of more than 200 components. Some of these components even with low amount may exhibit very important pharmaceutical properties. Therefore, thorough analysis of EOs seems to be essential. Nowadays, GC–MS technique is without any doubt the most common and powerful method for the analysis of EOs. However, some fundamental problems such as baseline drift, spectral background, noise, non-Gaussian peaks and co-elution accompany each GC–MS analysis. Two strategies can be used to solve these problems and improve the quality of the analysis: (1) using more sophisticated and of course, more expensive instruments such as GC–MS-MS, GC × GC–MS and (2) using the chemometric methods, such as MCR, which offer robust and reliable data analysis. This review has focused on the applications of the MCR techniques in improving the quality of analysis of the very complicated mixtures of EOs. In this review a simple example is presented to show how these techniques can be applied to resolve the components. Also, the resolution of three GC–MS peak clusters of the EOs of lemon, rose and grapefruit as real samples are presented. This review shows the strength of the MCR methods to those researchers interested in analysis of the EOs. It also reveals that different commercial or free softwares are available for the implementation of the MCR methods. Inspection of recent trends in application of MCR approaches shows an astonishing growth in the application of these techniques in the analysis of the complex mixtures. We believe that by introducing these techniques to different research groups and getting familiar with their strength, the rate of growth in the application of these techniques would increase in the near future.

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