



# Resolving of challenging gas chromatography–mass spectrometry peak clusters in fragrance samples using multicomponent factorization approaches based on polygonal inflation algorithm



Salehe Ghaheri, Saeed Masoum\*, Ali Gholami

Department of Analytical Chemistry, Faculty of Chemistry, University of Kashan, Kashan, Iran

## ARTICLE INFO

### Article history:

Received 28 August 2015  
Received in revised form  
19 November 2015  
Accepted 2 December 2015  
Available online 10 December 2015

### Keywords:

Multivariate curve resolution  
Polygonal inflation algorithm  
Rotational ambiguity  
Fragrance  
Gas chromatography–mass spectrometry

## ABSTRACT

Analysis of fragrance composition is very important for both the fragrance producers and consumers. Unraveling of fragrance formulation is necessary for quality control, competitor and trace analysis. Gas chromatography–mass spectrometry (GC–MS) has been introduced as the most appropriate analytical technique for this type of analysis, which is based on Kovats index and MS database. The most straightforward method to analyze a GC–MS dataset is to integrate those peaks that can be recognized by their mass profiles. But, because of common problems of chromatographic data such as spectral background, baseline offset and specially overlapped peaks, accurate quantitative and qualitative analysis could be failed. Some chemometric modeling techniques such as bilinear multivariate curve resolution (MCR) methods have been introduced to overcome these problems and obtained well resolved chromatographic profiles. The main drawback of these methods is rotational ambiguity or nonunique solution that is represented as area of feasible solutions (AFS).

Polygonal inflation algorithm (PIA) is an automatic and simple to use algorithm for numerical computation of AFS. In this study, the extent of rotational ambiguity in curve resolution methods is calculated by MCR-BAND toolbox and the PIA. The ability of the PIA in resolving GC–MS data sets is evaluated by simulated GC–MS data in comparison with other popular curve resolution methods such as multivariate curve resolution alternative least square (MCR-ALS), multivariate curve resolution objective function minimization (MCR-FMIN) by different initial estimation methods and independent component analysis (ICA). In addition, two typical challenging area of total ion chromatogram (TIC) of commercial fragrances with overlapped peaks were analyzed by the PIA to investigate the possibility of peak deconvolution analysis.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Perfumes and fragrances are increasingly applied in the various home and personal care products. The presence of a proper fragrance in a product has an important role in marketing and popularity so that the perfume business is a billion-dollar industry. Perfumes that are used in various products are complex mixture vary both in the number of ingredients and costs. Briefly, perfumes are applied in detergents, household cleaners and fabric conditioners include 10–50 ingredients whereas personal care perfumes contain about 80 perfumery raw materials and fine fragrances comprise more than 100 components. Perfume analysis is very important for formulation work, stability, product interaction,

packaging interaction, substrate interaction studies and headspace analysis [1].

Some studies show that the chromatographic techniques have been the most frequent applied analytical techniques for the volatile samples (essential oils and fragrances) analysis [2,3]. Gas chromatography (GC) has shown major contribution towards the determination of such samples. As these samples are often so complex, such separation is necessary before identification of components and GC usually provides highest resolution power for such samples. Different detection systems can be coupled to GC for a better qualitative and quantitative analysis. The main advantages of GC–MS are the potential of analyzing a great number of analytes, identifying the separated components using mass spectra, the high sensitivity and the low limit of detection. These advantages make GC–MS as one of the most widespread analytical techniques in many scientific fields [4,5]. Identification of separated component is done by similarity search in MS database but this identification

\* Corresponding author. Tel.: +98 3155912338; fax: +98 3155912397.  
E-mail address: [masoum@kashanu.ac.ir](mailto:masoum@kashanu.ac.ir) (S. Masoum).

method can be failed due to the complexity of such samples and different problems in GC–MS analysis such as spectral background, baseline offset, and some co-elution peaks. Among these issues, co-elution is one of the most observed chromatographic problems [6,7].

Even by use of optimized GC conditions, some problems such as overlapped and embedded peaks may be remained and therefore the analysis is encountered to fail. Chemometric resolution techniques are applied to solving these problems and extracting maximum information from a GC–MS dataset. Many iterative and non-iterative curve resolution methods have been introduced. In general, all these methods can be classified as the multicomponent factorization of multivariate data techniques [8–10]. Generally speaking, these methods may operate as follow: if  $D$  is an experimental matrix by  $n \times m$  dimension,  $f$  is a chemical rank of system,  $C \in \mathbb{R}^{n \times f}$  is a concentration matrix and  $S^T \in \mathbb{R}^{f \times m}$  is contained spectral profiles, then  $D = CS^T + E$ .

This is obvious that an infinite number of solutions could be found for above equation and the problem is this; which one is the chemically meaningful answer? This problem is called rotational ambiguity [11,12]. There are two main strategies to overcome this problem, the first one is relying on applying different constraints to remove or reduce the area of feasible solution (AFS). In some appropriate case by adding supplementary knowledge about system, it can lead to a unique decomposition or at least in some unique factors [13,14]. In the absence of further information, there is no choice except to compute all the feasible solutions [15–18]. The second strategy is the most common approach and there are some reports aim to compute the area of feasible solution in the literatures. First procedure to estimate and minimize rotational ambiguity has been introduced by Lawton and Silvestre [19]. In 1971 they solved this problem for a two-component system by presenting the so-called LS-plots only using nonnegativity constraint. This method has been developed to three-component system by Borgen et al. [20] and Rajko and Istvan [21,22] that proposed a clearer interpretation using computation geometry tools to find inner and outer polygons. Another method for the estimation of feasible bands is based on fast maximum and minimum of the relative signal contribution of components in system using nonlinear constrained optimization algorithms that has been proposed by Gemperline and Tauler [15,23]. Also, systematic grid search introduced by Vosough [12] is another method for all of the feasible solutions of a two-component system. Abdollahi et al. proposed the details of a drawing algorithm for a developmental from of Borgen plot and Lawton–Silvestre method [16,17] called triangle boundary enclosure algorithm. Recently Sawall et al. introduced a method that is based on expanding growing polygons which estimates the AFS [24,25] based on the polygon inflation algorithm (PIA) and is compared with triangle boundary enclosure algorithm. Efficiency and adaptively of the PIA have been evaluated and the results confirm that the PIA is an accurate algorithm with significantly faster performance than triangle boundary algorithm.

A key condition for Borgen and Kowalski's algorithms is the non-negativity of  $D$  as well as of  $C$  and  $S$ . Borgen plots were originally developed for an ideal noise-free bilinear data. Preprocessing steps such as background correction can lead to the small negative elements. Contrary to Borgen and Kowalski approach, the PIA can be applied to the perturbed data. In the evaluation function of the PIA, it is possible to work with relative negative entries.

In this research, the purpose is to obtain optimum resolved results from GC–MS data sets, which reflected co-elution peak problems using the PIA and other curve resolution methods by considering the rotational ambiguity. The performance and reliability of the PIA has been tested by simulated GC–MS data sets with different number of components. In addition, the obtained results are compared with multivariate curve resolution alternative

least square (MCR-ALS) [23,26,27], multivariate curve resolution objective function minimization (MCR-FMIN) which is based on a similar objective function but it uses local search optimization algorithms such as Quasi-Newton (QN) and Nelder–Mead simplex (NM) algorithms [28,29] and independent component analysis (ICA) [30]. Also, the MCR-BAND toolbox [31] is used for estimation of the extent of rotational ambiguity. Because the results of simulated data obtained by the PIA were enough satisfactory, analyses of real challenging GC–MS data sets from commercial fragrances have been done by the PIA. The desired fragrances are called Fleuron and Fresh feel 2 which are widely used in surface cleaner products.

## 2. Materials and methods

### 2.1. Apparatus and software

Gas chromatograph-mass spectrometric analyses of the desired fragrances were performed by an Agilent HP-6890 gas chromatograph system coupled with an Agilent HP-5973 mass selective detector equipped with a HP-5MS fused silica column (30 m  $\times$  0.25 mm i.d., 0.25  $\mu$ m film thickness). Oven temperature set at 60 °C and increased to 246 °C at a rate of 3 °C/min, and kept constant at 280 °C for 10 min for post run step. The injector and detector temperatures were set at 260 °C and 280 °C, respectively.

PIA numerical calculation was executed with FAC-PACK software that is presented by Sawall et al. [32]. The MCR-BAND and MCR-FMIN toolboxes were downloaded from MCR homepage [33]. The Matlab code of JADE-ICA algorithm was downloaded from website [34]. The MCRC software was used for preprocessing for real datasets, chemical rank determination and MCR-ALS procedures [35]. All computations and calculations were performed on 4-GHz Pentium IV with 4 GB of RAM and operate under MATLAB 7.8.0 environment.

### 2.2. Methodology

MCR bilinear methods are based on bilinear decomposition methods of  $n \times m$  data matrix ( $D$ ), that  $n$  refers to different retention times or samples and  $m$  represents the number of channel wavelength or mass to charge as follow:

$$D = CS^T + E_{MCR} = D_{MCR} + E_{MCR} \quad (1)$$

where  $C$  ( $n \times f$ ) is concentration profiles of  $f$  components,  $S^T$  ( $f \times m$ ) contains their spectral profiles and  $E_{MCR}$  ( $n \times m$ ) is a residual matrix.

Another bilinear decomposition method that is guided to unique solutions because of using restrictive constraints is singular value decomposition (SVD) and is formulated as:

$$D = U\Sigma V^T + E_{PCA} = D_{PCA} + E_{PCA} \quad (2)$$

$U\Sigma$  usually called a score matrix,  $V$  is recognized as a loading matrix [36] and  $C$  and  $S$  could be obtained from them by using a suitable transformation matrices  $T$ . This may be stated by the following equations where  $T$  is a nonsingular matrix by  $f \times f$  dimension.

$$D_{PCA} = U\Sigma V^T = U\Sigma T^{-1}TV^T \quad (3)$$

where

$$C = U\Sigma T^{-1} \text{ and } S^T = TV^T \quad (4)$$

It is clear that the  $D$  matrix can be reconstructed with various nonsingular  $T$ , therefore infinite number of feasible solutions are achieved for  $C$  and  $S$ . Mathematically all of these solutions are acceptable but not chemically meaningful. One way to limit the unacceptable chemically solutions, is using natural constraints such as nonnegativity.

Download English Version:

<https://daneshyari.com/en/article/7610561>

Download Persian Version:

<https://daneshyari.com/article/7610561>

[Daneshyari.com](https://daneshyari.com)