



Analysis of the volatile chemical constituents in *Mindium laevigatum* by gas chromatography – Mass spectrometry and correlative chemometric resolution methods

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ABSTRACT

The essential oil of *Mindium laevigatum* was extracted by applying simultaneous distillation extraction (SDE) method and studied with gas chromatography–mass spectrometry (GC–MS). The whole of 61 constituents was identified by applying similarity search between the obtained mass spectra and database. This number was expanded to 91 using multivariate curve resolution – alternation least square (MCR–ALS) method. Different chemometric methods such as simple-to use interactive self-modeling mixture analysis (SIMPLISMA), morphological score (MS) and Fixed Size Moving Window Evolving Factor Analysis (FSMWEFA) were used for determining the number of constituents, pure variables, zero concentration and selective regions. Self-modeling curve resolution (SMCR) was suggested for resolving the co-eluted GC–MS peak into pure chromatograms and mass spectra. MCR–ALS prosperously applied for this aim. Pure variables from SIMPLISMA were applied as initial mixing matrix in iterative process. The resolved mass spectra were properly identified applying mass spectral search in NIST and Wiley library. The outcomes of this work proved that the combination of hyphenated chromatographic methods and resolution techniques provides a complementary method for the exact analysis of essential oils.

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1. Introduction

Gas chromatography–mass spectrometry (GC–MS) has contributed substantially to the analysis of different mixtures of organic compounds especially essential oils and natural compounds [1]. This kind of hyphenated technique demanding separation is suitable for the analysis of complicated samples and is often applied as a strong tool for chemical analysis.

In GC–MS analysis, identification is executed solely by the direct similarity searches in MS databases connected to the GC–MS instruments. Considering the best experimental conditions, the possibility of peak overlap in chromatographic separations may become entirely parous, specifically for extremely complicated samples. This is caused by the baseline offset, background, and some overlapping/embedded peaks. These problems may cause mistaken similarity matches in the MS library and exact determination of the constituents cannot be done. Furthermore, even applying advanced chromatographic technologies, it is not possible to obtain maximum information from the instrument and the interpretation of the results could not improve by using suitable data analysis tools. Luckily, with the development of chemometric resolution techniques, extracting needed information

about constituents in a complicated sample became possible [2]. Common non-iterative procedures in curve resolution based on progressed nature of data, consist of evolving factor analysis (EFA) [3], orthogonal projection resolution (OPR) [4], window factor analysis (WFA) [5], heuristic evolving latent projections (HELP) [6], sub window factor analysis (SFA) [7], and evolving window orthogonal projections (EWOP) [8]. The iterative procedures in curve resolution are composed of alternating regression (AR) [9] and iterative target transformation factor analysis (ITTFA) [10]. Multivariate curve resolution–alternating least square (MCR–ALS) technique is one of the most common self-modeling curve resolution (SMCR) techniques that permits mathematical resolution of spectral and chromatogram profiles of pure chemical species in complex chemical evolving processes [11–14]. Determination of chemical rank is a vital step in curve resolution. Incorrect chemical rank estimation will give misleading information for further quantitative and qualitative analysis. Subspace comparison [15] and morphological score [16] that have been introduced by Shen et al. are useful and simple tools for chemical rank determination. It might induce extraneous constituents in principle component analysis and cause over determined estimation of the chemical rank of the two-way data from hyphenated tools.

The raw data must be pretreated before resolving the two-dimensional data. Many smoothing and denoising methods were suggested like roughness penalty smoothing method [17], convolution smoothing approach dependent on least squares expanded by Savitzky

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and Golay [18] and wavelet denoising technique [19]. Therefore, the combination of hyphenate tools and related chemometric methods opens some new approach for fast and correct analysis of real complex samples.

In this study, the volatile constituents of *Mindium laevigatum* complex mixture were identified using GC–MS combined with the chemometric approaches. The morphological score was used for chemical rank determination of GC–MS data. In addition, MCR–ALS method was successfully applied for the resolution of spectral and chromatographic profiles of *M. laevigatum* oil. The old name of this plant is *Michauxia laevigata* and some of the characteristic features of this plant are anti-inflammatory, wound healing and antioxidant activities [20].

2. Experimental and methodology

2.1. Experimental

The plants of *M. laevigatum* were collected during the fruiting period in July month of 2011 from Kashan (Iran). Root, stem and fruit of *M. laevigatum* were subjected to separate by simultaneous distillation–extraction for 2 h applying a SDE apparatus. The volatile components dried over anhydrous sodium sulfate and was analyzed by GC/MS. GC/MS analysis of volatile constituents was performed on a Agilent HP-6890 gas chromatograph coupled with Agilent HP-5973 mass selective detector equipped with a HP-5MS fused silica column (30 m×0.25 mm i.d., 0.25 μm film thickness). Oven temperature was started at 60 °C and programmed to 246 °C at a rate of 3 °C/min, and for post run step, kept constant at 280 °C for 10 min.

2.2. Methodology

The following steps were performed for every overlapped peak cluster as a subset of the total ion chromatogram (TIC):

- 1) Data processing: This step includes baseline correction, denoising and smoothing. In general raw two-way chromatographic data can be divided into two parts: one of them is chemical components in the mixture called spectral background, and the other one is the instrumental artifacts called chromatographic baseline. One of the powerful technique for removing the baseline drift and spectral background in the chromatographic data is baseline correction using congruence analysis and least square fitting [21]. Homoscedastic noise (independent on variable, sample and signal) and heteroscedastic noise (dependent on variable, sample and signal) are removed by morphological score [16] and Savitzky–Golay filter [18], respectively.
- 2) Number of chemical component determination: Morphological score method was used to chemical rank determination. In this method key spectra are used instead of full rank matrices. Therefore the acquired results are more reliable [16].
- 3) Resolution: By applying MCR–ALS algorithm as an alternative process, the chromatographic and spectral profiles of the components will be recovered [11].
- 4) Evaluation of the results: To confirm the quality and reliability of results, the similarity match with MS database was used.

MCR analysis was executed with MCRC software that presented by Jalali–Heravi group [22]. All computation and calculation were performed on 4–GHz Pentium IV with 4 GB of RAM.

3. Results and discussion

The total ion chromatogram of *M. laevigatum* oil is shown in Fig. 1. This figure indicates the intricacy of the chromatogram by showing various overlapped peaks. The resemblance indices acquired from direct searching applying MS database are very low due to these kinds

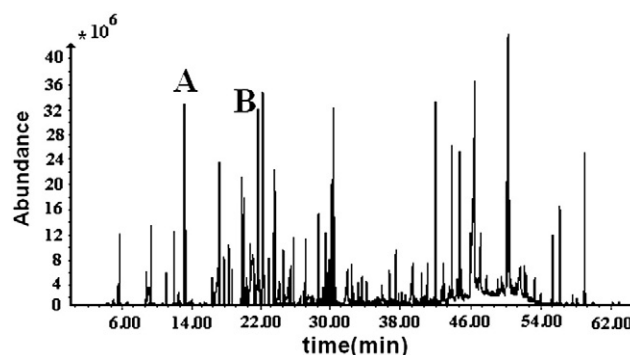


Fig. 1. Total ion chromatogram of *Mindium laevigatum*.

of overlapped peaks. Also, at several scan points of a single peak one can get different compounds applying library searching. If these overlapping and embedded peaks could not separate into constituent parts, the conventional searching employing MS database would be failed. Moreover, because of residual gases and column background, both resolution and identification, specifically for constituents of low concentration, cannot be done. In this work, Kvalheim and Liang method has been applied for the baseline correction [6]. So adequate information for uni-variate linear regression with regard to retention time is provided by the local rank analysis of zero component regions and therefore the baseline become corrected. Using this method, a lot better background correction could be obtained. The Keller method of selective normalization is used on the smoothed chromatograms. The spectra are normalized in chromatographic regions with large abundance according to:

$$x_{ki} / \sum_i x_{ki} \text{ if } \sum_i x_{ki} \geq 1. \quad (1)$$

In which x_{ki} represents the elements of the data matrix of abundances at the retention time k and mass-to-charge i . This way of normalization reduces the problem with heteroscedasticity of the noise, while at the same time the features in data will be retained [23]. It is worth mentioning that the separated and identified constituents with using chemometric resolution techniques would enlarge the number of constituents to 91 which is displayed in italic form in Table 1. Investigating Fig. 1 shows that chromatographic peaks for many constituents of *M. laevigatum* oil are overlapped. From the TIC of *M. laevigatum* oil (Fig. 1), two peaks clusters entitled A (32×201), within range 13.28–13.44 min and B (63×201), within range 21.60–21.88 min are taken as examples to illustrate the data analysis procedure in this study. Fig. 2 displays the TIC for these clusters.

In the first stage, morphological scores (MS) [16] were applied to determine the number of constituents in each peak cluster. In MS method, to prevent accretion of noise, key spectra rather than full rank matrix were analyzed. The plots of MS for peak clusters A and B are displayed in Fig. 3.

Investigating this figure reveals two and three constituents for the clusters A and B, respectively. Fixed size moving window evolving factor analysis (FSMWEFA) control the peak purity of two-dimensional data [24]. The curved shapes in FSMWEFA plots for which the logarithm values of eigenvalues are in a higher location than the noise level represent the appearance of constituents. Fig. 4 indicates the FSMWEFA plots for Clusters A and B. The plot of FSMW for cluster A (Fig. 4A) displays the heteroscedastic noise, because total curved shapes are higher than the noise level. Thus, in order to identify the number of significant constituents, the heteroscedasticity must be corrected. We have applied Keller method of selective normalization and Savitzky–Golay filter to correct the heteroscedasticity. Fig. 4B shows the plot of FSMW for the cluster A after correction. From this figure, we can deduce that the cluster A is

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