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Quantitative analysis of essential oils in perfume using multivariate curve resolution combined with comprehensive two-dimensional gas chromatography

Luiz Antonio Fonseca de Godoy[a], Leandro Wang Hantao[a], Marcio Pozzobon Pedroso[a,b], Ronei Jesus Poppi[a], Fabio Augusto[a,*]

[a] Institute of Chemistry and Instituto Nacional de Ciência e Tecnologia de Bioanalítica (INCTBio), State University of Campinas (Unicamp), CP 6154, 13084-971 Campinas, São Paulo, Brazil
[b] Department of Chemistry, Federal University of Lavras (UFLA), 37200-000 Lavras, Minas Gerais, Brazil

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ABSTRACT

The use of multivariate curve resolution (MCR) to build multivariate quantitative models using data obtained from comprehensive two-dimensional gas chromatography with flame ionization detection (GC × GC-FID) is presented and evaluated. The MCR algorithm presents some important features, such as second order advantage and the recovery of the instrumental response for each pure component after optimization by an alternating least squares (ALS) procedure. A model to quantify the essential oil of rosemary was built using a calibration set containing only known concentrations of the essential oil and cereal alcohol as solvent. A calibration curve correlating the concentration of the essential oil of rosemary and the instrumental response obtained from the MCR-ALS algorithm was obtained, and this calibration model was applied to predict the concentration of the oil in complex samples (mixtures of the essential oil, pineapple essence and commercial perfume). The values of the root mean square error of prediction (RMSEP) and of the root mean square error of the percentage deviation (RMSPD) obtained were 0.4% (v/v) and 7.2%, respectively. Additionally, a second model was built and used to evaluate the accuracy of the method. A model to quantify the essential oil of lemon grass was built and its concentration was predicted in the validation set and real perfume samples. The RMSEP and RMSPD obtained were 0.5% (v/v) and 6.9%, respectively, and the concentration of the essential oil of lemon grass in perfume agreed to the value informed by the manufacturer. The result indicates that the MCR algorithm is adequate to resolve the target chromatogram from the complex sample and to build multivariate models of GC × GC-FID data.

1. Introduction

Quantification has always been a field of intensive study in analytical chemistry. The conventional approach is the univariate calibration model for a single analyte. Essentially, it consists on the correlation of the instrumental responses with the concentrations of the target analyte. In gas chromatography (GC) the instrumental response is the peak area, which can be estimated through conventional integration [1]. However, obtaining quantitative results can be problematic when the target is not a single analyte, but a complex mixture, such as the case when evaluating the presence of essential oils in perfumes [2].

The first step in conventional approaches to perform this task is to identify specific chemical markers present only in the targeted essential oil or essence. Temperature-programmed retention indices of the unknown peaks determined with polar and non-polar columns, combined with electron-impact ionization mass spectra, are required to correctly identify each peak [2]. For essential oils originating from several countries, characteristic components of the essential oil and their common biosynthetic precursors that must be met to define essential oil quality can be chosen as markers [3]. Once identified, some markers, or their ratios required to characterize an essential oil, are quantified in the complex mixture, i.e., commercial perfumes and the result is then used to estimate the amount of the essential oil in the complex mixture. The reference values for each marker or their ratios include the average, minimum and maximum, taking into account seasonal or climatic variations in essential oil composition [3]. This classical procedure can be misleading if co-elution is present or if the amount of the chemical marker is under the limit of quantification. For example, when co-elution is present, quantification of the chemical markers will be hampered as the resulting peak integration may be erroneous. Therefore, techniques which improve separation capacity can be of special relevance to these problems.

* Corresponding author. Tel.: +55 19 35213057; fax: +55 19 35213023.
E-mail address: augusto@iqm.unicamp.br (F. Augusto).

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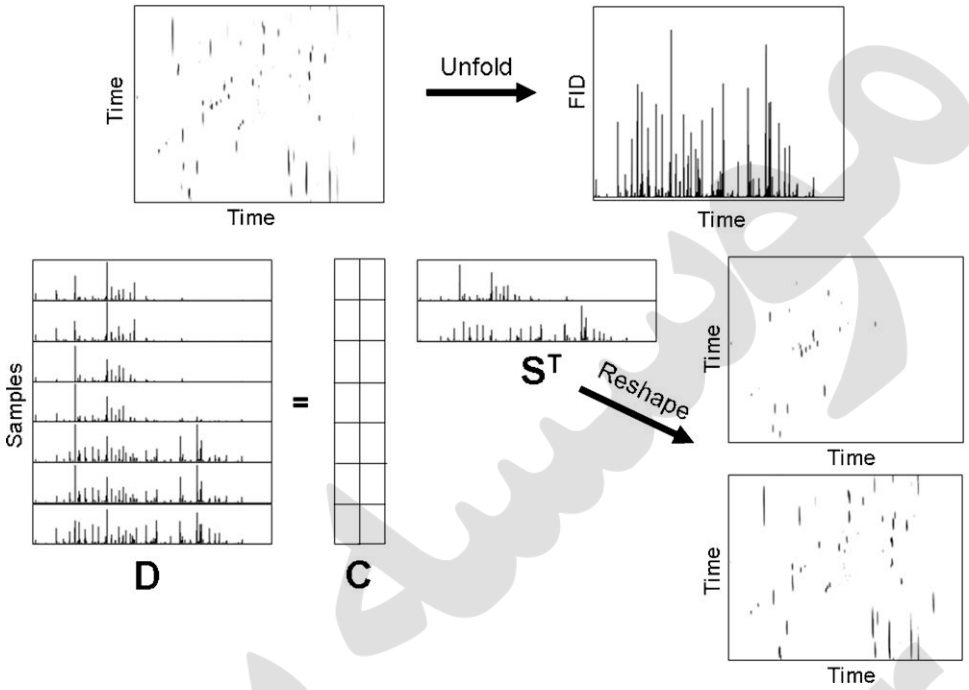

Fig. 1. Scheme for MCR-ALS analysis of GC × GC-FID chromatograms.

Introduced in 1991 by Phillips and coworker [4], comprehensive two-dimensional gas chromatography (GC × GC) has become the benchmark technique for unraveling complex samples. The GC × GC system consists of conventional gas chromatograph fitted with two capillary columns connected in series, such that all sample portions emerging from the first column enter the second and are analyzed sequentially. The key interface that allows the injection of small and narrow fractions from the first to the second column is the modulator. A GC × GC analysis provides higher sensitivity, detectability and separation power [5]. Because GC × GC provides a true orthogonal separation system (when the retention mechanisms from the first and second dimension are independent), it is possible to observe well ordered distributions of chemically similar compounds in the retention plane [6]. In this way, numerous small ingredients present in some essential oils can be separated, because every peak is submitted to two different mechanisms of separation and then detected, due to the higher sensitivity [7–9]. Even without positive identification of the compounds, as in a GC × GC-FID analysis, this technique can be very useful for the analysis of essential oils, for example to reveal some regional or seasonal variations and to detect adulterations that would be unnoticed by GC analysis [2].

Even though GC × GC may provide the peak capacity and the sensitivity needed, the use of the conventional approach (use of marked compounds) to quantify a complex sample as an essential oil in a more complex mixture such as perfume sample is still a tedious and time-consuming task. The quantification of the individual chemical marker is, usually, obtained by conventional integration [10], but in this approach the chromatographic signal of the marker has to be well resolved. de Godoy et al. [11] proposed an alternative for quantification of targeted-compounds by using an interval multi-way partial least squares calibration whereby coelution did not affect the results. Furthermore, Zeng et al. [12] proposed an alternative moving window factor analysis and two-step iterative constraint method to extract the pure profile (either mass or absorbance spectra) in order to quantify targeted-analytes, in cases where co-elution is present. When compared to conventional gas chromatography with mass spectrometric detection (GC–MS) the amount of information obtained from a GC × GC-FID chromatogram is considerably larger. Thus, instead of using a chemical marker to quantify a complex mixture in a complex sample, the whole two-dimensional chromatogram can be used in these analyses. As the intrinsic information obtained from GC × GC chromatograms is considerably larger and more complex, their manual (or conventional) interpretation can be problematic or even impossible. Consequently, the use of a chemometric approach is recommended, because it provides a reliable and non-subjective result [13]. Pedroso et al. applied multivariate calibration strategies to identify of gasoline adulteration, using GC × GC-FID data [14].

An important multivariate technique that has not been widely used with GC × GC-FID data is the algorithm proposed by Tauler et al. in 1995 called multivariate curve resolution (MCR) [15]. This method has been employed in analysis of complex mixtures through different analytical techniques [16–20], such as high performance liquid chromatography coupled to diode array detection [21]. The theory behind the MCR algorithm has been discussed in previously papers [22–25]. The most important feature of the MCR is the second order advantage, in which the calibration step can be built with few samples instead of a large calibration set and, furthermore, it is possible to quantify the compounds of interest even in the presence of interferences not present in the calibration sample set. In the MCR algorithm the data set is decomposed into two matrixes, one related to concentration profiles and another related to instrumental profiles. These two matrixes are iteratively adjusted to the data set through an alternating least squares (ALS) procedure, which starts with an initial estimate of pure analyte instrumental profiles. During the ALS optimization, several constraints, such as non-negativity, unimodality, closure and selectivity, can be applied to obtain chemically meaningful solutions. Fig. 1 exemplifies how the MCR algorithm can be used with GC × GC-FID data in the case of a two component mixture. The first step is the unfolding of the GC × GC-FID chromatograms from a matrix to a vector. Next, the vectors of all samples are placed in the lines of the bidimensional data matrix **D**, which is decomposed into the matrix of concentration profiles **C** and the matrix with the chromatograms of each pure component **S**. Finally, after ALS optimization, the vectors obtained in matrix **S** are reshaped into two-dimensional GC × GC-FID chro-

Table 1
Composition of the validation samples, in % (v/v), used to evaluate the chemometric model.

Sample	Essential oil of rosemary	Pineapple essence	Perfume #1
V1	8.0	–	–
V2	12.0	–	–
V3	5.0	2.0	–
V4	4.0	4.0	–
V5	5.0	10.0	–
V6	5.0	6.0	–
V7	8.0	4.0	–
V8	4.0	–	6.0
V9	6.0	–	80.0
V10	5.0	–	95.0

matograms and the calibration curve can be built using the data contained in with matrix **C**. Thus, the combination of GC × GC-FID and MCR-ALS provides the analyst the instrumental profiles of each pure compound besides the quantitative information. Consequently, this may be the best combination to unravel these complex issues regarding one of the ultimate goals in analytical chemistry.

In this paper, we proposed the use of the MCR-ALS method to analyze data obtained by GC × GC-FID. To evaluate the feasibility of this method, quantification of the essential oil of rosemary was performed in samples containing interferences (pineapple essence or a commercial perfume) not present in the calibration set, which evaluates the second order advantage of the algorithm. Additionally, the amount of essential oil of lemon grass was quantified in commercial perfumes to evaluate the accuracy of the proposed method.

2. Materials and methods

2.1. Samples and materials

The essential oil of rosemary, synthetic pineapple essence, cereal alcohol and a commercial perfume (perfume #1) were obtained from stores in Campinas, Brazil, to evaluate the chemometric model. The calibration samples were prepared by the dilution of the essential oil of rosemary in cereal alcohol at the concentrations of 2.5, 5.0, 7.5, 10.0 and 15.0% (v/v). For the validation samples, pineapple essence or a commercial perfume were added as interferences. The first interference was chosen to simulate a complex "perfume"-like sample. This particular mixture is not used in any commercial perfume known to the authors. The second interference was chosen to provide a higher complexity sample, in order to evaluate the chemometric model. The compositions of the validation samples are listed in Table 1.

To evaluate the accuracy of the proposed MCR-ALS method, a second data set was built to quantify the essential oil of lemon grass in a local commercial perfume (perfume #2), which contains this essential oil. The essential oil of lemon grass, an essence containing the major constituents of this perfume (without the lemon grass essential oil) and two samples of the perfume from different batches were supplied by the perfume manufacturer. Firstly, a calibration model was built by diluting the essential oil at the concentrations of 2.5, 5.0, 7.5, 10.0 and 15.0% (v/v) in cereal alcohol. The validation samples were prepared by introducing pineapple essence and the essence of the commercial perfume as interferences, to simulate a low complexity and high complexity sample, respectively. The compositions of the validation samples are listed in Table 2. Afterwards, the model was used to quantify the amount of essential oil of lemon grass in the perfume #2 samples.

Table 2
Composition of the validation samples (%, v/v) used to evaluate the accuracy of the model.

Sample	Essential oil of lemon grass	Pineapple essence	Perfume# 2 essence
V11	8.0	–	–
V12	10.0	–	20.0
V13	5.0	–	20.0
V14	5.0	20.0	–
S1[a]	8.0–9.0	–	–
S2[a]	8.0–9.0	–	–

[a] Perfume #2 samples from different batches. Essential oil concentration range informed by manufacturer.

2.2. GC × GC-FID

The GC × GC-FID prototype is based on a HP-6890 Series GC-FID coupled to a model 7263 liquid auto-sampler (Hewlett-Packard, Wilmington, DE) and fitted with a split–splitless injector (operated in split mode, split ratio 200:1). Hydrogen (0.6 mL min^{-1}) was used as carrier gas. This prototype uses a lab-made four jet cryogenic modulator. The cryogenic fluid was N_2 cooled in liquid nitrogen (LN_2). N_2 flow was toggled by two three-way Asco solenoid valves (Florham Park, NJ). The command to these valves was controlled by a DAQPad-6015 16 bits AD/DA board controlled by lab-made software developed using the LabView v8.2 programming environment (National Instruments, Austin, TX) and connected to an AMD Athlon 4600 Dual Core personal computer. The column set consisted of a 30 m × 0.25 mm × 0.25 μm HP-5 poly(5% diphenyl/95% dimethylsiloxane) column (Agilent Technologies, Wilmington, DE) connected by a press fit connector to a 1 m × 0.1 mm × 0.1 μm Supelcowax 10 polyethylene glycol column (Supelco, Bellefonte, PA, USA). For all runs, the modulation period was set to 6.0 s and data acquisition frequency was 100 Hz. The oven temperature program was: 60 °C to 250 °C at 3 °C min^{-1}. The injection and detection temperatures were 250 °C. The chromatograms were acquired and digitalized through Chemstation software (Agilent Technologies, Wilmington, DE). To estimate the deviation of the retention times in both dimensions, five replicates of the essential oil of rosemary, at 30% (v/v) in cereal alcohol, were injected.

2.3. Multivariate analysis

The GC × GC chromatograms were exported from Chemstation software to MatLab 6.5 (Mathworks, Natick, MA, USA) as ASCII files. The chromatograms were unfolded and aligned using a peakmatch algorithm downloaded from http://synoveclab.chem.washington.edu/ [26]. The MCR-ALS routine is also available on the internet (http://www.mcrals.info/).

3. Results and discussion

The GC × GC chromatogram obtained for the sample containing 15% (v/v) of the essential oil of rosemary in cereal alcohol is shown in Fig. 2, where a broad peak starting at $^1t_R \approx 10.5$ min appears as a streak through all ^{2}D space. This peak was identified as a co-elution of glycols, which are used for solubilization purposes and also act as fixing agents. Therefore, their presence is expected in most perfume and cologne products. Because of the highly polar nature of these species, they present very strong interactions with the second dimension column and, therefore, they elute in ^{2}D as extremely large and tailed peaks. These constituents were not added to the samples during their preparation, but they were already present in the fragrances (rosemary oil, pineapple essence) and in the perfume used. During data processing, it was observed that the region that contains these signals (10.2 min < ^1t_R < 14.4 min) as well as

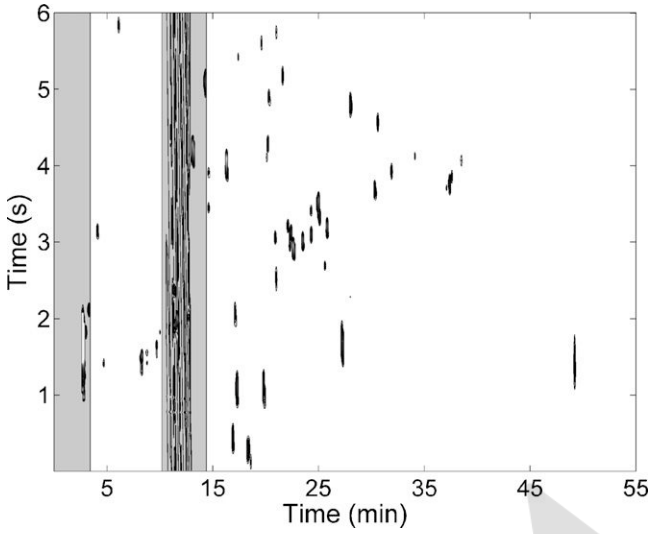

Fig. 2. GC × GC chromatogram obtained for the sample containing 15% (v/v) of essential oil of rosemary in cereal alcohol. The areas excluded before building the multivariate model are highlighted.

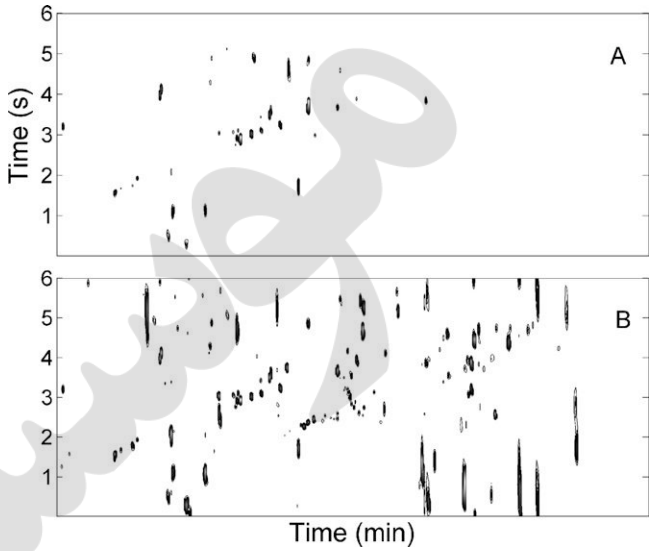

Fig. 4. GC × GC chromatograms obtained for (A) validation sample V5 and (B) validation sample V9.

the beginning of the chromatogram (^1t_R < 3.5 min), where solvent elutes, do not present any quantitative information; therefore, they were suppressed from the data set used to build the chemometric model.

Fig. 3 presents the chromatograms obtained for essential oil of rosemary, pineapple essence and the perfume #1 without the excluded regions, where it can been noted that the samples have some identical compounds and some compounds with ^1t_R and ^2t_R close to the same positions. Consequently, it was expected that a sample containing the essential oil of rosemary and pineapple essence or perfume would have a GC × GC chromatogram with co-elution in some regions. Fig. 4 shows the chromatograms obtained for validation samples V5 and V9 confirming that these co-elutions do indeed exist. The MCR algorithm was selected to build the chemometric model to quantify the essential oil of rosemary in samples with interferences absent in the calibration samples, because this routine presents several important proprieties as the second order advantage.

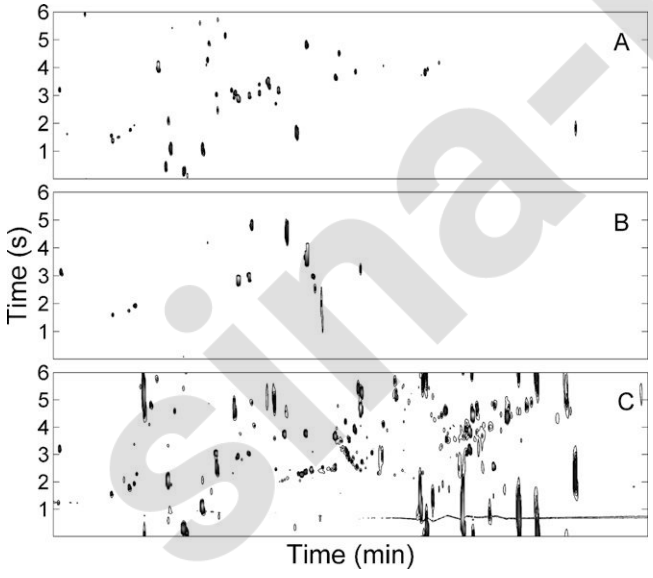

Fig. 3. Typical GC × GC chromatograms with the excluded areas suppressed of (A) the essential oil of rosemary, (B) pineapple essence and (C) commercial perfume.

Deviation in the retention times in both dimensions is a very common subject in day-to-day chromatography runs, thus it would lead to wrong results when chemometric is applied to raw chromatographic data. Therefore, the deviation was estimate through the variation of the retention times in both dimension by injection of diluted essential oil of rosemary and eight peaks with different polarities and boiling points were monitored. No deviations of the retention time in the first dimension were observed; however, the values for the estimated standard deviation of the retention time in the second dimension ranged from 20 to 77 ms for the monitored peaks. Although these values would seem to be insignificant for conventional gas chromatographic analysis, it is worth to highlight that the peak width for GC × GC is typically 80–400 ms and, therefore, it would jeopardize the results. To fix this problem, all GC × GC chromatograms were unfolded and aligned using the peakmatch routine before building the model [26].

As mentioned earlier, to employ the MCR-ALS algorithm an initial estimate of the experimental data is necessary. In the first part of this work, the chromatograms obtained for pure samples of the essential oil of rosemary, pineapple essence and perfume #1 were used for the initial estimates. During the ALS optimization of the model, selectivity constraints for concentrations and non-negativity constraints for concentrations and chromatograms were applied. As all samples were used to build the model and not only the calibration ones, the selectivity constraint was employed to provide to the model the presence or absence of the interferences in the samples, avoiding problems of rotational ambiguity in the resolution results. The chromatograms resolved by the model for the essential oil of rosemary, pineapple essence and perfume #1 are shown in Fig. 5. Comparing Figs. 3 and 5, the high similarity between the chromatograms for pure samples and for the chromatograms resolved by the MCR model can be seen. Then a calibration curve was carried out using the concentration results obtained from the model and the reference concentration of the calibration samples (Table 1), where a correlation coefficient of 0.996 was obtained.

The prediction of the concentration of the essential oil of rosemary in the validation samples was performed by interpolating into the calibration curve the concentration results provided by the MCR model for these samples. Table 3, which displays the predicted concentration for the essential oil of rosemary and the absolute error for each validation sample, allows the assessment of the accuracy and suitability of the proposed method. A graphic of

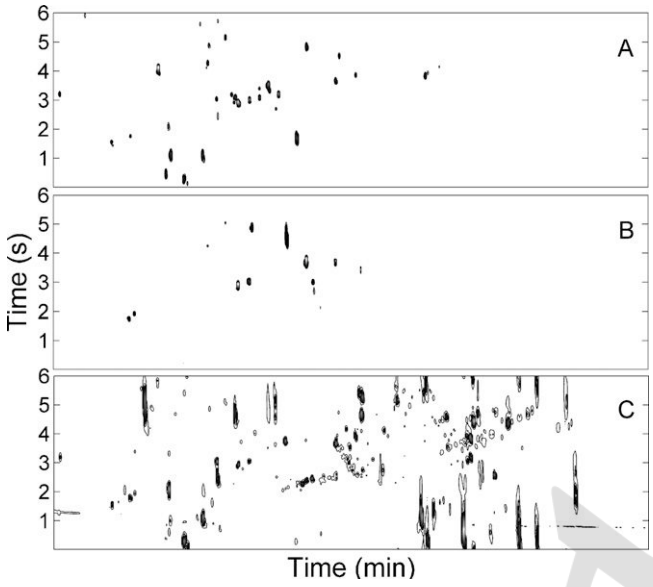

Fig. 5. GC × GC chromatograms recovered by MCR-ALS for (A) the essential oil of rosemary, (B) pineapple essence and (C) commercial perfume.

Table 3
Predicted and real concentrations of the essential oil of rosemary for the validation sample set in % (v/v), and the absolute errors (%, v/v).

Sample	Real	Predicted	Absolute errors
V1	8.0	7.3	−0.7
V2	12.0	11.4	−0.6
V3	5.0	5.5	0.5
V4	4.0	3.7	−0.3
V5	5.0	4.4	−0.6
V6	5.0	5.0	0.0
V7	8.0	7.9	0.1
V8	4.0	4.3	0.3
V9	6.0	6.2	0.2
V10	5.0	4.6	−0.4

predicted concentration *versus* reference concentration was plotted and a correlation coefficient of 0.988 was obtained (Fig. 6). The root mean square error of the percentage deviation (RMSPD) (Eq. (1)) and the root mean square error of prediction (RMSEP) values

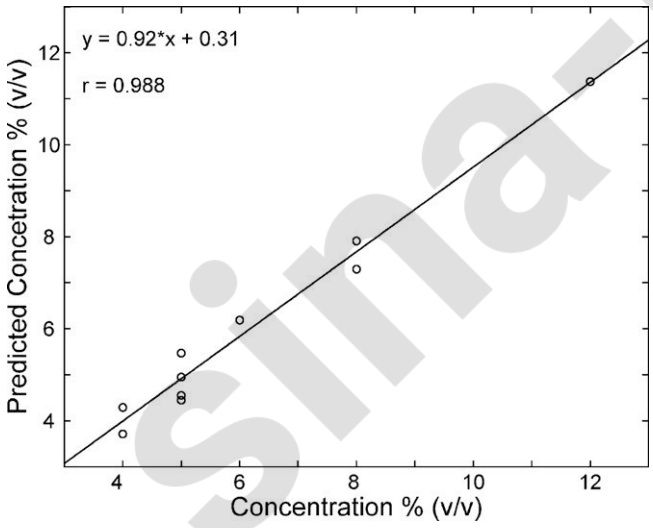

Fig. 6. Concentration of the essential oil of rosemary (%, v/v) in validation samples *versus* concentrations of these samples predicted by MCR-ALS (*r* = correlation coefficient).

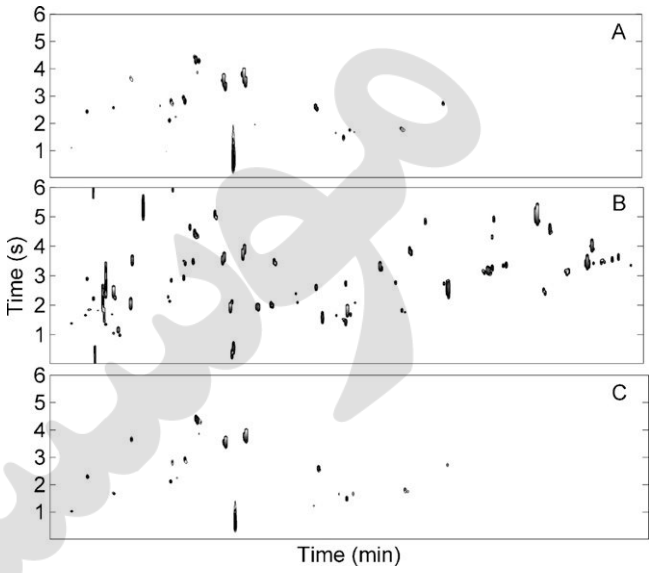

Fig. 7. GC × GC chromatograms for (A) the essential oil of lemon grass, (B) real commercial sample of perfume and (C) the recovered chromatogram for the essential oil of lemon grass in the real commercial perfume.

obtained were 7.2% and 0.4% (v/v), respectively

$$\mathrm{RMSPD} = 100 \times \sqrt{\sum_{i=1}^{n} \frac{(y_{pred(i)} - y_{ref(i)})^2}{(y_{ref(i)})^2} \times \frac{1}{n}} \quad (1)$$

where $y_{pred(i)}$ and $y_{ref(i)}$ are the reference and the predicted concentrations of the essential oil of rosemary in the *i*th sample and *n* is the number of prediction samples.

The MCR-ALS method was also evaluated by predicting the concentration of the lemon grass essential oil in validation samples and in two real perfume #2 samples. The procedure for calibration was performed similarly as described for the rosemary essential oil. The chromatograms of the pure samples of essential oil of lemon grass, pineapple essence and perfume #2 essences were obtained for the initial estimates needed to the MCR-ALS algorithm. The concentration of each component in the validation set and perfume sample is presented in Table 2. A calibration curve was build using the concentration results for the lemon grass essential oil, using the chromatogram resolved by the model for the essential oil, *versus* the reference concentration of the calibration samples; finally, a correlation coefficient of 0.983 was achieved. Fig. 7(A) illustrates the pure essential oil of lemon grass, (B) the commercial sample and (C) the recovered profile for the essential oil of lemon grass in the real perfume sample. To predict the essential oil concentration in validation and perfume samples, the results provided by MCR-ALS were interpolated in the calibration curve and the results are presented in Table 4. The root mean square error of the percentage deviation (RMSPD) (Eq. (1)) and the root mean square error of prediction (RMSEP) values obtained were 6.9% and 0.5% (v/v),

Table 4
Predicted and real concentrations of the essential oil of lemon grass for the validation sample set (%, v/v), and the absolute errors (%, v/v).

Sample	Real	Predicted	Absolute errors
V11	8.0	8.5	0.5
V12	10.0	9.3	−0.7
V13	5.0	5.4	0.4
V14	5.0	5.3	0.3
S1	8.0–9.0	8.7	–*
S2	8.0–9.0	8.2	–*

respectively. Values obtained for perfume samples were not used to calculate RMSPD and RMSEP because the supplier provided only a concentration range for the essential oil of lemon grass.

The results achieved by the MCR-ALS algorithm demonstrate that the proposed approach can be used to recovery a signal profile even from complex mixtures. The chromatograms of essential oils of rosemary and lemon grass were resolved from complexes mixtures with pineapple and/or perfume essence and they were used to quantify these oils, which are complex mixtures of several compounds, as they were single species. The proposed approach is an alternative to the single marker quantification in complex mixtures: the whole recovered chromatogram is used to predict the concentration of the mixture instead of few peaks or their ratios.

These results reveal that the MCR-ALS algorithm is able to work with data obtained by GC × GC-FID, thus combining the advantages of the GC × GC-FID, such as high detectability, sensitivity and selectivity, with the features of the MCR-ALS method, such as second order advantage and resolution of the chromatograms for each pure compound even in complex samples.

4. Conclusions

The results indicate that the MCR-ALS algorithm can be employed to estimate multivariate calibration models with data obtained from a GC × GC-FID, which presents several advantages in relation to conventional GC-FID, such as higher detectability, sensitivity and resolution power. In this way, these advantages can be combined with the features of MCR-ALS method, such as second order advantage, to analyze complex components in complex samples. This combination GC × GC-FID + MCR-ALS was successfully tested in the quantification of the essential oil of rosemary even in the presence of interferences not present in the calibration samples. After the optimization of the model, the chromatographic profiles obtained for the pure components were very similar to GC × GC-FID analysis of pure samples. The quantification of the essential oil of rosemary in the validation sample set was performed and the RMSEP and RMSPD obtained were 0.4% (v/v) and 7.2%, respectively, which validated the model proposed. For lemon grass essential oil, RMSEP and RMSPD obtained were 0.5% (v/v) and 6.9%, respectively; analysis of perfume samples were carried out and the results obtained agreed to the expected values.

The results suggest that the combination GC × GC-FID + MCR-ALS employed herein can be a powerful tool to resolve chromatographic signals in samples with unknown interferences or not present in the calibration samples, as well as for quantification of complex constituents in formulations such as perfumes and toilet products.

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