MULTIVARIATE CURVE RESOLUTION APPLIED TO ION MOBILITY SPECTRA

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Abstract

In this work, a Multivariate Curve Resolution (MCR) with Alternating Least Squares (ALS) method is described and used to identify the concentrations of a two-component (ethanol and acetone) mixture analysed with an Ion Mobility Spectrometer. Results allow us to distinguish qualitatively both components at lower concentrations, whereas fail to detect ethanol at higher concentrations. The impossibility of detecting ethanol at higher concentrations is caused by higher acetone's proton affinity.

1 Introduction

Ion Mobility Spectrometry is an instrumental analytical technique to analyse volatile substances based on the drift velocities of gas ions in weak electric fields. Firstly implemented during 1970's (Revercomb & Mason, 1975) under the name of "Plasma chromatography", IMS offered a low-cost, portable, sensitive and fast way of detecting trace organic compounds. Since then, it has been deployed to help in the detection of drug trafficking and chemical warfare agents, among other fields.

Its fundamental principle it's simple: A bundle of ions (called swarm) taken from the mixture to be analysed is introduced into a tube under an electric field. The ion swarm attains a drift velocity v_d proportional to the applied electric field E as equation 1 states.

$$v_d = KE \tag{1}$$

The proportionality coefficient K characteristic of each pure substance is called 'mobility coefficient'.

The electric current at the end of the tube, which is caused by the ions colliding with a detector, is monitored obtaining a measure of the charged ions that cross the tube through time. This $I(t)$ plot is called the 'mobility spectrum' and it presents a peaked shape. The mobility spectrum of different concentrations of ethanol and acetone conforms the dataset used at the present work.

Multivariate Curve Resolution (MCR) is a set of techniques which intend to extract information (concentrations and spectra) of a mixture's pure components. Instead of using the most common approach in chemical analysis, which is separating the mixture in its pure chemical components, MCR allows to extract the information directly from the mixture, in this case from the mobility spectrum. Avoiding the need of mixture separation has many significant advantages in the analysis time, cost and portability widening the applications of IMS.

The rest of the paper is structured as follows:

Section 2 presents the IMS device, linking the physical limitations of the measures with the mathematical properties and limitations of the data measured, described on section 3.

Section 4 deals with the explanation of the algorithms and the data processing used to extract the concentrations and spectra from the dataset.

Finally, results and a discussion are provided on section 5.

2 Ion Mobility Spectrometer
(Eiceman & Karpas, 2005)

The Ion Mobility Spectrometer is an analytical device used to identify ionized molecules in gas phase. It is based on the drift velocities of gas ions accelerated by an electric field inside a tube of known length. An 'IMS measure' consists of the distribution of the times needed by the ions to travel through the tube: a 'mobility spectrum'.

The IMS consists of two main regions: the ionization region and the drift region. These regions are separated by a shutter which marks the time when the ionized particles start to drift through the electric field. Particles travel through the electric field and neutralize colliding with a detector causing a current flow. The current flow is amplified (and usually converted to voltage) obtaining the mobility spectrum. Figure 1 summarizes this.

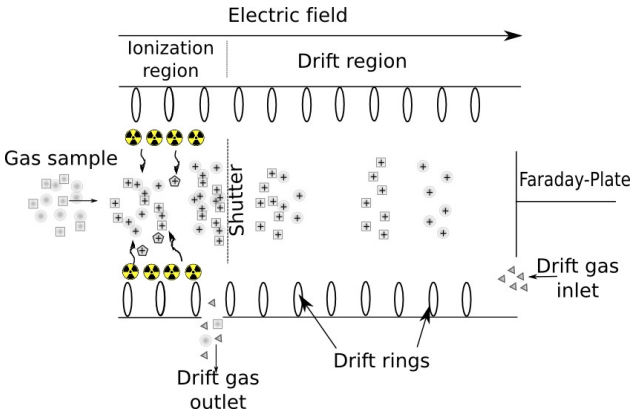


Figure 1: IMS working principle. Based on picture found at (Westhoff *et al.*, 2009)

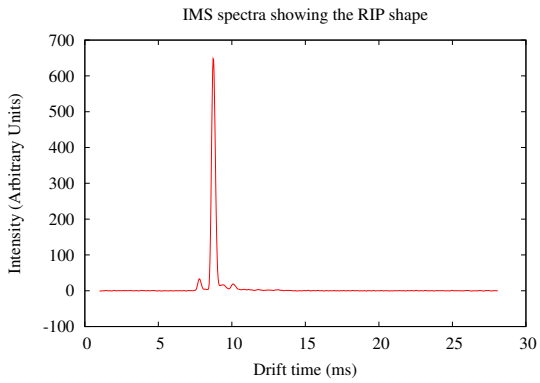


Figure 2: Spectrum sample taken without any concentration of ethanol nor acetone. The RIP is shown.

2.1 Ionization region

The ionization of the sample is usually performed at ambient pressure with the levels of moisture and oxygen found in ambient air. Several sources can be used to ionize the samples such as radioactive sources, corona discharges or photo-ionization; although the most common source is the radioactive because of its reliability, stability and absence of mobile parts and power supply which diminishes the maintenance cost.

For any source used, the total charge used to ionize the samples is fixed. This means that the number of particles that can be ionized at one experiment is finite. This restriction implies that there are non-linearities in the spectra: Superposition of two spectra with different concentrations (i.e. one sample exclusively with ethanol and one sample exclusively with acetone) will not lead to the spectrum of the combined sample (i.e. a sample of a mixture of ethanol and acetone).

Moreover, the proton affinity of a substance (which is the affinity of a substance to be ionized by a proton) will cause some components to be ionized easier than others. The components of the mixture with lower proton affinity may not be ionized, and therefore not detected at the end of the tube. These neutral particles may get stranded in the tube interfering with the moving ions, that's why they must be removed.

For each source, there are different reactant ions that lead to peaks at the mobility spectrum. These peaks are higher if there is no sample introduced. The reactant ion peaks (RIP), showed in figure 2 are reduced as the charge of these reactant ions is used to ionize the samples.

2.2 Drift region

Ions travel from the shutter to the detector under the electric field. In order to avoid interference between the travelling ions and neutral particles stranded on the tube, a drift gas is expelled from the detector in the opposite direction of the ions. The drift gas is chosen to be inert with the ions, guaranteeing that no chemical reaction will be produced in the drift region that would alter the travelling times. Close to the shutter a gas outlet is placed to eject the gas.

3 Dataset

Our dataset consists of 25 spectra with different concentrations of ethanol and acetone. The list of concentrations used is available as an appendix (see table 1). The ion mobility spectrometer used to take the spectra is the GDA2 from Airsense Analytics.

Each spectrum consists of 895 points, so all the spectra combined form a 25×895 matrix named D.

4 Multivariate Curve Resolution (Ferré, 1997)

MCR techniques are based on the assumption that the matrix D, which contains in each row a spectrum with a particular concentration of ethanol and acetone, can be factorized in the product of two matrices: C, which accounts for the concentrations of the pure substances and S^T, which accounts for the spectrum of each pure substance. This factorization is shown on equation 2. The E term accounts for experimental errors.

$$D = CS^T + E \tag{2}$$

Given D as an $m \times n$ matrix, with m the number of spectra, and n the number of points for each spectrum, the decomposition of C and S has a wide range of mathematical solutions. The number of pure substances, which determines the dimensions of C and S, is not fixed and has to be determined. If C is an $m \times k$ matrix and S^T is an $k \times n$, then k has to be understood as the number of pure substances in the mixture.

Once the number of components is fixed, an initial estimation of the concentrations must be given to

ALS to begin the iterations. The initial estimation is crucial to correctly identifying the spectra of the different substances, and the physical constraints to the solution (such as non-negativity or unimodality), will be imposed between ALS iterations.

The Matlab MCR-ALS Toolbox from Jaumot *et al.* (2005) has been used with the PLS_Toolbox from EigenvectorResearch (2011) to implement the data processing.

4.1 Preprocessing

The first step in the analysis consists on a preprocessing to clean the data. This preprocessing includes four different phases.

- Replicated spectra are removed.
- Baseline removal
- Noise filtering
- Peak alignment

The IMS device gives many replicas from each spectrum. These replicas are redundant and they must be removed from the dataset.

As with many other spectrometers, there exists a baseline which, in our case, is corrected by fitting and subtracting a fourth order polynomial to the first 200 points and the latest 450 points of each spectra.

To reduce the noise, a Savitzky-Golay filter of grade 2 and a window of 9 points is applied to the spectra. The Savitzky-Golay filter fits to each point a polynomial of degree 2 in our case, using the 9th points closer to the current point. The evaluation of the fitted polynomial at the treated point gives the output value of the filter. One of the main advantages of this filter in front of others is that it preserves the position and width of the relative maximum and minimum points of the spectra.

Finally, all the spectra are aligned. To do so, all the local maximum of all the spectra are detected. We consider that the two peaks should be aligned if the distance between them is smaller than $0.1ms$.

4.2 Number of components

We may know the number of pure chemical substances in the original mixture (i.e. in our experiment, we know we only have ethanol and acetone). This may give us a hint on the number of components, although we must take into account the different RIPs we may have. To estimate the number of components k with a more rigorous method, a singular value decomposition of the data matrix is performed and the number of components is estimated by counting the most significant singular values.

4.3 Initial estimation

There are different ways to obtain an initial estimation of the concentration and the spectra matrices. Given that the different spectra we use come from different experiments (i.e. not a temporal evolution), we may discard popular methods such as Evolving Factor Analysis (Keller & Massart, 1992) that are suitable for studying chemical mechanisms where mixture components form and disappear linking temporally different spectra. As this is not our case, we have opted by a more suitable method to obtain initial estimations: SIMPLISMA.

4.3.1 SIMPLISMA

SIMPLISMA (Windig & Guilment, 1991), which stands for "SIMPLe to use Interactive Self-modelling Mixture Analysis" allows to perform an initial estimation of the concentrations and spectra with little intervention from the user. It is based on the coefficient of variation of the spectra points which is defined in 3, where μ stands for the mean and σ stands for the standard deviation of the spectra points.

$$c_v = \frac{\sigma}{\mu} \tag{3}$$

The largest this coefficient is, the more information that drift time instant is supposed to add. As this coefficient is not well defined for $\mu \sim 0$, an offset α is added to μ to compensate. Therefore, the purity of a variable is defined as stated in equation 4.

$$p_j = \frac{\sigma_j}{\mu_j + \alpha} \tag{4}$$

For each drift time of the D matrix, the purity of the spectra is computed, defining a purity vector of components p_j, $j = 1...n$. The indexes of the k largest components of the purity vector are stored in an array s_l, $l = 1...k$. A matrix A is defined, and its elements $a_{i,l}$ are defined as $a_{i,l} = d_{i,s_l}$. In plain words, A contains a selection of the columns of the matrix D, this is the spectra of the drift times with largest purity.

The initial estimation of the spectra S_0^T is given as the solution of the overdetermined system presented on equation 5. This solution can be obtained using least squares.

$$AS_0^T = D \tag{5}$$

Finally an estimation of the concentrations can be obtained with $C_0 = DS_0^{T+}$.

4.4 Alternate least squares

The equation 2 can be solved using the equations 6 and 7 iteratively.

$$S = C^+ D \tag{6}$$

$$C = DS^{+} \tag{7}$$

In these equations, the symbol $^{+}$ stands for the pseudoinverse matrix.

The Moore-Penrose pseudoinverse

The Moore-Penrose pseudoinverse matrix is a generalization of matrix inversion which tries to reproduce many of the properties of a matrix inverse. It is generalized to non square matrices, and for square and invertible matrices both the inverse and the pseudoinverse are the same. A simple implementation of the Moore-Penrose pseudoinverse matrix consists on obtaining the singular value decomposition of the matrix (let A be the matrix, its singular value decomposition would be $A = USV^T$) and then computing $A^+ = VS^+U^T$ to obtain the pseudoinverse of A. Here, S^+ denotes the pseudoinverse of a diagonal matrix, which is computed by taking the reciprocal of the non-zero elements in the diagonal and transposing the matrix.

Between each iteration, several physical constraints are applied to the concentrations and spectra matrices.

4.4.1 Constraints

Non-negativity

The non negativity constraint adds physical meaning to concentrations and spectra. It can be applied by forcing to zero negative contributions or using a softer approach using non negative least squares algorithm (Lawson & Hanson, 1995).

Unimodality

As it has been shown that the ethanol, acetone and reactant ion peaks do not overlap, we may impose the unimodality constraint on the spectra by not allowing spectra overlaps with more than a fixed tolerance.

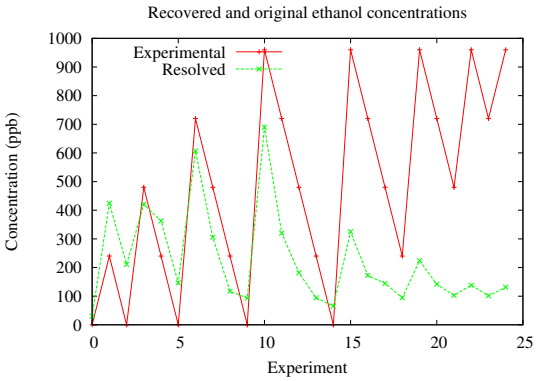
Spectra normalization

There is a scaling degree of freedom in the factorization $D = CS^T$, any valid solution will be valid if C is multiplied by a scalar and S^T is multiplied by its reciprocal. By imposing the spectra normalization condition, we constrain the scale ambiguity.

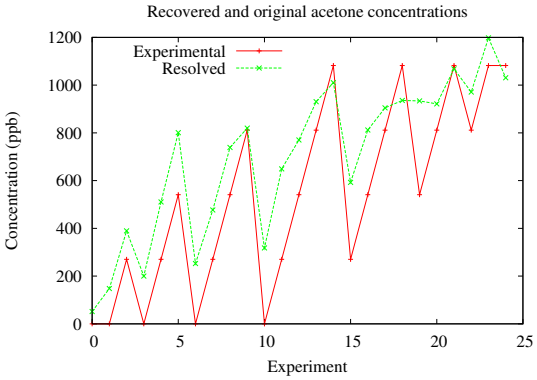
5 Results and Discussion

Figures 3a and 3b show the recovered concentrations compared to the experimental concentrations.

It can be seen how for lower experimental concentrations, the resolved concentrations are close to the expected result, even though the resolved concentrations never reach zero when the experimental does. This may be explained by the fact that, as it is shown on figure 4, there is some overlapping in the spectra.



(a) Ethanol



(b) Acetone

Figure 3: Original concentrations and recovered concentrations in different experiments.

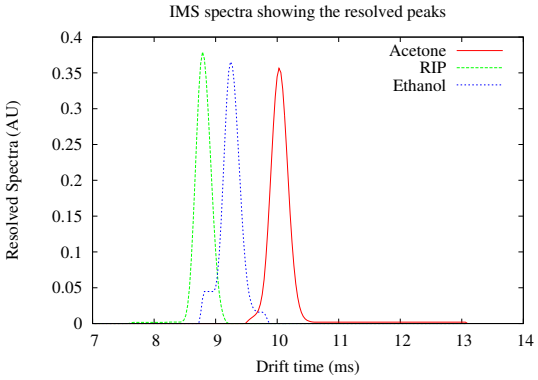
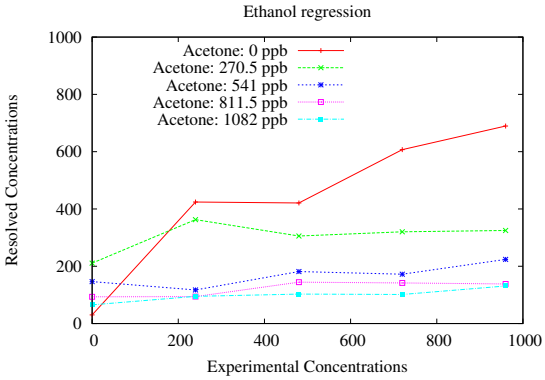


Figure 4: Resolved spectra for the three pure components: RIP, ethanol and acetone.

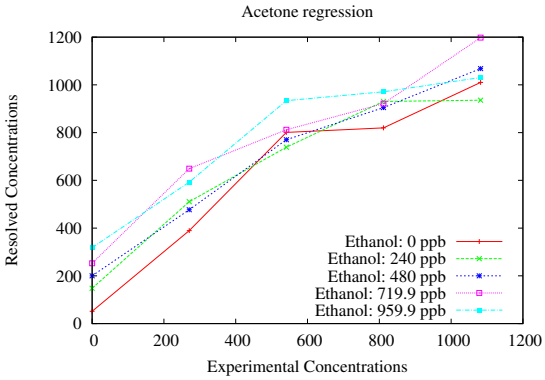
This overlapping increases the range of possible solutions, making it more difficult to distinguish between the components.

As concentrations increase, ethanol detection becomes more and more difficult and the only detected component (apart from RIP) is the acetone. This seems to be caused by the higher proton affinity of the acetone ($823kJ/mol$) with respect to ethanol ($788kJ/mol$) (Jolly, 1991). In other words, as acetone has more proton affinity, it takes all the available charge letting the ethanol unionized and therefore undetected.

An alternative view of the resolved concentrations is shown on figure 5. In those plots we can see the recovered concentrations of ethanol and acetone in terms of the respective experimental concentrations. Ideally these plots should overlap with the identity function (i.e. the resolved concentrations are the experimental ones). For the acetone (5b), the tendency to identity can be seen, especially in lower ethanol concentrations; however, for the ethanol (5a), the identity is clearly lost as the acetone concentration is different than zero. It is clear that as the concentration of the other component increases, the resolution degrades. In ethanol the effect is much more severe due to the smaller proton affinity.



(a) Ethanol



(b) Acetone

Figure 5: Recovered vs. Experimental concentrations.

6 Conclusions and Further work

In this work, the suitability of MCR-ALS method for separating two pure components of a mixture of ethanol and acetone analysed by an IMS has been tested.

Initial estimations for concentrations and spectra have been taken using the SIMPLISMA algorithm, and they have been refined and constrained with alternating least squares.

Results show that for lower concentrations, the recovered concentrations follow qualitatively the experimental concentrations, whereas for higher concentrations the IMS saturates, and only acetone, which has a higher proton affinity, is recognized.

Future work may be oriented to testing with different mixtures, using different components. It also would be interesting to try other non-linear factorization methods, to see if non-linearities affect strongly the results.

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Appendix

Exp. #	Etanol (ppb)	Acetona (ppb)
1	0	0
2	240	0
3	0	270.5
4	480	0
5	240	270.5
6	0	541
7	719.9	0
8	480	270.5
9	240	541
10	0	811.5
11	959.9	0
12	719.9	270.5
13	480	541
14	240	811.5
15	0	1082
16	959.9	270.5
17	719.9	541
18	480	811.5
19	240	1082
20	959.9	541
21	719.9	811.5
22	480	1082
23	959.9	811.5
24	719.9	1082
25	959.9	1082

Table 1: Experimental concentrations of the different experiments