

# Joint Cluster and Non-Negative Least Squares Analysis for Aerosol Mass Spectrum Data

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**Abstract.** Aerosol mass spectrum (AMS) data contain hundreds of mass to charge ratios and their corresponding intensities from air collected through the mass spectrometer. The observations are usually taken sequentially in time to monitor the air composition, quality and temporal change in an area of interest. An important goal of AMS data analysis is to reduce the dimensionality of the original data yielding a small set of representing tracers for various atmospheric and climatic models. In this work, we present an approach to jointly apply the cluster analysis and the non-negative least squares method towards this goal. Application to a relevant study demonstrates the effectiveness of this new approach. Comparisons are made to other relevant multivariate statistical techniques including the principal component analysis and the positive matrix factorization method, and guidelines are provided.

## 1. Introduction

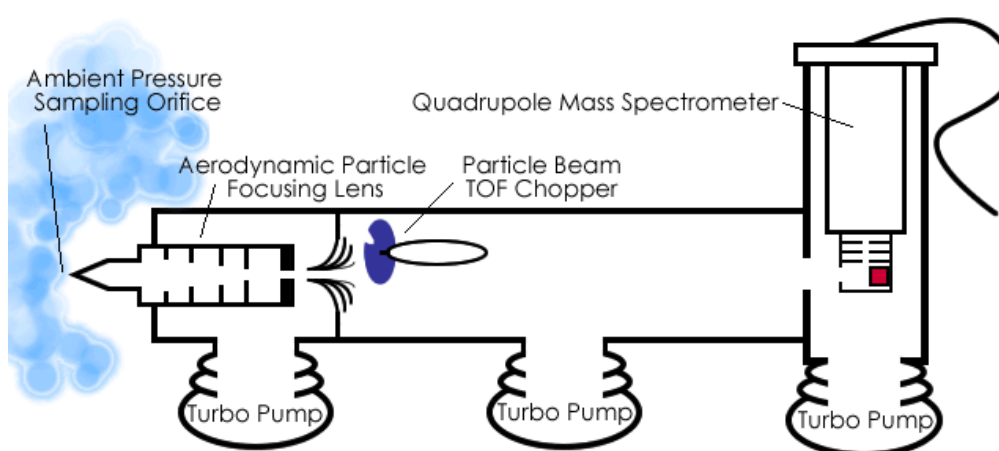
Atmospheric aerosols are significantly related to environmental issues such as rainfall, air pollution, and climate change. In recent years, quantitative aerosol studies based on mass spectrometry data have evolved rapidly in such field as particle formation research and air pollution analysis (see, e.g., [1]-[6]). Another area of great interest is dimension reduction. The goal is to obtain, from the original high dimensional aerosol mass spectrum (AMS) data, a much smaller set of representative tracers that will elucidate the source and interaction of different aerosol components, and to be plugged in as part of the model variables, to the next generation of climate models.

Several multivariate analysis techniques have been applied individually towards the dimension reduction of AMS data. These include principal component analysis [7] and cluster analysis [8]. The most widely used technique in the atmospheric research community however, is Positive Matrix Factorization (PMF), also known as the non-negative matrix factorization [9]. It has been developed [10] to yield factors with non-negative coefficients which would be more intuitive and interpretable than factors with a mixture of positive and negative coefficients. Plenty of work using PMF have been done [10-14] with two review papers published recently [15, 16]. However, a number of undesirable features inherent in PMF including subjectivity and non-uniqueness [17] have made it clear that better method must be developed to better serve the climate research communities.

In this paper, we propose a joint cluster analysis on variables (VARCLUS) [18-20] and non-negative least squares (NNLS) [21] approach to better achieve the goal of dimension reduction. Each method alone is not new; however, their combination is novel and as shown later, is rather effective in solving the problem at hand. The rest of the paper is arranged as follows. Section 2 provides a brief introduction to the AMS data from Milagro. Section 3 describes the proposed method in details while Section 4 presents the analysis of the Milagro data using the new method. Finally, Section 5 concludes with a comparison between the proposed method and the existing methods, especially the PMF.

## 2. Aerosol Mass Spectrum Data

### 2.1 Aerodyne Mass Spectrometer



**Figure 1.** Basic schematic of the Aerodyne aerosol mass spectrometer.  
(<http://cires.colorado.edu/~jjose/ams.html>)

The aerosol mass spectrum data analyzed in this work are recorded by the Aerodyne mass spectrometer. Its basic mechanism is illustrated in Figure 1. In summary, the air flows into the orifice. Particles are then focused in the focusing lens and passed through the chopper which is set to either an open or a closed mode. Vaporized and ionized, particles are introduced into the spectrometer sequentially with their weights and frequencies recorded. The instrument alternates in the MS mode and the TOF mode. During the MS mode, the chopper alternates between the open and blocked position every 5 seconds and the particle rates are record, while during the TOF mode mass spectrometer is set to a single  $m/z$  and sampled at a user defined rate. In this work, only data from the MS mode are involved. A full description of the Aerodyne mass spectrometer can be found in [1].

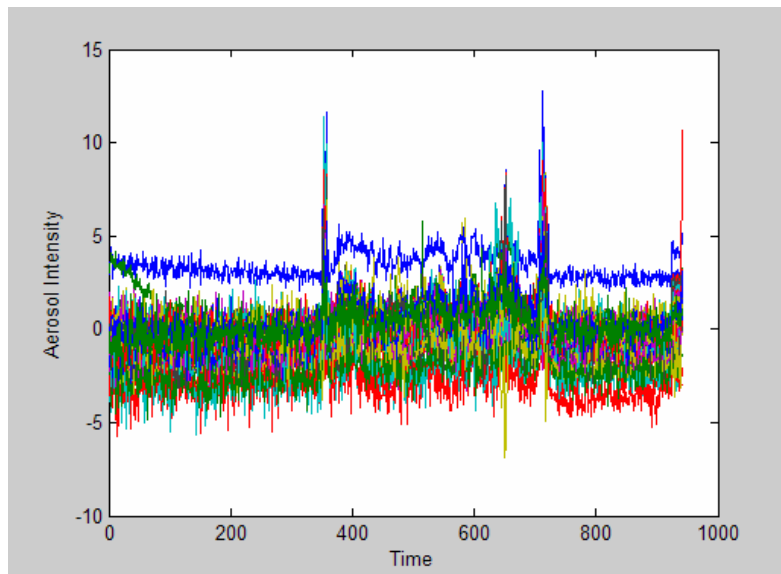
### 2.2 Data Preprocessing

The data we analyzed were collected on March 19, 2006 from Milagro containing signals with mass to charge ratios ( $m/z$ ) ranging from 1 to 452 measured every 12 seconds for a total of 943 measurements in time. Two modes of data were obtained -- data recorded when the aerosol beam was unobstructed (MSSopen) and data collected when the beam was blocked by the chopper (MSSclosed). Each mode also has its own baselines, designated as MSSopenBaseL and MSSclosedBaseL. We used the difference between the open mode and the closed mode to remove the contribution from background gas in the detector. Thus the data file we analyzed in this paper is named MSSDiff and defined as:

$$\text{MSSDiff} = (\text{MSSopen} - \text{MSSopenBaseL}) - (\text{MSSclosed} - \text{MSSclosedBaseL})$$

Data in MSSDiff contain negative values, which are expected for signals that are close to zero. Since MSSDiff contains negative signals, it does not satisfy the requirement to apply PMF directly. Although replacing all negative values with zeros would be a viable approach, it will nonetheless destroy the linearity of the AMS data. Since the proposed joint cluster and NNLS approach would allow negative values, we are able to retain all negative values for the analysis.

Our analysis is focused on the subset organic aerosols ranging in  $m/z$  values from 1 to 100. Twenty-eight inorganic aerosols in the range ( $m/z$ 's 1-11, 14, 16-18, 20-23, 28, 32-36, 39-40, and 47) were removed by setting the corresponding intensities to 0. The dataset was further normalized by dividing by the standard deviation at each  $m/z$  value. In addition, two time steps (time = 353, 643 seconds) appeared as outliers and were removed. The processed data are shown in Figure 2.



**Figure 2.** Pre-processed organic aerosol data where each colour represents the time series of a unique  $m/z$  value.

### 3. Method

#### 3.1 Notations and Overview

Let **ORG** represent the pre-processed AMS data with  $N_i$  columns for  $m/z$  values ranging from 1 to  $N_i$ , and  $N_t$  rows for  $N_t$  temporal measurements. Thus the  $i^{\text{th}}$  column of the matrix **ORG** is the time series corresponding to  $m/z$  value  $i$ , and the  $t^{\text{th}}$  row of **ORG** is the mass spectrum at time point  $t$ . Our goal is to find a mass spectrum basis, **MS**, with lower dimension of  $N_c$ , such that

$$\mathbf{ORG} = \mathbf{C} * \mathbf{MS} + \mathbf{E} \quad (1)$$

Here, **ORG** is an  $N_t * N_i$  matrix (in our work  $N_t=941$ ,  $N_i=100$ ). **MS** is an  $N_c * N_i$  matrix,  $N_c \ll N_t$ . Our goal includes two parts: first, we need to decide  $N_c$ , the dimension of the basis; next, we need to estimate **MS**.

The above decomposition can be solved by the principal component analysis (PCA), factor analysis (FA) or positive matrix factorization (PMF). PCA and FA could yield a suggestive  $N_c$  based on the variation explained by the basis. However, there are two apparent disadvantages to these methods. First, it is hard to interpret the output basis; second, the output basis usually contains negative values that are often unacceptable for practical purposes. The PMF method could avoid the second problem but not the first one. Furthermore, PMF returns different output using different starting matrix. That is, it is not unique [9, 17, 22].



This is achieved through the NNLS algorithm by minimizing  $\|ORG - \widehat{ORG}\|^2$ , with the constraints that each  $\beta$  is non-negative. The details of the NNLS algorithm can be found in [21]. For better fit, we add constant terms in the above linear equation system as follows.

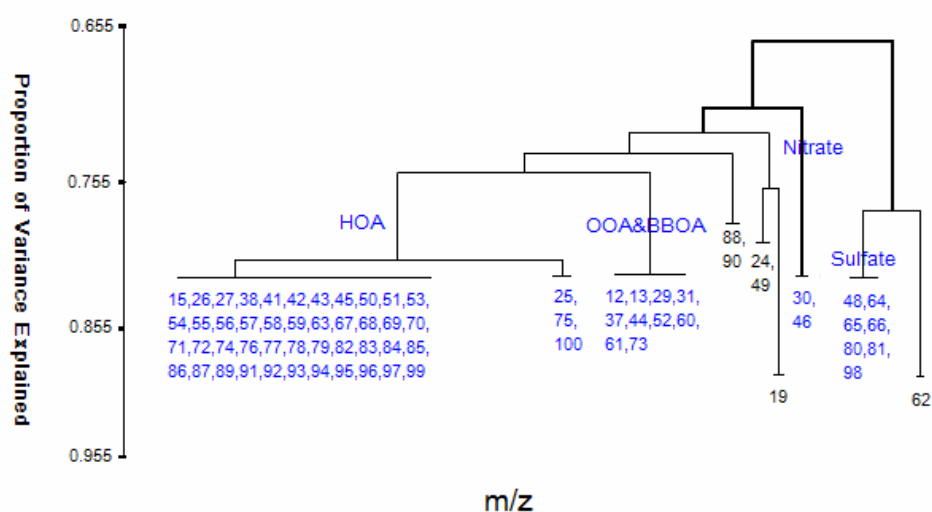
$$\begin{aligned} MZ_1 &= \beta_{1,0} + \beta_{1,1}C_1 + \beta_{1,2}C_2 + \dots + \beta_{1,N_c}C_{N_c} + e_1 \\ MZ_2 &= \beta_{2,0} + \beta_{2,1}C_1 + \beta_{2,2}C_2 + \dots + \beta_{2,N_c}C_{N_c} + e_2 \\ &\dots \\ MZ_{100} &= \beta_{100,0} + \beta_{100,1}C_1 + \beta_{100,2}C_2 + \dots + \beta_{100,N_c}C_{N_c} + e_{100} \end{aligned} \quad (2)$$

In matrix form we have:  $ORG = \begin{matrix} \widetilde{C} \\ 941 \times 100 \end{matrix} * \begin{matrix} \widetilde{MS} \\ (N_c+1) \times 100 \end{matrix}$ , where  $\widetilde{C}$  is  $C$  with an extra column of 1, and  $\widetilde{MS}$  is  $MS$  with the added row  $(\beta_{1,0}, \beta_{2,0}, \dots, \beta_{100,0})$ . Notice that  $(\beta_{1,0}, \beta_{2,0}, \dots, \beta_{100,0})$  is allowed to be negative. We used the NNLS command in MATLAB to estimate  $\beta$ .

## 4. Results

### 4.1 VARCLUS and NNLS output

The VARCLUS output, a hierarchical tree, is shown in Figure 3. Based on the output tree and the related aerosol information, we have, clearly, 4 major clusters.



**Figure 3.** VARCLUS output: the hierarchical tree. From the tree structural, we decided four major clusters. Numbers in blue indicate the  $m/z$  values of cluster members while numbers in black are  $m/z$  values not belonging to any major cluster. The proportion of variance explained at each step of the binary tree split is displayed along the vertical axis.

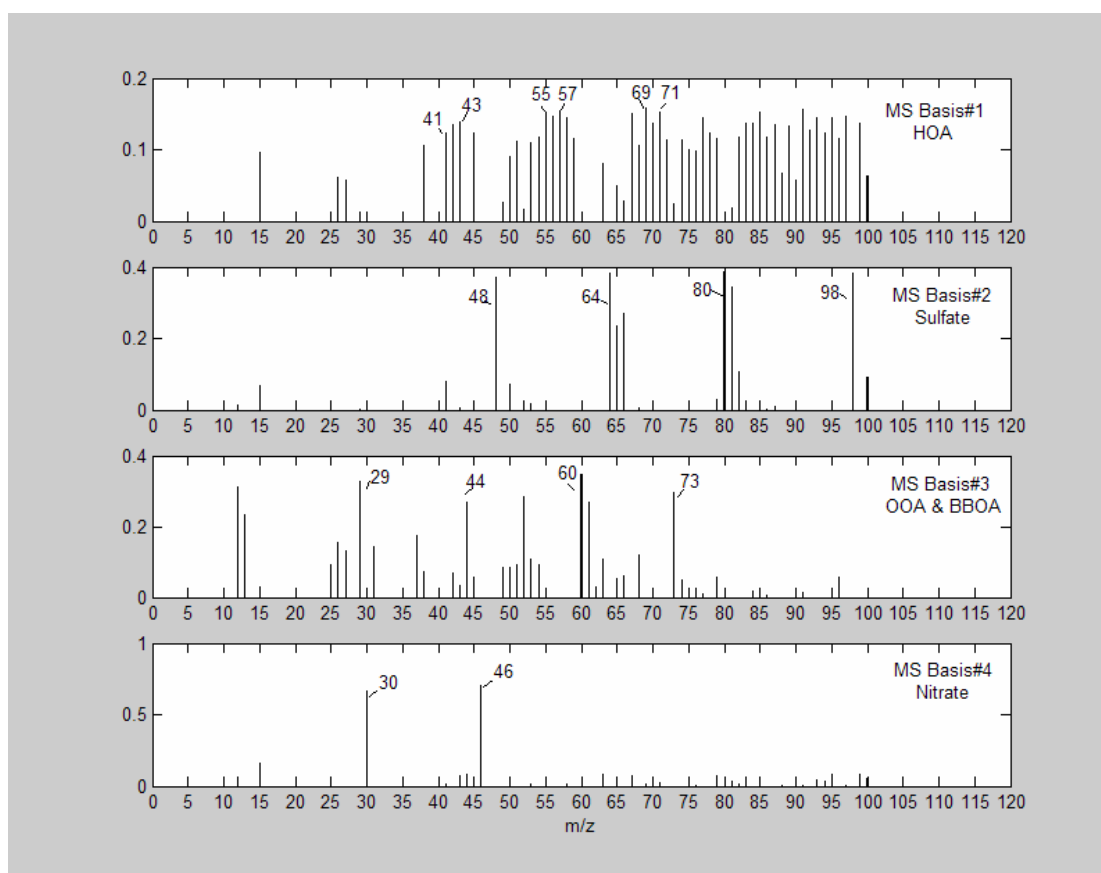
Table 1 contains detailed information on these four major clusters. As discussed in Section 3.2, the advantage of using VARCLUS is that the clustering results are usually explainable if there is inherent linearity in the data. The AMS data are inherently linear with organic aerosols usually coming from several main sources. For example, hydrocarbon-like organic aerosols (HOA) mostly come from fossil fuel, while oxygenated organic aerosols (OOA) mostly come from secondary organic aerosols (SOA) [7]. This property supports the VARCLUS data assumptions and in our output we can clearly

identify these 4 clusters. All 1<sup>st</sup> PCs in these clusters represent a high percentage of variation explained with non-negative coefficients. Thus, it is reasonable to use these four 1<sup>st</sup> PCs as the basis (tracer set) for the given AMS data.

**Table 1.** VARCLUS and PCA output.  
Total variation explained by the basis consisting of four PC's is **71.14%**.

Cluster	Members (m/z values)	Variation Explained	1 <sup>st</sup> PC Variation in Each Cluster	Label
Cluster#1	15,25:27,38,41:43,45,50 51,53:59,63,67:72,74:79, 82:87,89,91:97,99,100	49.72%	76.16%	HOA
Cluster#2	48,64,65,66,80,81,98	9.15%	94.16%	Sulfate
Cluster#3	12,13,29,31,37,44, 52,60,61,73	9.50%	68.36%	OOA and BBOA
Cluster#4	30, 46	2.77%	99.68%	Nitrate

Based on the VARCLUS output, we obtained the matrix **C** mentioned above. The matrix **MS** was estimated using NNLS. The output is shown in Figure 4.



**Figure 4.** The basis of four 1<sup>st</sup> PC's are linear combinations of individual m/z values within each cluster. Significant peaks on each 1<sup>st</sup> PC are labelled.

#### 4.2 Validity of Tracers

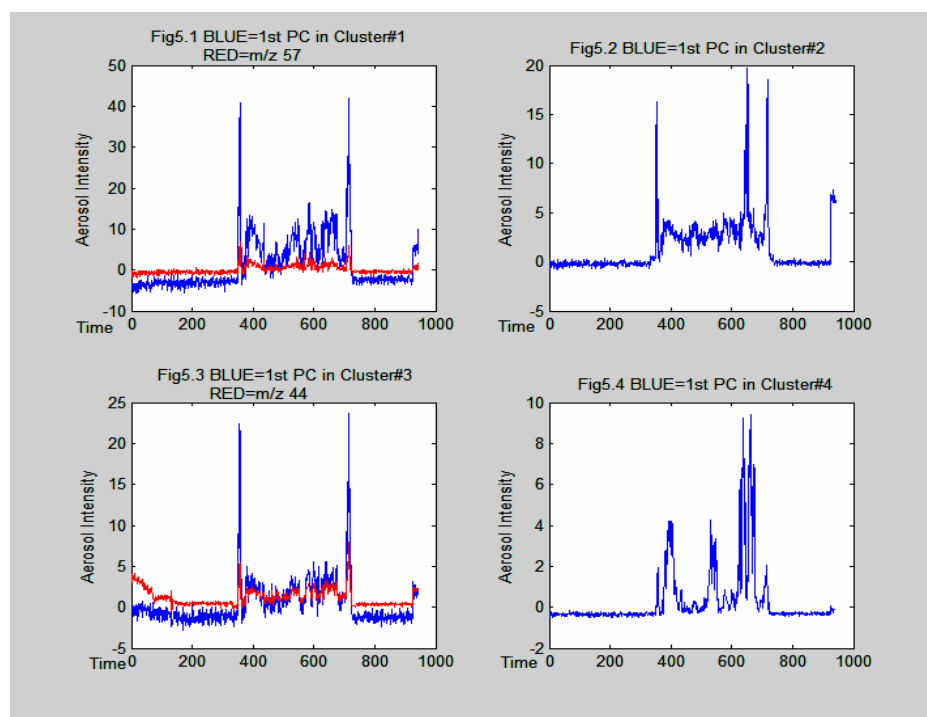
We checked the validity of the four tracers from three aspects: (a) whether they are interpretable for the given aerosol study; (b) how much of the total variation they could explain; (c) whether they could represent most of the aerosols in the original AMS data.

The organic aerosol factors from theoretic analysis are listed in Table 2 to check for (a). Compared with Table 1, the VARCLUS and PCA outputs are consistent with these factors for each major cluster containing all the corresponding critical  $m/z$ 's correctly.

For (b), we found that 71.14% of the total variation is explained by the tracers as shown in Table 1. Figure 4 shows the time series of the four tracers. Compared to the single  $m/z$  tracer used by Zhang et al (2005), we found that the new tracers have larger variability as illustrated in Figure 5.

**Table 2.** Organic aerosol factors. The emphasized  $m/z$ 's are important signals for the given factor.

Organic aerosol factors	Ionized at 600C	$m/z$	O: C ratio
HOA hydrocarbon-like organic aerosols	$C_n H_m \rightarrow C_{n-x} H_{m-y}^+$	27,29,41,43,55,57,69,71,...	↓ Less Oxidized  More Oxidized
OOA2 Oxygenated organic aerosols type II	$C_n H_m O \rightarrow C_2 H_3 O^+, C_3 H_3 O^+, R^+$	43,55,...	
BBOA biomass burning organic aerosols	$R \rightarrow R^+, C_2 H_4 O_2^+, C_3 H_3 O_2^+$	44,45,...	
OOA1 Oxygenated organic aerosols type I	$C_n H_m O_2 \rightarrow CO_2^+, HCO_2^+, R^+$	60,73,...	



**Figure 5.** Time series of 1<sup>st</sup> PCs in clusters. Comparison between 1<sup>st</sup> PC in cluster#1 (HOA) and  $m/z$  57 is shown in Fig5.1; comparison between 1<sup>st</sup> PC in Cluster#3 and  $m/z$  44 is shown in Fig5.3. The single  $m/z$  values of  $m/z$  44 and  $m/z$  57 were used as tracers for OOA and HOA in Zhang et al (2005).

To check for (c), we need to verify that most of the peaks in the aerosol mass spectrum could be represented by our tracers. We first used the ordinary least squares regression (OLS) for this purpose. For each  $m/z=i$ , we fit the equation  $MZ_i = \alpha_{i,0} + \alpha_{i,1} * C_1 + \alpha_{i,2} * C_2 + \alpha_{i,3} * C_3 + \alpha_{i,4} * C_4 + e_i$ , where  $C_j$  represents the 1<sup>st</sup> PC in the  $j^{\text{th}}$  major cluster and  $i=1, 2, \dots, 100$ . The goodness of fit for each regression, as evaluated by the coefficient of determinant  $R^2$  for each regression equation, is reported in Figure 6. We found that most  $R^2$  are bigger than 0.8 (the mean of  $R^2$  is 0.81, the standard deviation is 0.23). For the few  $m/z$ 's with small  $R^2$  such as  $m/z=19$ , it is because they are not in any major cluster and thus their signals can not be expected to be explained by the tracers. Lastly, stepwise regression was performed. The results support that these four tracers are not reducible.

We therefore conclude that the given tracers are highly satisfactory gauged by the three criteria (a), (b) and (c).

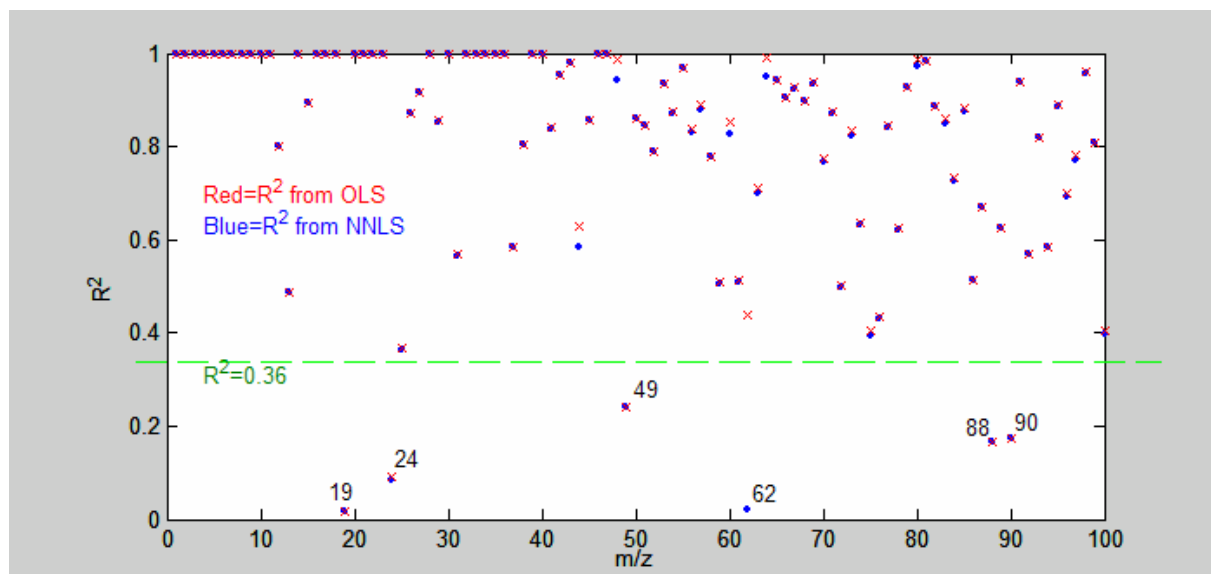
#### 4.3 Error Analysis

To further validate our analysis, especially the NNLS portion of the analysis, we performed an error analysis by examining and comparing the coefficient of determination ( $R^2$ ) from both OLS and NNLS.

Let  $SSE_i = \sum_{j=1}^{941} (ORG_{ji} - \overline{ORG_{ji}})^2$  be the sum of squared errors (SSE) for  $m/z=i$  (the  $i$ -th column in **ORG**), and  $SST_i = \sum_{j=1}^{941} (ORG_{ji} - \overline{ORG_{ji}})^2$  be the corresponding total sum of squares (SST). The coefficient of determination (at  $m/z=i$ ) is defined as [25]:

$$R_i^2 = 1 - \frac{SSE_i}{SST_i}$$

$R^2$  for each  $m/z$  using OLS or NNLS were calculated to examine the regression goodness-of-fit. We can see OLS and NNLS give similar  $R^2$  for most  $m/z$ 's in the given example.  $R^2=0.36$ , which corresponds to a multiple correlation of 60%, was used as a threshold to determine outliers. Six outliers were found: they're  $m/z$  19, 24, 49, 62, 88, 90. The reason causing these outliers is quite clear. These are the six  $m/z$ 's that are not assigned to any of the four major clusters as shown in Figure 7. Hence, all the other  $m/z$ 's could be well represented by the four tracers (first PC's of the 4 major clusters) with non-negative constraints except for these outsiders.



**Figure 6.** The coefficient of determination ( $R^2$ ) for each  $m/z$  using OLS or NNLS. Outliers are specified.

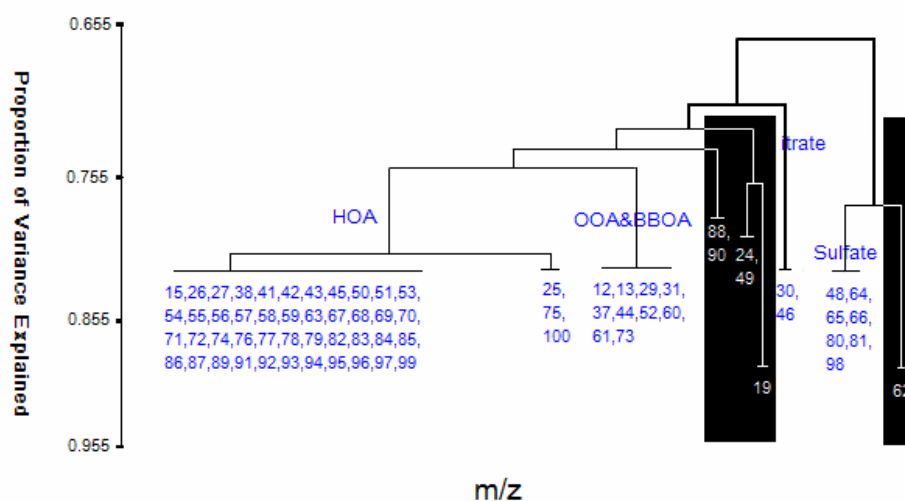


Figure 7. Outliers are displayed in the hierarchical clustering tree.

## 5. Discussion

Many commonly used multivariate statistical methods are not suitable in the intended AMS data analysis of dimension reduction and tracer extraction due to negative coefficients of the resulting basis. Both the PMF and the proposed method of joint cluster and NNLS analysis can achieve non-negative tracer coefficients. The major draw-back of the PMF lies in its non-uniqueness and subjectivity.

Generally speaking, PMF is not unique. For example, if  $X=ABC$ , where  $A$ ,  $B$  and  $C$  are all positive matrix, then we have at least two different PMF's in  $X=(AB)*C=A*(BC)$ . Different factorizations are called "rotations" in factor analysis. For the proposed joint analysis method, there is little flexibility in deciding the major clusters and thus the basis. Subsequently, given the fixed  $C$  matrix, the  $MS$  matrix determined by the NNLS procedure would be unique.

As P. Paatero (See [17]) pointed out "It is unfortunate that introducing a priori information also introduces some subjectivity in the analysis." To apply the PMF analysis, one needs to first decide upon at least two things: the number of factors and the "rotation" parameter. Otherwise one will find the solution non-unique. Both of these two choices have determinant effect on the final output. For our method, we still have to refer to some prior knowledge from the field. However, the "subjectivity" exists in only one step – the determination of major clusters based on the VARCLUS output. Furthermore, even for this step, our decision is based mainly on objective criterion such as the percent variation explained by each cluster as shown in the given study.

There is space yet for us to improve upon in the proposed method. First, since the sources of organic aerosols are complicated, the disjoint clustering method may not perform well for overlapping aerosol groups. Secondly, if the first principal component for a given cluster could only explain a modest amount of variation, one would need to find additional tracer(s) for the given cluster. Perhaps a combined VARCLUS and PMF approach with the PMF done within each cluster would better serve our purposes. Further research is warranted in this area.

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