



Combining Raman microspectrometry and chemometrics for determining quantitative molecular composition and mixing state of atmospheric aerosol particles



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ABSTRACT

Determining quantitative molecular composition of atmospheric particles is required for assessing their environmental and health impacts. The presented algorithm was designed to analyse numerous Raman spectra of metal-rich atmospheric particles. Multivariate curve resolution-alternating least squares procedure (MCR-ALS) has been applied to resolve complex data from Raman microanalysis by means of a computer-assisted analytical procedure called Single Particle Analysis (SPA). The SPA – contrary to Raman mapping – provides data in which each single particle is assigned to a single spectrum, in the group with a statistically significant size. During the procedure, the relative contributions of individual compounds in the recorded Raman spectra have been specified. Grouping and relationship determination of the collected data have been performed by hierarchical cluster analysis (HCA) and principal component analysis (PCA). A new methodology is proposed to quantitatively determine the molecular composition and chemical mixing of single airborne particles based on the data from the automated Raman microspectrometry measurements.

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1. Introduction

Single Particle Analysis (SPA) applied to atmospheric aerosol composition is an approach to analyse particulate matter by measuring individual particles [1–10]. Determining the composition of particles collected in ambient air using SPA, as opposed to bulk analysis, presents essential advantages that have been demonstrated in numerous works [11]. The analytical techniques appropriate for SPA must show a lateral resolution adapted to the particulate matter size. They must also show sensitivity suitable to detect both major and minor compounds within the particles. The SPA approach requires large quantities of data in order to obtain statistical significance for the description of collected particles. This assumption bears two major issues. First off, an automation of measurements is needed to achieve a sample size above the level of statistical significance. The second issue concerns development of robust data treatment since the large data matrix entails reducing the number of objects into the groups. In the case of atmospheric particles, it leads to detailed study of a few representatives only. It also helps provide reliable spatial and temporal chemical evolution of particle composition.

Among SPA techniques, Scanning Electron Microscopy (SEM) equipped with an energy dispersive X-ray detection (EDX) and Raman microspectrometry (RMS) have been recognized as powerful methods for studying particulate matter of different origin (airborne particles, sediments, soils, etc.) [3,6,7,9,12–21]. Both techniques belong to micro-analytical methods where the source of information is a result of a beam interaction (i.e. electrons or photons) with micro-size objects, producing elemental and molecular spectra, respectively. Automation of SEM/EDX applied to particulate matter was implemented more than twenty years ago and has been successfully developed ever since. However, there are some limitations related to the elemental quantification. Calculation of particle elemental composition requires a fit-for-purpose quantification methodology based on X-ray spectra. Quantification procedure based on Monte-Carlo simulations was developed for suitable measurements of low-Z elements [3–9], while the gun-shot residue (GSR) software enables detection of particles with high-Z elements [22]. Based on the elemental composition and morphology, the particles can be classified into different groups related to their chemical characteristics. Nevertheless, a significant number of publications reporting a successful application of computer-controlled SEM/EDX measurements of a large number of particles, followed by quantification and appropriate data classification, prove the need for fast and reliable tools in the field of SPA [3–9] [23–31].

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Confocal Raman microspectrometry (RMS) is another SPA technique providing molecular composition (speciation) of atmospheric particles, with a capability for automation of measurements. A Raman spectrometer coupled with an optical microscope and an automated XY stage, allows for computer-controlled measurements. The manual spot mode has been used for decades for characterizing the molecular composition of individual particles collected in ambient air [33,34]. In an imaging mode, RMS is able to describe chemical heterogeneity of micro-sized aerosol particles [20–38]. Considering a complex molecular composition resulting from heterogeneity of airborne particles, a Raman spectrum of one particle often reflects a mixture of several compounds. The multivariate curve resolution approach, such as SIMPLISMA, has substantially improved chemical description of particles by resolving the contribution of pure variables in the mixed spectra [13–21] [35–37]. Confocal Raman microspectrometry has been considered as less appropriate compared to SEM-EDX because of the three main issues: (i) identification of molecular species can be assessed using RMS but quantitative data is not accessible; this is because the Raman band intensities are not indicative for the proportion of species in solid and heterogeneous particles (ii) as mentioned previously, the analysis of particles results in a Raman spectrum of mixed species that requires automated procedure for unmixing in order to analyse a large number of particles, (iii) clustering of particles based on their Raman spectra requires automation of measurements and preprocessing of the Raman spectra. As a consequence, an application of RMS has only recently been extended to a large number of particles. Reisner et al. [39] described an integrated software for processing, analyzing, and classifying of multiple Raman spectra. The developed system was equipped with multiple preprocessing methods, including: a median filter to reduce noise and remove spikes due to cosmic rays, a wavelet filter for further noise reduction, an automated background fluorescence subtraction [40], normalization of spectra and subtraction of artifacts. Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA) were implemented as the two main multivariate analysis methods. Additionally, some classification methods, such as an artificial neural network classifier and a support vector machine classifier were implemented. Another significant feature was made by implementation of a relational model database for storing of any kind of information about the spectra, such as a date of data collection or a type of the specimen. Reisner et al. [39] made a compelling step to integrate tools for multiple Raman spectra processing, management and classification into a freely available, cross-platform system. Despite the versatility of the described system, there is a lack of spectral unmixing as well as clustering methods which are crucial in handling of the data from the environmental sample analysis [39]. Finally, Reisner et al. [39] evaluated the described system using the data from biological specimens. The results demonstrated the vast potential of the system in processing and classification of the spectra, based on well specified parameters. Ofner et al. [41] presented multisensor hyperspectral images of atmospheric particulate matter coupled with chemometrics analysis of an extensive chemical description of the collected particles. The authors provided a comprehensive image-based analysis of aerosol particles with a sectional description of samples. The combination of RMS and SEM-EDX used in multisensor hyperspectral data analysis made a way for detailed and well-grounded assignment of chemical species in the sample and the relationships among them. Notwithstanding, the described methodology is dedicated to the data from hyperspectral imaging, which significantly reduces the number of particles during a single run, compared to SPA. The structuration of the data was based on the pixel relationship taken from hyperspectral images which may not be directly translated into the description of the particle population. Additionally, operations on hyperspectral images are less efficient due to a large number of spectra collected during a single analysis, from which only few correspond to atmospheric particles. Finally, the mixing chemical state of particles is not considered. Jentzsch et al. [42] studied classification of mean Raman spectra of model particles composed of the most representative salts

expected to be produced in the atmosphere. The chemometrics data analysis was used to distinguish the potential of the Raman spectra classification from a single particle analysis. Jentzsch et al. [42] did not include any spectral unmixing algorithm, which might be a limitation for analysis of ambient aerosol particles [42]. Furthermore, Craig et al. [43] applied computer controlled Raman microspectrometry (CC-Raman) for a single particle analysis of a large number of both laboratory-generated and real-life particles. The authors conducted comprehensive characterization and clustering of aerosol particles based on the distinct features of their Raman spectra. Moreover, Craig et al. [43] juxtaposed the results from Raman microspectrometry with SEM/EDX and a condensation particle counter (CPC), which equalled in similar cluster formulation. Nonetheless, due to the lack of spectral unmixing algorithm, the specification of particular compounds and their chemical mixing in the ambient aerosol particles was limited.

Regarding the previous work, an application of RMS for a chemical description of particles collected in ambient air is not complete yet, since the quantitative composition of the samples, i.e. the relative abundance of particle types defined from their molecular composition, has not been provided. The multivariate curve resolution methods (MCR) applied to a Raman data set offers a considerable advantage as mentioned above. The mathematical principle of MCR is based on the presence of pure variables. In terms of spectroscopy, a pure variable (e.g. a wavenumber of a Raman spectrum) is a variable which has an intensity contribution from only one component of a mixture. Once the pure variables of every component are known, their content in the mixture spectra is calculated. Reliability of the contribution profiles may be used as calibration process as previously demonstrated [15]. Alternatively, resolved contributions may be considered to be indicative for a presence or an absence of chemical species within particles and used for determining a relative abundance of particle types. It should be noted that the application of the multivariate analysis – mostly clustering – after the matrix decomposition procedure, has already been described by other authors [44,45]. For instance, Liu et al. 2003 [44] proposed to initially perform principal component analysis in order to obtain a matrix of scores for further clustering. Furthermore, Tamayo et al. 2007 [45], suggested to apply the matrix decomposition by the non-negative matrix factorization on high-dimensional data for clustering of a basis matrix only.

The present study aims to provide a quantitative chemical description of collected airborne particles. The proposed methodology consists of analyzing a large number of particles through automated measurements. Grouping of the collected data is made by chemometrics methods through the application of the MCR approach on the Raman spectra data matrix. Firstly, the methodology requires first to distinguish particles composed of only one species (pure molecular compounds) from those with molecular composition comprised of more than one species (mixed particles). The second step is to define particle types according to their chemical similarity. The final part involves quantification of each group of the particles according to their composition and chemical mixing in order to describe the chemical composition and heterogeneity of the collected particles. For that purpose a multivariate curve resolution and an unsupervised multivariate analysis are used in combination for description of real particle samples collected in the mining environment.

2. Experimental

2.1. Sample description

The particles were sampled in the galleries of San Jose Mine (150 m, underground), located in the Oruro area, Bolivia (17°46'0"S – 67°28'60"W – 3674 MAMSL). The particle collection was performed using a personal cascade impactor (SIOUTAS, 3 l.min⁻¹), allowing simultaneous walking along underground passages and sampling of four size fractions of particles, i.e. PM₁₀, PM_{2.5}, PM₁ and PM_{0.5} corresponding to 10–2.5 μm,

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