

# Chemistry at level of individual aerosol particle using multivariate curve resolution of confocal Raman image

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## Abstract

Airborne particles with aerodynamic diameter in the 10–1  $\mu\text{m}$  range have been collected in an industrial/urban zone by impaction and have been investigated by automated confocal Raman microspectrometry. The computer-microcontrolled XY scanning and Z focusing of Raman images provided many pixel Raman spectra which are characteristics of complex mixture at level of individual particle. The large heterogeneity was not resolved by the spatial resolution of the instrument which is limited by the optical diffraction. The severe spectral overlaps generated by heterogeneity were resolved by multivariate curve resolution (MCR) methods. The purity based method (SIMPLISMAX) was used to resolve both luminescence spectra and pure Raman spectra without prior information. The MCR-alternating least square (ALS) was used as a refined method of both spectra and spectral concentrations. The reconstructing Raman images of the respective spectral contribution supply a versatile potential to characterize the chemistry of atmospheric aerosols at the level of the individual particles.

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## 1. Introduction

It is now well known that atmospheric aerosol particles aggregate and react with tropospheric reagents leading to complex heterogeneous and multiphase chemical phenomena which occur at aerosol size scale. Currently, the international regulation takes in consideration only particulate matter with aerodynamic diameter smaller than 10  $\mu\text{m}$  ( $\text{PM}_{10}$ ). With anthropogenic activities development, atmospheric particulate pollution has become of great concern particularly in urban zone. Particulate matter of the atmosphere can have serious environmental and health-related consequences. Urban aerosol samples are heterogeneous mixtures of different types of particles, so that the average chemical composition and average diameter do not describe well the dispersion of the particles in the sample. Energy dispersive electron probe X-ray microanalysis has proven to be an especially powerful technique. It is capable of simultaneously detecting the quantitative chemical composition and the morphology of a microscopic volume such a single atmospheric

particle [1–6]. The elemental analysis of single particles has deepened the understanding of the sources, reactivity, transport and removal of atmospheric chemical species. A new challenge resides in supplying analytical tools able to provide molecular information at the particle scale. The Raman microspectrometry which combines the molecular analysis capabilities of Raman scattering spectroscopy with an optical microscope provides a potential solution for obtaining molecular information on particles of microscopic volume with in situ conditions [7,8]. Tropospheric particles are collected as crystalline, amorphous, wet and dry phases. Then, Raman scattering exhibits a characteristic “fingerprint” of crystalline, amorphous and liquid phases which is suitable for chemical characterization of particles. Currently, large Raman spectral mapping can be collected by computer-controlled (XYZ) scanning [9,10]. However, the large heterogeneity at level of individual aerosol particle generates severe overlap of spectral information within a microscopic volume under analyses that cannot be resolved by the conventional Raman imaging methods [9]. Multivariate curve resolution methods (MCR) are gaining more widespread use for multivariate images. There are several methods that have a similar objective [11–13]. Applying MCR to the multivariate image yields information about *what* pure species are present

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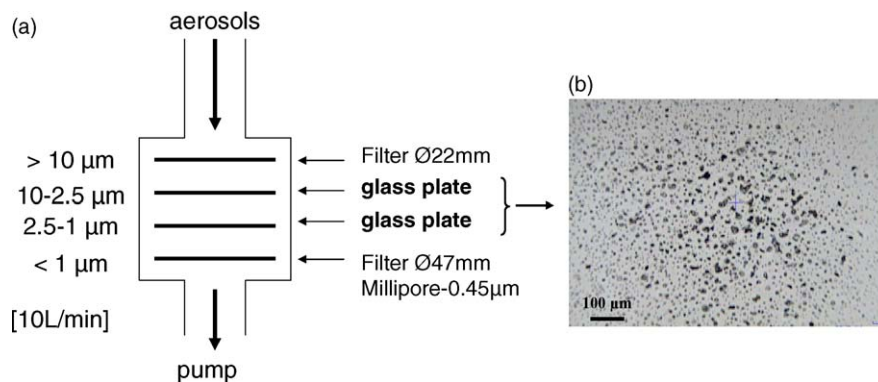


Fig. 1. Experimental set-up for particle collection. (a) Schematic representation of the cascade impactor (Dekati PM<sub>10</sub>) equipped with glass plates suitable for Raman microspectrometric measurements. (b) Optical image of aerosol particles collected at the 10–2.5 μm stage.

and *where* in the image they are located with a spatial resolution imposed by the optical diffraction limit of the microscope.

In this paper, we demonstrate the effectiveness of the combined use of computer-controlled Raman microspectrometry mapping and MCR methods of the Raman images to determine the chemical and heterogeneous characteristics of individual tropospheric aerosol particles collected in urban zones.

## 2. Experimental

### 2.1. Samples

Aerosol samples have been collected in the urban zones located in a former coal mining region of the North of France. The sampling sites were fixed at 1.5 km of large zinc and lead smelters in operation during the sampling periods. The details about sampling campaigns are described elsewhere [14]. Aerosol particles have been collected by impaction on glass plates using a Dekati PM<sub>10</sub> impactor mounted at a height of 2.5 m from the ground level. The PM<sub>10</sub> cascade impactor consists of three successive stages with aerodynamic cut-off diameters of 10, 2.5 and 1 μm when it operates at 10 L/min flowing air (see Fig. 1a). The sampling time was fixed at 30 min for one sample. An optical image of the impacted particles on glass plate is given in Fig. 1b.

### 2.2. Automated scanning Raman microspectrometry

Raman microspectrometric measurements were carried out with a LabRAM confocal spectrometer manufactured by Jobin Yvon, Horiba Gr, France (Fig. 2). An Olympus 100× objective, numerical aperture (NA)=0.90 was used. The spot size of the laser focused by the 100× objective at the sample was estimated to be 1 μm<sup>2</sup> in size. A color camera was used to feed a signal to a video monitor and thus provided an optical view of the samples. A liquid nitrogen-cooled CCD (Jobin-Yvon, 2048 pixels × 512 pixels) was used for detection, allowing simultaneous spectral dispersion by a 1800 grooves mm<sup>-1</sup> holographic grating over a wide wavenumber range of about larger than 1000 cm<sup>-1</sup> in the spectral region of interest. The Raman backscattering was excited with a 632.8 nm excitation

wavelength supplied by an internal, air-cooled, linearly polarized helium–neon laser. Laser power delivered at the sample was 8 mW and could be monitored via a filters' wheel with the optical densities 0.3, 0.6, 1, 2, 3 and 4. The microscope stage was XY-motorized and computer-controlled for point by point scanning with 0.1 μm resolution, 1 μm reproducibility and 90 mm × 60 mm spatial range. Due to the roughness of the impacted particles, the system uses a high precision piezo translator and feedback signal to automatically track and adjust the laser focus on the sample, ensuring perfect laser focus for each measurement. The glass plate with the impacted particles was directly mounted on the microscope stage without any further preparation. The data acquisition consisted in recording many spectra with point-by-point scanning mode with 1 μm as a minimum step, one accumulation and 30 s spectrum acquisition time. Many tropospheric aerosol particles containing organic species (e.g. bacteria, spores, carbonaceous particles covered with polycyclic aromatic hydrocarbons, clays with humic substances) generate intense fluorescence emission. Fluorescence cross-sections are typically several orders of magnitude larger than Raman scattering cross-sections. Then, the sharp Raman peaks were superimposed to fluorescence broad bands. An insight into

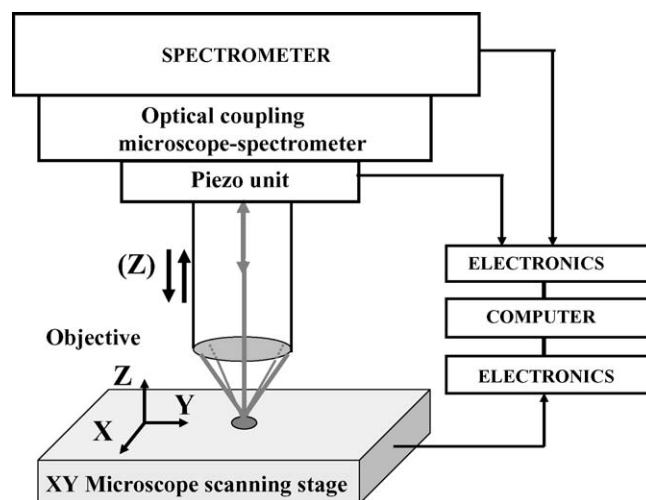


Fig. 2. Experimental set-up for the automated scanning Raman microspectrometry measurements.

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