Analytica Chimica Acta 1014 (2018) 41–49

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Influence of collecting substrate on the Raman imaging of micron-sized particles

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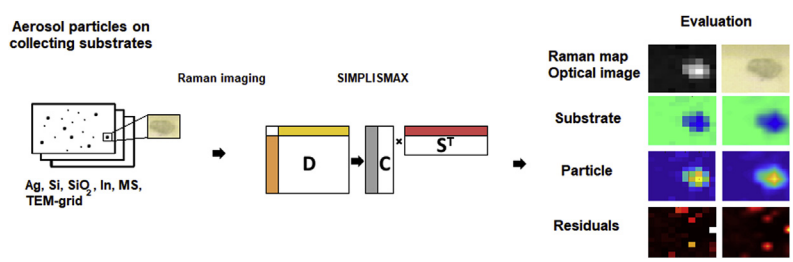
HIGHLIGHTS

- Evaluation of 6 substrates for Raman imaging and multivariate curve resolution.
- Substrate contribution is superior to micron-sized aerosol particle contribution.
- TEM Grid is the suitable substrate for micron-sized aerosol particle.
- Resolved spectra of compounds are always impaired by Si substrate contribution.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 September 2017
Received in revised form
2 February 2018
Accepted 4 February 2018
Available online 14 February 2018

Keywords:
Raman spectroscopy
Micron-sized
Particles
Multivariate curve resolution
Substrates
Imaging

ABSTRACT

The influence of six common substrates on the Raman imaging of micron-sized inorganic aerosol particles was examined. Laboratory-generated single-component particles of calcite ($CaCO_3$) and mixed particles of calcite ($CaCO_3$), nitratine ($NaNO_3$), hematite (Fe_2O_3) and anglesite ($PbSO_4$) were deposited by cascade impaction on Ag, In, Si, SiO_2, microscope slide and TEM-grid substrates. The spectral contribution of substrates to Raman images of the deposited particles was evaluated by Multivariate Curve Resolution. The shape and intensity of the substrate spectra affect the effectiveness capability of the spectral deconvolution. The substrates were characterized and compared with respect to their effect on the reconstruction of Raman images of aerosol particles. The TEM-grid substrate yielded spatially stable sample measurements with a homogeneous spectral contribution, satisfactory Raman map reconstruction and the potential for application in other techniques (e.g., SEM-EDX).

1. Introduction

Atmospheric aerosol particles suspended in the air, with their wide variety of sources and physico-chemical properties, strongly contribute to environmental quality [1]. They may scatter or absorb light and may affect the radiative balance of the atmosphere [2]. It

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https://doi.org/10.1016/j.aca.2018.02.015
0003-2670/

has been shown that selected aerosol particles act as cloud condensation nuclei, affecting the lifetime of clouds [3]. Aerosol particles might have a substantial impact on human health [4]. Both the atmospheric and health-related impacts of aerosol particles are related to their chemical composition, morphological features, size and sources [5]. Furthermore, the chemical heterogeneity of ambient aerosol particles is an essential parameter, as the particle size and elemental concentration are not sufficient to properly estimate the environmental impact of aerosol particles, namely, bioaccessibility [6], toxicological effects [7], reactivity [8] and optical properties [9]. Several microanalytical techniques can be used to determine chemical heterogeneity at the single-particle scale because their lateral resolution is comparable to the size of particles collected from ambient air [10]. Among the single-particle analysis (SPA) techniques, Raman microspectroscopy (RMS) is a powerful technique that provides both the molecular composition and imaging of micron-sized aerosol particles [11–13]. RMS has been used to resolve the molecular composition and heterogeneity of individual aerosol particles [12,14–17]. Raman spectra may be complex due to the contribution of multiple compounds within one particle. Thus, chemometric methods such as Multivariate Curve Resolution (MCR) have found an application in the separation of spectral contributions from chemical compounds within aerosol particles and can significantly improve Raman images [13,14,17,18], even beyond resolution limits [19]. Since SPA techniques are off-line techniques, particles must be collected on suitable substrates for analysis. Thus, the choice of an analytical substrate for single particle analysis has to be made wisely. Obviously, the substrate should be characterized by optimal contrast adjustment, if optical images are considered, and by chemical inertness, to avoid any modification of the chemical composition and morphology of the particles. The substrate may have a large signal contribution compared to the relevant information in the sample and thus impair final results. This is particularly crucial when the particle size is lower than the beam spot size that is typically encountered for atmospheric micron-sized particles. The issue of substrate selection has already been considered for several single particle analysis techniques [20–22]. Only one publication has referred to the evaluation of substrate for both RMS and sequential electron probe X-ray microanalysis using thin-window energy-dispersive X ray detection (TW-EDX-EPMA) for analysis of aerosol particles [23]. Several substrates were examined in the study: carbon tape, nucleopore filter, silicon wafer, beryllium disc, TEM-grid, aluminium wafer and silver wafer. The study focuses on the features of the substrate, such as roughness, as well as the influence of measurement parameters, i.e., laser wavelength (514 nm and 785 nm), laser power density, objective (× 100 or × 50) and finally the size of the single particle. In this study, the effect of substrate contribution on spectral intensity, and thus on Raman imaging, was not investigated.

One reason for the application of MCR methods is the ability to separate the contribution of each compound and substrate, then reconstruct their respective spatial distributions. The use of an inadequate substrate may impair the accuracy of the calculated spatial distribution. The use of a suitable substrate for Raman microspectrometry imaging combined with MCR methods has not yet been evaluated. Developing interest in molecular imaging in nanoscience, including the environmental fate of produced micro- and nano-objects, has necessitated improvements in submicrometric analysis, including the selection of a suitable substrate. The substrate's spectral contribution influences analysis, its contribution might increase while the size of the object analysed decreases. Therefore, the choice of substrate cannot be neglected when MCR methodology is applied. This work concerns the evaluation of 6 substrates commonly used for particle collection: Si-wafer, Ag layer, In layer, TEM-grid, SiO_2 and microscope slide (MS). We have investigated for the first time the influence of substrate contribution on the spectral characterization of single-component and mixed micro-sized particles by using both RMS and MCR.

2. Material and methods

2.1. Substrates

Six substrates that fulfil the criteria for application in RMS analysis were used: (i) silver (thickness ~ 1 mm) (named Ag) and (ii) indium (thickness ~ 1 mm) layers (named In), each separately sputtered on a microscope slide (10 × 10 mm); (iii) grid for transmission electron microscopy (TEM-grid, AGAR Scientific F1 type G2761C, diameter = 3.05 mm), which was covered with a thin formvar film and a nanometric layer of carbon (named TEM-grid); (iv) Si-wafer (10 × 10 mm, Interuniversity Micro-electronic Centre, Belgium) (named Si); (v) SiO_2 (10 × 10 mm, silica slide, optical quality, from Alfa Aesar) (named SiO_2); and (vi) standard microscope slide, 10 × 10 mm (named MS).

The selection criteria were as follows: chemical homogeneity and inertness, substrates inert to laser excitation, a flat surface, and compatibility with the impaction sampling system.

2.2. Materials

Calcite ($CaCO_3$), hematite (Fe_2O_3), nitratine ($NaNO_3$) and anglesite ($PbSO_4$), fine powders with a purity of 99.99%, were used as model compounds usually found in natural and industrial aerosols [24]. The particle size was below 10 μm.

2.3. Preparation of the samples

The substrates were first ultrasonically cleaned in a mixture of ethanol and deionized water (50/50 vol) for 15 min to remove potential contamination by indoor particles. In this paper, “clean substrates” refers to substrates without any impacted particles. “Impacted substrates” refers to substrates with impacted particles.

Aerosolized calcite particles were generated in a homemade turbulent airflow reactor [15]. A mass of 0.125 g of calcite powder was introduced into the reactor to generate particles. The particles were collected by an inertial cascade impactor (PM10 Dekati). The substrates were mounted on one impaction plates corresponding to particles with an aerodynamic diameter ranging from 10 to 2.5 μm. The collection time was set for 3 min to avoid substrate overloading. A similar protocol was used for mixed aerosol particles composed of calcite, hematite, nitratine and anglesite. The content of each compound was fixed to 25% (w/w) (0.125 g), and the resulting mixture was then introduced into the airflow reactor. As described previously, the particles were collected on the 10–2.5 μm stage for 3 min. This methodology allows the production of mixed aggregates, as demonstrated in our previous work [15]. Both clean and impacted substrates were analysed by Raman microspectroscopy without further preparation. In this study, the stage 10–2.5 μm was used for the Raman analysis. Particles with a diameter of 5 μm were selected for the sake of the comparison between all substrates.

2.4. Raman microspectroscopy

Each substrate (with and without aerosol particles) was analysed by means of a Labram confocal Raman microspectrometer (Horiba, Jobin-Yvon) equipped with a 100 × , 0.9 numerical aperture Olympus objective. Raman scattering was excited with the 632.8 nm wavelength of a He–Ne laser. Acquisitions were