Inorganic salts in atmospheric particulate matter: Raman spectroscopy as an analytical tool

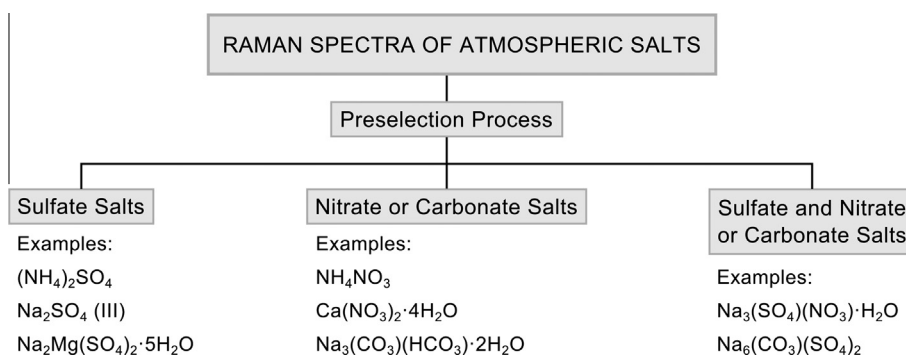Paul Vargas Jentzsch [a,1], Bernd Kampe [a,1], Valerian Ciobotă [a], Petra Rösch [a], Jürgen Popp [a,b,*]

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HIGHLIGHTS

- The Raman spectra of 45 atmospheric salts were recorded and the bands assigned.
- The carbonate salts can play an important role in the atmosphere.
- Structural similarities among salts can be expressed in the classification tree.
- The 45 salts were classified into 3 groups.

GRAPHICAL ABSTRACT

RAMAN SPECTRA OF ATMOSPHERIC SALTS

Preselection Process

Sulfate Salts
Examples:
$(NH_4)_2SO_4$
Na_2SO_4 (III)
$Na_2Mg(SO_4)_2 \cdot 5H_2O$

Nitrate or Carbonate Salts
Examples:
NH_4NO_3
$Ca(NO_3)_2 \cdot 4H_2O$
$Na_3(CO_3)(HCO_3) \cdot 2H_2O$

Sulfate and Nitrate or Carbonate Salts
Examples:
$Na_3(SO_4)(NO_3) \cdot H_2O$
$Na_6(CO_3)(SO_4)_2$

ARTICLE INFO

ABSTRACT

Atmospheric particulate matter is composed of inorganic and organic components of natural and anthropogenic origin. Wind-transport is probably the most important process responsible for the emission of solid particulate matter into the troposphere, but there are also important contributions from chemical reactions due to the interaction of different atmospheric components in presence of water and solar radiation. Sulfate, nitrate and carbonate salts can be both reactants and products in this complex dynamic system, and there is no doubt about their important impact on the climate. Both simple and mixed salts can be produced in atmosphere by dissolution–crystallization processes. The Raman spectra of 45 representative salts of the atmospheric environment were recorded and the bands assigned. The chemometric analysis of the spectroscopic data of these 45 salts demonstrates the suitability of Raman spectroscopy to classify and identify sulfate, nitrate and carbonate salts of atmospheric importance. Salts were classified into three groups: "sulfates", "nitrates or carbonates" and "sulfate-nitrates or sulfate-carbonate". This kind of information is relevant in atmospheric studies because specific characteristics of the salts can provide valuable information about the origin of the salts, the atmospheric chemistry and climate forcing, thus contributing to the evaluation of environmental impacts.

Introduction

The existence of several dynamic processes on the planet Earth is a well-known fact for a long time, but the interest in these processes is growing as mankind is becoming aware that their activities can affect and even modify them. Some general aspects of the environmental impacts caused by human activities were exposed by Crutzen [1].

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At present, environmental topics such as the global warming have importance worldwide, as there may be dramatic consequences to human future. A complete study of the weather includes the investigation of its changes over the time, i.e. the development of weather conditions through different eras and their possible trends. Researchers can use geologic information to identify climate changes in ancient times [2] and the occurrence in soil of a specific kind of ions is an indicator of the precipitation pattern of a specific region, e.g., nitrate salts are characteristic of arid soils [3,4]. However, the study of minerals seems not to be limited to the lithosphere, but also comprises the atmosphere, as huge amounts of particulate matter (aerosols) are not only released to the atmosphere, but they are also produced by chemical reactions within the atmosphere. About two decades ago, Preining [5] estimated that the annual global aerosol production totaled approx. 2 Pg (1 Pg = 10^{15} g), whereof 40% was attributed to direct natural emissions (sea salt, mineral dust and volcanic material), 40% to natural gas emissions converted to aerosols (sulfates, nitrates and hydrocarbons), and 20% to anthropogenic emissions (direct and gas-to-particle conversion). A few years later, Tegen and coworkers [6,7] demonstrated by using model calculations that not all mineral dust has a natural origin, in fact more than 50% of the total atmospheric dust mass originates from disturbed soils, in other words, it is produced by human activities.

Atmospheric particles are important for heterogeneous reactions which can alter the atmospheric composition; as an example the reaction between gaseous nitric acid, $HNO_3(g)$, and solid sodium chloride, $NaCl(s)$, is reported by Gard et al. [8]. Photochemical reactions of mineral dust have been the subject of different investigations on the daytime chemistry [9]. Atmospheric particles affect also the weather conditions and climate, since they influence the cloud lifetime and the Earth radiation budget [10,11].

Many authors, generally using X-ray diffractometry, reported the occurrence in atmospheric particle samples of minerals such as $Na_2Mg(SO_4)_2 \cdot 4H_2O$ (bloedite), $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$ (boussingaultite), $(NH_4)_2Ca(SO_4)_2 \cdot H_2O$ (koktaite), $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (mohrite), $Na_3(NO_3)(SO_4) \cdot H_2O$ (darapskite), $K_2Ca(SO_4)_2 \cdot H_2O$ (syngenite), $Na_2Ca(SO_4)_2$ (glauberite), $K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$ (polyhalite) among others [12–22]. While these minerals partly originate from blown dust, the atmospheric formation of particles cannot be ruled out. It is well known that salts containing characteristic aerosol ions are released to atmosphere by breaking waves and bursting bubbles on the ocean surface [23]; NO_3^- (especially as HNO_3) and SO_4^{2-} (as H_2SO_4) ions are produced in atmosphere by oxidation processes [24], and certain human activities release specific ions to atmosphere [19,25]. According to estimations these materials interact with atmospheric water, during the residence and transport of aerosols in atmosphere, undergoing around ten condensation–evaporation cycles [26], which are likely to produce important changes in their chemical composition. Based on these considerations we postulated in earlier articles [27–29] that mixed salts are formed in atmosphere as a result of dissolution–precipitation processes.

As mentioned, X-ray diffractometry is probably the most popular analytical method for mineral analysis, but infrared spectroscopy has also been proposed as a complementary analytical tool [30,31]. Recently, Raman spectroscopy is acquiring growing importance in mineral analysis; it has already been used to elucidate the composition of mineral deposits when studying geological processes [32] and is proposed for mineralogical studies in the planetary exploration [33,34]. In addition, several investigations reported the suitability of this technique for chemical characterization of atmospheric particles [27,28,35–42].

In this article we evaluate the Raman spectra of the most representative salts expected to be produced in atmosphere by the interaction of atmospheric material with water. It is known that sulfate and nitrate salts can be found in atmospheric particulate matter, and we believe that carbonate and bicarbonate salts (generally of terrigenous origin) can also play an important role in atmospheric chemistry; accordingly we selected representative salts for this study. The spectroscopic information is analyzed using chemometric methods to classify the atmospheric salts and to determine whether this kind of salts can be identified adequately using Raman spectroscopy.

Materials and methods

Chemicals and salt synthesis

Ammonium bicarbonate, NH_4HCO_3 ($\geqslant 99.0\%$), ammonium nitrate, NH_4NO_3 ($\geqslant 99.0\%$), ammonium sulfate, $(NH_4)_2SO_4$ ($\geqslant 99.0\%$), calcium nitrate tetrahydrate, $Ca(NO_3)_2 \cdot 4H_2O$ ($\geqslant 99.0\%$), calcium sulfate dihydrate, $CaSO_4 \cdot 2H_2O$ ($\geqslant 99\%$), iron (III) sulfate hydrate, $Fe_2(SO_4)_3 \cdot xH_2O$ (Fe 21–23%), iron (II) sulfate heptahydrate, $FeSO_4 \cdot 7H_2O$ ($\geqslant 99.0\%$), sodium bicarbonate, $NaHCO_3$ ($\geqslant 99.5\%$), sodium carbonate decahydrate, $Na_2CO_3 \cdot 10H_2O$ ($\geqslant 99.0\%$), sodium chloride, NaCl (min 99.5%), sodium sulfate anhydrous, Na_2SO_4 ($\geqslant 99.0\%$), magnesium nitrate hexahydrate, $Mg(NO_3)_2 \cdot 6H_2O$ ($\geqslant 99.0\%$), manganese (II) sulfate monohydrate, $MnSO_4 \cdot H_2O$ ($\geqslant 99\%$), potassium nitrate, KNO_3 ($\geqslant 99.0\%$), potassium sulfate, K_2SO_4 ($\geqslant 99.0\%$), hydrochloric acid, HCl ($\geqslant 37\%$), and sulphuric acid, H_2SO_4 (95.0–98.0%), were purchased from Sigma–Aldrich. Calcium carbonate, $CaCO_3$ ($\geqslant 99.0\%$), copper (II) sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$ ($\geqslant 99\%$) and zinc sulfate heptahydrate, $ZnSO_4 \cdot 7H_2O$ ($\geqslant 99\%$) were purchased from Merck. Sodium nitrate, $NaNO_3$ (min. 99%) was purchased from VWR. These reactants were used without further purification. Magnesium sulfate anhydrous, $MgSO_4$ (min. 99.5%) purchased from VWR was dried in an oven at 250 °C during 2 h before use, due to its high hygroscopicity.

$(NH_4)Fe(SO_4)_2 \cdot 12H_2O$ (lonecreekite) was crystallized at room temperature (20 °C) by slow evaporation of an acidic solution (pH < 2) containing $Fe_2(SO_4)_3$ and $(NH_4)_2SO_4$ in a molar ratio of 1:1. $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (mohrite) was crystallized at room temperature by slow evaporation of a slightly acidic solution containing $FeSO_4$ and $(NH_4)_2SO_4$ in a molar ratio of 1:1. In both cases, H_2SO_4 was used to acidify the solutions.

Considering that the commercial $FeSO_4 \cdot 7H_2O$ can contain impurities (Fe^{3+}), this salt was recrystallized. A slightly acidic saturated aqueous solution of the commercial $FeSO_4 \cdot 7H_2O$ ($\geqslant 99.0\%$) was prepared and vaporized at room temperature (20 °C). The resulting flat green crystals (a few millimeters long) were washed with small amounts of distilled water and dried carefully with a piece of absorbent paper.

$FeSO_4 \cdot H_2O$ (szomolnokite) was obtained using three methods: (1) heating crystals of $FeSO_4 \cdot 7H_2O$ at 40 °C during 2 h; (2) exposition of $FeSO_4 \cdot 7H_2O$ crystals to a very low humidity air environment (in a desiccator) overnight; and (3) recrystallization of the heptahydrate using a 50% v/v solution of H_2SO_4. [43] In all three cases the resulting product was grey and the Raman spectra showed the same features.

$FeSO_4 \cdot 4H_2O$ (rozenite) was obtained by exposition of $FeSO_4 \cdot H_2O$ powder to humid air (relative humidity 70%) during 10 min. The resulting powder was light yellow.

$K_3Na(SO_4)_2$ (aphthitalite) was obtained by slow vaporization of a saturated solution containing K_2SO_4 and Na_2SO_4, molar ratio 1:1.

For the preparation of Na_2SO_4 in phase III, a saturated solution of Na_2SO_4 at 100 °C was fast vaporized on a hot glass surface at 100 °C. Na_2SO_4 in phase III crystallized as tiny, less than 1 mm long needles.

$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (mohrite) was crystallized at room temperature (20 °C) by slow evaporation of a slightly acidic solution containing $FeSO_4$ and $(NH_4)_2SO_4$ in a molar ratio of 1:1.