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The topic of the doctoral dissertation: “Chemical Characterization of Isoprene Secondary Organic Aerosol in the Atmosphere using LC-MS/MS Approaches”

## **Abstract**

Atmospheric particulate matter (PM) is a key air pollutant. The solid and/or liquid particles suspended in the air form **an atmospheric aerosol**. The latter is a complex chemical mixture encompassing compounds of different molecular masses, structures and physicochemical properties. The diversity of the chemical composition of atmospheric aerosol is influenced by multifold factors, including sources of gaseous precursors, availability of atmospheric oxidants, and meteorological conditions. For a given aerosol fraction collected at a site (defined by the maximum size of particles contained in it and the same concentration depending on the place of sampling and the conditions prevailing in it), its chemical composition may vary at either a qualitative or quantitative level. Aerosol particles strongly impact air quality, living organisms, and the Earth’s climate, which is strongly dependent on the chemical composition of particles. Air pollution and smog evolution have become an increasingly popular subject of the research, due to the poor recognition of the composition of atmospheric aerosol, including respirable fractions, as well as due to the increasing number of cases of respiratory and cardiovascular diseases and premature deaths related directly to progressive air pollution. Air cleanliness is affected by both primary processes in which atmospheric dust is emitted directly into the atmosphere, e.g. through volcano emissions, and secondary processes where the particles are formed through the chemical reactions. Gaseous precursors, including sulfur and nitrogen oxides emitted to the atmosphere as a result of human activity, also enter secondary processes. In many regions of the world, regulations regarding the air purity standards are not obeyed. For example, this applies to the concentration limits for particulate matter (fraction  $PM_{10}$  and  $PM_{2.5}$ ).

Despite considerable knowledge about the sources of atmosphere pollution, as well as its adverse effects, due to the complexity of processes occurring in the atmosphere, many issues remain unsolved. The submitted thesis encompasses a series of studies aimed at a detailed

chemical characterization of secondary organic aerosol arising from the isoprene multiphase oxidation and proposing the likely mechanisms leading to its formation in the atmosphere. More specifically, I concentrated here on the characterization of the polar fraction of the PM matter, which is chiefly surpassed by organosulfates and nitroxy-organosulfates, mostly of undefined structures and origins. Owing to this knowledge, it would make it possible to better assess their potential effects on the environment and human health, while the knowledge of the mechanisms of atmospheric aerosol formation should allow us to extend the atmospheric models to better predict smog episodes, and perhaps also to prevent them. To achieve the goal, I applied a combined approach linking the capacity of the liquid chromatography, mass spectrometry and organic synthesis for getting more insights into the aqueous-phase reactions between sulfate radicals ( $\text{SO}_4^{\cdot-}$ ) and isoprene ( $\text{C}_5\text{H}_8$ ) as well as isoprene oxygenates, i.e., methyl vinyl ketone and methacrolein ( $\alpha$ ,  $\beta$ -unsaturated carbonyls;  $\text{C}_4\text{H}_6\text{O}$ ), leading to a novel chemical class of atmospheric particulate matter components – monoalkyl esters of sulfuric(VI) acids, hereinafter referred to as **organosulfates (OSs)**.

The research was conducted in several projects. First one encompassed a series of laboratory experiments, which equivocally proved that despite poor solubility of isoprene in the atmospheric waters, sulfate radicals-induced reactions of isoprene and its oxygenated derivatives, i.e., methyl-vinyl ketone and methacrolein, become important sources of aerosol-bound organosulfates. The results obtained from laboratory-conducted experiments revealed the presence of several atmospherically-relevant organosulfates. A series of LC-MS analyses carried out for fine ambient aerosol collected from various field campaigns confirmed their presence in natural samples. The comparison of chromatographic and mass spectral data obtained from both ambient and laboratory-generated aerosol allowed for the firm structural elucidation of several atmospherically relevant organosulfates, including the stereoisomeric assignments.