



Method development for the qualification and quantification of reactive α -dicarbonyls methylglyoxal and glyoxal in snow and ice using stir bar sorptive extraction (SBSE) and HPLC-ESI-IT/MS

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In recent years the analysis of secondary organic aerosol (SOA) has been of great interest due to its impact on the radiative budget of the earth's atmosphere. The water soluble α -dicarbonyls glyoxal (gly) and methylglyoxal (mgly) play an important role in the formation and growth of SOA. They are formed through gas phase oxidation of volatile organic compounds (VOCs) of anthropogenic (i.e. aromatics, alkenes) as well as biogenic (i.e. isoprene) origin.^[1] Aqueous-phase chemical processes lead to uptake of gly and mgly by aqueous aerosols, fog and cloud droplets. In the aqueous phase (particularly in cloud water) gly and mgly are oxidised by OH-radicals to form organic acids, especially oxalic and pyruvic acid, which are found in SOA. Oligomerisation of either gly/mgly or their oxidation products can also lead to SOA formation.^[2]

Only little research has been conducted regarding the qualitative and quantitative occurrence of gly and mgly in polar regions. Hence a quantification of these compounds in snow samples is of interest and may provide new information on the role of gly and mgly or their oxidation products in ice nucleation processes or the long-distance transport of aerosols for example.

By analysing samples from different layers in ice cores it is also possible to determine the temporal variation in the concentration of certain trace compounds. This provides information about the chemical composition of the atmosphere – interrelated with the climate – in the past.

Here the development of a new method for the qualification and quantification of gly and mgly in aqueous samples (molten snow and ice) is presented. Stir bar sorptive extraction (SBSE) with in situ derivatisation is applied for extraction and enrichment of the analytes. SBSE is an equilibrium technique which uses a polydimethylsiloxan (PDMS) - coated stir bar. The extraction is based on the partitioning of the solutes between the silicon phase and the aqueous sample.^[3] In contrast to the commonly used solid phase extraction (SPE), SBSE is less time-consuming and labour-intensive because of the simultaneous derivatisation, extraction and enrichment of the analytes. Lower limits of detection can be achieved compared to solid phase micro extraction (SPME), due to a larger volume of the silicon phase.

Measurements were conducted on a reversed phase high performance liquid chromatography coupled to electrospray ion trap mass spectrometry (RP-HPLC-ESI-IT-MS) system. Method parameters such as extraction time, backextraction time, and backextraction solvent were optimised and the influences of NaCl addition and amount of derivatisation agent were investigated. The limits of detection and quantification were determined.

[1] T. M. Fu et al., *J. Geophys. Res.* **2008**, (113), D15303.

[2] K. E. Altieri et al., *Atmospheric Environment* **2008**, (42), 1476-1490.

[3] F. David, P. Sandra, *J. Chromatogr. A* **2007**, 1152, 54-69.