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Application of Lithium Attachment Mass Spectrometry for Knudsen Evaporation and Chemical Ionisation Mass Spectrometry (KEMS, CIMS)

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Lithium ion attachment mass spectrometry provides a non-specific, non-fragmenting and sensitive method for detection of volatile species in the gas phase. The design, manufacture, and results from lithium ion attachment ionisation sources for two mass spectrometry systems are presented. Trace gas analysis is investigated using a modified Chemical Ionization Mass Spectrometer (CIMS) and vapour pressure (VP) measurements using a modified Knudsen Effusion Mass Spectrometer (KEMS) are presented.
The Li+ modified CIMS provided limits of detection of 4 ppt for acetone, 0.2 ppt for formic acid, 15 ppt for nitric acid and 120 ppt from ammonia. Despite improvements, the problem of burnout remained persistent. The Li+ CIMS would unlikely be suitable for field or aircraft work, but could be appropriate for certain lab applications.
The KEMS currently utilizes an electron impact (EI) ionisation source which provides a highly sensitive source, with the drawback of fragmentation of ionized molecules (Booth et al., 2009). Using Li+ KEMS the VP of samples can be measured without fragmentation and can therefore be used to identify VPs of individual components in mixtures. The validity of using Li+ for determining the VP of mixtures was tested by making single component VP measurements, which showed good agreement with EI measurements of Poly ethylene glycol (PEG) 3 and PEG 4, both when individually measured and when mixed. The Li+ KEMS was then used to investigate a system of atmospheric relevance, α-pinene secondary organic aerosol, generated in a reaction chamber (Alfarra et al., 2012). The VPs of the individual components from this generated sample are within the range we expect for compounds capable of partitioning between the particle and gas phase of an aerosol (0.1-10-5 Pa). Li+ source has a calculated sensitivity approximately 75 times less than that of EI, but the lack of fragmentation using the Li+ source is a significant advantage.