

Measurements of HO_x (OH, HO₂) and RO₂ radicals by ion molecule reactor-mass spectrometer (IMRMS)

Alexandre Kukui and co-workers at CNRS-ICARE Orléans

A mobile IMRMS has been developed to measure the HO_x and RO₂ radicals. The principle of the detection is the conversion of these radicals to gaseous H₂SO₄ by adding SO₂ and NO in the sampling air in a chemical conversion reactor. H₂SO₄ is further ionised into HSO₄⁻ ions by reaction with the NO₃⁻ ion in the ion-molecule reactor (IMR). The HSO₄⁻ ions are extracted through an ion optics interface and pass through the quadrupole filter before being detected. The primary NO₃⁻ ions are produced in a specially developed corona discharge ion source. The performance of the instrument have been optimized by developing 1/ a chemical conversion reactor with a reduced (a few ms) conversion time in order to minimize artificial formation of OH from HO₂ in presence of high NO concentrations (> 10ppb) in the sample medium; 2/ a radio frequency funnel with high sensitivity and complete declustering capacity of the NO₃⁻ ions. According to laboratory measurements the overall accuracy and detection limits are estimated to be , respectively, 25% and 2×10⁵ cm⁻³ for OH and 30% and 1×10⁵ cm⁻³ for HO₂ (integration time 10 mn). The detection limit for OH measurements under polluted conditions is 5×10⁵ cm⁻³ at 10 mn integration time.

The IMRMS has been coupled to the simulation chamber of ICARE (V= 7 m³) for radical measurements. The chemical conversion reactor has been installed inside the chamber and connected to the ion molecule reactor by a 2m long , 1 in. diameter PFA tube. OH and RO₂ radicals were produced in the chamber by ozonolysis of ethene and their kinetics were monitored with the IMRMS. Tests of the sampling line has been made using a calibrated OH and HO₂ radical source (photolysis of H₂O in air at 185 nm). The tests have shown that for reliable measurements under various conditions the IMR should be as close as possible to the chemical conversion reactor. Such new configuration has been realized for the IMRMS/LIF inter-comparison campaign of the second half of April 2009. At least preliminary results from this campaign should be also presented.

(The description and the first applications of the IMRMS have been recently submitted for publication to the Journal of Atmospheric Chemistry).