

Total sulphate vs. sulphuric acid monomer in nucleation studies

K. Neitola¹, D. Brus^{1,2}, U. Makkonen¹, M. Sipilä³, T. Jokinen³, R. L. Mauldin III^{3,4}, K. Kyllönen¹, H. Lihavainen¹ and M. Kulmala³

¹Finnish Meteorological Institute, Erik Palménin aukio 1, P.O. Box 503, 00100 Helsinki, Finland

²Laboratory of Aerosol Chemistry and Physics, Institute of Chemical Process Fundamentals Academy of Sciences of the Czech Republic, Rozvojová 135, 165 02 Prague 6, Czech Republic

³Department of Physical Sciences, University of Helsinki, P.O. Box 64, 00014 Helsinki, Finland

⁴Institute for Arctic and Alpine Research, University of Colorado, Boulder, CO 80309, USA

Keywords: nucleation, sulphuric acid.

Presenting author email: kimmo.neitola@fmi.fi

Exact determination of sulphuric acid concentration is crucial for predicting the nucleation rates and subsequent growth. In our study, we have noticed a discrepancy of about one to two orders of magnitude between sulphuric acid monomer and total sulphate concentrations measured from the same source of sulphuric acid vapour, with similar particle formation rates.

A thermally controlled saturator half filled with neat sulphuric acid (~97%) was used to produce the sulphuric acid vapour. The production method was first tested and then used in combination with a flow tube in a H₂O – H₂SO₄ nucleation experiment. Particle formation rates and size distributions were measured with several CPCs (TSI models 3776, 3025A and PSM) and with a DMPS system, respectively.

Sulphuric acid concentrations were detected with two independent methods. First, with two different mass spectrometers, CIMS (e.g. Eisele and Tanner, 1993) and CI-APi-TOF (Junninen et al., 2010). Second, with online ion chromatograph MARGA 2S ADI 2080 (ten Brink et al., 2007). MARGA was used also to detect background concentration of ammonia. Mass spectrometers were used to detect sulphuric acid monomer concentration, whereas MARGA measures the total sulphate concentration.

Results were compared to the previous measurements done in our laboratory (Brus et al., 2010), where a furnace was used as a source of sulphuric acid vapour and Bubblers were used to measure total sulphate concentration. Bubbler method is analogous to the MARGA with the difference that it is offline method. Results were also compared to the predicted values calculated using vapour pressure of sulphuric acid (Kulmala and Laaksonen 1990).

Figure 1 shows comparison of observed nucleation rates as a function of total sulphate or sulphuric acid monomer concentration between two different production methods and between two independent sulphuric acid detection methods. All results were obtained in similar conditions (RH 30%, T = 298K). Here one can observe that with similar nucleation rates and experimental conditions total sulphate and sulphuric acid monomer concentrations has a discrepancy of one to two orders of magnitude.

The discrepancy between the total sulphate and sulphuric acid monomer concentration cannot be explained by formation of larger clusters (dimer, trimer,

etc.) as the concentration of dimer was always 1% or less of monomer concentration, with decreasing trend when moving to larger clusters. Losses of sulphuric acid to particles and to the walls were determined and it is shown that losses cannot explain the discrepancy either.

We suggest that the sulphuric acid is hidden into pool of clusters that are not detected by the particle counters nor identified from the mass spectra of CI-APi-TOF.

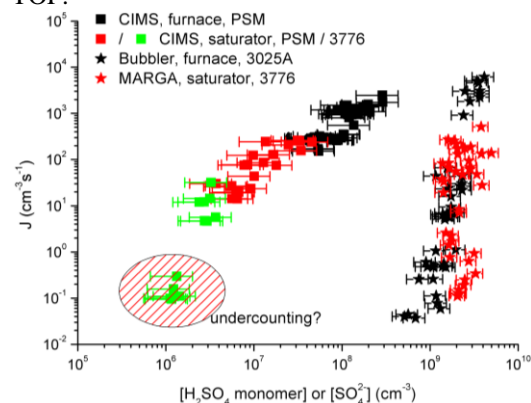


Figure 1. Comparison between our previous results and the results from this study from H₂O - H₂SO₄ nucleation experiment (Neitola et al., 2013).

This work was financially supported by the Finnish Academy Centre of Excellence program (project no. 1118615) and by the Maj and Tor Nessling Foundation.

Brus, D., Hyvärinen, A.-P., Viisanen, Y., Kulmala, M. and Lihavainen H. (2010) *Atmos. Chem. Phys.*, 10, 2631–2641.

Eisele, F. and Tanner, D. (1993) *J. Geophys. Res.*, 98, D5, 9001-9010.

Junninen, H., Ehn, M., Petäjä, T., Luosujärvi, L., Kotiaho, T., R. Kostianen, R., Rohner, U., Gonin, M., Fuhrer, K., Kulmala, M. and Worsnop, D. (2010) *Atmos. Meas. Tech.*, 3, 1039–1053.

Kulmala M. and Laaksonen, A. (1990) *J. Chem. Phys.*, 93 (1), 1.

Neitola, K., Brus, D., Makkonen, U., Sipilä, M., Jokinen, T., Mauldin III, R. L., Kyllönen, K., Lihavainen, H. and Kulmala, M. (2013) *Atmos. Chem. Phys. Discuss.*, 13, 2313–2350.

ten Brink, H., Otjes, R., Jongejan, P. and Slanina S. (2006) *Atmos. Env.*, 41, 13, 2768-2779.