Supporting information

Simultaneous determination of gaseous ammonia and particulate ammonium in ambient air using cylindrical wet effluent diffusion denuder and continuous aerosol sampler

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Supporting information for the publication including:

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Chemicals used for experiments

All solutions were prepared from deionized water. All reagents were of analytical grade. Ammonium sulphate, methanol, monosodium phosphate, phosphoric acid and sodium sulfite were obtained from Lach-Ner (Neratovice, Czech Republic), potassium hydroxide from Penta (Chrudim, Czech Republic), formaldehyde from Merck (Darmstadt, Germany) and ortho-phthaldialdehyde from Sigma-Aldrich (St. Luis, USA).

Description of CWEDD

The CWEDD consisted of a specially treated glass tube (50 cm length × 1.1 cm i.d.) and untreated inlet and outlet tubes, assembled together by two heads (Ketron PEEK). The tubes were sealed in the heads by Teflon tape to avoid leakage. To ensure a wettable surface, the inner wall of the denuder tube was roughed. The absorption liquid (deionized water) was dosed by peristaltic pump (with the flow rate of 0.33 ml min^{-1}) to the denuder tube through the porous Teflon o-ring located between the outlet tube and the denuder tube in the top head. A compact film of the absorption liquid flowed down continuously on the inner wall, and the analyte concentrate was aspirated at the bottom of the denuder tube through a slit between the end of the denuder tube and the inlet subduction zone at the bottom head.

Description of CGU-ACTJU

The ACTJU collector[43] captured aerosols by water droplets within the collision of two jets of fine water droplets formed by spraying of deionized water at room temperature by high-velocity air in two opposed Venturi nozzles. The deionized water (with the flow rate of 1 mL min^{-1}) with collected particles then entered into the cyclone where air and liquid concentrate were separated. The effluent was continuously aspirated from the bottom of the cyclone by a peristaltic pump for subsequent analysis using FLD, while air was aspirated out by the membrane pump. The air flow rate through the CGU-ACTJU sampler was 10 L min^{-1}.

The CGU consisted of two aluminum segments in series.[44] The first segment (length 34 cm; humidifier) was heated electrically to 52 °C and the second segment (length 34 cm; condenser) was thermoelectrically cooled to 18 °C by means of Peltier cooling devices. The inner space of each segment included two porous Teflon tubes (Aeos ePTFE extruded tube, i.d. 0.28″, wall 0.016″, length 5.91″, Zeus, USA) forming two parallel PTFE lines. The space between PTFE tubes and aluminum body was filled with deionized water continuously refilled by peristaltic pump. The analyzed air (with flow rate of 10 L min^{-1}) passed first through the heated humidifier where the air was saturated with water vapor and warmed up. Subsequently, the humidified air passed through the cooled condenser where the air temperature dropped down. The sharp drop in temperature resulted in the supersaturation of the air in the condenser, which activated condensational growth of small particles. The rapid condensational growth due to condensation of water vapor enlarged particles as small as a few nanometers to larger droplets in the super-micrometer range. The droplets at air flowing from the CGU were then collected in the ACTJU collector into deionized water.

Determination of NH_3/NH_4^+

The determination of NH_3 using the developed method was compared with results from reference method (DDP). The standard NH_3 (the concentration of 0.38, 0.82, 2.93, 8.35 and 18.2 μg m^{-3}) was in parallel analyzed by the GAA and reference method. The standard NH_4^+ aerosol (NH_4^+ concentration of 186, 633, 1171, 1746 and 2357 ng m^{-3}) was in parallel sampled on Zefluor filter/DDP and to the CGU-ACTJU sampler.

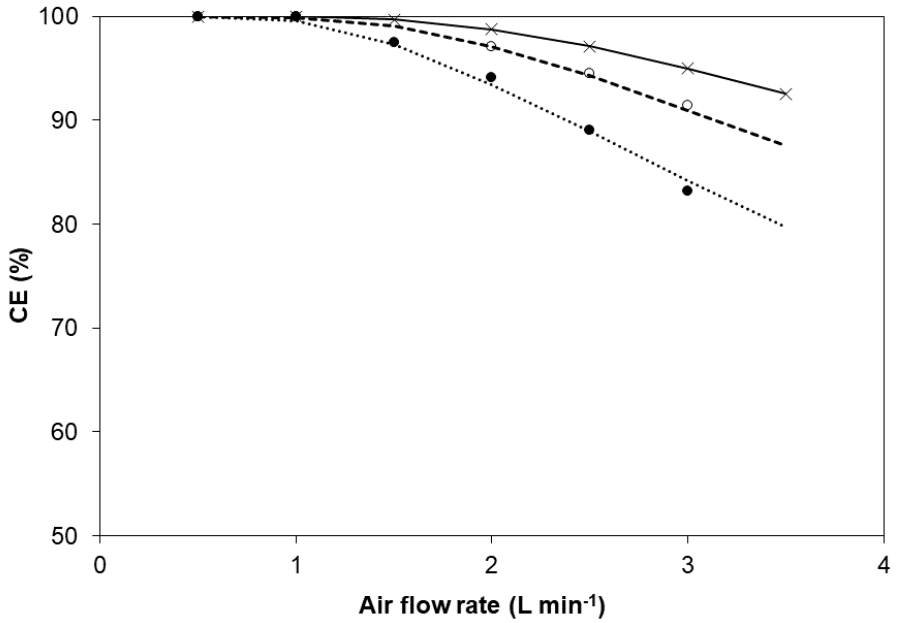

Figure S1. The dependence of CE of ammonia on the air flow rate in the CWEDD using two absorption liquids. (×) theoretical data calculated according to GK; (●) experimental data of deionized water; (⋯) theoretical curve for water calculated according to CKD; (○) experimental data of 10 mM $KHSO_4$; (---) theoretical curve for 10 mM $KHSO_4$ calculated according to CKD.

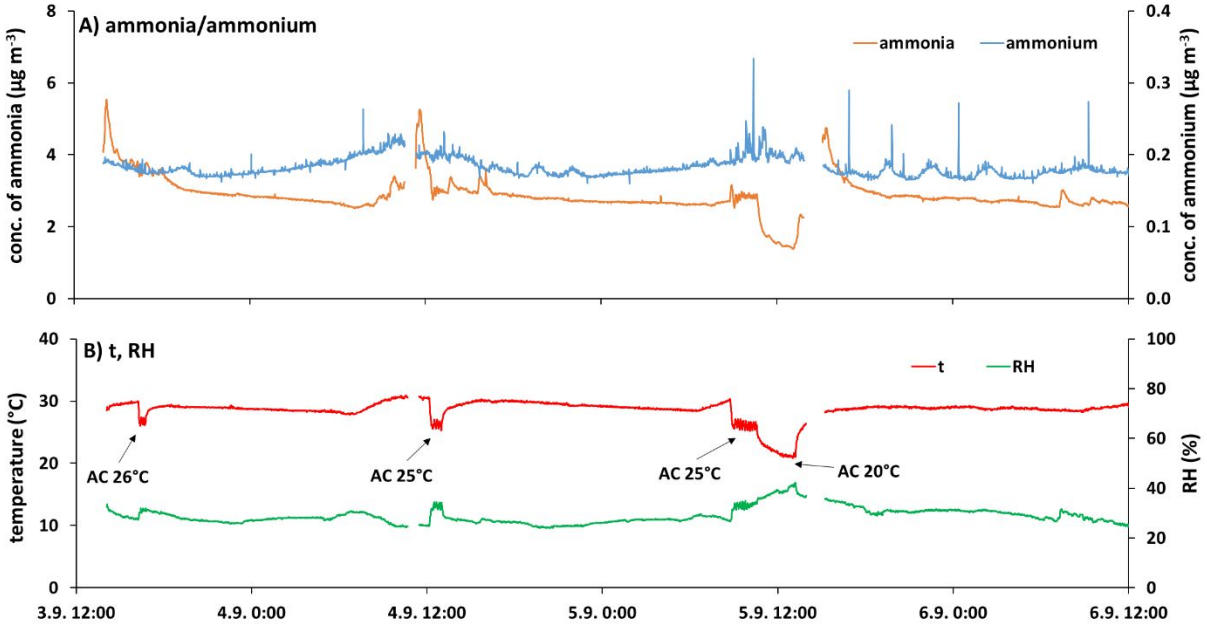

Figure S2. Changes in the concentration of NH_3/NH_4^+ in laboratory air (Brno, September 2017). A – concentration of ammonia and ammonium (µg m^{-3}), B – temperature (°C), relative humidity (%).

Table S1. Daily average concentrations of NH_3 and NH_4^+ during the winter and summer campaign

winter	NH_3 (µg m^{-3})	NH_4^+ (µg m^{-3})	$NH_3/(NH_3+NH_4^+)$ (%)
8.2.2018	0.185	3.175	5.5
9.2.2018	0.208	2.577	7.5
10.2.2018	0.186	2.511	6.9
11.2.2018	0.196	3.013	6.1
12.2.2018	0.063	2.146	2.9
13.2.2018	0.071	2.015	3.4
14.2.2018	0.042	2.730	1.5
15.2.2018	0.072	2.563	2.7
average	0.128	2.591	4.6
summer			
17.9.2018	2.223	0.551	80.2
18.9.2018	1.922	0.311	86.1
19.9.2018	1.974	0.709	73.6
20.9.2018	2.068	0.324	86.5
22.9.2018	1.253	0.005	99.6
23.9.2018	0.511	0.011	97.9
24.9.2018	0.127	0.029	81.6
average	1.440	0.277	83.9