Chemical Characterization of PM_{10} at Melpitz site in Germany – Test of an Online Wet Chemical System for Simultaneous Quantification of Gases and Water Soluble Ions (MARGA)

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1. Introduction

The new sampling system MARGA (Monitor for Aerosols & Gases in ambient Air, Applikon Analytical, NL)[1] for a semi-continuous and simultaneous quantification of water soluble ions in particulate matter and their related gas phase components is tested.
The MARGA is able to measure the gases HCl, HNO_2, SO_2, HNO_3 and NH_3 as well as the inorganic components Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} in the particle phase with a time-resolution of one hour. After passing a Teflon coated PM_{10} inlet the sample air enters a Wet Rotating Denuder (WRD) where the water-soluble gases diffuse into an absorbance liquid. Connected to the WRD is a Steam-Jet Aerosol Collector (SJAC) which is used to collect the particles (Figure 2) [2]. Due to a supersaturation of water vapour in the SJAC particles grow rapidly into droplets. These droplets containing the dissolved inorganic ions are collected in a cyclone. The resulting liquid solutions of the denuder and of the SJAC are analyzed online using an anion and a cation chromatograph.
The MARGA transfers 1 m³ air per hour into two 25 ml liquid samples and has a detection limit below 0.1 µg/m³. The ion chromatography is continuously calibrated by the use of an internal standard (LiBr).
The MARGA opperates at the research station of the Leibniz Institute for Tropospheric Research in Melpitz, Germany [3]. The station is located 50 km north-east of the city of Leipzig near the river Elbe in a flat terrain without noteworthy anthropogenic emissions in the nearby surroundings (Figure 1).
In Melpitz it is possible to compare the MARGA with other instruments for the monitoring of the troposphere, e.g. with gas analysers for SO_2 (Figure 4) or with daily samples of PM_{10} (DIGITEL-high-volume-samplers, Figure 5).

The new system has some advantages for the chemical aerosol characterization:

(i) Time resolution of one hour for concentrations of water-soluble ions particles and their related corresponding trace gases.
(ii) Artifact-free quantification of volatile species.
(iii) Online analysis with remote control.

Fig. 1: Location of the IfT-research-site Melpitz in Germany.

2. Instrumentation

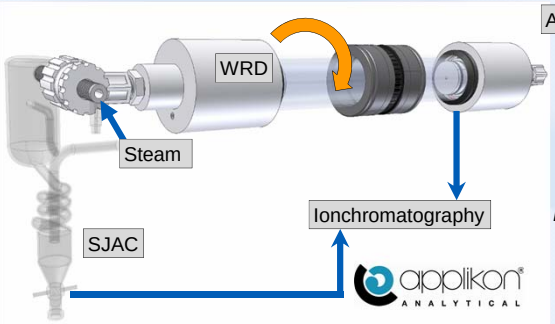

Fig. 2: Combination of Wet Rotating Denuder (WRD) and Steam-Jet Aerosol Collector (SJAC) in the MARGA-instrument

3. Results of continuous measurements

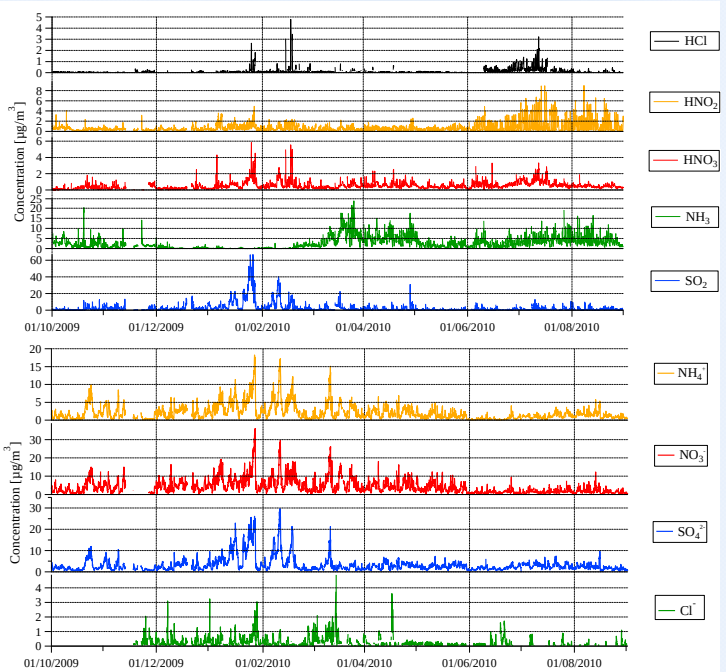

Fig. 3: Results of continuous measurements (hourly means) for gases and for the main water soluble ions in PM_{10} for eleven month (October 2009 until August 2010).

4. Comparison

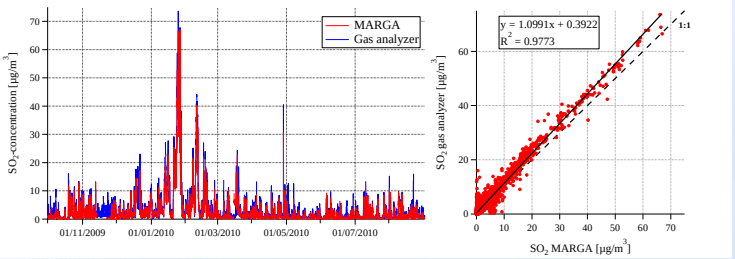

Fig. 4: SO_2-concentration measured with MARGA in comparison to results of measurements using a gas-monitor (UV-Fluorescence).

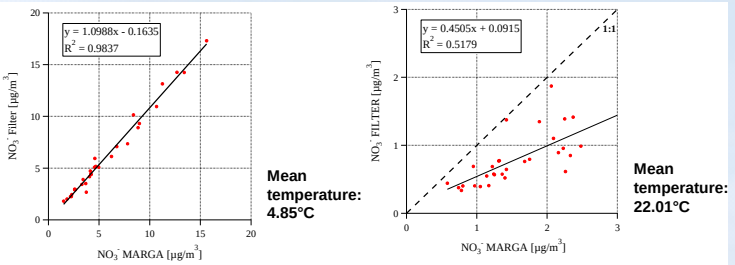

Fig. 5: NO_3^- measurements in PM_{10}: Comparison of daily High-Volume Filter measurement (quartz-fibre Filter, DIGITEL DHA-80) with results of MARGA. A) in winter (March 2010) and B) in summer (July 2010)

5. Summary

The MARGA was operated in Melpitz, Germany for 11 month. A data yield of over 90% was achieved since the launch of the MARGA in October 2009. Figure 3 shows the gases and the main ionic PM_{10} species NH_4^+, NO_3^-, SO_4^{2-} and Cl^- over the whole measuring period. The MARGA was remotely accessible. The site was visited once a week.
The MARGA showed very good agreement with common measuring instruments, e.g. with a SO_2-monitor (UV-fluorescence, Figure 4) and with PM_{10} filter measurements (DIGITEL-high-volume-samplers, Figure 5A).
The comparison between the MARGA and filter measurements of nitrate indicates a negative artifact in the filter measurements in July 2010 (Figure 5B). Due to the volatile behaviour of NH_4NO_3 and the high mean temperature of 22°C in this summer nitrate evaporates from the particle phase as HNO_3 and thus nitrate cannot be quantified correctly with filter measurements.

6. References

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[2] Khlystov, A., Wyers, G.P., Slanina, J. (1995) The Steam-Jet Aerosol Collector. *Atmos Environ.* **29**, 2229-2234.
[3] Spindler, G., Brüggemann, E., Gnauk, T., Grüner, A., Müller, K., Herrmann, H. (2010). A four-year size-segregated characterization study of particles PM_{10}, $PM_{2.5}$ and PM_1 depending on air mass origin at Melpitz.. *Atmos. Environ.*, **44**, 164-173.

7. Acknowledgements

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