

Laboratory and field based evaluation of chromatography related performance of the **Monitor for Aerosols and Gases in Ambient Air (MARGA)**

Introduction

Time-resolved simultaneous measurements of the gas and aerosol components of the ammonium-sulfate-nitrate system are required to investigate the processes governing inorganic aerosol formation and characteristics (e.g., phase partitioning, acidity) and the dry component of nitrogen deposition. The Monitor for Aerosols and Gases in Ambient Air (MARGA) provides near real-time simultaneous measurement of water soluble particulate species as well as their gaseous precursors.

The objective of this study is to evaluate MARGA performance with a focus on accuracy and precision characteristics related to automated chromatography analysis. To aid efficiency and flexibility in the reprocessing of raw chromatograms, an alternative to the MARGA chromatography tool was employed. Using laboratory standards, analytical accuracy, precision, and method detection limits derived from the two chromatograph processing methods were compared. Field measurements were used to further evaluate instrument performance and to demonstrate the ability of the MARGA instrument to resolve important atmospheric processes.



Issues with MARGA chromatography tool

- Incorrectly defined baseline due to peak fronting and tailing and shifting between "drop perpendicular" and "valley to valley" integration options.
- MARGA integration parameters are applied to all chromatograms.
- Inability to manually adjust integration for individual peaks
- An alternative chromatography software (Chromeleon V7.2, Thermo Scientific Dionex) was evaluated for batch reprocessing of MARGA chromatograms.

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Results and discussion

Laboratory study of chromatography characteristics

• MARGA chromatograms were systematically examined by running a multipoint series of liquid external standards.

 Table 1. Method

detection limits (MDL) for chromatograms processed by MARGA tool and Chromeleon.

	Chron	neleon	MARGA tool		
	MDL(µg/m³)	# of samples	MDL(µg/m³)	# of samples	
NH ₄ +	0.02	78	0.04	78	
NH ₃	0.02	78	0.04	78	
SO ₄ ²⁻	0.08	80	0.13	76	
SO ₂	0.05	80	0.08	76	
NO ₃ -	0.08	80	0.14	76	
HNO ₃	0.08	80	0.14	76	

• Method detection limits calculated using the MARGA software are substantially larger than corresponding detection limits calculated with Chromeleon.

Field Study

The site was impacted by an arctic air mass late in the study period.

	Cold Event			Non-Cold event		
	Average	Median	Max	Average	Median	Max
NH ₃	0.12	0.09	0.29	0.35	0.24	1.62
HNO ₃	0.35	0.30	0.82	0.17	0.13	0.97
SO ₂	3.22	1.32	32.56	0.73	0.42	8.09
NH4 ⁺	0.99	0.88	2.20	0.48	0.45	1.21
NO ₃ -	1.07	0.72	3.18	0.13	0.09	0.98
SO ₄ ²⁻	1.93	1.66	4.39	1.33	1.29	3.58
Temperature	4.54	5.00	13.9	12.88	12.20	29.40
RH	50	51	77	70	71	100



• During cold event periods 1 and 2, the majority (estimated inorganic portions summing SO_4^{2-} , NO_3^{-} and NH_4^{+} were 61±31% and 83±24%, respectively for period 1 and 2) of the PM_{25} mass was inorganic compounds, while in contrast, inorganic compounds only accounted for $22 \pm 11\%$ of PM_{2.5} mass during period 3.

 Table 2. Summary

of concentrations $(\mu g/m^3)$ of aerosol and precursor gases during and outside of cold air mass periods.

Figure 2. High concentration periods (cold event) observed during mid-November 2014. Period 1: highest SO_4^{2-} ; Period 2: highest NH_4^+ and NO_3^- ; Period 3: highest OC. Corresponding back trajectories (arrival at 500AGL, backwards for 168hrs) of individual period peaks (±2hrs) are also presented.



Impact of chromatography related biases were assessed using aerosol neutralization state as a case study.



- R1 and R2, respectively.
- reprocess the raw chromatograms.
- metrics of particle acidity.

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 NH_4^+ $R1 = \cdot$ $R2 = \frac{1}{NO_3^- + 2 \times SO_4^{2-}}$

results from MARGA

concentrations below

software $\approx 30\%$

Chromeleon for

larger than

Figure 4. Partitioning molar ratios of a) NO_3^- , b) SO_4^{2-} and c) NH_4^+ in particle phase, calculated as particle/(particle+gas); d) molar ratios (R1 and R2) of particulate NO_3^- , SO_4^{2-} and NH_4^+ to determine particle neutralization state and acidity; e) relative difference of partitioning molar ratios of NO₃⁻, SO_4^{2-} and NH_4^{+} in particle phase as well as particle neutralization state indicators R1 and R2 by Chromeleon and MARGA tool.

Average differences in neutralization state were $\approx 13\%$ and 14% for

Conclusions

Close examination of chromatograms revealed a number of issues with the MARGA chromatography software tool. Hence, an alternative software, Chromeleon (Thermo Scientific Dionex), was used to

Biases in anion concentrations between the two chromatography methods produced non-trivial errors in concentrations $< 1 \mu g m^{-3}$ and

The cause of this bias is unclear but can be controlled by correcting anion concentrations with multi-point calibration curves rather than relying solely on the MARGA LiBr internal standard.