

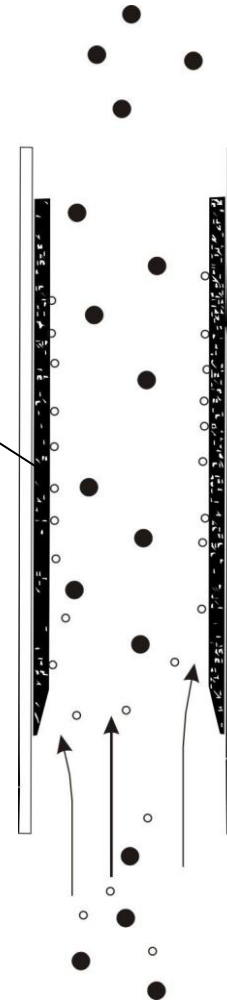
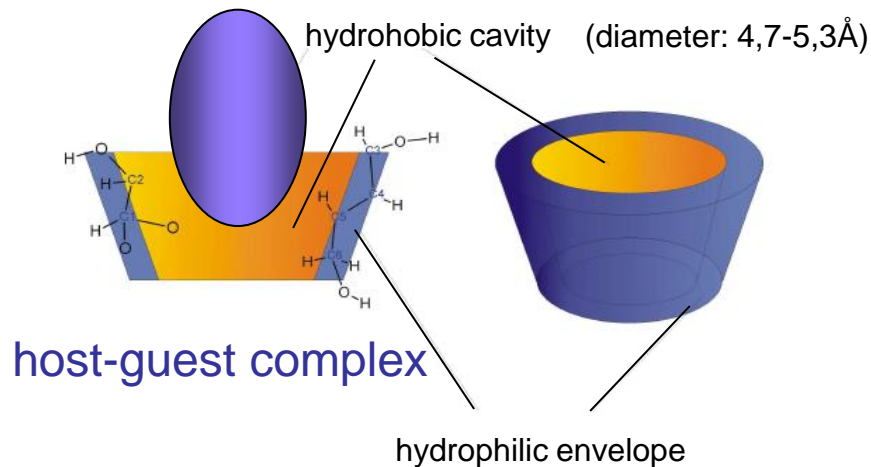
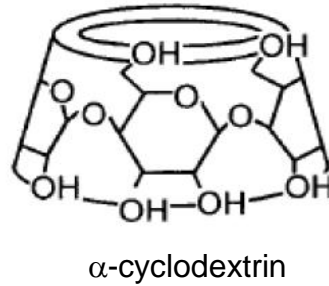
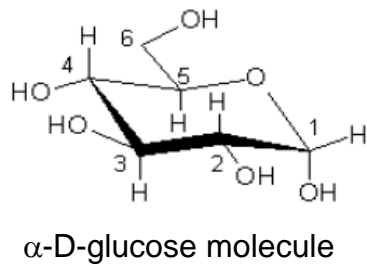
“Analysis of gaseous I₂ in the marine boundary layer”

Thorsten Hoffmann, Ru-Jin Huang, Michael Kundel, Christopher Kampf

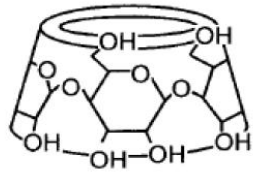
TORERO workshop, NCAR, October 31th, 2011

- I. Introduction
- II. Denuder-GC/MS Method
- III. Comparison with DOAS Method
- IV. Practical Aspects for TORERO Cruise
- V. Outlook: GTRAP-TOF-AMS Method




Sampling of molecular iodine using an cyclodextrin coated diffusion denuder

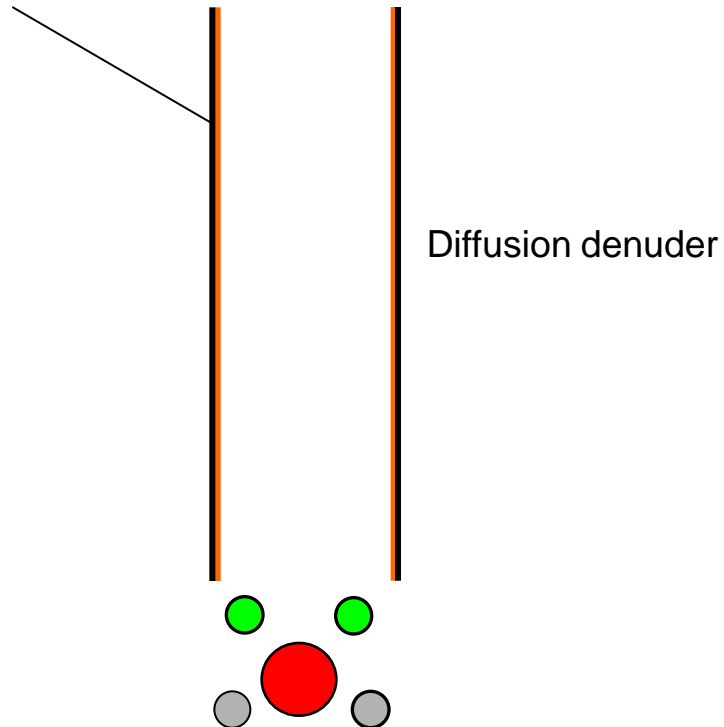


Sampling mechanism



α -cyclodextrin
[Yoshida 1999]

-  **Particles**
-  **Gaseous non-target compound**
-  **Gaseous target compound**



II. Denuder-GC/MS Method

Sample preparation and measurement

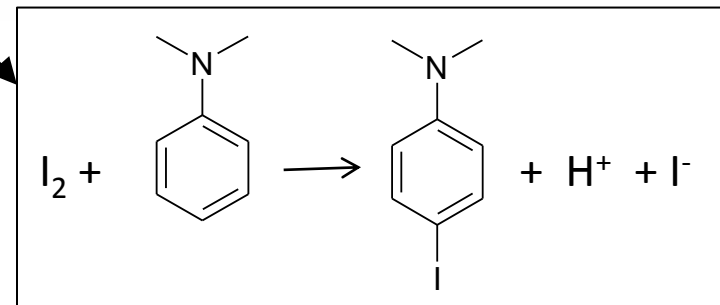
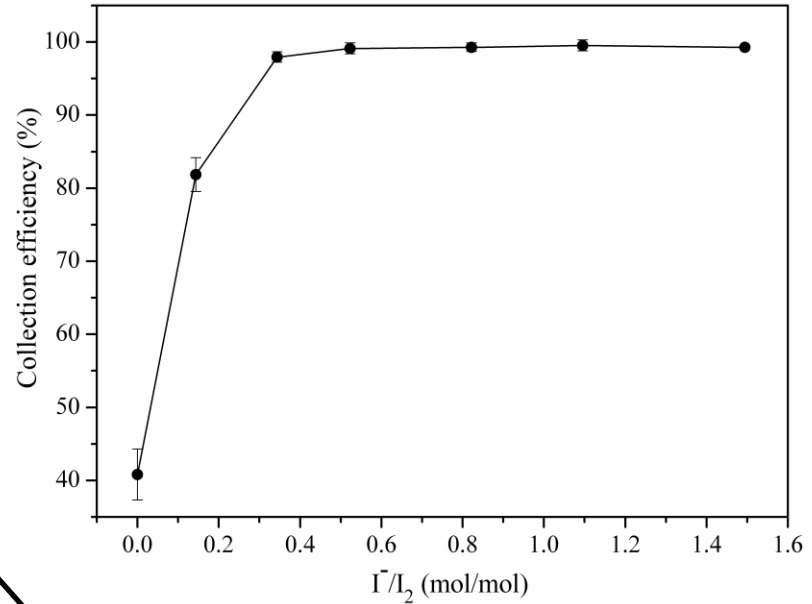
addition of Iodide-129 standard solution (SRM 4949C) $^{127}\text{I}/^{129}\text{I}$ ratio of **0.17**

Sampling

Elution, derivatization and extraction

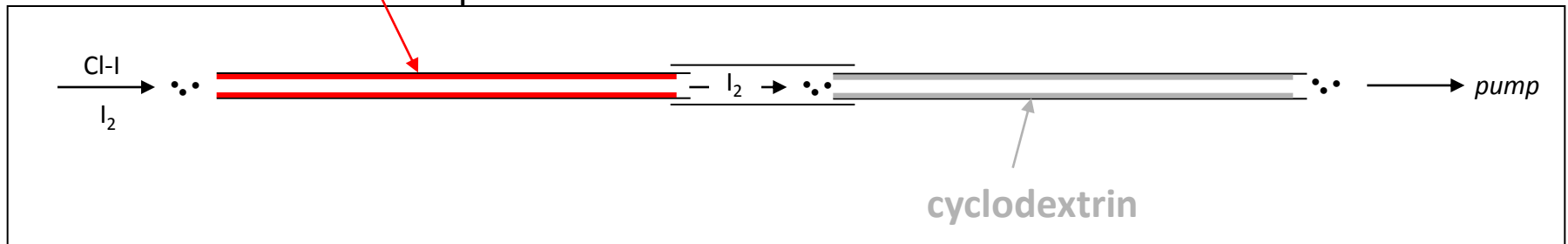
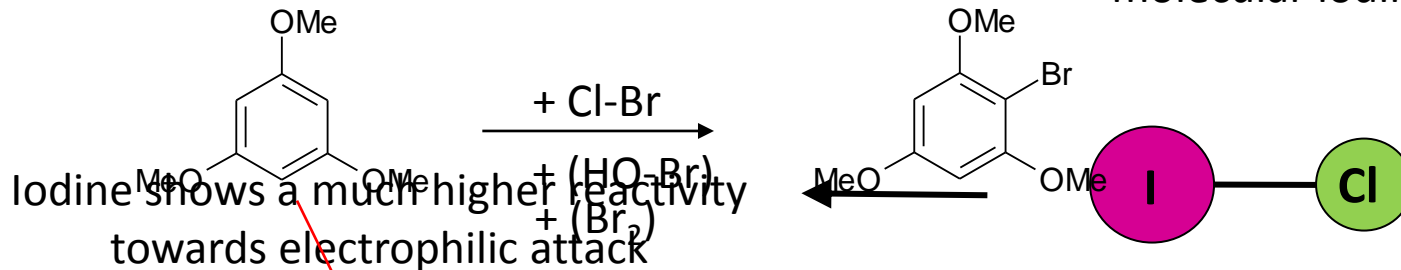
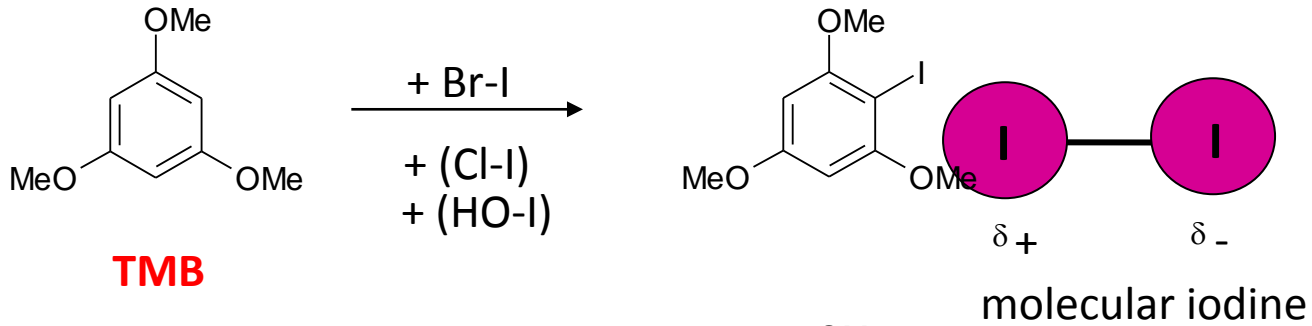
Concentrated to 100 μL

GC-MS

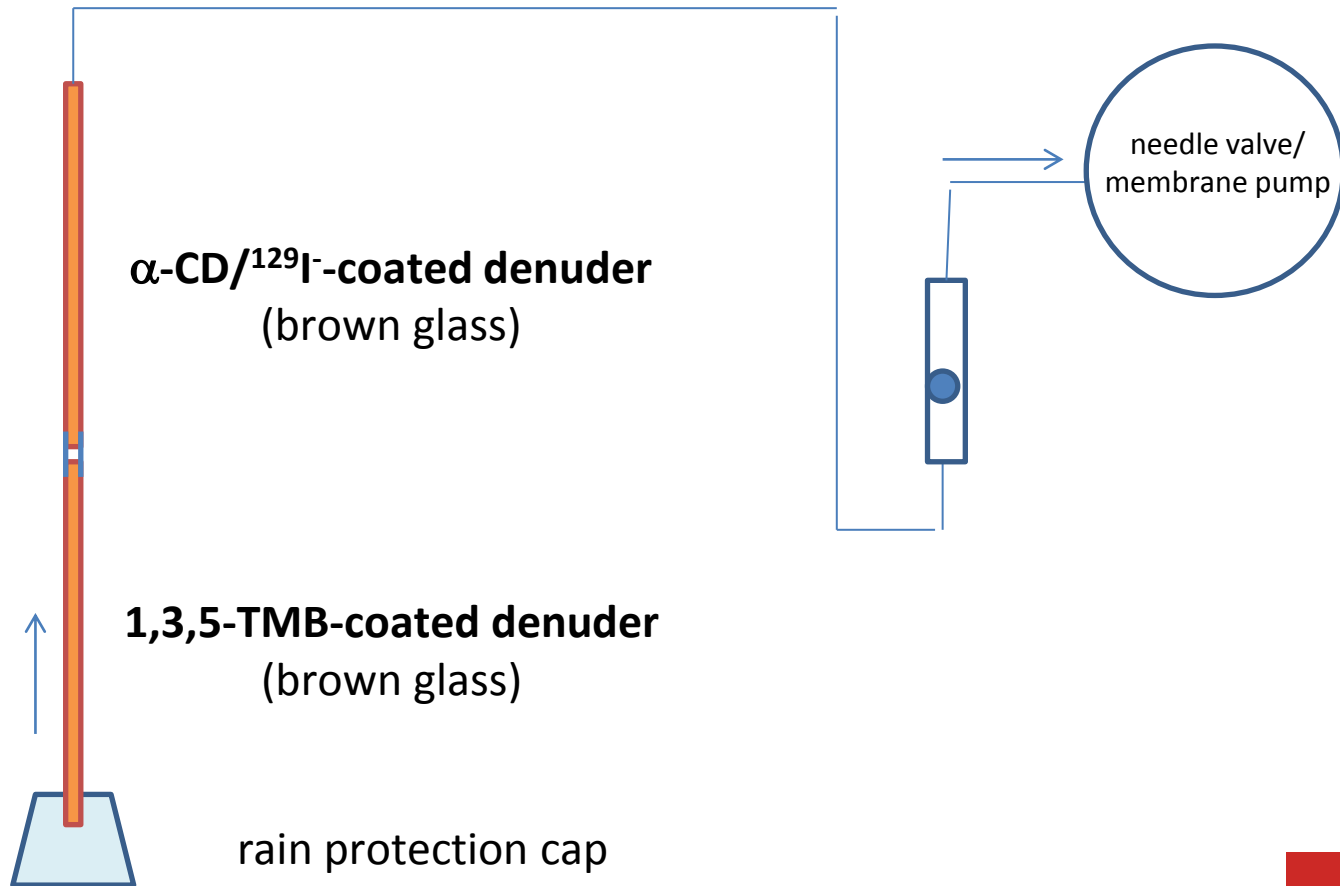


[Huang and Hoffmann, 2009]

Potential interference from highly reactive iodine compounds



Sampling setup



III. Comparison with DOAS Method

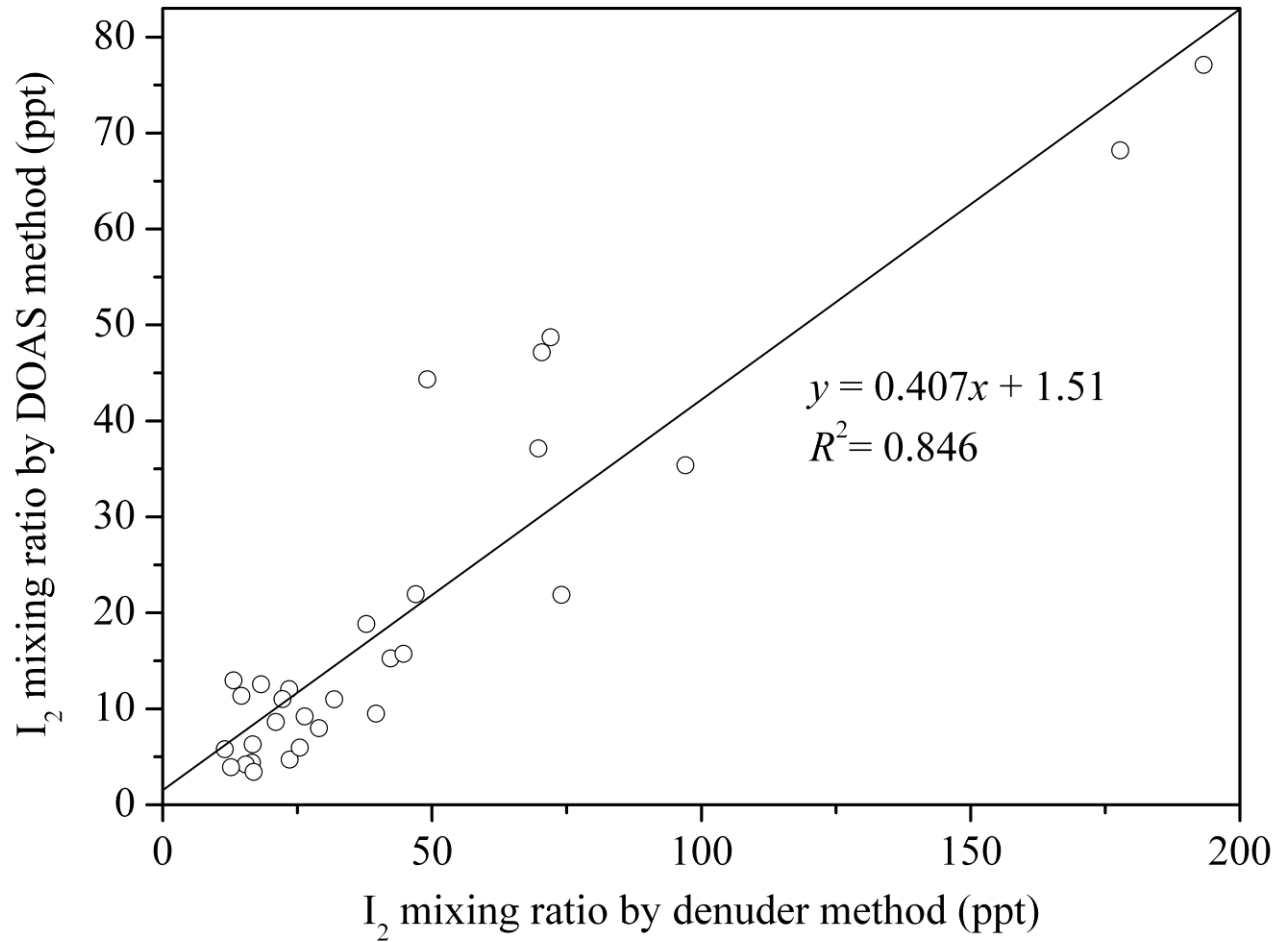
Analytical parameters

		Limit of Detection	Time Resolution	Spatial Resolution
Denuder-GC/MS	off-line	0.17 ppt	30 min	single-point
LP-DOAS	on-line	20 ppt	30 min	several km



Mace Head Atmospheric Research Station
(53°20' N, 9°54' W)

Data correlation



Sampling issues

- Sensitivity:

Time resolution of 30 min: Expected mixing ratios of I_2 between 1-5 ppt

Time resolution of 60 min: If expected mixing ratios are lower

- Temperature at sampling site:

Sampling so far at temperatures ≤ 25 °C

Shadowing of sampling setup recommended

- Contamination:

Diesel exhaust problematic – Suggestions for counter measures?

(especially when ship is not moving)

Storage and shipment

- Shipment:

GER – US: To Boulder or to Hawaii

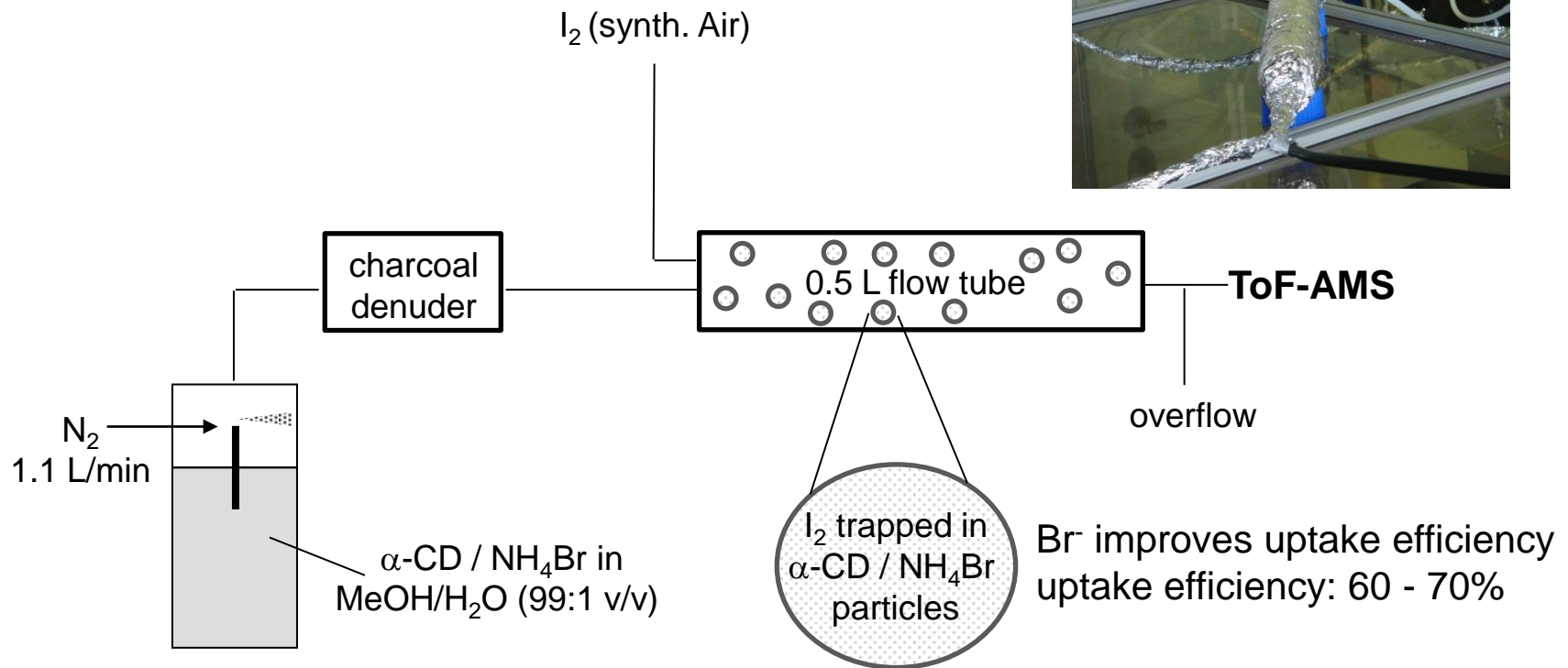
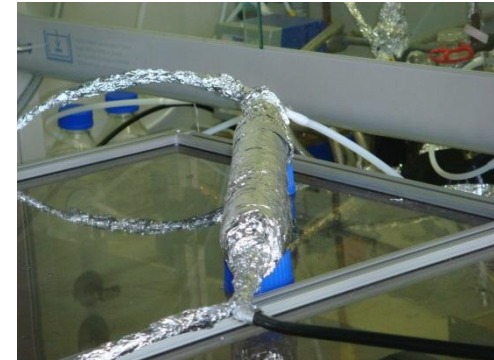
CR – GER: Cooling needed

- Storage:

Loaded denuders have to be stored in a refrigerator or freezer

V. Outlook: GTRAP-TOF-AMS Method

Gaseous compound trapping in artificially generated particles followed by **AMS analysis (GTRAP-AMS)**

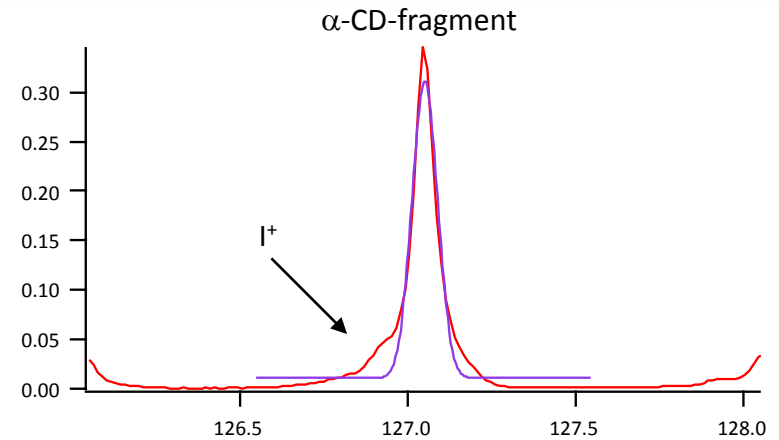


TOF-AMS measurement

m/z 127

m/z 126.9 \rightarrow I⁺

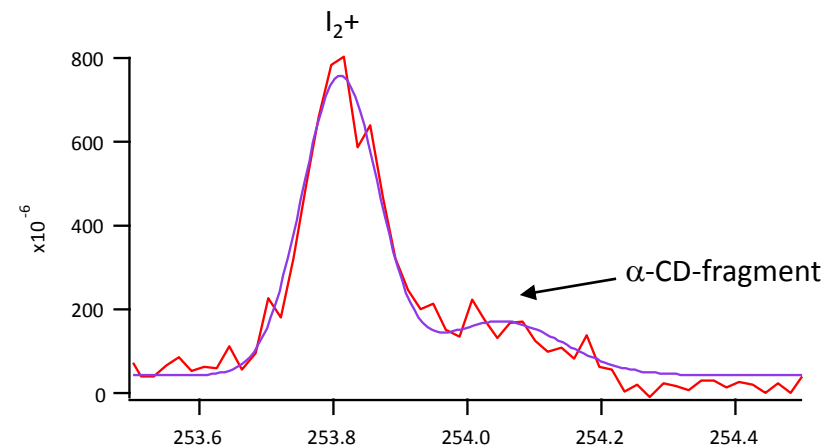
m/z 127.05 \rightarrow α -CD-fragment



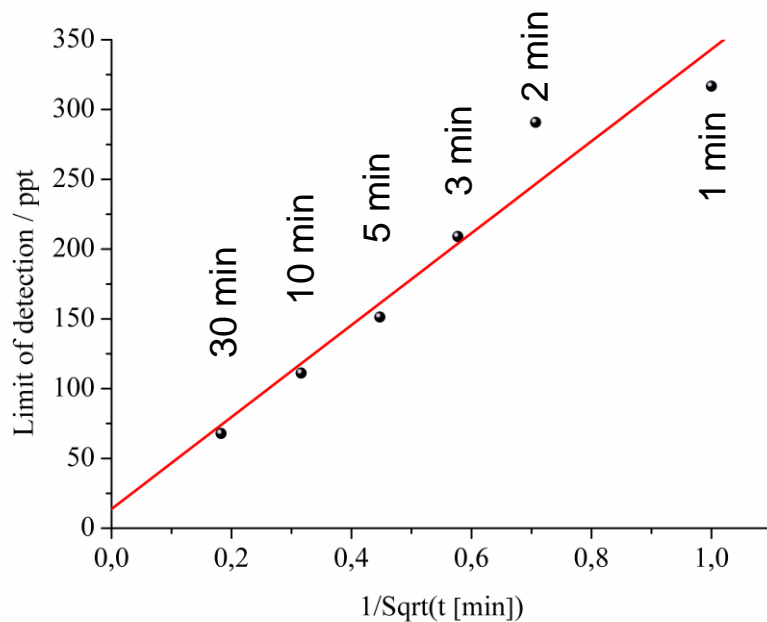
m/z 254

m/z 253.8 \rightarrow I₂⁺

m/z=254.05 \rightarrow α -CD-fragment



Analytical parameters



ToF-AMS detection limit mainly depends on ion counting statistics

→ increasing the averaging time of the data acquisition improves the detection limit (LOD $\sim 1 / \text{sqrt}(t)$)

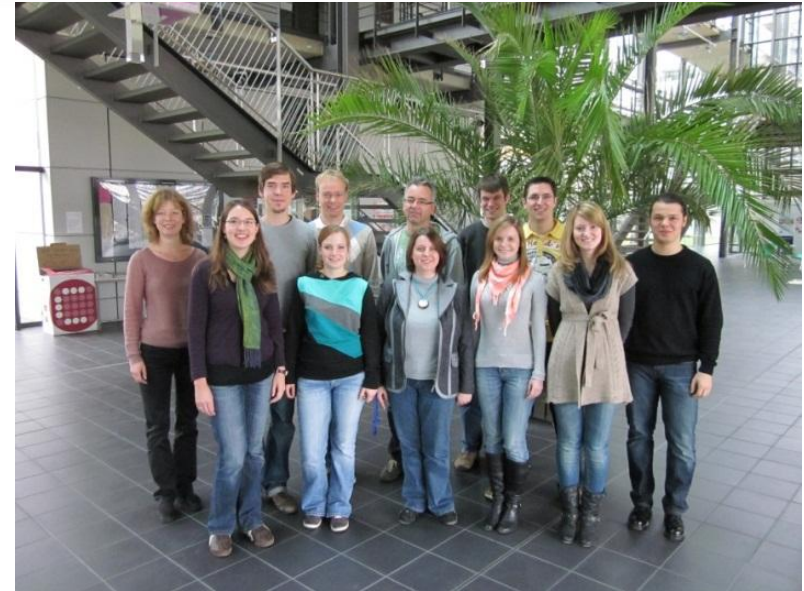
Successful application in laboratory experiments

Improvement of LOD necessary for field measurements



Acknowledgement

- Prof. Dr. Thorsten Hoffmann
- Work group Hoffmann



- supported by the German Research Foundation (DFG) within the Research Training Group 826: Trace Analysis of Elemental Species: Development of Methods and Applications



Thank you for your attention !