Determination of chlorine stable isotope ratios in aqueous samples by area-corrected continuous flow IRMS (ACCF-IRMS)

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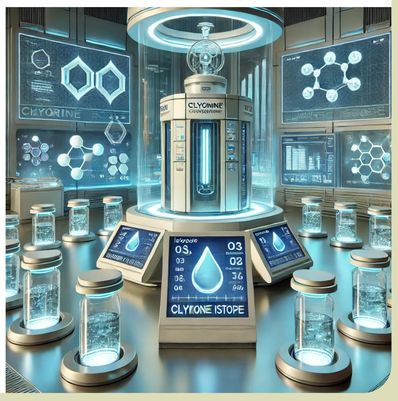
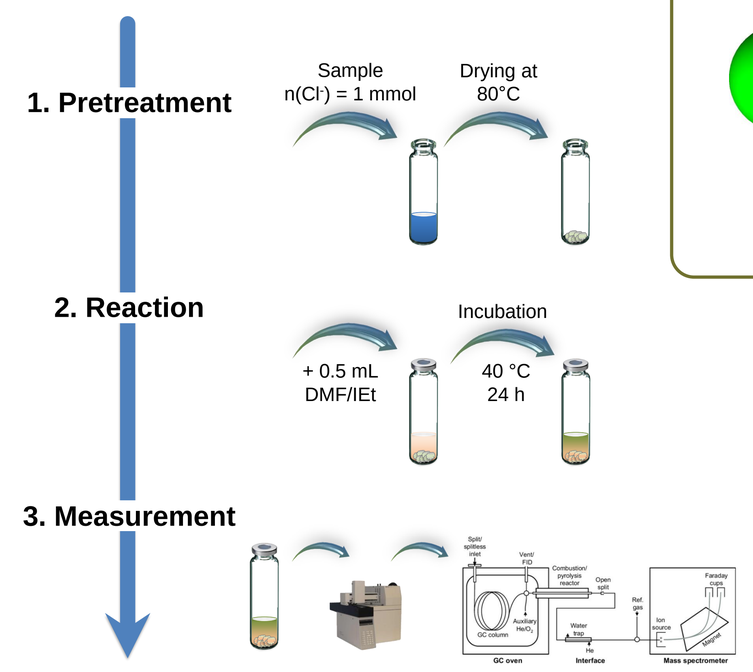
Objectives

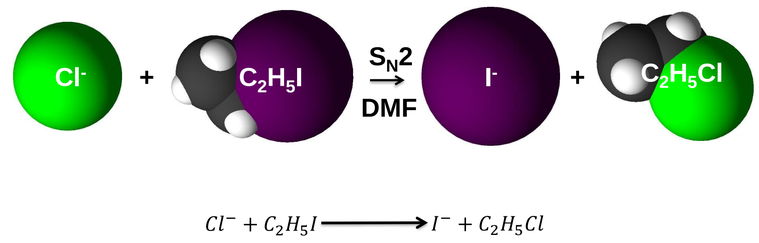
- **Chlorine isotopes as geochemical tracers:** Chlorine isotopes provide insight into the origin and transport of chloride in aqueous systems.
- **Natural reservoirs:** Major chlorine reservoirs include seawater, rocks, and sediments.
- **Isotopic variability:** Compared to other stable isotopes, chlorine isotopes exhibit limited natural variability.
- **Conventional analysis:** Existing methods are complex and often involve toxic reagents.
- **Innovative approach:** This method offers a precise, eco-friendly alternative without the use of hazardous chemicals.



Sample preparation



Reaction mechanism



$$Cl^- + C_2H_5I \longrightarrow I^- + C_2H_5Cl$$

- Minimal sample preparation required
- User-friendly operation
- Less toxic chemicals required

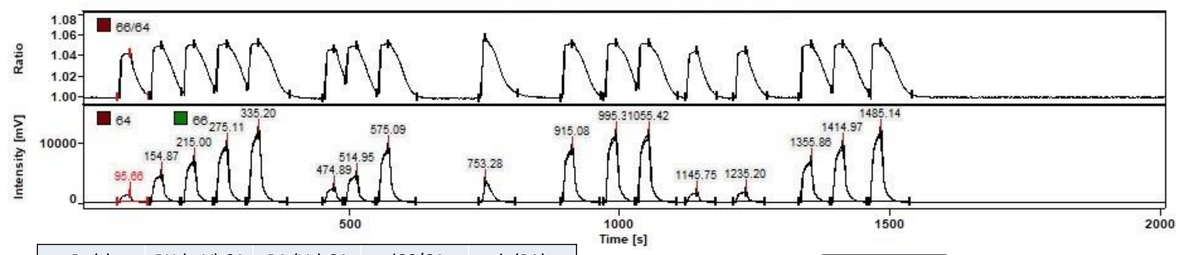
  C_2H_5I instead of CH_3I
- Low energy consumption (reaction at 40°)

Instrumental setup

- Headspace injection system (HS)
- Separation via gas chromatography
- Detection with quadrupole mass spectrometry (GC-qMS) and isotope-ratio mass spectrometry (IRMS)
- Area-corrected continuous flow (ACCF) with mass flow controller (MFC) connected to GC
- Measurements in SO_2 standard mode with changed resistors

Schematic representation of HS GC-qMS-ACCF-IRMS

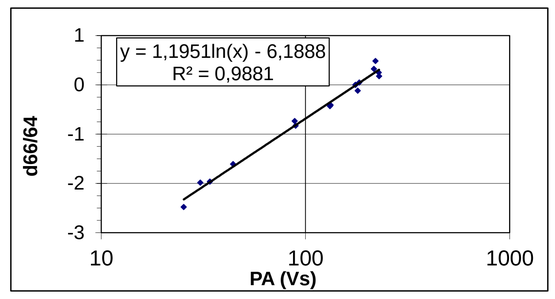
Area correction



Rt (s)	PH (mV) 64	PA (Vs) 64	d66/64	ln(PA)
95.6	1294	25.349	-2.479	3.23274
154.8	4625	89.480	-0.828	4.49401
214.9	6818	131.844	-0.431	4.88162
275.0	9393	180.217	-0.118	5.19416
335.1	11657	229.304	0.177	5.43505
475.8	2441	44.239	-1.608	3.78961
514.8	4545	88.486	-0.735	4.48284
575.0	8883	175.818	0	5.16945
915.0	8929	175.398	0	5.16706
995.2	11181	216.177	0.323	5.37610
1055.3	11162	219.984	0.484	5.39355
1145.6	1625	30.544	-1.984	3.41917
1235.0	1731	34.037	-1.962	3.52745
1355.7	6906	132.689	-0.410	4.88801
1415.8	9382	183.310	0.047	5.21118
1485.0	11572	228.200	0.250	5.43022

Rt (s)	PH (mV) 64	PA (Vs) 64	d66/64	Correction factor	Corrected value
758.2	2993	47.111	4.928	-1.5844547	6.51

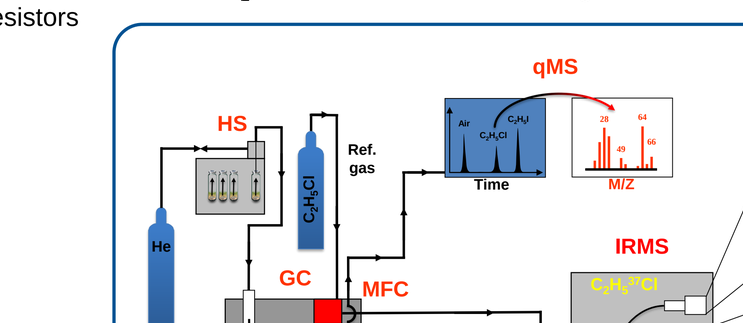
$$y = a\ln x + b$$



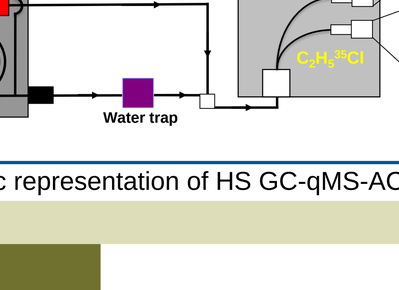
- ✓ Measurement specific correction of δ-Value
- ✓ Concentration independent measurement ≥ 25 µg/sample

Results

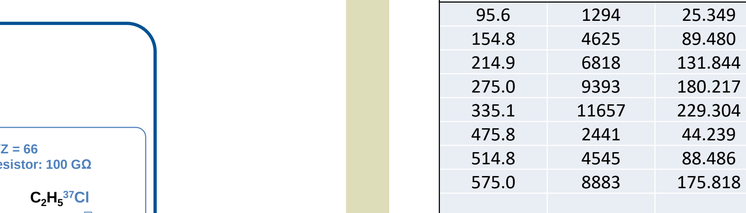
Reaction conditions



- Reaction temperature: **40°C**
- Concentration limit: **100 µg(Cl^-)/analysis**



Reproducibility



Reference material	Literature Reference with DI-method $\delta^{37}Cl \pm 1\sigma$ [‰-SMOC]	Literature Reference H_3PO_4 method $\delta^{37}Cl \pm 1\sigma$ [‰-SMOC]	Measured values with DMF/IEt ACCF-method $\delta^{37}Cl \pm 1\sigma$ [‰-SMOC]
ISL 354	+0,05 ± 0,02[3,4]	+0,06 ± 0,09 (n=10)[1]	+0,05 ± 0,04 (n=15)
LiCl	-0.55 ± 0.03 (IRMS)[2]	-0.49 ± 0.14 (n=4)[1]	-0.59 ± 0.05 (n=5)
RbCl	+0.89 ± 0.04 (IRMS)[2]	+1.04 ± 0.12 (n=4)[1]	+0.85 ± 0.06 (n=5)
CsCl	+0.45 ± 0.02 (IRMS)[2]	+0.46 ± 0.16 (n=4)[1]	+0.49 ± 0.10 (n=5)

- ✓ Comparable accuracy to DI-method with lower chloride concentrations

Interfering Ions

Contact

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1) Ertl. S.; Eichinger. F.; Pichlmaier. J.; Voropaev. A. A new method to determine $\delta^{37}Cl$ values of chloride in aquatic systems, Grundwasser 2024, 1-9.

2) Eggenkamp. H.; Bonifacie. M.; Ader. M.; Agrinier. P. Experimental determination of stable chlorine and bromine isotope fractionation during precipitation of salt from a saturated solution, Chemical Geology 2016, 433, 46-56.

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