An Ambient-Pressure Gas-Flow Electron-Yield Cell for *Operando* XAFS Studies of Liquid Jets with Tender X-Rays

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Aim

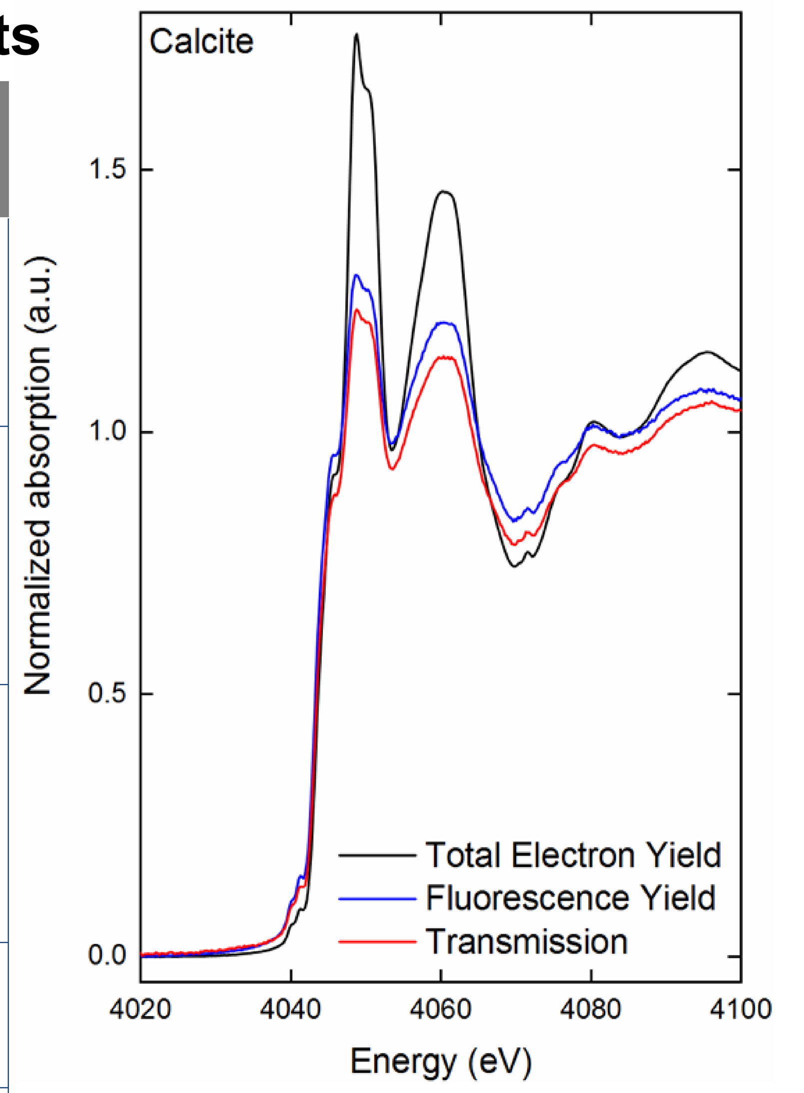
Determine the feasibility of characterising chemical species in concentrated suspensions gas-flow total electron-yield X-ray absorption spectroscopy (TEY-XAS) in the tender X-ray range (~2-5 keV).

Motivations

- Understanding structure-function relationships during the synthesis/ formulation of materials with diverse practical end applications such as catalysts, fuel additives and pharmaceuticals.
- *Operando* studies are pertinent in elucidating the behaviour of chemical species under varying process conditions representative of real-world conditions.
- X-ray absorption spectroscopy (XAS) using tender X-rays is valuable for probing elements from ~Mg to Ti.
- XA spectra can be collected in several different ways — TEY is less prone to distortions in some sample environments compared to transmission and FY spectra.(1)
- TEY-XAS is particularly suitable for liquid samples — demonstrated by various soft X-ray studies under vacuum.(2)
- As a modification of vacuum TEY-XAS, gas-flow TEY-XAS, is particularly suitable for measurements with tender and hard X-rays under ambient conditions but has not been used for liquid samples.

Different Detection Modes for XAS Measurements

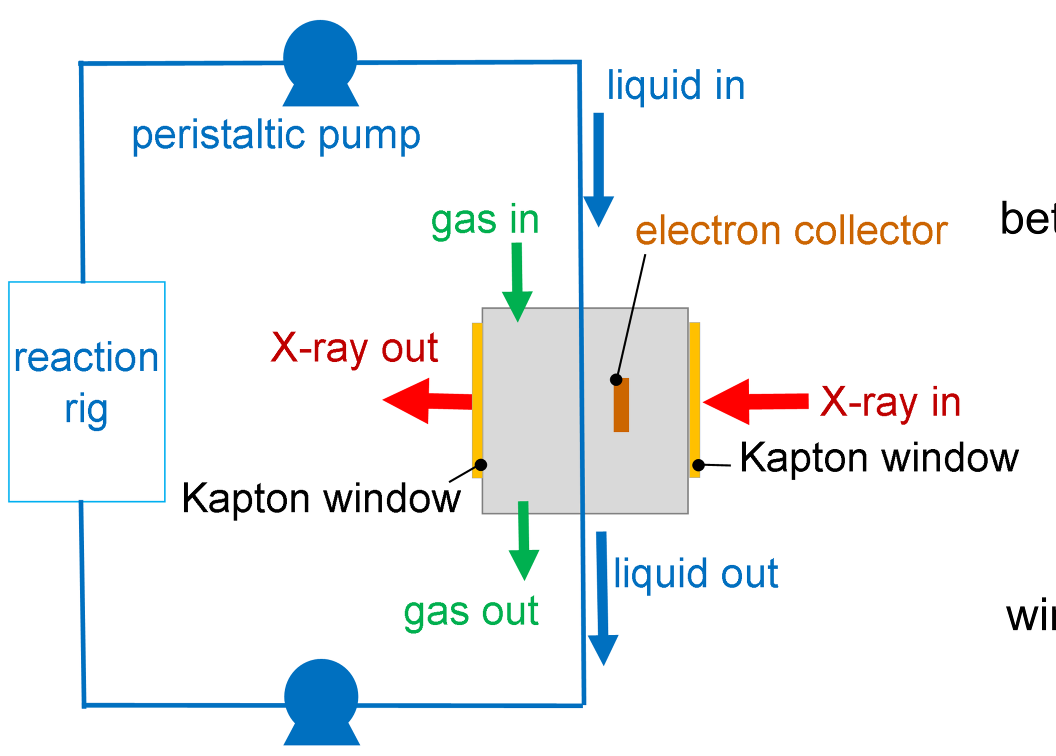
	Transmission	Fluorescence Yield (FY)	Total Electron Yield (TEY)
Sample Homogeneity Required?	yes (avoid 'pinhole' effects)	no	no
Ideal Sample Concentration	concentrated	dilute	concentrated
Max Sample Thickness	Tender X-rays = <10 µm (allow transmission through water)	n/a	n/a
Sensitivity	bulk	µm	surface (~nm)
Limitations	thickness effects	self-absorption effects	vacuum required unless gas-flow version used



Comparison of TEY, FY and transmission XA spectra of calcite powder mounted on carbon tape. Spectra were collected simultaneously.

Versatile XAS Liquid Jet Cell

Liquid Jet Cell Schematic



Sample is circulated between a reaction rig and the cell.

+ minimise/prevent radiation damage!

+

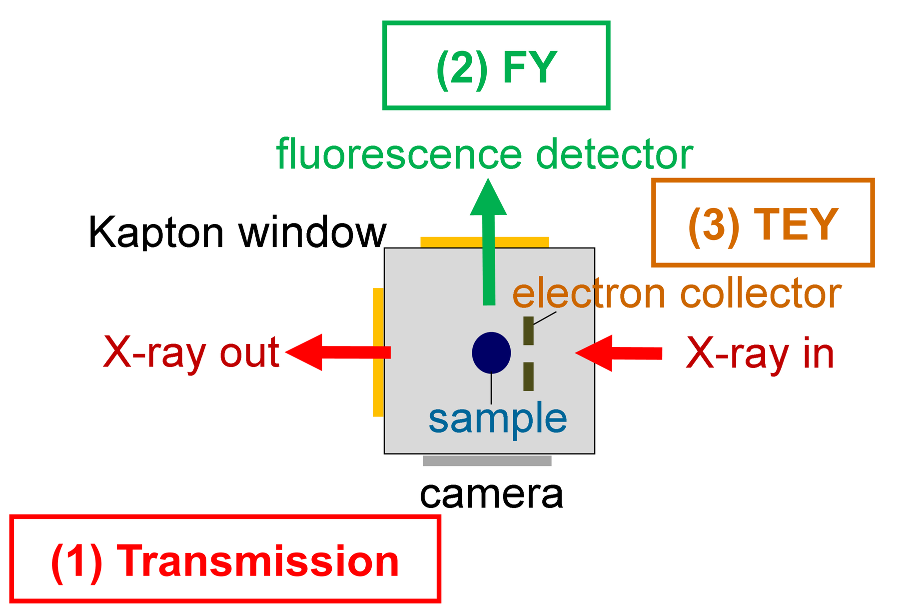
windowless measurement

+

cell flooded with helium for gas-flow TEY-XAS

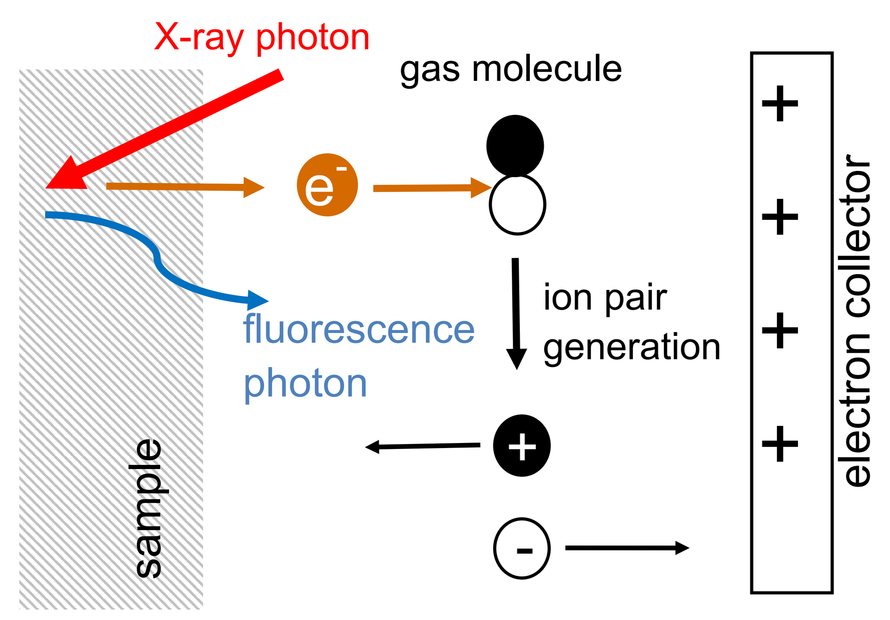
In situ/operando **liquid Jet TEY-XAS Setup**

XAS Detection Modes



Schematic of the cell viewed from the top showing optical paths for detection of XA spectra in transmission, FY and TEY.

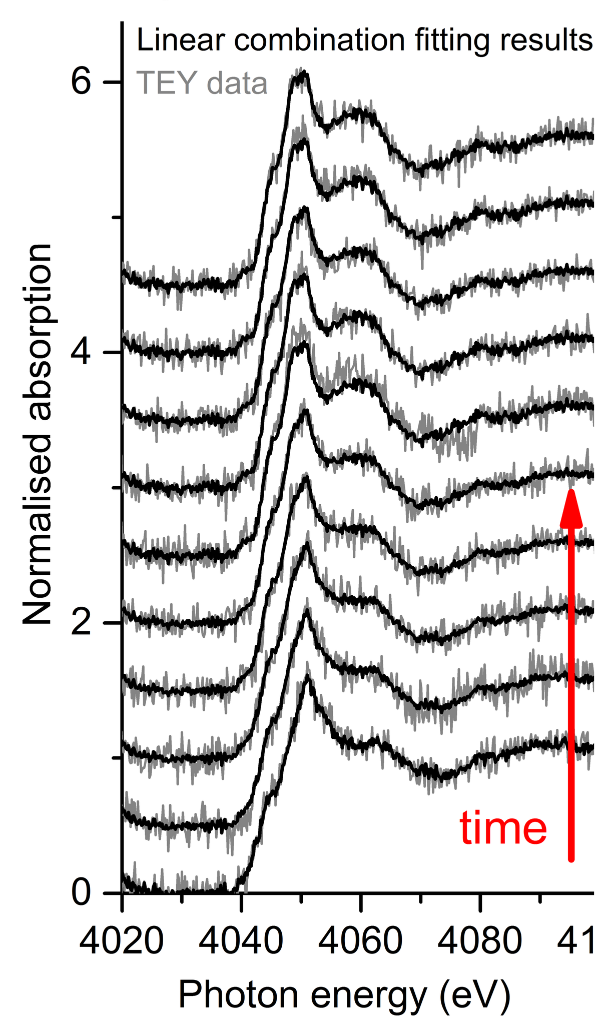
Gas-Flow TEY



An idealised schematic of gas-flow TEY collection. Gas molecules in the sample environment propagate the electron signal from the sample to the electron collector.

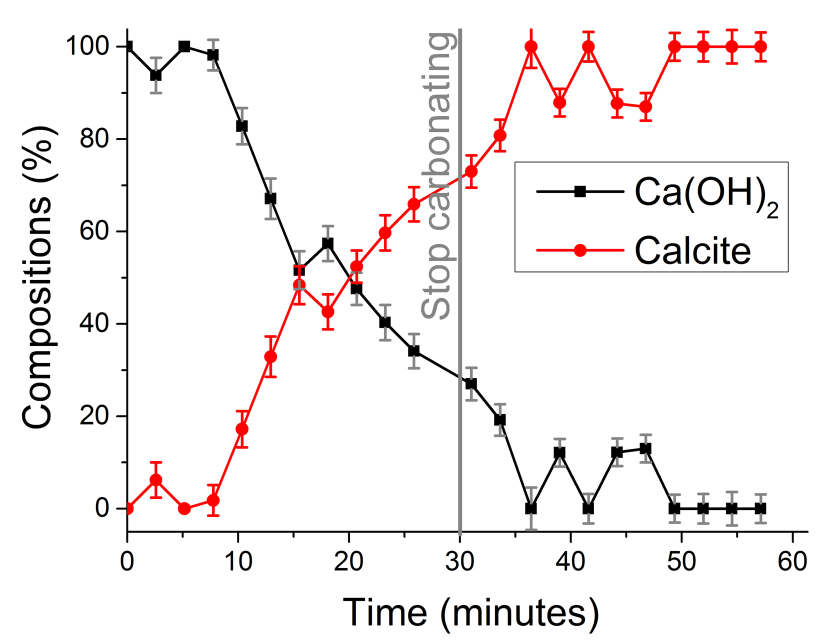
Feasibility Study: Carbonation of $Ca(OH)_2$

Beamline: B18 - Quick-XAFS at Diamond Light Source
Energy: Ca K-edge (~4 keV)
System: Carbonation of 360 mM $Ca(OH)_2$ aqueous suspension



Ca K-edge XANES measured in the TEY mode — transformation of $Ca(OH)_2$ to calcite in an aqueous suspension.

- Ca K-edge XANES captured the time-dependent transition of $Ca(OH)_2$ into calcite during a carbonation reaction.
- The relative change in composition was quantified with linear combination fitting of the



Change in sample composition vs time as quantified using linear combination fitting.

Conclusions

- We describe a liquid jet cell for characterising complex samples with gas-flow total electron-yield XAS under ambient temperature and pressure.
- The cell provides a windowless means of probing samples in a liquid-jet with TEY-XAS.
- Flow of helium gas in the sample environment is essential for the technique and propagates the electron signal from the sample to the electron collector
- The reactive crystallization of calcium carbonate from the carbonation of a multiphase (gas-liquid-solid) $Ca(OH)_2$ suspension was chosen for a feasibility study.
- Aliquots of the multiphase suspension were exposed to the X-ray beam in the form of a liquid jet— the jet was recycled between a reaction rig and the X-ray cell to prevent radiation damage.
- TEY XA spectra were collected at the Ca K-edge (~4 keV) and the transition of Ca species from $Ca(OH)_2$ to $CaCO_3$ over time was quantified with linear combination analysis of the XANES spectra.

References

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