Surface Enhanced Raman Spectroscopy (SERS) for astrobiological exploration

Rab Wilson², Stephen A. Bowden¹

¹Department of Geology & Petroleum Geology, University of Aberdeen, Aberdeen AB24 3UE, UK
²Department of Electronics and Electrical Engineering, Oakfield Avenue, University of Glasgow, Glasgow, G12 8LT, UK
Snow Algae Cairngorm Plateau

- Snow Algal bloom – Cairngorm Plateau

- Measurements performed on melted ice

- But this is best case scenario
  - Lots of analyte
  - Knew what and where it was before we performed analysis

20 x 20 km of snow field
Analysing Organic compounds for Astrobiology/geology

Inclusions in Halite

< ppm analysis – what it means
Solvent extraction/analyte concentration

-For physicists
  • Separation stages
  • Deconvolution not enough

-Difficult and complex analysis
  -In engineer speak:
    • Many mechanisms
    • High power
    • High Mass
Analysing organic compounds in geological materials

Soluble

1. Crush
2. Wash with solvent
3. Extract with solvent
4. **Concentrate**
5. **Transfer to analytical equipment**
Benefits of SERS over conventional Raman Spectroscopy

• SERS selectively enhances only specific molecules (factor $10^5$ enhancement)
  Can analyse organic compounds in solvents

Fluorescence quenching?
• Natural extracts complex mixtures
  - either fluoresce
  - not possible to interpret spectra

Limits of detection

• For scytonemin
• Detection of 2nM $> 3\sigma$ background noise

• Detect lower concentrations of R6G
Surface Enhanced Raman Spectroscopy (SERS)

Excited Electronic State

Chemisorption – charge transfer
Surface Plasmon Resonance

Roughened Metal

Electromagnetic
Raman signal
incident

Chemical
Energy (eV)

LUMO
Fermi level
HOMO

charge transfer
Equipment

• Light source - 514 nm, (typically about 10 mW laser)
• OTS Ocean Optics spectrometers
• Nitric acid, citric acid used to improve metal – analyte interaction

Silver Colloid in flow cell  Silver Beads and bead trap
1. Samples ground and crushed
2. Extracted with Acetone
3. Acetone analysed by SERS
Biomolecules in hydrothermal system II

C–S, C=O

C–O–C

D1

D2

Raman Shift (cm$^{-1}$)

500 600 700 800 900 1000 1100 1200 1300 1400 1500 1600 1700 1800 1900 2000

Green

Orange

Brown/purple

Sinter

Blank

b,b

scy

phyc

phyc

phyc
Bio/Geomolecules in hydrothermal system II

Measurement from grey goo most significant over time
Monitoring Arctic micro oases
Monitoring Arctic micro oases

Loss of carotene relative to scytonemin, consistent with trends seen in UV-VIS data
Meanest measurements possible - Towards a SERS \( \mu \)TAS

H-cell

- Extract \( \beta,\beta \) carotene from epsomite crystals
- By circulating less extracting solvent can concentrate sample
- Next stage to integrate components + LC-SERS
Conclusions

SERS can provide organic geochemical information – e.g. detect specific molecular structures in sediments at 10’s ppm. This is something Raman Spectroscopy can’t do.

This requires further sample processing – but this can all be automated.

Such a system could be a LOC device.
B-Presentation
Survival of Organic Compounds in ice-HVI

Stephen Bowden & John Parnell
University of Aberdeen

Mark J Burchell
Canterbury – University of Kent
Method

HVI-ice impact studies performed Canterbury, University of Kent

- Ice doped with organic compound
- 1.5 mm d projectile at ~5 kms$^{-1}$
- Ejecta collected and analysed
UV-VIS spectroscopy and GC-MS (data not shown) used to analyse products.
• Most altered fraction is very altered
• Suspect that radicalisation of water helps drive reactions
Acknowledgements

EPSRC for funding
Haughton Mars project; Communities of Griese Fjord; Resolute Bay
Icelandic Institute of Natural History; Krisjan Jonasson; Paula Lindgren;
Eric Strukel
Analysing organic compounds in geological materials

Residue

1. Crush/break
2. Dissolve matrix
3. Collect residue
4. **Screen through residue**
5. Involves microscope
6. Human discretion