

The fluorescent properties of a stalactite sample using the Agilent Cary Eclipse fiber-optic probe accessory

Application Note

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Introduction

The fluorescent properties of secondary carbonate cave deposits (speleothems) are related to the environmental conditions under which they form (for example, soil type, climate and vegetation, and formation of metal ion complexes).¹ Speleothem fluorescence is derived from organic acids (humic and fulvic) that precipitate with speleothem calcite after passing through surface layers in rainwater. Using non-destructive fiber-optic technology, the fluorescent properties of these speleothems can be investigated in order to further understand palaeoenvironmental trends.

The Agilent Cary Eclipse fiber-optic probe accessory takes light to the sample via an optical light guide. This allows the investigation of the fluorescent properties of samples that cannot be analyzed using more traditional means such as a cuvette or microplate reader², which are subject to size restrictions or complicated handling requirements.

The present study aimed to examine the fluorescent properties of the surface of a cross-sectioned speleothem (stalactite) sample using a Cary Eclipse equipped with fiber-optic coupler and probe.



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Materials and methods

(For part numbers please see Reference 5)

Equipment

- Agilent Cary Eclipse fluorescence spectrophotometer
- Fiber optic coupler
- Fiber optic probe (2 m)
- Solid sample tip

Protocol

The fiber-optic accessory with solid sample tip was installed into an Agilent Cary Eclipse fluorescence spectrophotometer and aligned as described in the user instructions supplied with the accessory. The 'Scan' application was opened and the following operating parameters set in the 'Cary' window (refer Figure 1). Both excitation and emission filters were set to 'Auto' to minimize the amount of scattered light reaching the detector. The PMT voltage was set to 880.

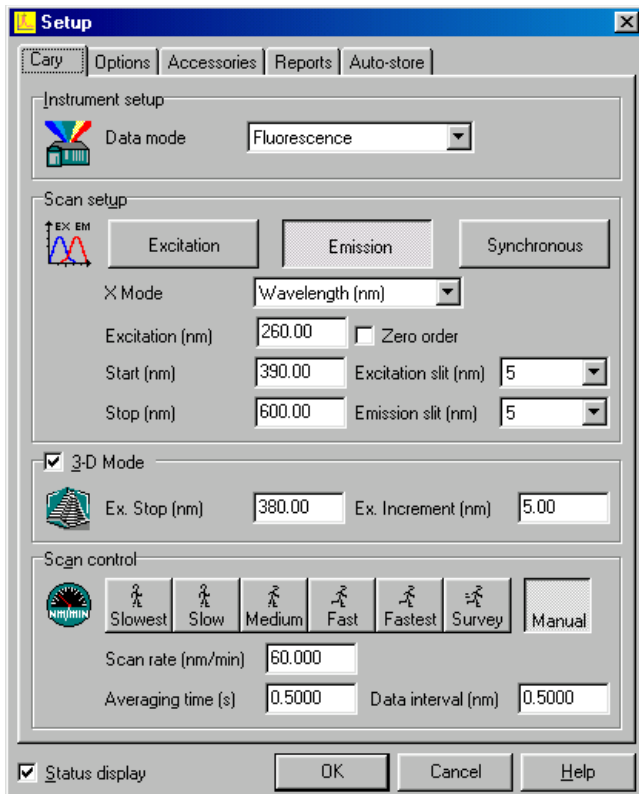


Figure 1. Instrumental parameters for speleothem analysis

Using the solid sample tip, the probe tip was positioned at 45° to the surface of the cross-sectioned stalactite sample using a retort stand and clamp. The solid sample tip was flush with the surface of the stalactite. Using the 'Scan' software in '3D Mode', contour plots of excitation versus emission were collected under ambient laboratory lighting conditions, as a function of distance along the stalactite.

Results and discussion

A typical excitation-emission matrix (EEM) contour plot is shown in Figure 2.

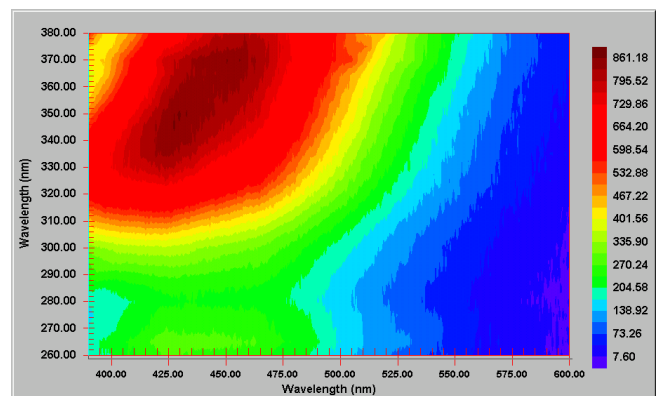


Figure 2: Excitation-emission matrix (EEM) of stalactite sample

Results in Figure 2 demonstrate measurable differences in the fluorescent properties of the stalactite sample over a range of wavelengths. Most notable is a broad band of emission between 390 nm and 500 nm, peaking at approximately 435 nm. This fluorescent centre is attributable to the presence of fulvic acids (hydrophillic organic acids derived from peats and loams)¹. The fluorescence of such fulvic material in speleothem samples has been correlated to geographical origin.³ This observation is consistent with that of McGarry and Baker,¹ who found similar characteristics in different stalactite samples.

When acquiring fluorescence spectra from solid samples, attempts must be made to reduce the effects of scattered light. Spectral artifacts can occur as a result of scattered light from the excitation monochromator reaching the detector. This can result in the appearance of spurious peaks in the fluorescence spectrum, and care must be taken not to interpret any

artifacts present as fluorescence. In this instance, internal excitation and emission filters were used to eliminate scattered light from the sample. Where appropriate (particularly when exciting below 280 nm), band-pass filters can be used to further reduce or eliminate scattered light. Any band-pass filter used should correspond to the excitation wavelength used, and have a reasonably narrow bandwidth (< 25 nm).

Conclusion

The Agilent Cary Eclipse, coupled with the fiber-optic accessory, permits the simple and rapid analysis of the fluorescent properties of a stalactite sample. In this instance, a fluorescent center attributable to fulvic acid was observed at approximately 435nm. Scattered light from the cross-sectioned surface of the sample was eliminated using internal excitation and emission monochromator filters, and the effect of laboratory room light was eliminated by the Cary Eclipse's room light immunity.⁴

Acknowledgements

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References

1. McGarry, S.F. and Baker A., 'Organic acid fluorescence: applications to speleothem palaeoenvironmental reconstruction', *Quaternary Science Reviews*, 19 (2000) 1087.
2. <http://www.agilent.com>
3. Miano, T.M., Sposito, G., and Martin, J.P., 'Fluorescence spectroscopy of humic substances', *Journal of the American Soil Science Society*, 52 (1988) 1016.
4. Comerford, J., 'Fluorescence room light immunity with the Cary Eclipse', *Application Note app02.pdf*.
5. Part numbers:

Product	Part Number
Agilent Cary Eclipse Fluorescence Spectrophotometer	00 100752 00
Fiber optic coupler:	00 100767 00
Fiber optic probe (2m)	79 100430 00
Solid sample tip	79 100432 00
Cary Eclipse Scan software	85 101772 00

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