

Determination of Aromatic Ring Number using Multi-channel Deep UV Native Fluorescence. R. Bhartia¹, G.D. McDonald¹, E. Salas², P. Conrad¹ - ¹Jet Propulsion laboratory (4800 Oak Grove Dr. MS 183-301, Pasadena, CA 91109; rbhartia@jpl.nasa.gov,) ²University of Southern California (3651 University Ave, Sci 223, LA, CA 90089).

Introduction: The *in situ* detection of organic material on an extraterrestrial surface requires both effective means of searching a relatively large surface area or volume for possible organic carbon, and a more specific means of identifying and quantifying compounds in indicated samples. Fluorescence spectroscopy fits the first requirement well, as it can be carried out rapidly, with minimal or no physical contact with the sample, and with sensitivity unmatched by any other organic analytical technique. Aromatic organic compounds with known fluorescence signatures have been identified in several extraterrestrial samples, including carbonaceous chondrites [1-3], interplanetary dust particles [4], and Martian meteorites [5]. The compound distributions vary among these sources, however, with clear differences in relative abundances by number of aromatic rings and by degree of alkylation. This relative abundance information, therefore, can be used to infer the source of organic material detected on a planetary surface.

Deep ultraviolet (DUV) native fluorescence can be used to determine the potential size (number of rings) of aromatics present in rock matrices. We suggest the use of specific band pass filters, coupled with PMT detectors, in order to meet size, mass and power constraints of portable field instruments.

In order to determine the efficacy of a filter based detection system it is essential that the PAH's of varying ring numbers can be differentiated. In addition, we need to determine which filters best differentiate varying ring numbers. We have undertaken a preliminary study to determine whether useful molecular information regarding a suite of aromatic compounds can be obtained from broadband fluorescence spectra.

Methods: The set of aromatics used are shown in table 1. Each sample was run in a Hitachi F-4500 fluorimeter to acquire high resolution (3 nm increments) emission spectra from 200-800nm at excitation wavelengths from 200-300nm. This data was used as an input to a modeling program (Filtersim ver. 4) which extracted the emission spectra at 224 nm excitation and determined a theoretical band pass acquired spectra based upon user definable Gaussian filters.

The theoretical spectra were then input into an analysis package inherent to Filtersim. Data analysis is performed by PCA, Band Difference, and Band Ratios.

The standard approach to data analysis using PCA is to use only the first few components. The expectation is that with the exception of the first few, most of

the components will capture very little variance, instead capturing mostly noise. This method of data compression can serve to reduce the number of dimensions that must be dealt with, while allowing for the retention of those features which appear to account for the majority of the variance in the data.

Ring Number	Homocyclic	Heterocyclic
1	Xylene Phenylalanine Tyrosine Ethylbenzene	Pyridine
2	Naphthalene	Tryptophan
3	Phenanthrene	1,10-phenanthroline
4	Naphacene	
5	Perylene	

Table 1. Aromatic Standards - pure

Mix 1 (1-5 rings)	Xylene, ethylbenzene, naphthalene, phenanthrene, naphacene, perylene.
Mix 2 (1-5 rings)	Mix 1 + increased xylene and ethylbenzene conc.

Table 2. Aromatic Mixtures

Band Difference and Band Ratios compare two filters with the largest wavelength separation. These analyses only work for 4 or 6 filter systems. Given six filters the x axis is a difference/ratio of filter 6 and 1. The Y axis compares filters 5 and 2 and the Z axis compares 4 versus 3. The resulting display clusters the data according to number of rings.

Results: The set of aromatics shows that separation via ring numbers can be accomplished using 6 filters outlined in table 3.

In addition to differentiation according to ring numbers, separation of heterocyclic and homocyclic aromatics can be made.

Separation of pure standards is not an adequate test of a fluorescence band pass system's efficacy. The mixture samples show it is possible to determine that a composite of PAH's can also be elucidated. Specifically, mixture 2 shows movement towards single ring aromatics correlating with an added concentration of xy-

lene and ethylbenzene (figure 1). Utilization of the Band Difference/Ratio correlation with results from PCA suggests that this simpler method may be adequate.

Filter center wavelength (nm)	Filter width (nm)
273	50
305	50
326	50
347	50
385	50
508	50

Table 3. Filter parameters.

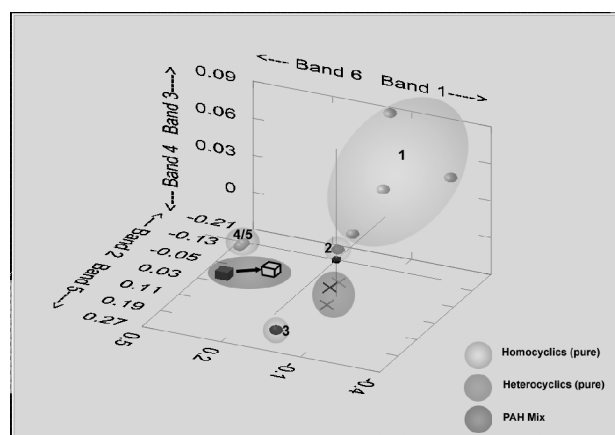


Figure 1. Band difference plot. Homocyclic aromatics are lightly shaded and Heterocyclics are darkly shaded. Mixtures are indicated by cubes – dark cube: Mix 1; Light cube: Mix 2. Numbers correspond to ring numbers on table 1.

Summary: Fluorescence is a broad band phenomenon that does not require high resolution spectra for discrimination of aromatics thus the dispersive grating techniques are not necessary.

The data indicate that the set of band pass filters used in conjunction with the analysis package can be used to differentiate aromatics based on ring number. Interestingly, the band pass center wavelengths are not at the emission maxima for pure aromatics thus indicating that the information content used to differentiate ring numbers lies primarily in the leading or lagging tails of the fluorescence emission curve. This analytical method is essential for future life detection missions.

References:

- [1] Shimoyama A. et al. (1989) *Geochem. J.*, 23, 181-193. [2] Hahn J. H. et al. (1988) *Science*, 239, 1523-1525. [3] Tingle T. N. et al. (1991) *Meteoritics*, 26, 117-127. [4] Clemett S. J. et al. (1993) *Science*, 262, 721-725. [5] McKay D. S. et al. (1996) *Science*, 273, 924-930.