



TechData Sheet

Naval Facilities Engineering Command
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Near-Real Time UV Fluorescence Technique for Characterization of PAHs in Marine Sediment

A rapid sediment characterization (RSC) tool

Introduction

UV fluorescence (UVF) spectroscopy is a screening or RSC technique that can be used in the ecological risk assessment to rapidly estimate total polycyclic aromatic hydrocarbons (PAH) levels in sediments. It provides semi-quantitative data at less cost, which helps limit sampling and lab analysis to the area of concern, fill in data gaps, and ensure that expensive, certified analyses have the greatest possible impact.

PAHs are common organic contaminants found at Navy sites, especially in sediments. PAHs in sediments may originate from many sources due to incomplete combustion of wood or petroleum products and from petroleum itself. They are common constituents in automobile tires (and, therefore, surface water runoff) and creosote (pier pilings).

Traditional site characterization is an expensive and time-consuming process. It often involves an iterative procedure of field sampling and laboratory analysis cycles, with subsequent sampling and analysis guided by previously obtained information.

Technical Description

Fluorescence is a standard analytical technique that can be used to measure the concentration of various analytes in many different matrices. For PAHs, only UV light is required to excite the emission of visible light. When UV light is passed through a sample, the sample emits light (fluoresces) proportional to the concentration of the fluorescent molecule (in this case, PAHs) in the sample. UVF is based on the measurement of fluorescence observed following UV excitation of organic solvent extracts of sediments. Figure 1 shows a generic schematic of the UVF system.

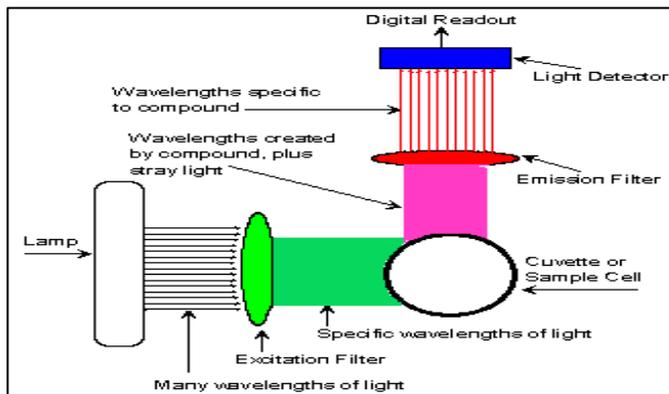


Figure 1. Generic schematic of the UVF system.

Methodology

Fluorescence measurements are matrix sensitive; it is necessary to make measurements on solvent extracts rather than directly on the wet sediment sample. Solvent extraction also allows for lower detection limits appropriate for marine sediment PAH benchmark criteria. Unfortunately, solvent extraction requires additional time for sample preparation, so although fluorescence is said to be a real-time measurement, the total time for analysis may be up to half an hour – hence the description of “near-real time.” This extraction step, however, makes it possible to improve detection limits by several orders of magnitude to the range of 1 ppm to 5 ppm total solid-phase PAH. Another limitation of this technology is the non-speciating nature of UVF. Because many different PAHs can fluoresce, this method is not able to quantify individual PAHs, but can serve to screen for bulk PAH levels in the sediment. Results of UVF can be downloaded to Excel or GIS software.

Comparison of UVF and Traditional Laboratory Analyses

UVF Screening

Benefits

- Rapid results can guide sampling locations
- Potential for high data density for mapping

Limitations

- Cannot speciate different PAHs
- Semi-quantitative
- Matrix sensitive
- Site-specific calibration required

Traditional Lab Analysis

Benefits

- Standard methods are quantitative
- Can often remove interferences

Limitations

- Often blind sampling
- Long delays for results

Application

UVF is most appropriate for preliminary assessments of contaminant distribution as in environmental field screening applications. It can also be used at other steps in the Environmental Protection Agency (EPA) eight-step ecorisk process depending on what specific questions are being addressed. A subset of 10-25% of the samples should be sent for confirmatory analyses by an outside laboratory. Combining screening data with a selected number of

laboratory analyses will result in the most efficient analysis plan to characterize the nature and extent of contamination at a site.

UVF screening and validation data have been successfully generated (Figure 2) at the Naval Air Station (NAS) Alameda and several San Diego sites. The results obtained by UVF have closely correlated with laboratory results. However, a site-specific calibration curve will be required at each site to predict accurate total PAH values; this can be achieved using split sampling and analysis.

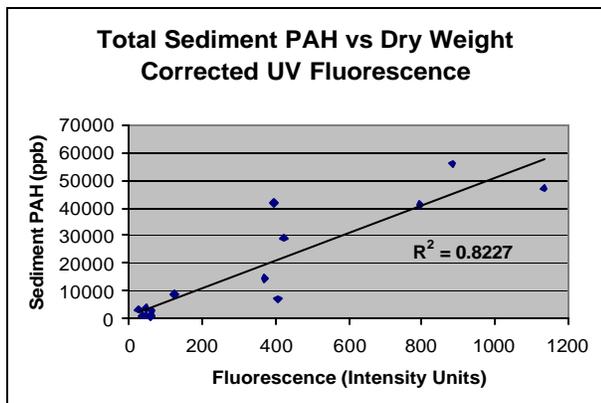


Figure 2. Correlation between lab analysis and UVF data from NAS Alameda, San Diego.

Advantages

- Commercially available portable equipment
- Near-real time; results can guide further sampling
- Low-cost analysis allows higher density sampling
- Detection limits between 1ppm and 5ppm
- Data are appropriate for mapping trends and designing better sampling strategies and plans

Limitations

- Semi-quantitative data
- Data are considered “screening data”
- Site-specific calibration required
- Sample collection and extraction required
- Possible interference from natural organic compounds (e.g. humics)

Case Study - NAS Alameda

A deep-water pier area at NAS Alameda was investigated with UVF as a technique to detect PAHs. Surface sediment samples were collected using a Van Veen grab. At each location several samples were collected and the solvent was extracted by centrifugation. Extract fluorescence was measured in the field, which took about half an hour per sample.

Figure 2 shows the relationship between the RSC and laboratory data that was used to develop a site-specific calibration curve for the site. The data show good correlation. Most of the scatter was due to differences in the mix of individual PAHs in the samples. At this site, little was known about the PAH composition and the results were to be used as a demonstration of the technique, 50% of the samples were sent on for laboratory confirmation to ensure that an acceptable calibration curve could be developed.

Figure 3 contains a contour map of PAH values in the pier area that was sampled at NAS Alameda. The contour map was created by using the calibration curve in Figure 2 to convert all the fluorescence values collected at 31 sites to total PAH values, and then using plotting software to generate a contour map.

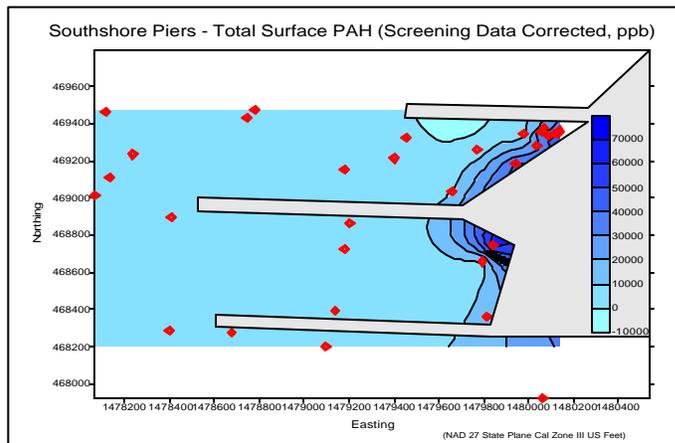


Figure 3. Surface Sediment PAH Contour Map using UVF helps focus sampling location and delineating hotspots

This map was generated after laboratory data were available, but similar contour maps can be developed for relative PAH values in the field in near real-time. These types of maps helped convince regulators that regulatory sampling (for additional chemistry and bioassay tests) could focus on the relatively smaller hotspot area outlined in the map. These types of RSC contour maps can be generated at a lower cost when compared to traditional laboratory analyses.

Cost Information

Screening

Approx \$100/sample
(20 to 30 samples per day)

Laboratory

GCMS (PAHs) \$400 – 550
(30 to 90 days turnaround time)

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