Application of Ion Trap Mass Spectrometry (LC/Ms^n) to the Characterization of Coastal Optical Properties (Equipment Only)

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LONG-TERM GOALS

The emphasis in our ONR funded research is placed on characterizing the factors affecting the optical properties (i.e. attenuation and fluorescence) of coastal seawater. Particular emphasis is being placed on developing a better understanding of the differences and similarities between colored dissolved organic matter CDOM of marine and terrestrial origin, and the impact these properties have on the chemical and optical characteristics of coastal environments where their effects are most pronounced. The equipment assembled under this grant is being used both in the laboratory and in shipboard experiments to provide detailed characterization of the optical properties of coastal seawater. Such information once acquired can be applied to remote sensing modeling applications and the design of optical sensing detectors for probing the ocean.

APPROACH

Funds were requested for components to upgrade an ion trap mass spectrometer (MS^n) in a system used for the optical and structural characterization of colored dissolved organic material (CDOM) in coastal waters. This system currently consists of a flow field flow fractionator (FlFFF) and HPLC as the liquid-phase separation techniques, with in-line 3D excitation-emission fluorescence and absorbance detectors for optical characterization and an LC/MS^n for structural studies. With LC/MS^n, FlFFF or HPLC eluents are directly injected, with resulting fragments repeatedly isolated and re-fragmented to yield detailed compositional information. The requested instrumentation included: ionization sources, a Hewlett-Packard Liquid Chromatography system and a high-purity nitrogen gas generator.

WORK COMPLETED

Funds from this grant

1. applied toward the purchase of two ion sources for the Hewlett-Packard/Bruker Esquire LC/MS^n Ion Trap Mass Spectrometer: APCI ESI
2. purchased a Whatman Compressed High Purity Nitrogen supply system

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14. ABSTRACT

The emphasis in our ONR funded research is placed on characterizing the factors affecting the optical properties (i.e. attenuation and fluorescence) of coastal seawater. Particular emphasis is being placed on developing a better understanding of the differences and similarities between colored dissolved organic matter CDOM of marine and terrestrial origin, and the impact these properties have on the chemical and optical characteristics of coastal environments where their effects are most pronounced. The equipment assembled under this grant is being used both in the laboratory and in shipboard experiments to provide detailed characterization of the optical properties of coastal seawater. Such information once acquired can be applied to remote sensing modeling applications and the design of optical sensing detectors for probing the ocean.

15. SUBJECT TERMS

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3. purchased a complete Hewlett-Packard Liquid Chromatography System with a Fluorescence detector. A Diode Array Detector (absorbance) has not yet been purchased because research is still ongoing to identify a second detector for the LC/MS^n system which will best extend instrumental capabilities.

4. A no-cost extension was granted for this year, to complete identification of research pacific components and purchase them. No additional major equipment has been purchased this year on this grant.

RESULTS

The Liquid Chromatography system permits the operation of the LC and our F;FFF instrumentation as two independent systems with the MS^n as a common detector for structural characteristics. This has resolved problems arising from solvent incompatibilities between the LC and FFFF which were causing severe cross-contamination problems; deteriorated quality and low-level detection capabilities. It allows continuous operation of both instrument systems for method development and independent research and has eliminated substantial down-time for transitions between operation modes. It has also permitted the FFFF to be operated as a stand alone instrument on a research cruise (F. G. Walton Smith, June 2000) , producing the first near-real time measurements in the field.

The High Purity Nitrogen supply has successfully replaced liquid nitrogen as a source of pure nitrogen for the mass spectrometer carrier flow. It produces a consistent background, eliminates dependence on timely deliveries of liquid nitrogen dewars, and reduces operation costs.

The LC/MS was purchased with an electrospray ionization source (ESI). An atmospheric pressure chemical ionization source (APCI) was loaned to us with the understanding that we would purchase it at the end of the first year. The two sources give us the capabilty to analyze a much broader range of samples The ESI requires the analyte to be readily ionized and has lower noise, which results in lower detection limits. APCI can ionized more stable and larger compounds (PAHs, etc) at the cost of noiser signal.

IMPACT/APPLICATIONS

This unique instrumentation will be used to examine factors affecting the optical characteristics (attenuation/fluorescence) of coastal and open ocean waters in detailed characterization studies that could be applied to remote sensing modeling applications and optical sensor design. This is the first application of LC/MS^n to the study of DOM. Particular emphasis will be placed on developing a better understanding of the structural differences/similarities for marine vs. terrestrial CDOM, and the impact these properties have on the chemical and optical characteristics of coastal environments where their effects are most pronounced. The affect of photochemical degradation on CDOM size, structure and hence optical properties will also be examined.

TRANSITIONS

Two cruises during the last year have involved ONR funded investigators from optical physics, marine biology and marine chemistry. A thorough understanding of the nature of CDOM in the oceans

requires a multi-disciplinary approach. Future endeavors should also include the area of remote sensing.

RELATED PROJECTS

The equipment purchased under this grant will be used in research funded by ONR grant # N000149810625 “Characterization of Optical and Associated Properties of Marine Colored Dissolved Organic Material (CDOM)”.