SCIMS - A Semi-Autonomous System for Sampling and Extraction of Surfactants in the Sea-Surface Microlayer

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ABSTRACT

Sea surface films affect the air-sea exchange of heat, mass, and momentum. The occurrence, spatial distribution, concentration and composition of sea surface films are not well known (Frew, 1997; Frew et al., 2001). Modeling the impact of the surface microlayer on air-sea exchange processes requires an understanding of many factors including:

- film formation rates and persistence as a function of wind stress
- patchiness of film distributions over a range of spatial scales (10m-1km)
- elasticity variations on these spatial scales
- film composition as a function of film pressure, wind stress, and seasonal factors.

To meet these needs, a new survey tool, **SCIMS (Slick Chemical Identification and Measurement System),** which detects the presence of surface microlayer films and allows mapping of their spatial and temporal distributions is described. Examples of time-series surface film enrichment and mass spectra of film materials collected during two recent field deployments are presented.

SCIMS OVERVIEW

SCIMS consists of a surface microlayer skimmer (SMS) coupled to a fluorometry package and an automated extraction interface. Deployed on a remotely-piloted catamaran, SCIMS processes the skimmer flow stream, carrying out cyclical, microscale solid-phase extraction, concentration, desalting, and elution of microlayer surface-active organics for short-term archiving in an autosampler-compatible vial array. The time-series 'snapshots' of the extracted microlayer are then processed by a lab or shipboard ion trap mass spectrometer (ITMS) to develop the surface compositional profile of the area surveyed by the skimmer, with a temporal resolution of about 10 minutes. The mass spectral information can be further used with elasticity data to develop correlative relationships between film composition and elasticity. SCIMS also provides real-time measurements of microlayer and subsurface colored dissolved organic matter (CDOM) fluorescence with 1-second resolution.

The SMS [*Carlson et al.*, 1988] consists of a partially-submerged, rotating glass cylinder supported by a small catamaran. The cylinder collects a thin layer of water (40-60 µm thickness) by viscous retention. The theoretical basis for the sampling mechanism has been described by *Levich* [1962] and verified experimentally by *Cinbis* [1992]. A flow stream duplexer selects either the microlayer or subsurface line from the SMS and routes the water to both the extraction system and the fluorometry package. The SCIMS extraction package (**Figs. 1-6**) employs a collection of digitally-controlled peristaltic and syringe pumps, multiport switching valves, and a three-axis positioner. Two syringe pumps are used in a push-pull arrangement to draw and filter microlayer water and to force it through a Michrom BioResources (M-B) solid phase sorption macrotrap (polystyrene-divinylbenzene, 50 µl bed volume (**Fig. 2**)). The M-B macrotrap is then alternately purged and rinsed with high purity N_2 and distilled water using two additional syringe pumps before elution of adsorbed surfactants from the trap with methanol from a fifth pump. Control of the extraction cycle is realized using a laptop PC with two RS-485 serial multidrop lines for the pumps, 3-axis arm and multiport valves (**Fig. 3**). A National Instruments DAQCard-1200 multifunction card drives the servo amplifier for the skimmer motor and provides digital I/O for the flow duplexer and power relays. A full-featured software package with graphical user interface and display has been developed for the WIN32 environment (**Fig.6**). The software integrates three separate applications: the SCIMS control interface, the fluorometry data acquisition interface, and a set of test bench tools for development/modification of the SCIMS extraction sequence.

The remote vehicle is a 13' Hobie Wave catamaran (**Fig. 7**) supporting an instrument platform on which the SCIMS package, two GPS units, 12V battery banks, and solid-state chargers are mounted. Twin radio-controlled electric motors and servo-driven rudders provide propulsion and steering. The SMS is supported on an articulated boom between the Hobie hulls and forward of the platform. In addition to SCIMS, the vehicle carries a flux measurement system consisting of a 2-D sonic anemometer and relative humidity gauge mounted on a 3-meter mast and a subsurface temperature and conductivity probe. The GPS units are integrated with the data acquisition systems. Communications and real-time control of SCIMS operations are made via wireless LAN components mounted on the catamaran and the support vessel. In deployments, the vehicle has proved to be highly maneuverable in winds up to 6 m/s. Endurance is about 6 hours and limited mainly by the current drain of the propulsion system.

THE SAMPLING PACKAGE

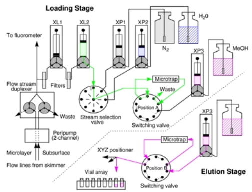


FIG. 1

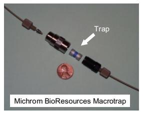


FIG. 2

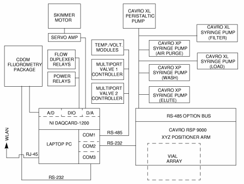


FIG. 3

FIG. 4

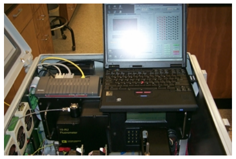


FIG. 5

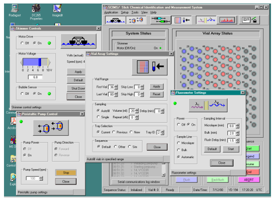


FIG. 6

Software Interface Capabilities:

- **Control dialogs for all subsystems**
- **Status displays/system monitoring**
- **Single vial and auto-fill (≤100 vial) modes**
- **CDOM fluorescence acquisition/display**
- **Date/time stamping/annotation**
- **Error handling**
- **Fully remote operation via WLAN**

THE REMOTE VEHICLE

FIG. 7

SPATIAL SURVEYS - CDOM FLUORESCENCE

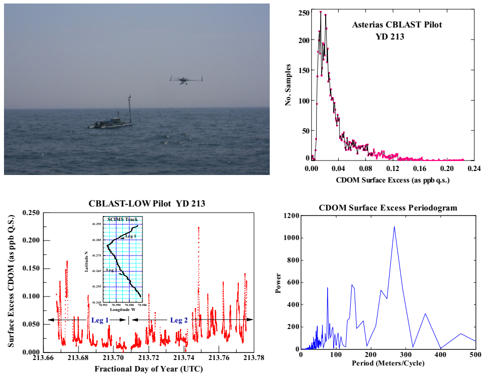


FIG. 8 SCIMS meets the low-flying NOAA LongEZ experimental aircraft (upper left) during a spatial survey in the recent ONR CBLAST-LOW Pilot Experiment off Martha's Vineyard, Massachusetts (July-August, 2001). CDOM fluorescence was used as a proxy for surfactants enriched in the microlayer. The CDOM surface excess as ppb q.s. (quinine sulfate external standard) during two legs of a SCIMS CBLAST-Low deployment (lower left) illustrates the patchiness of surface film conditions along the transect in light winds. Over large scales (1-2 km), decreasing and increasing surface enrichment trends were observed for the southwestward leg (Leg 1) and southeastward leg (Leg 2), respectively. Variations in patchiness over smaller spatial scales are evident from the periodogram (lower right), after detrending the time series. The histogram (upper right) of CDOM surface excess shows surface enrichments generally below 0.04 ppb q.s. but ranging as high as 0.23 ppb q.s.

ELECTROSPRAY IONIZATION - ION TRAP MS^2

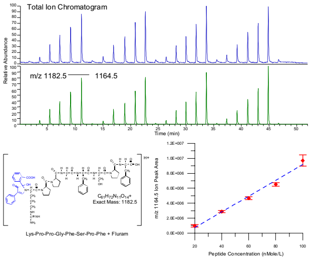
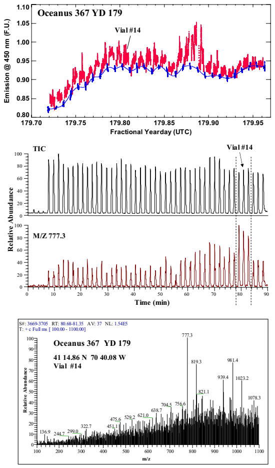


FIG. 9 Tests involving sequential flow injections of microextracts of Vineyard Sound surface water demonstrated a linear mass spectrometer response for both total ion current and specific ion fragmentation pathways for target surfactants in the water. The figure shows a 25-sample time series in which quantitation of a model surfactant, a small surface-active oligopeptide spiked into the seawater, was carried out using the automated macrotrap extraction system and ITMS with electrospray ionization (ESI) with virtually no chemical noise. The sample size was modulated in a sawtooth pattern to simulate varying surface microlayer concentrations. The mass spectrometer response is quite linear for both the total ion current and for specific detection of the peptide using two stages of MS (MS^2) to follow loss of water (Δ18 amu) from the sodium-cationized molecular ion. Each peak in the mass chromatograms represents one flow-injected extract, such that the envelope of peak intensities (or peak areas) corresponds to the concentration 'profile' and could be used to determine the original concentration of the peptide in the microlayer.

FILM COMPONENTS FROM ESI-MS ANALYSIS

FIG. 10 The panels at the right illustrate SCIMS results from R/V Oceanus Cruise 367 south of Martha's Vineyard in June, 2001. The upper panel shows microlayer (red) and subsurface (blue) CDOM fluorescence during a 5-hr transect at 41º14.18'N, 70º 38.16'W. Surface enrichments were evident throughout the transect. The middle panel presents the total ion and mass chromatograms (TIC and m/z 777) for the first 15 of 30 samples collected. These were flow-injected in triplicate into a Finnigan LCQ ITMS and ionized using electrospray. Variation in the TIC is minimal since total organic carbon is only slightly enriched in the microlayer. The mass chromatogram for m/z 777 shows more variation, suggesting preferential enrichment. The lower panel is the electrospray spectrum of sample extract #14, which shows a broad envelope of ions from m/z 100-1100 representing primarily protonated or sodiated parent ions. Prominent ions from a series of unknown but related compounds are observed at 777, 819, 939, and 981. Low mass defects along with mass differences of 162 amu suggest the presence of glycosyl (sugar) moieties in these structures. Ions at 777 and 939 for example, may derive from mono- and diglycosyldiglycerides. This will be explored further using a combination of ionization modes and multistage (MS^n) techniques.



POTENTIAL APPLICATIONS

Automated microlayer sampling with SCIMS combined with ion trap mass spectrometry provides the capability to examine the molecular identity and concentrations of organic compounds in the sea surface microlayer and to make better estimates of surface elasticity. The availability of such information during field studies will allow more detailed investigations of air-sea interactions and improved groundtruthing of microwave remote imagery. More rapid information acquisition will allow process studies of links between biological processes, surfactant production and film distributions, the role of hydrodynamic processes in film formation and dispersal, photochemical degradation processes in the microlayer, and the relative importance of insoluble lipid and soluble biopolymeric surfactants in determining sea surface viscoelasticity. Expected major applications include studies of the role of the marine microlayer in modulating small-scale waves and microwave scattering, microwave signatures of internal waves, wind stress-drag relationships, turbulent surface renewal and air-sea gas exchange.

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