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USE OF MICELLULARIZED P-TOSYL-8-AMINOQUINOLINE FOR DIRECT DETECTION OF NANOMOLAR LEVELS OF ZINC AND CADMIUM IN AQUEOUS SOLUTIONS

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Our research has been directed toward developing a remote, real-time fiber-optic sensor for detection of metal species in seawater. Detection is dependent upon measuring the fluorescence of water soluble metal-ligand complexes in solutions. Discrimination of different ions complexing with the same ligand is accomplished with time-resolved fluorescence, using a pulsed technique. Instrumentation consists of an OMA III system with an intensified linear photodiode array detector, monochrometer, pulsed nitrogen laser, and bifurcated fiber-optic cable for transmission of light to the sample and back to the detector.

Direct detection of a specific ion in a complex matrix such as seawater, using fluorescence techniques, requires a ligand that is water soluble and will fluoresce with few species other than the target ion. Boshevolnov (1965) and others have indicated that fluorescence of the ligand p-tosyl-8-aminoquinoline (pTAQ) is limited to complexes formed with zinc and cadmium. Unfortunately, pTAQ is insoluble in water in the pH range between 3 and 11, making direct use of it in natural waters impossible. Use of a micellular system consisting of the nonionic surfactant Triton X-100 and pTAQ allowed it to be directly dissolved in water.

Characterization of the solubilized ligand for the sensor system in the laboratory concentrated upon measuring the effective pH range, detection limits, and decay times for the two ions; and deconvolution of individual concentrations from mixtures of the two. The maximum concentration of the micellularized ligand that can be dissolved in water is limited to 5.0 micromolar, above this concentration the ligand system eventually precipitates. The quantum efficiency of both complexes was shown to be similar. Both complexes showed maximal

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19. ABSTRACT (Continued)

fluorescence over a range 4 pH units wide, centered at pH 8.7; the zinc response centered at pH 8.2 and cadmium at pH 9.2. To date, the detection limit for these complexes as established for zinc in deionized water, buffered to pH 8.1, is 0.153 nanomolar. Linear standard addition plots for concentrations from 0.153 nM to 15.3 nM had correlation coefficients of 0.999. The coefficient of variation at the 1.53 nM level was 4.6%. A linear response (R^2 = 0.999) was measured for standard additions of 15.3 to 1530 nM zinc to Chelex cleaned seawater. Based on current data it is believed that levels as low as 5.0 nM can be detected in seawater. Analysis time for individual samples is less than 1 minute.

Time-resolved fluorescence was used to separate concentrations of the individual metals from each other in mixtures of the two. The decay time for the zinc complex was established to be 23.3 ns, and that of the cadmium complex to be 16.0 ns. Deconvolution of the two metals was accomplished using a double exponential fit. Analysis time for mixtures is approximately 5 minutes. Mixtures with levels of both metals of concentrations as low as 15.3 nM can be distinguished from one another.

Improvement of the system for faster analysis time and lower detection levels, as well as results from field tests of the system at sea will be discussed.