Mapping the Specific Molar Extinction Coefficients of Organometallic Chemicals

Savannah Steinly, Kiranmayi Mangalgiri, Mamatha Hopanna, Lee Blaney

The University of Maryland, Baltimore County (Baltimore, MD)
Department of Chemical, Biochemical and Environmental Engineering

Abstract
Organometallic chemicals are used for a variety of applications, including agriculture, medicine, and electronics. This project focuses on four organometallic classes (i.e., organoarsenic, platinum, selenium, and tin). These compounds are introduced to the environment through wastewater treatment plants (Pt, Se), the shipping industry (Sn), and agricultural runoff (As). The unique properties of these compounds, and the corresponding inorganic metals, present distinct environmental and human health concerns; however, few studies on the photolytic transformation of these organometallics in the environment have been undertaken. One critical aspect of photolysis is determination of molar extinction coefficients across the solar irradiation spectrum. In this study, we used the Beer-Lambert law to measure the apparent UV-visible absorbance for 190-900 nm along a pH gradient for organometallics. With these data, we mapped molar extinction coefficients and deconvoluted the apparent molar extinction coefficients with respect to pH to determine extinction coefficients for protonated/deprotonated species. The results of this study yield important information about how organometallics absorb solar irradiation. That information will be used in ongoing work to identify the photodegradation kinetics of organometallics in environmental systems.

Motivation
• In this project, we aim to identify the molar extinction coefficients of organometallic compounds across pH and wavelength gradients.
• The molar extinction coefficients (also known as molar absorptivity) measure how efficiently a molecule absorbs photons at a particular wavelength.
• Understanding how these chemicals absorb solar irradiation is required to address photolytic chemical transformation pathways in the environment.

Experimental Materials and Methods
Organometallics. Analytical grade chemical compounds were ordered from Sigma-Aldrich (St. Louis, MO, USA) or Fisher Scientific (Pittsburgh, PA, USA); physicochemical properties are listed in Table 1. Stock solutions (1 g/L) were prepared using deionized water (DI) or methanol, based on solubility.

Buffered experimental solutions. Several 10 mM phosphate buffers ranging from pH 2 to 12 were created and spiked with organometallic stock solutions to generate solutions with organometallic concentrations high enough to quantify absorbance.

Results and Discussion

Figure 1: The UV-vis spectrophotometer

Figure 2: Absorbance spectra for the four organometallics prepared at 20 mg/L in DI and measured using 1-cm quartz cuvettes. The molecules only absorbed in the UV range, with maximal absorbance below 250 nm. These data indicate that the organometallics do not absorb much solar light, and that photolysis may be driven by indirect reactions with reactive species generated by dissolved organic matter. A schematic of the setup is shown.

Figure 3: (A) Map of molar extinction coefficients (M⁻¹cm⁻¹) for CIS as a function of wavelength (220 – 250 nm) and pH (2-12). (B) Absorbance of CIS at 254 nm, which is used in wastewater treatment plants for disinfection. Note that the absorbance increases as the pH approaches pKᵦ₊, indicating that ε₂₅₄ nm is greater than ε₁₂₅₄ nm.

Deconvolution of molar extinction coefficients
We hypothesized that the apparent molar extinction coefficient could be calculated from the summation of the contributions from the protonated/deprotonated species, as shown in Eq. 2:

ε_app = ε₁α₁ + ε₂α₂

To calculate the specific molar extinction coefficients at individual wavelengths, we recorded the full spectrum of absorbance for organometallics at various pH. With the use of a macro-based loop, the Excel solver function was used to fit the data.

Results and Discussion (cont.)

Figure 4: The specific molar extinction coefficients of (A) CIS and (C) SEM plotted against wavelength, along with model fits of the apparent molar extinction coefficients at near-neutral pH for (B) CIS and (D) SEM.

Conclusions and Future Work
Organometallics absorb solar irradiation, and their extinction coefficients have been measured and deconvoluted with respect to pH and wavelength. We are currently investigating the impact of the metal atom by analyzing the carbon analogs of these organometallics.

The next steps in this research project are to commence photodegradation studies and calculate pseudo-first order rate constants and quantum yields for the organometallics of concern.

References

Acknowledgements
We acknowledge the National Science Foundation (CHE 1508090) for funding this project and the CWT Scholars program for supporting Ms. Steinly.