Mapping the Specific Molar Extinction Coefficients of Organometallic Chemicals

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Abstract

Organometallic chemicals are used for a variety of applications, including agriculture, medicine, and electronics. This project focuses on four organometallic classes (*i.e.*, organo-arsenic, 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.

Table 1: Physicochemical properties of four organometallic compounds (pK_a values retrieved from chemicalize.org).

Organometallic	Abbrev. name	Chemical formula	Molecular weight (g/mol)	pK_a values	Chemical structure
Carboplatin	CPT	$C_6H_{12}N_2O_4Pt$	371.253	9.88 11.13	
Cisplatin	CIS	$H_6Cl_2N_2Pt$	300.050	11.30 12.56	
Azocyclotin	ASN	$C_{20}H_{35}N_3Sn$	436.222	3.19	
Selenomethionine	SEM	$C_5H_{11}NO_2Se$	196.106	1.56 9.50	

Experimental Materials and Methods (cont.)

UV-visible absorbance spectra

UV-vis spectrophotometry (Evolution 600; Thermo Scientific; Figure 1) was used to determine the absorbance spectra. Separate solutions of 50 mg/L CPT, CIS and ASN and 25 mg/L SEM were prepared in phosphate buffer at distinct pH values in the range of 2 to 12, placed in 10 cm quartz cuvettes, and recorded for 190-900 nm.

Figure 1: The UV-vis spectrophotometer.

Molar extinction coefficients

Measurement of molar extinction coefficients involved application of the Beer-Lambert law (Eq. 1) to describe apparent UV-visible absorbance along a pH gradient.
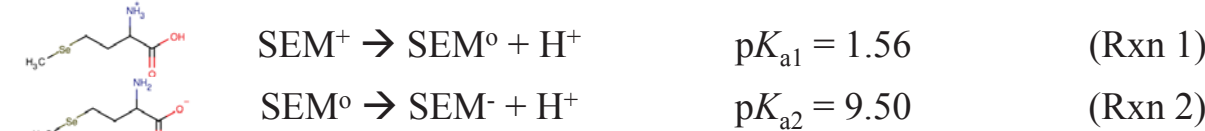
$$A_\lambda = \varepsilon_{app,\lambda}\, C\, l \qquad \text{(Eq. 1)}$$

In Eq. 1, A is the absorbance at wavelength λ, ε_{app} is the apparent molar extinction coefficient at wavelength λ, and l is the path length. The molar extinction coefficients are significant because they characterize the amount of light (at certain wavelengths) that a substance absorbs. This property aids in determination of the photochemical fate of organometallic chemicals.

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.

$$\varepsilon_{app,\lambda} = \varepsilon_{0,\lambda}\alpha_0 + \varepsilon_{1,\lambda}\alpha_1 + \varepsilon_{2,\lambda}\alpha_2 \qquad \text{(Eq. 2)}$$

In Eq. 2, the 0, 1, and 2 subscripts correspond to the protonated, deprotonated, and doubly deprotonated organometallic species. The alpha values are the relative fraction of each species, and stem from the deprotonation reactions (see example for SEM in Rxn 1-2).

$$SEM^+ \rightarrow SEM^o + H^+ \qquad pK_{a1} = 1.56 \qquad \text{(Rxn 1)}$$
$$SEM^o \rightarrow SEM^- + H^+ \qquad pK_{a2} = 9.50 \qquad \text{(Rxn 2)}$$

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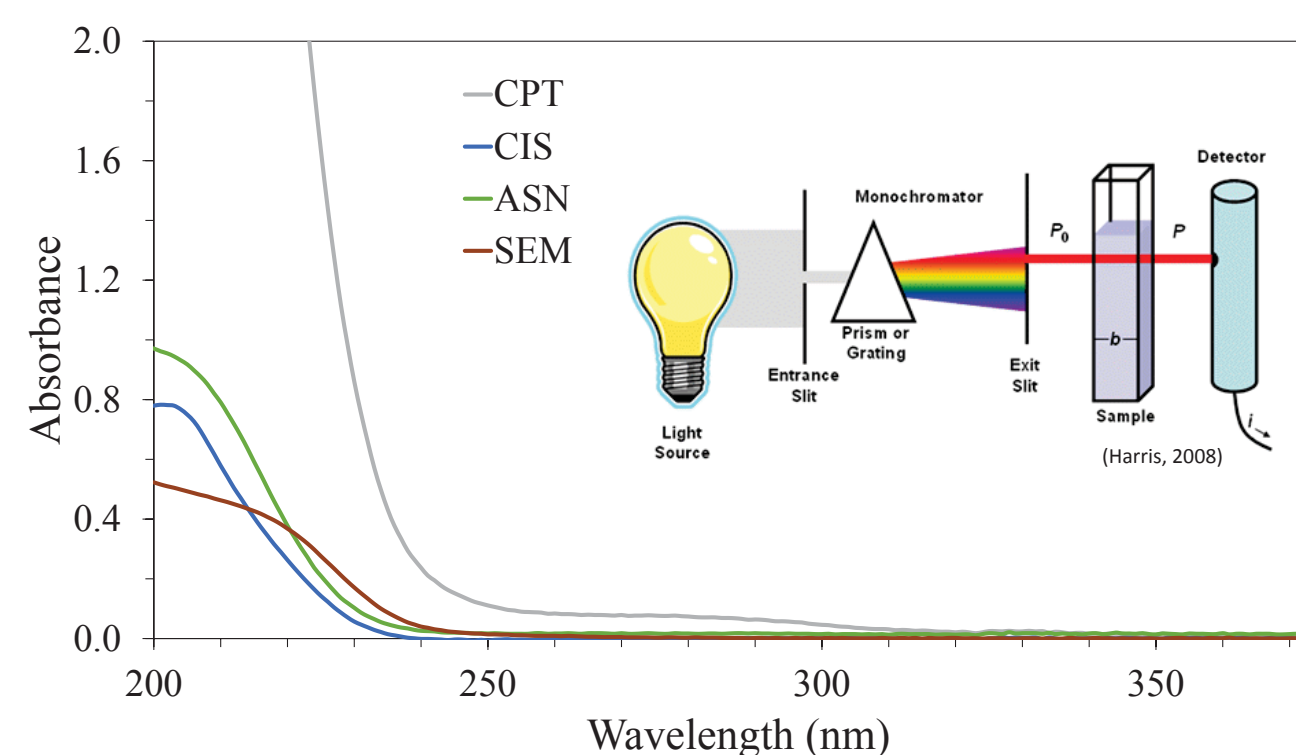
Figure 2: Absorbance spectra for the four organometallics prepared at 20 mg/L in DI and measured using 1-cm quartz cuvettes. The molecules only absorbed in the UV range, with maximal absorbance below 250 nm. These data indicate that the organometallics do not absorb much solar light, and that photolysis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

(Harris, 2008)

Results and Discussion (cont.)
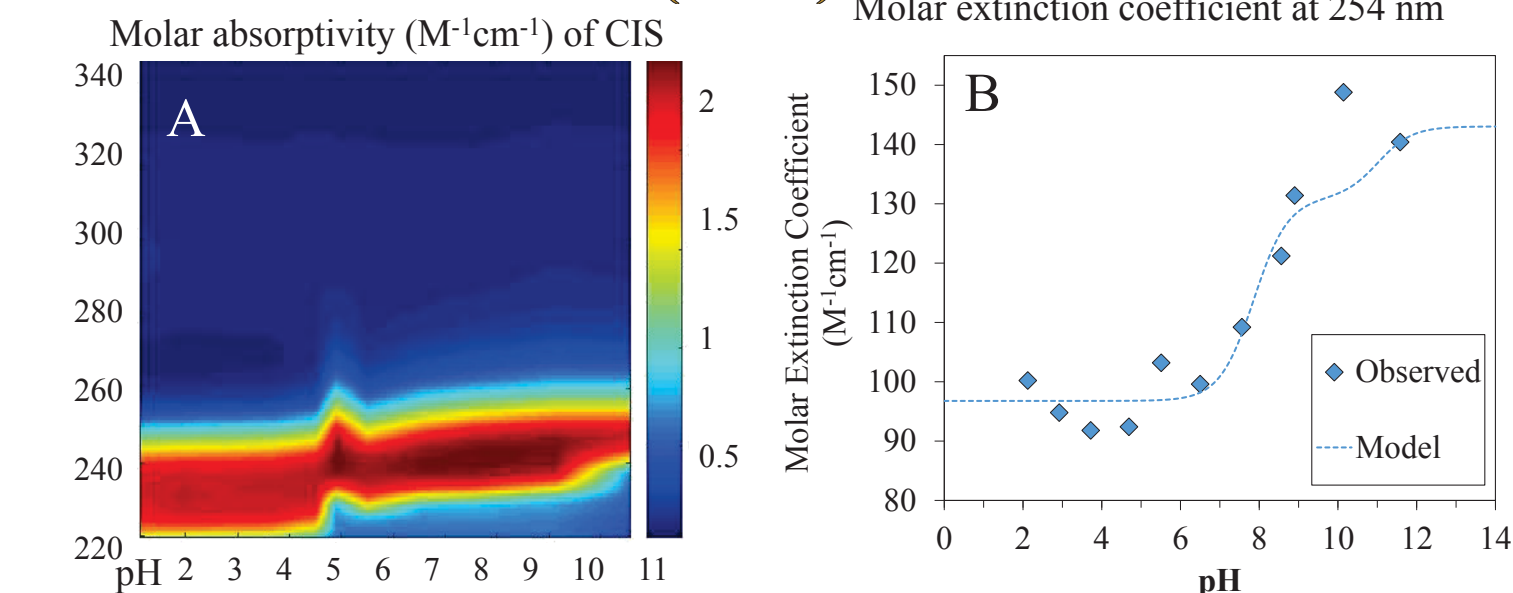
Figure 3: (A) Map of molar extinction coefficients ($M^{-1}cm^{-1}$) for CIS as a function of wavelength (220 – 250 nm) and pH (2-12). (B) Absorbance of CIS at 254 nm, which is used in water/wastewater treatment plants for disinfection. Note that the absorbance increases as the pH approaches pK_{a1}, indicating that $\varepsilon_{1,254\,nm}$ is greater than $\varepsilon_{0,254\,nm}$.

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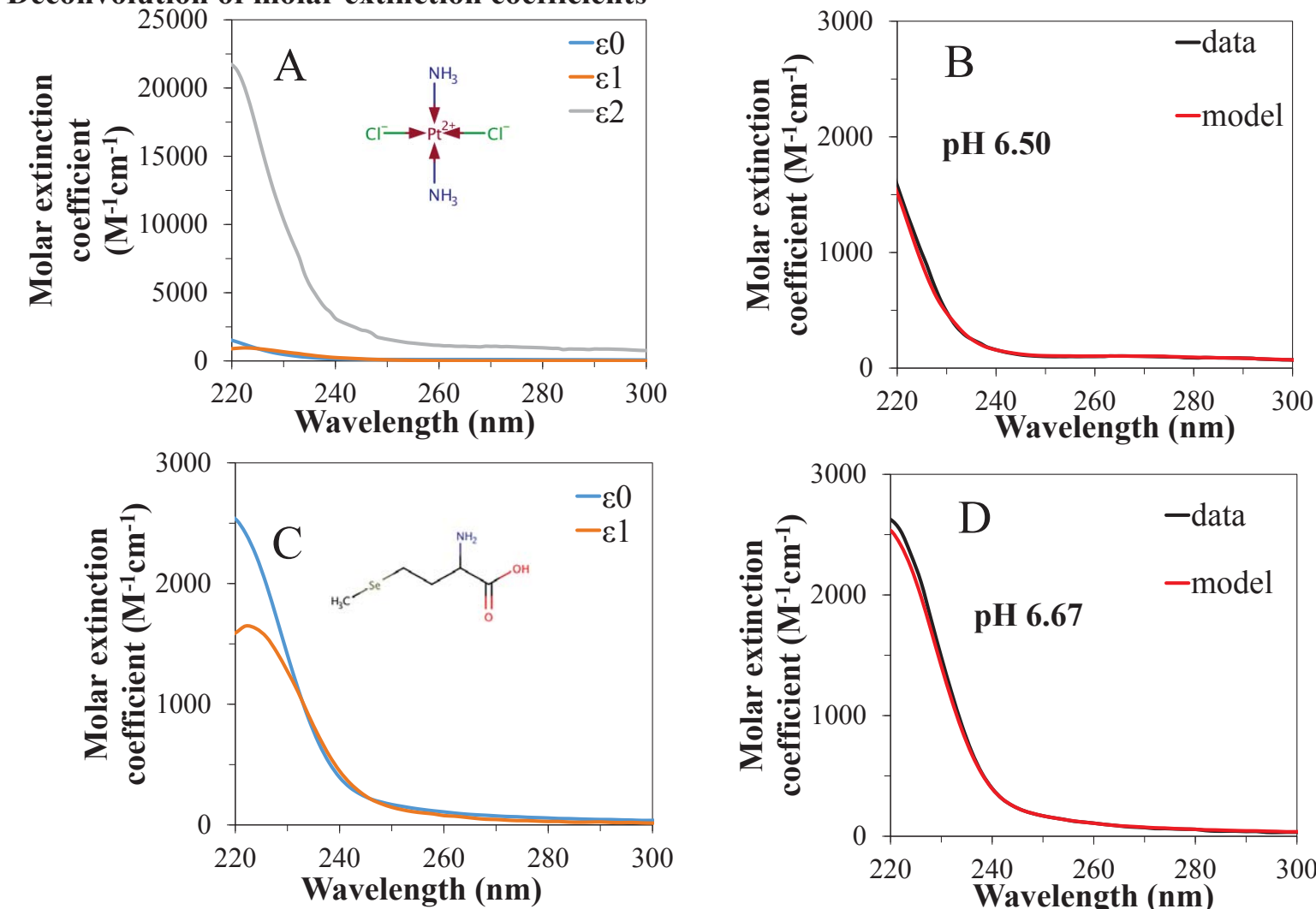
Figure 4: The specific molar extinction coefficients of (A) CIS and (C) SEM plotted against wavelength, along with model fits of the apparent molar extinction coefficients at near-neutral pH for (B) CIS and (D) SEM.

Conclusions and Future Work

✧ Organometallic chemicals 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 organometallic chemicals of concern.

References

Daniel C. Harris (2008). *Determination of Caffeine and Benzoic Acid in Soft Drinks by Multicomponent UV Analysis.* China Lake. W. H. Freeman; 7th edition.

Acknowledgements