Metal Complexation and Extraction Studies of bis-dithiophosphinite Ligands

by

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Abstract

Six bis(dithiophosphonite) ligands OR1a-OR3b were synthesized using Lawesson's Reagent and analogs of Lawesson's Reagent. Two of the ligands OR2a and OR3a, were used in extraction studies with uranyl nitrate. UV-Vis measurements were taken to determine how much uranyl was extracted into the organic layer from the aqueous layer at pH 2, 3, 4, and 5. The extraction studies indicated that a longer time frame of extractions would be beneficial for these ligands. There were modest extractions of 70% for most of the ligands however, it would be best to confirm with ICP in a continuing study. These ligands could also be used for future studies of separating the trivalent lanthanides from the trivalent actinides because of the sulfur donors.

Acknowledgments

I would like to thank Dr. Anne Gorden, for putting up with me and getting me through all this work, I have learned a lot about the actinide series of elements and look forward to continuing to work with her. Dr. John Gorden for giving me off the wall ideas of things to try from a coordination chemist's standpoint. My fellow lab mates for support and answering any questions I may have had. My parents and family for support and encouragement. My committee members, Dr. Christopher Easley, Dr. Christian Goldsmith, and Dr. Rik Blumenthal, for taking time out of their busy schedules to read this and listen to my presentation, I hope to work with each of you more in the future.

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List of Abbreviations

An	Actinide(s)
DCM	Dichloromethane or methylene chloride
DMF	N,N-dimethylformamide
DI	Deionized
DMSO	Dimethylsulfoxide
D2EHPA	di-(2-ethylhexyl)phosphonic acid
FP	Fission Products
HSAB	Hard soft acid base theory
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
Ln	Lanthanide(s)
L.R.	Lawesson's Reagent
LWR	Light Water Reactor
MOX	Mixed Oxide Fuel
PUREX	Plutonium Uranium Recovery by Extraction
SDS	Sodium Dodecyl Sulfate
SNF	Spent Nuclear Fuel
TBP	Tri-n-butyl phosphate
UV-VIS	Ultra Violet-Visible Spectroscopy

Uranium Extractions

Introduction

The availability of adequate energy at a reasonable price is considered a requirement of modern society.[1] Experts predict that the maximum allowable oil production using current methods will occur in the next 5 to 25 years, and consequently, the need to have alternative energy sources to eventually replace oil is growing.[1] Currently 25-30% of the world's electricity is produced using nuclear sources, and nuclear power is the dominant source of electrical power for most of Europe.[2] As of January 1, 2010, there were 437 nuclear power reactors in operation worldwide with 104 in the United States alone.[3] At the end of 2005, 85% of the domestic energy in the United States was produced from fossil fuels, while 8% was from nuclear power, and 6% from renewable energy such as hydroelectric, solar and wind power.[1] The applications of nuclear energy for the production of electricity for general civilian use, military applications, as well as in satellite and space exploration applications are plagued with waste management risks that must be addressed.[2] Fifty-years of nuclear weapons production has generated more than 100 metric tons of purified plutonium in the United States alone.[4] The production of plutonium from power reactors amounts to perhaps as much as 7000 metric tons worldwide most of which is dilute and contained in spent reactor fuel.[4]

In a typical light-water reactor, the operational life-span of a fuel rod is only three years,[5] and only about 5% of the energy content of the nuclear fuel rod is used.[1] Although recycling the remaining 95% of fissile material seems reasonable from an efficiency standpoint, the generation of weapons grade plutonium and proliferation risks led to the cessation of this technology in the United States during the cold war.[1,6] Other nations using nuclear power technology reprocess their spent fuel to recycle remaining fissile fractions.[1] Such a process can provide up to 96% more energy than the once-through cycle using the same initial amount of enriched uranium fuel.[1]

Reprocessing refers to the chemical separation of fissionable uranium and plutonium from irradiated nuclear fuel.[6] The two main reasons for commercial reprocessing are: (1) to increase the available energy from fissile and fertile atoms and (2) to reduce hazards and costs for handling the high level wastes from fission products (FP).[7] The economic advantage of reprocessing depends on the cost and availability of natural uranium, on enrichment and making fuel rods, and the prevailing energy price (usually based on fossil fuels).[7]

One of the first problems associated with the separation of Spent Nuclear Fuel (SNF) is separating lanthanides from actinides. This is difficult due to their similar oxidation states and ionic radii.[8] The first separation of uranium and plutonium was done by the chemists of the Manhattan Project in the 1940s.[7] In the early separations, the stability of UO_2^{2+} was exploited as well as the redox lability of plutonium (+3, +4, and +6 oxidation state).[4,7] In these earliest processes, only plutonium was isolated by precipitating it in the reduced state as PuF_3 or PuF_4 along with all the other FP insoluble fluorides.[7] In order to get relatively pure plutonium, this precipitation process had to be repeated several times.[4]

This precipitation technique is not suitable for large-scale, continuous remote operations, in which uranium and plutonium both have to be isolated in a very pure state.[7] In the late 1940's this process was replaced by solvent extraction methods in which the fuel rods where dissolved in nitric acid, and contacted with an organic solvent which selectively extracted the desired elements.[7] Because actinide production in reactors is accompanied by fission, the ability to isolate the transuranium actinides from both fission products and uranium, remains a separation problem central to actinide production.[4] Accordingly, efficient separation processes continue to be sought.[4,9]

PUREX Process

The most widely used and effective process for the removal of plutonium and uranium around the world is the PUREX process, which stands for Plutonium Uranium Recovery by EXtraction.[10-12] This process utilizes the extractant tributyl phosphate (TBP) (Figure 1) in a hydrocarbon solvent (usually kerosene or dodecane) (See Figure 2).[7,13] It relies on the extraction of plutonium and subsequent reduction to the trivalent state, leaving the excess uranium in the extractant phase for subsequent recovery.[4]

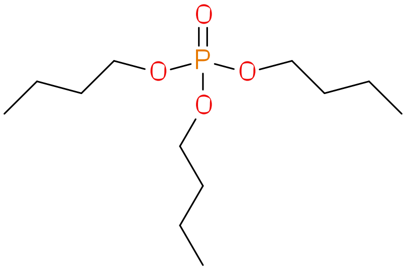


Figure 1: Tri-butyl Phosphate

As a result of using PUREX, the volume and radiotoxicity of highly radioactive and long-lived waste to be disposed were significantly reduced as compared to a once-through fuel cycle.[13] TBP acts like an adduct and is normally used as a 30% solution in kerosene.[7] It takes three purification cycles for both uranium and plutonium to be extracted efficiently, and the first cycle is where >99% of the fission products are separated as well as where high levels of beta and gamma activity are present.[7] The aqueous phase of the first separation is prepared in 3-4M HNO_3. The next two cycles are the same as the first but at lower acid concentration and are used to achieve additional decontamination and overall purity.[7]

After using this process for several decades with industrial feedback, there were several major milestones. First, high efficiency and reliability is achieved through the processing of large volumes of spent fuel with good statistics. Second is the production of high quality UO_2 and mixed oxide (MOX) fuels for light water reactors (LWRs) and fast reactors. Finally, continuous decrease of solid waste volume, effluents, and environmental impact in terms of radiation doses.[13] Though it is the industry standard at present, the PUREX process remains far from perfect, because it does not address the isolation of other actinide cations.[4]

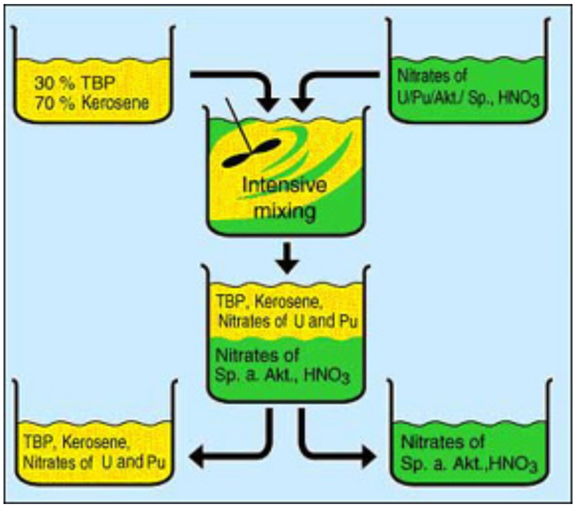


Figure 2: Typical PUREX process used with TBP. www.euronuclear.org/info/encyclopedia/p/purex-process.htm

TBP works very well at binding uranium and plutonium because the two metals are hard acids. Oxygen being a hard base forms a very stable complex. In 1963, Pearson came up with the Hard Soft Acid Base Theory (HSAB theory) that essentially describes the binding affinity of a hard Lewis acid (UO_2^{2+}, Mg^{2+}, Co^{3+}, Pu^{4+}...etc.) will more selectively bind with a hard Lewis Base (F, O, N…etc.) and the same for soft Lewis acids and bases.[14] Ni^{2+} and Co^{2+}, being soft Lewis acids, should be attracted to soft donors, sulfur substitution and the organophosphorous reagents began to emerge. This proved beneficial to the extraction of these metal ions.[15] All known An(III) | Ln(III) group separations are based on the stronger interactions of actinide with soft donor atoms like Cl^-, S, or N.[4,16]

Organophosphorous extractants have played a major role in actinide extraction.[9] These extractants are generally stable, cheap, and commercially available, and have been widely studied in the past few decades, in particular with respect to cobalt-nickel separation in weakly acidic sulfate media.[15] The earliest work was performed by Ritley and co-workers, as well as Flett and co-workers where they used an alkylphosphoric acid, di-(2-ethylhexyl)-phosphoric acid (D2EHPA). This resulted in a number of patents, and the commercial implementation of several processes with D2EHPA.[15,17] Next came the development of the phosphonic and phosphinic acid extractants 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC88A) and bis-(2,4,4,-trimethylpentyl)-phosphinic acid (Cyanex 272) which led to better separation factors in the order: phosphoric< phosphonic< phosphinic acid.[15,18,19] Handley and Dean lead the way into the investigation of the extraction of a number of metals from H_2SO_4 and HCl by trialkthiophosphates,[20] a dialkylthiophosphoric acid,[21] and dialkyldithiophosphoric acids.[22]

Cyanex 301

Cyanex 301 and 302 are the respective dithio and monthio analogs of Cyanex 272 with the main components of the reagents shown below:[15] Cyanex 301 was originally developed for the selective extraction of zinc from effluent streams containing calcium.[15] Increasing sulfur substitution increases the acidity of the extractants, making them more suited to the extraction of soft Lewis acid metal ions such as Ag(I), Ni(II), Zn(II), Cu(I), Au(I), and platinum group metals in accordance with the HSAB theory.[23]

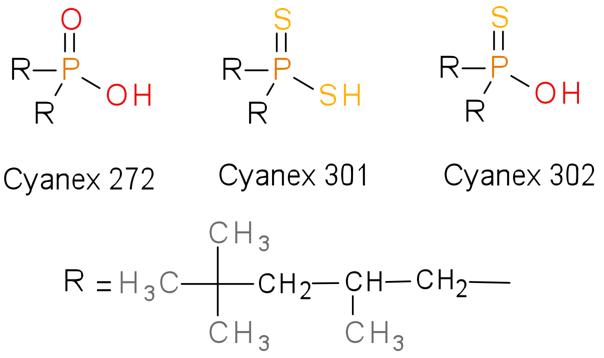


Figure 3: Cyanex 272, 301 and 302 structures

In recent years, Cyanex 302 and Cyanex 301 have received considerable attention both for their ability to extract soft transition metals,[23] and for their ability to differentiate between chemically similar trivalent lanthanides and actinides.[24] Recently, there have been numerous publications using thiosubstituted organophosphinic reagents to extract metal ions such as cobalt (II)[25], nickel (II),[25] titanium (IV),[26] silver,[27] mercury (II),[28] molybdenum (VI),[29] actinides and lanthinides,[30] copper,[31] and halfnium.[32,33]

With the sulfur atoms on Cyanex 302 and 301, these compounds are much stronger acids than Cyanex 272, and as such, are capable of extracting many metals at low pH (<2). At this low pH, they show a high degree of selectivity for heavy metals vs. alkaline and alkali earth metals,[33] however, Cyanex 301 will only differentiate between Am(III) and lanthanides in solutions less acidic than pH of 3 (pK_a of Cyanex 301 is 2.6).[34] Because the waste stream of the Cyanex process contains sulfur, a problem arises during incineration which can lead to the release of coke ash and sulfur dioxide, major contributors, to acid rain.[13]

To date, separations of SNF have focused on extraction agents containing a single dithiophosphinic acid group like Cyanex 301. We wanted to see if we could synthesize a ligand with two or more of these groups, such that they structurally complement the metal, and provide a chelate effect that would dramatically enhance the extraction efficiency.[35] Using computational calculations from Dr. Benjamin Hay,[36] we were able to identify a series of target ligands with two thiophosphonates to synthesize. A summary of his calculations in a graph of ΔU(reorg) vs. number of CH_2 groups in linkage are shown in figure 4. The structural reorganization is convenient to partition into a two-step process as shown in figure 5. In the first step, the ligand (host) goes from the free form, defined as the lowest energy conformation of the host, to the binding form. The difference in the strain energy of these two forms on the ligand, ΔU(conf), is a measure of the degree of pre-organization. The second step, where the host goes from the binding form to the bound form, the difference in the strain energy between these two forms is ΔU(comp), is a measure or the degree of complementarity offered by the binding conformation. The sum of the two energies $\Delta U(reorg) = \Delta U(conf) + \Delta U(comp)$, provides a measuring stick for determining the degree of structural reorganization that occurs on binding the guest (metal).[36] In this research, Lawesson's reagent and analogs of Lawesson's Reagent have been used to synthesize bisdithiophosphonate ligands for metal complexation as well as extraction studies of uranium.

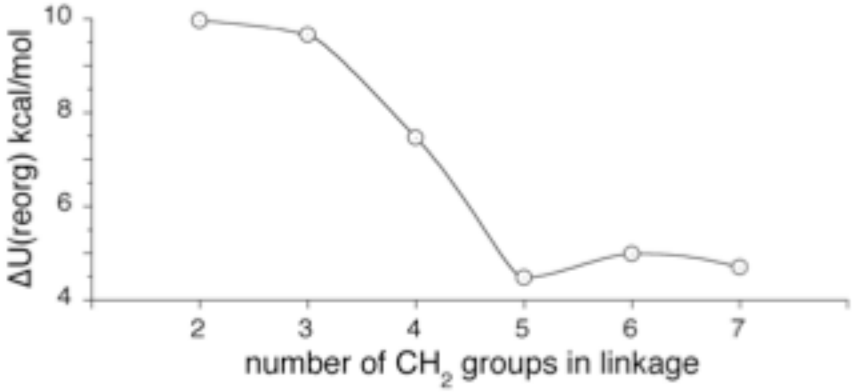


Figure 4: Plot of ΔU(reorg) values versus number of methylene groups in the linkage.[36] ΔU(reorg) = ΔU(conf) + ΔU(comp)[36]

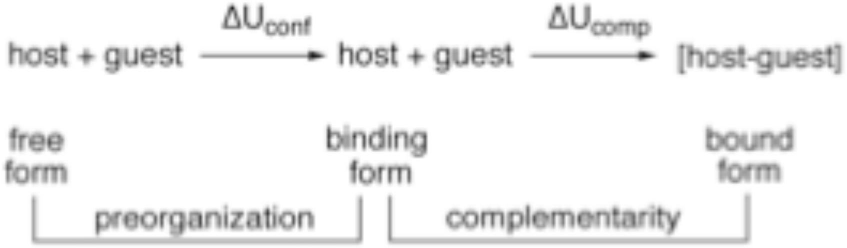


Figure 5: Irrespective of the actual complexation mechanism, the structural reorganization in the host that occurs upon binding the guest can be viewed as taking place in two steps defining three distinct structural states for the host: bound form, binding form, free form. The bound form is the structure of the host when complexed with the guest, the binding form is the host conformation obtained after removing the guest and optimizing the host, and the free form is the global minimum conformation of the host.[36]

Lawesson's Reagent

The chemical conversion of carbonyl to thiocarbonyl has been an area of interest in synthetic organic chemistry for over a century.[37] The usual method involves boiling toluene, xylene, or pyridine as solvent, and a large excess of a carbonyl reagent and long reaction times, resulting in variable yields.[37-39] Previous investigations have shown that the reaction of carbonyl compounds with phosphorous pentasulfide can be carried out at 30°C in polar solvents such as acetonitrile or tetrahydrofuran in the presence of a base catalyst.[37]

In the search for new, useful, and general thionation reagents, the chemistry of 2,4-bis(*p*-methoxyphenyl)-1,3-dithiadiphosphetane-2,4-disulfide (Lawesson's Reagent, LR) appeared to indicate that it could be a superior reagent for the conversion of a wide variety of carbonyl to thiocarbonyl compounds.[37] The first report on the synthesis of arylthionophosphine sulfides dates back to 1956, when Lecher and co-workers described the reaction of phosphorous pentasulfide with a number of aromatic substrates at elevated temperatures.[39,40] The crystalline products were isolated in varying yields.[40]

Lawesson's reagent has a couple of advantages over phosphorous pentasulfide. First, it easily and safely prepared by the reaction of phosphorous pentasulfide with refluxing anisole in a 1:10 molar ratio at 155°C for 6 hours for a 70-80% yield,[39,41] both are commercially available. The second advantage is that it can react with a wide range of carbonyl compounds in nearly equimolar proportions.[37] The attractiveness of this system is associated with its availability, simplicity and convenience of use, the high yields of sulfur-containing products, and a comparative ease of isolating the products from the reaction mixture;[42] however, LR is not stable for very long in a solution at temperatures at over 110°C, because it slowly undergoes polymerization or decomposes.[37,39]

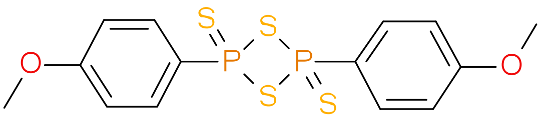


Figure 6: Lawesson's Reagent structure

Bis(Dithiophosphinite) Ligands

Organodithio derivatives of phosphorous compounds, such as dithiophosphinates, dithiophosphonates, and dithiophosphates have been studied for many years.[43,44]

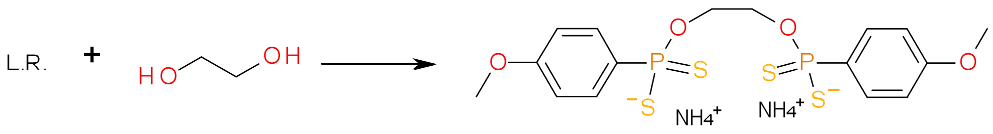
Phosphodithioates and their corresponding acids and metal complexes, have been used as additives to lubricant oils,[45,46] floatation reagents for the recovery of metals from solutions,[47] pesticides,[47,48] and for chemical warfare.[43] Mono(dithiophosphinates), mono(dithiophosphonates), and mono(dithiophosphates) and their complexes with various metals have been extensively studied;[44] however, the properties of the bis(dithiophosphinates, bis(dithiophosphonates), and bis(dithiophosphates), with special regard to containing bridging moieties, have not been investigated in detail.[44,47] The inspiration for this research was to prepare bid(dithiophosphonates) and to evaluate these in simple extractions systems to develop new targets for novel selective extraction systems.

Experimental

Lawesson's reagent, uranyl nitrate, uranyl sulfate, ethylene glycol, 1,3-propanediol, 1,5-pentanediol, phosphorous pentasulfide, and tert-butyl benzene were purchased from Acros and used without any purification. The pH was recorded on a Fischer Scientific AR15 pH meter. UV-Vis data was collected on a Cary 50 UV-Vis spectrophotometer with a xenon lamp in the range of 200-1200 nm. The ^{1}H, ^{13}C, and ^{31}P NMR was recorded on a Bruker AV 250 spectrophotometer with d_1-MEOD, d_1-$CDCl_3$, or d_6-DMSO as the solvent with tetramethylsilane as the reference. All melting points were recorded on a Mel-temp II melting point apparatus, and the values are uncorrected.

Synthesis of Ligands

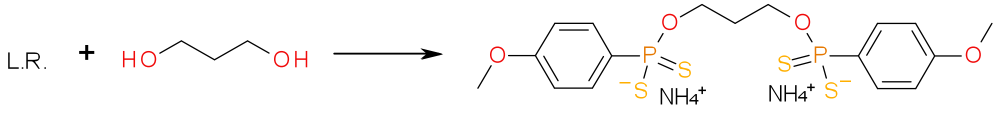
OR1b[47]



Scheme 1: Synthesis of ammonium salt OR1b

Lawesson's Reagent (2.0 g, 5 mmol) was mixed with toluene (5 mL) in a 100 mL round bottom flask. To this mixture ethylene glycol (0.275 mL, 5 mmol) was added. The temperature was set to 80°C and stirred until all of the solids had dissolved. The solution turned a dark green and more toluene (75 mL) was added. A white precipitate formed immediately upon the bubbling of dry ammonia gas converting the acid to the ammonium salt. Bubbling of the gas continued for 30 minutes. The white precipitate was filtered, washed with cold toluene and dried at room temperature under vacuum. Crystals for x-ray diffraction were grown from methanol but were not suitable for diffraction. The yield was 2.05g (82 %); product did not melt below 200°C

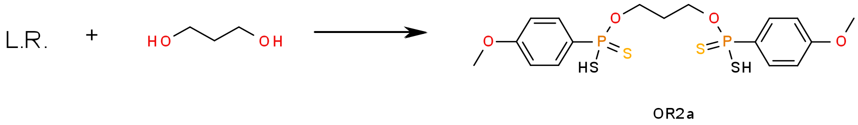
OR2b[47]



Scheme 2: Synthesis of ammonium salt of OR2b.

Lawesson's Reagent (4.2 g, 10 mmol) was mixed with toluene (5 mL) in a 150 mL round bottom flask. To this mixture 1,3-propanediol (0.74 mL, 10 mmol) was added. The temperature was set to 80°C and stirred until all the solids had dissolved. At this point the mixture was a dark green color and more toluene (125 mL) was added. A white precipitate formed immediately upon the bubbling of dry ammonia gas converting the acid to the ammonium salt. Bubbling of the gas continued for 30 minutes. The white precipitate was filtered, washed with cold toluene and dried at room temperature under vacuum. Crystals for x-ray diffraction were grown from methanol but were not suitable for diffraction. The yield was 4.05 g (80 %); mp 157-162 °C

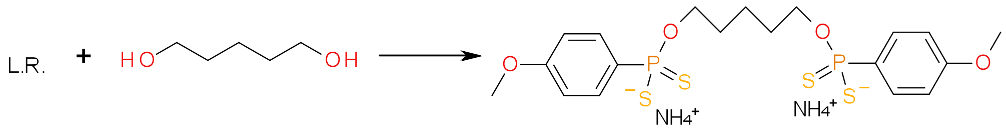
OR2a[44]



Scheme 3: Synthesis of organically soluble OR2a.

To a solution of 1,3-propanediol (0.7232 mL, 10 mmol) in toluene (30 mL), 4.0 g (10 mmol) of Lawesson's Reagent was added. The mixture was stirred at 60°C until all the solids had dissolved and left overnight. The solvent was removed on a roto-vap until the remaining volume was ~10 mL. Hexane (30 mL) was added to precipitate the product as a green oil. Yield 4.206 g (88%).

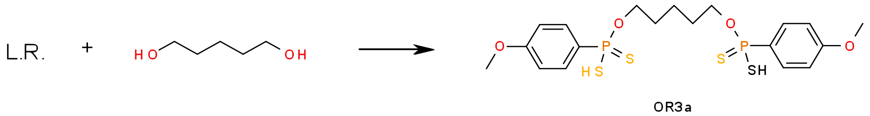
OR3b[47]



Scheme 4: Synthesis of ammonium salt of OR3b.

Lawesson's Reagent (4.2 g, 10 mmol) was mixed with toluene (5 mL) in a 100 mL round bottom flask. To this mixture 1,5-pentanediol (1.05 mL, 10 mmol) was added. The temperature was set to 80°C and stirred until all the solids had dissolved. At this point the mixture was a dark green color and more toluene (150 mL) was added. A white precipitate formed immediately upon the bubbling of dry ammonia gas converting the acid to the ammonium salt. Bubbling of the gas continued for 30 minutes. The white precipitate was filtered, washed with cold toluene and dried at room temperature under vacuum. Crystals for x-ray diffraction were grown from methanol but were not found to be suitable for characterization by single-crystal X-ray diffraction. The yield was 4.1 g (80 %); mp 171-176°C

OR3a

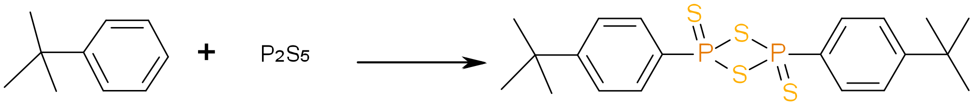


Scheme 5: Synthesis of organically soluble OR3a.

To a solution of 1,5-pentanediol (1.05 mL, 10 mmol) in toluene (30 mL), 4.0 g (10 mmol) of Lawesson's Reagent was added. The mixture was stirred at 70°C until all the solids had dissolved and left overnight. The solvent was removed on a roto-vap until the remaining volume was ~10 mL. Hexane (30 mL) was added to precipitate the product as a green oil. Yield was 4.2 g (84%).

Lawesson's Reagent Analogs

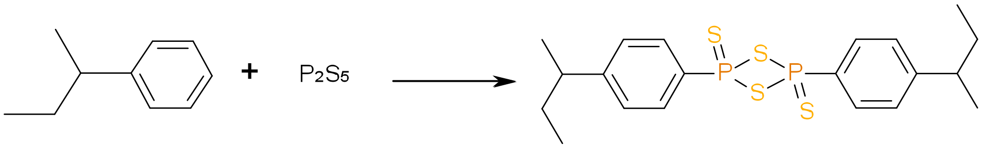
tert-butyl Lawesson's



Scheme 6: Synthesis of *tert*-butyl Lawesson's.

In a 100 mL round bottom flask, 158 mL (1mol) of *tert*-butyl benzene and 6.6 g (7.5 mmol) of phosphorous pentasulfide (P_2S_5) and 20 mL of 1,2-dichlorobenzene as solvent were heated to 170°C and stirred until all the solid had dissolved. The solution was decanted into a 250 mL beaker and cooled to room temperature, where a yellow precipitate formed. The product was filtered and washed three times with 10 mL each of 50:50 mixture of ethyl ether:methylene chloride. The product became crystalline like and was dried in a vacuum oven at room temperature overnight. Yield 0.79 g (23 %). mp - decomposed

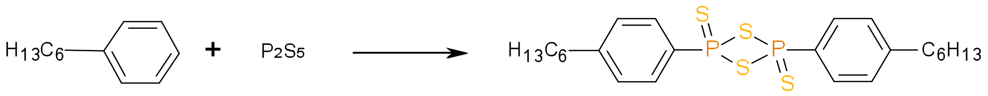
sec-butyl Lawesson's



Scheme 7: Synthesis of sec-butyl Lawesson's

In a 100 mL round bottom flask, 50 mL (0.32 mol) of sec-butyl benzene and 4.3 g (9.67 mmol) of phosphorous pentasulfide (P_2S_5), and 20 mL of 1,2-dicholorbenzene as solvent were heated and stirred at 170°C until there was no more evolution of hydrogen sulfide. The solution was decanted into a 250 mL beaker and cooled to room temperature where the product precipitated as a yellow solid. The product was filtered and washed three times with 10 mL each of 50:50 mixture of ethyl ether:dichloromethane. The product became crystalline like and was dried in a vac-oven at room temperature overnight. Yield 0.16g (15%) mp Decomposed at 200°C

hexyl Lawesson's



Scheme 8: Synthesis of hexyl Lawesson's

In a 100 mL round bottom flask, 50 mL (265 mmol) of hexyl benzene, 2.4 g (5.4 mmol) of phosphorous pentasulfide, and 20 mL of 1,2-dichlorobenzne as solvent were heated and stirred at 170°C until there was no more evolution of hydrogen sulfide. The solution decanted into a 250 mL beaker and cooled in an ice bath, where the product precipitated as a brown solid. The precipitate was filtered and washed three times with 10 mL of 50:50 mixture of ethyl ether:dichloromethane mixture. The precipitate was dried in a vac-oven at room temperature overnight. Yield 0.5876 g (21%) mp decomposed.

The NMR data can be located in appendix; OR1a, OR2a, and OR3a were found to compare well to the literature values.

Using the analogs of Lawesson's reagent, we tried to make the bisdithiophosphonate-linked ligand soluble in other organic solvents; however, due to the analogs not being soluble in solvents other than DMF or DMSO, we could not synthesize the ligands, because reactions with the solvent led to numerous side products generated by thionation of the solvent.

Metal Complexes

All metal complexes were formed using the ammonium salts of the ligands.

OR1a: Cu(II)

In a 20 mL scintillation vial, 0.200 g (0.4 mmol) of OR1a was dissolved in 5 mL of DI water. In a second vial, 0.100 g (0.4 mmol) of copper (II) sulfate was dissolved in 5 mL of DI water. The copper solution was added dropwise to the OR1a solution. Immediately a brown precipitate formed. The solid was filtered off and washed with cold DI water. This precipitate was not found to be soluble in standard organic solvents such as toluene, methylene chloride, or DMSO.

OR1a: Ni(II)

In a 20 mL scintillation vial, 0.200 g (0.4 mmol) of OR1a was dissolved in 5 mL of DI water. In a second vial, 0.159 g (0.4 mmol) of Nickel (II) ammonium sulfate was dissolved in 5 mL of DI water. The Nickel solution was added dropwise to the OR1a solution and a light brown/light purple precipitate formed almost immediately. The precipitate was filtered off and washed with cold DI water. The solid was slightly soluble in DMSO.

OR2a: Cu(II)

In a 20 mL scintillation vial, 0.209 g (0.4 mmol) of OR2a was dissolved in 5 ml of DI water. In a separate vial, 0.101 g (0.4 mmol) of Copper sulfate was dissolved in 5 mL of DI water. The copper solution was added dropwise to the OR2a solution. A brown precipitate formed immediately. The solid was filtered and washed with cold DI water. The dried solid was slightly soluble in DMSO.

OR2a: Ni(II)

In a 20 mL scintillation vial, 0.202 g (0.4 mmol) of OR1a was dissolved in 5 mL of DI water. In a second vial, 0.155 g (0.4 mmol) of Nickel (II) ammonium sulfate was dissolved in 5 mL of DI water. The Nickel solution was added dropwise to the OR1a solution and a light brown/light purple precipitate formed almost immediately. The precipitate was filtered off and washed with cold DI water. The solid was slightly soluble in DMSO.

OR2a:UO_2^{2+}

In a 20mL vial, 0.2 g (0.4 mmol) of OR2A was dissolved in 5mL of DI water. In a separate 20mL vial, 0.15 g (0.4 mmol) of Uranyl (VI) Sulfate was dissolved in 5mL of deionized water. The uranyl solution was added dropwise to the ligand solution and immediately a yellow precipitate formed. The uranyl vial was washed with 2mL of deionized water and added to the now OR2A: Uranyl solution. The precipitate was filtered, washed with cold water and air-dried. The solid was recrystallized from diffusion of DMSO: Ether.

OR3a:UO_2^{2+}

In a 20 mL vial, 0.22 g (0.4 mmol) of OR3a was dissolved in 5 mL of DI water. In a separate 20 mL vial, 0.15 g (0.4 mmol) of Uranyl (VI) Sulfate was dissolve in 5 mL of DI water. The uranyl solution was added drop wise to the ligand solution and a yellow precipitate immediately formed. The uranyl vial was washed with 2 mL of DI water and added to the solution. The precipitate was filtered, washed with cold water, and air-dried. The solid was recrystallized from diffusion of DMSO: Ether. No crystals were good enough for single x-ray diffraction.

Extractions

Two-phase extraction studies (DCM:H_2O) were performed to determine the extraction capability for the removal of UO_2^{2+} ion from aqueous solution. The ligands OR2a and OR3a, soluble in DCM were used for extraction studies. Fresh solutions of $UO_2(NO_3)_2 \cdot 6H_2O$ were prepared in DI water, and the pH was adjusted with HNO_3 and KOH (± 0.05). Two different methods were employed for studying extraction.

Hydrolysis Study

Stock solutions of OR2a, and OR3a were prepared by dissolving the respective compound in dichloromethane solution (100 mL each). An equivalent amount of aqueous solution at pH 1-14 (± 0.05) was added to separate vials containing 5 mL of OR2a or OR3a in organic solvent and shaken for 60 seconds. The solution was left undisturbed overnight, and the organic layer isolated for hydrolysis studies employing UV-Vis. The extent of hydrolysis at different pH was interpreted relative to the spectra at neutral pH.

Results and Discussion

Hydrolysis

The two-phase hydrolysis study of OR2a indicates that the ligand hydrolyzes in extreme pH conditions (pH 1,2 and 12-14) while OR3a also hydrolyzes in extreme pH conditions (pH 1,2 and 11-14). The hydrolysis profile of compounds OR2a and OR3a are shown in figures 7-9.

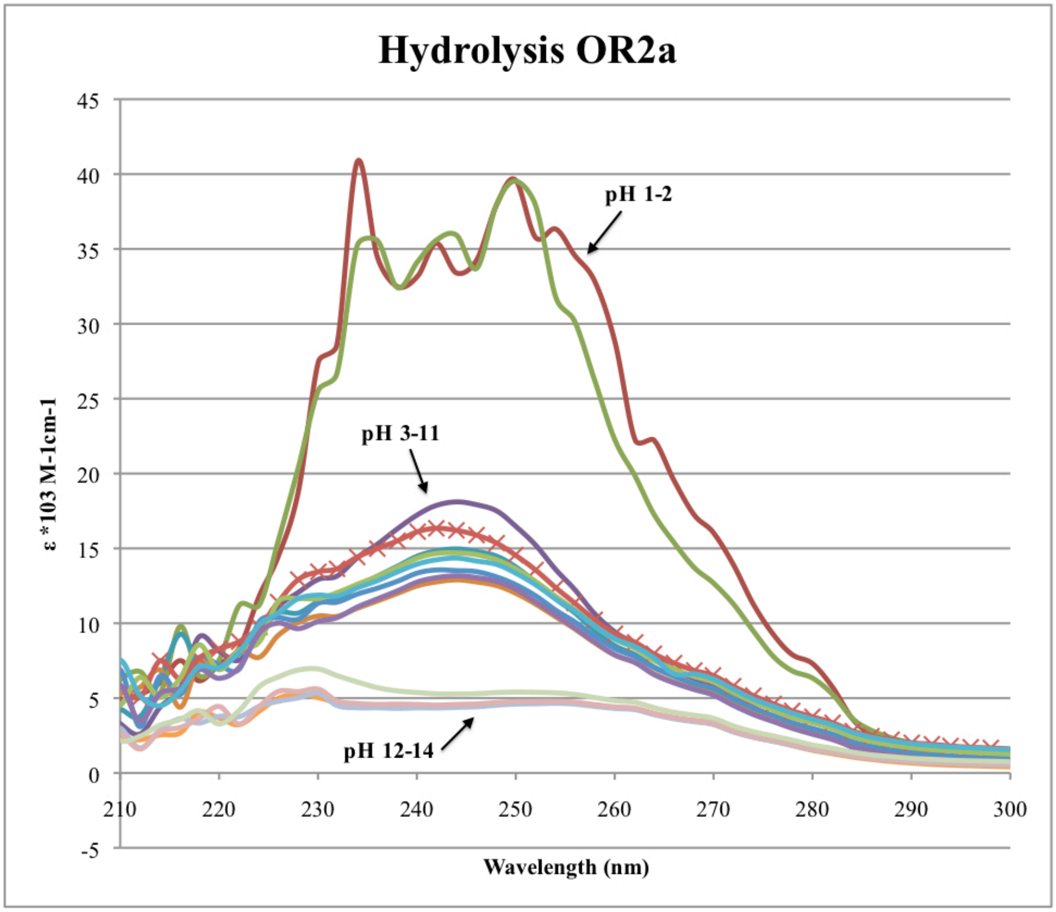


Figure 7: Hydrolysis of OR2a as extinction vs. wavelength. The band indicated by the x corresponds to neutral pH.

In the UV-VIS spectra of OR2a, there is a significant change in extinction maximum at pH 1 and 2 compared to that observed at pH 7. Another significant change in extinction is also observed in pH 12-14 compared to pH 7 as well as the characteristic extinction maximum wavelength peak around 245 nm is absent.

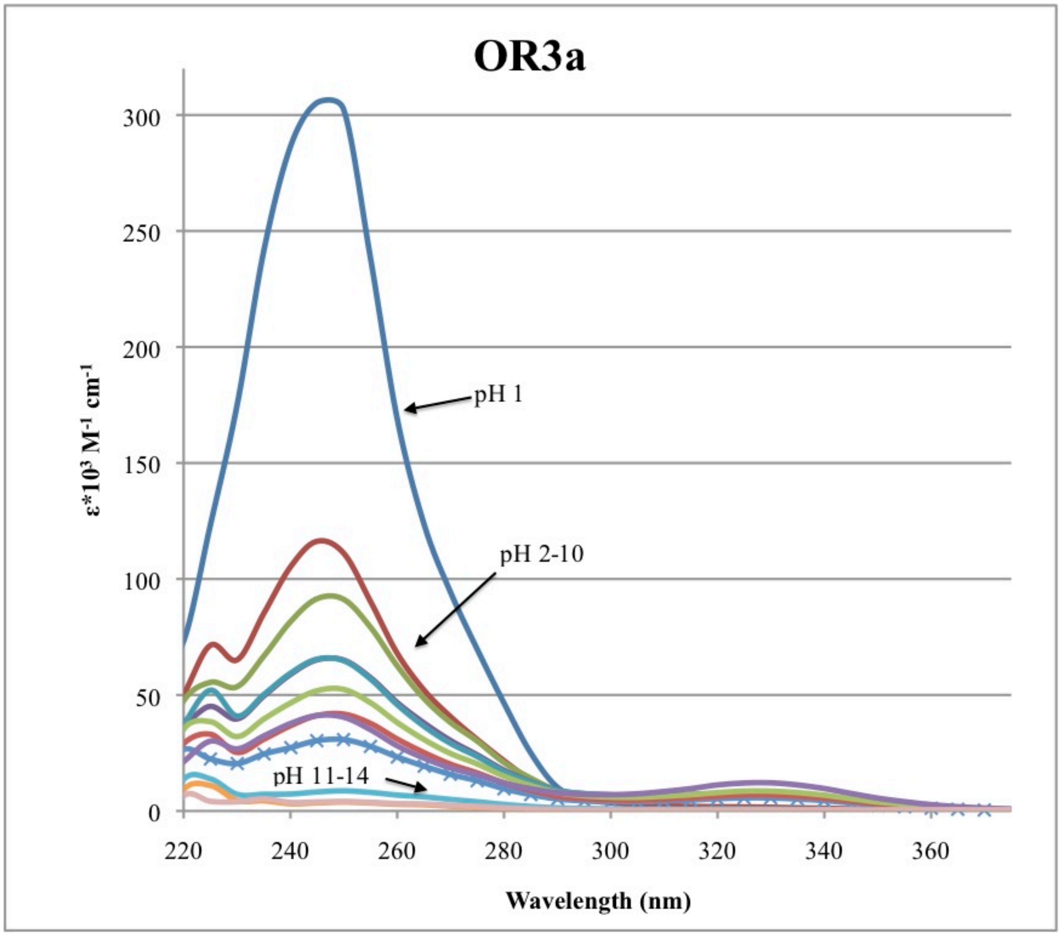


Figure 8: Hydrolysis of OR3a as extinction vs. wavelength. The band indicated by x corresponds to neutral pH.

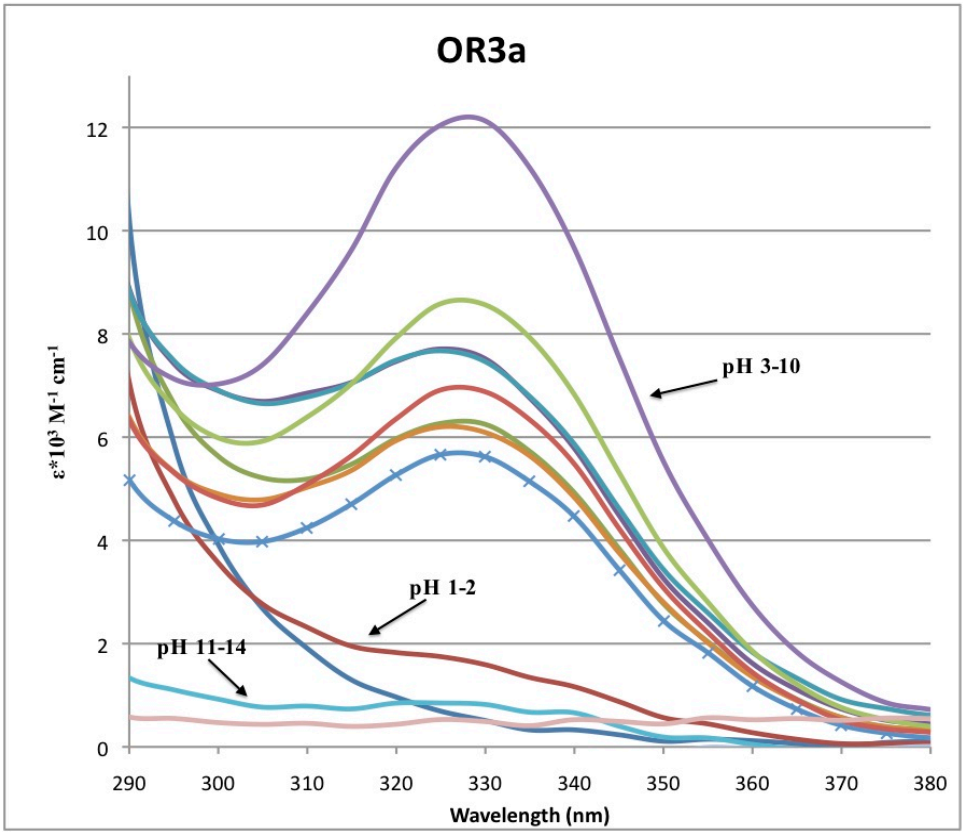


Figure 9: Close-up of extinction maximum that forms at 330 nm with pH 3-10. X indicates neutral pH in the hydrolysis of OR3a

In the UV-VIS spectra of OR3a, there is a significant change in extinction maximum between pH 1 and pH 2. Then there is another extinction maximum change between pH 10 and 11. Perhaps even more significant is the formation of extinction maximum at 330 nm. This extinction maximum is only formed for pH 3-10 giving indication that the ligand would still hydrolyze at pH 2. For pH 11-14, the characteristic extinction maximum at 245 nm is absent.

Extractions

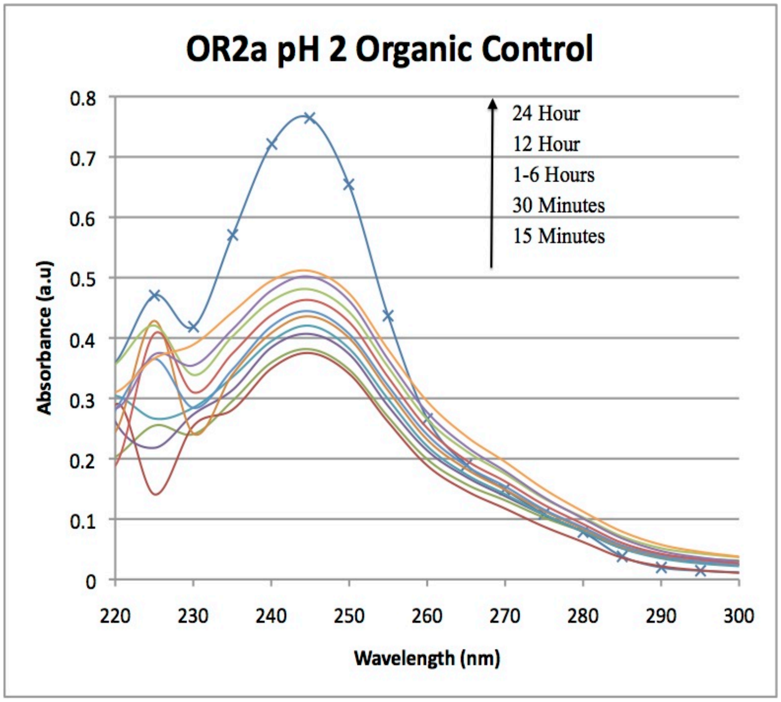
Based on the hydrolysis of the ligand and literature reference, simple extractions were tested in the pH range of 2-5 with ratios of 2:1, 1:1, and 1:2 uranyl (as UO_2^{2+}) to ligand for compounds OR2a and OR3a. The phases were agitated by stirring for time periods indicated on graphs, stopped, allowed 10 minutes to equilibrate, and each layer drawn off into a cuvette for UV-Vis measurement.

Typically, in these types of uranyl extractions, the efficacy of the ligand is quantified by the disappearance and eventual absence of the characteristic UO_2^{2+} extinction maximum at *ca.* 420 nm;[8] however, due to the high absorbencies (i.e. extinction coefficients) of these ligands, the concentration of the ligand must be decreased to micro molar scale and the smaller extinction coefficient of the characteristic extinction maximum is such that it cannot be distinguished from that of the ligand. Therefore, extraction efficacy is characterized by the formation of the metal/ligand complex and characterization of the organic and aqueous layers. Typically binding would be indicated by a shift of 20-25 nm from the ligand peak. With such a significant shift, it is commonly accepted that the ligand binds the metal tightly and is not partially binding. An equilibrium equation for metal binding in the aqueous phase is shown in equation 1; however, this only works at pH 3 or higher, as there is hydrolysis at pH 2.

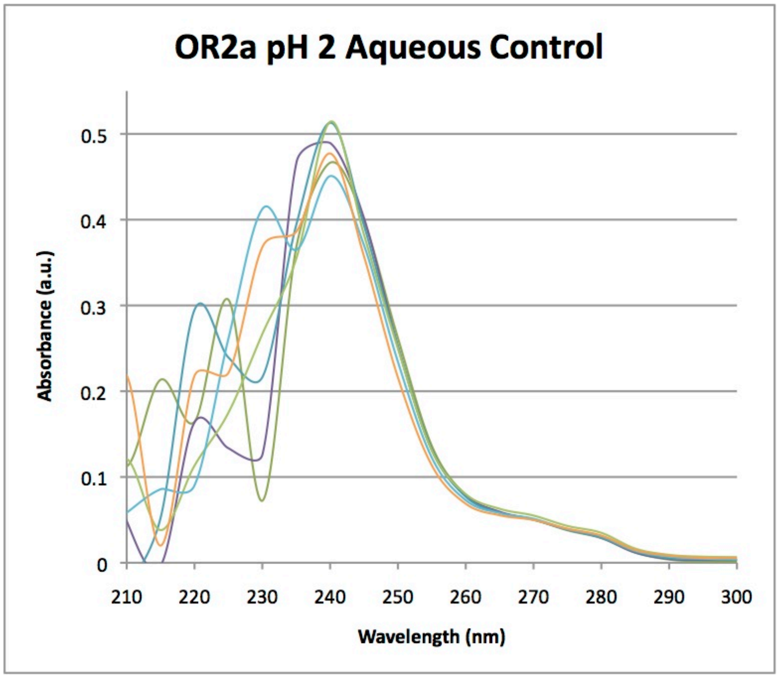
The estimated extraction percentage was calculated by taking the difference in the absorbance between the final measurement in the organic phase and the first measurement in the organic phase at 15 minutes. This was divided by the extinction coefficient of the ligand and then divided by the concentration of the ligand to get the estimated percent extraction. Without the characteristic uranyl peak, the percent extraction is much more complicated to estimate.

$$yUO_2(H_2O)_8^{2_x+} + xL^{2-} \rightleftharpoons (UO_2)_y(L)_x(H_2O)_{8y-4x}^{2-x} + 4xH_2O$$

OR2a pH 2


OR2a pH 2 Organic Control
Absorbance (a.u)
Wavelength (nm)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220
230
240
250
260
270
280
290
300
24 Hour
12 Hour
1-6 Hours
30 Minutes
15 Minutes

A)


OR2a pH 2 Aqueous Control
Absorbance (a.u.)
Wavelength (nm)
0.5
0.4
0.3
0.2
0.1
0
210
220
230
240
250
260
270
280
290
300

B)

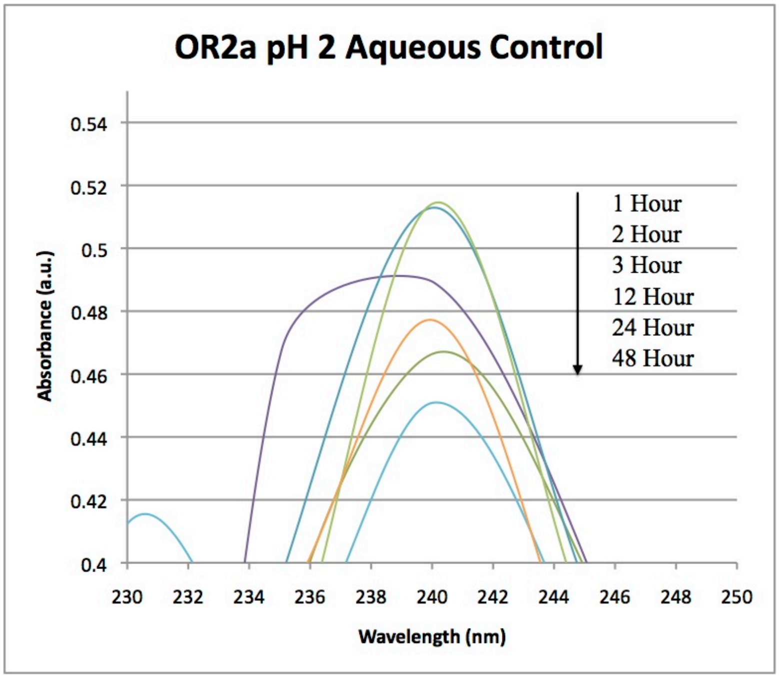
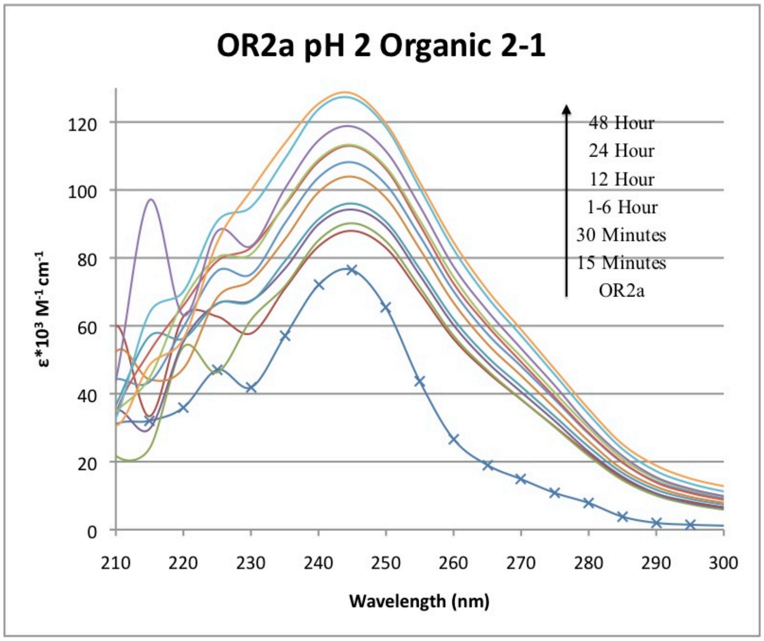
C)


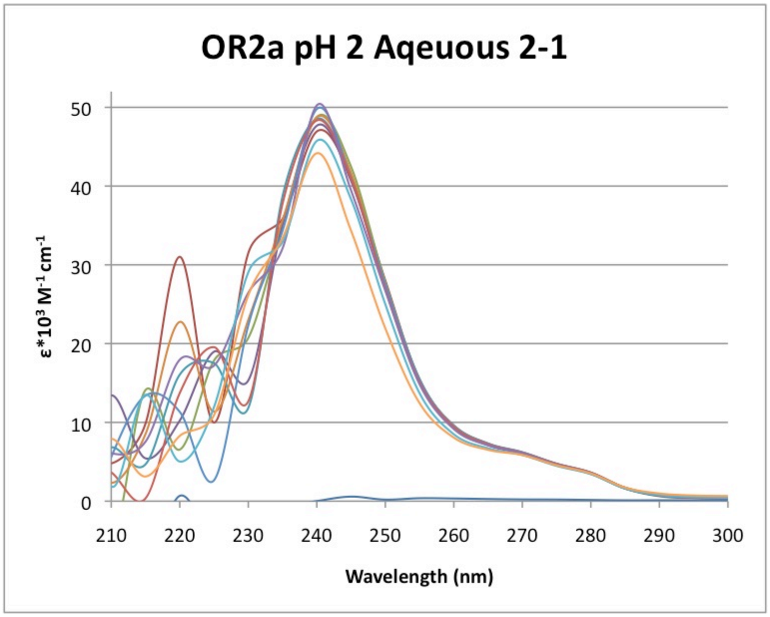
Figure 10: Graph of the control absorbance vs. wavelength of OR2a (10 µM) at pH 2 to determine the wavelength of the ligand in the aqueous phase (no uranyl). A) Organic phase, time plot at 245 nm B) Overall aqueous phase spectrum; C) Close up of aqueous phase around 240 nm. Time plotted at 240 nm.

The UV-Vis spectra above in figure 10, shows that even though the ligand should be somewhat hydrophobic; it will transfer into the aqueous layer and remain there. It will however, transition back into the organic phase slowly over time as evidenced by the decrease in extinction over time.

A)


OR2a pH 2 Organic 2-1
ε*10³ M⁻¹ cm⁻¹
0
20
40
60
80
100
120
210
220
230
240
250
260
270
280
290
300
Wavelength (nm)
48 Hour
24 Hour
12 Hour
1-6 Hour
30 Minutes
15 Minutes
OR2a

B)


OR2a pH 2 Aqeuous 2-1
ε*10³ M⁻¹ cm⁻¹
0
10
20
30
40
50
210
220
230
240
250
260
270
280
290
300
Wavelength (nm)

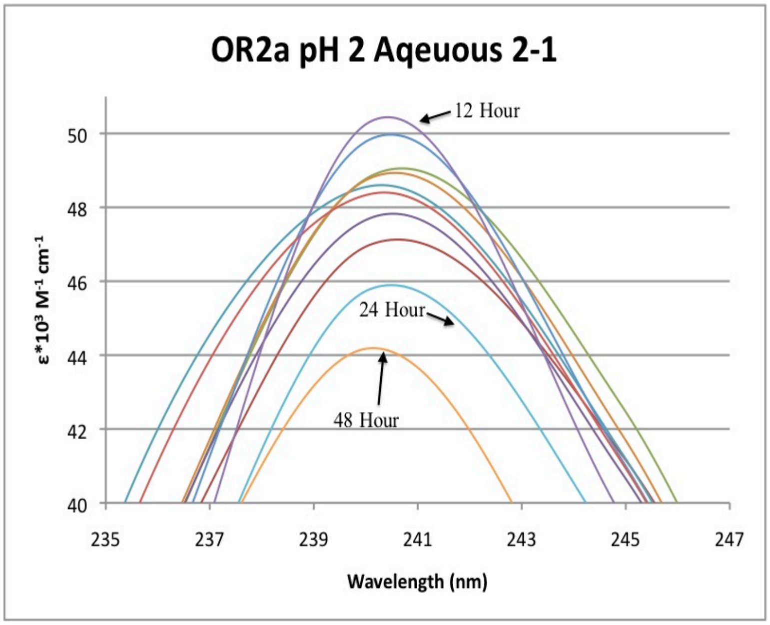
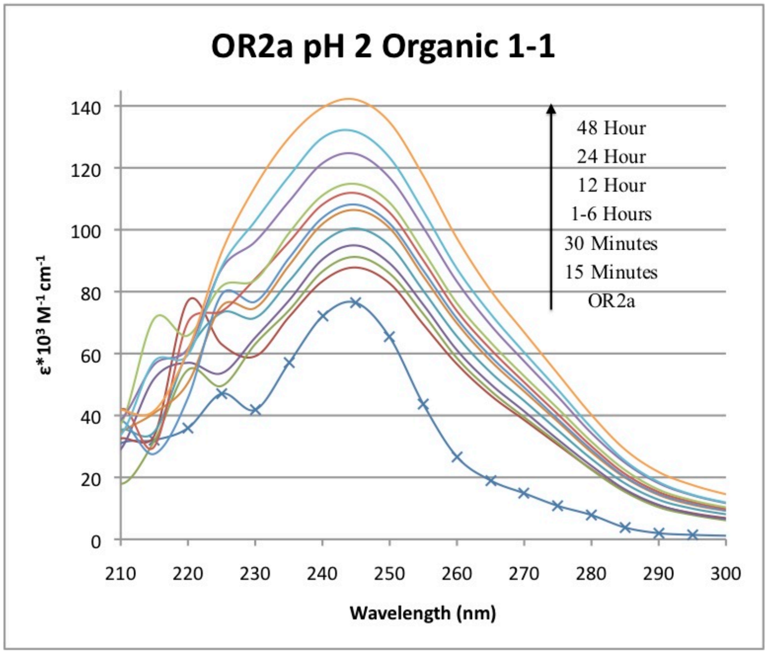
C)


Figure 11: Graph of extinction vs. wavelength for the extraction of uranyl (20 μM) from the aqueous phase (H_2O) at pH 2 by OR2a (10 μM) in the organic phase (DCM). A) Organic phase time plotted at 245 nm; B) aqueous phase; C) close up of aqueous phase around 240 nm.

In the figure above, with OR2a at pH 2 and a ratio of 2-1 (metal to ligand), in the organic layer (DCM), the extinction maximum is increasing at a steady rate based on the time between measurements. Up until the 24th hour, there is an increase of 20000 extinction units from the first measurement, indicative of the metal-ligand complex transferring into the organic phase; however between the 24th hour and the 48th hour there is only an increase of 1000 extinction units indicating that the ligand may be close to maximum extraction efficiency. The extinction maximum in the aqueous layer is decreasing, confirming that the ligand coordination and metal complex is being taken into the organic phase. The decrease between the 12th hour and the 24th hour is about 5000 extinction units, and between the 24th hour and 48th hour there is a decrease of just a little over 1000 extinction units, just like the organic phase. Unlike other similar systems, there is no wavelength shift in the extinction; however the change in extinction is far greater than effects seen due to changes in pH. This indicates that at this ratio of metal to ligand maintained at this pH, the ligand binding is not very strong for uranyl. Instead of all four sulfurs coordinating to uranyl, it is possible that only two, or only one sulfur is binding. From the hydrolysis data above, a second possibility is that the ligand could by hydrolyzing with the addition of the metal salt (decreasing below pH 2), the ligand-metal complex is not stable for very long. In comparison to control solutions containing ligand in the organic phase, we find that at this pH there is some evidence for the transfer of the ligand into the aqueous phase. This makes it difficult to interpret the data, as there is not clear evidence of the formation of metal complex and subsequent sequestration of the metal-ligand complex entirely in the organic phase. With the control as a basis for the shift in the aqueous phase, the maximum extinction in the controls is at 240 nm, and it is the same for the aqueous phase. From the data above, we presume that there is about 50-60% uranyl extraction, but is difficult to say this with certainty because of the potential for hydrolysis.

A)



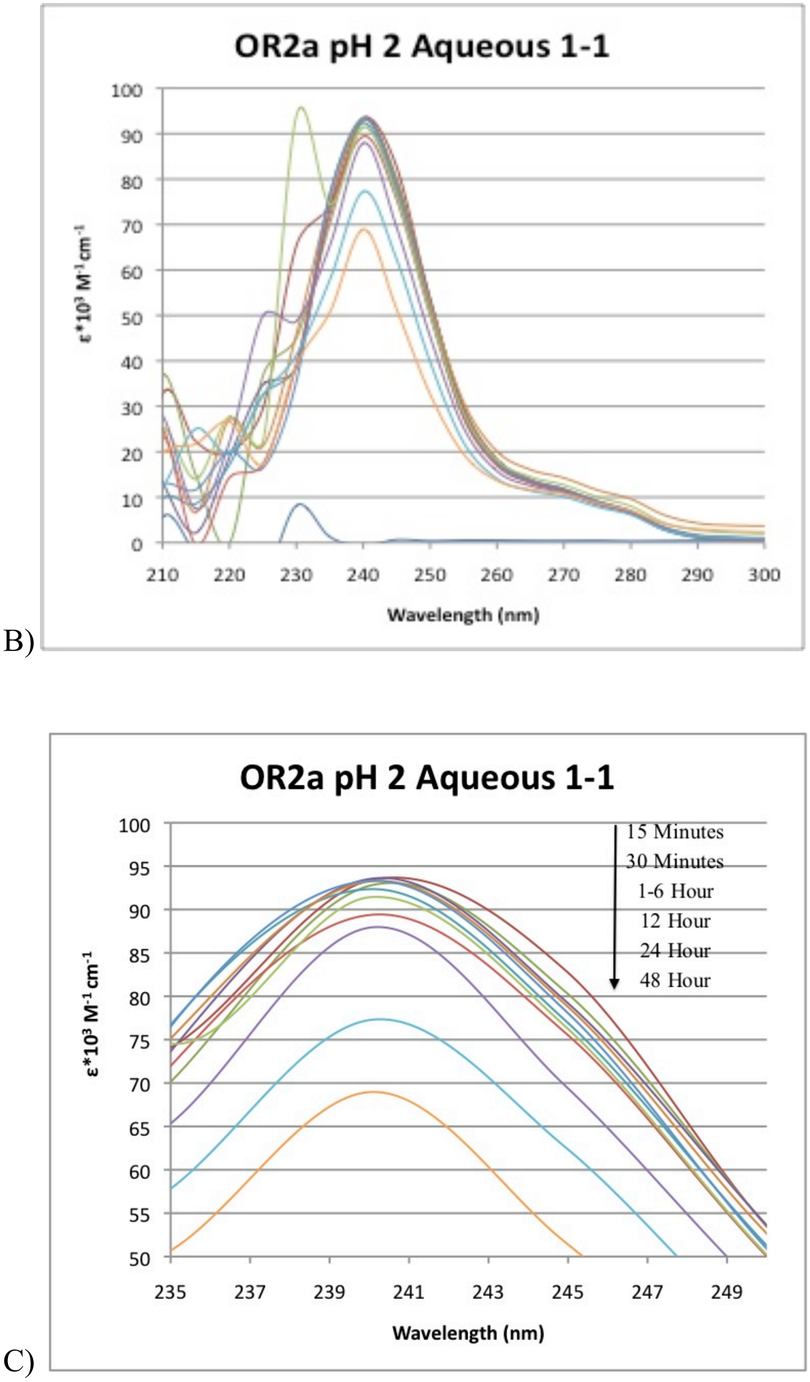
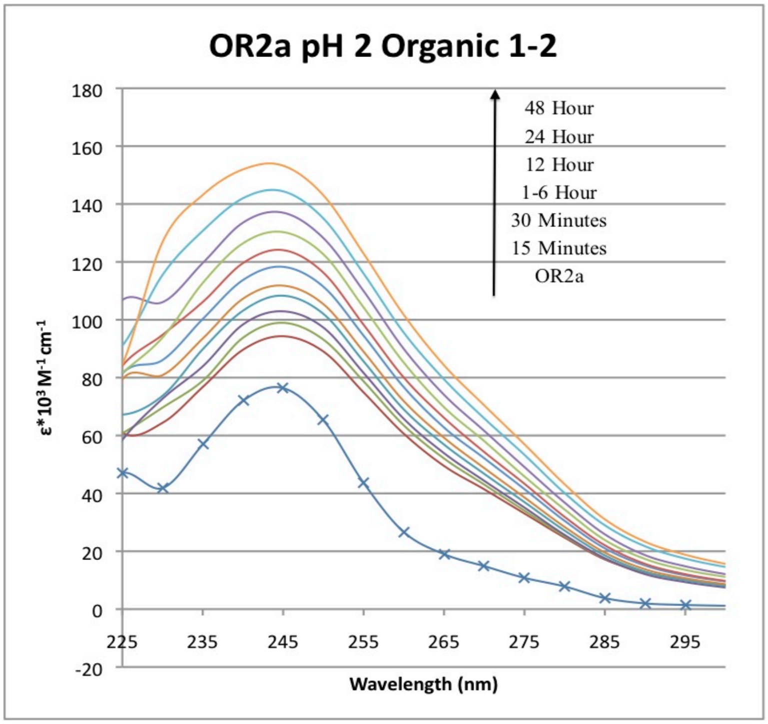


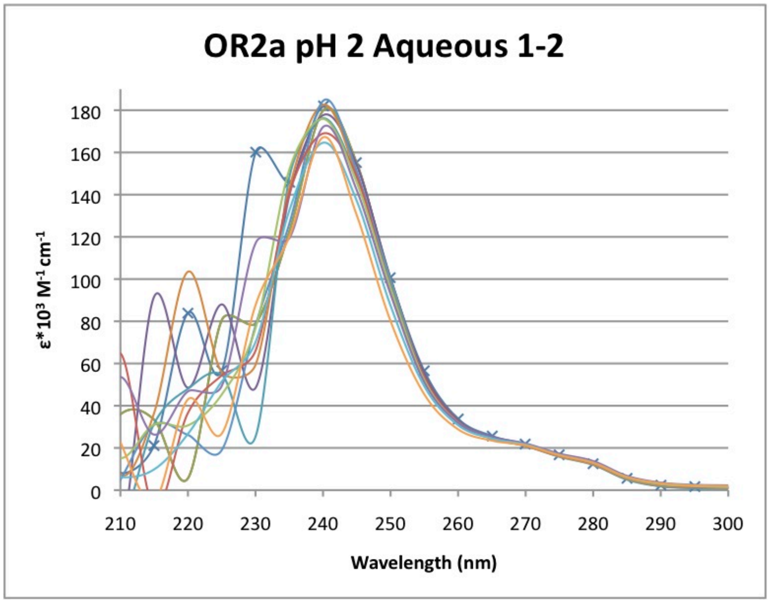
Figure 12: Graph of extinction vs. wavelength for the extraction of uranyl (10 μM) from the aqueous phase (H_2O) at pH 2 by OR2a (10 μM) in the organic phase (DCM). A) Organic phase. Time plotted at 245 nm; B) Aqueous phase; C) Close up of aqueous phase around 240 nm. Time plotted at 240 nm

When the ratio of uranyl to ligand is equal, there is no change in the maximum extinction wavelength typically indicative of binding between the ligand and metal. At this ratio, as time of exposure is increased, there is evidence of the metal complex continuing to separate into the organic layer. This hypothesis is confirmed in both the aqueous and organic layers by the 12, 24, and 48-hour measurements. Significant increases in extinction maximum of 10000 extinction units between 6 and 12 hours, 7000 extinction units between 12 and 24 hours, and 11000 units between 24 and 48 hours at 245 nm are noted in the organic phase. Based on the difference from the control, the change of 28000 extinction units to reach equilibrium, it is estimated to indicate that 60-70% of the uranyl has been extracted.

Significant decreases in extinction maximum of 5000 extinction units between 6 and 12 hours, 10000 extinction units between 12 and 24 hours, and 9000 extinction units between 24 and 48 hours in the aqueous phase at 240 nm are noted. In neither phase does the maximum extinction shift from the initial extinction wavelength seen in the control with the ligand at the target pH.


OR2a pH 2 Organic 1-2
48 Hour
24 Hour
12 Hour
1-6 Hour
30 Minutes
15 Minutes
OR2a
ε*10³ M⁻¹ cm⁻¹
180
160
140
120
100
80
60
40
20
0
-20
225
235
245
255
265
275
285
295
Wavelength (nm)

A)


OR2a pH 2 Aqueous 1-2
ε*10³ M⁻¹ cm⁻¹
180
160
140
120
100
80
60
40
20
0
210
220
230
240
250
260
270
280
290
300
Wavelength (nm)

B)

C)

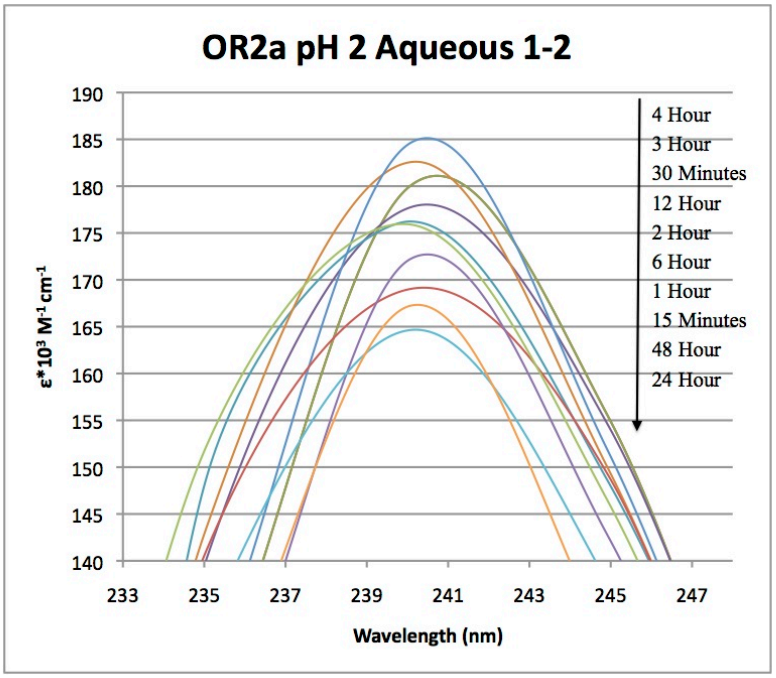


Figure 13: Graph of extinction vs. wavelength for the extraction of uranyl (5 µM) from the aqueous phase (H_2O) at pH 2 by OR2a (10 µM) in the organic phase (DCM). A) Organic phase. Time plotted at 245 nm; B) Aqueous phase; C) Close up of aqueous phase around 240 nm. Time plotted at 240 nm

Comparing the organic phase to the UV-Vis spectra seen in a system with an excess of ligand, as depicted in figure 13, an increase in the extinction maximum at each time interval at 245 nm is noted. The extinction wavelength shift at its maximum of 245nm is minimal. The ligand may be coordinating the uranyl ion, but not strongly enough to cause a shift in the extinction wavelength. From the blank, there is an initial increase of approximately 18000 extinction units at 15 minutes. The total increase in extinction after 48 hours is 76900 extinction units from the blank. Since the extinction is still increasing, this is indicative of the ligand not reaching equilibrium or maximum extraction efficiency yet.

The spectral changes with time of the aqueous layer are also quite interesting. In the control experiment the ligand will freely go into the aqueous layer at pH 2 and remain there. With an excess of ligand, ligand goes into the aqueous layer, and some of the ligand will remain there, while the rest will coordinate metal and equilibrate with the organic layer. During the first two hours, the extinction maximum has decreased about 6700 extinction units, but increased by 8000 extinction units from the 2nd to the 4th hour. After the 5th hour, there is a dramatic drop of 15000 extinction units followed by a small subsequent increase in the 6th hour of 6000 extinction units. The extinction decreased by 11000 extinction units from the 6th hour to the 48th hour. From the data above, we believe to be about 70-80% extraction of uranyl, but with the hydrolysis of the ligand, it is inconclusive.

With the dramatic drop of extinction maximum after the 5th hour, there is not a dramatic increase in extinction in the organic layer as one might expect, possibly indicating that the ligand-metal complex is soluble both in the organic and aqueous phases, or that some of the complex is precipitating or forming a third-phase system.

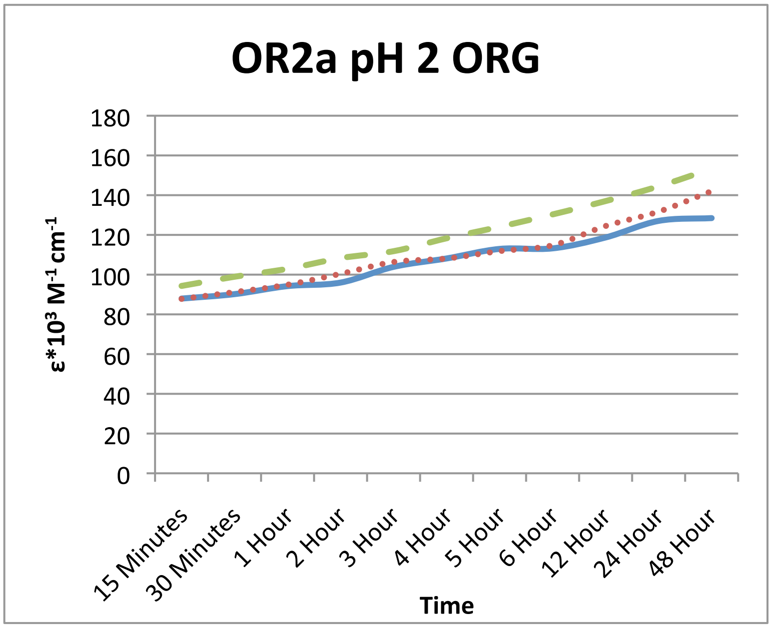
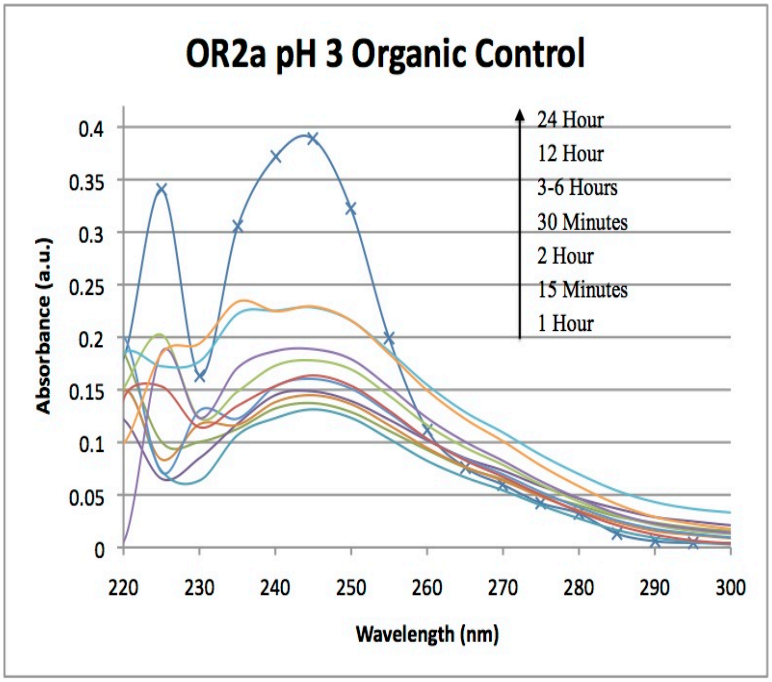


Figure 14: Graph of extinction vs. time for OR2a at pH 2 in the organic phase. –– 2-1 ratio, ++ 1-1 ratio, - - 1-2 ratio (metal to ligand)

OR2a pH 3

A) 

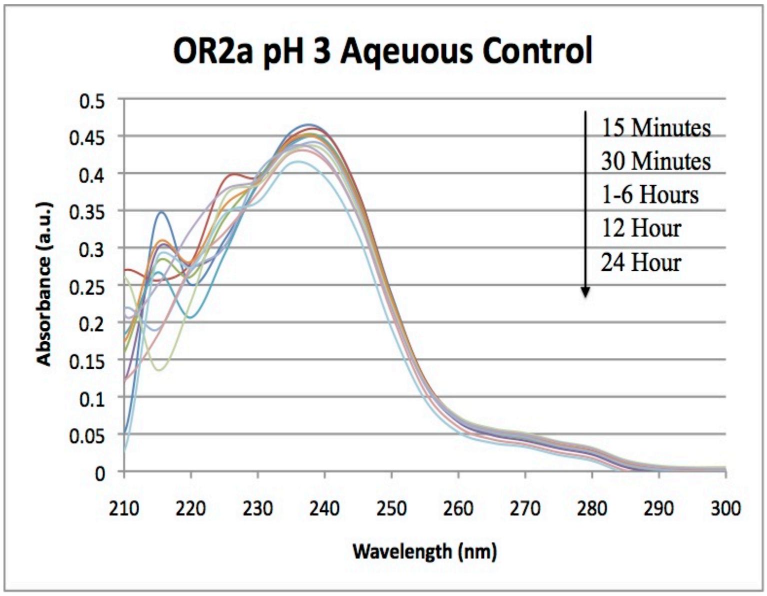
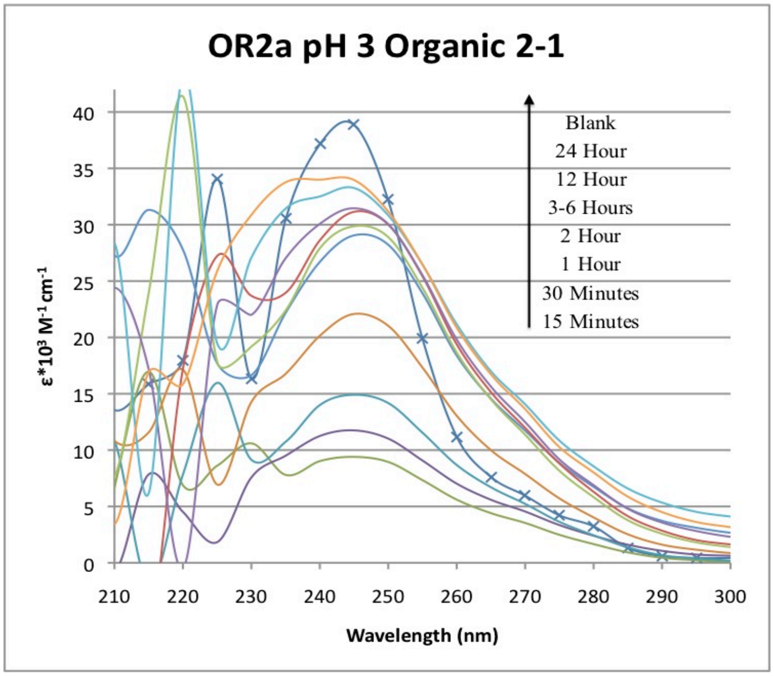
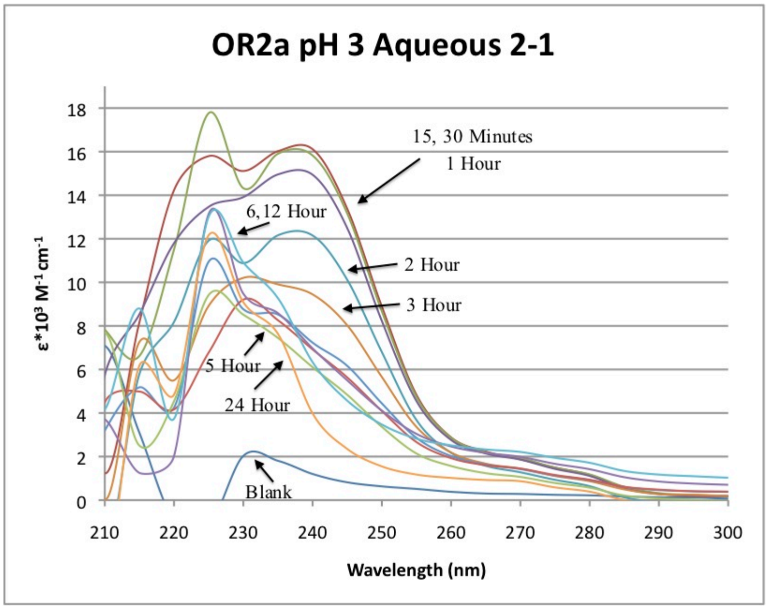
B) 

Figure 15: Graph of the control extinction vs. wavelength of OR2a (10 μM) at pH 3 to determine the wavelength of the ligand in the aqueous phase (no uranyl). A) Organic phase, time plotted at 245 nm. B) Aqueous phase, time plotted at 240 nm.

The UV-Vis spectra above in figure 15, shows that even though the ligand should be somewhat hydrophobic; it will transfer into the aqueous layer and remain there. It will however, transition back into the organic phase slowly over time as evidenced by the decrease in extinction over time.



A)

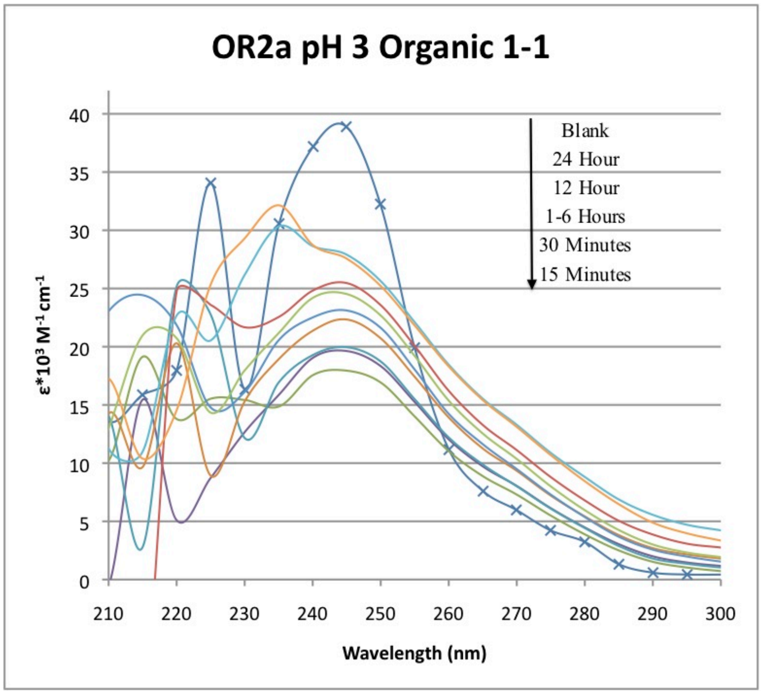


B)

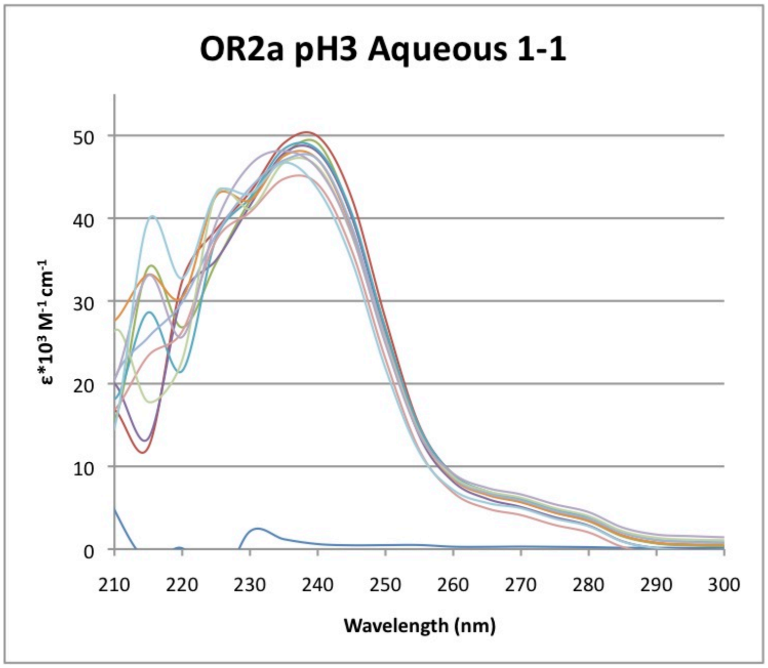
Figure 16: Graph of extinction vs. wavelength for the extraction of uranyl (20 μM) from the aqueous phase (H_2O) at pH 3 by OR2a (10 μM) in the organic phase (DCM). A) Organic phase. Time plotted at 245 nm; B) Aqueous phase

At pH 3 with OR2a and a ratio of 2-1 (metal to ligand), (as shown in figure 16) all of the recorded extinction measurements are not above the blank at 39000 extinction units but are increasing in extinction maximum at every interval in the organic phase. The extinction increased by 19600 extinction units from 15 minutes to the 2nd hour measurements; however, after 3 hours, the extinction maxima tightly overlay again, possibly indicating the ligand is getting close to maximum extraction efficiency at this pH, having already extracted all the uranyl it can into the organic layer. The extinction peaks are also broadening at time increases, which could indicate binding of the uranyl in the organic phase. However, without the shift, the ligand binding is not very strong for uranyl. Instead of all four sulfurs binding to uranyl, possibly only one or two sulfurs are binding. In comparison to control solutions containing ligand in the organic phase, we find that at this pH there is some evidence for the transfer of the ligand into the aqueous phase.

In figure 15b, depicting the extinction of the aqueous phase from the extraction at pH 3 with a two-fold excess of uranyl is not straightforward. The overall trend is that the extinction maximum decreases with time. While the first few measurements at 15 minutes, 30 minutes, and 1-3 hours are extinction maxima at a wavelength of 240 nm, the 5, 6, 12, and 24 hour extinction maxima appear to have shifted to approximately 230 nm. This is promising but it does not indicate a strong binding and shift of 20-25 nm, as one would expect. This is a definite improvement over the results seen in the characterization of extraction at pH 2. In comparison to control solutions containing ligand in the organic phase, we find that at this pH there is some evidence for the transfer of the ligand into the aqueous phase. The ligand does fluctuate between the organic and aqueous layers at this pH, which is a problem if it does not form a hydrophobic complex with uranyl. From the data above, we believe that there is about 55-65% extraction of uranyl.


OR2a pH 3 Organic 1-1
40
35
30
25
20
15
10
5
0
ε*10³ M⁻¹ cm⁻¹
Blank
24 Hour
12 Hour
1-6 Hours
30 Minutes
15 Minutes
210
220
230
240
250
260
270
280
290
300
Wavelength (nm)

A)


OR2a pH3 Aqueous 1-1
50
40
30
20
10
0
ε*10³ M⁻¹ cm⁻¹
210
220
230
240
250
260
270
280
290
300
Wavelength (nm)

B)

C)

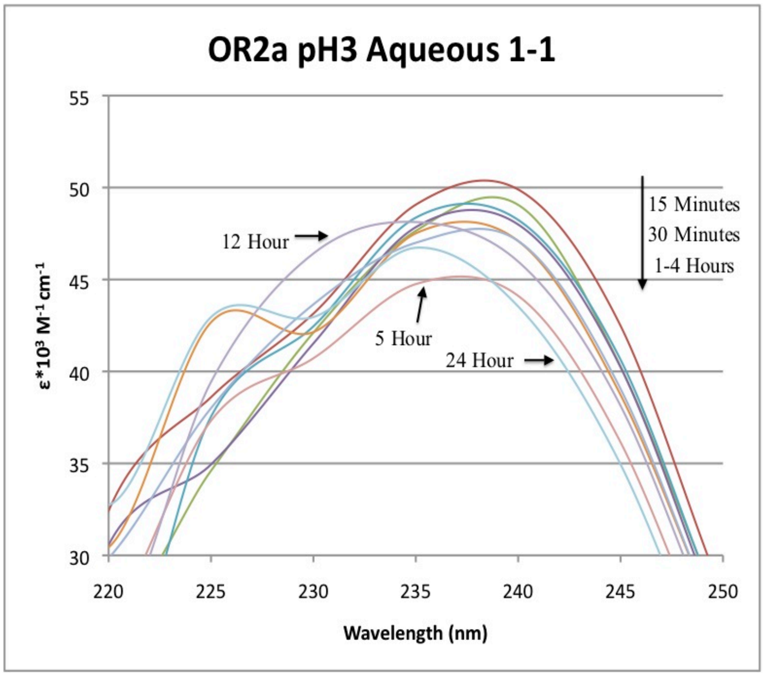
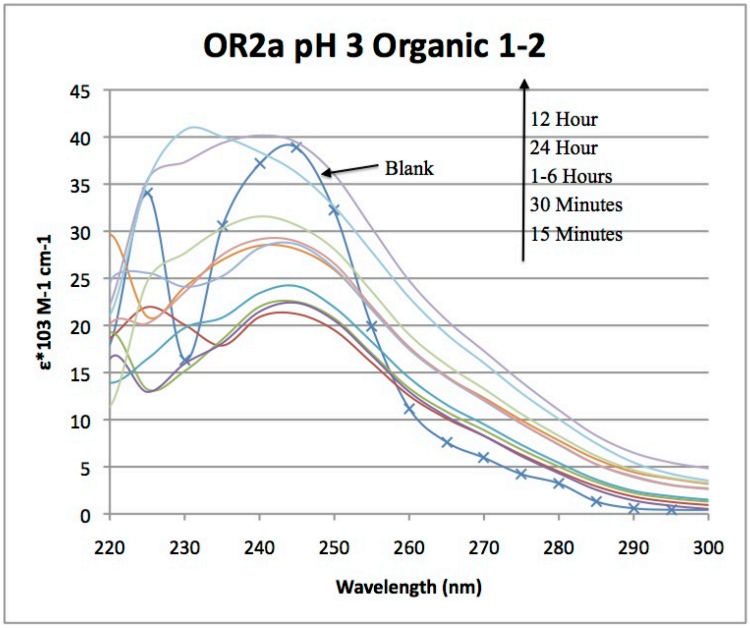
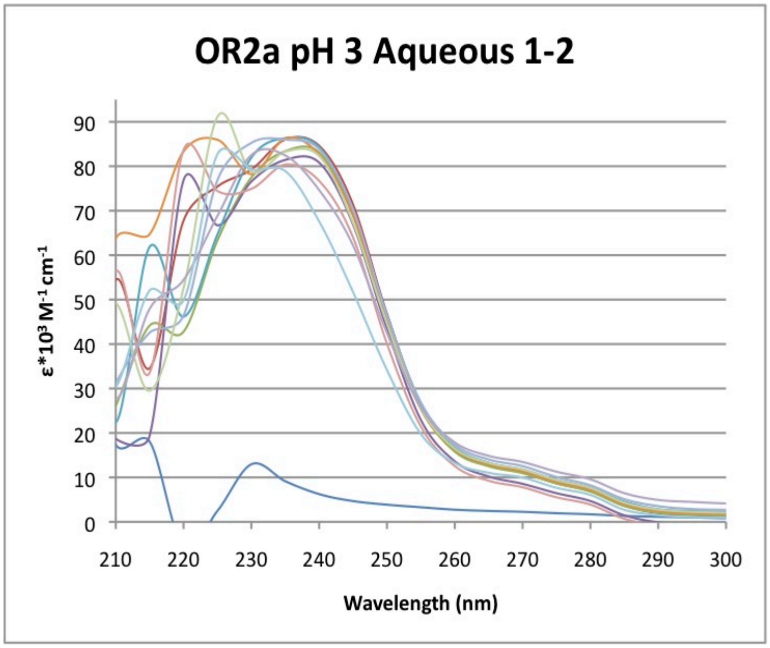


Figure 17: Graph of extinction vs. wavelength for the extraction of uranyl (10 μM) from the aqueous phase (H_2O) at pH 3 by OR2a (10 μM) in the organic phase (DCM). A) Organic phase. Time plotted at 245 nm; B) Aqueous phase; C) Close up of aqueous phase around 240 nm. Time plotted at 240 nm

In the UV-Vis spectral data from the organic phase (figure 17) for an extraction of ligand:metal 1:1 for the aqueous layer at pH 3, a demonstrable increase in extinction maximum at 245 nm is noted. Also noted is a shift of approximately 10 nm after 12 hours with an extinction of 30350 a difference of 12400 extinction units from the first measurement. Again this is indicative of a kinetics problem associated with the ligand binding. If it requires 12 – 24 hours to bind effectively, although not fully, this will not be good for extractions on an industrial scale. Between the 12th and 24 hour measurement, there is only a small increase of 2000 extinction units indicating that the ligand may be reaching full extraction efficiency and equilibrium.

In the aqueous phase, the decrease in maximum extinction of 800 extinction units at 240 nm is noted, and then at the 12 hour measurement, an increase in maximum extinction of 4100 extinction units from the 5th hour, but at 235 nm indicating a shift in the wavelength of 5 nm from the initial measurements. At the 24-hour mark, a decrease in extinction maximum to 46700 (overall decrease of 3100 extinction units) was observed also at 235 nm, indicating that the metal complex was transitioning back into the organic phase. This helps confirm that there is a metal complex in the organic phase as indicated by the shift as stated earlier. It is believed that 30-40% of the uranyl was extracted into the aqueous phase.

A)


B)


C)

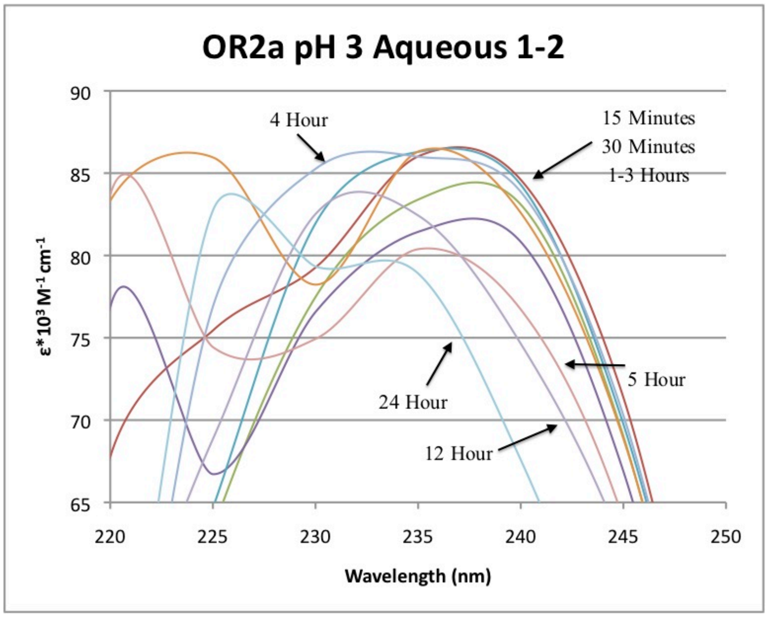


Figure 18: Graph of extinction vs. wavelength for the extraction of uranyl (5 μM) from the aqueous phase (H_2O) at pH 3 by OR2a (10 μM) in the organic phase (DCM). A) Organic phase Time plotted at 245 nm; B) Aqueous phase; C) Close up of aqueous phase around 240 nm.

In figure 18, with an excess of ligand is a similar as compared to the data shown in figure 15 with excess uranyl. The early measurements still feature the extinction maxima at the same wavelength as the control without any uranium, and later measurements such as the 6, 12, and 24-hour measurements, have a shift of 5, 5, and 15 nm respectively. This 15 nm shift is indicative of metal complexation and extraction into the organic phase, but the slow change confirms slow coordination, a kinetic problem with the ligand. The shift is still not in the 20-25 nm range typical of strong binding. Further investigations would be needed to probe the nature of this reaction, given the initial slow kinetics and if the rate can be improved with heat. Between the 15th minute and 12th hour, there is an increase in extinction of 19000 extinction units. The slowing of the increase extinction maximum between 12 and 24 hours appears to indicate that the extraction is complete or has achieved equilibrium.

Changes seen in the UV-Vis spectra for the aqueous phase at pH 3 and excess ligand in figure 16 are quite remarkable. It demonstrates that even with excess ligand, more of the ligand is likely to remain in the aqueous phase than to transfer back into the organic phase. As time increases, the extinction maximum is decreased and there is a small shift of 5 nm indicating binding in the aqueous phase, although not very strong. Because binding is indicated at the 4th hour, uranyl coordinating ligand may drop immediately into the organic layer which is why at the 5th hour, there is a decrease in extinction maximum of 4000 extinction units and shift back to the original 240 nm wavelength. The overall decrease in extinction between the 15th minute and 24th hour is 5700 extinction units, much less than the increase seen in the organic phase. Based on the aqueous phase of the control, it is believed that 50-60% of the uranyl is extracted. This is difficult to confirm because of the small decrease in extinction in the aqueous phase.

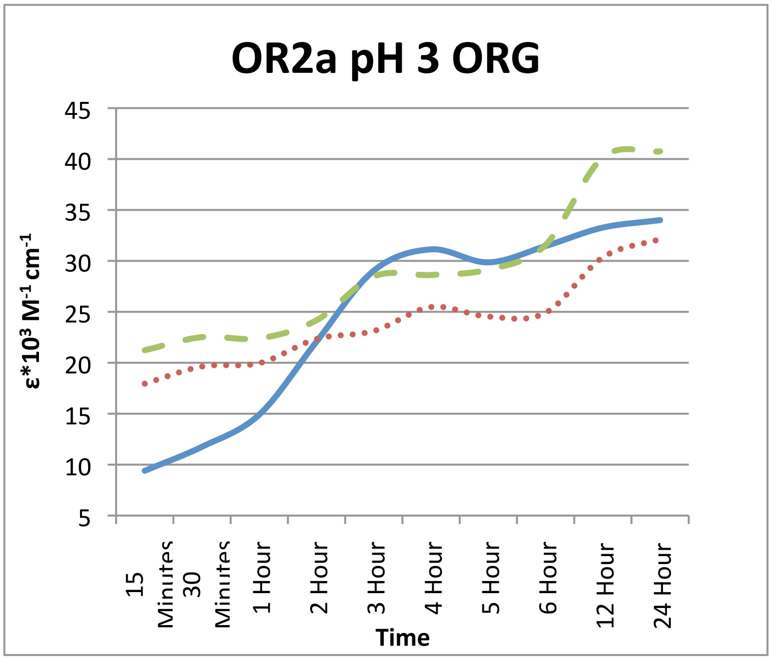
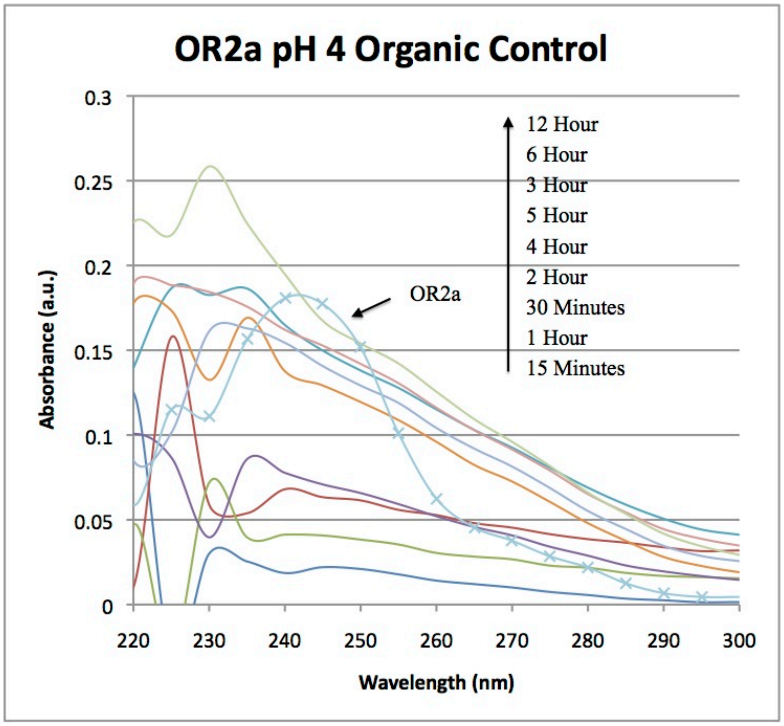


Figure 19: Graph of extinction versus time for OR2a at pH 3 in the organic phase. — 2-1 ratio, ++ 1-1 ratio, - - 1-2 ratio (metal to ligand)

OR2a pH 4

A)



B)

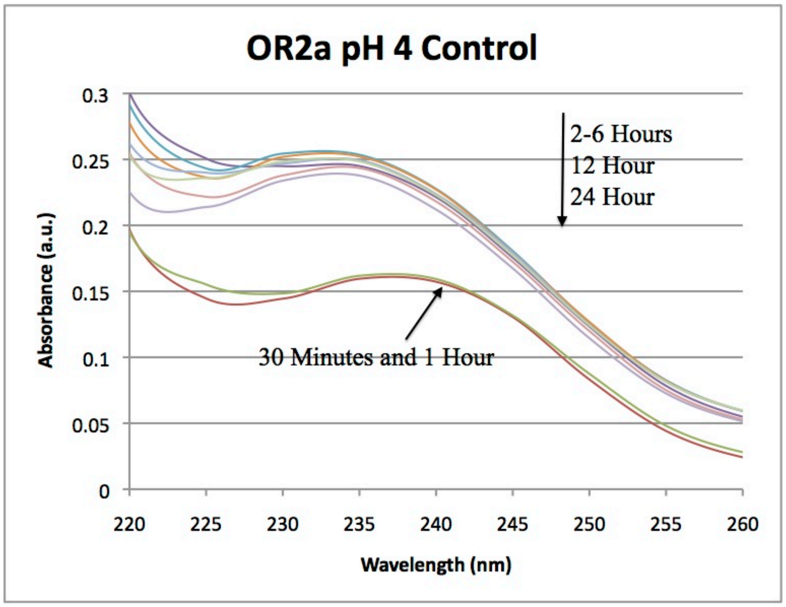
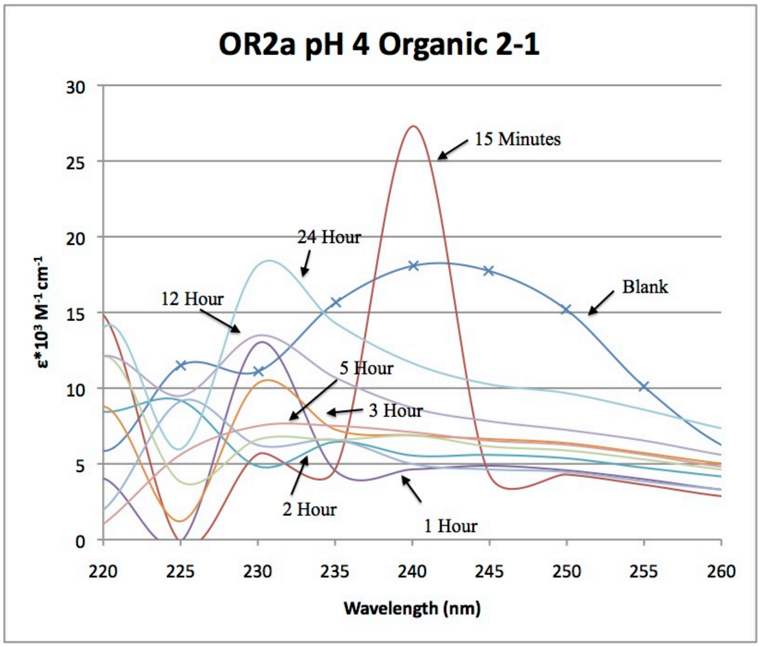
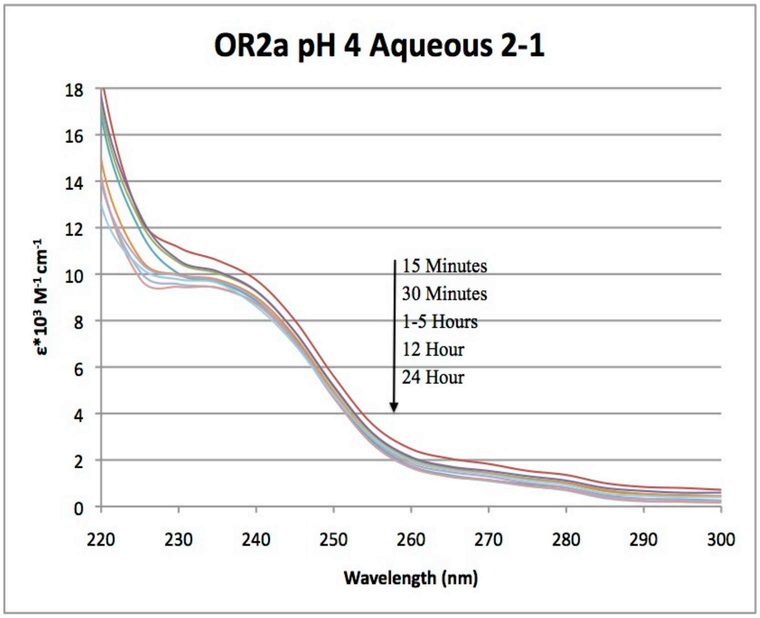


Figure 20: UV-Vis spectrum absorbance vs. wavelength of the control of OR2a at pH 4. A) Organic phase, time plotted at 245 nm. B) Aqueous phase, time plotted at 235 nm.

The UV-Vis spectra above in figure 20, shows that even though the ligand should be somewhat hydrophobic; it will transfer into the aqueous layer and remain there. The ligand even takes some time before equilibrium is reached in the aqueous phase. It will however, transition back into the organic phase slowly over time as evidenced by the decrease in extinction over time.



A)



B)

Figure 21: Graph of extinction vs. wavelength for the extraction of uranyl (20 μM) from the aqueous phase (H_2O) at pH 4 by OR2a (10 μM) in the organic phase (DCM). A) Organic phase; B) Aqueous phase. Time plotted at 235 nm.

In the figure above, with OR2a at pH 4, and a ratio of 2-1 (metal to ligand) in the organic layer, an immediate shift of 5 nm and an extinction of 27300 units are noted. At the 1-hour measurement, the extinction maximum is decreased to an extinction of 4870 and the shift is returned to the ligand blank at 245 nm. At the 2nd hour measurement a shift of 10 nm is noted with an extinction of 6450, an increase of 1580 extinction units over the 1st hour. At the 3rd hour, a shift in extinction maximum of 5 more nm is noted with an increase in the extinction maximum by 4000 units. At the 4th hour measurement a 5 nm shift back towards the ligand blank and a decrease in extinction maximum is noted. An increase of 10600 extinction units at a wavelength of 230 nm between the 5th and 24th hour is a good indication of extraction of uranyl into the organic phase and binding of the metal-ligand complex. More measurements past this time frame would be good for determining if the ligand had reached its extraction efficiency at this pH.

This is very different from the aqueous phase in figure 20c, where there is a decrease in extinction maxima without any fluctuations. Similar to what was seen in the control with OR2a and no uranyl, the first measurement at 15 minutes an extinction maximum at 240 nm is noted. After this measurement, a shift of 5 nm to 235 nm is noted for all measurements up until the 12th hour measurement where another shift of 5 nm of extinction maximum wavelength is noted. An overall decrease of 1000 extinction units, while small compared to the organic phase, is still an indication of the bound metal-ligand complex, going from the aqueous phase into the organic phase. The shift shows the ligand is binding stronger than at pH 2 or 3 in the aqueous phase. While it is good for the ligand to bind to uranyl in the aqueous phase, it is not good if the metal-ligand complex is hydrophilic, as that will hinder extraction. It does not seem to have affected extraction in this case as the extinction maximum increases in the organic phase and decreases in the aqueous phase as noted. 65-75% of the uranyl is believed to be extracted after 24 hours.

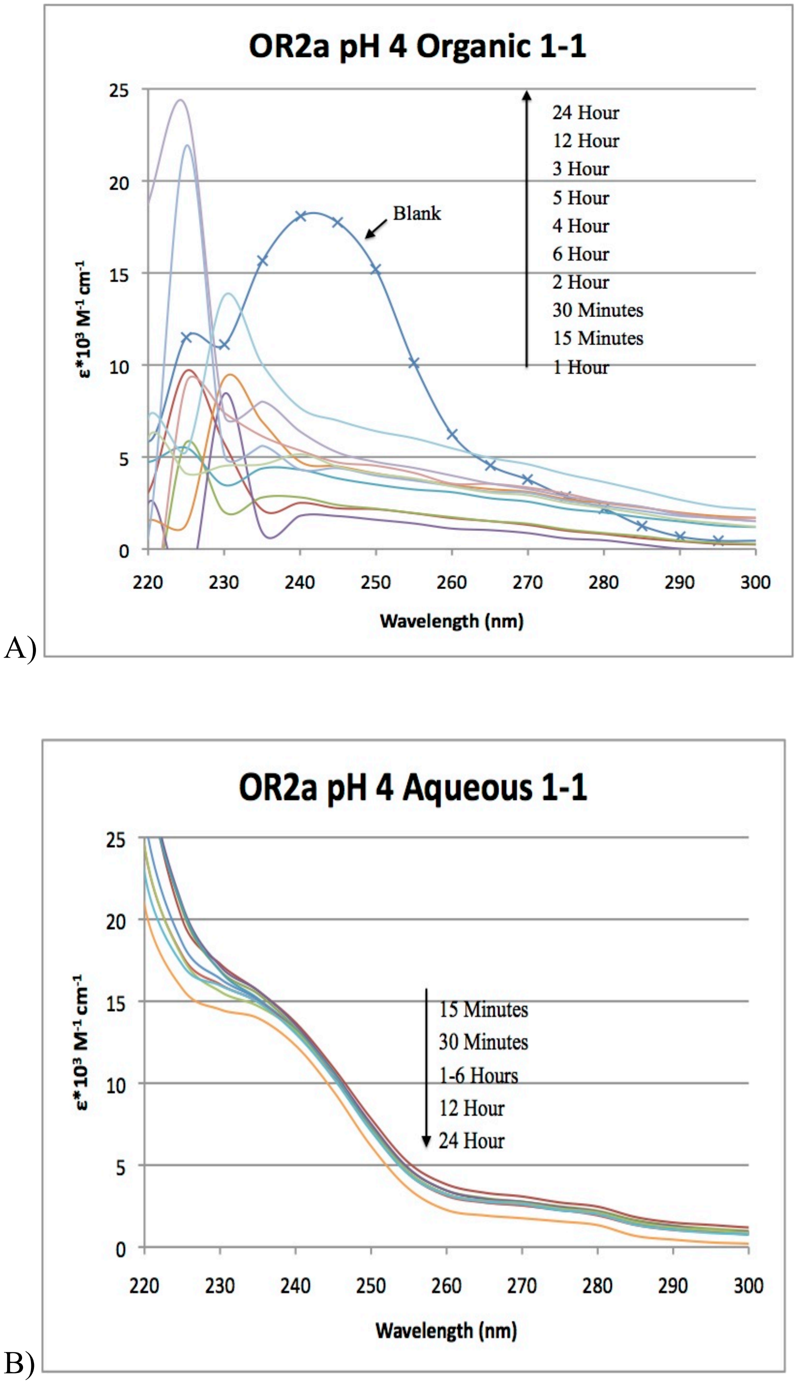
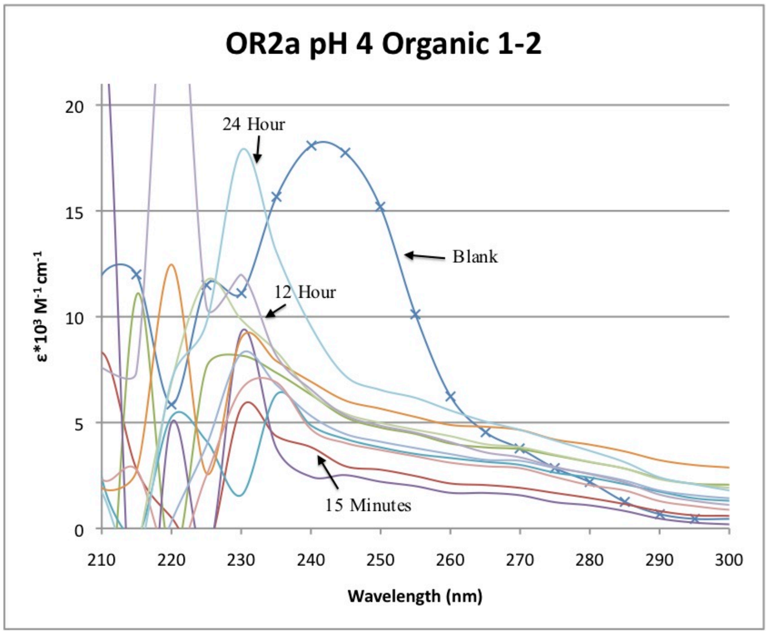


Figure 22: Graph of extinction vs. wavelength for the extraction of uranyl (10 µM) from the aqueous phase (H_2O) at pH 4 by OR2a (10 µM) in the organic phase (DCM). A) Organic phase; Time plotted at 235 nm. B) Aqueous phase. Time plotted at 240 nm

In figure 22 above, with OR2a (10 μM) at pH 4 and that ratio now equal (1:1 metal to ligand), in the organic layer, there are a lot of similarities to both the excess ligand in figure 21 and excess uranyl in figure 19, in that there are well defined maximum extinction shifts with increasing time. While there is an extinction maximum wavelength shift at 30 minutes, and an increase in extinction maximum by 300 extinction units, the 1 hour time measurement the extinction maximum is shifted back to the extinction maximum wavelength of the blank and a decrease of 1000 extinction units. An overall increase of 12000 extinction units from the lowest extinction measurement at 1 hour, and an increase in the maximum extinction wavelength shift to 10 nm from the blank confirm an extraction and binding of uranyl by the ligand in the organic phase. Since the extinction maximum is increasing and decreasing over time, coupled with the wavelength shifts, it can be concluded that a complex is being formed. However, the binding cannot be determined as it would appear some of the metal ligand complexes being formed are not stable for very long. There could also be a third phase formation hindering the extraction kinetics.

This aqueous phase spectrum is slightly different than what is seen in the organic phase. In the aqueous phase, there is a decrease of 1700 extinction units between the first measurement and the last measurement. Although a greater increase is seen in the organic phase, it is correlated well with the data in the aqueous phase. No shift in the extinction maximum wavelength from the blank is noted in the aqueous phase, and while this is not indicative of strong binding to uranyl in the aqueous phase, the metal-ligand complex could be somewhat hydrophobic and transfer into the organic phase as soon as it is formed. Instead of all four sulfurs coordinating to uranyl, only two, or possibly even one sulfur is binding, which would cause the extinction to shift in the organic phase. With a decrease in extinction as time increases, the hypothesis of third layer formation could be dispelled. After 24 hours, only 60-70% of the uranyl is believed to have been extracted into the organic phase.

A)



B)

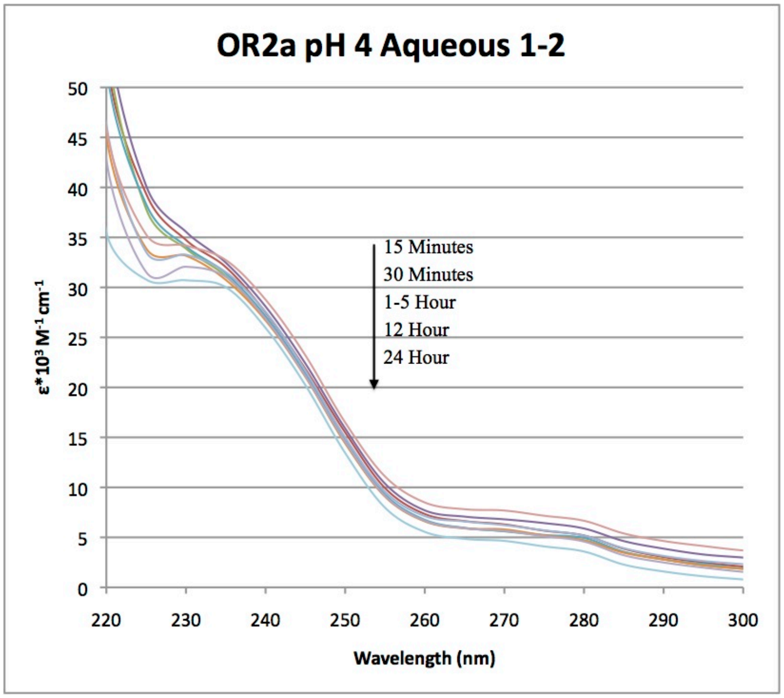


Figure 23: Graph of extinction vs. wavelength for the extraction of uranyl (5 μM) from the aqueous phase (H_2O) at pH 4 by OR2a (10 μM) in the organic phase (DCM). A) Organic phase; B) Aqueous phase. Time plotted at 235 nm.;

In figure 23 above, with OR2a at pH 4 and a ratio of 1-2 (metal to ligand) in the organic layer, the extinction maximum is increasing as an overall trend. An overall increase in extinction of 15100 extinction units is indicative of good extraction. With the initial measurement at 15 minutes, we see a 10 nm shift to 230 nm is noted. This is a shift of 10 nm from the ligand blank. This shift stays consistent throughout all the measurements indicating binding with uranyl, although it is not strong, thus indicating that not all four sulfurs are binding uranyl. Perhaps, only one or two sulfurs are binding uranyl. Further investigation is needed to probe the rate of extraction, as the biggest increase in extinction maximum was not seen until the 24-hour measurement. The extinction maximum in the aqueous phase is decreasing, indicating that the ligand coordination and metal complex is being taken into the organic phase. A decrease of 1300 extinction units, while not a lot compared to the organic phase, confirms that the metal-ligand complex is transitioning into the organic phase. It is not until the 5th hour that a shift of 5 nm is noted. This indicates that at this ratio and pH, the ligand binding is not very strong for uranyl in the aqueous phase. However, when the metal complex is transferred into the organic phase, the binding seems to be stronger as indicated by the longer shift in extinction maximum wavelength of 10 nm. After 24 hours, it is believed that 70-80% of the uranyl was extracted.

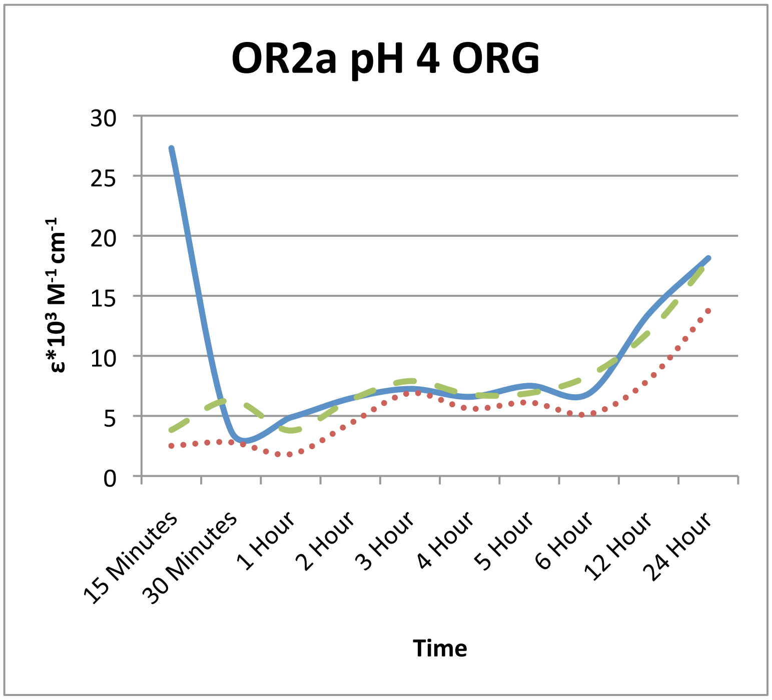
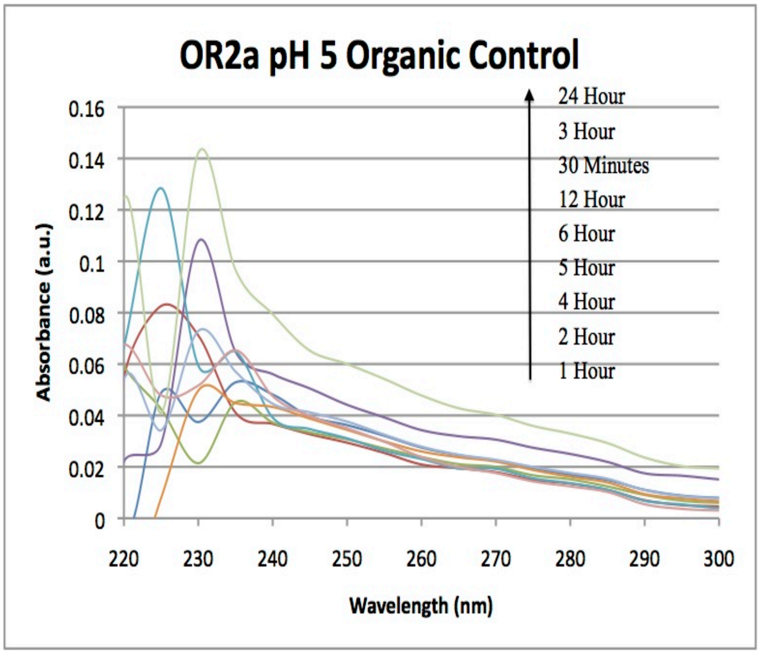
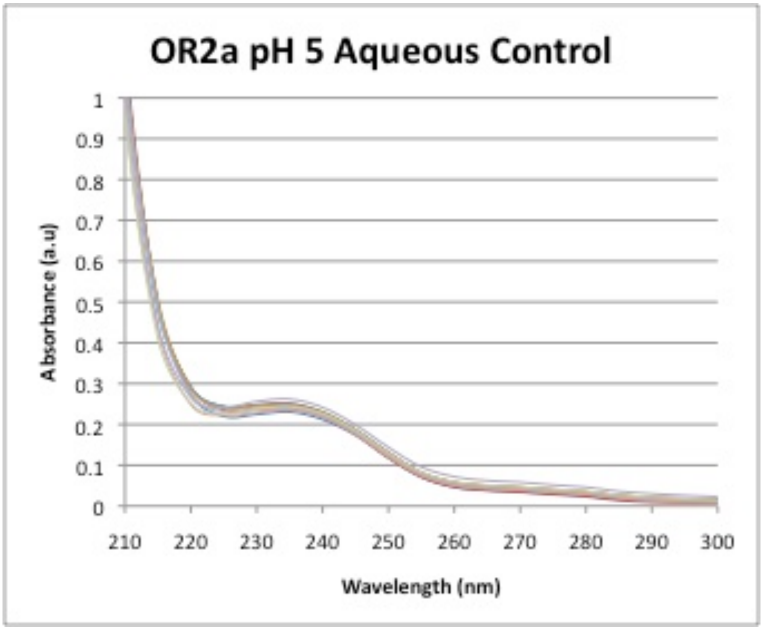


Figure 24: Graph of extinction versus time for OR2a at pH 4 in the organic phase. ── 2-1 ratio, ++ 1-1 ratio, - - 1-2 ratio (metal to ligand)

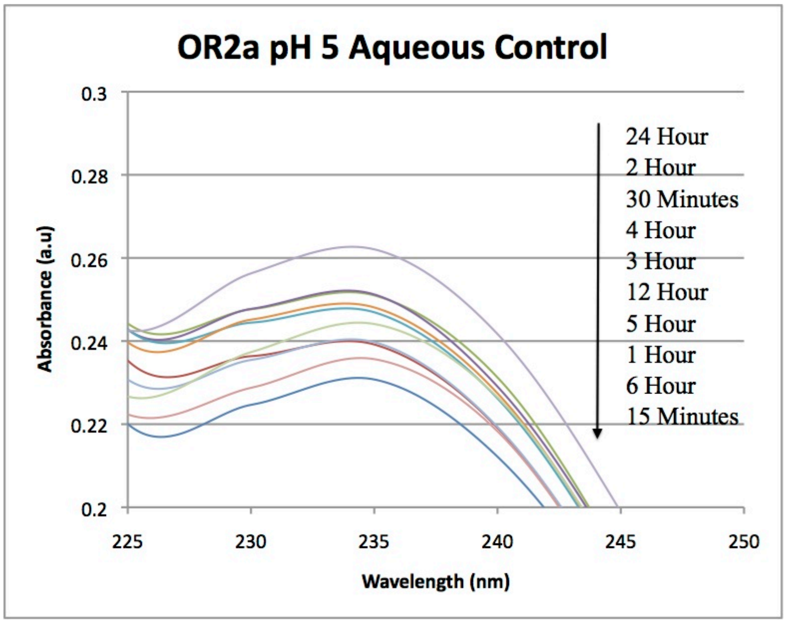
OR2a pH 5



A)



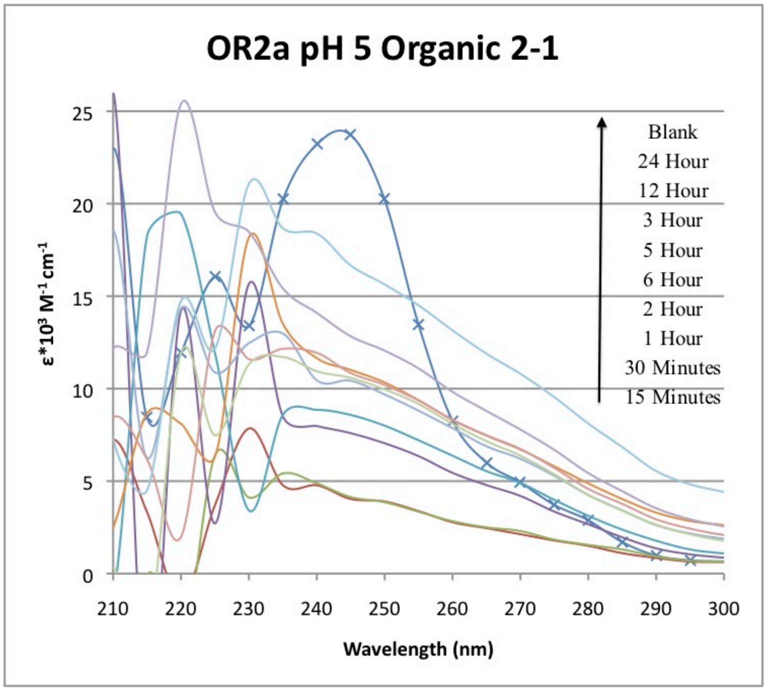
B)



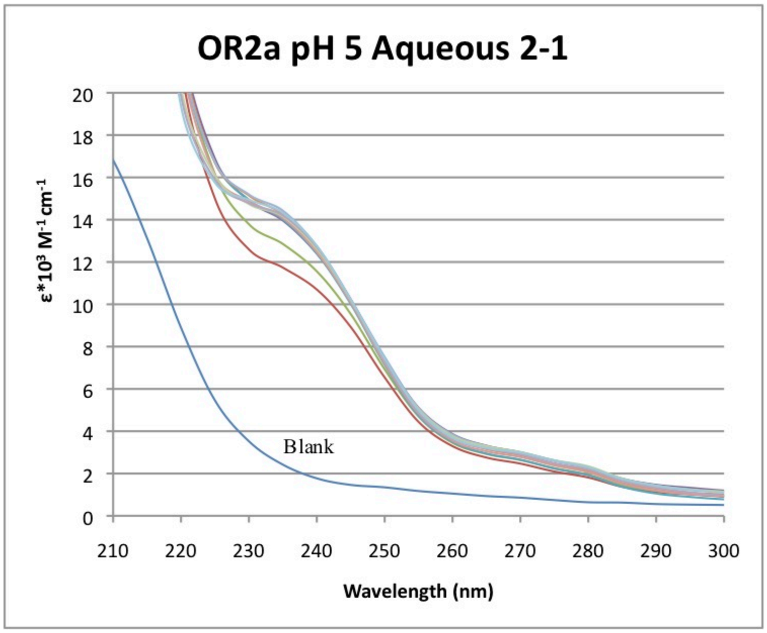
C)

Figure 25: UV-Vis spectrum of the control of OR2a at pH 5. A) Organic phase, time plotted at 240 nm. B) Overall aqueous phase spectrum; B) Close up around 235 nm. Time plotted at 235 nm.

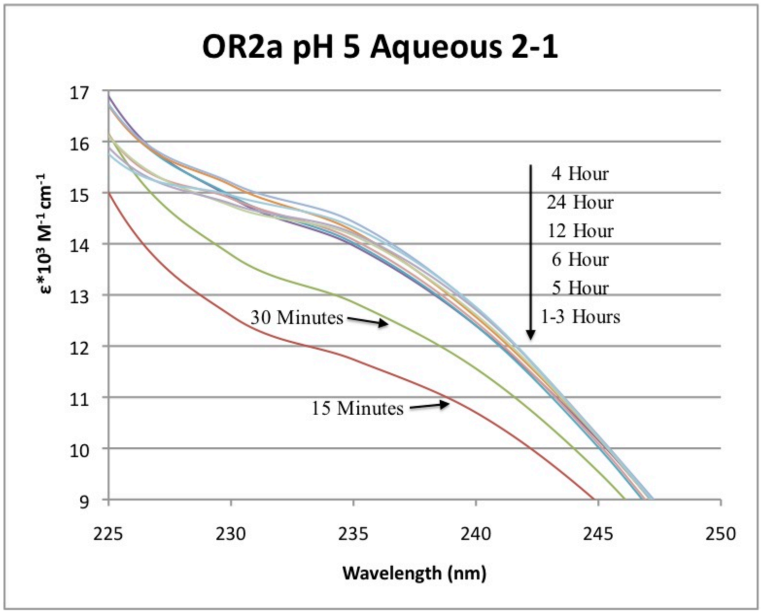
The UV-Vis spectra above in figure 25, shows that even though the ligand should be somewhat hydrophobic; it will transfer into the aqueous layer and remain there. The ligand is not reaching equilibrium as evidenced by the changing between increases and decreases in extinction maximum at different time measurements. With a longer time frame, we would expect to see equilibrium reached and decrease in extinction indicating the ligand would transfer back into the organic phase.



A)



B)

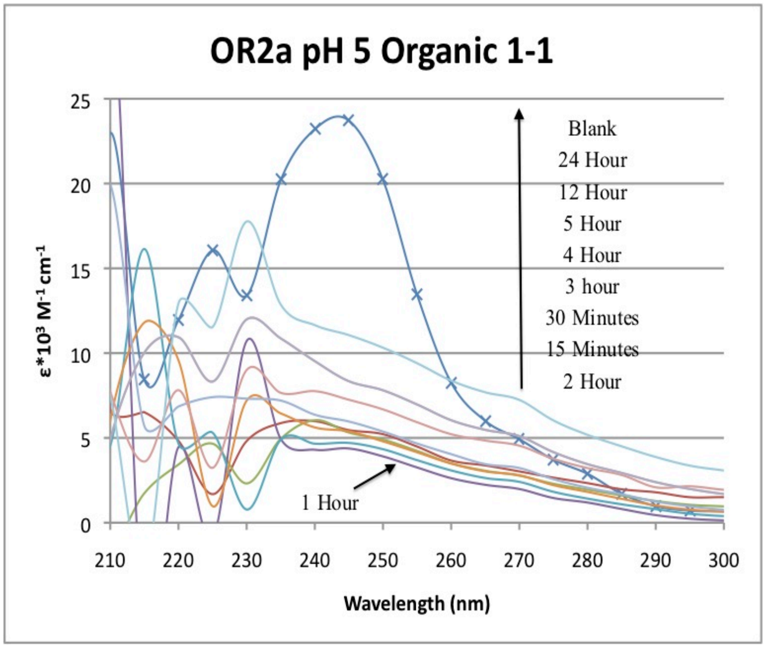


C)

Figure 26: Graph of extinction vs. wavelength for the extraction of uranyl (20 μM) from the aqueous phase (H_2O) at pH 5 by OR2a (10 μM) in the organic phase (DCM). A) Organic phase; Time plotted at 245 nm. B) Aqueous phase; C) Close up of aqueous phase around 235 nm. Time plotted at 235 nm.

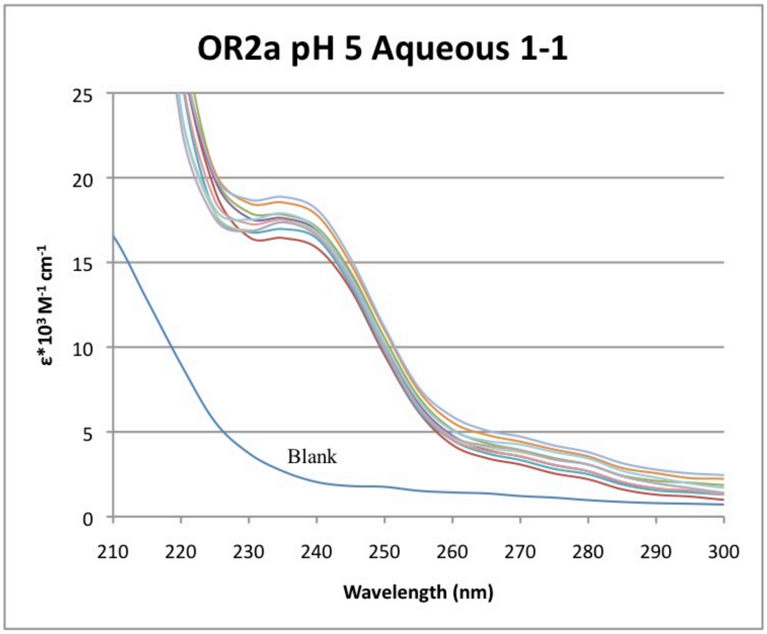
In the organic phase with OR2a at pH 5 and a ratio of 2-1 (metal to ligand) in figure 26, there is a general increase in extinction maximum especially for the 6, 12, and 24-hour measurements. An overall increase of 3800 extinction units from the first measurement at 15 minutes till the 24th hour is noted. A shift of 5 nm in extinction maximum wavelength is noted at 15 minutes, as well as a shift of 5 nm more for 30 minutes. This shift remains there until the 6th hour measurement when it shifts back towards the blank extinction maximum wavelength of 5 nm. This shift at 240 nm remains for the 12 and 24-hour measurements. The 10 nm shift would indicate stronger coordination, but since it does not remain at that wavelength for very long, we can conclude that the metal-ligand complex is not very stable with stronger binding, and is more stable with a weaker binding over a long period of time.

The aqueous phase indicates that the ligand takes at least an hour to equilibrate at this pH and ratio or metal to ligand. 15 Minutes is the lowest extinction maximum with 11700 extinction units. The overall increase in extinction maximum of 2600 units is not typical of what has been observed before. It would appear as though the ligand is establishing equilibrium in the aqueous phase with any metal-ligand complexes formed being hydrophobic and transferring into the organic phase. To correlate the two phases, there would need to be a decrease in extinction maximum in the aqueous phase, at the same time as in increase in the organic phase. No shift in extinction maximum wavelength is noted; indicating coordination of the uranyl ion is not weak, when using the maximum extinction in the controls at 235 nm. The % extraction at pH 5 and with an excess of uranyl is estimated to be roughly 80%.



A)

B)



C)

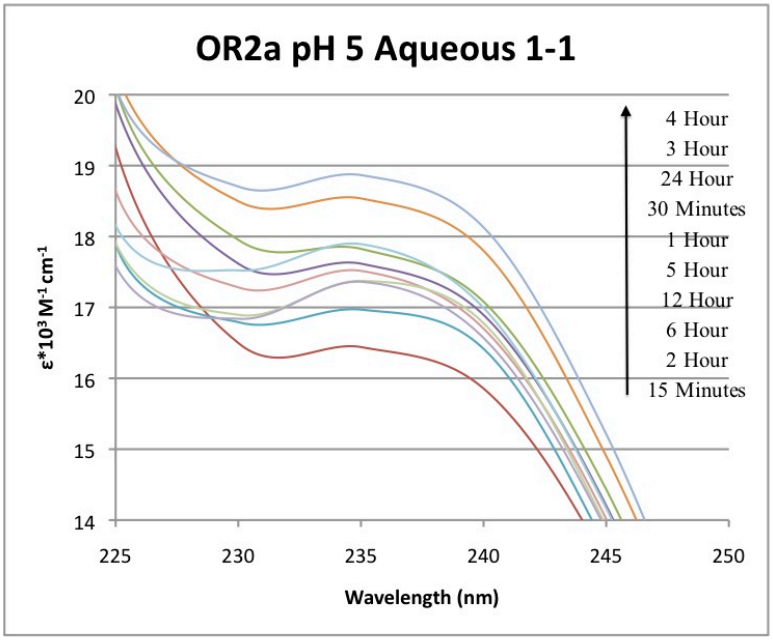
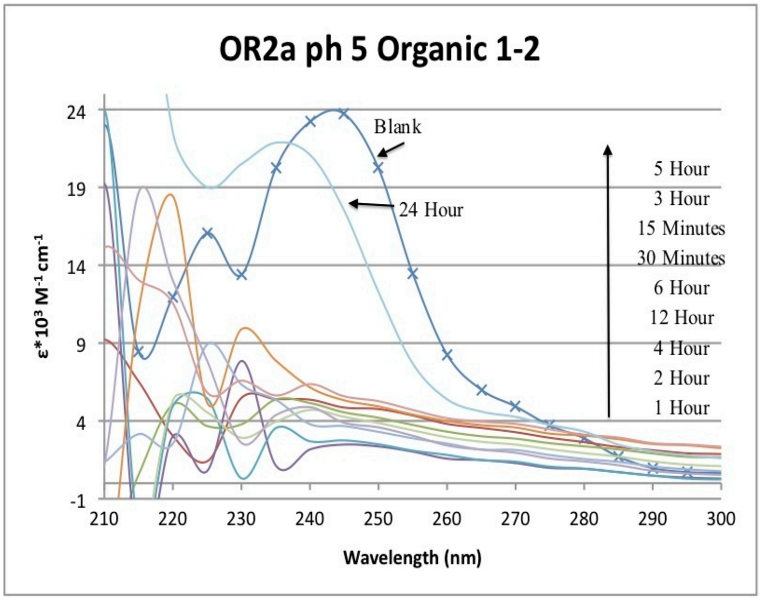


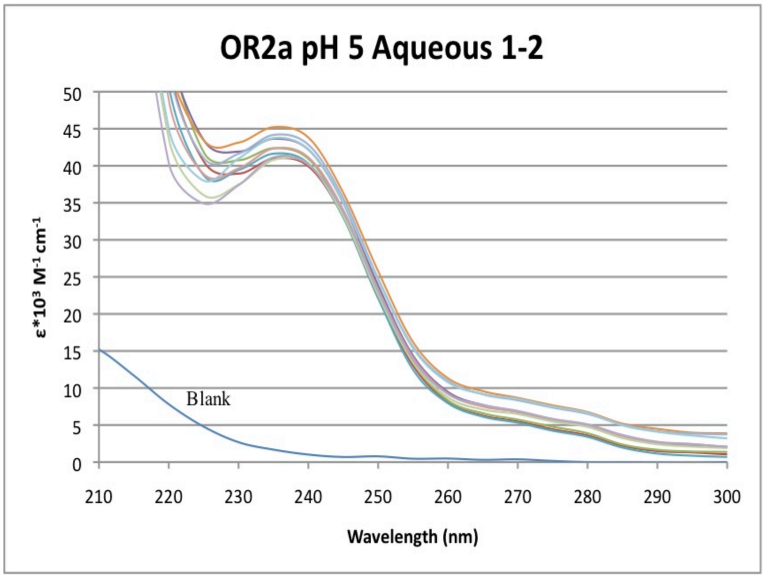
Figure 27: Graph of extinction vs. wavelength for the extraction of uranyl (10 μM) from the aqueous phase (H_2O) at pH 5 by OR2a (10 μM) in the organic phase (DCM). A) Organic phase;Time plotted at 240 nm. B) Aqueous phase; C) Close up of aqueous phase around 235 nm. Time plotted at 235 nm.

In the organic phase with OR2a at pH 5 and a ratio of 1-1 (metal to ligand) in figure 27, there is a general increase in extinction maximum especially for the 12 and 24-hour measurements. A significant increase of 13100 extinction units from lowest extinction measurement (1 hour) till the 24th hour is noted. It is not until the 4th hour that an extinction maximum shift in wavelength of 5 nm is noted. This shift increases at the 12-hour measurement by 10 nm to 230 nm. That is an overall shift of 15 nm from the extinction maximum wavelength of the ligand. While this indicates stronger binding than anything seen before, it is not in the 20-25 nm extinction maximum wavelength shift that would indicate strong binding. To speculate, the 15 nm shift could be three of the sulfurs coordinated to one uranyl, or one sulfur coordinated to one uranyl and one sulfur coordinated to another uranyl. It is hard to determine from the data what the binding is.

In the aqueous phase, there are increases in extinction maxima for the first 30 minutes before decreasing at the 1 and 2 hour measurements. The sharp increase in the 3rd and 4th measurements is noted, as well as the decrease in the next two hours. This increase and decrease in maximum extinction is indicative of the ligand trying to find equilibrium in the aqueous phase, or possibly, there is a hydrophilic metal-ligand complex but is not coordinated strongly to cause a shift in the extinction maximum wavelength. Instead of all four sulfurs binding to uranyl, only one or two sulfurs are binding to uranyl, if it is binding at all in the aqueous phase. At an equimolar ratio at pH 5, like the other 1-1 ratios at other pHs, there is less extraction compared to excess uranyl or excess ligand, and in this case, it is estimated that only 50-60% uranyl was extracted.


OR2a ph 5 Organic 1-2
ε*10³ M⁻¹ cm⁻¹
24
19
14
9
4
-1
210
220
230
240
250
260
270
280
290
300
Wavelength (nm)
Blank
24 Hour
5 Hour
3 Hour
15 Minutes
30 Minutes
6 Hour
12 Hour
4 Hour
2 Hour
1 Hour

A)


OR2a pH 5 Aqueous 1-2
ε*10³ M⁻¹ cm⁻¹
50
45
40
35
30
25
20
15
10
5
0
210
220
230
240
250
260
270
280
290
300
Wavelength (nm)
Blank

B)

C)

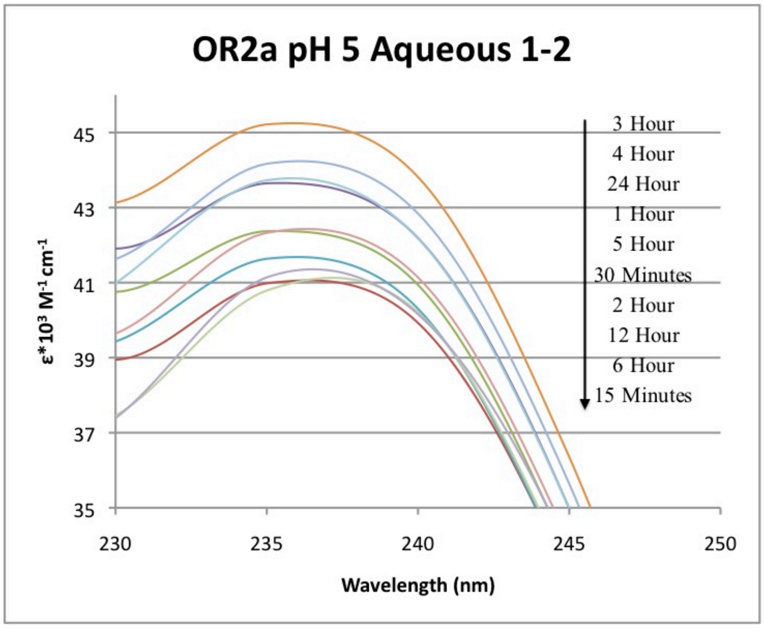
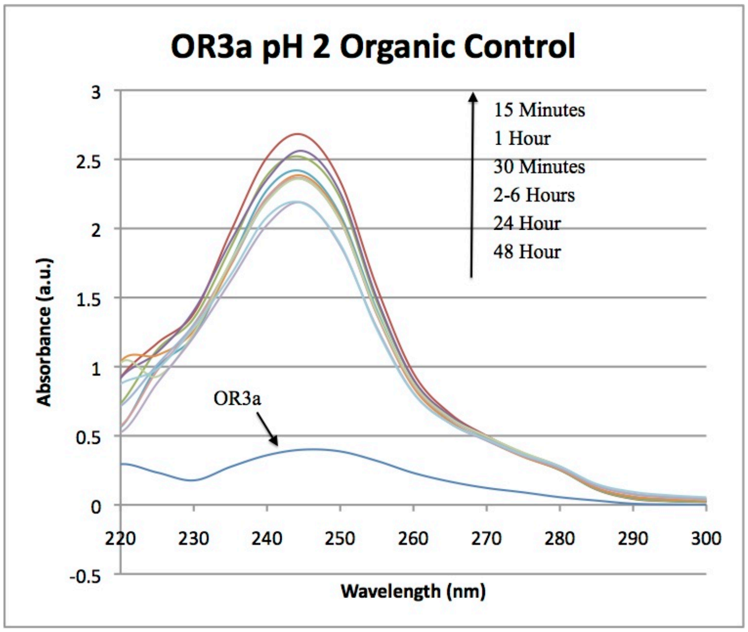


Figure 28: Graph of extinction vs. wavelength for the extraction of uranyl (5 μM) from the aqueous phase (H_2O) at pH 5 by OR2a (10 μM) in the organic phase (DCM). A) Organic phase. Time plotted at 240 nm; B) Aqueous phase; C) Close up of aqueous phase around 235 nm. Time plotted at 235 nm.

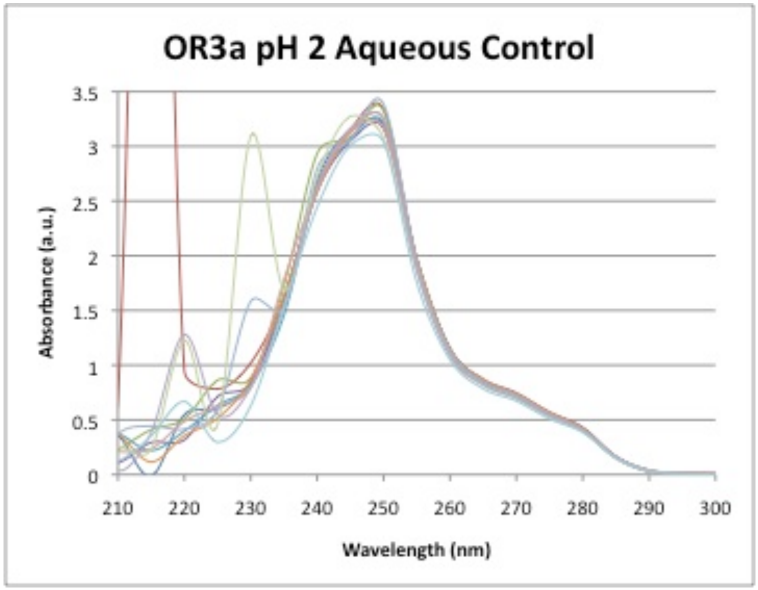
In the figure above, with OR2a at pH 5 and a ratio of 1-2 (metal to ligand) in the organic layer, an overall decrease in extinction maximum of 4000 extinction units for 15 minutes, 30 minutes, and 1 hour at a wavelength of 245 nm is noted. An increase of 19100 extinction units from the lowest maximum extinction measurement at 1 hour is noted. The 12th hour measurement is also when the first maximum extinction wavelength shift of 5 nm is noted. The ligand was able greatly increase extraction, but it took 24 hours for it to happen, leading to a belief of a kinetic problem. The wavelength shift is an indication of binding in the metal-ligand complex, but only 1 or 2 sulfurs is binding, and not all four that would cause a 20-25 nm shift.

The aqueous phase is very similar to the aqueous phase of the control seen in figure 22. The extinction maximum is increasing and decreasing trying to establish equilibrium. When there is the significant increase in extinction maximum in the organic layer, there is not a decrease in extinction maximum in the aqueous phase, there is actually an increase of 2000 extinction units. No shifts in extinction maximum wavelength are noted for the aqueous layer indicative of not weak coordination of uranyl by the ligand. With the increase of extinction maximum between the 12th and 24th hour, it can be concluded that, because there is an excess of ligand in solution, when the metal-ligand complex forms and transfers into the organic phase, more or equal amount of free ligand is equilibrated in the aqueous phase. While it is estimated that only 10-15% of the uranyl was extracted after 12 hours, the % extraction jumps up to about 80-90% after 24 hours.

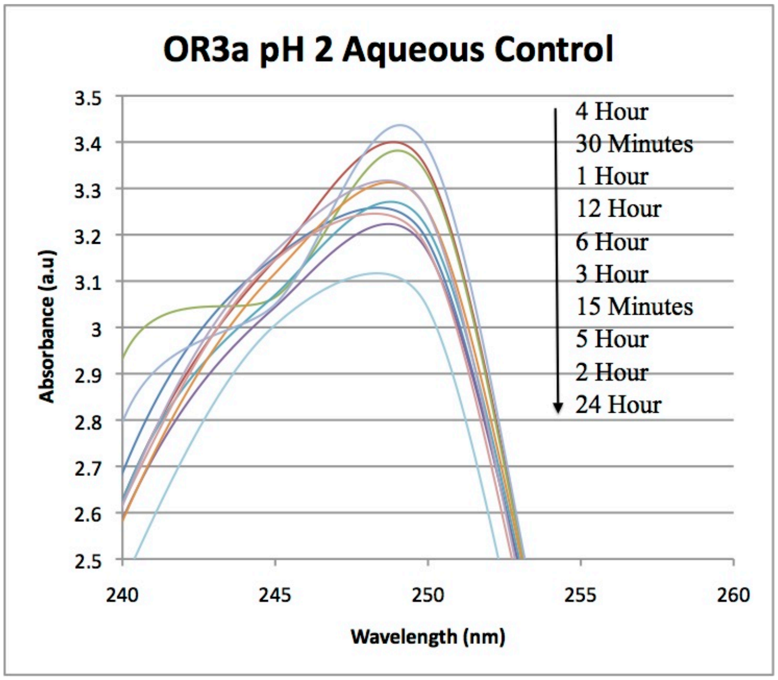
OR3a pH 2



A)



B)

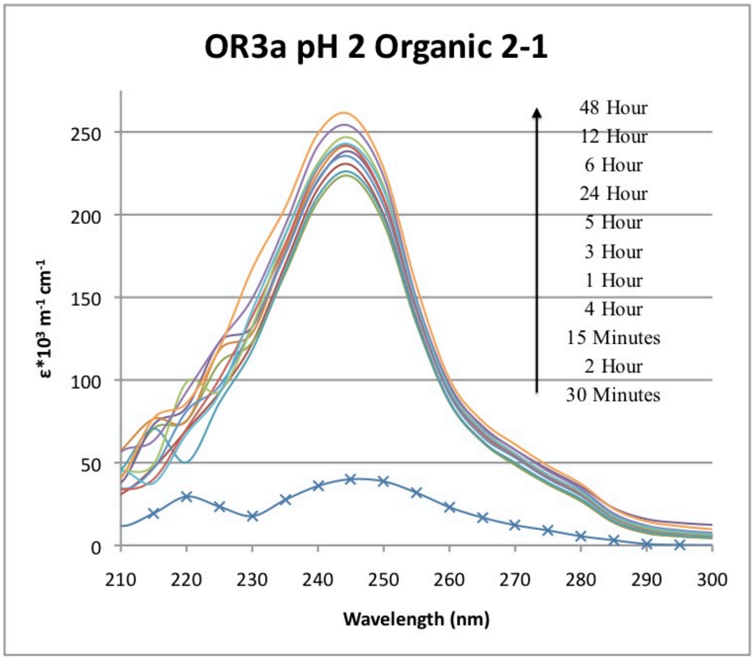


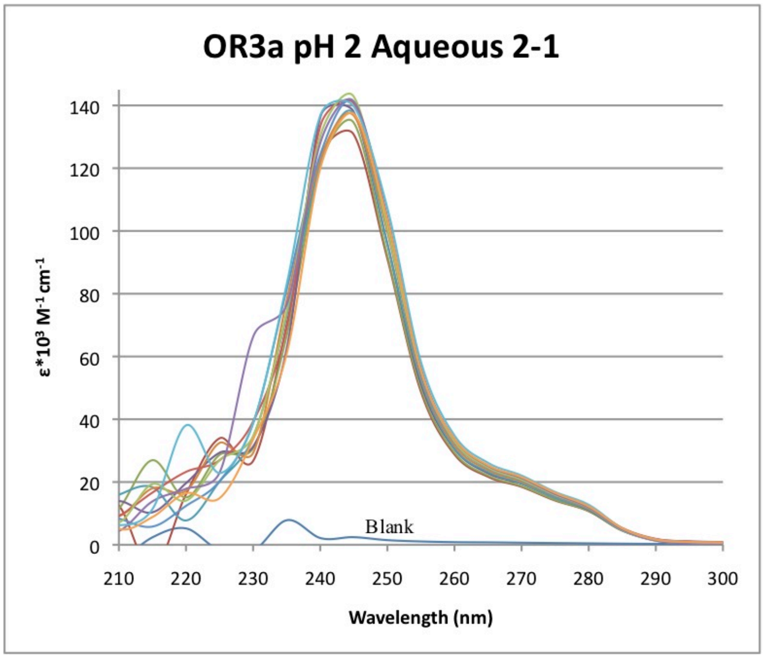
C)

Figure 29: UV-Vis spectrum absorbance vs. wavelength of the control of OR3a at pH 2. A) Organic phase, time plotted at 245 nm B) Overall aqueous phase spectrum; B) Close up around 250 nm. Time plotted at 250 nm.

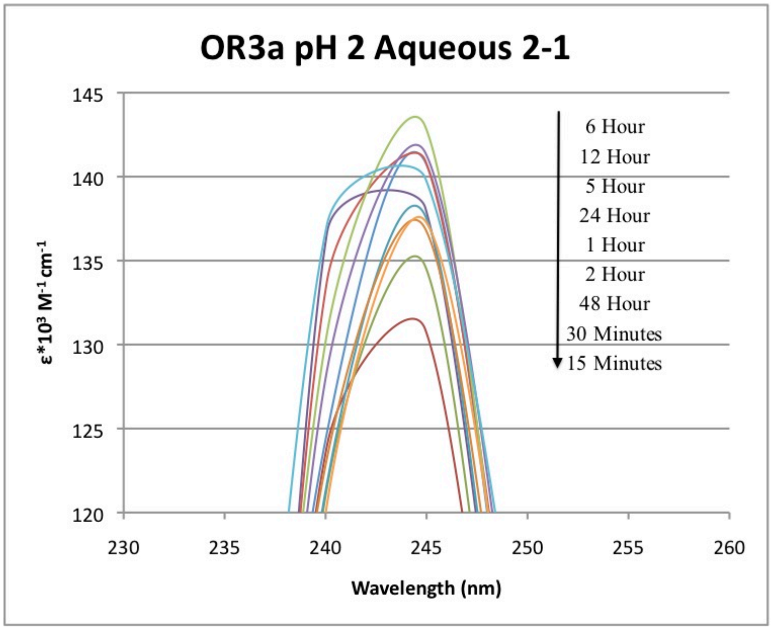
The UV-Vis spectra above in figure 29, shows that even though the ligand should be somewhat hydrophobic; it will transfer into the aqueous layer and remain there and even form an equilibrium for a relatively short period of time. It will however, transition back into the organic phase slowly over time as evidenced by the decrease in extinction over time.

A)





B)



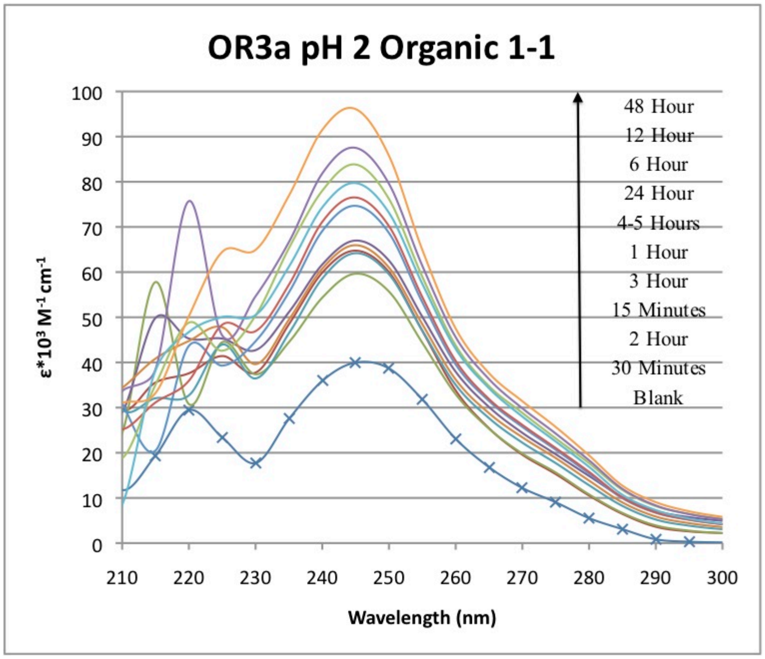
C)

Figure 30: Graph of extinction vs. wavelength for the extraction of uranyl (20 µM) from the aqueous phase (H_2O) at pH 2 by OR3a (10 µM) in the organic phase (DCM). A) Organic phase. Time plotted at 245 nm.; B) Aqueous phase; C) Close up of aqueous phase around 245 nm. Time plotted at 245 nm.

In the figure above, with OR3a at pH 2 and a ratio of 2-1 (metal to ligand), in the organic layer, the extinction maximum is generally increasing. The largest increase in extinction maximum is between the 12th and 24th hour measurements where the increase is 18200 extinction units. This correlates to the decrease of 2600 extinction units of extinction maximum seen in the aqueous phase at the same time frame. This is an indication that the metal-ligand complex is being taken into the organic phase. The organic phase does not exhibit an extinction maximum wavelength shift; however the change in extinction maximum is far greater than the effects seen due to changes in pH. This indicates that at this ratio of metal to ligand maintained at this pH, the ligand binding is not very strong for uranyl. Instead of all four sulfurs coordinating to uranyl, only two, or possibly even one sulfur is binding.

In the aqueous phase we see an increase in extinction maximum until the 6th hour when we start getting dramatic drops in extinction maximum. There is a consistent decrease from the 6th hour on of 1600 extinction units each measurement. While we see the increases in the organic phase at these times, we see a drop at the 24-hour measurement in the organic phase. From the hydrolysis data above, a second possibility is that the ligand could by hydrolyzing with the addition of the metal salt (decreasing below pH 2), the ligand-metal complex is not stable for very long. It is believed that only 60% uranyl was extracted at this pH. It is difficult to ascertain precisely at such a low concentration and the ligand hydrolyzing.

A)



B)

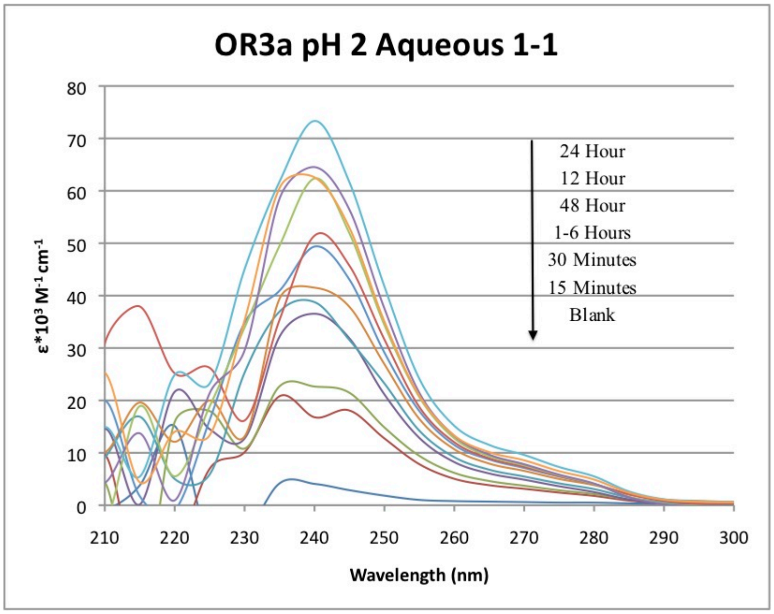


Figure 31: Graph of extinction vs. wavelength for the extraction of uranyl (10 μM) from the aqueous phase (H_2O) at pH 2 by OR3a (10 μM) in the organic phase (DCM). A) Organic phase. Time plotted at 245 nm; B) Aqueous phase. Time Plotted at 240 nm.

In the organic phase of figure 31 above, with OR3a at pH 2 and a ratio of 1-1 (metal to ligand), the extinction maximum at 30 minutes decreases by 5100 extinction units. It then increases at 1 hour to 67000, a difference of 9100 extinction units. At the 2 hour measurement is another decrease of 2800 extinction units, followed by an increase of 1700 extinction units at the 3rd hour measurement. A difference of 36500 extinction units separates the highest maximum extinction at 48 hours from the lowest at 30 minutes. The drop at 24th hour measurement in the organic phase is confirmed with an increase in extinction maximum of 8800 units in the aqueous phase at the same time interval. The increase and decrease of extinction seen in the organic phase could be because of the ligand hydrolyzing, or the formation of a third phase, that would make extractions difficult. The only real difference between the two phases is that besides the drop in extinction maximum at 24 hours, the aqueous phase is constantly increasing in maximum extinction. A shift of 5 nm from the aqueous control experiments for 15 and 30 minutes is noted. After this time, all extinction maximum wavelengths have shifted 10 nm from the aqueous control. While this is not in the 20-25 nm extinction wavelength shift that indicates strong coordination, a small shift is indicative of weak coordination of uranyl to the ligand. Since it occurs in the aqueous phase, we can assume that the ligand-metal complex could be somewhat hydrophilic, before being transferred into the organic layer. The ligand is believed to have only extracted 70-80% of the uranyl, while it undergoes hydrolysis.

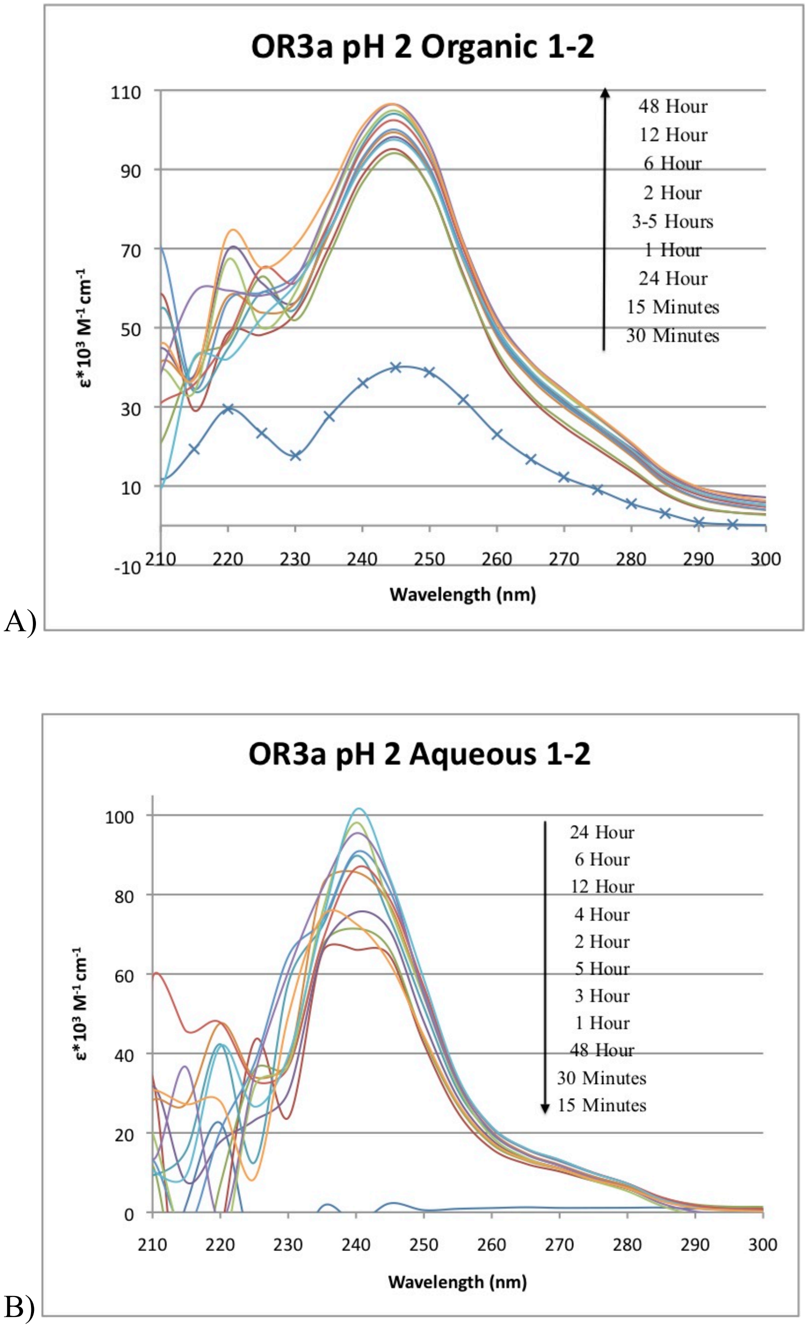


Figure 32: Graph of extinction vs. wavelength for the extraction of uranyl (5 μM) from the aqueous phase (H_2O) at pH 2 by OR3a (10 μM) in the organic phase (DCM). A) Organic phase. Time plotted at 245 nm; B) Aqueous phase. Time plotted at 240 nm.

In figure 32 above, with OR3a at pH 2 and a ratio of 1-2 (metal to ligand), in the organic layer, an overall increase in extinction maximum of 12300 extinction units from the first measurement at 15 minutes. An unexpected decrease in extinction maximum in the organic phase, would lead to formation of a third phase, but there is a correlation in the aqueous phase where the extinction maximum increases by 6000 extinction units at the same time interval. This is followed by a decrease of 6900 extinction units at the 48 hour measurement in the aqueous phase, similar to the 8900 extinction units increase noted in the organic phase. There is not an observed shift of extinction maximum in the organic phase; however, in the aqueous phase, we see an immediate 10 nm extinction maximum wavelength shift for all measurements except for the 48-hour measurement, where there is an extinction maximum wavelength shift of 15 nm. While there is also a shift of 15 nm seen at the 3rd hour, with the next five measurements having only a 10 nm shift from the controls, this could be an anomaly but is duly noted. The extinction maximum wavelength shifts are indicative of stronger coordination with uranyl than was seen in a similar ratio with OR2a. A reason could be with the extra two carbon atoms in the linker, the ligand is able to wrap around the uranyl ion better and promote binding. The ligand is hypothesized to have only extracted 20-30% of the uranyl in this case.

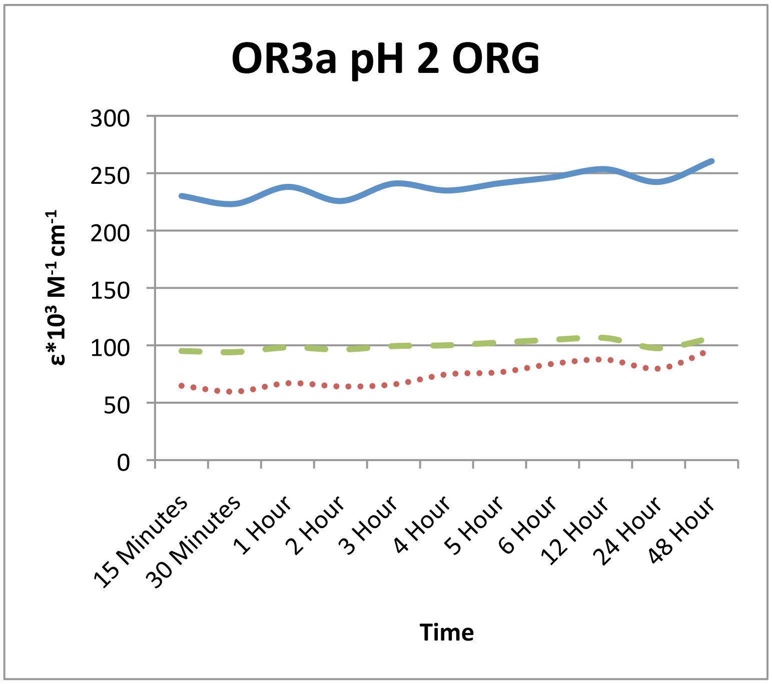
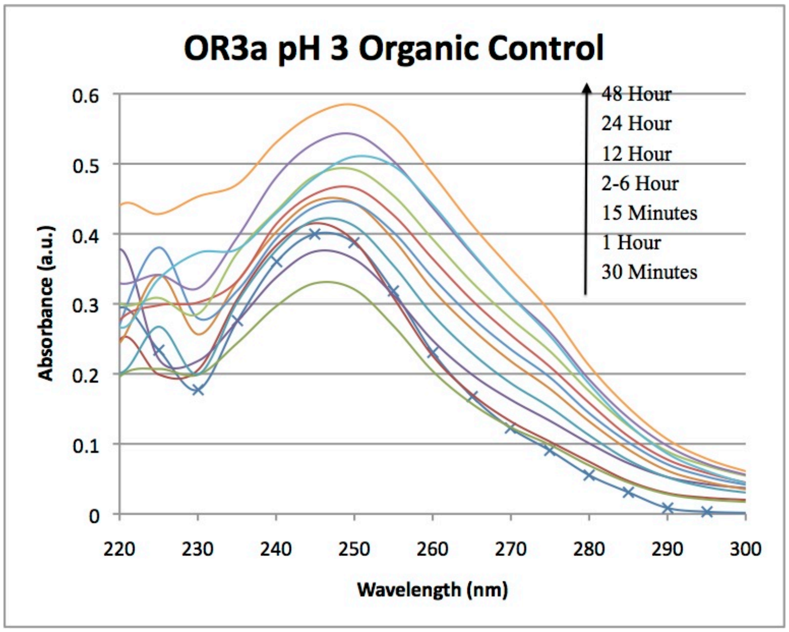


Figure 33: Graph of extinction versus time for OR3a at pH 2 in the organic phase. –– 2-1 ratio, ++ 1-1 ratio, - - 1-2 ratio (metal to ligand)

OR3a pH 3

A)


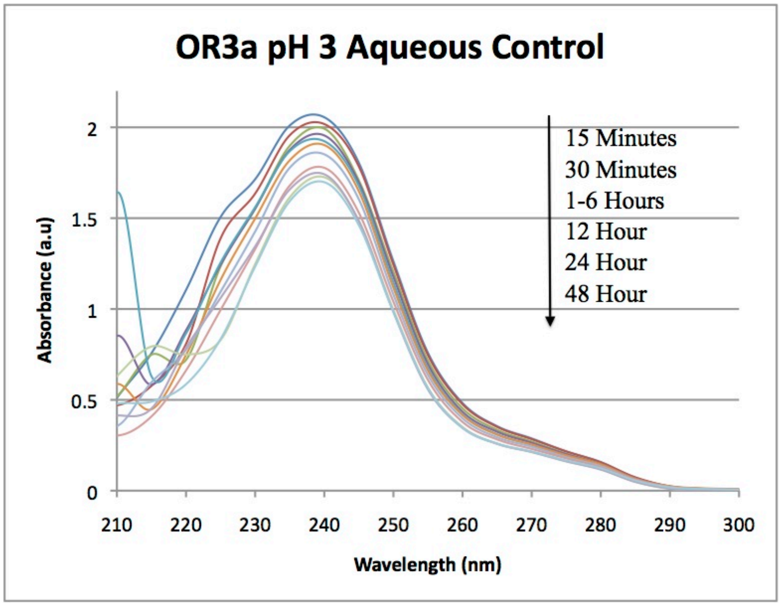
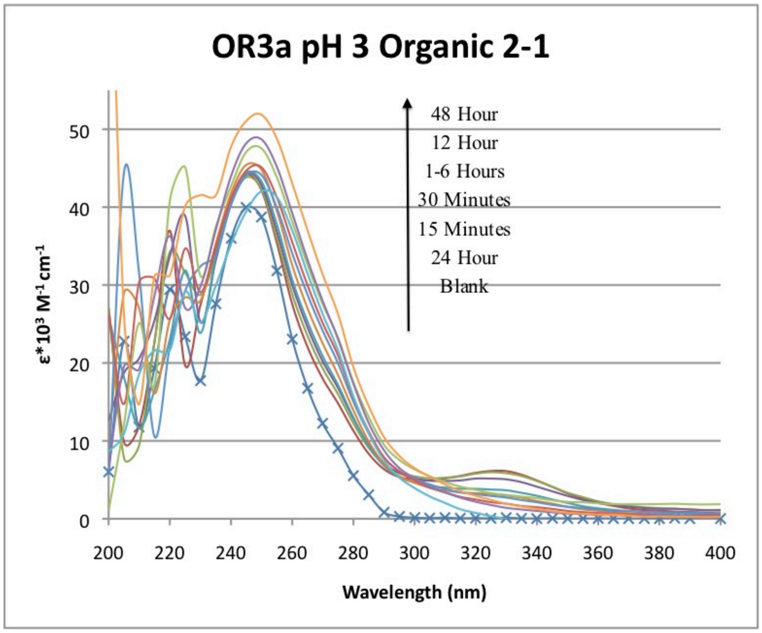
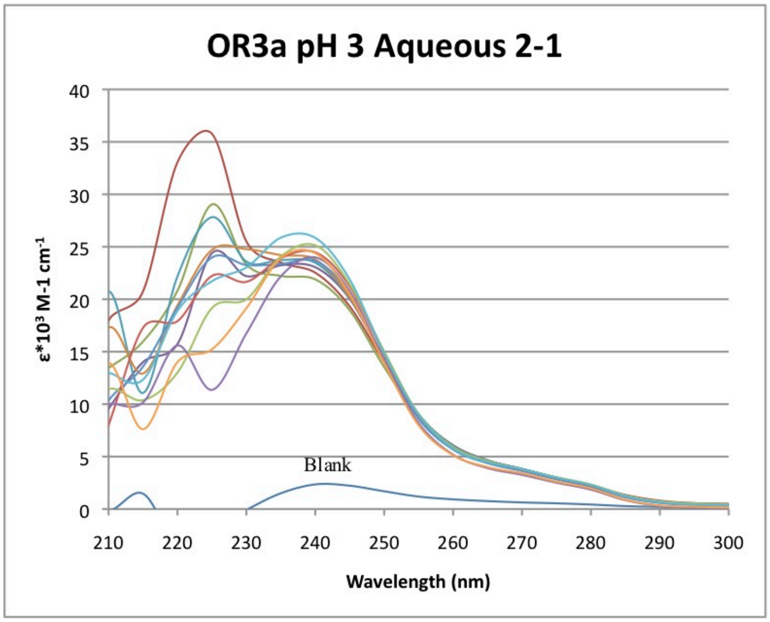
B)


Figure 34: UV-Vis spectrum absorbance vs. wavelength of the control of OR3a at pH 3. A) Organic phase, time plotted at 245 nm. B) Aqueous phase time plotted at 240 nm.

The UV-Vis spectra above in figure 34, shows that even though the ligand should be somewhat hydrophobic; it will transfer into the aqueous layer and remain there. It will however, transition back into the organic phase slowly over time as evidenced by the decrease in extinction over time.



A)



B)

C)

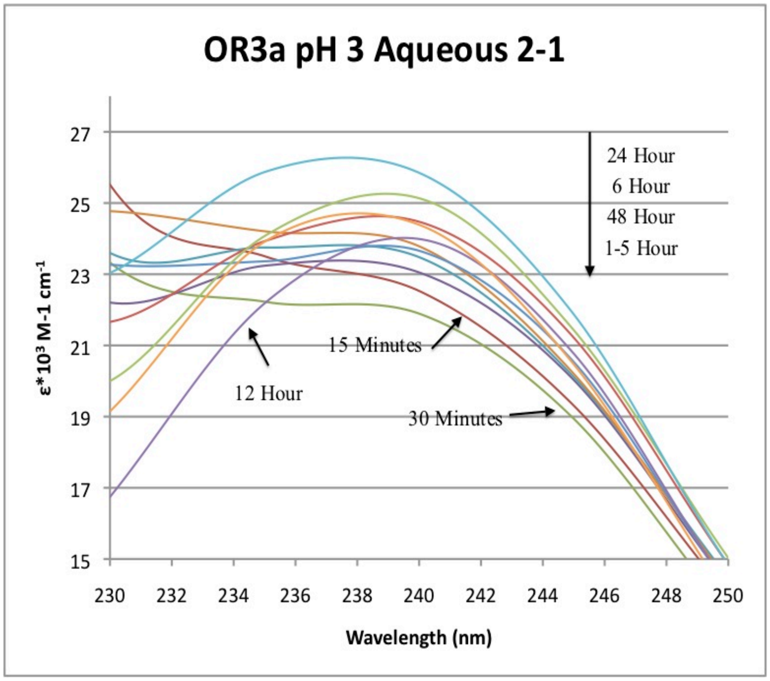
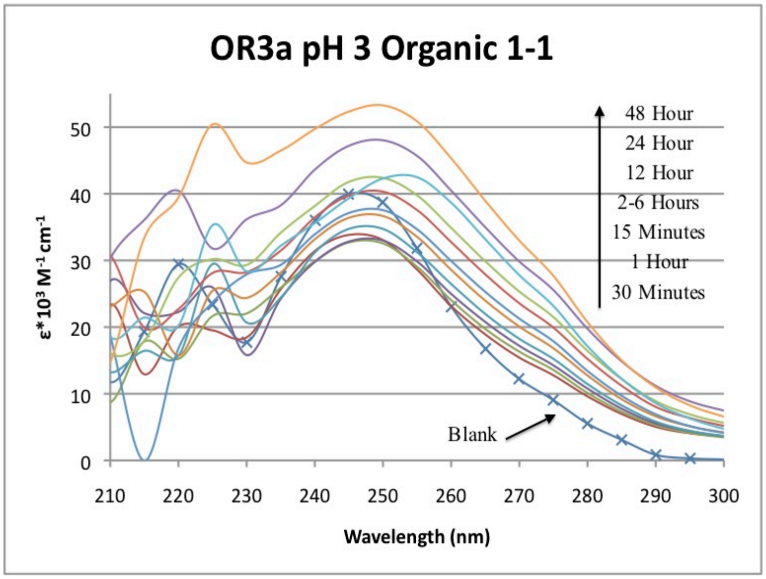


Figure 35: Graph of extinction vs. wavelength for the extraction of uranyl (20 μM) from the aqueous phase (H_2O) at pH 3 by OR3a (10 μM) in the organic phase (DCM). A) Organic phase. Time plotted at 240 nm; B) Aqueous phase; B) Close up of aqueous phase around 240 nm. Time plotted at 240 nm.

In the organic phase with OR3a at pH 3 and ratio of 2-1 (metal to ligand) (figure 35A), the majority of the measurements overlap each other at 245 nm until the 3rd hour, when there is a more noticeable increase in extinction maximum to an extinction of 44800 extinction units. An increase of 6500 extinction units occurs between 15 minutes and 12 hours. However in the 24th hour, there is a demonstrable decrease in extinction maximum of 7400 and a shift in extinction maximum wavelength of 5 nm more, a total of 10 nm from the ligand blank. Next though, is a decrease in the maximum extinction wavelength of 5 nm, but a monumental increase of 10500 extinction units, indicative of extraction. With the time length to cause significant increases in extinction, a kinetic problem may be indicated.

In the aqueous phase, between 15 minutes and 48 hours, there is an increase of 1900 extinction units. We want to see the spectra decrease in extinction, indicative of ligand metal complex transferring into the organic phase. There is a decrease in the extinction maximum after the ligand establishes equilibrium at the 24-hour measurement. The sudden increases and shifts correspond to the shift and increase noted in the organic phase at the same time interval. It can be concluded that while there was strong coordination of uranyl by the ligand, it was not a stable complex in either phase. It is hypothesized that OR3a extracted approximately 20-30% of the uranyl from the aqueous phase into the organic phase.



A)

B)

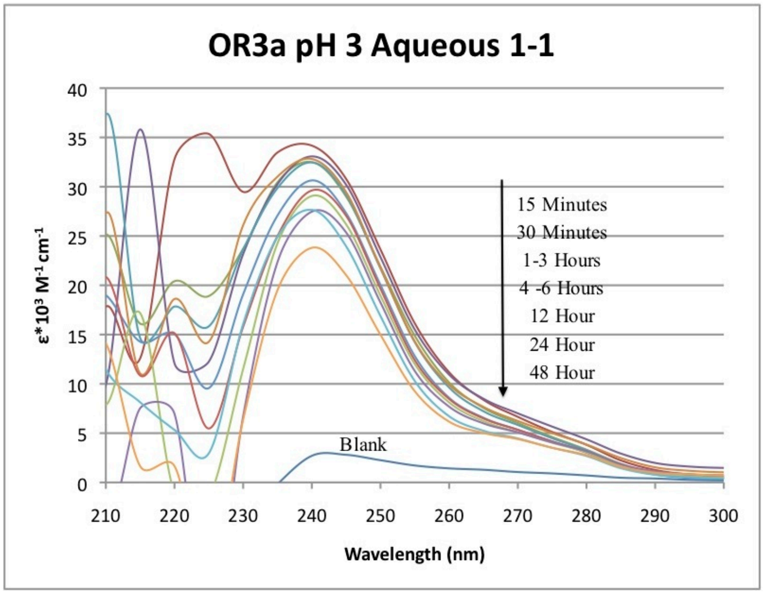
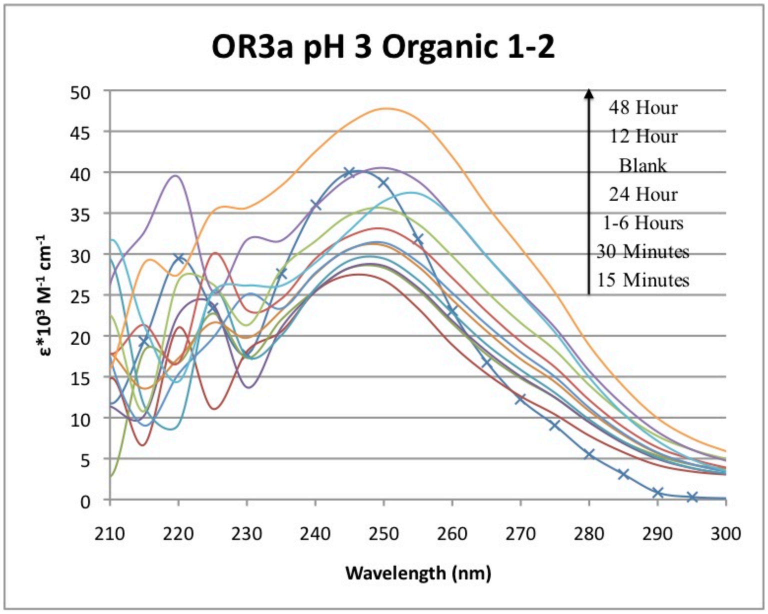


Figure 36: Graph of extinction vs. wavelength for the extraction of uranyl (10 μM) from the aqueous phase (H_2O) at pH 3 by OR3a (10 μM) in the organic phase (DCM). A) Organic phase. Time plotted at 245 nm; B) Aqueous phase. Time plotted at 240 nm.

In the figure above, with OR3a at pH 3 and a ratio of 1-1 (metal to ligand) in the organic phase, there is an increase in extinction maximum between 15 minutes and 48 hours of 20300 extinction units. The most significant increase in extinction maximum is at 12 hours where there is an increase of 5600 extinction units before a sharp decrease of 5500 extinction units and a shift of 5nm more in extinction maximum for a total of 10 nm from the blank. The 48-hour measurement shows a shift of 5 nm back towards the ligand blank and an increase in extinction maximum of 10800 extinction units. The decrease and shift in extinction seen at the 24th hour, is what has been observed in all ratios at this pH. The ligand could have stronger coordination but is not a stable complex for long which is why there is a shift back towards the ligand blank at 48 hours. Another explanation could be of a third layer formation, causing the extra shift and decrease in extinction.

In the aqueous phase, there are some overlaps in extinction maxima at 30 minutes and 1-3 hours, 4-6 hours, and 12 and 24 hours. It would seem as though the ligand established and equilibrium, and then maybe some extraction happens, and it has to establish another equilibrium. There is a general decrease in the extinction with a change of 10300 extinction units between the first measurement at 15 minutes and the last measurement at 48 hours. At the even ratio, there is much less extraction and is predicted that about 40-50% of the uranyl was extracted.

A)



B)

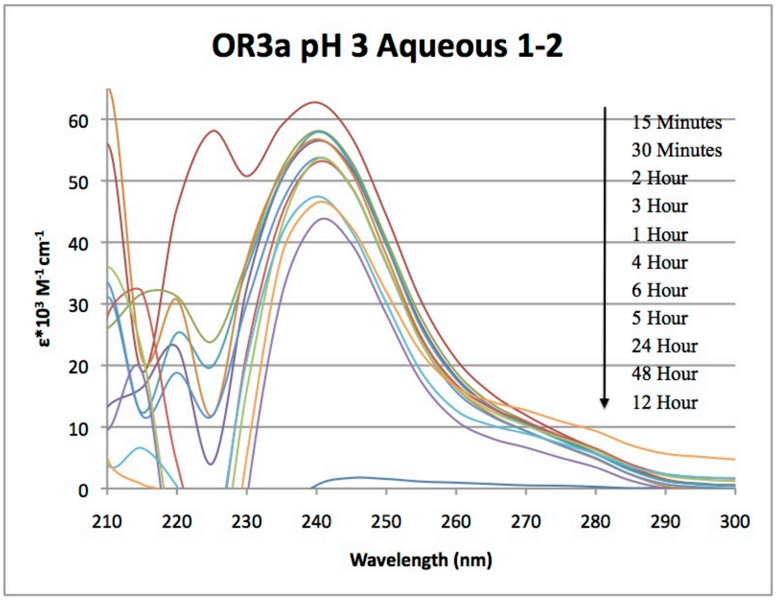


Figure 37: Graph of extinction vs. wavelength for the extraction of uranyl (5 μM) from the aqueous phase (H_2O) at pH 3 by OR3a (10 μM) in the organic phase (DCM). A) Organic phase. Time plotted at 250 nm; B) Aqueous phase. Time plotted at 240 nm.

In the figure above, with OR3a at pH 3 and a ratio of 1-2 (metal to ligand), in the organic phase there is an overall increase in extinction maximum as time increases. While the 15-minute measurement exhibits no shift in extinction maximum wavelength, subsequent measurements measure a 5 nm shift except for the 24-hour measurement, where a 10 nm shift in extinction maximum wavelength is noted. The extra 5 nm shift at the 24th hour would indicate a stronger coordination of ligand to uranyl, however, it does not appear to be stable for more than a day as the 48 hour measurement is equal to the 5 nm extinction maximum wavelength shift seen in previous measurements in this spectra. The extinction maxima at 30 minutes and 1 hour almost overlap each other. Also the extinction maxima at the 3rd and 4th hour almost overlap each other, indicative of very little or no increase of metal-ligand complex coming into the organic phase. An overall increase in extinction maximum of 20400 extinction units shows that there is an excellent amount of extraction as compared to pH 2.

There is almost the same overlap in extinction maxima that is seen in the organic phase, but in the aqueous phase, it's between 30 minutes and 2nd hour, 3rd and 1st hour, and 4th, 5th, and 6th hour. What is interesting is that none of these correlate with the overlaps in extinction maxima seen in the organic phase. A difference of 20200 extinction units separates the first measurement at 15 minutes from the last measurement at 48 hours. The extinction maximum in the aqueous phase does not have a shift off of the controls aqueous phase at 240 nm. This would mean that the ligand binding is not very strong for uranyl in the aqueous phase, or when the ligand binds to uranyl, it is a hydrophobic complex and transfers into the organic phase. The ligand could be binding with just one or two sulfurs, instead of all four sulfurs. We believe that about 50-60% of the uranyl was extracted from the aqueous phase.

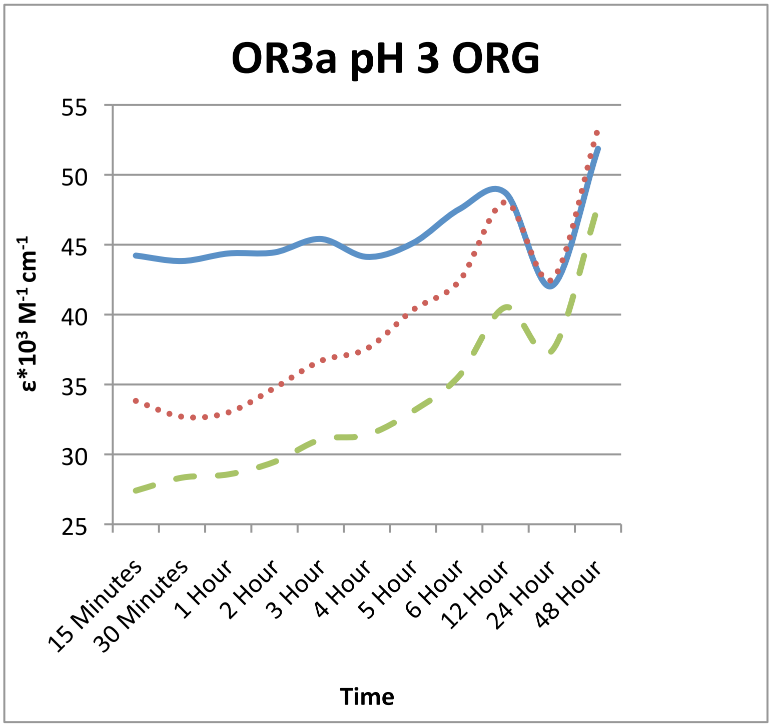


Figure 38: Graph of extinction versus time for OR3a at pH 3 in the organic phase. –– 2-1 ratio, ++ 1-1 ratio, - - 1-2 ratio (metal to ligand)

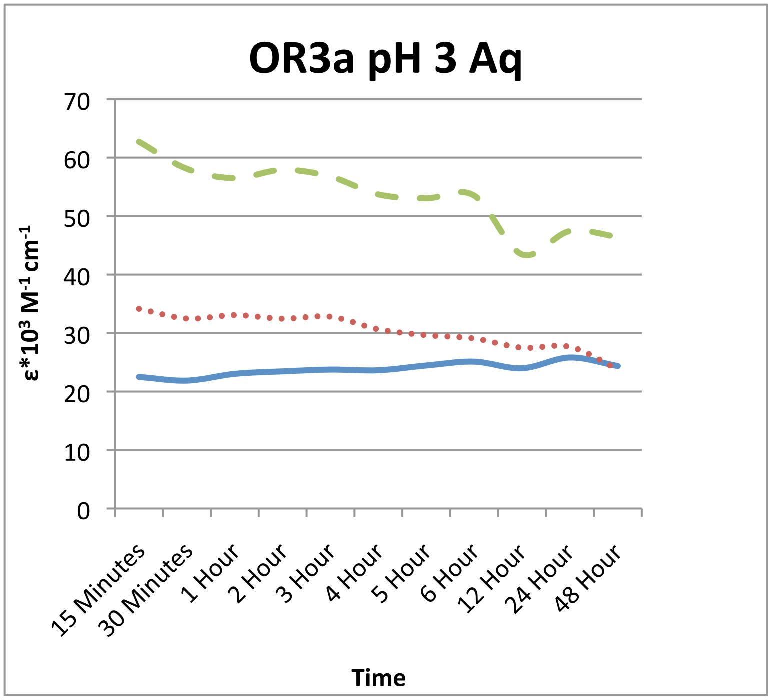
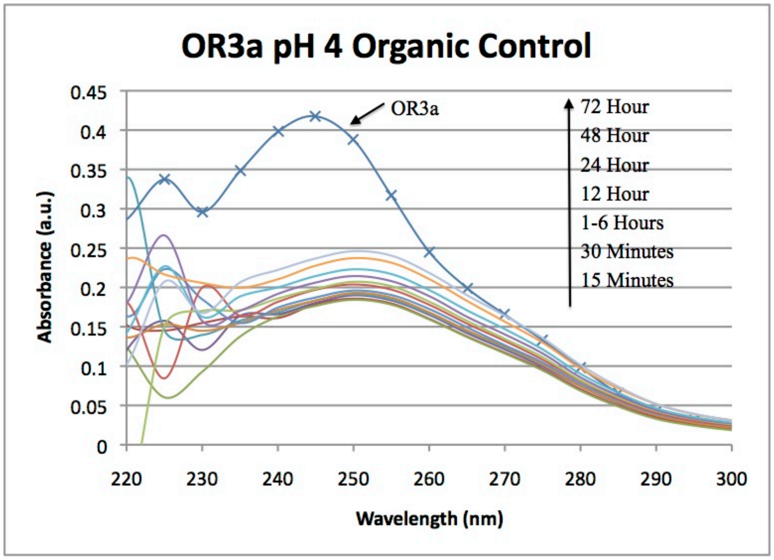


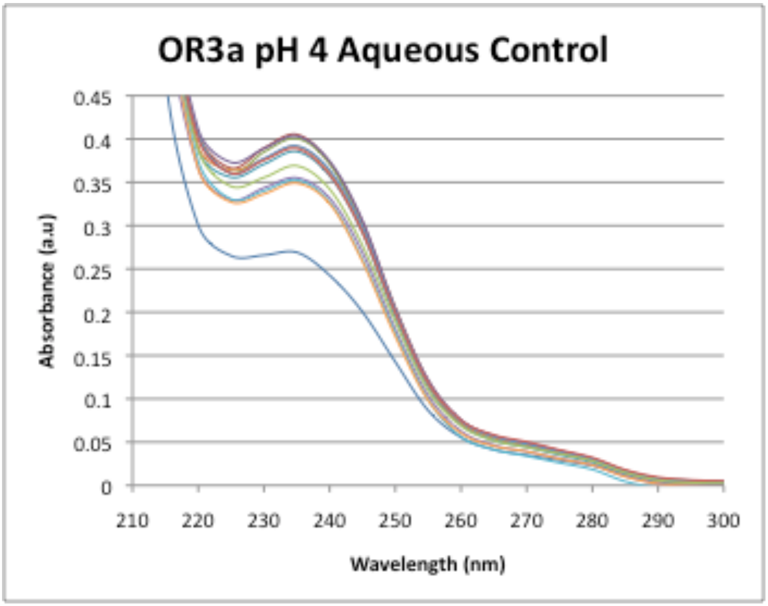
Figure 39: Graph of extinction versus time for OR3a at pH 3 in the aqueous phase. —— 2-1 ratio, ++ 1-1 ratio, - - 1-2 ratio (metal to ligand)

OR3a pH 4



A)

B)



C)

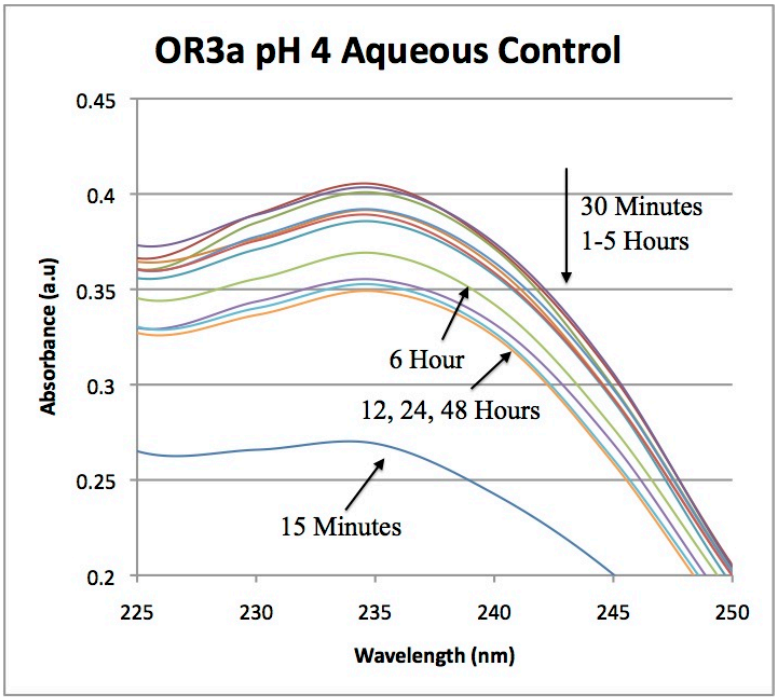
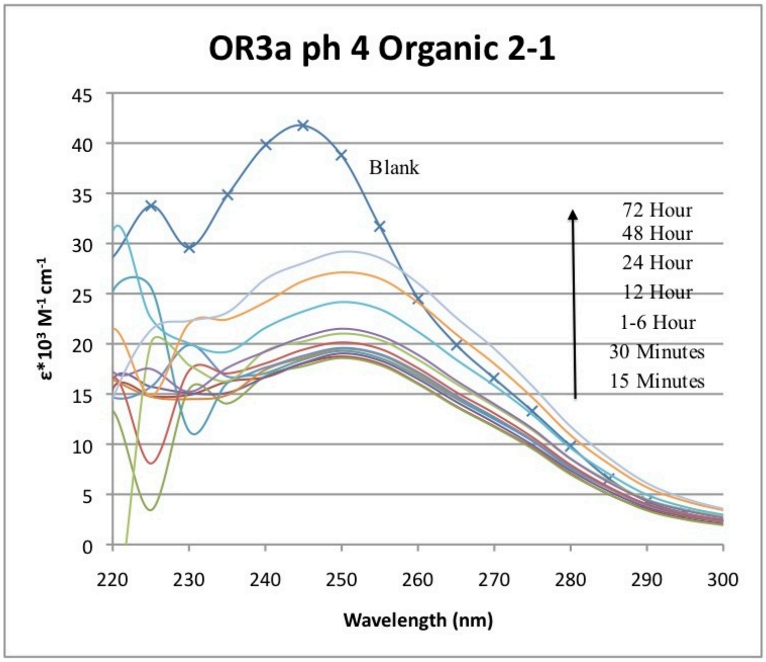
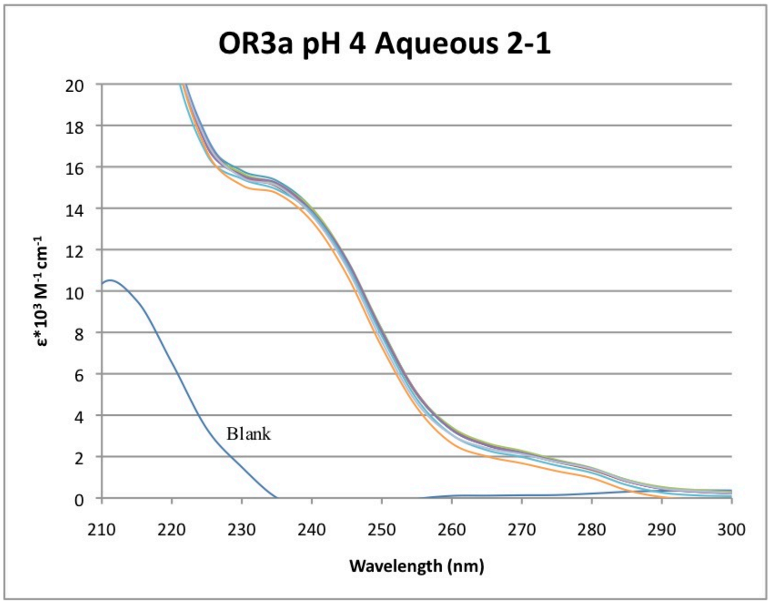


Figure 40: UV-Vis spectrum of the control of OR3a at pH 4. A) Organic phase, time plotted at 250 nm. B) Overall aqueous spectrum; B) Close up around 235 nm. Time plotted at 235 nm.

The UV-Vis spectra above in figure 40, shows that even though the ligand should be somewhat hydrophobic; it will transfer into the aqueous layer and remain there. It will however, transition back into the organic phase slowly over time as evidenced by the decrease in extinction over time and form an equilibrium as seen in the smaller decreases in extinction between 12, 24, and 48 hours.



A)



B)

C)

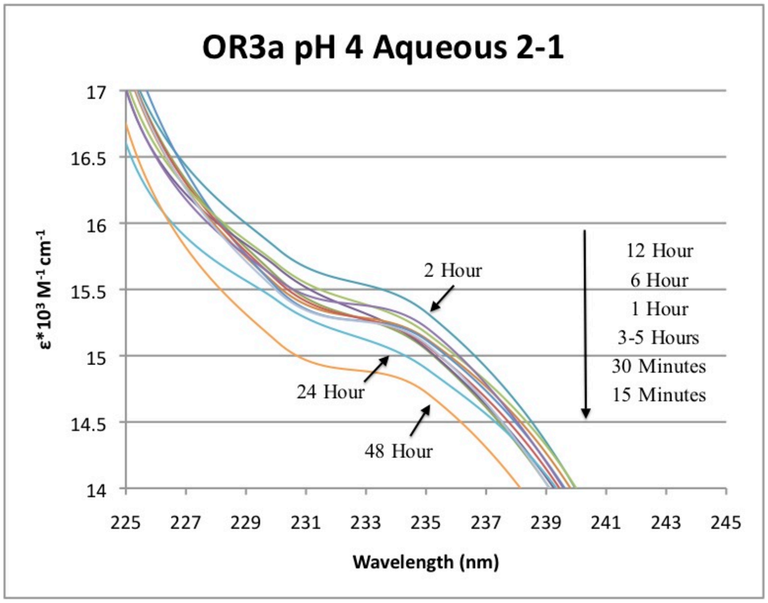
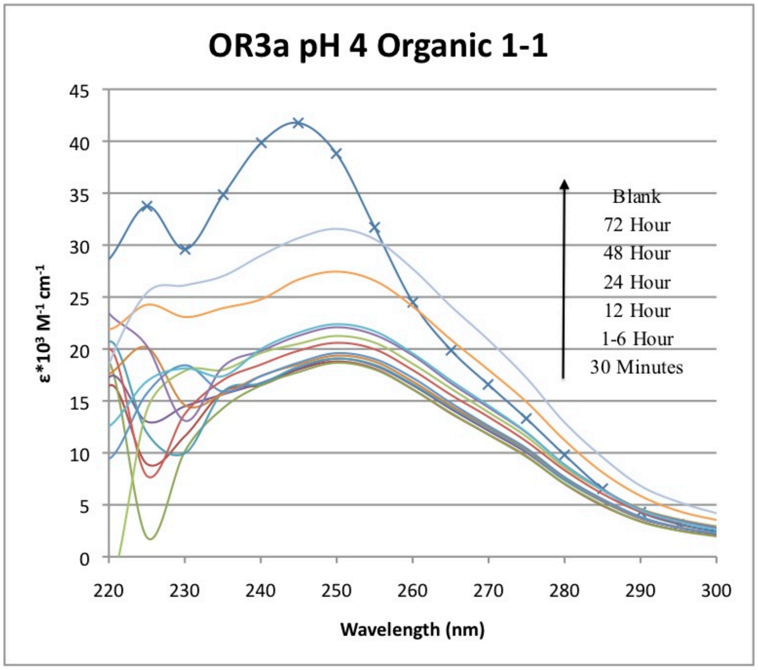


Figure 41: Graph of extinction vs. wavelength for the extraction of uranyl (20 μM) from the aqueous phase (H_2O) at pH 4 by OR3a (10 μM) in the organic phase (DCM). A) Organic phase. Time plotted at 250 nm; B) Aqueous phase; C) Close up of aqueous phase around 235 nm. Time plotted at 235 nm

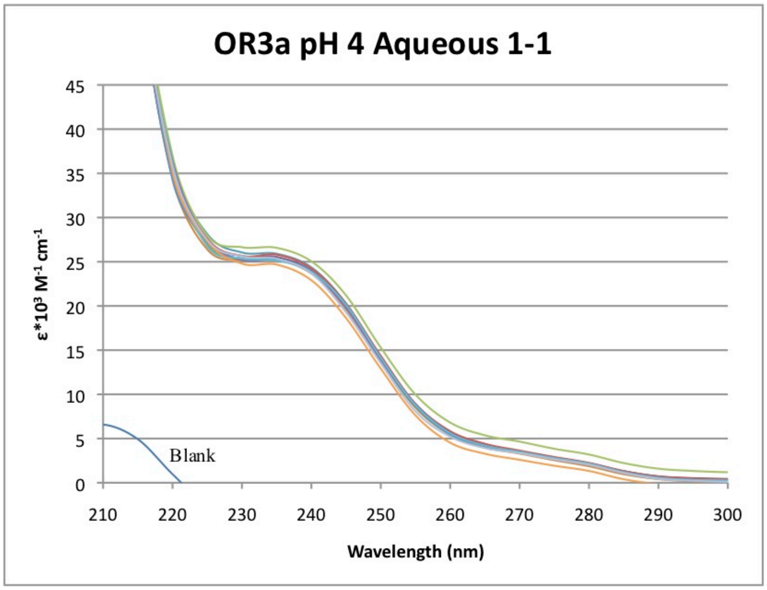
In figure 41, with OR3a at pH 4 and a ratio of 2-1 (metal to ligand), in the organic phase, there is an increase of 10600 extinction units between 15 minutes and 72 hours. The smaller increase noted between 48 and 72 hours could be an indication that the ligand is beginning to reach maximum extraction efficiency. There is a small 5 nm extinction maximum wavelength shift that is indicative weak coordination of uranyl to the ligand.

In the aqueous phase, there is an overall increase in extinction until the 12th hour when there are decreases in extinction. The absorbencies overlap with each other, indicative of the ligand being in equilibrium between the two phases. When there is the monumental decrease in absorbencies between 12 and 24 hour and 24 and 48 hours is a good indication of the metal-ligand complex transferring into the organic phase. The decreases are 300 and 200 extinction units respectively, also an indication that the ligand may be reaching extraction efficiency, especially since the 72nd hour measurement goes back to the equilibrium extinction seen in the earlier measurements. These decreases in extinction maxima correlate well with the increase of extinction maxima in the organic phase.

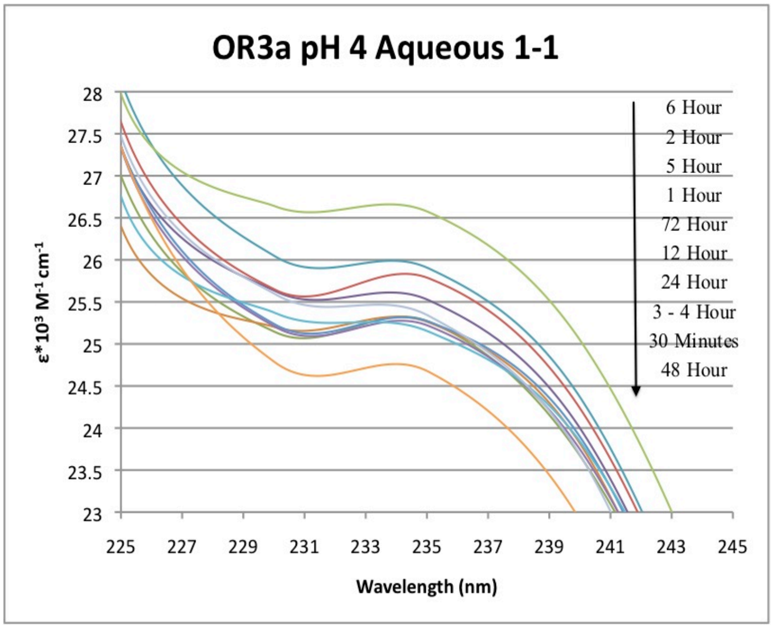
There is not a shift a shift from the control containing no uranyl, indicative of weak coordination between uranyl and the ligand. With the extinction being higher, it is estimated that extraction is in the 20-30% range.



A)



B)



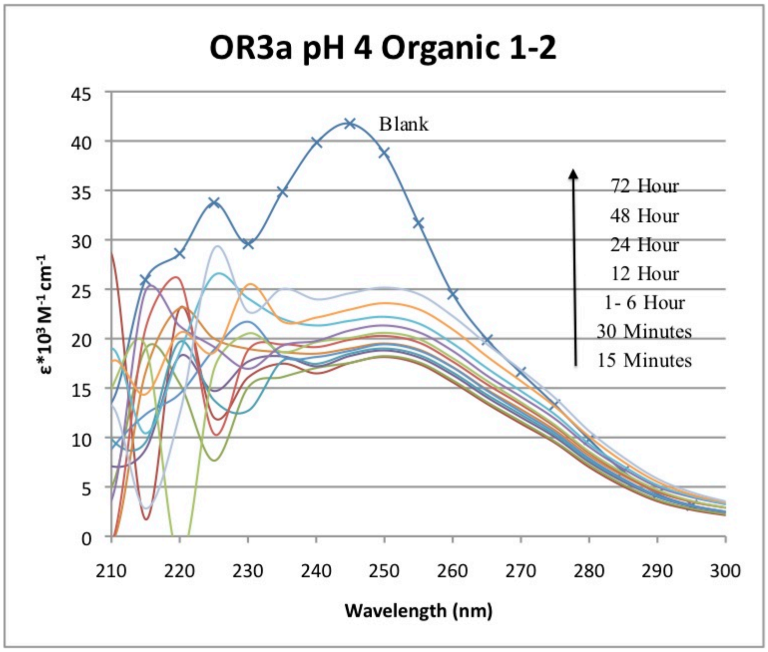
C)

Figure 42: Graph of extinction vs. wavelength for the extraction of uranyl (10 μM) from the aqueous phase (H_2O) at pH 4 by OR3a (10 μM) in the organic phase (DCM). A) Organic phase. Time plotted at 250 nm; B) Aqueous phase; C) Close up of aqueous phase around 235 nm. Time plotted at 235 nm.

With OR3a at pH 4 and a ratio of 1-1 (ligand to metal) (figure 42) in the organic layer, there is an always-increasing extinction maximum at 250 nm at each measurement, a 5 nm shift from the blank. An increase of 12900 extinction units between 15 minutes and 72 hours is noted. The 12 and 24-hour measurements overlap each other, indicative of no increase of ligand-metal complex in the organic phase. It would appear that the ligand takes up to 48 hours to provide significant extractions and then could be slowing down, indicative of reaching extraction efficiency. More data at longer time intervals would be needed to support that hypothesis.

The spectral changes with time of the aqueous layer are quite interesting. In the control, the ligand will freely go into the aqueous layer at pH 4 and remain there. With an excess of ligand or uranyl, ligand goes into the aqueous phase, and some of the ligand will remain there, while the rest will coordinate metal and equilibrate with the organic phase. There should be a decrease in extinction maximum in the aqueous phase, but instead there is an increase as noted. There is a decrease until the 72nd hour, when the extinction goes back to the equilibrium extinction seen at earlier measurements. This would be an indication of the ligand reaching the maximum extraction efficiency. This is the first time that a 1-1 ratio has a higher extinction than an excess of either ligand or uranyl, and therefore estimated to have 30-40% extraction.

A)



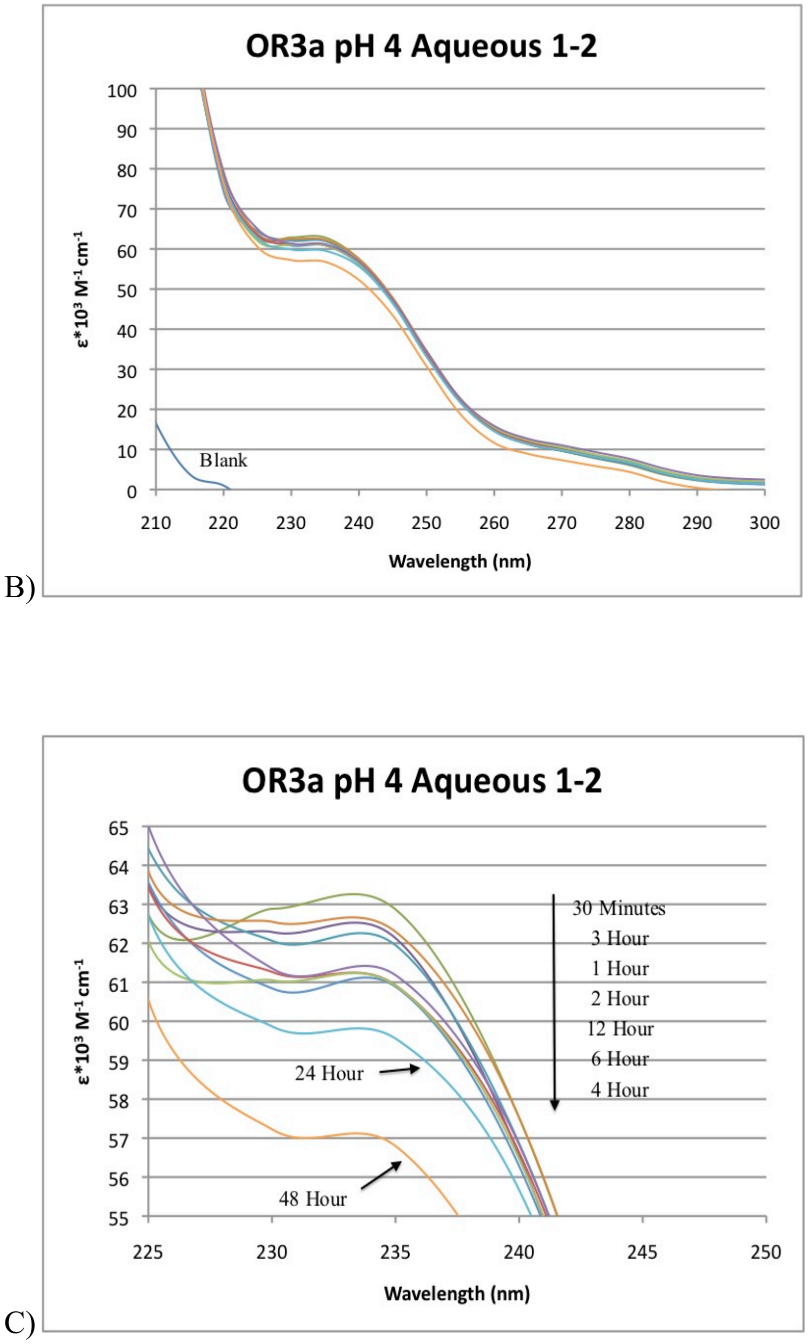


Figure 43: Graph of extinction vs. wavelength for the extraction of uranyl (5 μM) from the aqueous phase (H_2O) at pH 4 by OR3a (10 μM) in the organic phase (DCM). A) Organic phase. Time plotted at 250 nm; B) Aqueous phase; C) Close up of aqueous phase around 235 nm. Time plotted at 235 nm.

With OR3a at pH 4 and a ratio of 1-2 (ligand to metal) in the figure above, in the organic phase, there is a constant increase in extinction maximum at each measurement. Each measurement has also had an extinction maximum wavelength shift of 5 nm indicative of coordination, although weak. The overall increase in maximum extinction is 7000 extinction units, this constant increase in maximum extinction indicates that the uranyl is being extracted, but is disconcerting that it does take up to 24 hours to see a significant difference in the extinction indicative of better extractions. A longer time frame would be needed to see if and when maximum extraction efficiency is achieved.

In the aqueous phase, there is an overall trend of decreasing extinction with increasing time. The extinction decreases for the first two hours, but then suddenly increases by 400 extinction units in the third hour, before decreasing by 1400 extinction units in the 4th hour. It's not until the 12th hour before there is a consistent decrease in the extinction with a difference of 4400 extinction units between the 12th hour and the 48th hour. No shift from the aqueous control is noted, where it can be concluded that in the aqueous phase, coordination of uranyl by the ligand is weak, and that the metal-ligand complex could be hydrophobic and immediately transfer into the organic phase when the complex is formed. At this higher pH, the ligand does not appear to extract uranyl as well as at pH 3, and therefore it is estimated that only 20-30% of the uranyl is extracted.

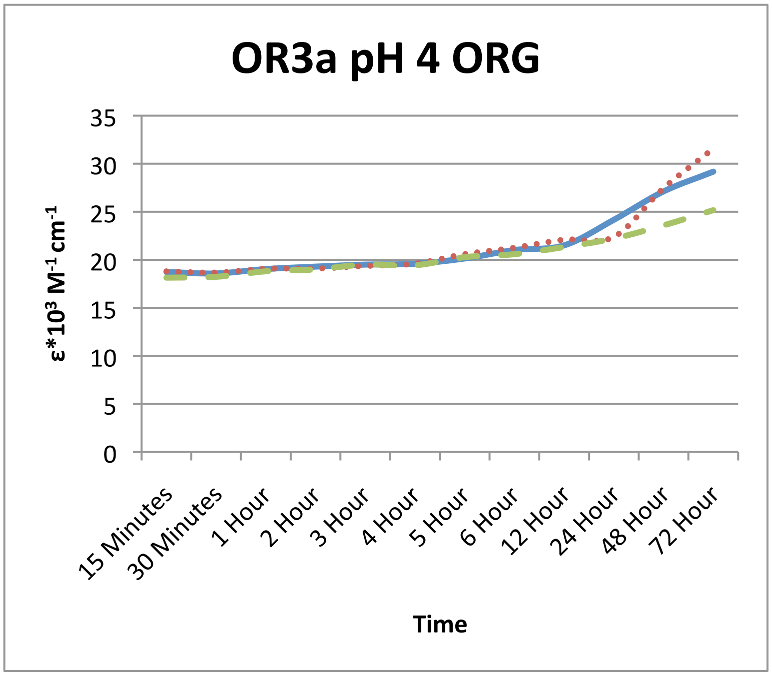
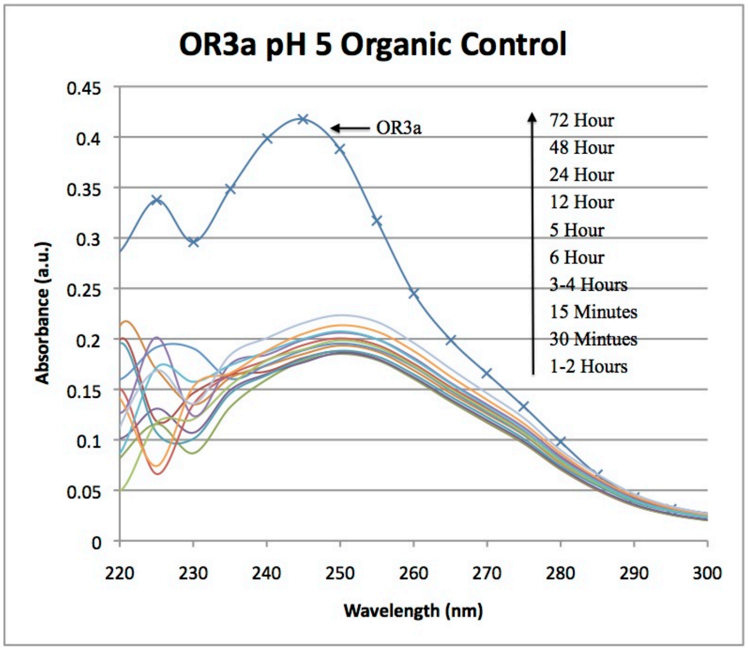
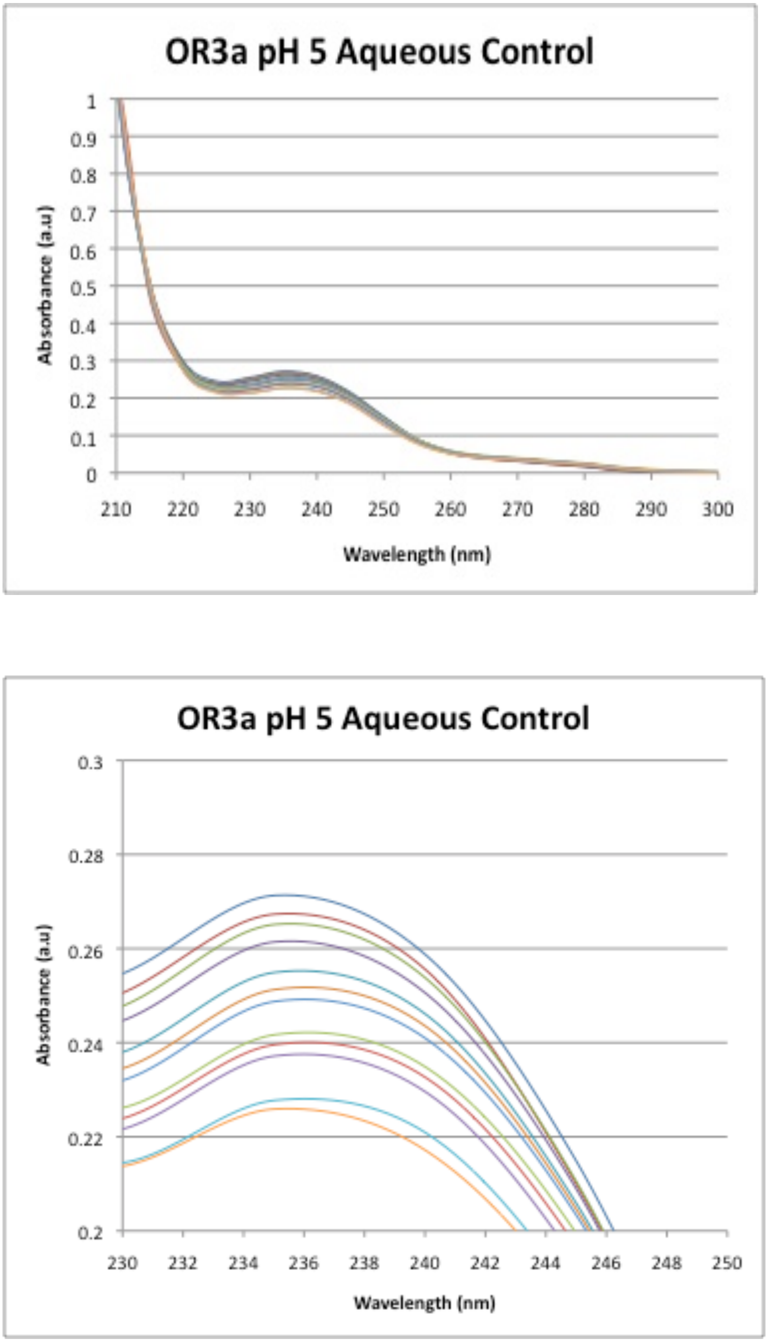


Figure 44: Graph of extinction versus time for OR3a at pH 4 in the organic phase. –– 2-1 ratio, ++ 1-1 ratio, - - 1-2 ratio (metal to ligand)

OR3a pH 5



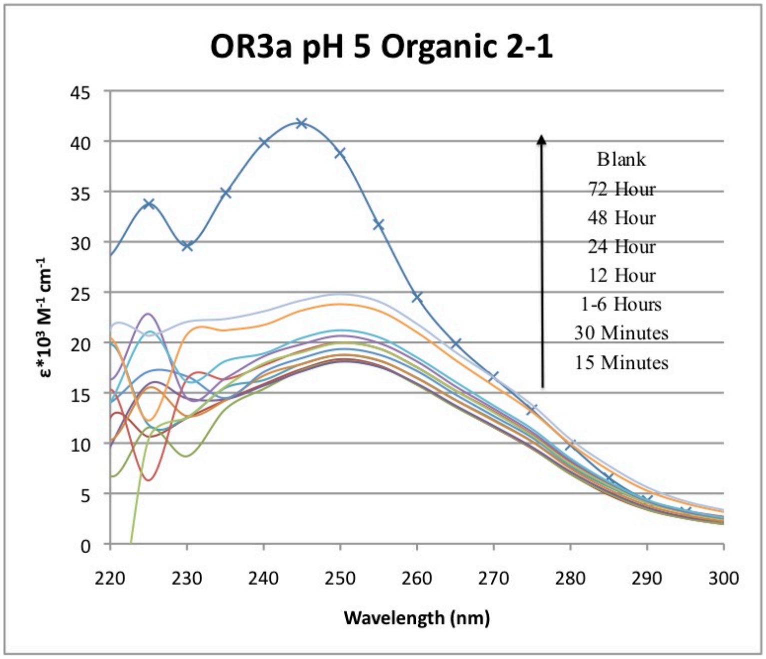
A)


B)

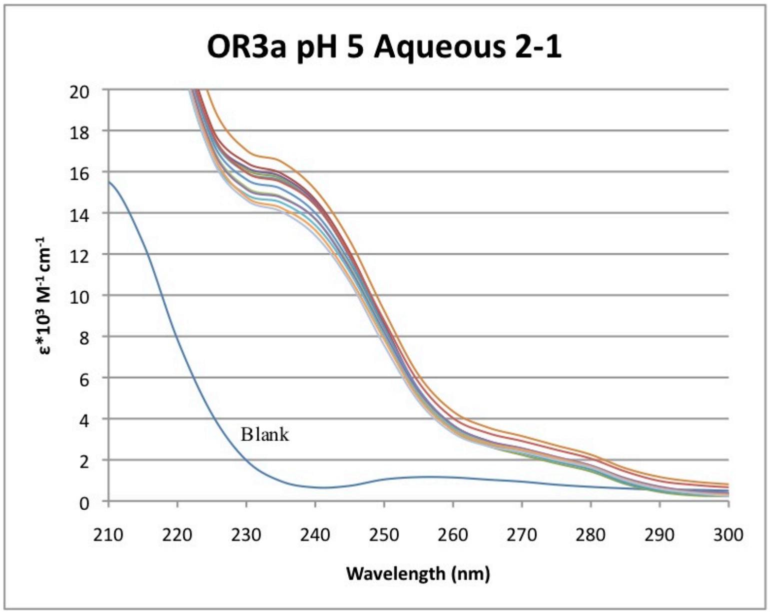
C)

Figure 45: UV-Vis spectrum of the control of OR3a at pH 5. A) Organic phase, time plotted at 250 nm. B) Overall aqueous spectrum; C) Close up around 235 nm.

The UV-Vis spectra above in figure 45, shows that even though the ligand should be somewhat hydrophobic; it will transfer into the aqueous layer and remain there. It will however, transition back into the organic phase slowly over time as evidenced by the decrease in extinction over time. The extinction decrease appears to happen in groups of a few measurements at a time. The first 1-hour measurements are all closely associated with each other, and then hours 2-4, then hours 5-24, and finally 48 and 72 hours. Perhaps the ligand is equilibrating after a certain amount is transferred back into the organic phase.



A)



B)

C)

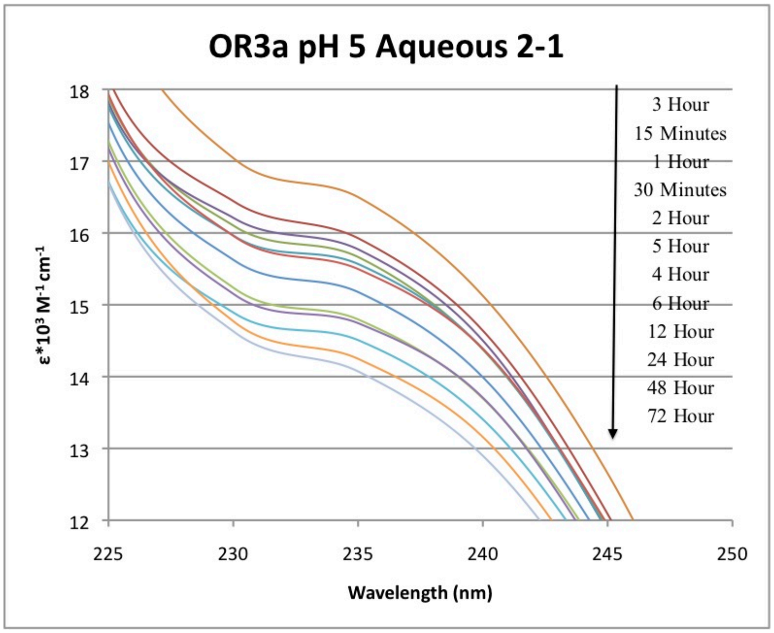
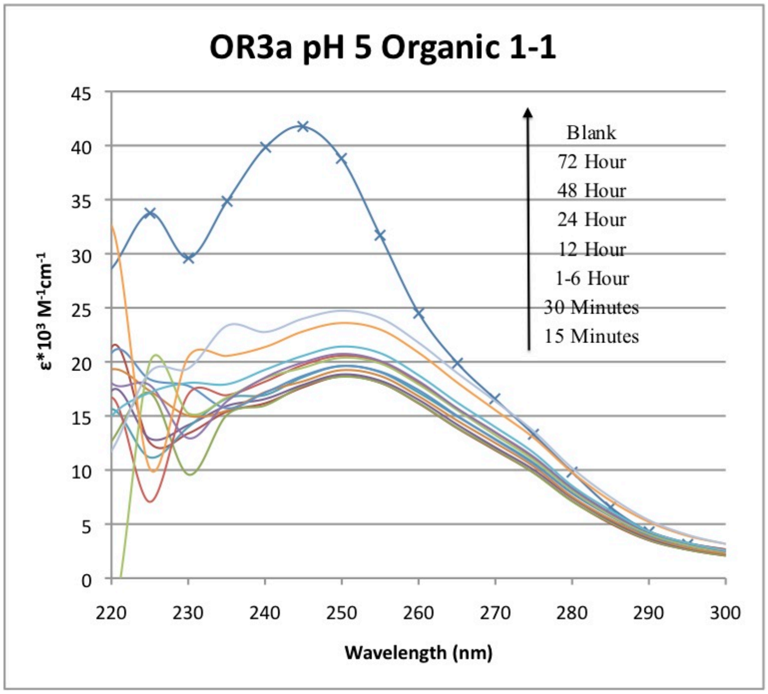


Figure 46: Graph of extinction vs. wavelength for the extraction of uranyl (20 μM) from the aqueous phase (H_2O) at pH 5 by OR3a (10 μM) in the organic phase (DCM). A) Organic phase. Time plotted at 235 nm; B) Aqueous phase; C) close up of aqueous phase around 235 nm. Time plotted at 235 nm.

In figure 46, with OR3a at pH 5 and a ratio of 2-1 (metal to ligand), in the organic phase, there is a consistent increase in steady increase in extinction maximum for the first 24 hours of 700 extinction units each measurement. It's not until the 48th hour is there a dramatic increase in maximum extinction and an overall increase of 6700 extinction units. The smaller increase at 72 hours compared to 48 hours is indicative of the ligand reaching maximum extraction efficiency. For all measurements, there is a 5 nm extinction maximum wavelength shift, indicating weakly coordinated uranyl to the ligand. Instead of all four sulfurs binding, only two or perhaps even one sulfur is binding the metal.

The spectral changes with time of the aqueous layer are quite intriguing. The maximum extinction has a decrease of 1900 extinction units between 15 minutes and 72 hours. The aqueous layer does correspond to the smaller increase of extinction maximum in the organic phase with a smaller decrease in the aqueous phase between 48 and 72 hours of 200 extinction units as compared to the previous measurement. The aqueous phase shows no extinction maximum wavelength shift from the aqueous layer of the control, containing only ligand and no uranyl. This could be from weakly coordinated uranyl to the ligand, or the formation of a hydrophobic metal-ligand complex in the aqueous layer. At pH 5, more than likely out of the best pH for extractions, it is estimated that only 10-20% of the uranyl is extracted based on the data above.

A) 

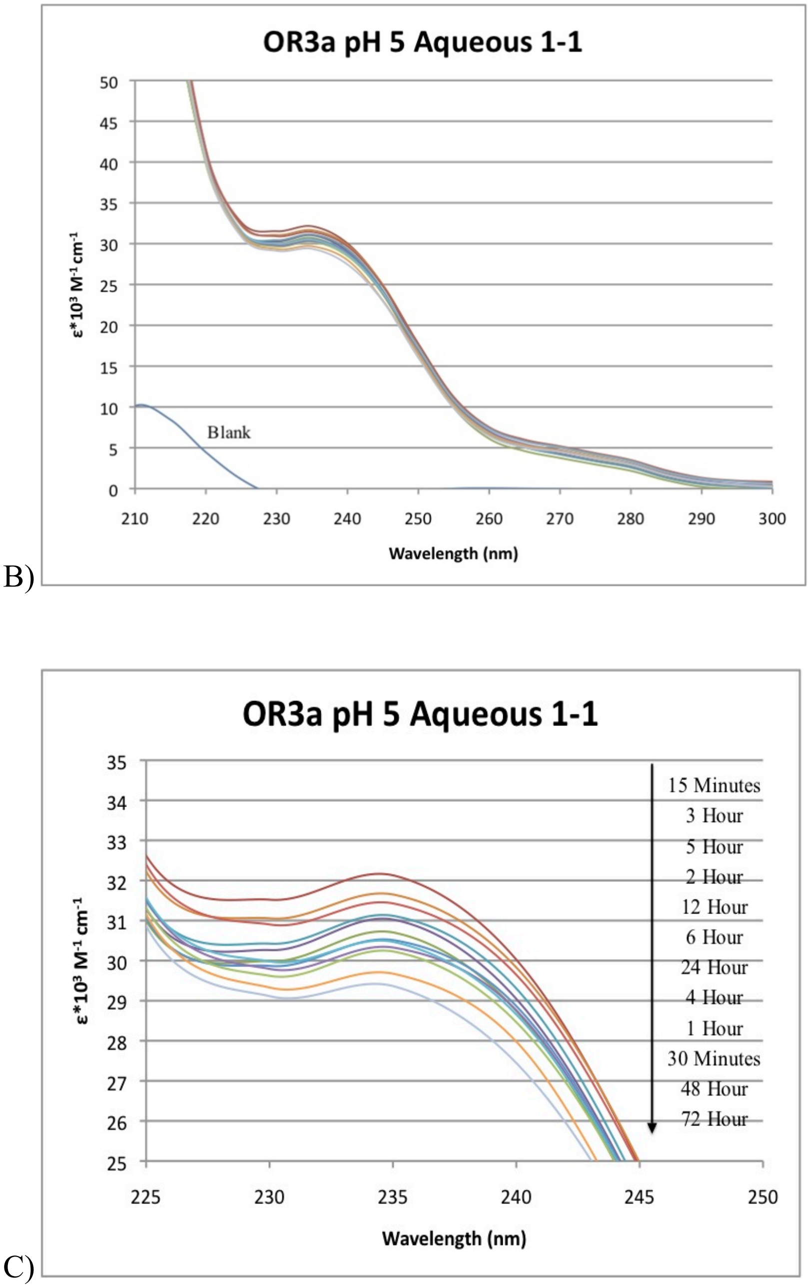
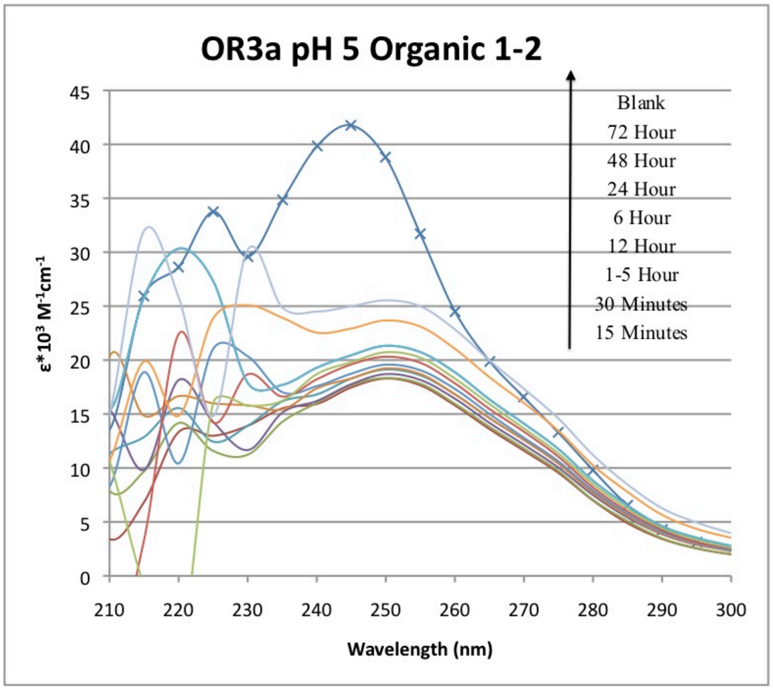


Figure 47: Graph of extinction vs. wavelength for the extraction of uranyl (10 μM) from the aqueous phase (H_2O) at pH 5 by OR3a (10 μM) in the organic phase (DCM). A) Organic phase. Time plotted at 250 nm; B) Aqueous phase; C) Close up of aqueous phase around 235 nm. Time plotted at 235 nm.

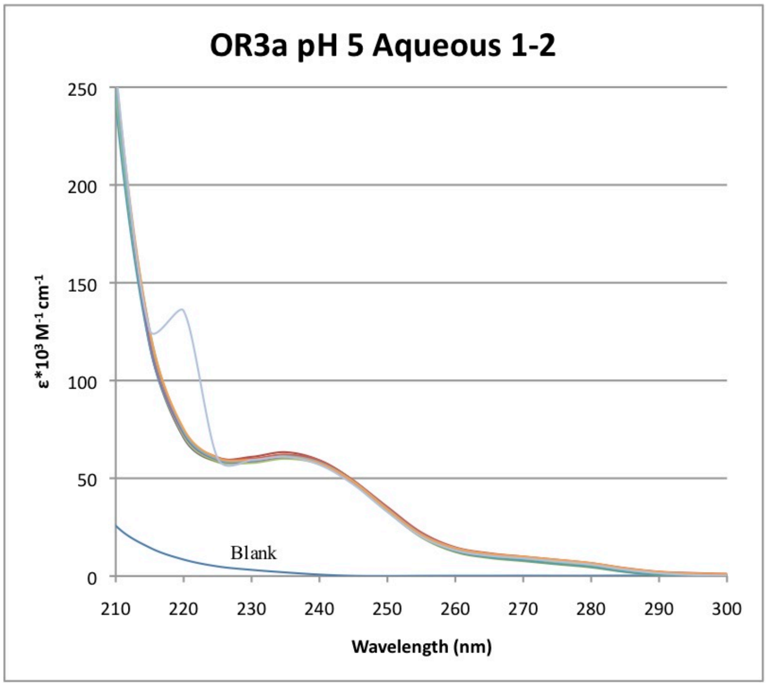
With OR3a at pH 5 and a ratio of 1-1 (metal to ligand) in figure 47, in the organic layer, much like what was seen at the other ratios of excess ligand and excess uranyl, there is a consistent increase in extinction maximum with the biggest increases coming between the

24th and 48th hour, and the 48th and 72nd hour, with an increase overall of 6100 extinction units. There is also a shift of 5 nm in extinction maximum wavelength from the very first measurement indicative of a weakly binding metal-ligand complex in the organic phase. The late increase in extinction maximum at the 48-hour measurement indicates a kinetic issue with the extraction and the smaller increase in the 72nd hour, would be indicative of the ligand possibly reaching maximum extraction efficiency at this pH and ratio.

In the aqueous phase, as is seen in all the other aqueous phases at this pH, the extinction maximum fluctuates until the 12th hour where there is consistently a decrease. The most important spectra are the 48th and 72nd hour measurements. These spectra correlate well with the organic phase, where there were big increases in extinction maximum between 24 and 48 hours, and a smaller increase between the 48th and 72nd hours, there are big decreases in the aqueous phase between 24 and 48 hours, and a smaller decrease between the 48th and 72nd hour measurements. While this decrease is small compared to the other ratios at this pH, it does fall in line with what would be expected. The overall decrease in extinction is 2700 extinction units between the measurements at 15 minutes and 72 hours. While less than what is seen in the organic phase, this could just be an indication of ligand at equilibrium in the aqueous phase. According to the data, it is hypothesized that only 10-20% of the uranyl was extracted.


OR3a pH 5 Organic 1-2
Blank
72 Hour
48 Hour
24 Hour
6 Hour
12 Hour
1-5 Hour
30 Minutes
15 Minutes
ε*10³ M⁻¹cm⁻¹
0
5
10
15
20
25
30
35
40
45
210
220
230
240
250
260
270
280
290
300
Wavelength (nm)

A)


OR3a pH 5 Aqueous 1-2
Blank
ε*10³ M⁻¹cm⁻¹
0
50
100
150
200
250
210
220
230
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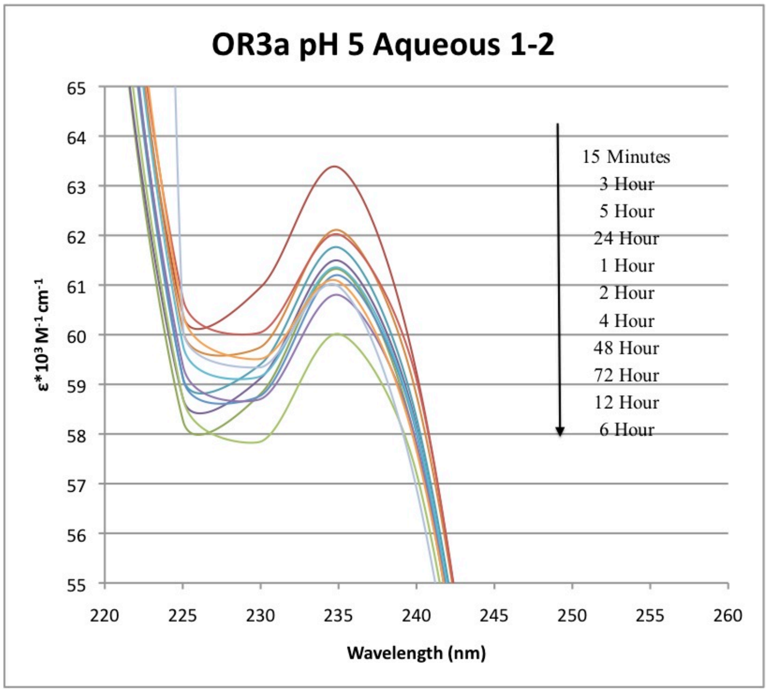
280
290
300
Wavelength (nm)

B)



C)

Figure 48: Graph of extinction vs. wavelength for the extraction of uranyl (5 μM) from the aqueous phase (H_2O) at pH 5 by OR3a (10 μM) in the organic phase (DCM). A) Organic phase. Time plotted at 250 nm; B) Aqueous phase; C) Close up of aqueous phase around 235 nm. Time plotted at 235 nm.

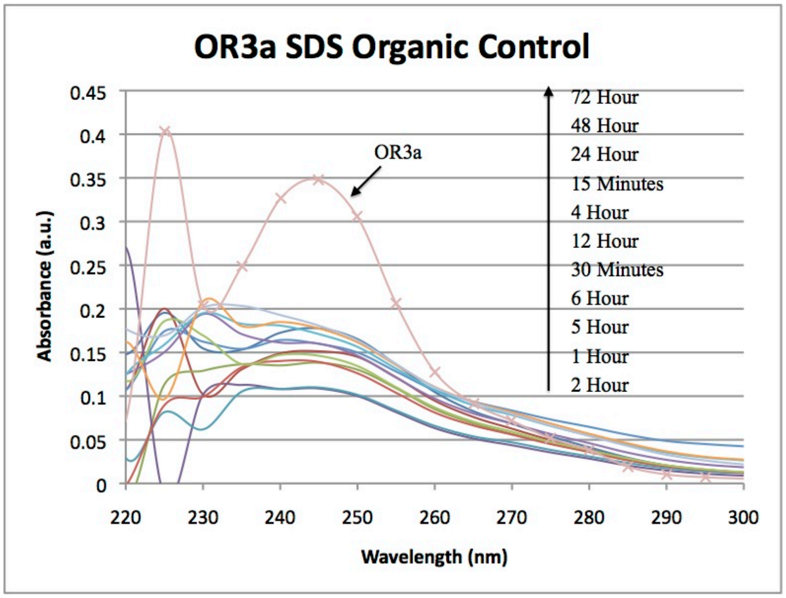
In figure 48 above, with OR3a at pH 5 and a ratio of 1-2 (metal to ligand) in the aqueous phase, an immediate shift in extinction maximum wavelength from the ligand blank of 5 nm at the first measurement is noted. This is indicative of a weakly coordinated uranyl to the ligand where only two, or possibly even one sulfur is bound to the metal instead of all four sulfurs. There is an always-increasing maximum extinction at each time measurement except for the 12th hour measurement. An overall increase of 7600 extinction units is noted. As was seen in the 2-1 (metal to ligand) ratio, all the measurements are grouped together with a slight increase over time, and then at 48 hours, there is a huge increase in extinction maximum, with a slightly less increase in the 72nd hour.

While the general trend of the aqueous phase is decreasing extinction maximum, it’s not until the 24th hour that there is a consistent decrease. An overall decrease of 6600 extinction units between 15 minutes and 72 hours, with a note that at 6 hours the extinction is actually lower, which could be an outlier. This could be an indication that the ligand is in equilibrium, and because of the excess ligand, the equilibrium hypothesis makes sense because the overall decrease is also consistent with the overall increase seen in the organic phase, indication extraction of uranyl. Using the data above, it is estimated that only 20-30% of the uranyl was extracted from the aqueous phase.

Extractions with SDS

To see if there was a possibility of the ligand aggregating with itself, we had a surfactant, sodium dodecyl sulfate (SDS) or sodium lauryl sulfate, as it is also known. These extractions were done at a pH of 3, and a 5µM concentration of SDS in the organic layer.

OR3a pH 3 SDS



A)

B)

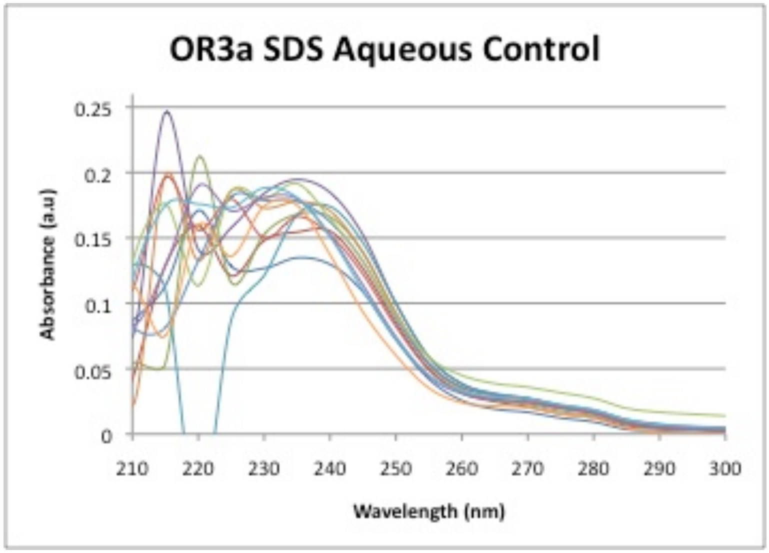
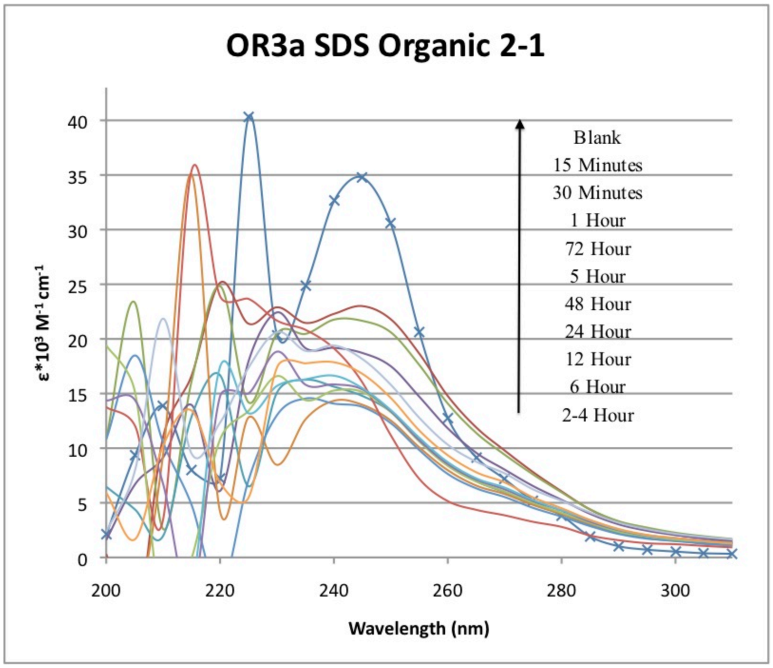


Figure 49: UV-Vis spectrum of OR3a with SDS control at pH 3. A) Organic phase, time plotted at 240 nm. B) Aqueous phase

The UV-Vis spectra above in figure 49, shows that even though the ligand should be somewhat hydrophobic; it will transfer into the aqueous layer and remain there. It will however, transition back into the organic phase slowly over time as evidenced by the decrease in extinction over time

A)



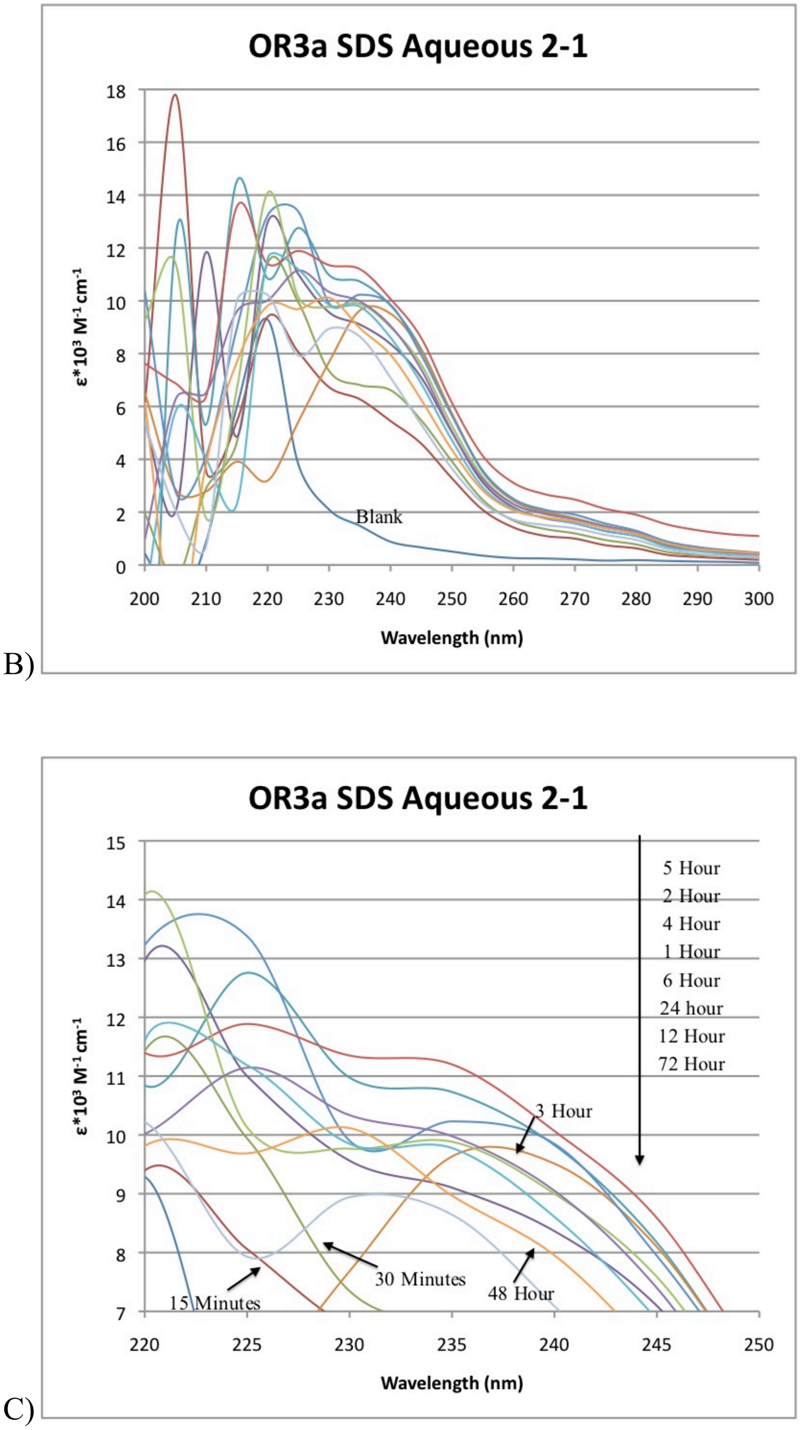
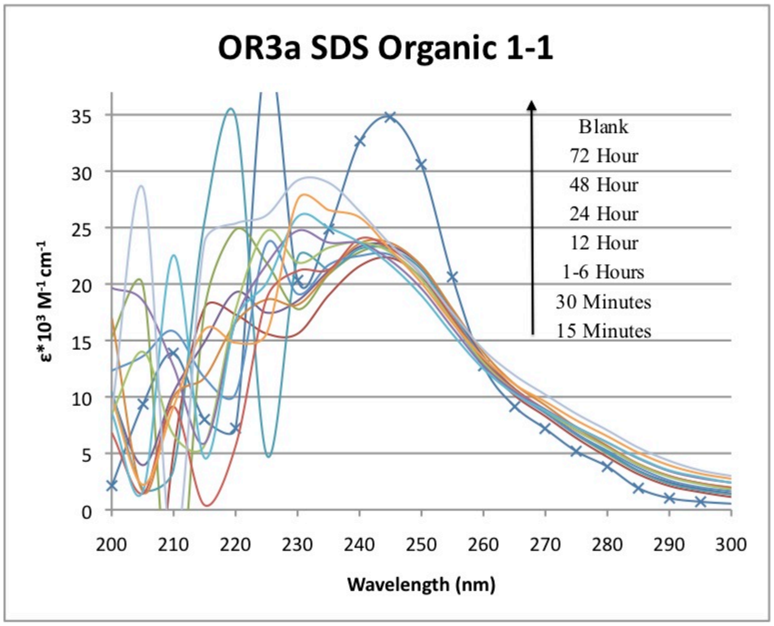


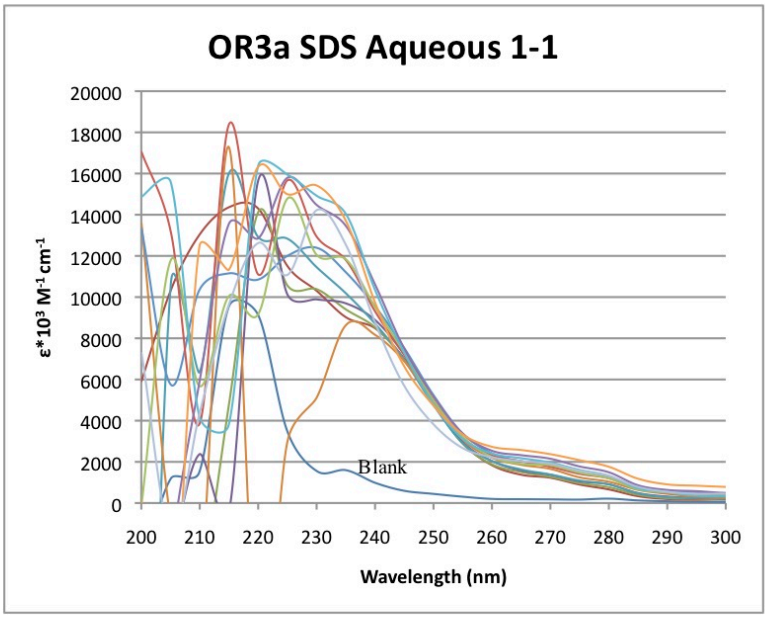
Figure50: Graph of extinction vs. wavelength for the extraction of uranyl (10 μM) from the aqueous phase (H_2O) at pH 3 by OR3a (10 μM) with SDS (5 μM) in the organic phase (DCM). A) Organic phase. Time plotted at 240 nm; b) aqueous phase; c) close up of aqueous phase around 235 nm. Time plotted at 235 nm.

In the organic phase of figure 50, with OR3a, SDS, and a ratio of 2-1 (metal to ligand), there is a general decrease in extinction maximum until the 5th hour, where an increase in extinction maximum in noted. Another decrease in maximum extinction at the 6th hour measurement, before there is a consistent increase in extinction for the 12, 24, 48, and 72-hour measurements. What there should be is a consistent increase in maximum extinction and not a fluctuation to have good extractions data. The fluctuation could be the ligand establishing equilibrium before any binding. It is not until the 6th hour is there a shift in maximum extinction wavelength of 5 nm. The 5th hour measurement, that is high in extinction and has a shift in wavelength of 10 nm from the ligand blank, would be an indication of a stronger coordinating complex, but is not stable in the organic phase for long, as evidenced by the sharp decrease and maximum extinction wavelength shift back towards the ligand blank by 5 nm.

In the aqueous layer, there is a shift in maximum extinction wavelength of 15 nm from the aqueous control, which contained no uranyl and only ligand with SDS. This shift disappears after 1 hour and goes back to the control wavelength of 235 nm. There may have been a complex formed in the aqueous layer, but it was not stable and did not transfer into the organic phase. There is a decrease of 1500 extinction units in the extinction maximum between the 48 and 72nd hour measurements. This shift and decrease in maximum extinction are indicative of a weakly binding metal-ligand complex and that it is transferring into the organic phase, much like the increases seen in the organic phase. The fluctuation would indicate that the ligand is trying to reach equilibrium or is at equilibrium. With the data in hand, it is estimated that about 30-40% of the uranyl was extracted.


OR3a SDS Organic 1-1
ε*10³ M⁻¹ cm⁻¹
35
30
25
20
15
10
5
0
200
210
220
230
240
250
260
270
280
290
300
Wavelength (nm)
Blank
72 Hour
48 Hour
24 Hour
12 Hour
1-6 Hours
30 Minutes
15 Minutes

A)


OR3a SDS Aqueous 1-1
ε*10³ M⁻¹ cm⁻¹
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
200
210
220
230
240
250
260
270
280
290
300
Wavelength (nm)
Blank

B)

C)

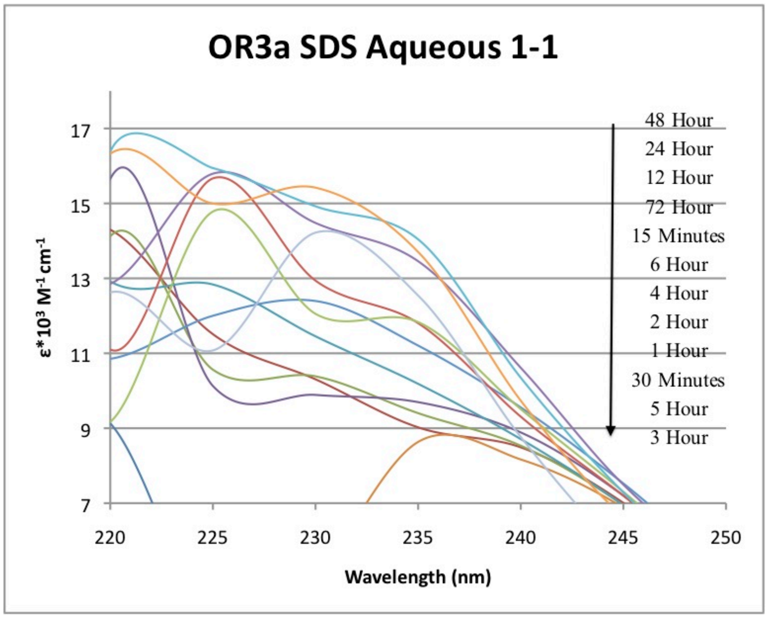


Figure 51: Graph of extinction vs. wavelength for the extraction of uranyl (10 μM) from the aqueous phase (H_2O) at pH 3 by OR3a (10 μM) with SDS (5 μM) in the organic phase (DCM). A) Organic phase. Time plotted at 235 nm; B) Aqueous phase; C) Close up of aqueous phase around 235 nm. Time plotted at 230 nm

In the figure above with OR3a and SDS at pH 3 and a ratio of 1-1 (metal to ligand), in the organic phase, up until the 24-hour measurement, there is no shift in extinction maximum wavelength, a shift of 15 nm after which is observed. There is a possible shift of 10 nm back towards the ligand blank at 48 hours, but the shift goes back to 15 nm from the ligand blank at the 72-hour measurement. Perhaps, the complex at the 48-hour measurement was not as stable as it could be, and went back to the stronger coordinating complex. The biggest increase of extinction maximum is 2800 extinction units between the 48th and 72nd hour measurement.

In the aqueous phase, the ligand takes a few hours to come to equilibrium, but this could be due to the extraction of uranyl into the organic phase. The overall difference between 15 minutes and 72 hours was an increase in the extinction of 2100 extinction units. The 72-hour measurement was actually on a decline in the extinction from the two previous measurements. While it is tough to tell, there appears to be a shift of 5 nm from the aqueous controls, indicating that ligand is weakly coordinating uranyl in the aqueous phase. The shift along with the increases and decreases in extinction maxima would indicate a slightly hydrophilic metal-ligand complex, but it does not seem to detract from the extraction seen in the organic phase. At this ratio, it is estimated that about 60-70% of the uranyl was extracted at this ratio.

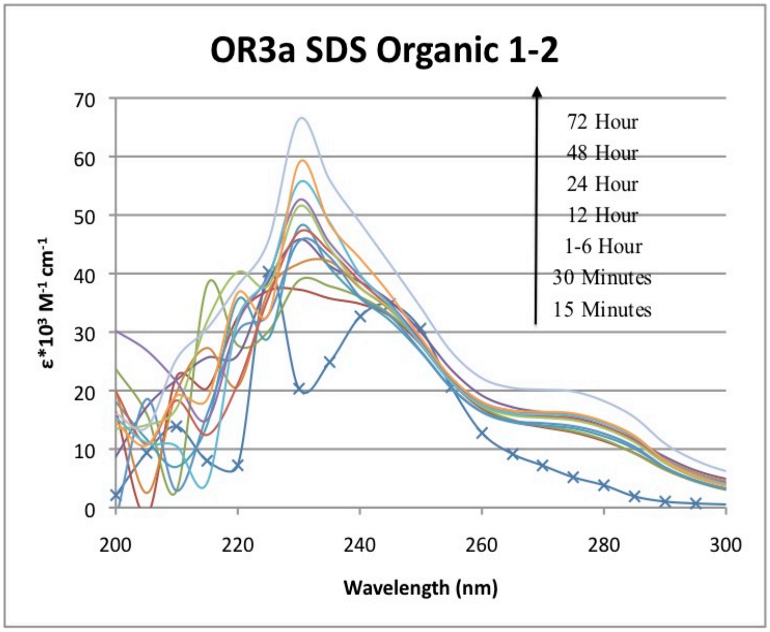
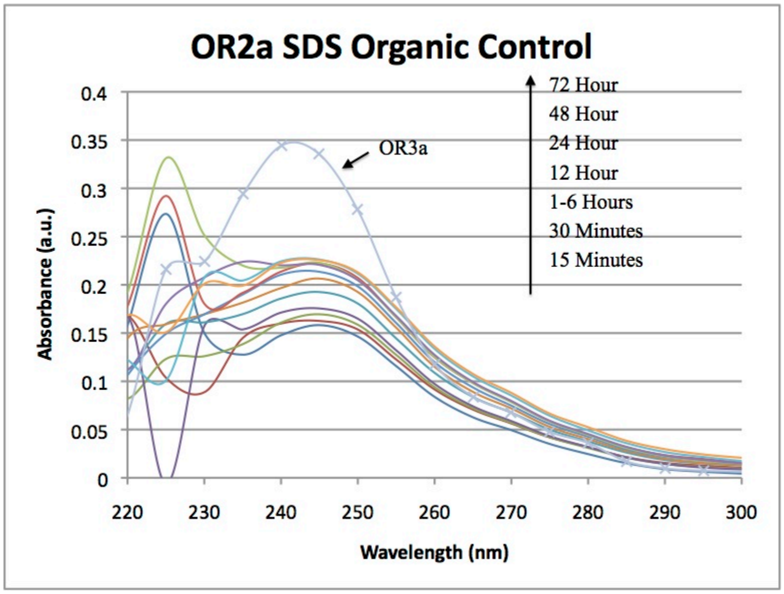


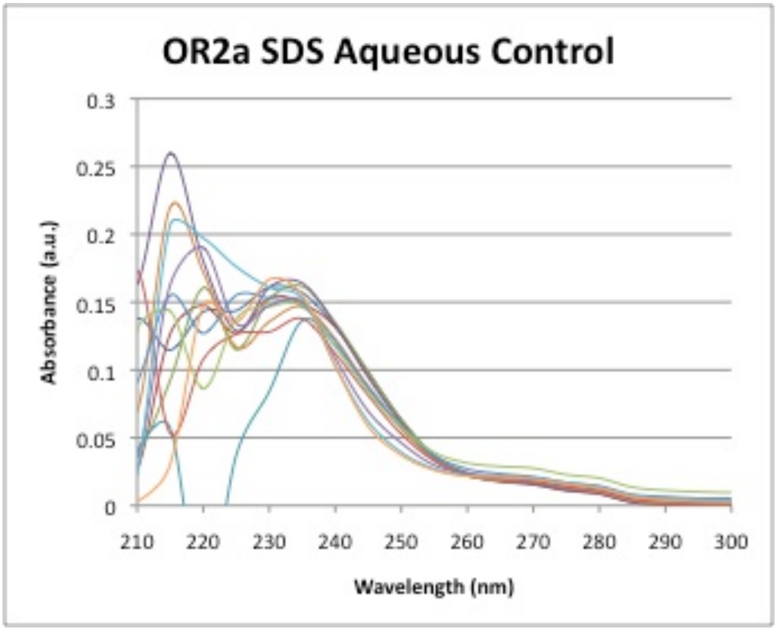
Figure 52: Graph of extinction vs. wavelength for the extraction of uranyl (10 μM) from the aqueous phase (H_2O) at pH 3 by OR3a (10 μM) with SDS (5 μM) in the organic phase (DCM). Time plotted at 230 nm.

In the figure above, with OR3a, SDS, at pH 3 and a ratio of 1-2 (metal to ligand), in the organic phase, there is an immediate shift of 15 nm in extinction maximum wavelength from the ligand blank. Then there is an ever-increasing extinction maximum as well. This is great extraction data, although there is not the 20-25 nm shift that would indicate strong coordination of the uranyl ion, but much stronger than there was without SDS. The biggest increase occurs between 48 and 72 hours with an increase in extinction of 7500 extinction units. The reason for there not being an aqueous phase is that in the aqueous phase, there was some problem, that caused it to be cloudy and therefore would make the UV-Vis spectra go off the chart.

OR2a pH 3 SDS



A)

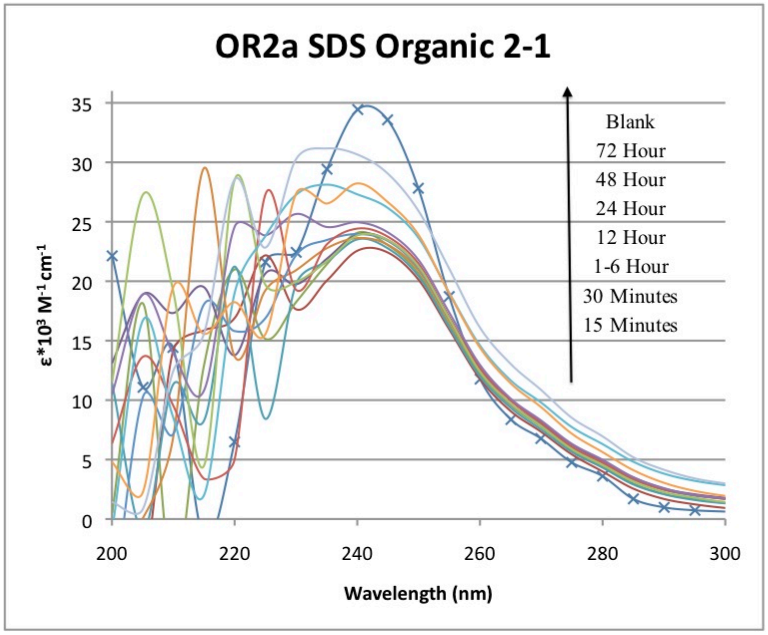


B)

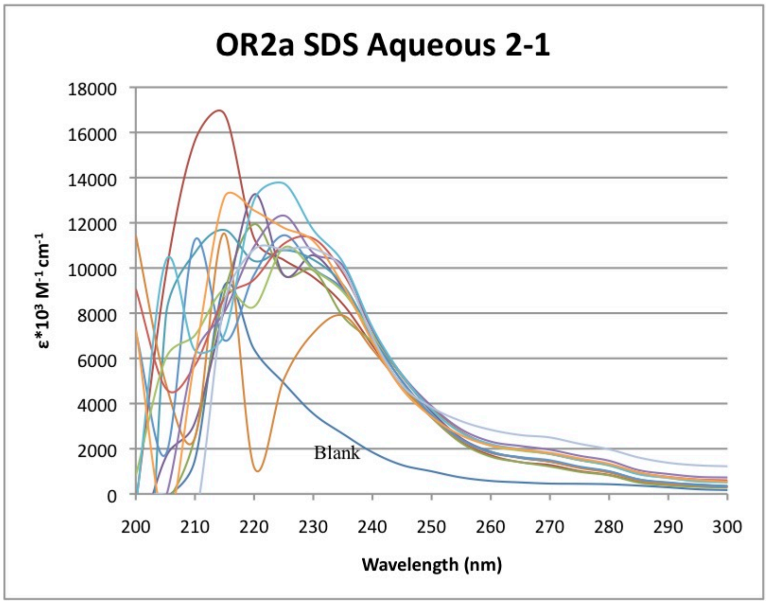
Figure 53: UV-Vis spectrum of OR2a SDS control at pH 3. A) Organic phase, time plotted at 245 nm. B) Aqueous phase

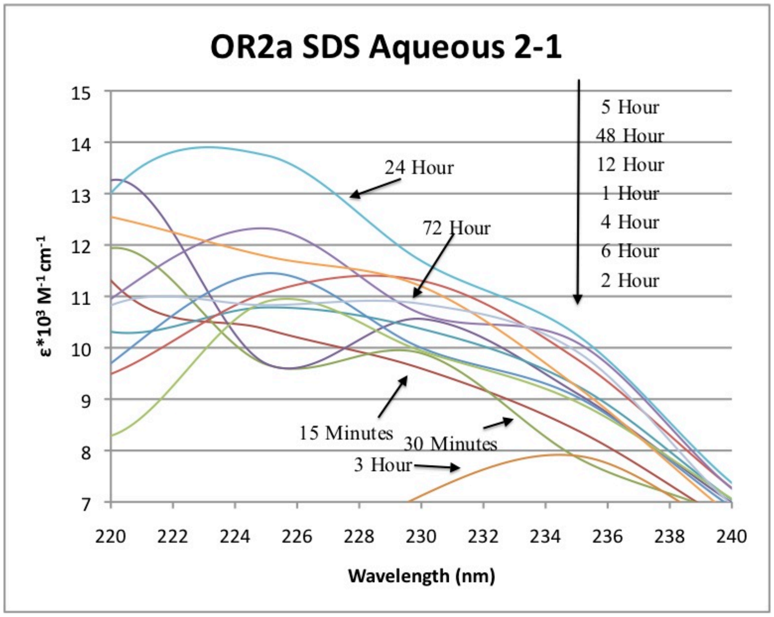
The UV-Vis spectra above in figure 53, shows that even though the ligand should be somewhat hydrophobic; it will transfer into the aqueous layer and remain there. It will however, transition back into the organic phase slowly over time as evidenced by the decrease in extinction over time

A)



B)





C)

Figure 54: Graph of extinction vs. wavelength for the extraction of uranyl (20 μM) from the aqueous phase (H_2O) at pH 3 by OR2a (10 μM) with SDS (5 μM) in the organic phase (DCM). A) Organic phase. Time plotted at 240 nm; B) Aqueous phase; C) Close up of aqueous phase around 230 nm. Time plotted at 230 nm.

In the figure above, with OR2a and SDS at pH 3 and a ratio of 2-1 (metal to ligand), in the organic layer, the maximum extinction is increasing at every measurement with an overall increase of 8600 extinction units. Even with the SDS to help prevent aggregation of the ligand, there is still a kinetic issue associated with extractions. The first shift in extinction wavelength doesn't occur till the 24th hour, a 5 nm shift, and doesn't last because the spectra shifts back at the 48th hour and doesn't increase in extinction; however, at the 72nd hour, the shift returns along with an increase in extinction, indicative that the complex is possibly more stable with the increase in time, and with stronger coordination than was noted at previous measurements.

The aqueous phase is similar to the aqueous phases seen with OR3a and SDS. After 15 minutes, there is a shift in extinction maximum wavelength of 5 nm from the control aqueous phase, but this quickly goes away after 30 minutes. The extinction maximum increases in the 1st hour but then decreases in the 2nd hour. It decreases even more in the third hour but this could be an outlier. The maximum extinction increases in the 4th and

5th hour before decreasing in the 6th hour. It then increases once again in the 12th and 24th hour before decreasing in the 48th and 72nd hours. This does not correlate well with the organic phase, a consistent decrease in extinction maximum would be expected, but the fluctuations could indicate and equilibrium trying to be established by free ligand and possibly a partially hydrophilic metal-ligand complex. Using the data above, it is predicted that 70-80% of the uranyl was extracted from the aqueous phase after 72 hours.

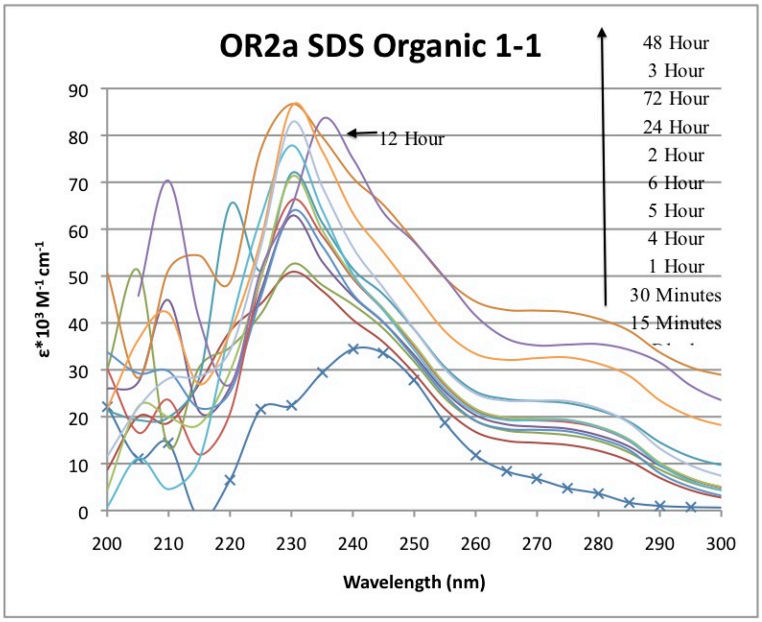
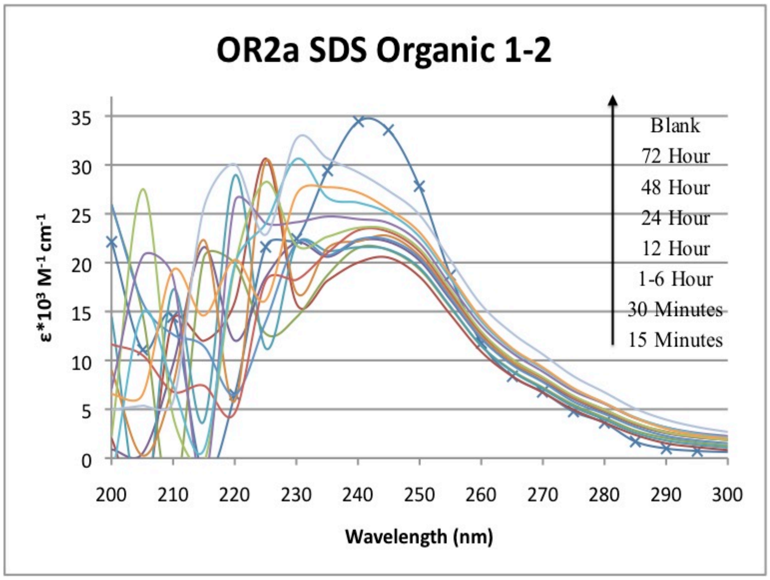
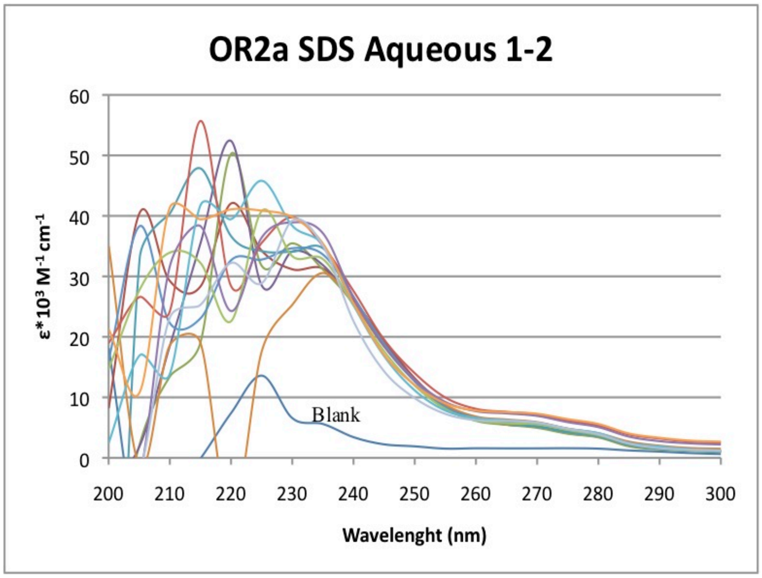


Figure 55: Graph of extinction vs. wavelength for the extraction of uranyl (10 μM) from the aqueous phase (H_2O) at pH 3 by OR3a (10 μM) with SDS (5 μM) in the organic phase (DCM). Time plotted at 230 nm.

In the figure above, with OR2a and SDS at pH 3 and a ratio of 1-1 (uranyl to ligand), in the organic phase, the general trend is an increase in extinction maximum at each time measurement. There is a shift in extinction maximum wavelength of 10 nm from the ligand blank at 240 nm. A shift of only 5 nm at the 12th hour is noted. The last 4 measurements could be considered outliers, as they were above the absorbencies of the other measurements at the higher wavelengths. The increase in maximum extinction and the shift is indicative of both good extraction and a somewhat stronger coordination metal-ligand complex. There is not any aqueous phase data for this run, as there was a mishap in the aqueous phase, causing it to be cloudy, and would make the extinction of that layer to go off the charts. Since the organic layer seemed unaffected for the most part, we decided to measure the organic layer and look for the trends.



A)



B)

C)

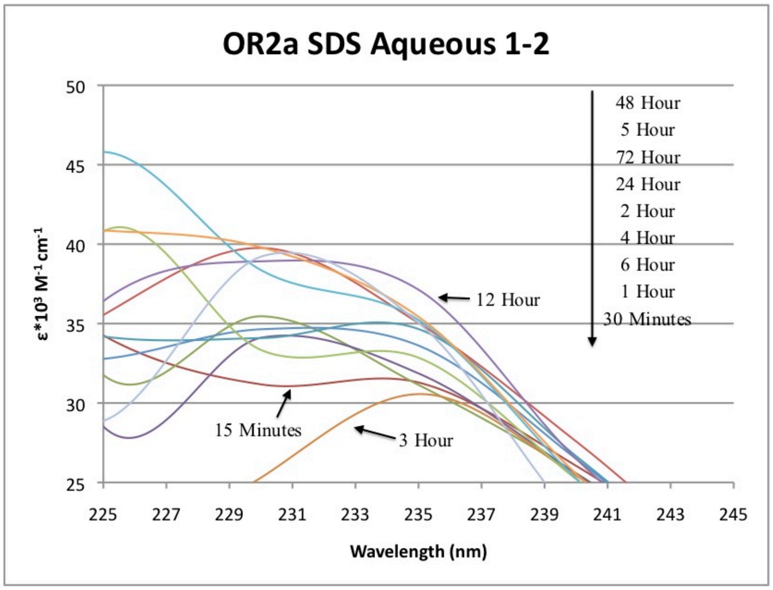


Figure 56: Graph of extinction coefficient vs. wavelength for the extraction of uranyl (5 μM) from the aqueous phase (H_2O) at pH 3 by OR3a (10 μM) with SDS (5 μM) in the organic phase (DCM). a) Organic phase; b) aqueous phase; c) close up of aqueous phase at 235 nm. Time plotted at 230 nm

In figure 56 above, with OR2a and SDS at a ratio of 1-2 (metal to ligand), in the organic phase, there are similarities to what was noted at the 2-1 ratio like there is not a shift in extinction wavelength until the 12th hour, and then there is a shift of 5 nm. There is an increase of 12200 extinction units overall in the organic phase. The shift noted would be rationale for a weakly coordinated uranyl to the ligand, as it is not in the 20-25 nm range of a strongly coordinated complex. Two sulfurs, or perhaps even one sulfur could be binding to uranyl, instead of the four that would cause the 20-25 nm shift. While it is unclear if the SDS is helping with the binding or acting as a co-extractant.

The aqueous phase is no different than any of the other aqueous phases that have been noted with either OR3a or OR2a with SDS. There is an increase in extinction for the first 2 hours, while a decrease is seen at the 3rd hour (possible outlier). There are increases in both the 4th and 5th hour before another decrease in extinction in the 6th hour. There are increases until the 72nd hour, when there is a decrease, although small. The fluctuation in the extinction maximum is more than likely the ligand trying to equilibrate in the aqueous phase. This does not correlate to what is noted in the organic phase, where there is a constant increase in maximum extinction. At the later measurements, there is an extinction maximum wavelength shift of 5 nm, indicative of a weakly binding slightly hydrophilic metal-ligand complex. With the extinction of the last measurement higher at this ratio than with excess uranyl, we believe that 80-90% of the uranyl may have been extracted after 72 hours.

After all the extraction data with SDS, while there is help in binding as indicated by the increased extinction maxima shifts, it is tough to tell if the SDS is helping with the binding by preventing the ligand from aggregating, or acting as a co-extractant. More data would be needed to fully understand the effect.

Sequential Extraction

Since it is sometimes difficult to quantify uranyl extraction, much can be said for the value of empirical observations. Uranyl in solution is yellow and it is this color that will turn clear in the aqueous phase indicating extraction. The organic phase with the ligands is clear to slightly cloudy. This phase should turn yellow. These solutions were 5mM ligand in methylene chloride and 5 mM uranyl at pH 3 and 4. 10 mL of each was put into a separatory funnel and mixed by shaking for 30 seconds, with venting every 15 seconds. The layers were allowed to separate for 10 minutes, and the organic layer siphoned off. Fresh organic solvent with ligand was added and the procedure repeated. Below the observations are described.

OR2a pH 3

Figure 57: Aqueous layer contains uranyl nitrate (5 mM), organic layer contains OR2a (5 mM) in DCM; Left: Before shaking. Right: Layers separated after shaking.

As can be seen in the first picture, the aqueous (top) layer is a slight shade of yellow although hard to see and the organic (bottom) layer is clear. We can see that most of the uranyl is extracted after the first organic layer, and then more in the second organic layer. Based on clarity of the final solution, it may be completely extracted based on the aqueous layer; however, at this pH, this ligand formed a third layer that would not go away. Because of this, both the organic and aqueous layers are cloudy and why we cannot acquire meaningful UV-Vis data. This indicates a solvent problem when a third layer forms, or the third layer is forming a polymer of ligand and uranyl. This could be the best pH for extractions with this ligand.

OR2a pH 4

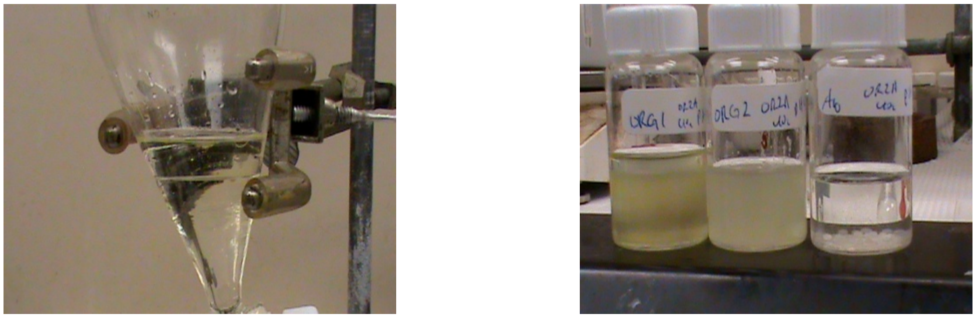


Figure 58: Aqueous layer contains uranyl nitrate (5 mM), organic layer contains OR2a (5 mM) in DCM; Left: Before shaking. Right: Layers separated after shaking.

The first picture like the rest of the first pictures shows a yellow aqueous layer and a clear organic layer. After the first extraction, we see that most of the uranyl was extracted into the organic phase by the darker yellow color as compared to the second organic layer. The aqueous layer has no tint of yellow, but however is slightly cloudy and would prevent any data on the UV-Vis.

OR3a pH 3

Figure 59: Aqueous layer contains uranyl nitrate (5 mM), organic layer contains OR3a (5 mM) in DCM; Left: Before shaking. Right: Layers separated after shaking.

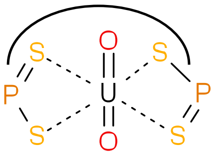
For this ligand, we see a darker yellow, almost orangish yellow organic layer. There was very little of a third layer formed in the first extraction. The second extraction shows more uranyl being extracted with a slightly lighter yellow color. This second extraction also formed a third layer although not nearly as much as OR2a. The aqueous layer after the second extraction still has a tint of yellow indicating there is still uranyl in the aqueous phase that would take further extractions remove all of it.

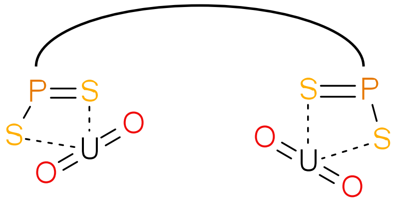
OR3a pH 4

Figure 60: Aqueous layer contains uranyl nitrate (5 mM), organic layer contains OR3a (5 mM) in DCM; Left: Before shaking. Right: Layers separated after shaking.

At this pH, we see the dark, almost clear organic layer after the first extraction. There was a little bit of a third layer formed. After the second extraction, the yellow color is of a lighter tint and therefore not as much uranyl was extracted. The aqueous layer still shows a tint of yellow indicating there is still some uranyl left, which could be extracted with fresh solution of ligand. This could be the best pH for extractions with this ligand.

There are at least seven possible ways the ligand may be binding and there are probably more. A shift of 20-25 nm in the UV-Vis data is expected for specific binding.





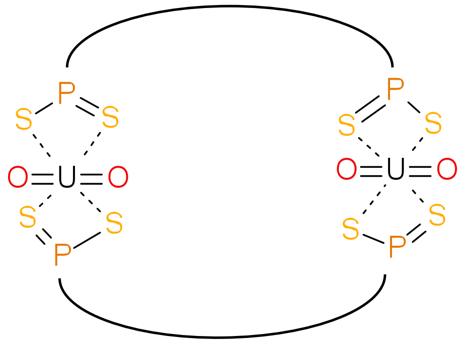
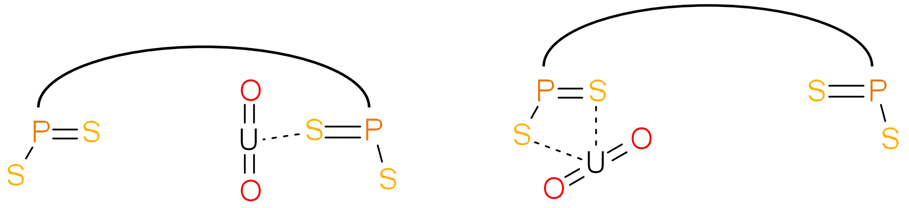


Figure 61: Proposed modes of binding that would result in > 20 nm wavelength shift.

Since the peak shift was less than 20-25 nm, one must consider additional modes of interaction. In the figure below, are possibilities of how the ligand might bind to uranyl. These are not complete binding and therefore would not cause the complete shift that we want to see, and therefore might cause a less significant shift of 5-15 nm.



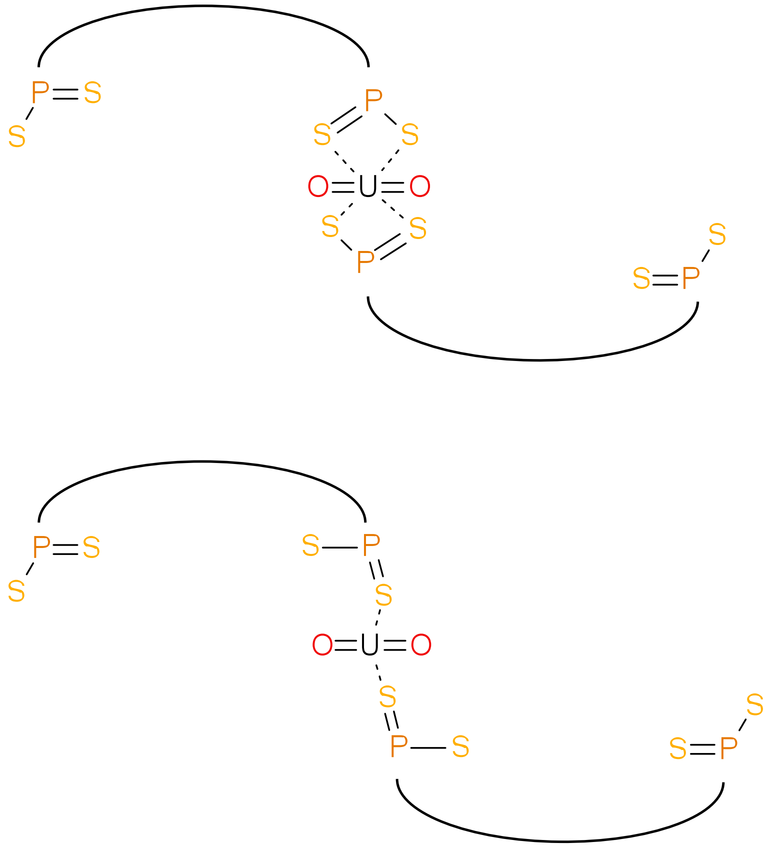


Figure 62: Possible modes of secondary binding

Conclusions

From this data one can observe that the ligand may not be the best for uranyl extraction. While possible, this ligand is not an improvement over current methods. The ammonium salt of the ligand was recrystallized from methanol, but single crystals were not sufficient for single crystal x-ray diffraction experiments. At no point could a metal complex be crystallized except for the ammonium salt of OR2a with uranyl nitrate, with the single crystals not being of high quality for single crystal x-ray diffraction.

With the extraction data, we determined that there is both a solubility problem and a kinetic problem. There is a solubility problem, because while methylene chloride is immiscible with water, there is still a small fraction that interacts with water, and could be part of the reason with the third phase formation. There was also the problem that when the concentrations were increased, there was a third layer formed between the organic and aqueous phases of the sequential extractions. While this was present in different amounts, it was nonetheless present and is a problem for extractions, if the third layer consists of an inorganic polymer with uranyl in it, it would take away from the overall extraction efficiency and recovery of uranyl.

There is also the possibility of a kinetic problem. Often, it took 12-24 hours to see a shift in either the organic phase or the aqueous phase. There were a few times that an immediate shift was observed at a higher pH, than are typical for SNF extractions. Most PUREX extractions are done at 3-6 M HNO_3 at significantly lower pH than the 2-5 that the extractions were done. The SDS surfactant added seemed aid in the binding but not necessarily the kinetics or rate of reaction. The SDS increased the shift by 5 nm to 15 nm from the blank as compared to extractions without SDS was only a 10 nm shift from the blank. This could mean it is acting as a co-extractant and not necessarily keeping the ligands from aggregating.

The tables below show the overall differences in extinction between the first measurement and the last measurement.

Difference in Extinction ε M^{-1} cm^{-1}	pH 2			pH 3		
Ligand/phase	2-1	1-1	1-2	2-1	1-1	1-2
OR2a/Aq	-2800	-24400	-14800	-6800	-3100	-6800
OR2a/Org	40800	54200	57000	24600	14100	19600
OR3a/Aq	6500	44400	8500	1900	-10400	-16200
OR3a/Org	30400	31400	11200	7700	19400	20400

Difference in Extinction ε M^{-1} cm^{-1}	pH 4			pH 5		
Ligand/phase	2-1	1-1	1-2	2-1	1-1	1-2
OR2a/Aq	-1000	-1600	-4000	1600	1500	2700
OR2a/Org	14400	11300	14000	13600	11800	16500
OR3a/Aq	50	70	16500	2600	1500	2800
OR3a/Org	10500	12800	7100	16300	11800	16500

Table 1: Difference in extinction between the first measurement and the last measurement for each ligand and phase at corresponding pH.

Max Shift (nm)	pH 2			pH 3		
Ligand/Phase	2-1	1-1	1-2	2-1	1-1	1-2
OR2a/Aq	0	0	0	5	5	5
OR2a/ Org	0	0	0	0	10	15
OR3a/Aq	0	0	5	0	5	0
OR3a/Org	0	0	0	10	10	10

Max Shift (nm)	pH 4			pH 5		
Ligand/Phase	2-1	1-1	1-2	2-1	1-1	1-2
OR2a/Aq	0	0	5	0	0	0
OR2a/ Org	15	10	10	10	15	5
OR3a/Aq	0	0	0	0	0	0
OR3a/Org	10	5	5	10	15	15

Table 2: Maximum shift observed from the blank for each ligand and phase at corresponding pH.

To prove in a way that can be seen with one's own eyes, we increased the concentration of both the ligand and uranyl to see if the yellow color of uranyl in aqueous solution would transfer to the organic phase. As it turns out, the uranyl appears to be transferred relatively quickly, and would not require too require significant quantities of fresh solvent to extract all of the uranyl from the aqueous phase. If we can eliminate the third layer formation, we can do UV-Vis and determine just how much is extracted after each fresh solvent is added.

Future Work

Future work in these efforts would include making these compounds more soluble in organic solvents other than methylene chloride or chloroform. One option could be including an ether linkage as opposed to a pure carbon tail on the phenyl rings. TBP has three such ether linkages with butyl groups attached and is soluble in kerosene or dodecane.

Another possible piece of the puzzle would be addressing the kinetic effect thermodynamically, can modest increases in temperature aid in extraction. There is an energy cost, however, and one must consider the costs for increasing the temperature. Also, a deeper look at the sequential extractions to determine how many times fresh solvent with ligand would have to be applied to achieve the maximum extraction of uranyl from the aqueous phase. Ultimately, future work would include extractions of the trivalent actinides (Am^{3+}) and trivalent lanthanides. Most of the ligands in the literature used for those extractions contain soft donors and more specifically sulfur donors.

Using inductively couple plasma mass spectrometry (ICP-MS), we could perform extractions on UO_2^{2+}, Gd^{3+}, Ce^{3+}, and Fe^{3+} with these ligands at higher concentrations. ICP-MS will give clear percent extraction regardless of either the ligand or the binding modes. This would be used to determine how selective the ligand could be between the actinides and lanthanides and how it can be applied towards trivalent actinide and lanthanides.

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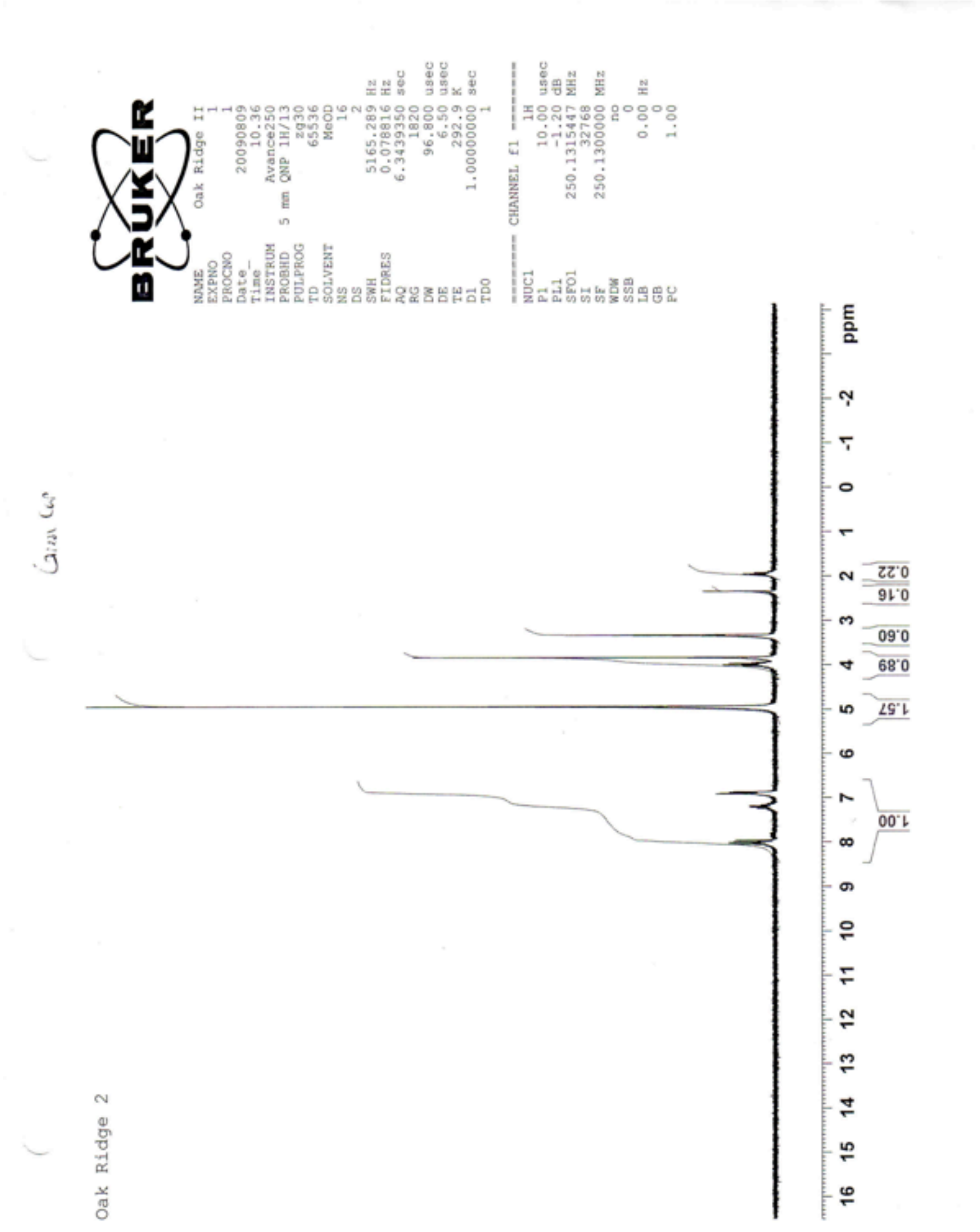
Appendix



Oak Ridge 2

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PROCNO                  1
Date_            20090809
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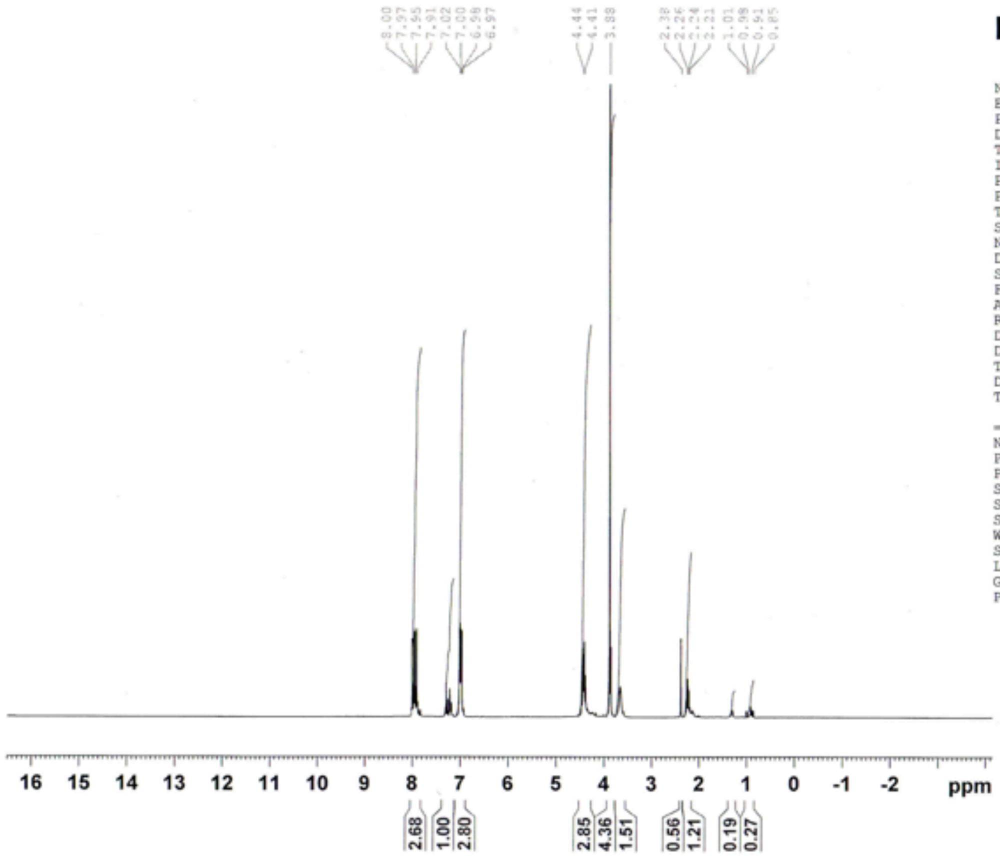
INSTRUM         Avance250
PROBHD   5 mm QNP 1H/13
PULPROG              zg30
TD                  65536
SOLVENT              MeOD
NS                     16
DS                      2
SWH             5165.289 Hz
FIDRES          0.078816 Hz
AQ             6.3439350 sec
RG                   1820
DW                 96.800 usec
DE                   6.50 usec
TE                  292.9 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.00 usec
PL1                 -1.20 dB
SFO1          250.1315447 MHz
SI                  32768
SF            250.1300000 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```


new procedure or2a

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PROCNO                 1
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INSTRUM       Avance250
PROBHD   5 mm QNP 1H/13
PULPROG               zg
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     0
SWH             5165.289 Hz
FIDRES          0.078816 Hz
AQ             6.3439350 sec
RG                   287
DW                96.800 usec
DE                  6.50 usec
TE                 293.7 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.00 usec
PL1                -1.20 dB
SFO1         250.1315447 MHz
SI                131072
SF           250.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.20 Hz
GB                     0
PC                  1.00
```

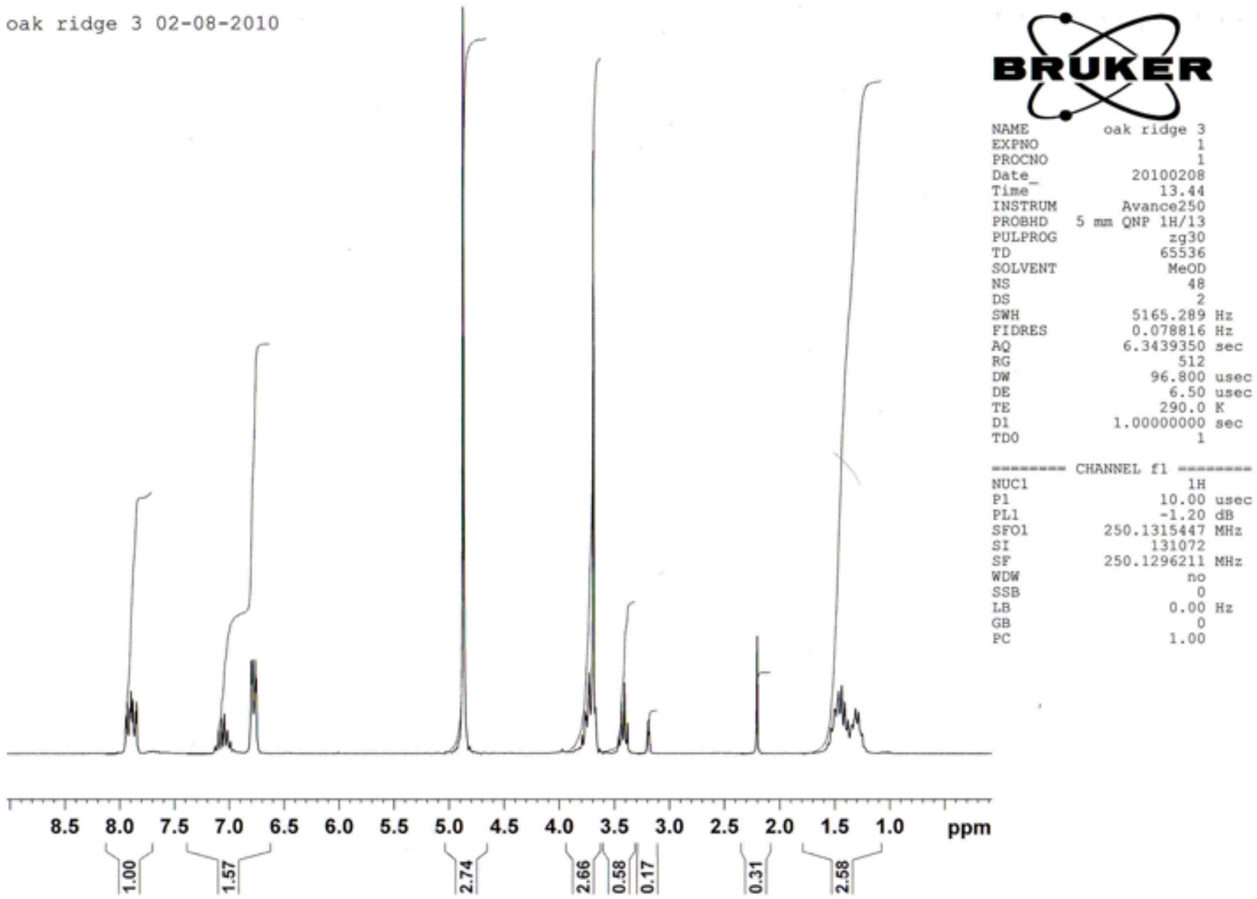
oak ridge 3 02-08-2010

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PROCNO                  1
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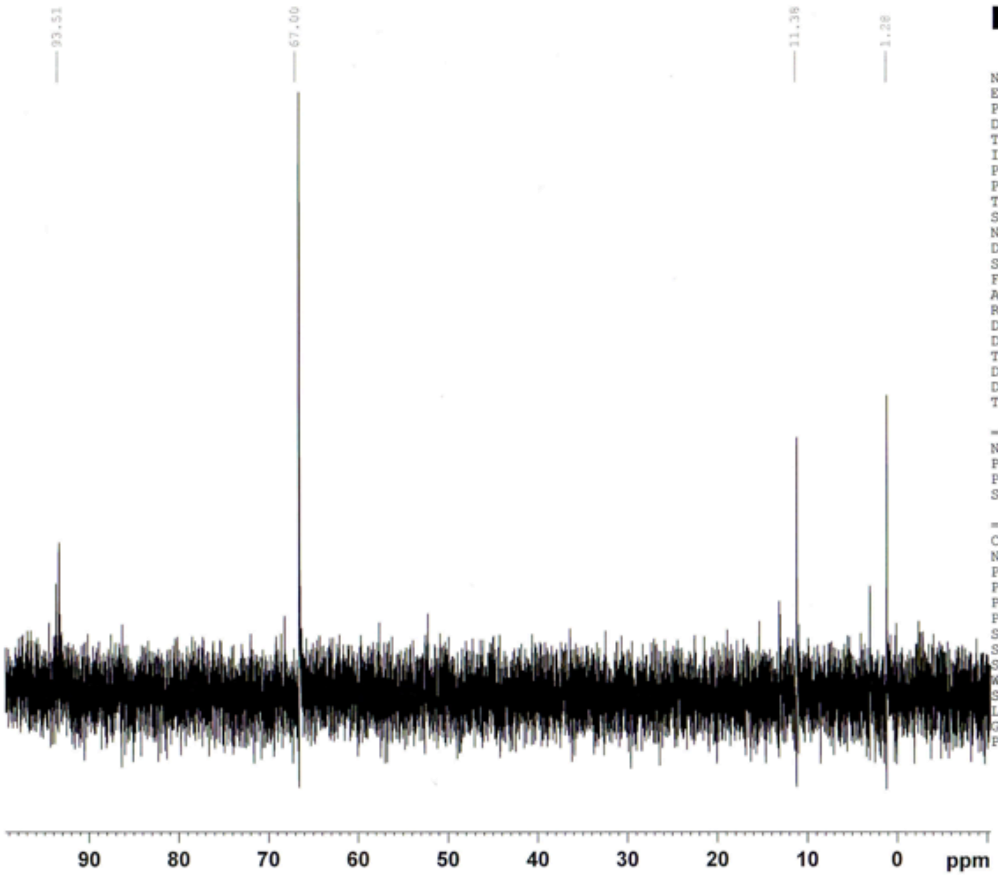
INSTRUM        Avance250
PROBHD   5 mm QNP 1H/13
PULPROG              zg30
TD                  65536
SOLVENT              MeOD
NS                     48
DS                      2
SWH              5165.289 Hz
FIDRES           0.078816 Hz
AQ              6.3439350 sec
RG                    512
DW                 96.800 usec
DE                   6.50 usec
TE                  290.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.00 usec
PL1                 -1.20 dB
SFO1          250.1315447 MHz
SI                 131072
SF            250.1296211 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```

oak ridge 3 02-08-2010



```
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EXPNO                    5
PROCNO                   1
Date_             20100208
Time                 14.20
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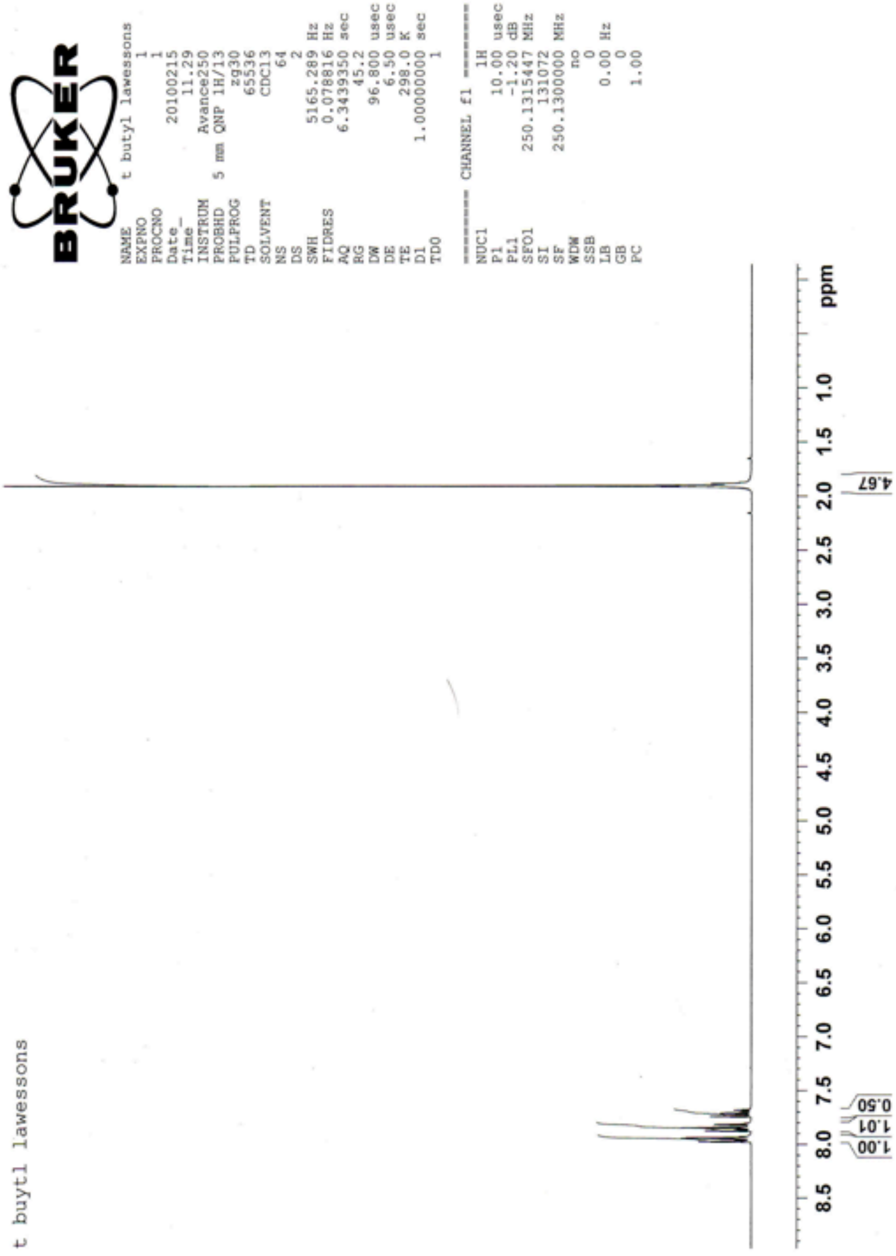
PROBHD   5 mm QNP 1H/13
PULPROG               zgpg
TD                   65536
SOLVENT               MeOD
NS                      30
DS                       0
SWH           20161.291 Hz
FIDRES         0.307637 Hz
AQ            1.6253428 sec
RG                     128
DW              24.800 usec
DE                6.50 usec
TE               291.2 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   31P
P1                8.00 usec
PL1               4.00 dB
SFO1       101.2544800 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2            80.00 usec
PL2              -1.20 dB
PL12             16.86 dB
PL13             17.00 dB
SFO2       250.1310005 MHz
SI                  131072
SF         101.2544691 MHz
WDW                     EM
SSB                      0
LB                0.50 Hz
GB                       0
PC                    1.40
```



t buytl lawessons

```
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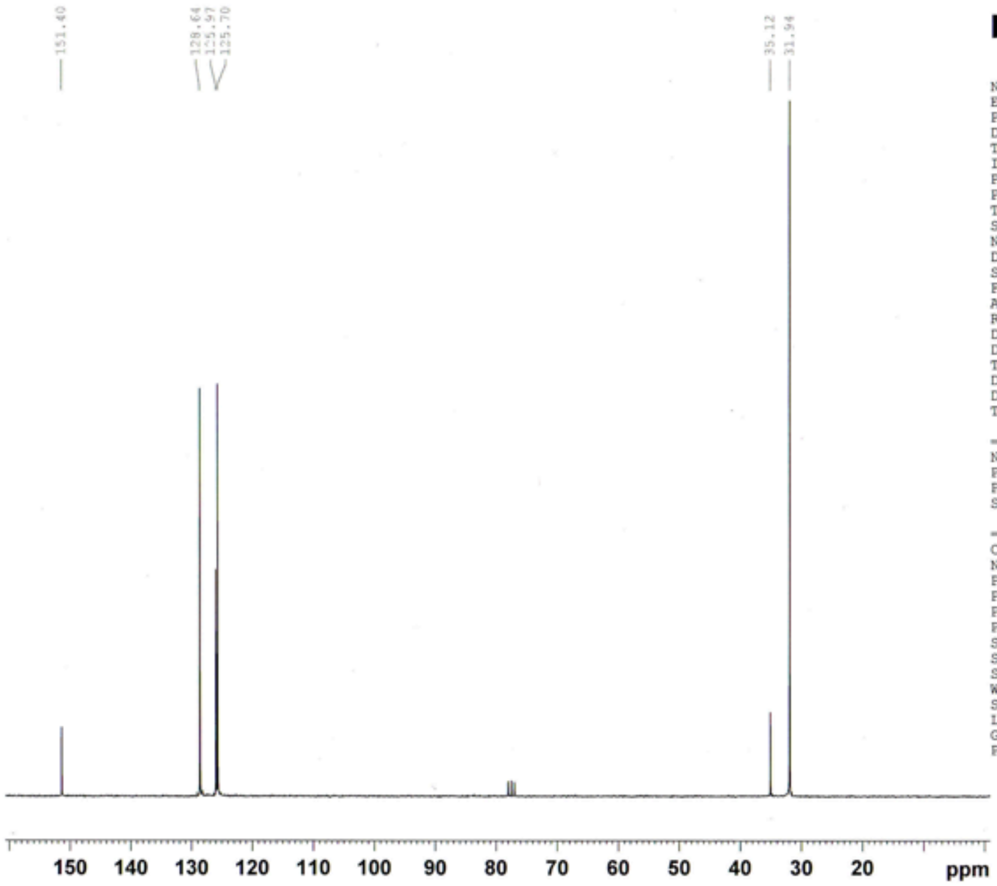
EXPNO                      1
PROCNO                     1
Date_               20100215
Time_                  11.29
INSTRUM           Avance250
PROBHD      5 mm QNP 1H/13
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        64
DS                         2
SWH                 5165.289 Hz
FIDRES              0.078816 Hz
AQ                 6.3439350 sec
RG                      45.2
DW                    96.800 usec
DE                      6.50 usec
TE                     298.0 K
D1               1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     10.00 usec
PL1                    -1.20 dB
SFO1             250.1315447 MHz
SI                    131072
SF               250.1300000 MHz
WDW                       no
SSB                        0
LB                      0.00 Hz
GB                         0
PC                      1.00
```

t buytl lawessons



```
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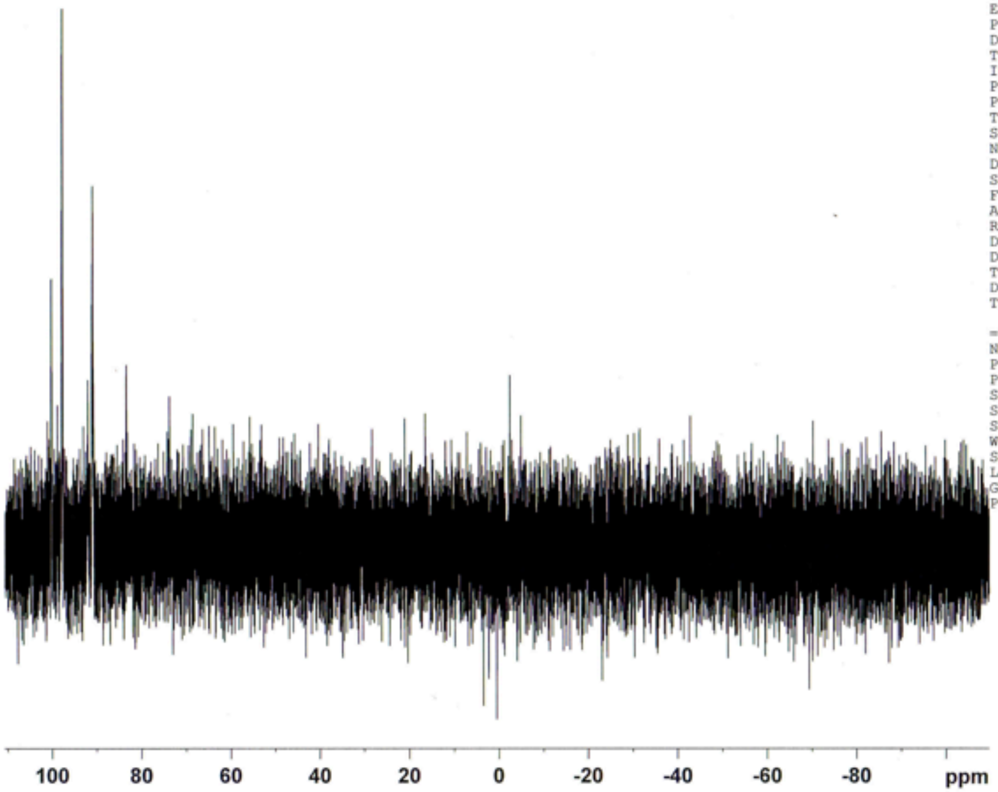
EXPNO                     5
PROCNO                    1
Date_              20100215
Time                  11.45
INSTRUM          Avance250
PROBHD   5 mm QNP 1H/13
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      61
DS                       4
SWH             15000.000 Hz
FIDRES           0.228882 Hz
AQ              2.1845834 sec
RG                    2050
DW                  33.333 usec
DE                    6.50 usec
TE                   298.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.20 usec
PL1                   2.00 dB
SFO1            62.9015280 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                  -1.20 dB
PL12                 16.86 dB
PL13                 17.00 dB
SFO2           250.1310005 MHz
SI                   32768
SF              62.8952390 MHz
WDW                     EM
SSB                      0
LB                    1.50 Hz
GB                       0
PC                    1.40
```

t-butyl lawessons coupled



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PROCNO                    1
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Time                  23.23
INSTRUM          Avance250
PROBHD    5 mm QNP 1H/13
PULPROG                  zg
TD                    65536
SOLVENT                MeOD
NS                       22
DS                        0
SWH               22321.428 Hz
FIDRES             0.340598 Hz
AQ                1.4680564 sec
RG                      144
DW                   22.400 usec
DE                     6.50 usec
TE                    298.0 K
D1              10.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    31P
P1                     8.00 usec
PL1                    4.00 dB
SFO1            101.2544800 MHz
SI                   131072
SF              101.2544233 MHz
WDW                      EM
SSB                       0
LB                     0.50 Hz
GB                        0
PC                     1.40
```