

Solvent Extraction of Copper: An Extractive Metallurgy Exercise for Undergraduate Teaching Laboratories

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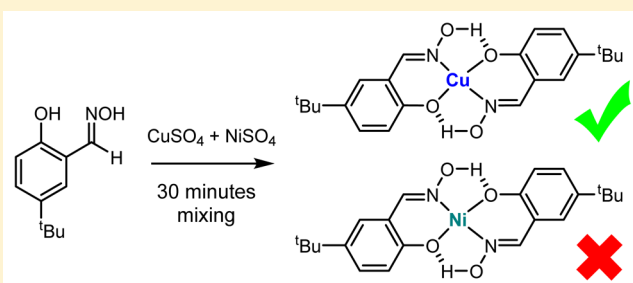
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S Supporting Information

ABSTRACT: A multidisciplinary experiment for advanced undergraduate students has been developed in the context of extractive metallurgy. The experiment serves as a model of an important modern industrial process that combines aspects of organic/inorganic synthesis and analysis. Students are tasked to prepare a salicylaldoxime ligand and samples of the corresponding copper and nickel complexes, before performing test extractions and UV–vis spectroscopic analysis. The oxime ligand demonstrates a clear preference for extraction of Cu²⁺ in the presence of Ni²⁺ from aqueous solution under the conditions described. It is also possible to demonstrate that the ligand can be recovered and reused. The experiment has successfully been employed in a final year project-based laboratory course involving small groups of students.

KEYWORDS: Upper-Division Undergraduate, Interdisciplinary/Multidisciplinary, Laboratory Instruction, Hands-On Learning/Manipulatives, Problem Solving/Decision Making, Coordination Compounds, Metallurgy, Phenols, Qualitative Analysis, Synthesis



INTRODUCTION

Many engaging teaching laboratory exercises have been directed toward the topic of production of economically important metals.^{1,2} Copper, in particular, has been the focus of many such experiments;¹ this is due to copper salts being generally inexpensive, easily obtained, and tending to be less hazardous than many other transition metal compounds. An excellent article recently reported an experiment that introduced the industrially and economically important concept of hydrometallurgy.² This work described a simple and engaging experiment for high school students to identify suitable ligands for nickel extraction. Hydrometallurgy³ is a broad term that covers several processes for recovering metals from ores that include leaching, precipitation from solution, or concentration/purification by solvent extraction. The latter technique is a key step in the production of a variety of important metals, including zinc, uranium, the platinum group metals, and copper.⁴ Previous work published in this journal⁵ has reported that resacetophenone oxime (prepared in two steps from resorcinol) could selectively precipitate the corresponding copper complex from a solution containing Cu²⁺ and Cd²⁺ ions. Although not reported in the context of hydrometallurgy, the Cd/Cu system provides a useful precedent for selective chelation of a metal ion in the presence of another. In contrast, industrial solvent extraction processes for copper recovery require ligands that will form complexes

that are soluble in hydrocarbon solvents; therefore, an alternative model system was investigated.

In this paper, we report an interdisciplinary laboratory exercise that is set in the context of a solvent extraction process for the separation and recovery of copper. This work has the following pedagogical goals:

- To make links between teaching laboratory work and a “real world” application of organic synthesis and coordination chemistry.
- To demonstrate key organic and inorganic chemistry principles (theoretical and practical) within the same laboratory activity.
- To foster collaborative working skills by getting students to work in small groups, perform individual tasks, and then combine results.

Background: Solvent Extraction of Copper

Copper metal has traditionally been produced on a large scale by smelting sulfidic ores, and although well understood, this process can be costly in energy and capital terms.⁴ Since the 1960s, an alternative process involving solvent extraction has been employed to concentrate and purify copper ore.^{4–7} This process relies on treatment of the ore with sulfuric acid (“ore leaching”) to afford an aqueous solution containing copper

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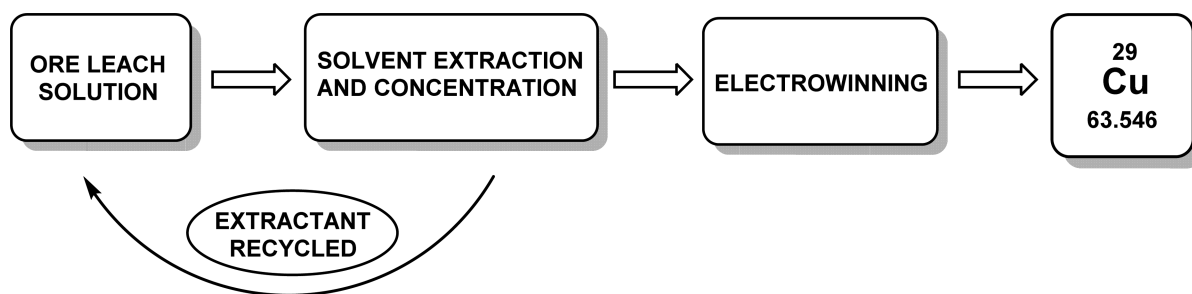


Figure 1. Simplified hydrometallurgy flowsheet for recovery of copper from ore leach solution containing copper sulfate.

sulfate and many other transition metal ion species. Separation and concentration of dissolved copper from other species can be effected by treatment with a ligand (alternatively known as an “extractant”) with a high affinity for Cu^{2+} .^{4–7} The extractant is dissolved in a hydrocarbon solvent, typically kerosene, and mixed with the ore leach solution. The Cu^{2+} is therefore transferred to the organic phase and is physically separated from the other metal ions which remain in aqueous solution. Subsequent treatment of the copper complex with sulfuric acid releases Cu^{2+} back into aqueous solution for purification by electrolysis (“electrowinning”), and the extractant can be recycled in subsequent extraction cycles (Figure 1).

A variety of extractants have been evaluated and employed in copper extraction, but the majority of those in commercial use^{7,8} are phenolic oximes which conform to the general structure illustrated in Figure 2.^{4,6}

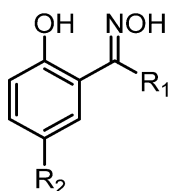


Figure 2. General structure of phenolic oxime copper extractants (R_1 and R_2 = H, alkyl, or aryl).

Phenolic oximes are known to form hydrogen-bonded dimers in solution, and in this arrangement the oxime ligands are preorganized for subsequent binding to transition metal ions. The resulting copper(II) complexes adopt a square-planar arrangement, where two oxime ligands form a 14-membered pseudo-macrocycle around the metal ion (Scheme 1). This arrangement is stabilized by hydrogen bonds between the oxime OH group and the phenolate oxygen atom. It is believed that the size and “goodness-of-fit” of a Cu^{2+} ion within the pseudo-macrocylic cavity formed by the ligands is responsible for the selectivity toward copper(II).^{4,6} The observed trend is also consistent with the Irving–Williams series⁹ of first-row transition metal complex stabilities. On treatment with an excess of acid, protonation of the phenolate oxygen atoms

occurs, and this leads to release of copper ions into aqueous solution and recovery of the oxime ligand. This “pH swing” process facilitates the use of phenolic oxime ligands in copper production.

EXPERIMENTAL OVERVIEW

The key objective of the experiment is to demonstrate the use of a phenolic oxime ligand to selectively extract Cu^{2+} in the presence of other transition metal ions. In this case, the Ni^{2+} ion serves as a representative contaminant (Scheme 2). The first step requires the model copper extractant to be prepared and characterized, and the subsequent steps then demonstrate that selective extraction of Cu^{2+} in the presence of Ni^{2+} has taken place and that the metal release (solvent “stripping”) step can be accomplished. The individual experimental components are summarized in the following sections.

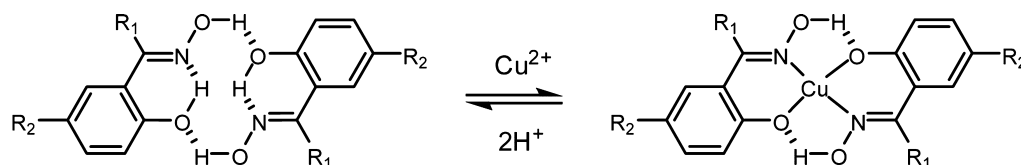
Preparation of the Extractant

As described above, the extractants employed in industrial copper solvent extraction processes are usually phenolic oximes (Figure 2). Initial studies investigated a series of oximes to identify a ligand that was readily prepared, was selective for Cu^{2+} over Ni^{2+} , and that formed a complex that was readily soluble in a hydrocarbon solvent. The conclusion was that 5-(*tert*-butyl)-2-hydroxybenzaldehyde oxime possessed all the desired properties and was selected for use. Oximes are well-known derivatives of carbonyl compounds, and as a result, many procedures are available for their preparation.^{10–12} The most common protocols involve treatment of the parent carbonyl compound with a hydroxylamine salt in the presence of a base. However, oxime formation under phase-transfer conditions¹¹ has also been reported. In this work, the procedure described by Stokker¹² was found to be most convenient (Scheme 3).

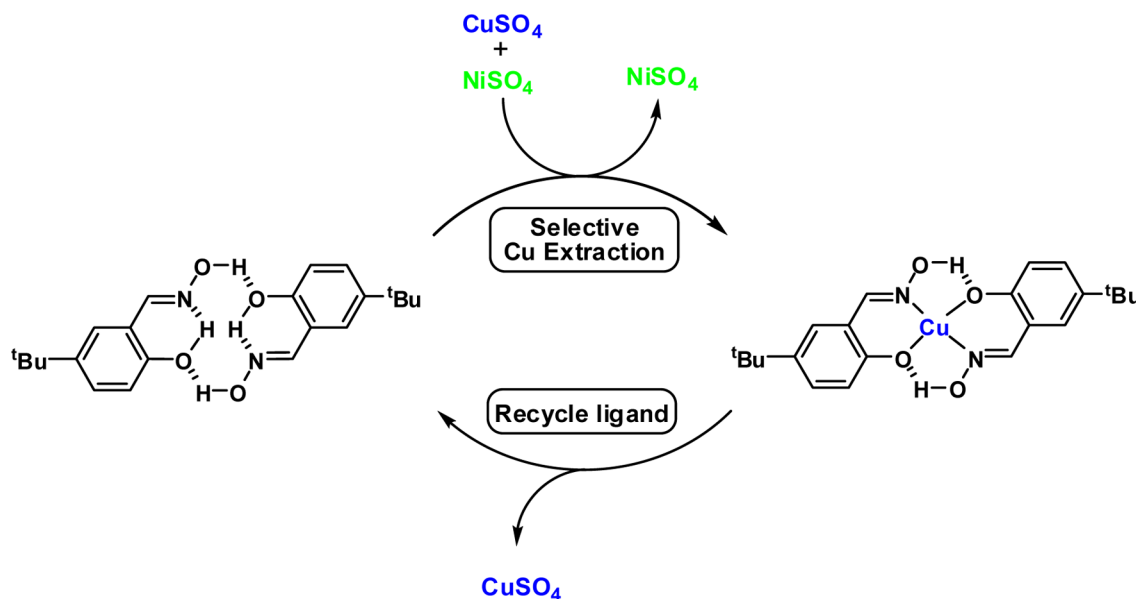
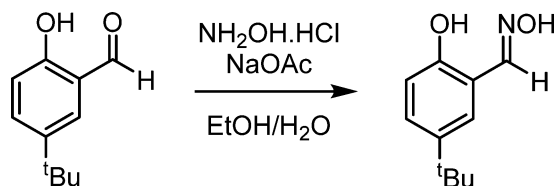
Preparation of the Copper and Nickel Complexes

Successful selective copper extraction can be confirmed when the organic layers from the extraction experiments are analyzed by UV–vis spectroscopy. Before performing the model extractions, it is necessary to prepare authentic samples of the copper and nickel complexes for later comparison with extracted samples. The procedure of Ramesh et al.¹³ was

Scheme 1. General Structure of Phenolic Oxime Copper Extractants (R_1 and R_2 = H, Alkyl, or Aryl)



Scheme 2. Summary of the Key Processes Involved in the Model Selective Extraction of Copper

Scheme 3. Preparation of 5-(*tert*-Butyl)-2-hydroxybenzaldehyde Oxime Ligand for Cu²⁺ Extraction

found to be relatively straightforward and allowed sufficient quantities of the required complexes to be prepared in an appropriate time frame (Scheme 4).

Model Extraction

A series of parallel extractions are required to demonstrate that the ligand prepared in the first step can selectively extract Cu²⁺ in the presence of Ni²⁺. The extractions attempted by the students are listed below:

1. Ligand dissolved in toluene mixed with 0.025 M aqueous copper sulfate.
2. Ligand dissolved in toluene mixed with 0.025 M aqueous nickel sulfate.
3. Ligand dissolved in toluene mixed with equal portions of aqueous 0.025 M copper sulfate and 0.025 M nickel sulfate.

Industrial extractions usually employ kerosene as the organic phase; in our model system, toluene has proven to be a convenient substitute. The toluene extracts can easily be separated and diluted for analysis by UV–vis spectroscopy, and

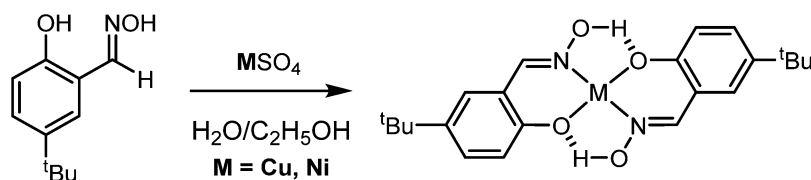
the resulting spectra can be compared to those obtained from the authentic samples prepared in the preceding step.

Copper “Stripping”

The final part of the experiment demonstrates that Cu²⁺ can be released back into aqueous solution by reducing the pH. This is achieved by mixing the toluene extract from extraction 1 or 3 with 2.5 M sulfuric acid. Addition of acid quickly leads to transfer of Cu²⁺ from the organic to aqueous phase, where subsequent analysis of the toluene layer by UV–vis spectroscopy can confirm that the copper complex is no longer present and thus the extractant can be recycled.

HAZARDS

A laboratory coat and safety glasses must be worn at all times. All operations should be conducted in a fume hood. Do not allow any of the substances in use to come into contact with skin. All the solvents in use should be considered flammable and harmful by inhalation, ingestion, or skin absorption. Sulfuric acid solutions are corrosive and should not come into contact with skin or eyes. CDCl₃ is a volatile solvent and is a suspected carcinogen. Care must be taken to avoid inhaling transition metal dusts during weighing operations. Dusts of nickel compounds are particularly hazardous since they are potentially carcinogenic and can cause skin allergy in some individuals. All transition metal wastes should be considered as toxic in an aquatic environment and should be collected in appropriate containers for proper disposal.

Scheme 4. Preparation of Comparison Samples of 5-(*tert*-Butyl)-2-hydroxybenzaldehyde Oxime Complexes of Copper and Nickel

RESULTS AND DISCUSSION

In the initial laboratory session, students were tasked to prepare the extractant and were then divided into subgroups: (1) to prepare authentic samples of the copper and nickel complexes; (2) to conduct test extractions/obtain UV–vis spectra, and (3) to complete the final stripping step.

Synthesis of 5-(*tert*-butyl)-2-hydroxybenzaldehyde oxime proved to be straightforward with reaction, workup, and final purification completed within two 3 h laboratory sessions. Yields between 55 and 70% were typically reported, and it was noted that students who allowed the product to recrystallize overnight from petroleum spirit (60–80) were able to obtain the best quality material. During the teaching laboratory sessions, the reaction was usually conducted on a 5 mmol scale; however, the procedure has been successfully attempted on scales between 2.5 and 7.5 mmol. In all cases, ^1H NMR spectra and melting point data were collected that were consistent with the target compound. The starting material for the synthesis of the extractant is 5-(*tert*-butyl)-2-hydroxybenzaldehyde; this compound can be sourced commercially, or it can be prepared in advance on a large scale¹⁴ (the procedure is outlined in the Supporting Information).

A simple procedure for the preparation of authentic samples of the copper and nickel complexes was employed. Addition of an ethanolic solution of the oxime to a warm aqueous solution of the corresponding metal sulfate furnished sufficient quantities of the complexes for the next stage of the experiment. The copper complex was found to precipitate rapidly as a brown solid. In contrast, the ligand is less reactive toward nickel(II), so it was found that the formation of the nickel complex (as a green solid) required a longer reaction period.

Model extractions were conducted in 100 mL conical flasks. A 10 mL aliquot of 0.01 M solution of the ligand in toluene was added to a 10 mL portion of 0.025 M aqueous solution of copper sulfate, nickel sulfate, or an equimolar mixture of both metal sulfates. The resulting biphasic solutions were stirred vigorously for 30 min to ensure thorough mixing. The toluene layers of extractions of aqueous solutions containing Cu^{2+} were observed to become brown within a few minutes and became darker as the extraction proceeded. During extraction of the aqueous solution containing only Ni^{2+} , a yellow/green solution was noted instead (Figure 3). The colorless to brown color change of the toluene layer indicates transfer of Cu^{2+} from the aqueous phase to the organic phase, and this can be confirmed after the organic layers are separated off, analyzed by UV–vis spectroscopy and comparisons with authentic samples are made.

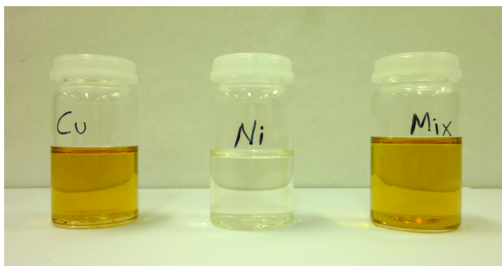


Figure 3. Left to right: Toluene extracts from (a) CuSO_4 extraction, (b) NiSO_4 extraction, and (c) $\text{CuSO}_4/\text{NiSO}_4$ mix extraction.

UV–vis absorption spectra of the toluene extracts were compared with those from authentic samples of the oxime ligand, nickel(II) complex, and copper(II) complex (Figure 4).

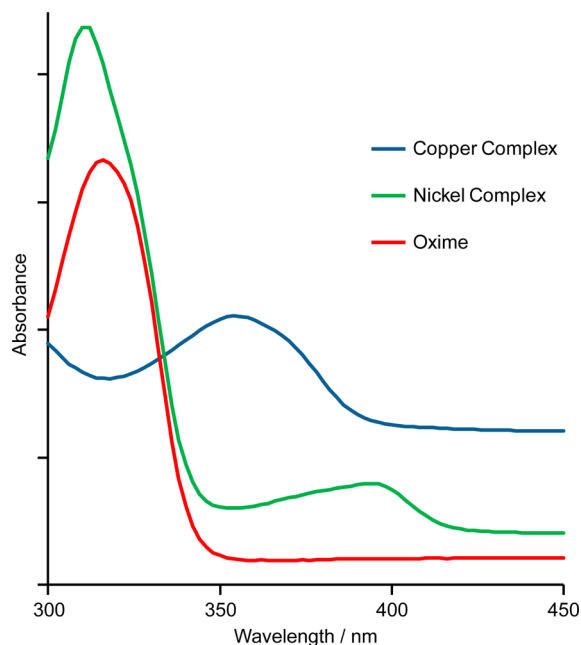


Figure 4. Overlay of UV–vis spectra of (a) 5-(*tert*-butyl)-2-hydroxybenzaldehyde oxime (red line), nickel complex (green line), and copper complex (blue line).

The spectra were all acquired between 300 and 500 nm. In this region, the absorbance attributed to the oxime ($\text{C}=\text{N}$) $n \rightarrow \pi^*$ transition in the free ligand or complex could be identified.¹³ The spectra of the free ligand and nickel(II) complex showed similar values ($\lambda_{\text{max}} = 316$ and 312 nm, respectively) for the oxime $n \rightarrow \pi^*$ transition; however, they could be distinguished by appearance of an additional absorbance ($\lambda_{\text{max}} = 392$ nm) in the spectrum of the nickel(II) complex, which was tentatively assigned as a ligand to metal charge-transfer band.¹⁵ The spectrum obtained from the copper(II) complex exhibited a significant bathochromic shift ($\lambda_{\text{max}} = 354$ nm) in comparison to the spectra obtained from the nickel(II) complex and the free ligand. These observations are in agreement with studies by Ramesh et al.,¹³ where it has been proposed that the observed oxime UV–vis absorbances can be used as a measure of the strength of binding between the oxime ligand and the metal ion. The UV–vis spectra of the toluene extracts from mixing the ligand with (1) copper sulfate and (2) copper sulfate/nickel sulfate mix showed identical spectra that were consistent with exclusive formation of the copper complex.^{4,16} Analysis of the toluene extract from mixing the extractant with nickel sulfate solution indicated that only the free ligand was present and that no significant complexation of Ni^{2+} had taken place within 30 min.¹⁶ Overall, the UV–vis spectra obtained were able to provide good evidence for the selectivity of the ligand for Cu^{2+} over Ni^{2+} under the reaction conditions investigated.

The model stripping step was conducted in a 100 mL conical flask, and the toluene extract from the $\text{NiSO}_4/\text{CuSO}_4$ mixture was transferred to the reaction flask containing a 10 mL portion 2.5 M sulfuric acid. The brown color of the toluene layer usually completely faded within 15 min of vigorous stirring. This observation indicated transfer of Cu^{2+} from the organic

phase to the aqueous phase was complete. UV–vis spectroscopic analysis of the toluene layer after separation demonstrated that only the free oxime was present ($\lambda_{\text{max}} = 316$ nm) and, hence, the ligand had been recycled.

Possible Variations

The experiment format as described can be adapted to meet the needs of the instructor; for example, the synthesis of 5-(*tert*-butyl)-2-hydroxybenzaldehyde can be included as part of the laboratory exercise if desired (a tested procedure¹⁷ has been included in the [Supporting Information](#)). It should also be possible to direct the students to use the copper complex they isolate to construct a calibration curve for the determination of the degree of copper recovery from the solvent extraction step. Extending the experiment would be time-consuming, so such additions are likely to be most suited to an extended group project format where the tasks can be divided among the team members.

CONCLUSIONS

An interdisciplinary experiment has successfully been developed for advanced undergraduate students that serves as a model of key steps in industrial solvent extraction of copper. The synthesis and purification of the salicylaldoxime ligand were found to work well, and subsequent selective extraction of Cu^{2+} in the presence of Ni^{2+} could be clearly determined by UV–vis spectroscopic analysis. It was also possible to demonstrate that the ligand could subsequently be recovered. The experiment has been employed in an advanced level project-based laboratory course involving small groups of students, and our findings were that this format was successful in encouraging them to adopt a collaborative approach to achieving a practical goal. Our work also suggests that the project tasks could be extended further to include additional synthetic and analytical steps if the instructor desired.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: [10.1021/acs.jchemed.5b00688](https://doi.org/10.1021/acs.jchemed.5b00688).

Example laboratory manual entry, instructor notes, experiment photographs, and relevant spectra (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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