

Permanganometric Titration for the Quantification of Purified Bis(2,4,4-trimethylpentyl)dithiophosphinic Acid in *n*-Dodecane

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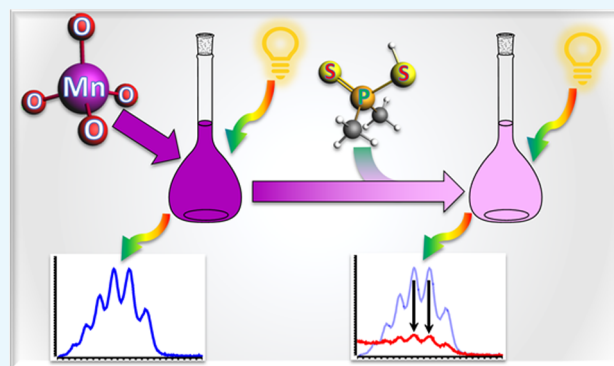
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ABSTRACT: The organic soluble extractant bis(2,4,4-trimethylpentyl)dithiophosphinic acid, often called Cyanex 301 (HC301), has shown selectivity for preferentially extracting trivalent actinides over the lanthanides in the treatment of used nuclear fuel. To maintain control and efficiency of a separation process using this extractant, it is necessary to accurately know specific parameters of the system, including the concentration of HC301 in the organic phase, at any given time. Here, the ability to quickly determine the concentration of HC301 in *n*-dodecane was tested by a one-step permanganometric titration in an organic solution using a double-beam UV–vis spectrophotometer. The addition of HC301 in *n*-dodecane to solutions of KMnO_4 was found to decolorize the KMnO_4 solutions, but the HC301 was best quantified in terms of decolorization in acetone. This decolorization allowed for the creation of a linear analytical curve relating the amount of KMnO_4 consumed to the amount of HC301 added. Cross-validation of this analytical curve reproduced the known amount of HC301 with an average difference of 1.73% and a maximum of 4.03%.



INTRODUCTION

Bis(2,4,4-trimethylpentyl)dithiophosphinic acid, which commonly goes under the trade name Cyanex 301 and abbreviation HC301, Figure 1, is used industrially for the

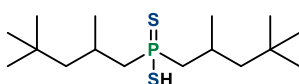


Figure 1. Structure of HC301 (bis(2,4,4-trimethylpentyl)-dithiophosphinic acid).

extraction of cobalt and nickel.¹ It has also shown promise for selectively extracting actinides during the difficult separation of trivalent actinides and lanthanides found in used nuclear fuel,^{2,3} as have other related dithiophosphinic acids.^{4–8} Generally, the separation procedure comprises an organic phase containing the chosen dithiophosphinic acid dissolved in a hydrocarbon diluent, possibly with the addition of a second, synergistic extractant.^{7–11} This organic phase would selectively extract actinides from an aqueous phase containing the metals to be separated and adjusted to a defined pH. To maximize the efficiency and maintain stability of such a process, it is necessary to frequently and quickly determine and adjust various process conditions such as extractant concentration, pH, and phase ratios. Of interest here is the determination of the HC301 in the organic phase, as it decreases due to oxidation and hydrolysis^{12–14} or radiolysis^{8,15,16} to form the

monothiophosphinic and phosphinic acids. Gas chromatography has been found to be ineffective in detecting HC301 or its impurities without prior derivatization due to their low volatility,¹⁷ and there are no published reports on the quantification of HC301 using gas or liquid chromatography at this time. Titrations of HC301 with sodium hydroxide in ethanolic media have been used to quantify its concentration or purity,^{3,15,18} but the development of faster methods may be beneficial to the implementation of HC301-based processes that require close monitoring and adjustment of solvent composition.

Permanganometry is a type of redox titration in which the strongly colored and oxidizing permanganate anion (MnO_4^-) is used to quantify the amount of an oxidizable species in a sample. HC301 presents several reduced sulfur sites prone to be oxidized by nitric acid,^{12–14} so the more powerfully oxidizing MnO_4^- would also be capable of this oxidation—making permanganometry an ideal candidate for HC301 quantification. Due to the intense visible absorption bands of MnO_4^- , even at low concentrations, HC301 can be quickly

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determined by UV–vis spectrophotometry. As MnO_4^- reacts with HC301 and the concentration of MnO_4^- before and after the reaction can be easily and quickly determined spectroscopically, MnO_4^- seems well suited to be exploited in a method for fast determination of HC301.

Permanganometry is traditionally used to determine oxidizable species in aqueous solution, whereas HC301 is dissolved in an organic diluent, frequently *n*-dodecane or kerosene. The diluent *n*-dodecane is considered here as it has a defined composition unlike kerosene. Therefore, the ability to accomplish a permanganometric titration in two different organic phases was studied. The first organic phase was based on purple benzene, where a phase transfer catalyst, in this case the crown ether 18-crown-6, is used to solubilize permanganate in benzene,^{19,20} and bis(2-ethylhexyl)phosphoric acid was used to solubilize the reduced Mn species. KMnO_4 was expected to have high stability in this benzene-based solvent, but due to the hazards associated with benzene, acetone was also considered despite being able to react with KMnO_4 .²¹ This reaction between MnO_4^- and acetone is complex, yielding hydroxyacetone, methylglyoxal, and lactic, pyruvic, oxalic, and acetic acids.²¹ The stability of KMnO_4 in these two organic solvents and water was tested as was the ability to quantify purified HC301 in *n*-dodecane via permanganometry.

RESULTS AND DISCUSSION

Molar Extinction Coefficient. To relate the concentration of KMnO_4 to the height of a UV–vis peak using the Beer–Lambert Law, the value for the molar extinction coefficient is required for KMnO_4 in each solvent. To determine the molar extinction coefficients, the absorptivity of solutions containing varying concentrations of KMnO_4 was measured and is shown in Figure 2. The analytical curves for the water and acetone

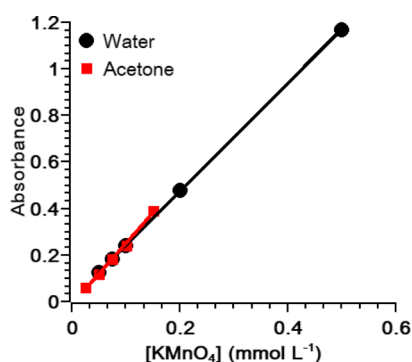


Figure 2. Analytical curves of KMnO_4 in water ($\lambda = 526$ nm) and acetone ($\lambda = 528$ nm) measured immediately after preparing the solution.

solutions are both linear and intercept the *y*-axis at close to zero as would be expected from the Beer–Lambert Law. From these plots, the molar extinction coefficient was determined with the largest standard deviation being 3%. The molar

extinction coefficients increased by decreasing the solvent polarity (Table 1).

Permanganate Stability. The stability of KMnO_4 was evaluated in water, acetone, and benzene and the results are shown in Figure 3. KMnO_4 in water is stable and no decrease in its concentration was observed during 20 h of observation. The stability is highly reduced in both organic solvents and negligible quantities of KMnO_4 remain after approximately 5 h. The stability of KMnO_4 in benzene is higher than for acetone, as the rate at which the MnO_4^- concentration decreases is slower in benzene than in acetone. The decreasing concentration of KMnO_4 in acetone over time follows an unusual, but reproducible, trend. This reveals the complexity of the reaction between KMnO_4 and acetone as noted by Wiberg and Geer.²¹ Other solvents considered included dodecane and hexane, which did not dissolve KMnO_4 but would likely have had better stability, and tetrahydrofuran, which had poorer stability than acetone. More volatile solvents like diethyl ether and dichloromethane were not considered, as their volatility would likely reduce the accuracy of the determination.

Although the stability was the lowest in acetone, KMnO_4 is far more soluble in acetone than in the benzene mixture. Since a higher concentration of KMnO_4 would allow a greater range of HC301 concentrations to be quantified, the use of acetone appears to be better if considerations are taken for the decreasing concentration of KMnO_4 . The use of acetone would also be beneficial as it is desirable to eliminate the use of benzene when possible and use a less-hazardous solvent like acetone.

Quantification of HC301. To quantify HC301 as quickly as reasonably possible, it is desirable not to perform a full titration to the endpoint, while maintaining accuracy and precision. Instead of titrating to the endpoint, an aliquot of the HC301-containing sample can be added to a solution containing a known, sizable excess of KMnO_4 and allowed to react. Thereafter, the concentration of remaining KMnO_4 can be determined, and the difference between its initial and final amounts is proportional to the HC301 concentration in the sample aliquot.

This one-step titration was first tried with aqueous KMnO_4 . Upon addition and mixing of an HC301 containing sample, but not a blank of *n*-dodecane, an immediate lightening of the KMnO_4 solution's color was observed. Despite the successful reaction, attempts to quantify the HC301 by this method were largely unsuccessful as the UV–vis spectra collected after the addition were unusually variable. This was likely due to the formation of droplets of negligibly water-soluble *n*-dodecane and oxidized HC301 suspended in the aqueous bulk as a result of mixing the two phases. These droplets would be capable of scattering light and causing the poorly reproducible UV–vis spectra observed.

KMnO_4 and HC301 were observed to react with each other in water as evidenced by the decolorization of the solution, but the insolubility of *n*-dodecane and oxidized HC301 in water

Table 1. Molar Extinction Coefficient (ϵ) at λ_{max} and Intercept for Potassium Permanganate in Water, Acetone, and Benzene Measured Immediately after Preparing the Solution

solvent	λ_{max}	ϵ ($\text{L}\cdot\text{mmol}^{-1}\cdot\text{cm}^{-1}$)	<i>y</i> -intercept	r^2	<i>n</i>
water	526	2.323 ± 0.005	0.011 ± 0.001	0.99998	5
acetone	528	2.62 ± 0.08	-0.010 ± 0.007	0.997	5
benzene	525	13.6			1

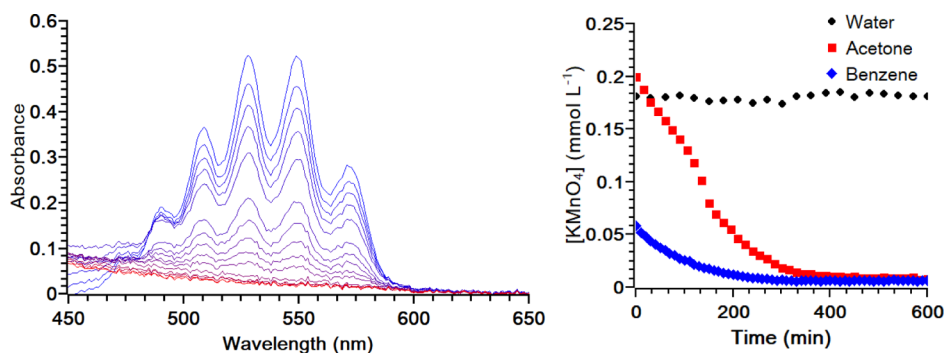


Figure 3. Left: Spectra of KMnO_4 in acetone. The initial spectra are shown in blue and the final spectra are shown in red. The spectra shown were collected at 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, 5.5, 6.5, 7.5, 8.5, and 10 h. Right: Stability of KMnO_4 in water, acetone, and a mixture of 40.024 mmol L^{-1} 18-crown-6 ether and 5.046 mmol L^{-1} bis(2-ethylhexyl)phosphoric acid in benzene.

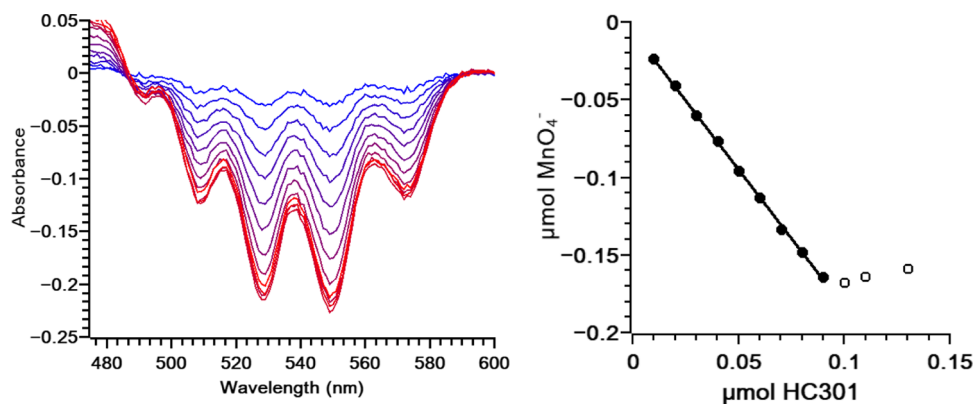


Figure 4. Left: Spectra of KMnO_4 in acetone after addition of 1.002×10^{-2} to 9.018×10^{-2} $\mu\text{mol HC301}$ and mixing for 15 s. After each addition of HC301, the KMnO_4 solution in both the sample and reference cells was replaced with a freshly prepared solution for the next addition. Spectra with less HC301 added are shown in blue and those with more HC301 are shown in red. Right: The amount of MnO_4^- dissolved in acetone consumed as a function of the amount of HC301 added.

prevented the reproducible quantification of the remaining KMnO_4 by UV–vis. Therefore, this reaction was tested in another solvent in which all components are soluble. Either acetone- or benzene-based solvents could have been used as *n*-dodecane and HC301 are soluble in both, but acetone was chosen as it could dissolve more KMnO_4 and is less hazardous than benzene. A major drawback of using either of these organic solvents is the reduced stability of the MnO_4^- anion. To avoid this instability from affecting the determination of HC301, the same solution containing an excess of KMnO_4 was put into both the sample and reference cells of the spectrophotometer. The initial concentration of KMnO_4 in both cells was 0.1998 mmol L^{-1} and no additions were made to the reference cell during the titration. With this approach, although the KMnO_4 is continuously degrading in the sample cell, it is degrading at the same rate in the reference cell too. Therefore, if nothing else is added to either of the cells and the spectra are recorded over time, the baseline spectra should be recorded at all time points. Indeed, when the same solution of KMnO_4 in acetone was placed in the sample and reference cells, stable baseline spectra are observed over at least 3 h. When an oxidizable species was added to the sample cell, the concentration of KMnO_4 in the sample cell decreases relative to the reference cell and a negative absorption peak proportional to the amount of oxidizable species will be detected. Upon addition of an aliquot containing HC301 to the sample cell, a negative absorbance peak was observed and had a consistent absorbance from immediately after mixing to

30 min later. After each HC301 addition, the solutions in both the sample and reference cells were replaced with a fresh KMnO_4 solution to minimize any differences between the two cells.

Since issues arising from the instability of KMnO_4 in acetone were avoided using the same KMnO_4 solution in both the sample and reference cells, this system was assessed for its ability to quantify HC301. Figure 4 shows the spectra resulting from the addition of HC301 and the amount of MnO_4^- consumed as a function of HC301 added. The amount of HC301 added was calculated from the molar extinction coefficient previously determined. The first nine spectra show a continuous decrease which, when converted to the graph on the right, shows a consistent linear response to the addition of HC301. This linear portion of the graph can serve as an analytical curve to relate the amount of HC301 added to the amount of KMnO_4 reduced. Additionally, as the slope of this linear portion is -1.96 , it indicates that the reaction between HC301 and KMnO_4 requires two equivalents of KMnO_4 to react with one equivalent of HC301. The later spectra and points did not have sufficient KMnO_4 to react with all the HC301 added, which caused this linear response to cease. The positive slope for these final three points is due to the degradation of KMnO_4 in the reference cell, which is no longer matched to the sample cell as all KMnO_4 within the sample cell has been depleted.

As the reduction of the remaining permanganate was found to have a linear relationship to the amount of HC301 added, it

has the potential to quantify this amount. To test this, leave-one-out cross-validation²² (LOOCV) was applied to the linear portion of the reduction in KMnO_4 versus amount of added HC301 relationship. In this method of cross-validation, a single data point is removed from the data set and an analytical curve is created from the remaining points. This new analytical curve is then used to determine the amount of HC301 added for the data point that was removed from the data set. The value resulting from the new analytical curve can be compared to the known value, Figure 5 and Table 2. The amount of HC301

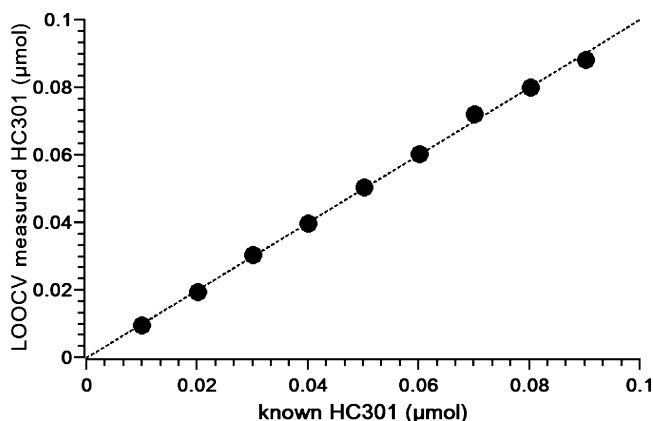


Figure 5. Comparison of the amount of HC301 measured by LOOCV and the known amount of HC301 that was added. The dashed line represents the ideal (i.e., LOOCV measured amount is equal to the known amount) relationship.

Table 2. Amounts of HC301 Added and Evaluated by LOOCV along with the Difference between These Two Values

known HC301 (μmol)	LOOCV measured HC301 (μmol)	difference (μmol)	difference (%)
1.002×10^{-2}	9.62×10^{-3}	4.04×10^{-4}	4.03
2.004×10^{-2}	1.94×10^{-2}	6.49×10^{-4}	3.24
3.006×10^{-2}	3.04×10^{-2}	-3.37×10^{-4}	-1.11
4.008×10^{-2}	3.98×10^{-2}	2.90×10^{-4}	0.72
5.010×10^{-2}	5.05×10^{-2}	-3.86×10^{-4}	-0.77
6.012×10^{-2}	6.03×10^{-2}	-1.61×10^{-4}	-0.27
7.014×10^{-2}	7.22×10^{-2}	-2.03×10^{-3}	-2.89
8.016×10^{-2}	8.00×10^{-2}	1.94×10^{-4}	0.24
9.018×10^{-2}	8.81×10^{-2}	2.05×10^{-3}	2.27

measured by the LOOCV method is close to the known amount, with the first data point having the largest relative difference from the known value (4.03%). When greater amounts of HC301 were added, LOOCV results had lower relative differences, especially for points in the middle of the series where the relative difference was frequently within $\pm 1\%$. Overall, the average of the absolute value of the relative differences was 1.73%.

Under the conditions used here, the limit of detection is $0.002 \mu\text{mol}$ and the maximum quantity of HC301 that can be quantified is slightly over $0.09 \mu\text{mol}$. If a typical HC301 process solution with a concentration of approximately 0.5 mol L^{-1} was to be quantified, an aliquot of at most $0.18 \mu\text{L}$ must be used. As this volume is too small to easily dispense, the sample must be diluted prior to analysis.

Quantification of HC301 under Process Conditions. Actual conditions for processes utilizing HC301 will likely be

more complex due to the presence of degradation products, oxidizable metal species, and impurities in the organic phase. If these species react with MnO_4^- , they would interfere with the quantification of HC301. This problem could be easily overcome using standard addition in which a set of samples are prepared and known; varying amounts of additional HC301 are added to each sample. Upon analysis of such a sample set, the amount of HC301 in the original sample can be determined. Although this approach would allow the determination of HC301 in a more complex matrix, it would increase the amount of time and effort required to analyze a sample. Therefore, it is worth considering how greatly this method of quantification is impacted by the presence of these unwanted species and if they may be ignored.

Of the mentioned interferents, the most prevalent would be the degradation products of HC301. HC301 can undergo oxidation and hydrolysis^{12–14} or radiolysis^{8,15,16} to form the monothiophosphinic and phosphinic acids. The monothiophosphinic acid would be the most problematic as it retains one of the reducing sulfur sites and could react with KMnO_4 . Fortunately, there is unlikely to be too much buildup of the monothiophosphinic acid because it is both a stronger and non-selective extractant,^{23,24} so the functionality of the separation system would be compromised before the concentration of the monothiophosphinic acid becomes excessive.¹⁵ Other HC301 degradation products are not expected to be troublesome as they lack reducing sulfur sites.

Along with the degradation products, extracted metal ions could also interfere if they are capable of being oxidized by KMnO_4 . Among the actinides and lanthanides being separated, it is unlikely that any would interfere due to the difficulty of oxidizing them past their initial, trivalent oxidation state. Ce(III) could be oxidized to the tetravalent state, but as it is a lanthanide and not strongly extracted, it will not have a very high concentration in the organic phase. Bk(III) could also be oxidized to the tetravalent state, but it is not present to any great extent in used nuclear fuel, so very little of it would be in the system. Lighter actinides have higher accessible oxidation states, so Pu(III), Pu(IV), and U(IV) would likely interfere, but they are likely to have been removed previously. As the mixture of lanthanides and actinides to be separated will have undergone extensive purification prior to reaching a HC301-based separation, many interfering metal species will have already been removed.^{25–27} After these other metal ions will have been removed, it is possible that Fe, Cr, and Ni could be reintroduced by corrosion of stainless-steel piping and process equipment in the presence of HC301 or nitric acid. Ni(II), Fe(II), and Fe(III) are capable of being extracted by HC301.^{28,29} Ni(II) and Fe(II) are both capable of being oxidized and could interfere if their concentration becomes too high.

Other reducing impurities could also interfere, but the identity and concentration of any impurities are likely dependent upon the sources and batches of chemicals used in the system. However, as HC301 must be extensively purified to provide selectivity,³⁰ it is likely that the vast majority of impurities have already been removed from HC301.

CONCLUSIONS

The ability to quantify the amount of HC301 in *n*-dodecane by permanganometry was tested here. Traditional aqueous permanganometry was found to be unsuitable for this fast, spectrophotometric titration due to light scattering from

droplets of the water-insoluble *n*-dodecane and oxidized HC301. To avoid the formation of droplets within the cuvette, two solvents which can dissolve *n*-dodecane and HC301 were tested, an 18-crown-6 ether and benzene-based solvent mixture and acetone. The stability of KMnO_4 was found to be reduced in both the organic solvents relative to water, particularly for acetone, but can be accounted for using the same solution of KMnO_4 in both the reference and sample cells of the spectrophotometer. By adding aliquots containing a known quantity of HC301 to the sample cell, a linear analytical curve can be obtained relating the amount of MnO_4^- consumed to the amount of HC301 added until all KMnO_4 is consumed by reaction with HC301 or the solvent. Cross-validating this analytical curve by LOOCV shows that this technique was able to determine the known amount of HC301 with reasonable accuracy. The average of the absolute value of the difference between the amount of HC301 calculated by LOOCV and the known value is 1.73%. The largest relative difference was 4.03%, with other points having lower relative differences. Although this system has shown the ability to quantify purified HC301 in a pure solvent, HC301 degradation products, oxidizable metal species, and other impurities could interfere. These interferences can be dealt with by standard addition or may be small enough to not warrant additional concern.

EXPERIMENTAL SECTION

Reagents. Potassium permanganate (ACS grade) was obtained from Alfa Aesar and dried in vacuo prior to use. Bis(2-ethylhexyl)phosphoric acid (97%) was purchased from Sigma-Aldrich and purified by the third-phase method.³¹ Benzene (HPLC grade), anhydrous dodecane ($\geq 99\%$), and anhydrous hexanes ($\geq 99\%$) were obtained from Sigma-Aldrich and used as supplied. Ethanol (200 proof) and acetone (ACS grade) were purchased from Pharmco by Greenfield Global. The crown ether 18-crown-6 (99%), concentrated nitric acid (ACS grade), and hydrochloric acid (ACS grade) were purchased from Acros organics, Mallinckrodt Chemicals, and Macron Fine Chemicals, respectively. Sodium sulfate (ACS grade) and ammonium sulfate (ACS grade) were obtained from Fisher Chemical. Neodymium oxide (99.995%) was purchased from Treibacher Industrie AG and converted to the nitrate by dissolution in nitric acid.

Bis(2,4,4-trimethylpentyl)dithiophosphinic acid was obtained from Solvay as the major component of the extractant Cyanex 301 GN and purified as follows.³² The crude HC301 was converted to the ammonium salt by bubbling with excess dry ammonia gas generated from the reaction between ammonium sulfate and sodium hydroxide. The precipitate of the ammonium salt of HC301 was filtered and washed with hexane and then dissolved in a mixture of ethanol in water with 6.8% ethanol, and sodium hydroxide was added to achieve a pH of 10. To this, hexane and 0.005 equivalents of neodymium nitrate were added and mixed for several minutes. Once the phases separated, the hexane phase was removed, and this process was repeated 15 times. Then, the remaining aqueous phase was acidified with hydrochloric acid to reprotonate the HC301, which was extracted with fresh hexane. This hexane phase was removed and dried with anhydrous sodium sulfate before evaporation of the hexane to recover the purified HC301. The resulting purity was found to exceed 99.9% by ³¹P NMR as evidenced by a singlet at 65 ppm from HC301 and a lack of other peaks especially at 93.5 and 59.8 as these

correspond to the monothiophosphinic acid and phosphinic acid, respectively.¹⁵

Water and acetone permanganate solutions were prepared by dissolving the required quantity of KMnO_4 in the solvent. Benzene solutions were prepared by dissolving KMnO_4 in a 40.024 mmol L^{-1} 18-crown-6 ether plus 5.046 mmol L^{-1} bis(2-ethylhexyl)phosphoric acid solution.

UV–Vis Spectrophotometry. UV–vis spectra were collected with a Cary 300 Bio spectrophotometer. Quartz cuvettes with a 1 cm pathlength and a maximum capacity of 3.5 mL were used for all samples. Spectra were collected using a bandwidth of 1 nm and an integration time of 0.200 s. The reference cell was loaded with the same solvent as used in the sample except when quantifying HC301 using potassium permanganate dissolved in acetone. When doing this, KMnO_4 was present in the reference cell at the same concentration as in the sample cell. All samples were measured at room temperature, and any temperature differences between sample and reference cells in the same sample chamber are minimal.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.1c00254>.

Spectra after addition of dodecane blanks (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Jakovljevic, B.; Bourget, C.; Nucciarone, D. CYANEX 301 binary extractant systems in cobalt/nickel recovery from acidic chloride solutions. *Hydrometallurgy* **2004**, *75*, 25–36.
- (2) Bessen, N. P.; Jackson, J. A.; Jensen, M. P.; Shafer, J. C. Sulfur Donating Extractants for the Separation of Trivalent Actinides and Lanthanides. *Coord. Chem. Rev.* **2020**, *421*, 213446.
- (3) Zhu, Y.; Chen, J.; Jiao, R. Extraction of Am(III) and Eu(III) from Nitrate Solution with Purified Cyanex 301. *Solvent Extr. Ion Exch.* **1996**, *14*, 61–68.
- (4) Peterman, D. R.; Greenhalgh, M. R.; Tillotson, R. D.; Klaehn, J. R.; Harrup, M. K.; Luther, T. A.; Law, J. D. Selective Extraction of Minor Actinides from Acidic Media Using Symmetric and

- Asymmetric Dithiophosphinic Acids. *Sep. Sci. Technol.* **2010**, *45*, 1711–1717.
- (5) Klaehn, J. R.; Peterman, D. R.; Harrup, M. K.; Tillotson, R. D.; Luther, T. A.; Law, J. D.; Daniels, L. M. Synthesis of symmetric dithiophosphinic acids for "minor actinide" extraction. *Inorg. Chim. Acta* **2008**, *361*, 2522–2532.
- (6) Pu, N.; Xu, L.; Sun, T.; Chen, J.; Xu, C. Tremendous Impact of Substituent Group on the Extraction and Selectivity to Am(III) over Eu(III) by Diaryldithiophosphinic Acids: Experimental and DFT Analysis. *J. Radioanal. Nucl. Chem.* **2019**, *320*, 219–226.
- (7) Ionova, G.; Ionov, S.; Rabbe, C.; Hill, C. m.; Madic, C.; Guillaumont, R.; Modolo, G.; Claude Krupa, J. Mechanism of Trivalent Actinide/Lanthanide Separation Using Synergistic Mixtures of Di(Chlorophenyl)Dithiophosphinic Acid and Neutral O-Bearing Co-Extractants. *New J. Chem.* **2001**, *25*, 491–501.
- (8) Modolo, G.; Odoj, R. The Separation of Trivalent Actinides from Lanthanides by Dithiophosphinic Acids from HNO₃ Acid Medium. *J. Alloys Compd.* **1998**, *271–273*, 248–251.
- (9) Choppin, G. R. Studies of the Synergistic Effect. *Sep. Sci. Technol.* **1981**, *16*, 1113–1126.
- (10) Clark, A. E.; Yang, P.; Shafer, J. C. Coordination of Actinides and the Chemistry behind Solvent Extraction. *Experimental and Theoretical Approaches to Actinide Chemistry*; John Wiley & Sons, 2018; pp 237–282.
- (11) Nash, K. L.; Braley, J. C. Challenges for Actinide Separations in Advanced Nuclear Fuel Cycles. *Nuclear Energy and the Environment*; ACS Publications, 2010; pp 19–38.
- (12) Sole, K. C.; Brent Hiskey, J.; Ferguson, T. L. An Assessment of the Long-term Stabilities of Cyanex 302 and Cyanex 301 in Sulfuric and Nitric Acids. *Solvent Extr. Ion Exch.* **1993**, *11*, 783–796.
- (13) Groenewold, G. S.; Peterman, D. R.; Klaehn, J. R.; Delmau, L. H.; Marc, P.; Custelcean, R. Oxidative Degradation of Bis(2,4,4-Trimethylpentyl)Dithiophosphinic Acid in Nitric Acid Studied by Electrospray Ionization Mass Spectrometry. *Rapid Commun. Mass Spectrom.* **2012**, *26*, 2195–2203.
- (14) Marc, P.; Custelcean, R.; Groenewold, G. S.; Klaehn, J. R.; Peterman, D. R.; Delmau, L. H. Degradation of Cyanex 301 in Contact with Nitric Acid Media. *Ind. Eng. Chem. Res.* **2012**, *51*, 13238–13244.
- (15) Chen, J.; Jiao, R.; Zhu, Y. A Study on the Radiolytic Stability of Commercial and Purified Cyanex 301. *Solvent Extr. Ion Exch.* **1996**, *14*, 555–565.
- (16) Modolo, G.; Odoj, R. Influence of the Purity and Irradiation Stability of Cyanex 301 on the Separation of Trivalent Actinides from Lanthanides by Solvent Extraction. *J. Radioanal. Nucl. Chem.* **1998**, *228*, 83–89.
- (17) Menoyo, B.; Elizalde, M. P. Composition of Cyanex 301 by Gas Chromatography-mass Spectrometry. *Solvent Extr. Ion Exch.* **2002**, *20*, 35–47.
- (18) Tait, B. K. The Extraction Of Some Base Metal Ions By Cyanex 301 Cyanex 302 And Their Binary Extractant Mixtures With Aliquat 336. *Solvent Extr. Ion Exch.* **1992**, *10*, 799–809.
- (19) Doheny, A. J.; Ganem, B. Purple Benzene Revisited. *J. Chem. Educ.* **1980**, *57*, 308.
- (20) Gokel, G. W.; Durst, H. D. Crown Ether Chemistry: Principles and Applications. *Aldrichimica Acta* **1976**, *9*, 3–12.
- (21) Wiberg, K. B.; Geer, R. D. The Kinetics of the Permanganate Oxidation of Acetone. *J. Am. Chem. Soc.* **1965**, *87*, 5202–5209.
- (22) Webb, G. I.; Sammut, C.; Perlich, C.; Horváth, T.; Wrobel, S.; Korb, K. B.; Noble, W. S.; Leslie, C.; Lagoudakis, M. G.; Quadrianto, N.; et al. Leave-One-out Cross-Validation. *Encyclopedia of Machine Learning*; Springer US: Boston, MA, 2011; pp 600–601.
- (23) Jensen, M. P.; Bond, A. H. Influence of Aggregation on the Extraction of Trivalent Lanthanide and Actinide Cations by Purified Cyanex 272, Cyanex 301, and Cyanex 302. *Radiochim. Acta* **2002**, *90*, 205–209.
- (24) Jensen, M. P.; Bond, A. H. Comparison of Covalency in the Complexes of Trivalent Actinide and Lanthanide Cations. *J. Am. Chem. Soc.* **2002**, *124*, 9870–9877.
- (25) Schulz, W. W.; Horwitz, E. P. The Truex Process and the Management of Liquid Tru Uwaste. *Sep. Sci. Technol.* **1988**, *23*, 1191–1210.
- (26) Philip Horwitz, E.; Kalina, D. C.; Diamond, H.; Vandegrift, G. F.; Schulz, W. W. The TRUEx Process—a Process for the Extraction of the Transuranic Elements from Nitric Acid Wastes Utilizing Modified PUREX Solvent. *Solvent Extr. Ion Exch.* **1985**, *3*, 75–109.
- (27) Huff, E. A.; Huff, D. R. TRU Spec and RE Spec Chromatography: Basic Studies and Applications. *34th ORNL/DOE Conference on Analytical Chemistry In Energy Technology*, Gatlinburg, TN, 1993; p 58.
- (28) Fleitlikh, I. Y.; Grigorieva, N. A.; Logutenko, O. A. Extraction of Non-Ferrous Metals and Iron with Systems Based on Bis(2,4,4-Trimethylpentyl)Dithiophosphinic Acid (CYANEX 301), A Review. *Solvent Extr. Ion Exch.* **2018**, *36*, 1–21.
- (29) Panesar, K.; Singh, O. V.; Tandon, S. N. Liquid-liquid extraction and reversed phase chromatographic behaviour of some 3d metal ions using bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301). *Talanta* **1994**, *41*, 1341–1344.
- (30) Zhu, Y.; Chen, J.; Choppin, G. R. Extraction of Americium and Fission Product Lanthanides with Cyanex 272 and Cyanex 301. *Solvent Extr. Ion Exch.* **1996**, *14*, 543–553.
- (31) Zhengshui, H.; Ying, P.; Wanwu, M.; Xun, F. Purification of Organophosphorus Acid Extractants. *Solvent Extr. Ion Exch.* **1995**, *13*, 965–976.
- (32) Chen, J.; Jiao, R. Z.; Zhu, Y. J. Purification and Properties of Cyanex 301. *Chin. J. Appl. Chem.* **1996**, *13*, 45–48.