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Extraction of ^{197}mHg with TIBPS in HNO_3 and HCl media

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October 27, 2021

Journal of Radioanalytical and Nuclear Chemistry

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Title page

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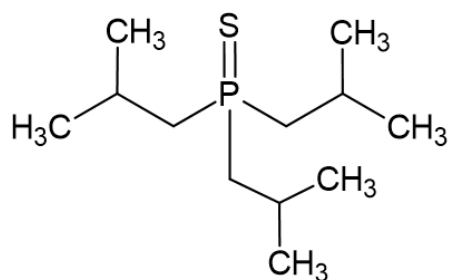
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11

34 mercury is of particular interest for transactinide chemistry homolog studies [2] [3] and
35 radiopharmaceuticals [4] [5]. While the affinity of TIBPS for mercury is well-known in
36 the literature, with proposed environmental applications based on liquid membrane
37 separations [6] [7], comprehensive studies of this extraction are lacking with only Refs. [8]
38 and [9] examining the extraction over a wide range of acid concentrations and studying the
39 speciation. Both of these studies only include data for mercury samples with
40 concentrations $\geq 10^{-4}$ M; there is no comparable data for NCA mercury, which is known to
41 behave differently than samples of mercury with significant mass. Furthermore, there is a
42 lack of data for the extraction of mercury by TIBPS at high concentrations (>1 M) of HNO_3
43 as CL resin is not compatible with HNO_3 at these concentrations and Ref. [9] is limited to
44 concentrations of 0.001 to 1 M HNO_3 .



49 **Fig. 1** Tri-isobutyl phosphine sulfide (CL resin extractant molecule [10]).

50 Therefore, experiments were performed to better characterize the extraction of NCA
51 $^{197\text{m}}\text{Hg}$ by TIBPS over a wide range of acid concentrations (0.001 to conc.) in both HCl
52 and HNO_3 , as well as to determine the uptake kinetics and the extracted species. The
53 uptake was high in low acid concentrations with a decrease in extraction at higher
54 concentrations; the uptake kinetics were rapid. The behavior in HNO_3 and HCl media was
55 very similar. Speciation studies indicated that the extraction is 1:1 ($^{197\text{m}}\text{Hg}$:TIBPS) in
56 HNO_3 and 1:2 in HCl.

57 **Experimental**

58 For all experiments, acid solutions were prepared from Aristar ultra-pure acids (VWR) and
59 diluted with Aristar ultra-pure water (VWR) as necessary. Carbon tetrachloride (ACS

60 reagent grade, 99.9%) was obtained from Sigma-Aldrich. Tri-isobutyl phosphine (CAS#: 4125-25-1) was purchased from Strem Chemicals (Newburyport, MA) and used to 61 synthesize TIBPS based on a modified protocol from the literature for the synthesis of the 62 triethyl analog (TEPS) of TIBPS [11]. TIBPS was obtained as a white solid and analyzed 63 with gas chromatography–mass spectrometry (GC-MS) and nuclear magnetic resonance 64 (NMR). The details of this analysis are included in the Supplementary Information. 65 Solutions of TIBPS dissolved in CCl₄ were prepared for use in experiments with 66 concentrations ranging from 5 x 10⁻⁶ M to 0.001 M. 67

68 Mercury-197m (t_{1/2} = 23.8 h [12]) was produced from the proton irradiation of gold foils 69 (99.999%, Goodfellow) at the Center for Accelerator Mass Spectrometry (CAMS) at 70 Lawrence Livermore National Laboratory. After the irradiation, mercury was separated 71 from the gold foils according to the procedure in Ref. [4] and two stock solutions were 72 prepared, one in 1 M HCl and the other in 1 M HNO₃, with activities >300 cps per 20 μL.

73 Activity measurements were made with an HPGe detector with Ortec NIM electronics and 74 ASPEC multi-channel analyzer. Maestro software (Ortec) was used to analyze the 75 resultant spectra. All samples were counted in the same geometry and all counts were 76 decay corrected to account for decay during experiments. The highest intensity gamma- 77 ray line (133.98 keV; 33.5%) was used to determine the activity. All gamma-ray 78 spectrometry was done immediately after completion of the batch, kinetics, and speciation 79 studies.

80 **GC-MS Analysis Method** A 6890 Agilent GC with 5975 MS detector equipped with a 81 split/splitless injector was used for the analysis (splitless mode). The GC column used for 82 the analysis was an Agilent HP- 5ms UI capillary column (30 m × 0.25 mm id × 0.25 μm 83 film thickness). Ultra-high purity helium, at 0.8 mL/min, served as the carrier gas. The 84 injector temperature was 250 °C and the injection volume was 1 μL. The oven temperature 85 program was as follows: 40 °C, held for 3 min, increased at 8 °C/min to 300 °C, held for 3 86 min. The MS ion source and quadrupole temperatures were 230 °C and 150 °C, 87 respectively. Electron ionization (EI) was used with an ionization energy of 70 eV and the 88 MS was operated to scan from *m/z* 29 to 600 in 0.4 s as described previously [13] [14].

89 **Nuclear Magnetic Resonance** Spectra were obtained using a Bruker Avance III 600 MHz
90 instrument equipped with a Bruker QNP 5 mm cryoprobe (Bruker Biospin, Billerica, MA)
91 at $30.0 \pm 0.1^\circ\text{C}$. NMR data is reported as follows: chemical shift (δ) (parts per million,
92 ppm); multiplicity: d (doublet), dd (doublet of doublets), non (nonet); coupling constants
93 (J) are given in Hertz (Hz). ^1H NMR (600 MHz) chemical shifts are calibrated with respect
94 to residual chloroform in CDCl_3 centered at 7.26 ppm, while ^{31}P NMR (242 MHz) is
95 calibrated to a phosphoric acid (H_3PO_4) internal standard.

96 **Caution!** Tri-isobutyl phosphine is an ignitable liquid when it comes into contact with air.
97 Although the bottle containing the chemical was only in contact with air only once and for
98 a very brief moment during the synthetic procedure, great caution should be exercised
99 when transferring it to the reaction mixture.

100 **Synthesis of TIBPS.** In a 50 mL round-bottom flask equipped with a stir bar and a rubber
101 septum, sulfur (3.2 g, 100 mmol, 12.5 equiv. to tri-isobutyl phosphine) was made into a
102 suspension in anhydrous dichloromethane (20 mL). The flask was placed under a gentle
103 stream of circulating nitrogen and cooled to $\sim 4^\circ\text{C}$ with an ice bath. The yellow suspension
104 was treated dropwise using an oven dried glass syringe with tri-isobutyl phosphine (2 mL,
105 1.6 g, 8 mmol). The resulting thick suspension was stirred at ambient temperature under
106 nitrogen for 4 hours. The suspension was partitioned ($\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$), the organic phase
107 was dried over anhydrous Na_2SO_4 , and evaporated *in vacuo* to give a yellow residue that
108 was purified by flash column chromatography ($\text{DCM} \rightarrow 3:7 \text{ MeOH:DCM}$) to give tri-
109 isobutyl phosphine sulfide as a white solid (567 mg, 30%) that was placed in a vial under
110 Argon and kept refrigerated. The identity of the TIBPS was confirmed by NMR (^1H and
111 ^{31}P), GC-MS (Supplementary Information Figs. 1 and 2), and HR-LCMS. ^1H NMR (600
112 MHz, CDCl_3) δ 2.19 (non, $J = 6.0$ Hz, 3H), 1.75 (dd, $J = 12.0, 6.0$ Hz, 6H), 1.06 (d, $J = 6.0$
113 Hz, 18H); ^{31}P NMR (242 MHz) δ 45.6; HRMS (CI) m/z calcd for $\text{C}_{12}\text{H}_{27}\text{PS}$ [M^+]:
114 234.1571; found 234.1574.

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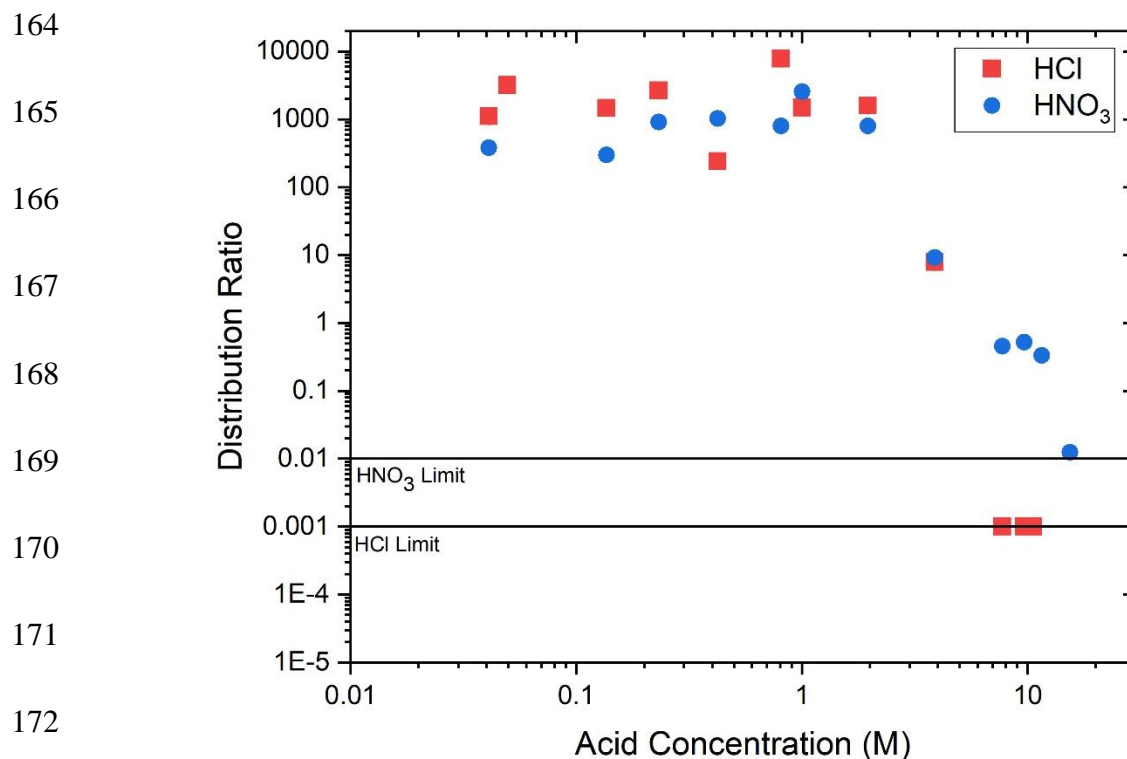
147 **Speciation Studies**

148 Speciation experiments were performed in the same manner as the batch studies. Studies
149 in HCl were done from 4 M HCl and studies in HNO₃ were done from 8 M HNO₃. The
150 acid (480 μL) was added to a 1.5 mL micro centrifuge tube along with 500 μL of a TIBPS
151 stock solution in CCl₄ (with concentrations ranging from 5 x10⁻⁶ M to 0.001 M) and a 20
152 μL spike of ^{197m}Hg stock solution, in the appropriate acid, was added. Each sample was
153 mixed for 5 min. before separation of the phases. As before, a 300 μL aliquot of each phase
154 was removed, placed in a clean 1.5 mL tube and counted for 30 s to 600 s.

155 **Results and Discussion**

156 **Batch Uptake and Kinetics**

157 The results from the batch uptake studies are shown in Fig. 2. The uptake from HCl and
158 HNO₃ follows a similar trend with high extraction ($D > 100$) at low concentrations, and a
159 strong reduction in extraction above 2 M acid that continues to higher concentrations. The
160 extraction behavior in HCl and HNO₃ is extremely similar at low acid concentrations (≤ 4
161 M), but the extraction from HCl decreases more at higher concentrations (≥ 8 M) than from
162 HNO₃. This agrees well with Ref. [9], which notes that the extraction behavior of mercury
163 from HNO₃ and HCl was extremely similar from 0.001 M to 1 M acid.



173 **Fig. 2** Uptake of ^{197m}Hg by 10^{-4} M TIPBS in CCl_4 as a function of HCl and HNO_3
 174 concentration. Error is from counting statistics; many of the error bars are smaller than
 175 the data points. The limit for each acid was established by the blank with no TIPBS
 176 present; the limit is HNO_3 is higher as the activity was lower in that study.

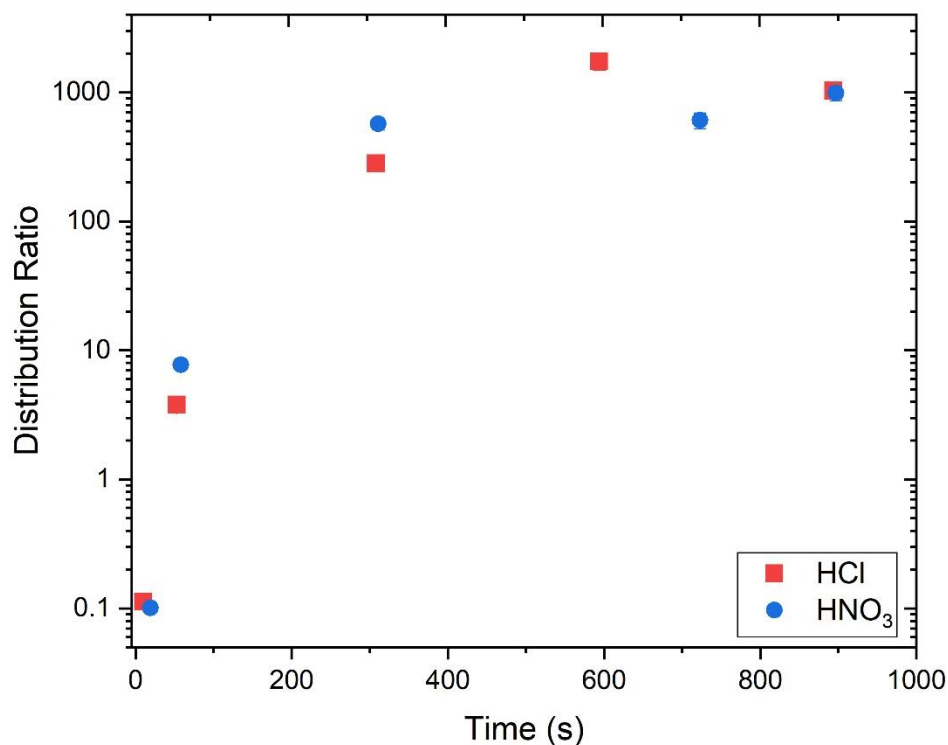
177 The extraction of mercury by TIPBS in HCl [8] and HNO_3 [9] has been studied extensively
 178 in toluene and Ref. [9] also studied the extraction of mercury from HNO_3 (0.001 M to 1
 179 M) with 10^{-4} M TIPBS from kerosene, xylene, toluene, n-hexane, chloroform and
 180 cyclohexane. Reference [9] notes that the extraction trends with the dielectric constant of
 181 the solvent, with the exception kerosene, and noted similar extraction from toluene,
 182 chloroform and cyclohexane. Due to the low specific activity of mercury available in this
 183 work, CCl_4 was chosen as the solvent as it is denser than the aqueous phase, which makes
 184 manual phase separation simpler. Despite the slightly lower dielectric constant of CCl_4 , as
 185 compared to toluene, high extraction was still observed and the simpler phase separation,
 186 which leads to less contamination between phases, resulted in better results than what could
 187 be obtained on this small scale with manual phase separation from a toluene organic phase.

188 A blank study also showed that the uptake of acid by the organic phase is negligible,
189 allowing the separations to be performed with no pre-equilibration of the phases.

190 The results from Ref. [9] are very similar to what was measured in this work over the
191 relevant concentration range when kerosene was used as the solvent, and slightly lower,
192 particularly at very low concentrations (0.001 M to 0.01 M), when toluene was employed
193 instead. Reference [8] studied the extraction of mercury in HCl (~0.01 M to 10 M) from
194 TIBPS (0.01 to 0.08 M) in toluene and while the trend in extraction is similar, the measured
195 distribution ratios in Ref. [8] are significantly lower than what was measured in this work
196 despite the use of higher concentrations of TIBPS in the toluene organic phase. The exact
197 source of this discrepancy is difficult to determine as the experimental conditions in Ref.
198 [8] were very different; in particular, significantly higher amounts of mercury were used
199 (10^{-3} M) and detection was done with a combination of titration and atomic absorption
200 spectrometry (AAS). These detection methods introduce more error than gamma-ray
201 spectrometry, particularly for mercury as there have been many developments in the field
202 of mercury detection with AAS since Ref. [8] was published in 1986. Notably, Ref. [9],
203 from 1997, used AAS and gamma-ray spectrometry for lighter transitional metals that were
204 studied but gamma-ray spectrometry was used exclusively for the determination of
205 mercury. The mass of mercury present in the system can also have a large effect on the
206 extraction as the tendency for changes in the behavior of mercury depending on the mass
207 present in the system are well-known. In this work, mercury was prepared as NCA, and
208 the mercury concentration was $<10^{-6}$ M based on the known levels of mercury
209 contamination in the Aristar Ultra-pure acids and the high purity gold foils.

210 The extraction behavior of mercury on CL resin was previously studied in HCl [1]. As in
211 the liquid-liquid batch study (Fig. 2), the extraction on CL resin is high at lower HCl
212 concentrations with a decrease in extraction at concentrations above 2 M HCl. However,
213 the decrease in extraction at ≥ 4 M HCl is not as sharp in the resin study as in the liquid-
214 liquid study. The difference in the concentration of TIBPS is likely contributing to this as
215 the resin loading of TIBPS is far higher than in the liquid-liquid extraction study.

216 The results from the kinetics studies are shown in Fig. 3. For studies in both HCl and
217 HNO₃ the kinetics were studied in 0.001 M acid as it was a point of high extraction for
218 both acids. The uptake kinetics are rapid with equilibrium achieved at ~5 minutes. The
219 kinetics of mercury uptake by TIBPS have not been well-characterized in the literature, but
220 this aligns with the uptake kinetics of ^{197m}Hg from HCl on CL resin [1].



221 **Fig. 3** Uptake kinetics of ^{197m}Hg by 10⁻⁴ M TIPBS in CCl₄ as a function of HCl and
222 HNO₃ concentration. Error is from counting statistics; many of the error bars are smaller
223 than the data points.

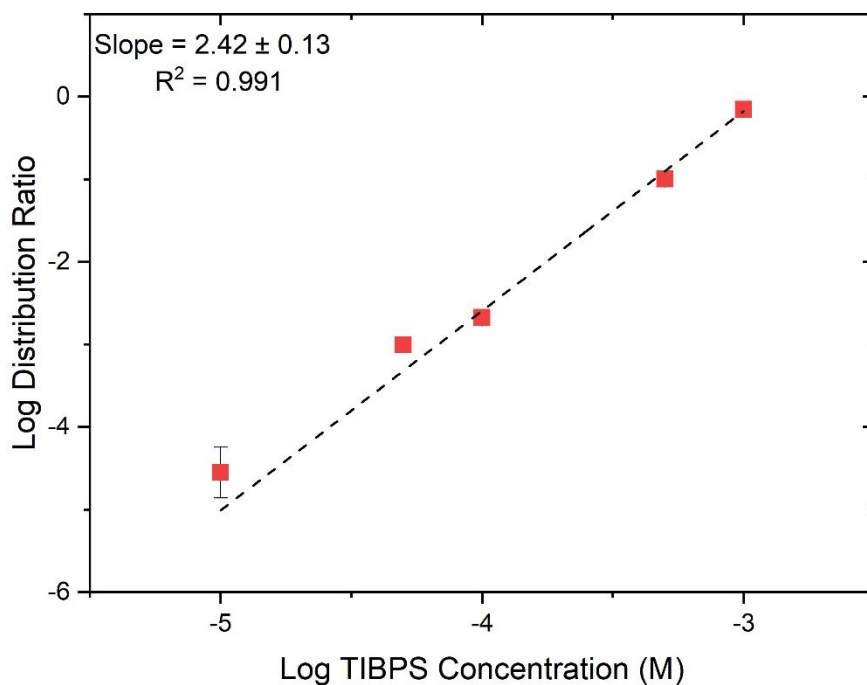
224 Speciation

225 The speciation of mercury was also studied in HCl and HNO₃, and the results are shown in
226 Figs. 4 and 5. For these studies, 4 M HCl and 8 M HNO₃ were chosen for the aqueous
227 phases. At lower acid concentrations, the extraction sufficiently high at all of the studied
228 concentrations of TIBPS that the differences in extraction for each data point are dominated
229 by the error arising from the counting statistics rather than the difference in extraction

230 magnitude, which is essential to elucidate the mechanism from the data. Therefore, a
231 concentration of intermediate extraction was chosen for each acid.

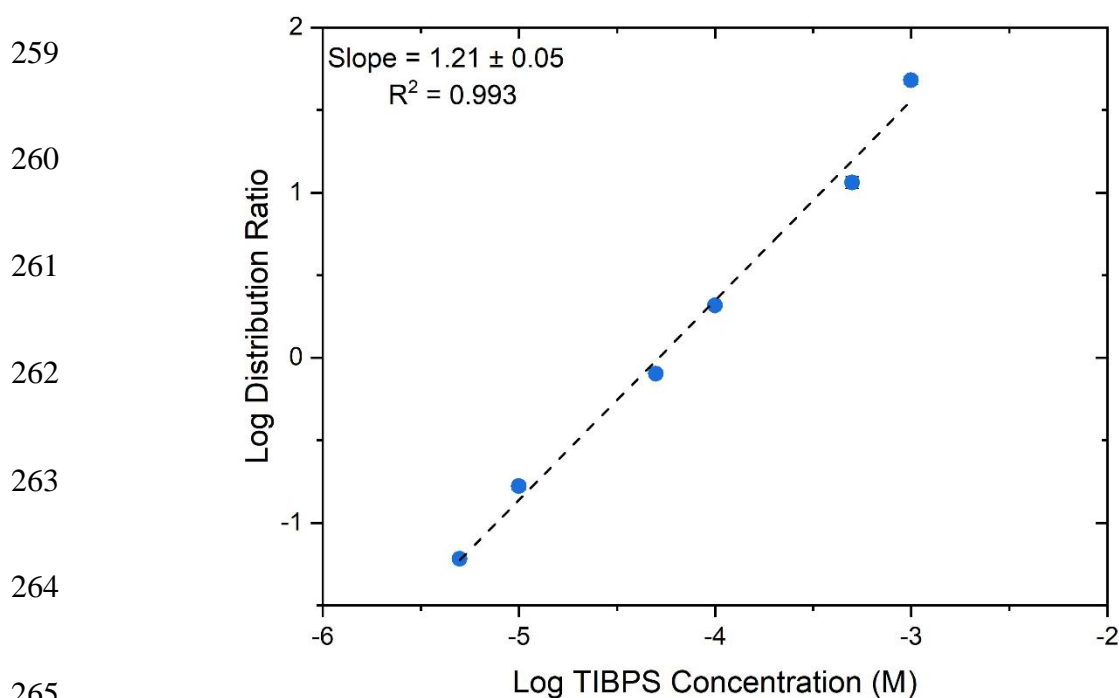
232 In a plot of $\text{Log}(D)$ versus $\text{Log}([\text{TIBPS}])$, the slope indicates the number of TIBPS
233 molecules involved in the extraction of one atom of mercury [9]. In HCl (Fig. 4), the slope
234 is 2.42 ± 0.13 . This suggests the extraction is 1:2 ($^{197\text{m}}\text{Hg}:\text{TIBPS}$) with the extracted
235 species being $\text{HgCl}_2 \cdot 2\text{TIBPS}$. While the slope is higher than expected for a 1:2 extraction,
236 small variations in the data, particularly due to counting statistics, can lead to large changes
237 in the slope. Speciation experiments with higher masses of mercury [8] have indicated two
238 possible species that can be extracted by TIBPS from HCl: $\text{HgCl}_2 \cdot 2\text{TIBPS}$ and
239 $(\text{HgCl}_2)_2 \cdot 2\text{TIBPS}$. The results from this work clearly trend toward a 1:2 extraction
240 mechanism rather than 1:1; presumably the dimerized species, $(\text{HgCl}_2)_2 \cdot 2\text{TIBPS}$, does not
241 form at extremely low concentrations of mercury as studied in this work. Further studies
242 would need to be performed at varying concentration of HCl and mercury to determine the
243 extraction more precisely under varying conditions.

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251 **Fig. 4** Speciation plot for the extraction of $^{197\text{m}}\text{Hg}$ by TIPBS in CCl_4 from 4 M HCl. The
252 error on the distribution ratio is from counting statistics, the error on the TIPBS
253 concentration is 0.0217; most of the error bars are smaller than the data points.

254 In HNO_3 (Fig. 5), the slope is 1.21 ± 0.05 , which suggests a 1:1 extraction mechanism,
255 likely $\text{Hg}(\text{NO}_3)_2 \cdot \text{TIPBS}$. This agrees with studies in the literature as Ref. [9] measured a
256 slope of 1.3 for the extraction of mercury by TIPBS from 0.01 M HNO_3 and concluded that
257 the mechanism was a 1:1 extraction. Unlike in HCl, the previous studies with mass did not
258 indicate the extraction of a dimerized form.



266 **Fig. 5** Speciation plot for the extraction of $^{197\text{m}}\text{Hg}$ by TIPBS in CCl_4 from 8 M HNO_3 .
267 The error on the distribution ratio is from counting statistics, the error on the TIPBS
268 concentration is 0.0217; most of the error bars are smaller than the data points.

269 The speciation and extraction differences between HCl and HNO_3 may be impacted by the
270 speciation of mercury in aqueous acidic solutions. In HNO_3 , mercury forms primarily
271 neutral species [2], but in HCl numerous cationic, neutral and anionic species can form
272 depending on the acid concentration [15] [16]. At concentrations from 0.001 M to 0.01 M,

273 HgCl₂ dominates [15], and from 0.01 M to 1 M HgCl₃⁻ is the primary species [16]. Above
274 1 M, HgCl₄²⁻ dominates, but with a significant fraction of HgCl₃⁻ remaining until the
275 concentration approaches 10 M HCl [16]. It may be that the extraction drops more
276 significantly in HCl at high concentrations (≥8 M) due to the various changes in mercury
277 speciation. Further studies would be needed to determine the effect of the identity and
278 concentration of the counterion on the extraction.

279 TIBPS Synthesis

280 While TIBPS is a well-known molecule, there are no detailed references concerning its
281 synthesis. There are many references for the sulfurization of other trialkylphosphines, such
282 as Ref. [11] which was used as a basis for the synthesis in this work. Literature methods
283 to produce phosphine sulfides involve strictly inert conditions throughout the procedure
284 with heating (120-140 °C) on an overnight basis (>16 hr), followed by purification with an
285 overnight crystallization (additional time >16 hr) [11]. The procedure employed in this
286 work differs from the published protocol for other phosphine analogs [11] as it is carried
287 out at ambient temperature for only 4 hours in inert conditions (gentle N₂ stream). The
288 material is ~80-85% pure prior to a final column purification with silica gel to give a final
289 product with very high purity (>96% by ¹H and ³¹P NMR). In addition, as TIBPS analytical
290 data such as GC-MS analysis is not available in the NIST library for GC instruments, the
291 full spectrum is included in the Supplementary Information along with the NMR data.

292 Conclusions

293 Based on previous work on the uptake of NCA mercury by CL resin [1], studies were
294 performed to better characterize the extraction of ^{197m}Hg by TIBPS, the extractant molecule
295 of this resin. Previous work in the literature has characterized the extraction of mercury by
296 TIBPS in HCl (0.01 M to 10 M) and HNO₃ (0.001 M to 1 M), but with significant masses
297 of mercury. Experiments in this work studied the extraction of NCA ^{197m}Hg by TIBPS (in
298 CCl₄) over a wide concentration range (0.001 M to conc.) for both HCl and HNO₃ as well
299 as determining the uptake kinetics and speciation. The uptake is similar for both acids,

300 with high extraction from 0.001 to 2 M acid, and a decrease in extraction at higher
301 concentrations (≥ 4 M). The decrease in extraction is more pronounced for HCl than HNO₃,
302 which may be due to the successive formation of higher charged anions in HCl versus only
303 neutral species in HNO₃.

304 The kinetics are also similar in HCl and HNO₃ with rapid uptake and equilibrium
305 established at ~5 min. Speciation studies indicated a possible 1:2 extraction mechanism
306 from HCl, likely HgCl₂·2TIBPS. Unlike in studies with higher concentrations of mercury,
307 there was no indication of the co-extraction of a dimerized 1:1 species. The extraction is
308 likely 1:1 from HNO₃, presumably the extracted species is Hg(NO₃)₂·TIBPS. This aligns
309 with the speciation reported previously in the literature from HNO₃ [9].

310 The experiments in this work contribute to a greater understanding of the extraction
311 chemistry of mercury with TIBPS by examining the behavior of NCA mercury over a wide
312 concentration range, which had not been comprehensively shown by previous studies.

313 **Acknowledgements**

314 The authors would like to thank the CAMS facility staff at LLNL, particularly Scott
315 Tumey, for providing beam time and expertise for the production of radionuclides used in
316 this study. This study was performed under the auspices of the U.S. Department of Energy
317 by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. This
318 work was funded by the Laboratory Directed Research and Development Program at LLNL
319 under project tracking code 19-ERD-003.

320 **References**

- 321 1. Kmak K, Despotopulos J (2021) Extraction of gold, mercury and lead on CL resin in
322 HCl. J Radioanal Nucl Chem DOI: 10.1007/s10967-021-07999-z
- 323 2. Ferrier M, Kmak K, Kerlin W, Valdez C, Despotopulos J (2020) Transactinide studies
324 with sulfur macrocyclic extractant using mercury. J Radioanal Nucl Chem 326:215–222

- 325 3. Despotopulos J, Kmak K, Gharibyan N, Moody K, Sudowe R, Shaughnessy D (2018)
326 Studies of the homologs and pseudo-homologs of flerovium with crown ether based
327 extraction chromatography resins. *J Radioanal Nucl Chem* 318:1821–1826
- 328 4. Despotopulos J, Kmak K (2021) Rapid isolation of ^{197m}gHg from proton irradiated
329 Au foils. *J Radioanal Nucl Chem* 327:1349–1354
- 330 5. Mandal S, Nayak D (2010) Production, separation and speciation of no-carrier-added
331 Hg radionuclides using greener methodologies. *Radiochim Acta* 98:45–51
- 332 6. Bhandare A, Argekar A (2002) Transport of mercury(II) ion through a supported liquid
333 membrane containing a triisobutylphosphine sulfide (Cyanex 471X) as a mobile carrier.
334 *Journal of Chemical Technology & Biotechnology* 77(7):811-816
- 335 7. Lothongkum A, Suren S, Chaturabul S, Thamphiphit N, Pancharoen U (2011)
336 Simultaneous removal of arsenic and mercury from natural-gas-co-produced water from
337 the Gulf of Thailand using synergistic extractant via HFSLM. *Journal of Membrane*
338 *Science* 369(1-2):350-358
- 339 8. Baba Y, Umezaki Y, Inoue K (1986) Extraction Equilibrium of Mercury(II) with
340 Triisobutylphosphine Sulfide. *Solvent Extr Ion Exch* 4(1):15–26
- 341 9. Singh R, Tandon S (1997) Extraction and separation of mercury(II) using triisobutyl
342 phosphine sulfide (TIBPS/Cyanex) as an extractant and its application to industrial
343 effluent. *Talanta* 44(5):843–848
- 344 10. Mastren T, Stein B, Parker T, Radchenko V, Copping R, Owens A, Wyant L, Brugh
345 M, Kozimor S, Nortier F, Birnbaum E, John K, Fassbender M (2018) Separation of
346 protactinium employing sulfur-based extraction chromatographic resins. *Anal Chem*
347 90(11):7012–7017
- 348 11. Goodwin C, Reant B, Vettese G, Kragoskow J, Giansiracusa M, DiMucci I, Lancaster
349 K, Mills D, Sproules S (2020) Heteroleptic Samarium(III) Chalcogenide Complexes:
350 Opportunities for Giant Exchange Coupling in Bridging σ - and π -Radical Lanthanide
351 Dichalcogenides. *Inorg Chem* 59(11):7571-7583

- 352 12. National Nuclear Data Center (2019) Brookhaven National Laboratory.
353 https://www.nndc.bnl.gov/nudat2/indx_dec.jsp. Accessed 29 October 2021
- 354 13. Valdez CA, Leif RN, Alcaraz A (2016) Effective methylation of phosphonic acids
355 related to chemical warfare agents mediated by trimethyloxonium tetrafluoroborate for
356 their qualitative detection and identification by gas chromatography-mass spectrometry.
357 *Anal Chim Acta* 933:134-143
- 358 14. Valdez, CA, Leif RN, Hok S, Vu AK, Salazar EP, Alcaraz A (2019) Methylation
359 protocol for the retrospective detection of isopropyl-, pinacolyl- and
360 cyclohexylmethylphosphonic acids, indicative markers for the nerve agents sarin, soman
361 and cyclosarin, at low levels in soils using EI-GC-MS. *Sci Total Environ* 683:175-184.
- 362 15. Powell K, Brown P, Byrne R, Gajda T, Hefter G, Sjoberg S, Wanner H (2005) Chemical
363 Speciation of Environmentally Significant Heavy Metals with Inorganic Ligands. *Pure*
364 *Appl Chem* 77(4):739-800
- 365 16. Sato T, Nakamura T (1980) The stability constants of the aqueous chloro complexes of
366 divalent zinc, cadmium and mercury determined by solvent interaction with tri-n-
367 octylphosphine oxide. *Hydrometallurgy* 6:3-12

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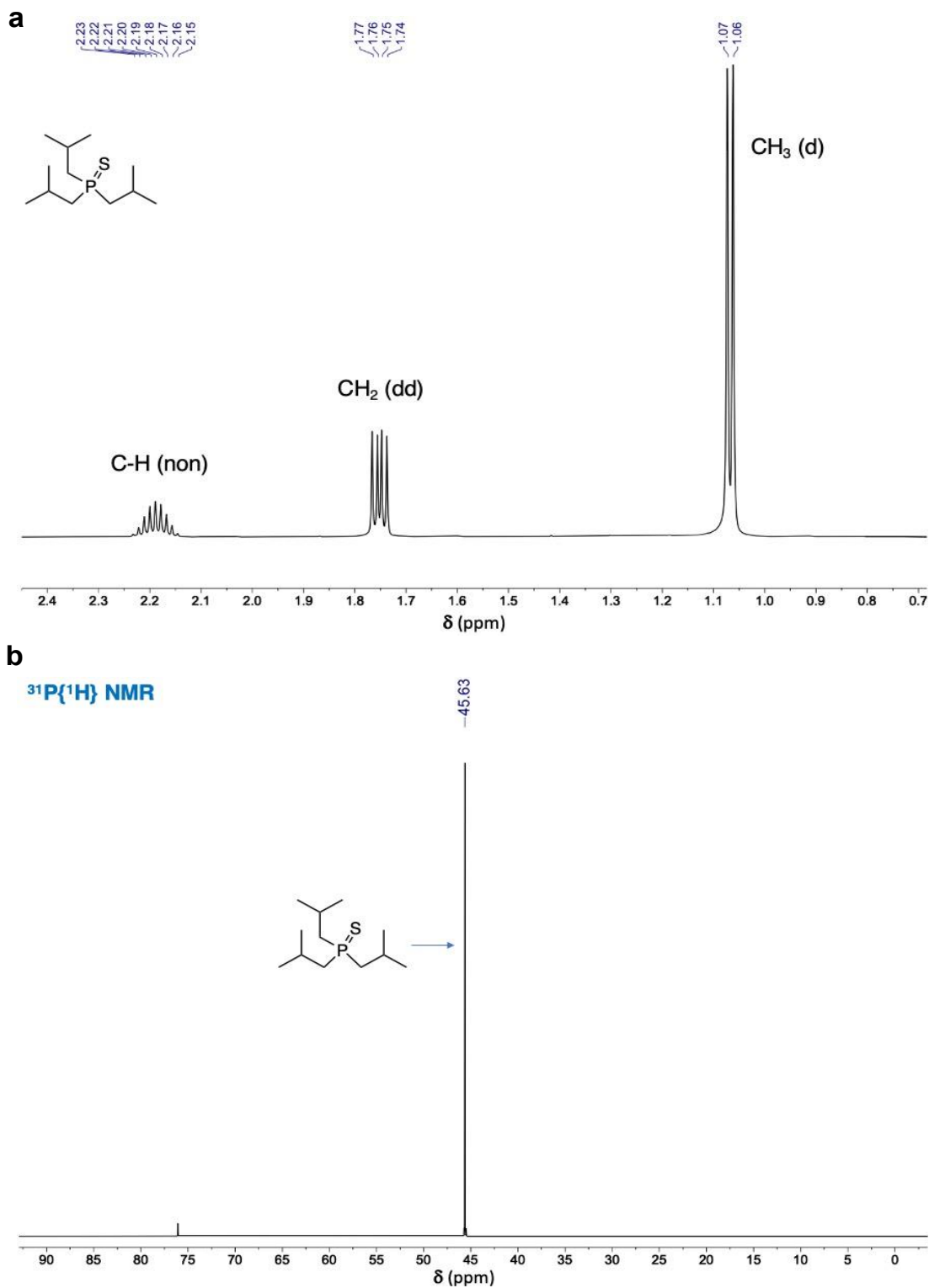
Supplementary information

376 TIBPS Identification by NMR and GC-MS

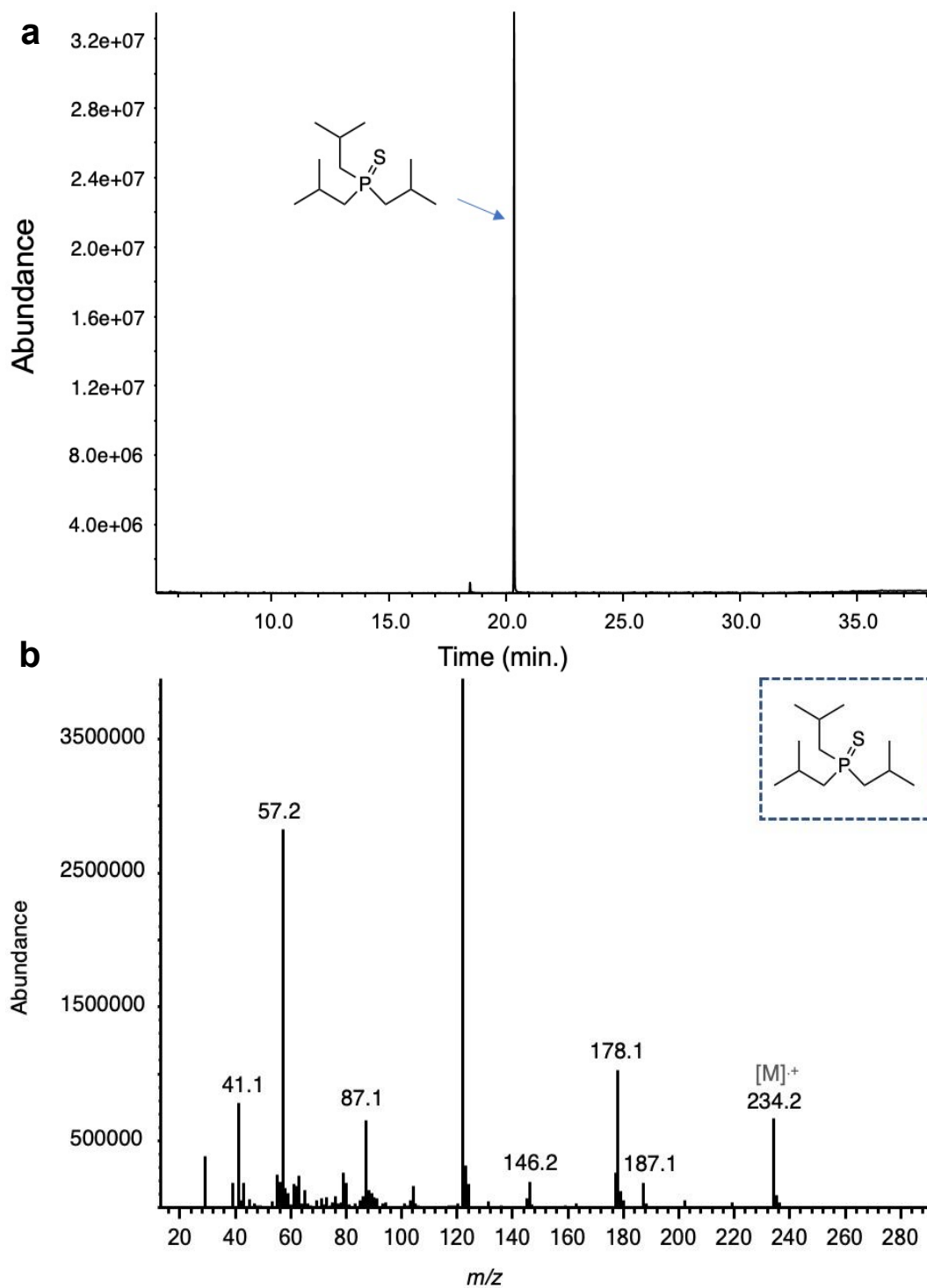
377 The identity of TIBPS was confirmed via its ^1H -NMR spectrum with the presence of three
378 main signals (Supplementary Information Fig. 1a). The first one is a complex multiplet (a
379 nonet centered at $\delta = 2.19$ ppm) featuring a coupling constant of 6.0 Hz attributed to all
380 three, equivalent methine (C-H) protons from the isobutyl arm in TIBPS. The second
381 signal is a doublet of doublets centered at $\delta = 1.75$ ppm) featuring two coupling constants
382 of 12.0 and 6.0 Hz attributed to all three, equivalent methylene (CH_2) protons from the
383 isobutyl arm in TIBPS. This signal possesses not only the coupling constant of 6.0 Hz to
384 the methine protons adjacent to the methylene protons but also the large 2-bond coupling
385 constant between these (*i.e.* 12.0 Hz). The third, and last signal, is an expected doublet
386 centered at $\delta = 1.06$ ppm featuring a coupling constant of 6.0 Hz attributed to all three,
387 equivalent methyl group (CH_3) protons from the isobutyl arm in TIBPS. The signal is a
388 doublet as it is adjacent to the methine proton featuring that key 6.0 Hz coupling constant.
389 Furthermore, the integration of all three signals in the order of methine, methylene and
390 methyl protons is 3:6:18, in accordance with the structure of TIBPS. Further confirmation
391 for the purity and identity of TIBPS was done by ^{31}P -NMR (Supplementary Information
392 Fig. 1b). The material was found to provide a singlet centered at $\delta = 45.6$ ppm. This
393 chemical shift falls within the expected range for P=S containing phosphorus species (see
394 Ref. [11]).

395 Electron-ionization GC-MS was performed to also assess the purity of the material and it
396 was found to provide only one peak (Supplementary Information Fig. 2a) whose associated
397 mass spectrum (Supplementary Information Fig. 2b) contained the nominal mass for
398 TIBPS ($m/z = 234.2$). In addition to this, an exact mass was obtained for the material and
399 found to be in accordance with TIBPS' calculated value and within the allowed range for
400 mass variability (*vide infra*).

401



402 **Supplementary Information Fig. 1** Characterization of synthesized TIBPS: (a) ^1H NMR
 403 spectra in CDCl_3 (600 MHz) with signal assignments and multiplicity given in
 404 parentheses, (b) $^{31}\text{P}\{^1\text{H}\}$ -NMR (proton decoupled) showing the singlet for TIBPS.



405 **Supplementary Information Fig. 2** Electron-Ionization Gas Chromatography-Mass
406 Spectrometry (EI-GC-MS) analysis for TIBPS: (a) GC chromatogram for TIBPS (elution
407 time: 20.3 min.) and (b) mass spectrum for TIBPS.