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**Characterization of a set of improved, CMPO-based,
extraction chromatographic resins
Applications to the separation of elements important for
geochemical and environmental studies**

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21 **Abstract:**

22 This article describes several extraction chromatographic materials aiming to offer improved
23 potential for isolating trace elements with high charge/ionic radius ratio from accompanying
24 matrix elements in natural samples. Starting from the commercially available, field proven,
25 TRU- and RE-Spec materials (Eichrom Technologies), three resins containing less TBP in the
26 CMPO-TBP mixtures, or even neat CMPO only, have been prepared and characterized through
27 measurement of the distribution ratios of some fifty elements in HNO₃ and HCl media of
28 variable strength. These resins were further evaluated for analytical applications on
29 geochemical samples. The results highlight a strong enhancement of weight distribution ratios
30 of many elements of interest in geochemistry, cosmochemistry and environmental sciences
31 (Lanthanides, naturally occurring Actinides, High Field Strength Elements). Combined with
32 good chromatographic characteristics, these high D_w's make it possible to achieve excellent
33 group separations by using very small columns operated at high, gravity driven flow rate.
34 Moreover, in an attempt to further improve the selectivity against Fe(III) and Ti(IV),
35 preliminary investigations were made on an additional pair of resins impregnated with a
36 CMPO-substituted calixarene. Although promising distribution ratio data were obtained, these
37 prototypes did not permit to prepare columns with satisfactory chromatographic characteristics,
38 and this approach still waits for a better impregnation method of the porous inert support.

39

40 **Keywords:** EXC resins, Lanthanide, Actinide, HFS Elements

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44 INTRODUCTION

45 Because it combines the versatility and selectivity of solvent extraction with the ease of
46 operation and multi-stage characteristics of chromatographic columns, extraction
47 chromatography (EXC) provides a powerful approach to separation chemistry at the analytical
48 scale. ^[1] In the 1990's, a suite of specific EXC materials was developed by E.P. Horwitz and
49 his group at Argonne ^[2] and made available on a commercial basis. ^[3, 4] These ready-to-use
50 resins allowed great improvements, both in terms of miniaturization and selectivity, of the
51 separation protocols of many trace elements important in Earth, environmental, and planetary
52 sciences. ^[5] The first of these EXC materials was developed in order to quantitatively isolate
53 the actinides as a group from urine samples before measurements by α -spectrometry. It was
54 based on a mixture of CMPO dissolved in TBP and sorbed on to a porous, polyacrylic ester
55 inert substrate (Amberlite XAD-7). ^[6] This EXC resin was further improved by using another
56 support with smaller particle size (50-100 μm) and larger average pore diameter (Amberchrom
57 CG71), and marketed as TRU Spec (for TRans Uranic Specific) resin. ^[7] The new method was
58 derived from the liquid-liquid extraction process referred to as TRUEX, ^[8, 9] based on the
59 neutral organophosphorus extractant octyl(phenyl)-N, N-diisobutylcarbamoylmethylphosphine
60 oxide (CMPO) ^[10] dissolved in a solvent composed of tri-n-butyl phosphate (TBP) and aliphatic
61 hydrocarbon diluent. This mixture allowed the extraction/recovery of all actinides from acidic
62 nuclear wastes solutions. Likewise, the TRU Spec resin provides an efficient means to achieve
63 the isolation of U and Th from complex matrices such as geological samples dissolved in nitric
64 acid media. ^[11] Most interestingly for geochemists, by virtue of the chemical similarity of the
65 light Rare Earths (LREE) with Am(III), one of the main targets of TRU Spec, this resin also
66 proved to permit their easy separation from most elements but Fe(III) and Ti(IV). ^[12, 13] A
67 closely related resin, referred to as RE Spec (for Rare Earth Specific), differing from TRU Spec
68 by a slightly higher proportion of CMPO in the extractant mixture, was also released by

69 Eichrom. In their most useful work, Huff & Huff determined with ICP-Atomic Emission
70 Spectrometry the distribution coefficients of both resins for 42 and 32 elements in nitric and
71 hydrochloric acid media, respectively. ^[14] However, even the RE Spec resin suffers from a
72 rather low affinity for the heaviest lanthanides (e.g., D_w 's = 10-30 for Lu ^[15]) in the range of
73 nitric acid (1-3M) convenient to handle geological sample solutions, and permitting to use
74 ascorbic acid as a masking agent for Fe(III) through reduction to Fe(II). This is a serious
75 shortcoming limiting the practical use of RE Spec in miniaturized separation schemes aiming
76 to quantitatively recover the whole Lanthanide series by using very small columns. A
77 comparison of the distribution data available for both TRU- and RE Spec ^[14] reveals a
78 significant increase of the D's of elements of interest, including the HREE, from TRU Spec (13
79 wt% CMPO-27% wt% TBP) to RE Spec (16% wt% CMPO-24% wt% TBP). This observation
80 suggests that CMPO plays the major active role in the blend of extracting agents, in line with
81 the fact that CMPO was the key ingredient in the original liquid-liquid extraction process ^[6].
82 Indeed, in the TRU EX process, TBP was mainly used as a phase modifier in order to increase
83 the metal ion loading capacity and extractant compatibility with alicyclic and aliphatic diluents
84 and prevent the formation of a second organic phase. ^[16] Such problems should not be a source
85 of concern in EXC of trace elements, and it was anticipated that EXC resins containing less
86 TBP in the CMPO-TBP mixtures, or even prepared from neat CMPO, might offer improved
87 distribution ratios for the HREE and the rest of the elements of interest. On this basis, three new
88 resins have been prepared and characterized for the distribution ratios of some fifty elements in
89 HNO₃ and HCl media. Two of these resins were further evaluated for potential analytical
90 applications. Moreover, in an attempt to improve the selectivity against Fe(III) and Ti(IV),
91 exploratory investigations were made on an additional pair of resins impregnated with a more
92 complex molecule, specifically a CMPO-substituted calixarene belonging to a new class of
93 highly efficient extractants for lanthanides and actinides developed in the late 1990's. ^[17-19]

94

95 **EXPERIMENTAL**

96

97 **Preparation of EXC materials**

98 In every case, the polyacrylic ester resin Amberchrom CG-71 (50-100 μm particle size)
99 was used as the porous inert support. A 40 wt% loading of this support corresponds to complete
100 filling of the pores ^[20] and this total impregnation was chosen in every case, in line with all
101 other previous EXC resins prepared by using the same porous support. Variable proportions of
102 the conventional CMPO and TBP extracting agents were used to prepare three new EXC
103 materials, hereafter referred to as P-1 (20 wt% CMPO-20 wt% TBP), P-2 (35 wt% CMPO-5
104 wt% TBP), and P-3 (40 wt% CMPO). These were prepared on demand at Triskem International
105 (Bruz, France), following a procedure similar to that outlined by Horwitz et al. ^[6] A summary
106 of the CMPO/TBP ratio of these prototypes against the commercially available materials TRU
107 and RE is given in Table 1.

108 On an exploratory basis, an additional pair of resins were prepared with a third ligand, hereafter
109 referred to as «Calix-CMPO», consisting in a calix[4]arene bearing four CMPO-like
110 functional groups attached on the wider rim. This compound was chosen on the basis of earlier
111 solvent extraction studies showing a largely enhanced affinity for tri- and tetravalent actinides
112 compared with CMPO, ^[17] along with strong size selectivity among the lanthanide series. ^[18,19]
113 The molecule (mass 1756; J.F. Dozol, pers. comm.), not available commercially, was
114 synthesized on demand by, and purchased from Marshallton Research Laboratories Inc. (King,
115 NC, USA). Two prototypes, hereafter referred to as PC-1 and PC-2, were prepared at Triskem.
116 The first one was impregnated with 7.5 wt% Calix-CMPO dissolved in chloroform, while the
117 second contained, in addition to 7.5% Calix-CMPO in chloroform, 2.5 wt% octanol (A.
118 Bombard, pers. com.). Unlike the CMPO +/- TBP-based resins, PC-1 and PC-2 did not behave

119 as free flowing powders, possibly reflecting the presence of excess ligand at the surface of the
120 resin beads, as also could be inferred from the difficult wetting of both resins. In spite of this
121 obvious shortcoming, these prototypes were used for distribution ratios measurements, in order
122 to evaluate the potential of the novel molecule in terms of selectivity against major elements.
123 The results of these preliminary investigations are given in Appendix A1.

124

125 **Measurements of weight distribution ratios**

126 **Reagents**

127 Solutions of mineral acids (HNO₃, HCl, HF) were prepared from reagent grade acids
128 (Fluka) purified by subboiling distillation in PFA Teflon DST-100 systems (Savillex, Eden
129 Prairie, MN, USA) and diluted with 18.2 MΩ cm water obtained from a deionization device
130 (Aqua System Distribution, Bondoufle, France). Ascorbic acid (Aldrich), chosen as a reducing
131 agent, was used as received.

132 Metal ion solutions used for the determination of distribution ratios were prepared from a set
133 of five, separate, multi-element standard solutions traceable to NIST (Inorganic Ventures,
134 Christiansburg, VA, USA) containing 10 μg mL⁻¹ of (1) the 14 lanthanides, Sc, Y, Th, and U in
135 5% v/v nitric acid; (2) Au, Ir, Pd, Pt, Re, Rh, Ru, and Te in 10% v/v HCl ; (3) Ge, Mo, Nb, Hf,
136 Ta, Ti, Sn, W, and Zr in 5% v/v in 5% v/v nitric acid containing traces of hydrofluoric acid for
137 stability; (4) As, B, Ba, Be, Bi, Cd, Ga, In, Pb, Sb, Se, Tl, and V in 5% v/v nitric acid; (5) Ag,
138 Al, Ca, Cs, Co, Cr, Cu, Fe, Li, Mg, Mn, Na, Ni, K, Rb, Sr, and Zn in 5% v/v nitric acid.

139

140 **Batch uptake of metal ions**

141 In order to investigate the acid dependence of the uptake by the resins of metal ions from
142 both HNO₃ and/or HCl media, weight distribution ratios (D_w 's) were determined by using the
143 batch extraction method. An amount of resin in the 10-50 mg range was precisely weighed
144 (W_{res}) in a polypropylene micro tube (Eppendorf) and contacted with a precise weight (1-2 g)
145 of acid solution (W_{liq}) of variable strength containing the elements of interest at the 10 ng g⁻¹
146 level. The ratio of resin to solution was intentionally varied in order to produce, as far as
147 possible, a significant difference between the initial and final concentrations. Then, the micro
148 tubes were placed in a 3D rotary mixer at room temperature (20 +/- 0.5°C) in order to
149 intermingle the solid and liquid phases. After 1 hour contacting time, the resin was separated
150 by centrifugation for 10 minutes at 12 000 rpm. In >/ 5M acids, however, the resins floated at
151 the surface of the denser acid, and the liquid phase was separated by filtration through a 0.45
152 µm porosity PTFE membrane within a polypropylene housing (Puradisc 25 TF, Whatman)
153 fitted on a syringe. Finally, a weighed aliquot of the supernatant or filtered solution was taken,
154 precisely diluted by weight to ~ 4 mL, and analysed by ICP-MS with a quadrupole instrument
155 (Agilent 7500 Ce). Aliquots of the initial solutions were processed in the same manner to
156 determine their concentration before equilibration with the resin. In order to overcome isobaric
157 interferences by polyatomic ions, low mass elements (<80) were measured as often as possible
158 by using the collision cell filled with He gas. Based on these ICP-MS data, the mass initially
159 contacted with the resin M_0 and the mass left behind in the liquid phase M_{liq} were found for
160 each element. The mass of element extracted by the resin was obtained by difference $M_{extr}=M_0$
161 - M_{liq} , and the weight distribution ratio was calculated as the ratio of the concentration of
162 element in the resin to the concentration of element left in the solution after equilibration.

163
$$D_w = (M_{extr} / W_{res}) / (M_{liq} / W_{liq})$$

164 Based on duplicate measurements in 0.5M HNO₃, the precision of distribution ratios is, in
165 general, about 10% or better for most elements, but can be markedly worse when the
166 concentration difference between the initial and equilibrated solutions was difficult to quantify
167 (corresponding to very low D_w's) and when the amount of elements left in the equilibrated
168 solution was very small (corresponding to very high D_w's). However, from a practical point of
169 view, a precise determination of both very low and very high D_w's is generally not required to
170 set up separation schemes.

171

172 **Metal ion capacity**

173 The capacity of P-2 and P-3 resins was determined by measuring the volume of a
174 solution of Pr (1 mg mL⁻¹ in 1M HNO₃) needed to saturate a slurry-packed column of each resin,
175 on the one hand, and by measuring the amount of Pr stripped from the column with 0.05M
176 HNO₃ and 1M HCl, after having washed out the volume of Pr interstitial solution, on the other.
177 These two determinations differed by less than 5%, and their average was reported.

178

179 **Kinetics of uptake**

180 The uptake kinetics for Pr on P-2 and P-3 resins was studied by equilibrating, in a series
181 of centrifuge tubes, 20 mg of each resin with 1.8 mL of a 100 ng mL⁻¹ solution in 1M HNO₃, at
182 20°C. At various shaking time intervals, the solution was promptly separated from the resin by
183 centrifugation at 12 000 rpm. A 0.5 mL aliquot was carefully withdrawn from the tube with a
184 pipette, and the amount of Pr left in the aqueous phase measured by ICP-MS. The percentage
185 of Pr extracted was calculated by difference from the nominal amount (180 ng) contacted with
186 the resin.

187

188 **Column parameters**

189 The resin bed density was determined by measuring the volume occupied by 1.00 g of
190 dry P-2 and P-3 resins slurry-packed in a calibrated cylinder. The volume of stationary phase,
191 V_s , was calculated from the nominal wt% of extracting agent sorbed onto the inert support and
192 the extractant density, not different within uncertainty from 0.98 g mL^{-1} for both TBP^[21] and
193 CMPO.^[22] The volume of mobile phase, V_m , also referred to as the free column volume (FCV)
194 was determined by measuring the volume of 1M HNO_3 preceding the breakthrough of Cs, an
195 element not extracted by the resins.

196

197

198 **RESULTS AND DISCUSSION**

199

200 As a first step of this work, the trend of increasing D_w 's for tri- and tetra-valent elements
201 as a function of CMPO loading, noticed from the data^[14] published for the commercially
202 available TRU (13 wt% CMPO-27 wt% TBP) and RE (16 wt% CMPO-24 wt% TBP) resins
203 was investigated. For this purpose, a first prototype of resin was prepared featuring a further
204 small increment of CMPO in the mixture of extracting agents, that is, 20 wt% CMPO-20 wt%
205 TBP. This EXC material, hereafter referred to as P-1, was used for the determination of weight
206 distribution ratios in nitric acid media of increasing molarity. The results are compared with
207 those available^[14, 15] for the Lanthanide series on the TRU and RE resins in 1M HNO_3 (Fig. 1).
208 Overall, the data confirm that increasing the proportion of CMPO in the CMPO-TBP mixture
209 enhances the extraction of all lanthanides, with a broadly homogeneous, twofold increase of
210 D_w 's for the light and medium REE (from La to Dy) on the P-1 resin compared to RE Spec, but

211 this enhancement is less pronounced for the heavy REE (from 1.7 for Ho to 1.25 for Lu,
212 respectively).

213 Based on these observations, two further resins were prepared with a strongly reduced
214 amount of TBP (P-2, 35 wt% CMPO-5 wt% TBP) and no TBP at all (P-3, 40 wt% neat CMPO),
215 respectively. These two resins were further investigated in detail for their distribution ratios,
216 capacity, and uptake kinetics. Their main characteristics are given in Table 1 of Appendix A2
217 (as supplemental material). Not unexpectedly, most of these data do not differ within
218 uncertainty from those given for the original TRU resin ^[7], based on the same porous inert
219 support and a mixture of the same ligands.

220 The results of the uptake kinetics experiments are displayed in Fig. 2. It can be seen that
221 >90% of uptake is achieved in 5 minutes by both resins. This is in line with previous data
222 reported for three other EXC materials using the same support Amberchrom CG71.^[20] It has
223 been reported that the time required to reach equilibrium was somewhat longer for a « solvent
224 free » Sr EXC resin than for the conventional, octanol-bearing resin.^[23] It is therefore
225 noteworthy that the extraction by P-3, prepared with neat CMPO (solid at room temperature),
226 proceeds as rapidly as for the resins containing variable amounts of TBP (liquid at room
227 temperature) as a diluent (TRU: 27 wt%, P-2: 5 wt%).

228

229 **Acid dependence of distribution ratios in nitric and hydrochloric acids**

230 The weight distribution ratios measured for a range of elements on P-1, P-2 and P-3 as a
231 function of increasing concentration of nitric and hydrochloric acids are listed in Tables 2 to 8
232 of Appendix A2 (as supplemental material). It turns out that the affinity scale is qualitatively
233 similar in both acids. That is, all metal ions not extracted from HNO₃ at any concentration also
234 do not display any uptake in the 0.05M-6M HCl range and, conversely, those elements

235 extractable from nitric acid media show significant, albeit variable, uptake. Also, P-3
236 consistently achieves higher D_w 's than P-2, confirming that CMPO, rather than TBP, is the
237 major extractant involved in the uptake of most elements, irrespective of the acid medium.

238

239 *Behavior of common elements, particularly iron*

240 Many elements do not display any significant extraction by the CMPO-based resins, from both
241 nitric and hydrochloric media, at any acid strength. These include all the alkali and alkaline
242 earth metals, many transition metals (Mn, Co, Ni, Cu, Zn) and groups 13 (B, Al, Ga, In, Tl) and
243 14 (Si, Ge, Sn, Pb) elements. In the divalent state, Fe is not extracted from both acids. In
244 contrast, its uptake as Fe(III) is quite significant and increases markedly with increasing
245 concentration of HNO_3 ; this effect is even more pronounced for the undiluted CMPO (P-3)
246 resin, thereby confirming the relatively poor selectivity of CMPO with regard to this major
247 element in its trivalent state (Fig. 3). In HCl, however, the uptake of Fe(III) is different (Fig. 3),
248 as shown by its higher extraction by the P-1 resin (20 wt% TBP-20 wt% CMPO) suggesting
249 that, in this medium, its uptake is preferentially caused by the TBP component. This inference
250 is broadly consistent with very large distribution ratios reported in the 100% TBP-HCl solvent
251 extraction system. ^[24]

252

253 *Group 4, 5 and 6 elements*

254 Above 0.5M HNO_3 , the uptake of Group 4 elements (Ti, Zr, Hf) is important and increases as
255 a function of nitric acid strength, with a strong preference of both resins for Zr (Fig. 4). Albeit
256 their hydrolysis propensity at relatively low acid strength makes the data less robust, Group 5
257 and 6 elements (Nb, Ta, Mo, W) follow a similar trend (Fig. 4). The P-3 resin shows a stronger

258 affinity than P-2 for Zr and Hf, but the reverse is true for Nb and Ta, while the two resins do
259 not differ appreciably for Mo and W. High D_w 's are also achieved in >1M HCl for all these
260 elements (Fig. 5), hereafter collectively referred to as High Field Strength Elements (HFSE).
261 This observation is in agreement with earlier data documenting largely enhanced extraction of
262 these elements by the RE resin in even more concentrated (i.e., 8M) HCl. ^[14] Further, the HFSE
263 display two different kinds of acid dependence (Fig. 5). Indeed, while Zr, Hf, and Mo are
264 characterized by a sharp increase of their D_w 's from very low values to several hundred when
265 the HCl concentration rises from 0.05 to 1 M, W, Nb, and particularly Ta, display very high
266 D_w 's whatever the HCl molarity.

267

268 *Lanthanides and natural actinides*

269 In nitric acid, the Actinides (Th, U), light Lanthanides (from La to Eu), and Sc are all very
270 strongly extracted, with extremely high D_w 's (> 1000) achieved for both resins, even at
271 moderate acid strength. Again, the resin prepared from neat CMPO (P-3) proves to be more
272 retentive than that based on the 35 wt% CMPO - 5 wt% TBP mixture (P-2). Besides their usual
273 acid dependence, D_w 's show a marked decrease as a function of increasing atomic number (and
274 decreasing ion size) along most of the Lanthanide series, from Pr to Lu (Fig. 6). This selectivity
275 trend is opposite to that obtained with EXC materials based on other widely used ligands.
276 Indeed, both the acidic organophosphorus extractants HDEHP or HEH[EHP] ^[25-27], and the
277 diglycolamide ligand TODGA ^[28, 29] display a continuously increasing affinity from La to Lu,
278 interpreted to reflect the increasing charge density of the cations along the series. However, as
279 already observed with the conventional TRU and RE resins, the Lanthanides do not exhibit a
280 simple, monotonic variation of D_w 's as a function of their atomic number and ionic size when
281 they are extracted by CMPO. Instead, D_w 's first increase from La to Pr and then decrease from

282 Pr to Lu, resulting in upwards concave, « hockey stick » shaped patterns. Such curved trends
283 differ from predictions based on a simple relationship of D_w 's to ionic radii. Indeed, the
284 lanthanide ion size in aqueous solutions smoothly decreases across the series (the so-called
285 « lanthanide contraction ») from 125 pm for La to 99.5 pm for Lu. ^[30] This very regular
286 variation should rather suggest a monotonic extraction trend, with a maximum uptake of La.
287 Similarly shaped patterns of D 's for the lanthanide series, peaking at Pr or Ce, have been
288 reported for a solvent extraction system using the diamide-type extractant DOODA(C8) in n-
289 dodecane in 3M HClO₄ and 3M HNO₃.^[31, 32] This somewhat « anomalous » behavior of La and
290 Pr in systems based on fairly different ligands, awaits for an explanation.

291 Another salient feature is the differential behavior of the light and heavy lanthanides as a
292 function of increasing nitric acid strength. Specifically, the uptake of the lightest lanthanides
293 decreases at high acid concentration (in >2M and >3M HNO₃ for P-2 and P-3, respectively)
294 while, in contrast, the heavy lanthanides display an enhanced extraction (Fig. 7). This increase
295 of D_w 's has a marked atomic number dependence, thereby causing a large fall of the mutual
296 fractionation of the heavy lanthanides as the nitric acid concentration increases: for both resins,
297 D_{Gd}/D_{Lu} decreases from ~17 in 0.5M HNO₃ to 2.4 in 5M HNO₃, or even 1.4 in 7M HNO₃ for
298 P-3. These changes result in an anticlockwise rotation of D_w 's profiles, around an axis located
299 close to Eu when the nitric acid molarity increases. Eventually, almost flat patterns from Sm to
300 Lu are achieved in 7M HNO₃, in marked contrast with the steeply inclined profiles typically
301 obtained in less concentrated acids (Fig. 8).

302 For both resins, in the 0.05M-3M HCl acidity range, distribution ratios of those elements having
303 a clear affinity for the resin (lanthanides, actinides, Group 4) are much lower than those
304 achieved in HNO₃ (Fig. 9). This might reflect the different properties of the Cl⁻ and NO₃⁻ anions
305 which must be co-extracted in order to ensure the charge neutrality of the extracted CMPO-

306 metal complex. Indeed, albeit of similar charge and ionic radius, Cl^- differs from NO_3^- by a
307 higher hydration energy (-317 vs -270 kJ mol^{-1}) [33] which must be overcome in order for it to
308 act as a counter anion. This effect would be less pronounced at high HCl concentration, as
309 suggested by the strong, positive acid dependence of the extraction of the light lanthanides in
310 HCl, opposite to the slight decrease of D_w 's observed in nitric acid at elevated molarity (Fig.
311 9). From a practical point of view, the low D_w 's of the light lanthanides in 1-3M HCl offer an
312 efficient mean to strip quantitatively these elements following their extraction from nitric acid
313 solutions.

314

315 *Noble metals, Selenium and Tellurium*

316 A set of six noble metals (Au, Ir, Pd, Pt, Re, Rh, Ru) and two metalloids (Se, Te) have been
317 investigated for their behavior on the P-2 resin, in HNO_3 and HCl media. Due to problems with
318 the solubility of this element in nitric acid, data for gold are considered suspect and are not
319 reported. The results can be summarized as follows. First, three of these elements do not show
320 any extraction from both nitric and hydrochloric acids, namely Ru, Rh, and Se. In contrast, Pt
321 and Re are extracted from both media, but with quite different acid dependences: while their
322 D_w 's decrease monotonously from 0.1M to 5M HNO_3 (Fig. 10 a), they define upward convex
323 curves with a broad maximum in 1-3M HCl (Fig. 10 b). The behavior of Pd, Ir, and Te (not
324 shown) is somewhat intermediate, that is, the extraction of Pd is significant in HNO_3 , with a
325 negative dependence on acid strength, but negligible in HCl throughout the 0.1-6M range.
326 Unlike this, Iridium and Tellurium are not extracted from HNO_3 media, but are weakly (Ir) or
327 strongly (Te) retained from 3-4M HCl, with a marked dependence of the extraction of Te on
328 acid strength. For the sake of comparison, the distribution ratios have also been determined for
329 the conventional RE Spec resin (16% CMPO-24% TBP). As exemplified by the uptake of

330 platinum from HCl (Fig. 11), it appears that, for most extracted elements, the values obtained
331 with P-2 (35% CMPO-5% TBP) are consistently larger than those achieved with RE Spec, thus
332 indicating that CMPO plays a major role in the enhanced extraction.

333

334 **Effect of fluoride ion**

335 By virtue of its strong affinity for silicon, fluorine is commonly used to decompose silicate
336 samples, either as an aqueous solution of HF, or in solid compounds (e.g., ammonium acid
337 bifluoride NH_4HF_2) the higher boiling point of which allows higher temperatures to be achieved
338 without resorting to high pressure devices. ^[34, 35] The resulting sample solutions contain variable
339 amounts of F^- ion which, as a strong complexing agent for many elements, is likely to interfere
340 with subsequent separation processes based on ion exchange or extraction. For this reason, the
341 dependence of D_w 's has been investigated for the P-1 resin (20 wt% CMPO-20 wt% TBP) in
342 nitric acid containing varying concentrations of HF. It is noteworthy that even the nominally
343 fluorine-free, multi-element nitric acid solutions used to measure D_w 's do contain HF because
344 this acid was typically used in 6 :1 or 8 :1 molar proportion to stabilize standard solutions of
345 Ti, Zr, Hf, Nb, Ta, Mo, Sn and W. ^[36]

346 The results highlight a clear adverse effect on the uptake of all the elements that are extracted
347 to a significant degree from nitric acid media. In every case, this effect is more pronounced in
348 dilute HNO_3 than in more concentrated ($>1\text{M}$) acid. However, in detail, the various groups of
349 elements display different behavior. The uptake of Ti-group elements (Ti, Zr, Hf, Nb) is
350 essentially suppressed (D_w 's < 10) for the range (0.25-5M) of HNO_3 concentrations investigated
351 (Fig. 12), in line with the notorious affinity of these elements for fluorine. This drastic fall of
352 D_w 's is followed by a weak recovery when the molarity of HF increases. The behavior of Ta is

353 in sharp contrast, with an enhanced extraction as the HF concentration increases from 0.07 to
354 0.29M, both in 0.25M and 1M HNO₃ (Fig. 12). This increasing trend is much weaker in 2.5M
355 HNO₃, and cancels out in 5M HNO₃, in which Ta follows the same decreasing trend as the rest
356 of the Ti-group elements when the HF concentration increases (Fig. 12).

357 As elements prone to complexing by the fluoride ion, the Actinides also display reduced
358 extraction with increasing HF content. Thorium is very sensitive, as shown by the steep decline
359 of its distribution ratios as a function of increasing HF (Fig. 13). In contrast, in spite of a
360 significant effect, the tremendous affinity for U is largely preserved, with D_w's > 1000 in nitric
361 acid – hydrofluoric acid mixtures ranging from 1M to 5M HNO₃ at a fixed HF concentration of
362 0.29M. In dilute (0.25M) HNO₃ however, both Th and U display a different behavior, namely,
363 a marked decrease of D_w's in 0.07M HF, then a « rebound » at 0.145M HF, followed by a
364 further decrease in 0.29M HF (Fig. 14).

365 The extraction of the Lanthanides also decreases as a function of HF concentration in the HNO₃-
366 HF mixtures (Fig. 15). In further detail, depicted in Figs 1 to 6 of Appendix A2, it can be seen
367 that the light and the heavy Ln's do not respond in the same manner to the presence of increasing
368 contents of HF in nitric acid of variable strength. That is, in 1M HNO₃, the D_w's of light Ln
369 (La-Nd) decrease regularly with increasing HF (Fig. A2-1) while the heavy Ln's (Er-Lu) show
370 an upward concave trend with an increase of D_w's when HF rises from 0.145 to 0.29M (Fig.
371 A2-2). In 2.5M HNO₃, the initial decrease of light Ln D_w's is followed by an almost flat trend
372 reflecting a vanishingly small effect of the F⁻ ion on the uptake of these elements at relatively
373 high nitric acid strength (Fig. A2-3). The heavy Ln's still display the same upward concave
374 trends as those obtained in 1M HNO₃ (Fig. A2-4). Finally, in 5M HNO₃, the differential
375 behavior along the Ln series tends to cancel out (Fig. A2-5 & 6), reflecting the vanishing effect
376 of fluoride complexing in more concentrated nitric medium.

377 As already observed for Th and U, the variation of Ln D_w 's as a function of increasing HF in
378 dilute (i.e., 0.25M) nitric acid is peculiar (Fig. A2-7). For the light and middle Ln's (from La to
379 Dy), D_w 's first decrease at 0.07M, then rebound in 0.145M, and eventually decrease again in
380 0.29M HF. In contrast, the heavy Ln's show regular, upward concave trends similar to those
381 observed at higher HNO_3 concentrations. The similarly sinuous, non monotonic trends
382 displayed, not only by the light and middle Ln, but also by Th and U (Fig. 14) suggest that, at
383 low nitric acid concentration, the extraction of these elements is controlled by a complex
384 interplay of their nitrate and fluoride species. Whatever its explanation, which is beyond the
385 scope of this article, the differential response of these groups of elements to the presence of HF
386 could be used to improve their mutual separation.

387 Albeit not belonging to the lanthanide series, scandium and yttrium are two additional Rare
388 Earth Elements, which are significantly extracted by the CMPO-based resins. In every respect,
389 Y behaves much like the heavy Ln Thulium. In contrast, albeit sharing some common features
390 with the heavy Ln's, Sc follows more closely thorium concerning its overall strong affinity for
391 the resin, and the dependence of its distribution ratios on the presence of HF. However, it is
392 noteworthy that the extraction of Sc from nitric acid media is much more sensitive to the
393 presence of F^- ion than that of the LREE and Th (Fig. 13). This property might offer a way to
394 selectively strip these two elements by an appropriate tuning of HNO_3 -HF mixtures.

395

396

397 **Resin stability and column re-use**

398 Earlier studies on the TRU resin (13 wt% CMPO-27 wt% TBP) reported appreciable shifts in
399 the position of elution peaks after column rinses, interpreted to reflect preferential leaching of

400 the more soluble TBP at first, possibly followed by a loss of CMPO after further extensive
401 rinses.^[7] A *ca.* 30% increase of V_m , suggestive of the presence of empty pores, provided further
402 evidence for a significant loss of stationary phase after prolonged (1000 FCV) column rinsing.
403 ^[7] We lack hindsight to assess the long-term shelf-life of the resin prototypes. Also, no specific
404 study of relatively short-term resin aging due to extractant leaching as been done, but the
405 columns were re-used (up to 5 times) for separating sample solutions of geological samples
406 without observing any significant change of the elution profile. Based on the extremely low
407 solubility of CMPO in aqueous medium (estimated water solubility at 25°C ~0.01mg/L ^[37]),
408 compared to that of TBP (280 mg/L at 25°C ^[38]), it is anticipated that P-2 and P-3, containing a
409 strongly reduced amount of TBP, or no TBP at all, respectively, should not suffer from serious
410 loss of stationary phase, and could be re-used. However, due to the very strong uptake of the
411 elements of interest, it will probably be quite challenging to reduce memory effects to extremely
412 low levels, making the re-use of columns not recommendable, at least for those applications
413 most demanding in terms of analytical blank. This does not seem to be a major concern,
414 however, because the extreme column miniaturization permitted by the very high retention of
415 the new EXC materials should make it possible to routinely use fresh resin, thereby ensuring
416 low analytical column blanks, at rather reduced cost. Indeed, CMPO is not a very rare
417 compound, which can be obtained from many companies ^[39] at a rather moderate price (~ 10
418 US \$ / gram). This would imply an extractant contribution of less than 0.5 US \$ to the cost of
419 a micro-column filled with 100 mg of P-3 resin with 40 wt% loading of CMPO.

420

421

422 **EXAMPLES OF ANALYTICAL APPLICATIONS**

423

424 **Group separation of many high valence trace elements from natural silicate samples**
425 **decomposed by alkaline fusion or by hydrofluoric acid attack**

426 In order to highlight the real analytical potential of the new EXC materials developed
427 in this work, column chromatography has been used to study the contrasting behavior of
428 unwanted major and minor elements, and selected trace elements of interest in geological and
429 environmental sciences. To achieve this goal, natural samples with complex matrices are well
430 suited. Accordingly, three samples covering the compositional range of common silicate rocks
431 have been chosen, namely an in-house standard of granitic composition (FAY), and two basaltic
432 and andesitic international standard reference materials prepared by the U.S. Geological
433 Survey (BCR-2, and AGV-1, respectively). While the basaltic and andesitic samples were
434 brought into solution by conventional dissolution with hydrofluoric acid, the granite was
435 decomposed by alkaline fusion with lithium metaborate. Although this procedure involves the
436 addition of a three-fold excess of flux and does not remove Si from the sample as volatile silicon
437 fluoride, it ensures a much more efficient attack of refractory accessory minerals hosting major
438 amounts of Zr, Hf, Th, U, and Lanthanides in rocks typical from the continental crust. Also,
439 this decomposition method gives a final, quenching solution without any added fluorine,
440 thereby offering an opportunity to compare the extraction behavior of elements in F⁻ free and
441 F⁻ bearing environments.

442 The final resulting sample solutions, both in nitric acid medium containing a few tens of mg of
443 ascorbic acid to reduce Fe(III) to Fe(II), have been passed through a column containing 100 mg
444 of the neat CMPO resin, P-3. By virtue of the enhanced distribution ratios of that resin, it was
445 possible to use a very short column (~ 7 mm high, ~ 7 mm internal diameter). The practical
446 interest of such a stocky column was to permit a fast, gravity driven flow rate, most useful to
447 load the relatively large volume of solution obtained after sample fusion with LiBO₂.

448 The elution behavior of major and trace elements on the short P-3 column loaded with
449 the granite sample decomposed by fusion is displayed in Table 2. As predicted by D_w 's data,
450 almost all the matrix elements (Al, alkalis, alkali earths, etc.) are quantitatively removed from
451 the column during the loading and initial rinse steps. Iron is retained to a minor degree (~6%)
452 indicating that ascorbic acid was not able to reduce this element quantitatively, possibly due to
453 the adverse effect of the relatively high (2.5M) nitric acid concentration. Tantalum, and to a
454 lesser degree Nb, are weakly extracted, presumably because of their strong hydrolytic tendency
455 in the absence of suitable complexing agent. Among major elements, only Ti is retained to a
456 large extent. It is stripped almost quantitatively (~98%), along with Zr, Hf, and Nb in the next
457 fraction of 2.5M HNO_3 -0.1M HF. At this stage, Th, U and the Lanthanides are still retained on
458 the column, except the heaviest Ln's, particularly lutetium, as a reflection of their lower D_w 's.
459 It is inferred that this incipient breakthrough of Lu reflects, at least in part, a decrease of the
460 capacity of the column caused by the extraction of significant amounts of Fe(III) and, in the
461 absence of fluoride, titanium. These minor HREE losses could be prevented by using a longer
462 column, a slightly lower molarity of HNO_3 , slightly reducing the volume of that fraction, or a
463 combination thereof. In spite of the obvious disadvantage of such a short (~7 mm) column for
464 this purpose, a gradient of decreasing HNO_3 molarity was used to study the sequential elution
465 of the lanthanides. Specifically, a suite of fractions of 1M to 0.125M HNO_3 achieves the
466 stripping of 95% of the heaviest Ln's and Y, while the lighter Ln's (from La to Gd) are still
467 fully retained. These are almost quantitatively (99%) recovered by switching the eluant from
468 0.125M HNO_3 to 3M HCl. This medium would permit the on-line loading of a column of
469 TODGA resin used in tandem to achieve the separation of individual elements, e.g., Nd in view
470 of mass spectrometric measurements of radiogenic isotope ratios. ^[40] Then, dilute HCl allows
471 recovering some two-thirds of Th but the addition of 0.145M HF is required to strip the last
472 third, together with some 6% of U. Finally, the bulk of U is stripped with 1.45M HF. Bismuth,

473 which was not included in the measured distribution ratios, was also found in this fraction.
474 Additional work would be required to characterize the behavior of this element.

475 The elution of major and trace elements on the same very short (~7 mm) P-3 column
476 loaded with the basaltic rock standard dissolved with a mixture of HF and HNO₃ is displayed
477 in Table 3. Unlike the previous case, for which the volume of sample solution was
478 commensurate to the high total dissolved solid content (TDS, consisting of the sample plus a
479 threefold (wt/wt) amount of LiBO₂), silicon was removed by evaporation from the sample
480 dissolved with HF. This smaller TDS allows loading the column with a significantly reduced
481 volume of solution, in this case 2.5 mL of 2.5M HNO₃, instead of 6 mL. A few minutes before
482 column loading, ascorbic acid (50 mg) was added to the solution to reduce Fe, present (along
483 with other transition elements) in greater amount than in the granite sample.

484 The data show that matrix elements (Al, alkalis, alkali earths,) including iron as Fe(II), behave
485 passively and pass through the column during the loading step, along with minor transition
486 elements (Ni, Co, Cu, Zn), Tl, and Pb. In marked contrast with the granite sample decomposed
487 by fusion with LiBO₂, the Ti-group elements (Ti, Zr, Hf), W, and Nb are essentially not
488 retained, indicating they occur as non extractable species formed during the sample dissolution
489 step with HF. However, Ta is quantitatively removed (along with Mo) from the sample solution,
490 in line with its peculiar behavior compared to the rest of the HFSE (Fig. 12 a).

491 The next fractions of 0.5 ml 2.5M HNO₃ totaling 3 mL (equivalent to roughly 25 free column
492 volumes), do not contain any appreciable element except *ca.* 3% of Lu, highlighting the strong
493 retention of the elements of interest extracted during the loading step. This indicates that
494 samples of larger size, e.g., 200 mg of basaltic rock, could be processed on the same
495 microcolumn. This suggestion is further supported by the fact that the next 2 mL of 2.5M
496 HNO₃-0.1M HF only contain the small amount of Ti, Zr, Hf, and Nb that was initially extracted,

497 along with *ca.* 1% of Lu, the least adsorbed Ln. The next two mL of 1M HNO₃ contain a few
498 % of the heaviest Ln, and this fraction could be omitted to proceed directly to the stripping of
499 the heavy Ln's with 2 mL of 0.125M HNO₃.

500 Then, the light lanthanides are eluted in a very pure state with 1.5 mL of 3M HCl. The next
501 fraction of 0.5 mL of the same acid contains 99% of Th, accompanied by *ca.* 15% of U, and 8%
502 of Bi. The rest of U and Bi are stripped by means of 0.5 mL of 0.05M HCl-0.145M HF. This
503 fraction also contains the bulk of Sc and about one fourth of Mo found in this experiment. The
504 complement of Mo can be stripped with 2 mL of 0.72M HF, but Ta remains strongly held by
505 the resin. It was found necessary to resort to a very strong, water soluble, organic complexant
506 designed as a stripping/holdback reagent for multivalent ($M^{>/+3}$) metal ions in SEX schemes,
507 ^[41] namely, 1-hydroxy ethane-1,1 diphosphonic acid (HEDPA, also known as etidronic acid) to
508 back-extract that element.

509 In conclusion, these preliminary experiments conducted on natural, complex matrices
510 demonstrate the potential of the neat CMPO resin (P-3) for the selective, high yield separation
511 of many trace elements of interest (the REE: Ln + Sc and Y ; Th, U, plus Zr-Hf in case F⁻-free
512 solutions are processed) from all those common elements forming geological and
513 environmental samples. These elements are obtained in a very pure state, as shown by the
514 decontamination factors (that is, the ratio of the amount of unwanted element accompanying
515 the element of interest after and before the separation) achieved in the different fractions (Table
516 4). Irrespective of the sample decomposition method, the results lie in the 10⁻⁴ to 10⁻⁵ range in
517 most cases, which is a good achievement for a single pass column separation. However, in the
518 case of a decomposition of the sample by melting, a significantly poorer decontamination of Ti
519 and Zr is achieved, reflecting the strong initial extraction of these elements from F⁻ free
520 solutions. Although additional work is still required to refine the composition of successive

521 elution media, the data available at present suggest that sequential stripping of the main groups
522 of elements extracted should be possible. The comparison between the experiments conducted
523 with solutions prepared by LiBO_2 fusion or dissolution with HF confirm that the extraction of
524 certain high valence elements by CMPO is highly sensitive to the presence of the fluoride ion.
525 Specifically, their extraction is greatly (Ti, Zr, Hf) or notably (Nb) reduced when hydrofluoric
526 acid was involved in the sample preparation steps preceding the column separation. In contrast,
527 and as anticipated from the measurements of distribution ratios in HNO_3 containing HF, the
528 extraction of Ta is enhanced when the sample was treated with an excess of hydrofluoric acid
529 during the dissolution step.

530

531 **Extraction from hydrochloric acid medium**

532 The distribution ratios of trace elements extractable by CMPO such as the REE, Th, and
533 U are in general much lower in HCl medium than in nitric acid, at least at low to moderate acid
534 strength. However, the new resins might offer interesting prospects to separate a few trace
535 elements which are not extracted in nitric media, but display relatively high D_w 's in HCl, such
536 as certain noble metals. Among them, rhenium, occurring at ultra-trace level in geological
537 materials, is important in radiogenic isotope geochemistry, due to the natural chronometer and
538 isotopic tracer offered by the long-lived radioactive decay of ^{187}Re into ^{187}Os . To investigate
539 the potential interest of the CMPO resins in this scope, a 100 mg aliquot of the AGV-1 andesitic
540 SRM has been dissolved with HF, evaporated to dryness, spiked with 30 ng Re, and redissolved
541 with 1 mL of 1M HCl. After addition of 35 mg of ascorbic acid as a reducing agent for Fe(III),
542 this solution was loaded onto a ca. 5 mm i.d. column containing 100 mg of P-2 resin. Then, the
543 column was rinsed with 0.5 mL of 1M HCl, and further washed with 4 x 0.5 mL of 0.05M HCl.
544 The results listed in Table 5 show that this step allows to get rid of most major, minor, and trace

545 elements, while Re is quantitatively extracted. Several trace elements are also retained to a
546 significant extent, namely, Sn, Cd, Sb, Nb, W, Bi, and, especially, Mo and Ta. Although the
547 extraction behavior of Nb, Mo, Ta, and W is consistent with their high distribution ratios
548 measured in HCl medium, it turns out that Zr and Hf were not extracted, in spite of similarly
549 high D_w 's. This suggests that these two elements occurred as non extractable fluoride
550 complexes. The major part of the retained elements can be removed from the column by means
551 of 6 x 0.5 mL 0.1M HNO₃, while Re is still held by the resin. Finally, Re is stripped with 1.5
552 mL of 4M HNO₃. This Re fraction still contains impurities of Ta, W, Mo, Nb, and Sn, but
553 preliminary work indicates that these unwanted elements could be efficiently filtered off by
554 loading the Re fraction on-line onto a column of HDEHP-based EXC material (LN resin of
555 Eichrom). Indeed, Re is not extracted by HDEHP from 4M HNO₃, whereas Ta, W, Mo, and Sn
556 are retained. Although promising, this scheme should be significantly up-scaled in order to
557 handle the much larger samples sizes necessitated by the exceedingly low concentrations of Re
558 in most natural samples. But it is suggested, that this protocol might prove useful for isolating
559 Re from matrix elements in view of precise concentration measurements by isotope dilution
560 mass spectrometry, either by N-TIMS or ICP-MS.

561

562 **Mutual separation of the heavy lanthanides**

563 Finally, a preliminary experiment has been conducted to explore the possibility to
564 isolate individual Ln from adjacent elements. This trial was prompted by the observation that
565 distribution ratios of the mid and heavy lanthanides on both the P-2 and P-3 resins in dilute
566 nitric acid decrease markedly as a function of increasing atomic number, i.e., following a trend
567 reverse to that observed for other EXC systems based on HDEHP or TODGA. This suggests
568 that a CMPO based resin might offer an alternative, or complementary, way to fractionate the

569 heavy Ln's. Taking the heaviest lanthanide, lutetium, as example, a roughly similar magnitude
570 of extraction (e.g., $D_w \sim 12$) would be achieved in 1M, 0.2M, and 0.15M (interpolated values)
571 HNO_3 for RE, P-2, and P-3 resins, respectively, with a modest improvement of its separation
572 factor from Yb (taken as the ratio of their D_w 's) from 1.2 with RE to ca. 1.5 with P-2 and P-3.
573 A moderately long (~7 cm), ~4 mm i.d. column containing 310 mg of P-2 resin was tested with
574 an artificial mixture containing 50 ng of each of the six heavier Ln's : Dy, Ho, Er, Tm, Yb, and
575 Lu. Following sample loading in 50 μL of 1M HNO_3 followed by 150 μL of the same acid to
576 ensure the sorption of the elements on top of the column, the resin was washed with 3 mL of
577 0.25M HNO_3 which did not desorb any element. Then, the chromatographic separation was
578 continued by decreasing the nitric acid strength from 0.15M to 0.05M, with two intermediate
579 steps of 0.10M and 0.08M HNO_3 .

580 This caused the sequential elution of the Ln's in the reverse order of their D_w 's. The results
581 show (Fig. 16) that the most strongly held elements, Dy and Ho, are well separated from each
582 other in 0.05M HNO_3 . However, the peaks of Ho and Er are not perfectly resolved, and the
583 overlap between adjacent peaks is even more important for the less retained Lu and Yb. This
584 indicates that a longer column (and possibly of wider internal diameter, depending on the
585 amount of heavy Ln's to be separated) would be required to improve the resolution of the
586 chromatographic peaks of these elements. Also, the concentration gradient of the eluting
587 medium could be optimized. In case only one of these elements is targeted, the P-2 column
588 could be used in tandem with another column of LN resin (featuring a reverse order of
589 selectivity of the HREE) to get rid of the tail of the unwanted adjacent element peak.

590

591 **Other potential use**

592 Besides separation applications, it would also be possible to take advantage of the extreme
593 affinity of the neat CMPO resin for many important trace elements in fairly concentrated, 5-7M

594 nitric and 6M hydrochloric acids, to remove traces of contaminants from these reagents, as an
595 alternative to, or combined with, sub-boiling distillation. For example, this approach might be
596 helpful for an ultimate “polishing”, just prior to use, of small volumes of acids in very
597 demanding applications such as radiogenic or stable isotope chemistry where ultra-low blanks
598 of selected elements are required.

599

600 **CONCLUSIONS**

601 Compared to the well-established TRU- and RE-Spec EXC materials based on CMPO largely
602 diluted with TBP, the new resins developed in this work with little or no TBP display greatly
603 enhanced distribution ratios for the trace elements of interest over the range of nitric acid
604 concentration (1-3M) most appropriate for handling samples in solution. This includes the
605 heaviest lanthanides which suffered from limited uptake by TRU and RE resins in <3M HNO₃.
606 The excellent selectivity against those elements constituting the bulk of natural samples is
607 maintained. Only Fe (III) is potentially troublesome, but thanks to the improved D_w's in
608 relatively dilute (ca. 2M) HNO₃, this problem can be more easily circumvented by using
609 ascorbic acid to reduce trivalent iron to the non extracted, divalent species. The high D_w's allow
610 a very high degree of miniaturization of separation protocols to be achieved. Combined with
611 fast uptake kinetics, they permit to use very short columns, thereby ensuring the selective
612 extraction of trace elements of interest at a high flow rate. This is most useful when relatively
613 large volumes of sample solution are to be processed, as is the case when silicate samples are
614 decomposed by alkaline fusion. From such fluoride-free, nitric acid media, all the main target
615 elements of many geochemical studies (REE, Th-U, and HFSE) can be quantitatively separated
616 from unwanted matrix elements. When sample are dissolved by using HF, the extraction of
617 REE, Th, and U is still quantitative, but that of most HFSE is greatly reduced, as a result of the

618 extreme sensitivity of these elements to fluorine complexing. The same nitric acid solutions
619 could also be loaded onto Sr Spec column for the concomitant separation of Sr and Pb. Besides
620 their obvious interest for fast, group separations with very short columns, the new CMPO resins
621 could also be used in sufficiently long columns to achieve the mutual separation of the heavy
622 lanthanides in dilute nitric acid, by virtue of the marked fractionation of their D_w 's as a function
623 of increasing atomic number. Finally, the CMPO resins might prove useful in HCl media for
624 the separation of certain noble metal from matrix elements, thus broadening their potential field
625 of application.

626

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636

637

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639 There is no conflict of interests to declare.

640

641

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