# EXTRACTION OF HAFNIUM WITH CHELATING AGENTS FROM AQUEOUS–ALCOHOLIC SOLUTIONS*

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Received October 9th, 1974

Extraction of hafnium into solutions of N-benzoyl-N-phenylhydroxylamine, 2-thenoyltrifluoroacetone and di-n-butylphosphoric acid in benzene, toluene, chloroform and tetrachloromethane from aqueous alcoholic solutions with a formal acidity of 2M-$HClO_4$ was studied. Methyl-, ethyl-, n- and isopropyl- and tert-butyl alcohol were used as organic components in the mixed aqueous–organic phase. In the extraction into N-benzoyl-N-phenylhydroxylamine the presence of the alcohols leads to synergistic effects analogous to the previously described extraction by substituted benzoylpyrazolone. With the other two extractants, the effect of the alcohols is antagonistic, due to interaction of alcohol or water with the reagent in the organic phase, and to the decrease in the reagent distribution constant.

In the previous communication[1], synergistic and antagonistic effects were described for extraction of hafnium into 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone from aqueous–alcoholic medium and general prospects of the utilization of mixed media in the extraction were outlined. In the present paper the study of these systems is continued and the results of the investigation of the extraction of hafnium from aqueous–alcoholic media containing 2M-$HClO_4$ with other chelating reagents, namely, N-benzoyl-N-phenylhydroxylamine (BPHA), 2-thenoyltrifluoroacetone (TTA) and di-n-butylphosphoric acid (DBP), are given.

## EXPERIMENTAL

As extractants, BPHA (Lachema, Brno), TTA (Arcochemie, Berlin) and DBP (Koch-Light, Great Britain) were used.

The DBP distribution between aqueous–alcoholic 2M-$HClO_4$ and benzene was followed by titration of DBP in the equilibrium organic phase employing an initial concentration of 0·12M--DBP. The DBP distribution ratio was corrected for volume changes.

The UV spectra were measured in quartz cuvettes on a recording UV-VIS spectrophotometer model 365 (Varian-Techtron, USA).

Coextraction of the alcohols with BPHA and DBP was studied using $^{14}C$-labelled alcohols[1] and the water content in the equilibrium organic phases was determined by the Fischer method. All other data are given in the previous paper[1].

* Part XX in the series Extraction of Hafnium; Part XIX: This Journal *40*, 3329 (1975).

## RESULTS AND DISCUSSION

### *Extraction by N-Benzoyl-N-phenylhydroxylamine*

The effect of the initial alcohol concentration in the polar phase* on the hafnium distribution ratio ($D$) for extraction into a toluene solution of BPHA is shown in Fig. 1. For ethyl and methyl alcohol, $D$ remains constant up to an alcohol concentration of c. 2·4M and for isopropyl and tert-butyl alcohol up to about 1M. n-Propyl alcohol is an exception; here $D$ slowly increases up to a concentration of 2·1M. At alcohol concentrations higher than the above values, the distribution ratio decreases more rapidly. The extraction into BPHA solutions in benzene and in $CCl_4$ has the same character[2]. However, the region of decreasing $D$ is shifted to higher alcohol concentrations with benzene and to lower with $CCl_4$. In the n-$C_3H_7OH$—$CCl_4$ system, the increase in $D$ is less pronounced than with extraction into benzene and toluene.

Extraction into chloroform differs from that with the above-mentioned solvents in that all the alcohols used cause a synergistic increase in $D$ (Fig. 2). This is apparently caused by the equilibrium alcohol concentration in the organic phase,

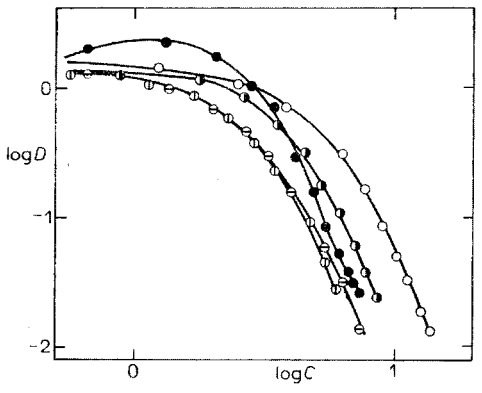


FIG. 1

Dependence of the Hafnium Distribution Ratio on the Alcohol Concentration in the Polar Phase

7 . $10^{-3}$M-BPHA in toluene; ○ $CH_3OH$, ◑ $C_2H_5OH$, ● n-$C_3H_7OH$, ○ iso-$C_3H_7OH$, ⊙ tert-$C_4H_9OH$.

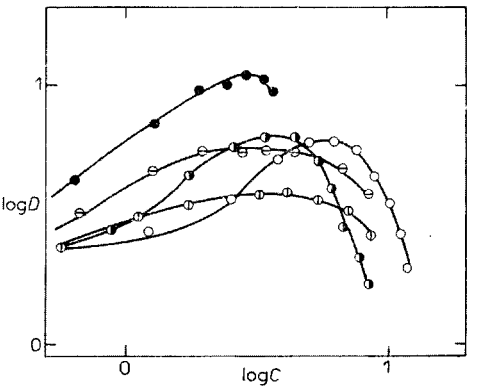


FIG. 2

Dependence of the Hafnium Distribution Ratio on the Alcohol Concentration in the Polar Phase

5 . $10^{-3}$M-BPHA in chloroform; symbols on the curves as in Fig. 1.

* The aqueous–alcoholic phase is termed the polar phase[1], in contrast to the organic phase of low polarity (benzene *etc.*).

which is several times higher compared with the other solvents[1]. At most the *D* value is increased by about one half of one order of magnitude and the effect decreases in the series, n-$C_3H_7OH$ > $C_2H_5OH$ ≈ $CH_3OH$ > iso-$C_3H_7OH$ > tert-$C_4H_9OH$. It can also be seen that the alcohol concentration at which the synergistic effect begins to operate increases in the series, n-$C_3H_7OH$ < $C_2H_5OH$ < $CH_3OH$, *i.e.* the synergistic effect of straight-chain alcohols increases with the chain length, similar to extraction with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP). With these alcohols, the position of the synergistic maximum shifts to lower alcohol concentrations with increasing length of the carbon chain: 6·5M-$CH_3OH$, 3·8M-$C_2H_5OH$ and 3·0M-n-$C_3H_7OH$. If the BPHA concentration decreases, the synergistic effect becomes more pronounced and the maximum shifts to higher alcohol concentrations (Fig. 3).

It follows from comparison with PMBP (ref.[1]) that apparently analogous, though less pronounced, effects occur during extraction with BPHA. In Fig. 4 is depicted the variation in the distribution ratio of BPHA in the toluene/polar phase system with increasing alcohol concentration. While with PMBP some alcohols did not affect the reagent distribution in a wide concentration range, with BPHA all the alcohols cause a decrease in its distribution, even when present at low concentrations. Therefore this effect competes much more strongly with the synergistic effect for

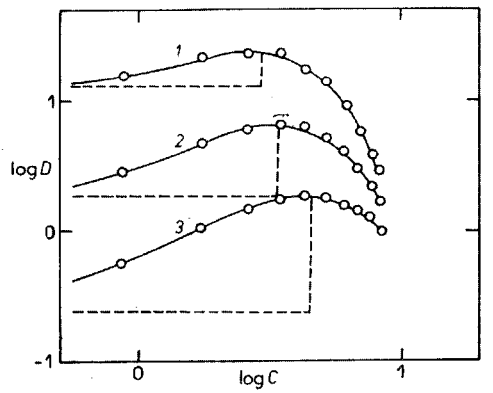


FIG. 3

The Effect of the BPHA Concentration on the Magnitude of the Synergistic Effect During Extraction from Aqueous–Ethanolic Medium into Chloroform

BPHA concentration ($mol^{-1}$): curve *1* $1 . 10^{-2}$, $2 5 . 10^{-3}$, $3 2·5 . 10^{-3}$.

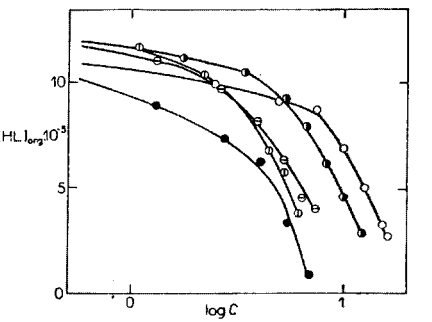


FIG. 4

The Effect of the Initial Alcohol Concentration on the Distribution of BPHA Between the Aqueous–Alcoholic Phase and Toluene

BPHA (≡HL) initial concentration, $1·2 . . 10^{-4}$M; symbols on the curves as in Fig. 1.

BPHA than for PMBP and consequently the synergistic effect is less pronounced for BPHA.

The dependences of $D$ on the BPHA concentration for various alcohol concentrations and with chloroform as the organic phase are given in Fig. 5. The following slopes were obtained (alcohol concentrations in % (v/v) and the corresponding slopes

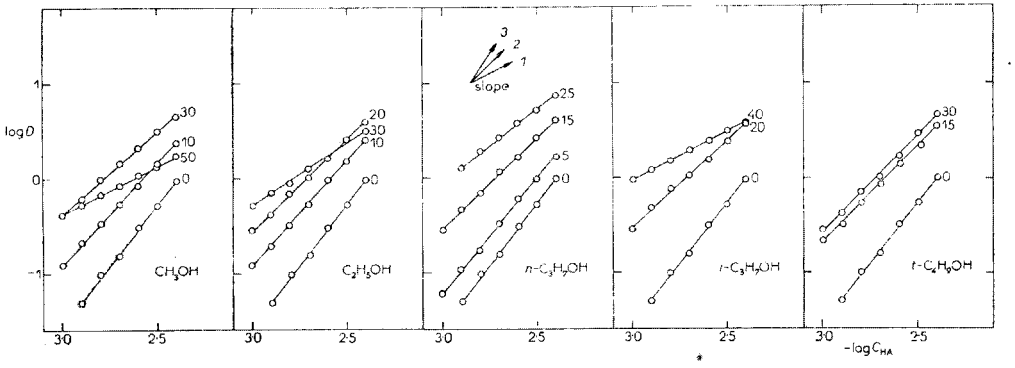


FIG. 5

Dependence of the Hafnium Distribution Ratio on the BPHA Concentration in Chloroform
The numbers at the curves specify the alcohol concentration in % (v/v).

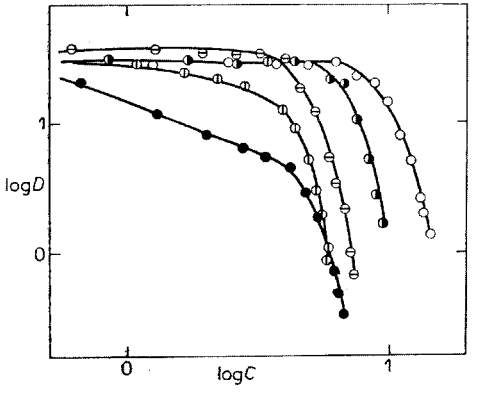


FIG. 6

Dependence of the Hafnium Distribution Ratio on the Initial Alcohol Concentration $4 . 10^{-2}$M-TTA in benzene; symbols on the curves as in Fig. 1.

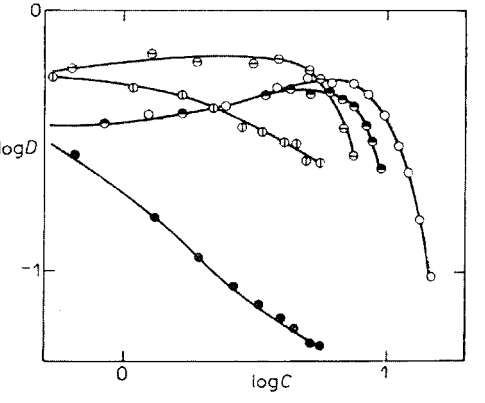


FIG. 7

Dependence of the Hafnium Distribution Ratio on the Initial Alcohol Concentration $2 . 10^{-2}$M-TTA in tetrachloromethane; symbols on the curves as in Fig. 1.

are given): $CH_3OH$ 10, 2·1; 30, 1·8; 50, 1·2; $C_2H_5OH$ 10, 2·2; 20, 1·9; 30, 1·6; n-$C_3H_7OH$ 5, 2·5; 15, 2·0; 25, 1·5; iso-$C_3H_7OH$ 20, 1·9; 40, 1·0; tert-$C_4H_9OH$ 15, 2·0; 30, 2·0. The $HfL_4$ chelate is extracted from aqueous 2M-$HClO_4$ (ref.[3]) (BPHA≡≡HL) and the slope of the log $D$ *vs* log [BPHA] dependence has a value of 2·5 to 2·7, owing to stepwise hafnium complex formation with the BPHA anion in the aqueous phase[4]. The slope further decreases in the presence of an alcohol, due to transfer of BPHA into the polar phase (Fig. 4) and to an increase in the degree of complexation of $Hf^{4+}$ in this phase. In agreement with the discussion in the previous paragraph, this effect is more pronounced than that encountered with PMBP, where a decrease in the slope of the corresponding dependences occurs at higher alcohol concentrations.

The qualitatively identical character of the effect of alcohols on the extraction of hafnium with the two reagents and the fact that various physico-chemical parameters (the relative permittivity of the organic phase, variations in the polar phase acidity due to partial miscibility of the two phases, variations in the chelate distribution constant) exert no basic influence on the extractability in these systems[1] justify

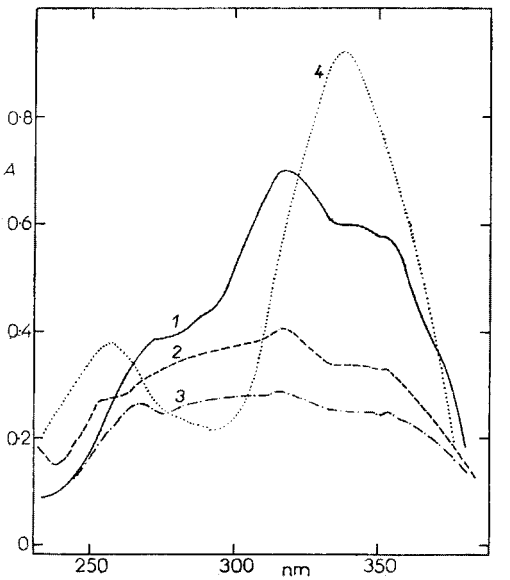


FIG. 8

UV Spectra of TTA

Curve: *1* $6 \cdot 10^{-5}$M-TTA in n-octane; *2* $1 \cdot 10^{-4}$M-TTA in n-octane after shaking with a polar phase containing 50% (v/v) $CH_3OH$; *3* the same conditions as for curve 2, but 60% (v/v) $CH_3OH$; *4* $5 \cdot 10^{-5}$M-TTA in absolute $C_2H_5OH$.

the assumption that the cause of the synergistic effects – if they occur at all – is identical for BPHA and PMBP (ref.[1]), namely, the solvation of the $HfL_4$ chelate by alcohol molecules in the organic phase. Both systems are also analogous with respect to antagonistic effects. If $D$ is corrected for changes in the BPHA concentration in the organic phase, the same family of curves as that given in Fig. 1 is obtained, except that the descending parts of the curves are somewhat shifted. This indicates that the decreasing distribution constant of BPHA with increasing alcohol concentration is not the sole reason for the antagonistic effect, as $D$ would have to be independent of the alcohol concentration after the correction. Another cause of the decrease in $D$ at higher alcohol concentrations is the formation of a molecular complex (or solvate) of BPHA with the alcohol in the organic phase, leading to a decrease in the BPHA activity in this phase. This fact is verified by coextraction of alcohols with BPHA into chloroform: with an initial concentration of 20% (v/v) alcohol it holds that $[CH_3OH]_{org} = 0{\cdot}136$M and $[C_2H_5OH]_{org} = 0{\cdot}33$M in extraction with chloroform alone and $[CH_3OH]_{org} = 0{\cdot}170$M and $[C_2H_5OH]_{org} = 0{\cdot}35$M in extraction into 0·2M-BPHA in chloroform.

*Extraction by 2-Thenoyltrifluoroacetone*

As can be seen from Fig. 6, antagonistic effects play a role during the extraction into benzene, occurring at $[CH_3OH]$ and $[C_2H_5OH] > 5{\cdot}5$M and $[\text{iso-}C_3H_7OH]$ and $[\text{tert-}C_4H_9OH] > 3{\cdot}5$M. $\text{n-}C_3H_7OH$ causes a decrease in $D$ even at low concentrations. The results are analogous with other solvents; the only difference found is for chloroform, namely, that $CH_3OH$ and $C_2H_5OH$ also cause a decrease in $D$ even at low concentrations[2]. With $CCl_4$ (Fig. 7), $D$ increases minutely with increasing concentrations of $CH_3OH$ and $C_2H_5OH$ before the antagonistic region is reached. A similar increase was observed with the toluene–$C_2H_5OH$ or $\text{iso-}C_3H_7OH$ systems[2].

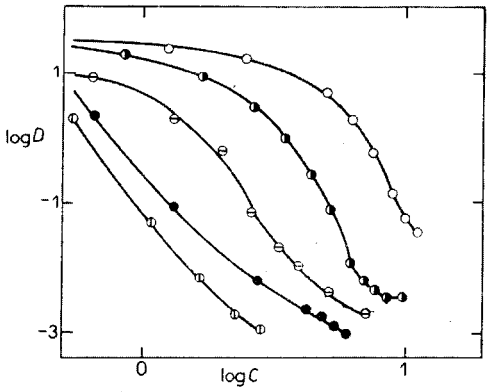


FIG. 9

Dependence of the Hafnium Distribution Ratio on the Initial Alcohol Concentration $1 . 10^{-3}$M-DBP in toluene; symbols on the curves as in Fig. 1.

However, the increase in the extractability is small and hence has not been further studied.

The cause of the antagonistic effect is apparent from the UV spectra of TTA in octane solutions shaken with polar phases of various compositions (Fig. 8). The TTA spectrum in octane shaken with aqueous 2M-$HClO_4$ (curve *1*) is identical with the spectrum of TTA (dried over $P_2O_5$) in anhydrous octane. A sharp maximum at 315 nm and incompletely resolved maxima at 275 and 340 nm correspond to the TTA enol form[5,6]. After shaking with a polar phase containing 50% (v/v) $CH_3OH$ (curve *2*), the maxima at 315 and 340 nm remain; however, a new maximum appears at 265 nm and the spectrum exhibits increased absorbance in the region below 300 nm compared with the spectrum of dry TTA. These changes are due to conversion of a part of the TTA to the ketohydrate form during the extraction; the spectrum of this form is characterized by maxima at 262 and 287 nm (ref.[7]). The ketohydrate absorption maximum at 267 nm is quite pronounced on curve *3* (60% (v/v) $CH_3OH$.) The same changes in the spectra were also observed for the other alcohols[2]. The formation of ketohydrate is certainly caused by increased water concentration in the organic phase due to its coextraction with the alcohols. This is shown in Table I for the coextraction of water into tetrachloromethane. However, no quantitative correlation was found between the water content in the organic phase and the appearance of the TTA ketohydrate form in the spectrum: for example, with n-$C_3H_7OH$, where $[H_2O]_{org}$ is by one or two orders of magnitude higher than with $CH_3OH$ and $C_2H_5OH$, there is virtually no difference in the magnitude of the corresponding absorption bands for the two TTA forms in the spectra and the formation of ketohydrate with

TABLE I

Coextraction of Water with Alcohols into Tetrachloromethane

| Alcohol | Initial alcohol concentration % (v/v) | $[H_2O]_{org} \cdot 10^3$ mol $l^{-1}$ |
|---|---|---|
| $CH_3OH$ | 60 | 1·9 |
| $C_2H_5OH$ | 40 | 2·6 |
| | 60 | 8·1 |
| n-$C_3H_7OH$ | 30 | 48 |
| | 50 | 76 |
| iso-$C_3H_7OH$ | 30 | 11·5 |
| | 60 | 31 |
| tert-$C_4H_9OH$ | 30 | 63 |
| | 60 | 89 |

tert-$C_4H_9OH$ is much less pronounced than with the other alcohols. Similarly, it is interesting that pronounced changes in the spectra of octane extracts (Fig. 8) are caused by a relatively small change in the water concentration in the organic phase; while no ketohydrate is formed during extraction from 2M-$HClO_4$ (the solubility of water in octane is $\approx 7 . 10^{-4}$M (ref.[7]), its formation during the extraction from mixed solutions is considerable, even though the water concentration in the octane phase shaken with a polar phase containing 50 and 60% (v/v) $CH_3OH$ is not much larger and is constant ($1{\cdot}2 \pm 0{\cdot}2 . 10^{-3}$M). Curve *4* represents the spectrum of dry TTA in anhydrous $C_2H_5OH$. The maxima at 257 and 338 nm correspond to a TTA molecular complex with the alcohol[5]. As the alcohol concentration in the equilibrium organic phase is always higher than that of water (for $CCl_4$ compare *e.g.* the data in Table I with Fig. 12 in ref.[1]; for octane, the alcohol concentration in the organic phase is 0·08M-$CH_3OH$, 0·18M-$C_2H_5OH$ and 0·50M-n-$C_3H_7OH$ with initial alcohol concentrations of 50% (v/v)), the changes in the spectra are probably also complicated by TTA interaction with the alcohol, so that all three TTA forms determine the resultant shape of the spectrum. The antagonistic effect in these systems is thus caused by inactivation of a part of TTA through the formation of keto hydrate and of molecular complex with the alcohol. Comparison of curves *2* and *3* in Fig. 8 also indicates that a decrease in the overall TTA concentration in the organic phase due to its transfer into the polar phase also contributes to the antagonistic effect.

*Extraction by Di-n-butylphosphoric Acid*

It is characteristic for all the alcohols without exception that their presence in the polar phase causes a strong decrease in $D$ in all the solvents. This is shown in Fig. 9

TABLE II

Coextraction of Alcohols with DBP into Benzene

| $C_{DBP,tot}$ | $[DBP]_{org}$ | $[CH_3OH]_{org}$ | $[DBP]_{org}$ | $[C_2H_5OH]_{org}$ |
|---|---|---|---|---|
| mol $l^{-1}$ | mol $l^{-1}$ | | mol $l^{-1}$ | |
| | 20% (v/v) $CH_3OH$ | | 30% (v/v) $C_2H_5OH$ | |
| 0 | — | 0·107 | — | 0·356 |
| 0·105 | 0·088 | 0·133 | 0·084 | 0·423 |
| 0·21 | 0·175 | 0·146 | 0·167 | 0·482 |
| 0·315 | 0·262 | 0·177 | 0·25 | 0·51 |
| 0·42 | 0·35 | 0·194 | 0·334 | 0·56 |
| 0·525 | 0·44 | 0·216 | 0·416 | 0·60 |

for the extraction into toluene. The decrease becomes more pronounced with increasing length and branching of the alcohol chain and the order of the antagonistic efficiency of alcohols $CH_3OH < C_2H_5OH <$ iso-$C_3H_7OH <$ n-$C_3H_7OH <$ $<$ tert-$C_4H_9OH$, is preserved also with the other solvents[2].

The fact that dialkylphosphoric acids are monomeric in alcoholic solutions, in contrast to solutions in non-polar solvents, has been verified cryoscopically[8] and by extraction studies[9,10]. It is assumed that monomeric dialkylphosphoric acid is solvated by alcohol. With regard to the high alcohol concentration in the equilibrium organic phase[1,2], one of the causes for the observed decrease in $D$ can be attributed to the destruction of active DBP dimers. The order of the antagonistic efficiency of non-branched alcohols, which can be correlated with increasing alcohol solubility in the organic phase[1], is in agreement with this assumption. In Table II are given the results of the study of the distribution of $^{14}CH_3OH$ and 1-$^{14}$C—$C_2H_5OH$ between the polar alcoholic phase and benzene DBP solutions. Increased extractability of alcohols in the presence of DBP is evident and clearly verifies the solvation of monomeric DBP in the equilibrium organic phase during extraction from aqueous–alcoholic solutions.

It is evident from the following data that, during extraction from aqueous–alcoholic media, the decrease of the DBP distribution ratio, with increasing alcohol concentration in the polar phase, also contributes to the antagonistic effect:

| $CH_3OH$ overall concentration % (v/v): | 0 | 10 | 20 | 30 | 40 | 50 | 60 |
|---|---|---|---|---|---|---|---|
| DBP distribution ratio: | 6·1 | 6·1 | 5·05 | 3·84 | 2·66 | 1·29 | 0·57 |

2M-$HClO_4$ was used as the polar phase; the initial DBP concentration in benzene was 0·121M.

Dialkylphosphoric acids were used in several works for the extraction separation of $^{95}Zr$ from the fission products[11–13]. For the back-extraction of $^{95}Zr$, hydrofluoric acid was employed[12,13]. In order to facilitate the back-extraction on the basis of monomerization of dialkylphosphoric acids in similar systems, addition of an alcohol to the organic phase has already been proposed (*e.g.* in the thorium(IV)-di-(2-ethylhexyl)-phosphoric acid–kerosene–decanol[14] system). Among the systems studied in the present work, tert-$C_4H_9OH$ seems to be most suitable for the back-extraction of hafnium – and apparently also zirconium – as it is very effective at concentrations of only 20–25% (v/v) in the polar phase.

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Translated by M. Štulíková.