# EXTRACTION OF HAFNIUM(IV) WITH ORGANOPHOSPHORUS REAGENTS FROM SOLUTIONS OF MINERAL ACIDS MIXTURES

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Extraction of hafnium(IV) was studied from solutions of mixtures of perchloric and nitric acids and of perchloric and hydrochloric acids for constant ionic strength, $I = 2, 4, 6,$ or $8$, and for $c_{Hf} \leqq 4 \cdot 10^{-4}$ mol l$^{-1}$. The organic phase was constituted by solutions of some acidic or neutral organophosphorus reagents or of 2-thenoyltrifluoroacetone, 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone, or N-benzoyl-N-phenylhydroxylamine in benzene, chloroform, or n-octane. A pronounced synergic extraction of hafnium proceeds only on applying organophosphorus reagents from an aqueous phase whose acidity is not lower than $3M$-$(HClO_4 + HNO_3)$ or $5M$-$(HClO_4 + HCl)$. The synergic effect was not affected markedly by a variation of the initial concentration of hafnium in the range $1 \cdot 10^{-8}$—$4 \cdot 10^{-4}$ mol l$^{-1}$, it lowered with increasing initial concentration of the organophosphorus reagent and decreasing concentration of the H$^+$ ions. It is suggested that the hafnium passes into the organic phase in the form of mixed complexes, the salting-out effect of perchloric acid playing an appreciable part.

Synergic extraction of metal elements from mixtures of mineral acids has been so far confined to the application of tri-n-butylphosphate (TBP) and concerns a limited number of elements. Of these, zirconium(IV) and hafnium(IV) predominate; their extraction has been studied from mixtures of nitric acid and perchloric[1-3], hydrochloric[4], and hydrofluoric[5,6] acids, respectively, and of sulfuric and hydrochloric acids[7], for constant ionic strengths. Synergic extraction has been also observed for cerium(IV), from HClO$_4$–HNO$_3$ system in the presence of di-n-butylphosphoric acid[8]. Of the trivalent metal cations extractable with TBP, attention has been paid to gallium in the presence of mixture of various mineral acids[9,10], and to scandium from HClO$_4$–HCl and HClO$_4$–HNO$_3$ mixtures[11].

To account for the synergic effect, the authors of the papers cited have considered the possibilities of *a*) a change of the activity coefficients of the metal and the mineral acids in the mixture, *b*) the formation of a mineral acid–organophosphorus reagent solvate, hence a lowering of the free reagent concentration, *c*) the formation of mixed, better extractable complexes involving anions of both acids in the mixture, *e.g.*, HX, HY. The last mechanism mentioned — the formation of the MX$_x$Y$_y$(TBP)$_z$ type complexes — is commonly considered to be most probably responsible for the synergism.

Since the synergism, found[1-7] for the extraction of zirconium and hafnium in the presence of TBP, should be observable also if other analogous reagents are used, we examined in this work the extraction of microquantities of hafnium(IV) from $HClO_4$–$HNO_3$, $HClO_4$–$HCl$, and $HClO_4$–$H_2SO_4$ mixtures employing other, particularly acidic organophosphorus reagents and also other chelating agents not involving phosphorus.

## EXPERIMENTAL

### Chemicals and Apparatus

Di-n-amylphosphoric (HDAP) and di-n-octylphosphoric (HDOP) acids were prepared at the Institute of Nuclear Research, Řež, n-Decylphenylphosphonic acid (HPDP) was prepared and purified according to ref.[12], 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBPz) according to ref.[13]. The other chemicals used were commercial preparations reagent grade purity; of organic reagents, these were: di-n-butylphosphoric acid (HDBP), tri-n-butylphosphine oxide (TBPO), tri-n-octylphosphine oxide (TOPO), triphenylphosphine oxide (TPPO), 2-thenoyltrifluoroacetone (HTTA), and N-benzoyl-N-phenylhydroxylamine (HBPHA). The stock solutions of $^{175+181}Hf$ chloride, nitrate, and perchlorate were prepared from commercial $^{175+181}HfO_2$ by dissolving in HF, multiply heating and evaporating with $HClO_4$ and final diluting with the corresponding mineral acid; the concentrations and activities of the working solutions were $1 . 10^{-8}$ to $4 . 10^{-4}$ mol l$^{-1}$ and $1 . 10^2$ to $3 . 10^6$ s$^{-1}$ ml$^{-1}$, respectively. The gamma radiation of the samples was measured by means of an NaI(Tl) well-type crystal. The spectrometric measurements were conducted on an instrument Spectromom 201 (MOM, Budapest) in 1 cm glass or quartz cells. For the conductivity measurements served a conductoscope OK 102 (Radelkis, Budapest) with smooth platinum electrodes.

### Working Procedure

Equal volumes (5 ml) of the aqueous and organic phases were agitated for 12 h at $20 \pm 1°C$; this period was found sufficient for the extraction equilibrium to establish. After the separation of the phases, aliquots were taken from either of them and measured in the well-type crystal.
    For the determination of the chloride ions, use was made of their reaction with Hg(OH)CN (ref.[14]), the nitrate ions were determined photometrically by means of phenyl disulfonic acid[15]. The partition of the perchlorate ions between the two liquid phases was examined with malachite green, which forms with the ions a defined ionic associate extractable into benzene; this was monitored photomerically at 620 nm and the data were evaluated by using a calibration curve. Chloride and nitrate ions do not interfere. The working procedure applied was identical with that developed for methylene blue[16].

## RESULTS AND DISCUSSION

### Partition of the Mineral Acids

Fig. 1 shows the dependences of the distribution ratio logarithms of the mineral acids anions on the composition of the $HClO_4$–$HCl$ and $HClO_4$–$HNO_3$ mixtures

for the total initial acid concentration 7 mol l$^{-1}$; benzene served as the organic phase. The perchloric acid present in the mixtures is seen not to be extracted into benzene to an appreciable degree. The varying initial concentration of hydrochloric or nitric acid essentially does not affect the partition of the perchlorate; the small minima, apparent on the extraction curves (Fig. 1, curve *1*, *2*) in the region of the highest HClO$_4$ concentrations are not quite evident. On the contrary the distribution ratios of chlorides and nitrates (curve *3*, *4*) with raising HClO$_4$ concentration increase monotonically up to one order of magnitude, which indicates rather strong salting-out effect of perchloric acid in the above systems. This fact is likely to play a part also in the partition of the metals, as observed, *e.g.*, for the extraction of zirconium and hafnium with TBP solutions in *o*-xylene[2,17]. In contrast to our results, it has been found in[18] that in the system HClO$_4$–HCl, the former acid is extracted better than the latter into a 50% solution of TBP in *o*-xylene; this may be due to the somewhat different proton solvation in the two solvents compared.

*Partition of Hafnium Between the Aqueous Phase Containing a* HClO$_3$–HNO$_3$ *Mixture and the Reagent Solution in Benzene*

During the investigation of the extraction of hafnium from HClO$_4$–HNO$_3$ mixture, attention was given to the application of phosphoric acid diesters (HDBP, HDAP, HDOP). Fig. 2a — d shows the dependences of the logarithms of the hafnium distribution ratios on the composition of the HClO$_4$–HNO$_3$ mixtures for a constant acidity of the aqueous phase, 2, 4, 6, or 8M. HDOP solutions in benzene of various initial concentrations served as the organic phase. HDBP and HDAP gave virtually identical results. The dependences obtained lead to the conclusion that the synergic effect for the extraction of hafnium increases with the total acidity of the aqueous phase and that it is most pronounced for the lowest intial concentrations of the phosphoric
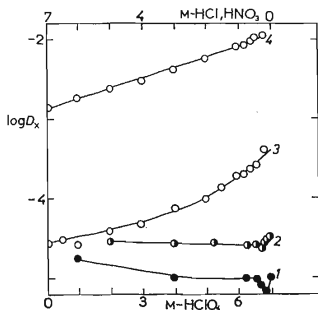


Fig. 1

Partition of Anions of Mineral Acids Between Mixtures of 7M-(HClO$_4$ + HNO$_3$) or (HClO$_4$ + HCl) and Benzene

*1* ClO$_4^-$ (system HClO$_4$–HNO$_3$), *2* ClO$_4^-$ (system HClO$_4$–HCl), *3* Cl$^-$, *4* NO$_3^-$.

acid di-n-alkyl esters and in the region of initial concentration of $HNO_3$ in the mixture $1 \pm 0.5$ mol $l^{-1}$.

Since small quantities of nitrobenzene were found to form during the agitation of the two phases if the total acidity of the aqueous phase exceeded 6 mol $l^{-1}$, we examined its effect on the hafnium partition in the above conditions. Nitro-
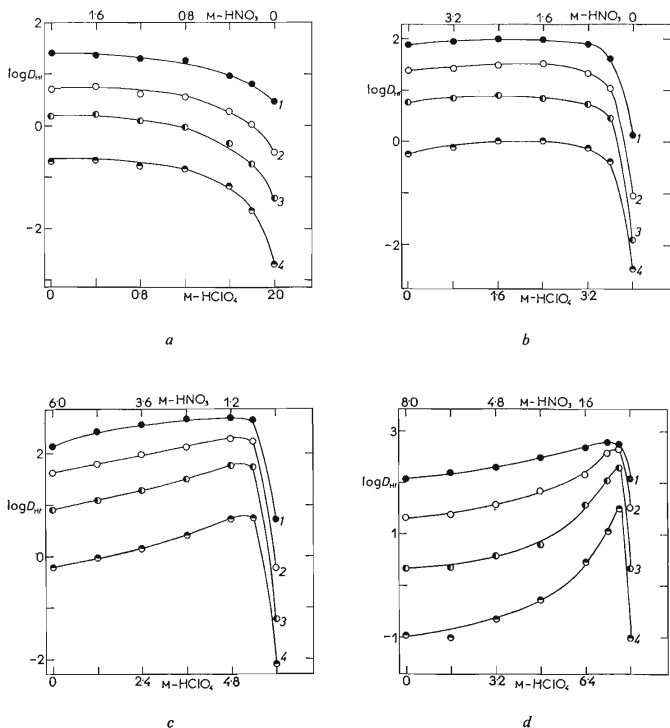


Fig. 2

Partition of Hafnium Between the Aqueous Phase Containing a $HClO_4$–$HNO_3$ Mixture and Benzene Solutions of HDOP

$c_{Hf} = 4 \cdot 10^{-7}$ mol $l^{-1}$, $c_{HDOP}$ (mol $l^{-1}$): $1\ 2 \cdot 10^{-4}$, $2\ 1 \cdot 10^{-4}$, $3\ 5 \cdot 10^{-5}$, $4\ 2 \cdot 10^{-5}$.

benzene addition as high as 4% vol. was found not to affect considerably the hafnium distribution ratio; thus the small changes in the composition of the organic phase associated with the nitration of benzene, if any, can be ignored. The effect of the initial concentration of hafnium on its partition between the aqueous and the organic phases was also examined; the distribution ratio was found unaffected up to the hafnium concentration $3 \cdot 10^{-5}$ mol $l^{-1}$, with higher concentrations it decreased slowly by tenths of log $D_{Hf}$, the highest concentration tested being $4 \cdot 10^{-4}$ mol $l^{-1}$.
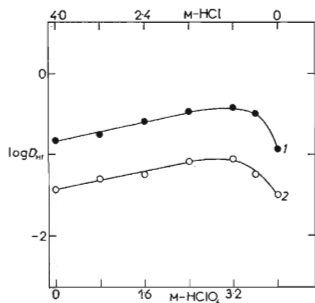
*Partition of Hafnium Between the Aqueous Phase Containing a $HClO_4$–$HCl$ Mixture and the Reagent Solutions in Benzene or Other Organic Solvents*

Analogously as in the preceding case, attention was focussed first of all on phosphoric acid diesters. Fig. $3a-c$ gives the dependences of the logarithms of the hafnium distribution ratios on the composition of the $HClO_4$–$HCl$ mixtures for constant total acidity of the aqueous phase, 4, 6, or 8M. The organic phase was again constituted by HDOP solutions in benzene, HDBP and HDAP behaved analogously. Similar results were obtained as with the $HClO_4$–$HNO_3$ mixtures; differences only lay in the less marked effect of the total acidity of the aqueous phase and less distinct maxima on the extraction curves. This is probably primarily due to the smaller difference between the hafnium distribution ratios for sole $HClO_4$ and HCl.

Of the other acidic organophosphorus reagents, attention was further paid to HPDP. Fig. 4, curve *1*, presents dependences identical with those of Fig. *3b* as concerns the composition of the two phases. HPDP is seen to behave analogously as HDOP; the $D_{Hf}$ values are, however, higher, as has been also observed previously[19]. Of the group of neutral organophosphorus reagents we examined TBPO, TOPO, and TPPO, and also TBP for a comparison. The respective extraction curves are shown in Fig. 4, curves $2-5$; they indicate that analogously as the acidic organophosphorus reagents behave TOPO and TPPO, whereas TBPO in $10^{-4}$ to $1 \cdot 10^{-3}$M solutions in benzene or in chloroform does not exhibit a maximum on the extraction curve. This anomaly could be interpreted in terms of the very low distribution ratio of hafnium in perchloric acid alone, which makes the course of the synergic extraction little pronounced; this phenomenon has not been explained. The shape of the extraction curve pertaining to TBP serves well to illustrate the difference between the application of trialkylphosphine oxides and trialkylphosphates: roughly the same hafnium distribution ratios can be attained with TBP in case that its initial concentration is two to three orders of magnitude higher.

In addition to benzene, chloroform and n-octane were also employed as the organic phase. The shapes of the extraction curves obtained with these solvents did not differ substantially from those for benzene.
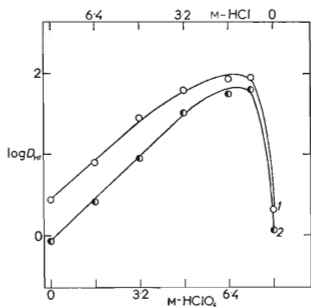
Similarly as with the $HClO_4$–$HNO_3$ mixtures, we examined the effect of the initial concentration of hafnium on its partition between the aqueous and the organic

*a*
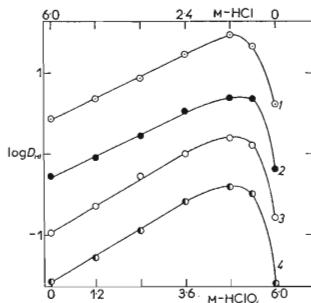


*b*



*c*

FIG. 3

Partition of Hafnium Between the Aqueous Phase Containing a $HClO_4$–HCl Mixture and Benzene Solutions of HDOP

$c_{Hf} = 2 . 10^{-6}$ mol l$^{-1}$, $c_{HDOP}$ (mol l$^{-1}$): ⊙ $4 . 10^{-4}$, ● $2 . 10^{-4}$, ○ $1 . 10^{-4}$, ◑ $5 . 10^{-5}$.

FIG. 4

Partition of Hafnium Between Mixtures $HClO_4$–HCl, Total Concentration 6M, and Benzene or Chloroform Solutions of Some Organophosphorus Reagents

$c_{Hf} = 4 . 10^{-6}$ mol l$^{-1}$; *1* $2 . 10^{-4}$M--HPDP, *2* $1 . 10^{-4}$M-TOPO, *3* $1 . 10^{-2}$M--TPPO, *4* $1 . 10^{-3}$M-TBPO, *5* $1 . 10^{-1}$M--TBP; *3* chloroform, otherwise benzene.
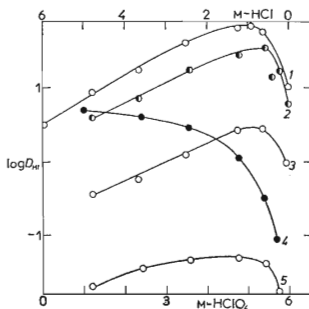
phases. If the reagent was present in an at least twentyfold excess over the initial concentration of hafnium, no differences were found in the $D_{Hf}$ values in the hafnium concentration range $1 . 10^{-8}$ to $1 . 10^{-4}$ mol l$^{-1}$; with additional rise of the hafnium concentration the $D_{Hf}$ values decreased slowly.

For a comparison of the behaviour of organophosphorus reagents and other chelating agents that did not contain phosphorus, we treated HTTA, HBPHA, and HPMBPz. The corresponding extraction curves are reproduced in Fig. 5. None of them represents a synergic extraction of hafnium such as described for the organophosphorus reagents. The maximum appearing on curve *1*, pertaining to $5 . 10^{-3}$M--HPMBPz in benzene, corresponds to the aqueous phase of $1\cdot2$M-HClO$_4$ + $4\cdot8$M-HCl. For HTTA and HBPHA, the hafnium distribution ratios did not vary.

*Partition of Hafnium Between the Aqueous Phase Containing a* HClO$_4$–H$_2$SO$_4$
*Mixture and a Benzene Solution of* HDOP

This partition was investigated for systems of $6$M-(HClO$_4$ + H$_2$SO$_4$). Obviously, the synergic effect does not take place here, probably because of the considerable stability of the hafnium sulfate complexes, which are not extractable into the organic phase.

*Study of the Acidity of the Mineral Acid Mixtures and Conductivity*
*Measurements*

The acidity of the mixtures of $6$M- and $8$M-(HClO$_4$ + HCl) was studied by using the dependence of the Hammett function $H_0$ on the mixture composition. The mixtures HClO$_4$ + HNO$_3$ were not subject to the study, regarding the conceivable
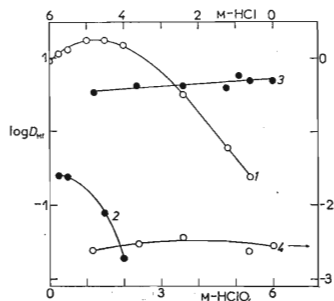


Fig. 5

Partition of Hafnium Between Mixtures HClO$_4$–HCl, Total Concentration $6$M, and Benzene or n-Octane Solutions of Some Chelating Agents

$c_{Hf} = 4 . 10^{-4}$ mol l$^{-1}$; *1* $5 . 10^{-3}$M--HPMBPz, *2* $2 . 10^{-3}$M-HPMBPz, *3* $1 . 10^{-2}$M-HBPHA, *4* $1 . 10^{-2}$M-HTTA; *2* n-octane, otherwise benzene.

changes accompanying the nitration of the indicator. The $H_0$ values were determined photometrically, using 2,4-dichloro-6-nitroaniline ($\lambda$ 426 nm) for the 6M acid mixture and 2,4-dinitroaniline ($\lambda$ 350 nm) for the 8M concentration. The p$K$ values of the bases were taken from[20], the equilibrium concentrations of the individual forms of the indicator were determined conventionally[21]. In the whole composition span the $H_0$ value varies linearly, decreasing towards the higher initial concentrations of perchloric acid; thus the activity of the hydrogen ions in the aqueous phase grows regularly with the increasing concentration of perchloric acid in the mixture, attaining the maximum value for $HClO_4$ alone.

The conductivity measurements, performed with $HClO_4$–$HNO_3$ and $HClO_4$––$HCl$ mixtures, total acidity 6M, also exhibited smooth variation of the conductivity, free from distinct maxima or minima (Fig. 6).

## CONCLUSIONS

The following conclusions can be drawn from the above results: Where organophosphorus reagents are used, acidic or neutral, the synergic effect takes plase if the total acidity of the aqueous phase exceeds 3M for $HClO_4$–$HNO_3$ mixtures or 5M for $HClO_4$–$HCl$ mixtures; with $HClO_4$–$H_2SO_4$ this effect does not occur. The synergic effect does not appear if other chelating agents not containing phosphorus are used, such as HTTA, HBPHA, HPMBPz; the inexpressive extraction maxima, if occurring, are shifted towards low initial concentrations of perchloric acid in the mixture. The characteristic maxima appear on the extraction curves in case that in the mixture, acidity as stated above, HCl or $HNO_3$ is present in the initial concentration $1\cdot0 \pm 0\cdot5$ mol l$^{-1}$. The extractability of hafnium, expressed *via* the $D_{Hf}$ value in the extraction curve maximum, lowers for the various organophosphorus reagents in the order
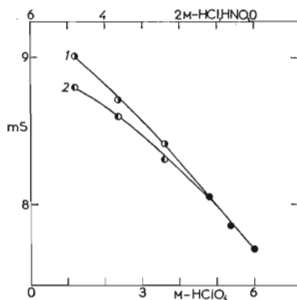


Fig. 6

Conductivities of 6M-($HClO_4$ + $HNO_3$) and ($HClO_4$ + HCl) Mixtures at $20 \pm 0\cdot1°C$
 1 $HClO_4$ + $HNO_3$, 2 $HClO_4$ + HCl.

HPDP = TOPO > HDBP = HDAP = HDOP > TPPO > TBP; the anomalous behaviour of TBPO is probably due to the very low $D_{Hf}$ values for the hafnium extraction from perchloric acid alone into TBPO solutions in current organic solvents. In the case of synergic extraction of hafnium, the maxima on the extraction curves are the more pronounced, the lower is the initial concentration of the organophosphorus reagent and the higher is the initial acidity of the aqueous phase. The principal cause of the synergic effect in the above cases is probably the salting-out effect of perchloric acid in the acid mixture concerned, rather than the anomalous value of the hydrogen ion activity in the aqueous phase. Although we were not able to directly prove the formation of mixed extractable complexes of the $HfY_x(ClO_4)_y(HA)_z$ type ($Y = Cl$, $NO_3$), their existence is feasible and they may be responsible for the mentioned anomalous extraction of hafnium from a mixture of two mineral acids.

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