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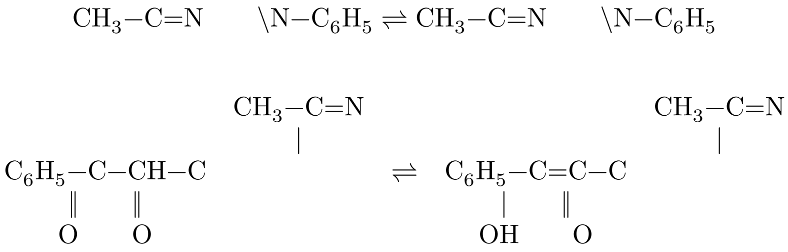
EXTRACTION OF INNER-COMPLEX COMPOUNDS OF ELEMENTS WITH 1-PHENYL-3-METHYL-4-BENZOYLPYRAZOLONE-5

(Presented by Academician A. P. Vinogradov, 29 III 1965)

For the extraction of inner-complex compounds, the search for organic reagents that ensure the extraction of elements from relatively acidic solutions is of essential importance. The use of such reagents makes it possible to eliminate the influence of hydrolysis and polymerization and, in a number of cases, to increase the selectivity of the extraction separation. Reagents of this type include, for example, thenoyltrifluoroacetone, which, however, is difficult to synthesize, insufficiently stable in storage, and not easily purified. On the other hand, reagents are needed that, under certain conditions, permit group extraction of a large number of elements at once, for example for subsequent spectral determination. Such group reagents include 8-oxyquinoline or sodium diethyldithiocarbamate. Despite all their popularity, these reagents are not universal.

We have studied the extraction of a large number of elements in the form of inner-complex compounds with 1-phenyl-3-methyl-4-benzoylpyrazolone-5 (PMBP), with a view to using the data obtained for solving analytical and radiochemical problems. It proved that PMBP is a highly effective extraction reagent; it has a number of substantial advantages that make it one of the most interesting reagents for the extraction of inner-complex compounds. The reagent is one of the eleven 4-acyl-substituted phenylmethylpyrazolones studied by Scytte Jensen (¹).



$$\mathrm{CH_3{-}C{=}N} \qquad \backslash\mathrm{N{-}C_6H_5} \rightleftharpoons \mathrm{CH_3{-}C{=}N} \qquad \backslash\mathrm{N{-}C_6H_5}$$

$$\mathrm{C_6H_5{-}}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}}{-}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{CH}}{-}\mathrm{C} \quad \begin{array}{c}\mathrm{CH_3{-}C{=}N}\\ |\end{array} \rightleftharpoons \mathrm{C_6H_5{-}}\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{C}}{=}\underset{\substack{\|\\ \mathrm{O}}}{\mathrm{C}}{-}\mathrm{C} \quad \begin{array}{c}\mathrm{CH_3{-}C{=}N}\\ |\end{array}$$

PMBP is a β-diketone; it exists in the keto form and in the enol form. The yellow-green enol form is obtained by recrystallization from heptane, in which, however, the reagent is rather poorly soluble. The white keto form is obtained by recrystallization from a mixture of ethyl or methyl alcohol with water. We did not observe differences in the extraction behavior of these forms. By the spectrophotometric method, at ionic strength 1.0 (perchlorate solution) and at a temperature of 25°, the acid dissociation constants of the reagent and the distribution constants of it in the systems benzene—water and isoamyl alcohol—water were determined (Table 1). PMBP is a fairly strong acid (pK 4.11).

The reagent has a high extraction capacity. Many elements are extracted from relatively acidic solutions with large distribution coefficients. In its ability to extract a number of elements from acidic media, PMBP surpasses thenoyltrifluoroacetone.

We have studied in detail the extraction of Ca, Sr, Sc, Mn, Fe(III), Zr, and Pu(IV). As extractants we used solutions of PMBP in isoamyl alcohol, cyclohexanone, C_6H_6, $CHCl_3$, mixtures of isoamyl alcohol with $CHCl_3$, and other solvents. Extraction was studied at 25° as a function of pH, reagent concentration, aqueous-phase composition, phase contact time, and other factors. Some data are given below as examples.

Plutonium(IV) is well extracted, especially from nitric acid solutions. For example, a 0.1 M solution of PMBP in isoamyl alcohol extracts

Table 1

Acid dissociation constants and distribution constants of PMBP

Constant	Solvent	Value obtained
$K_1 = \frac{[HA][H^+]}{[H_2A^+]}$	Water	$pK_1 = 0.28 \pm 0.03$
$K_2 = \frac{[A^-][H^+]}{[HA]}$	Water	$pK_2 = 4.11 \pm 0.02$
$P_{HA} = \frac{[HA]}{[HA]_0}$	Benzene—water	$\lg P_{HA} = 3.01 \pm 0.02$
$P_{HA} = \frac{[HA]}{[HA]_0}$	Isoamyl alcohol—water	$\lg P_{HA} = 2.33 \pm 0.02$

Table 2

pH values for 50% extraction of certain elements by 0.01 M PMBP solutions in various solvents

Solvent	Sc	Mn	Ca	Sr
Isoamyl alcohol	0.34	3.50	5.15	5.78
Cyclohexanone	0.34	3.64	5.40	(6.00)

Solvent	Sc	Mn	Ca	Sr
Ethyl acetate	0.70	4.10	5.58	(5.94)
Chloroform	1.09	(6.30)	7.36	–
Benzene	0.76	6.57	(9.70)	–

plutonium with distribution coefficients greater than 1000 from 1-9 N HNO_3 solutions. PMBP solutions in benzene, chloroform, and amyl acetate also extract plutonium well. It is especially interesting that plutonium extraction is almost not hindered by oxalates (even a saturated solution of oxalic acid), acetates (1.5 M), citrates (0.5 M), or phosphates (1 M). Plutonium is also extracted fairly well from sulfuric acid solutions. Figure 1 shows the dependence of the degree of extraction of plutonium on the concentration of HNO_3, H_2SO_4, and HCl. Extraction was carried out with a 0.1 M solution of PMBP in benzene. It is seen that plutonium is well extracted from nitric and sulfuric acid solutions.

Zirconium is extracted by PMBP solutions in benzene from nitric and sulfuric acids over a wide range of their concentrations. In the extraction of iron(III), equilibrium is established very slowly, but under equilibrium conditions iron is well extracted from nitric acid solutions up to 10 N.

Scandium is quantitatively extracted by 0.01 M PMBP solutions in isoamyl alcohol over a wide pH range (from pH 0–1 and higher, depending on the reagent concentration). The distribution coefficients are on the order of several thousand. Scandium is also well extracted by PMBP solutions in cyclohexanone, chloroform, and benzene. Scandium, like plutonium and certain other elements, is extracted as a compound with PMBP in a more acidic medium and with larger distribution coefficients than as a compound with thenoyltrifluoroacetone. Figure 2 shows the distribution coefficients obtained under identical conditions for 0.1 M solutions of these reagents in benzene. It is seen that PMBP extracts better.

Calcium is quantitatively extracted by PMBP solutions in a mixture of isoamyl alcohol with chloroform already at pH 6–7 and higher. As far as we know, there is no other reagent, except alkylphosphoric acids, that would provide calcium extraction at such low pH values for this element. Calcium is also extracted by PMBP solutions in isoamyl alcohol, cyclohexanone, and ethyl acetate. The inner-complex compound of calcium with PMBP is apparently coordinatively unsaturated and hydrated in the aqueous phase, since

chloroform and benzene extract it much worse than oxygen-containing solvents.

The effectiveness of extraction with PMBP and the influence of the nature of the solvent on the extraction of some elements can be illustrated by the data in Table 2, which gives the pH values for 50% extraction of Sc, Mn, Ca, and Sr. In many cases these values are very low, indicating the high extracting ability of the reagent.

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

Fig. 1. Extraction of plutonium(IV) ($1 \cdot 10^{-5}$ g-ion/l) by 0.1 M solutions of PMBP in benzene from solutions of various acids.
1 −H_2SO_4, 2 −HNO_3, 3 −HCl

As an example, Fig. 3 shows the extraction curves of Sc, Mn, Ca, and Sr by 0.01 M solutions of PMBP in isoamyl alcohol.

In addition to extracting a number of elements from more acidic media than in the case of TTA, PMBP also has other advantages over this reagent. Thus, PMBP is stable in storage and is easily purified by recrystallization; some elements, especially plutonium, are extracted rapidly. An important advantage of PMBP is its availability and the simplicity of its synthesis. The reagent is synthesized easily, in a single stage, from readily available starting materials.

The useful properties of PMBP and its availability open up possibilities for developing effective methods for separating elements, as well as for their determination. PMBP can be recommended as a new group reagent for the extraction concentration of trace elements prior to spectral determination. Our qualitative study of the interaction of PMBP with several dozen elements in neutral solutions showed that practically all the elements studied give precipitates soluble in organic solvents. Most extracts are colorless; Fe, V, Ti, and Mo give colored compounds. A more detailed study showed that, from neutral solutions, PMBP solutions in isoamyl alcohol quantitatively extract Cu, Ca, Zn, Cd, Al, Pb, Bi, Mn, Fe, Co, Ni, and other elements whose impurities often need to be determined. As a group reagent, PMBP is apparently more universal and more convenient than 8-hydroxyquinoline and sodium diethyldithiocarbamate.

Fig. 2. Extraction of scandium by 0.01 M solutions of PMBP and TTA in benzene. Ionic strength 1.0 (perchlorates), temperature 25°.
1 −PMBP, [Sc] $1.0 \cdot 10^{-5}$ g-ion/l;
2 −TTA, [Sc] $5.6 \cdot 10^{-6}$ g-ion/l.

Methods have been developed for the activation determination of calcium and manganese in sodium iodide of special purity. Sodium iodide is poorly suited for direct irradiation in a reactor because it becomes strongly activated. Extraction separation of the elements to be determined from the macrocomponent before irradiation was applied; the extract, evaporated in a quartz box, was irradiated.

Fig. 3. Extraction of Sc (1), Mn (2), Ca (3), Sr (4) with 0.01 M solutions of PMBP in isoamyl alcohol from perchlorate solutions with ionic strength 1.0 (25°). Element concentrations (g-ion/l): Sc $1 \cdot 10^{-5}$, Mn $1.5 \cdot 10^{-5}$, Ca $5.2 \cdot 10^{-4}$,

Fig. 3. Extraction curves

Figure 3: Fig. 3. Extraction curves

Sr $1 \cdot 10^{-5}$.

Since we were developing methods for determining impurity elements in high-purity alkali-metal halides, the influence of the macrocomponent on the extraction of the concentrated trace elements was preliminarily checked. Isoamyl alcohol was used as the solvent. The effect of large amounts (3 mol/l) of LiCl, NaCl, KCl, NaBr, and NaJ was studied. In many cases the salts, especially LiCl, lead to a decrease in the distribution coefficients, but the extraction remains practically complete (with the exception of the extraction of Ca and Sr in the presence of LiCl).

Procedure for the synthesis of PMBP (according to (1), taking into account (2) and our experience). A weighed portion (60 g) of carefully ground 1-phenyl-3-methylpyrazolone in a porcelain mortar (the technical product is first purified by recrystallization from a 5:1 mixture of water and ethanol) is dissolved in 300 ml of dioxane, and the solution is transferred to a three-necked flask fitted with a reflux condenser, thermometer, and stirrer. The solution is heated to 50° and, with vigorous stirring, 48 g of finely ground calcium oxide hydrate is introduced into the flask. Then, dropwise with stirring, 39.6 ml of benzoyl chloride is added over 1 min (the mixture warms up). The mixture is heated with a reflux condenser for 30 min, then cooled and poured into a large beaker containing 300 ml of methanol, 200 ml of hydrochloric acid, and 200 g of ice. The beaker is left overnight; then the precipitate that has formed is collected on a Büchner funnel and twice recrystallized from a mixture of ethanol and water.

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Note: Figure translations are in progress. See original paper for figures.