# PRILOG APPENDIX

## VIJESTI INFORMATION

## SYMPOSIUM

### Mechanism of Separation Processes in Radiochemistry

Under this title the I Polish — Yugoslav Symposium was held from October 17 to 21, 1963 in Herceg Novi in the Center for Personnel Training and Organization of International Conferences. The Symposium was sponsored by the Yugoslav Federal Nuclear Energy Commission and organized by M. Branica on behalf of the »Ruđer Bošković« Institute, Zagreb.

Participants of the Symposium from the

Institute for Nuclear Research Warsaw: R. Gwóźdź, S. Siekierski, A. Siuda, and W. Smulek;

The representative of the Yugoslav Federal Nuclear Energy Commission; Belgrade: D. Dobričanin;

Institute for Nuclear Sciences »Boris Kidrič«, Vinča: D. Cvjetičanin, I. Paligorić;

Nuclear Institute »Jožef Stefan«, Ljubljana: F. Krašovec, Š. Paljk and M. Senegačnik;

»Jugovinil«, Chemical Manufacturers, Split: V. Mitrović;

Institute »Ruđer Bošković«, Zagreb: H. Bilinski-Matošić, M. Branica, R. Despotović, H. Füredi, V. Jagodić, Lj. Jeftić, Z. Konrad, V. Pravdić, Z. Pučar and B. Tomažič; Secretary of the Symposium: L. Đačić

During five sessions the following topics have been discussed:

Session 1. *The Use of Partition Chromatography in Radiochemical Separations*
Session 2. *The Use of Electrophoresis in Radiochemical Separations*
Session 3. *The Structure of the Extractable Species and Their Interaction With Solvents*
Session 4. *Various Separation Methods in Radiochemistry*
Session 5. *Adsorption and Coagulation Phenomena*

The abstracts of papers appear in their order of presentation at the Symposium.

## ABSTRACTS

### 1.1 The Application of Various Extracting Agents in Reversed-Phase Partition Chromatography

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The reversed-phase partition chromatography, contrary to the ion-exchange method, allows the chemical properties of both the moving and stationary phases to be changed. The change in the properties of the stationary phase can be accomplished by adsorbing extracting agents of different chemical properties on an appropriate supporting material.

In the present paper a survey of the applications of various extracting agents to partition chromatography will be given. The extracting agents studied are:

1. Tri-*n*-butylphosphate
2. Tri-*n*-octylphosphine oxide
3. Di (2-ethylhexyl) phosphoric acid
4. 2-ethylhexylphenylphosphoric acid
5. Tri-*n*-octylamine

The advantages and drawbacks of the various systems are discussed and new application and development possibilities are suggested.

## 1.2. Chromatographic Separation of Rare Earths by means of Paper Treated with Di-*n*-butyl phosphate

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The chromatographic behaviour of rare earths was investigated on paper treated with di-*n*-butyl phosphate. Hydrochloric acid in a concentration of 0.2—10 *N* was used as the eluent. The relationships between the $R_f$ values and the molarity of the eluting agent and the atomic number of rare earths were investigated. The experimental results show the possibility of the separation of rare earths species from one another.

## 1.3. Factors Influencing the Work of an Amine Column

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Althout high molecular weight amines in organic diluent have been found to be efficient extractants for a wide variety of substances from aqueous solutions, their use in partition chromatography is not as yet very popular. The mechanism of extraction with amines shows a close analogy to the action of liquid anion exchangers. The resulting ammonium salt in the organic phase can exchange its anion $X^-$ for another anion $Z^-$.

$$R_3N_{(o)} + HX_{(aq)} \rightleftarrows R_3NHX_{(o)}$$

where HX is a mineral acid, R an alkyl or aryl radical.

The aim of the present work was to prepare an amine column having characteristics that would warrant its use in radiochemical separations. One of the main feature characterizing any column is the number of theoretical plates. The greater this number the higher the efficiency of the column.

It may be mentioned that as a rule values of 200 or more theoretical plates are required for rare earths separations. The numerical value of N, the number of theoretical plates, is given approximately by the formula of Matheson

$$N = \frac{2C\,(C + 1)}{W^2}$$

where W is the width of the elution at 1/e of the maximum, C is the number of column volumes to the peak of the activity curve, and e is equal to 2.718.

The stationary phase of the column was tri-*n*-octylamine on the kieselguhr *Hyflo Super Cell.* Hydrochloric acid was used as the mobile phase. To determine the free volume of the column $^{137}$Cs at a tracer concentration was applied. As a model for a number of metals, forming chloride complexes, Co(II) marked with $^{58}$Co at a tracer concentration has been used. The columns used in the course of the present work were of about 4 mm in diameter and contained 0.50 g of kieselguhr and usually 0.05 g. of tri-*n*-octylamine. The length of the bed was 100 mm. The packing of the bed was always the same. From the commercial kieselguhr 8 fractions have been separated by decantation and the medium fraction was used. Before use the kieselguhr was treated with dichlorodimethylsilane. The number of theoretical plates has been determined as a function of the following factors:

1. Concentration of the eluting agent (HCl);
2. Concentration of the amine in the column bed;
3. The effect of column length;
5. The effect of temperature;
6. The effect of flow rate;
7. The effect of grain size of the kieselguhr;
8. The effect of an additional extractant.

Optimal conditions for the amine column (about 600 theoretical plates) have been established. As an example of application of the column a satisfactory separation of Ni, Co and Fe has been carried out.

## 1.4. Partition Chromatography as a Method for Production of Some Radioisotopes

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At the early stages of the development of the reversed phase partition chromatography attention was paid mainly to the separation of radioelements in microamounts. In this paper a survey is made of new applications of this method to the separation of microamounts of some elements from milligram and even gram quantities of irradiated targets. The separation made included the following pairs of elements:

1. microamounts of Tb from macroamounts of Er in three systems: TBP — $HNO_3$, DBP — $HNO_3$, HDEHPA — $HNO_3$.
2. $^{45}$Ca from a scandium target in the TBP — HCl system.
3. $^{234}$Th from the natural uranium in the TBP — HCl system.
4. $^{77}$As from a germanium target (TBP — HCl).

In the above systems the partition coefficient of the microcomponent was lower than the one for the macrocomponent. Experiments were also carried out in which the situation was reversed. The following examples can be given:

1. $^{233}$Pa from a thorium target (TBP — HCl),
2. $^{199}$Au from a platinum target (TBP — HCl).

The possibility of separation of following other pairs is also discussed: Co — Fe, Sn — Sb, Bi — Po, Th — Fe, Nb — Mn. The relation between the mechanism of the extraction of the macrocomponent and the column capacity is also discussed.

## 2.1. General Introduction on the Use of Continuous Electrophoresis in Radiochemical Separations

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The continuous electrophoresis techniques have the advantage that during a separation process contamination of a slowly moving zone by a more rapidly moving one, through partial or reversible adsorption on the porous supporting medium, is avoided. The continuous electrophoresis ensures that each component separated moves along its own path, thus offering a simple method for achieving absolute separations. This is of decisive importance for the separation of carrier free tracers, where the smallest contamination can be the source of far reaching error.

Absolutely pure radionuclides or carrier-free radionuclides can be obtained by continuous electrophoretic separation using volatile or combustible background electrolytes, as the mobilities of simple inorganic ions and complexes obey individual laws in relatively large concentration ranges.

The movement of an electrically charged particle, which is considered to be reversibly adsorbed onto the supporting medium, can be expressed in continuous electrophoresis as the vectorial sum of the horizontal (or electrochromatographic) and the vertical (or chromatographic) components. For the sake of simplicity first the horizontal movement of an unadsorbable particle is discussed, which can then be considered as a purely electrophoretic component. The vertical or chromatographic component is discussed separately, and then the results are synthetized with the conclusion that the continuous electrophoretic process on an adsorptive, porous, supporting medium is a true electrophoretic process depending only on the electrokinetic mobilities, the adsorption on the supporting medium having no influence on the final result of separation.

During electrophoretic separations of inorganic ions in relatively high concentrations the ions which form the moving zone can to a considerable degree take part in the transport of electrical current across their moving boundaries. This would affect a change in concentrations and in the electrical field strength across their front- and rear moving boundaries. This results in various disturbances of the moving zones, and thus considerably impairs the electrophoretic separation. These problems are discussed in studying the mechanism of the transport of electrical current through concentration gradients in an electrolytic solution by application of the fundamental Kohlrausch regulating function, of Svenssonn's equation for the moving and standing boundaries, and of Pučar's electrophoregraphic equation, which gives the electrical field strenght in a moving zone.

## 2.2. Tracer Level Separations of Cyclotron Target Components by means of Continuous Electrophoresis

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Application of the continuous electrophoretic separation of cyclotron target components to the preparation of carrier free radionuclides was studied. The separation process consists of irradiation of the target in the cyclotron, dissolution of the irradiated target, and its electrophoretic separation. For this purpose the following tracer level separations were performed:

1. Na-Mg-Al to obtain $^{22}$Na and $^{26}$Al from a magnesium target,
2. Rb-Sr-Y to obtain $^{90}$Sr and $^{90}$Y from a rubidium target, $^{88}$Y from a strontium target and $^{90}$Y from $^{90}$Sr,
3. Cs-Ba to obtain $^{133}$Ba from a cesium target,
4. Mn-Fe to obtain $^{55}$Fe from a manganese target,
5. Fe-Mn-Co to obtain $^{54}$Mn and a mixture of $^{56}$Co, $^{57}$Co and $^{58}$Co from an iron target,
6. Pb-Bi-Tl to obtain $^{207}$Bi and $^{204}$Tl from a lead target, and
7. Cd-In to obtain $^{111,114}$In from a cadmium target .

Maximum separation capacity conditions for the above processes were investigated. It was possible to separate the whole cyclotron target within 10—12 hours.

## 2.3. Paper Chromatography and Paper Electrophoresis of Some Arsenic and Phosphorus Compounds

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In connection with some investigations on the radioactive chemical products formed due to nuclear transformations of arsenic and phosphorus in organic media, it was necessary to develop both paper chromatography and high-voltage electrophoresis techniques for separation and identification of several phenyl and inorganic derivatives of both these elements.

The following synthetic mixture of arsenic compounds has been investigated: triphenylarsine, diphenylarsine oxide, phenylarsine oxide, phenylarsonic acid, diphenylarsonic acid, arsenic acid and arsenous acid.

The paper chromatography applied was carried out by ascending technique, using strips of Whatman No. 3MM paper and a solvent mixture of ethyl acetate, pyridine and water (50:23:50).

The paper electrophoresis was made on strips of Whatman No. 3MM chromatographic paper soaked in 0.02 *M* ammonium carbonate at the potential gradient about 55 V/cm. .

The following mixture of phosphorus compounds has been separated: triphenylphosphine, triphenylphosphine oxide, phenylphosphonous acid, phenylphosphonic acid, diphenylphosphonic acid, orthophosphoric acid, pyrophosphoric acid, hypophosphoric acid, phosphorous acid, and hypophosphorous acid.

The paper chromatography was made by a similar technique as in the case of arsenic compounds. The solvent mixture consisted of *n*-propanol and 25% aqueous ammonia (100:50).

The paper electrophoresis was carried out using 0.5 *M* lactic acid as supporting electrolyte. The potential gradient was about 35 V/cm.

Detection of spots containing arsenic or phosphorus was achieved by neutron activation.

## 2.4. Continuous Electrophoretic Separation of Radioactive Rare Earths

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The electrophoretic behaviour of rare earths in 0.5 *N* lactic acid is investigated in view of their continuous separation. Relative electrophoretic mobilities of rare earths in lactic acid of the same concentration are determined. Accompanying diagrams give information about the possibility of continuous electrophoretic separations of all rare earths between the ordinal numbers 57 and 71. In the same electrolyte the rare earths complexibility increases with decreasing ionic radius.

The following continuous electrophoretic separations are described:

$^{144}$Ce — $^{160}$Tb — $^{170}$Tm
$^{144}$Ce — $^{152}$Eu — $^{169}$Y
$^{147}$Nd — $^{169}$Er — $^{177}$Lu
$^{144}$Ce — $^{153}$Gd — $^{177}$Lu
$^{144}$Ce — $^{147}$Pm — $^{160}$Tb — $^{169}$Er — $^{177}$Lu

Each figure containing experimental data consists of the radioautogram and of the corresponding diagram of the activity of separated mixture components.

The possibility of achieving continuous electrophoretic separation of a mixture of all rare earths, the possibility of applying the continuous electrophoretic separation of radioactive rare earths both to obtain carrier-free radionuclides, and in qualitative and quantitative radiometric analysis, is discussed.

## 2.5. The Application of Electrochemical Methods to Separation Processes in the light of Recent Developments

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Electrochemical (electrolysis) methods, although the oldest, classical, methods of separation of metals, alloys, or certain compounds as oxides from solutions, have been superseeded by electromigration methods in the past 20 years, the main reason being the simplicity of equipment and the possibility of varying the selectivity of these methods.

The development in the field of electrolysis methods employing electronically controlled equipment offers certain advantages in special cases. Consideration is to be given to methods of potentiostatic, galvanostatic and coulostatic methods of electrolysis control. Recent development offers standardized instrumental equipment. Application has so far been mostly in the field of analysis of solutions. However, the developed methods offer opportunities in a number of selective separations. This can be achieved either by changing the oxidation state of the ions, or the *p*H at the surface of the electrode. When combining this with either precipitation, adsorption or extraction in the following step, a number of positive applications is offered. The recent development of research work in this laboratory has been directed towards studying the possibility of uranium separation.

### 3.1.1. Factors Responsible for Complex Formation

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A general picture is given of a complex molecule. The influence of the metal ion on complex formation is discussed shortly. The role of the ligand is considered in more details. The types of ligands are summarised and attention is given to chelating agents.

To illustrate the use of experimental techniques in studying problems of such kind, as an example the study of europium(III) and terbium(III) derivatives of mono octyl anilino benzyl phosphoacid is given. These investigations are still in progress. Modern analytical methods and infrared spectroscopy have been applied and the data obtained are used to establish the way in which the unstoichiometric amount of the ligand is bound in the molecule, and to get more information about metal — ligand bonds inside the molecule.

### 3.1.2. Structure of the Extractable Species and their Interaction with Solvents. II.

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The standard free energy change accompanying an extraction reaction depends on many factors. Some of the most important are: the interaction between cation and water, the interaction between cation and the organic extracting agent (complex formation), the interaction between the complex and the molecules of the organic phase. The present part of this paper will be devoted to the last mentioned type of interaction and its role in the overall extraction process. The forces which are responsible for this type of interaction are: dispersion forces, dipole — dipole attraction and hydrogen bonding. These forces are, as a rule much weaker than those responsible for the formation of a chemical bond between a cation and an extracting agent, but nevertheless they substantially contribute to the observed value of the distribution ratio. Which of the three types of forces mentioned above will play the most important role depends on the structure of the extracted complex. Several kinds of methods can be applied to measure the type and energy of the interaction between the complex and the molecules of the organic phase:

1. *Optical methods.* These methods, especially studies of infrared spectra, are very important in revealing the presence of hydrogen bonds, but have a rather qualitative value.
2. *Determination of the solubility.* In this method the complex under study is prepared and its solubility in various solvents is determined. The solubility method gives quantitative results, but is restricted to a limited number of solvents.
3. *Extraction.* In this method the magnitude of interaction between a complex and surrounding molecules is calculated from the measured activity of the extracting agent and from the distribution ratio of the cation.
   The extraction method gives quantitative results and can be applied to any solvent.

A few experimental results which are available and some theoretical considerations lead to the following conclusions as to the interaction of the extracted species with the organic molecules:

1. *Simple molecules* such as $GeX_4$ ($X=Cl$, Br, I), $AsCl_3$, $SnI_4$, $OsO_4$ and $RuO_4$. For complexes of this type dispersion forces and, in part, dipole-dipole interactions are responsible for the interaction with the molecules of solvent. The interaction can be quantitatively described in terms of the solubility parameters of both the complex and the solvent.
2. *Chelate complexes.* Complexes of this type are generally highly symmetrical and non-polar. The dispersion forces are the chief mode of interaction. It was shown that, as in the case of simple molecules, the interaction of the chelate complexes with the solvent molecules can be described in terms of solubility

parameters. It seems also that hydrogen bonding between the molecules of the complexing agent in the inner coordination shell of the cation and the molecules of the solvent may be of importance in some cases.

3. *Solvated salts* e.g. $Eu(NO_3) \cdot 3TBP$. Complexes of this type are generally highly polar and their chief mode of interaction should be of the dipole-dipole type. The solubility parameter of such a complex is greater than about 10, and, as a consequence, the applicability of the Hildebrand equation is more difficult to prove than in the case of chelate complexes.
4. *Hydrated and solvated salts* e.g. $Eu(ClO_4)_3 \cdot nH_2O \cdot mTBP$. In this case the principal mode of interaction is through hydrogen bonds. The extracted cation retains part of its hydration water and the extracting agent is bonded in the second coordination shell. The affinity of the diluent towards water determines its influence on extraction.

### 3.2. Solvent Extraction and Separation of Europium(III) and Terbium(III) from Uranium(VI) by Monooctyl Anilino Benzyl Phosphonate

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The solvent extraction of europium(III) and terbium(III) with anilinobenzylphosphonate has been investigated in ligroin solution using radio nuclides $^{152}Eu$ and $^{160}Tb$.

The influence of the reagent concentration in organic phase, and of the $H^+$ ions concentration in aqueous phase, on the extraction of europium and terbium in the presence of chloride nitrate and sulphate anions is discussed. The metal-ligand ratio of the extractable species for europium and terbium are calculated graphically by plotting log distribution ratios versus log concentration of the reagent. Same complexes of europium and terbium with monooctyl anilinobenzyl phosphonate have been isolated and the metal-ligand ratio determined by radiometric analysis of metals. The separation of europium and terbium from uranium (VI) by monooctyl anilinobenzylphosphonate is also described. The separation coefficients for different concentrations of metals and reagent are of the order of $10^3$ to $10^4$. The possibility of reextraction of uranium, bond to monooctyl anilinobenzylphosphonate in ligroin solution, is discussed.

### 3.3. Influence of the Reagents Structure on the Extraction of Lanthanide Ions

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Several lanthanide ions were extracted from 1 *M* perchlorate aqueous phase with the solutions of different orthophosphoric acid esters in chloroform. The results indicate $MA_3(HA)_2$ to be the predominant metal species in the organic phase except in the case of aliphatic di-*n*-butylphosphate, where the complex $MA_3(HA)_3$ exists in the organic phase. The principal reaction occurring during the extraction of lanthanide ions with diarylphosphates may be written as:

$$M^{3+} + 2.5\, H_2A_{2\ \mathrm{org}} \rightleftarrows MA_3(HA)_{2\ \mathrm{org}} + 3\, H^+$$

The overall equilibrium constant $\varkappa$ of this reaction was calculated.

$$\varkappa = q\, [H^+]^3\, [H_2A_2]^{-2\cdot 5}_{\mathrm{org}}$$

It may be assumed that the principal reaction includes the folowing two steps:

$$M^{3+} + 3\, A^- \rightleftarrows MA_3$$
$$MA_3 + H_2A_{2\ \mathrm{org}} \rightleftarrows MA_3(HA)_{2\ \mathrm{org}}$$

If $\beta_3$ and $\lambda'_3$ are the equilibrium constants of these reactions, the knowledge of the dissociation ($K_a$), distribution ($K_d$) and dimerization ($K_2$) constants of the reagents enables to calculate the product $\lambda'_3\beta_3$ from the $\varkappa$ values.

$$\log \varkappa = \log \lambda'_3\beta_3 + 3 \log K_a - 3 \log K_d - 1.5 \log K_2$$

It was shown that the linear relationship

$$\log \lambda'_3\beta_3 = a + 4 \log K_d$$

exists between $\log \lambda'_3\beta_3$ and $\log K_d \cdot a$ is an empirical constant, characteristic for the individual lanthanide ion and can be obtained from the plot $\log \lambda'_3\beta_3$ against $\log K_d$.

Thus the overall equilibrium constant $\varkappa$ of the extraction reaction can be written as follows:

$$\log \varkappa = a + 3 \log K_a + \log K_d - 1.5 \log K_2$$

This equation enables to predict the value of the equilibrium constant $\varkappa$, *i.e.* the extraction ability for lanthanide ions of an arbitrary chosen diaryl phosphoris acid, supposing that its $K_a$, $K_d$ and $K_2$ are known.

The relationship between a and the inverted value of the ionic crystal radius is discussed.

### 3.4. The Influence of Diluent on Extraction of Europium with Dibutylphosphate (DBP)

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The extraction of europium with DBP can be represented by the following equations:

$$Eu^{+3}_{aq} + 3(DBP)_{d,o} \longrightarrow Eu \cdot 3(DBP)_{d,o} + 3H^{+}_{aq}$$

$$K = \frac{a_{c,o}\ a^3_{H,aq}}{a_{Eu,aq}\ a^3_{d,o}} = \frac{X_{c,o} \cdot f_{c,o} \cdot a^3_{H,aq}}{X_{Eu,aq}\ f_{Eu,aq} \cdot a^3_{d,o}}$$

at constant composition of the aqueous phase:

$$K = C \cdot D_{x,Eu} \cdot \frac{f}{a^3} \quad \text{or,} \quad D_{x,Eu} = \frac{I}{A}\ \frac{a^3 d,o}{fc,o}$$

where a is thermodynamic activity, x — mole fraction, d — dimer of DBP, $D_{x,Eu}$ — distribution ratio of Eu in mole fractions.

It follows from the last equation that the distribution ratio measured is a function of both the thermodynamic activity coefficient of the complex and the thermodynamic activtiy of DBP dimer in the organic phase. Both $f_{c,o}$ and $a_{d,o}$ depend on the diluent which generally is the main component of the organic phase. To study the influence of diluent on extraction with DBP, the same procedure was applied as in the case of TBP extraction. This includes the determination of the activity of the extracting agent and of the distribution ratio of europium. Using these two values, the activity coefficient of the complex can be calculated and thus the mode of interaction between the complex and diluent molecules revealed. In the present study the activity of 0.05 *M* DBP (total concentration) in 18 diluents was determined and the distribution ratio of europium in the same systems studied. The results can be summarised as follows.

1. Partition of DBP
   - 1.1. The dependence of the activity coefficient of the DBP dimer (calculated from the measured activity) on the solubility parameter of the diluent can approximately be represented by the equation $RT\ln f_{d,o} = V_d (\delta_d - \delta_o)^2$ where $V_d$ is molar volume of the dimer, $\delta_d$ and $\delta_o$ are solubility parameters of the dimer and diluent, respectively.
   - 1.2. The aliphatic hydrocarbons do not conform to the theoretical relation.
   - 1.3. The behaviour of $CHCl_3$ $C_2H_2Cl_4$, and to some extent of $CHBr_3$, is also exceptional. This can be explained by assuming hydrogen bond formation.
2. Partition of europium complex with DBP
   - 2.1. The activity coefficient of the complex ($f_{c,o}$) generally changes with the diluent as predicted by the theory of regular solutions.
   - 2.2. The aliphatic hydrocarbons, $CHCl_3$, $C_2H_2Cl_4$ and $CHBr_3$ behave exceptionally. These results indicate the possibility of hydrogen bond formation between the DBP dimer in the complex and the diluent molecules.

### 3.5. The Influence of Diluent on Extraction of $GeX_4$ Molecules (X=Cl, Br, I)

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Simple molecules such as $GeCl_4$, $GeBr_4$, $GeI_4$ can be extracted from concentrated solutions of halogen acids by inert solvents (aliphatic and aromatic hydrocarbons). Since the presence of the organic extracting agent is not necessary for extraction, the theory of regular solutions can be applied in a simple way. From this theory the following expression can be derived for the partition coefficient of $GeX_4$:

$$RT \ln k_x = V_c[(\delta_c - \delta_{aq})^2 - (\delta_c - \delta_o)^2] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad 1.$$

where $k_x$ is the partition coefficient defined as the ratio of molar fractions, $V_c$ — molar volume of $GeX_4$, $\delta$ — solubility parameter, c — complex ($GeX_4$), o — diluent (inert solvent), aq — water.

Choosing one of the diluents as a standard, one arrives at the following equation:

$$\ln \frac{k_x}{k_{x,s}} = \frac{V_c}{RT} [(\delta_c - \delta_s)^2 - (\delta_c - \delta_o)^2] \quad . \; . \; . \; . \; . \quad 2.$$

where s stands for »standard solvent«.
Equation (2) can be rearranged to obtain the following relation:

$$\frac{2.3\,RT}{\delta_o - \delta_s} \log \frac{k_s}{k_{x,s}} = - V_c\,(\delta_o + \delta_s) + 2\,V_c\,\delta_c \quad . \; . \; . \; . \quad 3.$$

From the plot of the left part of this equation against $(\delta_o + \delta_s)$, the values of $\delta_c$ and $V_c$ can be determined.

To check the applicability of theoretical predictions to the extraction of $GeX_4$ molecules, the distribution ratio of Ge between concentrated solutions of halogen acids and various inert solvents has been determined. The main results can be summarised as follows:

1. The logarithm of the distribution ratio of Ge from each halogen acid is a parabolic function of the solubility parameter of the solvent, as predicted by theory.
2. The values of $\delta_c$ and $V_c$ for $GeCl_4$, as determined from equation (3), are in good agreement with those determined by other methods. (7.9 and 8.1; 114 $cm^3$ and 115 $cm^3$).

### 3.6. Determination of Stability Constants of Metal Complexes by Different Polarographic Methods. Determination of Complexibility of Uranyl, Copper(II), Ferric, Lead(II) and Indium(III) Acetylacetonato Complexes

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Stability constants of uranyl, copper, ferric, lead and indium acetylacetonato complexes were determined by:

the shift of the half-wave potential,
the change in the diffusion current,
the change in the A.C. peak height,
the change in the S.W. peak height and
the influence of S.A.A. on the S.W. peak height in dependence on the free ligand concentration in the solution.

a) The shift of the polarographic half-wave potential with the change of the free ligand concentration was applied for the investigation of copper, lead and indium acetylacetonates which were reduced at D.M.E. to amalgam. The stability constants were calculated from the intersection points of two straight lines which were graphically obtained from the plot of $E_{1/2}$ *vs.* logarithm of the free ligand concentration.

b) Separated polarographic waves were obtained by the reduction of two ionic specia which are in sluggish equilibrium, and whose half-wave potential differs enough to form two well separated waves. The stability constants were calculated from the ratio of the corresponding diffusion currents. This method was applied in the investigation of ferric acetylacetonato complexes.

The stability constants were calculated from the distribution curve for the consecutive acetylacetonato complexes. Such curves could be obtained on the basis of different reversibility of the polarographic reduction, *i.e.* the specific A.C. and square-wave sensitivity, or directly from the A.C. or square-wave peak height, in the case when the consecutive complexes give separate peaks.

c) Stability constants for copper and indium acetylacetonato complexes were obtained by A.C. polarography.

d) By square-wave polarography the stability constants for uranyl and copper acetylacetonato complexes were obtained.

e) The influence of surface active agents on the S.W. polarographic peak height of uranyl acetylacetonato complexes was investigated. Tritone—X—100 decreased specifically the S.W. peak height of each uranyl acetylacetonato species, and form this depression the overall stability constant of uranyl acetylacetonato complexes was calculated.

### 3.7. Synergistic Effects in the Extraction of Rare Earths by Amines

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The extraction of some lanthanides from nitrate or nitrite solutions by mixtures of tri-*n*-octylamine with a number of other extractants (mono-dodecyl phosphoric acid, di-*n*-butyl phosphoric acid, tri-*n*-butyl phosphate) has been studied. The study revealed that some of the systems investigated (*e.g.* tri-*n*-ocylamine + mono-dodecyl phosphoric acid), under the experimental conditions, extract the lanthanides more efficiently than either constituent alone. The effect of the aqueous phase and its concentration on the extraction coefficient, as well as the probable mechanism of the extraction are discussed. The influence of diluent is also considered.

### 3.8. Studies of Some Intermolecudar Interactions by the Extraction Method

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During the extraction of iron(III) from hydrochloric acid solutions by a series of amines in various diluents the following equation was derived for the extraction coefficient:

$$k = A \cdot \frac{a}{y_c}$$

where: a is the thermodynamic activity of the extractant, $y_c$ is the molar activity coefficient of the complex and A is a constant for the aqueous phase of constant composition. Both a and $y_c$ may depend on the diluent used. Further, it was assumed that the extractant-diluent interaction is responsible for the value a , whereas the complex-diluent interaction accounts for the value $y_c$. This assumption is correct when dilute solutions are involved and the extractant--complex interaction is neglected. Three different kinds of interaction are assumed to take place in the above examples:

1. dipole-dipole interactions;
2. dispersion forces;
3. hydrogen bonding.

It can be said that when the interaction between the diluent and the extractant and the complex extracted is of similar kind and strength, k is roughly independent of the diluent. However, when different kinds of interaction are taking place, k is diluent dependent. Thus, by measuring k and a or $y_c$, the influence of diluent can be studied, supplying also some relevant data as to the kind of interactions involved. Information on the latter were derived from relations between k, a or $y_c$ and the dielectric constant, dipole moment and solubility parameter of the diluent. The general trend is: the stronger the interaction, the lower a and $y_c$. During this study k was determined by the usual extraction procedure described elsewhere and the thermodynamic activitiy, a, was determined by measuring the solubility of the extractant in the aqueous phase, using an indirect method with a standard diluent (chlorobenzene). Aromatic and aliphatic hydrocarbons and their derivatives (Cl, Br, $NO_2$) were used in the study.

Assuming that the complex extracted is an ion pair, $R_4N^+FeCl_4^-$, where $R_4N^+$ is the ammonium cation, from the results obtained the following conclusions can be drawn.

The tribenzylamine hydrochloride-diluent interaction is mainly of electrostatic nature. $a_{TBA \cdot HCl}$ is a function of the dielectric constant and the dipole moment for $2 < pH < 2.8$; $Zr_3(OH)_{10}^{+2}$ for

The tri-*n*-hexylamine and tri-*n*-octylamine hydrochlorides-diluent interaction is mainly through dispersion forces. $a_{THA \cdot HCl}$ is a function of the solubility parameter of the diluent.

All the amine hydrochlorides interact with chloroform or bromoform through hydrogen bonding. The hypothesis was put forward that this bond is through the chlorine atom, $R_3NHCl \ldots HCCl_3$. The thermodynamic activity is 1—3 orders of magnitude lower in chloroform than in, say, chlorobenzene — a diluent of similar physical parameters.

The complexes of tribenzylamine and tri -*n*-butyl amine, being highly polar ion pairs, interact with the diluent predominantly through dipole-dipole interactions. $y_c$ for both these amines is a function of the dipole moment of the diluent.

The complexes of tri-*n*-hexylamine and tri-*n*-octylamine interact with the diluent mainly through dispersion forces. The role of the latter increases with the length of the carbon chain of the amine, $y_c$ is a function of the solubility parameter of the diluent.

No hydrogen bond is formed between chloroform or bromoform and the complexes extracted with all the amines.

The complexes with a quarternary amine, tetra-*n*-butylammonium chloride, is also a highly polar ion pair, interacting with the diluent electrostatically. $y_c$ is a function of both the dielectric constant and the dipole moment of the diluent. Neither the amine salt nor the complex extracted form hydrogen bonds with chloroform.

The extraction experiments with a series of secondary amines (dibenzylamine, dihexylamine, dioctylamine, dodecylamine, dibenzylaniline and diethylamine) show the trend indicated for the tertiary amines. The interaction between chloroform and the amine hydrochlorides is still through hydrogen bonding but the difference in the numerical values of a for this diluent and chlorobenzene is less pronounced than in the case of tertiary amines.

The extraction of iron(III) from hydrobromic acid solutions revealed that between the amine hydrobromides and chloroform a strong interaction takes place, presumably through the bromine atom ($R_3NHBr \ldots HCCl_3$).

No hydrogen bonding with chloroform appears to take place in the system where the halogens were replaced by the nitrate ion.

Carbon tetrachloride shows a kind of interaction, especially with the polar complexes, *e.g.* with TBA. Induced dipole moments arising from the high polarizability of this diluent may be an important factor in this interaction.

## 4.1. Solubility of Thorium(IV), Zirconium(IV), Yttrium(III) and Rare Earths(III) Hydroxides and their Soluble Ionic Species in Equilibrium with the Solid Phase

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By tyndallometric and *p*H measurements the hydrolysis and precipitation of various metal hydroxides in aqeuous solutions at 20°C were investigated. The following systems were studied:

a) thorium nitrate — potassium hydroxide
b) zirconyl chloride — potassium hydroxide
c) zirconyl chloride — potassium hydroxide — 1 *M* sodium perchlorate
d) rare earth and yttrium nitrate — potassium hydroxide.

The solubility products of metal hydroxides and hydrolytic constants, from the solubility curves, were determined by using a simple graphical method. The predominant soluble hydrolytic species which is in equilibrium with the solid phase was directly evident from the slope of the solubility curve. The solubility curves were determined for a wide range of concentrations of both precipitating components.

a) The predominant ionic species in aqeuous solution in equilibrium with the solid phase $Th(OH)_4$ are: free ion $Th^{+4}$ for $pH < 3.4$; hydrolized ion $Th(OH)_2^{+2}$ for $3.4 < pH < 4.1$, and highly hydrolized polynuclear thorium ion species at $pH > 4.1$

b) The simplest predominant ionic species in equilibrium with the solid phase of $Zr(OH)_4$ are obtained as follows: hydrolized ion $Zr(OH)_2^{+2}$ for $pH < 2$; $Zr(OH)_3^+$ for $2 < pH < 2.8$; $Zr_3(OH)_{10}^{+2}$ for $2.8 < pH < 4.1$; and $Zr_4(OH)_{15}^+$ for $4.1 < pH < 7$. At *p*H higher than 7 the decreased precipitation of both thorium and zirconium hydroxide was noticed. It is considered to be the effect of the carbonate ions present in the solutions.

c) By adding 1 *M* sodium perchlorate, the solubility curve of zirconium hydroxide is slightly shifted toward the lower concentrations of zirconyl chloride, because of higher association in concentrated solutions.

The predominant species (in the simplest form) in equilibrium with the solid phase zirconium hydroxide are: $Zr(OH)_2^{2+}$ for $pH < 1.8$; $Zr(OH)_3^+$ for $1.8 < pH < 3.2$; $Zr_3(OH)_{10}^{+2}$ for $3.2 < pH < 4.6$; $Zr_4(OH)_{15}^+$ for $pH > 4.6$.

It seems that the predominant species of lanthanides in the solution in equilibrium with the solid phase is always a free unhydrolized ion $Ln^{+3}$.

From the obtained experimental data it is evident that the solubility product is constant only in a narrow concentration range of the precipitating components. This range depends directly upon the relative stability of the ionic species present in the solution.

### 4.2. Ion Exchange Separations of Radio-Cerium, Radio-Cesium, Radi-Strontium, Radio-Barium and Radium in Fall-out Analysis of Waters

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A description is given of four rapid ion exchange separations applied to:
1. determination of $^{137}Cs$ and $^{90}Sr$ in rain and cistern waters;
2. determination of $^{144}Ce$, $^{137}Cs$, $^{90}Sr$, $^{140}Ba$ and Ra in rain and cistern waters;
3. determination of $^{137}Cs$ and $^{90}Sr$ in surface and tap waters;
4. determination of $^{144}Ce$, $^{137}Cs$, $^{90}Sr$, $^{140}Ba$ and Ra in surface and tap waters.

After the addition of carriers (30 mg for Ce, Sr, Ba, 10 mg for Cs) the samples (volume 5—25 liters) are filtered. The sorption of samples (sorption rate 50—60 ml/min column) and the subsequent elutions (elution rate 5 m/min, column, the volumes of eluate fractions of separated radio-elements vary from 350—650 ml) have been caried out on a column of special shape, filled with 110 ml of Dowex 4, X-8, 50—100 mesh in $NH_4^+$-form.

The following elutrients have been used:

Procedure 1: Cs + Ca are eluted with 0.6 *M* ammonium glycolate, *p*H 5
Sr is eluted with 1 *M* ammonium glycolate, *p*H 5
Procedure 2: Ce and Cs + Ca are separated with 0.6 *M* ammonium glycolate, *p*H 5
Sr, Ba and Ra are separated with 0.15 *M* ammonium citrate, *p*H 7.5
Procedure 3: Cs + Ca are eluted with 1 *M* ammonium lactate, *p*H 7.5
Sr is eluted with 2 *M* ammonium lactate, *p*H 7.5
Procedure 4: Ce and Cs + Ca are separated with 1 *M* ammonium lactate, *p*H 7.5
Sr, Ba and Ra are separated with 0.15 *M* ammonium citrate, *p*H 7.5

The radio-nuclides are isolated from the respective eluates as follows:

Ce is precipitated from eluate as cerium perhydroxide, oxidized to Ce(IV) in 10 $M$ $HNO_3$ and separated from accompanying rare earth fission products by extraction with 0.1 $M$ DBP solution in $n$-hexane and finally converted to $CeO_2$.

Cs is coprecipitated with ammonium hexacobaltinitrite, separated from $NH_4^+$, K and Rb by precipitation with silicotungstic acid and isolated as cesium dipicrylaminate.

Sr is precipitated from ammonium glycolate or ammonium lactate eluate by ammonium carbonate and then determined by somewhat modified standard procedures.

Ba (Sr in procedures 2,4). The eluate is first acidified to $pH$ 1—2,, then Ba (Sr) is readsorbed on a smaller column (h = 15 mm) containing about 3 ml of Dowex 50, X-8, 50—100 mesh, $NH_4^+$ form. After the elution with 6$M$ HCl Ba (Sr) is determined by modified standard procedures.

Ra is coprecipitated with $BaSO_4$ from slightly acidified eluate and then purified by the standard method.

Radiochemical yields are about 95%, the decontamination factors for most important long lived fission products are in all cases greater than $10^3$.

## 4.3. The Separation of Radionuclides on Zirconium-pyrophosphate

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The distribution coefficients of $Pu^{3+}$, $Pu^{4+}$, $PuO_2^{2+}$, $UO_2^{2+}$, $^{234}Th^{4+}$, $^{95}Zr$, $^{95}Nb$, $^{106}Ru$, $^{144}Ce^{3+}$, $^{90}Sr^{2+}$ and $^{137}Cs^+$ were determined in the system zirconium pyrophosphate--aqueous solution of $HNO_3$. From the distribution coefficients, it can be concluded that some of them can be separated. This was confirmed on small zirconium pyrophosphate columns. The following radionuclides were separated: $UO_2^{2+}$ from $^{234}Th^{4+}$; $^{90}Sr^{2+}$ from $^{90}Y^{3+}$ and $^{137}Cs^+$; $Pu^{4+}$ from $UO_2^{2+}$, $^{144}Ce^{3+}$, $^{90}Sr^{2+}$, $^{137}Cs^+$, $^{106}Ru$, $^{95}Zr$ and $^{95}Nb$.

## 5.1. Adsorption of Ions from Aqueous Solutions on Metal Surfaces

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As a part of a long-term programme, studies have been carried out on the adsorption of ions from aqueous solutions on metal surfaces, as a function of $pH$, electrolyte concentration, chemical properties of ions and the nature of the metal surface. The adsorption of $^{131}I^-$, $^{35}S - SO_4^{2-}$, $^{32}P - PO_4^{3-}$, $^{60}Co^{2+}$, $^{65}Zn^{2+}$ and $^{137}Cs^+$ ions on gold, platinum, stainless steel, tin, copper, aluminium, zinc, lead, perspex and glass surfaces was studied. As a complementary investigation, adsorption of $H^+$ and $OH^-$ ions on aluminium, nickel, iron and their oxides was also carried out, again as a function of $pH$, solution concentration and the nature of electrolyte.

The result of these investigations have shown that there are three different processes of adsorption on metals and on oxide covered metal surfaces:

a) the primary, potential-determining adsorption of $H^+$ and $OH^-$ ions which gives rise to the Stern layer of the electrical double layer. The adsorption of $H^+$ ions is high in the low $pH$ region and is decreasing with rising $pH$; the adsorption of $OH^-$ ions, on the contrary, is low in the low $pH$ region and is rising with increasing $pH$. At a certain $pH$, which depends on the nature of the surface and the nature and the concentration of the electrolyte, the adsorption of $H^+$ ions is equal to that of the $OH^-$ ions; this is the isoelectrical point of the surface.

b) the primary, ion-exchange adsorption between the ions (anions and cations) present in the solution and the potential determining ions in the Stern layer. The primary adsorption of cations, as well as of the anions, is low in both the low and the high $pH$ region; it is rising on moving to the middle $pH$ region and attains its maximum in the vicinity of the isoelectrical point.

c) the secondary adsorption of the anions in the low $pH$ range and of the cations in the high $pH$ range give rise to the inner Helmholtz layer of the electrical

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* Presented by S. Siekierski

double layer; in the case when more than one species of ions is present in the solution, the secondary adsorption is an ion-exchange process. The exchange capacity of the surface is given, in the case of anion exchange, by the primary, potential-determining adsorption of the $H^+$ ions, and, in the case of cation exchange, by the potential-determining adsorption of the $OH^-$ ions. The secondary adsorption of anions is high in the low *p*H region and decreases with rising *p*H, whereas the cation secondary adsorption presents an inverse behaviour.

As a result, the real adsorption behaviour of a given surface in a given solution is a combination of these three processes, which are interrelated. An attempt of a more quantitative approach was made in the case of $H^+$ and $OH^-$ ions. The adsorption isotherms of these ion species were derived as Langmuir isotherms modified to take into account the influence of the anions and cations present in the solution on the adsorption of $H^+$ and $OH^-$ ions. The constants entering the adsorption isotherms were calculated.

### 5.2. Heterogeneous Exchange in Radionuclide Separation

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The process of heterogeneous exchange in the systems 'silver halide — halide ion' and 'silver halide — silver ion' was investigated. Some characteristic factors influencing the final equilibrium conditions as well as the kinetics of the process were established.

The influence of the age of the precipitate, of the concentration of the potential determining constituent ion and of the charge and concentratrion of counter ions on the kinetics of exchange were described. The $AgI — Ag^+$ system was found to be an exception because the exchange is not influenced by factors which otherwise influence the sign and magnitude of the electrokinetic tension. Contrary to the halide exchange, this exchange was observed on fresh and aged (three weeks) systems.

In general, after a critical aging time, the exchange cannot be observed. This process can be used for the separation of radionuclides if the precipitates are aged for less than the critical aging time.

The relation between the autodiffusion and the particle size was discussed. From the exchange kinetics information on the crystallographic modification and particle size of silver iodide could be obtained.

### 5.3. The Composition of Precipitates Formed in the Aqueous Systems: Uranyl nitrate — Potassium hydroxide — Potassium, Calcium, Strontium and Barium nitrate

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The precipitation of uranium(VI) in the systems: uranyl nitrate — potassium hydroxide — potassium (or calcium, strontium, barium) nitrate was investigated. The results showed that uranium was not precipitated at $20^0$ C and 24 hours after mixing in the form of uranyl hydroxide from uranyl nitrate — potassium hydroxide solutions, at *p*H higher than 5. It was proved that different uranates were formed and precipitated, in dependence on the *p*H value of the solution.

Different neutral electrolytes were added to optically clear systems prepared by mixing solutions of uranyl nitrate and potassium hydroxide with a final equinormal concentration of $2 \times 10^{-3}N$. The critical precipitation concentrations were determined by simple tyndallometric techniques. The results of analysis of precipitates (determined were: potassium, calcium, strontium, barium, and uranium) and the influence of the concentration of *neutral* electrolytes on the extent of precipitation of uranium(VI), were interpreted in terms of formation of sparingly soluble uranates.

NMR-spectra, at room temperature and at —$160^0$ C, showed the existence of hydroxyl groups and crystal water in the dried precipitates.

## 5.4. The Mechanism of Coprecipitation of Uranium(VI) from Aqueous Solutions of Uranyl nitrate, Sodium carbonate and Alkaline Earth chlorides

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By means of threedimensional precipitation diagrams the regions of coprecipitation of uranium(VI) from carbonate solutions with barium, strontium, calcium and magnesium chloride were located at constant concentration of $2 \times 10^{-3}N$ uranyl nitrate. The coprecipitation regions decrease in the following order of alkaline earths: $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$. The influence of the concentration of uranyl nitrate was investigated on the system uranyl nitrate — sodium carbonate — strontium chloride. The concentration region, within which more than 75% of uranium(VI) is coprecipitated with strontium carbonate was graphically represented by a threedimensional diagram. The concentration relations of the precipitating components in this region were defined by two simple expressions. The capacity of strontium and calcium carbonate expressed as g atom U/mole $MeCO_3$ was found to be a function of the precipitated quantity of $MeCO_3$. It was shown by means of electron micrographs that the presence of uranyl nitrate influences the aggregation degree of the particles of alkaline earth carbonates. The mechanism of coprecipitation of uranium(VI) with alkaline earth carbonates was interpreted in accordance with the above mentioned results and Težak's conceptions on occlusion phenomena.