# Radiochemistry for Neutron Activation Analysis


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# Objectives of this lecture

**Learn basic principles and approaches in radiochemical methods/procedures (pre-treatment, solubilisation, separation&pre-concentration, (co)precipitation, volatilisation, liquid-liquid extraction, ion exchange, and extraction chromatography) to improve measurement results obtained by NAA**

# OVERVIEW

- Introduction
- NAA optimisation
- Definitions
- Radiochemistry
  1. Pre-treatment
  2. Solubilisation
  3. Separation and pre-concentration
  4. Precipitation
  5. Volatilisation
  6. Solvent (liquid-liquid) extraction
  7. Ion exchange chromatography
  8. Extraction chromatography

# Main characteristics of NAA

1. Multi-element capability
2. Sensitivity for many elements
3. General good selectivity
4. No effects of the chemical binding of the analyte element
5. Absence/minimisation of the blank value
6. Relatively minor matrix effects
7. Ability to overcome inhomogeneities
8. Possibility to use carriers after irradiation
9. Good traceability
10. Special physical basis of the technique

# Competitive role of NAA

- **Independent technique for QC and metrology purposes**
- **Ultra-trace levels of As, Au, Co, Cr, Cs, Hg, Mn, Mo, Ni, Rb, REE, Sb, Sc, Se, Th, U, V**
- **Long-lived NORM or artificial RNs $^{53}$Mn, $^{99g}$Tc, $^{129}$I**
- **Combination with α- spectrometry for $^{238}$U, $^{232}$Th, $^{230}$Th, $^{237}$Np and $^{231}$Pa**

**The detection limit in units of mass fraction, $m_D$, is given by:**

$$m_D = \frac{L_D}{K}$$

**where $L_D$ is the detection limit expressed by the signal magnitude (e.g., a number of counts in γ-ray spectrometry) and $K$ is a calibration factor (a number of counts per mass unit) obtained in NAA by:**

$$K = \frac{N_A \theta_a \gamma_a}{M_a} SDC\left(G_{th}\phi_0\sigma_{0,a} + G_{e,a}\phi_e I_{0,a}(\alpha)\varepsilon_{\gamma,a}Y_a\right)$$

**The detection limit $m_D$ can be decreased both by increasing $K$ and decreasing $L_D$ (e.g., background due to matrix activities, such as $^{24}Na$, $^{42}K$, $^{82}Br$, $^{32}P$ in NAA of biological and environmental samples, interferences in γ-ray spectrometry, nuclear interference reactions, etc.) and by performing both.**

# Optimisation of NAA

1. Physical optimisation
2. Chemical optimisation (separation)
   a. After irradiation (blank-free, carriers, chemical yield, but: radiation burden, $T_{1/2}$)
   b. Prior to irradiation (no radiation burden, no time limitations, speciation, but: blank, risk of contamination, problems related to low concentrations and yield determination)

# Definitions

**Nuclear Chemistry:** The application of procedures and techniques common to chemistry to study the structure of the nucleus and to define the nature of the fundamental particles.

**Radiochemistry:** The application of the phenomenon of radioactive decay and techniques common to nuclear physics to solve problems in the field of chemistry.

**Radiochemistry:** The chemistry of radioactive substances.

# Definitions of the International Union of Pure and Applied Chemistry (IUPAC)

**Nuclear Chemistry:**

The part of chemistry which deals with the study of nuclei and nuclear reactions using chemical methods.

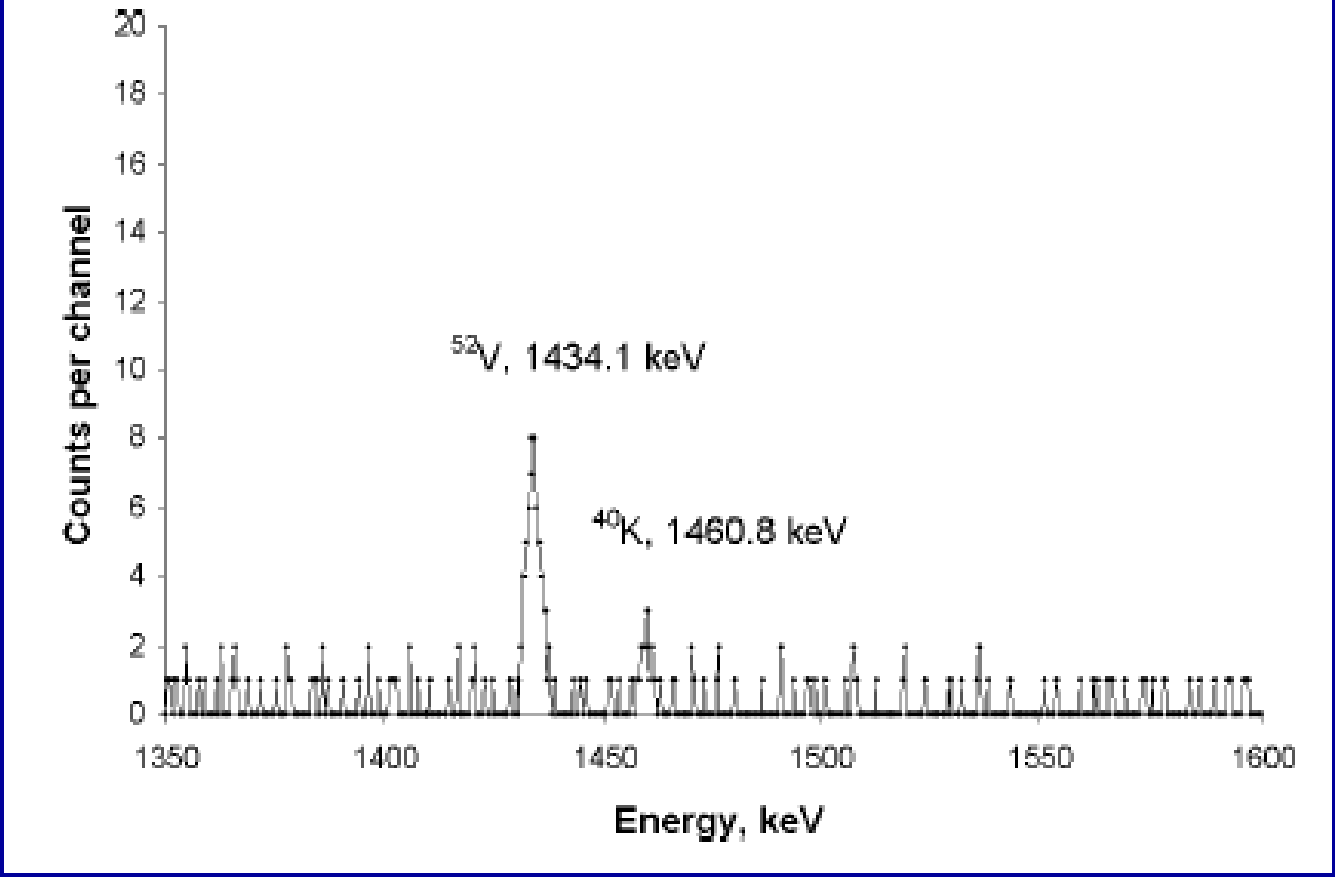
**Radiochemistry:**

That part of chemistry which deals with radioactive materials. It includes the production of radionuclides and their compounds by processing irradiated materials or naturally occuring radioactive materials, the application of chemical techniques to nuclear stdies, and the application of radioactivity to the investigatiion of chemical, biochemical or biomedical problems.

# Strategies of radiochemical separation

1. Element- and conc.- dependant
2. Simple to remove e.g. $^{24}Na$, $^{42}K$, $^{32}P$
3. Complex schemes for up to 40 elements
4. Combinations: INAA (ENAA) followed by CSC and RNAA for As, Cd, Hg, Sb; ENAA+RNAA for I; FNAA followed by CSC and RNAA for Si
5. Element difficult to analyse by other methods at low levels, e.g. V

250 mg of freeze-dried blood irradiated 12 min, wet-ashed in $H_2SO_4$+ $HNO_3$+$HclO_4$, V extracted with N-benzoylphenylhydroxylamine (N-BPHA) in toluene from HCl (total processing time 8 minutes), $^{52}V$ counted in 120 $cm^3$ HPGe well-type detector for 7 minutes.




Separated ~ 0.05 ng $cm^{-3}$ of V in blood

# Radiochemical procedure must allow for:

- The radionuclide of interest is isolated in high yield and with high purity
- The radionuclide of interest should be detected with as high efficiency as possible, considering also background
- Procedure should be applicable to a wide range of material types and radionuclide concentrations

# Pre-treatment of samples

**Pre-treatment is aimed at (1) removing organic constituents and convert samples into inorganic form and/or (2) as pre-concentration step. Frequently used approach is ashing:**

a. **Dry ashing (300 - 550 ºC) - losses**
b. **Wet ashing (mineral acids + oxidants)**

# Solubilisation

**Solubilisation is dissolution of a sample i.e., bringing it into a liquid form.**

1. **Total dissolution (quantitative): treatment with mineral acids (e.g. $HNO_3$, $HClO_4$, HF) or fusion with a suitable flux; Heated pressure vessels, microwave ovens; Alkaline fusion (800-1000 ºC) to eliminate losses of volatiles followed by acid dissolution of fused melt**
2. **Leaching (not necessarily quantitative)**


Thermolyne
Type 2200 Hot Plate

# Separation and preconcentration (1)

**Methods for separating substances utilise differences between the distribution coefficients of the individual constituents of a mixture between two phases.**

1. **Macro-micro separation: major constituent isolated, traces remain in the solution**
2. **Micro-macro separation: trace constituents isolated, major constituents retained in solution**
3. **Micro-micro separation: trace constituents separated from one another after isolation**

# Separation and preconcentration (2)

**Separation method is characterised by:**

- **Separation factors of the mixture constituents to be analysed**
- **Separation specificity or selectivity**
- **Rate of process**
- **Performance ease and equipment availability**
- **Suitability for isolated fraction treatment**
- **Coefficient of enrichment**

# Separation and preconcentration (3)

- Specific isolation of a single constituent from a mixture. Macro-micro separation or one trace element separation.
- Group separation of all trace elements.
- Masking of interfering constituents for complete specificity. Masking agent is substance, which reacts to form stable complex with interfering constituent.
- Contamination problems from (1) atmosphere, (2) laboratory vessels/containers, (3) reagents.

# (Co)precipitation (1)

**Precipitation is formation of a separable solid substance from a solution, either by converting the substance into an insoluble form or by changing the composition of the solvent to diminish the solubility of the substance in it.**

1. **Crystalline precipitate (nucleation, crystal growth, aging)**
2. **Colloidal precipitate: continuous transition from molecular particles to macroscopic aggregates.**
   a) **Hydrophilic (strong affinity to water, reluctant to flocculate, difficult to wash, hard to separate).**
   b) **Hydrophobic (low affinity for water, easy to flocculate by adding suitable electrolyte).**

# (Co)precipitation (2)

**Co-precipitation: incorporation of impurities into a precipitate by substances, which under experimental conditions are usually soluble in the liquid phase: trace constituents are precipitated together with a collector. Three mechanisms:**

1. **Mixed-crystal formation: substitution of ions in the crystal lattices of the carrier by co-precipitating ions. Ions may be about the same (true mixed crystals) or different size. Favoured at slow growth rate process.**
2. **Occlusion: mechanical entrapment of foreign ions at the surface of precipitate during rapid growth of crystals.**
3. **Adsorption: depends on the surface of the resulting precipitate.**

# (Co)precipitation (3)

## Application of (co)precipitation

- **Separation of major sample constituent by precipitation (macro-micro separation), i.e. for removing the major constituent of a sample without losses of trace constituents to be determined subsequently. Examples: Pb removal by HCl; AgCl removal; BiI removal.**
- **Co-precipitation of trace elements with inorganic collectors (group or single element). Collectors: sulphides, hydroxides, manganese dioxide, halides.**
- **Co-precipitation of trace elements with organic collectors. Two reagents are usually used: one forms complexes with the metal ions to be separated (chelating agent or a simple anion, e.g. thiocyanate, $Cl^-$, $Br^-$, $I^-$) which forms anionic complexes, and the other is an organic compound, which is sparingly soluble in water.**
- **Electro deposition: electrolysis, whether normal or "internal" is used for precipitation of components of a solution.**

# (Co)precipitation (4)

**Most frequently used precipitations**

- **$CO_3^{2-}$ and $PO_4^{3-}$ to preconcentrate target elements or to remove alkali metals – they remain in solution**
- **$Fe(OH)_3$ to preconcentrate target elements or to remove alkali and alkaline earth elements – they remain in solution**
- **$C_2O_4^{2-}$ to concentrate target elements or to remove alkali and alkaline earth elements – they remain in solution**
- **$LaF_3$ for tri- and tetravalent ions**
- **Dimethylglyoxime for Ni**
- **$SO_4^{2-}$ for Ra and Pb**
- **AgX for $Cl^-$ and $I^-$ separations**
- **Ammonium phosphomolybdate (AMP) and transition $[Fe(CN)_6]^{4-}$ to preconcentrate e. g., Cs**

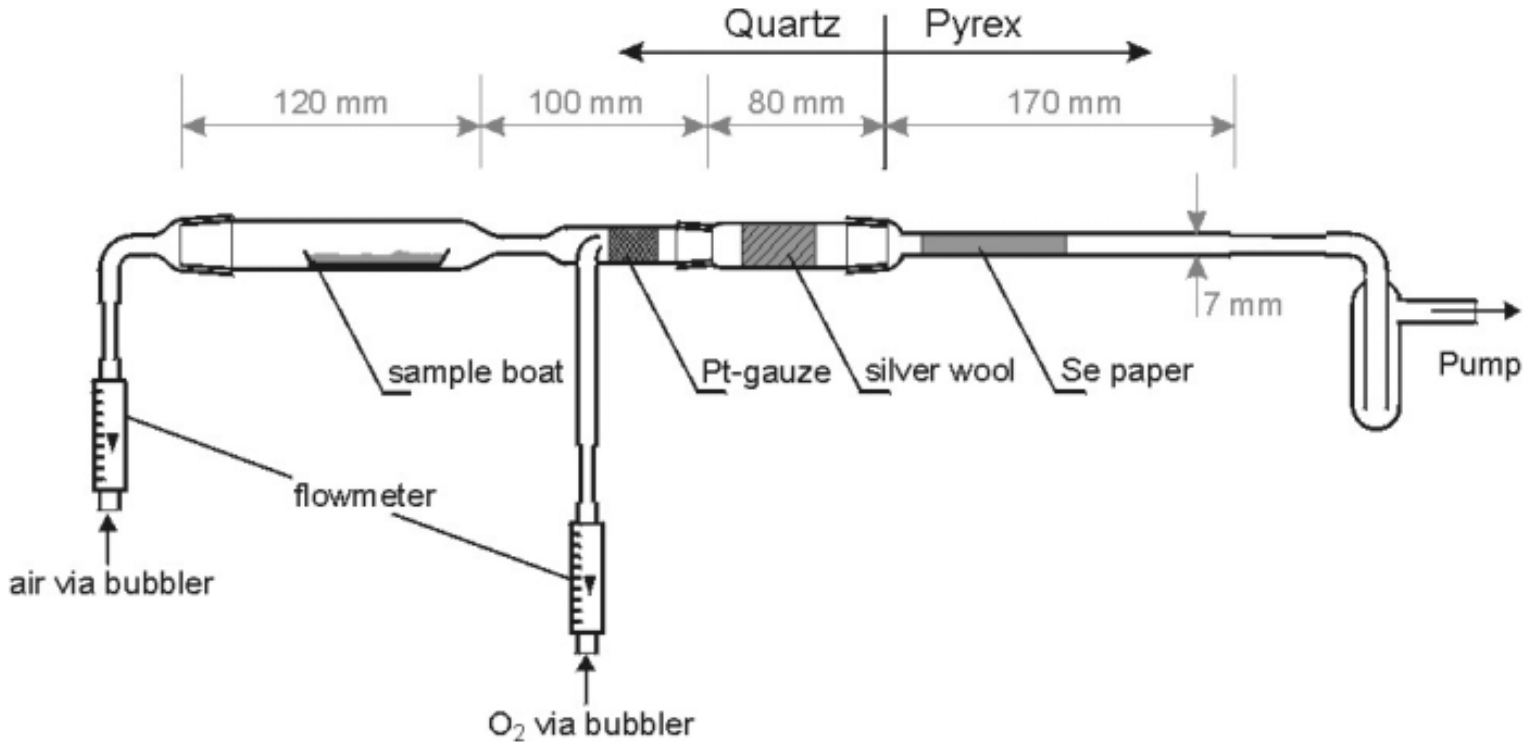
# Volatilisation (1)

**Matrix or trace constituents are separated, depending on which is more volatile. Typical example: impurities in water). There are two possibilities:**

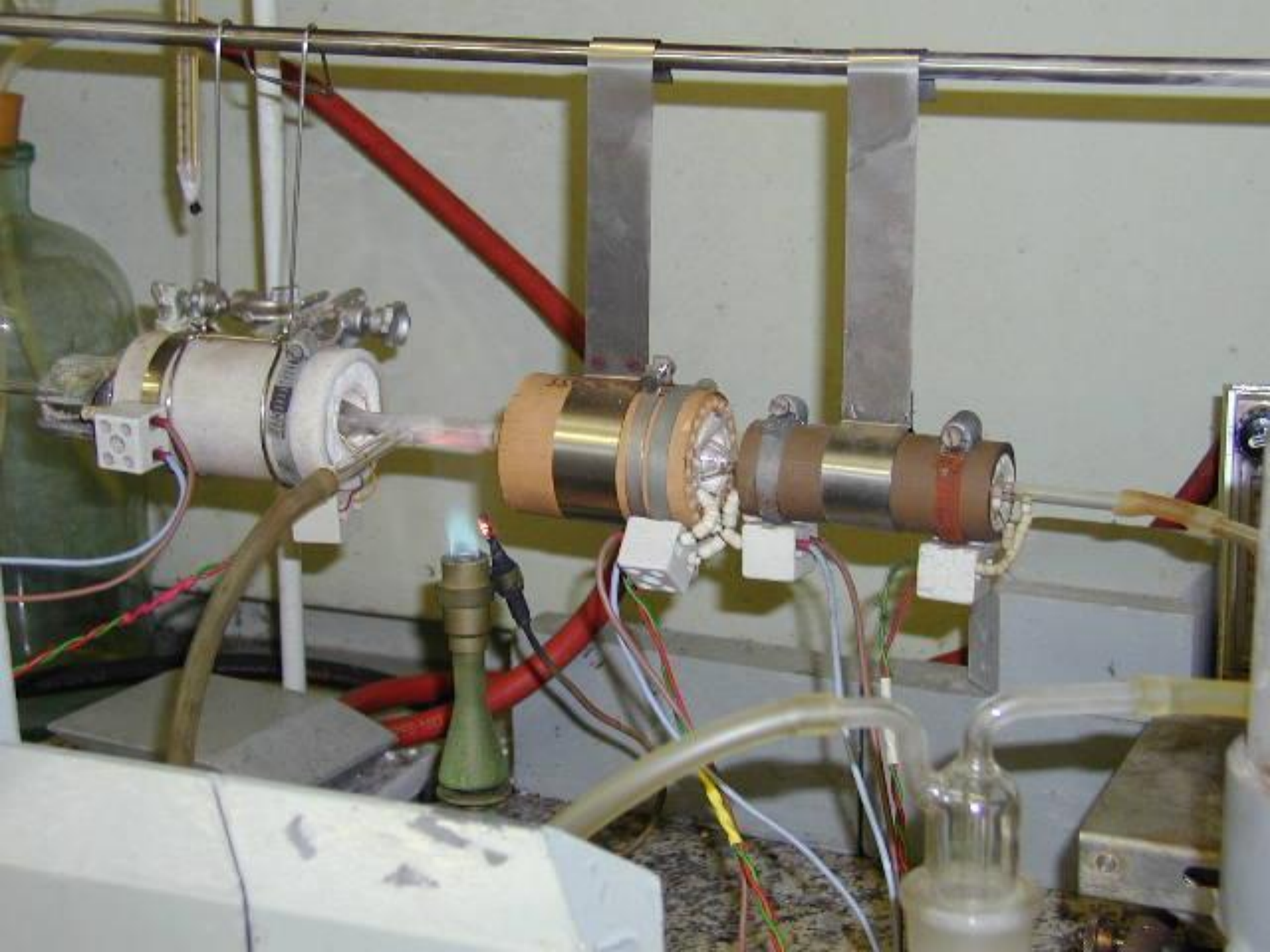
- **Direct distillation of one or more trace constituents from the sample.**
- **Conversion of the sample constituents into chemical species that can be separated by virtue of the difference in their volatilities (F, Cl, Br and hydrogen halides).**

# Volatilisation (2)

1. Direct distillation of sample matrix. For certain high-purity metals and volatile compounds. Zn, Cd, Se, and Na at 350-500 ºC. Hg selenide in a quartz beaker, at 400 ºC, the selenide sublimes completely, and the trace impurities remain intact in the beaker.
2. Distillation of the sample matrix. As, Cr, Ge, Os, Rh, Ru, Sb, and Sn can be distilled from solution as the chlorides or bromides.
3. Isolation of trace constituents. Elements are directly distilled and afterwards collected in a cooled receiver. As, Bi, Cd, Ge, Hg, In, Pb, Sb, Te, Tl in a stream of hydrogen at 1000 ºC. Volatile hydrides and halides can be distilled off.




# Isolation of Hg



# Volatilisation (3)

4. **Ashing of organic matrices. Determination of inorganic constituents in organic materials requires removal of the organic matter. The simplest way to remove organic matter is to ash or oxidise it. C and H are oxidised to $CO_2$ and $H_2O$, and organic N free $N_2$. Since all the products are gasses, ashing is considered as a method based on volatilisation. It should meet the following requirements:**
   - **Quantitative: all the organic matter should be oxidised and volatilised; all inorganic portion should remain.**
   - **Rapid: it affects time and cost of analysis.**
   - **Feasible: simple and inexpensive apparatus.**
   - **No trace constituent must be lost or introduced into the sample.**

# Solvent (liquid-liquid) extraction (1)

**This is a process of transferring a chemical compound from one liquid phase to a second liquid phase, immiscible with the first one. One phase is usually water and the other a suitable organic solvent. In terms of extractability, inorganic compounds may be classed into the two groups:**

1. **Compounds, which occur in the aqueous phase as undissociated covalent species, e.g. $I_2$, $Br_2$, halides of some metals, e.g. $AgCl_3$, $AsBr_3$, and some oxides, e.g. $OsO_4$.**
2. **Ionic compounds.**

# Solvent (liquid-liquid) extraction (2)

**Three main mechanisms for extraction of inorganic cations:**

1. **Chelate systems. Chelates are uncharged covalent compounds. Complexes of a metal ion with a multidentate ligand which occupies two or more co-ordination sites, and in which rings are formed. A stable ring is often formed when the ligand contains a charged group, which can form an electrovalent bond with the metal, and also an electron-donating group, which can form a covalent bond with the metal. Typical charged groups are –OH, –COOH, =NOH, =NH. Typical electron donating groups are (usually contain O, N, S) =O, –O–, –N=, =S.**

# Solvent (liquid-liquid) extraction (3)

2. Ion-association extraction systems. Systems in which the compounds extracted may be a variety of species; non-solvated co-ordination salts, solvated co-ordination salts and anion complexes are the most important in separation processes. An important group of ion-association compounds for separation processes are the anionic complexes. Such complexes are formed by certain transition metals with halide or pseudohalide ions (e.g. $CN^-$, $SCN^-$).
3. Simple molecules and compounds such as $I_2$ or $RuO_4$.

# Solvent (liquid-liquid) extraction (4)

**Two types of extraction systems:**

- **Species extracted are uncharged covalent compounds (e.g. chelates)**
- **Species extracted are electrovalent compounds (anionic complexes, ion pairs with amines, co-ordinatively solvated salts)**

# Solvent (liquid-liquid) extraction (5)

**Extraction separation has one of the following three aims:**

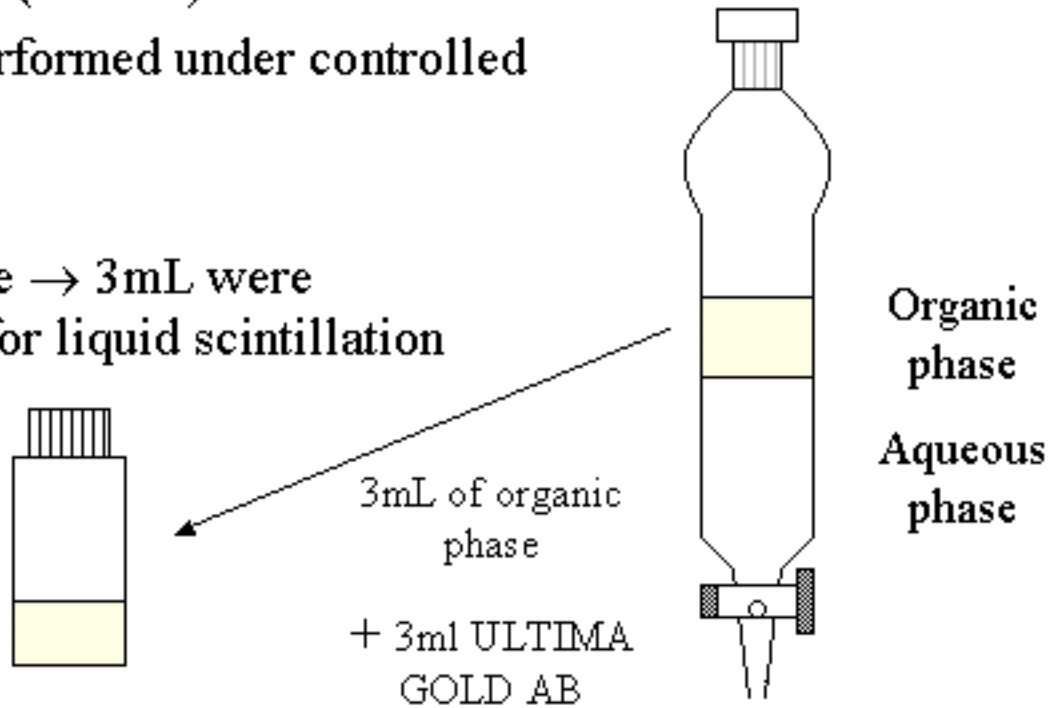
- **Extraction of the major component, to allow the impurities left in aqueous phase to be determined.**
- **Isolation of a group of elements which are to be determined.**
- **Selective isolation of a single element from the material to be analysed.**

# Extraction procedures and measurements

Extractions were performed:

- at room temperature using constant aqueous nitric acid composition (2mol/L)
- all extractions were performed under controlled conditions:

  10 min / 160min$^{-1}$
- 10 mL of organic phase → 3mL were transferred into a vial for liquid scintillation counting



# Theoretical separation model

Organophosphorous extractants:

TOPO - tri-n-octylphosphine oxide

HDEHP - bis-(2-ethylhexyl) hydrogen phosphate

DEDA- N,N-diethyldodecanamide

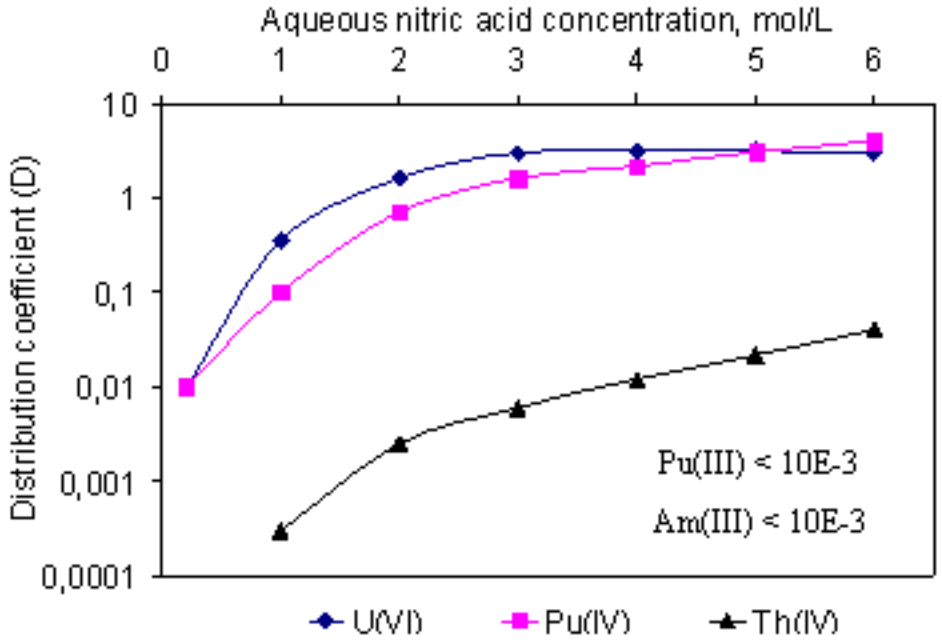



***Figure 1***: *Distribution coefficients as a function of initial aqueous nitric acid concentration for a 0.3 M DEDA solution in toluene*

# Separation scheme

Soil sample, leaching 8M $HNO_3$, filtration

drying, 2M $HNO_3$, $Al(NO_3)_3$

ascorbic acid 0.1g, $NaNO_2$

↓

extraction of U(VI), Pu(IV), 0.5M DEDA → aqueous phase Am(III)

organic phase ↓ + stripping of trace amounts of Th(IV), 6M HCl

stripping of U(VI), Pu(IV), 0.3M $HNO_3$ ↓

aqueous phase ↓ 2M $HNO_3$ extraction of Th(IV), 0.05M TOPO

ascorbic acid, extraction of U(VI), 0.05 TOPO pH adjustment

aqueous phase

organic phase LSC

organic phase LSC

aqueous phase $NaNO_2$

extraction of Am(IV) 0.3M TOPO

↓

extraction of Pu(IV), 0.1M HDEHP

organic phase ↓

LSC

organic phase LSC

# Neutron activation analysis

Determination of elements at trace levels by NAA can be performed via the induced $^{52}V$, $^{239}U$ and $^{56}Mn$:

$$^{51}V(n,\gamma)^{52}V(t_{1/2} = 3.75 \text{ min}) \rightarrow {}^{52}Cr \text{ (stable)}$$

$$\sigma = 4.88 \pm 0.04 \text{ b}$$

$$^{238}U(n,\gamma)\ ^{239}U\ (t_{1/2} = 23.5 \text{ min}) \rightarrow {}^{239}Np \rightarrow$$

$$\sigma = 2.70 \pm 0.02 \text{ b}$$

$$^{55}Mn(n,\gamma)\ ^{56}Mn\ (t_{1/2} = 2.58 \text{ h}) \rightarrow {}^{56}Fe \text{ (stable)}$$

$$\sigma = 13.3 \pm 0.2 \text{ b}$$

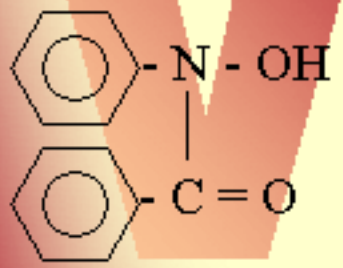
# Radiochemical NAA

- highly sensitive technique
- offers virtual freedom from blanks
- applicable to trace analysis using selective separations

## Separation procedures for V,U and Mn:

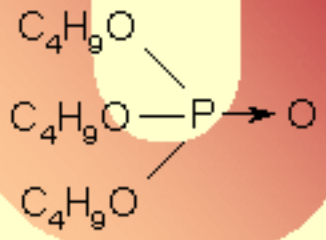
- formation of chelate complex

N-Benzoyl-N-Phenylhydroxylamine (BPHA)



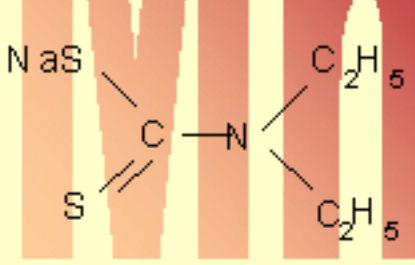

- formation of co-ordinatively solvated salts

tri-N-Butyl Phosphate (TBP)




-formation of sulphides

Sodium Diethyldithiocarbamate (Na-DDTC)



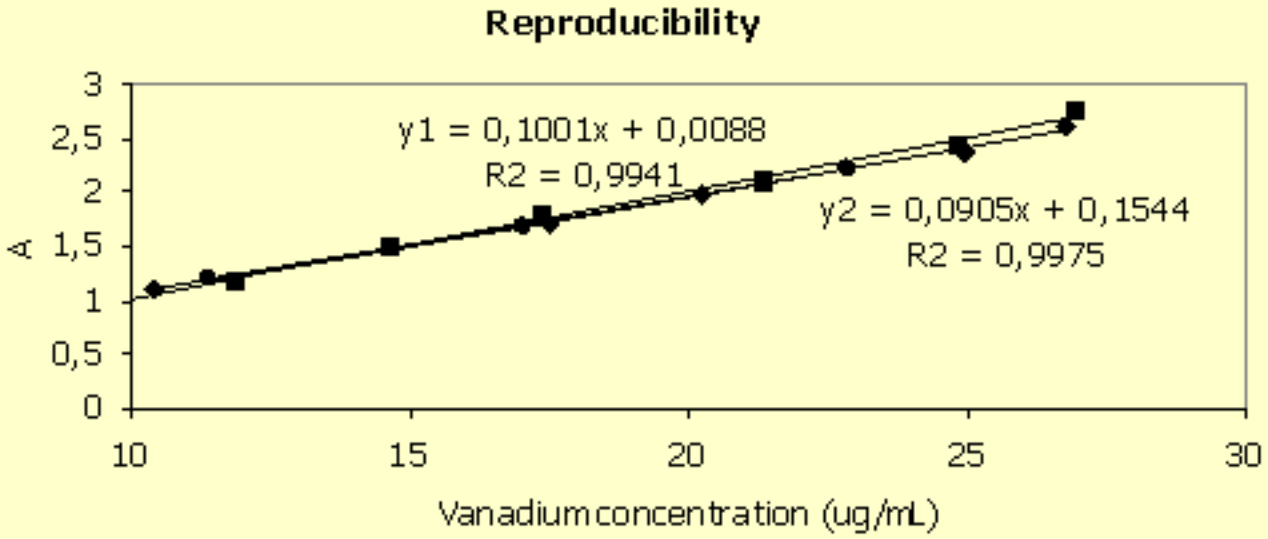
# Evaluation of the chemical yield

- **spectrophotometrically for vanadium**

  purplish-violet chelate V-BPHA complex

  ($\lambda_{max}$ = 525 nm, molar absorptivity = $5.1 \cdot 10^3$ )

V-BPHA/toluene
10 – 27 µgV/mL




- **isotopic tracer technique for uranium**

  $^{235}U$ from natural uranium carrier, $E_\gamma$ = 185.7 keV

## - isotopic tracer technique for manganese:

Irradiate $Fe_2O_3$ to induce:

$^{54}Fe(n,p)\ ^{54}Mn\ (t_{1/2} = 312.5\ d) \rightarrow\ ^{54}Cr$ (stable)

↓ cooling

dissolve in conc. HCl, evaporate, dissolve in 7 M HCl

↓ load on DOWEX 1X8, 50-100 mesh

retain Fe on anion-exchange column in 7 M HCl

↓

elute **$^{54}Mn$** with 7 M HCl

evaporate, add 2 mL conc. $HNO_3$, dilute with $H_2O$

1 g $^{54}Mn$ tracer (10 mL geometry, HPGE well)....10 cnt/s

# Sequental separation – V, U, Mn

sample (~ 0.25 g) + standards (V, U, Mn)

t (irrad.) = 4-10 min ↓ ∅ = 4 x $10^{12}$ n $cm^{-2}$ $s^{-1}$

add 100 μg of V-, 25 mg U- and 300 μg of Mn-carrier+ **Mn-54 tracer**

wet-ash irradiated sample ($H_2SO_4$, $HNO_3$)

add $HClO_4$, fume off

↓

~ 3 min

transfer to separatory funnel with 8 mL $H_2O$

add 3 mL 10 M HCl

6 mL BPHA reagent, shake for 5 s

aqueous phase → U, Mn

organic phase ↓

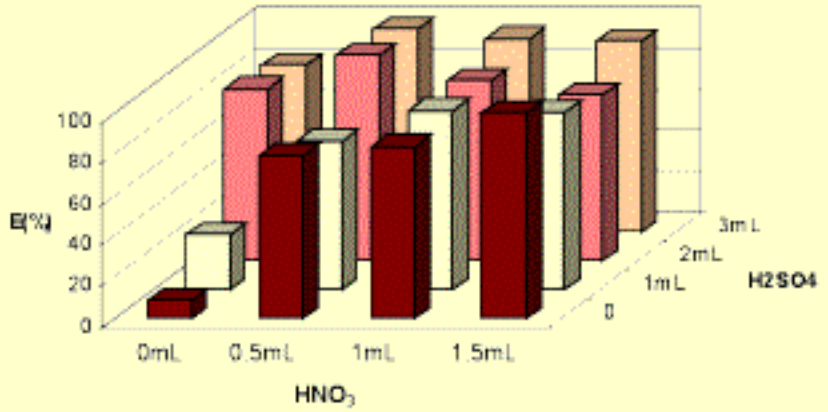
wash with 5 mL 5 M HCl

~ 6 min

pipette 5mL, **count $^{52}V$** → spectrophotometry

# Sequental separation – V, U, Mn (cont.)

add 2 mL of conc. $HNO_3$




add 5.5 mL of TBP/toluene
shake for 5 s

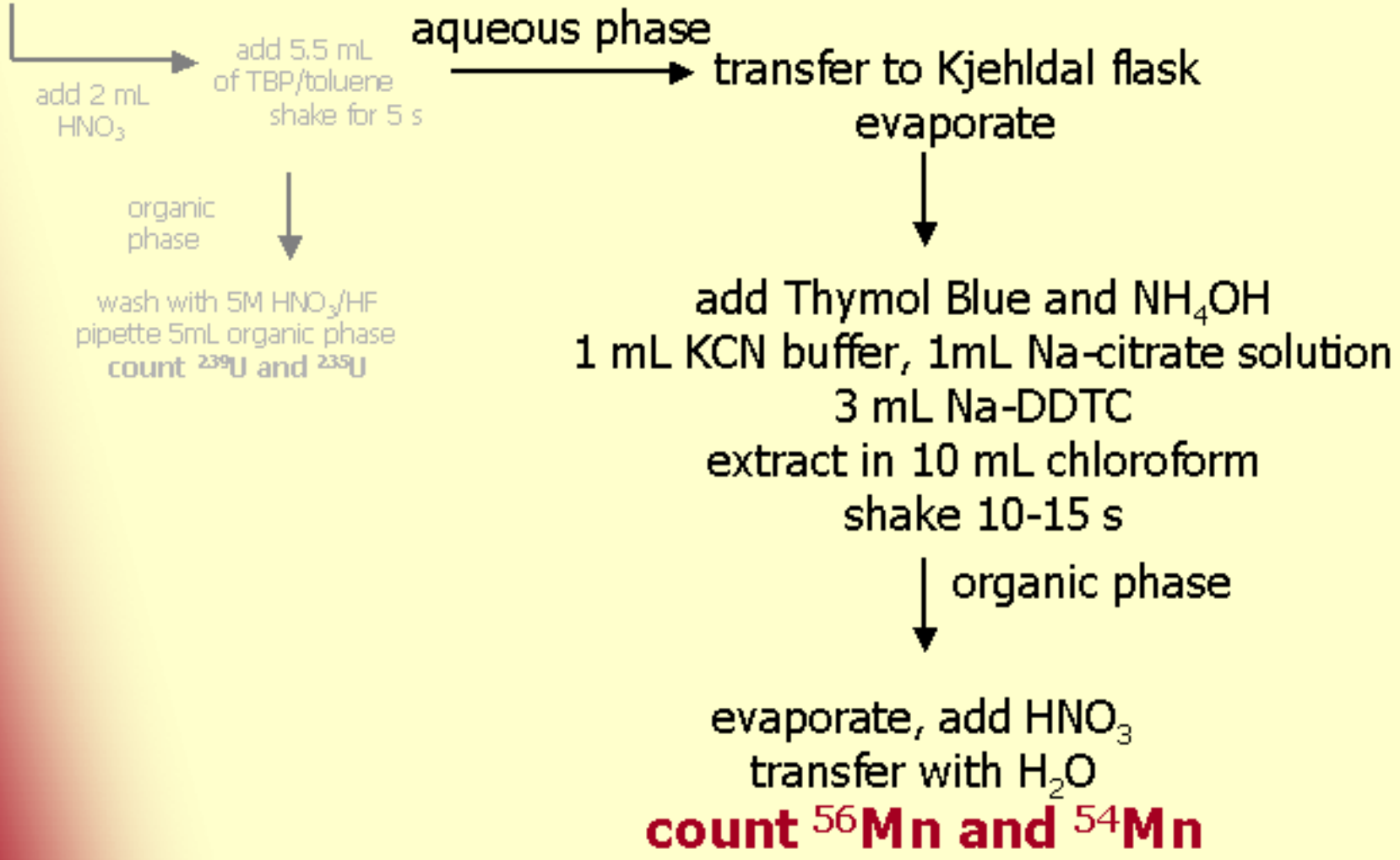
aqueous phase → Mn

organic phase

wash with 5 M $HNO_3$/HF
pipette 5 mL organic phase
**count $^{239}U$ and $^{235}U$**

~ 10 min

# Sequental separation – V, U, Mn (cont.)



# Ion exchange chromatography (1)

Ionic substances are separated on cationic or anionic sites of the packing. Charged substances are separated via column materials that carry an opposite charge. The sample ion will exchange with ions already on the ionogenic group of the packing. Ion-exchangers are insoluble solid materials, which contain exchangeable cations or anions. These ions can be exchanged for a stoichiometrically equivalent amount of other ions initially present in an electrolyte solution when an ion-exchanger is brought into contact with it. Substances containing exchangeable cations are called cation-exchangers and those containing exchangeable anions are called anion-exchangers.

# Ion exchange chromatography (2)

1. Inorganic ion exchangers: natural (clays, zeolite-type minerals, etc.) and synthetic (synthetic zeolites, molecular sieves, hydrous multivalent metal oxides, heteropoly acid salts, etc.) compounds. Zeolites are crystalline aluminosilicates with ion-exchange properties. Heteropoly-acid salts are e.g. molybdophosphates, molybdoarsenates, molybdosilicates, etc. Most widely used are the synthetic ion-exchange resins, which have as charge carriers ionogenic groups bonded to a framework (matrix) that is a three-dimensional network of hydrocarbon chains.

# Ion exchange chromatography (3)

## 2. Organic ion exchangers

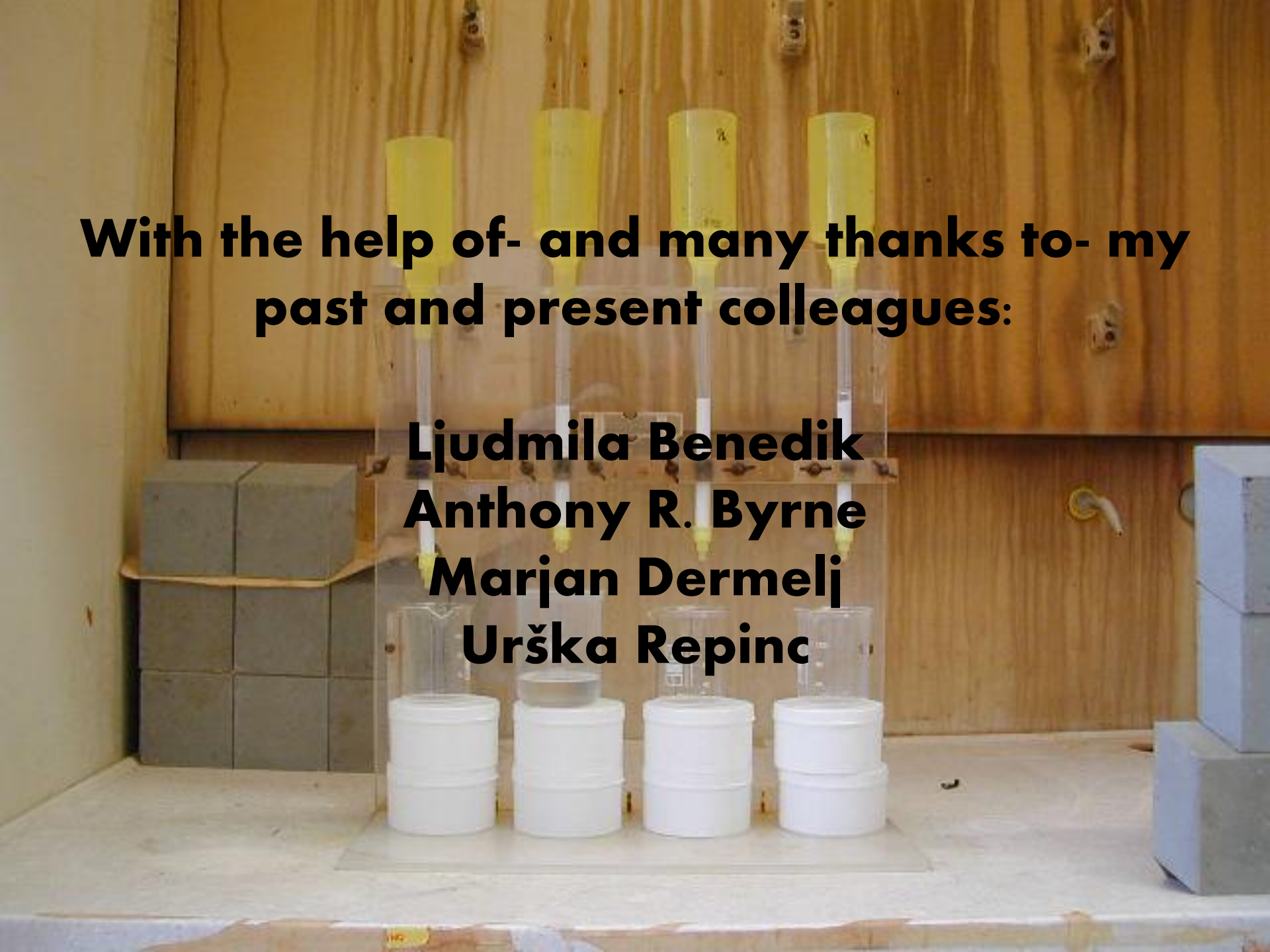
a) Synthetic cation exchangers are cross-linked polyelectrolytes, which consist of a three-dimensional network of hydrocarbon chains carrying groups such as sulphonate, carboxylate, phenolate, phosphonate, and others. The properties of an ion-exchanger depend on the nature and number of functional groups, the degree of ionisation, the type and extent of cross-linking in the matrix, and the configuration of the functional groups. Ion-exchangers are synthesised by condensation or polymerisation. Condensation type is e.g. obtained by sulphonation of phenol and subsequent condensartion with formaldehyde: Amberlite IR-100, Dowex-30. Polymerisation type is e.g. based on a styrene-divinyl-benzene copolymer: Dowex 50, Zerolit 225, Amberlite IR-120.

# Ion exchange chromatography (4)

b) Condensation-type anion exchange resins are prepared e.g. by condensing aromatic amines with formaldehyde or aliphatic polyamines with aldehydes. Polymer type anion exchange resins are mostly based on S-DVB (divinylbenzene) copolymers. Examples are Amberlite IRA-400, Dowex 1.

# Extraction chromatography (1)

The separation process is solvent extraction, carried out in a chromatographic column. Stationary phase is an extractant, which coats or is bonded to a porous hydrophobic support, and the mobile phase is a suitable solution of an acid, base or salt. As stationary phase supports serve silica gel or an organic polymer (Hostaflon, Teflon, etc). The most used extractants are tributyl phosphate, methyl isobutyl ketone, TOPO, crown ethers, etc. Samples are usually dissolved in nitric or hydrocloric acid. There are several commercial element-specific resins on the market.



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