

Microwave Acceleration of the Cloud Point Extraction Preconcentration Procedure

Determination of Rh, Pd and Pt by ICP-MS

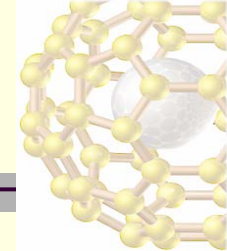


V. Stefanova, K. Simitchiev, V. Kmetov – Department of Analytical Chemistry, University of Plovdiv, Bulgaria

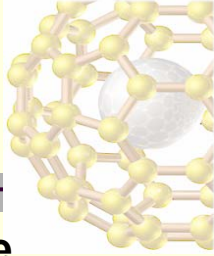


A. Canals -Departamento de Quimica Analitica, Nutricion y Bromatologia, University of Alicante, Spain

Lecture content

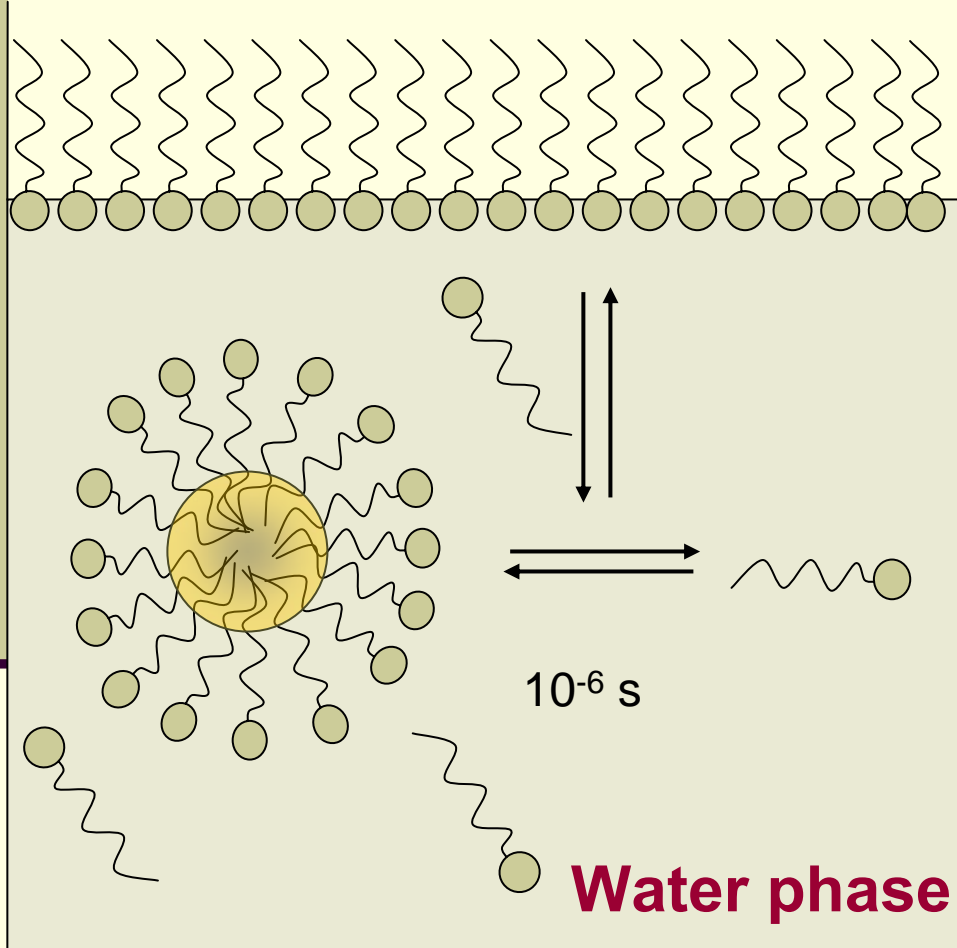


- **Why Cloud point extraction?**
- **Selection of the surfactant and appropriate ligands**
- **Optimisation of the experimental conditions**
- **Energy source – hot plate versus MW**
- **The influence of auxiliary reduction process on the rate of CPE**
- **Analysis of Pharmaceutical products**



Why Cloud point extraction

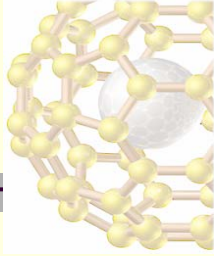
✓ The surfactant forms a mono-molecular layer on the surface and constitute **MICELLES** - oriented assemblies with hydrophilic shield and hydrophobic core.



✓ When a surfactant concentration exceeds **Critical Micellar Concentration** the thermodynamic equilibrium is established.

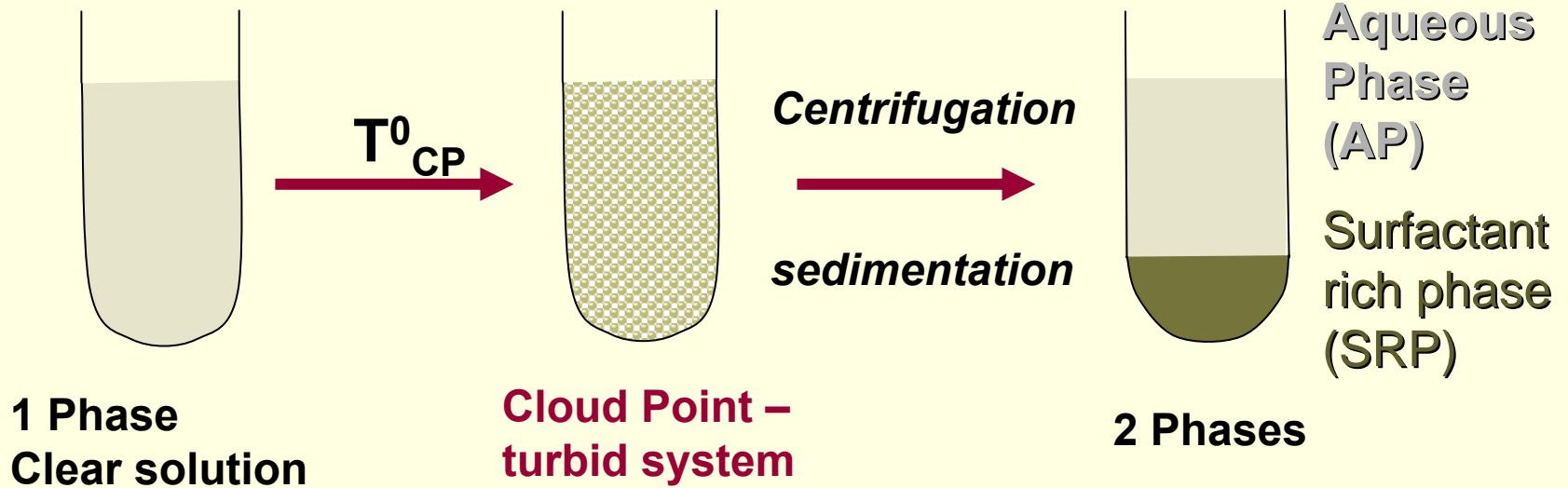
✓ The important result is that the micelle core provide **A NEW REACTION MEDIUM** with different properties in comparison to the bulk solution

✓ Into this micro medium the rates of chemical reactions and equilibrium constants as well as products formation can be altered

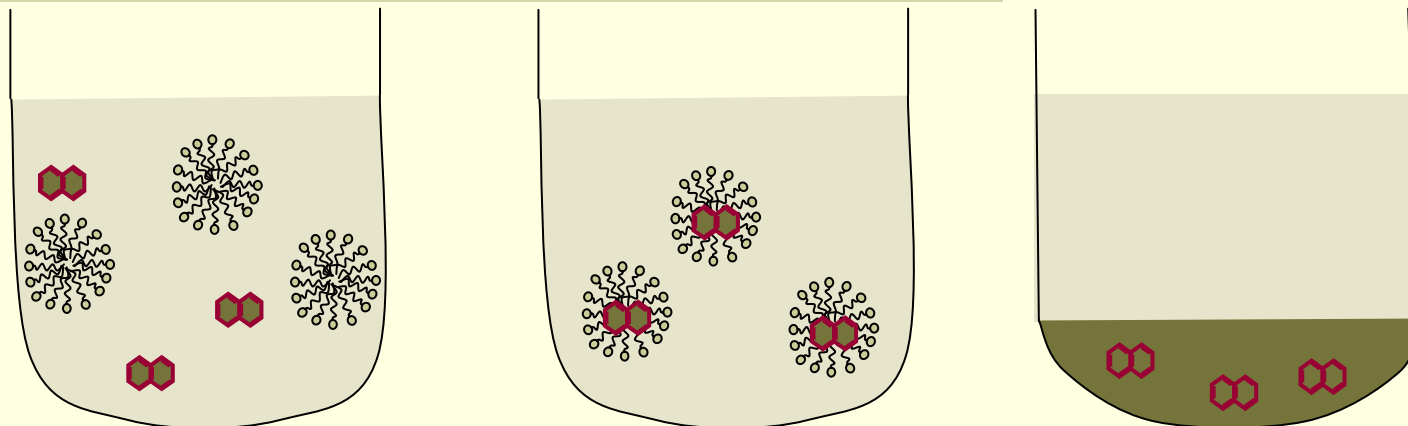


Cloud Point separation procedure

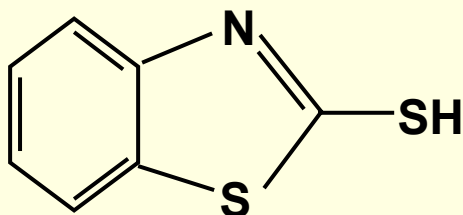
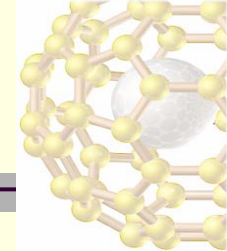
➤ Macroscopic view



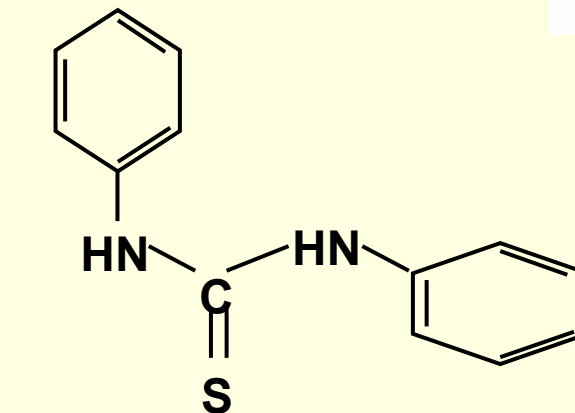
➤ Microscopic view



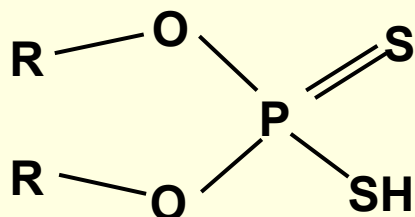
2. Selection of the ligands forming stable complexes with Rh, Pd and Pt



2-mercaptobenzothiazole
(2-MBT)



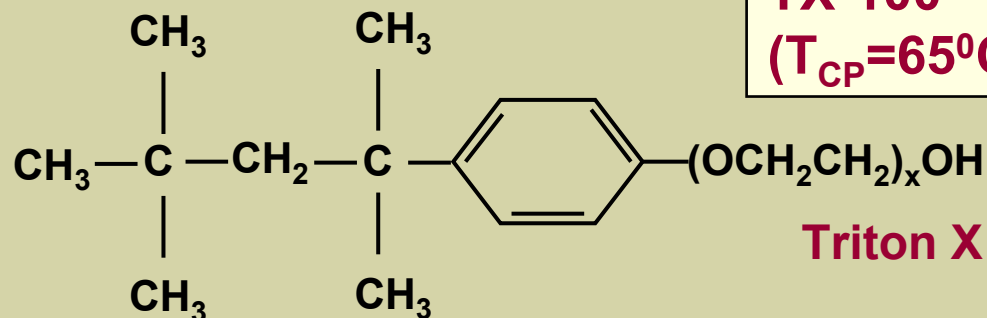
N,N'-diphenylthiourea
(NNDPTU)



O,O' – dialkyldithiophosphoric acid
(DDTP)

- ✓ The chloro-complexes of **Pd** are **labile**
- ✓ The chloro-complexes of **Rh** and **Pt** are **inert**

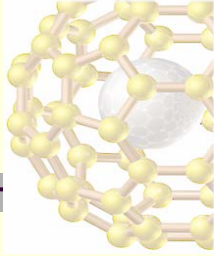
3. Selection of the surfactant



TX-100
($T_{CP}=65^{\circ}\text{C}$)

Triton X

Comparison between Cloud Point Extraction (CPE) and liquid-liquid extraction



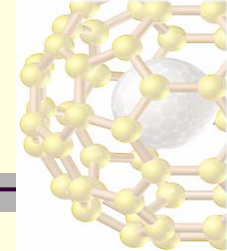
➤ Advantages of CPE:

- ✓ High preconcentration factors (10-100) could be obtained, using a small amount of initial solution (< 50 ml)
- ✓ Safety and low cost analysis
- ✓ Simplicity and feasibility of the extraction procedure
- ✓ **Compatibility of the SRP with ICP**

➤ Disadvantages of CPE:

- ✓ Complicated and unclear mechanism of CPE
- ✓ **Achieved SRP is with high viscosity. It must be diluted before further analysis**

Experimental



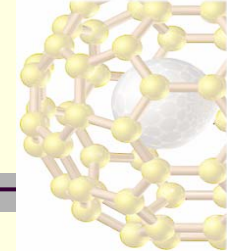
- **All measurements were accomplished with:**
 - ✓ *Perkin-Elmer SCIEX ELAN 500 inductively coupled plasma mass-spectrometer, upgraded with ELAN 5000 software.*
 - ✓ *Thermo PQ-ExCell*

- **Cloud point extraction was performed by:**
 - ✓ *Hot plate with an water bath (HP-CPE)*
 - ✓ *CEM MDS-81D (600 W) system was used for microwave-assisted cloud point extraction (MW-CPE)*

- **CPE was carried out with model solutions of platinum group metals (PGM) in hydrochloric media**

- **The degree of extraction (R%) of was calculated by measuring of the residual PGM concentration in water phase after separation form the SRP**

Cloud Point Extraction - *Hot Plate* versus *MW*



➤ The extraction of **Rh (III)**, **Pd (II)**, **Pt (II)** and **Pt (IV)** in HCl was studied

➤ Surfactant – **Triton X-100** 1% or 0,5% m/v

TX-100 was introduced in the extraction system before organic ligand

➤ Three organic ligands were tested (**2-MBT**; **NNDPTU**; **DDTP**)

➤ The following variables were optimised:

A) Related to the main chemical reaction

✓ **Acidity of water phase**

✓ **Excess of the ligand**

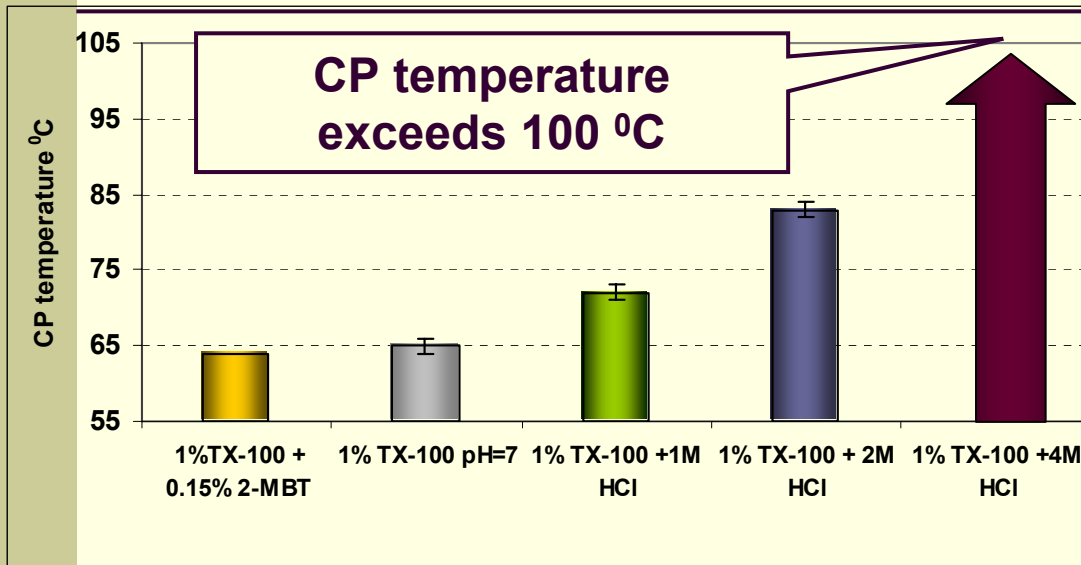
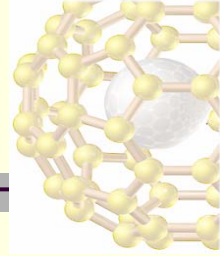
B) Dependent on the energy transfer to the system

✓ **Time for incubation after cloud point temperature is obtained**

✓ **Chemical reduction of the analyte**

Optimisation of the CPE procedure:

✓ *Acidity of the water phase and T_{CP}*



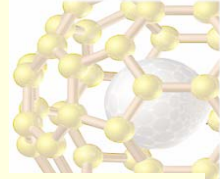
Cloud point temperature depends on:

- **Structure, properties and concentration of the surfactant**
- **Concomitant polar compounds in the bulk solution**

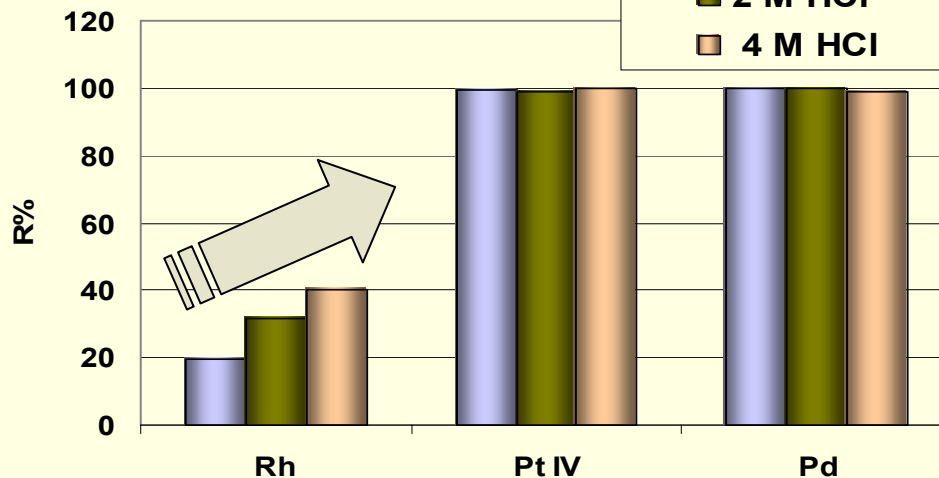
Fig. 1 Influence of the additive reagents (HCl and 2-MBT) on the Cloud point temperature of 1 % Triton X-100 solution

- **The Hot Plate Cloud point extraction procedure was performed in a thermostated at 95°C water bath**
- **Microwave-assisted CPE procedure was developed:**
 - ✓ *6 samples – each with volume 40 ml placed in an external container with 70 ml H₂O*
 - ✓ *maximum power (600W) for 5 min*
 - ✓ *350W for additional incubation and phase separation*

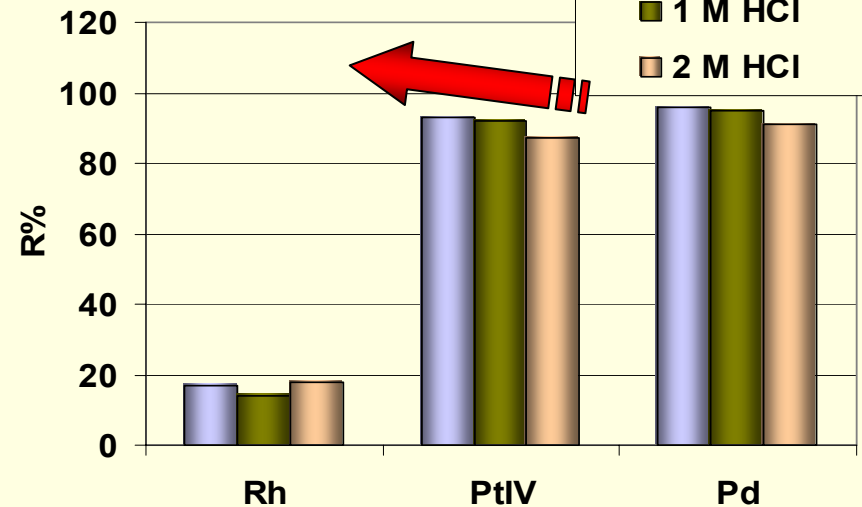
✓ *The influence of HCl concentration on the CP-extraction degree (R%) of Rh, Pt IV and Pd*



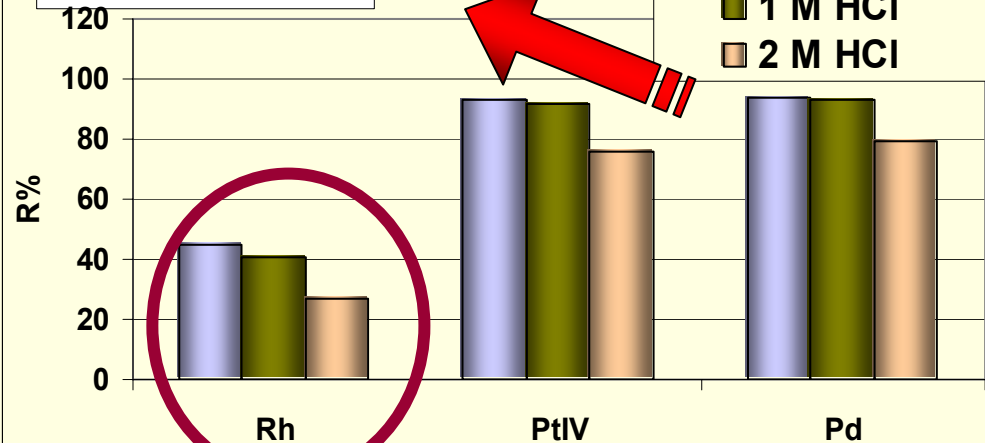
A) 2-MBT (1000/1)



B) NNDPTU (1000/1)



C) DDTP (1000/1)



- **Quantitative CPE of Pd and Pt with 2-MBT is obtained with**
- **For NNDPTU and DDTP the low acid concentration is preferable**
- **PE extraction of Rh seems to be the most problematic**

✓ Excess of the ligand needed for CPE

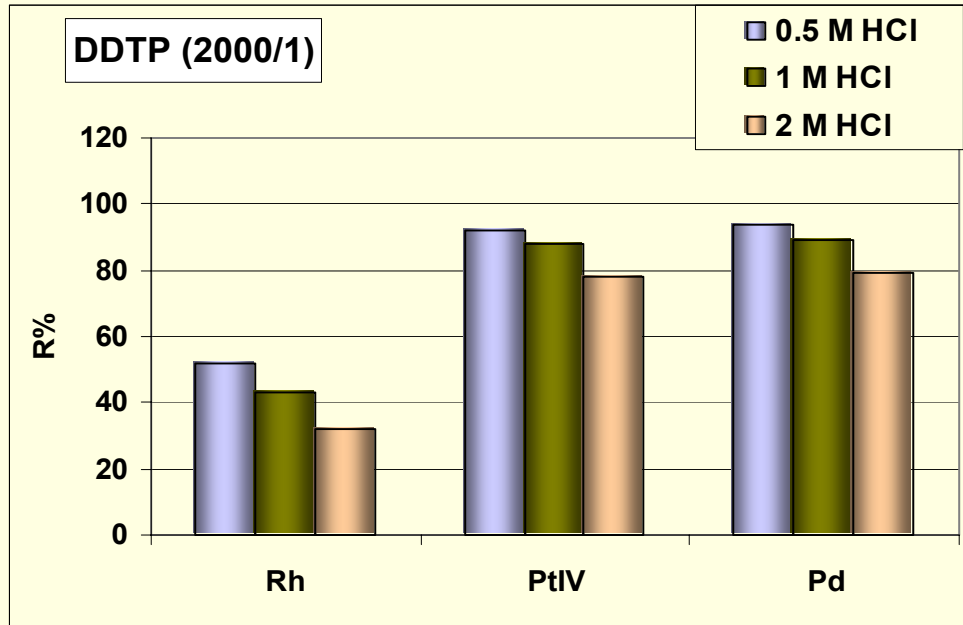
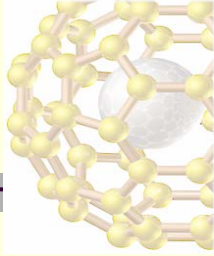


Fig.3. Influence of the excess of the DDTP on the extraction degree (R%) of Rh, Pd and Pt (MW-CPE, 30 min)

- Only for DDTP the weak effect on the extraction degree was observed
- The extraction of Rh is still **very low** (<55%)

LET THE ENERGY, TIME and auxiliary CHEMICAL REDUCTION to HELP!

Pd – CPE

✓ Incubation time and reducing agents (KI or SnCl₂)

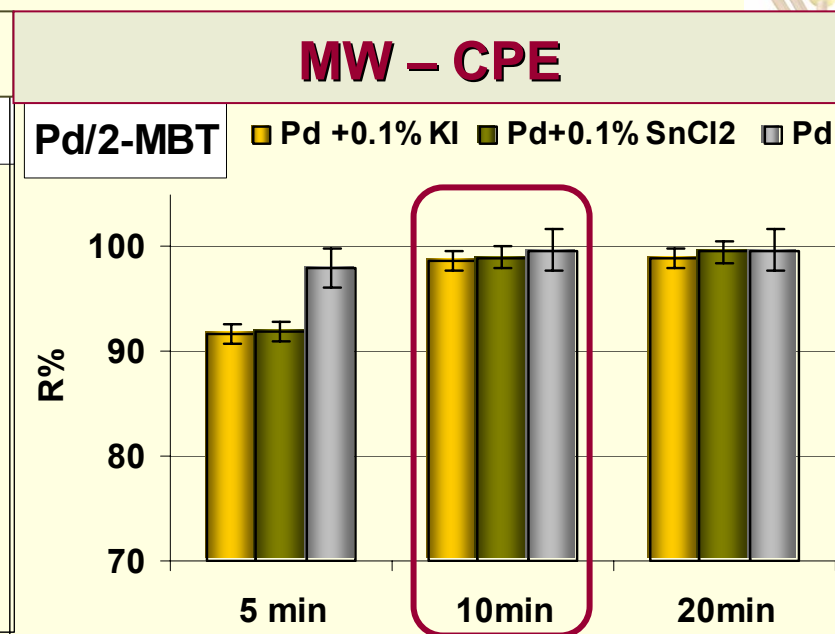
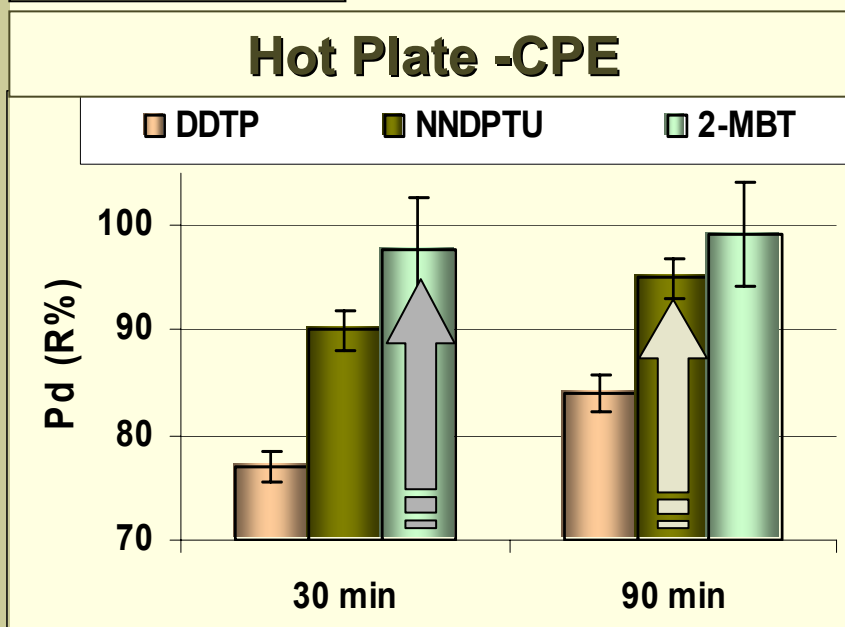


Fig.4. Extraction degree (%) of studied Pd complexes as a function of time for HP-CPE

Fig.5. Extraction degree (%) of Pd 2-MBT complex, as a function of time for MW incubation

➤ HP-CPE the time for quantitative extraction (<95%) of Pd is:

✓ 90 min for NNDPTU

✓ 30 min for 2-MBT

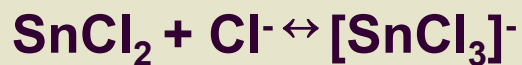
➤ MW-CPE decreases the time for quantitative extraction of Pd with 2-MBT by a factor of 3

➤ NO significant influence of the reducing agents

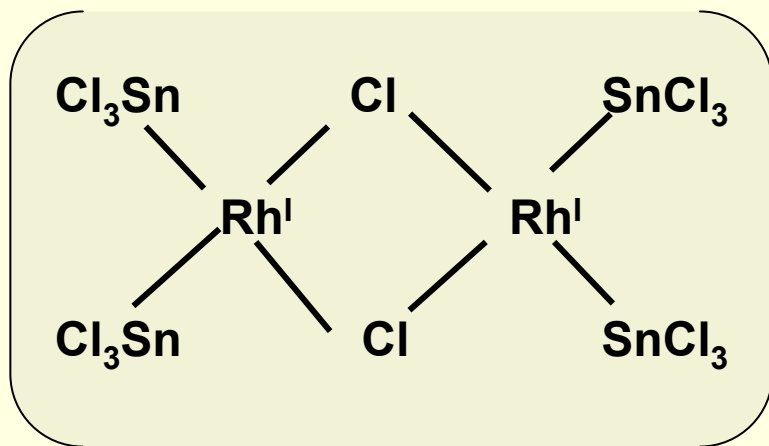
Rh - CPE

✓ Incubation time and reducing agents (KI or SnCl₂)

Introduction of reduction agent is the key point for the successful CPE of Rh



[SnCl₃]⁻ replaces Cl⁻ in the internal coordination sphere of Rh



✓ [SnCl₃]⁻ would be more effective as a reducer when it is bounded directly with the central ion

MW - CPE

2-MBT

SnCl₂ is more effective

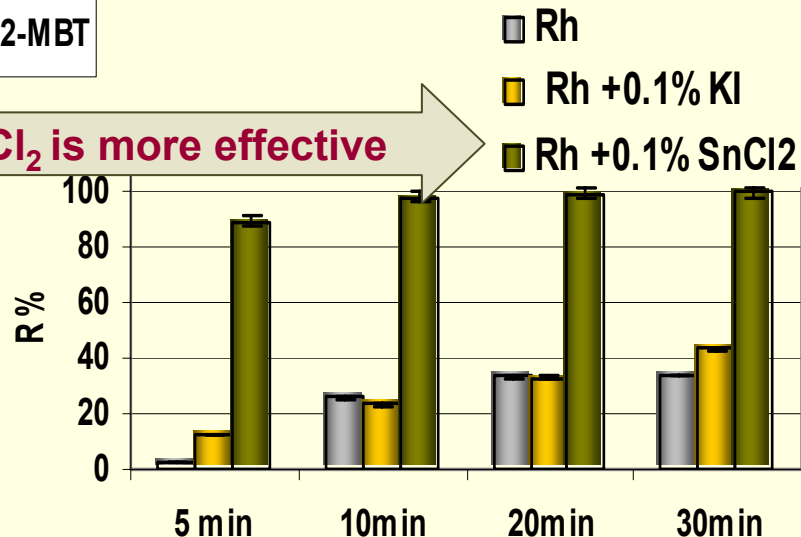


Fig. 6 Extraction degree (%) of Rh 2-MBT complex, as a function of time for MW irradiation

✓ The Rh complexes with [SnCl₃]⁻ are larger so the migration into the hydrophobic micellar core could be stimulated

Rh - CPE

✓ *Incubation time and reducing agents (KI or SnCl₂)*

➤ The quantitative MW-CPE of Rh in the presence of 0.1% SnCl₂ was obtained for 10 min.

➤ Similar trend was proven for Hot Plate CPE of Rh in the presence of 0.1% SnCl₂ quantitative R% was obtained for 90 min.

Hot Plate -CPE

Rh/2-MBT + 0.1%SnCl₂

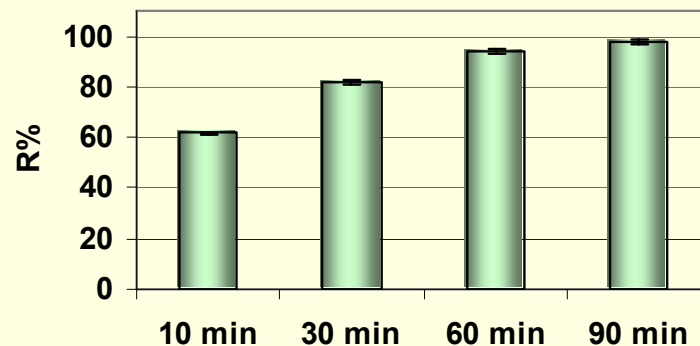


Fig. 7 Extraction degree (%) of Rh/ 2-MBT complex in a presence of SnCl₂, as a function of time for MW irradiation

The obtained time factor of MW acceleration of the CPE for Rh is **9 !**

- The extraction rate of Pt with 2-MBT depends on the oxidation state of the central ion
- The extraction degree of Pt complexes with 2-MBT depends on the presence of Pd as a concomitant element

Table 1. Synergic effect of Pd on HP-CP extraction degree (%) of Pt (II) and Pt (IV)

	Extraction degree %			
	Pt II	Pt IV		
	<i>30 min</i>	<i>30 min</i>	<i>45 min</i>	<i>120 min</i>
<i>solution of Pt</i>	86 ±3	45 ±3	53±3	95±1
<i>solution of Pd u Pt (1:1)</i>	93 ±2	70 ±3	79±2	99±1
<i>solution of Pd u Pt (1:10)</i>			79±1	
<i>solution of Pd u Pt (10:1)</i>			80±1	

- Synergistic effect of Pd on the extraction of Pt 2-MBT complexes is independent of the mass ratio of both elements

Pt - CPE

✓ Synergistic effect of Pd with NNDTP and DDTP

Hot Plate -CPE

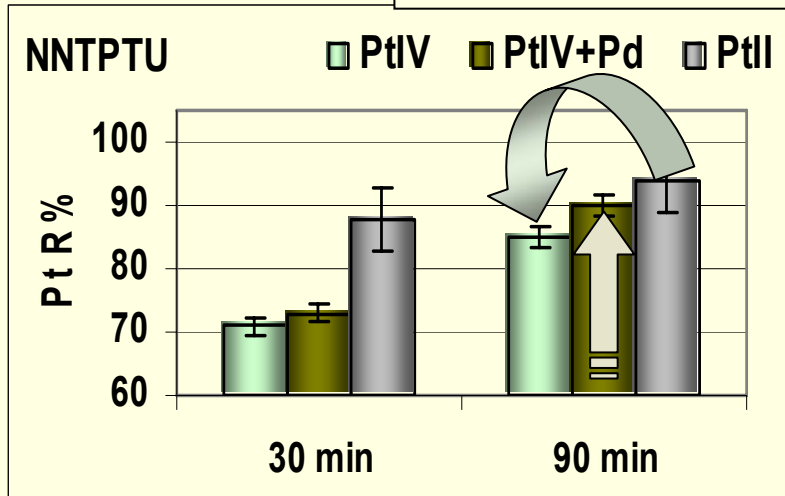


Fig. 8 HP-CPE extraction degree (%) of *Pt-NNDPTU* as a function of time

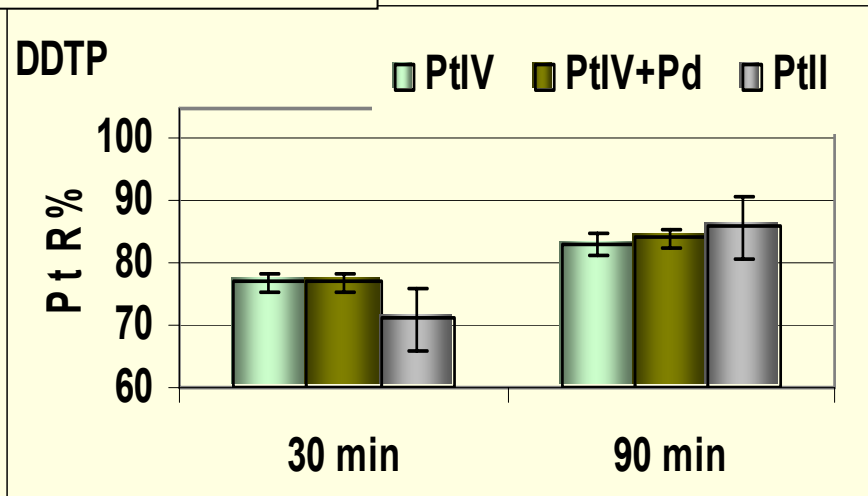


Fig. 9 HP-CPE extraction degree (%) of *Pt-DDTP* as a function of time

➤ For the HP-CPE extraction of Pt (IV) with NNDPTU (90min)

✓ Less expressed synergistic effect could be seen

✓ The lower R% was observed for higher oxidation state of Pt as well

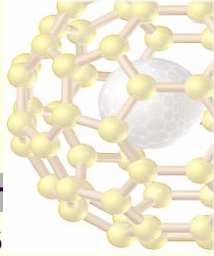
➤ For the HP-CPE extraction of Pt with DDTP (90min)

✓ Neither influence of the oxidation state of Pt nor the synergistic effect of Pd

✓ The obtained extraction degree of Pt was the lowest (R< 86%)

Pt-CPE

✓ Reducing agents optimisation



MW – CPE

Pt MW-CPE; 2-MBT

■ Pt IV ■ Pt II
■ PtIV+Pd ■ PtIV+Pd+KI
■ PtIV+Pd+SnCl₂

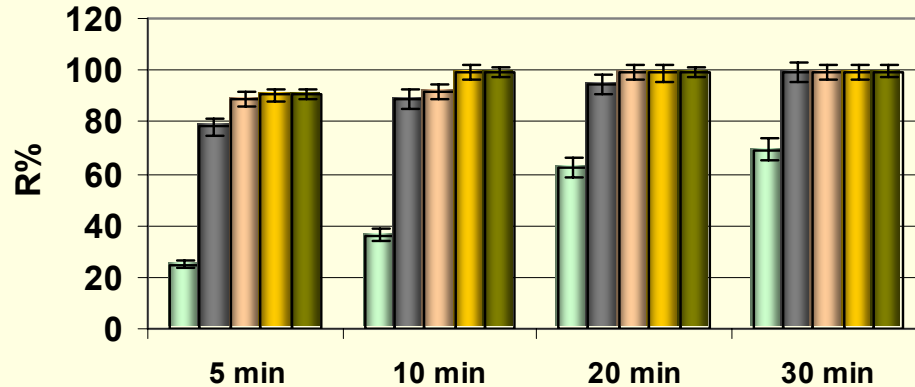


Fig 10. Influence of the reducing agents on the Extraction degree (%) of Pt (II) and Pt (IV) (MW-CPE 30 min with 2-MBT and presence of Pd)

✓ The reducing agents equalize the behaviour of both oxidation states of Pt

✓ NO difference between KI or SnCl₂

✓ The obtained acceleration factor of MW-CPE compared to HP-CPE depends on:

- ❖ the oxidation state of Pt in the initial solution
- ❖ the use of reducing reagent

➤ For Pt (IV)/2-MBT without reduction the time factor is 6

➤ In the presence of KI or SnCl₂ the MW accelerates the CP extraction of Pt (IV)/2-MBT and Pt (IV)/NNDPTU by the time factor of 3.

Hot Plate vs. MW -CPE for

PGM multi-element analysis with 2-MBT and SnCl₂

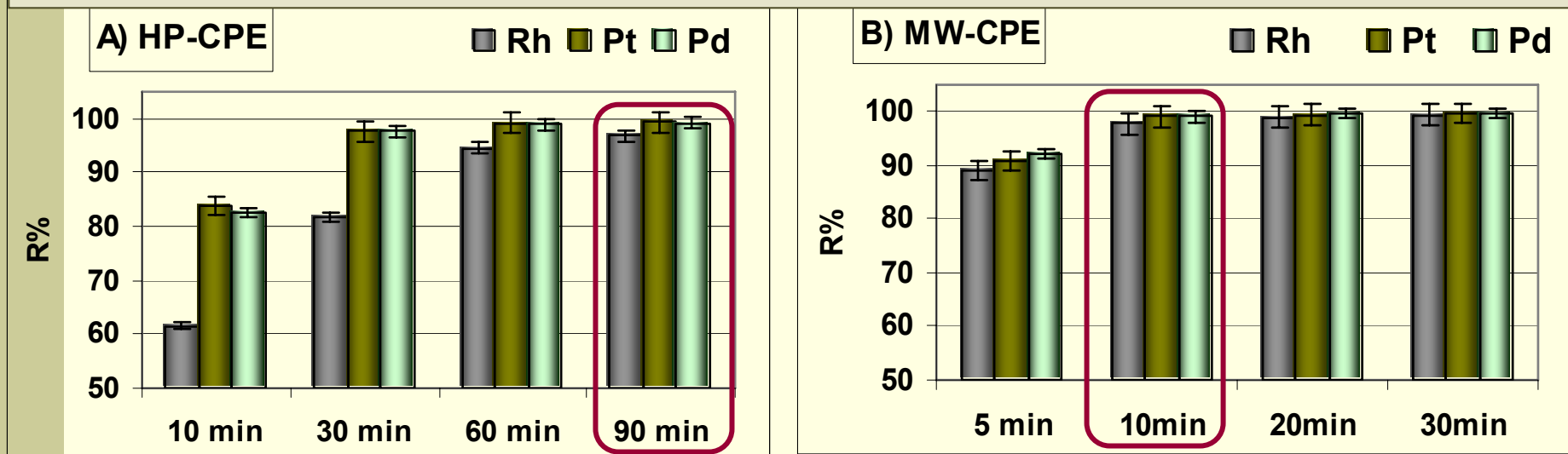


Fig 11. Degree of extraction (%) of PGM with 2-MBT in the presence of 0.1% SnCl₂ as a function of time

➤ The group CPE of the Rh, Pt and Pd with a combination of 2-MBT or NNDPTU and SnCl₂ was successfully completed with R > 95 % for

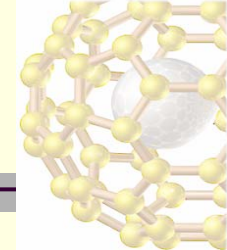
✓ 90 min on a **HOT PLATE**

✓ 10 min in a **MICROWAVE SYSTEM**

➤ Separated Surfactant rich phase, diluted in **1M HCl** was introduced into ICP-MS by continuous nebulisation

➤ **Preconcentration factor 8 was obtained**

Drugs for treatment of arterial hypertension-analysis of PGM after MW-CPE



The European Agency for the Evaluation of Medicinal Products
Evaluation of Medicines for Human Use

London, 17 December 2002

CPMP/SWP/QWP/4446/00

Corrigendum to the version dated 26th June 2002

NOTE FOR GUIDANCE ON SPECIFICATION LIMITS FOR RESIDUES OF METAL CATALYSTS

Elements	Oral Concentration Limit (ppm)	Parenteral Concentration (ppm)	Limit
Pt, Pd, Ir, Rh, Ru, Os	5 (group)	0.5 (group)	
Mo, V, Ni, Cr	10	1.0	
Cu, Mn	15	1.5	
Zn, Fe	20	2.0	

Digestion of the samples

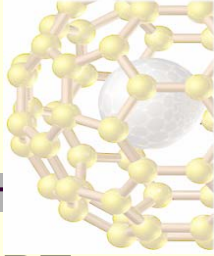
HCl + H₂O₂

➤ Hot plate

➤ MW-assisted

Table 3. Analytical results of drugs for treatment of arterial hypertension (possible contamination of PGM by used catalyst)

ICP-MS analysis	Direct	MW-CPE			
		2-MBT			N,N'-DPTU
Sample	Pd ng/g	Pd ng/g	Pt ng/g	Rh ng/g	Pd ng/g
Tritace	78 ± 4	78 ± 2	< 2	< 0.3	
Vivace	15 ± 0.9	15 ± 0.5	< 2	< 0.3	14 ± 0.5
Laprilén	< 8.4	<3.1	< 2	< 0.3	<4.2



Conclusions

- Quantitative recovery for Rh, Pd and Pt in CPE with 2-MBT or N,N'-DPTU is achieved when SnCl₂ is used as reducing agent
- For the first time the whole CPE is accomplished in a MW system
- The obtained ACCELERATION of the MW-CPE in comparison with Hot Plate with a **time factor of 3-9**
- The MW-CPE procedure was successively applied for quantitative preconcentration and analysis of PGM trace contaminations in pharmaceutical products

Acknowledgements to:

- ❖ *COST office for COST-STSM-D32-02151 short mobility visit of PhD student K. Simitchiev to University of Alicante (Spain)*
- ❖ *University of Plovdiv for X-7105*