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Non-stoichiometric synthesis of rhenium heptasulfide hydrosol

7th International Symposium On Technetium and Rhenium
Science and Utilization
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Re_2S_7 application

Catalysis :

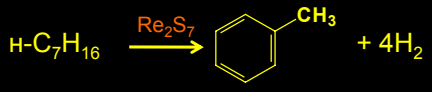
1)±H_2 – hydrogenation and dehydrogenation

2)Organic synthesis of complex organic compounds, reduction

3)Rheniforming

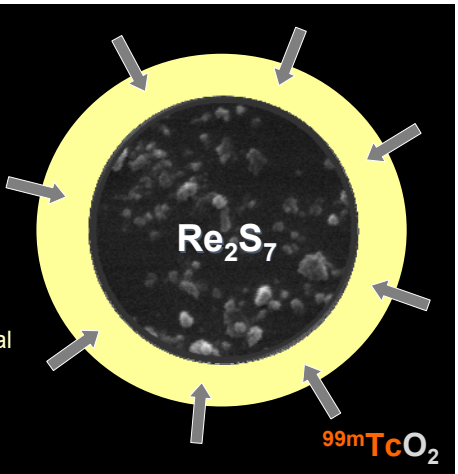
R, nm	S_{sp}, m^2/g
10	62
20	31
30	21
40	15
50	12

$$C_{17}H_{35}COOH + 3H_2S \xrightarrow{Re_2S_7} C_{17}H_{35}CH_2SH + 2H_2O + 2S$$



Re_2S_7 application

- **Nuclear medicine:** nanoparticles labeled by radionuclides can be used in nuclear medicine for diagnostic and therapeutic purposes. Recently the nanocolloids of technecium – 99m have been widely adopted in the technique of intraoperational visualization.



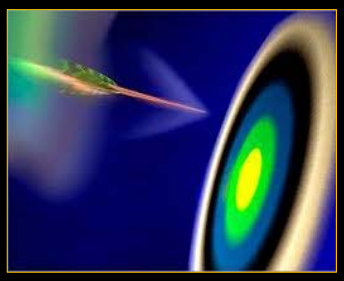
radionuclide generator
$^{99}Mo/^{99m}Tc$

$$2Na^{99m}TcO_4 + 3SnCl_2 + 2H_2O \downarrow$$
$$2^{99m}TcO_2\downarrow + 3SnO_2\downarrow + 2NaCl + 4HCl$$

Objective of the research:

—to find optimal conditions for the Re_2S_7 nanoparticles formation

—to determine kinetic parameters of the reaction



Characteristics of disperse phase depend on

- concentration of reagents
- their ratio
- order of mixing
- synthesis time
- temperature
- method of stopping reaction

REACTIONS

Re_2S_7 synthesis

$$2NaReO_4 + 7Na_2S_2O_3 + 2HCl \rightarrow Re_2S_7 + 7\,Na_2SO_4 + 2\,NaCl + H_2O$$

Possible elementary reaction

The formation of intermediate substances

$$NaReO_4 + Na_2S_2O_3 \rightarrow NaReO_3S + Na_2SO_4$$

etc

other water-soluble forms of Re are formed

Side reaction of hyposulfite decomposition

$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + S_{coll} + H_2O$$

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Rhenium distribution over different phases

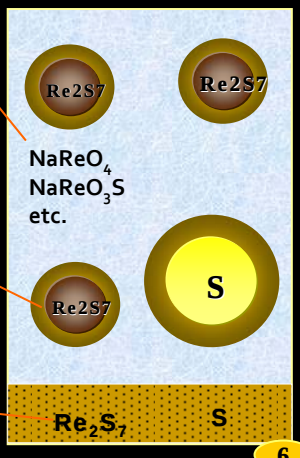
Continuous medium (**ReCM**)

Reaction mixture after synthesis

Dispersoid (**ReD**)

ΣRe_2S_7 = ReD + RePP

Primary precipitate Re_2S_7 (**RePP**)



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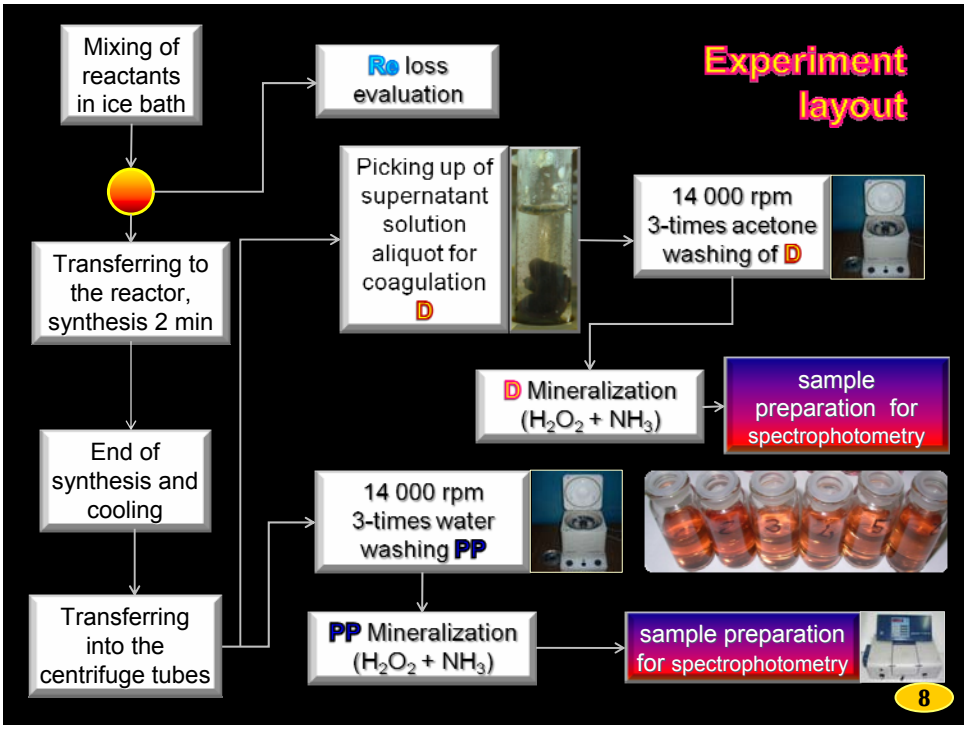
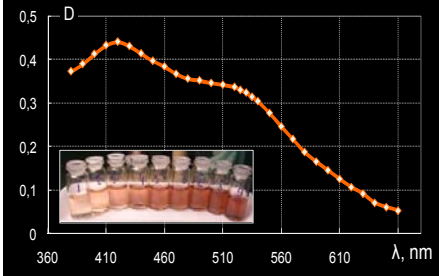
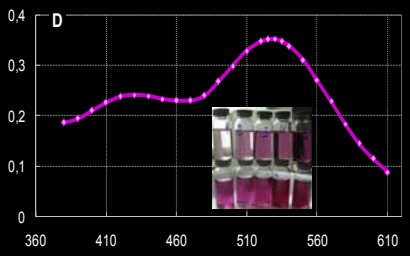
Experiment layout



Re_2S_7 dissolving techniques and reduced rhenium coloured compounds



1) $Re_2S_7 + H_2O_2 + NH_3$
2) $HCl + Na_2S_2O_3 + SnCl_2$



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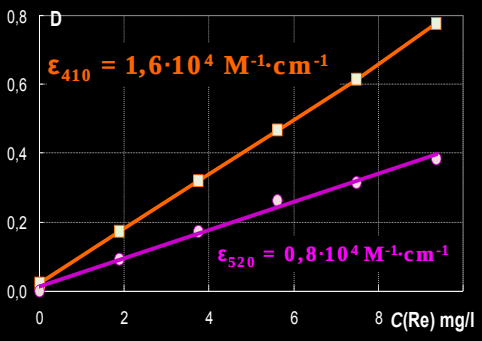

$3\ HCl + HNO_3 \rightarrow 2\ [Cl] + NOCl \uparrow + 2\ H_2O$
$2\ NOCl \rightarrow 2NO\uparrow + Cl_2\uparrow$

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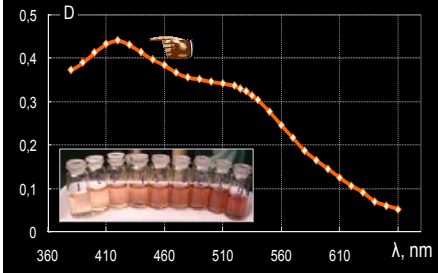
Re_2S_7 dissolving techniques and reduced rhenium coloured compounds



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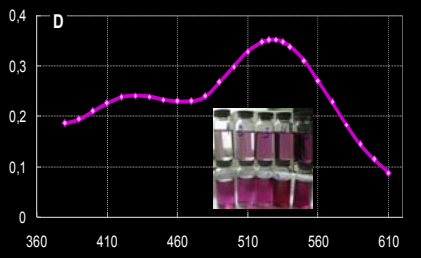

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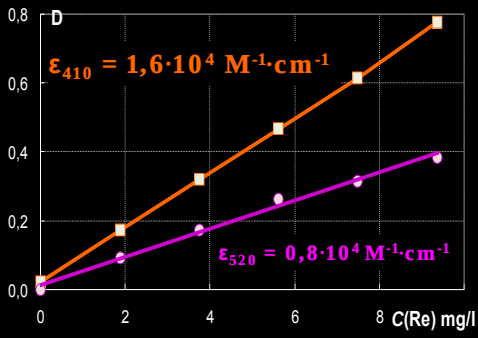

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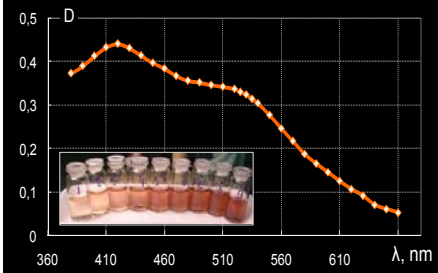
Re_2S_7 dissolving techniques and reduced rhenium coloured compounds



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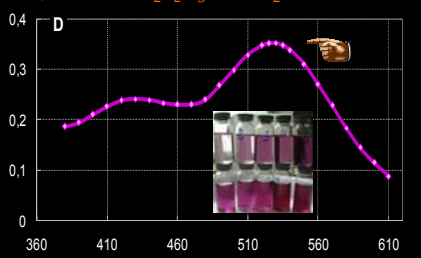

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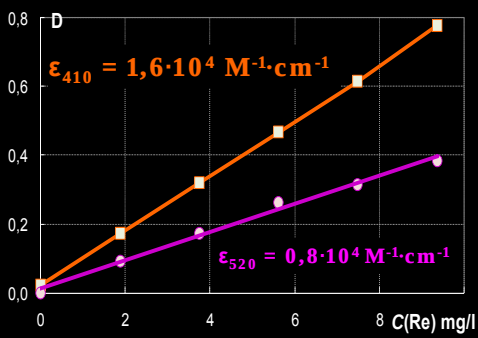
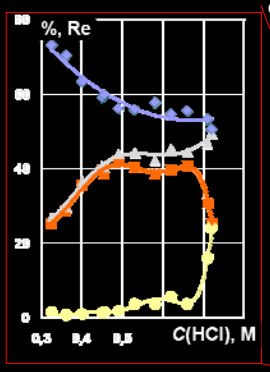
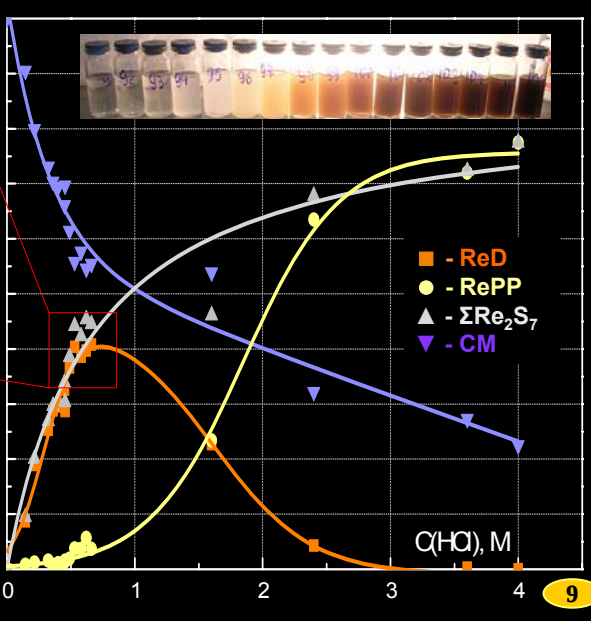


$3\ HCl + HNO_3 \rightarrow 2\ [Cl] + NOCl \uparrow + 2\ H_2O$
$2\ NOCl \rightarrow 2NO\uparrow + Cl_2 \uparrow$

Influence of acidity on heptasulfide yield



Finding optimal acidity



C_{opt}(HCl) = 0,45 M

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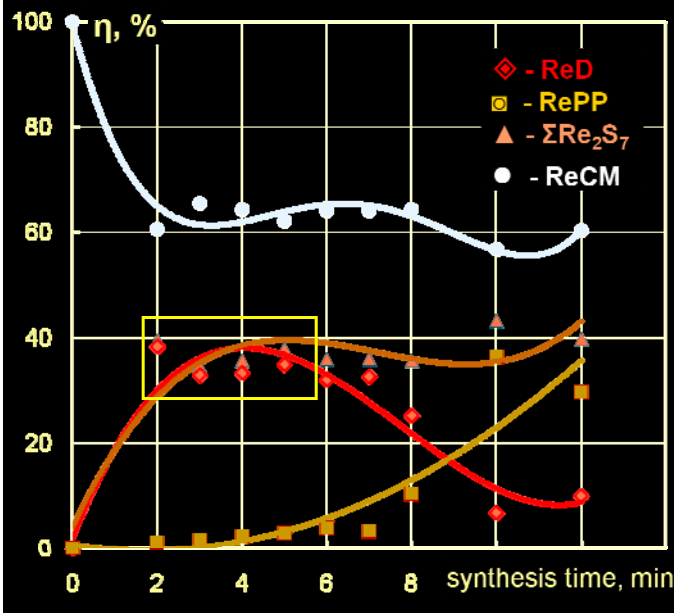
Finding optimal synthesis time



- Prolonged heating in acidic conditions provokes sol coagulation

τ_{opt}= 2÷3 min

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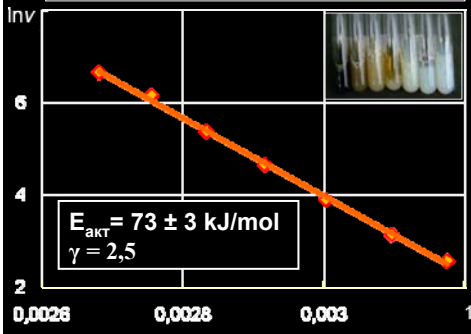
Activation energy of the main and side reactions

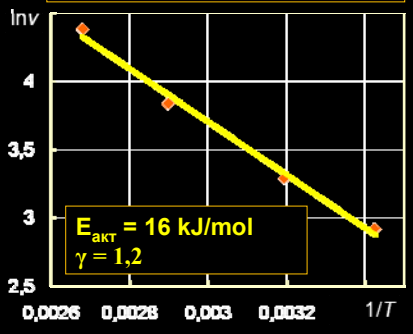
Re_2S_7 formation

$$2\ NaReO_4 + 7\ Na_2S_2O_3 + 2\ HCl \rightarrow Re_2S_7 + 7\ Na_2SO_4 + 2\ NaCl + H_2O$$



hyposulfite decomposition

$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + S + H_2O$$



When temperature rises up from 20 to 100 °C
- the rate of Re_2S_7 formation increases in 800 times
- the rate of $Na_2S_2O_3$ decomposition increases only in 4 times

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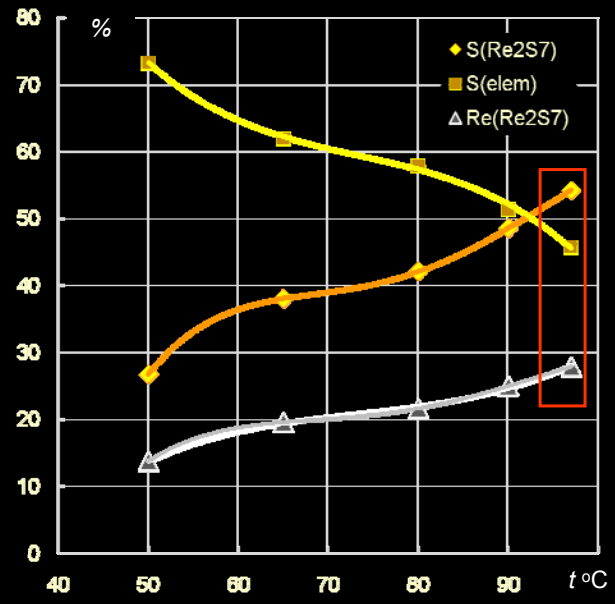
Temperature dependences of the Re_2S_7 and S yields



$$\frac{Na_2S_2O_3}{NaReO_4} = 2{,}2$$

C(HCl) = 0,45 M

$C_{жел}$ = 2,2 %

Time – 2 min

t_{opt}= 100 °C

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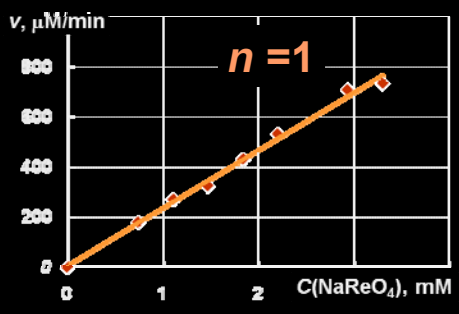
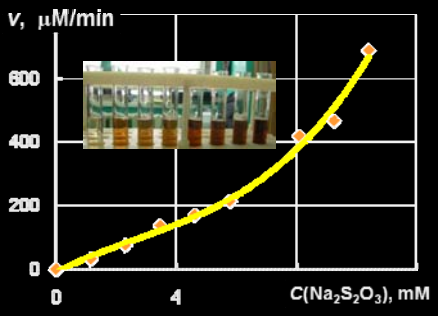
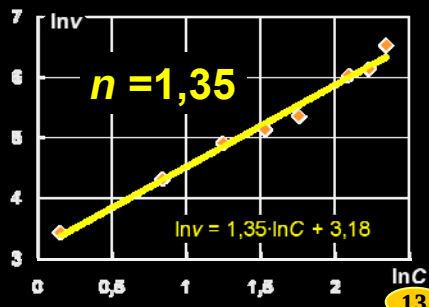
The order of reaction with respect to $NaReO_4$ and $Na_2S_2O_3$







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- There is a consecutive substitution of oxygen atoms by sulfur atoms iIn the molecule of rhenium acid formed after perrhenat-ion protonation .
- One of the possible reaction mechanism is:

- $HReO_4 + H_2S_2O_3 = \mathbf{H[ReO_3S]} + H_2SO_4$
- $H[ReO_3S] + H_2S_2O_3 = H[ReO_2S_2] + H_2SO_4$
- $H[ReO_2S_2] + H_2S_2O_3 = H[ReOS_3] + H_2SO_4$
- $H[ReOS_3] + H_2S_2O_3 = \mathbf{H[ReS_4]} + H_2SO_4$

The last one is formation of a sulphidic bridge between rhenium atoms

- $H[ReS_4] + H[ReOS_3] = Re_2S_7 + H_2O$

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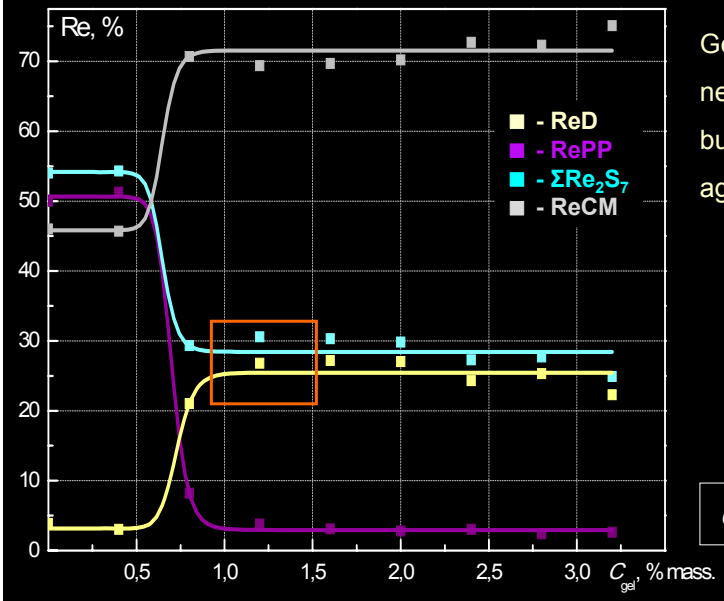
Finding optimal concentration of gelatin



Gelatine is necessary, but undesirable agent

$C_{opt}(gel) = 1,2\ \%$

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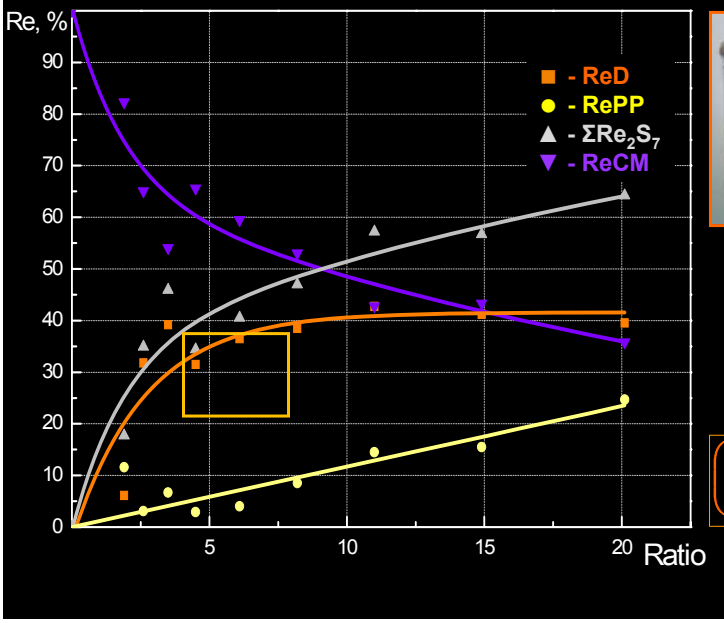
Re_2S_7 yield dependence from the ratio $\frac{Na_2S_2O_3}{NaReO_4}$



$\left(\frac{Na_2S_2O_3}{NaReO_4}\right)_{opt} = 4,5$

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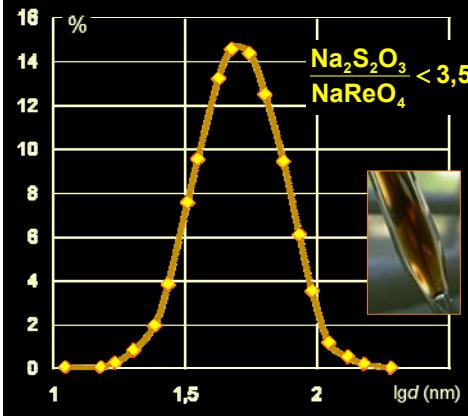
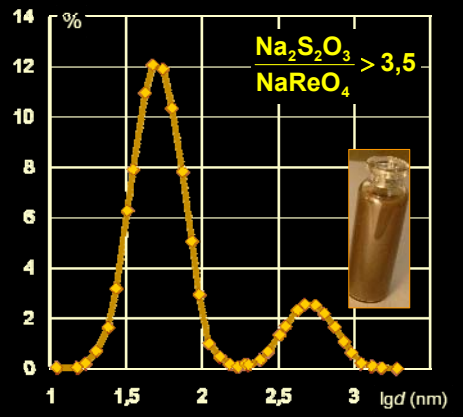
Particle size distribution

(Unicor SP)





- Bimodal distribution (50±15nm and 500±200nm) denotes different formation mechanisms or different nature of the particles
- Large particles are sulphur

$$\left(\frac{Na_2S_2O_3}{NaReO_4}\right)_{opt} = 4,5$$

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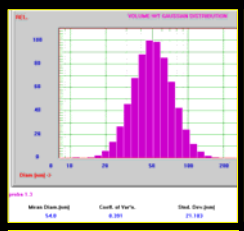
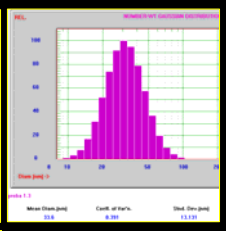
Particle size determination

Zeta Potential/ Particle Sizer Nicomp™ 380 ZLS и TECNAI-12-3R



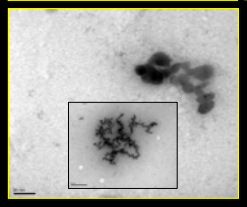


Effective hydrodynamic diameter

ø mass-average = 55±20 nm

ø number-average = 35±15 nm

Small discrepancy means that the distribution of particles over their sizes is narrow



◄ Diameter of a nanoparticle dense core (electron microscopy)

ø = 10-20 nm

▲The sample of high polydispersity (not ours)

Nanoparticles easily pass through sterilizing filter Millipore 0.22 ►

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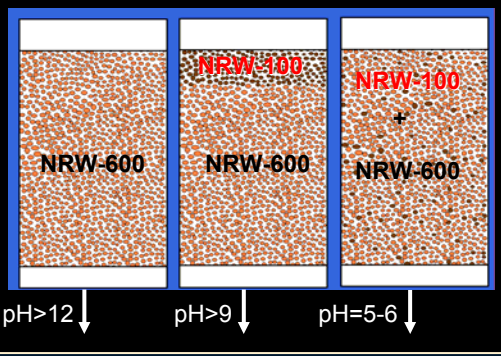
Possible impurities

ReO_4^- HCl

SO_4^{2-} Fe^{3+}

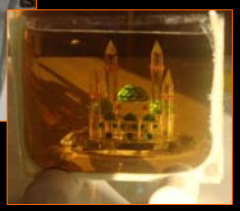
SO_3^{2-} S^{2-} α-aminoacids

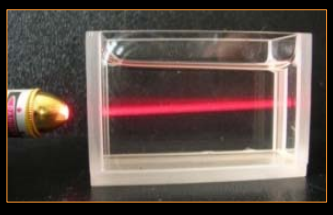


The hydrosol was deionized by mixed bed ion-exchange columns

Re_2S_7 HYDROSOL

Visually transparent hydrosol ▼





◄Tyndall effect shows dispersoid

Coagulation after stabilizer destroying ►

Comparison of hydrosols, obtained by different methods

№: 1 **4** 2 3

№	Experiment	C_o(Re), g/l	$\frac{Na_2S_2O_3}{NaReO_4}$	C(HCl), M	C_{gel}, %	Time min	ø, nm
1	«Coren» radiopharmaceutical	**0,36**	**6,0÷7,0**	**0,07÷ 0,11**	**0,81**	**3,5**	**≤1000**
2	Zabel P.L. 2004	**0,59**	**7,1** / **3,0**	**0,125**	**0,17**	**6÷10**	**<100 (60%)** **100÷200 (14%)**
3	Tsopelas 2001	**0,48**	**4,8 ÷7,7**	**0,20**	**4,0**	**3 ÷5**	**<50 (20 %)**
4	**MUCTR**	**0,60**	**4,5**	**0,40÷0,45**	**2,2**	**2**	**50±20 (100 %)**

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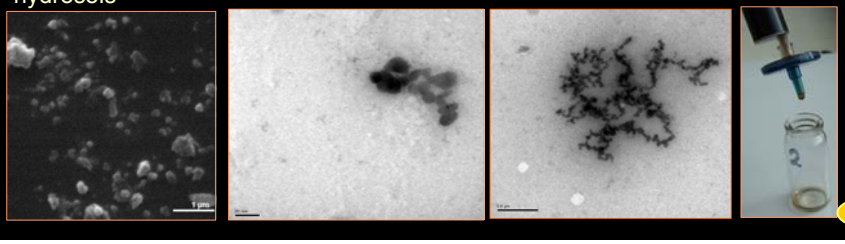
As a result of the work

- visually transparent non-opalescent deionized product,
- stable within a wide range of pH (1-9),
- not coagulating in saturated solutions of salts (including polyvalent cations) even at long heating up to 100 °C has been synthesized.
- Effective hydrodynamic diameter of the nanoparticles (PCS) is at least 2-3 times more than diameter of the dense core (TEM).
- **Re_2S_7 nanoparticles are irregular shaped, X-ray amorphous, stabilized by gelatin**
- Polydispersity is low: 75% (mass) of the particles have hydrodynamic diameter between 35 to 75 nm.
- Deionized hydrosols can be stored in an inert atmosphere for indefinitely long time (years).
- This work may be helpful in developing synthesis of other metal sulfides hydrosols



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Thank you for your attention