SPECTRAL STUDY OF FUNCTIONAL NANOCOMPOSITES BASED ON HUMIC ACIDS FOR WATER TREATMENT

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OUTLINE

- Why nanocomposites? definitions, examples
- What are functional nanocomposites?
- How to produce functional nanocomposites?
- What set of spectroscopic data are good for?
- How functional nanocomposites utilize for waste water treatment?

What are nanocomposites?

- **Nanocomposites** are a class of materials in which **one or more phases** with **nanoscale** dimensions are embedded in a metal, ceramic or polymeric matrix.

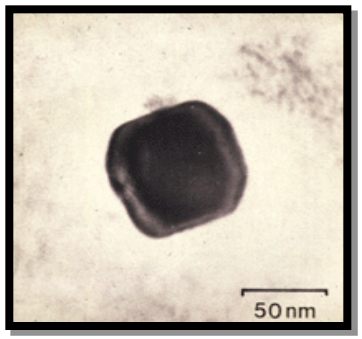
- The **general idea** is to create a **synergy** between the various constituents, such that novel properties capable of meeting or exceeding design expectations can be achieved.

- The **properties** of nanocomposites rely on a range of variables, particularly the matrix material, loading, degree of dispersion, size, shape, and interaction between the matrix and the second phase.

Nanocomposites

Resulting nanocomposite may **exhibit drastically** different (often ***enhanced***) properties than the individual components.

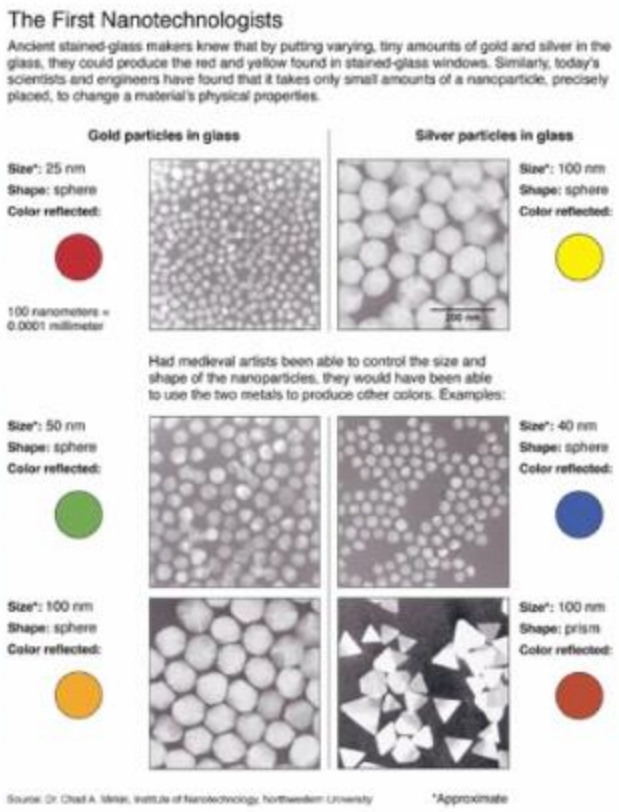
Appears green in reflected light and red in transmitted light.



Lycurgus Cup is made of glass.
Roman ~400 AD,
Myth of King Lycurgus

http://www.britishmuseum.org/explore/highlights/highlight_objects/pe_mla/t/the_lycurgus_cup.aspx

First nanocomposites: example

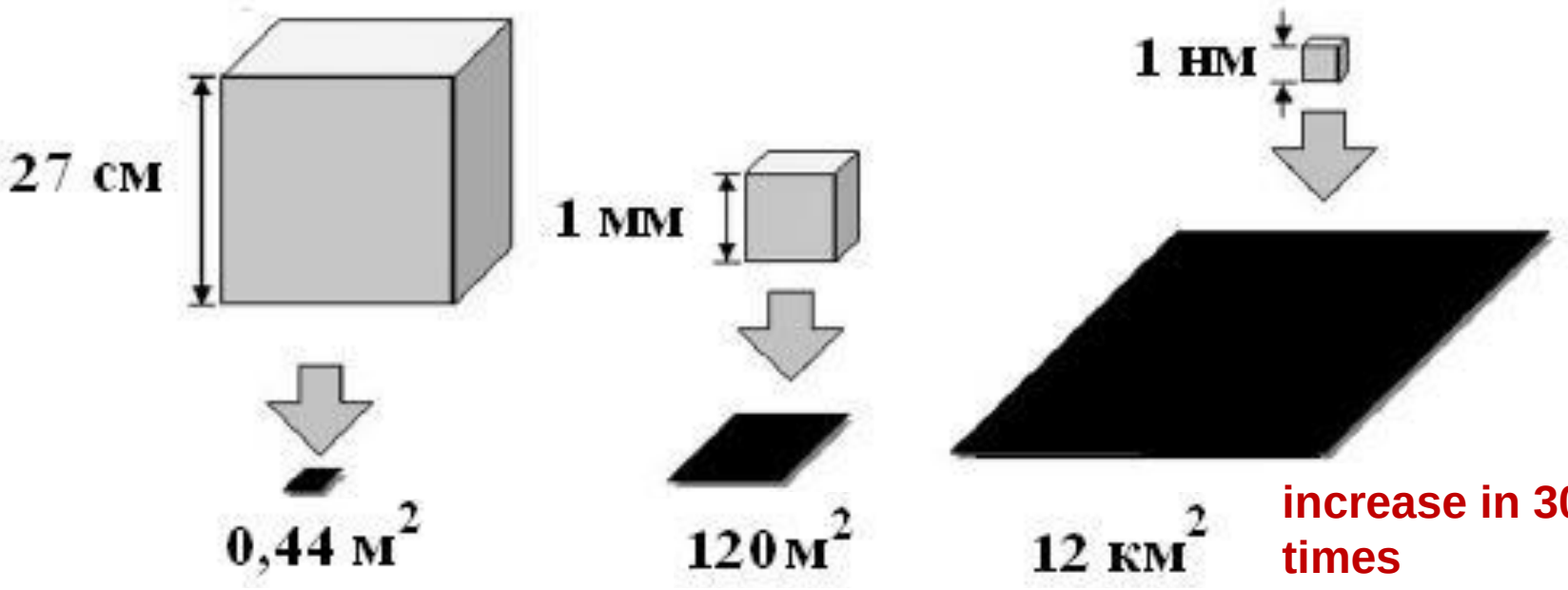


Technology re-discovered in the 1600s and used for colored stained glass windows.

The Institute of Nanotechnology http://www.nano.org.uk/

Nanoeffect

- Very high surface area to volume ratios in nanostructures
- Nanocomposites provide large interface areas between the constituent, intermixed phases



prefix “nano” for system is not only thanks to size, but to dependence of system properties from size

MAGNETIC HUMICS-BASED NANOCOMPOSITES

fabrication, composition, sorption**, structure:**

- **Ultrasound spectrometry**
- **Mossbauer spectrometry**
- **Fluorescence**
- **Infrared spectrometry**

Case study:

Kara-Balta uranium tailing dump

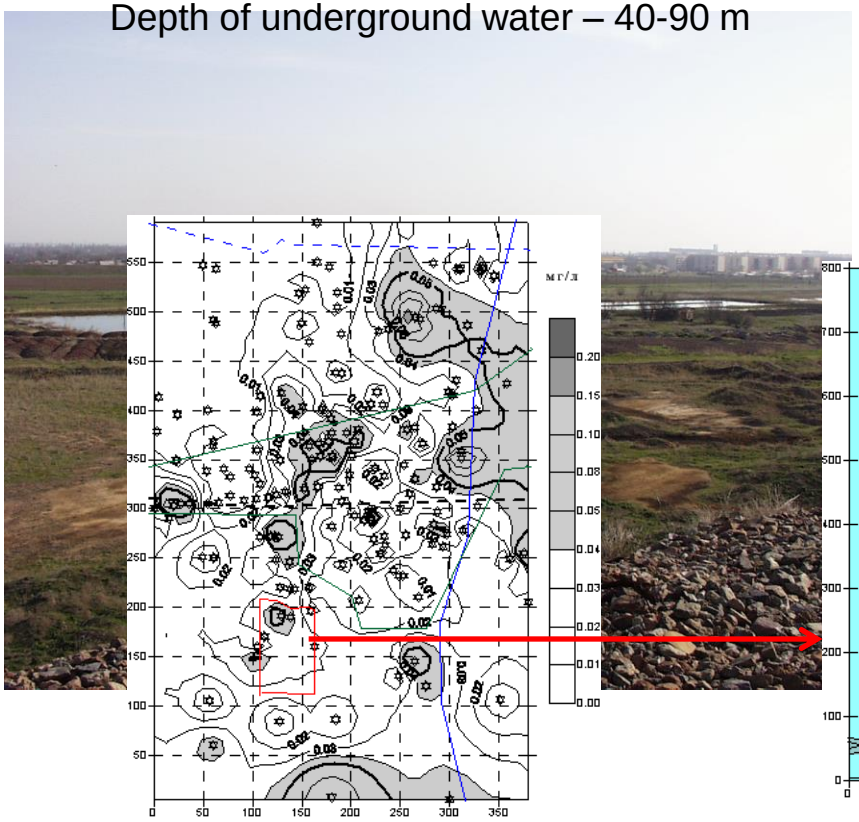
Accumulating storage reservoir :

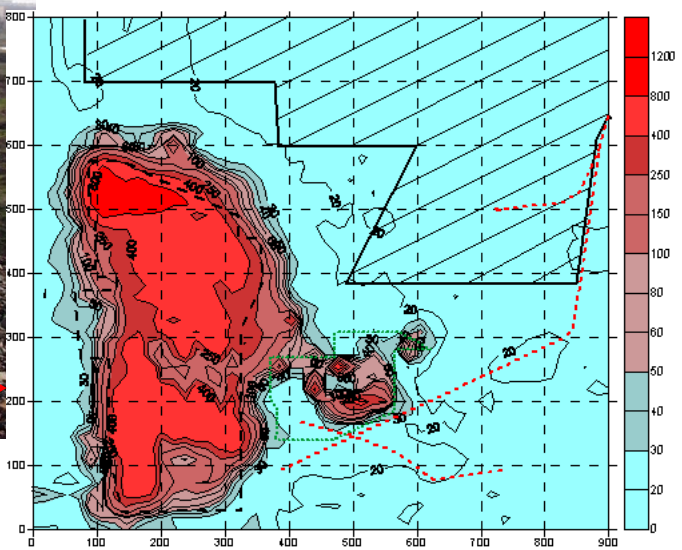
Contaminated area is 40-50 km^2,

Total area of TD is 240 ga

Depth of reservoir is 110-120 m

Depth of underground water – 40-90 m





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APPROACHES TO TECHNOLOGY DEVELOPMENT

HA + **Fe_3O_4**

Nanocomposite formulation

- Chemical coprecipitation (*ex situ*, *in situ*)
- Mechanochemical dispersion

↓

Fe_3O_4@HA

↓

Sorption of radionuclides and HM

↓

Fe_3O_4@HA/M

↓

Magnet separation

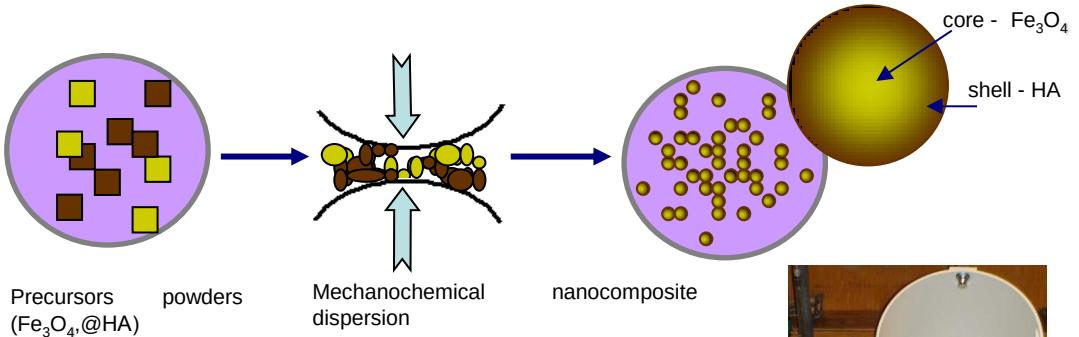
↓

Sorbent regeneration

↓

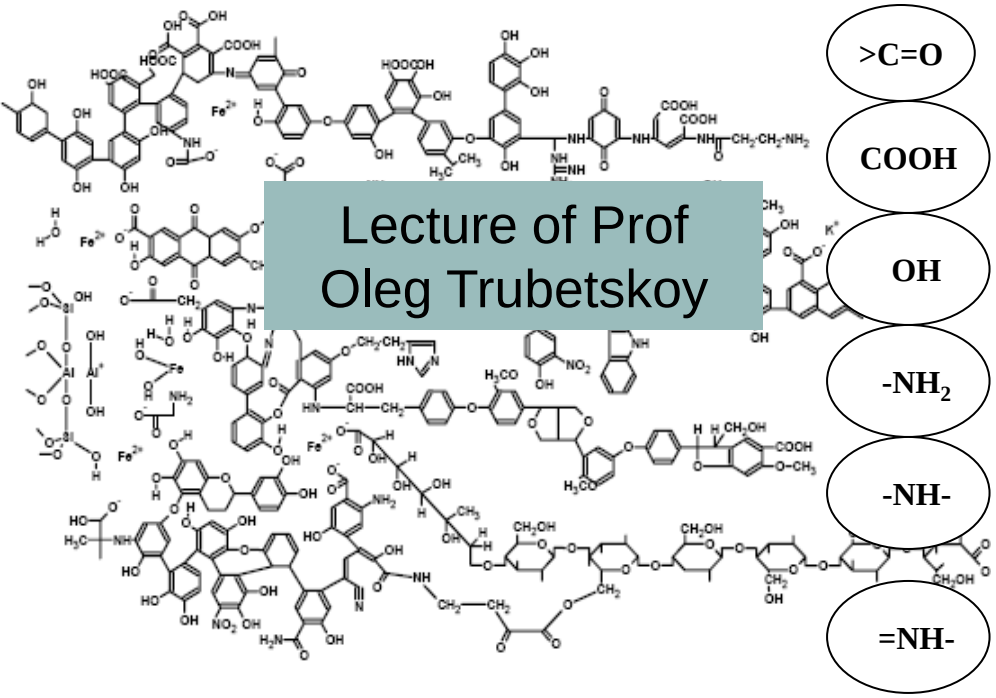
Fe_3O_4@HA

Principal scheme for magnet separation technology



COMPONENTS OF NANOCOMPOSITE

Humic acids of brown coal (HA)



Lecture of Prof Oleg Trubetskoy

Structure unit of humic acids (Kleinchempel, 1991)

- high complex ability (to **10 mmol/g** for coal-derived);
- S_{spec} ~ **40 m²/g**
- sorption capacity – to **7 mg-eq/g**;
- raw material: coal, peat, sapropel, compost etc.
- non-toxic, nature-abundant

Magnetite (Fe_3O_4)

- M_s=**92-100** A·m²/kg **(Fe_3O_4)** (60-80 for γ-Fe_2O_3)
- simple synthesis
- high speed of reaction
- high yield of target material
- scalability
- non-toxic, nature-abundant

Fe_3O_4 nanoparticles

- magnetic;
- provide specific surface
- (Sspec – 62 m²/g)

Humic acids:

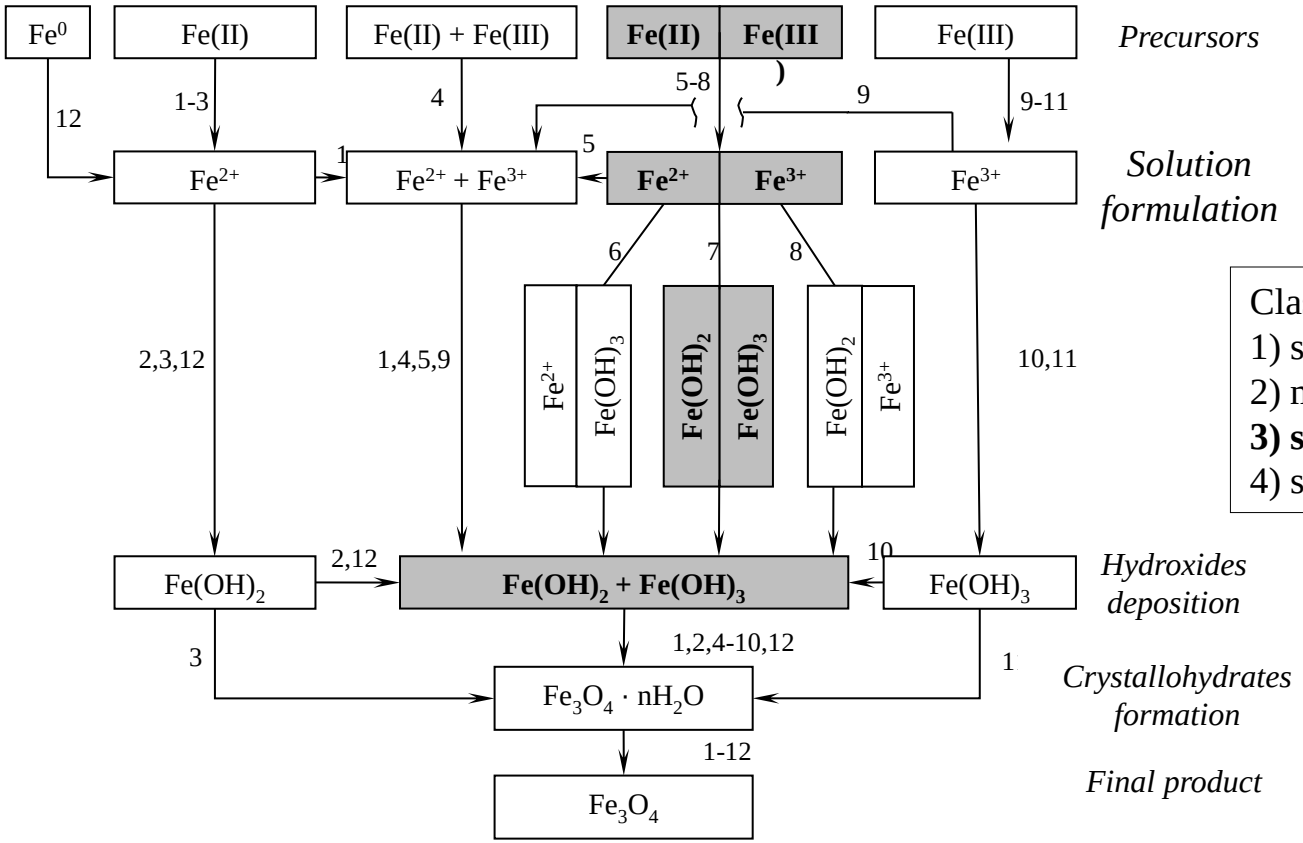
- enhance sorption potential for composite;
- stabilization of Fe_3O_4 nanoparticles

HYBRID FUNCTIONAL MATERIALS

Sspec to 180 m²/g

initial ratio Fe_3O_4/HA, wt% (80/20, 50/50, 30/70, 20/80, 10/90);

CHEMICAL METHODS FOR FORMULATION MAGNETITE*



Classification by type of precursors:
1) salt of Fe (II) (variants 1-3);
2) magnetite (variant 4);
3) salts of Fe (II, III) (var. 5-8);
4) salts/oxides of Fe (III) (var. 9-12)

chemical coprecipitation

$Fe + HCl \rightarrow FeCl_2 + H_2$ (inert conditions)

$2Fe\mathbf{Cl}_3 + Fe\mathbf{Cl}_2 + 8NH_4OH \rightarrow Fe_3O_4\downarrow + 8NH_4Cl + 4H_2O$

$Fe_3O_4 + HA + 8NH_4OH \rightarrow \mathbf{Fe_3O_4@HA}$

$2FeCl_3 + FeCl_2 + 8NH_4OH + HA \rightarrow \mathbf{Fe_3O_4@HA}\downarrow + 8NH_4Cl + 4H_2O$

*Grabovskiy, 1998, modified

SYNTHESIS of NANOCOMPOSITE Fe_3O_4@HA

Synthesis methods

Chemical coprecipitation

$2FeCl_3+FeCl_2+NH_4OH+HA=Fe_3O_4/HA+NH_4Cl+H_2O$

- initial ratio Fe_3O_4/HA, wt% (80/20, 50/50, 30/70, 20/80, 10/90);
- synthesis atmosphere: argon and air;
- 40°C and 22±2°C

Tombach et al. (2006), Liu et al. (2008)
- chemical precipiation *ex situ*
- synthesis at ~10 wt % HA

Mechanochemical synthesis

- high energetic planetary grinder SPEX SamplePrep 8000 Mixer/Mil,
- agate mortar with agate balls from wolfram carbide;
- rate - 1425 rpm;
- initial ratio of Fe_3O_4 and HA, wt% (80/20, 50/50, 20/80);
- m_{balls}/m_o (7/1 и 4/1);
- τ (2÷60 min)

Table 2. List of samples synthesized

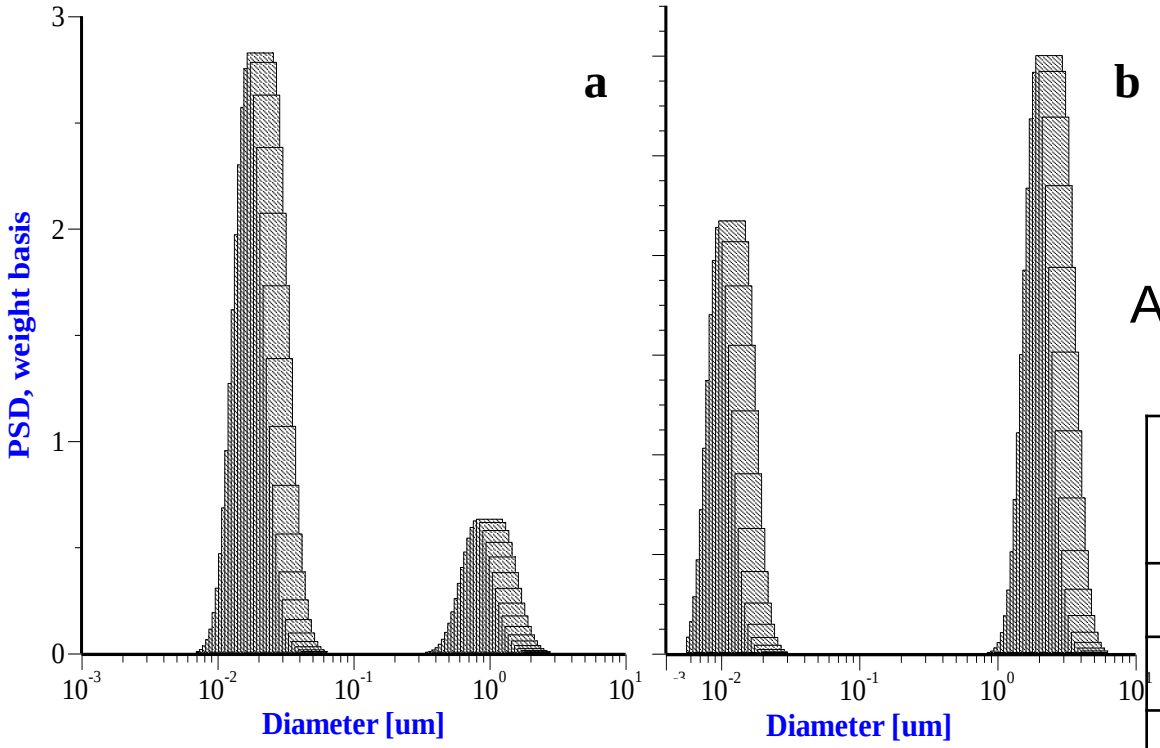
Sample description*	Initial ratio of	Method and condition of …esis
Fe_3O_4-HA20*-		…tion in …sphere:
Fe_3O_4-HA50-C		
Fe_3O_4-HA80-C		
Fe_3O_4-HA20-C		…tion in …ere:
Fe_3O_4-HA50-C		
Fe_3O_4-HA70-C		
Fe_3O_4-HA80-C		
Fe_3O_4-HA90-C_B	10% Fe_3O_4, 90% HA	
Fe_3O_4-HA20-M10	80% Fe_3O_4, 20% HA	Mechanochemical synthesis: m_{balls}/m_s = 7/1; τ_d = 10 min
Fe_3O_4-HA50-M10	50% Fe_3O_4, 50% HA	
Fe_3O_4-HA80-M10	20% Fe_3O_4, 80% HA	
Fe_3O_4-HA20-M30	80% Fe_3O_4, 20% HA	Mechanochemical synthesis: m_{balls}/m_s = 7/1; τ_d = 30 min
Fe_3O_4-HA50-M30	50% Fe_3O_4, 50% HA	
Fe_3O_4-HA80-M30	20% Fe_3O_4, 80% HA	

Magnet separation of solution
(Nd 2X2 см, 0.3 T, 7 min, 20% DS, 10 mL)

T – synthesis temperature, rpm – rate of stirring, rotation per minute, τ – synthesis time, τ – dispersion time, m_{balls}/m_{sample} - m_{balls}/m_s, * number index in sample description indicates initial ratio of HA into composition, in wt%

Zaripova, Kydralieva, et al. *J Biol Physics & Chem*, 2008
Patent RU 2547496C2RU от 10.07.2012.
Kydralieva, Yurishcheva, et al. *J Inorg Org Polym Mater.* 2016. Review

ULTRASOUND SPECTROSCOPY: HYDRODYNAMIC SIZE



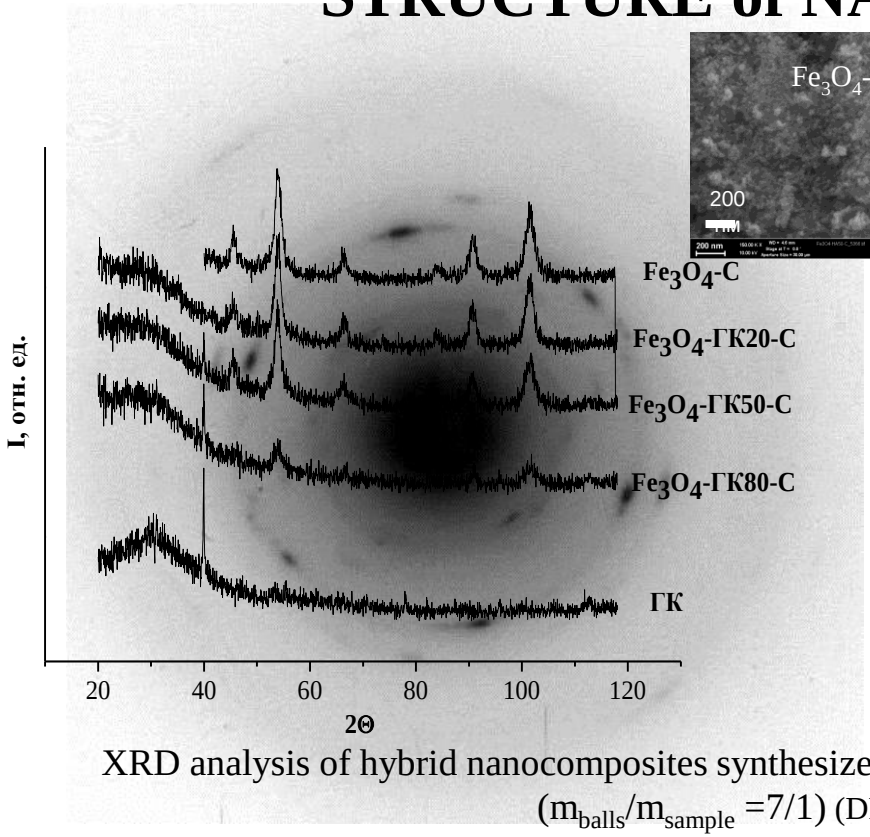
Histograms of particle size distribution for as-prepared magnetite (a) and in 14 days of solution (b)
(DT-1200, Dispersion Technology, 22±2°C, 10 g/L)

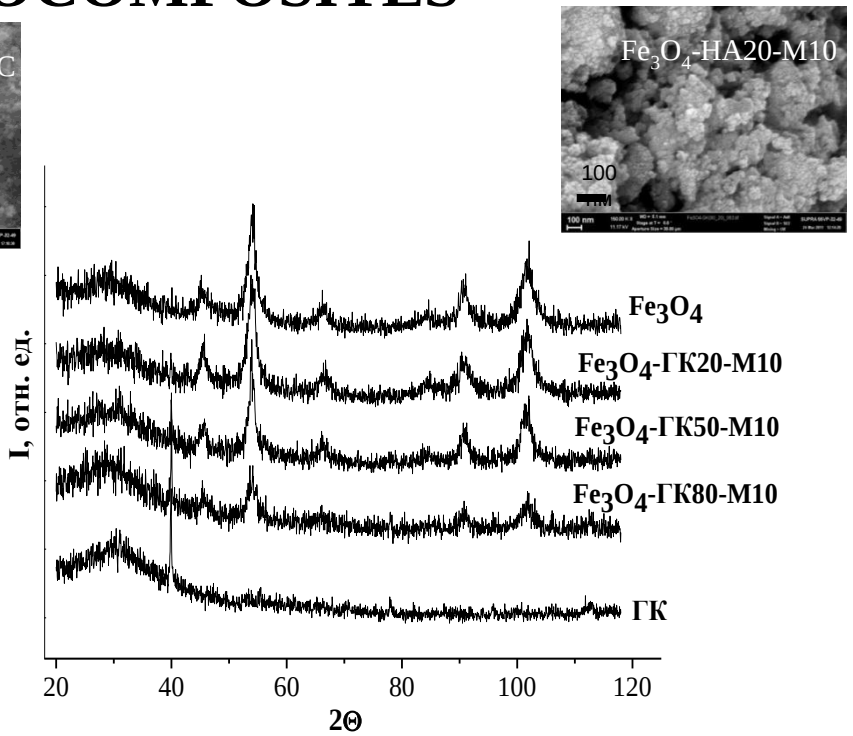
Average hydrodynamic size for nanocomposites

Sample	<*d*> ± 12, nm
Fe_3O_4	184
Fe_3O_4/ГК20	157
Fe_3O_4/ГК50	122
Fe_3O_4/ГК80	106

There is a narrow particle size distribution for as-prepared Fe_3O_4.
The average hydrodynamic particle size was ~ 180 nm.
In 14 days of storage of the original magnetite the redistribution in size and enlargement of the dispersed system are observed.

STRUCTURE of NANOCOMPOSITES





XRD analysis of hybrid nanocomposites synthesized by coprecipitation and mechanochemical dispersion (m_{balls}/m_{sample} =7/1) (DRON-UM-2, Cu(K_a), 1°/min)

Major phase formed during both synthesis method in the presence of humic acids *in situ* is a magnetite Fe_3O_4.
The HA bind to the particles just after nucleation of the Fe_3O_4 nanoparticles preventing further growth.
According to SEM more uniform distribution was observed for samples synthesized by coprecipitation (SUPRA 55VP-32-49, 150000×).

Table 3. Particle size of magnetite according XRD (data processing by Fityk)

Sample	Particle size, nm
Fe_3O_4	9,2±0,18
Fe_3O_4-HA20-C	8,2±0,12
Fe_3O_4-HA50-C	7,3±0,13
Fe_3O_4-HA80-C	5,7±0,20
Fe_3O_4-HA20-M10	8,7±0,21
Fe_3O_4-HA50-M10	7,8±0,28
Fe_3O_4-HA80-M10	5,8±0,25

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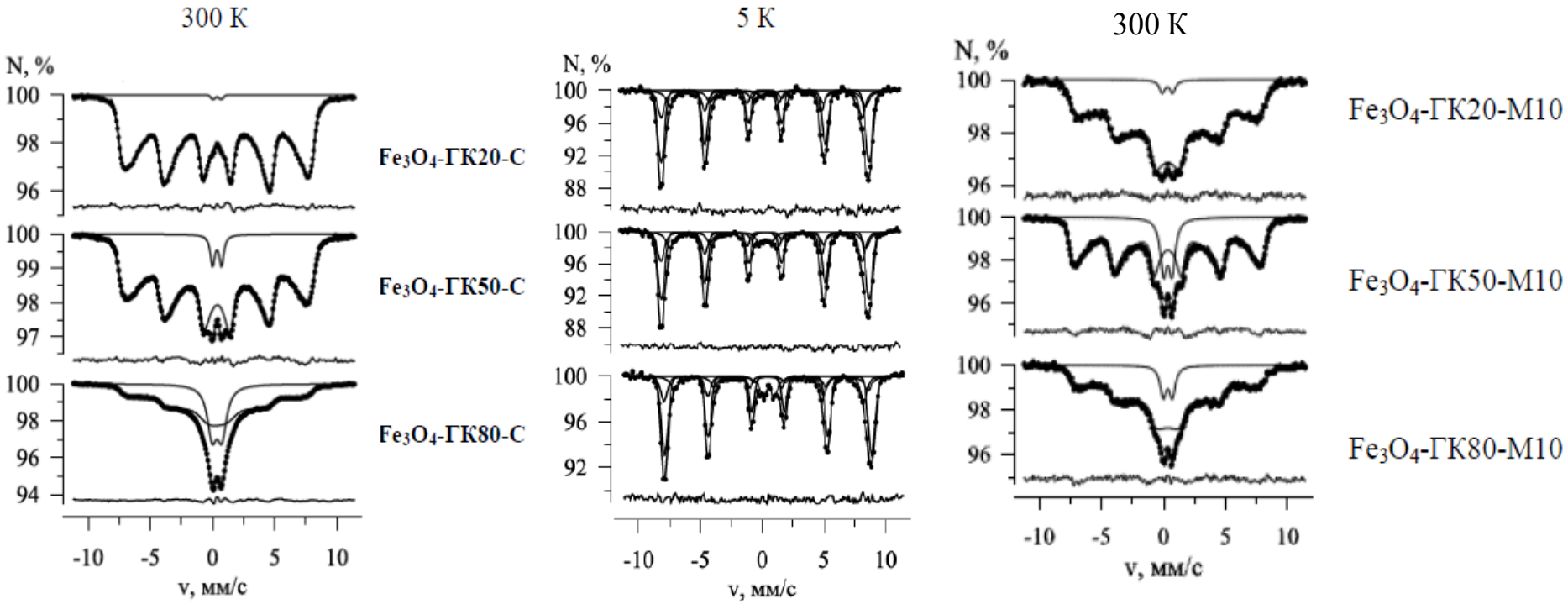
STRUCTURE of NANOCOMPOSITES



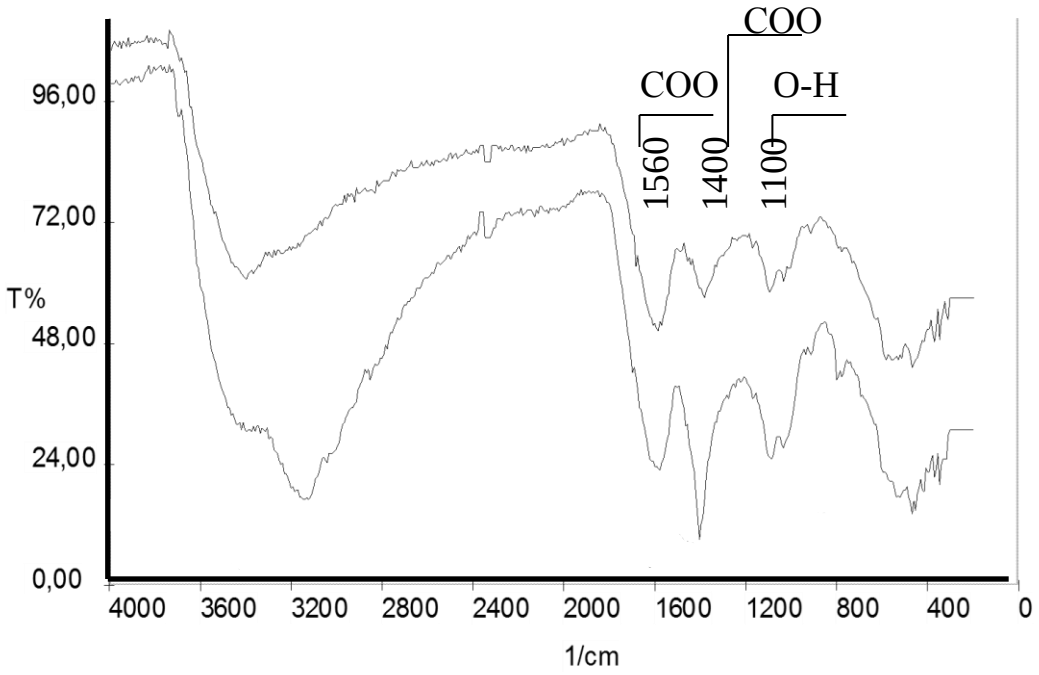
Mossbauer spectra for nanocomposites at 300 K and 5 K

(MS-1101-E, Mostec, helium cryostat SHI-850-5 (4.5÷500 K), ^{57}Co in matrix of Rh, etalon is α-Fe)

In collaboration with Dr Natalia Chistyakova

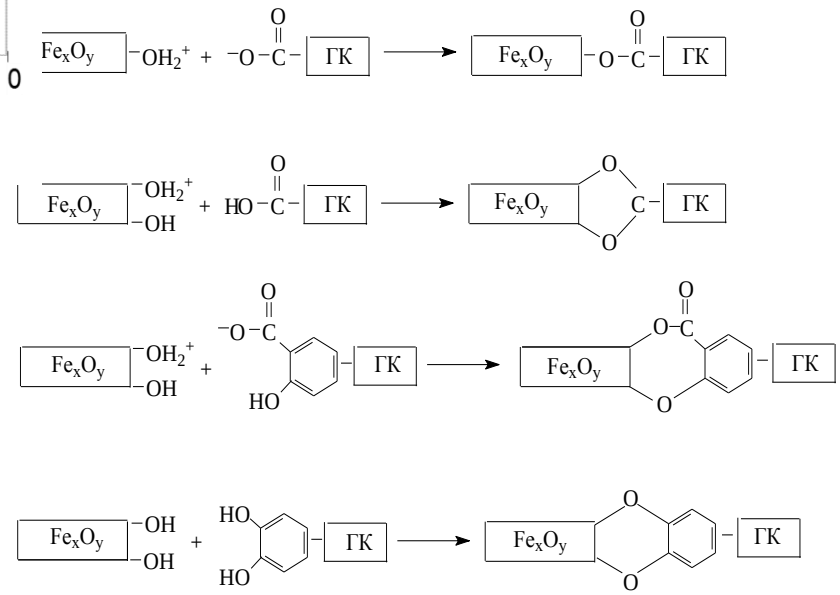
In Mossbauer spectra quadruple doublet corresponding to ^{57}Fe atoms in octahedral surrounding of oxygen is observed. Intensity of doublet correlates with increase of HA content. Size of particles made *d* (Fe_3O_4-HA20-C) = 13,5 ± 0,1 nm, *d* (Fe_3O_4-HA50-C) = 12,3 ± 0,1 nm. Fe_3O_4-HA50-M10 is maggemite (γ-Fe_2O_3).

FTIR – SPECTRA of NANOCOMPOSITES



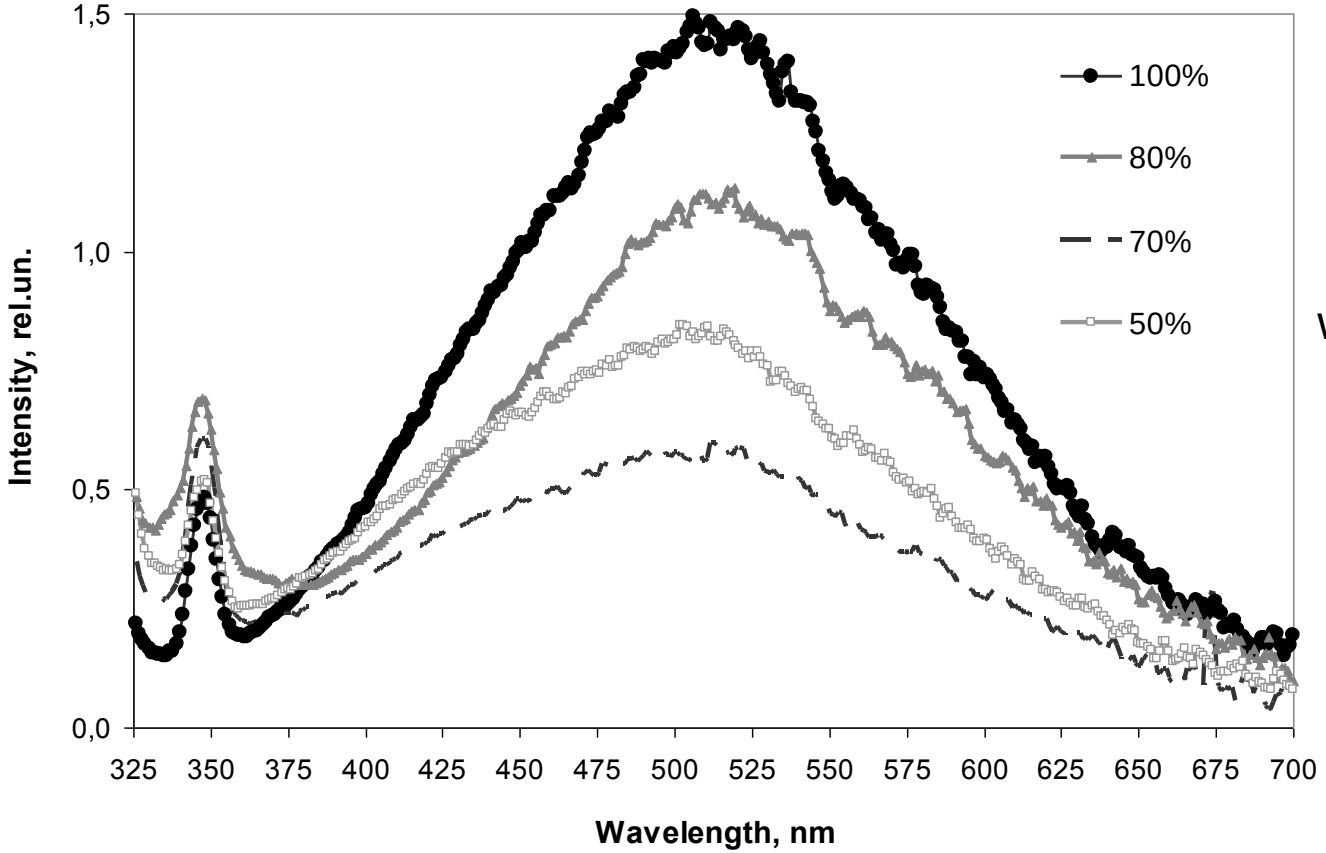
FTIR-spectra of samples: 1 – Fe_3O_4-HA80; 2 - Fe_3O_4-HA90 (IR-200, ThermoNicolet, KBr, 4 cm^{-1})

- Intensive bands in 1530-1570 cm^{-1} region (C=O), 1400 cm^{-1} (C=O).
- Weakening / disappearance of characteristic bands of carbonyl group (νCO =1710 $см^{-1}$)
- Appearance of bands – symmetric (ν_sCOO=1390-1400 $см^{-1}$) and asymmetric (ν_{as}COO=1560-1590 cm^{-1}) bands of COO-ions



Proposed scheme for mechanisms of interaction of iron oxides with humic acids (Gu et al., 1994, adopted)

FLUORESCENCE SPECTRA OF NANOCOMPOSITES



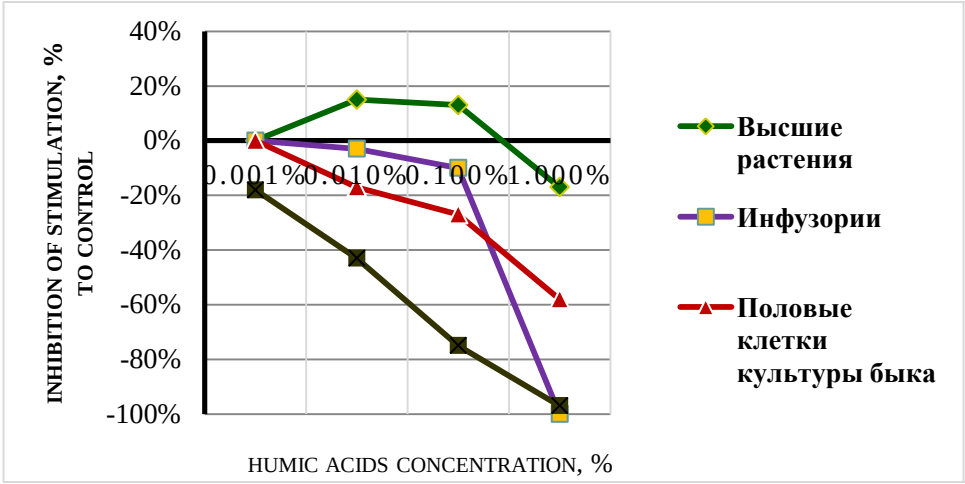
In collaboration with Dr Svetlana Patsaeva

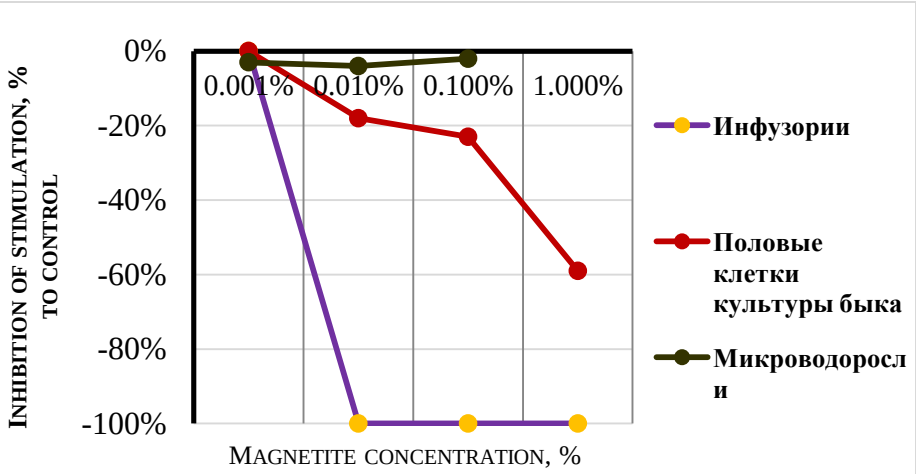
Fluorescence spectra of the HA solution and nanocomposite with the different HA content in water upon excitation at a wavelength of 310 nm

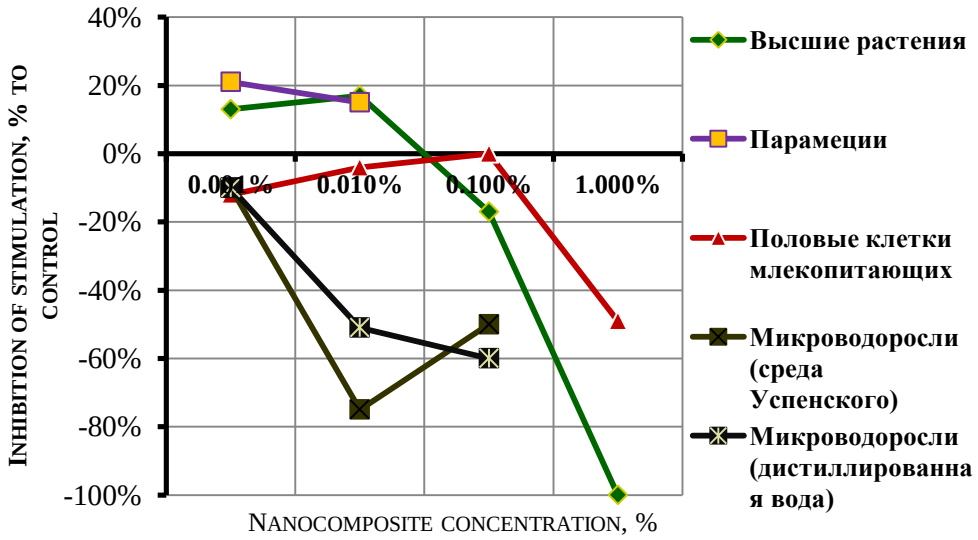
The observed changes in the fluorescence emission maximum indicated that magnetite altered the conformation of humic acid macromolecules and occurred as wavelength-selective fluorescence quenching.
Thus, the HA interact with Fe^{3+} of magnetite in the nanocomposite.

ECOTOXICOLOGICAL ESTIMATION OF Fe3O4@HA and THEIR PRECURSORS

Test-samples - Fe_3O_4-HA90-C, HA and Fe_3O_4 (concentration range – 0.001÷1 wt%)
Test-systems – white mustard seeds (*Sinapis alba*), protococcus algae (*Scenedesmus quadricauda)*, protozoa (*Paramecium caudatum)*, bulls sperm cells (*Bos taurus taurus*) *in vitro*







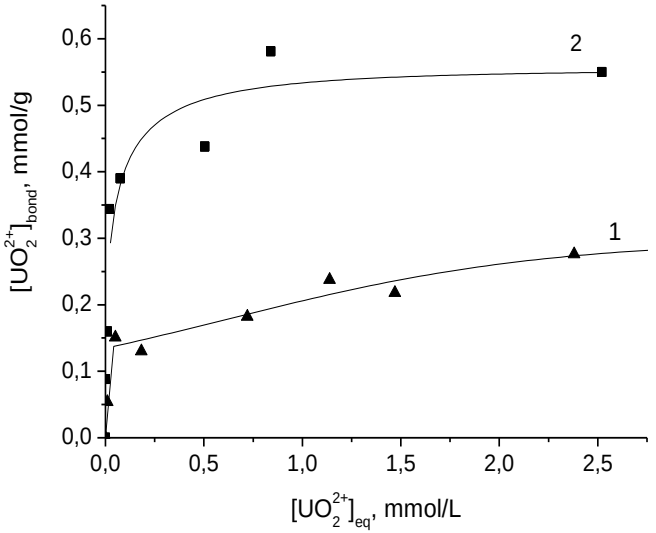
- Fe_3O_4-HA concentration in 0.001% was absolutely safe for all test organisms; the range from 0.001 to 0.01% was still safe for higher plants and bull spermatozoa but toxic for algal cells which appeared to be the most sensitive to Fe_3O_4-HA.
- Further concentration increases up to 0.1% and 1.0% was toxic for the whole battery of organisms.

ЛЭТАП

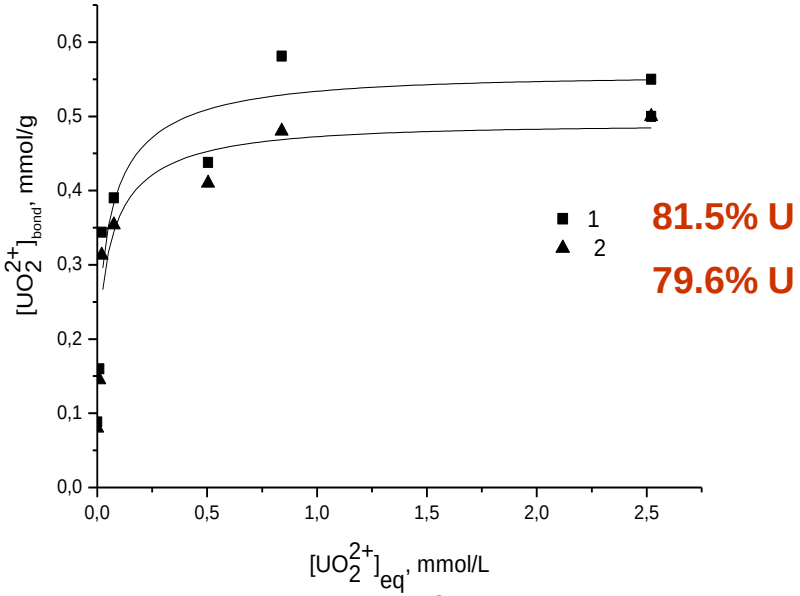
In collaboration with Dr Vera Terekhova

Terekhova V.A., Kydralieva K.A., Matorin D.N., Lisovitskaya O.V., Yurishcheva A.A. *J Env Indicators*: 2014, 8: 4-14.

SORPTION EXPERIMENTS WITH NANOCOMPOSITE



Adsorption isotherms of UO_2^{2+} ions onto HA (1) and Fe_3O_4/HA (2) (insert: linear form of the Langmuir equation)



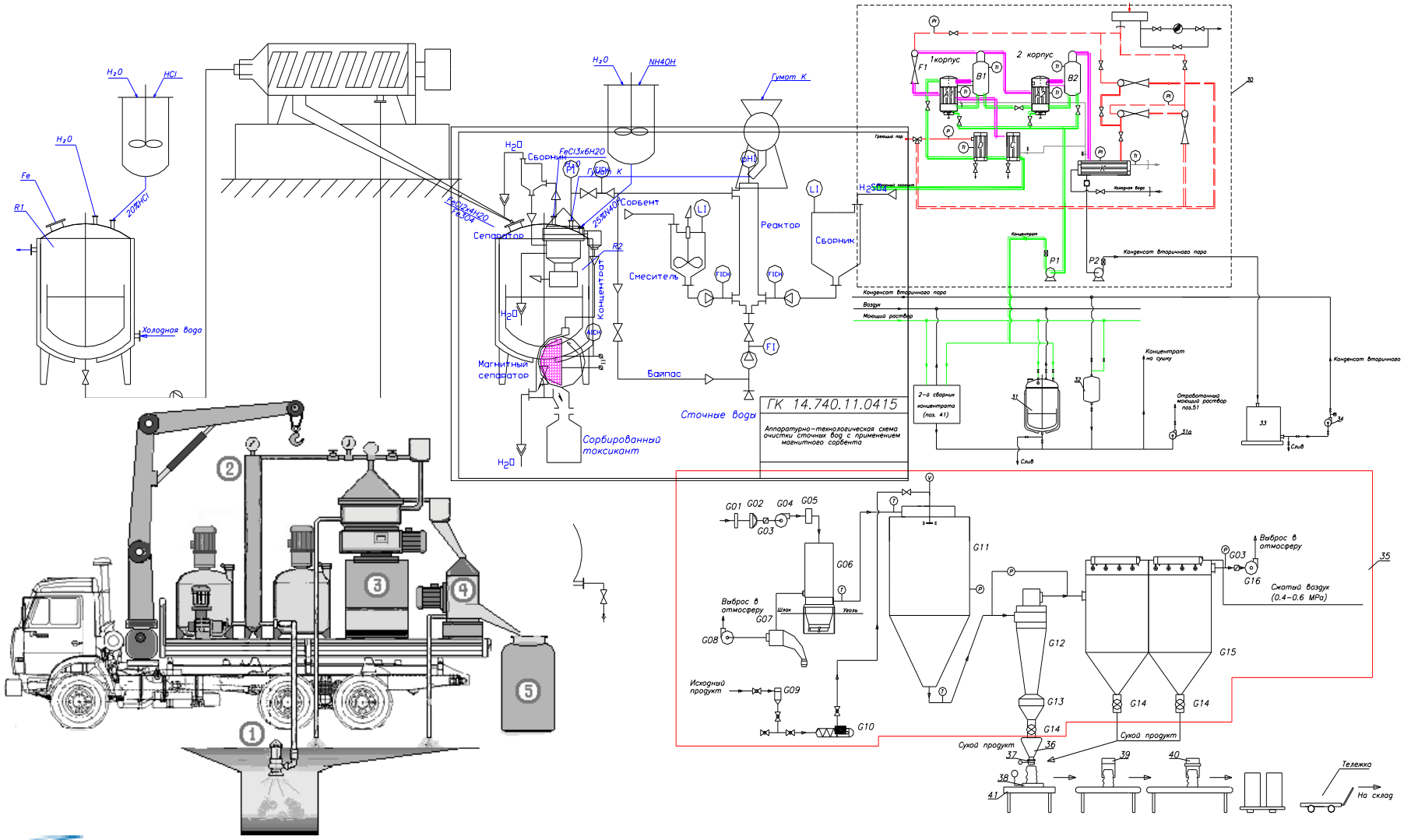
Adsorption isotherms of UO_2^{2+} ions onto Fe_3O_4/HA in the absence (1) and in the presence of Mg^{2+} (x100) (2)

Sample cipher	Q_{max}, mmol/g
HA/UO_2^{2+}	0.31± 0.05
HA@Fe_3O_4/ UO_2^{2+}	0.56± 0.02
HA/Cd^{2+}	0.17-0.22
HA@Fe_3O_4/ Cd^{2+}	0.56± 0.02
HA/Pb^{2+}	0.10-0.18
HA@Fe_3O_4/ UO_2^{2+}	1.78± 0.02

Adsorption of UO_2^{2+} by the nanocomposite is enhanced in comparison with the parent HA.
Fe_3O_4/HA had beneficial adsorption selectivity for UO_2^{2+} with the coexistence of Mg^{2+}.
No serious effect on the adsorption of UO_2^{2+}-ions was observed even when the concentration of the coexisting ions was about 100-fold.

Yurishcheva, Kydralieva, Dzhardimalieva et al., *J Biol Physics & Chem* 2013;
Kydralieva, Dzhardimalieva, et al. *J Inorg Org Polym Mater.* 2016. Review

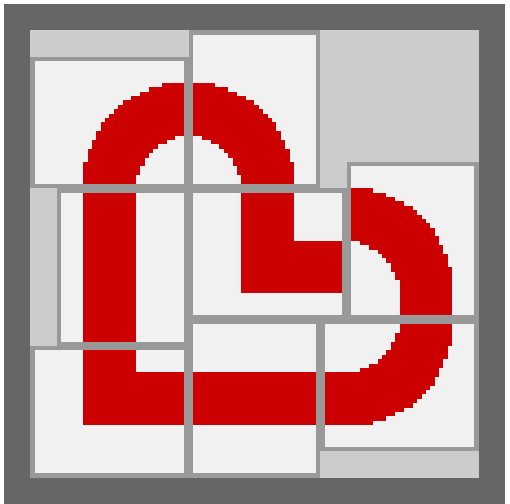
DEVELOPMENT OF HARD-WARE-TECHNOLOGICAL SCHEMES FOR SORBENT PRODUCTION



Hard-ware-technological schemes, unit for production, concentration and drying of sorbent

ION IMPRINTED SORBENTS

preparation, structure, sorption



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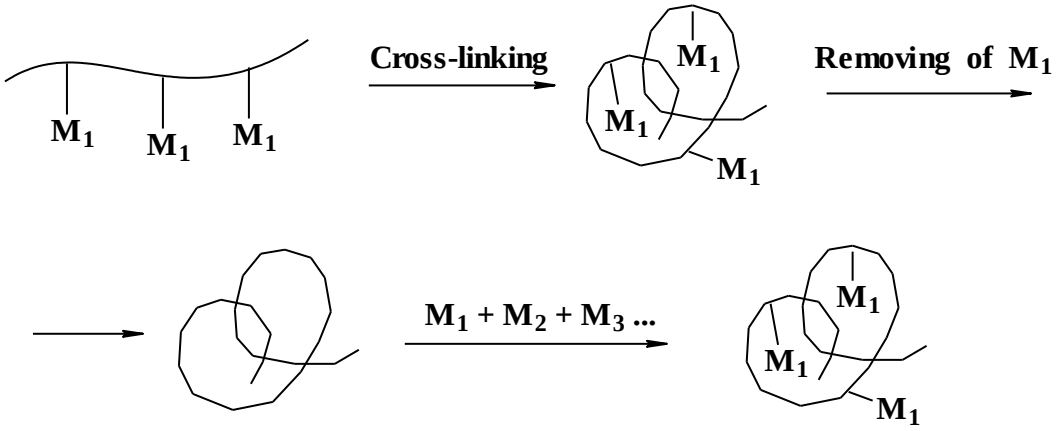
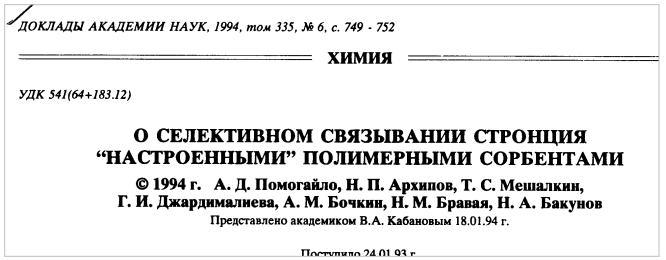
MOLECULAR IMPRINTING SYNTHESIS



"Template" polymer



ДОКЛАДЫ АКАДЕМИИ НАУК, 1994, том 335, № 6, с. 749 - 752

ХИМИЯ

УДК 541(64+183.12)

О СЕЛЕКТИВНОМ СВЯЗЫВАНИИ СТРОНЦИЯ "НАСТРОЕННЫМИ" ПОЛИМЕРНЫМИ СОРБЕНТАМИ

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Представлено академиком В.А. Кабановым 18.01.94 г.

Поступило 24.01.93 г.

Сополимеризация ($Sr(CH_2=CHCOO)_2$) (M_1) с диметакрилатом этиленгликолем (M_2) и сорбционные свойства настроенных полимеров

The composition of monomer mixture, mol.%		The composition of copolymers, mol.%		The content of Sr^{2+}, mg-eqv/g	After sorption, mg-equ/g		*f**
M_1	M_2	m_1	m_2		[Sr]	[Ba]	
95	5	61	39	6.03	**	**	-
89	11	58	42	5.73	2.74	0.10	27.4
73	26	49	51	4.84	3.07	0.14	21.9
49	51	46	54	4.5	1.23	0.06	20.5
23	77	18	82	1.78	0.54	0.78	0.69
12	88	7	93	0.68	0.80	0.96	0.83

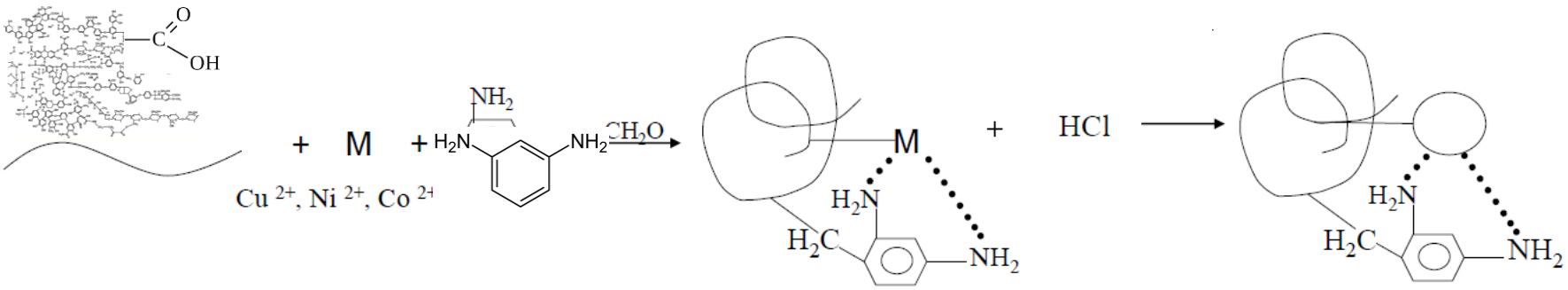
*f the factor of selectivity, i.e., the ratio of amount of "own" metal ion to amount of another metal ion

** the soluble polymers are formed after metal ion removing

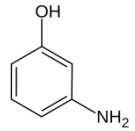
I S T C

M H T Ц

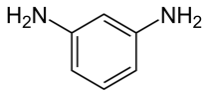
IMPRINTED SORBENTS Fe_3O_4@HA/M



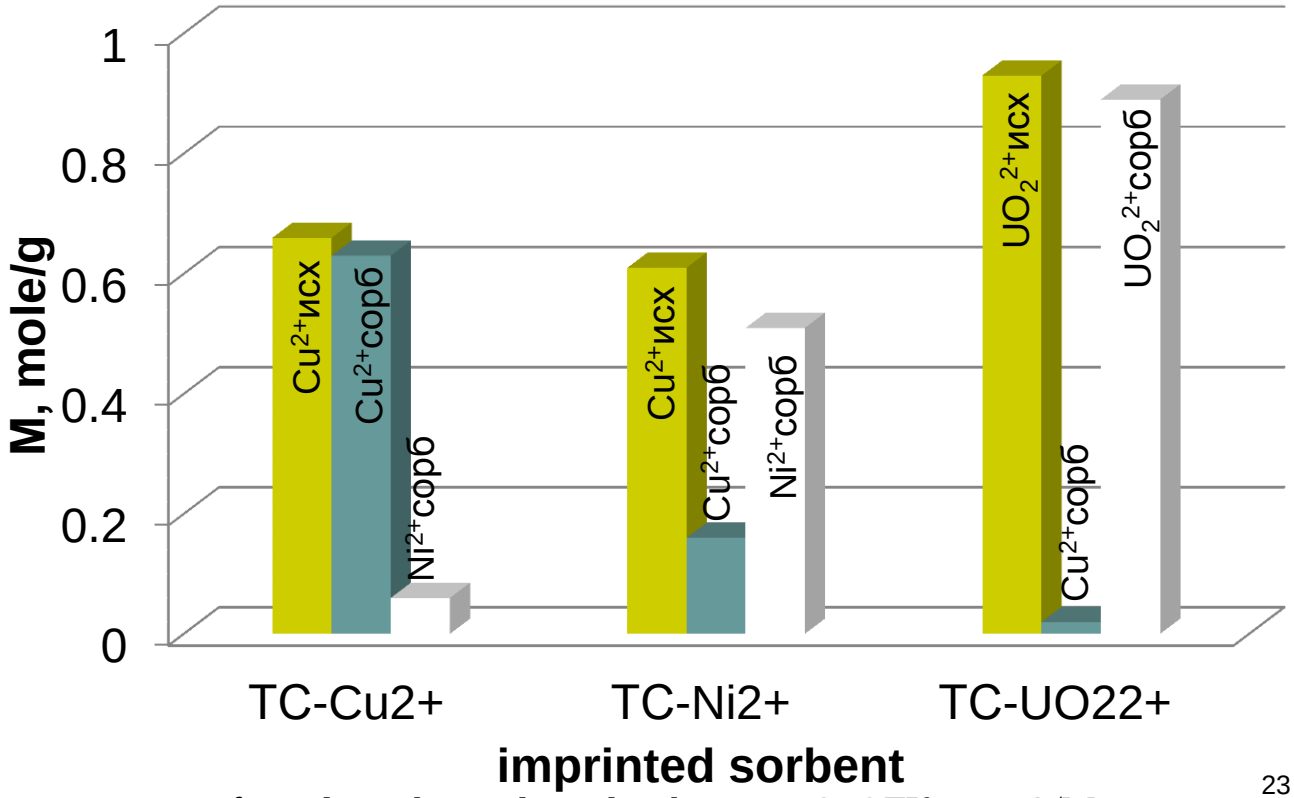
Copolymers:



m-aminophenol, MAP

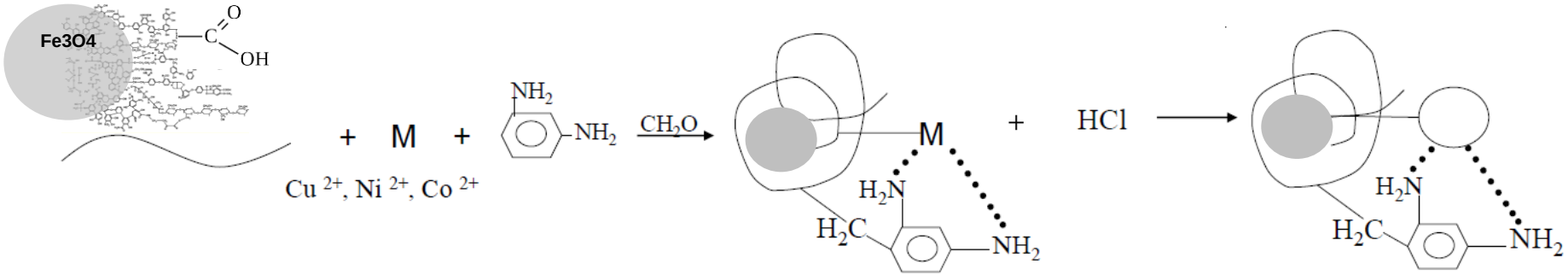


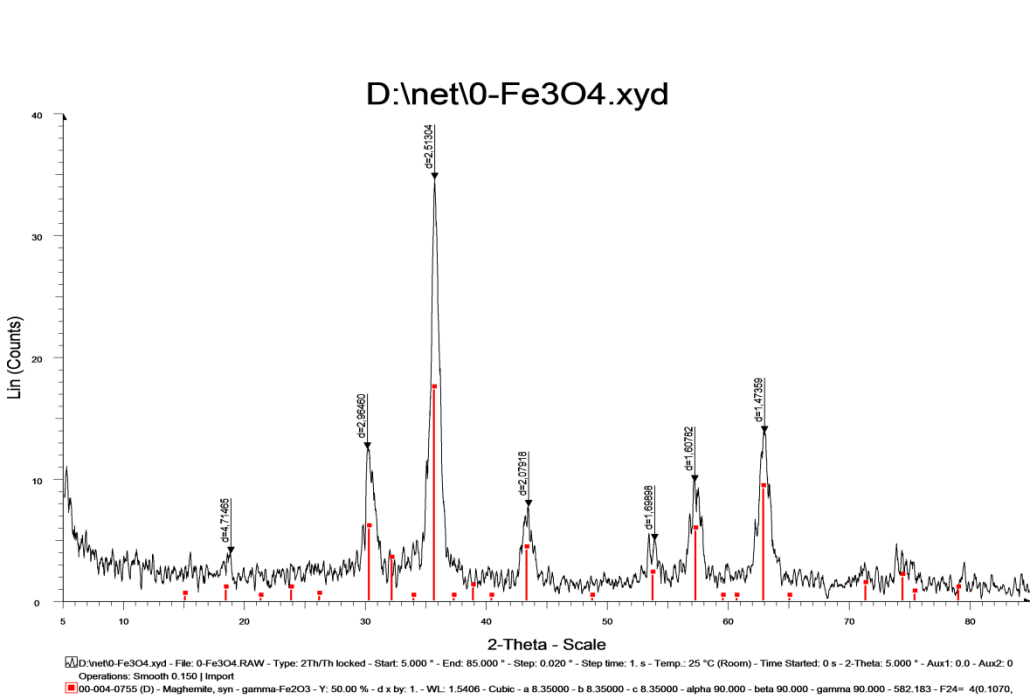
m-phenylenediamine, MPDA

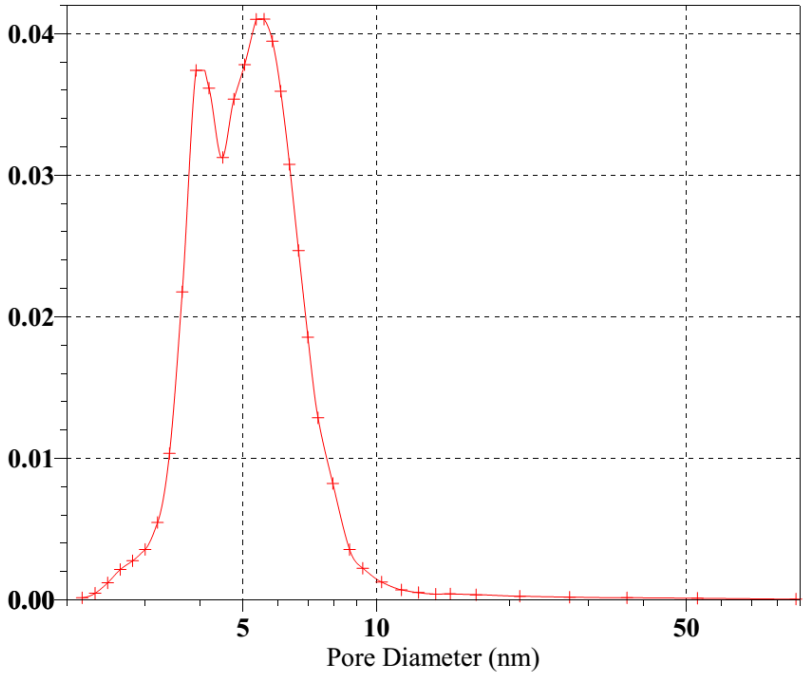


Selective sorption of metal ions by implrinted sorbents Fe_3O_4@ГК-MPDA/M from binary solutions

MAGNETIC ION IMPRINTING OF Fe3O4@HA-MPDA







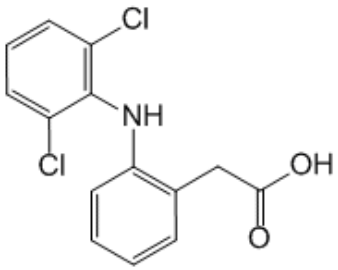
На рентгенограмме определяются линии, соответствующие фазовому составу магнетита. По уширению линий согласно уравнению Дебая-Шерера определен размер частиц для магнетита, равный 15 нм. Мезопористая структура

New project proposal:

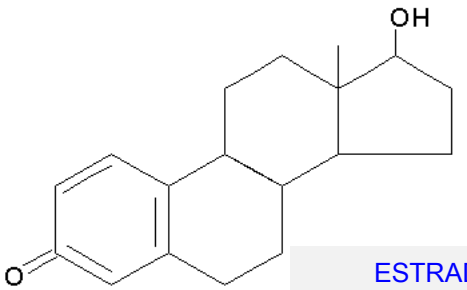
Development of MIPs for removal of pharmaceuticals from wastewater

Model pharmaceuticals:

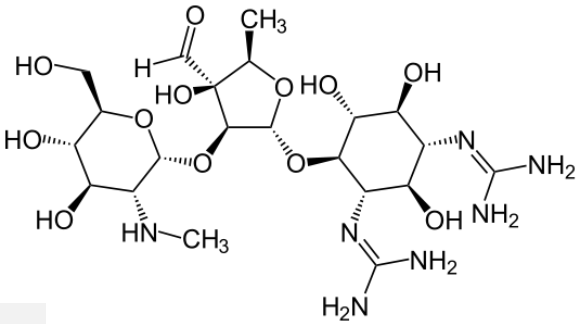
- anti-inflammatory drug (diclofenac)
- estrogen hormone (17 β-estradiol)
- antibiotics (streptomycin)



DICLOFENAC



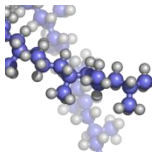
ESTRADIOL



STREPTOMYCIN

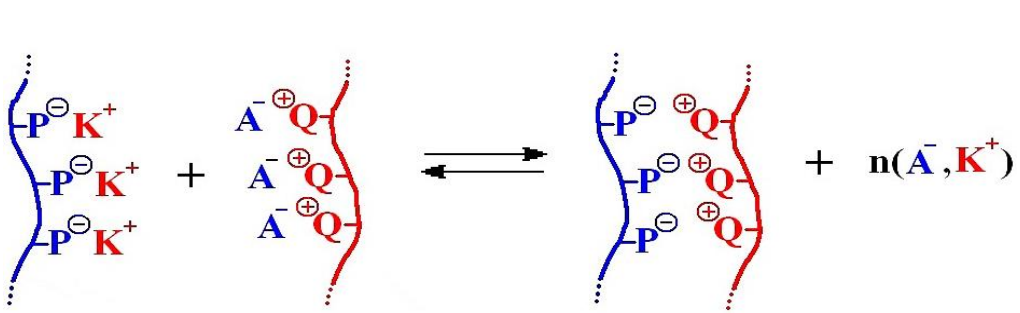
MIPs - Molecular Imprinted Polymers

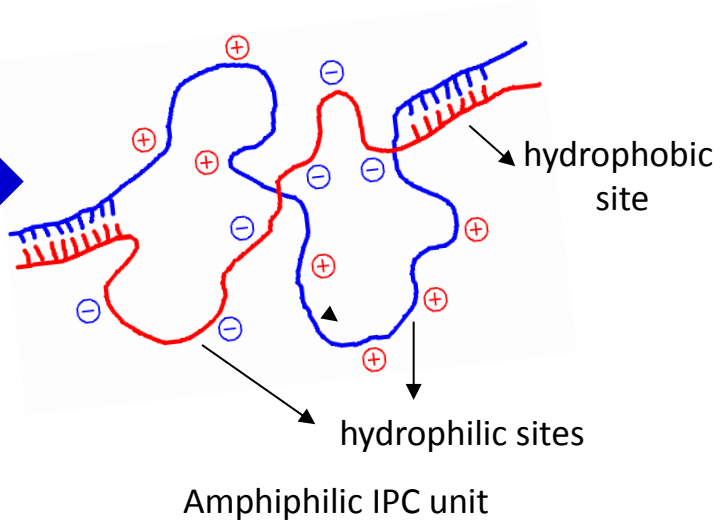
NON-STOICHIMETRIC INTERPOLYELECTROLYTE COMPLEXES (NIPECs)



BASIS FOR TECHNOLOGY DEMONSTRATION

IPC are products of cooperative interaction between oppositely charged polyelectrolytes.

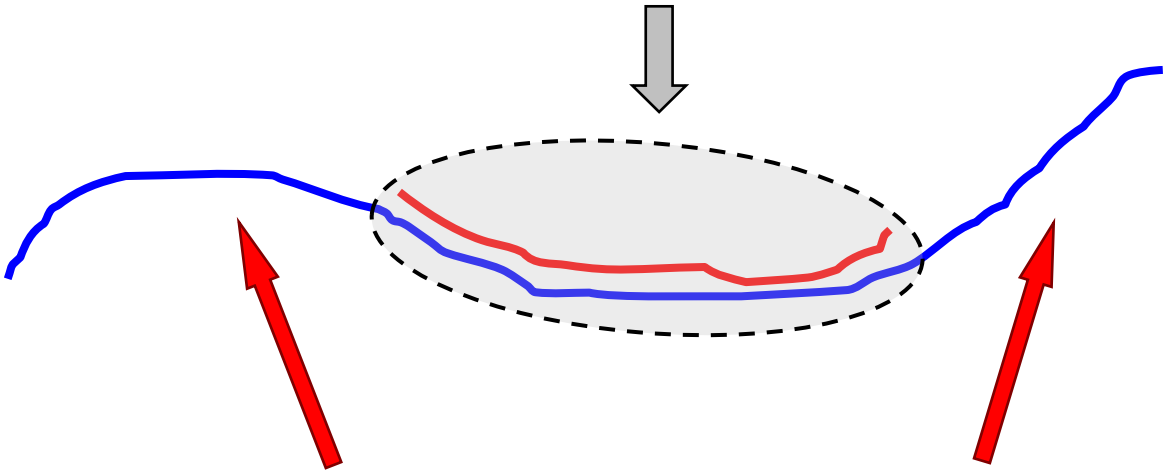




http://www.istc.ru/istc/db/projects.nsf/All/BBD1730AA6328F63C3256C8C003EC55A?OpenDocument&search=1

Anionic NIPEC

a block from mutually neutralized negative and positive charges of both polyelectrolytes, capable of binding to hybrophobic colloidal particles



negative blocks capable of binding to heavy metal cations *and* positive colloidal particles

<u>Expectation</u>: *stabilization* of soil against wind and water erosion and *extraction* of heavy metals from contaminated water/soil

EXTREME PHYSICAL PARAMETERS FOR IPEC

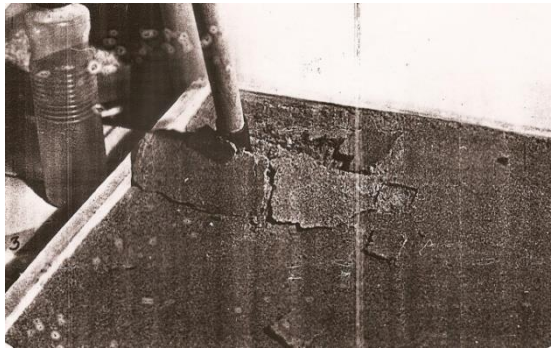
sample	environmental resistance				
	wind rate, m/s	water speed , cm/s	time, year	temperature, ^{o}C	pH
IPCs formulations	30	30-40	2	-20 ÷70	3,5-10

Economical parameters for IPEC

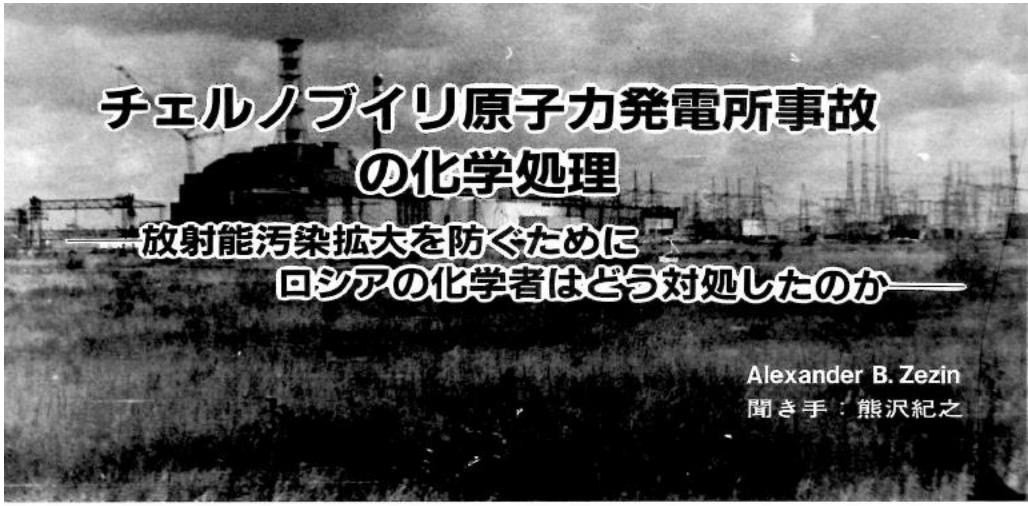
Sample	S	Price, $
IPCs formulations	1 m^2	0.025-0.1
	1 ha	250 (1%)-1000 (2%)

STORY: CASE STUDY IN CHERNOBYL

As a result of the treatment the 5-10 mm topsoil becomes soaked with formulation.
After drying this layer is turned to the solid soil-polymeric crust.



Soil-NIPECs crusts were long-lived systems, they were found on the topsoil (sandy soil) treated with NIPECs by helicopter in two years after the treatment of soil in Chernobyl area.



1986年4月26日，世界を震撼させたチェルノブイリ原子力発電所の事故から13年が過ぎた．この事故による放射能汚染は，ベラルーシ，ウクライナ，ロシアをはじめとする旧ソ連圏の諸国や東欧諸国（図1）に現在もなお暗い影を落としている．がん死亡率の増加をはじめとした住民の健康被害や立入り不能

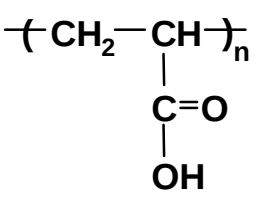
＊　このインタビューは，文部省科学研究費（国際学術研究：研究代表者　吉川研一（京都大学理学部），“単一分子鎖の折り畳みによるナノ秩序構造の自己創出”）により，ロシア側の研究分担者であるZezin教授が来日されたのを機会に行ったものである．

地域の存在は，長い年月に及ぶ世界の負の遺産である．しかし大きな負の遺産であるがゆえに，この事故から学ぶところも大きい．化学者にとっては，事故後の放射性物質の拡散を旧ソ連の科学者がどのような方法で防ごうとしたのかが興味深い点である．

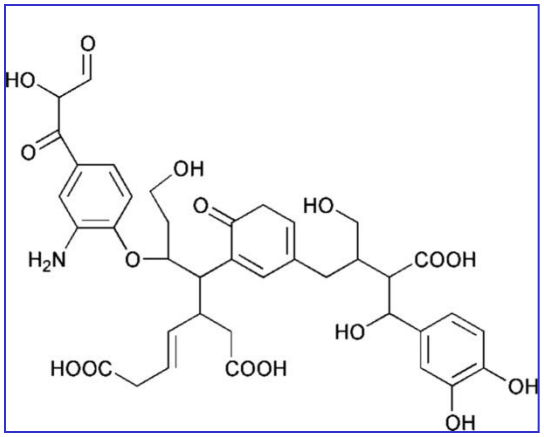
モスクワ大学化学部高分子化学科の教授でありロシア科学アカデミーの一員でもあるA. B. Zezin教授は，チェルノブイリ事故の化学処理に指導的立場で直接携われた科学者の一人である．Zezin教授の経験を伺うことは，放射能汚染事故に対する迅

Polyelectrolytes

Anionic

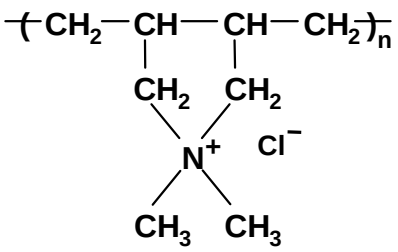


polyacrylic acid (PAA)

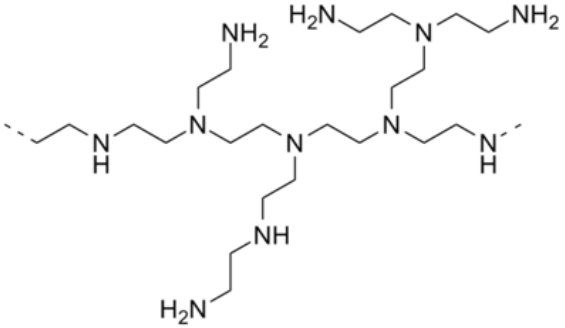


humic acids (HA)

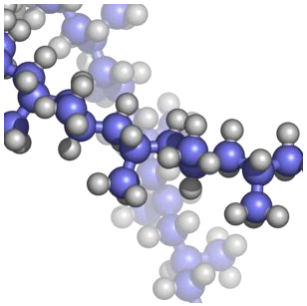
Cationic



polydiallyldimethylammonium chloride (PDADMAC)



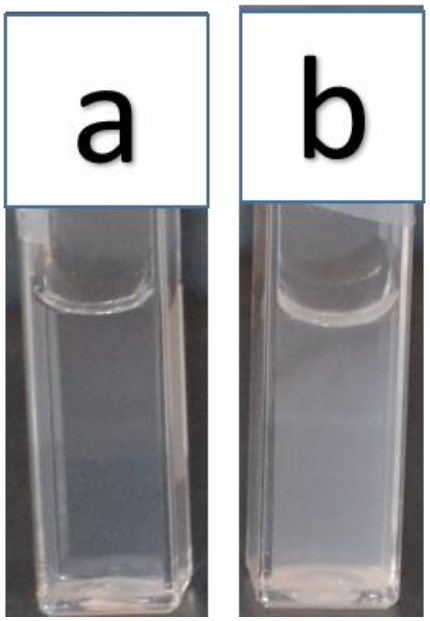
polyethyleneimine (PEI)



In collaboration with Prof Alexander Yaroslavov, Lomonosov MSU

Polyanion-to-polycation complexation

Visual control

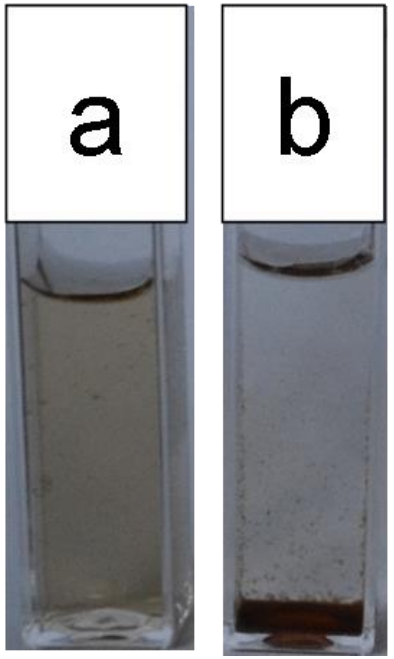


PAA + PDADMAC

PAA + PEI

HA + PEI

HA + PDADMAC



PAA + PDADMAC: opalescence

Photos of a PAA + PDADMAC binary system. PAA conc. 0.72 wt%, PDADMAC conc. 0.32 (a) and 0.81 (b) wt%. TRIS aqueous buffer solution with pH 7.

HA + PEI: precipitation

Photos of a HA + PEI binary system. HA conc. 0.01 wt%, PEI conc. 0.01 (a) and 0.03 (b) wt%. TRIS aqueous buffer solution with pH 7.

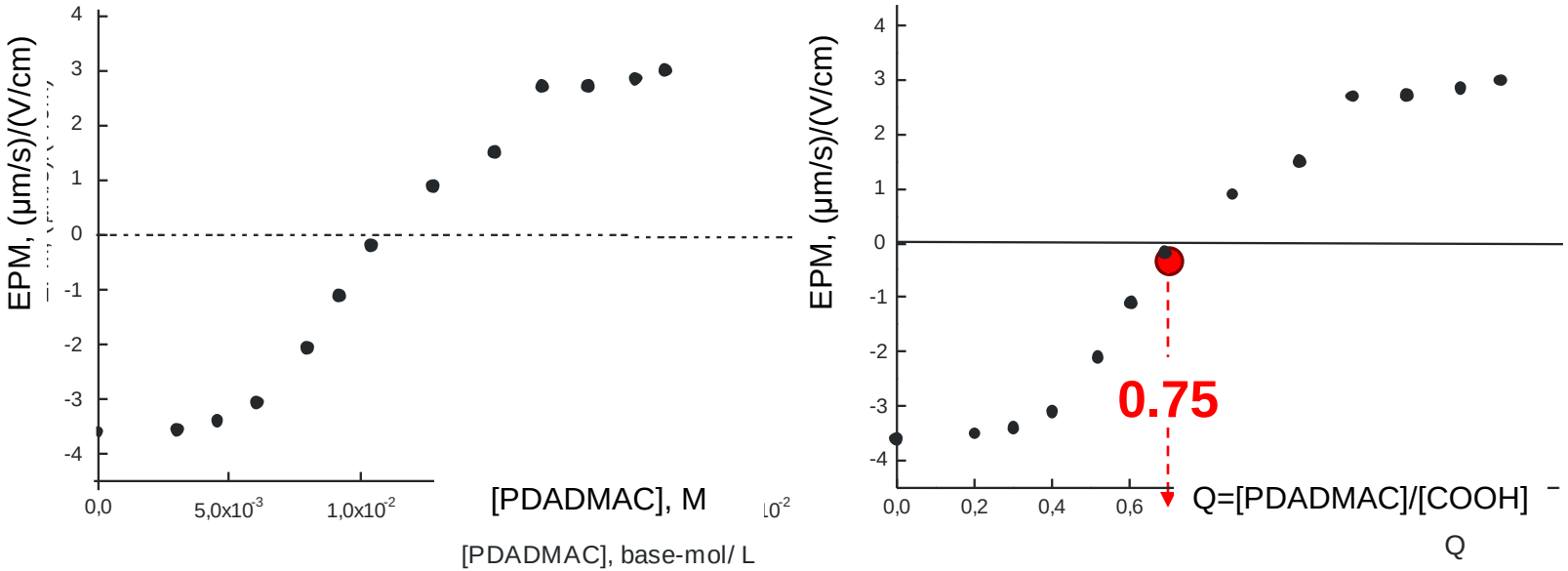
At lower Q values colloidally stable nonstoichiometric interpolyelectrolyte complexes (NIPECs) with an excess of an anionic component (PAA or HA) were formed.

Q - anionic polymer-to-cationic polymer ratios

Panova, Kydralieva,.Jorobekova, Zezin, Yaroslavov. *Geoderma*, 2017 *submitted*

PAA-to-PDADMAC complexation

Electrophoresis



EPM of PAA/PDADMAC binary complex vs. PDADMAC concentration (a) and Q ratio (b). PAA conc. 0.0072 wt%, TRIS aqueous buffer solution with pH 7.

EPM=0 points allowed to find the concentration of COO^- groups capable of electrostatic binding to PDADMAC: $[COO^-] = [N]$ at the EPM=0. An excess of either component gave charged complexes, positive in the excess of PDADMAC or negative in the excess of PAA, that demonstrated stability against aggregation.

At EPM = 0, Q = [PDADMAC]/[COOH] = 0.75 → electroneutral (saturated) IPEC

a photon correlation spectrometer Brookhaven Zeta Plus 90

Panova, ..Kydralieva,.. Jorobekova, Zezin, Yaroslavov. *Geoderma*, 2017 *submitted*

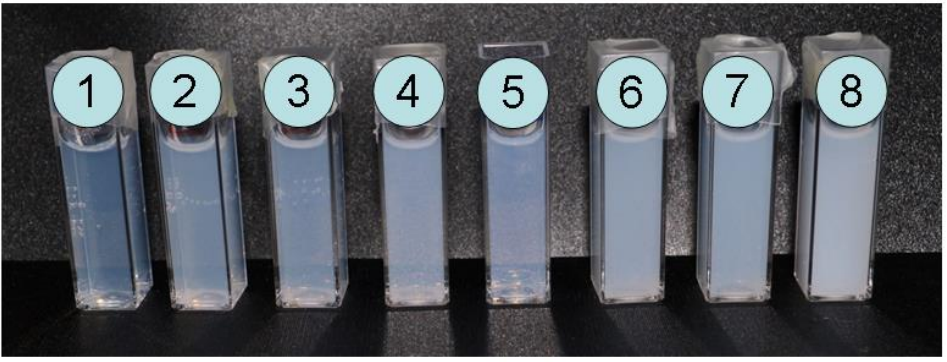
Negative NIPEC

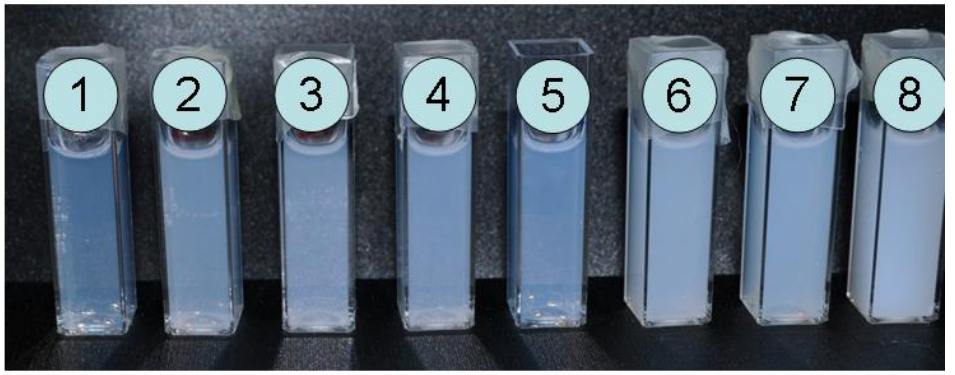
"block copolymers with **hydrophilic** regions, represented by free anionic units, and **hydrophobic** fragments of mutually neutralized anionic and cationic units"

EPM and size of negative PDADMAC-PAA NIPEC

Q	Electrophoretic mobility, (μm/s)/(V/cm)	Hydrodynamic diameter, nm		
		5 min after preparation	1 month after preparation	3 month after preparation
0.15	-3.5	40	50	45
0.23	-3.3	55	60	60
0.30	-3.1	95	90	95

NIPEC samples with Q = [PDADMAC]/[PAA] ≤ 0.3 demonstrated excellent aggregation stability for at least within 3 months after preparation





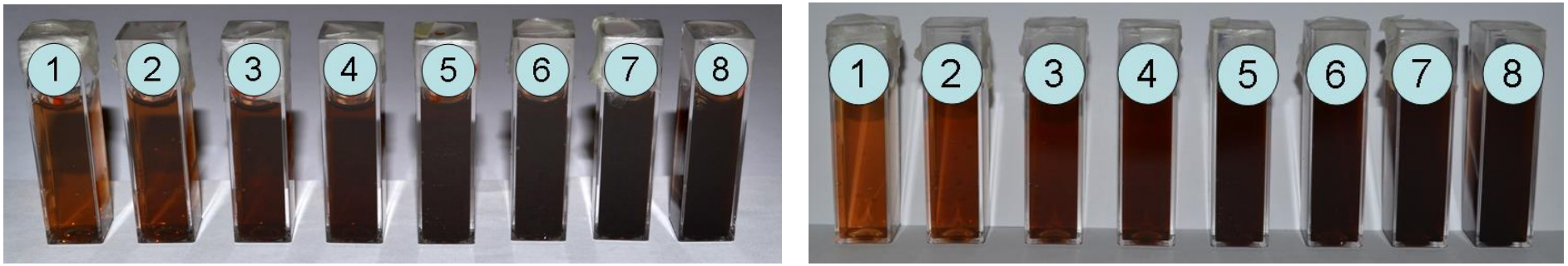
Suspensions of PAA/PDADMAC NIPECs 5 min (left) and 2 weeks (right) after preparation. Q_{comp} = 0.2, PAA conc. 0.022 (1), 0.029 (2), 0.036 (3), 0.043 (4), 0.050 (5), 0.058 (6), 0.065 (7) and 0.072 wt.% (8)

Stability of NIPEC against aggregation

Size (hydrodynamic diameter) of NIPECs measured within 6 month period

HA/PDADMAC (negative)	Q_{comp}.	Diameter after 5 min incubation, nm	Diameter after 14 days incubation, nm	Diameter after 3 months incubation, nm	Diameter after 6 months incubation, nm
1	0.2	75+520	80+550	85+540	90+540
2	0.3	215+580	230+630	225+620	230+640
3	0.4	323+700	320+690	295+680	300+690

All unsaturated polycomplexes (NIPECs), both negative and positive, showed high aggregation stability at least within 6 months after preparation.



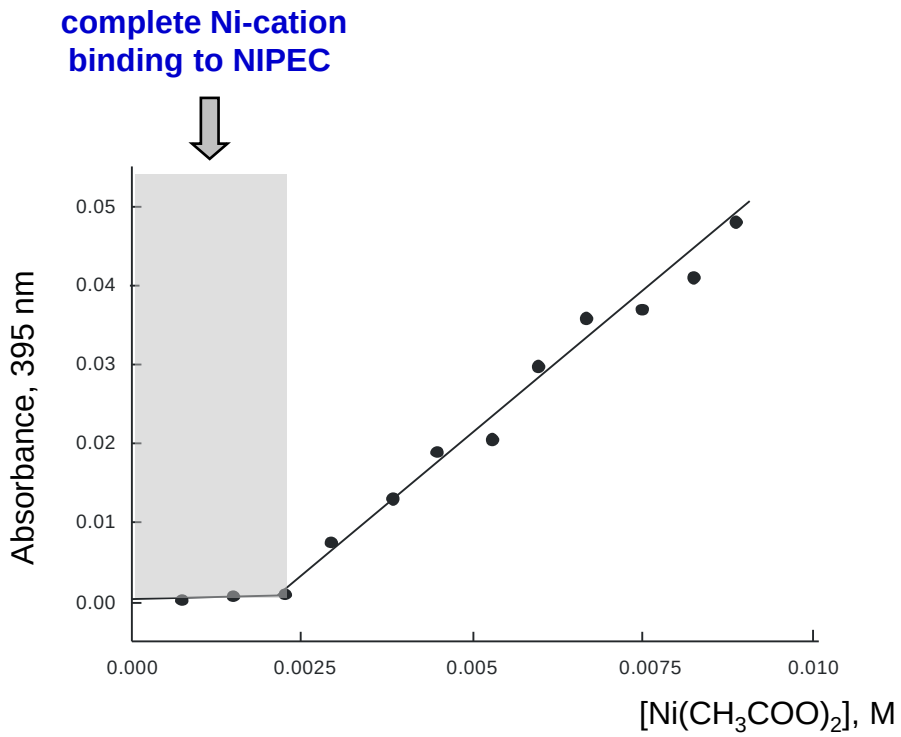
Binary NIPECs HA/PDADMAC 5 min (left) and 2 weeks (right) after preparation. Q_{comp} = 0.2, HA conc. 0.03 (1), 0.04 (2), 0.05 (3), 0.06 (4), 0.07 (5), 0.08 (6), 0.09 (7) and 0.1 wt.% (8).

NIPECs form stable colloids in a wide range of concentrations.

Capacity of negative NIPEC to Ni-cations

Procedure:

NIPEC + $Ni(OAc)_2$ → NIPEC formation (Q=0.15) → centrifugation → spectrophotometric measurement of Ni-cations in supernatants

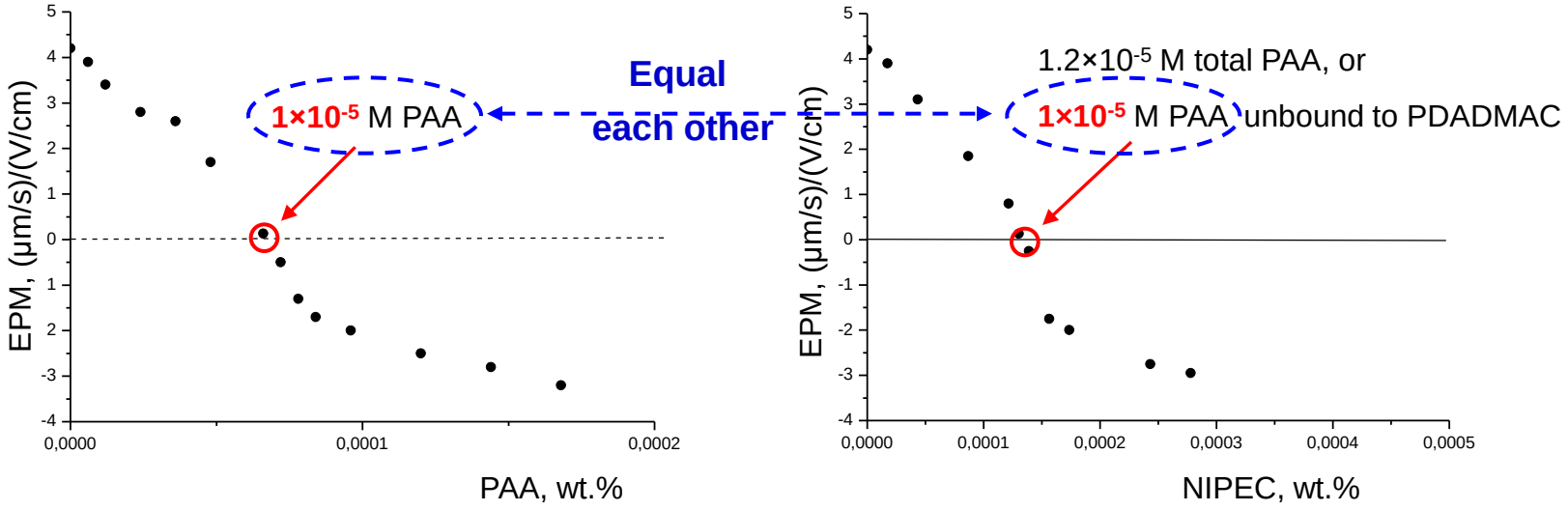


Absorbance of the supernatant after separation of PAA/PDADMAC/Ni(2+) ternary complex vs. Ni(2+) concentration. PAA conc. 0.036 wt. %, PDADMAC conc. 0.011 wt. %

Panova, ..Kydralieva,.. Jorobekova, Zezin, Yaroslavov. *Geoderma*, 2017 *submitted*

Complexation of negative NIPEC with 90 nm cationic colloidal particles

Electrophoresis



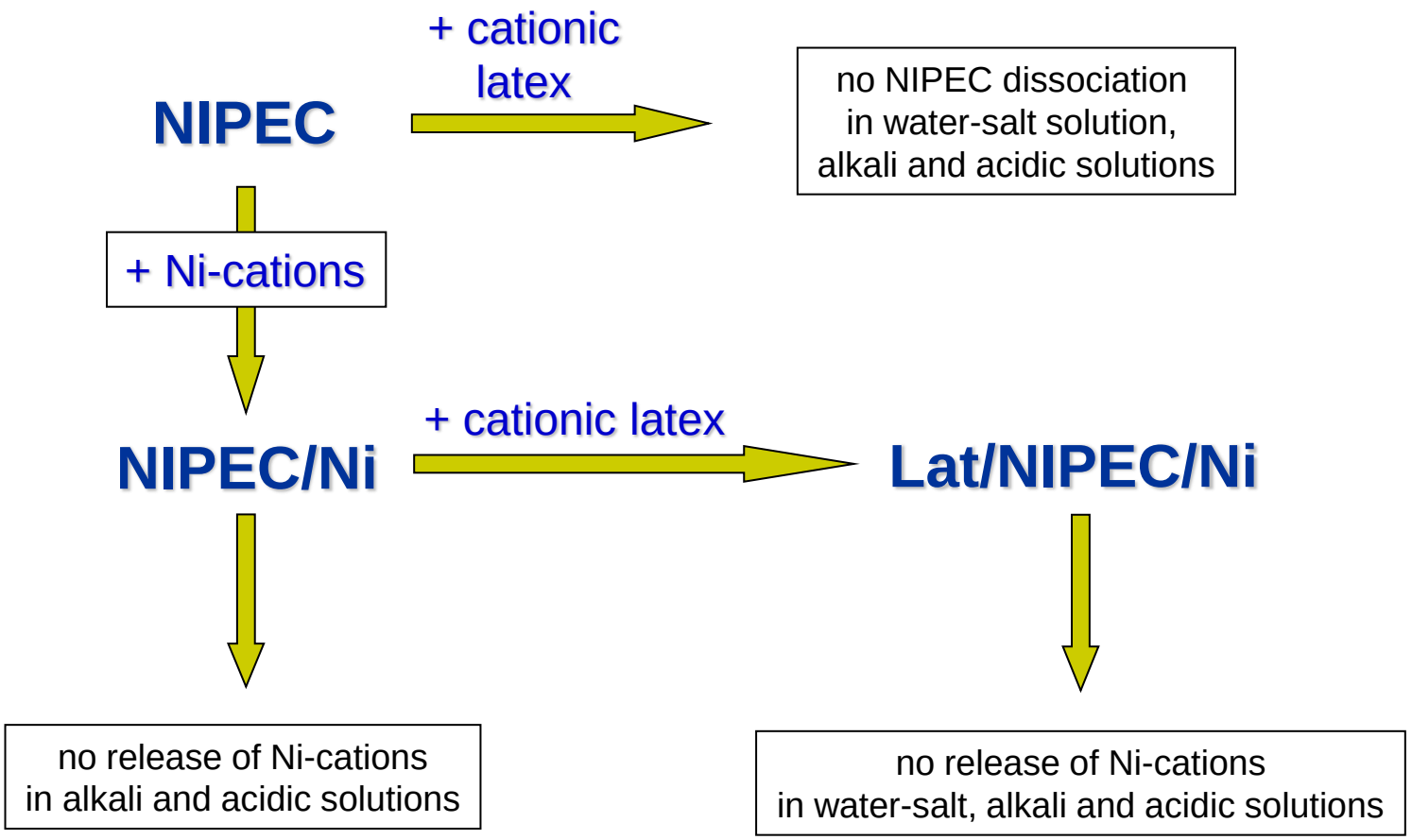
Cationic latex + PAA

Cationic latex +
PAA/PDADMAC NIPEC (Q=0.15)

► negative NIPEC complexes with cationic latex;
NIPEC retains stable under complexation

No dissociation of the quaternary Lat(+)/PAA/PDADMAC/Ni(2+) complexes and quaternary Lat(+)/HA/PDADMAC/Ni(2+) complexes in aqueous salt media was detected.

HA-PDADMAC NIPEC:
Complexation with Ni-cations and colloidal particles



HA-PEI NIPEC

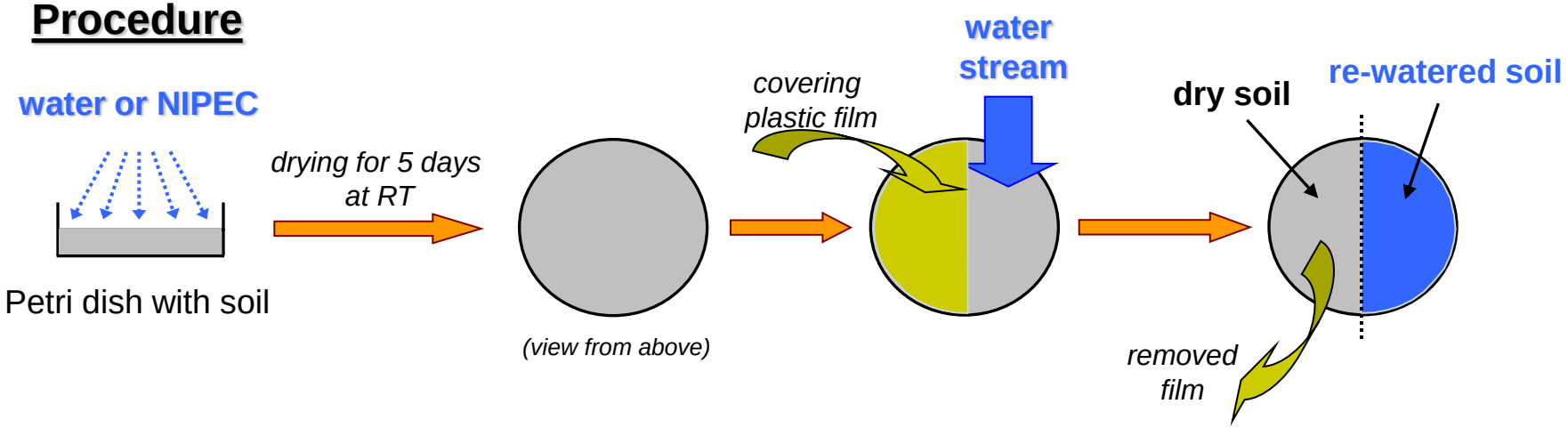
shows a **much higher** (approx. 30-fold) capacity towards Ni-cations in comparison with PAA/PDADMAC NIPEC, most likely due to:

(a) additional binding of Ni-cations to HA carboxylic groups unavailable to PEI macromolecules, or

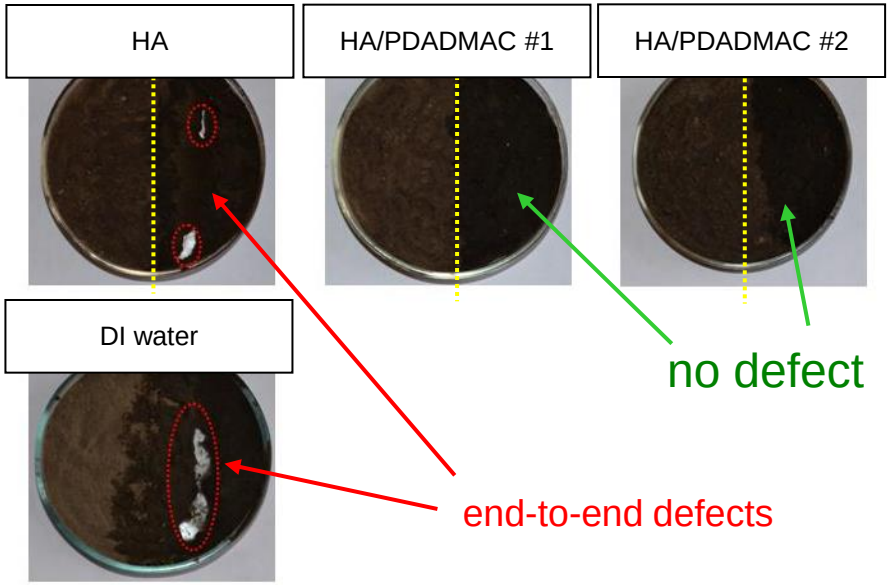
(b) additional adsorption of Ni-cations on the surface of aggregated HA/PEI NIPEC particles

Protective properties of NIPEC formulation: Stabilization of soil against water erosion

Procedure

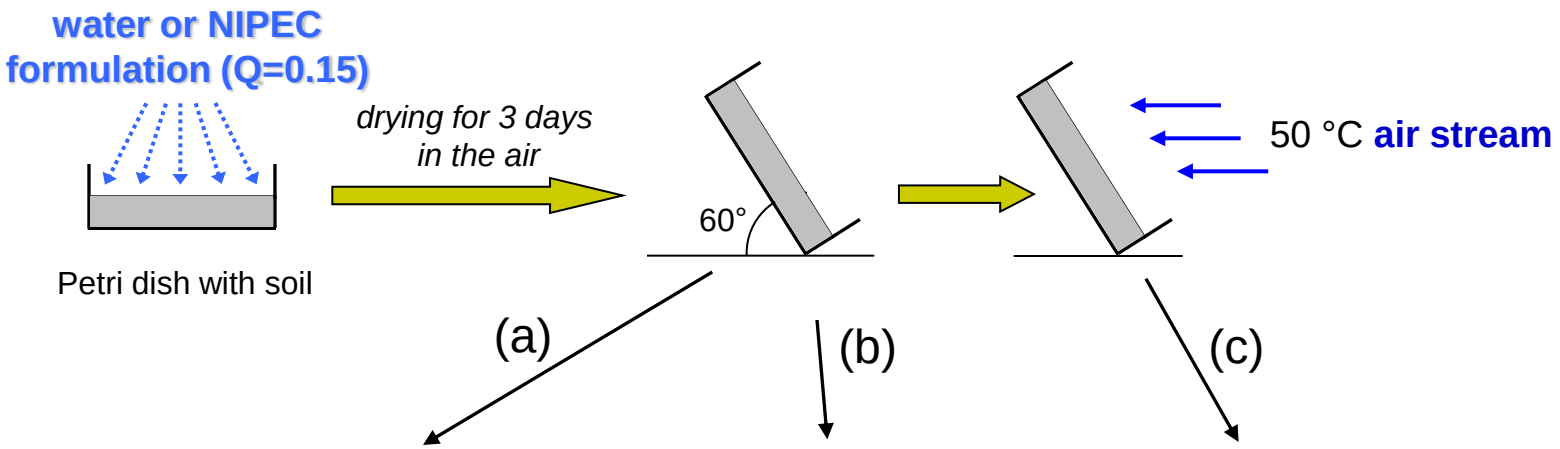


Experimental results



treatment with HA/PDADMAC formulations prevents soil from water erosion;
neither water no one-component polymer solution does not protect soil from water erosion

Protective properties of NIPEC formulation: Stabilization of soil against wind erosion



treated by water

treated by NIPEC formulation

treated by NIPEC formulation and subjected to 50 °C air stream

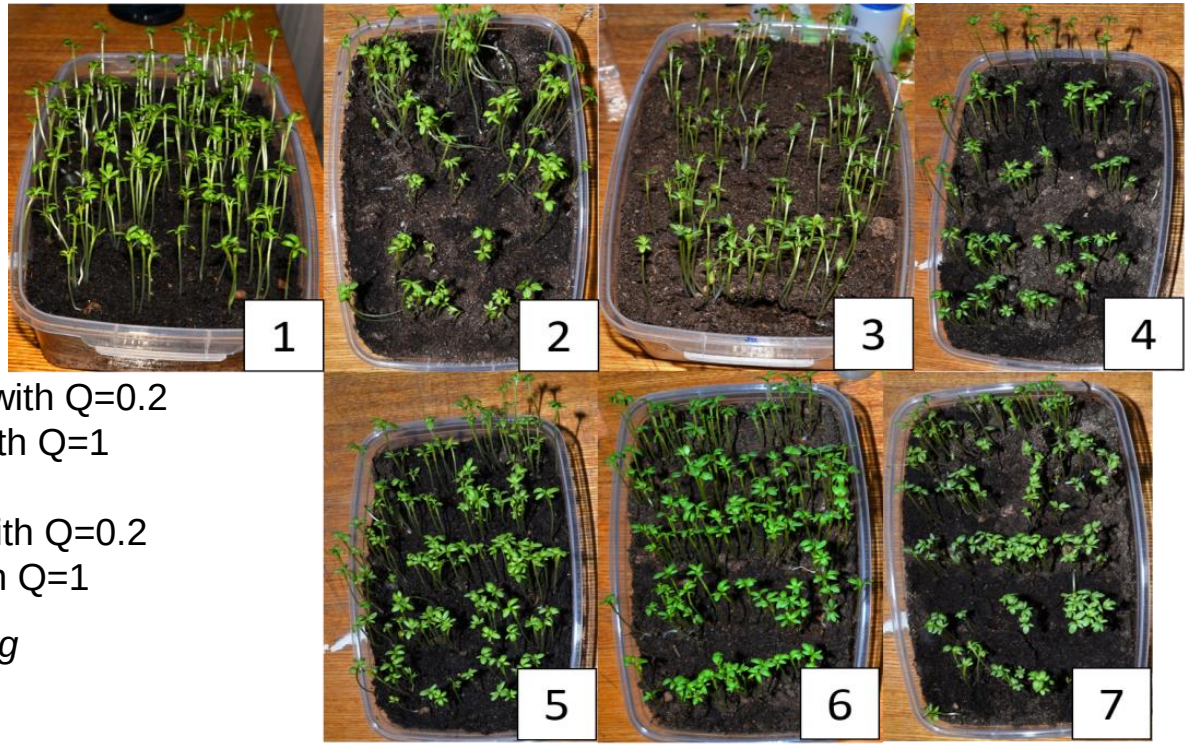
Effect of NIPEC on growth and development of cress-salad crops

Procedure

Soil (8 cm in height) → cress-salad seeds → 2 cm soil layer on top → water or polymer/NIPEC formulation → regular watering for 2 weeks

(1) DI water (control)
(2) 1% PAA solution
(3) 1% PAA/PDADMAC NIPEC solution with Q=0.2
(4) 1% PAA/PDADMAC IPEC solution with Q=1
(5) 1% HA solution
(6) 1% HA/PDADMAC NIPEC solution with Q=0.2
(7) 1% HA/PDADMAC IPEC solution with Q=1

1 week after seeding and polymer treating



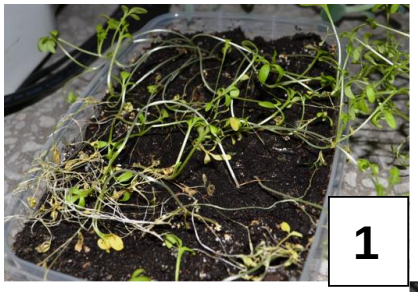
HA solution and HA/PDADMAC NIPEC solution stimulate seed germination

Polymer formulations do not prevent seed germination through the 2 cm soil layer

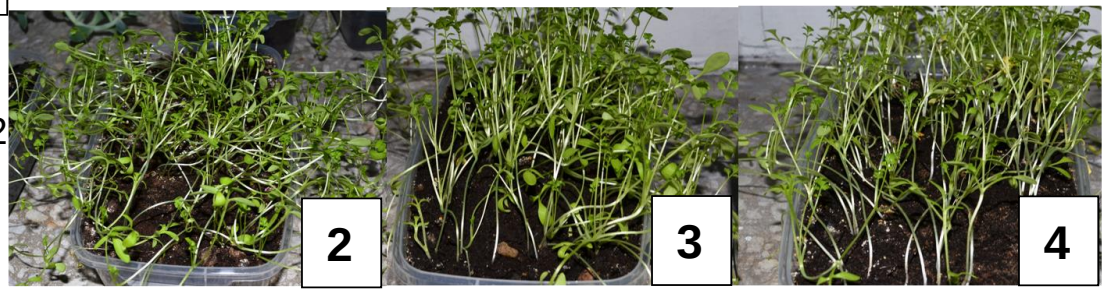
Ability of polymer-treated soil to retain moisture

Procedure

Soil (8 cm in height) → cress-salad seeds → 2 cm soil layer on top → water or polymer/NIPEC formulation → regular watering for 2 weeks → no watering for 1 week



(1) DI water (control)
(2) 1% PAA solution
(3) 1% PAA/PDADMAC NIPEC solution, Q=0.2
(4) % HA/PDADMAC NIPEC solution, Q=0.2

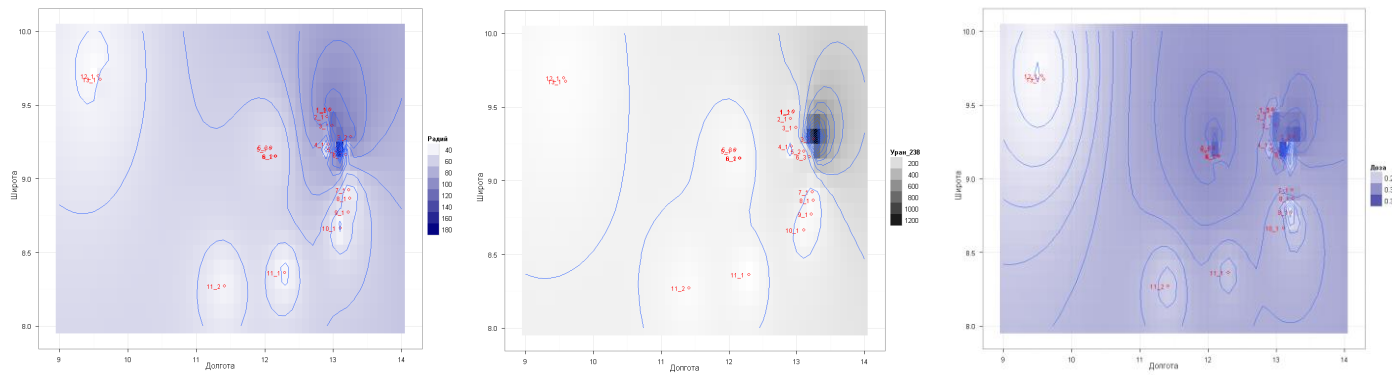


3 weeks after seeding and polymer treating

The soil, untreated by polymer formulation, lost water that led to inhibition of plant growth and yellowing of the foliage, while soils, treated by polymer formulations, retained moisture that maintained the quality of the green cover.

Case study:

Kadzhi-Say uranium technogenic province

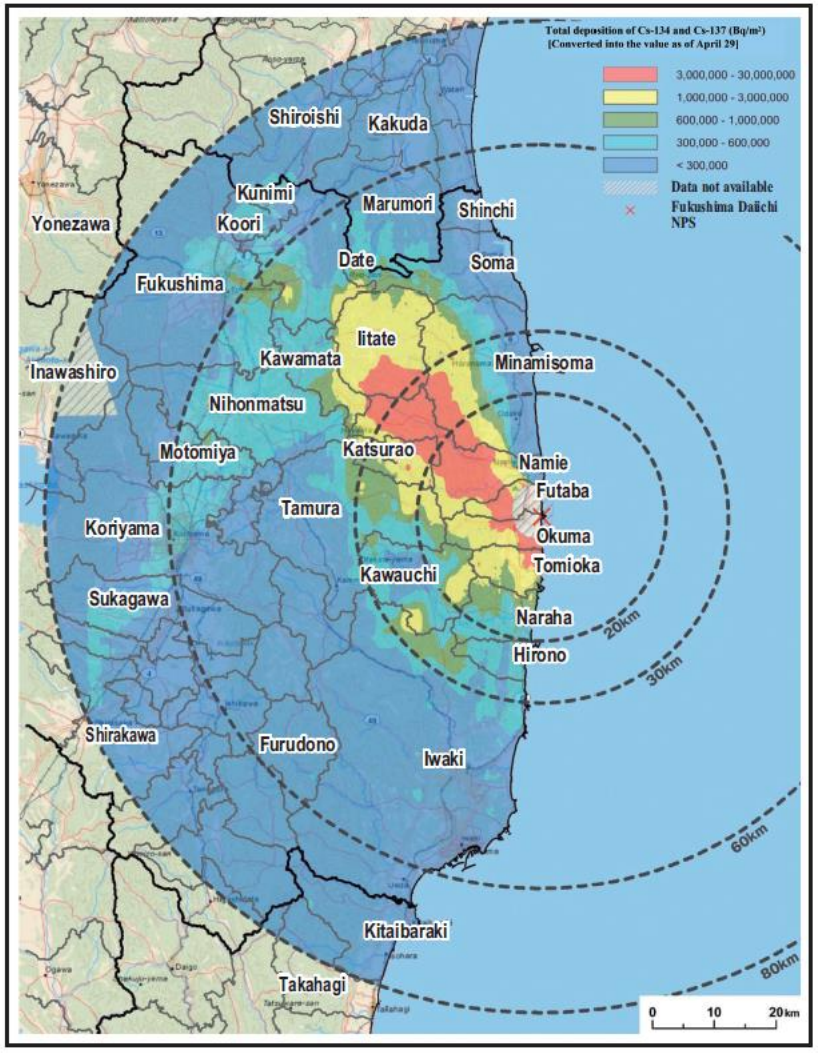


Uranium tailings waste of 400 000 cubic meters and an area of 10800 m^2

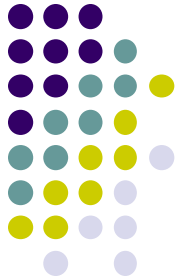
Spatial interpolation of geochemical and radiological indicators for Ra226, U238, exposure dose

Shitikov, Kydralieva et al. *Principles in Ecology*, 2015; Terekhova, Kydralieva et al. *Ecology*, 2017;
Geraskin, Kydralieva et al. *Problems of Regional Ecology*, 2015; Terekhova, Kydralieva et al. *Reports on Ecological Soil Science*, 2014

Fukushima Daiichi
NPS
pilot projects sites, Iwaki

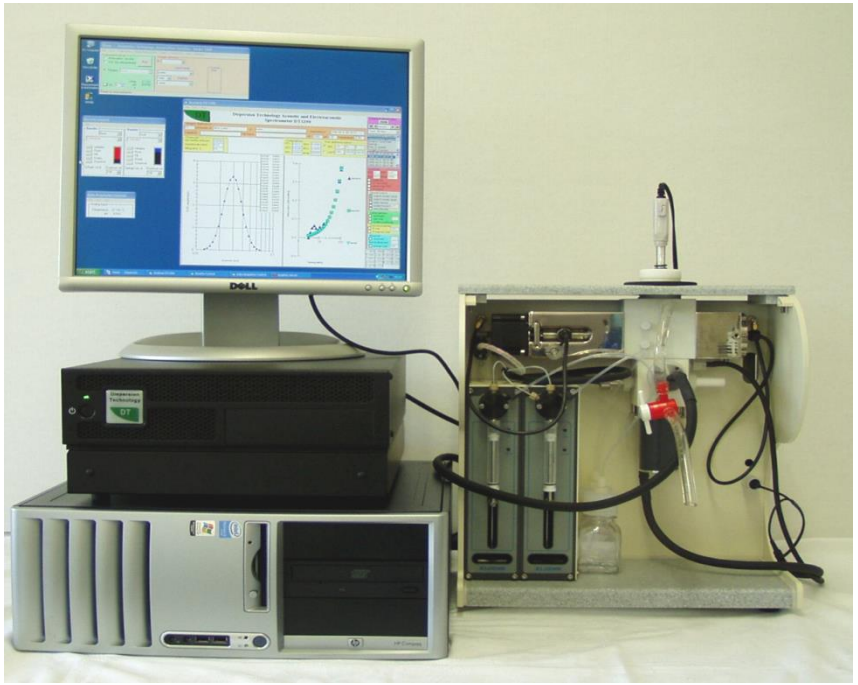


E-mail: kamila.kydralieva@gmail.com



ULTRASONIC SPECTROSCOPY (USS)

measures the change in ultrasound signal per unit distance as it propagates through a material. The interaction between the ultrasonic and the material causes a energy loss in the wave which is specific to the material.



What can USS be used for?

USS can be used to characterize hydrodynamic size and particle size distribution.

Why USS?

- Non-destructive
- Applicable to optically opaque materials

Ultrasonic or Ultrasound is derived from Latin word Ultra means Beyond and Sonic means Sound. Ultrasound is beyond the audible range. Is simply spectroscopy employing SOUND WAVES. Particularly uses a High Frequency ACOUSTIC WAVE, that means the sense of hearing designed to respond. Similarly those used by dolphins for communication.

Infrared Spectroscopy

is the analysis of infrared light interacting with a molecule to find out what kinds of bonds are present in a molecule and to determine functional groups in molecules.

In addition, the mechanism of chemical reactions and the detection of unstable substances can be investigated with such instruments.

IR Spectroscopy measures the vibrations of atoms.

The fundamental measurement obtained in infrared spectroscopy is an infrared spectrum, which is a plot of measured **infrared intensity** versus **wavelength** (or frequency) of light.

X-ray diffraction (XRD analysis) is a unique method in determination of crystallinity of a compound.

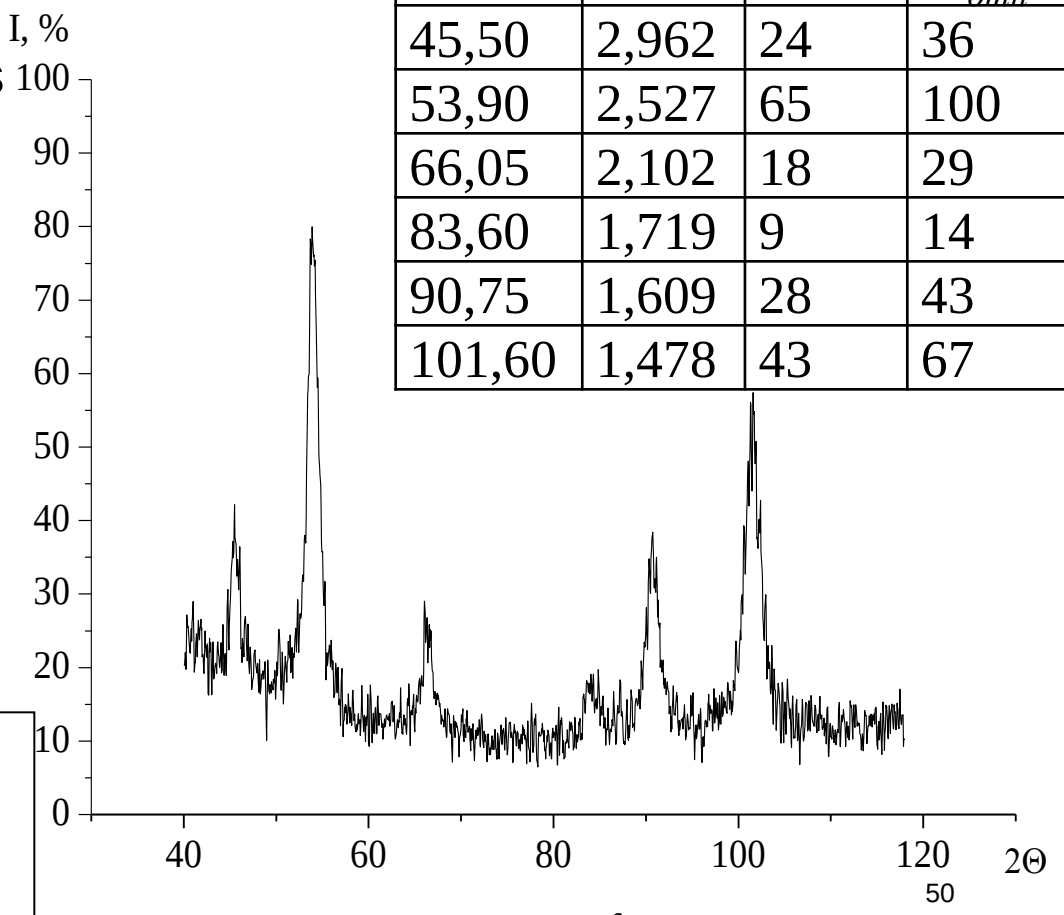
XRD is primarily used for

- ID of crystalline material**,** incl. average crystallite size
- ID of different polymorphic forms (“fingerprints”).

The result from an XRD analysis is a diffractogram showing the intensity *I* as a function of the diffraction angles.

Positive ID of a material using XRD analysis is based on accordance between the diffraction angles of a reference material and the sample in question.

2θ	d	I	$I_{отн}$
45,50	2,962	24	36
53,90	2,527	65	100
66,05	2,102	18	29
83,60	1,719	9	14
90,75	1,609	28	43
101,60	1,478	43	67



XRD for magnetite
(DRON-UM-2, Cu(K_a), 1°/min)

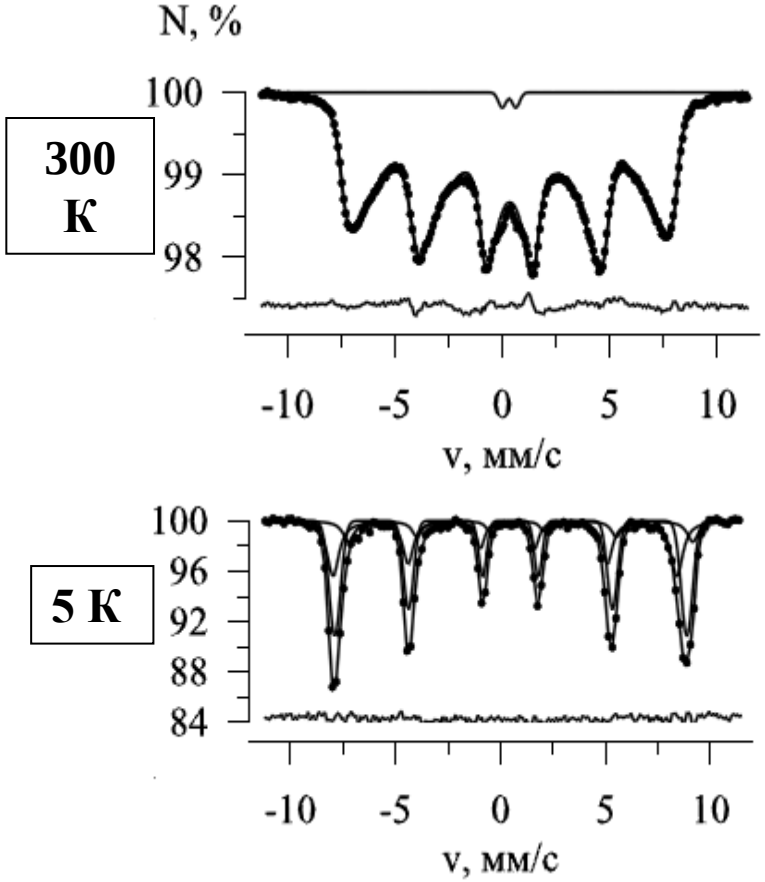
Main component of synthesized material is magnetite Fe_3O_4, size of nanoparticles is ~9 nm according to Sherrer equation.

MOSSBAUER SPECTRA: phase composition and structure of Fe_3O_4

The technique of Mössbauer spectroscopy is widely used

- to examine the valence state of iron, which is found as Fe^0metal), Fe^{2+}, and Fe^{3+}
- to assist in the identification of Fe oxide phases on the basis of their magnetic properties.

The technique probes the hyperfine transitions between the excited and ground states of the nucleus.
Mössbauer showed experimental evidence for recoilless resonant absorption in the nucleus, later to be called the Mössbauer Effect (Nobel Prize).



Mossbauer spectra of magnetite:
300 K (a) и 5 K (b) (MS-1101-E, Mostec, helium cryostat SHI-850-5 (4.5÷500 K), ^{57}Co in Rh matrix, etalon - α-Fe)

In the spectrum (sextet) there are five non-equivalent positions of Fe atoms corresponding to structural formula of Fe_3O_4 and characteristic for superparamagnetic particles.