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The use of thermal release technique with atomic absorption detection for the study of mercury transformation in contaminated environment

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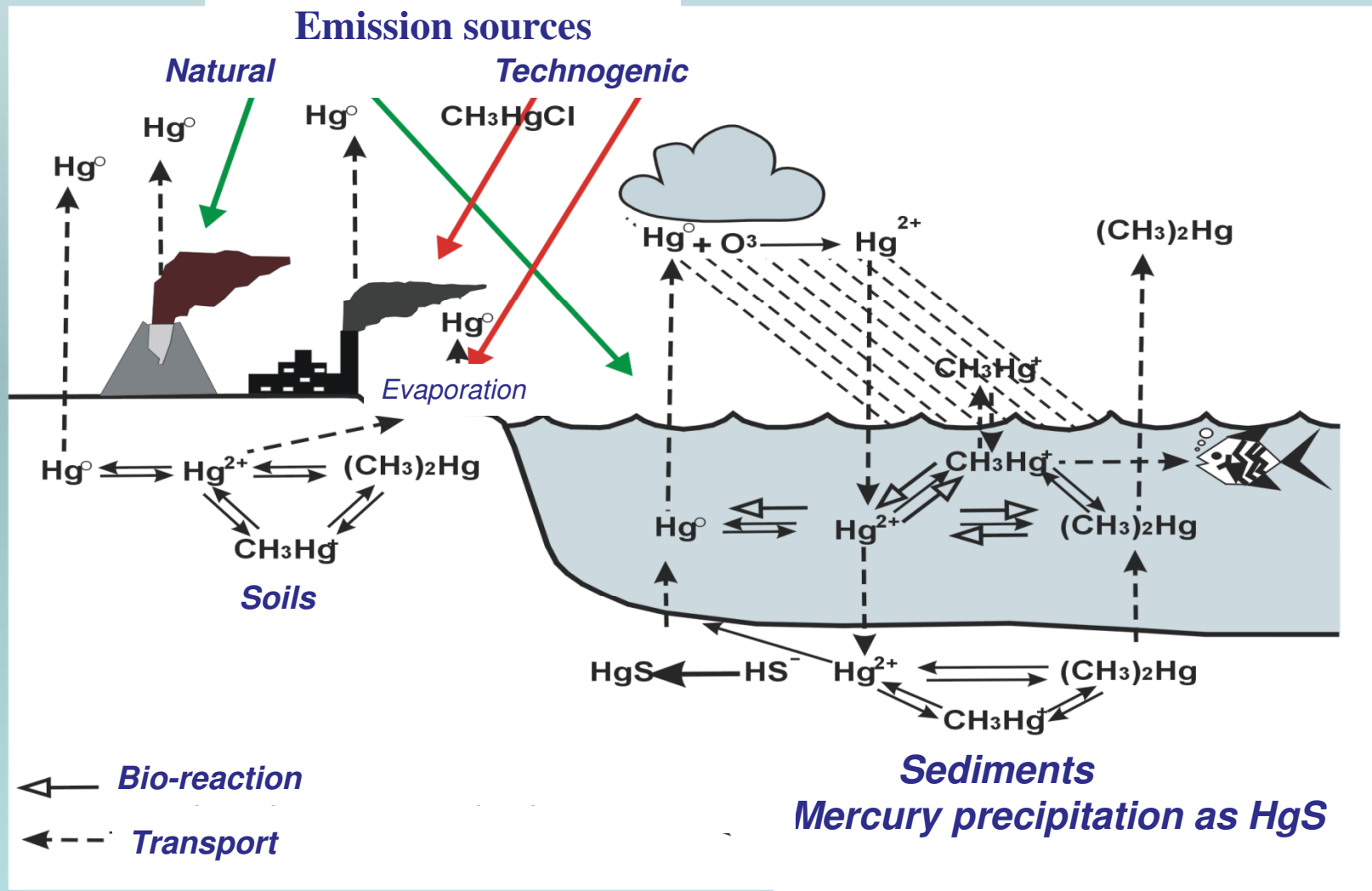
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Biogeochemical cycle of mercury

*Barkay T., Turner R., Saouter E. et al. Mercury biotransformation and their potential for remediation of mercury contamination // *Biodegradation*.-1992.-Vol.3-P 147-159.



The sources of mercury emission:

Natural: gas emission from the earth

Anthropogenic: mining, metallurgy, power plants, pharmacy

Clark (earth core) *0,045 ppm*

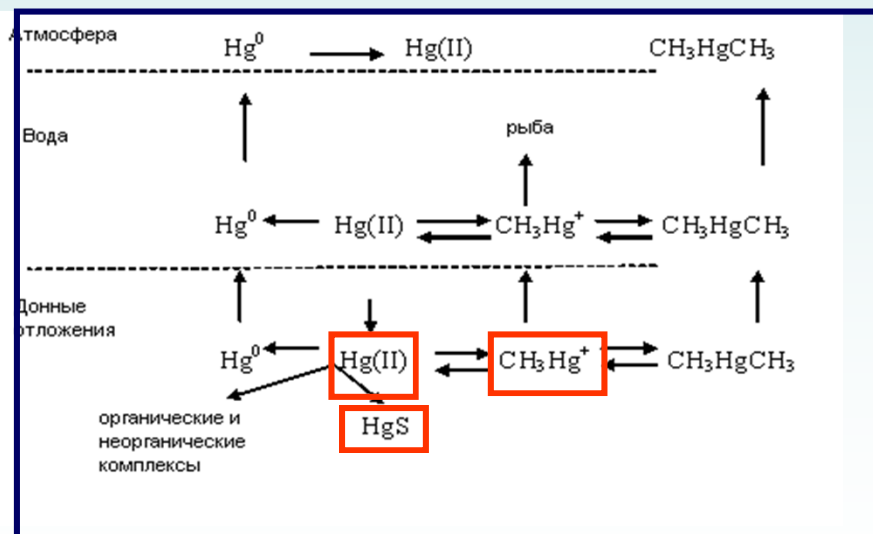
Permissible contents:

Natural (tape) waters - 0,01ppb

Soils - 2,1 ppm

Fish - 0,5 -1,0 ppm

The typical mercury species in environmental and biological samples



The type compound	Chemicals
Elemental	Hg^0
Inorganic compounds	Hg_2^{2+} , Hg^{2+} , HgS
Organic compounds	CH_3Hg^+ , $\text{C}_2\text{H}_5\text{Hg}^+$, $\text{C}_6\text{H}_5\text{Hg}^+$, $(\text{CH}_3)_2\text{Hg}$

The number of toxicity: $(\text{CH}_3)_2\text{Hg} > \text{CH}_3\text{Hg}^+ > \text{Hg}^{2+} > \text{Hg}^0$

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Mercury speciation in solid samples. Current state.

Soils and sediments: different modifications of sequential extraction procedure, distilling off.

Separation: high performance liquid chromatography (HPLC), gas chromatography (GC) usually after derivatization, capillary electrophoresis (CE).

Detection: atomic fluorescence, atomic absorption, inductively coupled plasma atomic emission, mass-spectrometry.

The method based on the thermal evaporation of mercury species from solid samples seems to be a more attractive one because of the absence of the stage of dissolution.

This technique has historically been used for total mercury determination in ores after the trapping by amalgamation on a gold column and decomposition of the amalgam followed by AAS detection.

There have been examples where the thermal release technique was used in combination with AAS for mercury speciation in ores, soils and sediments but no attempts have been made to identify methylmercury.

G.Bombach, K.Bombach, W.Klemm, Fresenius J. Anal. Chem., 350 (1994) 18.

V.L.Tausson, V.I.Menshikov, V.S.Zubkov, Geochemistry (Russia), 8 (1992) 1203.

C.C.Windmoller, R-D.Wilken, W.F.Jardim, Water, Air Soil Poll., 89 (1996) 399.

SUMMARY

Two important conclusions follow from the results of the studies presented in the literature:

- the temperature ranges of mercury compounds release from the samples under analysis are only very slightly different for different species resulting in an overlapping;
- the temperature ranges are dependent on the matrix composition and may differ for the same compounds from one object to another.

The available literature data on the application of the thermal release analysis rather demonstrate the possibility of identification of bonding forms of mercury than the determination of mercury species.

The aim of present work was to develop an assay to determine the most essential mercury species Hg^{2+} , CH_3Hg^+ and HgS in solid samples having different matrixes: soils, sediments, biological probes (fish tissue, plankton) using Thermal Release Atomic Absorption Spectrometry (TR-ETA-AAS).

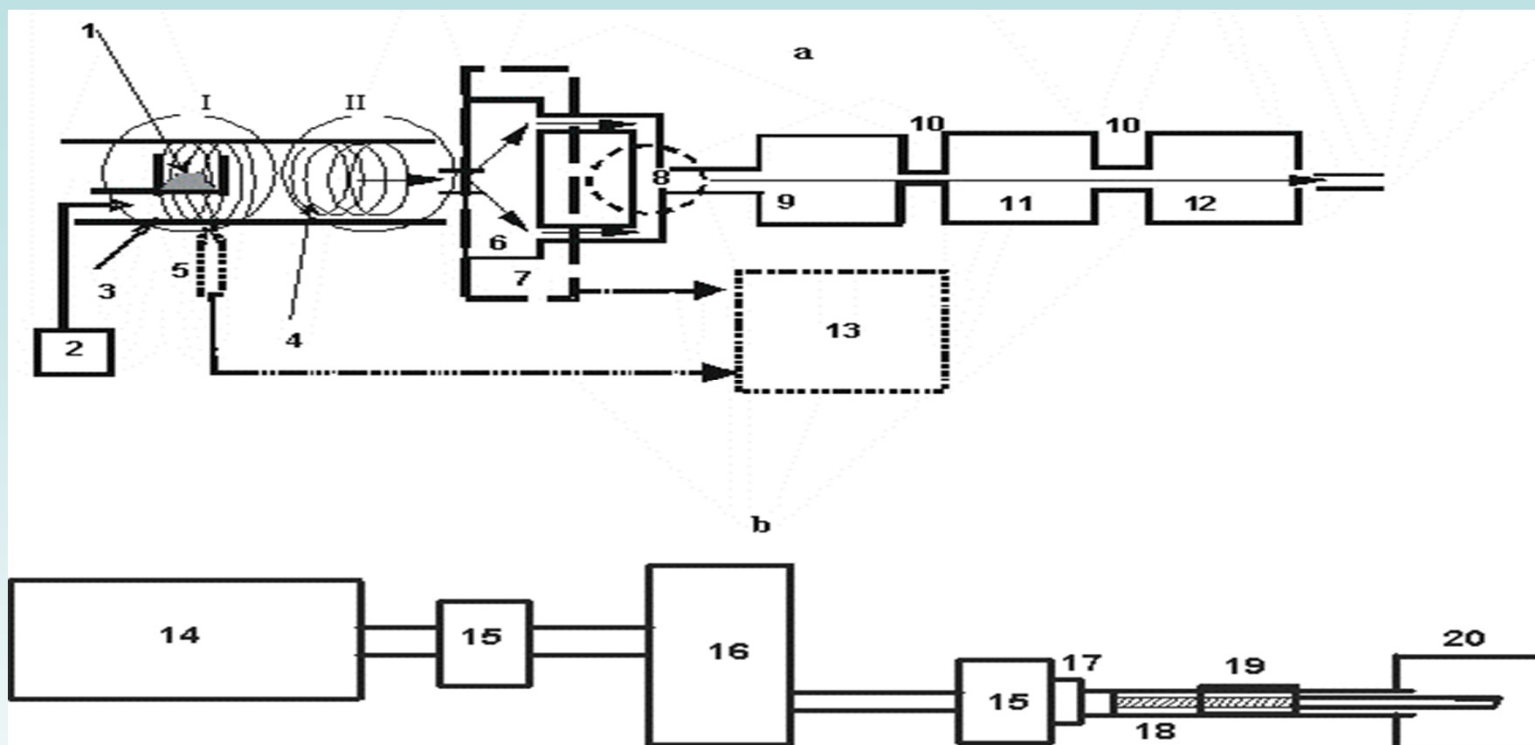
Compliance with 11th principle of Green Chemistry

The main goal of green chemistry – to prevent a pollution during the process of chemical products manufacturing, i. e. pollution prevention at the earliest stages of planning and performing of the chemical processes



To avoid a generation of hazardous wastes the analytical methods of monitoring and control in real time should be developed

The scheme of mercury analyzer RA-915+ (Lumex, S-Petersburg, Russia)

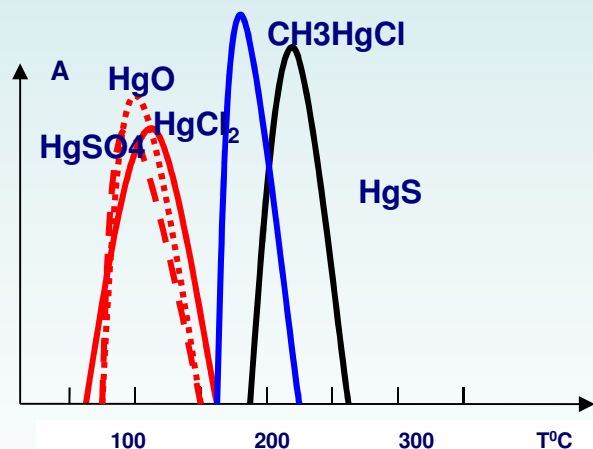


a: 1 – dosing unit, 2 – device for dosing unit replacement, 3 – the first atomizer section ($t \sim 750^{\circ}\text{C}$), 4 – the second atomizer section ($t \sim 800^{\circ}\text{C}$), 5 – thermocouple, 6 – analytical cell of atomic absorption analyzer, 7 – AAS analyzer, 8 - gas tee, 9 – adsorption filter, 10 – connecting tubes, 11 – rotameter, 12 – air pump, 13 – computer;

b: 14- electric motor, 15 – drive shaft coupling, 16 – reducer, 17 – bearing, 18 – micro screw, 19 - sliding nut, 20 – the entrance into the pyrolytic attachment.

The formation of analytical signal includes:

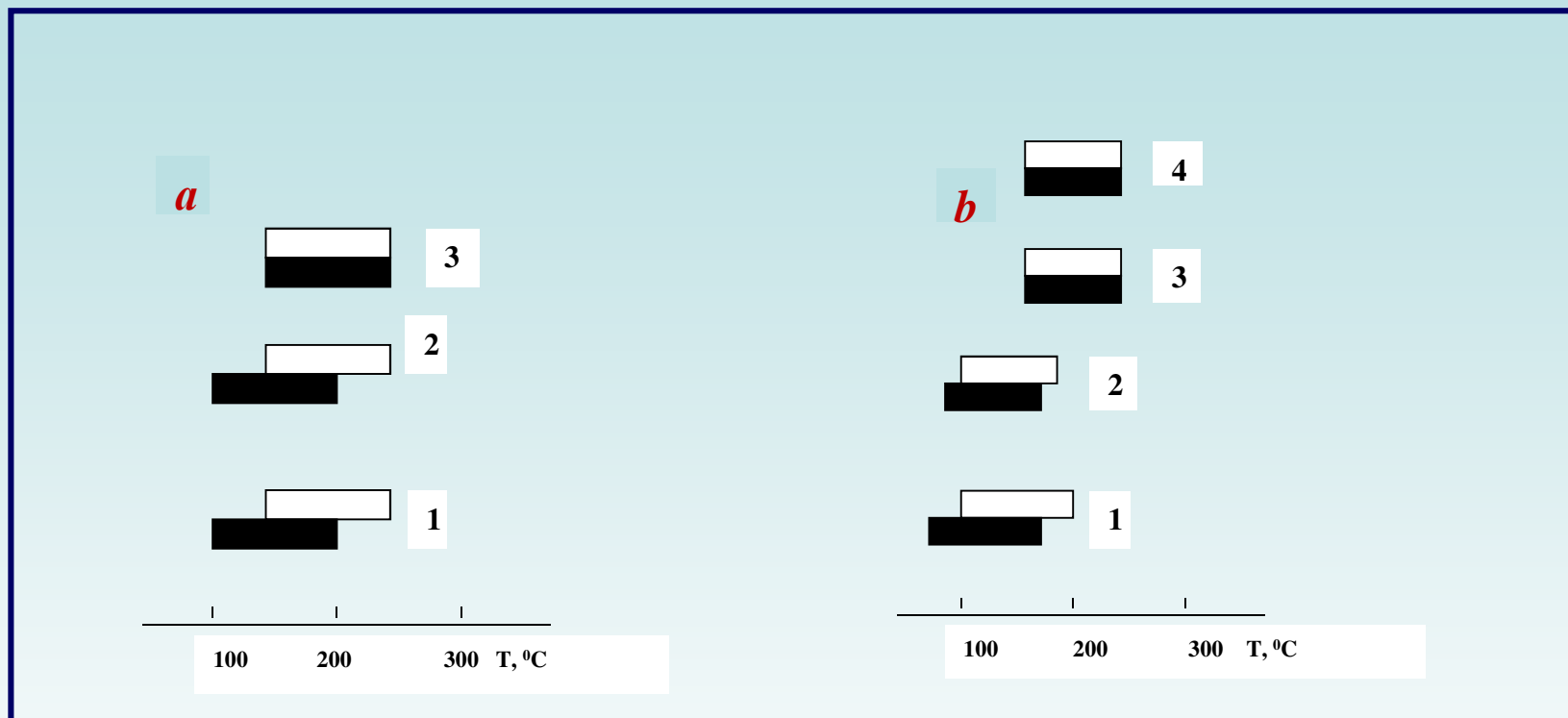
1. Successive evaporation of mercury compounds at the heating in atomizer (section I), where their transformation and partly or complete dissociation occurs;
2. Transportation of evaporated species into the section II by the air flow, complete atomization of mercury compounds;
3. Transportation of Hg^0 into the analytical cell, measuring of the signal intensity (λ 253,7 nm), thermo-peak formation.



Compound	Literature		Experiment
	$T_{\text{melt}}, ^\circ\text{C}$	$T_{\text{boil}}, ^\circ\text{C}$	$T_{\text{max}}, ^\circ\text{C}$ (thermopeak width)
Hg^{2+}	276	302	120 (75 – 150)
HgS	583, subl.	1450	230 (220-280)
CH_3HgCl	170	300, digest.	180 (150 – 220)

No correspondence between physicochemical properties and thermo-peaks' parameters for Hg^{2+} и HgS was observed

The influence of the matrix composition on the parameters of thermo-peak . Unification of sample preparation procedure



The dependence of the methylmercury thermo-peak position for the sample with organic and inorganic matrix (■ - plankton □ - sediment) on the type of the additive:

a – inert material (1 – graphite; 2 – SiO_2 ; 3 – Al_2O_3),

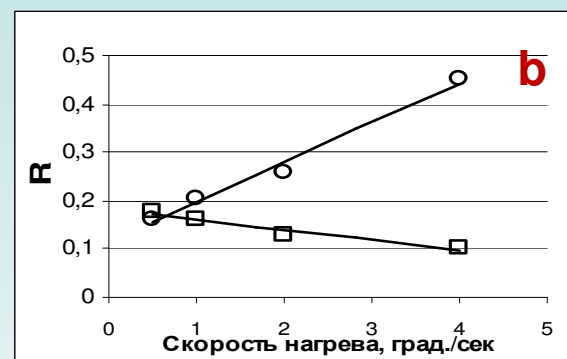
b – sample to additive ratio for Al_2O_3 (1- 1:2; 2 – 1:3; 3 - 1:4; 4 – 1:10)

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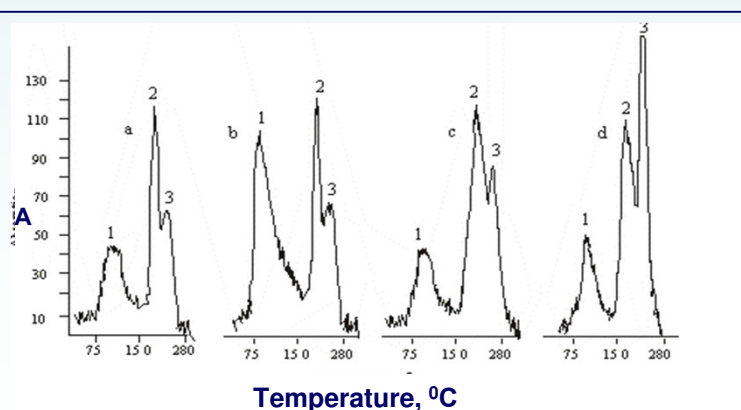
Optimization of the conditions of mercury species separation and detection

1. Eliminating of the matrix effect on the position and value of the analytical signal through the sample dilution with aluminum oxide (1:4)

2. The choice of the optimal heating rate and carrier gas (air) flow



The dependence of: (a) the peak area **S** on the air flow: ● – HgCl₂; ▲ – CH₃HgCl; ■ – HgS; (b) resolution **R** for the pares HgCl₂ – CH₃HgCl (□) и CH₃HgCl – HgS (○) on the heating rate



The model mixture separation under optimal conditions
(heating rate 1,0 %/sec, air flow 1,0 L/min,
the ratio samle:Al₂O₃=1:4)

a – HgCl₂ (1), CH₃HgCl (2) and HgS (3), 5 ng (as Hg);
spiked with :

b – HgCl₂,

c – CH₃HgCl

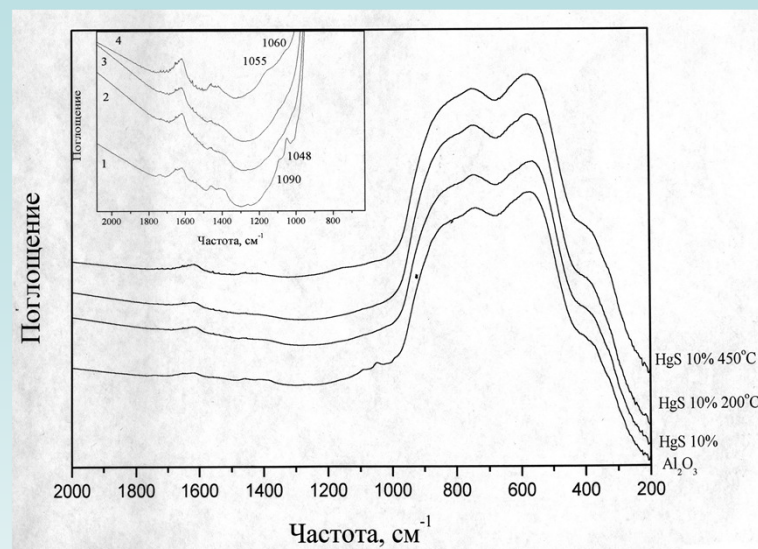
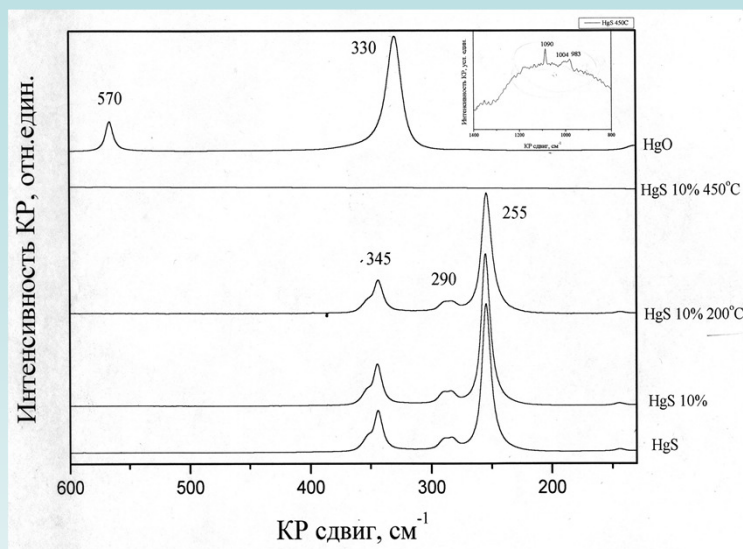
d – HgS

} 5 ng (as Hg)

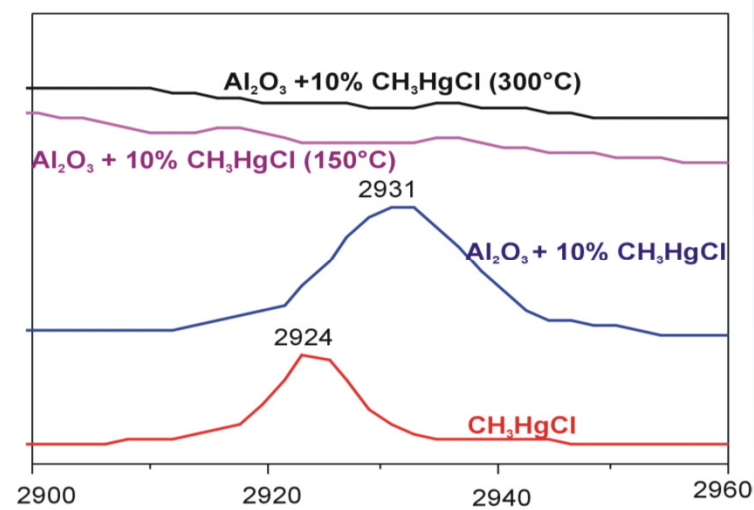
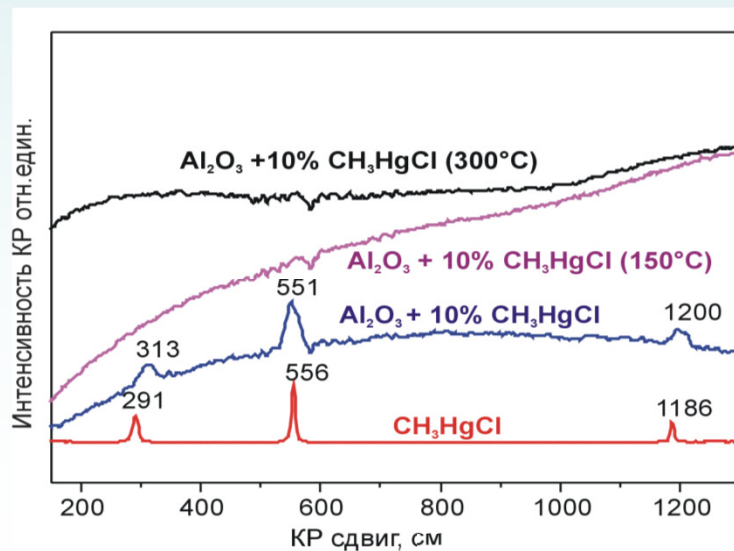
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The study of the analytical signal formation by Raman spectroscopy

HgS



CH₃HgCl



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Figures of merit of the developed assay, n=10; P=0,95

Species	Concentration range, ppm	RSD	C _{min} , ppm	Calibration graph parameters	
				The slope	Coefficient of regression
CH ₃ HgCl	0,035 - 30	0,25	0,035	8,7·10 ²	0,998
HgCl ₂	0,07- 30	0,14	0,07	5·10 ²	0,989
HgS	0,02 –30	0,18	0,02	12,6·10 ²	0,999

Accuracy control

Certified reference materials analysis		
Sample	Mercury, ppm	
	Found	Certified
СДПС-3, Hg ²⁺ (soil)	0,30±0,05	0,29±0,03
BCR-320, Hg ²⁺ (river sediment)	0,90±0,20	1,03±0,13
DOLT-2, HgCH ₃ ⁺ (dogfish liver)	1,5±0,8	1,99±0,10
DORM-2, HgCH ₃ ⁺ (dogfish, muscle)	4,2±0,8	4,47±0,32

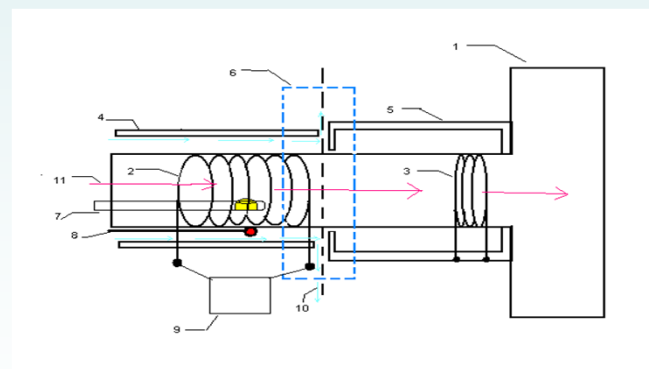
Inter-comparison of the results of independent techniques (n=3)		
Sample	Methylmercury, ppm	
	TR-ETA-AAS	CV-AAS
Plankton №1	1,50±0,30	1,60±0,20
Plankton №2	1,60±0,30	1,30±0,20
Lake sediment №1	0,53 ±0,10	0,53 ±0,07
Lake sediment №2	0,30 ±0,05	0,32 ±0,04

The adventures of the developed assay of mercury speciation in environmental solid samples using TR-ETA-AAS :

- the absence of the sample (analytes) dissolving stage;
- selectivity;
- low *DL* (at the level of 0,02 – 0,07 ppm);
- ease of operation, commercial available instrumentation.

Perspectives:

- constructive improvements due to the separation of the atomizers I and II
- the study of the of the separation in the presence of Al_2O_3



The comparison of the methods used in worldwide practice for mercury speciation in solid environmental samples

Method	Species	Details	DL, ppb
TR-ETA-AAS	HgCl ₂ , HgCH ₃ Cl, HgS	Direct determination by thermal release	20 – 70
HG-CT-GC-ETA-AAS	Hg(II), HgCH ₃ ⁺	Extraction from the solid phase, hydride generation, cryogenic trapping, GC separation	0,5 – 3,0
CV - AAS	Hg _{opr} , Hg _{heopr} .	Sequential selective reduction from the solid phase, fraction by fraction analysis	≥1
HG-CT-GC-ETA-AAS	Hg(II), HgCH ₃ ⁺	Microwave assisted extraction, hydride generation, cryogenic trapping, GC separation	3
GC-CV-AAS	HgCH ₃ ⁺	Distilling off in gas flow (t ~150°C), trapping, alkylation, GC separation (<i>the formation of Hg(CH₃)₂ is possible during the procedure</i>)	2,5
GC-MP-AES	HgCH ₃ ⁺	Supercritical fluid extraction (CO ₂), alkylation, GC separation	0,1

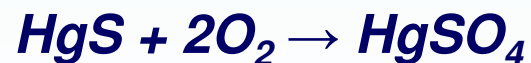
The study of mercury species distribution in the vicinity of the tailing impoundment (Ursk, Kemerovo region, Russia)



The original ores:

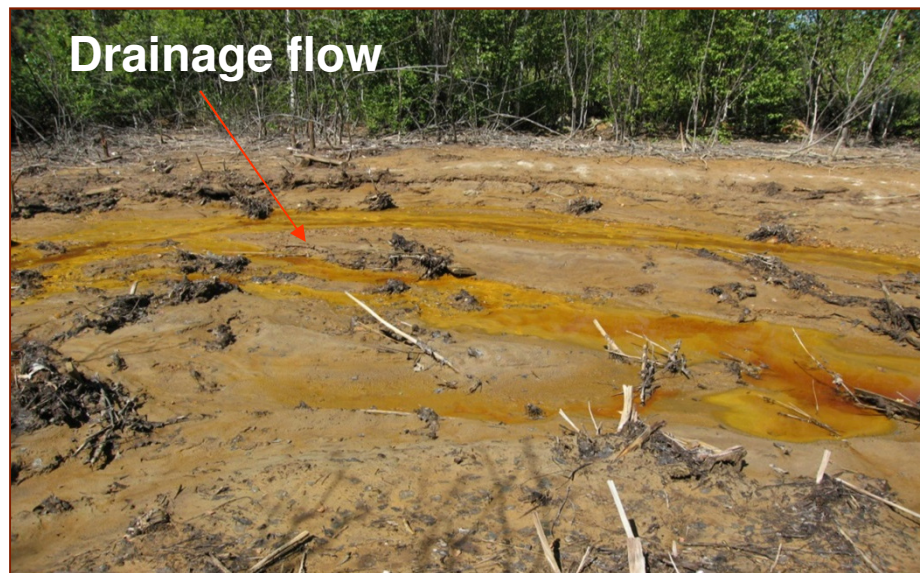
FeS_2 , ZnS , $CuFeS$, HgS ,
 $FeAsS$, PbS

The residual matter oxidation :





Sulfide waste of the ores cyanidation process

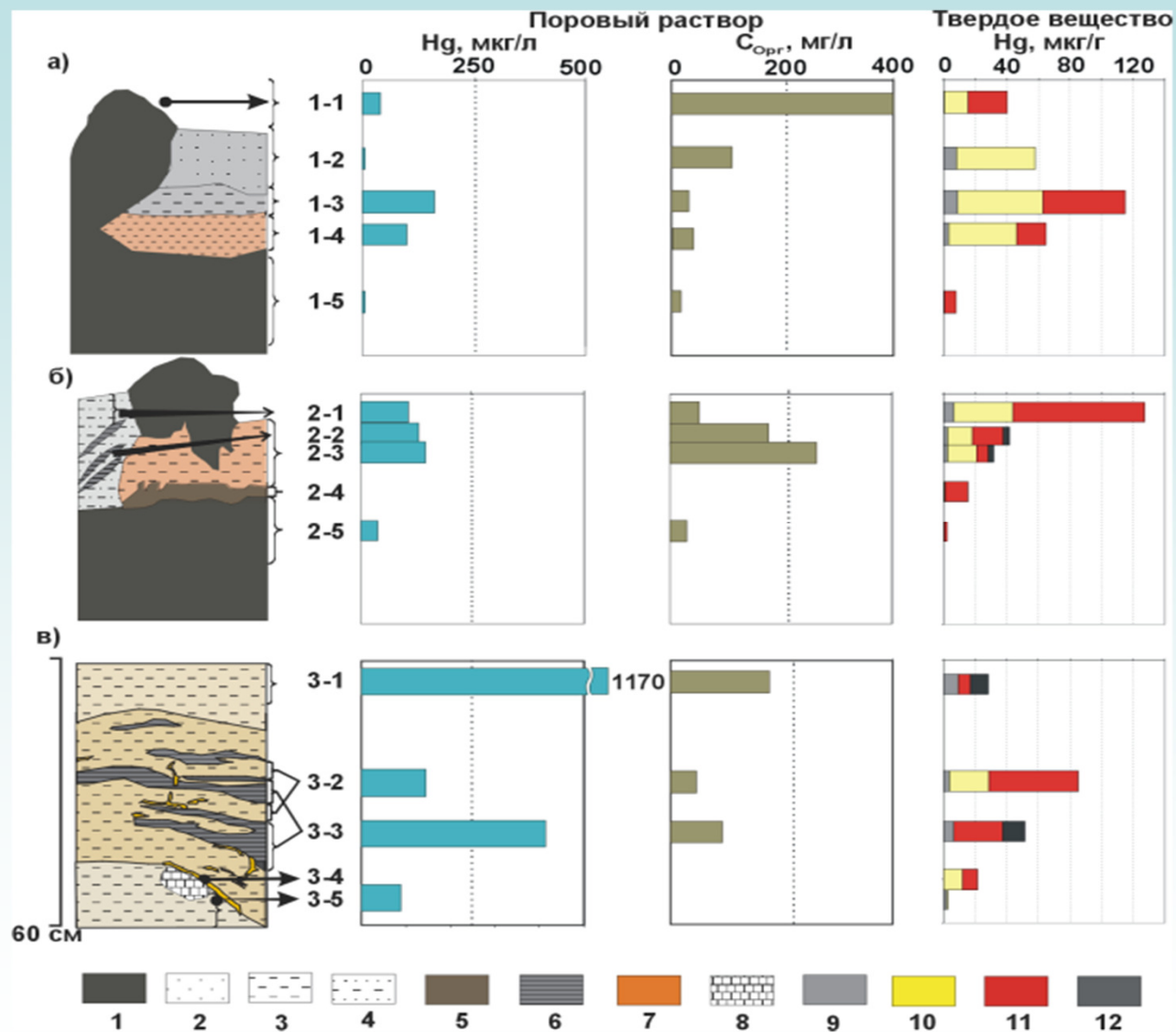


Drainage flow

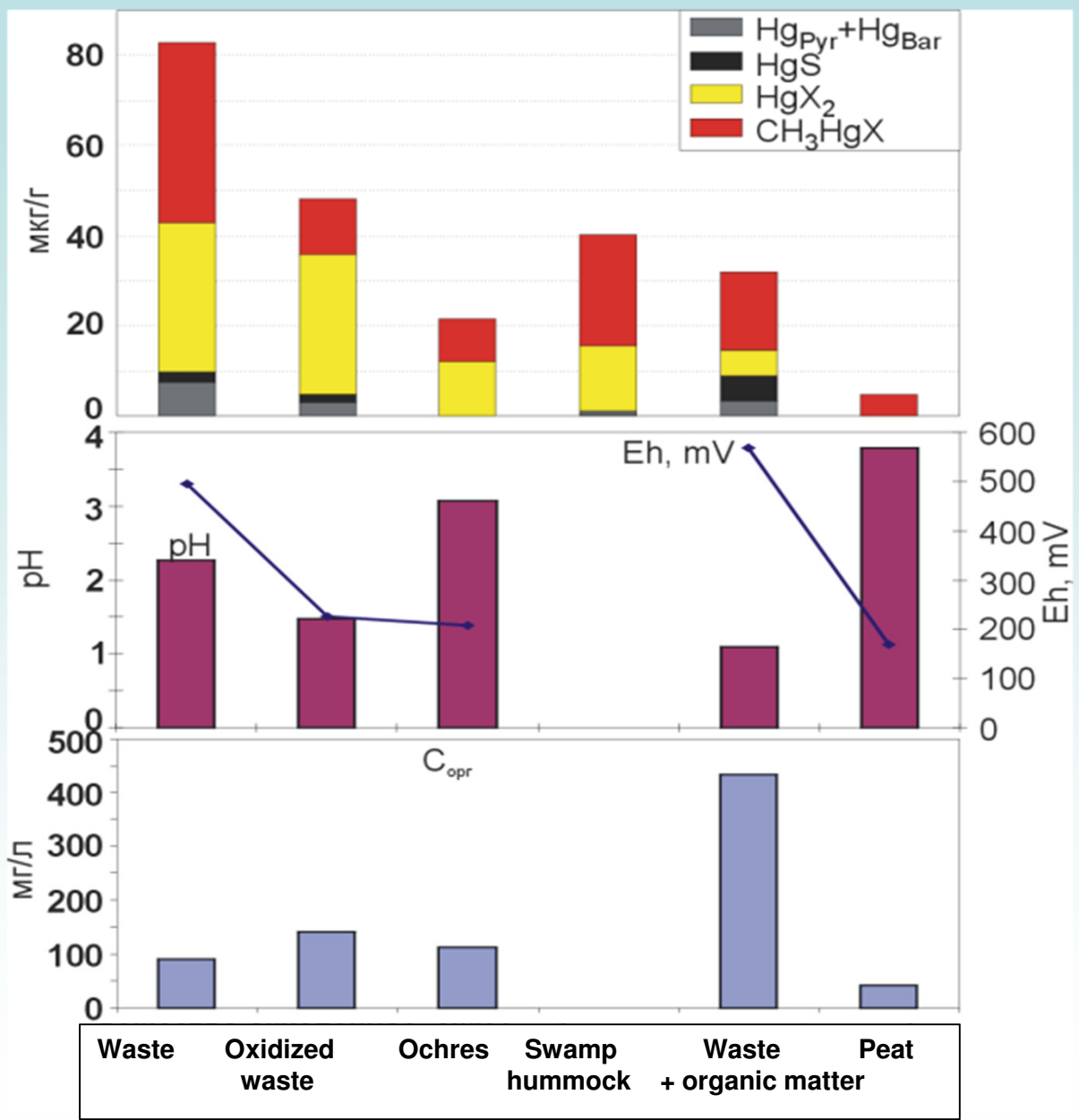


Man-made swamp

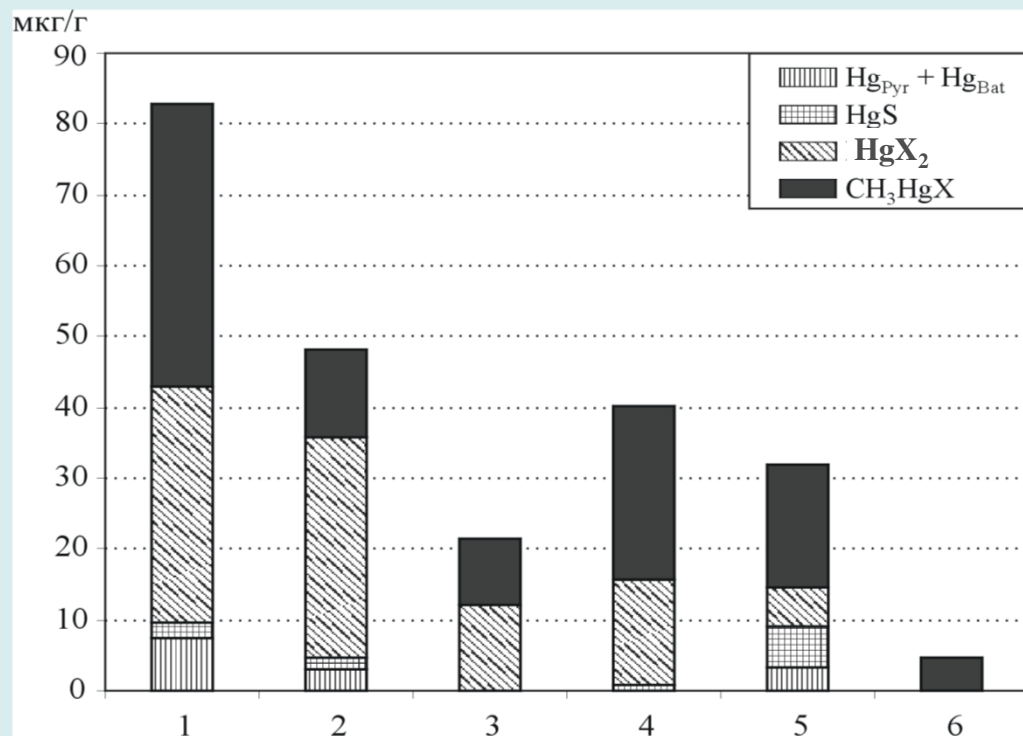
Mercury distribution in solid matter and pore waters of the tailing



Mercury species distribution in solid matter of the tailing



Mercury species distribution in the tailing impoundment



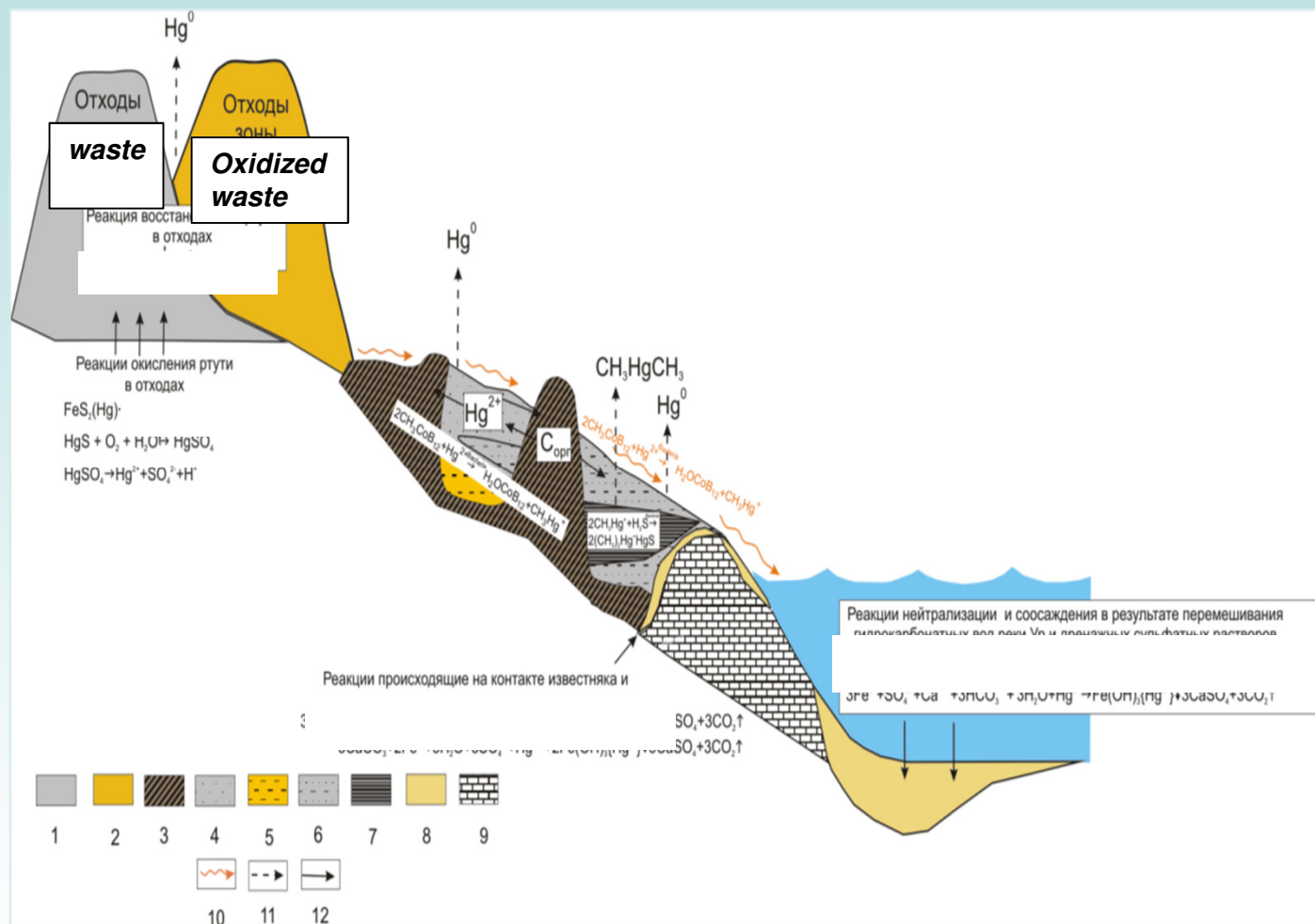
Chemical forms of mercury in:

- 1- waste materials;
- 2 – oxidized waste materials;
- 3 – ochres;
- 4 – detritus;
- 5 – waste material + organic matter;
- 6 – buried organic matter.

Results

1. The predominant mercury compounds are HgX_2 and monomethylmercury;
2. The formation of methylmercury probably takes place in pore solution at $pH = 2-4$, $E_h = 0,6-0,8 B$; $t = 20-70^\circ C$, $C_{org} = 20-400 mg/l$ which are the most favorable for methylation process (Suchenko S. A. Mercury in water reservoirs ; new aspect of anthropogenic contamination of biosphere, Novosibirsk, 1995. – 59 p.);
3. The presence of HgS as the second mineral phase is due to the process under participation of bacteria in anaerobic conditions

The scheme of mercury transformation in the tailing



1 – waste; 2 – oxidized waste; 3 – organic matter; 4 – sand matter; 5 – sludge; 6 – sand + sludge;
7 - sludge+ organic matter; 8 – ochres + Fe(OH)₃; 9 – limestone; 9 – Hg(pyrite) + Hg (barite);
10 – drainage flow; 11 - volatilization; 12 – chemical reaction

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Conclusions

- The developed method can be considered as a practical and reliable technique for direct speciation of mercury in solid samples.
- It demonstrates significant advantages as compared with the methods in worldwide use: the ease of operation, simple instrumentation and the absence of a sample pretreatment stage which allows to avoid analytes' transformation and losses during isolating of mercury species from the samples.
- The method allows *DL* at a level of 0.20 - 0.70 ng, *RSD* values of 14-25% and recoveries of 84-94%. The accuracy of the proposed method validated using certified reference materials and inter-methods comparison.
- The proposed method was employed for mercury speciation in original contaminated environmental system. It was shown that methylmercury is one of the predominant mercury species in solid matter as a result of methylation during the storage of waste materials.



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A photograph of a forest at sunset. The sun is low on the horizon, partially obscured by tall, thin trees, creating a warm, golden glow. The light reflects on a body of water in the foreground. In the immediate foreground, there are green, leafy branches of a bush or small tree. The overall mood is peaceful and serene.

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