

## DETECTION OF TOXIC METALS IN THE ENVIRONMENTAL OBJECTS

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*In this paper we discuss measurement results on the content of some heavy metals in water and air above it obtained during an expedition to the upper reaches of Volga river. The measurements have been carried out using the atomic absorption and emission spectroscopic techniques. Thus, for example, the concentration of mercury was measured with a compact RGA-11 analyzer, which uses Zeeman correction for the background.*

With the increase of anthropogenic influence on the environment the problem on permanent or periodic monitoring of the quality of air and water basins, ground, and biological objects arises. The central problem of this monitoring is the detection of toxic metals in the environmental objects using up-to-date express highly sensitive instrumentation. In this paper we consider measurement results on the heavy metals concentration in the environment. The measurements have been carried out from June 27 till July 7, 1993 onboard "Il'ya Repin" ship under the program of ecological measurements of Symposium on the Molecular Spectroscopy of High and Ultra-High Resolution.

We measured the content of toxic metals using the atomic absorption and emission spectroscopic techniques.

The atomic emission spectroscopic techniques were used for detection of copper, titanium, lead, zink, chromium, manganese, iron, vanadium, barium, nickel, bismuth, molybdenum, thallium, strontium, gallium, and germanium in water. We recorded spectra with an ISP-30 spectrograph, UGE-4 generator, MPh-2 microphotometer, PFS-02 photographic plate. These spectroscopic measurements were carried out in a certified laboratory of the environmental monitoring at Tomsk Polytechnic University after the expedition. Water samples have been preserved in accordance with the State Standard. Samplings have been done in seven towns upstream Volga river, namely, Uglich, Kostroma, Yaroslavl, Nizhny Novgorod, Ples, Tver. We detected metals using a certified technique with the measurement error of 25% for concentration level 0.1–0.001 mg/l.

Mercury was detected using the atomic absorption spectroscopic technique with an RGA-11 analyzer directly aboard the ship. This analyzer was designed and manufactured by DTI "Optika" of SB RAS. This instrument was constructed as a small unit of nine kilograms mass and allows continuous measurements of mercury content in air. To detect mercury in liquids and ground, the device is supplied with two additional blocks, which have small size, capable of operating in field. Basic characteristics of the analyzer are presented below.

### Specification of an RGA-11 analyzer

Range of mercury vapor density in the atmospheric air, ng/m <sup>3</sup>	30 to 10 000
Full time of air sample analysis, s	5
Minimum detectable concentration	
in liquids, µg/l	0.02
in fish, ng/g	1.0
in vegetation, ng/g	2.0
in ground, ng/g	1.0
Full time of analyzing water or ground samples, s	180
Power consumption, W	15
Mass, kg	9
Size, mm <sup>3</sup>	700×365×100
Voltage from a power supply, V	12

Maximum permissible concentration of mercury in air is 300 ng/m<sup>3</sup>, in water – 0.5 µg/l, in ground – 2000 ng/g, in fish – 500 ng/g, and in vegetation – 20 ng/g.

Analysis of air samples in the concentration range between the background value and up to the level of maximum permissible concentration is done under conditions of natural existence of mercury in the atmosphere without mercury preconcentration on a sorbent. High steadiness of the analyzer to vibrations allows the measurements to be conducted on any moving platform. The principle of RGA-11 analyzer operation (see Fig. 1) is based on the differential absorption technique and uses Zeeman effects and isotopic splitting of a mercury spectral line at 254 nm. Mercury occurs in air as a mix of several isotopes. Differences in the nuclei masses cause splitting of the resonance line at 254 nm into several spectral components. The figures from 196 to 204 denote atomic mass of an isotope, and the height of a vertical line presents the intensity, in relative units, of a spectral line from corresponding component of natural mercury in air.

Each isotopic component exhibits collisional broadening at atmospheric pressure (see Fig. 1, curve 1 corresponds to  $^{202}\text{Hg}$ ), and the total profile of the absorption line at 254 nm takes the shape presented by curve 2. High-frequency,  $^{204}\text{Hg}$  isotope-filled, VSB-1 lamp is a source of radiation in RGA-11 analyzer. In the absence of a magnetic field the Doppler profile of the emission line 3 delivered by such a lamp is on the slope of the total profile. In the analyzer the lamp is placed in a longitudinal magnetic field splitting the line 3 into two Zeeman components  $\sigma^+$  and  $\sigma^-$ , which have different circular polarizations. Splitting corresponding to maximum of differential absorption of the Zeeman components by atmospheric mercury is shown in Fig. 1.

Optical arrangement facilitating the described technique is shown in Fig. 2. A permanent magnet 2 produces a longitudinal magnetic field. A monoisotopic mercury lamp 1, placed in this field, emits the Zeeman components, which are separated in time by a resonance photoelastic modulator of polarization 3, 4, and the Glan prism 5, made of synthetic calcite. The photoelastic modulator consists of a fused silica plate and a quartz resonator, glued with the plate. Oscillations, generated by the piezoelectric crystal at a resonance frequency of 50 kHz, create mechanical tensions in the plate of fused silica. These oscillations cause the birefringence of the plate alternating at the same frequency.

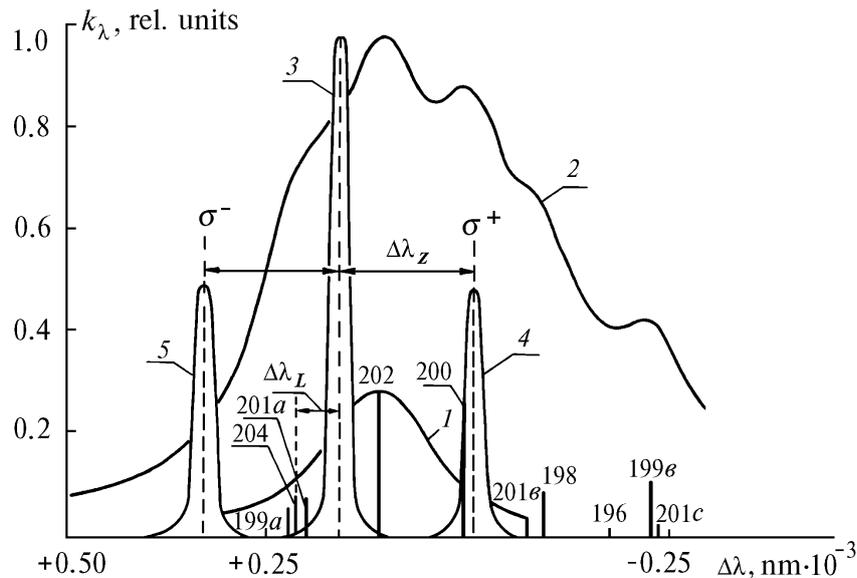


FIG. 1. Spectral characteristics of mercury atoms near the wavelength of 254 nm. 1 – profile of the  $^{202}\text{Hg}$  absorption line broadened by collisions at atmospheric pressure; 2 – total profile of absorption line for an isotopic mix of the atmospheric mercury. The mix consists of isotopes with nuclei masses from 196 to 204; height of vertical lines shows the relative intensity of the isotopes spectral lines; 3 – profile of the line emitted by a  $^{204}\text{Hg}$  isotope-filled, low pressure mercury lamp; and, 4 and 5 – components of Zeeman splitting of the line 3 in the presence of a longitudinal magnetic field;  $\Delta\lambda_1$  is the shift of absorption line by collisions at atmospheric pressure.

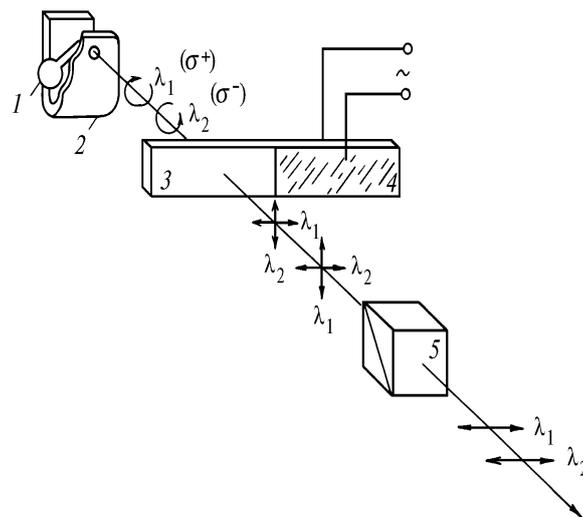


FIG. 2. Block-diagram of time separation of  $\sigma^+$  and  $\sigma^-$  Zeeman components of a mercury line at  $\lambda = 254$  nm emitted by a  $^{202}\text{Hg}$  isotope-filled VSB-1 low pressure mercury lamp,  $\lambda_1$  and  $\lambda_2$  are the wavelengths of  $\sigma^+$  and  $\sigma^-$  Zeeman components.

Changing the amplitude of electrical signal applied to the piezoelectric crystal one can obtain linearly polarized  $\sigma^+$  and  $\sigma^-$  components that are alternately, at a modulation frequency, emitted from the source. The radiation then passes through the open six-pass cell and is incident onto a photodetector. The device operates in a narrow spectral interval of 0.004 nm width that provides a very high selectivity of the analysis.

The content of mercury in the atmospheric air was measured aboard the ship during whole day. Content of mercury in water and fish was determined using certified techniques. The main idea of these techniques is that organomercuric compounds are first decomposed in an alkali medium, then mercury ions are reduced to atoms by dichloride

of tin in the presence of bivalent cadmium. The accuracy of mercury content determination was better than 20% at the level of maximum permissible concentration.

The main bulk of results on toxic metals detected are listed in Tables I and II. The results of ecological expedition allow us to conclude that the detection of mercury in the environment in field conditions with an RGA-11 mercury analyzer is an easy measurement procedure free of systematic errors. Use of spectroscopic technique based on atomic emission spectra to detect metals in the environment is still practicable because of a large number of components that can be detected with the sensitivity of the detection being quite sufficient for ecological survey.

TABLE I. Content of toxic metals in water of Volga river as measured from June 27 till July 7, 1993 (mg/l).

No.	Place of sampling	Date, loc. time	Cu	Al	Zn	Pb	Cr	Mn	Fe	V	Ba	Ti
1	Uglich	29.06.93 19.10	0.009	0.108	0.100	0.008	0.025	0.05	0.342	0.015	0.05	0.017
2	Yaroslavl	30.06.93 09.00	0.0047	0.122	0.121	0.9975	0.005	0.023	0.101	0.015	0.05	0.012
3	Kostroma	30.06.93 17.00	0.0035	0.417	0.121	0.013	0.008	0.133	6.175	0.017	0.05	0.018
4	Nizhny Novgorod	01.07.93 13.00	0.006	0.202	0.100	0.0092	0.005	0.038	0.167	0.012	0.16	0.019
5	Nizny Novgorod	02.07.93 19.00	0.004	0.125	0.108	0.142	0.005	0.033	0.167	0.015	0.05	0.012
6	Ples	03.07.93 17.00	0.0012	0.125	0.108	0.0077	0.005	0.043	0.0083	0.012	0.05	0.013
7	Tver	06.07.93 10.00	0.0019	0.095	0.142	0.142	0.005	0.043	0.112	0.015	0.08	0.016
MPC			0.001	0.5	1.0	0.003	0.1	10.0	0.5	0.1	0.1	0.1

Note: Ga, Ge, Mo, Tl, and Sr < 0.0025 mg/l; Ni and Bi < 0.008 mg/l.

TABLE II. Content of mercury in the air, water, and fish.

Place of sampling	Date	Loc. time	Air	Water	Fish
Uglich (stop)	20.06.93	19.00	20-40	0.00024	—
Yaroslavl (in motion)	30.06.93	09.30	140-160	0.00007	—
	30.06.93	11.15	20-40	—	—
Kostroma (stop)	30.06.93	19.00	70-80	0.00005	0.020
Volgorechensk (in motion)	30.06.93	21.00	100-120	—	—
Kineshma (in motion)	30.06.93	23.45	90-100	0.00005	—
	01.07.93	10.30	20-40	—	—
N. Novgorod (stop)	01.07.93	20.30	100-120	0.00005	0.035
(in motion)	02.07.93	21.30	100-134	0.00005	—
Ples	02.07.93	21.45	100-130	—	—
	03.07.93	19.00	60-100	—	—
	03.07.93	19.45	150-160	—	—
Rybinsk	04.07.93	11.00	100-120	0.00006	—
	04.07.93	13.00	100-120	—	—
	04.07.93	19.30	100-120	—	—
Novookatovo	05.07.93	09.30	40-50	0.00005	0.092
Tver	06.07.93	09.45	80-90	0.00005	—
Tver (stop)	06.07.93	15.15	130-150	—	—