

MERCURY MONITORING

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The urgency of mercury monitoring is assessed. The information about typical values of mercury concentration in various objects is summarized. The principles of operation and design of Zeeman atomic-absorption mercury analyzer is described. The analyzer and techniques for determination of mercury content in the atmosphere, water, soil, and biological objects have been certified by the Russian State Committee on Standardization. The possibilities of mercury monitoring are illustrated by a number of examples.

The goal of our work was to develop the methods and instrumentation for measuring the mercury content in the atmosphere, water, soil, and biological objects to solve the problems of monitoring the technological processes in which mercury and its compounds take part as well as in ecological monitoring. This could also provide efficient measurements and regular monitoring of mercury content in the medium within the range from background concentrations to maximum permissible ones.

The metallic mercury and some of its compounds are related to a group of extremely toxic substances. They flow into the atmosphere as a part of gaseous emissions and smokes, in the form of industrial dust. They are supplied with sewage to water basins; then, from the water and the atmosphere they find their way into the soil where their migration becomes much slower. The content of mercury in the natural medium is represented below.

MERCURY CONTENT IN NATURAL MEDIUM (FROM REFERENCES)

Atmosphere

Mean concentration	20 ng/m ³ (background level of 5 ng/m ³)
In the atmosphere of cities:	
Chicago	3–39 ng/m ³
San Francisco	0.5–50 ng/m ³
Over mercury-enriched soils	20–200 ng/m ³
Near the rice fields where mercury fungicides were used	up to 10 000 ng/m ³
Near the busy superhighway (Japan)	up to 18 000 ng/m ³
In the village near a large ore mine (Spain)	up to 800 000 ng/m ³
At 24°C, the mercury vapor saturated atmosphere contains	18 000 000 ng/m ³
Maximum permissible concentration for free atmosphere	300 ng/m ³
Maximum permissible concentration for operating area	5 000 ng/m ³ (shift-average) 10 000 ng/m ³ (single discharge)

Water

Mean mercury content in oceanic water (as a rule, below 50 ng/l)	
300 ng/l)	
Natural content in river water	up to 200 ng/l
Rivers in the valleys of West Europe flowing into the North Sea	400–700 ng/l
Minamata Bay	up to 600 ng/l
Solubility of mercury vapors in air-free water	
at room temperature	20 µg/l
in the presence of oxygen	40 µg/l
Maximum permissible concentration in water (USA)	1 000 ng/l

Soil, rocks

Mean mercury concentration in the Earth's crust	0.08 mg/kg (8·10 ⁻⁶ %)
In minerals of ore deposits	from 8·10 ⁻⁶ to 2%
In minerals served as a raw material for mercury extraction	up to 85%
In gas deposits of the Dneprovsko–Donetsk hollow	from 0.01 to 110 µg/m ³
Background content (USA)	0.1 mg/kg
Maximum permissible concentration for soil	2 mg/kg

Vegetation and foods

Vegetation	0.001–0.04 mg/kg (dry mass)
Maximum permissible concentration for vegetation	0.5–1 mg/kg
Vegetables	0.001–0.033 mg/kg (wet substance)
Maximum permissible concentration for vegetables	0.02 mg/kg
Fruits	0.001–0.012 mg/kg (wet substance)
Maximum permissible concentration for fruits	0.01 mg/kg
Berries	0.001–0.017 mg/kg (wet substance)
Grain	0.001–0.06 mg/kg (wet substance)
Maximum permissible concentration for grain	0.01 mg/kg
Potato	0.001–0.015 mg/kg (wet substance)
Lichen	0.05–0.2 mg/kg

Fish

Benthic	0.2 µg/g
Living on plankton and invertebrates	0.2–0.5 µg/kg
Predatory	more than 1 µg/kg

In addition to producers of mercury and its compounds, the most substantial mercury consumers, which are responsible for mercury pollution are:

- electrotechnical industry (luminescent lamps),
- production of chlorine and caustic,
- production and refining of non-ferrous metals,
- agriculture (fungicides),
- defensive industry.

The detonators made from mercury fulminate used for extracting the mineral resources with the help of explosions increase the mercury vapor concentration in a face to the level of 28–100 maximum permissible concentrations. Currently, widely developed are the systems for extracting the mercury from used luminescent lamps. Technological and ecological services of these and many other productions as well as numerous regional ecological services need for means of reliable efficient and routine monitoring of mercury content in different media. These means must be provided with special analytical methods. It should be noted that the systems and methods must be certified by State Committee on Standardization, Metrology, and Certification.

As of the present time, the technological and ecological services do not possess universal methods and instrumentation for reliable efficient and routine monitoring of mercury content in the environment. Thus, the instrumentation with high portability (JEROME–411) do not have sufficient sensitivity and selectivity, while highly sensitive and highly selective instruments (ZEEMAN–6000) are related to the class of stationary laboratory instrumentation.

The Design and Technology Institute "Optika" of the Siberian Branch of the Russian Academy of Sciences has designed the RGA–11 mercury analyzer; a small lot of the analyzers are manufactured. This instrument possesses efficiency, selectivity, and sensitivity higher than those of native and foreign analogs. It has been registered in the State List of Measurement Instrumentation of Russia. The over-all dimensions of the analyzer are 700×365×100 mm, mass is 10 kg, power supply is from the direct-current source at voltage of 12 V and power of 12 W.

In analyzing the gaseous media and soils, no sample preparation and preliminary mercury concentration on sorbents are required. A small-size analyzer can be used in pedestrian survey as well as with the use of different carriers (automobile, motodeltoplane, or helicopter). It can be easily included into both stationary and mobile complexes of engineering instrumentation. The level of its automatization provides for free connection to computer lines and complexes of enterprises and branches.

The principle of operation of the RGA–11 gas analyzer is based on the method of differential absorption with the use of the Zeeman effect and isotopic splitting of spectral line at the wavelength of 253.7 nm (Fig. 1).

The atmospheric mercury represents a mixture of several isotopes. Due to difference in nucleus masses, the absorption line of such a mixture is splitted into several spectral components. Figures from 196 to 204 are related to atomic mass of isotopes and the height of vertical lines presents relative intensity of the corresponding component of isotopic splitting of the mercury line. At atmospheric pressure, each of the isotopic components undergoes collisional broadening (for ^{202}Hg it is curve 1) and the total contour of the absorption line at 253.7 nm takes the form shown with curve 2. The radiation source in the analyzer is a VSB–1 high-frequency electrodeless lamp filled with ^{204}Hg isotope.

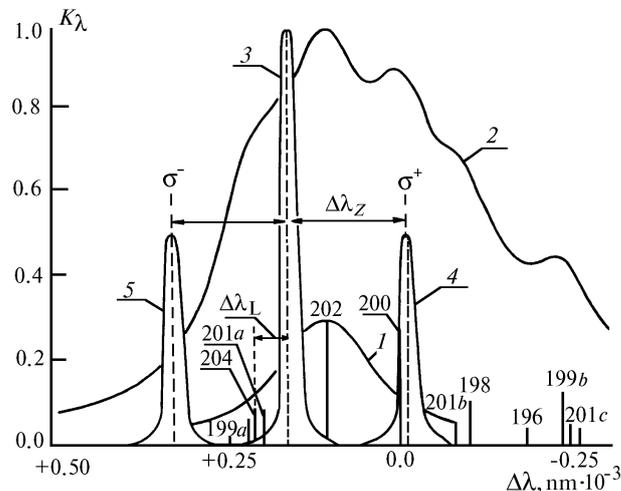


FIG. 1. Spectral characteristics of mercury atoms near the wavelength of 254 nm: the contour of ^{202}Hg isotope absorption line broadened by collisions at atmospheric pressure (1); the total contour of absorption line of isotope mixture containing in atmospheric mercury (2). Here (196–204) are the masses of isotope nuclei, the height of vertical lines under the figures is related to relative intensity of spectral lines of isotopes; the line contour emitted by a mercury lower-pressure lamp filled with a ^{204}Hg isotope (3); 4 and 5 are the components of Zeeman splitting of the line 3 when the lamp is placed in the longitudinal magnetic field; $\Delta\lambda_z$ is the shift of absorption line by collisions at atmospheric pressure.

With no magnetic field, the Doppler contour of the emission line of this lamp 3 falls on the slope of the total contour. By superimposing a longitudinal magnetic field, the line 3 is splitted into two Zeeman spectral components σ^+ and σ^- with different circular polarization. Depicted in Fig. 1 is the splitting related to maximum differential absorption of components by the total contour.

Figure 2 represents an optical scheme, which realizes the method described.

The Zeeman components emitted by a monoisotopic mercury lamp 1 placed in a longitudinal magnetic field created by a permanent magnet 2 are separated in time using a resonance photoelastic modulator of polarization 3, 4 and the Glan prism made of iceland spar 5. The photoelastic modulator consists of a fused-quartz plate and a quartz resonator glued with it. Vibrations excited with a quartz crystal at resonance frequency of 50 kHz create mechanical tensions in the fused-quartz plate, which result in birefringence modulated at the same frequency in the plate. Changing the amplitude of electrical signal applied to the piezoelectric crystal, we can obtain linearly polarized components σ^+ and σ^- , which are alternately, at the modulation frequency, emitted from the source. Then, the radiation passes through the optical cell and falls into the photomultiplier. It should be noted that all of the spectroscopic effects used for modulation are observed in the spectral range only 0.004 nm in width. The attachments to the gas analyzer make it possible to determine the mercury content in liquids, soils, and biological objects.

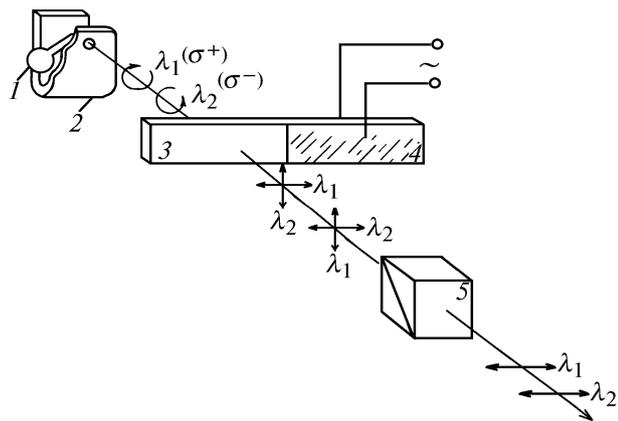


FIG. 2. The scheme of time separation of the σ^+ and σ^- components of Zeeman splitting of mercury line $\lambda = 254$ nm emitted by the lamp VSB-1 filled with ^{204}Hg isotope: a lamp (1), a permanent magnet (2); resonance modulator of polarization (3 and 4); the Glan prism (5); λ_1 and λ_2 are the radiation wavelengths of the σ^+ and σ^- components of Zeeman splitting.

The range of the measurable concentrations of mercury vapors in the atmospheric air is between 30 and 10 000 ng/m³ during the 5-s analysis. An inorganic mercury in water media is determined with a 2-ml volume. The range of measurable contents is between 0.1 and 50 ng during the 180-s analysis. There exist several methods to determine organic forms of mercury in water or biological objects: decomposition with strong oxidants, the use of alkali medium with a catalyst, and so on.

The mercury in solid samples is determined by annealing of the sample at 700°C in an airtight system UV-1. The minimum detectable concentration is 0.001 mg/kg

during 20 s. When analyzing the soil near a shooting stand, we observed the mercury concentration exceeding the background one in the soil around the stand by a factor of 40. The mercury source is a mercury fulminate containing in percussion caps of hunting cartridges.

The technique for determining the mercury in air, soil, water, fish, and meat with RGA-11 has been certified by State Committee on Standardization of Russia. The techniques for determining the mercury in natural, sewer, and drinking waters as well as in agricultural products are being prepared to certification.

Table I lists the results of comparative analyses of muscular tissue of fish with respect to Hg content, which were obtained with an RGA-11 and an atomic-absorption spectrometer PERKIN ELMER. The disagreement between the results is smaller than 5%.

TABLE I.

Number of sample	Mercury concentration in muscular tissue of fish, $\mu\text{g}/\text{kg}$	
	RGA-11	PERKIN ELMER
1	0.26	0.26
2	0.16	0.15
3	0.26	0.22
4	0.30	0.33
5	0.22	0.21
6	0.22	0.19
7	0.42	0.35
8	0.35	0.35

The use of an RGA-11 gas analyzer for monitoring of mercury pollutants indoors is illustrated in Fig. 3. The gas analyzer was placed in the passage between the microelectronics block and the optical block of the Design and Technology Institute "Optika". The mercury-vapor source was the Gevelo capsule. The moment of shot made in the room on the ground floor of the optical block was taken as the start of temporal read-out. The figure depicts variations in mercury vapor concentration at the observation point. On Sunday when the exhaust fan was disconnected, the maximum mercury-vapor concentration at the same point attained 2 500 ng/m³. The results depicted in Fig. 3 illustrate the possible use of mercury vapors as a tracer when estimating the operation of plenum and exhaust ventilation in the rooms.

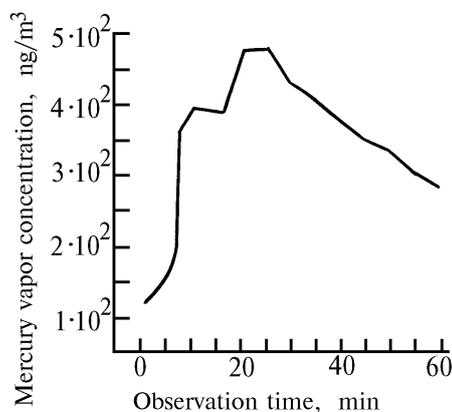


FIG. 3. Variations in mercury vapor concentration after a shot.

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