RGA gas analyzer and its application to environmental mercury monitoring

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Atomic absorption analyzer with Zeeman background correction and techniques for determining mercury content in different media are presented. A possibility is demonstrated of widely using the analyzer for organization of multipurpose environmental mercury monitoring. The results of investigation of peatbogs are presented as an example.

Introduction

Pollution of the environment on the local, regional, and even global scales under impact of anthropogenic factors tend to widen in recent decades. In such a situation their monitoring, forecast, and control became not only a desire, but also a necessity. In the framework of this big problem the mercury monitoring is of primary importance because mercury is extremely toxic and its content in the environment, foodstuff, etc. is strictly normalized. Mercury monitoring problems include three aspects. These are the following: determination of background and anthropogenic components what is of interests to sanitary and ecological public services; evaluation of mercury exhausts from industrial plants and their further migration; investigation of the global mercury transfer what suggests that a lot of results obtained with different devices and with the use of various methods should be agreed.[1–6] Thus, to solve the problems on modern mercury monitoring, one needs portable devices having large dynamic range and high sensitivity, as well as techniques that provide for determining mercury content in various media without preliminary concentration, preservation, and storage of the samples. Such a device, matching the above requirements, has been developed at the Institute of Optical Monitoring (IOM) SB RAS. Among other devices developed at the institute, this device was the first one, which has been certified by the National Service for Legal Metrology and included into the State Measuring Technique Register.

Basic technical decisions

Method of atomic absorption spectroscopy with Zeeman background correction[7,8] was used as the basis for a device developed as it is most sensitive, fast, and suitable for creating a portable mercury analyzer. However, when realizing this method, we came across some problems that stimulated us to carry out supplementary investigations and calculations. Thus, based on the literature data, we calculated an integral profile for the mercury absorption line with the wavelength of 253.7 nm and its change with the decrease of atmospheric pressure.[9] We also studied the emission lines for lamps filled with different even mercury isotopes and measured their widths.[10] The dependences of differential signal on the value of applied magnetic field for different even mercury isotopes have been calculated as well. Our calculations have been confirmed by the experimental results presented in Ref. 7. The results obtained allowed us to improve the emitter parameters in order to get maximum possible sensitivity.

Then we considered how the differential signal is formed in the Zeeman atomic absorption analyzer.[11] This study was necessary because in the real device the output signal was not equal zero even in the absence of mercury. We called this signal a parasitic one. Analysis has shown that the parasitic signal may be caused by both optical causes and noise of electronic units, PMT, etc. Since the electronic units' noise can be compensated for electrically, this problem is not very difficult. Therefore we studied thoroughly an optical noise caused by distortion of circular polarization of $\sigma^{\pm}$ components because of both optical anisotropy of the lamp capillary walls (in the general case the $\sigma^{\pm}$ components are a set of components with different elliptical polarization) and different intensities of $\sigma^{\pm}$ components. As has been shown in Ref. 9, when circular polarization is distorted, those portions of both $\sigma^{\pm}$ components, whose electric field vectors oscillate in the principal plane of the Glan prism, pass through the prism simultaneously. This results in the appearance of parasitic signal at the receiver's output and does not allow one to set the analyzer signal to zero even in the absence of mercury. We suggested to supplement the analyzer optical layout, presented in Ref. 12, with an optical compensator as one of the probable methods of parasitic signal compensation. An optical compensator

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is a quartz plate in which mechanical strength is produced by means of a screw. This results in induced birefringence. It was shown by calculations and confirmed in experiments,[9] that it is possible to choose the birefringence and rotation angle of the compensator in such a way that the radiation at its output will be circularly polarized. The optical arrangement with a compensator was used in RGA-11 analyzer.

In recent years three versions of the analyzer have been developed. RGA-10 was the first in this series. Ten such analyzers were produced. They were intended for measuring mercury content in air. This analyzer was big in size, had a weight of 18 kg, and was installed onboard a helicopter or a car. Each of the RGA-10 analyzers had been metrologically tested. RGA-11 analyzer was the next in this series. As compared with RGA-10 analyzer, it has smaller sizes and extended list of applications. For example, it allows one to determine mercury content not only in air but also in solid and liquid samples by the use of a supplementary unit. Since the RGA-11 analyzer is made as a knapsack, it can be used in pedestrian mercury survey. The RGA-11 analyzer developed has been tested by the National Service for Legal Metrology and included into the State Measuring Technique Register, No. 13083-91. It should be noted that after the development and production of RGA-11 analyzer, analogous devices, intended for measuring mercury content in different media, have been developed by other Russian companies (for example, RA-915, AGP-01M). Their parameters are comparable with the parameters of our device. The third analyzer in the RGA series is RGA-11M analyzer that now is under design. As compared with RGA-11 analyzer, the latter one has smaller size and weight, lower detection limit, and wider field of application.

Metrological guarantee

Metrological guarantee of RGA-type analyzers was one of the most important stages in their development and subsequent certification. Unlike mercury analyzers with preliminary mercury concentration, metrological guarantee of atomic absorption analyzers with Zeeman background correction has some peculiarities. When calibrating the analyzer for analysis of liquid samples, one can use Certified Reference Material of Metal Solutions, a mercury solution in our case, or Certified Reference Material of mass fraction of mercury for solid samples.[13] Calibration of analyzers for determination mercury in gases is a more complicated problem. The matter is that the mercury sorptive properties do not allow one to make a standard gas mixture with a stable in time mercury concentration that can be further used for verification. Therefore, at the initial stages of the analyzer development we used techniques intended for calibrating mercury analyzers with a preliminary mercury accumulation on a sorbent.[13] These techniques include the following ones: dynamic doser, pulsed doser, and thermal mercury sublimation from powder of Certified Reference Material of mass fraction of mercury.

To remedy the disadvantages inherent in the above listed techniques, we suggested new technique based on the fact that the saturated mercury vapor placed into a closed volume has a constant pressure at a fixed temperature.[14] Thin cells presented in Fig. 1 were used as a closed volume. The cell consists of two quartz windows *2* that are separated by a teflon spacer *3* of known thickness (from tens to hundreds of microns). The windows are hermetically sealed and pasted in a frame *1*. The mercury drop *4* is placed between windows and gives saturated mercury vapor due to mercury vaporization from its surface. To calibrate the analyzer, the cells of different thickness are inserted into RGA-11 analyzer (beam path is 2.7 m) and their transmittance is determined, i.e., a signals from atmospheric mercury having different concentrations are simulated.[15]

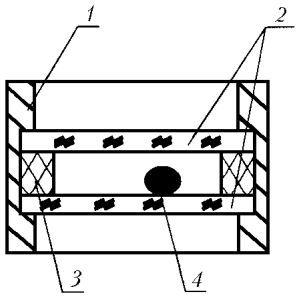

Fig. 1. Cell filled with saturated mercury vapor.

To verify new calibration technique, we carried out experimental measurements of the dependence of RGA-11 signal on the cells' temperature.[16] We also estimated the dependence of saturated mercury pressure on a mercury drop radius for the cells with thickness from 0.01 to 0.6 mm included into the calibration kit. The results obtained confirmed that:

1) mercury vapor inside the cells is saturated and its pressure (concentration) obeys well-known empirical laws;

2) mercury vapor pressure is uniform across the volume of the cell;

3) the signal from the cells is repeatable with a high accuracy over the period of time that far exceeds the verification periodicity. Thus, thin cells filled with saturated mercury vapor can be used as certified reference materials for verification and calibration of atomic absorption analyzers with Zeeman background correction.

Measurement techniques for different media

The techniques for determining mercury content in air and in water[15] have been developed at our institute

and the ones for determining mercury content in soil[17] and biological objects[18] (meat and fish) have been developed in collaboration with the laboratory of environmental monitoring at Tomsk Polytechnic University, Chemical department. When developing these techniques, the following factors have been investigated: influence of flow rate on peak amplitude and on the integral of the signal over the time, influence of the degree of sample dilution on the output signal value, choice of oxidizing agent for organic samples, etc.

As was mentioned above, the advantage of the method developed is that the determination of mercury content in air is carried out without pumping the sample under analysis through sorbent and preliminary mercury concentration. The measurement results are indicated on a digital display, the measurement time is 5 s. Analysis of solid and liquid samples is performed using a supplementary unit shown in Fig. 2.

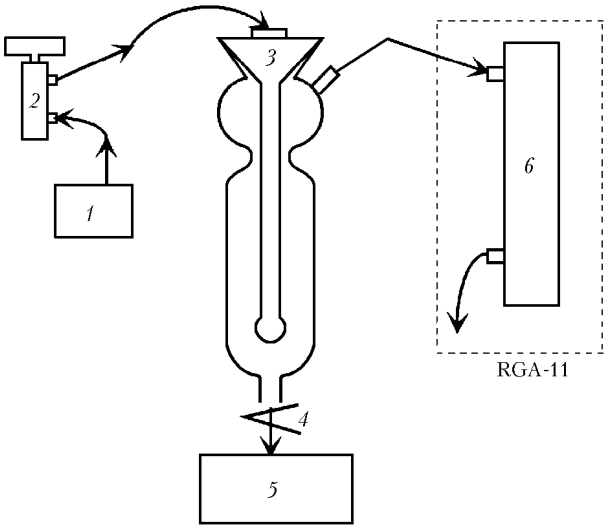

Fig. 2. Determination of mercury content in liquid samples: microcompressor (*1*); air flow meter (*2*); reaction vessel (*3*); clip (*4*); vessel for the processed sample (*5*); analytical cell (*6*).

The technique for analyzing liquid samples is described in Ref. 15. When analyzing solid samples, the reaction vessel *3* in Fig. 2 is replaced by an atomizer. An atomizer is a special oven, intended for annealing the sample in order to convert the mercury inherent in the sample into the elemental form. The sample (20 ng weight) is placed into the atomizer and a signal is recorded. The calibration curve is obtained in accordance with Ref. 17 using certified reference materials. Then this curve is used to determine mercury content in the samples under analysis. Recently the measuring technique for solid samples have been improved and applied to determining mercury content in peat. The detection limit is 1 ng/g.

Special software has been developed aimed at automation of the analyzer calibration as well as analysis of air, liquid, and solid samples. All measurement techniques have been certified and now they are used by sanitary and ecological services.

Mercury monitoring of peatbogs

In order to illustrate the potentialities of the developed and metrologically guaranteed RGA mercury gas analyzer, let us present some results of investigation of mercury content in peatbogs. These investigations are being carried out in the framework of the Integration Program on Complex Studying of Great Vasyugan Bog. Researchers from different scientific fields joined forces in order to study this giant natural formation.

As known, the atmospheric mercury transfer is of great importance in the mercury geochemical cycles. A major portion of mercury emitted by technogenic sources enters the atmosphere and may be transported for large distances.[19] From the atmosphere mercury deposits on the Earth surface as gas or aerosol. It also may be washed out by precipitations. Therefore an investigation of natural constituents that may be indicators of mercury pollution is very important. From this point of view the peat deposits are of special interest because they are giant natural filters. Owing to its high adsorptive capacity, peat adsorbs microelements and cleans the atmosphere. Because of this, the peat layers may be used as archives of atmospheric mercury deposition.[20]

For this purpose an investigation of mercury content in peat has been carried out. The peat samples were collected in the bogs of Bakchar and Tomsk regions. Bakchar region is eco-friendly because it is situated far from anthropogenic sources of pollution. All objects studied in Bakchar region are spurs of Vasyugan Bog. The Tagan peat deposit is situated 13 km to the southwest of Tomsk. It can be considered as an ecosystem subjected to direct attack of pollution coming from the city via the atmosphere. All the objects studied were not subjected to mercury pollution in any other way than via the atmospheric transfer. The objects studied are presented in Table 1.

Our expeditions to Bakchar region were located in Polynyanka village on the Vasyugan'e scientific-research station of Siberian Scientific Research Institute of Peat. At Tagan peat deposit we have chosen two sites, namely, natural and cut over ones.[21] At the cut over site the drainage was made in 1975 and then a peat layer has been removed. The residual peat layer has a thickness of 150 cm. We collected the samples at the typical sites of oligotrophic and eutrophic bogs that have dominating peat deposits. All sites are related to geographic coordinates. The peat samples were collected with the help of TBG-1 drill. The soil extracted has been divided into separate samples. Besides, the moss samples and soil, underlying peat deposit, have also been collected. All samples were packed in polyethylene bags. Then the samples were dried and ground. Mercury concentrations presented in figures are for the weights of dried samples.

Table 1. The objects studied

Object	Peat deposit depth, m	Feature	Location
Landscape profile of Kluch river, oligotrophic bog			
Site 1	0.2	Water logged forest	Bakchar region
Site 2	1.0	High ryam	
Site 3	3.0	Low ryam	
Site 4	2.7	Fen	
Vasyuganskoe peat deposit, oligotrophic bog			
Natural	2.5	Low ryam	Bakchar region
Dried	2.8	Low ryam (forest amelioration)	
Samara peat deposit	3.7	Eutrophic bog	
Tagan peat deposit, eutrophic bog			
Natural	3.4	Mixed forest	Tomsk region
Cut over	1.0	Used as a pasture	

Distribution of mercury concentration in depth is uniform for all objects studied. Concentration profile for natural site of Tagan peat deposit shown in Fig. 3 is most typical one.

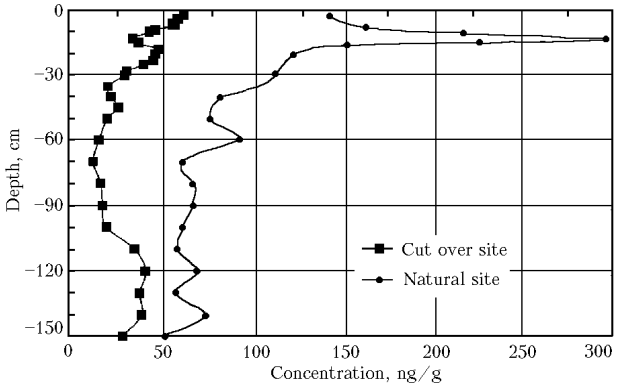

Fig. 3. Tagan peat deposit. Mercury distribution in depth.

For the majority of studied objects the mercury concentration gradually increases from the surface and reaches its maximum at the depth of 2 to 25 cm. Then it goes down to natural background value as the depth further increases. The underlying rock (clay or sand) contains less mercury than peat at the deposit bottom. The peat deposit of oligotrophic bog of the Klyuch river basin is very interesting object for investigation. This is because this ecosystem includes all landscapes, which are typical of an oligotrophic bog. These are the following: water logged forest, high ryam, low ryam, and fen.[22] The mercury concentration profiles for all these landscapes are shown in Fig. 4. Using this bog as an example, one can trace a mercury concentration increase from the central part of the oligotrophic bog to its outskirts, which coincides with the bog hydrological flow.

Mercury contents in all components of peat deposit are shown in Fig. 5 for all objects studied. It follows from this figure that peat accumulates mercury more strongly than moss. The most high mercury contents were found in water logged forest (in outskirts of oligotrophic bog on Klyuch river) and at the natural site of Tagan peat deposit. It can be seen that at the natural site of Tagan peat deposit mercury accumulation increases due to pollution coming from Tomsk city.

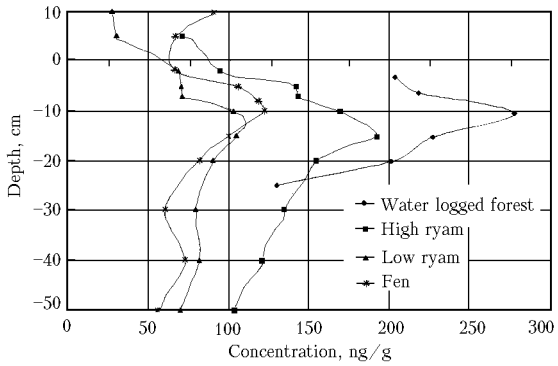

Fig. 4. Landscape profile of Klyuch river basin. Mercury distribution in depth.

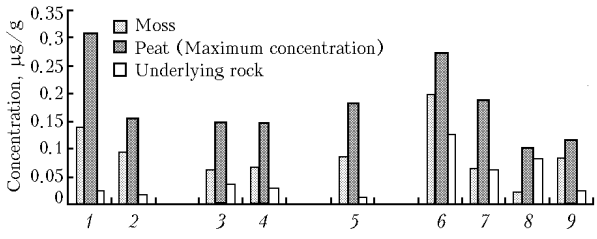

Fig. 5. Mercury content in components of peat deposit: Tagan peat deposit: natural site (*1*), cut over (residual peat layer of 105 cm) (*2*); Vasyuganskoe peat deposit: natural site (*3*), forest amelioration (*4*); Samara eutrophic bog (*5*); Landscape profile of Klyuch river basin: water logged forest (*6*), high ryam (*7*), low ryam (*8*), fen (*9*).

From the results obtained, one can date the mercury pollution based on the dependence of the mercury concentration in peat on the depth. The

growth rate of peat deposit is approximately 1 mm per year (from 0.6 to 2.4 mm).[20,23] For the objects studied the maximum mercury concentration in peat is at the depth of 2 to 25 cm. An average depth of the maximum location is 12 cm. Such a mercury concentration profile corresponds to dynamics of mercury production and consumption on a global scale.[24]

Conclusion

Operating experience of RGA atomic absorption analyzer with Zeeman background correction, as well as developed techniques for determining mercury content in air, water, soil, and biological objects confirmed its operating reliability, high exploitation characteristics, and metrological guarantee. All these parameters make possible a wide use of this device for multipurpose mercury monitoring.

In particular, this device is already used for mercury content determination both at background sites and near industrial plants in order to monitor their emissions; inspection of rooms and peoples after disasters associated with mercury overflow; food stuff certification.

In field operation the device was efficiently used for survey of mercury anomalous concentrations in seismic areas, as well as when searching minerals. The example presented above on using this device for peatbogs monitoring shows great promises of its exploitation under stationary conditions.

References

1. E.P. Yanin, *Mercury in Environment of Industrial City* (IMGRE, Moscow, 1992), 169 pp.
2. O.F. Vasiliev, A.A. Obolensky, and M.A. Yagolnitser, Sci. Total Environ. **213**, 73–84(1998).
3. S.I. Kovalev, I.N. Malikova, G.N. Anoshin, Zh.O. Badmaeva, and A.S. Stepin, Dokl. Akad. Nauk **363**, No. 1, 104–106 (1998).
4. *Regional and Global Mercury Cycles: Sources, Fluxes and Mass Balances* (NATO ARW, Novosibirsk, 1995).
5. N.A. Roslyakov and A.N. Dmitriev, eds, *Katun': Eco-geochemistry* (Nauka, Novosibirsk, 1992), 183 pp.
6. K.K. Kvetkus, "*Investigation of mercury in the atmosphere*," Author's Abstract of Cand. Phys.-Math. Sci. Dissert., Moscow (1986), 17 pp.
7. *Investigation of analytical characteristics of airborne Zeeman atomic absorption analyzer intended for aerogeochemical survey on gas mercury aureole,* Report on contract No. 366/85 (R&D Institute of Earth Crust at Leningrad State University, Leningrad, 1985).
8. E.L. Al'tman, A.A. Gannev, Yu.I. Turkin, and S.E. Sholupov, Zh. Prikl. Spektrosk. **XXX**, Issue 6, 987–990 (1979).
9. E.Yu. Genina, "*Peculiarities of measurement of mercury microquantities by method of atomic absorption spectroscopy*," Author's Abstract of Cand. Phys.-Math. Sci. Dissert., Tomsk (2000), 18 pp.
10. A.B. Antipov, E.Yu. Genina, and D.O. Kuchmezov, Atmos. Oceanic Opt. **11**, No. 7, 582–589 (1998).
11. A.B. Antipov and E.Yu. Genina, Atmos. Oceanic Opt. **11**, No. 5, 436–440 (1998).
12. A.B. Antipov, E.Yu. Genina, G.V. Kashkan, and N.G. Mel'nilov, Atmos. Oceanic Opt. **7**, Nos. 11–12, 886–889 (1994).
13. L.A. Konopel'ko, D.O. Kuchmezov, M.M. Morozova, and S.E. Sholupov, in: *Proceedings of Conference on Mercury and Complex Safety System* (St. Petersburg, 1996), pp. 52–59.
14. I.K. Kikoin, ed., *Tables of Physical Constants. Handbook* (Atomizdat, Moscow, 1976), 1006 pp.
15. *RGA-11 mercury gas analyzer.* Technical Description and Manual, AMYa2.770.001 TD (1992), 41 pp.
16. A.B. Antipov and E.Yu. Genina, in: *Proceedings of Third Scientific and Practical Conference on Mercury and Complex Safety System* (St. Petersburg, 1999), pp. 98–103.
17. Certificate No. 08–48/034 on metrological verification of technique of quantitative chemical analysis of soils for determination of mercury microquantities using method of atomic absorption spectroscopy (1993).
18. Certificate No. 08–47/010 on metrological verification of technique of quantitative chemical analysis of fish tissue, human and animal organs for determination of mercury microquantities using method of atomic absorption spectroscopy in the cold vapor version (1992).
19. M. Horvat, in: *NATO ASI Series 2: Environment. Global and Regional Mercury Cycles: Sources and Mass Balances* (Kluwer Academic Publisher, Dordrecht–Boston–London, 1996), pp. 1–30.
20. H. Biester, R. Kilian, C. Hertel, and H.F. Schöler, in: *Proceedings of 11th Annual International Conference on Heavy Metals in the Environment* (University of Michigan, School of Public Health, Ann Arbor, MI, 2000), Contribution #1029 (CD-ROM).
21. *Geological Report on Detailed Survey of Tagan Peat Deposit of Tomsk Region and Tomsk District* (Gor'ky, 1981).
22. L.I. Inisheva, ed., *Vasyugan Bog (Natural Conditions, Structure, and Functioning)* (Center of Scientific and Technical Information, Tomsk, 2000), 136 pp.
23. P. Boyarkina, N.V. Vasil'ev, V.I. Rezchikov, and E.B. Tyulyupo, in: *Neutron Activation Analysis of Peat as a Witness of Technogenic Pollution of the Atmosphere* (Tomsk State University Publishing House, Tomsk, 1977), pp. 76–81.
24. *Mercury in Siberian Environment: Estimation of Natural and Anthropogenic Sources Contribution.* Final Report of Temporary Scientific Group working on SKOPE Project on Estimation of Mercury Spreading and Its Role in Ecosystems (1994–1995), 30 pp.