Short communication

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Automatic monitors for direct continuous mercury measurement in ambient air, hydrocarbon, and industrial gases

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ABSTRACT. Mercury (Hg) has various sources of natural and anthropogenic emissions, can be transferred for a long distance in the atmosphere, and accumulate in deponent media and food chains. Due to its toxicity, mercury is considered a global pollutant. The Minamata Convention on Mercury (Articles 19 and 22) stipulates mercury monitoring to obtain information on the environmental cycle, transport, deposition, transformation, and fate of mercury and mercury compounds in various ecosystems. The developed monitors based on Zeeman atomic absorption spectrometry allow the fully automatic real-time determination of mercury in such different media as ambient air, industrial, and process gases.

Keywords: Zeeman atomic absorption spectrometry, mercury monitoring, ambient air, hydrocarbon and process gases

1. Introduction

The use of atomic absorption spectrometry with Zeeman correction of background absorption (ZAAS) enables us to avoid the Hg accumulation on sorbent traps and to design a family of real-time RA-915AM monitors that are intended for monitoring of ambient air, natural, process, and stack gases.

2. Materials and methods

The RA-915AM mercury monitor (Fig. 1) is based on ZAAS (Sholupov and Ganeyev, 1995; Sholupov et al., 2004) and is designed for the long-term non-attended Hg measurement; it has a built-in PC for data acquisition and processing, self-diagnostics, and data transfer.

Analysed air or gas is continuously pumped at the flow rate of ca. 8 L/min through the multipath analytical cell having an effective optical length of 9.6 m. The readings are collected continuously each 1 sec and are averaged for reporting at any chosen time interval, e.g. 5 min. The combination of the multipath cell with the ZAAS ensures direct continuous real-time measurement of the background mercury concentration in ambient air, as well as the mercury concentration in a wide range of natural and industrial gases. An activated carbon filter is used for zero drift control to detect Hg in ambient air and industrial gases; a special zero filter is used for natural hydrocarbon gases to eliminate an effect of non-selective absorbance of BTEX (benzene, toluene, ethylbenzene, and xylene). Automatic zero drift correction and autocalibration functions provide stable analytical parameters, operational reliability, and safety. For multiple sampling at 2 to 16 sites, the MLT-915 multiplexer is applied.

Fig.1. The automated mercury RA-915AM monitor.

The limit of detection (LoD) was determined three times exceeding the standard deviation of the blank measurement, as 0.3 to 0.5 ng/m^3. Further reduction of the LoD can be achieved by increasing the averaging interval, e.g. for 30-min averaging, the LoD is 0.1 – 0.2 ng/m^3.

Unique features of the monitor, which provided direct real-time measurement with frequency of 15 times per second readings, were used for the specific mercury surface to air mercury flux calculation (Osterwalder et al., 2020).The monitor can also be used

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in applications when the analysed ambient air has a reduced pressure, down to 40 kPa (at an altitude up to 5300 m or in the plane measurements (Weigelt et al., 2016)). Since the monitor does not require consumables, including gas cylinders, the use of RA-915AM monitors makes it possible to simplify maintenance at high-altitude and remote monitoring stations.

3. Results and discussion

Most required application for automatic RA-915AM monitors are: the background air monitoring, the indoor measurement at industrial facilities, and mercury determination in hydrocarbon and process gases.

3.1. Air monitoring

Examples of the RA-915AM application for long-term background air mercury measurement at two monitoring stations during a year are shown in Fig. 2. The Listvyanka monitoring station run by Limnological Institute SB RAS (LIN) is located in a rural area on the coast of Lake Baikal. The nearest major anthropogenic source of atmospheric pollution is the city of Irkutsk located at a 70 km distance to the northwest of Lake Baikal (Mashyanov et al., 2021). The South African Weather Service (SAWS) monitoring station is located at the southernmost tip of the Cape Point; the nearest city, Cape Town, is located 60 km to the north. The mean background mercury concentration for the year is 1.50 ng/m^3 (Listvyanka) and 1.53 ng/m^3 (Cape Point).

An example of indoor mercury monitoring at two sampling sites of a mercury storage facility during one year is shown in Fig. 3. The maximum mercury concentration of about 14 ng/m^3 that does not exceed the threshold limit value (TLV = 0.025 mg/m^3) averaged over an 8-hour work shift. The differences in mercury concentrations at different levels are rather small, which indicates good ventilation in the storage facility.

3.2. Hydrocarbon gases

Mercury concentration in hydrocarbon gases varies in a wide range, covering six orders of magnitude (Ozerova et al., 1999). A high Hg concentration in hydrocarbon gases poses some technological and environmental problems (contamination of equipment and products, poisoning of catalysts) and initiates intense corrosion of technological equipment, thereby enhancing accident risk. An example of the mercury monitoring in natural gas is shown in Fig. 4. A special concern is mercury in gas used for liquefaction when the volume of liquefied gas has a 600-fold decrease, and liquid mercury can precipitate even from a gas with a low Hg concentration. Therefore, for liquefaction, the Hg concentration must be brought down to a value below 10 ng/m^3.

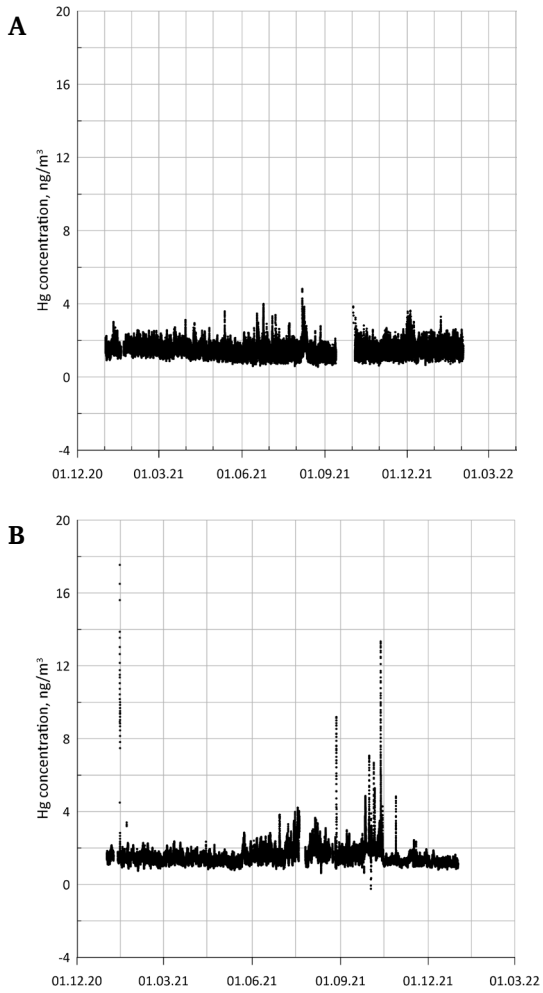

Fig.2. Background mercury monitoring of ambient air during a year at the Listvyanka (A) and SAWS Cape Point (B) monitoring stations. Courtesy of LIN and SAWS.

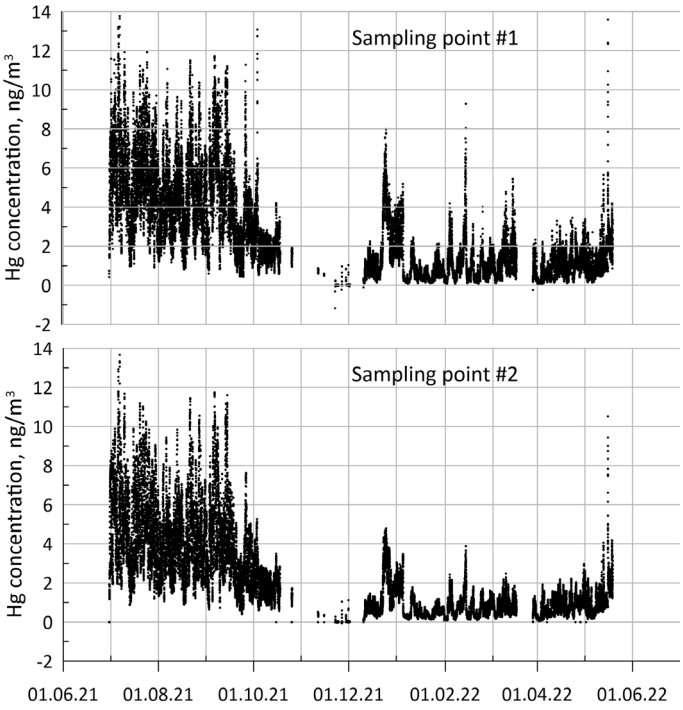

Fig.3. Two-channel mercury air monitoring in the storage for mercury containers at the sampling site #1 (at the level of the upper airways) and at the sampling site #2 (20 cm above the ground). Courtesy of Lumex Analytics.

3.3. Industrial gases

Industrial and process gases are the most complicated objects for mercury monitoring. Nevertheless, high selectivity of ZAAS enables direct online measurement under extremely complex gas composition (Fig. 5).

4. Conclusions

ZAAS technology ensures the development of mercury monitors with outstanding analytical features, combining low LoD, the highest selectivity, and a wide dynamic range. The monitors are used for direct continuous measurement of mercury concentration in ambient air and gases of complex composition. Fully automated data acquisition and processing, built-in self-diagnostics, as well as absence of consumables, enables long-term not attended operation at the remote monitoring sites.

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Conflict of interest

Authors declare no conflict of interest.

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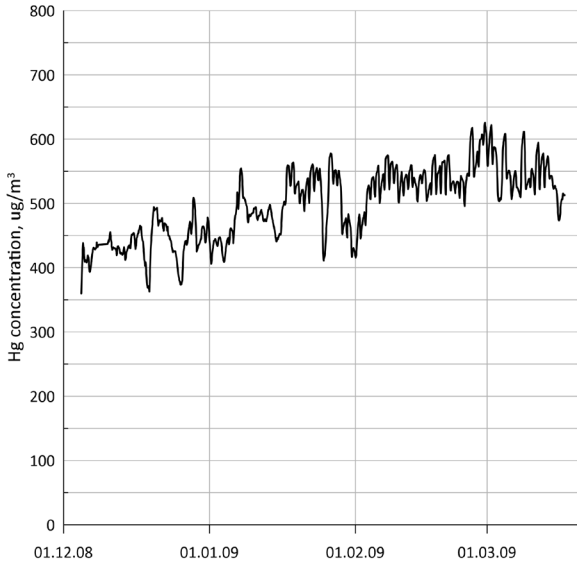

Fig.4. Mercury monitoring in natural gas. Courtesy of Petronas.

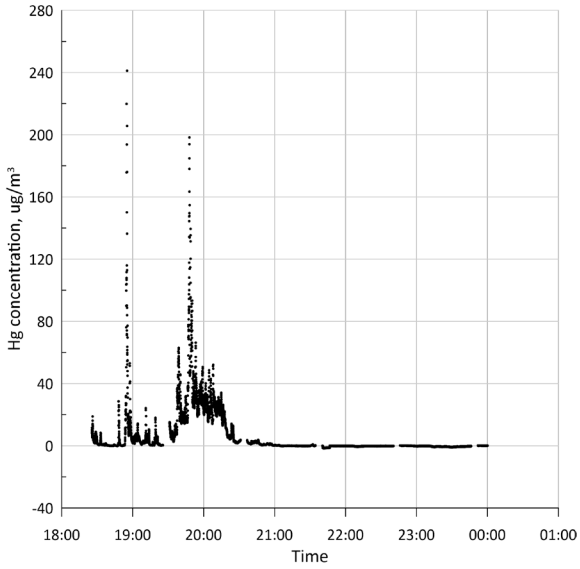

Fig.5. Mercury ambient air monitoring near the medical waste incineration plant. Courtesy of Lumex Analytics.