TRACEABLE CALIBRATION METHODS FOR OXIDISED MERCURY

Because of its toxicity, regulations on the use and exposure limits for mercury are becoming even more stringent [1]. For health and safety purposes, as well as for enforcement of regulations accurate measurements and hence calibrations are required. In recent years research has led to traceable calibration of elementary mercury (Hg^0) concentrations, including the primary standard currently operational at VSL. However, mercury also occurs in oxidised forms (Hg^{2+}) that are reactive and can be transformed into organic Hg species such as methylmercury (MeHg), which is very toxic and most prone to bioaccumulation in aquatic systems (Figure 1). Half of atmospheric mercury emissions are of natural origin whilst the rest are of anthropogenic sources, primarily from fossil fuel burning and other high-temperature industrial processes, such as cement clinker production, waste incineration, ore roasting and steel production.

The objective of the European Metrology Programme for Innovation and Research (EMPIR) the Metrology for Oxidised Mercury (MercOx, 2017 – 2020) project is the development of reliable and direct Hg^{2+} measurements techniques and reliable and traceable Hg^{2+} standards. This would close the traceability gap that currently exists in the measurement of total mercury (Hg^{tot}) and Hg^{2+} concentrations originating from various Hg sources. Furthermore, in the MercOx project methods for measuring Hg^{2+} and for accurately comparing the Hg^{tot} concentration in generated Hg^0 and Hg^{2+} reference gas standards are being developed, as well as improved sampling methods, traceable reference standards, validated methods for the on-line measurement of mercury under field conditions and a comparison for mercury species inter-conversion.

The basis of the MercOx project is the development of calibration methods to establish and implement a traceable calibration methodology for the most important oxidised mercury species, particularly for mercury chloride ($HgCl_2$). A two-channel analytical system was developed by LUMEX Analytics GmbH with two gas channels, for parallel determination of Hg^0 and Hg^{tot} concentrations (Figure 2). The Hg^{tot} channel contains an atomizer and both channels are equipped with an atomic absorption spectrometer utilizing the Zeeman effect. Proper calibration of instruments and methods for mercury measurements is crucial to establish metrological traceability to the international system of units (SI). Such a traceable Hg^0 source for the preparation of dynamic gas mixtures containing Hg^0 in air, in the range from 0.1 – 100 µg/m³, according to ISO 6145-8, was developed by VSL (the Dutch Metrology Institute) in previous collaboration projects [2]. This primary Hg^0 generator enables traceable mercury gas phase calibrations based upon gravimetry, i.e. traceable to the kilogram. This Hg^0 source was used to calibrate both channels of the two-channel analytical system in the range 0.8 - 14 µg/m³ for stack gas emission measurements (Figure 3). The conversion steps in the traceability chain from the Hg^0 sources via $HgCl_2$ or Hg^{tot} are described as follows:

Hg^0 (traceable source) → Hg^0 (measurement)

Hg^0 (traceable source) → $HgCl_2$ + Hg^0 → Hg^{tot} (measurement)

The next step in the traceability chain is certification of $HgCl_2$ generators. These generators are capable of generating calibration gas mixtures in wide ranges of total gas flow and chemical concentration for use in both laboratory and field conditions. As part of the project various types of generators were certified

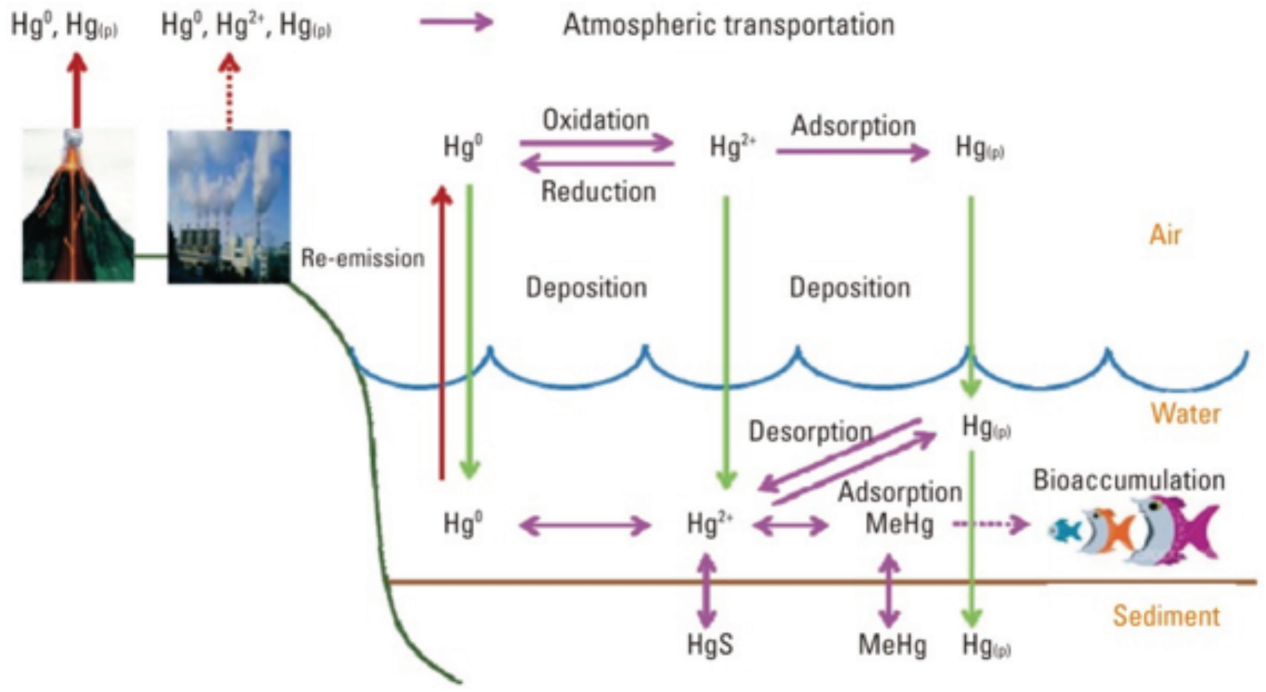

Figure 1 Mercury species in the environment.

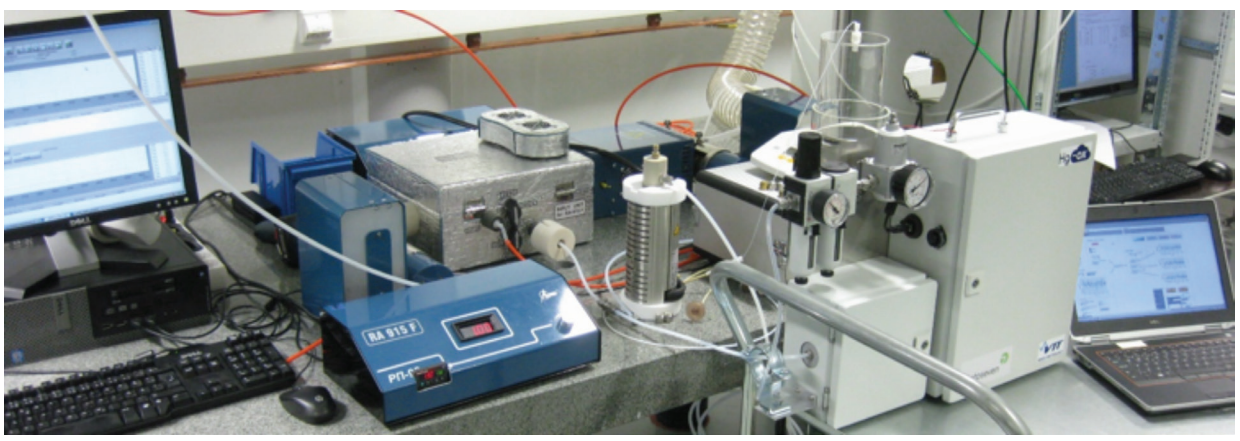

Figure 2 Setup of the two channel analytical system (left) and liquid evaporative $HgCl_2$ generators (right).

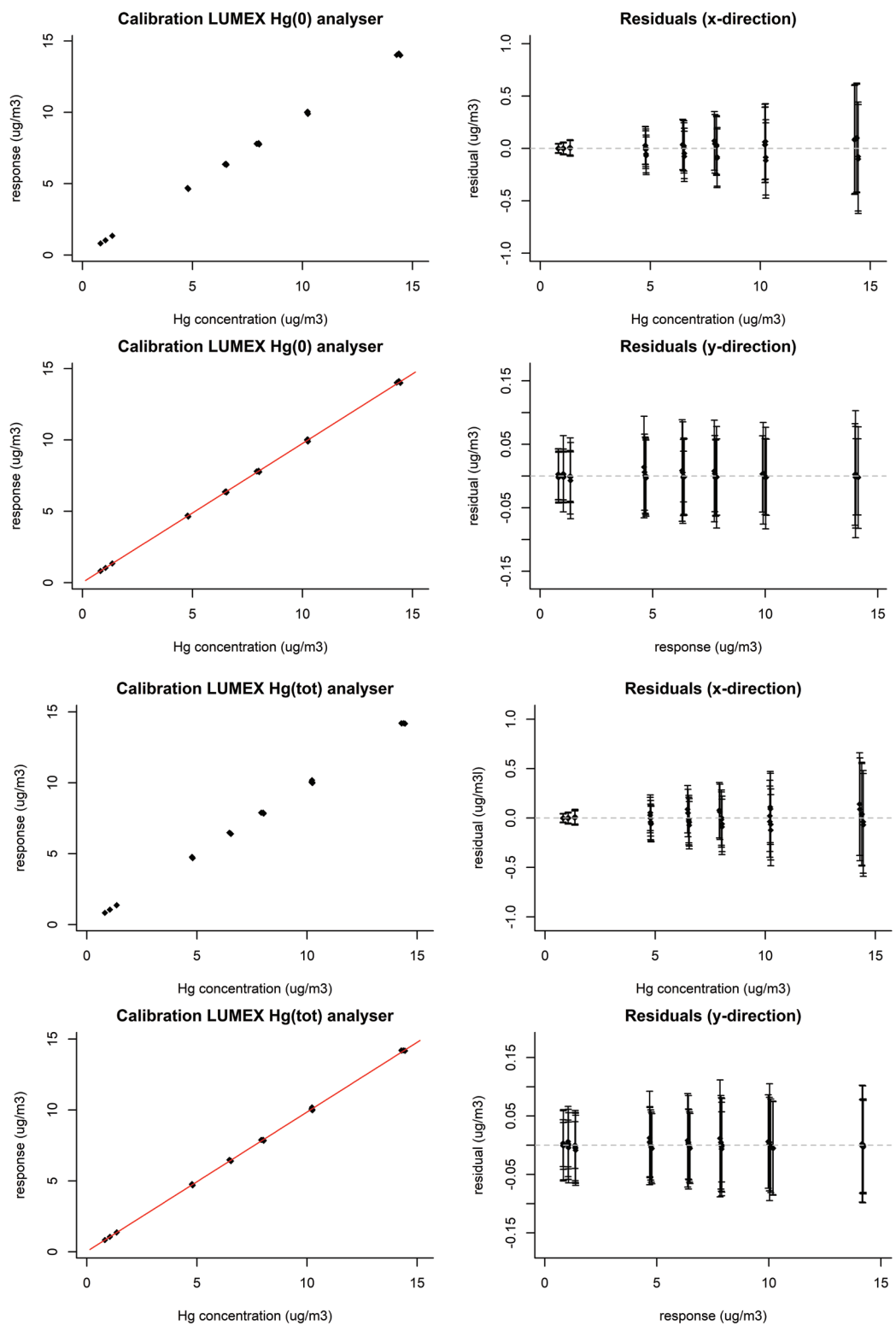

Figure 3 Calibration of both channels of the two channel analytical system, including the residuals calculated according to ISO6143.

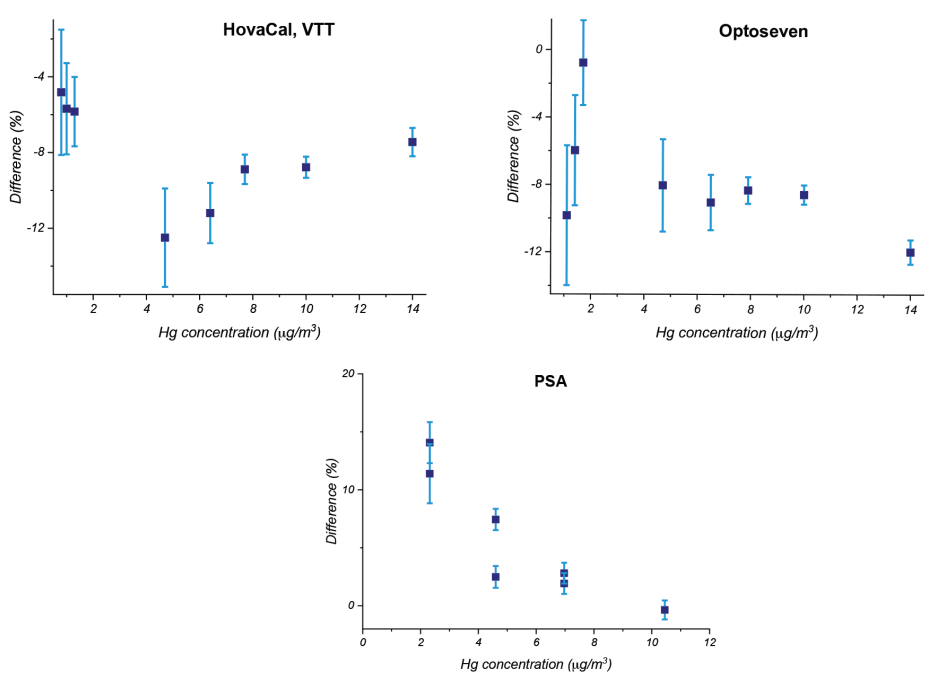

Figure 4 Results for recovery certification of various $HgCl_2$ generators.

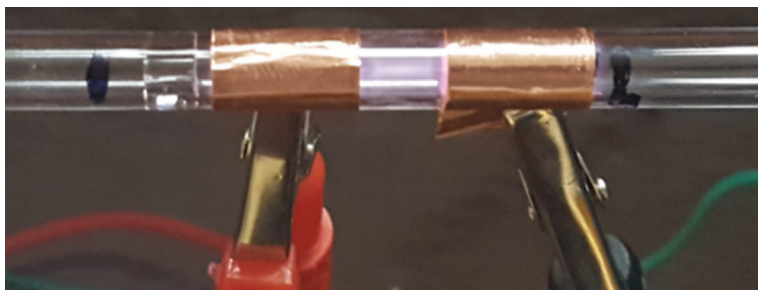

Figure 5 Cold helium plasma between two electrodes inside a quartz tube.

(Figure 4), among them two liquid evaporative generators: one commercially available system, provided by The Finnish National Metrology Institute VTT MIKES, with peristaltic pump and a newly developed system by Optoseven Oy using syringe injection. In both generators, the reference gas is generated by mixing a liquid solution with a known concentration of $HgCl_2$ into a carrier gas. The mixture is evaporated to yield the reference gas. The third system, from PS Analytical, is based on the continuous generation and dilution of saturated $HgCl_2$ vapour for the automated calibration of online mercury analysers. A low gas flow (ml/min range) passes over a mercury reservoir located in a temperature controlled oven. The mercury mass-flow is then diluted by a gas flow in the range of L/min to obtain a dynamic calibration gas mixture.

For the calibration of lower Hg^{2+} levels, which are more suitable for the determination of environmental Hg^{2+} concentrations, JSI developed a novel system for quantitative oxidation of Hg^0 based on cold plasma (Figure 5). Plasma systems have been used for the oxidation of mercury in flue gasses but have never been utilized for calibration purposes. Contrary to those systems, the developed cold plasma system is suitable for generating low Hg^{2+} amounts and due to its small dimensions, it is possible to make this system portable, enabling its use in laboratory and field.

The working principle of the cold plasma system is based on the quantitative oxidation of Hg^0 in cold helium plasma. Cold helium plasma is produced by applying radiofrequency on helium gas flow within a quartz tube. Hg^0 is produced by tin chloride reduction of a known amount of Hg^{2+}, which is traceable to the NIST Standard Reference Material (SRM) 3133. The produced Hg^0 is quantitatively collected on gold-coated aluminium oxide sand from which it is thermally released into the cold plasma helium stream. In the cold plasma, Hg^0 is quantitatively oxidized to Hg^{2+} which is retained on a potassium chloride (KCl) trap, which can also be used for calibration purposes. To determine the amount of Hg^0 that is not oxidized in the cold plasma, a second gold-coated aluminium oxide sand trap (breakthrough trap) is placed after the KCl trap. The first preliminary results of experiments with 50 and 100 ng of Hg^0 showed a recovery of 97.0 ± 3.37 % $Hg^{2+}$and a Hg^0 breakthrough of 2.67%.

The calibration methods described here, developed in the MercOx project, are currently used to validate the measurement methods, the sampling methods and the on-line Hg field measurements developed in the MercOx project.

Preceding the ICMGP conference (8 – 13 September 2019, Krakow, Poland) the consortium of the MercOx project is organizing an expert workshop "Achieving Comparability, Quality Assurance and Quality Control in Laboratory Measurements" (Sunday 7 September 2019 13:00-15:30). During the ICMGP special session 1.12 "Metrological traceability for mercury analysis and speciation" (Friday 13 September 2019 9:30-12:00) MercOx partners will present their latest results.

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For registration for the workshop or the ICMGP program click here (https://mercury2019krakow.com/gb/programme/program-overview.html).

For more information click here (http://www.mercox.si/) to visit the MercOx website or contact Iris de Krom (IdeKrom@vsl.nl) or Milena Horvat (Milena.Horvat@ijs.si). This work was funded by the European Programme for Innovation and Research (EMPIR).

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Hg-ox

References

[1] Mercury is one of the most toxic metals, and as such is regulated by the Industrial Emissions Directive (IED) 2010/75/EU, the Air Quality Directive 2004/107/EC, the Waste Incineration Directive 2000/76/EC and the Minamata Convention adopted in 2013 and started in 2017; the global treaty to protect human health and the environment from the adverse effects of Hg.

[2] European Metrology Research Programme (EMRP) projects: ENV02 PartEmission and ENV51 MeTra

Author Contact Details

Iris (I.M.J.) de Krom - Scientist, VSL • Thijsseweg 11 Delft, The Netherlands • Tel: 0031 (0)15 269 1500 • Email: idekrom@vsl.nl • **Web: www.vsl.nl/en**