Publishable Summary for 16ENV01 MercOx
Metrology for oxidised mercury

Overview

The overall goal of this project is to develop SI traceable measurements for the monitoring and control of mercury (Hg) and its different species in gas emission sources and in the atmosphere. In this way, the project will achieve significant improvements in the measurement comparability and uncertainty of Hg measurement results. Currently, traceable calibration methods only exist for elemental mercury (Hg(0)), however such measurements are also needed for oxidised Hg species, i.e. Hg(II) in order to meet the requirements of EU regulation and the implementation of the Minamata Convention. To address this, the project aims to validate and develop traceable oxidised Hg standards and methods for sampling and analysing oxidised Hg species in flue gas emissions and in the ambient air.

Need

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 (2013) - a global treaty to protect human health and the environment from the adverse effects of Hg. In addition to its elemental form, Hg also exists in oxidised forms, i.e. Hg(II) compounds that are reactive and can be transformed into organic Hg species such as methylmercury (MeHg), the most toxic Hg species and the one most prone to bioaccumulation in aquatic systems. Half of the atmospheric Hg emissions are of natural origin while the remaining half is from anthropogenic sources. The latter is primarily from the burning of fossil fuels and other high temperature industrial processes, such as cement clinker production, waste incineration, ore roasting and steel production.

The development of reliable and direct Hg(II) measurement techniques and reliable and traceable Hg(II) standards would solve the traceability problem that exists in the measurement of total mercury (Hg^{tot}) and oxidised Hg originating from different Hg sources. Currently, traceable calibration methods are only available for Hg(0), but they are also needed for oxidised Hg species to meet EU regulations. Furthermore, methods for measuring oxidised Hg and for accurately comparing the amount of Hg^{tot} in generated elemental and oxidised Hg reference gas standards are needed, in addition to improving sampling methods, traceable reference standards, validated methods for online field measurements and for studying interconversion of Hg species.

Knowledge of Hg speciation both in air and in stack gas emissions is critical when validating models for predicting Hg emissions, transport, deposition and fate at the European level as well as on a global scale. In addition, atmospheric Hg isotopic signatures that can be used to trace the origin and fate of atmospheric Hg also need metrological support and development.

Furthermore, in order to meet future global and European requirements (in relation to the Minamata Convention and European Directives) standardisation bodies have recognised the importance of and need to standardise the method for measuring Hg in industrial flue gases and in the atmosphere. This project will meet this need by facilitating the transfer of a measurement infrastructure as developed in the project to standards development organisations such as CEN/TC264/WG8 and the respective Articles of the Minamata Convention.

Objectives

The overall goal of this project is to develop traceable online measurement procedures for the monitoring and control of Hg and its different species in gas emission sources and in the atmosphere, and to improve the measurement comparability and uncertainty of Hg measurements. The project's specific objectives are to:

1. Develop, establish and implement a traceable calibration methodology for the most important oxidised mercury (Hg) species, especially for mercury chloride ($HgCl_2$). This includes quantitative confirmation of the output from liquid evaporative $HgCl_2$ generators and the development of reference gas standards.

2. Develop and compare different methods of measuring oxidised Hg and to accurately compare total mercury (Hg^{tot}) concentrations in generated standard gases for elemental mercury (Hg(0)) and oxidised mercury (Hg(II)). This includes methods for bulk and species-specific, e.g. Hg(0) and Hg(II), isotope ratio measurements to determine Hg migration pathways, its origin and species interconversion.
3. Optimise sampling methods for gaseous Hg species using traceable reference standards for Hg(0) and Hg(II). The project will look at the different measurement methods available and their long-term efficiency and reliability for sampling different matrices.
4. Test and validate new and existing methods for online Hg field measurements using the newly developed gas standards and/or generators. This will include measurement of Hg in stack emissions and in ambient air.
5. Facilitate the take up of the technology and measurement infrastructure developed during the project across the measurement supply chain (accredited laboratories) and by standards development organisations (CEN/TC264/WG8 and those linked to the IED 2010/75/EU, the Air Quality Directive 2004/107/EC and the Waste Incineration Directive 2000/76/EC) and end-users (environmental monitoring programmes, the research community, regional and global programmes).

Progress beyond the state-of-the-art

For the control and assessment of Hg concentrations in the environment it is essential to be able to monitor all Hg species. Unfortunately, traceable methods and calibration standards only exist for Hg(0), and even these are based on Hg vapour pressure equations that give different results. This discrepancy is of great concern and work to improve this situation is ongoing within EMRP JRP ENV51 MeTra which includes work on Hg(0) in air. However, insufficient work has been undertaken on oxidised Hg and there is a lack of reference gas standards for $HgCl_2$ or other oxidised Hg compounds. The main challenge with the evaporative gas generation systems used for measuring Hg is maintaining a high enough temperature during the transfer of the generated standard gas to the detection system..

The direct measurement of gaseous Hg(II) has recently become a major focus of international research programmes for continuous Hg source emission and ambient measurement and monitoring. However, these measurements are dependent on the availability of reliable Hg(II) gaseous reference standards and materials to assess and verify the quality of data and in most existing methods for Hg measurements, the different oxidised Hg species normally have to be reduced to the detectable elemental form i.e. Hg(0) in order to be quantified. Therefore, reliable Hg(II) reference gases are needed to quantify this conversion and to assess the ability to quantitatively transfer in particular the reactive Hg(II), through the entire measurement system.

The atmosphere contains three forms of Hg: gaseous elemental mercury (GEM), gaseous oxidised mercury (GOM), and particulate bound mercury (PBM). Through a series of photochemically initiated reactions in the atmosphere, involving halogens, GEM is converted to a more reactive species and is subsequently associated to particles in the air and/or deposited, particularly in polar environments. These phenomena are called atmospheric mercury depletion events (AMDE) and so far, only one commercially available instrument has claimed to be able to measure these Hg species, but it has since been demonstrated that measurements made with this technology underestimate GOM concentrations by as much as a factor of 2 to 13. Furthermore, sampling efficiency for GOM is affected by ozone and water vapour and underestimating GOM results in biased values that are too low for modelling dry deposition. The deposition of reactive mercury (RM = GOM + PBM) also produces inorganic Hg complexes that undergo abiotic and biological transformations on surfaces and in water. In order to address these knowledge gaps comparable and traceable measurements are needed for GEM, GOM and PBM. This is also true for stable direct Hg isotope ratio measurements of stack gas emissions and atmospheric measurements.

Results

To develop, establish and implement a traceable calibration methodology for the most important oxidised Hg species, especially for $HgCl_2$.

Traceable calibration methods for oxidized mercury species and a certification protocol for the output of liquid evaporative $HgCl_2$ are being optimized and two-channel analytical systems and calibration methods for the measurement of $HgCl_2$ from liquid evaporative $HgCl_2$ generators are under development. The step to set up a certification protocol has already been undertaken and steps are being examined to convert the obtained

protocol into a CEN or ISO norm.

To develop and compare different methods of measuring oxidised Hg and to accurately compare Hg^{tot} concentrations in generated standard gases for Hg(0) and Hg(II).

Feasibility investigations of laser ablation Inductively Coupled Plasma Mass Spectrometry (ICP-MS) as a method to determine Hg^{tot} in activated carbon traps were implemented. The method based on ICP-MS methodology was investigated for the accurate determination of Hg^{tot} and Hg species in activated carbon materials, frequently used as sorbent traps. A method of Hg^{tot} in reference aqueous solution of Hg using Isotope Dilution Cold Vapor Inductively Coupled Plasma Mass Spectrometry (ID-CV-ICP-QQQMS) was optimised. The same technique will support the study of interconversion processes during sampling and analysis of Hg(II) and Hg(0). A tandem ICP-MS was also purchased to allow for tracing the species interconversion at the different stages of the analytical measurement procedure.

An efficient nanomaterial with a 2D structure, high surface area, low cost and metal-free was successfully prepared. It is based on graphitic carbon nitrite (g-C3N4) and graphene oxide (GO), which shows very promising results with respect to selectively trapping Hg(II) present in impinger solutions.

A thermal desorption method was optimised for separating Hg(0) adsorbed on particles or solid substrates using a quadrupole mass spectrometer (QMS, Pfeiffer QMS 700). A clear separation of adsorbed Hg(0) was observed qualitatively, however further optimisation is needed for quantitative determination.

To develop optimised sampling methods for gaseous Hg species using traceable reference standards for Hg(0) and Hg(II). Regarding species inter-conversion, different measurement methods and their long-term efficiency and reliability in different matrices will be taken into account.

A theoretical review of practical issues related to Hg speciation and fractionation was done. Both atmospheric chemistry and stack gas emission chemistry were considered. Practical steps for the development of the chemical mechanism modules have been undertaken and will be included in a box model based on the Kinetic Pre-Processor (KPP) software.

A set of experiments was designed based on predefined experimental protocols for investigating Hg species conversion during sampling by either pre-concentration or filtration techniques.

Stability of Hg species on sorbent traps using conventional techniques based on CV AFS and temperature fraction analysis using quadrupole MS was implemented. It was observed that Hg(II) can convert to Hg(0) at room temperature under atmospheric conditions. Oxidation of adsorbed Hg(0) to Hg(II) has not been confirmed.

To test and validate new and existing methods for on-line Hg measurement under field conditions using the developed gas standards or generators.

The links with the Global Mercury Observation System (GMOS) programme was established and sites have been selected for field testing, which is planned in the last year of the project. First contacts were established with coal burning thermal power stations and cement industries in order to implement field testing of the validated methodologies.

Impact

Impact on industrial and other user communities

By developing optimised and traceable calibration methods for oxidised Hg species, including $HgCl_2$, and a certification protocol for the output from liquid evaporative $HgCl_2$ generators, this project will enable the use of liquid evaporative $HgCl_2$ generators as reference gas sources. Those stakeholders that will benefit directly from this were contacted and invited to the first stakeholder event. In addition, the MercOx project was presented at two workshops “Mercury emission from coal - MEC” where representatives from the government, industry and academia were present.

Impact on the metrology and scientific communities

The project will produce a good practice guide for Hg sample preparation and interspecies conversion correction as well as optimised and validated sampling methods for gaseous Hg species using traceable reference standards for Hg(0) and Hg(II). Both will significantly improve Hg speciation both in air and in flue gases, which is vital for the validation of models for predicting Hg emissions, transport, deposition and fate at the regional level (i.e. European level) as well as on a global scale. Arrangements were made to include a special session at the International Conference on Mercury as a Global Pollutant that will be organised in September 2019 in Krakow, Poland. During this conference, a training course on the traceability of Hg(II) will be organised for students and other users. Furthermore, the project was presented at five additional international meeting/conferences.

The validated bulk and species-specific isotope ratio measurements developed within the project will also be used to determine Hg migration pathways, its origin and the species interconversion of atmospheric Hg. Thus they will enable the scientific communities working on these issues to measure Hg(0) and Hg(II) more accurately and to predict Hg species pathways and the Hg biogeochemical cycle. Contact was established with the European ERA PLANET project that collaborates closely with the Global Earth Observation network (GEO).

Impact on relevant standards

Validation of field testing of new and existing methods for online and sorbent based Hg measurements in stack emissions and in the atmosphere will support stakeholders such as industry, standardisation bodies and policy makers. In Europe, industrial Hg emissions are covered by the IED 2010/75/EU, whereas Directives 2004/107/EC and 2000/76/EC are concerned with air quality and the incineration of waste, respectively. By developing traceable online measurement procedures for the monitoring and control of Hg in gas emission sources and in the atmosphere including oxidised Hg species, this project will make it possible to meet the levels of control in this legislation. In particular, this project will provide input to CEN/TC264/WG8 on Hg; who are currently developing standard methods for the measurement of Hg in emissions and are looking at ways to expand this to cover oxidised Hg emissions in the future. This will provide CEN/TC264/WG8 with the underpinning research and development requirement to produce standard methods to determine the different fractions of Hg in gaseous emissions. At the last CEN TC 264, WG8 meeting in Delft in 2018 the project was presented with clear explanations of the need for an elemental and $HgCl_2$ calibration gas protocol. Further actions to explore the best way forward were also proposed.

Wider impact of the project

The outputs of this project will also significantly improve Hg measurement and monitoring capabilities necessary for a reliable and consistent basis for reporting Hg emissions. This is particularly important for the implementation of Minamata Convention on Mercury, signed in 2013, which requires controls and reductions of Hg across a range of products, processes and industries where Hg is used, released or emitted. The results of this project will also be of interest to the Global Mercury Partnership of the Minamata Convention, especially the Partnership on Mercury Emissions from Coal and the Fate and Transport partnership. The secretariat of the Minamata Convention at UNEP has convened two meetings during which atmospheric Hg measurements were selected as one of the metrics for effectiveness evaluation of the Convention. At the meeting convened in Rome on 6-7 February 2018 (IGOSP meeting on EU ERA-NET project dealing with satellite measurements of Hg and persistent organic pollutants, POPs) and at the UNEP/WHO meeting on 13-14 February 2018 dealing with Global Environmental Facility (GEF) funded global Hg meeting, it was decided that this project MercOx plays a key role in measurement comparability. This was also stressed and notified at the UNEPs meeting on the 4th of April 2018 held at the UNEP's headquarters in Geneva, Switzerland.

Publications

[1]. Majda Pavlin, Arkadij Popovič, Radojko Jaćimović, Milena Horvat: Mercury fractionation in gypsum using temperature desorption and mass spectrometric detection, Open Chemistry, 2018; 16: 544–555

Project start date and duration:	01 October 2017, 36 months	
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