

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/TC 264 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 ($\text{Hg}(0)$) and oxidised mercury ($\text{Hg}(\text{II})$). This includes methods for bulk and species-specific, e.g. $\text{Hg}(0)$ and $\text{Hg}(\text{II})$, 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 $\text{Hg}(0)$ and $\text{Hg}(\text{II})$. 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/TC 264 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, prior to the start of this project, traceable methods and calibration standards only existed for $\text{Hg}(0)$, and even these were based on Hg vapour pressure equations that give differing results. This is a significant issue and work to improve this situation was done within the preceding project ENV51 MeTra which included work on $\text{Hg}(0)$ in air. However, there is still insufficient information oxidised Hg and 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 and this challenge is being addressed by this project.

The direct measurement of gaseous $\text{Hg}(\text{II})$ is a major focus of international research programmes for Hg source emission and ambient measurement and monitoring. However, these measurements are dependent on the availability of reliable $\text{Hg}(\text{II})$ gaseous reference standards and materials to be able to assess and verify the quality of data. In addition, in most existing methods for Hg measurements, the different oxidised Hg species have to be reduced to the detectable elemental form i.e. $\text{Hg}(0)$ in order to be quantified. Therefore, this project is going beyond the current state of the art by developing reliable $\text{Hg}(\text{II})$ reference gases that are needed to quantify this conversion and to assess the ability to quantitatively transfer in particular the reactive $\text{Hg}(\text{II})$, through the entire measurement system.

The atmosphere contains three forms of Hg: (i) gaseous elemental mercury (GEM), (ii) gaseous oxidised mercury (GOM), and (iii) 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 prior to the start of this project, only one commercially available instrument has claimed to be able to measure these Hg species. Although it was subsequently 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 ($\text{RM} = \text{GOM} + \text{PBM}$) also produces inorganic Hg complexes that undergo abiotic and biological transformations on surfaces and in water. This project is going beyond the current state of the art by addressing these knowledge gaps and developing comparable and traceable measurements for GEM, GOM and PBM. This project is also investigating 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 .

Several types of HgCl_2 generators were developed and tested including permeation tubes, salt saturation and liquid evaporators. The output of each type of HgCl_2 generator was then tested using the dual channel Zeeman AAS system which was calibrated with a SI traceable diffusion based gravimetric elemental Hg generator. This dual channel Zeeman AAS measurement system has provided an accurate real time measurement of total and elemental Hg which has been used to check the species integrity of the developed HgCl_2 generators.

The project's developed evaporative HgCl_2 generator is capable of generating Hg(II) reference gases in a wide concentration range, from sub ng/m^3 levels typical in ambient measurements to $\mu\text{g/m}^3$ levels typical in continuous process conditions. Moreover, a new method for calibration at low ambient concentrations for Hg was developed. The new method for calibration is based on the quantitative oxidation of traceable amounts of Hg(0) by cold plasma system in helium/oxygen atmosphere and is convenient for low level Hg concentrations representing ambient Hg levels.

Additionally, the performance of the HgCl_2 gas generators has been validated by direct coupling to a species independent inductively coupled plasma mass spectrometry (ICP-MS) detector. The direct coupling to the detector can provide sensitivity for both Hg(0) and Hg(II), and can compare the HgCl_2 gas generators output signal. The liquid evaporative HgCl_2 generator was validated using a highly specific ^{197}Hg tracer, which detected adsorption phenomena on tubing for HgCl_2 and especially for HgBr_2 species. This led to the design of additional validation testing specifically for when the liquid evaporative HgCl_2 generators are used for the loading of selective adsorption traps.

A certification protocol for the output of liquid evaporative HgCl_2 generators has also been prepared and the project is working on how to convert the protocol into a CEN or ISO standard.

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).

Laser ablation inductively coupled plasma mass spectrometry (LA ICP-MS) was developed as a method to determine Hg^{tot} in activated carbon traps and is currently being validated. Interlaboratory comparisons for accurate determination of Hg^{tot} and mercury species in activated carbon materials were also performed.

An efficient nanomaterial with a 2D structure and high surface area, that is also low cost and metal-free was successfully prepared and is based on graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) and graphene oxide (GO). This nanomaterial shows very promising results to selectively trap Hg(II) in impinger solutions and from the atmosphere.

Experiments are also on-going to develop isotope dilution inductively coupled plasma mass spectrometry (ID ICP-MS) for accurate measurements of Hg(II) and testing for interconversions during preconcentration steps.

Selective trapping systems using KCl loaded traps, denuders and impingers were validated using a ^{197}Hg tracer. The experiments using a liquid evaporative HgCl_2 generator (from objective 1) resulted in high losses of Hg(II) onto the tubing, especially at low Hg(II) concentrations. Traceable quantities of mercury loaded onto selective traps and denuders were only demonstrated by the oxidation of Hg(0) by cold plasma.

The feasibility and experimental protocols to determine the concentration of Hg species by specific adsorbent techniques and Hg isotopic composition in gas phase and Particulate Matter (PM) by multi-collector inductively coupled plasma mass spectrometry (MC ICP-MS) were successfully validated.

A method for the determination of stable isotope ratio of Hg in atmospheric bio-monitors (lichen, moss, needle) was also optimised and was subsequently used for the analysis of spruce needle samples from the German specimen bank. A reference material of urban atmospheric particles from the National Institute for Environmental Studies (NIES) in Japan, has been characterised for Hg isotopic composition in order to provide new reference values for this type of sample. The isotopic data obtained is currently being analysed.

A thermal desorption method was developed to separate Hg(0) adsorbed on particles or solid substrates using quadrupole mass spectrometer (QMS, Pfeiffer QMS 700) for detection. Very clear separation of adsorbed Hg(0) was observed qualitatively, however optimisation is needed for quantitative determination, which is currently in progress.

In addition, initial scoping studies using thermal desorption combined with ICP-MS have shown promising

results. Accurate species quantification, accounting for species conversion, can be achieved using species-specific isotope dilution mass spectrometry (ID-MS) with an ICP-MS detector.

A method for the determination of Hg^{tot} in reference Hg solutions using isotope dilution cold vapor inductively coupled plasma mass spectrometry (ID-CV-ICP-MS) was developed for the certification of Hg in a reference material (i.e. bituminous coal CRM 6200625a) for a proficiency testing. The same method for the determination of Hg^{tot} in reference Hg solutions (with or without cold vapour) will be used to study interconversion processes during sampling and analysis of Hg(II) and Hg(0).

Finally, a bituminous coal candidate reference material was developed for the determination of Hg^{tot} and Hg(II).

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.

Both atmospheric chemistry and stack gas emission chemistry have been investigated by the project. The modelling studies have focused on updating existing Hg chemistry mechanisms in transport/chemistry models to improve our understanding of the emission, transport and deposition of Hg emitted in industrial plumes. Since the start of this project several theoretical studies addressing the chemistry and photolysis of brominated Hg compounds have been published and the results from these theoretical studies have been added by this project to the Weather Research and Forecasting (WRF) model coupled with Chemistry (WRF/Chem model). The regional WRF/Chem has also been updated to include the most recent rate constants for BrHg* addition, product reactions and their subsequent photolysis, which yields BrHgO (a radical which reacts in the atmosphere with both inorganic and organic compounds). The project is currently comparing the WRF/Chem model with previous versions to understand how the recent changes affect the dynamics of Hg transport and deposition with respect to earlier simulations. This will subsequently be validated with experimental data.

The project has studied Hg species interconversion during the sampling steps based on pre-concentration on KCl solid traps. The results indicated the importance of proper preconditioning of solid traps as the sequential thermal heating severely affects the selectivity for Hg(II) trapping. Moreover, selectivity of the KCl trapping solutions used in the ASTM D6784-02 (Ontario Hydro) method showed that elemental Hg can be oxidised due to impurities in the KCl solution and stack gas matrix. This can potentially produce a positive and negative bias in the reporting of oxidised and elemental Hg respectively. The solubility of elemental Hg in KCl solution has also been experimentally determined by establishing the dimensionless Henry's law constant. The results showed that traces of $HgCl_2$ were measured in the KCl trapping solution using aqueous phase propylation liquid extraction with gas chromatography atomic fluorescence spectrometry (GC-AFS). The influence of stack gas components on the stability of $HgCl_2$ trapped in the KCl solution were studied, and in some cases a reduction of $HgCl_2$ was observed.

Studies on the stability of Hg species on sorbent traps using conventional techniques based on cold vapour atomic fluorescence spectrometry (CV AFS) and temperature fractionation analysis using QMS continued. Interconversion processes were confirmed and quantified using a highly sensitive radiotracer technique based on the use of highly sensitive radiotracer ^{197}Hg produced in the JSI nuclear research reactor from an enriched ^{197}Hg stable isotope. The highly sensitive radiotracer technique was used to study the outputs of $HgCl_2$ calibrators as well as the adsorption and desorption of Hg(II) during loading onto traps, denuders and impingers. This unique approach indicated severe losses of Hg(II) species in the sampling of commonly used methods. Work is now in progress on re-addressing the performance of the liquid evaporative Hg(II) calibration source under various conditions (e.g. gas flow, temperature, tubing material).

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

The logistics for the field work for emission measurements and atmospheric mercury speciation measurements have been set up. A preparatory meeting with the consortium and plant operators was held in Saloniit Anhovo a cement clinker production facility in Slovenia and a comprehensive list of activities for the field work was agreed. Both atmospheric and process gas measurements will be conducted at the Saloniit Anhovo cement clinker production facility and at air monitoring stations nearby. The field work will include e.g. active online monitoring of GEM, GOM and PBM with a commercial unit, collection of Hg from ambient air using epiphytic

lichens, passive samplers and wet precipitators, as well as process monitoring with sampling by sorbent traps and the plants continuous emission monitoring system.

In parallel in a coal fired power plant in Germany samples will be collected from different parts of the process using sorbent traps. The measurement results from the coal fired power plant's continuous emission monitoring system are available as well. Atmospheric measurements were organised in the transect from the emission source (cement production facility) to cover the range of atmospheric concentrations as well as various ratios of Hg(0)/Hg(II) species. The work has also been enhanced by adding the validation of commonly used passive samplers of gaseous Hg in the atmosphere as well as the biomonitoring protocols using lichens.

Impact

Impact on industrial and other user communities

The MercOx project has been presented at a number of workshops including "Mercury emission from coal - MEC" where representatives from the government, industry and academia were present. Moreover, the project was presented at the 3rd Conference of Parties of the Minamata Convention on Mercury (COP3) where governments and international agencies, non-governmental organisations and other stakeholders met to discuss the implementation of the Minamata Convention and its effectiveness. A need for comparable Hg measurements was strongly acknowledged at the conference.

In addition, the project organised a workshop entitled "Comparability of mercury measurements in air" during the International Conference on Mercury as a Global Pollutant (ICMGP2019) in Krakow; the largest global forum where researchers, industry, policy and other stakeholders meet, The latest developments in the area of traceable Hg measurements were presented by the project partners during the workshop.

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 levels as well as on a global scale.

At ICMGP2019 the project hosted a special session on: "Metrological traceability for mercury analysis and speciation". In addition, the project's coordinator (M. Horvat) received the Life Achievement Award for mercury research at ICMGP2019.

The project has produced 3 open access peer-reviewed publications, as well as submitting a patent related to the calibration method using cold plasma from objective 1.

The project has given 32 presentations or posters at conferences such as Gas 2019, the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy (Pittcon), the 13th Mercury and Multi-Pollutant Emissions from Coal Workshop, and the European Winter Conference on Plasma Spectrochemistry.

The validated bulk and species-specific isotope ratio measurements developed within the project (in objective 2) can 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.

The project has also established contact (and future collaboration) with the European ERA PLANET project the European network for observing our changing planet (<http://www.era-planet.eu/>) that collaborates with the Group on Earth Observations.

Impact on relevant standards

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 support the requirements in this legislation. In

particular, this project will provide input to CEN/TC 264 WG8 Emissions - Total mercury; 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. At the CEN/TC 264 WG8 meeting in 2018 the project was presented with clear evidence for the need for an elemental and HgCl₂ calibration gas protocol, as well as recommendations for the best way forward. Subsequently, in 2019 CEN/TC 264 have agreed on the adoption of: prEN xxxxx “Stationary source emissions — Calibration of elemental and oxidised mercury gas generators for SI-traceable mercury concentration measurements in air” which is a very important impact of the project on standardisation. (https://standards.cen.eu/dyn/www/f?p=204:22:0:::FSP_ORG_ID,FSP_LANG_ID:7829,25&cs=11B8EDE407406BC1569F064C43BC44ABF)

Further to this, the consortium has also presented the project and its outputs to ISO/TC 146 Air Quality SC1 Stationary source emissions WG32 Hg and EURAMET TC-MC (Metrology in Chemistry).

Longer-term economic, social and environmental impacts

In the long term, the outputs of this project will significantly improve Hg measurement and monitoring capabilities, which are 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 Minamata Convention has previously identified atmospheric Hg measurements as one of the metrics for effectiveness evaluation of the Convention. Further to this, at the Integrated Global Observing Systems for Persistent Pollutants (IGOSP) meeting for satellite measurements of Hg and persistent organic pollutants and at the joint United Nations Environment Programme (UNEP)/ World Health Organisation (WHO) meeting dealing with Global Environmental Facility funded global Hg meetings, it was decided that this project plays a key role in Hg measurement comparability. This was also stressed at the UNEPs 2nd and 3rd meetings of the Conference of the Parties to the Minamata Convention on Mercury (COP2 and COP3) in 2018 and 2019.

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; <https://doi.org/10.1515/chem-2018-0046>
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- [3]. Saxholm Sari, Rajamäki Timo, Hämäläinen Jussi and Hildén Panu, Dynamic calibration method for reactive gases, *Measurements Science and Technology*, 2020, 31, 034001, <https://dx.doi.org/10.1088/1361-6501/ab4d68>



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Internal Funded Partners: 1 JSI, Slovenia 2 LGC, United Kingdom 3 TUBITAK, Turkey 4 UBA, Germany 5 VSL, Netherlands 6 VTT, Finland	External Funded Partners: 7 CNR, Italy 8 Lumex, Germany 9 Optoseven, Finland 10 PSA, United Kingdom 11 UPPA, France	Unfunded Partners: 12 CENAM, Mexico
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