



SRM EN 13211 ISOKINETIC SAMPLING COUPLED WITH ON-LINE AND CONTINUOUS ANALYTICAL SYSTEM FOR MERCURY SPECIATION IN FLUE GAS: WASTE WATER TREATMENT SLUDGE IN A COMBUSTION / CO-COMBUSTION MUNICIPAL SOLID WASTE INCINERATOR CASE-STUDY

This work presents the results of 15 months from the start of the F.A.N.G.H.I. project (Lombardy Region: ERDF ROP 2014-2020 Innovation & Research Call Hub). The project provides for a total cost of € 9,904,708.53, a duration of 30 months starting in January 2020. The pandemic caused some of the project's objectives to be postponed and for this reason the project will end at the end of 2022.

F.A.N.G.H.I. proposes an integrated approach to assess the health and environmental impact of two alternative strategies for sewage sludge disposal, incineration, and amendment to agricultural soils, to identify the most sustainable from an energy, economic, health and environmental point of view. Mercury (Hg) in sewage waters and sewage sludge (SS) is a relevant topic which needs further studies to be understood in detail as well as to provide reliable estimates on the amount of mercury and its species released into the environment (Wang and Mao, 2019). In addition, there are very few studies on Hg emission linked to SS incineration. In Takaoda et al, 2012 authors reported results found for two Japanese fluidized-bed type incinerators equipped with different Air Pollution Control Devices (APCDs): they found that Total Hg (THg) concentrations in the flue gases ($36.6 \mu\text{g}/\text{Nm}^3$ and $21.1 \mu\text{g}/\text{Nm}^3$ on average) were higher than those reported for other type of incineration plants in Japan. These evidences show the importance of monitoring Hg concentrations in emissions deriving from SS thermal treatment.



Fig. 1 – WTE plant where Hg monitoring took place (courtesy of A2A Life company)

This work describes a method used to quantify THg emitted by SS thermal treatment in a mono-incineration and co-incineration condition. In Europe, the reference method EN 13211:2003 prescribes an isokinetic sampling for THg in order to properly collect also the dust phase and droplets generated by wet scrubbers. Unlike the reference method prescribes, THg speciation (i.e. Hg0 and Hg2+) and real-time acquisition is useful to better understand Hg emissions. Experimental tests were performed in isokinetic conditions, based on the continuous SnCl₂ reduction and real-time CVAAS measurements (1 sec. acquisition time) on a WTE plant with a fluidized bed combustion furnace treating dried and pelletized sludge (DPS) in a single combustion or in a co-combustion regime (DPS burned together with Refuse-Derived Fuel - RDF).

The approach to work was rather innovative: the Atomic Absorption Mercury Analyzer (NIC SGM-9) employed in this work is a real time device based on the atomic absorption spectroscopy principle, equipped with a gas treatment system in which the SnCl₂ and KOH reagents are supplied at precise concentrations. This configuration allows to measure at the same time the Elemental Mercury (EHg) and the Total Gaseous Mercury (TGHg) in the flue gas sample. In this setup the SnCl₂ captures mercury Hg and KOH removes possible interferences: These reagents are required by international standards such as ISO 21741: 2020

By simply entering on-site conditions (ambient temperature, measured gas humidity and measured gas temperature) system automatically set the timing and volume of discharging liquid from the gas scrubbing bottles. In the first setup (first scrubber), the Hg²⁺ is reduced to Hg⁰ using a wet method (10% SnCl₂ solution). Then, the sum of Hg⁰ is determined by means of the first detector. The second setup is responsible for determination of Hg⁰ only. Interfering substances (e.g. HCl, SO₂) are removed from the flue gas with a 10% KOH solution (second scrubber), the moisture is removed by the third scrubber, whose temperature is reduced to 5 °C.

The solutions in the scrubbers may be discharged and replaced automatically at a specified time. At determined intervals (typically every 60 s), the detector controls the background level using a gold trap which removes Hg from the flue gas and corrects the analytical signal. From the probe (TCR TECORA® titanium rotative probe) to the analyzer a heated line with thermoregulator is used in order to avoid condensation (temperature above 180 °C)

Particular attention has been given to the calibration of the instrument. An insulated chamber (gas box) with a vial inside with a

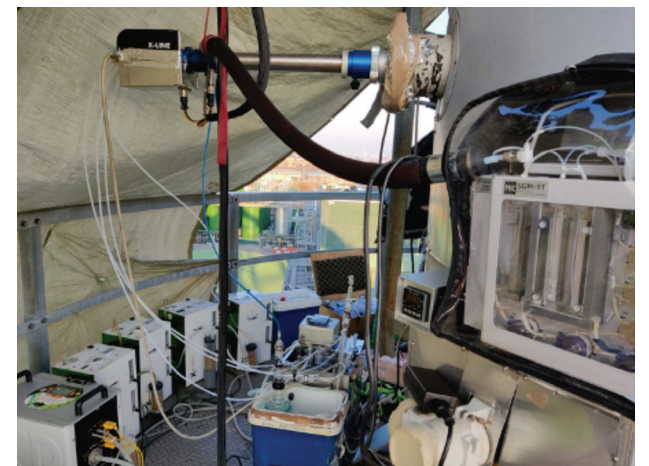


Fig 2 – Set of instruments used for monitoring

thermosealed thermocouple calibrated with an external temperature primary by NIST was used

Metallic mercury is taken with a gastight syringe and placed in the vial. From this, precise aliquots are taken from the vial and injected into a tedlar bag.

Amount of Hg contained in the air inside the chamber obtained from gas state equation allows to trace the amount of mercury injected into the tedlar bag that must be detected by the atomic absorption analyzer

Then, a series of mercury injections were carried out inside a tedlar bag.

A three-point calibration starting with a value of 4 micrograms and ending with approximately 16.50 micrograms was performed, with a good correlation between the estimated concentration and that measured by the atomic absorption of the analyzer.

At the same time isokinetic sampling collections on a quartz-fiber filter and by absorption on K₂Cr₂O₇ + HNO₃ solution (EN 13211:2003) was performed in order to compare results from experimental tests and reference method.

Two campaigns lasting approximately 5 hours each were prepared in which 100% of RDF was burned in the WTE plant and 2 campaigns in which, in addition to RDF, DPS was burned with different loads.

The comparison could only be done with an analyzer as continuous as the AMS installed in the plant, a CEM which uses the photometric principle with Zeeman effect and for the calibration uses a vaporizer generating a gas starting from a solution of mercury chloride

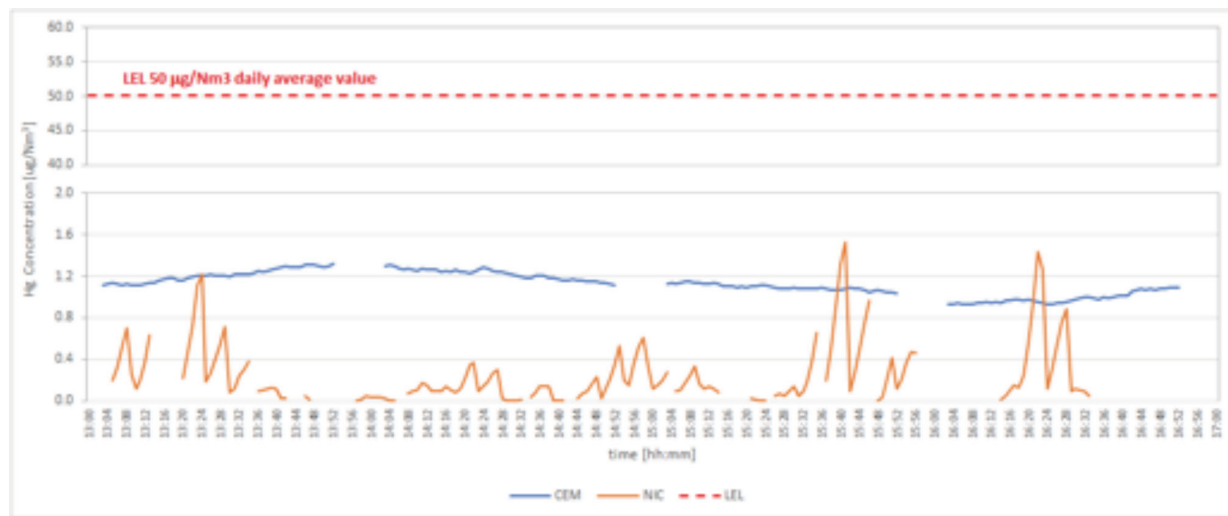


Fig 3 - 170640 kg RDF, 46074 kg dry sludge, average over 4 h: 1.12 $\mu\text{g}/\text{Nm}^3$ AMS 0.34 $\mu\text{g}/\text{Nm}^3$, SRM with NIC

Values of the hourly averages in the sampling periods (approx. 5 hours per campaign) between AMS and SRM with the analyzer remain around 0.5 - 1.0 $\mu\text{g}/\text{Nm}^3$ with a very small difference (between 0.5 and 1.0 $\mu\text{g}/\text{Nm}^3$). The results seem to maintain constant the AMS / SRM with NIC SGM-9 differences between

100% RDF combustion and different dry sludge combustion loads. SRM with NIC SGM-9 generally seems to show frequent peaks unlike AMS: this may be due in part to the interaction of NIC SGM-9 with some interfering metals (KOH molarity was

consequently increased from 1M to 2M), in part to NIC SGM-9 higher sensitivity.

Filter analysis always provided Hg values below the instrumental sensitivity limit such as not to generate a quantifiable contribution to the analyzer values.

This work compares the results of 4 test campaigns between a validated AMS and a discontinuous system based on SRM (isokinetic sampling) coupled to a real-time (AA) system for measuring mercury in gaseous form.

The comparison already shows satisfactory agreement and well below the LELs (50 $\mu\text{g}/\text{Nm}^3$ d.a.). However, further investigation of the field tests carried out is needed to investigate the deviations found between the two systems.

References

- Takaoka M., Domoto S., Oshita K., Takeda N., Morisawa S. Mercury emission from sewage sludge incineration in Japan. *Journal of Material Cycles and Waste Management* (2012), 14: 113–119.
- Wang X., Mao Y. Mercury in Municipal Sewage and Sewage Sludge. *Bulletin of Environmental Contamination and Toxicology* (2019), 102:643–649.

Author Contact Details

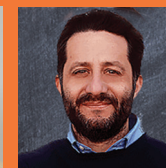
Paolo Lopinto – TCR TECORA® • Via delle Primule, 16 Cogliate, (MB) 20815, Italy • Email: paolo.lopinto@tcrtecora.com • Web: www.tcr-tecora.com/it

Federico Teoldi, Laboratory of Environmental Chemistry and Toxicology, IRCCS • Istituto di Ricerche Farmacologiche Mario Negri,

Via Mario Negri 2, 20156 Milan, Italy • Email: federico.teoldi@marionegri.it



Federico Teoldi



Paolo Lopinto