Literature Study

on

Dual Channel Mercury Analyzers (DCMA)

Task

Lumex, with input from PSA, LGC and VTT, will compile a list of performance characteristics (e.g. repeatability, reproducibility, accuracy, linearity, drift, bias and robustness) and uncertainty sources of state-of-the-art dual analytical systems (e.g. thermal converter efficiency and undesirable species interconversion) [1]

Definition

The term „Dual Channel Mercury Analyzer“, in the framework of the EMPIR projects 19NMR03 SI-Hg and the preceding 16ENV01 MercOx, is used for an instrument that can determine elemental and oxidized forms of mercury in parallel, either simultaneously or sequentially – but in both cases from the identical gaseous sample.

Not included in this study are hyphenated techniques like ICP-MS with or without prior chromatographic separation of species.

It was also not undertaken to extract instrument performance characteristics from the large number of papers published on the measurement of mercury species in the atmosphere. Several reviews are available on this topic, one of the latest, and most concise being the one by Lyman et al. [2]

Need

In the early years of mercury emission monitoring, the focus was almost exclusively on the measurement of total Hg (Hg^{tot}), which comprises various physico-chemical entities, like

- gaseous elemental Hg(0)
- gaseous forms of oxidized Hg (mainly Hg^{2+})
- particle-bound Hg
- Hg dissolved or absorbed by aerosols or droplets

The governing technology applied by instrument manufacturers was, and still is, Atomic Fluorescence (AFS) or Atomic Absorption Spectroscopy with or without Zeeman background correction (AAS), utilizing the strong elemental mercury absorption line at 253,7 nm. This method is very sensitive, with detection limits in the ppt range – but it can determine elemental Hg only. Thus, to measure Hg^{tot}, it was necessary to reduce oxidized mercury to the elemental form, either by passing the sample through a thermal converter, kept at temperatures of about 1.000°K, or through an aqueous reduction solution.

As evidence grew that oxidized species played an important role in the global atmospheric cycling of mercury, and that the various chemical compounds exhibited quite different toxicological profiles and threats, demand for a separate quantitative determination of the individual species came up. Two alternative procedures were established:

A) calculating Hg^{2+} as the difference between Hg^{tot} and Hg(0) (two measurements: first passing the sample through a converter/reduction solution, second bypassing the converter/reduction solution)

B) separating Hg^{2+} from the sample stream by physical or chemical bonding to a suitable matrix (eg KCl or an ion exchange resin/membrane), followed by desorption, conversion, and subsequent measurement.

An additional demand came from the field of metrology, which gave rise to the EMPIR 16ENV01 MercOx project:

"Thus, the development of reliable and direct Hg(II) measurement techniques and reliable and traceable Hg(II) standards would solve the traceability problem that currently exists in the measurement of total mercury and oxidised Hg concentrations originating from different Hg sources. Currently, traceable calibration methods only exist for Hg(0), but they are also needed for oxidised Hg species in order to meet the requirements of EU regulation. Furthermore, methods for measuring oxidised Hg and for accurately comparing the Hg^{tot} *concentration in generated elemental and oxidised Hg reference gas standards are needed, as well as improved sampling methods, traceable reference standards, validated methods for the on-line measurement of Hg under field conditions and a comparison of Hg species inter-conversion".* [3]

Consequently, the development of a *"two-channel analytical system… , capable of determining the concentration of both elemental Hg… and oxidised Hg simultaneously in real time"* was part of the WP1 of this project [4]. The system, which was successfully designed and assembled by Lumex, has been thoroughly tested by several MercOx partners as part of other WPs, and will continue to be used in the follow-up EMPIR project 19NMR03 SI-Hg. A detailed description of it is given further below.

The need for traceable field calibration techniques was also emphasized in the 2020 review of Lyman et al.: *"Many atmospheric mercury measurements have been made with inadequate specificity and insufficient field validation. This is true for measurements that have targeted Hg(0) and those that have targeted gas- and particle-phase Hg(II). Future mercury measurements must use methods wherein the captured species are clearly and quantitatively understood. Many emerging techniques and modifications of existing techniques appear able to meet this need. Future measurements must also be supported by routine calibration checks in ambient air in real field conditions. Field calibration techniques are readily available for Hg(0) , are becoming available for gas-phase Hg(II), and are unavailable (to our knowledge) for particle-phase Hg(II)* " [2]

DCMAs in operation

There are two commercially available systems from Tekran and PSA, plus two systems on a prototype level, which have been assembled using serial components by people from Utah State University (USU), and – within the scope of the MercOx project - Lumex, respectively. The PSA and Lumex systems work according to procedure A), the Tekran and Utah State University systems work according to procedure B).

It should be noted that the systems were designed with totally different applications in mind: the Tekran and USU for speciated mercury measurement in ambient air, the PSA for analysing flue gas, and the Lumex – at least initially – to control the composition of the output of Hg(0) and Hg^{2+}calibrators in the laboratory and the field. Thus, their performance characteristics are hardly comparable.

TEKRAN Model 1130

Tekran uses a KCl-coated annular denuder to capture oxidized mercury while allowing elemental mercury to pass through. During the sampling (adsorption) phase, their AFS Model 2537 provides real time measurement of elemental mercury. During the analysis (desorption) phase, the denuder is flooded with Zero Air and heated. The captured oxidized mercury is thermally desorbed and reduced to the elemental form. The Model 2537 detects this eluted mercury, providing a measurement of total oxidized mercury captured during the previous sampling period. The desorption process also regenerates the denuder coating. After cooling, the denuder is ready for another cycle.

For a schematic diagram of the system, see Fig.1, which includes the Model 1135, used to separate particle bound mercury from the sample stream.

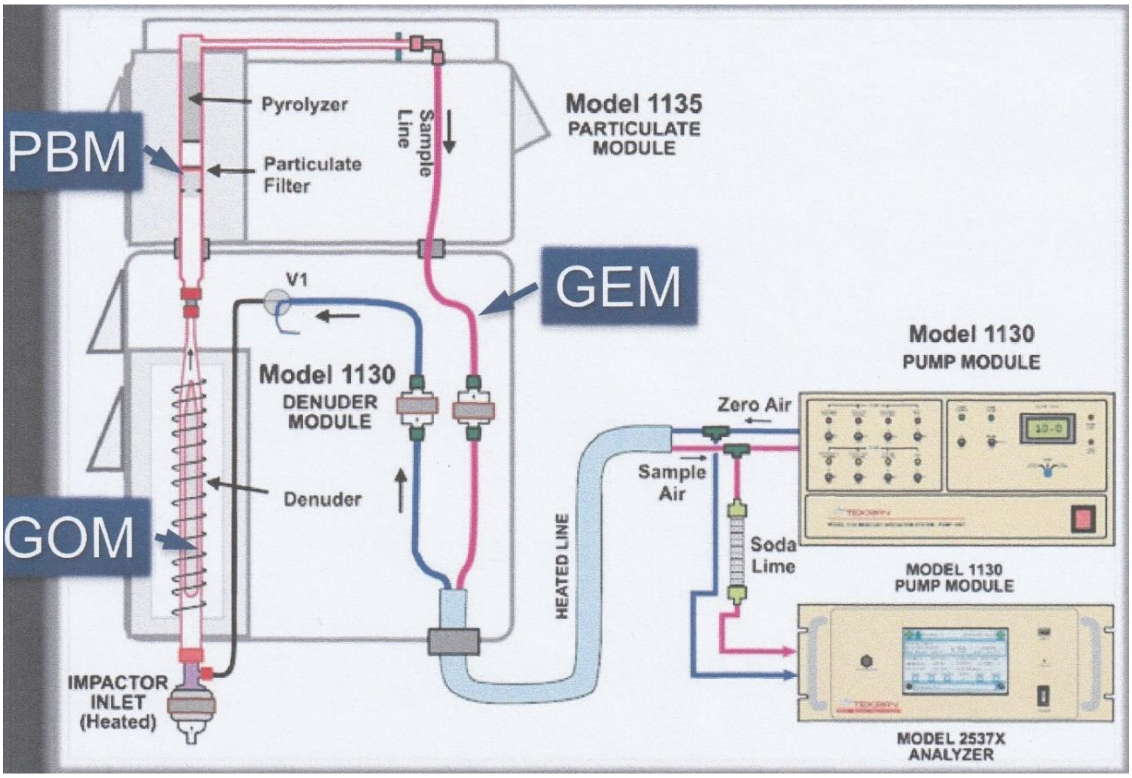


Fig. 1 Tekran DCMA [5]

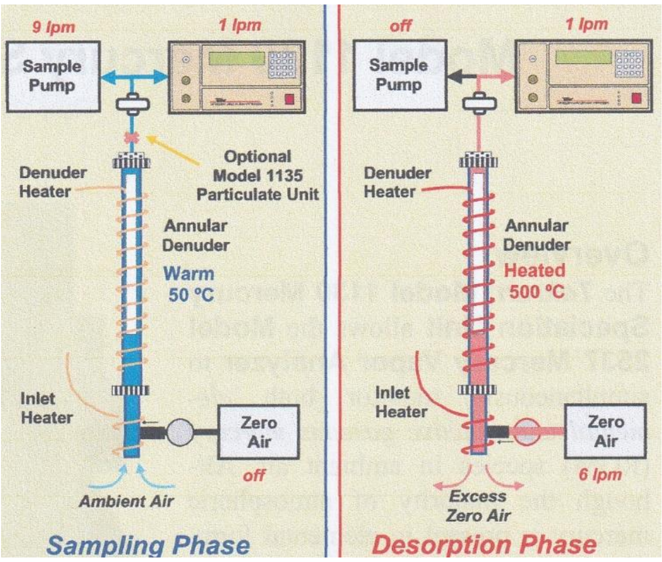


Fig. 2 Working principle of Tekran denuder [6]

None of the performance criteria listed under Task A2.1.1 of the 19NRM03 SI-Hg project could be found in the open literature and were also not disclosed by the manufacturer.

Over the last years, KCl denuder-based systems have come under criticism, as a substantial amount of the Hg^{2+} they capture in ambient air is apparently reduced to Hg^0 during sample collection, causing a low bias for Hg^{2+} (e.g. Lyman et al. {7]).

Utah State University DCMA

Lyman et al. approached this problem by replacing the KCl denuder by an activated poly(ether sulfone) cation-exchange membrane. Their system, which uses the Tekran 2537 AFS as the detector, is shown in Fig.3:

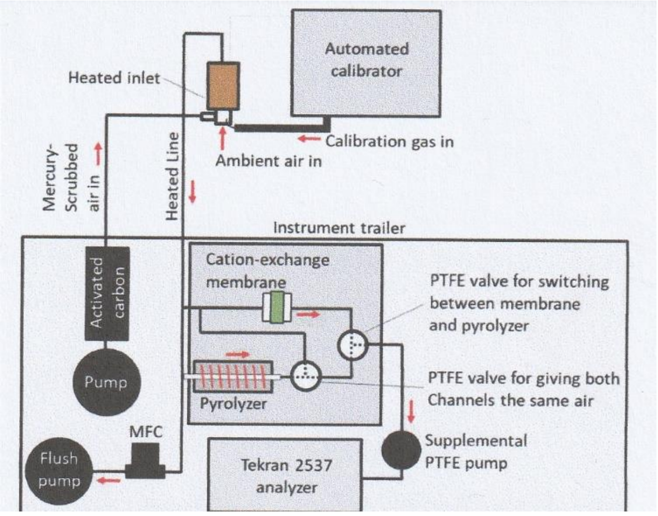


Fig.3 Diagram of the Utah State University DCMA [7]

It shows much improved recovery rates of $HgCl_2$ and $HgBr_2$, when injected from a permeation tube calibrator into an ambient air sample, compared to a KCl denuder-based system, as shown in Fig.4:

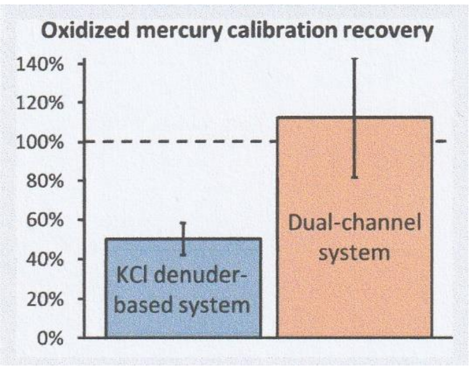


Fig. 4 Comparison of Hg^{2+} recovery [7]

The DCMA is comparatively new. All measurements reported so far have been done in the field with ambient air as sample, i.e., under constantly varying conditions. In addition, the short-term stability of their calibration device (permeation tube with $HgCl_2$ and $HgBr_2$, respectively) is questionable. Thus, from the data recorded so far, qualitative rather than quantitative performance characteristics can be derived: like absence of drift and bias, no evidence of non-linear response.

The only parameter that has been determined quantitatively is the detection limit DL (calculated as three times the standard deviation of measurements when the system routed pyrolyzed air to the membrane channel), which is 107 ± 23 pg m^{-3} for 10 min sampling time, and the 1 h detection limit (three times the standard deviation of 1 h averages) being 60 ± 34 pg m^{-3}.

The system has gone through a re-design, and further measurement results are expected in late 2021.

PSA 10.680 Hg-CEM

The PSA 10.680 Hg-CEM is a two channel Hg continuous emission monitoring system (Hg CEM) that provides measurement of Hg^0 and Hg^{tot}. This instrument is typically used for Hg in flue gas applications.

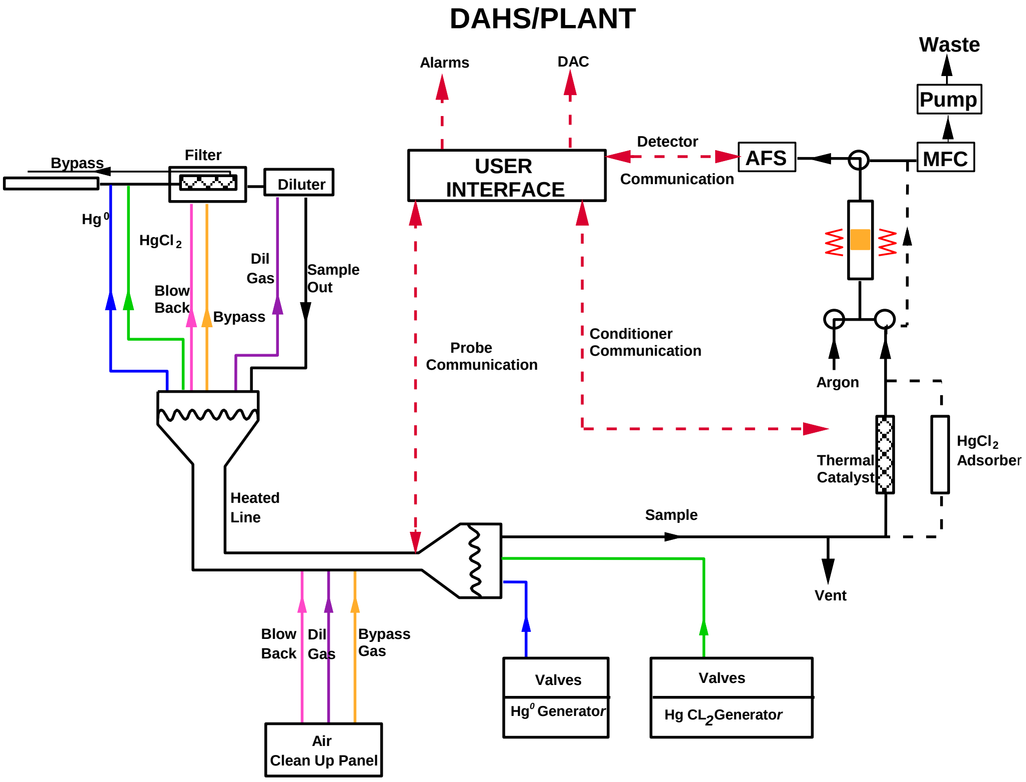


Fig. 5 Schematic of the PSA 10.680 Hg CEM [8]

The sample is drawn from the stack using a heated probe, filtered to remove stack gas particles and diluted 40:1 with instrument air. The diluted sample is then delivered to the Hg-CEM using a heated PTFE sample line. A portion of the sample gas is then split and sent to two channels. For the Hg^{tot} channel, the sample gas is passed through a thermal catalyst operating at 800 °C which thermally converts Hg^{2+} to Hg^0. For the Hg^0 channel the sample gas is passed through a bed of metal halide salt, which selectively collects Hg^{2+}. These two channels are then analyzed sequentially, using gold amalgamation with atomic fluorescence spectrometry (AFS). This fractionation approach provides a Hg^{tot} and Hg^0 results with the Hg^{2+} fraction being calculated as the difference. The typical measurement period per channel is 5 minutes, and with a 40:1 dilution the detection limit is 0.1 µg m^{-3}.

The system can be adapted to test the output of elemental and oxidized Hg generators by introducing the calibration gas to the oven which contains the thermal catalyst and $HgCl_2$ adsorber. In this case the detection will be improved to less than 2.5 ng m^{-3} using a 5-minute collection as no dilution is used Lower detection limits are achievable by loading a larger volume of sample. The upper flowrate limit for the gold trap is 0.8 L min^{-1}. The system when used in a sequential mode to monitor two channels (elemental and total mercury) will require a 0.5 minute flush period in between cycles.

PSA Sir Galahad Hg Analyser (PSA 10.525)

This instrument is based on gold amalgamation with AFS. The instrument measures total gaseous Hg as all forms of Hg are collected on gold and subsequently measured during the high temperature thermal desorption of the Hg species from the gold trap. Sample gas is pulled across the gold trap using a vacuum pump and the flow and volume of sample is controlled using a mass flow-controller (0.1 - 1.0 L min^{-1}) downstream of the gold trap. The typical sample measurement period is 4 min for Hg concentrations in the µg m^{-3} range and 10 minutes or greater for concentrations in the ng m^{-3} range. The analyser also has a built-in feature to permit the analysis of removable gold traps which are typically used for offline sampling methods. The detection limit for a 10 L sample is 0.1 ng m^{-3}. A schematic drawing showing the operation of the analyser and photograph is shown in Figure 6. Calibration is achieved using the manual bell jar method (PSA 10.555) by loading known masses of Hg directly onto the gold trap using a gas tight syringe. Alternatively, the system can be calibrated using the PSA 10.536 Hg^0 vapour generator by loading a known mass of Hg using a precisely timed flow-controlled method using the mass flow-controller.

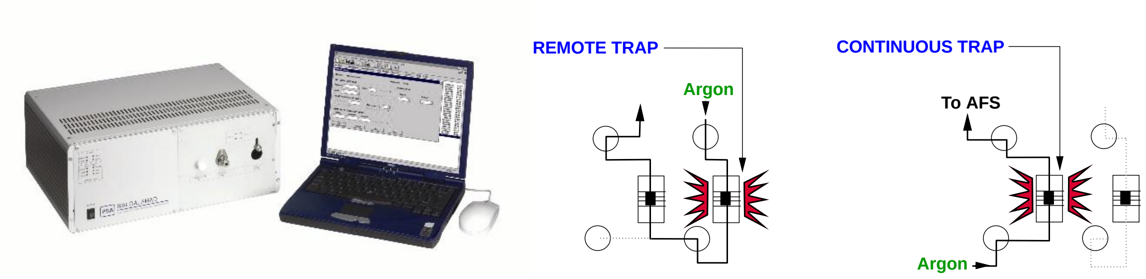


Fig. 6 Schematic and photograph of the PSA 10.525 Sir Galahad Hg Analyser

When testing an elemental Hg generator a detection limit of 0.1 ng m^{-3} is obtainable for a 10 L sample volume. It is also possible to analyse the output of a $HgCl_2$ generator provided that the gas is dry. The preferred approach is however to use a thermal conversion system to avoid adsorption of $HgCl_2$ at the sample inlet to the analyser. If used as a dual channel speciation analyser a $HgCl_2$ trap such as KCl is required for the elemental Hg channel.

PSA Thermal Conversion System

This is a standalone unit consisting of a 3/8inch OD length of quartz tube of length 18 cm. The heating zone is approx. 10 cm long and consisted on externally wound coil of NiCr wire. The quartz tube is packed with 3 mm alumina spheres held in place by crimps in the quartz tube. By applying DC voltage the temperature can be adjusted to a maximum of 900 ^{o}C. At the end of each side of the quartz tube PFA reducing unions are used. The inlet connector is bored through to allow a closer connection to the heated zone.

The thermal conversion efficiency in relation to temperature has been evaluated using developmental oxidized Hg generators. A stable response with no further increase to the signal output was found at 800 ^{o}C. Figure 7 shows a photograph of the thermal conversion system in operation.

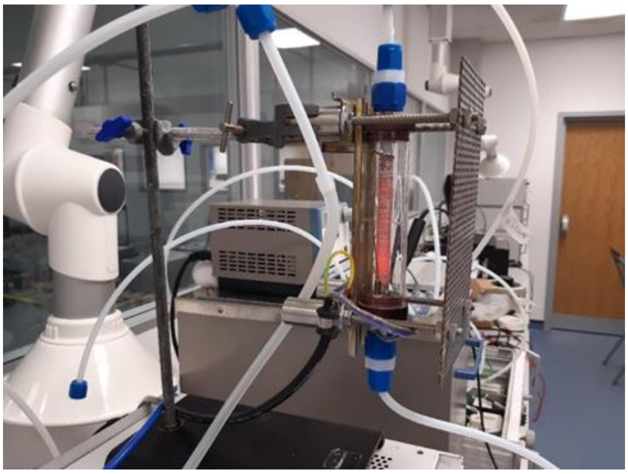


Fig. 7 PSA Thermal conversion system

When used with the arrangement shown in Figure 8 the system can be used for sequential elemental and total mercury measurements. The $HgCl_2$ adsorber is a KCl trap which collects oxidized Hg only and elemental Hg is unretained.

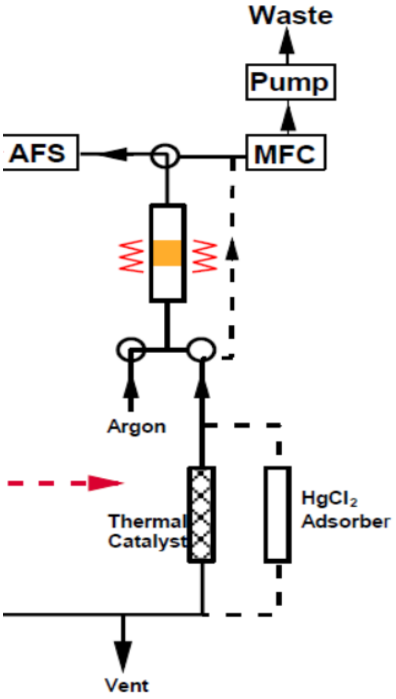


Fig. 8 PSA Thermal conversion system coupled to the sequential elemental and total mercury analyser system

The system has been used to test low level elemental Hg and oxidized Hg generators as part of the MercOx project operating the ng m^{-3} concentration range. An example calibration is shown in Figure 9 using a calibration gas of mercury chloride of concentration of 0.9 ng m^{-3}. The calibration was achieved by loading different volumes of calibration gas across the gold trap. A linear calibration was obtained between 0 - 40 pg Hg which is equivalent to 0.225 ng m^{-3} to 4.0 ng m^{-3} for a 10 L sample collection volume. The elemental channel response was similar to blank showing the effectiveness of the KCl trap in trapping oxidized Hg.

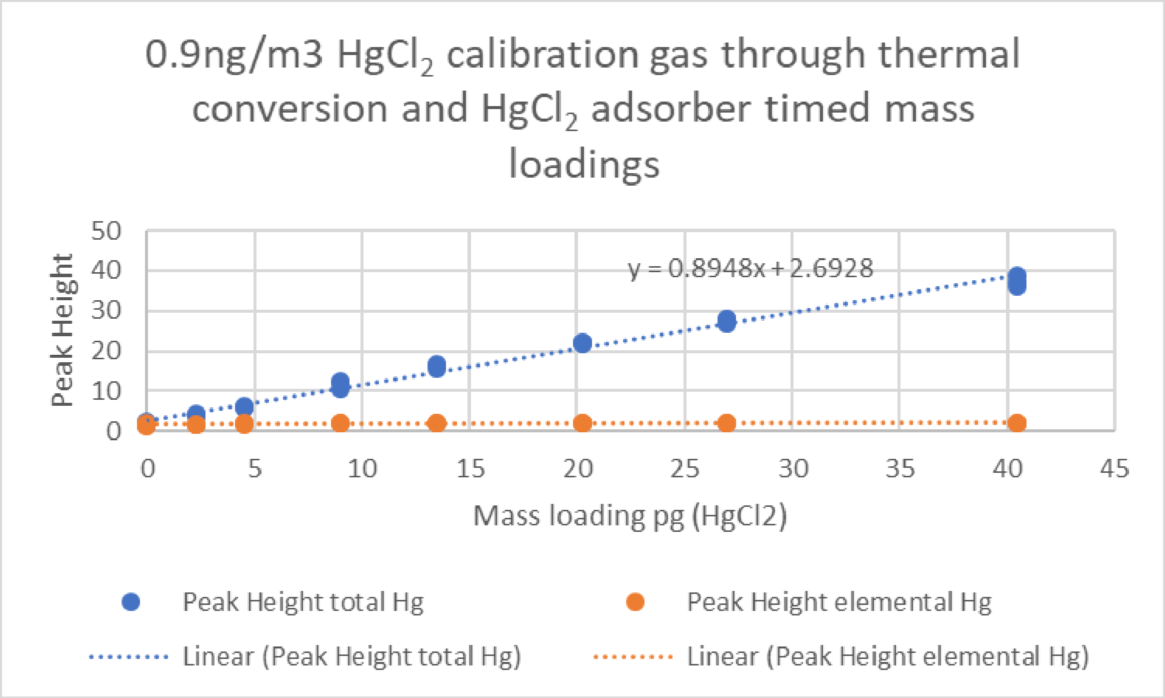
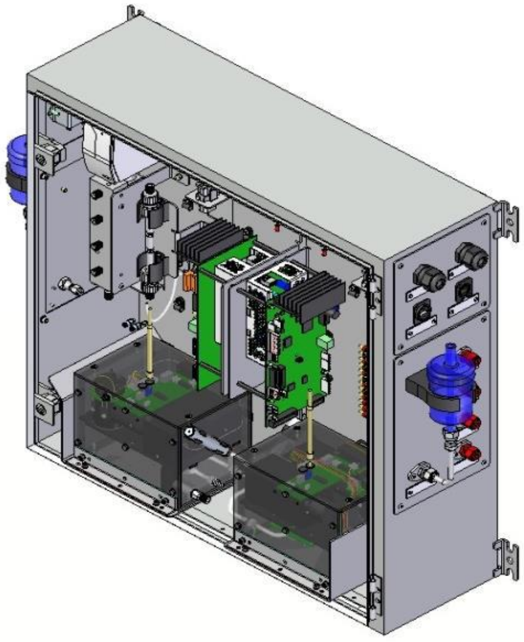


Fig. 9 Example calibration using sequential dual channel Sir Galahad with low level oxidized Hg generator

Direct AFS Measurement (PSA 10.216)

The PSA 10.216 is a direct AFS measurement system originally developed for online Hg in workroom. The standard product is designed to measurement elemental Hg only. This instrument is shown in Figure 10 and is designed with multi stream functionality. After selecting the sample stream using a valving arrangement the sample gas is passed directly to the AFS detector using a pump. The detector is calibrated using a commercially available Hg^0 generator (PSA 10.536).



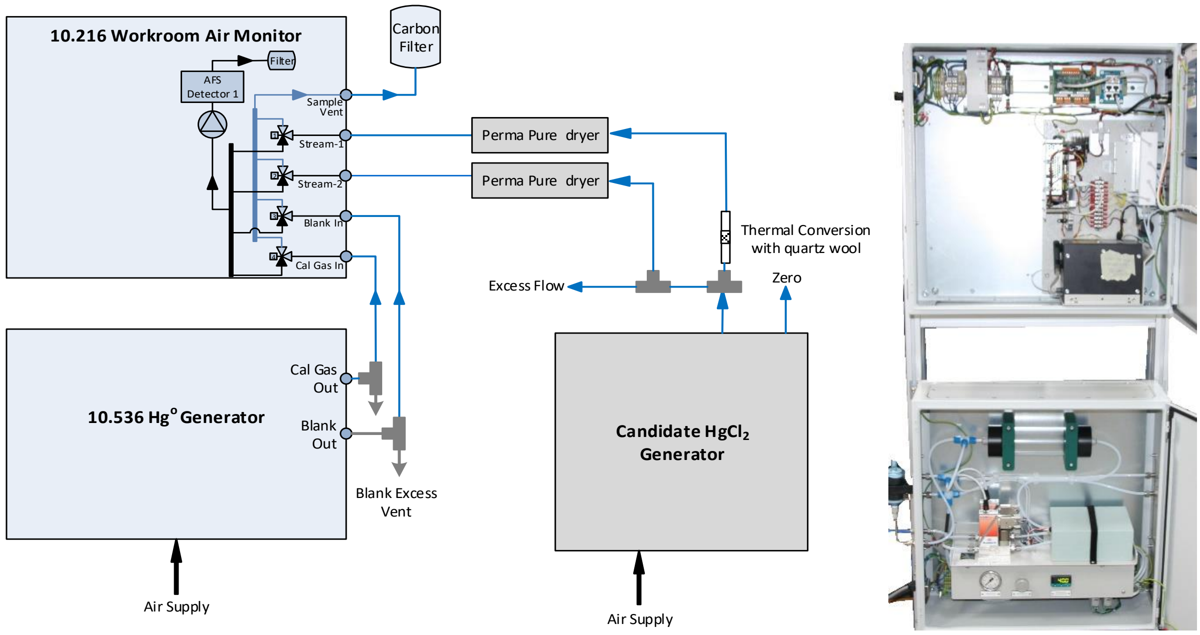


Fig. 10 PSA 10.216 Workroom Air monitor configured for sequential testing of elemental and oxidized Hg generators.

The advantage of this arrangement is that is provides a signal response every 0.25 s. In order to maximise sensitivity however a signal integration time of 30 s is typically applied. The unit provides a detection limit of <0.4 µg m^{-3} in an air matrix. If the Hg generator is operated using a nitrogen or argon lower detection limits are lessened and sensitivity is improved as the cross-quenching effect is much smaller. The expected detected limits based on quenching factors for nitrogen and argon are <0.125 µg m^{-3} and <0.033 µg m^{-3} respectively. To determine total gaseous Hg it is necessary to include a thermal conversion system upstream of the detector for the Hg^{tot} channel to convert $HgCl_2$ to Hg^0 and also to include a Permapure™ hygroscopic membranes on both channels to remove water vapour when testing evaporative $HgCl_2$ generators. This feature was not required when testing the dry based $HgCl_2$ generators.

Two models of the PSA 10.216 are available depending on the number of detectors which are included. The PSA 10.216A100 has a single detector and the PSA 10.216A200 has two AFS detectors (Figure 11)

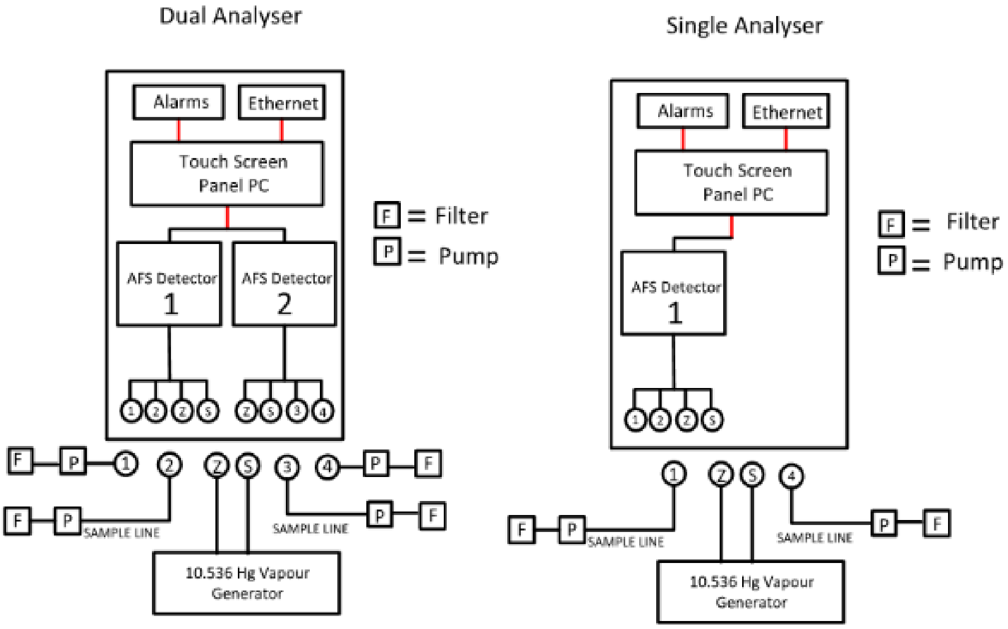
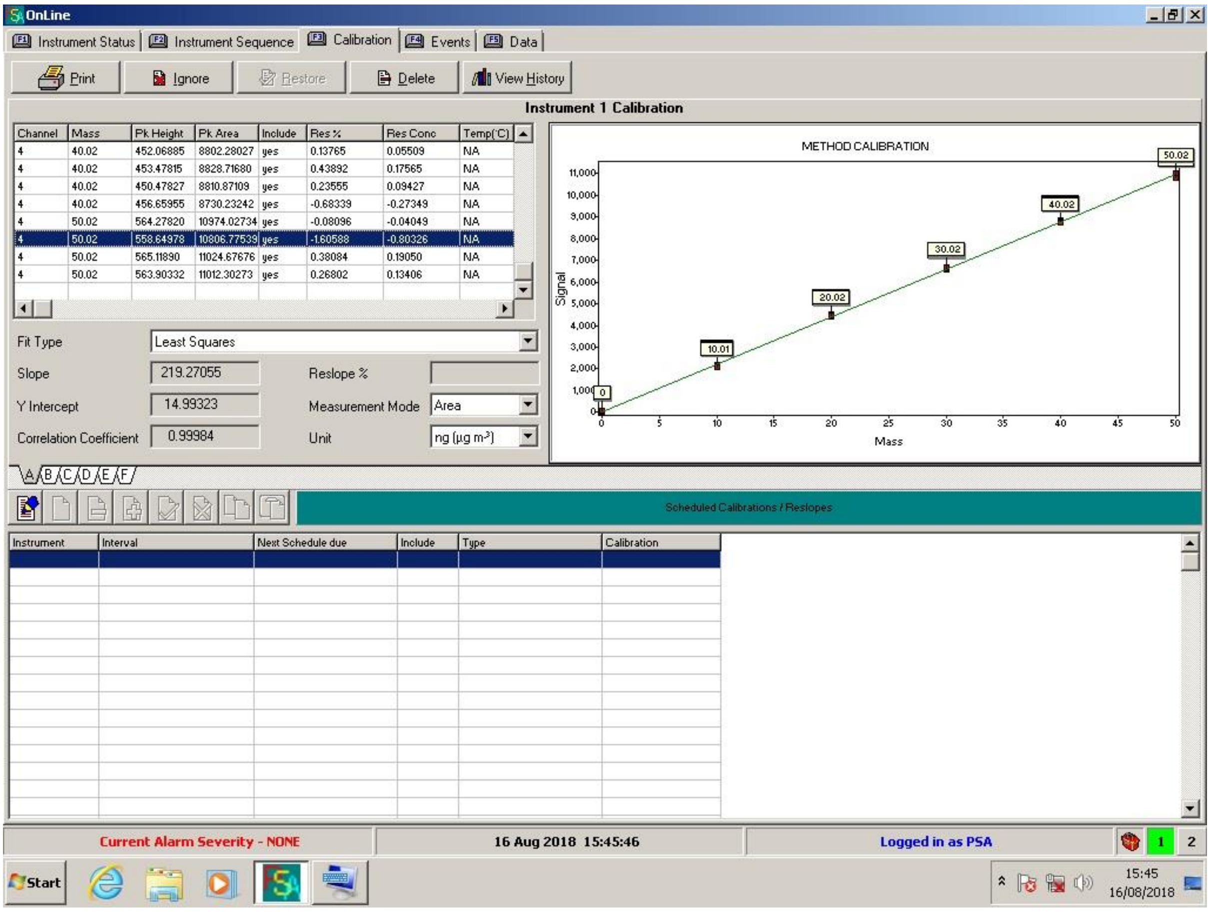


Fig. 11 Schematic drawings of single and dual analysers

The PSA C10S007 online software has the capability of running 2 analysers at the same time and therefore when used with the PSA 10.226A200 a simultaneous measurement system is provided. When testing an elemental or oxidized Hg generator a direct measurement will be provided for total and elemental Hg and oxidized Hg may be measured by difference.

Performance Data for PSA 10.226

A production PSA 10.226A200 was initially calibrated using the 10.536 Hg generator with a compressed air carrier gas. The concentration was varied between 0-50 µg m^{-3} by varying the reservoir flowrate on the generator. Each calibration point was based on 4 readings. The calibration is shown in Figure 12**.**



Instrument 1 Calibration

Channel	Mass	Pk Height	Pk Area	Include	Res %	Res Conc	Temp(°C)
4	40.02	452.06885	8802.28027	yes	0.13765	0.05509	NA
4	40.02	453.47815	8828.71680	yes	0.43892	0.17565	NA
4	40.02	450.47827	8810.87109	yes	0.23555	0.09427	NA
4	40.02	456.65955	8730.23242	yes	-0.68339	-0.27349	NA
4	50.02	564.27820	10974.02734	yes	-0.08096	-0.04049	NA
4	50.02	558.64978	10806.77539	yes	-1.60588	-0.80326	NA
4	50.02	565.11890	11024.67676	yes	0.38084	0.19050	NA
4	50.02	563.90332	11012.30273	yes	0.26802	0.13406	NA

Fit Type: Least Squares
Slope: 219.27055
Reslope %:
Y Intercept: 14.99323
Measurement Mode: Area
Correlation Coefficient: 0.99984
Unit: ng (µg m³)

Instrument	Interval	Next Schedule due	Include	Type	Calibration

Current Alarm Severity - NONE
16 Aug 2018 15:45:46
Logged in as PSA

Fig. 12 Calibration using compressed air between 0-50 ug m^{-3}

The system was then setup to automatically analyse the span gas at a concentration of 20 µg m^{-3} elemental Hg through the two channels for a period of 1 hour. Performance data is shown below in Table 1 and Figure 13

Table 1 Summary of performance data for 1 hour of span gas through both channels

Channel No	Mean µg m^{-3}	SD µg m^{-3}	RSD %	% Recovery
1	20.346	0.206	1.01	101.6
2	20.304	0.269	1.32	101.4

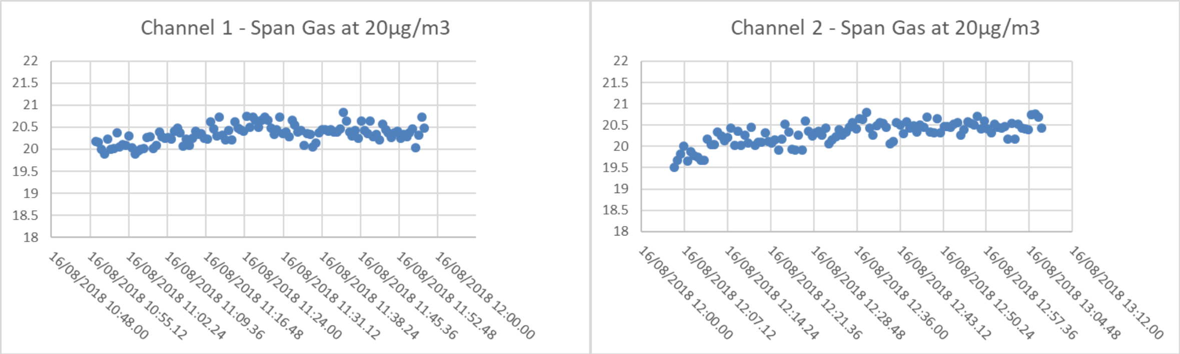


Fig. 13 One hour repeatability for elemental Hg at 20 ug^{-3} through both channels

The system was then setup to run four readings of a 20 µg m^{-3} span gas as a sample followed by four readings of lab air. Each reading was generated with an integration period of 20 seconds. A period of 10 seconds was added to switch between streams. This was required to flush the span gas out of the cell and the transfer lines. The response time is approx. 5 seconds. Every hour the system ran a zero gas and calibration span gas as a check. From this data it was possible to deduce the analytical performance data. The chart below (Figure 14) shows a period of 24 hours of test data of sequential measurements switching between lab air and span gas.

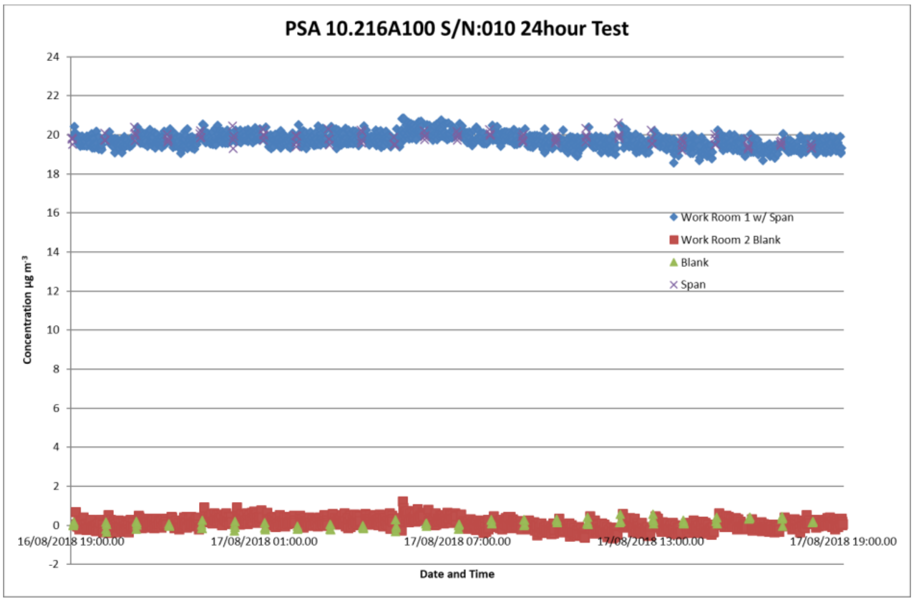


Fig. 14 24 hours of test data of sequential measurements switching between lab air and span gas

The zero-gas data was used to calculate the limit of detection defined as 3 times SD of 10 blank readings The LOD test was repeated 10 times and following data was obtained. The average LOD was found to be 0.321 µg m^{-3} (Table 2). The span gas check data is presented in Table shows that the average RSD% was 1.16% (Table 3).

Table 2 LOD study data using compressed air

LOD Study	**LOD µg m^{-3}**	**Mean LOD µg m^{-3}**	**SD µg m^{-3}**
1	0.416	0.321	0.097
2	0.400		
3	0.464		
4	0.329		
5	0.244		
6	0.231		
7	0.369		
8	0.195		
9	0.237		

Table 3 Span gas check data over 24-hour period

Span Test	**Conc µg m^{-3}**	**SD µg m^{-3}**	**RSD %**	**% Recovery**
1	19.736	0.142	0.72	98.68
2	19.813	0.179	0.90	99.07
3	20.041	0.285	1.42	100.21
4	19.800	0.166	0.84	99.00
5	19.996	0.176	0.88	99.98
6	19.865	0.484	2.44	99.33
7	20.007	0.220	1.10	100.04
8	19.730	0.276	1.40	98.65
9	19.833	0.338	1.70	99.17
10	19.924	0.325	1.63	99.62
11	19.598	0.190	0.97	97.99
12	19.955	0.192	0.96	99.78
13	19.946	0.185	0.93	99.73
14	20.073	0.127	0.63	100.37
15	19.828	0.180	0.91	99.14
16	19.766	0.156	0.79	98.83
17	19.955	0.282	1.41	99.78

18	20.085	0.349	1.74	100.43
19	19.793	0.326	1.65	98.97
20	19.537	0.257	1.32	97.69
21	19.720	0.259	1.31	98.60
22	19.467	0.230	1.18	97.34
23	19.573	0.110	0.56	97.87
24	19.371	0.100	0.52	96.86
Average	19.809	0.231	1.163	99.044

Comparison Performance Data for PSA 10.216A100 using elemental Hg calibration gas in air, nitrogen and argon.

The PSA 10.216 performance is influenced by the gas matrix. When using this system for testing Hg generators the detector must be calibrated using the same gas matrix as the generator. The detector has 4 amplification gain ranges between 1, 10, 100 & 1000. The sensitivity defined here as the slope of the calibration line was compared using different carrier gases for a generator concentration range between 0-50 µg m^{-3}. This was test was performed using the appropriate gain setting for the carrier gas used to prevent the detector from going off scale. The slope value represents the AFS response for 1 µg m^{-3}. This data is summarized in Table 4

Table 4 Comparison of sensitivity using different carrier gases

Cavkit Hg generator carrier gas	**Gain**	**Slope value**	**Slope equivalent to gain 10**
Air	1000	345.24	3.4524
Nitrogen	100	476.93	47.693
Argon	10	577.57	577.57

The LOD was studied by running the zero gas through the detector using different carrier gases against a calibration between 0-50 ug m^{-3}. The gain setting was selected according to conditions in Table 5. The LOD ($3\sigma_{n-1}$) was performed by taking 10 subsequent zero gas readings with an integration period of 30 seconds for each measurement. This was repeated ten times to establish the average LOD. The LOD improves in the order of air, nitrogen and argon due the lessening cross quenching effect. In addition to this less noise was observed with lower amplification gain settings. This data is summarized in Table 5.

Table 5 LOD using different carrier gases

LOD Study	**Air Carrier µg m^{-3}**	**Nitrogen µg m^{-3}**	**Argon µg m^{-3}**
1	0.239	0.013	0.0073
2	0.24	0.018	0.0035
3	0.255	0.015	0.0016
4	0.234	0.021	0.003
5	0.268	0.013	0.0024
6	0.281	0.012	0.0024
7	0.268	0.011	0.0019
8	0.293	0.018	0.0014
9	0.246	0.021	0.0014
10	0.264	0.022	0.009
Average LOD	**0.2588**	**0.0164**	**0.00339**

The accuracy and precision were studied at a concentration of 20 µg m^{-3} for each carrier gas against a calibration between 0-50 µg m^{-3}. This test was performed by measuring for a 1-hour period equivalent to approx. 120 readings. The precision was found to improve when argon and nitrogen was used as the system has less noise on the lower amplification ranges. Table 6 summarizes the accuracy and precision data.

Table 6 Summary of accuracy and precision data

Carrier Gas	**Gain**	**Mean µg m^{-3}**	**SD µg m^{-3}**	**RSD %**	**% Recovery**
Air	1000	19.967	0.113	0.57	99.8
Nitrogen	100	19.981	0.040	0.20	99.9
Argon	10	20.293	0.042	0.21	101.4

LUMEX DCMA

The Lumex Dual Channel Mercury Analyzer is, as of today, the most extensively tested instrument for the parallel analysis of oxidized and elemental mercury. In the EMPIR 16ENV01 MercOx project, it was specifically developed to analyze the output of Hg(0) and Hg^{2+}generators used for calibration purposes:

Lumex with support from VTT, JSI and VSL will develop a two-channel analytical system (based on Zeeman atomic absorption spectrometry) capable of determining the concentration of both elemental Hg (Hg(0)) and oxidised Hg simultaneously in real time. The system will consist of an inlet compartment where flow from a HgCl2 generator (or from another type of oxidised Hg generator) will enter. Part of this flow will be directed into the first analytical channel where the Hg(0) concentration will be measured. The other part of the flow will be directed into the second analytical channel where an atomiser (Cold Vapour (CV) or thermal) will measure the Hgtot concentration [4].

A stream of inert carrier gas containing oxidized mercury is supplied by the generator at a flow rate of ≥ 8 l/min. From the heated line, gas is pumped into two analytical channels - total and elemental mercury – at flow rates between 1 and 3 l/min each.

The thermocatalytic converter (Pyro) is operating at a temperature of 750°C. Material in contact with process gas is quartz and SS. To avoid losses of oxidized mercury at the interface between sample line and converter, the sample is introduced to the hot center of the converter by means of a long quartz tube. The converter is welded to the analytical cell, which is also kept at 750°C.

The elementary mercury channel is identical to the total mercury channel, except there is no thermocatalytic converter, the analytical cell is made of PTFE, and is kept at a temperature of 130°C.

Hg^{tot} Data from both spectrometers are processed by a custom-made software. Concentrations of elemental and oxidised mercury are displayed in real time and simultaneously.

In order to overcome memory effects, especially in the Hg^{tot} channel, and to allow for true parallel, real-time measurements of Hg(0) and Hg^{tot}, two independent AA spectrometers were used. As they have different performance characteristics, in particular regarding zero drift and sensitivity, an individual coefficient for each spectrometer was determined by calibration using the primary Hg(0) generator at VSL, and the coefficients were set at 1,27 for the Hg(0) channel, and 2,56 for the Hg^{tot} channel, respectively.

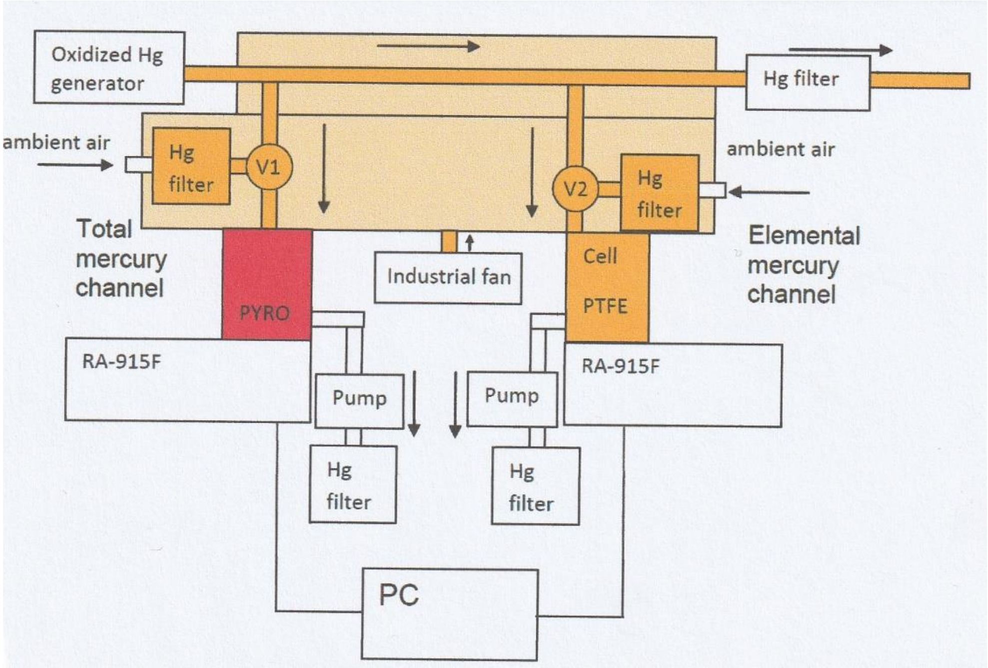


Figure 15 - Block diagram of Lumex DCMA [9]

yellow: parts kept at 150 – 180°C, red: parts kept at 750°C

The system has been tested and validated in the laboratories of various MercOx partners. The results have been published in the report "Optimised and traceable calibration methods for oxidized mercury species, including mercury chloride ($HgCl_2$)", which can be downloaded from the project's homepage www.mercox.si [9].

The Lumex DCMA is the only system that utilizes two spectrometers, and hence measures the concentration of oxidized and elemental mercury simultaneously.

Table 7 Main performance characteristics of the Lumex DCMA

	Hg^{tot}	Hg(0)	Hg^{2+}calc.
DL, µg/m³	0,07	0,07	0,1
QL, µg/m³	0,18	0,18	0,25
Linearity, µg/m³	0 – 1.000	0 - 500	0 - 500
Repeatability, %	2	2	
Reproducibility, %	3	3	
Stability, %/year	≤ 2	≤ 2	
Drift, µg/m³h	≤ 0,2	≤ 0,2	≤ 0,3
Bias, %	0,7 – 4,1	0,7 – 3,3	

Robustness: Variable Pyro Temp.	Conversion rates 250°C: 70% 700°C: 101%		
Accuracy, %	5	5	
Response time, sec	20	20	20
Cross-sensitivities: signal variation	-9% with 2,5 ppm HCl -14% with 30 ppm SO2	-14% with 30 ppm SO2	

Conclusions

Several attempts to design a suitable analytical system able to determine oxidized and elemental mercury in parallel have been described in this study. In the course of these developments, major obstacles in trace analysis of highly reactive chemical compounds have been overcome. Yet, several problems remain i.e., the tendency of interconversion between mercury species during sampling and analysis, and the evaluation of the efficiency of the converter under different conditions.

Another challenge is the qualification of a suitable SI-traceable calibration device for the instruments. Such a device would allow a more comprehensive metrological characterization of the DCMAs, and hence the critical assessment and validation of analytical results produced by these instruments, and finally the comparison with data generated by other research groups with different equipment.

Dr. Reinhold Möseler, for

Lumex Analytics GmbH, Germany

References

[1] Annex 1 – JRP protocol, EMPIR 19NRM03 SI-Hg, May 13, 2020, p. 23

[2] Lyman,S.N., Cheng,I., Gratz,L.E., Weiss-Penzias,P., Zhang,L., Sci.Tot.Env. 707 (2020), 135575

[3] Annex 1 – JRP protocol, 16ENV01 MercOx, May 17, 2017, p.7

[4] Annex 1 – JRP protocol, 16ENV01 MercOx, May 17, 2017, p.20

[5] Prestbo,E.M., Presentation on ICMGP, Edinburgh, 2013

[6] Tekran Model 1130 Product Brochure, 2008

[7] Lyman S.N., Gratz L.E., Dunham-Cheatham S.M., Gustin M.S., Luippold A., Env.Sci.Techn. 2020 54 (21), 13379

[8] PS Analytical Dual Channel AFS Analysers, Product Brochure, 2018

[9] Krom I.de, Efremov E., Zivkovic I., Gacnik J., Kotnik J., Horvat M., Rajamäki T., Makkonen J., Möseler R., Sholupov S., Corns W., Optimised and traceable calibration methods for oxidized mercury species, including mercury chloride ($HgCl_2$)
Euramet EMPIR MercOx Project Report, download on www.mercox.si