



D1: Protocol for the SI-traceable calibration of elemental mercury (Hg^0) gas generators used in the field

19NRM03 SI-Hg

Iris de Krom¹, Adriaan van der Veen¹, Federica Gugole¹, Warren T. Corns², Carsten Röllig³, Timo Rajamäki⁴, Reinhold Mösel⁵, Sophie Page⁶, Igor Živković⁷, Attilio Naccarato^{8,9}, Antonella Tassone⁸, Francesca Sprovieri⁸

¹ VSL, Department of Chemistry, Mass, Pressure and Viscosity, Thijsseweg 11, 2629 JA Delft, the Netherlands

² PS Analytical Ltd, Arthur House, Crayfields Industrial Estate, Main Road, Orpington, Kent BR5 3HP, UK

³ TÜV Rheinland, AM Grauen Stein, 51105 Köln, Germany

⁴ National Metrology Institute VTT MIKES, Tekniikantie 1, 02150 Espoo, Finland

⁵ Lumex Analytics GmbH, Naher Str. 8 D 24558 Wakendorf II, Germany

⁶ LGC Ltd, national Measurement Laboratory, Queens Road, Teddington, Middlesex, TW11 0LY, UK

⁷ JSI, Department of Environmental Sciences, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia

⁸ CNR-Institute of Atmospheric Pollution Research (CNR-IIA), Rende, Italy

⁹ University of Calabria, Rende, Italy

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Introduction

The monitoring of mercury concentrations in air is essential for the implementation of national and international legislation, and to demonstrate the progress in implementing international agreements such as the Minamata convention on mercury. Laboratories and other entities performing mercury concentration measurements usually calibrate their own equipment. For this calibration, mercury gas generators are generally used.

To set up a metrological traceability chain, the output of the gas generators needs to be comparable to reference standards, up to ultimately the primary measurement standards for mercury concentration held by national metrology institutes (NMI). Currently, there are no standardised procedures that ensures dissemination of the metrological traceability to testing laboratories and field measurements. This protocol describes such a standardised procedure for the characterisation and calibration of elemental mercury gas generators to demonstrate that their output is metrologically traceable to the International System of Units (SI).

This protocol describes 1) the experimental procedures to compare the output of elemental mercury gas generators and 2) the data processing for determination of mercury concentration and the expanded uncertainty of the mercury concentration obtained from the elemental mercury gas generator. Demonstrating that a particular generator meets the requirements establishes that the requirements for performance and metrological traceability to the SI are met, and that an unbroken chain of comparisons is created. For applications, this protocol applies only to mercury monitoring system span concentrations in the range of micrograms per cubic meter ($\mu\text{g m}^{-3}$) and nanograms per cubic meter (ng m^{-3}).

1. Scope

This protocol specifies the procedures for establishing traceability to the SI for the quantitative output of elemental mercury generators that are employed in regulatory applications for emission monitoring or testing.

This protocol provides methods for

- Calibrating the output of a candidate generator by comparison with a reference standard;
- Calculating the mercury concentration and the associated uncertainty of the mercury concentration generated with the candidate generator in relation to the known uncertainty of the reference standard.

This protocol specifies a measurement method for the determination of the output of candidate generators used to calibrate mercury analysers for the determination of the concentration of mercury in emission sources and ambient air.

The method is applicable for different types of mercury gas generators:

- Bell-jar generator, working according to ISO 6145-9 [1]
- Saturation gas generators, working according to ISO 6145-9 [1]
- Permeation gas generators, working according to ISO 6145-10 [2]
- Mercury amount fractions in cylinders, prepared according to ISO 6142-1 [3]
- Continuous injection gas generators, working according to ISO 6145-4 [4]. Based on the reduction of mercury chloride (HgCl_2). A HgCl_2 solution is vaporised and mixed with a known flow of matrix gas to obtain a humid HgCl_2 calibration gas. The HgCl_2 in the calibration gas is reduced to elemental mercury.
- Mass of mercury on sorbent tubes

The concentrations are expressed in ng m^{-3} or $\mu\text{g m}^{-3}$ (at 0 °C and 101.325 kPa).

2. SI traceable calibration chain

Traceability means that a result of measurement may be traced back, through an unbroken chain of comparisons, to a national or international standard. Each step in the comparison chain involves a measurement procedure, which contributes some uncertainty. As the overall uncertainty combines the uncertainty from all steps of the traceability chain, it gives information about the closeness of the results to the true value. To obtain SI traceability for mercury concentration measurement results NMI have developed primary standards for elemental mercury in air [5 -8]. These standards are called primary because they are directly traceable to the SI. From the primary standards the traceability chain can be established by comparison of a candidate generator to the primary standard or reference standard according to the measurement procedure described in this calibration protocol. After calibration the candidate generator receives an SI traceable certificate and can be used as a reference generator for calibration of other candidate generators, and so forth (Figure 1). This way a chain of calibrations is obtained from the primary standard to gas generators used every day for monitoring of mercury concentrations in emission sources and in the atmosphere.

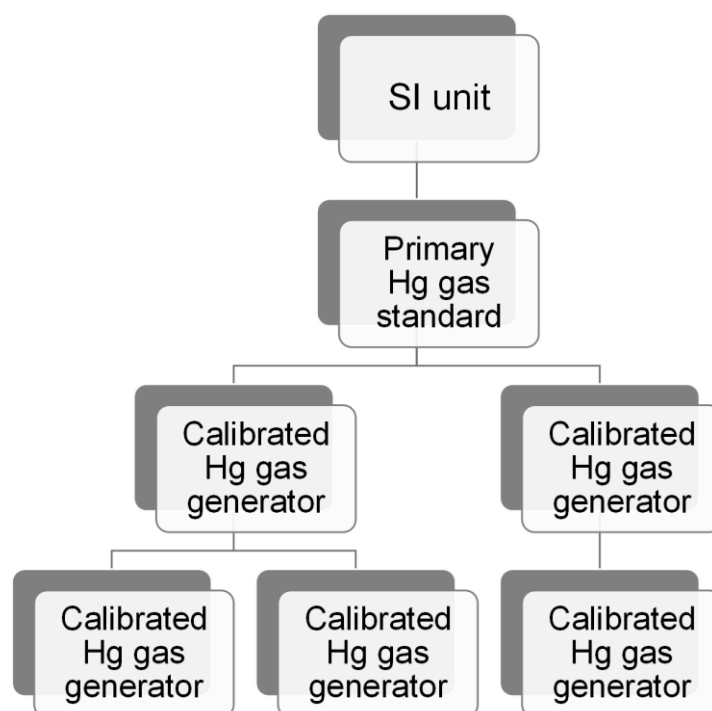


Figure 1: SI traceable calibration chain for mercury gas generators.

3. Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 13211, Air quality – Stationary source emissions – Manual method of determination of the concentration of total mercury

ISO 7504, Gas analysis – vocabulary

ISO/IEC 17025, General requirements for the competence of testing and calibration laboratories

4. Terms and definitions

For the purposes of this document, the terms and definitions given in EN 13211 and ISO 7504.

5. Symbols and abbreviations

5.1 Symbols

r_{zero}	response zero gas
$c_{cand(i)}$	setpoint candidate generator
$c_{ref(i)}$	setpoint reference generator
$r_{ref(i)}$	response gas mixture from reference generator
$r_{cand(i)}$	response gas mixture from candidate generator
t_i	time response was recorded
$r_{candcorr}$	response gas mixture from candidate generator corrected for zero response
$r_{refcorr}$	response gas mixture from reference generator corrected for zero response
R	output ratio
$c_{(i)}$	calibrated output candidate generator
$u(c_{ref})$	standard uncertainty of the mercury concentration from the reference standards
MS_{cand}	residual error for the candidate generator measurement points
MS_{ref}	residual error for the reference generator measurement points
$MS(\overline{r_{ref(1)}})$	standard error of the mean of each individual measurement from the before-candidate reference generator measurement
$MS(\overline{r_{cand}})$	standard error of the mean of each individual measurement from the candidate generator measurement
$MS(\overline{r_{ref(2)}})$	standard error of the mean of each individual measurement from the after-candidate reference generator measurement
R_{jk}	the measured ratio for the k^{th} individual bracket within the j^{th} contiguous set of brackets
$u(R_{jk})$	standard uncertainty R_{jk}
\bar{R}_j	average output ratio
K	number of brackets in this j^{th} set
$u\bar{R}_{j\text{stability}}$	standard uncertainty average output ratio
S_1	pooled standard error of the standard uncertainty average output ratio
S_2	level 2 standard deviation of the output ratios
$u_{repeatability}$	standard uncertainty repeatability of the output ratio
L	average number of individual responses used in each measurement average and output ratio determined

$u_{\overline{repeatability}}$	standard uncertainty of the average output ratio
$u_{reproducibility}$	standard uncertainty reproducibility
$u_{bracketing}$	standard uncertainty of each bracketing procedure
$u_{\overline{comparison}}$	standard uncertainty of a single comparison
$u_{reference}$	standard uncertainty component of the reference generator
$u(c)$	standard uncertainty output candidate generator
$U(c)$	expanded uncertainty output candidate generator
k	coverage factor
F	interpolation function, $c = F(c_{cand})$
b_j	coefficients of the interpolation function F ($j = 0, 1, \dots, N$)
S	weighted least squares
$\hat{c}_{(i)}$	adjusted data point calculated as a by-product of the regression analysis
S_{res}	residual sum of weighted squares deviations
$u_{interpolation}$	uncertainty of the coefficients of the interpolation function

5.2 Abbreviations

SI	International System of Units
HgCl ₂	Mercury(II) chloride
NMI	National Metrology Institute
AFS	Atomic fluorescence spectrometer
MFC	Thermal mass flow controller
AAS	Atomic absorption spectrometer
PFA	Perfluoro alkoxy
PTFE	Polytetrafluoroethylene
RSD	Relative standard deviation (%)
AICc	Akaike Information Criterion for small sample size
AIC	Akaike Information Criterion

6. Principle

6.1 General

The mercury concentration in a gas mixture prepared with a candidate generator is determined by comparison with a metrologically traceable reference standard to calibrate the output of the candidate generator.

The comparison can be performed at one concentration level (single-point calibration) or at several concentration levels (multipoint calibration) using the bracketing sequence. When applying the bracketing sequence, the outputs from the reference standard and candidate generator are introduced alternately to a mercury analyser so that each response from the candidate generator is bracketed by a pair of responses from the reference standard. At each concentration level, the bracketing procedure requires a minimum of four responses from the certified reference standard and a minimum of three responses from the candidate generator. An example of a bracketing procedure injection sequence for a given mercury concentration is provided below in Table 1.

Table 1 – Example of a bracketing sequence

Measurement nr.	Generator ID
1	Reference standard
2	Candidate
3	Reference standard
4	Candidate
5	Reference standard
6	Candidate
7	Reference standard

There are two approaches for the data processing

- Without zero correction
- With zero correction

Zero correction is required only for an instrument that does not perform an automatic baseline correction for every reading.

7. Equipment and materials

7.1 Mercury reference standard

The metrological traceable reference standard can either be a 1) primary mercury standard or 2) a metrologically calibrated reference standard, e.g., a calibrated mercury gas generator, a calibrated gas mixture in a high-pressure cylinder or sorbent tubes sampled with a calibrated mass of mercury.

7.2 Analyser equipment

Generally, two types of mercury analysers are available:

1. AFS: The instrument is based on pre concentration on gold amalgamation with an atomic fluorescence spectrometer detector. The instrument measures total gaseous mercury as all forms of mercury are collected on gold and subsequently measured during the high temperature thermal desorption of the mercury species from the gold trap. Sample gas is pulled across the gold trap using a pump and the flow and volume of sample is controlled using a MFC.
2. AAS: A direct measurement system with an atomic absorption spectrometer utilizing the Zeeman effect. The instrument passes the sample gas directly the AAS detector using a pump.

7.3 Zero gas

Zero gas is used to zero the detector or obtain a zero response (r_{zero}). As zero gas pure nitrogen can be used or a zero air generator to obtain purified air. The gas should be free of mercury and other chemicals that give a detector response.

8. General procedure

8.1 Gas generator requirements

First determine over what range of mercury concentrations the candidate generator is expected to be used.

The operating principle of the gas generator shall be determined.

8.2 Reference standard requirements

The user of a reference standard shall verify that the property values come with a statement concerning the metrological traceability of these values. This statement shall provide the value of the specified property, its associated uncertainty, and a statement of metrological traceability.

The reference standard used has a mercury concentration range greater than that selected for the candidate generator. If the output from the candidate generator extends beyond the specified reference standard range, considerable measurement errors might result from extrapolation outside the analytical measurement range.

8.3 Analyser requirements

Use a mercury analyser with a measurement range greater than that which is expected for the candidate generator and the reference standard. If the output from the candidate generator and reference standard extends beyond the specified operating range, considerable measurement errors might result from extrapolation outside the analytical measurement range.

Furthermore, the sensitivity, the response function in the used range, detection limit, precision and drift of the analyser shall be known.

8.4 Experimental design

8.4.1 General

Before operating the candidate generator, the measurement standard and the analyser, the operating instruction of the manufactures shall be followed particularly with regard to the set-up of equipment and the quality and quantity of the consumable produces necessary.

The gas mixtures obtained with the reference standard and candidate generator shall be transported using PFA or PTFE tubing.

It is recommended to use reference standards with the same complementary gas, e.g., nitrogen or air.

NOTE: clearly state on the calibration certificate which complementary gas is used during the calibration to operate the candidate generator.

The candidate generator, the reference standard and analyser shall be allowed to warm up during the time specified by the manufacturer before undertaking any experiments. If the warm-up time is not specified, a minimum of 30 minutes is recommended.

When applying gas mixtures to the analyser, the gas mixture system shall be operated sufficiently long before starting the tests in order to stabilise the concentrations applied to the analyser. Conduct a 15-minute stability check of both the reference generator and the candidate generator at the outset. The output may be assumed to be stable if no more than 2 % drift is observed or alternative until the signal has reached 98% of the expected value over the 15-minute time interval.

The manner in which the responses are recorded depends on the analyser (detector). If it is a continuous analyser, record readings at appropriate set intervals and compute the average over the desired time period. It is recommended that the recorded response for each gas mixture is based on a least 5 minutes of stable readings. If the analyser concentrates the sample and an integrated signal is obtained for the generator output, record the result of one analysis cycle or average multiple analysis cycles using all stable measurement system responses. For systems that have two traps or channels (“A” and “B”) to concentrate the sample, use the same designated trap (A or B) throughout the sampling procedure.

8.4.2 Selection set points reference standard and candidate generator

8.4.2.1 Single-point calibration

Select a mercury concentration using the same nominal setpoint for the candidate generator ($c_{cand(i)}$) and the reference standard ($c_{ref(i)}$) such that the measuring system produces responses which are within $\pm 50\%$.

8.4.2.2 Multipoint calibration

Select a mercury concentration using the same nominal settings for the candidate generator and the reference standard such that the measuring system produces responses which are within $\pm 50\%$.

Specify the number n of calibration points ($c_{cand(i)}, c_{ref(i)}$) required, depending on the type of mathematical function to be used for the interpolation function (Section 8.6.2 step S and Annex 2).

Select mercury concentrations from the candidate generator and the reference standard such that the concentrations $c_{cand(1)}, c_{cand(2)}, \dots, c_{cand(n)}$ and $c_{ref(1)}, c_{ref(2)}, \dots, c_{ref(n)}$ span an appropriate calibration range, i.e. approximately equally spaced.

Calibration designs using equally spaced values for mercury concentrations are not the optimum choice for cases of strongly non-linear response. They are, however, well suited for linear and moderately non-linear responses, as considered in this protocol (Annex 2).

8.4.3 Bracketing measurement sequence

Table 2 illustrates the bracketing measurement sequence for single-point and multipoint calibrations. More than one candidate generator can be certified in one sequence. If this approach is followed sequential responses from each candidate generator are recorded in-between the reference standard responses, and linear time interpolation of the reference standard responses is used to correlate with the exact time of each intervening candidate generator response. The manner in which the responses are recorded depends on the analyser (detector).

Table 2 – Bracketing measurement sequence for single-point and multipoint calibrations

Single-point	Multipoint
$c_{zero(1)}$	$c_{zero(1)}$
$c_{ref(1.1)}$	$c_{ref(1.1)}$
$c_{cand(1.1)}$	$c_{cand(1.1)}$
$c_{ref(1.2)}$	$c_{ref(1.2)}$
$c_{cand(1.2)}$	$c_{cand(1.2)}$
$c_{ref(1.3)}$	$c_{ref(1.3)}$
$c_{cand(1.3)}$	$c_{cand(1.3)}$
$c_{ref(1.4)}$	$c_{ref(1.4)}$
$c_{zero(2)}$	$c_{ref(2.1)}$

	$C_{cand(2.1)}$
	$C_{ref(2.2)}$
	$C_{cand(2.2)}$
	$C_{ref(2.3)}$
	$C_{cand(2.3)}$
	$C_{ref(2.4)}$
	$C_{ref(n.1)}$
	$C_{cand(n.1)}$
	$C_{ref(n.2)}$
	$C_{cand(n.2)}$
	$C_{ref(n.3)}$
	$C_{cand(n.3)}$
	$C_{ref(n.4)}$
	$C_{zero(2)}$

8.5 Stepwise procedure

Step A: Zero the detector by introducing zero gas and making any necessary zero adjustments. Alternatively, obtain the required responses of the zero gas from the detector ($r_{zero(1)}$).

Step B: Direct the output of the reference standard to the detector and obtain the required responses ($r_{ref(i.1)}$).

Step C: Direct the output of the candidate generator to the detector and obtain the required responses ($r_{cand(i.1)}$).

Step D: Switch back to direct the output of the reference standard to the detector and obtain the required responses ($r_{ref(i.2)}$).

Step E: Repeat steps C and D at least two more times to achieve at least triplicate responses for the mercury concentration from the candidate generator and at least quadruple responses for the mercury concentration from the reference standard.

Step F: In case the RSD of the responses from the reference standard (r_{ref}) are bigger than 2.0 % at least one extra repeat of steps C and D shall be performed.

Step G: When applying a multipoint calibration repeat steps B through E for the second, third and following concentration levels.

Step H: Check the zero response of the detector, without making any adjustments.

NOTE: Ensure stable responses are obtained with a RSD \leq 2.0 %. The first responses for the zero measurements, reference standard and candidate generator, on both channel A and channel B if applicable, can show instability when going from one concentration level to the other.

8.6 Data processing

8.6.1 Single-point calibration

Step I: To determine the actual output of the candidate generator, first correct each response for any zero offset of the detector. Zero correction is required only for an instrument that does not perform an automatic baseline correction for every reading. If zero correction is required, calculate

the interpolated zero offset based on the time when a specific response was recorded according to equation (1):

$$r_{zero(i)} = r_{zero(1)} + \left[(t_i - t_1) \frac{(r_{zero(1)} - r_{zero(2)})}{(t_1 - t_2)} \right] \quad (1)$$

Step J: then, correct the response at t_i for the zero offset using equation (2):

$$r_{cand_{corr}} = r_{cand} - r_{zero(i)} \quad (2)$$

The data set in Table 3 provides an example of how each response is corrected for zero offset over the course of a test period.

Table 3 – zero corrections for an example data set

Time (min)	r_{zero}	$r_{zero(i)}$	r_{ref}	$r_{ref_{corr}}$	r_{cand}	$r_{cand_{corr}}$
0	27.1					
10		28.3	5686.1	5657.8		
20		30.6			5966.5	5935.9
30		32.8	5636.1	5603.2		
40		35.1			6065.3	6030.1
50		37.4	5648.6	5611.2		
60		39.7			6012.3	5972.6
70		42.0	5692.2	5650.2		
80	44.3					

Step K: Next, calculate the output ratio (R) for each value of $r_{cand_{corr}}$ according to equation (3a):

$$R = \left[\frac{r_{cand_{corr}}}{\frac{r_{ref(1)_{corr}} + r_{ref(2)_{corr}}}{2}} \right] \quad (3a)$$

The average of the $r_{ref(1)_{corr}}$ and $r_{ref(2)_{corr}}$ responses in the denominator of Equation (3a) provides an estimate of the value of r_{ref_s} when r_{cand} was actually recorded. Note, however, that this equation only applies to equally-spaced measurements when one candidate generator is being certified. If the spacing is not equal or more than one candidate generator is being certified with a single reference standard, a more rigorous, time-interpolated formula in Equation (3b) is used to estimate r_{ref} when r_{cand} was actually recorded.

$$R = \frac{r_{cand_{corr}}}{\frac{t_{ref(2)} - t_{cand(1)}}{t_{ref(2)} - t_{ref(1)}} r_{ref(1)_{corr}} + \frac{t_{cand(1)} - t_{ref(1)}}{t_{ref(2)} - t_{ref(1)}} r_{ref(2)_{corr}}} \quad (3b)$$

The t values in Equation (3b) are timestamps associated with the r_{cand} and r_{ref} readings. Equations (3a) and (3b) are mathematically identical when the three t values are equally spaced.

Table 4, illustrates these calculations, for the example data set presented in Table 3.

Table 4 – Example calculation of the output ratio (R) (with zero correction)

Time (min)	r_{ref}	$r_{ref_{corr}}$	r_{cand}	$r_{cand_{corr}}$	Output ratio (R)
10	5686.1	5657.8			
20			5966.5	5935.9	1.054
30	5636.1	5603.2			
40			6065.3	6030.1	1.075

50	5648.6	5611.2			
60			6012.3	5972.6	1.061
70	5692.2	5650.2			

Step L: Next, average the calculated output ratios. For this data set, the value of \bar{R} is 1.063.

Step M: Finally, use Equation (4) to determine $c_{(i)}$, the calculated candidate generator output mercury concentration.

$$c_{(i)} = c_{ref} \bar{R} \quad (4)$$

For this example, c_{ref} , is 2226 ng m⁻³. Therefore, the value of $c_{(i)}$ from Equation (4) is 2367 ng m⁻³, based on the zero-corrected responses.

Step N: If zero correction is not necessary for the detector, use the uncorrected values (r_{ref} and r_{cand}) in the calculations, as shown in Table 5. For this example data set, the value of $c_{(i)}$ is 2367 ng m⁻³, based on the uncorrected responses.

Table 5 – Calculation of output ratio (R) (without zero correction)

Time (min)	r_{ref}	r_{cand}	Output ratio (R)
10	5686.1		
20		5966.5	1.054
30	5636.1		
40		6065.3	1.075
50	5648.6		
60		6012.3	1.060
70	5692.2		

Step O: For each concentration level calculate the RSD of the output ratios (R). The RSD shall not exceed 2.0 %. If the RSD value is exceeded, the test is invalid and shall be repeated. The calculated RSD values for the output ratios in Tables 4 and 5 are both 1.0 % and are therefore acceptable.

Step P: The uncertainty of mercury concentration from the candidate generator shall be calculated as explained in Annex 1.

8.6.2 Multipoint calibration

Step Q: Apply the calculation procedures from step I till step P to each concentration level.

Step R: The uncertainty of each mercury concentration from the candidate generator shall be calculated as explained in Annex 1.

Step S: Determination of the interpolation function as explained in Annex 2.

NOTE: When a concentration analyser is used with two traps the results from channel A and channel B should be treated separately. When the final result from channel A and channel B are comparable within the obtained uncertainty the results can be averaged.

Annex 1: Determining the uncertainty of the calibrated mercury concentration obtained with the candidate generator

This annex describes the calculation method that is used to determine the expanded uncertainty of elemental mercury concentrations produced by candidate gas generators.

NOTE: a script was developed to calculate 1) the mercury concentration, 2) the associated uncertainty of the mercury concentration and 3) the interpolation function for multipoint calibration according to this calibration protocol [9].

A1.1 Uncertainty sources

The uncertainty assigned to the output concentration of an elemental mercury gas generator is accumulated at each step in a chain of calibrations. The uncertainty of the mercury concentration from the reference standard, $u(c_{ref})$, is the starting point for the uncertainty calculations in this Annex. In addition to the uncertainty of the reference standard, the following three sources of uncertainty have been identified for assigning concentration values to candidate generator setpoints: 1) measurement stability; 2) repeatability; and 3) reproducibility. The first two components apply specifically to the bracketing sequence described in this protocol. The reproducibility component applies to the overall process of transferring traceability from the reference standard to the candidate.

A1.1.1 Measurement stability

The measurement stability uncertainty calculation applies a statistical test to the assumptions that are built into the bracketing sequence (e.g., no non-linear drift, wavering responses, or excessively “noisy” measurements). This uncertainty component is calculated based on the standard error of the reference standard and candidate measurement points, assumed to lie on two straight lines when plotted versus time. This uncertainty component is quantified in terms of the residual error estimate for these two lines Equation (1.1) and Equation (1.2):

$$MS_{cand} = \sqrt{\frac{\sum(r_{cand} - \bar{r}_{cand})^2 - \frac{[\sum(r_{cand} - \bar{r}_{cand})(t_{cand} - \bar{t}_{cand})]^2}{\sum(t_{cand} - \bar{t}_{cand})^2}}{(n_{cand} - 2)}} \quad (1.1)$$

$$MS_{ref} = \sqrt{\frac{\sum(r_{ref} - \bar{r}_{ref})^2 - \frac{[\sum(r_{ref} - \bar{r}_{ref})(t_{ref} - \bar{t}_{ref})]^2}{\sum(t_{ref} - \bar{t}_{ref})^2}}{(n_{ref} - 2)}} \quad (1.2)$$

Where t_{cand} and t_{ref} are the timestamps associated with the candidate and reference standard measurements. The t units and the $t = 0$ origin can be anything, as long as they are consistent within each standard error calculation. The m and n values refer to all of the points of the regression lines. The standard errors for these lines are used to calculate the standard error of the mean of each individual measurement interval Equation (1.3), Equation (1.4) and Equation (1.5).

$$MS(\bar{r}_{ref(1)}) = \frac{MS_{ref}}{\sqrt{n_{ref(1)}}} \quad (1.3)$$

$$MS(\bar{r}_{cand}) = \frac{MS_{cand}}{\sqrt{n_{cand}}} \quad (1.4)$$

$$MS(\bar{r}_{ref(2)}) = \frac{MS_{ref}}{\sqrt{n_{ref(2)}}} \quad (1.5)$$

where \bar{r}_i is the mean response for just that measurement interval, and n is the number of individual measurements in that interval. The subscript notations (i.e., *ref(1)*, *cand*, and *ref(2)*) relate to the before-candidate reference generator measurement, the candidate measurement, and the after-candidate reference generator measurement (respectively). For each ratio calculation, these standard errors are used to calculate a combined stability uncertainty for this ratio according to Equation (1.6) and Equation (1.7). Equation (1.6) is equal to Equation (3b) in Section 8.6.1.

$$R_{jk} = \frac{\overline{r_{cand_{corr}}}}{\frac{t_{ref(2)} - t_{cand}}{t_{ref(2)} - t_{ref(1)}} \overline{r_{ref(1)_{corr}}} + \frac{t_{cand} - t_{ref(1)}}{t_{ref(2)} - t_{ref(1)}} \overline{r_{ref(2)_{corr}}}} \quad (1.6)$$

$$u(R_{jk}) = R_{jk} \sqrt{\left(\frac{MS(\overline{r_{ref(1)}})}{\frac{t_{ref(2)} - t_{ref(1)}}{t_{ref(2)} - t_{cand}} \overline{r_{ref(1)_{corr}}}} \right)^2 + \left(\frac{MS(\overline{r_{cand}})}{\overline{r_{cand_{corr}}}} \right)^2 + \left(\frac{MS(\overline{r_{ref(2)}})}{\frac{t_{ref(2)} - t_{ref(1)}}{t_{cand} - t_{ref(1)}} \overline{r_{ref(2)_{corr}}}} \right)^2} \quad (1.7)$$

Where R_{jk} is the measured ratio for the k^{th} individual bracket within the j^{th} contiguous set of brackets.

Measurement stability is one of two uncertainty components that relate only to a single bracketing procedure, with average output ratio according to Equation (1.8) and measurement stability uncertainty according to Equation (1.9).

$$\bar{R}_j = \frac{\sum_{k=1}^K R_{jk}}{K} \quad (1.8)$$

$$u\bar{R}_{j_{stability}} = \sqrt{\frac{1}{K^2} \sum_{k=1}^K u^2(R_{jk})_{stability}} \quad (1.9)$$

Where K is the number of brackets in this j^{th} set.

NOTE: When a concentration analyser is used with two traps, all calculations of ratios and uncertainties must be performed independently for channel A and channel B, up to the point of calculating \bar{R}_j and the bracketing uncertainty $u(\bar{R}_j)$ for the set.

A1.1.2 Repeatability

Repeatability quantifies, independently of measurement issues such as linearity and stability, the precision of the output ratio determinations within a single bracketing procedure. It is calculated as the difference between 1) the standard deviation of the individual bracket ratios, and 2) the statistical contribution of measurement instability to the standard deviation of the ratios.

For the bracketing measurement procedure, standard errors are pooled at 3 levels:

Level 1: Individual ratio uncertainty

Level 2: Repeatability within set

Level 3: Set reproducibility (Section A1.1.3)

The level specific contributions to the uncertainty are computed from these pooled standard errors. Starting with the pooled level 1 standard error (Equation (1.10)) and the level 2 standard deviation (Equation (1.11)).

$$S_1 = \sqrt{\frac{1}{K} \sum_{k=1}^K (u\bar{R}_{j_{stability}})^2} \quad (1.10)$$

$$S_2 = \sqrt{\frac{\sum_{k=1}^K (R_{jk} - \bar{R}_j)^2}{(K-1)}} \quad (1.11)$$

The repeatability uncertainty of the output ratio measurements is computed according to Equation (1.12).

$$u_{repeatability} = \sqrt{\max \left[0, s_2^2 - \frac{1}{L} \cdot s_1^2 \right]} = \sqrt{\max \left[0, \frac{\sum_{k=1}^K (R_{jk} - \bar{R}_j)^2}{(K-1)} - \frac{\sum_{k=1}^K u^2(R_{jk})_{stability}}{L \cdot K} \right]} \quad (1.12)$$

Where L represents the average number of individual responses used in each measurement average and output ratio determination Equation (1.13).

$$L = \frac{1}{K} \sum_{k=1}^K (n_{ref-B,k} + n_{cand,k} + n_{ref-A,k}) \quad (1.13)$$

The uncertainty of the set-average ratio is calculated according to Equation (1.14).

$$u_{\overline{repeatability}} = \frac{1}{\sqrt{K}} u_{repeatability} = \frac{1}{\sqrt{K}} \cdot \sqrt{\max \left[0, \frac{\sum_{k=1}^K (R_{jk} - \bar{R}_j)^2}{(K-1)} - \frac{\sum_{k=1}^K u^2(R_{jk})_{stability}}{L \cdot K} \right]} \quad (1.14)$$

The “Max” function holds this term at zero when sort-term precisions uncertainty is dominated by measurement instability.

A1.1.3 Reproducibility

Reproducibility is a measure of how precisely a bracketing sequences result can be duplicated. Based on the results obtained a default value can be assigned. This value can be based on the reproducibility routinely achievable by commercially available systems, for example 0.5% of the output of the candidate generator (Equation (1.15)).

$$u_{reproducibility} = 0.005 \cdot c \quad (1.15)$$

A1.1.4 Combined Uncertainty

Once calculated, all of the uncertainties are combined using propagation of uncertainty according to the GUM [10]. First, the combined uncertainty of each bracketing procedure is calculated (Equation (1.16)).

$$u_{bracketing} = \sqrt{[u_{\bar{R}_j}_{stability} + u_{repeatability}^2]} \quad (1.16)$$

Then, these uncertainties are combined into a single comparison uncertainty (Equation (1.17)).

$$u_{\overline{comparison}} = \sqrt{\frac{1}{J^2} \sum_{j=1}^J [c_{ref} \cdot u_{bracketing}]^2} \quad (1.17)$$

The reference generator uncertainty component is calculated based on its reported value and the average comparison ratio (Equation (1.18)).

$$u_{reference} = \frac{c}{c_{ref}} \cdot u(c_{ref}) \quad (1.18)$$

The overall combined uncertainty for the mercury concentration generated with the candidate gas generator can be calculated according to Equation (1.19) and the expanded uncertainty according to Equation (1.20).

$$u(c) = \sqrt{u_{\overline{comparison}}^2 + u_{reproducibility}^2 + u_{reference}^2} \quad (1.19)$$

$$U(c) = k \cdot u(c) = 2 \cdot u(c) \quad (1.20)$$

A1.2 Example

This example shows how bracketing data are used to determine the uncertainty of the candidate generator output mercury concentration. The calculations are based on the data given in Section 8.6.

A1.2.1 Measurement stability uncertainty

Table A1.1 shows the intermediate calculation for the candidate responses as input for Equation (1.1).

Table A1.1 intermediate calculations

t_{cand}	r_{cand}	$(t_{cand} - \bar{t}_{cand})^2$	$(r_{cand} - \bar{r}_{cand})^2$	$(t_{cand} - \bar{t}_{cand})(r_{cand} - \bar{r}_{cand})$
20	5966.5	400	2323.2	964
40	6065.3	0	2560.4	0
60	6012.3	400	5.8	-48
Average		Sum		
40	6014.7	800	4889.4	916

These data are entered into the residual error of estimate equation for the candidate generator (Equation (1.1)) and similar for the reference generator (Equation (1.2)).

$$MS_{cand} = \sqrt{\frac{4889.4 - \frac{1012^2}{800}}{(3-2)}} = 62$$

$$MS_{ref} = 47$$

These two values are used to calculate the standard error for each measurement average which in turn is used to calculate the output ratios (Equation (1.3) – Equation (1.5)). For the first bracket the standard errors are:

- $MS(\bar{r}_{ref-B}) = \frac{47}{\sqrt{1}} = 47$
- $MS(\bar{r}_{cand}) = \frac{62}{\sqrt{1}} = 62$
- $MS(\bar{r}_{ref-A}) = \frac{47}{\sqrt{1}} = 47$

These values are propagated through the output ratio calculation (Equation (1.7)). For all three ratios the uncertainty is calculated

- $u(R_1) = 1.054 \sqrt{\left(\frac{47}{2:5658.0}\right)^2 + \left(\frac{62}{5938.2}\right)^2 + \left(\frac{47}{2:5607.5}\right)^2} = 0.0127$
- $u(R_2) = 0.0128$
- $u(R_3) = 0.0127$

The average of the measurement stability uncertainty ration calculated using Equation (1.9).

$$u\bar{R}_{j\text{ stability}} = \sqrt{\frac{1}{9}[(0.0127)^2 + (0.0128)^2 + (0.0127)^2]} = 0.007$$

A1.2.2 Repeatability

Equation (1.14) is used to calculate the repeatability uncertainty which is composed of Equation (1.10) till Equation (1.13).

$$S_1 = \sqrt{\frac{(0.0127)^2 + (0.0128)^2 + (0.0127)^2}{3}} = 0.0127$$

$$S_2 = \sqrt{\frac{(1.054 - 1.063)^2 + (1.075 - 1.063)^2 + (1.060 - 1.063)^2}{(3 - 1)}} = 0.0108$$

$$L = \frac{1}{3} \sum_{k=1}^3 (1 + 1 + 1) = 3$$

$$u_{\text{repeatability}} = \frac{1}{\sqrt{3}} \sqrt{\max\left[0, 0.0127^2 - \frac{1}{3} 0.0106^2\right]} = 0.005$$

A1.2.3 Reproducibility

For this example the reproducibility uncertainty was set to zero. Reproducibility measurements performed on 3 measurement days show that the results from Channel A and Channel B and the results from the 3 days are comparable within the uncertainty without adding a contribution for the reproducibility. Therefore it is not necessary to add extra uncertainty due to the reproducibility of the measurements.

NOTE when the measurements, especially those obtained on different days, are not comparable within the uncertainty it is advised to add uncertainty for the reproducibility to the uncertainty calculation.

A1.2.4 Combined uncertainty

For each bracketing, the combined uncertainty is calculated according to Equation (1.16).

$$u_{\text{bracketing}} = \sqrt{0.007^2 + 0.005^2} = 0.009$$

The comparison uncertainty can be obtained next (Equation (1.17)).

$$u_{\text{comparison}} = 2226 \cdot 0.009 = 19 \text{ ng m}^{-3}$$

The reference standard uncertainty is calculated according to Equation (1.18).

$$u_{\text{reference}} = \frac{2367}{2226} 56 = 59 \text{ ng m}^{-3}$$

Based on these values the combined calibration uncertainty can be calculated (Equation (1.19)).

$$u(c) = \sqrt{19^2 + 59^2} = 62 \text{ ng m}^{-3}$$

Giving an expanded uncertainty (Equation (1.20)) of $2 \cdot 62 = 124 \text{ ng m}^{-3}$ which gives a relative expanded uncertainty of $\frac{124}{2367} 100 = 5\%$.

NOTE: The raw data and results used for this example calculated with the data processing script can be found in an online repository [11].

Annex 2: Interpolation function for multipoint calibration

A2.1 Introduction

The interpolation function relates the mercury concentration as indicated by the candidate generator (c_{cand}) to the actual mercury concentration (c). In this protocol, the actual concentration is either provided by an SI-traceable measurement standard, or by a calibrated measurement standard. Thus, the mercury concentration provided by the generator is given by $c = F(c_{cand})$.

where F denotes the interpolation function, expressing the mercury concentration as a function of the indication of the generator.

The interpolation function $c = F(c_{cand})$ is a mathematical function approximately expressing the calibrated candidate generator output mercury concentration $c_{(1)}, c_{(2)}, \dots, c_{(n)}$ in relation to the setpoints of the candidate generator $c_{cand(1)}, c_{cand(2)}, \dots, c_{cand(n)}$. The interpolation function is required for calculating unknown output mercury concentrations c obtained with the candidate generator from the setpoint of the candidate generator c_{cand} .

NOTE: a script was developed to calculate 1) the mercury concentration, 2) the associated uncertainty of the mercury concentration and 3) the interpolation function for multipoint calibration according to this calibration protocol [9].

A2.2 Determination of the interpolation function

The interpolation function can be determined directly by means of weighted least squares or a similar regression technique.

The following description, in terms of a series of steps, of the calibration experiment and its evaluation resumes and elaborates the principles outlined in Section 8.4.2.2.

Step A: Specify the range of setpoints $c_{cand(1)}, c_{cand(2)}, \dots, c_{cand(n)}$ for which the candidate generator will be used.

Step B: Specify the type of mathematical function to be considered for the interpolation function, $c = F(c_{cand})$. Select the simplest function that describes the data obtained from the following candidate models:

- Polynomial 1 (linear) $c = b_0 + b_1 c_{cand}$
- Polynomial 2 (quadratic) $c = b_0 + b_1 c_{cand} + b_2 c_{cand}^2$
- Polynomial 3 (cubic) $c = b_0 + b_1 c_{cand} + b_2 c_{cand}^2 + b_3 c_{cand}^3$

The coefficient b_j of the interpolation function are determined by regression analysis using the values from the calibration data set, i.e., the calibrated candidate generator output mercury concentration and the setpoint of the candidate generator used for calibration.

Step C: Specify the number n of calibration points ($c_{cand(i)}, c_{(i)}$) required, depending on the type of mathematical function to be used for the interpolation function. If a mercury generator has been assessed before over the interval selected in step A, it is appropriate to assume that the interpolation function will be of the same shape.

The minimum number of calibration points recommended for the different types of functions considered is:

- 3 for a linear function;
- 5 for a second-order polynomial;
- 7 for a third-order polynomial.

The recommended number of calibration points is greater than the number of indeterminate coefficients of the interpolation function because it is also necessary to validate the function chosen. If calibration experiments were only based on the minimum number of calibration points, it would be necessary to validate the interpolation function using additional reference standards. It is better, instead, to incorporate these additional “reference points” into the set of calibration points so as to reduce the calibration uncertainty of the estimated coefficients.

Step D: Calculate the mercury concentration output of the candidate generator $c_{(1)}, c_{(2)}, \dots, c_{(n)}$, based on the calibration measurements performed, together with their standard uncertainties $u(c_{(1)}), u(c_{(2)}), \dots, u(c_{(n)})$. So as to establish the output $c_{(i)}$ and $u(c_{(i)})$ for a given $c_{cand(i)}$, according to the method described in Section 8.6.2.

Step E: Calculate the coefficient b_j of the interpolation function to be used for the interpolation function.

The set of input data for this calculation consists of:

- the setpoint of the candidate gas generator (expressed as mercury concentration in ng m^{-3} or $\mu\text{g m}^{-3}$), $c_{cand(1)}, c_{cand(2)}, \dots, c_{cand(n)}$;
- calibrated candidate generator output mercury concentrations (expressed as mercury concentration in ng m^{-3} or $\mu\text{g m}^{-3}$), $c_{(1)}, c_{(2)}, \dots, c_{(n)}$, according to the method described in Section 8.6.2;
- the standard uncertainties of the calibrated candidate generator output mercury concentration, $u(c_{(1)}), u(c_{(2)}), \dots, u(c_{(n)})$, according to the method described in Annex 1.

These coefficients are calculated by regression analysis, according to the method described in Section A.2.3.

A2.3 Calculation of the coefficients of the interpolation function

The coefficients of the interpolation function are determined using weighted least squares. It is essential to use weighted least squares to ensure that the uncertainty associated with the measurement of the mercury concentrations is properly propagated [12].

In weighted least squares, the following sum of squares is minimised

$$S = \sum_{i=1}^n \left[\frac{|\hat{c}_{(i)} - c_{(i)}|^2}{u^2(c_{(i)})} \right] \quad (2.1)$$

where $\hat{c}_{(i)} = F(c_{cand(i)}; b_0, \dots, b_m)$. The chosen function F is acceptable if

$$|\hat{c}_{(i)} - c_{(i)}| \leq 2u(c_{(i)}) \quad (2.2)$$

for all i . If the absolute differences $|\hat{c}_{(i)} - c_{(i)}|$, when plotted as a function of $c_{(i)}$ are not randomly distributed around zero, then another model should be chosen.

The required output of the regression is as follows:

- the chosen function F ,
- the values for the coefficients b_1, \dots, b_n , and

- the covariance matrix associated with the coefficients, containing the squared standard uncertainties of the coefficients and the covariances between pairs of coefficients.

Any software used for this kind of regression shall be capable of providing the required output and enable assessing the residuals $|\hat{c}_{(i)} - c_{(i)}|$. Weighted least squares is described in [13] and implemented in R and Python.

A2.4 Validation of the interpolation function

A2.4.1 Purpose

Before using the interpolation function determined according to Section A2.3, it is necessary to validate the interpolation function and examine compliance with uncertainty requirements.

Different statistical test can be used to validate the interpolation function, such as, 1) determination of the residual sum of weighted squared deviations, S_{res} , or 2) by using Akaike Information Criterion for small sample size (AICc).

A2.4.2 Validation of the response model

The response model shall be validated by assessing whether the selected type of interpolation function is compatible with the data set:

- the setpoints of the candidate generator $c_{(1)}, c_{(2)}, \dots, c_{(n)}$;
- the calibrated candidate generator output mercury concentration $c_{cand(1)}, c_{cand(2)}, \dots, c_{cand(n)}$;
- the standard uncertainties of the calibrated candidate generator output mercury concentration, $u(c_{(1)}), u(c_{(2)}), \dots, u(c_{(n)})$.

To assess the overall fit of a calculated interpolation curve to the calibration data, the residual sum of weighted squared deviations, S_{res} , is compared with the relevant degrees of freedom (equal to the number of data points minus the number of response curve coefficients), as given in Section A.2.2. For the purpose of this protocol however, satisfactory fit is required for each individual data point by using the following test procedure. For each output mercury concentration ($c_{(i)}$), an adjusted data point ($\hat{c}_{(i)}$) is calculated, as a by-product of the regression analysis used to determine the interpolation function (Section A.2.2). The coordinates $\hat{c}_{(i)}$ of the adjusted data point are estimates of the true output mercury concentration for the candidate generator. By construction the calculated response curve passes through the adjusted data points. The selected response model is considered compatible with the data set if Equation (2.2) is fulfilled for every data point ($i = 1, 2, \dots, n$).

If the model validation test fails, one possibility is to examine other response models until a model is found that is compatible with the data set. Another possibility is to examine, and possibly revise, the data.

An alternative for the residual sum of weighted squared deviations is using the Akaike Information Criterion for small sample size (AICc). The AIC is an estimator of prediction error. Given a collection of models a data set, AIC estimates the quality of each model. When the sample size is small, AIC tends to select models that have too many coefficients (i.e., it will overfit). To address this issue AICc was developed. AICc is AIC plus a penalty term for the number of coefficients. ISO TS 28038 (Determination and use of polynomial calibration functions) discusses the usage of AICc. The polynomial with the smallest value in the AICc test is the best fit for the data.

A2.5 Determination the output of the calibrated candidate generator

Determination of the (prospective) output of the calibrated candidate generator, consists in determining the mercury concentration, c , and its standard uncertainty, $u(c)$, at a setpoint c_{cand} . These data are determined in a series of two steps as follows.

Step F: Calculate the output, $c = F(c_{cand})$, using the interpolation function determined according to the procedure described in Section A2.3. The input value for this calculation is the setpoint of the gas generator, c_{cand} .

Step G: Calculate the standard uncertainty of the mercury concentration, $u(c)$, using the law of propagation of uncertainty, according to the GUM [10], on the setpoint of the candidate generator. The uncertainty sources are 1) the uncertainty of the reference standard, $u_{reference}$ (Equation (1.18)), and 2) the uncertainty on the coefficients of the interpolation function, $u_{interpolation}$, Equation (2.3).

$$u_{interpolation}^2 = \sum_{i=1}^N \left(\frac{\partial f}{\partial c_{cand}} \right)^2 u^2(c_{cand}) + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{\partial f}{\partial c_{cand(i)}} \frac{\partial f}{\partial c_{cand(j)}} u(c_{cand(i)}, x_{cand(j)}) \quad (2.3)$$

$u(c_{cand(i)}, x_{cand(j)})$ is the estimated covariance associated with $c_{cand(i)}$ and $x_{cand(j)}$.

The overall combined uncertainty for the mercury concentration generated with the candidate gas generator can be calculated according to Equation (2.4) and the expanded uncertainty according to Equation (1.20).

$$u(c) = \sqrt{u_{interpolation}^2 + u_{reference}^2} \quad (2.4)$$

A2.6 Example

A2.6.1 Determination of the interpolation function

In this example the calculation of the interpolation function of a six-point calibration is shown (Table A2.1). The data was obtained using a sampling analyser with two channels (channel A and channel B).

Table A2.1: Data used for the calculation of the coefficients of the interpolation function.

Setpoint	c_{cand} (ng m ⁻³)	c_A (ng m ⁻³)	$u(c_A)$ (ng m ⁻³)	c_B (ng m ⁻³)	$u(c_B)$ (ng m ⁻³)
1	1071	1015	26	1041	27
2	1367	1283	35	1272	33
3	1675	1539	41	1552	45
4	1964	1801	46	1833	47
5	2263	2107	54	2095	54
6	2563	2368	63	2426	64

The interpolation function was determined according to Section A2.3. For channel A a linear function ($c = b_0 + b_1 c_{cand}$) was determined and for channel B a quadratic function ($c = b_0 + b_1 c_{cand} + b_2 c_{cand}^2$) (Table A2.2) including the covariance matrix associated with the coefficients, containing the squared standard uncertainties of the coefficients and the covariances between pairs of coefficients (Table A2.3) [13].

Table A2.2: Coefficients of the interpolation function

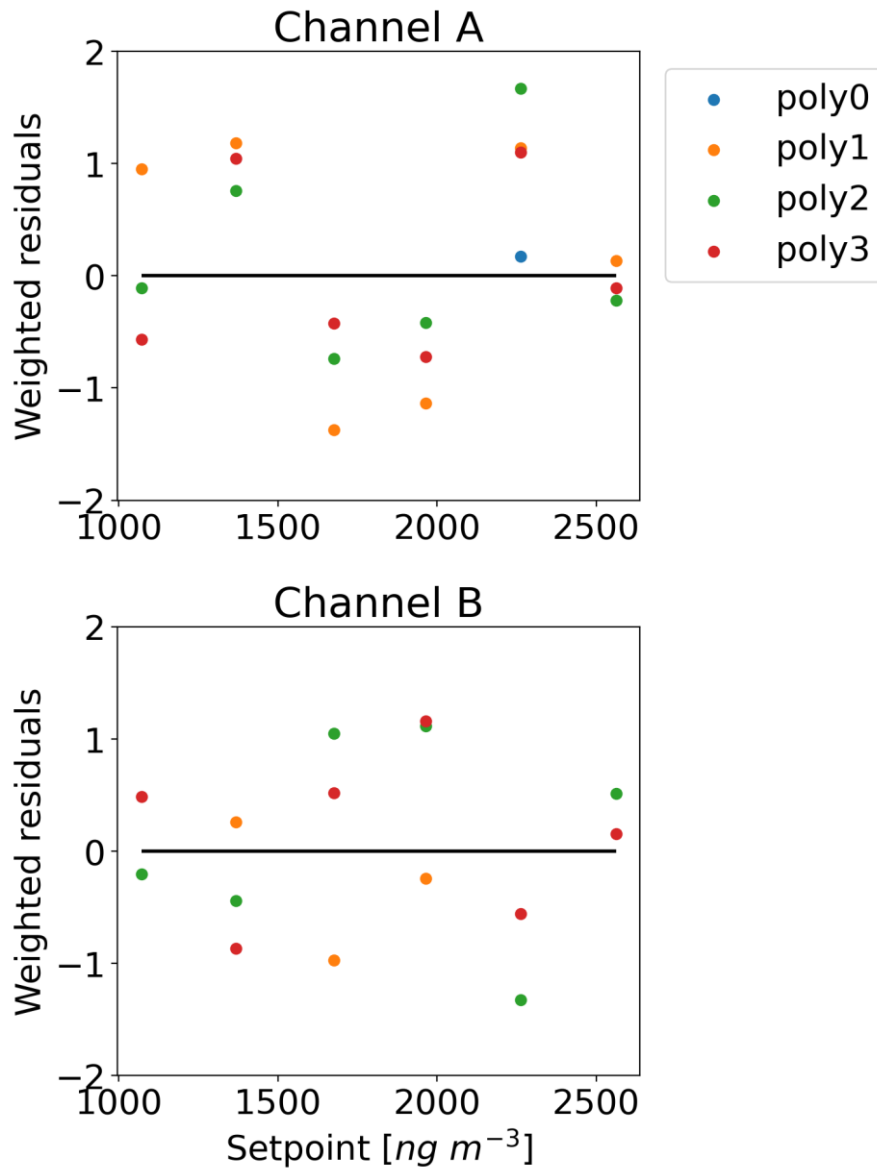
Channel A	Coefficients	Standard error
b_0	9.5	23
b_1	0.920	0.010
Channel B	Coefficients	Standard error
b_0	375	99
b_1	0.50	0.11
b_2	0.000116	0.000028

Table A2.3: Covariance matrix

Channel A	b_0	b_1	
b_0	507	-0.215	
b_1	-0.215	0.0000943	
Channel B	b_0	b_1	b_2
b_0	9881	-10.6	0.00266
b_1	-10.6	0.0115	-0.00000294
b_2	0.00266	-0.00000294	0.00000000076

A2.6.2 Validation of the response model

To assess the overall fit, of the calculated interpolation function to the calibration data, both the residual sum of weighted squared deviations, S_{res} , and AICc were used (Figure A2.1, Table A2.4 and Table A2.5).



Figures A2.1: Weighted residuals determined for the different interpolation functions of channel A and channel B

Table A2.4: Results of the sum squared residuals for the different interpolation functions of channel A and channel B

	Channel A	Channel B
Poly 0	15249	12993
Poly 1	<u>7</u>	32
Poly 2	4	<u>5</u>
Poly 3	3	3

Table A2.5: Results of the AICc test for the different interpolation functions

	Channel A	Channel B
Poly 0	96	96
Poly 1	<u>55</u>	65
Poly 2	62	<u>63</u>
Poly 3	90	90

The interpolation function or polynomial with the smallest value in the AICc test is the best fit for the data. For both Channel A this is polynomial 1 and for Channel B this is polynomial 2. Furthermore, a function is acceptable if the weighted residuals are in absolute value ≤ 2 (Figure A2.1). The best fit for the data is polynomial 1 as the data will be overfitted when using polynomial 2 or polynomial 3. Both statistical test show polynomial 1 or the linear function will be the best fit for the data.

A2.6.3 Calibration results

For this example data is used obtained with a concentration analyser using two traps (channel A and channel B). The results were treated separately for channel A and channel B. When the mercury concentration, c , obtained for channel A and channel B is comparable with the uncertainty calculated, $u(c)$, the results can be averaged to obtain the final calibration results (Table A2.6).

Table A2.6: Final calibration results averaged for channel A and B

Setpoint	c_{cand} (ng m^{-3})	c (ng m^{-3})	$U(c)$ (ng m^{-3}) ($k = 2$)
1	1071	1028	62
2	1367	1278	73
3	1675	1545	91
4	1964	1817	102
5	2263	2101	117
6	2563	2397	127

To determine if the interpolation functions for channel A and channel B are comparable, a value for the compatibility of the averaged functions can be calculated (Chi squared) [13]. When they are comparable, they can be combined (Figure A2.2).

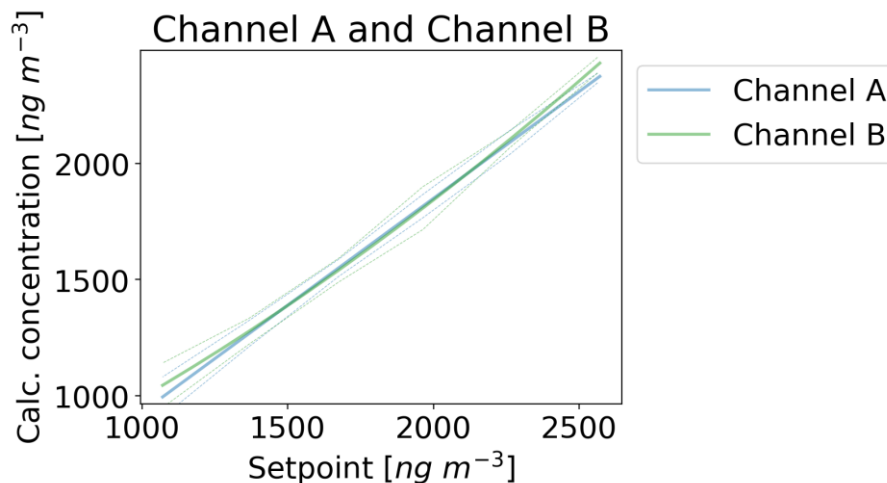


Figure A2.2: Overlay interpolation functions channel A and channel B.

For this example the data from channel A and channel B can be averaged using a linear function. This is acceptable with a Chi squared value of 4.3 and the probability that such a Chi squared value should occur by chance is 0.93. If the probability is larger than 0.90, then the goodness-of-fit is believable. If it is smaller than the comparability of the functions can rightly be called into question. The average regression coefficients for Channel A and Channel B and a covariance matrix was calculated (Table A2.7 and Table A2.8). The covariance matrix explains how the two data sets (b_0 , b_1) are correlated. This correlation should be included in the calculation of the total uncertainty associated to the interpolation function.

Table A2.7: Final calibration result for the average coefficients

	Parameters	Standard error
b_0	-1.8	36
b_1	0.930	0.016

Table A2.8: Final covariance matrix

	b_0	b_1
b_0	1268	-0.547
b_1	-0.547	0.000246

The final interpolation function is a linear function:

$$c = -1.8 + 0.930 c_{cand}$$

A2.6.4 Determination of the output of the candidate generator

The output of the candidate generator, c , at three setpoints of the candidate generator, c_{cand} , are calculated (Table A2.9). The mercury concentrations fall in the calibration range tested. Using the interpolation function and coefficients determined in section A2.3 the output of the candidate generator was calculated including the uncertainty of the mercury concentration, $u(c)$. The uncertainty is calculated using Equation (2.3) and Equation (2.4). In Equation (2.3) $c = F(c_{cand})$ is $c = b_0 + b_1 c_{cand}$ for this example, which gives:

$$u^2(c) = \left(\frac{\partial c}{\partial b_0}\right)^2 u^2(b_0) + \left(\frac{\partial c}{\partial b_1}\right)^2 u^2(b_1) + 2 \frac{\partial c}{\partial b_0} \frac{\partial c}{\partial b_1} u(b_0, b_1)$$

where $\frac{\partial c}{\partial b_0} = 1$ and $\frac{\partial c}{\partial b_1} = c_{cand}$. Substituting the values reported in the covariance matrix (Table A2.8), $u^2(b_0) = 1268$, $u^2(b_1) = 0.000246$ and $u(b_0, b_1) = -0.547$ this results in $u^2(c) = 1^1 \cdot 1268 + c_{cand}^2 \cdot 0.000246 + 2 \cdot 1 \cdot c_{cand} \cdot (-0.546)$.

The mercury concentration is calculated using the interpolation function:

$$c = -1.8 + 0.930 \cdot 1150 = 1068$$

The uncertainty of the interpolation is calculated according to Equation (2.3).

$$u_{interpolation} = \sqrt{1^1 \cdot 1268 + 1150^2 \cdot 0.000246 + 2 \cdot 1 \cdot c_{cand} \cdot (-0.546)} = 18.3$$

The reference standard uncertainty is calculated according to Equation (1.18).

$$u_{reference} = \frac{1068}{2226} 56 = 26.7 \text{ ng m}^{-3}$$

Based on these values the combined calibration uncertainty can be calculated (Equation (2.4)).

$$u(c) = \sqrt{18.3^2 + 26.7^2} = 32.4 \text{ ng m}^{-3}$$

Giving an expanded uncertainty (Equation (1.20)) of $2 \cdot 32.4 = 65 \text{ ng m}^{-3}$ which gives a relative expanded uncertainty of $\frac{65}{1068} 100 = 6.1 \%$.

Table A2.9 – Output and uncertainty candidate generator determined using the interpolation function

c_{cand} (ng m ⁻³)	c (ng m ⁻³)	$u(c)$ (ng m ⁻³)	$U(c)$ (ng m ⁻³)	$U(c)$ (%)
1150	1068	32	65	6.1
1750	1626	42	84	5.2
2450	2277	57	115	5.0

NOTE: The raw data and results used for this example calculated with the data processing script can be found in an online repository [11].

References

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3. ISO 6142-1, Gas analysis – Preparation of calibration gas mixtures – Part 1: Gravimetric methods for Class I mixtures
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