19NMR03 SI-Hg

Draft protocol for the SI-traceable certification of elemental mercury (Hg^0) gas generators used in the field (A1.1.4)

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CEN/TC/WG8

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Introduction

- Draft protocol for the SI-traceable certification of elemental mercury (Hg^0) gas generators used in the field
  - Scope
  - Principle
  - Equipment
  - General procedure
  - Data processing
  - Quality control and documentation
- Difference compared to NIST procedure
- Next steps

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Scope

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

- This protocol provides methods for
  - Determining the output of a mercury gas generator by comparison with a reference standard;
  - Calculating the uncertainty of the mercury concentration generated with the gas generator in relation to the known uncertainty of the reference standard.

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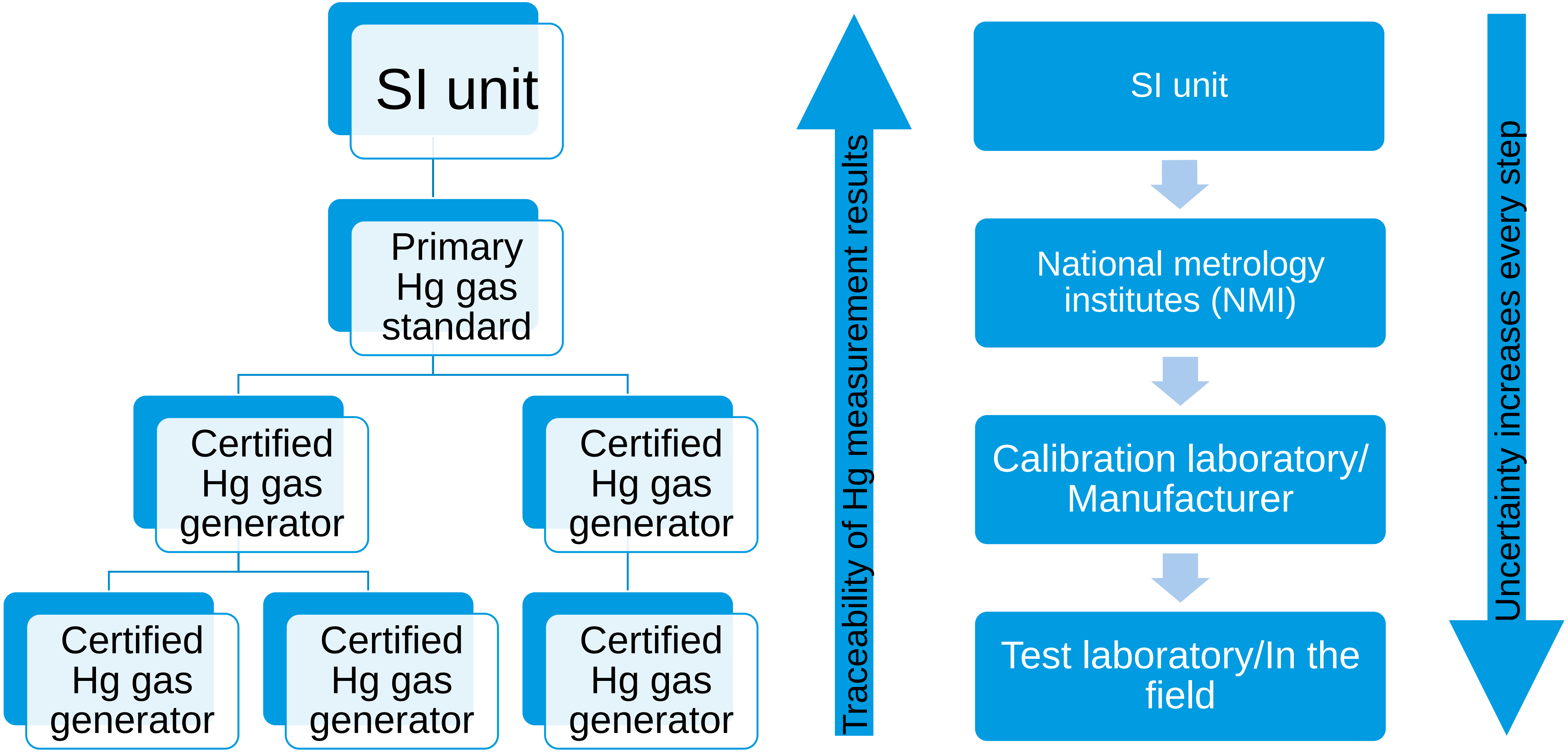
Traceability chain



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Principle

- The mercury concentration in a gas mixture prepared with a mercury gas generator is determined by comparison with a metrologically traceable reference standard to calibrate the output of a candidate gas generator.
  - At one concentration level – single-point calibration
  - At several concentration levels – multipoint calibration
- Bracketing measurement sequence

Generator ID	Response ID
Reference standard	RS_1
Candidate	C_1
Reference standard	RS_2
Candidate	C_2
Reference standard	RS_3
Candidate	C_3
Reference standard	RS_4

- There are two approaches for the data processing
  - Without zero correction
  - With zero correction

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Equipment

- The method is applicable for different types of mercury gas generators:
  - Bell-jar generator, working according to ISO 6145-9
  - Saturation gas generators, working according to o ISO 6145-9
  - Permeation gas generators, working according to ISO 6145-10
  - Mercury amount fractions in high-pressure cylinders, prepared according to ISO 6142-1
  - Reduction gas generators of Hg(II) to Hg(0)

- 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 or a calibrated gas mixture in a high-pressure cylinder.

- Analyser equipment
  - AFS or AAS
  - Direct measurement system or pre concentration system

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General procedure (1/4)

- Gas generator requirements
  - Mercury concentration range
  - Operating principle
  - Bell-jar: calibration of the syringe volume
  - Saturation or permeation gas generators: calibration of the MFC

- Reference standard requirements
  - Metrological traceability
  - Mercury concentration range > gas generator

- Analyser requirements
  - Measurement range > gas generator
  - Sensitivity, response function, detection limit, precision and drift shall be known

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General procedure (2/4)

- Set-up equipment according to operating instructions
- Gas mixtures transported using PFA or PTFE tubing
- Use reference standards with the same complementary gas
- Warm up time according to operating instructions
- Conduct a 15-minute stability check of both the gas generator and reference standard
- Analyse concentrations from low to high or mixed?
- Continuous analyser: record reading at appropriate set intervals and compute the average over 5 minutes
- Concentration analyser: record the result of one analysis cycle or average multiple analysis cycles. For a system with two traps use the same designated traps (A or B).
- Select set points
  - Single-point calibration: mercury concentrations using the same nominal settings for the candidate gas generator and the reference standard such that the measuring system produces responses which are within ± 30 %

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General procedure (3/4)

- To use a generator over an extended range, a multipoint evaluation is necessary
- Purpose is to determine the behaviour over the entire concentration range over which the generator is to be used
- Selection of data points:
  - Lowest setpoint at the lower end of the concentration interval, or just below it
  - Highest setpoint at the higher end of the concentration interval, or just above it
  - Number of data points large enough to fit an interpolation function
  - Other setpoints about equally spaced between the lowest and highest setpoint
- Example:
  - Concentration interval 5 ng m^{-3} to 250 ng m^{-3}
  - Lowest point: 5 ng m^{-3}
  - Highest point: 250 ng m^{-3}
  - For a cubic function: 6 points
  - Other setpoints: 50 ng m^{-3}, 100 ng m^{-3}, 150 ng m^{-3}, 200 ng m^{-3}

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General procedure (4/4)

- Measurement bracketing sequence
  - At one concentration level – single-point calibration
  - At several concentration levels – multipoint calibration

One level	Multiple levels
Z_1	Z_1
$RS_{c1.1}$	$RS_{c1.1}$
$C_{c1.1}$	$C_{c1.1}$
$RS_{c1.2}$	$RS_{c1.2}$
$C_{c1.2}$	$C_{c1.2}$
$RS_{c1.3}$	$RS_{c1.3}$
$C_{c1.3}$	$C_{c1.3}$
$RS_{c1.4}$	$RS_{c1.4}$
Z_2	$RS_{c2.1}$
	$C_{c2.1}$
	$RS_{c2.2}$
	$C_{c2.2}$
	$RS_{c2.3}$
	$C_{c2.3}$
	$RS_{c2.4}$
	$RS_{cn.1}$
	$C_{cn.1}$
	$RS_{cn.2}$
	$C_{cn.2}$
	$RS_{cn.3}$
	$C_{cn.3}$
	$RS_{cn.4}$
	Z_2

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Stepwise procedure

Step A: Zero the detector by injecting zero gas and making any necessary zero adjustments. Alternatively, obtain the response of the zero gas from the detector (r_z).

Step B: Direct the output of the reference standard to the detector and obtain a response (r_{rs1}).

Step C: Direct the output of the candidate gas generator to the detector and obtain a response (r_{u1}).

Step D: Switch back to direct the output of the reference standard to the detector and obtain a response (r_{rs2}).

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

Step F: In case the deviation between RS_1 and RS_4 is bigger than 1 % 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.

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Data processing
Single-point calibration **without** zero correction

Step I: calculate the mean response value of triplicate responses for the mercury concentration from the candidate generator and quadruple responses for the mercury concentration from the reference standard, r_u, and the standard uncertainty, $u(r_u)$, of the mean response value.

Step J: The mercury concentration from the candidate gas generator is calculated using equation (1).

$$c_u = c_{rs}\frac{r_{rs}}{r_u} \qquad (1)$$

Step K: The uncertainty of mercury concentration from the candidate gas generator is derived from the uncertainty of the mercury concentration from the reference standard, taking into account that measurements are carried out on both mercury concentrations from the reference standard and the candidate gas generator; see Formula (2):

$$u^2(c_u) = u^2(c_{rs}) + \frac{c_{rs}^2}{r_{rs}^2}[u^2(r_{rs}) + u^2(r_u)] \qquad (2)$$

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Data processing
Single-point calibration **with** zero correction (1/2)

Step L: To determine the actual output of the User generator, first correct each response for any zero offset of the detector. Calculate the interpolated zero offset based on the time when a specific response was recorded according to equation (3):

$$r_{zi} = r_{z1} + \left[(t_i - t_1)\frac{(r_{z1}-r_{z2})}{(t_1-t_2)}\right] \quad (3)$$

Step M: then, correct the response at t_i for the zero offset using equation (4):

$$r_{u_{corr}} = r_u - r_{zi} \quad (4)$$

Time (min)	y_z	y_{zi}	y_{rs}	$y_{rs_{corr}}$	y_u	$y_{u_{corr}}$
0	0.00					
10		0.04	10.00	9.96		
20		0.08			9.85	9.77
30		0.12	10.20	10.08		
40		0.16			9.96	9.80
50		0.20	10.25	10.05		
60		0.24			10.00	9.76
70		0.28	10.40	10.12		
80	0.32					

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Data processing
Single-point exact-match calibration **with** zero correction (2/2)

Step N: Next, calculate the output ratio (R) for each value of r_{corr} according to equation (5):

$$R = \left[\frac{r_{u_{corr}}}{\frac{r_{rs1_{corr}} - r_{rs2_{corr}}}{2}}\right] \qquad (5)$$

Step O: Next, average the three calculated output ratios arithmetically.

Step P: Finally, use Equation (6) to determine Y_{c_i}, the calculated candidate gas generator output mercury concentration.

$$Y_{c_i} = c_{rs}\,\bar{R} \qquad (6)$$

Step R: For each concentration level calculate the relative standard deviation (RSD) of the output rations. The RSD shall not exceed 1.0 %. If the RSD value is exceeded, the test is invalid and shall be repeated.

Step S: Determine the uncertainty of the mercury concentration from the candidate gas generator

Time (min)	y_{rs}	$y_{rs_{corr}}$	y_u	$y_{u_{corr}}$	Output ratio (R)
10	10.00	9.96			
20			9.85	9.77	0.975
30	10.20	10.08			
40			9.96	9.80	0.974
50	10.25	10.05			
60			10.00	9.76	0.968
70	10.40	10.12			

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Data processing
Multipoint calibration (1/5)

- With zero correction determine calculate the output ratio (R) and candidate gas generator output mercury concentration Y_{c_i} for each setpoint using step L till step S

- For data processing and uncertainty calculation software will be made available!

- Gas generator behaviour:
  - Ideal case: $c_{\mathrm{rs}} = c_u$
  - Can be assessed by fitting $c_{\mathrm{rs}} = a_0 + a_1 c_u$
  - If ideal case applies, then a_0 is not significantly different from zero, i.e., $|a_0| \leq 2u(a_0)$,
  - and the slope is unity $a_1 = 1 \pm 2u(a_1)$.

  - If not, then
    a) Use the coefficients a_0 and a_1 as obtained (if the fit is satisfactory)
    b) Use a different model that provides a satisfactory fit of the data

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Data processing
Multipoint calibration (2/5)

- Interpolation model
  - Purpose: to calculate the concentration, given any set point c_u within the interval $[c_{\mathrm{u,min}}, c_{\mathrm{u,max}}]$
  - If the straight line suffices, $c = a_0 + a_1 c_0$
  - Otherwise, use the interpolation model selected for the data
  - Uncertainty of the concentration c follows from propagating the uncertainty of the coefficients of the interpolation model
- Goodness of fit
  - We will consider only generalised linear models of the type $c_{\mathrm{rs}} = a_0 + a_1 c_u + a_2 c_u^2 + \cdots$
  - Defining the residuals as $\Delta c = \frac{\hat{c}_{\mathrm{rs}} - c_{\mathrm{rs}}}{u(c_{\mathrm{rs}})}$
  - We require that the residual is, in absolute sense, smaller than 2 for all points in the fit
  - Considering parsimony, we will choose the model with the smallest number of coefficients that meets the above requirement

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Data processing
Multipoint calibration (3/5)

- Use a different model that provides a satisfactory fit of the data
- Use AICc to determine satisfactory model
  - The Akaike Information Criterion (AIC) is an estimator of prediction error and thereby relative quality of statistical models for a given set of data. Given a collection of models for the data, AIC estimates the quality of each model, relative to each of the other models. Thus, AIC provides a means for model selection.
  - When the sample size is small, there is a substantial probability that AIC will select models that have too many parameters, i.e. that AIC will overfit. To address such potential overfitting, AICc was developed: AICc is AIC with a correction for small sample sizes.
  - Typical models:
    1. $\mathrm{c} = \mathrm{a}_0 + \mathrm{a}_1\mathrm{c}_0$
    2. $\mathrm{c} = \mathrm{a}_0 + \mathrm{a}_1\mathrm{c}_0 + a_2 c_0^2$
    3. $\mathrm{c} = \mathrm{a}_0 + \mathrm{a}_1 \frac{1}{c_o}$
  - Examples on the next slide

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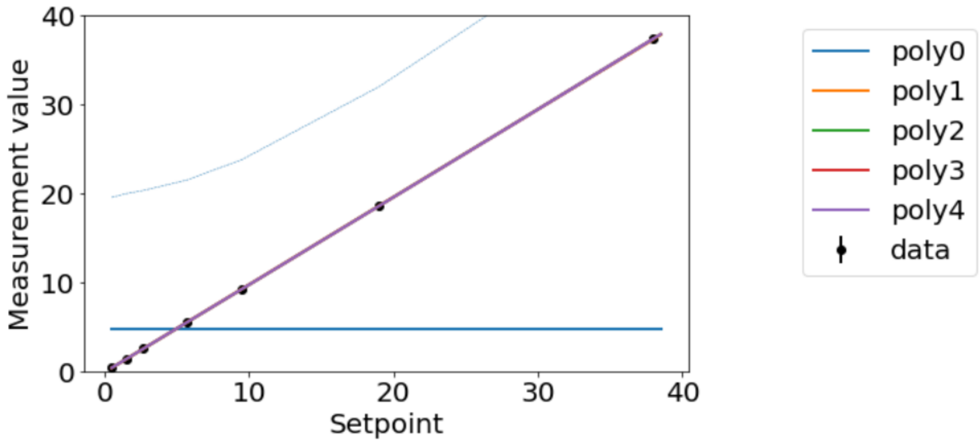
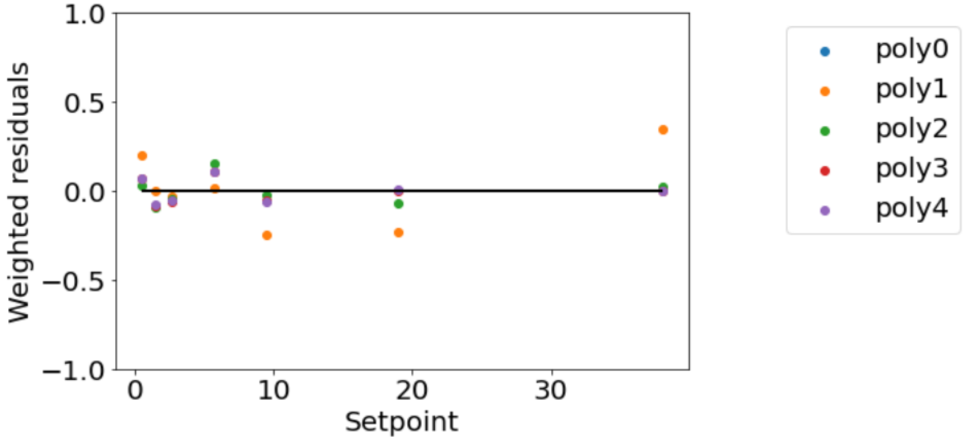
Data processing
Multipoint calibration (4/5)

- When predicting the measurement value
- AICc indicates to use a polynomial of degree 2
- $c = a_0 + a_1 c_0 + a_2 c_0^2$

Function	AICc
poly0	50.338
poly1	-31.113
poly2	-37.533
poly3	-25.824
poly4	16.134





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Quality control and documentation

- Ongoing quality assurance/quality control
  - According to QAL3 EN14181

- Test report
  - Report the results in accordance with the requirements of ISO/IEC 17025.
  - A test report, shall contain at least the following information:
  - a) a description of the analytical system used;
  - b) the composition, including uncertainty, of the reference gas standard used for calibration;
  - c) the results and mathematical function type used for the analysis function

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Difference compared to NIST procedure

Interim EPA Traceability Protocol for Qualification and Certification of Elemental Mercury Gas Generators - 2009

- Multipoint calibration is added to enable interpolation with use of regression
- Single procedure for both user generator and field reference generator
- Integrated with ISO and EN standards

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Next steps

- Elaborate calculations to determine calibration function and uncertainty
- Validation protocol (*2021/2022*)
- Performance evaluation of elemental mercury generators on the market (*2022/2023*)
- Finalize protocol based on validation and performance evaluation (*2023*)
- Protocol converted into a written documentary standard (*2025*)

- Validation of certification protocols for oxidised mercury gas generators used in the field
  - Evaluation state of the art dual analytical systems
  - Evaluation state of the art Hg^{II} gas generators used in the field
  - Development of a traceable certification protocol for oxidised mercury gas generators used in the field
  - Validation of the certification protocol for oxidised mercury gas generators used in the field
  - Performance evaluation of oxidised mercury generators on the market

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