D3: Protocol for the SI-traceable calibration of oxidised mercury (Hg^{II}) gas generators used in the field.

19NRM03 SI-Hg D3

Timo Rajamäki [1], Sari Saxholm [1], Warren Corns [2], Carsten Röllig [3], Igor Živković [4], Iris de Krom [5]

[1] National Metrology Institute VTT MIKES, Tekniikantie 1, 02150 Espoo, Finland

[2] P S Analytical, Arthur House, Crayfields Industrial Estate, main Road, Orpington, Kent, BR5 3HP, UK

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

[4] JSI Jozef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia

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

Lead partner:	VTT
Project number:	19NRM03
Version No.:	1.3
Due date deliverable:	31-08-2023
Actual submission date:	29-11-2023

VTT

PSA

LUMEX

TÜVRheinland®
Precisely Right.

Jožef Stefan Institute

VSL
National
Metrology
Institute

Istituto sull'Inquinamento Atmosferico
Consiglio Nazionale delle Ricerche

LGC

Activity number	Activity description	Partners (Lead in bold)
A2.3.1 M20	Using input from A2.1.4, A2.2.1, A2.2.2 and A2.2.3, VTT, in collaboration with TÜV Rheinland, PSA and Lumex will adjust the certification protocol developed within the EMPIR 16ENV01 MercOx project which determines the output of liquid evaporative $HgCl_2$ gas generators. The protocol will be adjusted to obtain a protocol that is applicable to different types of gas generators, commonly used in the field e.g. liquid based, dry based gas generators and Hg^0 to Hg^{II} converter systems.	**VTT**, TÜV Rheinland, PSA, Lumex
A2.3.2 M35	Based on the results of A2.1.4, A2.2.5, A2.4.4 and A3.2.5, VTT, in collaboration with TÜV Rheinland, PSA and Lumex will finalise the certification protocol developed in A2.3.1 by including relevant validation data such as repeatability, reproducibility, bias and uncertainty evaluation.	**VTT**, TÜV Rheinland, PSA, Lumex
A2.3.3 M36	VTT, with support of PSA, Lumex, TÜV Rheinland, JSI, VSL, CNR and LGC will review the certification protocol from A2.3.2. VTT will send the final document to the coordinator. The coordinator will then submit it to EURAMET as **D3** "*Protocol for the SI-traceable certification of oxidised mercury (Hg^{II}) gas generators used in the field.*".	**VTT**, PSA, Lumex, TÜV Rheinland, JSI, VSL, CNR, LGC

This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme.

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Summary

This document was developed to obtain a calibration protocol that is applicable to different types of dynamic oxidised mercury (Hg^{II}) gas generators commonly used in the field, e.g., liquid-based gas generators, dry based gas generators and elemental mercury (Hg^0) to Hg^{II} converter systems. The calibration protocol describes step by step calibration process needed to confirm the output of different types of dynamic Hg^{II} gas generators. The process consists of two main parts. Firstly, calibration of an analyser using a traceable mercury Hg^0 gas standard and secondly, measurement of the output from the dynamic Hg^{II} gas generator using the calibrated analyser.

Table of Contents

Summary 2

Table of Contents 3

Introduction 4

1. Calibration of the analyser 5

    1.1 Analyser selection 5

    1.2 Traceability 5

    1.3 Measurement plan 5

    1.4 Analyser preparation 6

    1.5 Calibration gas mixtures 6

    1.6 Measurements 6

    1.7 Data analysis 7

    1.8 Results 7

2. Calibration of a reference gas generator 8

    2.1 Traceability 8

    2.2 Measurement plan 8

    2.3 Generator preparation and generator details 8

    2.4 Measurements 9

    2.5 Data analysis 9

    2.6 Results 9

Annex A (informative) Calibration protocol: Step by step flow chart 10

References 11

Introduction

This document specifies a step-by-step calibration protocol to confirm the quantitative output of different types of dynamic Hg^{II} gas generators, to achieve a metrological traceability to the International System of Units (SI) and to determine the expanded uncertainty of the mercury concentration for the output. The process consists of two main parts. Firstly, calibration of an analyser with established converter efficiency using a traceable elemental mercury gas standard and secondly, measurement of the output from the dynamic Hg^{II} gas generator using the calibrated analyser.

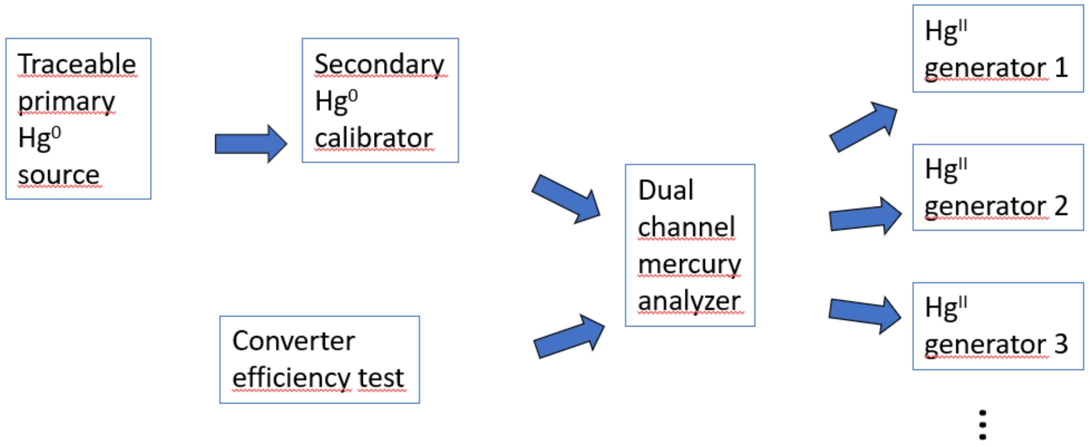
The calibration protocol is applicable for different types of dynamic Hg^{II} gas generators:

- liquid based gas generators, working according to ISO 6145-4
- saturated dry based gas generators, working according to ISO 6145-9, and
- Hg^0 to Hg^{II} converter systems.

The concentrations are expressed in ng/m^3 or $\mu g/m^3$ at standard conditions of pressure (101.325 kPa) and at temperature of 293.15 K.

The calibration protocol consists of two main parts. Firstly, calibration of an analyser using a traceable elemental mercury gas standard and secondly, measurement of the output from the dynamic Hg^{II} gas generator using the calibrated analyser, i.e., calibration of a generator.

Traceability chain of the procedure is following:



1. Calibration of the analyser

1.1 Analyser selection

An analyser is used as a measuring instrument. The specific analyser, which is suitable for the meant purpose, is selected. In the selection process, at least the operational principle and measurement range needs to be considered: these must cover the range, which is going to be calibrated, and the analyser must be capable to measure total mercury concentration (Hg^{tot}) and preferably elemental mercury concentration (Hg^0) as well. Analyser converter efficiency, sensitivity, response function in the used range, detection limit, precision and drift of the analyser must be known. Furthermore, typically available analysers are not measuring Hg^0 and Hg^{tot} in parallel but alternating.

EXAMPLE. The output of liquid evaporative $HgCl_2$ generator is going to be calibrated. When studying analytical parameters of oxidised mercury generators, the concentrations of elemental mercury and total mercury are measured. In the ideal case of Hg^{II} generator the Hg^0 concentration is absent and the Hg^{tot} concentration corresponds the Hg^{II} concentration. The output gas of a liquid evaporative generator is always humid to some extent, i.e., it contains water in vapour phase.

1.2 Traceability

The analyser needs to be calibrated to ensure the traceability of Hg^{II} measurements. A traceable primary or secondary Hg^0 or Hg^{II} gas standard should be used to perform the calibration.

EXAMPLE. The analyser is calibrated with the primary Hg^0 gas standard developed at the Van Swinden Laboratory (VSL). This primary Hg^0 gas standard is developed to establish metrological traceability of Hg^0 concentration measurement results, based upon a gravimetric approach, for ambient air levels as well as higher concentrations [1,2]. Using specially designed diffusion cells, Hg^0 is evaporated under well-controlled conditions (temperature, flow and pressure) according to ISO 6145-2. By weighing the diffusion cells at regular time intervals with a high-resolution balance, an accurate mass flow rate, traceable to the SI, is obtained. After mixing the mass flow of Hg^0 with an accurately measured mass flow rate of air, the primary Hg^0 gas standard is obtained in the range between 0.1 $\mu g/m^3$ and 100 $\mu g/m^3$.
By using the primary Hg^0 gas standard to calibrate the two-channel analytical system, the traceability of Hg^{II} measurements has been established as follows:

- $Hg^0 \rightarrow HgCl_2 \rightarrow Hg^0$ (measurement) $\leftrightarrow Hg^0$
- $Hg^0 \rightarrow (HgCl_2 + Hg^0) \rightarrow Hg^{tot}$ (measurement) $\leftrightarrow Hg^0$

1.3 Measurement plan

A measurement plan for calibration is made. In the plan, the calibration range and the calibration points within the range are determined, and measurement sequences needed to investigate the generators repeatability and reproducibility, linearity, and hysteresis, are planned.

The selected calibration points should include at least points close to both minimum and maximum values of the analyser's measurement range, and at least one point between those. Typically, the relevant measurement range for analyser is the range of the generator which shall be calibrated. The analyser range should cover the range of the generator to be calibrated and additionally zero and span point (appr. 80% of the analyser range used) should be recorded. In case the analyser output is not linear, at least five test points are required. It is recommended to distribute the selected points equally over the operational range. Additionally, it is recommended to include typical measurement points used during actual measurements. This ensures to get enough information for linearity analysis and optimises the corrections and fitting curves used for the analyser by avoiding large interpolations based on calibration data.

To observe the possible hysteresis from the calibrations results, the selected calibration points need to be generated in order, from minimum towards maximum value, and same in the opposite direction.

EXAMPLE. Eight different Hg^0 concentrations are selected as calibration points. During the calibration each measurement point is measured more than once, and the average of the recorded readings is used as a measured result for that point. Short time repeatability is calculated as a standard deviation from these.

The hysteresis and the linearity of the instrument are analysed from the results.

1.4 Analyser preparation

Before starting the actual calibration measurements, the analyser needs to be allowed to warm-up according to the manufacturer's recommendation. Zero level (baseline) of the analyser is checked after the warm-up time is completed. It is also recommended to check the zero level after every measurement and adjust it, if necessary.

EXAMPLE. Typically, a warm-up time of minimum two hours is needed for the system to warm-up. The warm-up time may change according to the set-up and/or the equipment, e.g., the manufacturer of the two-channel analyser recommends five hours warm-up time, or even longer.

Zero level is checked after the warm-up time. During the first few hours of measurements if a small drift of the zero level is still observed, the zero level should be checked after each measurement. Thermal conversion warmup and stability should be considered as well as moisture removal system if used. In most cases a sub sample of the calibration gas from a bypass flow will be taken as flow rates from the analyser and generator may not be compatible especially if a thermal conversion is used.

1.5 Calibration gas mixtures

Calibration gas mixtures are generated using the primary Hg^0 gas standard. The uncertainty of generated gas mixtures is known and documented.

EXAMPLE. The reference gas mixtures generated by the primary Hg^0 gas standard can be used to directly calibrate the analyser. Eight different Hg^0 concentrations are generated according to measurement plan.

The calibration is performed at laboratory conditions at ambient pressure and in room temperature (20 °C). Calibration medium is the same as during usage. The calibration points include both minimum and maximum flow control set points, and the actual flow set points during usage. However, this is not the case for fixed output generator and amalgamation systems can take a fixed output and then collect different volumes to have different mass loadings.

1.6 Measurements

The generated gas mixture is supplied from the primary Hg^0 gas standard to the analyser through the inert pipeline (e.g., Teflon tubing). The analyser reading is observed and waited to be stabilized. After the stabilization period the analyser reading is recorded such a period, that enough data for the result analysis is achieved considering the setup response time and measurement time, e.g., for five minutes.

EXAMPLE After stabilisation of the measurement response, the average response displayed by the two-channel analyser is recorded for both channels (Hg^0 and Hg^{tot}) over a period of approximately 15

– 20 minutes. Recorded measurement data includes the supplied concentration from the gas standard and the outputs from the analyser. In general, if the oxidised Hg generator is using heated transport lines, then the elemental primary generator should do the same to mitigate differences due to transportation.

The calibration is repeated three times during different days to get enough data for the analysis. In this way there is proper data for the hysteresis and the linearity analyses too (see 5.1.3 Measurement plan).

1.7 Data analysis

The recorded measurement data is analysed for hysteresis, linearity, standard deviation, repeatability, and reproducibility.

The hysteresis of the analyser is determined from measurements of the Hg concentrations by going through the measurement points from the lowest Hg concentration to the highest Hg concentration and back to the lowest Hg concentration.

The average and the standard deviation for the recorded analyser readings are calculated.

The calibration data is analysed according to EN ISO 6143:2006 [3]. The obtained regression coefficients can then be used to calculate the mercury concentrations in the real on-site measurements, or from an Hg^0 or Hg^{II} generator.

The analyser software settings and coefficients saved to the device memory needs to be checked and documented. The settings must remain the same during the actual use after calibration measurements, too.

EXAMPLE. The measurements points are repeated from the lowest Hg concentration to the highest Hg concentration and back to the lowest Hg concentration. The hysteresis is calculated from the difference of the ascending and descending responses.

The calibration data is analysed according to EN ISO 6143:2006 [3], which is an international standard providing methods to determine the analysis function and to calculate the concentration and corresponding uncertainty of calibration gas mixtures.

A linear fit is used to plot the data obtained with primary Hg^0 gas standard and the two-channel analyser. The regression coefficients and full covariance matrices are obtained for each measurement.

The repeatability is determined by interpolating the calibration data obtained on two latter measurement days as unknown in the calibration on the first measurement day. The repeatability is the standard deviation during one measurement period.

The reproducibility is the standard deviation between the six measurements of one concentration on three different days.

1.8 Results

Reporting the results including measurement uncertainty from characterization of dual channel mercury analyser and explanation of the process of obtaining the different uncertainty terms is presented in the 19NRM03 SI-Hg project Deliverable 4 document [4].

2. Calibration of a reference gas generator

2.1 Traceability

The generator output needs to be calibrated against a traceable standard to ensure the traceability of the generated gas mixture. To confirm the output of oxidised mercury generator the output is measured using the calibrated analyser from previous chapter. Furthermore, the preparation and purity, stability, and accuracy of the evaporated liquid mixtures as well as the converter efficiency is essential to obtain SI traceability.

EXAMPLE. The output of the liquid evaporative $HgCl_2$ generator is calibrated using the calibrated two-channel analyser.

2.2 Measurement plan

A measurement plan for the generator output calibration is made. In the plan, the calibration range and the calibration points within the range are determined. Additionally, measurement sequences are needed to investigate the repeatability and reproducibility, linearity, and hysteresis.

The selected calibration points should include at least points close to both minimum and maximum values of the generator's operational range, and enough points between those. It is highly recommended to include those concentration points, where the generator is most typically going to be used. This ensures to get enough information for linearity analysis and optimises the corrections and fitting curves used during the actual field usage of the analyser by avoiding large interpolations based on calibration data.

To observe the possible hysteresis from the calibrations results, the selected calibration points need to be generated in order from minimum towards maximum value, and the same in the opposite direction.

EXAMPLE Eight different Hg^0 concentrations are selected as calibration points. During the calibration each measurement point is measured at least three times, and the average of the recorded readings is used as a measured result for that point. Short time repeatability is calculated as a standard deviation from these.

The hysteresis and the linearity of the instrument are analysed from the results.

2.3 Generator preparation and generator details

Before starting the actual calibration measurements, the generator is allowed to warm-up according to the manufacturer's recommendation.

Zero level (baseline) and its stability are checked after the warm-up time is completed. For an evaporative generator this should be made using both dry and humid gas with water content set to value typical to measurement conditions since the actual calibration gas made through evaporation is humid gas as well. The humid gas can detach mercury, which is adsorbed on the system surfaces in contact with the generated gas. Ultrapure water is dosed to the evaporator. It is also recommended to check the zero level during the calibration measurements.

EXAMPLE Typically a warm-up time of minimum 30 minutes is needed for the system to warm-up. During the warmup, a clean, dry air flow is running through the system. The warm-up time may change according to the set-up and/or the equipment.

Specific properties of different types of generators, i.e., liquid-based gas generators, dry based gas generators and Hg^0 to Hg^{II} converter systems, are considered following manufacturer's instructions. Especially warm-up and stabilization times typically differ according to different operation principles.

2.4 Measurements

The generated gas mixture is supplied from the generator to the analyser. A slip stream is normally used as total generator flow is different to analyser flow. The analyser reading is observed and waited to be stabilized. After the stabilization period the analyser reading is recorded over such a period, that enough data for the result analysis is achieved considering the setup response time and measurement time.

EXAMPLE For the calibration of the liquid evaporative $HgCl_2$ generator, two different liquid mixtures are used. The preparation of the liquid solution normally has two stages. The first stage is a base solution, which may be a commercial solution, or self-made solution prepared, e.g., by dissolving powder of pure solid chemical (mercury salt) in acidic water. The Hg concentration and purity analysis can be ordered from the institutes or suppliers providing chemical analyses. It is possible to analyse the solution concentration using atomic absorption spectrometry after $SnCl_2$ reduction or CV-AFS measurement according to EN ISO 17852 and to calibrate the measurement system using NIST Standard Reference Material (SRM) 3133. More information on the uncertainty estimation for the self-made solutions and the stability of liquid mixtures used for the calibration of Hg^{II} gas generators can be found on the 19NRM03 SI-Hg project document *Good Practice Guide on the Storage and Stability of* $HgCl_2$ *Solutions and Salts for Use with Mercury Gas Generators* [5].

Selected liquid flows are evaporated with selected flow of carrier gas (nitrogen) to obtain 8 different Hg concentrations. For an evaporative generator this should include both dry and humid zero gases. These outputs from the generator are analysed using the calibrated two-channel analyser.

2.5 Data analysis

The calibration data is analysed according to EN ISO 6143:2006 [3]. Based on the analysis, the generators theoretical, calculated output concentration value is compared to the response from the analyser. The uncertainties of both the generator output and the analyser measurement capability needs to be considered when comparing these results. From these results, a calibration curve and uncertainty budget are calculated. These are specific values for the calibrated generator in relation to the conditions used.

EXAMPLE In the calibration of the liquid evaporative $HgCl_2$ generator, repeatability of the measurement data for the Hg^{tot} concentration is determined when using 1s sampling time in two-channel analytical system for consecutive measurement points. Averaging the measurement data gives even lover values for repeatability corresponding longer measurement time, e.g., 1 min.

2.6 Results

Reporting the results including measurement uncertainty for a reference gas generator is presented in the 19NRM03 SI-Hg project Deliverable 6 document [6].

Annex A
(informative)

Calibration protocol: Step by step flow chart

The calibration protocol to calibrate and confirm the output of different types of dynamic Hg^{II} gas generators is shown as a step-by-step flow chart in the Figure 1.

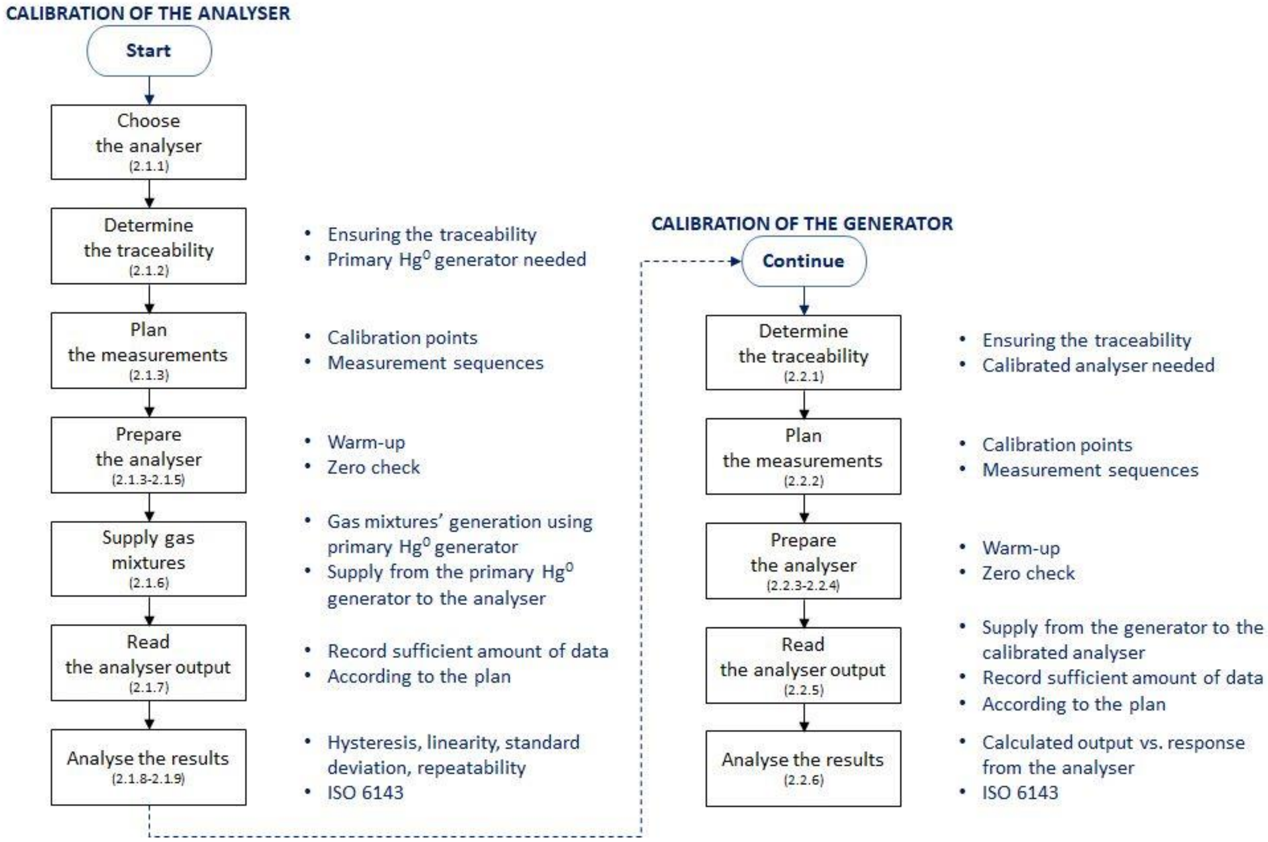


Figure A.1 — A step by step flowchart of the calibration protocol.

References

[1] I. de Krom, W. Bavius, R. Ziel, E. Efremov, D. van Meer, P. van Otterloo, I. van Andel, D. van Osselen, M. Heemskerk, A.M.H. van der Veen, M.A. Dexter, W.T. Corns, H. Ent, Primary mercury gas standard for the calibration of mercury measurements, Measurement 169 (2021) 108351, Doi: https://doi.org/10.1016/j.measurement.2020.108351

[2] I. de Krom, W. Bavius, R. Ziel, E.A. McGhee, R.J.C. Brown, I. Živković, J. Gačnik, V. Fajon, J. Kotnik, M. Horvat, H. Ent, Comparability of calibration strategies for measuring mercury concentrations in gas emission sources and the atmosphere, Atmos. Meas. Tech., 14 (2021) 2317, Doi: https://doi.org/10.5194/amt-14-2317-2021

[3] EN ISO 6143:2006. Gas analysis. Comparison methods for determining and checking the composition of calibration gas mixtures.

[4] T. Rajamäki, H. Söderblom, I. Živković, S. Page, W.T. Corns, M. Dexter, I. de Krom, Validation report for the calibration of oxidised mercury gas generators including (1) metrological evaluation of state-of-the-art dual Hg0 and HgII analytical systems, (2) repeatability, reproducibility, and uncertainty evaluation of the calibration procedures at representative concentration levels extended to the low ng/m^3, 2023, https://zenodo.org/records/10204446

[5] S. Page, P. Dunn, J. Entwisle, S. Hill, H. Goenaga-Infante, J. Koesters, C. Röllig, Good practice guide on the storage and stability of HgCl2 solutions and salts, 2023, Good Practice Guide on the Storage and Stability of HgCl2 Solutions and Salts (zenodo.org) DOI: 10.5281/zenodo.10039500

[6] T. Rajamäki, H. Söderblom, I. Živković, C. Röllig, I. de Krom, Report on the performance evaluation of at least three oxidized mercury gas generators on the market, 2023, https://zenodo.org/records/10204452