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Swiss Confederation

Federal Institute of Metrology METAS

Dutch Metrology Institute

Comparison of primary standards for liquid nano flow rates

Pilots

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1 Introduction

An intercomparison has been organized with the purpose to determine the degree of equivalence of several newly developed primary standards for liquid flow rates from 3 mg/h up to 200 mg/h (equivalent with 50 nl/min to 3.3 µl/min). The operating conditions are ambient pressure and temperature.

The development of (most of) the primary standards as well as this intercomparison is part of the MeDD project [4]. Hence, the ultimate goal is to validate the claimed uncertainties of the accompanying primary standards. This intercomparison is complementary to EURAMET project 1291/ EURAMET.M.FF.S7 [3] to cover even lower flow rates (project 1291 covers flow rates from 0.12 g/h up to 200 g/h, equivalent to 2 µl/min to 3.3 ml/min).

This report discusses the protocol (measurement procedures) as well as the results following the intercomparison. It is organized as follows. Section 2 gives the participants and followed time schedule. Section 3 discusses the transfer standards used, whereas Section 4 discusses the protocol. Next, Section 5 discusses the results which are evaluated in Section 6. Finally, in Section 7, the conclusion is drawn.

2 Participants and time schedule

For the intercomparison two different transfer standards have been used: a chip-based Coriolis flow meter from Bronkhorst High-Tech [5] [6] and a thermal volume flow meter from Sensirion [7].

The 3 participants for the Coriolis meter are shown in Table 1, whereas the 2 participants for the thermal volume flow meter are shown in Table 2. Following Table 1 there are several gaps in the dates. This is because several labs had (initially) issues with performing the calibrations which caused delays. Also there has been one major delay at one of the customs.

Following Table 1 and Table 2 only METAS participated in both intercomparison, despite the ranges overlap. FH Lübeck did not participate in the former intercomparison because at that time the focus was on syringe pumps. VSL did not participate in the latter intercomparison because of practical challenges.

Prior to the intercomparison based on the Sensirion volume flow meter, METAS performed calibrations at the flow rates 140 nl/min, 220 nl/min and 300 nl/min to study the reproducibility and the suitability of this flow meter as transfer standard. It was later decided to widen the range of flow rates by adding 60 nl/min (below the scope of the facility at METAS). Therefore, the selected flow rates are 60 nl/min, 100 nl/min and 500 nl/min. The flow rate of 220 nl/min has been omitted to shorten the measurement time of each laboratory. However, METAS has performed the calibration at 220 nl/min as well to get information on any possible drift of the thermal volume flow meter.

Table 1 Participants and time schedule intercomparison based on Coriolis flow meter.

id	Laboratory (country)	Contact Person	Date	remarks
1	VSL, Netherlands	Peter Lucas	April 2014	Calibration by partner, indicated flow rate 8 to 108 mg/h, measured in the opposite flow direction.
2	METAS, Switzerland	Hugo Bissig	June 2014	Calibration by partner, indicated flow rate 7 to 202 mg/h, measured in the opposite flow direction.
3	Bronkhorst High-Tech, Netherlands	Joost Lötters	October 2014	Calibration by partner, indicated flow rate 3 to 200 mg/h, measured in the default flow direction.

Table 2 Participants and time schedule intercomparison based on thermal volume flow meter.

id	Laboratory (country)	Contact Person	Date	remarks
1	METAS, Switzerland	Hugo Bissig	March/ April 2014	First calibrations for the flow rates 140 nl/min, 220 nl/min and 300 nl/min.
2	FH Lübeck, Germany	Martin Ahrens	December 2014	Calibrations for the flow rates 500 nl/min, 100 nl/min and 60 nl/min.
3	METAS, Switzerland	Hugo Bissig	March/ April 2014	Calibrations for the flow rates 500 nl/min, 220 nl/min, 100 nl/min and 60 nl/min.

3 Transfer standard

3.1 Chip based Coriolis flow meter

A chip-based Coriolis flow meter from Bronkhorst High-Tech has been used [5] (M10.7n, full scale flow rate 2 g/h, zero stability 2 mg/h), see Figure 1. The transfer standard has been transported only by road to avoid the possible impact of low pressure on the flow meter curve (low pressure may lead to different mechanical stresses and thus a reduced reproducibility).

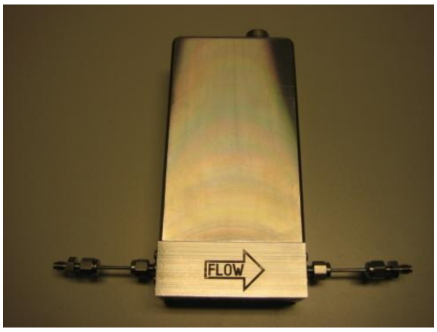

Figure 1 Chip-based micro Coriolis mass flow sensor with 1/16" OD stainless steel tubes with an internal diameter of 125 µm to connect the chip.

3.2 Thermal volume flow meter

A thermal flow meter from Sensirion AG has been used (type SLG 1430-025, serial number 1216-00025, flow rate range 50 nl/min to 1500 nl/min) [7], see Figure 2. The transfer standard has been transported only by road to avoid the possible impact of low pressure on the flow meter curve (low pressure may lead to different mechanical stresses and thus a reduced reproducibility).

Figure 2 Thermal volume flow meter SLG1430-025 from Sensirion AG.

4 Measurement procedure

4.1 Measured quantity

The intercomparison is based on comparing the relative error of the transfer standard as determined by the participating labs. The relative error is defined as:

$$\varepsilon = 100\,\frac{q_{indicated} - q_{ref}}{q_{ref}} \tag{1}$$

where $q_{indicated}$ is the indicated flow rate and q_{ref} is the reference flow rate.

4.2 Facilities

In Table 3 an overview is given of the participating laboratories, the type of facility, calibration procedure and references for further reading if existing. All laboratories are independent.

Table 3 Overview participating laboratories, type of facility, calibration procedure and references for further reading.

Laboratory (country)	Facility type	Calibration procedure	Further reading
Bronkhorst High-Tech	Gravimetric, submerged dispensing needle, layer of oil on top of the water surface to avoid evaporation	Dynamic	[5]
FH Lübeck	Front tracking of a moving meniscus in a capillary of known dimensions	Start/ stop	[1]
METAS	Gravimetric, continuous water flow by means of water bridge of 50 μm from dispensing needle to fast water absorbing material in beaker, nearly saturated air around beaker and fast water absorbing material to avoid evaporation	Dynamic	[8]
VSL	Volumetric flow rate based on expansion of a volume due to a temperature gradient	Dynamic	[2]

4.3 Calibration protocol and measurement conditions

In this section the calibration protocol is described and the (range of) measurement conditions are given. The following (range of) measurement conditions has been used:

- Upstream pressure: 0.5 to 2.5 bar depending on the required flow rate.
- Water temperature between 20 °C and 23 °C.
- Minimal measurement time depends on the set up, however sufficient to have a stable flow over at least one minute.
- A minimum of 3 repetitions.
- Target flow rates for the Coriolis flow meter: (3, 6, 20 and 200) mg/h (equivalent to (50, 100, 333 and 3333) nl/min). Target flow rates for the thermal flow meter: 60 nl/min, 100 nl/min and 500 nl/min (equivalent to (3.6, 6 and 30) mg/h).

Each participant used their own calibration procedures to calibrate the flow meter at the various flow rates. However, at least the following measures were taken:

- After receiving the flow meter visually inspect the meter for damages and whether the package is complete. If all looks well install the meter in the horizontal plane and turn it on. Perform leak tests and make sure the installation is water tight.
- Purge the meter with fully degassed and pure water (deminiralized, or single/ double distilled water). Purge sufficiently long to make sure there is no dissolved and/ or entrapped air upstream of the flow meter. For this particular flow meter a good check is to quickly open and close a valve just up and downstream of the meter (be careful not to damage anything in case a volumetric/ positive displacement type pump is used). In case the flow meter jumps to zero and back within 0.5 seconds, the system is typically properly degassed. Note 1, some labs pre-primed the system with CO_2 gas or created a (near) vacuum downstream of

the meter as this sometimes helps in a quicker degasification. Note 2, not all labs measured the flow meter error in the same direction, see Table 1, However, preliminary results showed this has a negligible impact on the meter error.

- For the flow rate at hand, wait for stable temperature conditions. At stable conditions, create zero flow rate and ambient pressure. Either zero the flow meter or measure the flow rate indication for a minute. Correct the results in case the flow meter has not been zeroed.
- Calibrate the flow meter using the laboratory calibration procedure. Determine the flow rate error as defined in Section 4.1.

5 Measurement results

5.1 Stability of the transfer standards

5.1.1 Coriolis mass flow meter

The stability of the Coriolis flow meter could not be checked by the pilot lab because the foreseen pilot could not perform the measurements. Therefore, the potential drift (reproducibility) of the meter is based on the claimed zero stability of the meter. Following [3][6] the potential drift is typically within the claimed zero stability.

The uncertainty due to drift then follows by assuming a uniform distribution. Hence,

$$U_{drift} = \frac{\Delta\varepsilon}{\sqrt{3}} \quad (2)$$

where U_{drift} (k=2) is the uncertainty due to drift (reproducibility) and $\Delta\varepsilon$ is the claimed zero stability of the meter.

Table 4 Maximum difference Coriolis flow meter error, zero stability and derived uncertainty due to drift.

target flow rate (mg/h)	zero stability (mg/h)	zero stability (%)	uncertainty due to drift (k=2) (%)
3	2	67	38.5
6	2	33	19.3
20	2	10	5.8
200	2	1	0.6

5.1.2 Thermal volume flow meter

The stability of the volume flow meter could not be fully checked by the pilot lab because of time constraints. Therefore, the drift (reproducibility) of the meter is assessed by studying repeated measurement at 220 nl/min, see Figure 3 and Table 5.

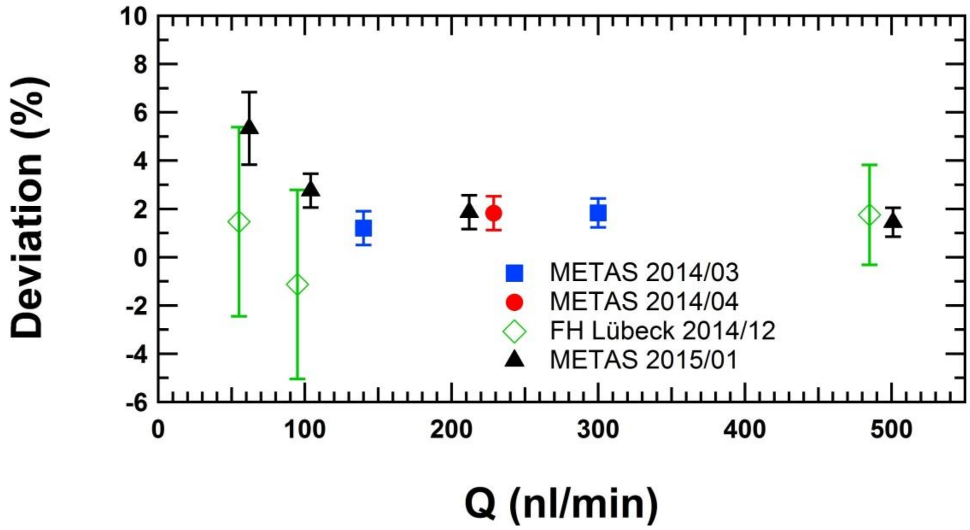

Figure 3 Calibration results at all flow points conducted by METAS and FH Lübeck.

Table 5 Repeated measurement results from METAS at the flow rate of 220 nl/min.

	METAS	
target flow rate (nl/min)	error 1st series (%)	error 2nd series (%)
202		1.84
224		1.88
225	1.54	
226	1.87	
229	1.93	
235	1.92	

The maximum difference at the flow rate *around* 220 nl/min is 0.39 %. The uncertainty due to drift then follows by assuming a uniform distribution from Eq. (2). As the flow meter was not tested for reproducibility at the other flow points, the determined drift of 0.23% (0.39% divided by $\sqrt{3}$) at 220 nl/min is taken for all the flow rates. This seems a fair assumption because the flow meter curve is rather flat.

Table 6 Maximum (estimated) difference thermal volume flow meter error and derived uncertainty due to drift

target flow rate (nl/min)	uncertainty due to drift (k=2) (%)
60	0.23
100	0.23
500	0.23

5.2 Laboratory results

5.2.1 Coriolis mass flow meter

In Table 7 the calibration results are shown for the Coriolis flow meter. The maximum indicated flow rate at VSL is significantly lower than the target flow rate. This is because this standard cannot reach larger flow rates.

Table 7 Error (%) as determined by the participating labs and for the indicated flow rate.

	Bronkhorst High-Tech		METAS		VSL	
Target flow rate (mg/h)	indicated flow rate (mg/h)	error (%)	indicated flow rate (mg/h)	error (%)	indicated flow rate (mg/h)	error (%)
3	3	-27.3	-	-	-	-
6	6	0.44	7	10.5	8	21.1
20	20	4.44	23	5.0	22	4.54
200	200	1.73	202	1.14	108	1.16

5.2.2 Thermal volume flow meter

In Table 8 the calibration results are shown for the thermal volume flow meter.

Table 8 Error (%) as determined by the participating labs and for the indicated flow rate.

	FH Lübeck		METAS	
Target flow rate (nl/min)	indicated flow rate (nl/min)	error (%)	indicated flow rate (nl/min)	error (%)
60	61.2	1.47	62.4	5.33
100	102.7	-1.13	104.2	2.76
500	488.8	1.75	501.0	1.45

5.3 Uncertainty

5.3.1 Coriolis flow meter

In Table 9 and Table 10 the calibration uncertainty (k=2) for the flow meter is given. The former table gives the calibration uncertainty including the uncertainty in reference flow and repeatability (sample deviation of the various repetitions divided by the square root of the number of repetitions), whereas in the latter table also the uncertainty due to drift is included.

METAS measured significant variations in the zero flow error and has included this uncertainty in the calibration uncertainty. These variations are expected because of the zero stability of the meter (see again Table 4). One could argue that the zero stability is included twice for METAS in Table 10, however the uncertainty due to drift (based on the *stated* zero stability) dominates the uncertainties given this table. Hence, including also the measured zero stability does not lead to an excessive uncertainty.

Table 9 Calibration uncertainty (%) Coriolis flow meter as obtained by the various labs.

Target flow rate (mg/h)	Bronkhorst High-Tech	METAS	VSL
3	149	-	-
6	104	7.90	21.3
20	32.3	2.40	6.31
200	3.14	0.45	3.12

Table 10 Calibration uncertainty (%) including drift Coriolis flow meter.

Target flow rate (mg/h)	Bronkhorst High-Tech	METAS	VSL
3	154	-	-
6	106	20.8	28.7
20	32.8	6.25	8.55
200	3.19	0.73	3.17

5.3.2 Thermal volume flow meter

In Table 11 and Table 12 the calibration uncertainty (*k*=2) for the thermal volume flow meter is given. The former table gives the calibration uncertainty including the uncertainty in reference flow and repeatability (sample deviation of the various repetitions divided by the square root of the number of repetitions), whereas in the latter table also the uncertainty due to drift is included.

It is worthwhile to mention at this point that the flow rate of 60 nl/min is below the stated measurement capabilities of the facility at METAS. Nevertheless, METAS has performed the calibration at this low flow rate to get information about the limits of the calibration possibilities of this gravimetric setup.

Table 11 Calibration uncertainty thermal volume flow meter as obtained by the two labs.

Target flow rate (nl/min)	FH Lübeck (%)	METAS (%)
60	4.0	1.5
100	4.0	0.7
500	2.1	0.6

Table 12 Calibration uncertainty including drift thermal volume flow meter.

Target flow rate (nl/min)	FH Lübeck (%)	METAS (%)
60	4.0	1.6
100	4.0	0.74
500	2.1	0.65

6 Evaluation

In this Section the results are evaluated. Key of this evaluation is to study whether the calibration results of the various labs are consistent with each other. To judge whether the results are consistent the E_n is used, defined as:

$$E_{n_{lab-i}} = \frac{\varepsilon_{lab-i} - \varepsilon_{RV}}{\sqrt{U^2(\varepsilon_{lab-i}) - U^2(\varepsilon_{RV})}} \tag{3}$$

where ε_{lab-i} is the error of lab-*i* for a certain flow point, ε_{RV} is the comparison reference value for the error and $U(\varepsilon_{lab-i})$ and $U(\varepsilon_{KCRF})$ and the expanded uncertainties (*k*=2) of those values. The (expanded) uncertainty include the uncertainty in reference flow rate, repeatability and the reproducibility (see Section 5.1). The repeatability is defined as the sample standard deviation divided by the square root of the number of repetitions. Note, in case only two labs participate the E_n value can be determined directly without the need to determine the reference value (RV).

The value of E_n has the following meaning:

- The results of a laboratory for a certain flow point are consistent (passed) if $E_n \leq 1$
- The results of a laboratory for a certain flow point are inconsistent (failed) if $E_n > 1.2$
- For results between $1 < E_n \leq 1.2$ a “warning level” is defined. For this particular situation the particular lab is recommended to check the procedures and methodology.

The comparison reference value is the uncertainty weighted average of the error and is determined as follows:

$$\varepsilon_{RV} = \frac{\sum_{i=1}^{n} \varepsilon_{lab-i} / U^2(\varepsilon_{lab-i})}{\sum_{i=1}^{n} 1 / U^2(\varepsilon_{lab-i})} \quad (4)$$

where *n* is the number of participating labs. The uncertainty of the reference value follows from:

$$u(\varepsilon_{RV}) = \frac{1}{\sqrt{\sum_{i=1}^{n} 1 / U^2(\varepsilon_{lab-i})}} \quad (5)$$

Finally, when there are more than 2 independent results for a certain flow point, the chi-squared test is applied to see whether the determined errors and accompanying uncertainties can be expected based on a Gaussian distribution. If so, the reference value can be accepted. The chi-squared test is defined as follows, for each flow point, chi-squared is defined as:

$$\chi^2_{obs} = \sum_{i=1}^{n} \left(\frac{\varepsilon_{lab-i} - \varepsilon_{RV}}{u(\varepsilon_{lab-i})} \right)^2 \quad (6)$$

Note, here $u(\varepsilon_{lab-i})$ is the standard uncertainty (*k*=1). The set of measurement results for a certain flow point is only accepted when:

$$Pr\left(\chi^2(n-1) > \chi^2_{obs}\right) < 0.05 \quad (7)$$

where *Pr* stands for probability and $\chi(n)$ is the expected value for a Gaussian distribution. Using the CHIINV(probability, degrees of freedom-1) function from Excel, this can be rewritten as follows for a consistent set (coverage factor 95%):

$$\chi^2_{obs} < CHIINV(0.05; n-1) \quad (8)$$

Hence, if the observed chi-squared value satisfies the above equation, the reference value is accepted. If not, the results leading with the largest contribution to χ^2_{obs} are discarded and the test is repeated.

6.1 Coriolis mass flow meter

In Figure 4 and Figure 5 the calibration results of the labs are shown. The plotted flow rates do not represent the indicated flow rate, however have been given an artificial off set (compared to the target flow rate) for reasons of visibility. For example, the last series of measurements all have a target flow rate of 200 mg/h.

Note, the indicated flow rates are not equal for the various labs (see again Table 7). Nevertheless, all flow points are treated as if the indicated flow rate is the same. For the larger flow rates the calibration curve of the meter is quite flat which makes this a fair assumption. For the lowest two flow points the significant calibration uncertainty covers for this mismatch.

The uncertainty include the uncertainty in reference flow rate, repeatability and the drift (see Section 5.1). Next, in Table 13 the E_n value is given, whereas in Table 14 the comparison reference value and its uncertainty are given (following Eq. (4)). Finally, in Table 15 the final results for the chi-squared test are given.

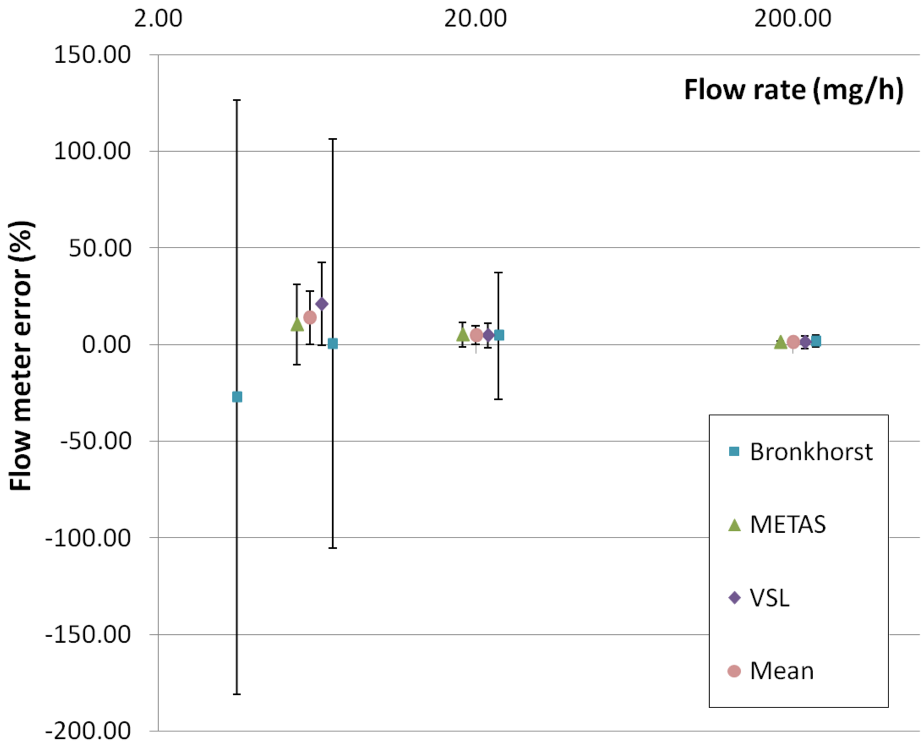

Figure 4 Results intercomparison. The uncertainty includes the uncertainty in reference flow rate, repeatability of the calibration and the uncertainty due to drift. The indicated flow rate has been modified for visibility.

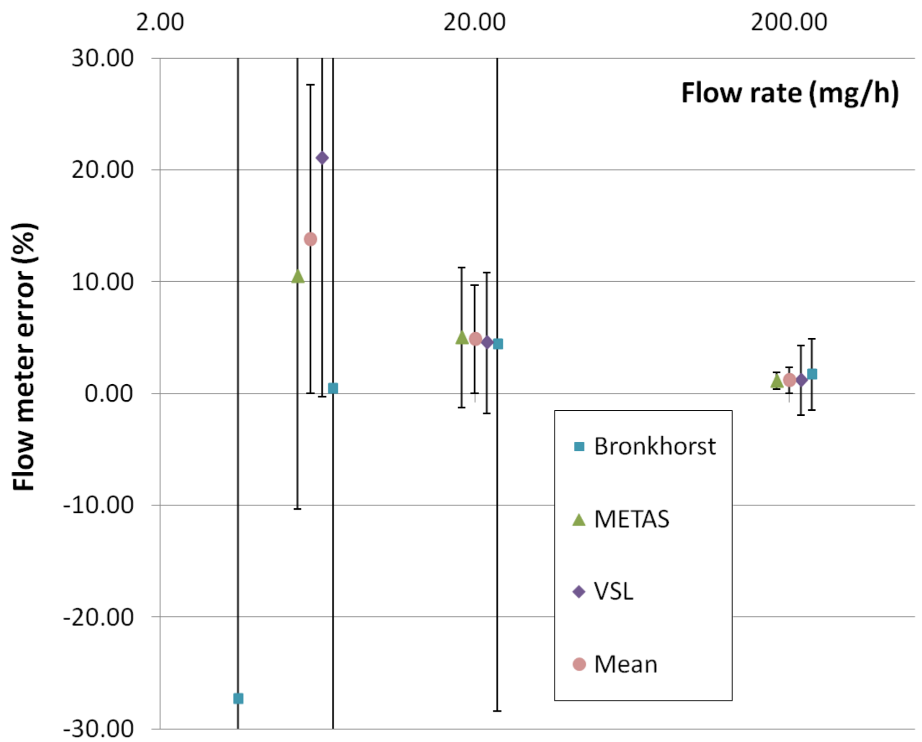

Figure 5 Results intercomparison, close up of Figure 4. The uncertainty includes the uncertainty in reference flow rate, repeatability and the uncertainty due to drift. The indicated flow rate has been modified for visibility.

From Table 15 it follows that the reference value can be accepted (the distribution around the RV is conform a Gaussian distribution). Next, from Figure 4 and Table 13 it follows all results are consistent with each other.

Table 13 Degree of equivalence (E_n value), determine with Eq. (3).

Target flow rate (mg/h)	Bronkhorst High-Tech	METAS	VSL
3	-	-	-
6	0.13	0.12	0.31
20	0.01	0.02	0.04
200	0.18	0.03	0.00

Table 14 Comparison reference value for the error (%) and uncertainty (%), determined with Eq. (4) and Eq. (5) respectively.

flow rate (g/h)	error	uncertainty
3	27.3	154
6	13.8	16.6
20	4.83	4.99
200	1.17	0.70

Table 15 Observed chi-squared value χ^2_{obs}, population size *n* and threshold $\chi^2(n-1)$, determined with Eq. (8).

flow rate (mg/h)	n-1	χ^2_{obs}	$\chi^2(n-1)$
3	2	-	-
6	2	0.31	5.99
20	2	0.01	5.99
200	2	0.04	5.99

6.2 Thermal volume flow meter

In Figure 6 the calibration results of the two labs are shown. The plotted flow rates do not represent the indicated flow rate, however have been given an artificial offset compared to the target flow rate for reasons of visibility.

The uncertainty include the uncertainty in reference flow rate, repeatability and the drift (see Section 5.1). Next, in Table 16 the En value is given, whereas in Table 17 the reference value and its uncertainty are given. For this intercomparison the chi-squared test is not performed because there are only 2 participants. From Figure 6 and Table 16 it follows the results are consistent with each other.

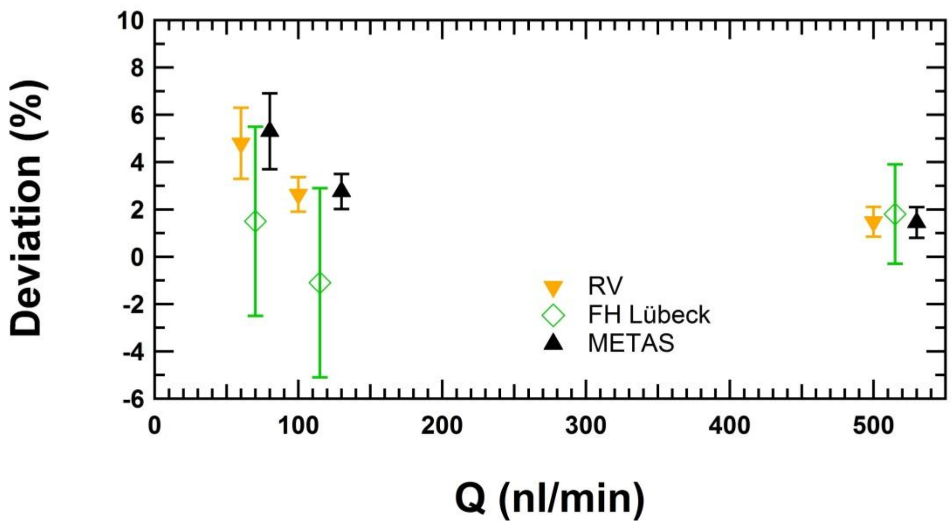

Figure 6 Results intercomparison. The uncertainty includes the uncertainty in reference flow rate, repeatability of the calibration and the uncertainty due to drift. The indicated flow rate has been modified for visibility.

Table 16 Error, uncertainty and degree of equivalence (En value), determine with Eq. (3).

	FH Lübeck		METAS		
Target flow rate (nl/min)	error (%)	uncertainty (%)	error (%)	uncertainty (%)	E_n
60	1.5	4.0	5.3	1.6	0.88
100	-1.1	4.0	2.76	0.74	0.95
500	1.8	2.1	1.45	0.65	0.16

Table 17 Comparison reference value for the error (%) and uncertainty (%), determined with Eq. (4) and Eq. (5) respectively.

flow rate (g/h)	error	uncertainty
60	4.8	1.5
100	2.63	0.73
500	1.48	0.63

7 Conclusion

A first research intercomparison for nano low liquid flow rates has been conducted. For this intercomparison both a thermal flow and Coriolis mass flow sensor have been used. For both these transfer standards good results have been achieved, i.e. the labs are in agreement within the uncertainty (even when taking into account that a flow rate of 60 nl/min is below the stated measurement capabilities of the facility at METAS).

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