Comparison of standards for low liquid flow rates

EURAMET project 1379

October 23, 2017

Pilot

VSL, Netherlands – Peter Lucas

1 Introduction

A comparison has been organized in order to determine the degree of equivalence of standards for liquid flow rates in the range of 0.5 to 10 kg/h (ambient pressure and temperature). A Bronkhorst Coriolis mass flow meter is used as the transfer standard. If laboratories were not able to cover the whole range, they calibrated the transfer standard over a part of the range.

This report discusses the protocol 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 standard used, whereas Section 4 discusses the protocol used. 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

The participants and schedule are shown in Table 1. It was scheduled VSL would determine the uncertainty due to drift, however later it was found the results of the first measurements (VSL, January 2016) were compromised. These results were therefore discarded and DTI repeated the measurements (December 2016) in order to determine the uncertainty due to the drift. IPQ and SP initially planned to participate in the comparison, however finally did not because their calibration facility was not ready.

Table 1 Participants intercomparison. BHT stands for Bronkhorst High-Tech.

id	Laboratory (country)	Contact Person	Date	remarks
1	VSL (PILOT)	Peter Lucas plucas@vsl.nl	January 2016	
2	DTI	Anders Koustrup Niemann aknn@teknologisk.dk	February 2016	Maximum flow rate 6 kg/h
3	CMI	Miroslava Benková mbenkova@cmi.cz	February 2016	Maximum flow rate 6 kg/h
4	CETIAT	Florestan Ogheard florestan.ogheard@cetiat.fr	March 2016	
5	VSL	Peter Lucas plucas@vsl.nl	April 2016	
6	BHT	Joost Lötters J.C.Lotters@bronkhorst.com	July 2016	Third party, no contribution to the reference value
7	METAS	Hugo Bissig Hugo.Bissig@metas.ch	Aug 2016	Maximum flow rate 6 l/h
8	LEI	Gediminas Zygmantas gediminas.zygmantas@lei.lt	Nov 2016	
9	DTI	Anders Koustrup Niemann aknn@teknologisk.dk	Dec 2016	Maximum flow rate 6 kg/h

3 Transfer standard

3.1 Coriolis flow meter

A Coriolis mass flow standard is used for the intercomparison. See below for the specifications, flow meter and flight case.

Type:	M14-AGD-22-0-S
Manufacturer:	Bronkhorst High-Tech
Zero stability	6 g/h
Q_{max}	10 kg/h
Serial number:	B15201358A
Connection type:	¼"OD Swagelok compression type
Communication:	RS232
Electrical connection:	9 pins sub-D (power connection included)

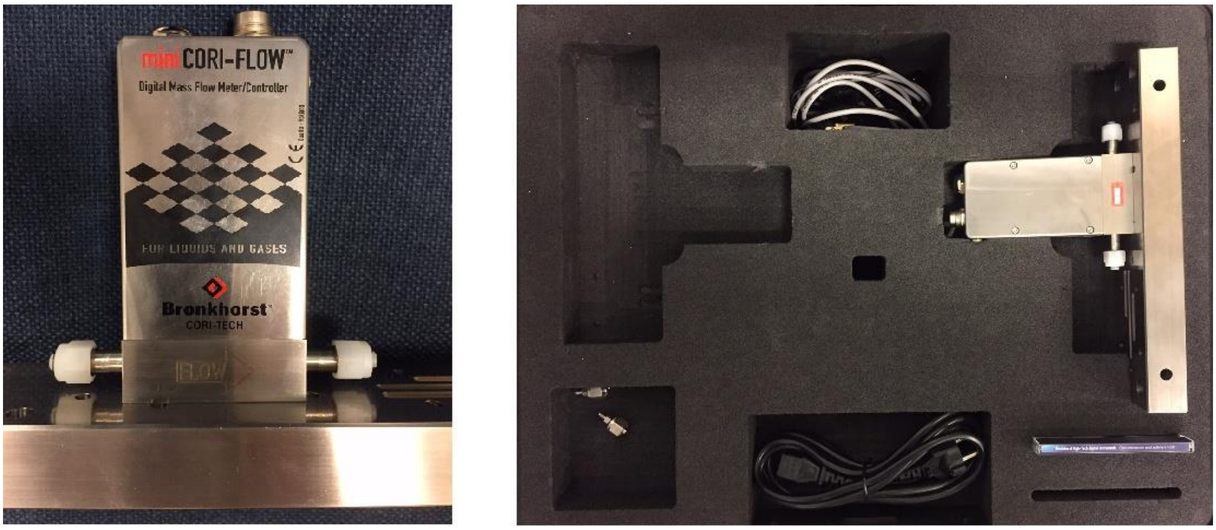

Figure 1 Bronkhorst High-Tech Coriolis mass flow meter (left) and flight case (right)

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 ε (%) 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

The participating National Metrology Institutes (NMI) used their own calibration procedures to calibrate the flow meter. In Table 2 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; however Bronkhorst High-Tech does not contribute to the reference value (RV) because it is not an NMI or DI.

Table 2 Overview participating laboratories, type of facility, calibration procedure and references for further reading if existing.

Laboratory (country)	Facility type	Calibration procedure	Further reading
BHT	Gravimetric, submerged dispensing needle, nearly saturated air around beaker to avoid evaporation	Dynamic	
DTI	Gravimetric, submerged dispensing needle, layer of oil on top of the water surface to avoid evaporation	Dynamic	[1]
CETIAT	Gravimetric, submerged dispensing needle, nearly saturated air around beaker to avoid evaporation	Start/ stop	[1]
CMI	Gravimetric method, with pumps, nearly saturated air around beaker to avoid evaporation, measurement through secondary mass standards	Start/ stop	
LEI	Gravimetric, not-submerged needle, nearly saturated air around beaker to avoid evaporation	Dynamic	
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	[1]
VSL	Gravimetric, submerged dispensing needle, nearly saturated air around beaker to avoid evaporation	Dynamic	[1]

4.3 Calibration protocol and measurement conditions

In this section the calibration protocol is described and the (range of) measurement conditions are given.

The M14 Coriolis flow meter has been used together with 1/4” OD Swagelok compression fittings, including adapters to 1/8” OD Swagelok compression fittings. No upstream or downstream tubing has been included. The M14 was fixed on a mass block.

The following procedure was used to calibrate the flow meter:

- After receiving the flow meter visually inspect the meter for potential damage 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 (demineralized, or single/ double distilled water). Purge sufficiently long to make sure there is no dissolved and entrapped air upstream of the flow meter and between the meter and the measurement beaker. For this particular flow meter a good check is to quickly open and close a valve just up and

downstream of the meter. In case the flow meter jumps to zero and back within 0.5 seconds, the system is typically properly degassed.

- For each flow, wait for stable temperature conditions. At stable conditions, create zero flow rate and ambient pressure. Zero the flow meter.
- Calibrate the flow meter using the laboratory calibration procedure and determine the flow rate error as defined in Section 4.1. For the calibrations the upstream pressure should be between 0.5 bar and 5 bar and the temperature between 20°C and 23°C.
- The flow points are: (0.5, 2, 4, 6, 8, 10) kg/h. If the laboratory cannot cover the whole range, they can perform measurements up to the maximum or down to the minimum flow rate.

5 Measurement results

5.1 Stability of the transfer standard

The uncertainty due to drift follows from the difference in measured error by assuming a uniform distribution. Hence,

$$u_{drift} = \frac{\Delta\varepsilon}{2\sqrt{3}} \tag{2}$$

where u_{drift} (k=1) is the uncertainty due to drift (reproducibility) and $\Delta\varepsilon$ is the difference in measured error at the beginning and end of the intercomparison.

The uncertainty due to the drift is added (quadratically) to the calibration uncertainty (uncertainty in reference flow rate and the repeatability which is defined as the sample standard deviation divided by the square root of the number of repetitions). Another approach to treat the uncertainty due to drift is to include it in the uncertainty of the reference value and in the determination of the degree of equivalence (E_n value). However, when the uncertainty due to drift is small compared to the calibration uncertainty, both approaches give similar results (which is typically the case for a carefully selected transfer standard).

The stability of the flow meter is checked by DTI rather than the pilot lab because the first measurement series of the pilot lab appeared compromised. In Table 3 the error (%) is shown for both measurement series as well as the corresponding uncertainty due to drift. In this table also the claimed zero stability of the meter is shown. Upon comparison of the claimed zero stability with the measured drift it follows the meter performs well within specifications.

From Table 3 it follows the uncertainty due to drift is quite small. In fact, compared to the calibration uncertainty of the laboratories the uncertainty due to drift is in most cases negligible. For the largest two flow rates there is no estimate for the uncertainty in drift because the maximum flow rate of DTI is limited to 6 kg/h. Based on the measured values, as well as comparison with the zero stability, an uncertainty due to drift of 0.01% is estimated for these flow rates. Because this uncertainty is small and in negligible to the calibration uncertainty, this estimate seems acceptable (a small uncertainty due to drift implies potential discrepancies between labs are revealed quicker).

Table 3 Reproduced measurement results

target flow rate (kg/h)	error 1st series (%)	error 2nd series (%)	Abs(Δ) (%)	zero stability (%)	uncertainty due to drift (*k*=2) (%)
0,5	-0.071	-0.095	0.024	1.2	0.014
2	-0.027	0.019	0.046	0.3	0.026
4	-0.017	-0.023	0.007	0.15	0.004
6	0.021	0.003	0.018	0.1	0.010
8	N/A	N/A	N/A	0.08	0.01[1]
10	N/A	N/A	N/A	0.06	0.01[1]

[1]Estimated

5.2 Laboratory results

In Table 4 the calibration results of the participating labs are shown. Following the initial analysis, the results for CETIAT appeared significantly off for one or more flow rates. After notification, CETIAT found one or more errors in the analyses and corrected the results twice. Following this correction the results for one or more flow rates of DTI were significantly off. After notifying this lab, DTI also found an error in the analyses and subsequently updated their results. Note, these corrections were performed before Draft A was released and without any prior information.

Note that the indicated flow rate, as well as the error, from LEI differs quite a bit from the other results. However, because of the relatively large uncertainty, this does hardly impact the analyses.

Table 4 Error (%) as function of the indicated flow rate as determined by the participating labs.

	BHT		CETIAT		CMI		DTI		LEI		METAS		VSL	
target flow rate (kg/h)	ind. flow rate (kg/h)	error (%)	ind. flow rate (kg/h)	error (%)	ind. flow rate (kg/h)	error (%)	ind. flow rate (kg/h)	error (%)	ind. flow rate (kg/h)	error (%)	ind. flow rate (kg/h)	error (%)	ind. flow rate (kg/h)	error (%)
0.5	0.50	-0.15	0.51	-0.20	0.50	-0.16	0.51	-0.07	0.55	1.36	0.50	-0.18	0.50	0.76
2	2.00	-0.08	2.01	-0.07	2.00	-0.10	2.03	-0.03	2.18	0.22	1.99	-0.08	2.01	0.12
4	4.00	-0.02	3.98	-0.05	4.01	0.03	4.02	-0.02	4.21	0.11	3.99	-0.04	4.01	0.03
6	6.00	-0.01	5.96	-0.05	6.01	-0.01	6.03	0.02	6.36	0.19	5.99	-0.01	6.02	0.01
8	8.00	0.01	8.00	-0.03	N/A	N/A	N/A	N/A	8.25	0.26	7.98	0.01	8.02	0.00
10	10.0	0.01	10.0	-0.04	N/A	N/A	N/A	N/A	10.2	0.04	9.98	-0.01	10.0	-0.01

5.3 Uncertainty

5.3.1 Calibration uncertainty

In Table 5 and Table 6 the calibration uncertainty (k=2) is given. In the former table the uncertainty due to drift is not included, whereas it is in the latter table. Comparison of these two tables reveals the uncertainty due to drift is indeed very small and in most cases negligible.

Table 5 Calibration uncertainty (k=2) (%) as obtained by the various labs.

flow rate (kg/h)	BHT	CETIAT	CMI	DTI	LEI	METAS	VSL
0.5	0.15	0.10	0.16	0.08	3.8	0.07	0.05
2	0.12	0.10	0.16	0.06	1.1	0.07	0.03
4	0.08	0.10	0.10	0.06	0.71	0.07	0.06
6	0.08	0.10	0.10	0.05	0.78	0.07	0.03
8	0.08	0.10	N/A	N/A	0.47	0.07	0.03
10	0.08	0.10	N/A	N/A	0.30	0.07	0.05

Table 6 Calibration uncertainty (k=2) (%) including drift flow meter for the various labs.

flow rate (kg/h)	BHT	CETIAT	CMI	DTI	LEI	METAS	VSL
0.5	0.15	0.10	0.16	0.08	3.8	0.07	0.05
2	0.12	0.10	0.16	0.06	1.1	0.07	0.04
4	0.08	0.10	0.10	0.06	0.71	0.07	0.06
6	0.08	0.10	0.10	0.06	0.78	0.07	0.03
8	0.08	0.10	N/A	N/A	0.47	0.07	0.03
10	0.08	0.10	N/A	N/A	0.30	0.07	0.05

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 well-known E_n is used. For independent laboratories with a contribution to the RV this value is given as [2]:

$$E_{n\,lab-i} = \frac{|\varepsilon_{lab-i} - \varepsilon_{RV}|}{\sqrt{U^2(\varepsilon_{lab-i}) - U^2(\varepsilon_{RV})}} \qquad (3a)$$

where ε_{lab-i} is the error of lab-*i* for a certain flow point, ε_{RV} is the comparison reference value (RV) for the error and $U(\varepsilon_{lab-i})$ and $U(\varepsilon_{RV})$ are the expanded uncertainties (*k*=2) of those values. For independent laboratories without a contribution to the RV (BHT) this value is given as [2]:

$$E_{n\,lab-i} = \frac{|\varepsilon_{lab-i} - \varepsilon_{RV}|}{\sqrt{U^2(\varepsilon_{lab-i}) + U^2(\varepsilon_{RV})}} \qquad (3b)$$

The (expanded) uncertainty includes 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. Remark, one lab uses the pooled standard deviation rather than the sample standard deviation (see also Table 2).

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:

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

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

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

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:

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

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:

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

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%):

$$\chi_{obs}^2 < CHIINV(0.05; n-1) \tag{8}$$

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

In Figure 2 the calibration results for the flow meter are shown. The plotted flow rates have been given an artificial offset compared to the target flow rate for reasons of visibility. For example, the last series of measurements all have a target flow rate of 10 kg/h. Note, the indicated flow rates are not exactly similar for the various labs (see again Table 4). Nevertheless, because the difference in indicated flow rate is quite small, all flow points are treated as if the indicated flow rate is the same. Further, the calibration curve of the meter is quite flat which makes this a fair assumption.

The uncertainty in Figure 2 include the uncertainty in reference flow rate, repeatability and the drift. Next, in Table 7 the E_n value is given, whereas in Table 8 the reference value (RV) (equation (4)) and uncertainty (equation (5)) are given. Note that Bronkhorst High-Tech (BHT) does not contribute to the reference value as they do not have an NMI or DI status. Finally, in Table 9 the final results from the chi-squared test are given, following equation (6) and (8) and discarding the results from BHT.

The results in Table 7 to Table 9 are obtained when the lowest two flow rates from VSL are discarded. Following the chi-squared test the results for these flow points have been identified as outliers and therefore need to be omitted which results in a consistent set (hence, 1 iteration has been performed where the lab with the largest chi-value is removed from the set). Consequently, the results for these flow points are not used to determine the RV. Next, from Figure 2 and Table 7, it follows most results are consistent; however there are the following warnings and fails:

- VSL, fail for flow rates (kg/h): 0.5, 2 and 6;
- DTI, warning for a flow rate (kg/h) of 0.5.

Figure 2 Results intercomparison. 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.

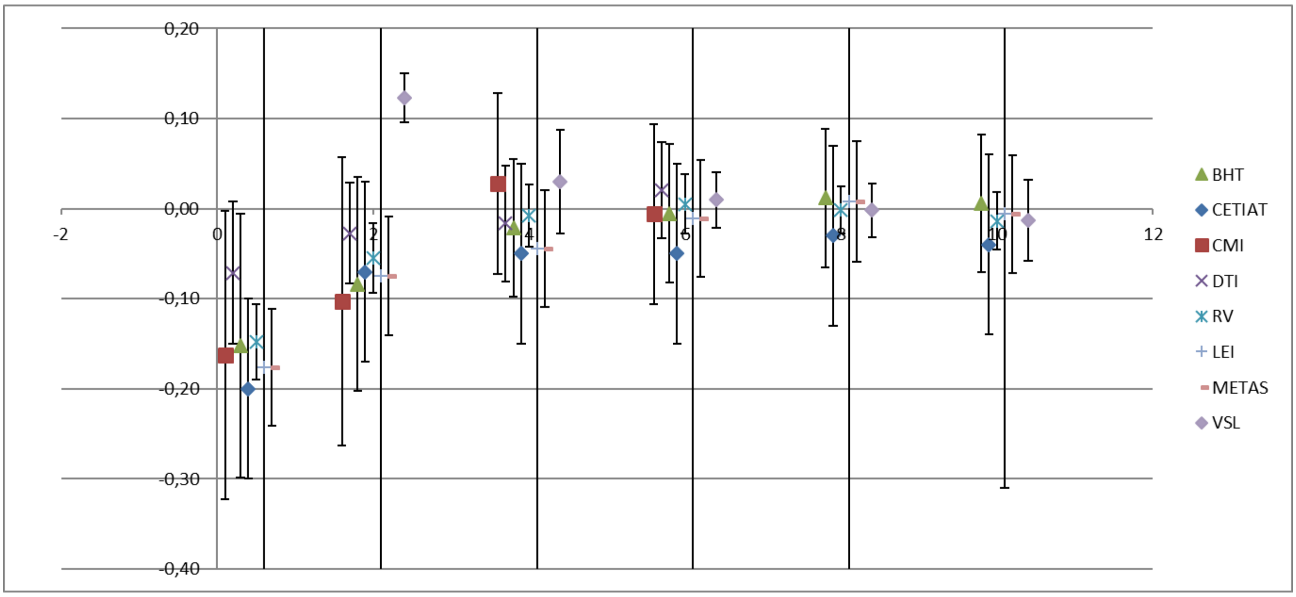

Table 7 Degree of equivalence (E_n value) for the flow meter intercomparison. Soft colored cells indicate a warning, hard colored cells indicate a fail. Values in red do no contribute to the RV.

flow rate (kg/h)	BHT	CETIAT	CMI	DTI	LEI	METAS	VSL
0.5	0.03	0.57	0.09	1.12	0.40	0.55	28
2	0.23	0.16	0.31	0.57	0.25	0.35	18
4	0.16	0.45	0.38	0.16	0.17	0.66	0.80
6	0.13	0.58	0.12	0.36	0.24	0.28	1.86
8	0.16	0.29	N/A	N/A	0.56	0.15	0.02
10	0.24	0.28	N/A	N/A	0.18	0.13	0.01

Table 8 Reference value (RV) and uncertainty for the flow meter.

flow rate (kg/h)	Error (%)	Uncertainty (k=2) (%)
0.5	-0.15	0.04
2	-0.05	0.04
4	-0.01	0.03
6	0.01	0.03
8	0.00	0.03
10	-0.01	0.03

Table 9 Observed chi-squared value χ^2_{obs}, population size n and threshold $\chi^2(n-1)$ for the flow meter intercomparison.

flow rate (kg/h)	n	χ^2_{obs}	$\chi^2(n-1)$
0.5	5	6.12	9.49
2	5	1.81	9.49
4	6	4.32	11.1
6	6	2.14	11.1
8	4	1.64	7.81
10	4	0.46	7.81

7 Conclusion

Seven laboratories participated in EURAMET project 1379. Six of these laboratories are independent NMIs whereas one is a manufacturer. In Table 10 the (preliminary) CMC claims (if existing) are shown for the (mass) flow rates. For all labs it typically holds that the uncertainty increases for a decrease in flow rate. In Table 5 the calibration uncertainty was presented (excluding the uncertainty due to drift). A comparison of Table 5 with Table 10 therefore shows whether the stated CMC claims are realistic, which is shown in Table 11.

From Table 11 it follows VSL is not consistent for a flow rate of 0.5 kg/h, 2.0 kg/h and 6.0 kg/h. Following initial investigations this was probably caused by entrapped air and/ or an unnoticed leakage. A leakage could cause a roughly constant flow rate, which would explain the mismatch is larger for lower flow rates. After this intercomparison VSL has repeated the calibrations and the results were found to be consistent. This, however, will have to be proved by a follow up intercomparison.

Table 10 (Preliminary) CMC claims (%) (k=2) of the participating labs. P stands for preliminary.

target flow rate (kg/h)	BHT	CETIAT (P)	CMI (P)	DTI	LEI	METAS	VSL (P)
0.5	N/A	0.1	0.16	0.5	N/A	0.07	0.01
2	N/A	0.1	0.16	0.5	N/A	0.07	0.05
4	N/A	0.1	0.10	0.5	N/A	0.07	0.05
6	N/A	0.1	0.10	0.5	N/A	0.07	0.05
8	N/A	0.1	N/A	0.5	N/A	0.07	0.05
10	N/A	0.1	N/A	0.5	N/A	0.07	0.05

Table 11 Consistency with (preliminary) CMC claims. Id stands for 'NMI Service Identifier' or an Identifier used for national accreditation.

NMI/ Inst.	(preliminary) CMC tables/ national accreditation			Comparison Euramet project 1379	Consistent with (prelim.) CMC tables
	Flow range (kg/h)	Expanded uncertainty (*k*=2) (%)	Id	Calibration uncertainty (%)	
BHT	0.001 to 10	0.65 to 0.1	N/A	0.08 to 0.15	Yes
CETIAT	0.001 to 10	0.6 to 0.1	COFRAC 2-57, to be submitted as CMCs	0.1	Yes
CMI	0.01 to 6	0.5 to 0.1	N/A	0.5 to 0.1	Yes
DTI	0.1 to 6	0.05	DK37	0.05 to 0.08	Yes
LEI	N/A	N/A	N/A	0.3 to 3.8	Yes
METAS	0.01 to 20	0.07	To be submitted	0.07	Yes
VSL	0.0025 to 5	1.4 to 0.05	RvA K999 FL10	0.03 to 0.06	Partial[1]

1 Inconsistent for 0.5 kg/h, 2.0 kg/h and 6.0 kg/h, consistent for 4.0 kg/h, 8.0 kg/h and 10 kg/h.

References

[1] Bissig, H. *et al.*, Primary Standards for Flow Rates from 100 nl/min to 1 ml/min - Gravimetric Principle, Journal of Biomedical Engineering, 60(4), August 2015, doi: 10.1515/bmt-2014-0145.

[2] Cox M.G., Evaluation of key comparison data, Metrologia, 2002, 39, 589-595