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An Intercomparison of Low Flow Gas Facilities at Eleven European Laboratories Using a Molbloc Transfer Package (EUROMET Project No 806)

A Report for

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Kingsgate House
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London
SW1E 6SW

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Date: May 2008

Approved by:

Date:

for M Valente
Managing Director

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2 SUMMARY

This report describes the results from the intercomparison of low flow gas facilities at eleven European laboratories. The organizations taking part were TUV NEL (UK), EIM (Greece), NMi (The Netherlands), CMI (The Czech Republic), INRIM (Italy), MIKES (Finland), METAS (Switzerland), PTB (Germany), LNE (France), FI (Denmark) and UME (Turkey). EIM acted as joint pilot laboratory with TUVNEL and NMi acted as assisting laboratory.

The transfer package consisted of two high-accuracy laminar-flow elements with associated hardware and software. The laminar-flow elements were Molblocs manufactured by DH Instruments Inc. The two Molblocs covered different flow ranges and were calibrated separately. The flow ranges covered were 2.1 to 21 mg/s for Molbloc A and 83 to 578 mg/s for Molbloc B.

3 INTRODUCTION

This report describes the results from the first part of an intercomparison exercise of low flow gas calibration facilities at eleven European laboratories. The participating laboratories were TUV NEL (NEL) (UK), EIM (Greece), NMi (The Netherlands), CMI (The Czech Republic), INRIM (Italy), MIKES (Finland), METAS (Switzerland), PTB (Germany), LNE (France), FI (Denmark) and UME (Turkey). EIM and TUVNEL were joint pilot laboratories and NMi acted as assisting laboratory.

The transfer-standard consisted of two meters, Molbloc A which was used over the flow range 2.1 to 21 mg/s and Molbloc B used over the range 83 to 575 mg/s. Calibrations were carried out using nitrogen as the test gas.

The second part of the intercomparison will involve fewer laboratories and use air as the test gas.

The transfer meter was circulated in the following order;

NEL	United Kingdom	September 2005
EIM	Greece	November – December 2005
NMi	The Netherlands	February 2006
CMI	The Czech Republic	March – May 2006
INRIM	Italy	June 2006
NEL	United Kingdom	July – Aug 2006
MIKES	Finland	September 2006
METAS	Switzerland	October 2006
PTB	Germany	December 2006
LNE	France	January 2007
FI	Denmark	March 2007
UME	Turkey	May 2007
NEL	United Kingdom	June 2007

4 TRANSFER STANDARD

The transfer standard (Fig 1) was a commercially available system based on Molbloc laminar-flow elements (LFE) and an instrumentation/control system. The complete package was manufactured by D&H Instruments and was supplied to NEL by Chell Instruments Ltd. The package consisted of two Molbloc sensor elements, each with an associated mass flow controller (MFC). A control and measurement unit, Molbox1, and an MFC switchbox were common to both elements. The devices are listed below.

4.1 Molbloc assembly A:

Model No: 1E3-VCR-V-Q
Serial No: 2198
Range: 0.1 to 1.0 l/min (2.1 to 21 mg/s)
MFC Model: HFC 302 Serial No 1164900001

4.2 Molbloc assembly B:

Model No: 3E4-VCR-V-Q3
Serial No: 2192
Range: 3 to 30 l/min (65 – 650 mg/s).
MFC Model: HFC302 Serial No 1164800001

4.3 The Molbox1 control and measurement unit

Model: FAM004
Serial No: 682.

The complete package assembly is shown in fig 1 below.

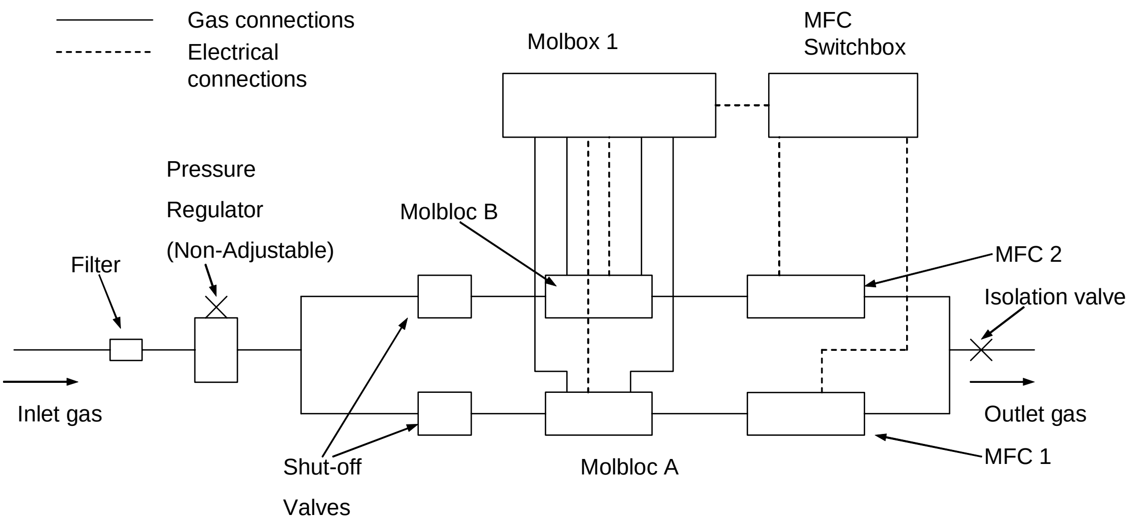


Figure 1: Schematic Diagram of the Transfer Standard

5 PROCEDURE

The procedure provided to the participants is as follows:

Five points were taken at each flow rate using the following procedure:

5.1 First Day

Start with Molbloc A and take one point at each flow rate going up the flow range and then take one point at each flow rate going down the range. Then change to Molbloc B and repeat the procedure.

After completing the tests switch off the Molbox1/Molbloc system and leave for 2 days.

5.2 Final Day

Repeat the test order for Day 1 and then chose the final test point at each flow rate by selecting the flow rate in a random order. Testing of Molbloc A should be completed before starting Molbloc B.

The flow rates used in the intercomparison are given in Table 1 below;

Molbloc	MFC Voltage (Volts)	Nominal Flow Rate (mg/s)	Nominal Flow Rate (l/min)	Nominal Molbloc Upstream Pressure (kPa)
A	0.5	2.0	0.1	269-271
A	2.5	11.0	0.5	269-271
A	5.0	20.0	1.0	269-271
B	0.62	83.0	4.0	269-271
B	2.5	320.0	15.0	269-271
B	4.5	570.0	25.0	259-261

Table 1: Nominal Flow Rates for the Intercomparison

6 FACILITIES

6.1 NEL, United Kingdom

Both Molbocs were calibrated against a piston prover reference (Califlow). The Molbloc was placed upstream of the reference Califlow and nitrogen (99.998%) used as the test gas. The Molbloc was supplied with its own instrumentation (Molbox1) for measuring the upstream and downstream pressures, from which the differential pressure was calculated, and the upstream and downstream temperatures of the Molbloc, from which the mean temperature was obtained. The Molbox1 was set to operate in average mode and so gave the average flow rate measured over the set time. The time was set to be as close as possible to the time required to fill the Califlow cylinder at the particular flow rate. Molbloc A was calibrated against the small cylinder of the Califlow and Molbloc B against the large cylinder. The reference pressure and temperature were measured at the inlet to the Califlow.

Nitrogen was passed through the test line and the flow conditions allowed to stabilize for at least 15 minutes before measurements were taken.

6.2 EIM, Greece

EIM assisted with the design of the experiment and with the analyses of the results.

The transfer standard was stored in the test room prior to calibration in order to be stabilized at the temperature of the test room. It was installed upstream of the appropriate primary flow standard. Two mercury sealed piston provers were used for the calibration of Molbloc A covering flow rates 2.0 – 20 mg/s and a Bell prover used for Molbloc B covering flow rates 65 – 650 mg/s, respectively. The calibration was performed by direct comparison of the indication of the transfer standard and the corresponding reading of the reference standard after the application of appropriate conversions to standard conditions (1013.25 mbar, 0 ^{o}C). Five points were taken at each flow rate. The percentage error in the flow rate between the transfer standard and the reference standard was calculated for each tested flow rate. High purity nitrogen (99.999%) was used as the test gas.

6.3 NMi, The Netherlands

Measurements were made on the transfer standard and a set of results returned on the standard EXCEL proforma that was supplied to all partaking laboratories. However no calibration certificate or report text was issued with the returned spreadsheet and subsequent communication with NMi established that there had been some operational difficulties with the test package coupled with changes in personnel at NMi. These factors meant that no documentation was produced on the original tests and therefore the results were withdrawn from the inter-comparison analysis.

6.4 CMI, The Czech Republic

A primary low mass flow standard based on dynamic gravimetric system DHI GFS 1 and primary low mass flow standard based on static gravimetric system CMI were used to calibrate the Molblocs. The Molblocs were located downstream of the reference standard. Pure nitrogen (purity 99.999%) was used as the calibration gas and the conditions of measurement were 20 ± 1 ^{o}C, 98 ± 1 kPa and 50 ± 10 %humidity. The flows in standard litres per minute were quoted for the reference conditions of 101.325 kPa and 0 ^{o}C.

6.5 INRIM, Italy

Molbloc A was calibrated against a 3 litre capacity piston prover (MICROGAS), with interferometer measurement of piston travel and active temperature control. The reference meter input port was connected to the outlet port of Molbloc A.

The gas used in this calibration was nitrogen, with a manufacturers claimed contents of less than 3 ppm H_2O, less than 2 ppm of O_2, and hydrocarbons below 0.5 ppm.

The calibration was carried out on two different days, during which ambient temperature was kept at (22.8 ± 0.3) °C whereas atmospheric pressure ranged between 98.8 and 99.2 kPa. The pressure at the outlet port of the instrument assembly (and in the MICROGAS) was higher than the current atmospheric value by no more than 50 Pa.

Absolute pressure at the Molbloc inlet was kept at 270 ± 1 kPa, while temperature at the Molbloc was taken from the Molbox1 and ranged between 22.9 and 23.4 °C.

Molbloc B was calibrated against a 150 litre bell prover (BELLGAS). The Molbloc was positioned upstream of the reference bell prover.

The calibration was carried out on 2 different days, during which ambient temperature was kept at 22.8 ± 0.3 °C while atmospheric pressure ranged between 98.6 and 99.1 kPa. The pressure at the outlet port of the instrument assembly (and in the BELLGAS as well) was higher than the current atmospheric value by no more than 300 Pa.

Absolute pressure at the Molbloc inlet was kept at about 270 kPa at the two lower flow rates and at about 260 kPa at the highest flow rate. Temperature at the Molbloc, as measured by the Molbox1, ranged between 22.0 and 22.6 °C.

A full description of the INRIM national standards used in this project have been published by Cignolo *et al.*[2,3]

6.6 MIKES, Finland

A dynamic weighing system (DWS) was used to calibrate both Molblocs.

The Molbloc laminar flow element (LFE) and the terminal were placed at the same level in the flow laboratory. The terminal was switched on and the thermal conditions were allowed to stabilize for one day before starting the calibration measurements. A leak test was performed for the calibration set-up using the balance of the DWS and pressure sensors of the terminal. The calibration was performed using nitrogen with purity of 99.999%. The absolute upstream pressure at the Molbloc was 270 ± 1 kPa.

The gas flow rate was controlled by the thermal mass flow controllers (MFC). A zero adjustment of pressure sensors (i.e. taring) was performed for the device under test (the Molbloc) according to the upstream pressure. Measurements were started after reaching a stable gas flow when indicated by Molbox1. The reference and the Molbloc were connected in series, with the transfer standard being located downstream of the reference weighing system. The same mass flow passed through both instruments. Five successive measurements were made at all calibration points.

6.7 METAS, Switzerland

The Molblocs were calibrated against a primary volumetric piston prover with interferometer measurement that was located downstream of the transfer standard.

For each Molbloc one measurement at each flow rate was taken going up the flow range and then one measurement at each flow rate going down the range. Three repeat runs were taken at each flow rate.

Then the Molbox1/Molbloc system was switched off and left for two days.

The test order described above was repeated. Finally a measurement at each flow rate by randomizing the test order was taken.

As a summary the mean values of the five measurement results at each flow rate from the standard and the Molbloc have been tabled with the corresponding uncertainties.

The device was turned on for at least 4 hours before use for complete stabilization. Extended leak test procedures were performed with the Molblocs between the isolation valves and the ball valve of the primary volumetric standard. The tare function to adjust the two pressure sensors to the upstream sensor was undertaken at each measurement point. The volume flow was regulated with the MFC and after a stabilization period of at least 15 minutes it was measured simultaneously with the primary volumetric standard of METAS and with the Molbloc.

4.8 PTB, Germany

Molbloc A (2198) was calibrated using the following different devices:
A Double Piston Flow Comparator,
A small Interferometric Piston Prover,
A medium Interferometric Piston Prover and
A Wet Gas Meter.

Molbloc B (2192) was calibrated against a Wet Gas Meter.

99.999 per cent nitrogen was used as the test gas.

The test schedule used is shown in Table 2 below;

Date	**D**ouble **P**iston **F**low **C**omparator **DPFC**	**I**nterferometric **P**iston **P**rover (**S**mall, 19mm) **IPP (S)**	**I**nterferometric **P**iston **P**rover (**m**edium, 44mm) **IPP (M)**	**W**et **G**as **M**eter **WGM**
05.12.2007		Molbloc A		
06.12.2007			Molbloc A	
07.12.2007	Molbloc A		Molbloc A	Molbloc B
08.12.2007				Molbloc A Molbloc B
11.12.2007				Molbloc A Molbloc B
21.12.2007		Molbloc A		

Table 2: PTB Reference Meters used to Calibrate Molblocs

6.8 LNE, France

The Molblocs were calibrated by directly weighing the mass of gas lost from a pressure vessel.

For Molbloc A the reference standards used were a 1.2 kg electronic balance (resolution 0.001 g) for measurements in the range 0.03 mg/s to 8 mg/s and an 8.2 kg electronic balance (resolution 0.01 g) for measurements in the range 8 mg/s to 250 mg/s and a timer (resolution 0.01 µs).

The expanded uncertainty of the reference mass flow was $\pm 8.0 \times 10^{-4} + 2.0 \times 10^{-3} q_m$ in the range 0.4 to 10 mg/s and $\pm 1.8 \times 10^{-3} q_m$ between 8 mg/s and 250 mg/s.

The ambient gas temperature during the calibration of Molbloc A ranged between 20.1 and 21.1 ^{o}C.

For Molbloc B the reference standards used were an 8.2 kg electronic balance (resolution 0.01 g) for measurements in the range 8 mg/s to 250 mg/s and a 16 kg capacity electronic balance (resolution 0.1 g) for measurements in the range 250 mg/s to 2200 mg/s and a timer (resolution 0.01 µs).

The expanded uncertainty of the reference mass flow was $\pm 1.8 \times 10^{-3} q_m$ between 8 mg/s and 250 mg/s and $\pm$ 0.1 + $2.0 \times 10^{-3} q_m$ over the range 250 mg/s to 700 mg/s.

The ambient gas temperature during the calibration of Molbloc B was between 20.5 ^{o}C and 21.2 ^{o}C.

Dry nitrogen (99.999 % purity) was used as the test gas with a compressibility factor of 0.9995.

The mass flow was calculated in volume flow at standard conditions of 101325 Pa and 273.15 K.

6.9 FI, Denmark

The calibration reference was a mercury-sealed piston prover, manufactured by Sierra Instruments consisting of 3 different tubes.

One small flow tube:	1ml/min – 750 ml/min
One medium flow tube:	100 ml/min – 10000 ml/min
One big flow tube:	1000 ml/min – 50000 ml/min

The Molbloc was installed upstream of the piston prover. The piston prover measures volume flow and so it normally measures the flow as a standard flow given at a certain condition. Therefore it only measures the temperature and pressure at the inlet to the piston prover. The whole calibration is controlled by a computer, after the inlet pressure at the meter has been set manually.

6.10 UME, Turkey

A reference Ritter Wet Gas Meter, calibrated by PTB, was used to calibrate Molbloc A while Molbloc B was calibrated against an EG & G Flow Technology bell prover that was calibrated at the UME Dimensional and Time & Frequency Laboratories. In both cases the reference standard was located downstream of the transfer package.

7 CALCULATION

The percentage error in the flow rate between the transfer standard and the reference meter was calculated using equation below.

$$E = \frac{M_t - M_r}{M_r} \times 100 \quad (1)$$

Where;

M_t is the mass flow rate indicated by the transfer standard (mg/s) and
M_r is the mass flow rate indicated by the reference standard (mg/s)

8 RESULTS

Most participants operated the transfer standard to indicate mass flow but some chose to run in volume flow so as to be compatible with their normal operating procedures. The participants then applied nominal mass flow values or converted them from volume flow using standard conditions of 101325 Pa and 0 ^{o}C. The calculated error has been left as calculated from the units used by each laboratory, hence avoiding any indirect errors in the conversion to mass. . After some consideration NMi withdrew their data for the calibration of Molblocs A and B so was not included in the key comparison reference value analysis (KCRV).

During the circulation of the package CMI reported a leak from Molbloc A that had not been present with previous users. CMI sealed the leak and the component was changed prior to the middle audit being undertaken by the pilot laboratory.

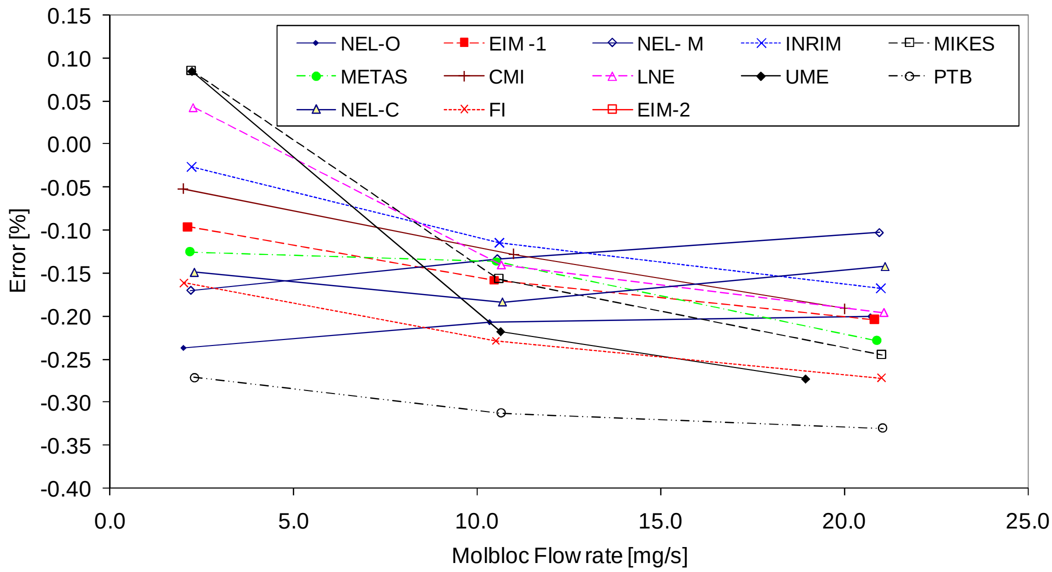
Throughout the intercomparison intermittent problems were reported with the stability of the flow at the highest flow rate of Molbloc B. This instability was thought to be due to the mass flow controller (MFC) being unable to give the required level of control. For their tests MIKES replaced the MFC with an MFC of their own, while LNE and FI replaced the MFC with a needle valve.

A leak was reported by METAS from the downstream pressure tapping of Molbloc B and this was replaced before the transfer standard was sent to the next laboratory. None of the laboratories that calibrated the transfer standard after METAS reported a leak, and no leak was observed at this point during the closing audit. A summary of all the results submitted by each laboratory for both Molblocs is given in Table 3 with actual flowrates in mg/s and percentage error as defined in section 6 (Eqn. 1). The data from Table 3 are plotted for Molbloc A in Figure 2 and, for Molbloc B, in Figure 3.

	Lab:	TUV NEL-O	Lab:	TUV NEL-M	Lab:	TUV NEL-C	Lab:	EIM 1066
	Molbloc Flowrate Actual (mg/s)	Error (%)	Molbloc Flowrate Actual (mg/s)	Error (%)	Molbloc Flowrate Actual (mg/s)	Error (%)	Molbloc Flowrate Actual (mg/s)	Error (%)
	1.997	-0.2370	2	-0.1703	2.3132	-0.150	2.099	0.070
Molbloc A	10.3353	-0.2075	10.5	-0.1332	10.6869	-0.180	10.453	-0.030
	20.7072	-0.2009	21	-0.1027	21.107	-0.140	20.829	-0.180
	83.054	-0.0076	85	0.0582	84.734	0.040	108	-0.120
Molbloc B	322.2	0.0356	325	0.1728	325.622	0.070	325	-0.190
	575.77	0.4617	578	0.2606	580.242	0.090	580	-0.160
	Lab:	EIM 1064	Lab:	METAS	Lab:	INRIM	Lab:	NMi
	Molbloc Flowrate Actual (mg/s)	Error (%)	Molbloc Flowrate Actual (mg/s)	Error (%)	Molbloc Flowrate Actual (mg/s)	Error (%)	Molbloc Flowrate Actual (mg/s)	Error (%)
	2.099	-0.162	2.172	-0.1251	2.222	-0.0268		
Molbloc A	10.453	-0.080	10.52	-0.1367	10.589	-0.1157		
	20.829		20.89	-0.2283	20.99	-0.1684		
			82.08	-0.0161	84.288	0.0841	81.5746	0.6208
Molbloc B			318.51	-0.0922	323.99	0.0064	319.213	0.1702
			568.52	0.0314	574.377	0.2012	569.8616	-0.0718
	Lab:	MIKES	Lab:	CMI	Lab:	PTB	Lab:	LNE
	Molbloc Flowrate Actual (mg/s)	Error (%)	Molbloc Flowrate Actual (mg/s)	Error (%)	Molbloc Flowrate Actual (mg/s)	Error (%)	Molbloc Flowrate Actual (mg/s)	Error (%)
	2.196	0.086	2	-0.052	2.2878	-0.271	2.28618	0.040
Molbloc A	10.56	-0.154	10	-0.128	10.6539	-0.313	10.6568	-0.140
	20.96	-0.246	20	-0.191	21.0483	-0.331	21.0424	-0.196
	82.36	-0.074	82.36	0.082	85.01	-0.129	84.156	0.028
Molbloc B	321.07	-0.172	321.07	0.005	325.0966	-0.193	323.85	-0.080
	572.94	0.140	572.94	-0.220	578.4005	0.060	576.12	0.078
	Lab:	UME	Lab:	FORCE				
	Molbloc Flowrate Actual (mg/s)	Error (%)	Molbloc Flowrate Actual (mg/s)	Error (%)				
	2	0.0842	2	-0.160				
Molbloc A	10	-0.2180	11	-0.230				
	20	-0.2730	21	-0.270				
	83	0.5016	85	0.150				
Molbloc B	320	0.4198	325	0.070				
	456	0.3436	578	0.110				

Table 3: Mean Error (Per Cent) for All Laboratories

Figure 2 shows that all the mean error values lie within a range of 0.4 per cent or better for the three flowrates.



Fig

Figure 2: Mean Error for Molbloc A All Laboratories

A summary of the results for Molbloc B are plotted in Fig 3 and show that all the mean error values lie within a range of 0.8 per cent. UME encountered some difficulties with the calibration of Molbloc B and achieved a maximum flow rate of 472 mg/s. Although this value was much lower than the 570 -580 mg/s reported by the other participants, it was decided to include it in the key comparison reference value analysis (KCRV).

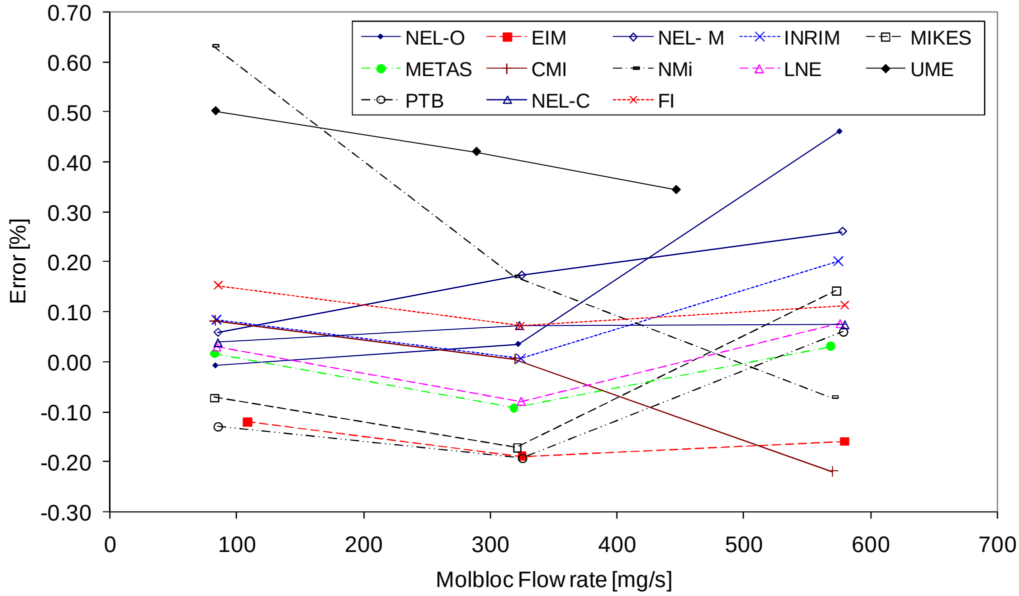


Figure 3: Mean Error for Molbloc B All Laboratories

8.1 KCRV Analysis

Because of the problems encountered by several institutions with Molbloc B, the KCRV analysis for this intercomparison has presented some difficulties. The first draft of this report presented 2 analyses which were discussed at the EUROMET meeting in Berlin in February 2008.. As a result of those discussions, the data from NMi has been excluded from the KCRV analysis and the report has been amended accordingly. However the results for NMi (Molbloc-B), along with NEL-O (open) and NEL-M (Middle), have been included in some tables for comparison purposes.

A KCRV analysis was carried out using the method recommended by Cox[1] using the weighted means of each institutes results (Cox Procedure-A). Tables 5 and 6 show the Procedure A analysis for Molbloc-A and Molbloc-B respectively. The following points should be noted in relation to Tables 5 and 6.

Note [1]

There was some discussion on what reported standard uncertainty value should be used for the Procedure A analysis as some institutes had reported smaller uncertainties on the comparison test than were published on the BIPM web-site for their standard service. After asking collaborative institutes to confirm the source of their standard uncertainty figures, in the subsequent KCRV analysis (column 2 in Tables 5 and 6) an initial decision was taken to use the larger of:

(a) the CMC value published on the BIPM web-site for the institution's relevant service ID, and

(b) the reported standard uncertainty that was indicated on the accompanying calibration certificate.

Table 4 shows a summary of the uncertainties supplied by each participant on their calibration certificate (where a certificate was supplied) together with the corresponding uncertainty figures posted on the BIPM web-site for the relevant BIPM service ID.

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Country	Organisation	Standard Meter(s) Used	Certificate #	Min %U on cert (±)	Max %U on cert (±)	Min abs U on cert (±)	Max abs U on cert (±)	2ndary included ?	Coverage Factor	BIPM (%U) (±)	BIPM Service ID
Denmark	Force Technology	Piston prover with 2 tubes Medium: 1- 10000 ml/min Large: 1-50000 ml/min	9.8-5607	0.16	0.52			yes	2	0.12 0.19	DK5
Finland	MIKES	Direct Weighing System	M-06D027 M-06D028	0.30 0.30	0.30 0.40			-	2	-	-
France	LNE	Direct Weighing System	H015030/43 H015030/44			0.0055 mg/s 0.15 mg/s	0.056 mg/s 1.4 mg/s	-	2	0.22 0.4	FR10
Germany	PTB	Double piston Flow comparator Interferometric piston prover (small) Interferometric piston prover (medium) Wet Gas meter	2192	0.12	0.16			-	2	0.15	DE33
Greece	EIM	BROOKES 1066 (piston prover) BROOKES 1064 (piston prover) BELL PROVER	D11-02-029/2006	0.12 0.18 0.17	0.13 0.20 0.20			-	2	0.2	GR6
Italy	iNRiM	MICROGAS 3 L piston prover BELLGAS 150 L bell prover	06-000A-01 06-000B-01	0.027 0.104	0.029 0.143			-	2	0.05 0.12	IT20 IT21
Switzerland	METAS	Volumetric Standard	232-10206			0.0032 mg/s	0.94 mg/s	-	2	0.15	CH6
The Czech Republic	CMI	Direct Weighing System	6013-KL-M166-06			0.0002 slm	0.0779 slm	-	2	0.18	CZ2
The Netherlands	NMi	??	None issued					-	2 assumed	0.18	NE06
Turkey	UME	Ritter Wet Gas Meter Bell Prover	None issued					-	2 assumed	0.25 0.50	TR1 TR2
United Kingdom	TUV NE.	Califlow (piston prover) reference meter	2007/196	0.17	0.17			no	2	0.1	UK34

Table 4: Uncertainty claims for EUROMET 806 intercomparison {from BIPM web-site}

The values in columns 5 and 6 are the minimum and maximum uncertainty values taken from the calibration certificates supplied and are assumed to refer to the mean of the repeated measurements at each flow rate. The coverage factor for all the expanded uncertainties was given as k=2 in all cases except two (UME and NMi) where the coverage factor was not stated and was assumed to be k=2. In response to the circulation of the first draft of this report, METAS requested that the uncertainties stated in the calibration certificate supplied with their test results should be used for the KCRV analysis and not the BIPM service values quoted in table 4. This request has be acceded to for METAS uncertainties only in this report. For all other participants we have used the BIPM service ID numbers. This substitution for METAS did not make a significant difference to the final results.

Note [2]
Those cells highlighted in column 7 in tables 5 and 6 (the degree of equivalence, d_i, value for institute *i*) show those data which are considered discrepant from the KCRV using the chi-squared test.

Note [3]
The NEL-C (Close) data were taken for the KCRV analysis. This set was chosen since only 1 of the three sets measured by NEL may be included in the KCRV analysis. And this was considered to be the most stable of the three measurements.

Note [4]
EIM 1064 and EIM 1066 data were both selected for the KCRV analysis as both sets of measurements were judged to be fully independent of each other and so satisfy Cox's condition 2 (see Appendix-I for details on Cox Procedure-A).

Note [5]
The NMi Molbloc-A and Molbloc-B data were excluded from the analysis after a preliminary calculation showed that both datasets were discrepant and subsequent communication with NMi. Removing this dataset from the KCRV analysis had the effect of bringing the other datasets that were also showing discrepant values back into agreement. The Molbloc B data from NMi are shown for completion in Table 6 but have not been used in the KCRV analysis.

Note [6]
The number of degrees of freedom used for the chi-squared test for the Molbloc-A is 10 for the two lower flow rates and 9 for the highest flow rate (EIM 1064 has no results for this flow). The number of degrees of freedom used for the Molbloc-B results is 9 for all flow rates

Figures 4 to 9 show the deviation of each laboratory with respect to the key calculated reference value for each of the flowrates specified in the intercomparison. On the charts for each flowrate the percentage expanded uncertainty, U, at coverage factor k = 2 is displayed as the error bar on either side of each point. Also, a semi-transparent rectangle with a dotted line border is superimposed on each chart to show how the expanded uncertainty in the reference value, XREF, compares for each participant.

8.1.1 Molbloc-A Comparison

Visual inspection of Table 5 together with Figures 4 to 6 shows that for the set of uncertainties chosen, there are three datasets which are discrepant: namely NEL-O (Open and INRIM at the lowest flowrate of 2.2 mg/s and also PTB at the lowest flow rates of 2.2 mg/s and 10 mg/s. All other laboratories datasets pass the chi squared test.

ID	Reported value	Reported standard uncertainty				Degrees of Equivalence		
Laboratory	x_i	$u(x_i)$	$x_i/u^2(x_i)$	$1/u^2(x_i)$	$(x_i-y)^2/u^2(x_i)$	d_i	$u^2(d_i)=u^2(x_i)-u^2(x_{ref})$	U(di)
NEL-O	-0.237	0.085	-32.803	138.408	4.11784	-0.17249	0.0068789	0.1658777
	-0.208	0.085	-28.720	138.408	0.54048	-0.06249	0.0068930	0.1660487
	-0.201	0.085	-27.806	138.408	0.00229	-0.00406	0.0068807	0.1658994
NEL-M	-0.170	0.085	-23.570	138.408	1.54859	-0.10578	0.0068789	0.1658777
	-0.133	0.085	-18.436	138.408	0.01931	0.01181	0.0068930	0.1660487
	-0.103	0.085	-14.209	138.408	1.22755	0.09418	0.0068807	0.1658994
NEL-C	-0.15	0.085	-20.761	138.408	1.01146	-0.08549	0.0068789	0.1658777
	-0.18	0.085	-24.913	138.408	0.16945	-0.03499	0.0068930	0.1660487
	-0.14	0.085	-19.377	138.408	0.44710	0.05684	0.0068807	0.1658994
EIM 1066	0.07	0.1	7.000	100.000	1.80941	0.13451	0.0096539	0.196508
	-0.03	0.1	-3.000	100.000	1.32274	0.11501	0.0096680	0.1966524
	-0.18	0.1	-18.000	100.000	0.02834	0.01684	0.0096557	0.19653
EIM 1064	-0.162	0.1	-16.200	100.000	0.95035	-0.09749	0.0096539	0.196508
	-0.080	0.1	-8.000	100.000	0.42263	0.06501	0.0096680	0.1966524
NMi								
CMI	-0.052	0.1	-5.200	100.000	0.01566	0.01251	0.0096539	0.196508
	-0.128	0.1	-12.800	100.000	0.02894	0.01701	0.0096680	0.1966524
	-0.191	0.1	-19.100	100.000	0.00341	0.00584	0.0096557	0.19653
INRIM	-0.027	0.025	-42.880	1600.000	2.27577	0.03771	0.0002789	0.0333977
	-0.116	0.025	-185.120	1600.000	1.37455	0.02931	0.0002930	0.0342371
	-0.168	0.025	-269.440	1600.000	1.29373	0.02844	0.0002807	0.0335056
METAS	-0.130	0.045	-64.2	493.8	2.11773	-0.06549	0.0016789	0.0819476
	-0.180	0.045	-88.89	493.827	0.60458	-0.03499	0.0016930	0.0822932
	-0.230	0.045	-113.580	493.827	0.54315	-0.03316	0.0016807	0.0819916
MIKES	0.086	0.15	3.822	44.444	1.00687	0.15051	0.0221539	0.2976834
	-0.154	0.15	-6.844	44.444	0.00359	-0.00899	0.0221680	0.2977787
	-0.246	0.15	-10.933	44.444	0.10743	-0.04916	0.0221557	0.2976955
PTB	-0.271	0.075	-48.178	177.778	7.57981	-0.20649	0.0052789	0.1453114
	-0.313	0.075	-55.644	177.778	5.01698	-0.16799	0.0052930	0.1455066
	-0.331	0.075	-58.844	177.778	3.20002	-0.13416	0.0052807	0.1453362
LNE	0.040	0.122	2.667	66.666	2.28190	0.10451	0.0146540	0.2421072
	-0.140	0.11	-11.570	82.645	0.00207	0.00501	0.0117680	0.2169612
	-0.196	0.120	-13.558	69.175	0.00005	0.00084	0.0141117	0.2375856
FI	-0.160	0.173	-5.346	33.412	0.30464	-0.09549	0.0295829	0.3439933
	-0.230	0.081	-35.056	152.416	1.10094	-0.08499	0.0062290	0.1578486
	-0.270	0.08	-42.188	156.250	0.83641	-0.07316	0.0060557	0.1556362
UME	0.084	0.1705	2.896	34.399	0.76077	0.14871	0.0287241	0.3389637
	-0.218	0.2088	-4.999	22.933	0.12217	-0.07299	0.0432738	0.4160473
	-0.273	0.2033	-6.603	24.188	0.14031	-0.07616	0.0409987	0.4049629

[mg/s]	$y=x_{ref}$	$\Sigma(x_i/u^2(x_i))$	$\Sigma(1/u^2(x_i))$	χ^2_{obs}	χ^2_{crit}	$u(x_{ref})$
2.2	-0.0645	-186.377	2888.9	20.1144	18.31	0.018605
10.5	-0.1450	-436.836	3012.451	10.1687	18.31	0.018220
20.8	-0.1968	-571.624	2904.071	6.5999	16.92	0.018557

Table 5: Molbloc-A KCRV Procedure-A Analysis

8.1.2 Molbloc-B Comparison

The situation with respect to Molbloc-B at the higher gas flowrates is shown in Table 6 together with Figures 7 to 9. There are a number of datasets which are flagged up as being discrepant. NEL Open at the highest flow rate of 572 mg/s and also NEL Middle at the two highest flow rates of 320 mg/s and 572 mg/s. The EIM dataset at 572 mg/s is also discrepant. The 572 mg/s dataset from INRIM is marginally discrepant. Note that NMi is highly discrepant but has not been included in the KCRV analysis itself.

ID	Reported value	Reported standard uncertainty				Degrees of Equivalence		
Laboratory	x_i	$u(x_i)$	$x_i/u^2(x_i)$	$1/u^2(x_i)$	$(x_i-y)^2/u^2(x_i)$	d_i	$u^2(d_i)=u^2(x_i)-u^2(x_{ref})$	U(di)
NEL-O	-0.0076	0.085	-1.0519	138.4083	0.115445	-0.02888	0.0068789	0.165878
	0.0356	0.085	4.9273	138.4083	0.967171	0.08359	0.0068930	0.166049
	0.4617	0.085	63.9031	138.4083	20.741471	0.38711	0.0068807	0.165899
NEL-M	0.0582	0.085	8.0554	138.4083	0.188656	0.03692	0.0068789	0.165878
	0.1728	0.085	23.9197	138.4083	6.748573	0.22081	0.0068930	0.166049
	0.2606	0.085	36.0753	138.4083	4.791352	0.18606	0.0068807	0.165899
NEL-C	0.040	0.085	5.5363	138.4083	0.048500	0.01872	0.0068789	0.165878
	0.070	0.085	9.6886	138.4083	1.926973	0.11799	0.0068930	0.166049
	0.090	0.085	12.4567	138.4083	0.032884	0.01541	0.0068807	0.165899
EIM 1066	-0.118	0.100	-11.80	100.0000	1.939909	-0.13928	0.0096539	0.196508
	-0.190	0.100	-19.00	100.0000	2.016595	-0.14201	0.0096680	0.196652
	-0.160	0.100	-16.00	100.0000	5.503067	-0.23459	0.0096557	0.19653
EIM 1064								
NMi	0.621	0.090	76.6420	123.4568	44.373273	0.59952	0.0077539	0.176112
	0.170	0.090	21.0000	123.4568	2.734224	0.14882	0.0077539	0.176112
	-0.072	0.090	-8.8519	123.4568	1.067332	-0.09298	0.0077539	0.176112
CMI	0.082	0.100	8.1804	99.7604	0.367801	0.06072	0.0096779	0.196752
	0.005	0.150	0.2216	44.3144	0.124447	0.05299	0.0222341	0.298222
	-0.220	0.156	-9.0622	41.1917	3.574654	-0.29459	0.0239324	0.309402
INRIM	0.0841	0.074	15.3579	182.6150	0.720650	0.06282	0.0051299	0.143246
	0.0064	0.053	2.3220	362.8118	1.073419	0.05439	0.0024243	0.098474
	0.2012	0.054	70.2943	349.3755	5.600861	0.12661	0.0025179	0.100357
METAS	0.016	0.045	7.9012	493.8272	0.013770	-0.00528	0.0016789	0.081948
	-0.092	0.045	-45.4321	493.8272	0.956348	-0.04401	0.0016930	0.082293
	0.031	0.045	15.3086	493.8272	0.938150	-0.04359	0.0016807	0.081992
MIKES	-0.074	0.150	-3.2889	44.4444	0.403484	-0.09528	0.0221539	0.297683
	-0.172	0.200	-4.3000	25.0000	0.384443	-0.12401	0.0396680	0.398337
	0.140	0.150	6.2222	44.4444	0.190176	0.06541	0.0221557	0.297696
PTB	-0.129	0.080	-20.1563	156.2500	3.528790	-0.15028	0.0060539	0.155613
	-0.193	0.080	-30.1563	156.2500	3.285468	-0.14501	0.0060680	0.155795
	0.060	0.080	9.3750	156.2500	0.033243	-0.01459	0.0060557	0.155636
LNE	0.028	0.110	2.3140	82.6446	0.003731	0.00672	0.0117539	0.21683
	-0.080	0.110	-6.6116	82.6446	0.084664	-0.03201	0.0117680	0.216961
	0.078	0.110	6.4463	82.6446	0.000963	0.00341	0.0117557	0.216847
FI	0.150	0.090	18.5185	123.4568	2.045517	0.12872	0.0077539	0.176112
	0.070	0.080	10.9375	156.2500	2.175372	0.11799	0.0060680	0.155795
	0.110	0.080	17.1875	156.2500	0.195959	0.03541	0.0060557	0.155636
UME	0.502	0.250	8.0256	16.0000	3.691308	0.48032	0.0621539	0.498613
	0.420	0.250	6.7168	16.0000	3.501287	0.46779	0.0621680	0.49867
	0.344	0.250	5.4976	16.0000	1.157895	0.26901	0.0621557	0.498621

[mg/s]	$y=x_{ref}$	$\Sigma(x_i/u^2(x_i))$	$\Sigma(1/u^2(x_i))$	χ^2_{obs}	χ^2_{crit}	$u(x_{ref})$
83	0.0213	30.588877	1437.4068	12.7635	16.92	0.026376
320	-0.0480	-75.61347	1575.5062	15.5290	16.92	0.025194
572	0.0746	117.72618	1578.3917	17.2279	16.92	0.025171

Table 6: Molbloc-B KCRV Procedure-A Analysis

Figures 4 to 9 show graphs of the mean errors for each institute at each of the 6 flow rates specified in the project (3 flows for Molbloc-A and 3 higher flows for Molbloc-B). Also drawn on the figures is a shaded region which shows the position of the KCRV's expanded uncertainty (k=2 coverage) in relation to each national institute's measurement. This is provided as a visual aid to identifying those measurements that are discrepant (see also the discrepant values that are shown in highlighted red background cells in Tables 5 and 6).

On the basis of statistical variability alone, we should expect that 5% of the measurements to be discrepant.

8.2 Molbloc-A Plots

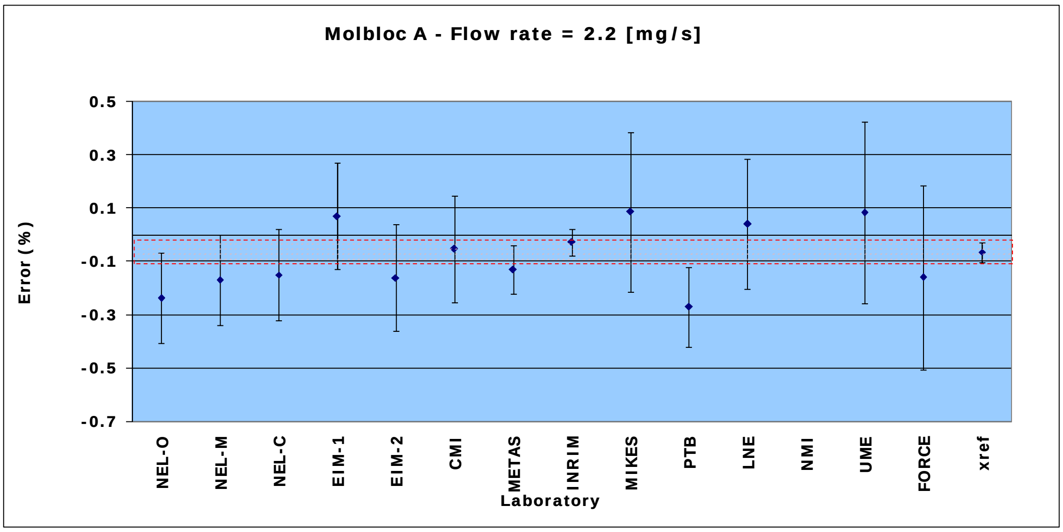

Figure 4: Molbloc-A 2.2 mg/s comparison

At the 2.2 mg/s flow rate NEL-Open, PTB and INRIM are discrepant., with the latter only marginally so with ($|d_i|$ $-U(d_i)$) = 0.004

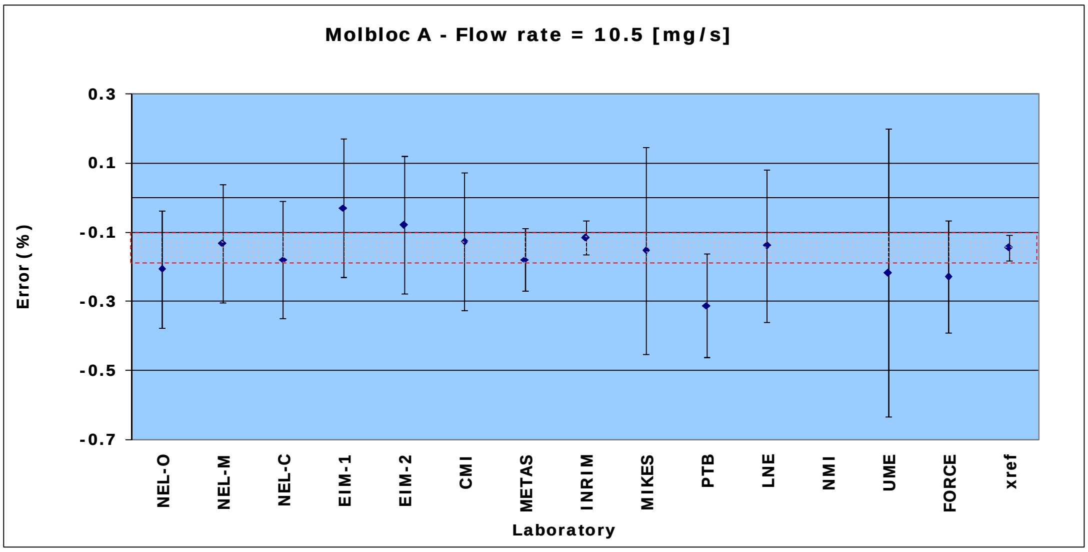

Figure 5: Molbloc-A 10.5 mg/s comparison

At the 10.5 mg/s flow, the PTB result is marginally discrepant with ($|d_i|$ $-U(d_i)$) = 0.022

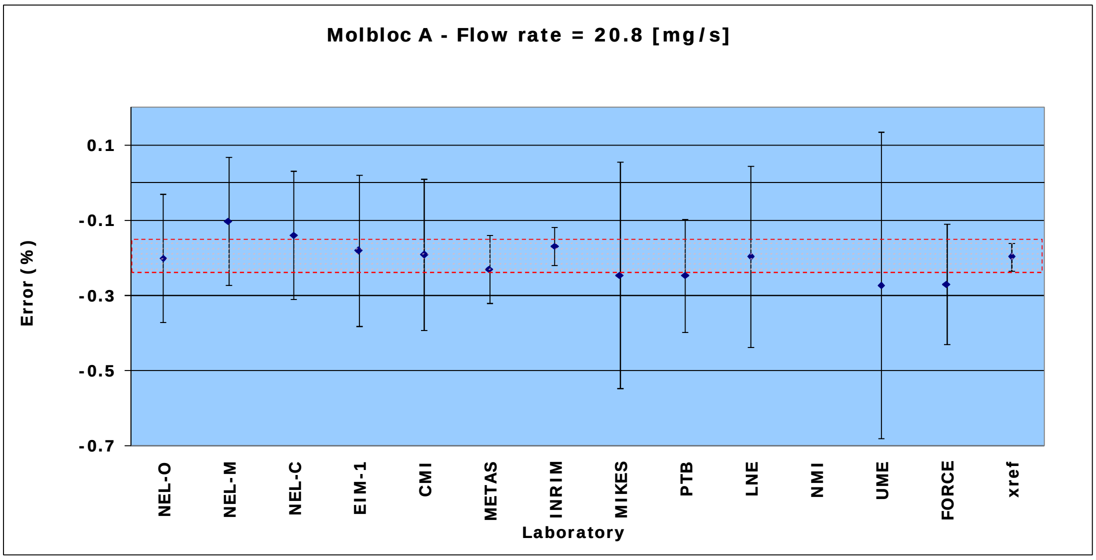

Figure 6: Molbloc-A 20.8 mg/s comparison

At the 20.8 mg/s flow, all institutes' measurements pass the discrepancy test.

8.3 Molbloc-B Plots

A similar set of 3 plots, one for each flow rate, was prepared for the Molbloc-B results. As indicated earlier, the results were not so consistent as Molbloc-A.

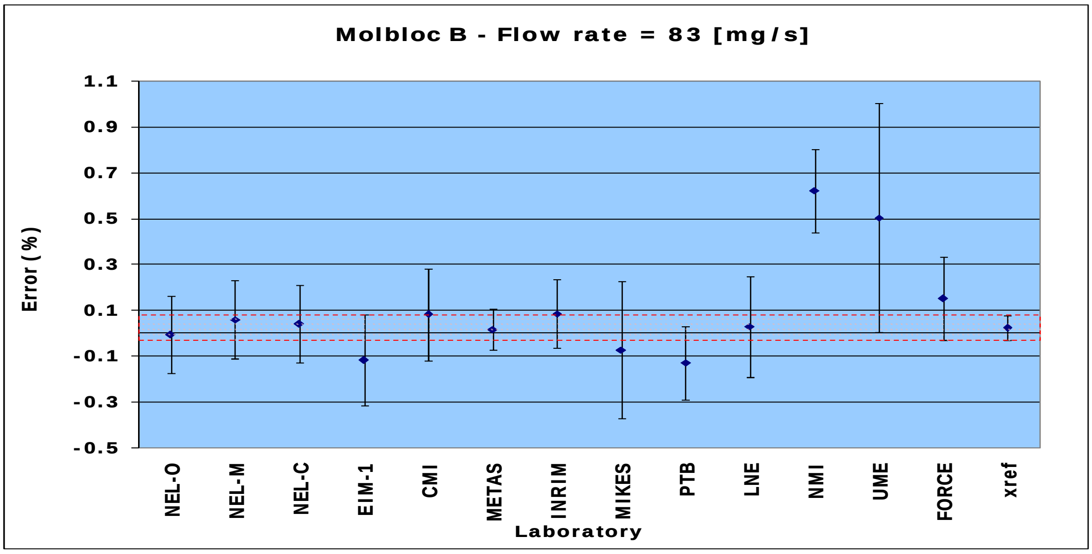

Figure 7: Molbloc-B 83 mg/s Comparison

At the 83 mg/s flowrate, the NMI data is shown as being clearly different to other laboratories. The NMI, NEL-O and NEL-M values were not used in the KCRV but are included for completeness.

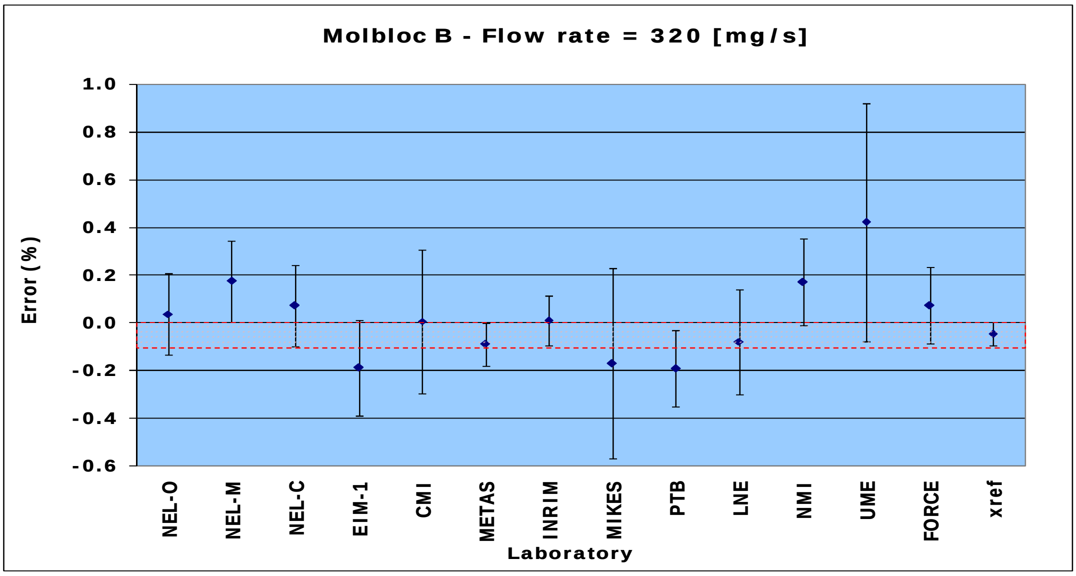

Figure 8: Molbloc-B 320 mg/s Comparison

At the 320 mg/s flowrate, only NEL-M is discrepant with ($|d_i|$ $-U(d_i)$) = 0.055 but was not included in the KCRV analysis

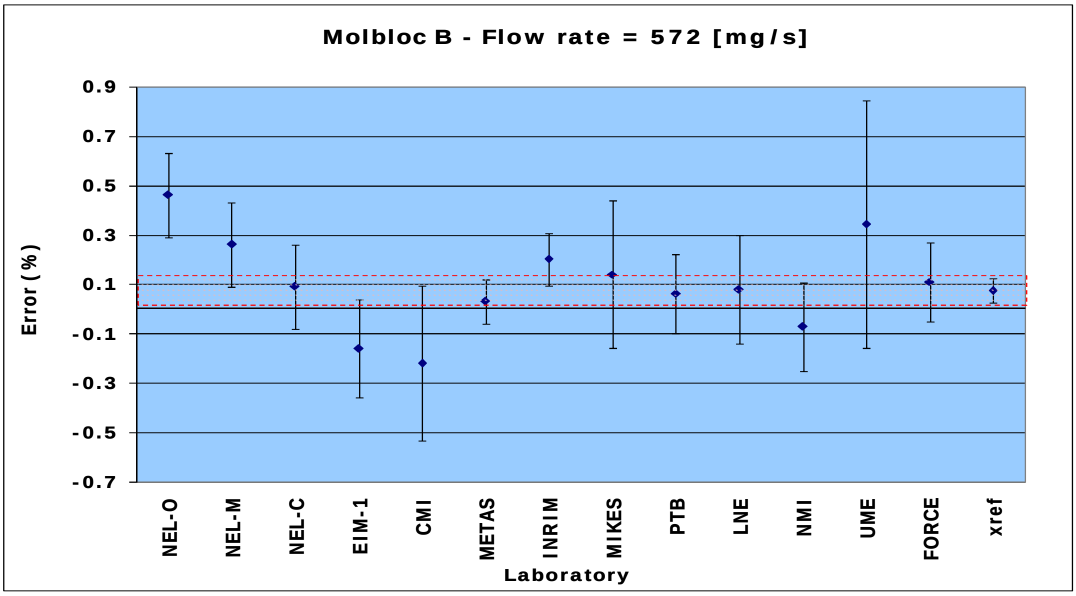

Figure 9: Molbloc-B 572 mg/s Comparison

At the highest flow of 572 mg/s NEL-O, NEL-M and EIM-1 are discrepant. Only the latter was used in the KCRV analysis and had a ($|d_i|$ $-U(d_i)$) = 0.037

8.4 Degrees of Equivalence and *En* Values

Column 7 in both Table 5 and Table 6 shows the degree of equivalence, d_i, between the KCRV and each individual national institute measurement. A useful dimensionless parameter, *En*, can be calculated to compare each institution's measurements with the computed KCRV. Table 7 lists the *En* values for each nation institute at each of the six measured flow rates. It is helpful to produce a single overall value which encapsulates a characteristic criteria for each laboratory taking part in the key comparison. Assuming that the degree of equivalence is a random variable with a log-normal probability density, a simple geometric mean value was considered an appropriate parameter for this purpose and is shown for each national laboratory measurement set (both Molbloc-A and Molbloc-B results) in the rightmost column of Table 7. Values greater than 1.0 have been highlighted. As already noted earlier, NEL-O, NEL-M and NMi were excluded from the KCRV calculation but are included in Table 7 for completeness.

Flow mg/s	2.2	10.5	20.8	83	320	572	Geometric Mean
NEL-O	**1.040**	0.376	0.024	0.174	0.503	**2.333**	0.354
NEL-M	0.638	0.071	0.568	0.223	**1.330**	**1.122**	0.452
NEL-C	0.515	0.211	0.343	0.113	0.711	0.093	0.255
EIM-1	0.685	0.585	0.086	0.709	0.722	**1.194**	0.525
EIM-2	0.496	0.331	-	-	-	-	0.405
NMi	-	-	-	**3.404**	0.845	0.528	**1.149**
CMI	0.064	0.086	0.030	0.309	0.178	0.952	0.143
INRIM	**1.129**	0.856	0.849	0.439	0.552	**1.262**	0.794
METAS	0.799	0.425	0.404	0.064	0.535	0.532	0.369
MIKES	0.506	0.030	0.165	0.320	0.311	0.220	0.195
PTB	**1.421**	**1.155**	0.923	0.966	0.931	0.094	0.710
LNE	0.432	0.023	0.004	0.031	0.148	0.016	0.037
FI	0.278	0.538	0.470	0.731	0.757	0.228	0.455
UME	0.439	0.175	0.188	0.963	0.938	0.540	0.438

Table 7: $En_{i,KCRV}$ values

A further comparison can be made between each pair of institutions, labelled i and j, that shows the degree to which each pair of laboratories are equivalent (d_{ij}). Note that, according to Cox's analysis[1], this measure of equivalence is independent of the key comparison reference value. Table 8 and Table 9 show these inter-laboratory values for Molbloc-A and Molbloc-B respectively at each flow rate.

	Flow mg/s	NEL-C	EIM-1	EIM-2	CMI	INRIM	METAS	MIKES	PTB	LNE	FI	UME
NEL-C	2.2		-0.220	0.012	-0.098	-0.123	-0.020	-0.236	0.121	-0.190	0.010	-0.234
	10.5		-0.150	-0.100	-0.052	-0.064	0.000	-0.026	0.133	-0.040	0.050	0.038
	20.8		0.040		0.051	0.028	0.090	0.106	0.191	0.056	0.130	0.133
EIM-1	2.2	0.220		0.232	0.122	0.097	0.200	-0.016	0.341	0.030	0.230	-0.014
	10.5	0.150		0.050	0.098	0.086	0.150	0.124	0.283	0.110	0.200	0.188
	20.8	-0.040			0.011	-0.012	0.050	0.066	0.151	0.016	0.090	0.093
EIM-2	2.2	-0.012	-0.232		-0.110	-0.135	-0.032	-0.248	0.109	-0.202	-0.002	-0.246
	10.5	0.100	-0.050		0.048	0.036	0.100	0.074	0.233	0.060	0.150	0.138
CMI	2.2	0.098	0.070	0.110		-0.025	0.078	-0.138	0.219	-0.092	0.108	-0.136
	10.5	0.052	-0.030	-0.048		-0.012	0.052	0.026	0.185	0.012	0.102	0.090
	20.8	-0.051	-0.180			-0.023	0.039	0.055	0.140	0.005	0.079	0.082
INRIM	2.2	0.123	-0.097	0.135	0.025		0.103	-0.113	0.244	-0.067	0.133	-0.111
	10.5	0.064	-0.086	-0.036	0.012		0.064	0.038	0.197	0.024	0.114	0.102
	20.8	-0.028	0.012		0.023		0.062	0.078	0.163	0.028	0.102	0.105
METAS	2.2	0.020	-0.200	0.032	-0.078	-0.103		-0.216	0.141	-0.170	0.100	-0.214
	10.5	0.000	-0.150	-0.100	-0.052	-0.064		-0.026	0.133	-0.040	0.090	0.038
	20.8	-0.090	-0.050		-0.039	-0.062		0.016	0.101	-0.034	-0.314	0.043
MIKES	2.2	0.236	0.016	0.248	0.138	0.1128	0.216		0.357	0.046	0.246	0.002
	10.5	0.026	-0.124	-0.074	-0.026	-0.0383	0.026		0.159	-0.014	0.076	0.064
	20.8	-0.106	-0.066		-0.055	-0.0776	-0.016		0.085	-0.050	0.024	0.027
PTB	2.2	-0.121	-0.341	-0.109	-0.219	-0.244	-0.141	-0.357		-0.311	-0.111	-0.355
	10.5	-0.133	-0.283	-0.233	-0.185	-0.197	-0.133	-0.159		-0.173	-0.083	-0.095
	20.8	-0.191	-0.151		-0.140	-0.163	-0.101	-0.085		-0.135	-0.061	-0.058
LNE	2.2	0.190	-0.030	0.202	0.092	0.067	0.170	-0.046	0.311		0.200	-0.044
	10.5	0.040	-0.110	-0.060	-0.012	-0.024	0.040	0.014	0.173		0.090	0.078
	20.8	-0.056	-0.016		-0.005	-0.028	0.034	0.050	0.135		0.074	0.077
FI	2.2	-0.010	-0.230	0.002	-0.108	-0.133	-0.030	-0.246	0.111	-0.200		-0.244
	10.5	-0.050	-0.200	-0.150	-0.102	-0.114	-0.050	-0.076	0.083	-0.090		-0.012
	20.8	-0.130	-0.090		-0.079	-0.102	-0.040	-0.024	0.061	-0.074		0.003
UME	2.2	0.234	0.014	0.246	0.136	0.111	0.214	-0.002	0.355	0.044	0.244	
	10.5	-0.038	-0.188	-0.138	-0.090	-0.102	-0.038	-0.064	0.095	-0.078	0.012	
	20.8	-0.133	-0.093		-0.082	-0.105	-0.043	-0.027	0.058	-0.077	-0.003	

Table 8: Molbloc-A Degrees of Equivalence d_{ij} - institution i; institution j

	Flow mg/s	NEL-C	EIM-1	CMI	INRIM	METAS	MIKES	PTB	LNE	FI	UME
NEL-C	**83**		0.158	-0.042	-0.044	0.024	0.114	0.169	0.012	-0.110	-0.462
	320		0.260	0.065	0.064	0.162	0.242	0.263	0.150	0.000	-0.350
	572		0.250	0.310	-0.111	0.059	-0.050	0.030	0.012	-0.020	-0.254
EIM-1	**83**	-0.158		-0.200	-0.202	-0.134	-0.044	0.011	-0.146	-0.268	-0.620
	320	-0.260		-0.195	-0.196	-0.098	-0.018	0.003	-0.110	-0.260	-0.610
	572	-0.250		0.060	-0.361	-0.191	-0.300	-0.220	-0.238	-0.270	-0.504
CMI	**83**	0.042	0.200		-0.002	0.066	0.156	0.211	0.054	-0.068	-0.420
	320	-0.065	0.195		-0.001	0.097	0.177	0.198	0.085	-0.065	-0.415
	572	-0.310	-0.060		-0.421	-0.251	-0.360	-0.280	-0.298	-0.330	-0.564
INRIM	**83**	0.044	0.202	0.002		0.068	0.158	0.213	0.056	-0.066	-0.418
	320	-0.064	0.196	0.001		0.098	0.178	0.199	0.086	-0.064	-0.413
	572	0.111	0.361	0.421		0.170	0.061	0.141	0.123	0.091	-0.142
METAS	**83**	-0.024	0.134	-0.066	-0.068		0.090	0.145	-0.012	-0.134	-0.486
	320	-0.162	0.098	-0.097	-0.098		0.080	0.101	-0.012	-0.162	-0.512
	572	-0.059	0.191	0.000	-0.170		-0.109	-0.029	-0.047	-0.079	-0.313
MIKES	**83**	-0.114	0.044	-0.156	-0.158	-0.090		0.055	-0.102	-0.224	-0.576
	320	-0.242	0.018	-0.177	-0.178	-0.080		0.021	-0.092	-0.242	-0.592
	572	0.050	0.300	0.360	-0.061	0.109		0.080	0.062	0.030	-0.204
PTB	**83**	-0.169	-0.011	-0.211	-0.213	-0.145	-0.055		-0.157	-0.279	-0.631
	320	-0.263	-0.003	-0.198	-0.199	-0.101	-0.021		-0.113	-0.263	-0.613
	572	-0.030	0.220	0.280	-0.141	0.029	-0.080		-0.018	-0.050	-0.284
LNE	**83**	-0.012	0.146	-0.054	-0.056	0.012	0.102	0.157		-0.122	-0.474
	320	-0.150	0.110	-0.085	-0.086	0.012	0.092	0.113		-0.150	-0.500
	572	-0.012	0.238	0.298	-0.123	0.047	-0.062	0.018		-0.032	-0.266
FI	**83**	0.110	0.268	0.068	0.066	0.134	0.224	0.070	0.122		-0.352
	320	0.000	0.260	0.065	0.064	0.162	0.242	-0.010	0.150		-0.350
	572	0.020	0.270	0.330	-0.091	0.079	-0.030	0.030	0.032		-0.234
UME	**83**	0.462	0.620	0.420	0.418	0.486	0.576	0.631	0.474	0.352	
	320	0.350	0.610	0.415	0.413	0.512	0.592	0.613	0.500	0.350	
	572	0.254	0.504	0.564	0.142	0.313	0.204	0.284	0.266	0.234	

Table 9: Molbloc-B Degrees of Equivalence d_{ij} - institution i; institution j

In a similar fashion to the calculation of an *En* value between a national institute and the KCRV, we can define an inter-laboratory *En* value pertaining to the measurements made between a pair of laboratories taking part in the key comparison. Table 10 and Table 11 show the calculated inter-laboratory *En* values between each pair of laboratories that have been included in the KCRV analysis for the results obtained for Molbloc-A and Molbloc-B respectively. The tables are symmetric, so only the upper triangle has been filled. Results that are greater than 1.0 are shown highlighted.

The interpretation of *En* values is relatively simple. If the measurements from a given pair of laboratories, designated *i* and *j*, are in complete agreement, then the inter-laboratory *En*(*i-j*) number for that pair would be zero. An *En* value between 0.0 and 1.2 signifies that, although the measured values are not in complete agreement, there is good overlap of the measurement uncertainties from the two institutions. Values above 1.2 signify that the data from the two laboratories are not is good agreement and differ by more than their combined expanded uncertainties (k=2 coverage factor).

The *En* values derived for Molbloc-B confirm the reports that this transfer package appeared to be less stable than Molbloc-A.

	Flow mg/s	NEL-C	EIM-1	EIM-2	CMI	INRIM	METAS	MIKES	PTB	LNE	FI	UME
NEL-C	2.2		0.838	0.046	0.373	0.695	0.104	0.684	0.534	0.637	0.026	0.615
	10.5		0.571	0.381	0.198	0.363	0.000	0.075	0.587	0.144	0.213	0.084
	20.8		0.152		0.194	0.160	0.468	0.307	0.842	0.190	0.557	0.302
EIM-1	2.2			0.838	0.431	0.470	0.912	0.044	**1.364**	0.095	0.576	0.036
	10.5			0.571	0.346	0.416	0.684	0.344	**1.132**	0.370	0.777	0.406
	20.8				0.039	0.056	0.228	0.366	0.604	0.051	0.351	0.205
EIM-2	2.2				0.389	0.656	0.146	0.688	0.436	0.639	0.005	0.623
	10.5				0.170	0.173	0.456	0.205	0.932	0.202	0.583	0.298
CMI	2.2					0.122	0.356	0.383	0.876	0.291	0.270	0.345
	10.5					0.060	0.237	0.072	0.740	0.040	0.396	0.194
	20.8					0.110	0.178	0.153	0.560	0.016	0.308	0.181
INRIM	2.2						**1.002**	0.371	**1.544**	0.267	0.381	0.322
	10.5						0.625	0.126	**1.248**	0.108	0.674	0.243
	20.8						0.598	0.255	**1.028**	0.112	0.606	0.255
METAS	2.2							0.690	0.806	0.651	0.084	0.607
	10.5							0.083	0.760	0.168	0.270	0.089
	20.8							0.051	0.577	0.132	0.218	0.103
MIKES	2.2								**1.064**	0.119	0.537	0.004
	10.5								0.474	0.038	0.223	0.124
	20.8								0.253	0.130	0.071	0.053
PTB	2.2									**1.083**	0.294	0.953
	10.5									0.650	0.376	0.214
	20.8									0.476	0.278	0.134
LNE	2.2										0.472	0.105
	10.5										0.329	0.165
	20.8										0.256	0.163
FI	2.2											0.503
	10.5											0.027
	20.8											0.007
UME	2.2											
	10.5											
	20.8											

Table 10: Molbloc-A, Inter-Laboratory *En* values

	Flow mg/s	NEL-C	EIM-1	CMI	INRIM	METAS	MIKES	PTB	LNE	FI	UME
NEL-C	83		0.602	0.160	0.196	0.125	0.331	0.724	0.043	0.444	0.874
	320		0.991	0.188	0.318	0.842	0.557	**1.127**	0.540	0.000	0.662
	572		0.952	0.873	0.554	0.307	0.145	0.129	0.043	0.086	0.480
EIM-1	83			0.707	0.812	0.611	0.122	0.043	0.491	0.996	**1.151**
	320			0.540	0.869	0.447	0.040	0.012	0.370	**1.015**	**1.132**
	572			0.162	**1.592**	0.871	0.832	0.859	0.800	**1.054**	0.935
CMI	83				0.008	0.301	0.433	0.823	0.182	0.253	0.779
	320				0.004	0.309	0.354	0.582	0.228	0.191	0.711
	572				**1.278**	0.774	0.832	0.799	0.781	0.942	0.957
INRIM	83					0.393	0.473	0.978	0.212	0.283	0.801
	320					0.712	0.431	**1.042**	0.354	0.332	0.809
	572					**1.217**	0.192	0.734	0.504	0.474	0.278
METAS	83						0.287	0.790	0.050	0.666	0.956
	320						0.195	0.550	0.050	0.882	**1.007**
	572						0.348	0.158	0.198	0.430	0.615
MIKES	83							0.162	0.274	0.640	0.987
	320							0.049	0.202	0.562	0.924
	572							0.235	0.167	0.088	0.349
PTB	83								0.577	**1.158**	**1.201**
	320								0.415	**1.162**	**1.167**
	572								0.066	0.221	0.540
LNE	83									0.429	0.867
	320									0.551	0.915
	572									0.118	0.486
FI	83										0.662
	320										0.666
	572										0.445
UME	83										
	320										
	572										

Table 11: Molbloc-B, Inter-Laboratory *En* values

9 CONCLUSION

Eleven laboratories entered into the comparison. One withdrew during the course of the project leaving ten participants in all.

The Molbloc-B package had some leakage problems during the course of the intercomparison and several laboratories reported stability problems especially at higher flow rates. NEL submitted three data sets and EIM submitted two. All were retained in the presentation of the results but only one of the NEL sets provided input to the determination of the KCRV. The second EIM set contained data on 2 flow rates for Molbloc-A only.

The results for Molbloc A and Molbloc B as plotted in figures 2 and 3, respectively, show a spread that is perhaps wider than originally anticipated. In an attempt to explain this behavior it was hypothesized that the spread could be, at least partially, attributed to the experimental conditions prevailing during the measurements and in particular to the inability of some laboratories to keep the upstream pressure at the recommended value. However, upon examination of the upstream pressure values reported, all laboratories kept the upstream pressure at the recommended levels despite some stability problems and the leak issues. Moreover, the spread of the data in both plots is rather uniform and no tendency for clustering between specific sets of data has been identified. Based on these findings the data spread could not be attributed to deviations from the recommended experimental conditions.

An adequate measure of consistency was achieved by using the CMC values for the standard uncertainty for each laboratory (except for METAS which requested that their calibration certificate value should be used) and by excluding the NMi data as being discrepant.

The majority of the 10 laboratories have E_n values which show consistency with one another (values less than 1.0) with 7 exceptions for Molbloc-A, from a total of 156 values, which represents ~4.5%. Of the 7 exceptions, only 3 had E_n values that were greater than 1.2.

There were 13 exceptions for Molbloc-B, from a total of 135 values, which represents ~9.6%. However of the 13 E_n values that exceeded 1.0, only 3 were greater than 1.2.

Six KCRVs have been generated for the two transfer standard packages; three for each package and are given below with their expanded uncertainties (k=2 coverage factor).

Transfer Standard	Flow [mg/s]	KCRV [%]	±Uncertainty (k=2) [%]
Molbloc-A	2.2	-0.064_5	0.037
	10.5	-0.145_0	0.036
	20.8	-0.196_8	0.037
Molbloc-B	83	0.021_3	0.053
	320	-0.048_0	0.050
	572	0.074_6	0.050

Table 12: Summary of the Key Comparison Reference Values (KCRVs)

There is a belief from some users that Molblocs, in experienced hands, perform much better than has been found in this work. If this is the case, then the procedure to be used in phase-2 of the project would benefit from some additional instructions according to the suggestions from those who have more expertise in their use.

10 APPENDIX - I

10.1 Introduction

Two procedures for the analysis of key comparisons have been described by Cox[1] that apply to the simple circulation of a single travelling standard around a number of participants. The procedure outcomes are a key comparison reference value (KCRV) and its associated uncertainty, the degree of equivalence of the measurements made by each participating national measurement institute and the degrees of equivalence between measurements made by all pairs of participating institutes. Procedure A applies when the following conditions are met:

1 Each participating national institute provides a measurement of a travelling standard having good short-term stability and stability during transport and the associated standard uncertainty.

2 Each institute's measurement is realised independently of the other institutes' measurements in the key comparison. (Implies no mutual dependence of the institute's measurements).

3 For each institute a Gaussian distribution (with a mean equal to the institute's measurement and standard deviation equal to the provided associated standard uncertainty) can be assigned to the measurand of which the institute's measurement is an estimate.

10.2 Procedure-A

Procedure A is based on a least squares adjustment when the three conditions, stated above, apply.

Step-1: Determine the weighted mean, y, of the institutes' measurements, using the inverses of the squares of the associated standard uncertainties as the weights:

$$y = \frac{x_1 / u^2(x_1) + \ldots + x_N / u^2(x_N)}{1/u^2(x_1) + \ldots + 1/u^2(x_N)} \qquad (2)$$

Step-2: Determine the standard deviation, $u(y)$, associated with y, from:

$$\frac{1}{u^2(y)} = \frac{1}{u^2(x_1)} + \ldots + \frac{1}{u^2(x_N)} \qquad (3)$$

Step-3: Apply a chi-squared test to carry out an overall consistency check of the results obtained:

3(a) Form the observed chi-squared value:

$$\chi^2_{obs} = \frac{(x_1 - y)^2}{u^2(x_1)} + \ldots + \frac{(x_N - y)^2}{u^2(x_N)} \qquad (4)$$

3(b) Assign the degrees of freedom:

$$v = N - 1 \tag{5}$$

3(c) Regard the consistency check as failing if:

$$\Pr\left\{\chi^2(v) > \chi^2_{obs}\right\} < 0.05 \tag{6}$$

Where in equation (6), Pr denotes "Probability of".

Step-4: If the chi-squared consistency check does **not fail**:

4(a) Accept y as the KCRV x_{ref}.

4(b) Accept $u(y)$ as the standard uncertainty $u(x_{ref})$ associated with x_{ref} .

4(c) Calculate the degrees of equivalence:

(i) For the $i = 1...,N$ form the degree of equivalence of institute i as the pair of values $(d_i, U(d_i))$, using:

$$\left.\begin{aligned} d_i &= x_i - x_{ref} \\ U(d_i) &= 2u(d_i) \\ &where \\ u(d_i) &= \sqrt{\left(u^2(x_i)\right) - u^2(x_{ref})} \end{aligned}\right\} \tag{7}$$

(ii) For $i = 1...,N$ and $j = 1...,N$ with $j \neq i$ form the degree of equivalence between institute i and institute j as the pair of values $(d_{ij},U(d_{ij}))$ using:

$$\left.\begin{aligned} d_{ij} &= x_i - x_j \\ U(d_{ij}) &= 2u(d_{ij}) \\ &where \\ u(d_{ij}) &= \sqrt{\left(u^2(x_i) + u^2(x_j)\right)} \end{aligned}\right\} \tag{8}$$

4(d) Record the results and the manner in which they were determined.

4(e) Finish

Step-5: If the consistency check in step-3 fails:

5(a) Identify discrepant measurements. If:

$$|d_i| > 2u(d_i) \tag{9}$$

Then classify x_i as discrepant at the 5% level of significance.

Note that, on *the basis of statistical variability alone*, 5% of the measurements would be expected to be classified as discrepant.

10.3 *En* Values

An alternative method of expressing the degree of equivalence between the corresponding measurements for a national laboratory and the evaluated KCRV is to define a dimensionless parameter, En, where:

$$En_{i,KCRV} = \frac{|d_i|}{2u(x_i)} \tag{10}$$

This parameter can also be employed to characterize the degree of equivalence of two participating laboratories, i and j, where the individual degrees of uncertainty d_i and d_j and the standard uncertainties for each laboratories are combined as given in equation (11):

$$En_{i,j} = \frac{|d_i - d_j|}{2\sqrt{\left(u^2(x_i) + u^2(x_j)\right)}} \tag{11}$$

The advantage of using En values are they are dimensionless and the interpretation of the value is relatively easy. For a given laboratory pair that is in complete agreement, the En value would be 0. For laboratories that are in good agreement, the values usually lie in the range 0 < En < 1 and may go up to 1.2. Any values above this upper limit show that the laboratories are not in agreement and the measurements lie outside the their mutual expanded uncertainty limits (k = 2 coverage factor).

11 REFERENCES

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