Interlaboratory Comparison Measurement SPB-1

Final report

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This report can be downloaded at http://www.ut.ee/katsekoda/ILC/

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1 The Aim of the Intercomparison

The aim of the SPB-1 intercomparison was to allow the participating laboratories to check the performance of their UV-Vis spectrophotometers, namely the accuracy of the absorbance scale.

2 Organization

2.1 General

The intercomparison measurement was organized jointly by University of Tartu Testing Centre (below UT), Vilnius Semiconductor Physics Institute and Latvian University.

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The Final report was compiled by UT and is available at the website of UT at http://www.ut.ee/katsekoda/ILC/. The participants are listed in the final report but the results are presented in random order, so that the results cannot be traced back to the participants. Every participant will receive a private letter revealing his/her result number and permitting assessment of performance.

2.2 The Sample

The sample was a neutral density filter and the measurands were the absorbance values of this glass filter at 410, 510 and 600 nm. The absorbance values of the filters have been calibrated at HUT/MIKES.

3 Participants

Invitations were sent to a number of laboratories in Estonia, Latvia and Lithuania. The participants are listed in Table 1.

Table 1. Participants to SPB-1.

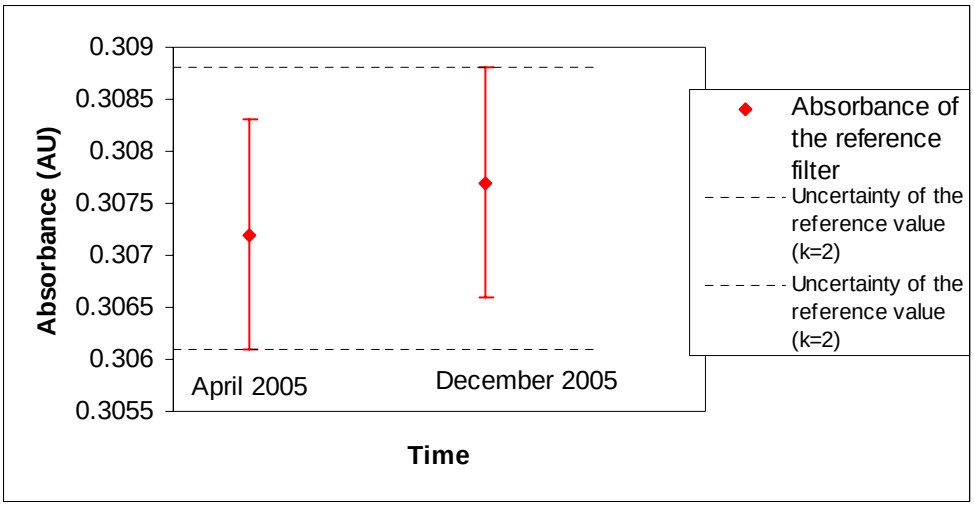
Institution	Country
Estonian Agricultural University,Institute of Veterinary Medicine and Animal Science, Department of Animal Nutrition, Laboratory of Milk Quality	Estonia
Põlva Piim Tootmine OÜ	Estonia
Werol Tehased AS	Estonia
Metrosert Ltd, Tartu Laboratory	Estonia
Tallinn University of Technology, Department of Oil Shale Technology Fuel Research and Testing Laboratory	Estonia
Silmet Ltd, Central laboratory	Estonia
Laboratory of Rakvere Meat Processing Company	Estonia
Areto OÜ	Estonia
Saaremaa Veterinary and Food Laboratory	Estonia
Saybolt Estonia Ltd	Estonia
Agricultural Research Center	Estonia
Joint Water Quality Control Laboratory of “Riga Water” Ltd. (Group 1)	Latvia
Joint Water Quality Control Laboratory of “Riga Water” Ltd. (Group 2, instrument Jenway 6300)	Latvia
Joint Water Quality Control Laboratory of “Riga Water” Ltd. (Group 2, instrument Thermo Spectronic Helios E)	Latvia
Joint Water Quality Control Laboratory of “Riga Water” Ltd. (Group 3, instrument Jenway 6300)	Latvia
Joint Water Quality Control Laboratory of “Riga Water” Ltd. (Group 3, instrument Jenway 6105)	Latvia
Ltd Vides audits	Latvia
Laboratory of Hygiene and Occupational Diseases of Riga Stradins University	Latvia
Laboratory of quantitative analysis, Faculty of Chemistry, UL	Latvia
Laboratory of the Chemistry State agency “Public Health Agency”	Latvia
JSC Itaina, Laboratory for quality control of alcohol products	Lithuania
Kaunas Public Health Center,Chemical and Physical Testing Laboratory	Lithuania
AB Mazeikiu Nafta, Environmental Laboratory	Lithuania
SE Pieno tyrimai	Lithuania

4 Results

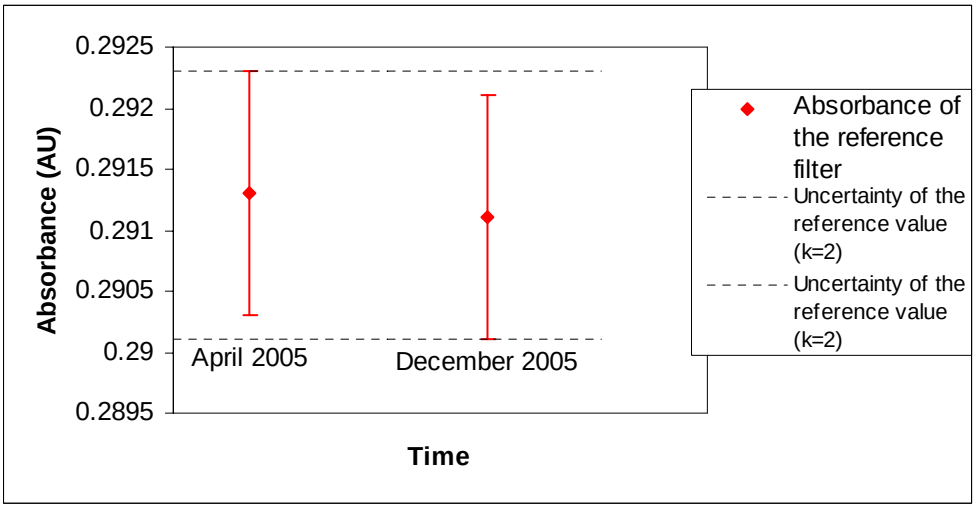
4.1 Deriving the Reference value

As stated above, the absorbance values of the sample filter were calibrated at HUT/MIKES (Finland). The calibration was performed two times – before the SPB-1 intercomparison in April 2005 and in December 2005 after the measurements by the participants were finished. The calibration results are given in Schemes 1, 2 and 3 and in Table 2.

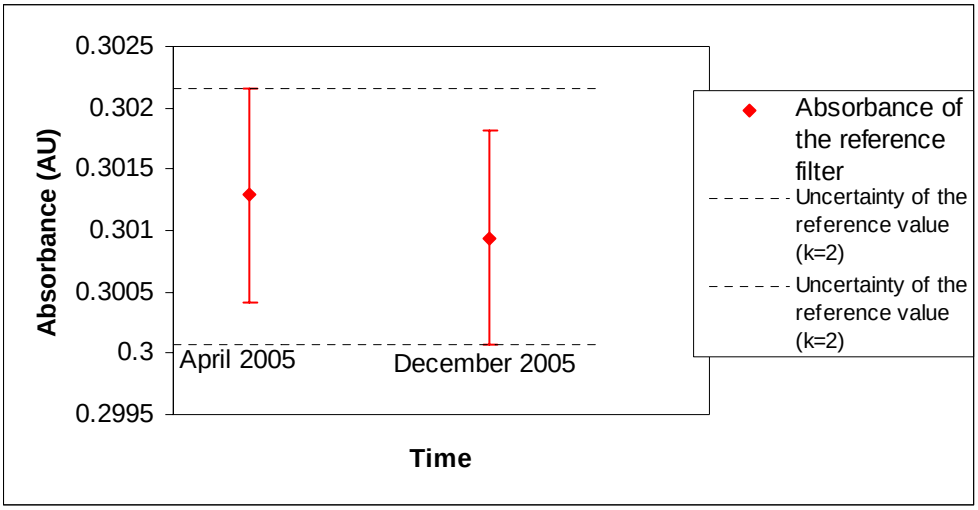
Scheme 1. Results of Calibration of the Absorbance Value of the Sample Filter at 410 nm.



Scheme 2. Results of Calibration of the Absorbance Value of the Sample Filter at 510 nm.



Scheme 3. Results of Calibration of the Absorbance Value of the Sample Filter at 600 nm.



In order to get the reference value for the SPB-1 measurement, the following approach was used. The reference absorbance value A_{ref} for the sample filter at given wavelength was calculated as the average of the two calibration values A_{high} and A_{low}:

$$A_{ref} = \frac{A_{high} + A_{low}}{2} \quad (1)$$

The uncertainty range (k=2) for the reference values was defined as the range between the higher absorbance value plus its uncertainty and the lower absorbance value minus its uncertainty (both uncertainties assigned by HUT/MIKES) for every wavelength:

$$A_{low} - U_{\mathrm{HUT}}(A_{low}) \quad \ldots \quad A_{high} + U_{\mathrm{HUT}}(A_{high}) \quad (2)$$

So the uncertainty range was slightly expanded as compared to the range of a single calibration. The reference values and their uncertainties U (k=2) are given in Table 2. The uncertainties are given as half of the ranges defined by equation 2. The results allow to conclude that the parameters of the filter have changed insignificantly during the intercomparison.

Table 2. Calibration Data for the Sample Filter and the Reference Absorbance Values for SPB-1 measurement.

		410 nm	510 nm	600 nm
April 2005	Absorbance value (AU)	0.3072	0.2913	0.3013
	Uncertainty (U_{HUT}) (k=2)	0.0011	0.001	0.00087
December 2005	Absorbance value (AU)	0.3077	0.2911	0.3009
	Uncertainty (U_{HUT}) (k=2)	0.0011	0.001	0.00087
Reference value	**Absorbance value (AU)**	**0.3075**	**0.2912**	**0.3011**
	Uncertainty (*U*) (k=2)	**0.0014**	**0.0011**	**0.0010**

4.2 Results of the Participants

Results of the participants are presented in Table 3 the same way as provided by the participants. The results of absorbance measurements at UT are given separately in Table 4.

Table 3. Participant Results together with the Expanded Uncertainties.[a]

	Absorbance values					
	410 nm		**510 nm**		**600 nm**	
Lab Number[b]	**Result**[c] **AU**	**Uncertainty AU**	**Result AU**	**Uncertainty AU**	**Result AU**	**Uncertainty AU**
1	0.308	0.0011	0.292	0.0009	0.302	0.001
2	0.301	0.01	0.293	0.01	0.301	0.01
3	0.3079	0.01078	0.2923	0.01078	0.3023	0.01078
4	0.309	Not given	0.293	Not given	0.294	Not given
5	0.309	Not given	0.291	Not given	0.302	Not given
6	0.318	0.004	0.295	0.004	0.306	0.004
7	0.301	0.004	0.29	0.004	0.298	0.004
8	0.309	0.004	0.292	0.002	0.302	0.003
9	0.141	0.00164	0.251	0.0082	0.273	0.00104
10	0.3081	0.0022	0.2921	0.0022	0.3019	0.0022
11	0.301	0.0064	0.285	0.006	0.294	0.0064

12	0.3084	0.0012	0.2924	0.0012	0.3019	0.0012
13	0.307	0.006	0.292	0.006	0.3	0.006
14	0.3091	0.003	0.293	0.003	0.3025	0.003
15	0.302	0.006	0.287	0.006	0.297	0.006
16	0.305	0.005	0.291	0.005	0.3	0.005
17	0.3081	0.0002	0.2921	0.0002	0.302	0.0002
18	0.312	0.003	0.296	0.003	0.304	0.003
19	0.309	0.001	0.293	0.001	0.302	0.001
20	0.308	0.006	0.293	0.006	0.302	0.006
21	0.309	0.005	0.292	0.005	0.301	0.005
22	0.309	0.004	0.294	0.004	0.301	0.003
23	0.307	0.004	0.292	0.002	0.301	0.004
24	0.3068	0.004	0.29	0.004	0.2994	0.004

[a]The coverage factor k=2 was used if the expanded uncertainty was not already given by the participant

[b] The participating laboratories are given numbers in random order that is different from the order given in Table 1. However, the order of countries was preserved: results 1 to 11 are from Estonia, 12 to 20 from Latvia and 21 to 24 from Lithuania.

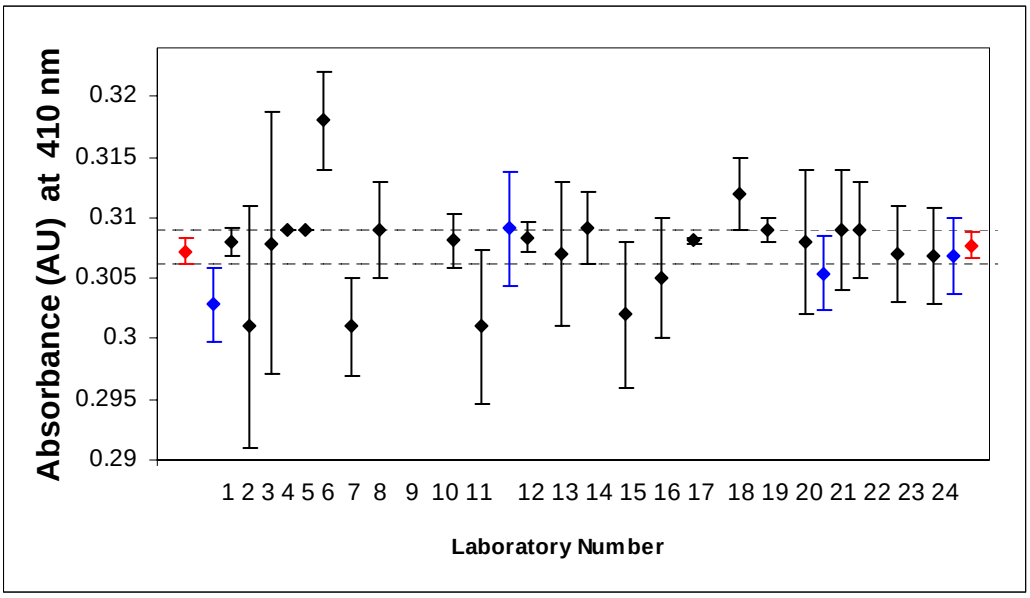
[c]The results are presented the same way as they were presented by the participants.

Table 4. Results of the Absorbance Measurements at UT.

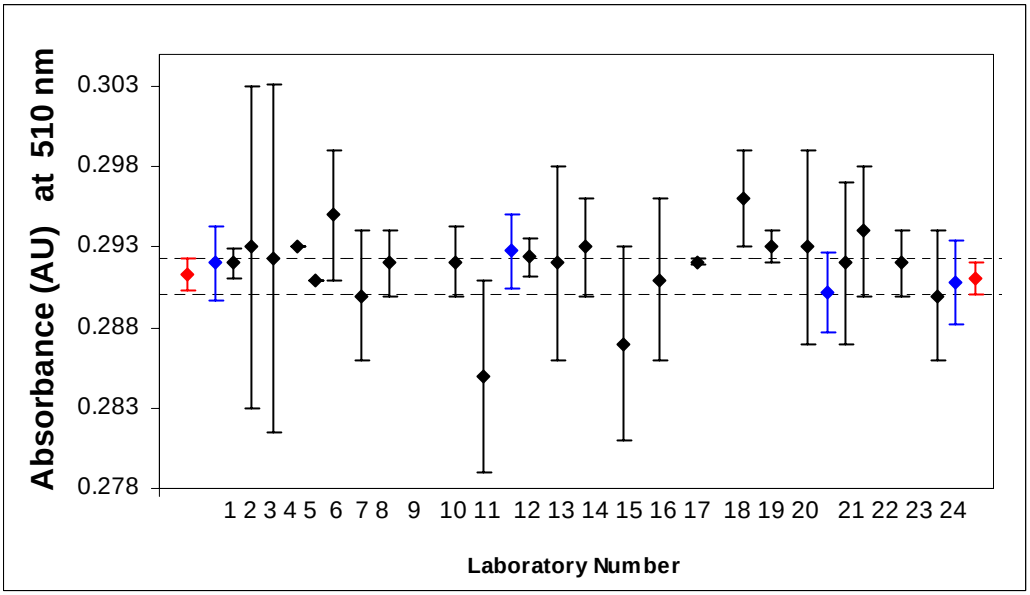
		410 nm	510 nm	600 nm
May 2005	Absorbance value (AU)	0.3028	0.2920	0.3015
	Uncertainty (k=2)	0.0031	0.0023	0.0044
June 2005	Absorbance value (AU)	0.3091	0.2928	0.3042
	Uncertainty (k=2)	0.0047	0.0023	0.0044
September 2005	Absorbance value (AU)	0.3054	0.2902	0.3012
	Uncertainty (k=2)	0.0031	0.0025	0.0044
October 2005	Absorbance value (AU)	0.3068	0.2908	0.3020
	Uncertainty (k=2)	0.0031	0.0026	0.0031

All the results are graphically presented in Schemes 4, 5 and 6. The absorbance values of calibrations at HUT/MIKES are given with red rectangles, the results of absorbance measurements at UT are given with blue rectangles and the results of absorbance measurements performed by the participants are given with black rectangles. The order of the laboratories is the same as in Table 3.

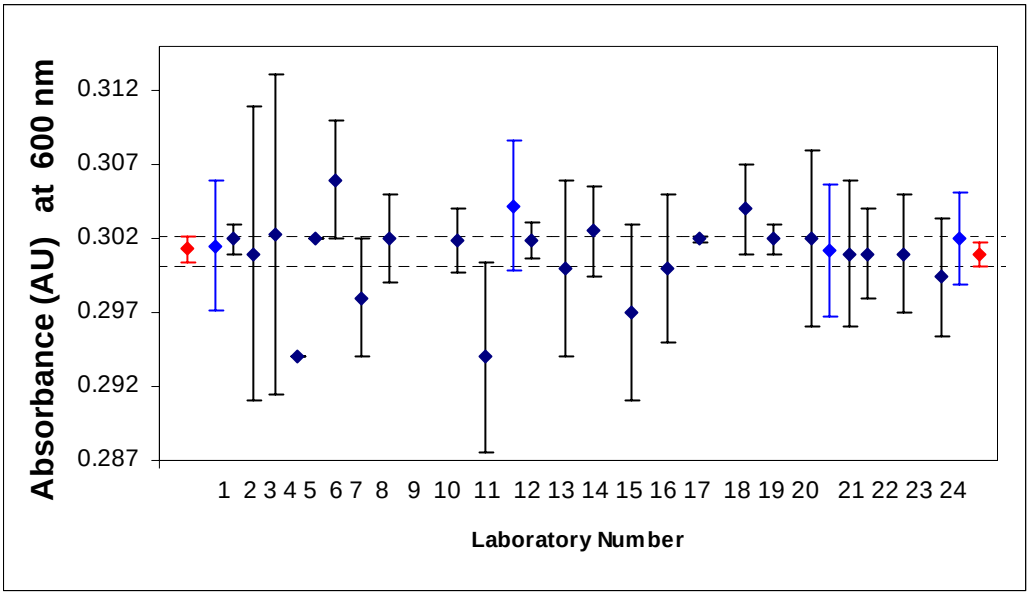
Scheme 4. The Results of the Absorbance Measurements at 410 nm (red rectangles – HUT/MIKES, blue rectangles – UT, black rectangles – participants of the measurement).



Scheme 5. The Results of the Absorbance Measurements at 510 nm (red rectangles – HUT/MIKES, blue rectangles – UT, black rectangles – participants of the measurement).



Scheme 6. The Results of the Absorbance Measurements at 600 nm (red rectangles – HUT/MIKES, blue rectangles – UT, black rectangles – participants of the measurement).



4.3 Data Treatment

The evaluation of participant data was done at UT according to the ISO Guide 43-1.[1] E_n numbers were used to assess the agreement between participant values and the reference values. The E_n numbers for absorbance are found as follows:

$$E_n = \frac{A_{lab} - A_{ref}}{\sqrt{U_{lab}^2 + U_{ref}^2}}, \quad (3)$$

where A_{lab} is the participant absorbance value, A_{ref} is the reference value of absorbance, U_{lab} is the expanded uncertainty of the participant value and U_{ref} is the expanded uncertainty of the reference value.

Criteria for laboratory performance based on the E_n numbers[2]:

a) $|E_n| \leq 1$: **satisfactory** (the result and the reference value agree);

b) $|E_n| > 1$: **unsatisfactory** (the result and reference value do not agree)

The $|E_n|$ numbers of the participants for absorbance measurements are given below:

[1] ISO Guide 43-1 *Proficiency Testing by Interlaboratory Comparisons. Part 1: Development and Operation of Proficiency Testing Schemes*, ISO/IEC 1997.

[2] The E_n number is strongly dependent on the uncertainty of the participant value. Therefore it does not directly indicate the quality of the participant value but only the agreement between it and the reference value (which, of course, is an important component of the quality of the result).

Table 5. The | E_n | Numbers of the Participants for Absorbance Measurements.

		$\|E_n\|$ number	
Lab number[a]	**410 nm**	**510 nm**	**600 nm**
1	0.32	0.56	0.61
2	0.64	0.18	0.01
3	0.04	0.10	0.11
4[b]	NA	NA	NA
5[b]	NA	NA	NA
6	2.50	0.92	1.18
7	1.53	0.29	0.75
8	0.37	0.35	0.28
9	78	29	19
10	0.25	0.37	0.32
11	0.99	1.02	1.10
12	0.53	0.74	0.49
13	0.07	0.13	0.18
14	0.5	0.56	0.44
15	0.89	0.69	0.68
16	0.47	0.04	0.22
17	0.48	0.80	0.83
18	1.38	1.50	0.91
19	0.92	1.21	0.61
20	0.09	0.30	0.15
21	0.30	0.16	0.02
22	0.37	0.73	0.04
23	0.11	0.48	0.03
24	0.15	0.31	0.41

[a] The participating laboratories are given in random order that is different from the order given in Table 1 but is identical to the order given in Table 3.

[b] It is not possible to calculate the E_n numbers because no uncertainties were reported by the participants.

The | E_n | numbers of the absorbance measurements performed at UT are given in Table 6.

Table 6. The | E_n | Numbers of UT for Absorbance Measurements.

		$\|E_n\|$ number	
	410 nm	**510 nm**	**600 nm**
May 2005	1.38	0.31	0.085
June 2005	0.33	0.62	0.68
September 2005	0.606	0.37	0.019
October 2005	0.19	0.14	0.27

5 Discussion

General. This interlaboratory comparison was the run to offer participants to test the performance of their UV-VIS spectrophotometers and uncertainty estimation at the international level. In total, 24 participants from three Baltic Countries took part in comparison measurement of three neutral density filters. Out of 72 results, 15 fell into category with $|E_n|>1$. Results of the country-wise comparison of participant performance are presented in Table 7.

Table 7. Country-Wise Comparison of Participant Performance.

Country	Number of submitted results	Number of results eligible for E_n-factor calculation	Number of results with $E_n>1$	Fraction of unsatisfactory results
EST	33	27	8	8/27
LAT	27	27	3	3/27
LIT	12	12	-	0/12

Stability of the sample. According to the results of calibrations presented in section 4.1 the stability of the sample during the intercomparison can be considered very good. From the calibration uncertainties reported by MIKES and the assigned uncertainty values presented in Table 2 it is possible to calculate the uncertainty component due to instability U_{instab} (k=2) of the filter according to the following equation:

$$U_{\text{instab}} = \sqrt{U^2 - U_{\text{HUT}}^2} \tag{4}$$

The following values of U_{instab} were found for the three wavelengths: 0.0009, 0.0005 and 0.0005 AU (for 410, 510 and 600 nm, respectively).