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Results of the first EC/OC comparison exercise for EU National Air Quality Reference Laboratories (AQUILA)

Summary

The JRC-IES European Reference Laboratory for Air Pollution (ERLAP) has organized in 2009 the first inter-laboratory comparison for the measurement of elemental carbon (EC) and organic carbon (OC) in particulate matter sampled on filters for the AQUILA Network. To this comparison AQUILA's European Union National Reference Laboratories for air quality or delegated organizations have participated, all using instrumentation of the same make (Sunset Laboratories Inc.[1]).
The objectives of this comparison have been to evaluate the performances of participants but also to study the effects of the use of different thermal analysis protocols currently used for analysis.

It has been shown – based on z-scores – that all participants using laboratory analyzers are able to meet a 25% expanded uncertainty as a "fitness-for-purpose" criterion for total carbon (TC, as the sum of OC and EC) and OC.
For EC this criterion is only met when results are evaluated by specific protocols (NIOSH or EUSAAR2) separately.
Field versions of the analyzer have been found for a number of samples to yield aberrant results.

Method evaluation according to ISO 5725-2 reveals that reproducibility relative standard deviations range:

- from 4% to 8% for TC
- from 5% to 12% for OC
- from 10% to 25% for EC.

Ratios of repeatability and reproducibility standard deviations indicate that the thermal-optical method used is quite robust.

Standard uncertainties calculated from results for duplicate samples range from 2,2 to 7,9% for OC, but from 4 to >50% for EC, indicating that some sample pairs may not be real duplicates for EC. This affects the uncertainties for TC that are higher for those pairs where the uncertainty for EC is high: 15,8% and 13,7% vs. 2,1% and 1,6%.

[1] The identification of commercial equipment does not imply recommendation or endorsement by the JRC-IES.

Introduction

Elemental Carbon (EC) and Organic Carbon (OC) are important constituents of the fine fraction of particulate matter (PM), both from the perspective of health risks due to inhalation and indication of sources of air pollution.
The latter has been the reason for including the requirement for measuring EC and OC in $PM_{2.5}$ at rural background locations in Air Quality Directive 2008/50/EC [1]. Results of these measurements can be used for source apportionment and assessment of contributions from long-range transport.

Directive 2008/50/EC does not specify a method for the measurement of EC and OC. However, thermal-optical determination of EC and OC on filters is almost exclusively used for this purpose. Currently, a European Technical Specification (TS) is being prepared for such measurements of EC and OC [2]. This TS will be transferred into a European Standard after validation of the method described, and may consequently become a European Reference Method.

For these reasons the JRC-IES European Reference Laboratory for Air Pollution (ERLAP) has organized in 2009 an inter-laboratory comparison among European Union National Reference Laboratories (NRL) for air quality or delegated organizations.
The objectives of this comparison are to evaluate the performances of participants but also to study the effects of the use of different thermal analysis protocols currently used for analysis [2].

Organization

Samples

High-volume samplers (Digitel DHA80) have been used to collect samples of PM_{10} on 150 mm diameter quartz-fibre filters at the following locations:

- Essen, urban background location
- Vienna, urban background location
- Ispra, rural background location.

A total of 13 samples have been collected over a period of 24 hours each:

- 5 in Essen, by sampling on 5 consecutive days (samples S1 – S5)
- 4 in Vienna, by sampling on 2 consecutive days using 2 samplers (samples S6 – S9)
- 4 in Ispra, by sampling on 2 days using 2 samplers (samples S10 – S13).

Samples S6 and S7, S8 and S9, S10 and S11, S12 and S13 may therefore be considered as duplicates. Upon receipt at ERLAP filters have been stored in a freezer.

Sub-samples and homogeneity testing

From each of the samples described in 2.1 square punches of 2x2 cm² have been prepared for dispatch to the participants. To the set one punch from a blank filter has been added.

Previous to the dispatch the homogeneity associated with the preparation of the sub-samples has been investigated using a separate sample collected in Ispra. The homogeneity has been assessed as the relative standard deviation (rsd) of the results of the determination of total carbon (TC). Filter punches have been taken from the centre of the filter and from the edges. The homogeneity for all punches is 3%; when only considering punches from the edges the homogeneity increases slightly to 4%.

Sub-samples and blank punches have been dispatched to participants in closed petri dishes.

Participants

Thermal-optical determinations of EC/OC are almost exclusively performed using one type of apparatus, the Sunset Labs Analyzer. Consequently, every member of AQUILA, the network of National Reference Laboratories for Air Quality Monitoring (NRL), equipped with the Sunset Labs thermal-optical analyzer has been invited to participate, together with laboratories of other institutions.

The list of participants is reported in Table 1. The Environmental Protection Agency of Lithuania did not take part in the comparison due to technical problems with the analyzer.

Table 1: List of participants and contact persons. Most laboratories are designated National Reference Laboratories (NRL)

	Name of laboratory	Notes	Contact persons
1	UBA GmbH, Austria	NRL	marina.froehlich@umweltbundesamt.at
2	NCSR-D, Athens		elefther@ipta.demokritos.gr
3	JRC EMEP Station		fabrizia.cavalli@jrc.it
4	Neri, Denmark	NRL	jakn@dmu.dk
5	Empa, Switzerland	NRL	christoph.hueglin@empa.ch
6	INERIS, France	NRL	Laura.CHIAPPINI@ineris.fr
7	CHMI, Czech republic	NRL	novakj@chmi.cz
8	UBA, Germany	NRL	elke.bieber@uba.de
9	LRA, Portugal	NRL	joana.brantes@apambiente.pt
10	VMM, Belgium	NRL	j.vercauteren@vmm.be
11	ERLAP		annette.borowiak@jrc.ec.europa.eu
12	NPL, UK	NRL	paul.quincey@npl.co.uk
13	Universita' di Milano		andrea.piazzalunga@unimib.it
14	GGD, Amsterdam		ddjonge@ggd.amsterdam.nl
15	ISCIII, Spain	NRL	sgarcia@isciii.es
16	IMI, Croatia		rgodec@imi.hr

Thermal-optical analysis

Although thermal-optical analysis is a widely used method to quantify elemental and organic carbon in PM samples, information on the comparability of different analytical protocols is scarce and there is no clear indication of the expected uncertainty range in currently available carbon measurements. In the European Union two protocols (and variations hereof) are mainly used: the NIOSH protocol [3] and the EUSAAR2 protocol [4].
NIST has produced a reference material (RM 8785) for the measurement of EC, OC and total carbon (TC) in PM on filters [5] with (tentative) uncertainties for each measurand for the so-called STN-NIOSH protocol: 12% for EC, 14% for OC and 12,7% for TC, all expressed at the 95% confidence level.

Since one of the objectives of the comparison is to quantify the uncertainties in present state EC/OC measurements and since no standard protocol is yet available, each laboratory has been asked to analyze the samples with its usual protocol. The type of analytical protocols and OC charring correction, the punch sizes and the presence of replicate measurements are summarized in The duration and the maximum temperatures of the ramps in the three analytical protocols are shown in table 4; as an example of the NIOSH-type protocols, the ERLAP protocol is reported in the table. In order to reduce the formation of pyrolized OC (“charring”) the EASAAR2 protocol is characterized by the lowest maximum temperature in the OC ramps and by a longer duration of the OC analysis (see [4] for details on the protocol).

Table 2.

Transmittance has been chosen by every participant to correct for OC charring and most laboratories have used 1,5 cm² punches.

Two laboratories have used the field version of the Sunset analyzer, all others have used the laboratory version. The main differences between the two types of analyzers are:

- the detector (NDIR in the field version, FID in the laboratory version)
- the way to insert the sample (the field version is meant for semi-continuous analysis, so no sample boat is provided for)
- the analytical protocol (in the field version is shorter and with less temperature ramps).

Basically, three analytical methods have been used in the comparison: small variations on the NIOSH method, the field version protocol, again similar to the NIOSH protocol, and the EUSAAR2 protocol. Given the different instrumental setup, the punch areas analyzed with the field versions are different from all the others (see The duration and the maximum temperatures of the ramps in the three analytical protocols are shown in table 4; as an example of the NIOSH-type protocols, the ERLAP protocol is reported in the table. In order to reduce the formation of pyrolized OC ("charring") the EASAAR2 protocol is characterized by the lowest maximum temperature in the OC ramps and by a longer duration of the OC analysis (see [4] for details on the protocol).

Table 2).

The majority of participants have used samples of 1,5 cm² ; of the laboratories using the EUSAAR2 protocol only JRC has employed 1 cm² samples. By contrast, half of the labs using NIOSH-type protocols have employed 1 cm². Replicate measurements have been performed by 8 laboratories, only two of them using the EUSAAR2 protocols. One lab has used both the NIOSH and the EUSAAR2 protocols (The duration and the maximum temperatures of the ramps in the three analytical protocols are shown in table 4; as an example of the NIOSH-type protocols, the ERLAP protocol is reported in the table. In order to reduce the formation of pyrolized OC ("charring") the EASAAR2 protocol is characterized by the lowest maximum temperature in the OC ramps and by a longer duration of the OC analysis (see [4] for details on the protocol).

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The duration and the maximum temperatures of the ramps in the three analytical protocols are shown in table 4; as an example of the NIOSH-type protocols, the ERLAP protocol is reported in the table. In order to reduce the formation of pyrolized OC ("charring") the EASAAR2 protocol is characterized by the lowest maximum temperature in the OC ramps and by a longer duration of the OC analysis (see [4] for details on the protocol).

Table 2 Analytical protocols, type of charring correction and punch sizes. Laboratories providing replicate measurements are labeled with X

	Laboratory	Analytical method	Charring correction	Punch area	Replicates
1	Umweltbundesamt GmbH, Austria	NIOSHlike (Field version)	transmittance	2.01	
2	NCSR-D, Athens	NIOSHlike (Field version)	transmittance	1.76	
3	JRC	EUSAAR2	transmittance	1	
4	Neri, Denmark	EUSAAR2	transmittance	1.5	S7, S12
5	Empa, Switzerland	EUSAAR2	transmittance	1.5	X
6	INERIS, France	EUSAAR2	transmittance	1.5	X
7	CHMI, Czech republic	EUSAAR2	transmittance	1.5	
8	UBA, Germany	EUSAAR2/NIOSH like	transmittance	1.5	two methods
9	LRA, Portugal	NIOSH like	transmittance	1.5	X
10	VMM, Belgium	NIOSH like	transmittance	1	
11	ERLAP	NIOSH like	transmittance	1	X
12	NPL, UK	NIOSH like	transmittance	1	X
13	Universita' di Milano	NIOSH like	transmittance	1	X
14	GGD, Amsterdam	NIOSH like	transmittance	1.5	
15	ISCIII, Spain	NIOSH like	transmittance	1.5	X
16	IMI, Croatia	NIOSH like	transmittance	1.5	X

Table 3: Details of the three analytical protocols used by participants

	Field		NIOSH		EUSAAR2	
	UBA-A Temp. ramps		ERLAP Temp. ramps			
Carrier gas	Seconds	ºC	Seconds	ºC	Seconds	ºC
Helium	10	-	70	310	120	200
Helium	95	600	60	475	150	300
Helium	85	840	60	615	180	450
Helium	42	-	105	870	180	650
Helium	3	550				
Tot. OC analysis	3,9	minutes	4,9	minutes	10,5	minutes
Oxygen in Helium	35	550	60	550	120	500
Oxygen in Helium	45	650	60	625	120	550
Oxygen in Helium	90	870	60	700	70	700
Oxygen in Helium			60	775	80	850
Oxygen in Helium			110	890		
Oxygen in Helium						
Tot. EC analysis	2,8 minutes		5,83 minutes		6,5 minutes	
Tot. analysis:	7 minutes		11 minutes		17 minutes	
Punch size (cm²)	2,01 or 1,76		1,0 or 1,5		1,0 or 1,5	
% Oxygen in Helium	10%		10% or 2%		10%	

Data evaluation

Laboratory performance

Usually z-scores are calculated to evaluate the capacity of the laboratory to comply with the data quality objective (DQO) of the measurements, as stated in ISO 13528 [6]. The z-score is calculated as:

$$z = \frac{(x - X)}{\sigma}$$

where

x is the result of the participant,
X is the assigned value for the sample
σ is the "fitness for purpose" standard deviation.

X is a robust average, calculated from participants' data with a recursive algorithm, as in Annex C of ISO 13528. To reproduce the actual conditions of currently available carbon

data, analyzed with different protocols, both NIOSH and EUSAAR2 data together have been used for the calculation of X.

Because of lack of data quality objectives and reference methods for EC/OC measurements the fitness for purpose standard deviation cannot be based on existing information. In order to bridge this gap values for σ have been calculated using an inverse approach: data have been tested against two hypothetical DQOs: 25%, i.e. the DQO for uncertainty in PM fixed sites measurements and 40%, the DQO for uncertainty in As, Cd and Ni analysis in PM.

The fitness for purpose standard deviation is then calculated as:

$$\sigma = \sqrt{\left(\frac{DQO^2}{4} - u_s^2 \right)}$$

where

DQO is 25% or 40%
u_s is the uncertainty of sampling (5%).

z-Scores between -2 and 2 (warning signal limit) are an indication of satisfactory performance, z-scores below -3 or above 3 are indications of unsatisfactory performance. Other scores qualify results as "questionable".

Method (protocol) performance

Differences in the analytical protocols are known to cause differences in the split between EC and OC, but do not affect the total carbon (TC) concentrations. Therefore, the preliminary assessment of the consistency of the dataset was carried out on TC. ISO5725-2 [7] has been followed to estimate TC data consistency, at first graphically, by means of Mandel's *h* and *k* statistics. The first parameter describes the between-laboratory consistency and has been calculated for every laboratory and every sample, while the latter estimates the within-laboratory consistency and has been calculated only for the laboratories that provided replicate measurements.

After elimination of outliers based on Mandel's *h* statistics, ISO5725-2 has been used to quantify the repeatability and reproducibility of NIOSH-type and EUSAAR2 protocols for TC, EC and OC analysis. Here, a potential for obtaining results biased towards the performance of the NIOSH-type protocol is present since 6 of 8 laboratories that have reported replicate results use NIOSH-type protocols. Because of this the relative standard deviation of laboratory means has been considered as an alternative approximation for the reproducibility standard deviation.

Finally, results from the pairs of duplicate samples (S6-S7; S8-S9; S10-S11; S12-S13) have been used to calculate uncertainties for each of the duplicates as:

$$u^2_{x(i),x(i+1)} = \frac{\sum_j \left[x(i)_j - x(i+1)_j\right]^2}{2n}$$

where

$u_{x(i),x(i+1)}$	is the uncertainty for the pair of replicate samples x(i) and x(i+1)
$x(i)_j$	is the result of laboratory j for sample x(i)
$x(i+1)_j$	is the result of laboratory j for sample x(i+1)
n	is the number of replicates for samples x(i) and x(i+1).

Results

All results are presented in Tables 11-13 in Annex 1.

Evaluation

Laboratory performance

As may be observed from Figures 1 and 2, TC and OC measurements, regardless of analytical protocol, can easily comply with a DQO of 25%, although the blank variability is high. EC data do not meet the 25% DQO, but comply with the 40% DQO (Figure 3).

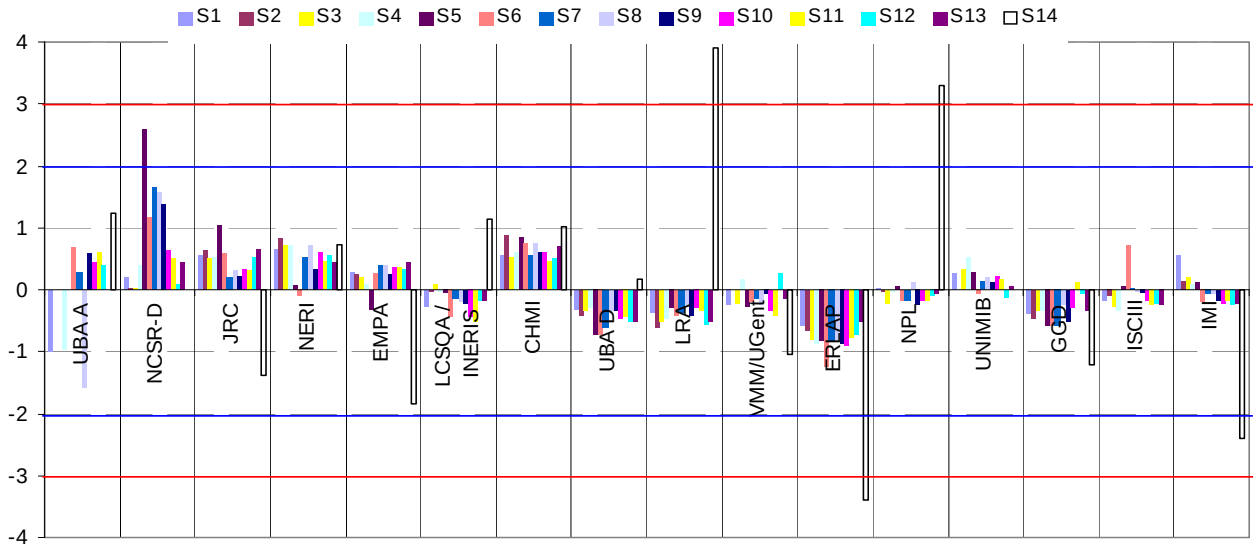

Figure 1. TC z-scores for DQO 25%. Regardless of analytical protocol, TC measurements comply with DQO 25%.

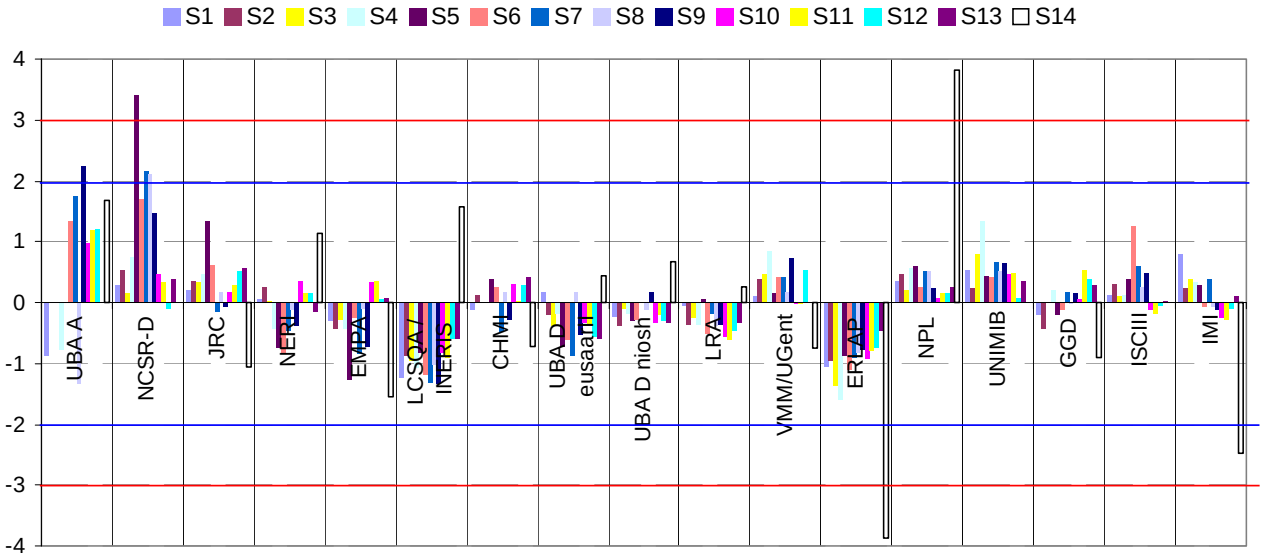

Figure 2. OC z-scores for DQO 25%. Regardless of analytical protocol, OC measurements comply with DQO 25%.

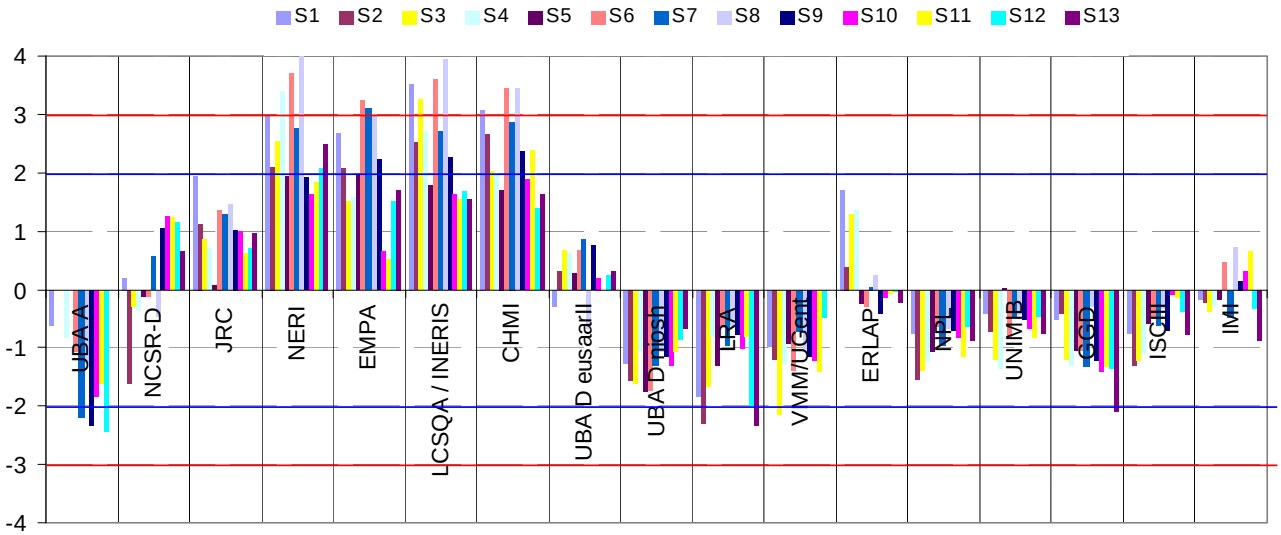

Figure 3. EC z-scores for DQO 40%. Regardless of analytical protocol, EC measurements comply with DQO 40%.

However, if separate calculations of the assigned values are made for NIOSH and EUSAAR2 data, also EC z-scores comply with the 25% DQO (Figure 4).

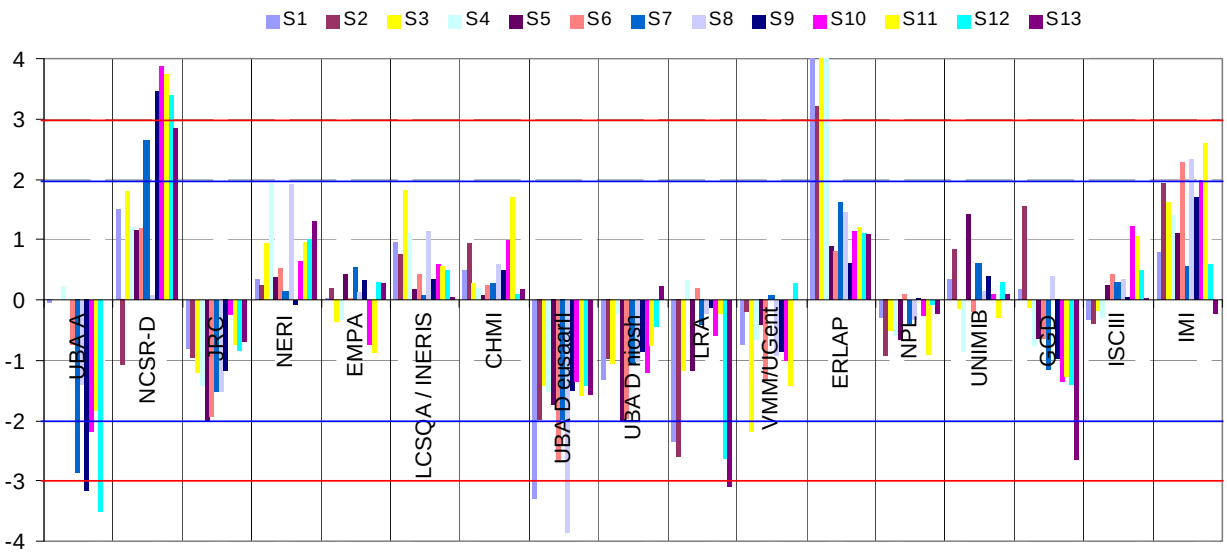

Figure 4. EC z-scores for DQO 25%. After recalculating z-scores separately for EUSAAR2 and NIOSH protocols, EC measurements tend to meet DQO = 25%.

Method performance

Mandel's statistics

The *h* statistics plot (Figure 5) shows that TC analysis made with the field version of the analyzer poses problems of both overestimation or underestimation of TC with respect to the results obtained with the laboratory version of the instrument. The outcome of the *h* statistic is confirmed by Grubb's test for outliers. In the TC data set, five outliers were identified, all of them from the field version analyzer, and have been removed from the data set before further evaluation (3.2).

The *k* statistic's results are plotted in Figure 6. Some samples were above the critical values, but there is no indication that either one particular sample, or one single laboratory was constantly above the limit. Results obtained using the field instruments have been omitted from the figure.

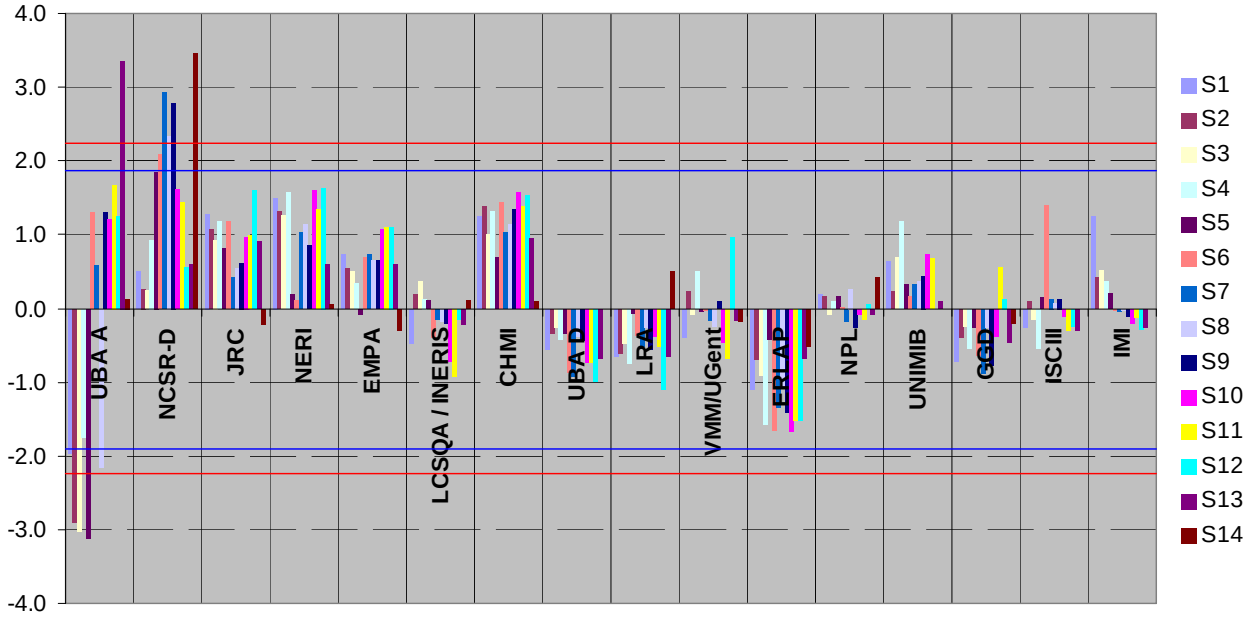

Figure 5: Mandel's h statistic values for between laboratory consistency on TC data. For 16 laboratories, h values should be < 2,33 at 1% significance level(red line) and < 1.86 at 5% significance level (blue line)

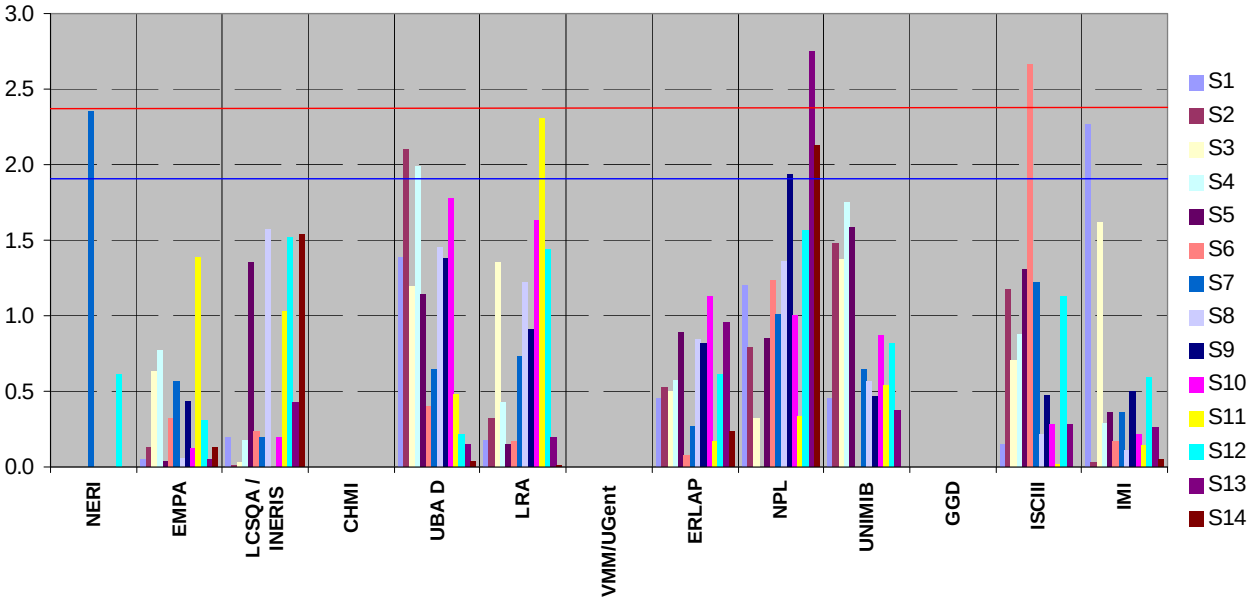

Figure 6: Mandel's k statistic values for within laboratory consistency on TC data. For 9 laboratories, k values should be < 2,29 at 1% significance level (red line) and < 1.90 at 5% significance level (blue line)

Repeatability and reproducibility

Repeatability and reproducibility standard deviations obtained from ISO 5725-2-based calculations are given in **Table 4**, 6 and 7, together with the reproducibility standard deviation of means.

For TC both reproducibility standard deviations are linearly related to carbon content and are about 5%. Contrary, TC repeatability and OC and EC repeatability and reproducibility vary between samples, but are not dependent on carbon concentration and, overall, no differences in replicabilities between analytical protocol performances are observed.

However, it is noteworthy that the general mean results for EC obtained when applying the NIOSH protocol are always lower than those obtained when using the EUSAAR2 protocol. The ratio between sample means for both protocols is quite constant: the average for the ratio NIOSH/EUSAAR2 is 0,638 with a standard deviation of 0,053. The reason for this discrepancy has not been further investigated within the frame of this comparison.

Table 4. Repeatability (*r*) and reproducibility (*R*) relative standard deviations, and relative standard deviation of means for TC

	General mean (µg/cm²)	*r* (%)	*R* (%)	*rsd* of means (%)
S1	27,8	3	5	4,8
S2	28,3	3	4	5,5
S3	31,8	3	5	5,0
S4	28,5	2	5	5,2
S5	13,9	3	5	6,3
S6	26,4	5	8	6,6
S7	33,1	2	5	5,0
S8	27,1	2	4	4,8
S9	33,1	1	4	4,4
S10	54,8	1	4	5,0
S11	53,6	2	4	4,5
S12	76,1	1	5	4,9
S13	74,3	2	4	4,9
S14	1,5	46	46	24,5

Table 5. Repeatability (*r*) and reproducibility (*R*) relative standard deviations, and relative standard deviation of means for OC grouped by analytical protocols

	General mean (µg/cm²)		*r* (%)		*R* (%)		*rsd* of means (%)	
	NIOSH	EUSAAR2	NIOSH	EUSAAR2	NIOSH	EUSAAR2	NIOSH	EUSAAR2
S1	23,6	22,6	3,9	0,6	7,9	8,3	6,1	6,3
S2	23,7	23,0	3,3	0,7	6,6	4,0	5,6	5,5
S3	26,8	25,8	3,8	2,3	9,0	6,2	7,0	5,2
S4	23,0	21,7	2,3	0,8	11,4	5,5	9,4	6,1
S5	11,2	10,2	3,4	4,0	6,5	5,0	5,3	11,5
S6	23,0	21,4	6,8	1,4	10,5	8,3	7,7	8,1
S7	26,0	22,7	2,7	2,6	7,1	5,9	5,5	5,1
S8	23,3	22,6	1,9	2,6	6,3	8,2	4,9	5,4
S9	25,6	23,2	2,0	0,5	6,3	0,5	5,5	5,4
S10	47,8	47,9	1,4	1,0	5,8	9,7	4,7	5,6
S11	46,6	46,1	1,7	2,3	5,7	10,7	5,2	5,5
S12	65,2	65,0	1,1	1,5	4,1	4,8	4,7	5,3
S13	63,3	62,5	2,1	1,1	4,0	5,6	3,7	5,7
S14	1,4	1,4	56,2	53,3	57,4	53,3	29,6	14,5

Table 6 Repeatability (*r*) and reproducibility (*R*) relative standard deviations, and relative standard deviation of means for EC grouped by analytical protocols

	General mean (µg/cm²)		*r* (%)		*R* (%)		*rsd* of means (%)	
	NIOSH	EUSAAR2	NIOSH	EUSAAR2	NIOSH	EUSAAR2	NIOSH	EUSAAR2
S1	3,7	6,0	7,6	3,3	25,3	8,1	21,2	18,5
S2	3,8	6,5	8,6	2,9	24,0	5,0	19,8	13,0
S3	4,3	7,2	5,0	5,8	26,0	17,7	24,3	14,3
S4	4,9	7,8	5,3	2,6	23,2	11,5	19,9	15,7
S5	2,6	3,8	2,9	1,8	12,0	2,4	13,3	13,5
S6	3,1	5,4	4,5	1,9	10,4	3,5	14,2	16,7
S7	6,6	11,2	12,2	3,9	12,2	4,0	10,0	12,8
S8	3,3	5,4	8,3	0,7	12,9	8,2	12,0	24,9
S9	7,0	10,8	10,1	0,9	10,4	0,0	9,8	10,1
S10	6,0	8,3	5,4	4,9	11,8	11,5	13,7	10,4
S11	6,2	8,4	4,2	2,3	14,7	11,7	15,4	14,5
S12	9,2	13,5	3,5	3,7	15,6	5,0	13,5	10,4
S13	8,9	14,4	4,4	4,5	17,4	4,5	18,0	11,2

Uncertainties from duplicates

Uncertainties for duplicates have been calculated for sample pairs (S6,S7), (S8, S9), (S10,S11) and (S12,S13) from results of laboratories using laboratory instruments. From these results aberrant values have been omitted for the calculation.
Summarized results are given in Tables 8-10 below.

Table 8 Uncertainty from results of duplicates for TC

	S6,S7	S8,S9	S10,S11	S12,S13
Mean	29,1	29,6	53,5	74,5
Number of replicates	25	24	25	24
Uncertainty, µg/cm^2	4,62	4,05	1,10	1,23
Relative uncertainty, %	15,8	13,7	2,05	1,64

Table 9 Uncertainty from results of duplicates for OC

	S6,S7	S8,S9	S10,S11	S12,S13
Mean	23,1	23,5	46,4	63,2
Number of replicates	25	24	25	24
Uncertainty, µg/cm^2	1,82	1,23	1,14	1,39
Relative uncertainty, %	7,90	5,22	2,46	2,20

Table 10 Uncertainty from results of duplicates for EC

	S6,S7	S8,S9	S10,S11	S12,S13
Mean	5,96	6,04	6,86	11,0
Number of replicates	25	24	25	24
Uncertainty, µg/cm^2	3,10	3,09	0,28	0,59
Relative uncertainty, %	52,0	51,2	4,10	5,37

Conclusions

A comparison has been performed on the determination of elemental carbon (EC) and organic carbon (OC) and total carbon (TC, as the sum of EC and OC). The comparison involved 16 participants, all using Sunset analyzers (field and laboratory version) and two analytical protocols: NIOSH-type and EUSAAR2.

Overall, based on z-scores results of participants are satisfactory for total carbon (TC) and organic carbon (OC) when applying a 25% expanded uncertainty (k=2) as the criterion for fitness-for-purpose. For elemental carbon a 25% criterion appears to be over-ambitious when all data are evaluated together. However, when the dataset is evaluated separately for the two protocols used (NIOSH; EUSAAR2) the 25% criterion is met for each protocol separately.

Using ISO 5725-2 statistics a good agreement is found for TC results, although five outliers have been identified based on Mandels's *h* statistics. These outliers are all attributable to the two laboratories using the field version of the instrument, which is originally meant for online analysis. Apparently, when the online system is used for offline measurements, there are some difficulties either when introducing the sample in the oven or in correctly evaluating the area of the punch being analyzed.

After elimination of these outliers the two analytical protocols have been tested separately for repeatability and between NIOSH-type and EUSAAR2 protocols, also the relative standard deviation of the laboratory means has been used as a measure of the reproducibility standard deviation.

Regardless of analytical protocol, the repeatability standard deviations for TC and OC range from 0,5% to 6,8% (apart from those for blank samples).
For EC the repeatability range is from 0,7% to 12,2%.

Reproducibility standard deviations are between 4% and 8% for TC , between 5% and 12% for OC, and between 10% and 25% for EC when considering a sufficient number of replicates (apart from those for blank samples). The values obtained for TC and OC are in the same range as the uncertainties given for NIST RM 8785, the uncertainties for EC are about twice the uncertainty reported for this RM.

When considering ratios between reproducibility and repeatability standard deviations, it can be concluded that the thermal-optical method is capable of producing quite robust results.

Standard uncertainties calculated from duplicate samples are good for sample pairs (S10,S11) and (S12,S13) – about 2% for TC and OC, 4-5% for EC. For sample pairs (S6,S7) and (S8,S9) uncertainties for EC are high (>50%), thereby affecting the uncertainties for TC. For OC uncertainties are from 2,2 to 7,9%.

This may indicate that sample pairs (S6,S7) and (S8,S9) are not really duplicates for EC. Otherwise, the uncertainties calculated indicate that the method performs well with respect to replicability of sampling and analysis.

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Annex 1. All results

Table 11 Total carbon (µg/cm^2)

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14
UBA A	24,7	20,9	23,7	25,5	6,1	28,8	34,2	22,2	35,5	58,1	57,8	80,1	96,1	1,7
NERI	30,0	31,0	34,7	31,1	14,0	26,4	34,0	29,4	34,7	59,2	57,0	81,1	78,7	1,6
							36,3					81,8		
EMPA	28,8	29,1	32,3	28,7	13,4	27,2	34,3	28,4	34,1	57,6	55,5	79,8	78,6	1,1
	28,9	29,2	33,1	29,4	13,4	27,9	34,8	28,4	34,4	57,8	57,2	79,4	78,7	1,2
LRA	26,6	26,6	29,4	27,0	13,5	25,3	31,4	26,8	31,5	52,6	50,6	70,9	70,5	2,2
	26,8	26,2	31,0	27,4	13,4	25,6	32,1	25,9	32,1	54,4	53,4	72,6	70,9	2,2
JRC	29,7	30,4	33,9	30,4	15,5	28,5	33,8	28,1	34,2	57,4	56,0	81,3	80,6	1,3
UBA D	27,8	28,1	31,5	28,7	13,1	24,8	31,1	26,6	32,4	53,5	51,8	72,3	70,7	1,5
	26,0	26,0	30,0	26,8	12,4	24,1	30,5	25,6	31,5	51,5	51,2	72,0	70,5	1,5
VMM/UGent	27,1	28,4	31,2	29,3	13,5	26,2	32,5	26,4	33,1	53,3	51,6	79,1	73,8	1,3
ERLAP	26,5	26,4	29,1	26,1	13,1	22,9	29,9	24,3	29,9	49,7	49,4	71,1	70,4	0,7
	25,5	26,2	29,3	25,6	12,4	23,0	30,0	24,5	29,9	48,8	49,2	70,1	69,1	1,0
	25,9	26,6	28,5	26,1	12,2	23,0	30,1	24,4	30,5	50,9	49,4	70,0	70,5	1,1
	26,3	25,7	29,5	25,4	12,5	22,8	29,7	25,3	29,6	49,6	49,5	70,0	72,4	0,8
NPL	27,2	27,9	31,4	28,6	13,7	25,0	32,0	27,0	33,0	53,8	52,8	74,9	71,6	1,0
	28,8	28,7	31,0	28,6	14,2	27,4	33,0	28,0	31,7	54,9	53,2	76,8	77,1	3,1
LCSQA / INERIS	26,9	28,3	32,3	28,7	13,4	25,6	32,7	27,1	32,5	52,5	51,6	74,2	73,0	0,9
	27,1	28,3	32,4	28,6	14,2	25,2	32,5	26,0		52,7	50,3	76,0	73,8	2,4
IMI	28,1	28,9	33,8	29,2	14,2	26,3	32,6	26,9	32,8	54,1	53,0	74,3	73,4	1,1
	31,1	28,9	31,8	28,9	14,0	26,0	33,0	26,8	32,5	53,9	53,2	75,0	72,9	1,1
CHMI	29,6	31,2	34,0	30,7	15,3	29,0	35,2	29,4	35,6	59,2	57,0	81,1	80,9	1,7
GGD	26,6	26,9	30,8	27,6	13,0	24,9	30,9	26,4	31,3	53,5	54,9	76,1	71,9	1,3
NCSR-D	28,5	28,5	32,1	30,0	18,0	30,3	39,4	32,0	38,6	59,3	57,2	77,6	78,7	5,8
ISCIII	27,4	27,5	30,6	27,2	14,3	26,4	32,6	27,2	33,0	54,2	52,6	74,1	72,6	
	27,2	28,7	31,5	28,0	13,6	31,6	33,8	27,0	33,3	54,5	52,6	75,5	73,1	
UNIMIB	28,5	29,3	32,0	29,4	14,1	26,5	33,3	27,6	33,7	57,2	54,7	75,1	75,0	
	29,1	29,4	32,7	30,1	13,9	26,5	33,5	27,4	34,0	57,4	55,4	74,9	75,7	
	29,0	27,4	34,7	30,1	14,1		34,3	28,0		56,2	55,7	75,9		
	28,2	27,6	33,7	32,1	15,3		33,4	28,0		56,1	54,8	76,4		

Table 12 Organic carbon (µg/cm^2)

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14
UBA A	21,2	17,3	19,2	20,8	4,1	26,0	29,9	19,6	31,2	53,7	53,1	74,5	90,5	1,7
NERI	23,7	24,4	26,9	21,6	9,9	20,4	22,9	22,8	23,7	50,3	47,6	65,8	62,1	1,6
							24,2					67,4		
EMPA	22,9	22,6	25,5	21,4	9,2	21,6	22,3	22,9	22,7	49,6	47,8	66,4	63,1	1,1
	22,6	22,5	26,3	21,7	9,4	22,1	22,6	22,9	22,9	50,5	49,6	65,3	64,4	1,2
LRA	23,4	22,9	25,1	21,8	11,0	21,1	24,5	22,3	23,3	44,3	42,1	61,4	60,6	1,6
	23,5	22,6	26,8	21,9	10,9	21,2	24,1	21,9	24,3	46,0	44,7	62,5	61,0	1,3
JRC	24,1	24,7	27,7	24,0	12,5	24,1	24,4	23,6	24,6	49,3	48,2	69,3	67,4	1,3
UBA D	24,0	23,1	25,6	22,3	10,0	20,9	22,3	23,6	23,3	46,4	44,8	61,1	58,9	1,5
	22,9	22,7	26,4	22,3	10,5	21,7	24,8	22,8	25,3	46,5	45,7	63,1	60,7	1,5
VMM/UGent	23,8	24,8	28,2	25,0	11,0	23,6	26,0	23,6	26,9	48,1	46,6	69,5	53,9	1,3
ERLAP	21,2	21,3	23,0	18,9	10,3	19,8	22,2	20,7	22,5	43,3	42,7	60,4	59,9	0,7
	20,2	21,1	22,6	18,7	9,8	19,6	22,5	21,0	22,6	42,4	42,3	59,9	58,8	0,8
	20,8	21,2	21,7	18,4	9,4	19,8	22,3	20,8	23,0	44,1	42,4	59,4	59,2	0,9
	20,5	21,1	22,9	18,3	9,5	19,5	22,2	21,5	22,4	42,7	42,7	59,4	61,7	0,8
NPL	24,2	24,6	27,6	24,3	11,4	22,0	26,0	24,0	25,3	48,3	47,8	65,8	62,9	1,0
	24,9	25,4	27,1	24,2	11,8	24,3	26,7	25,0	25,6	49,0	47,4	67,4	67,3	3,1
LCSQA / INERIS	20,2	21,2	24,2	20,0	9,5	19,6	21,3	21,0	21,0	43,6	42,4	60,3	58,7	0,9
	20,2	21,5	23,4	19,9	10,2	19,3	20,8	19,9		43,6	41,5	61,8	59,0	2,4
IMI	24,2	25,1	29,3	24,2	11,3	22,4	27,0	22,6	23,8	47,3	45,4	64,8	64,6	1,1
	27,2	23,8	26,7	23,0	11,1	22,1	24,6	23,2	25,1	46,4	45,1	64,9	63,8	1,0
CHMI	23,2	24,1	26,7	22,8	11,3	23,2	23,4	23,7	24,0	49,9	46,9	67,7	66,2	1,3
GGD	23,0	22,6	26,8	23,3	10,6	22,2	25,3	23,1	25,2	48,5	49,7	68,3	65,3	1,3
NCSR-D	24,3	25,2	27,2	24,7	15,1	26,9	31,0	28,8	29,0	50,8	48,6	64,6	66,1	5,1
ISCIII	23,9	24,0	26,8	22,7	11,8	23,4	26,2	23,9	26,4	47,7	45,8	64,4	63,2	
	23,9	25,2	27,3	23,5	10,9	28,2	26,9	23,8	26,1	47,5	45,9	65,6	63,5	
UNIMIB	24,9	25,3	28,2	25,3	11,2	23,6	26,5	24,2	26,7	51,2	49,0	65,5	65,6	
	25,5	25,4	28,7	25,9	11,0	23,5	26,8	24,1	26,5	51,0	49,5	66,1	66,0	
	25,2	23,4	30,1	26,6	11,1		27,0	24,9		50,6	49,6	65,8		
	24,4	23,4	29,8	27,1	12,3		26,7	25,0		50,4	49,2	66,3		

Table 13 Elemental carbon (µg/cm^2)

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14
UBA A	3,6	3,6	4,5	4,8	2,0	2,8	4,3	2,6	4,4	4,4	4,8	5,6	5,6	0,0
NERI	6,3	6,6	7,8	9,4	4,1	6,0	11,1	6,6	10,9	9,0	9,4	15,3	16,6	0,0
							12,1					14,4		
EMPA	6,0	6,5	6,8	7,3	4,2	5,6	12,0	5,4	11,4	8,1	7,7	13,3	15,5	0,0
	6,3	6,7	6,8	7,7	4,0	5,8	12,2	5,5	11,5	7,3	7,6	14,1	14,3	0,0
LRA	2,5	2,6	3,6	4,7	2,2	3,0	5,6	3,3	7,0	5,4	5,8	6,3	6,1	0,6
	2,7	2,6	3,5	5,0	2,2	3,2	6,7	2,8	6,5	5,5	5,9	6,8	6,2	0,8
JRC	5,5	5,7	6,1	6,5	3,0	4,4	9,4	4,4	9,5	8,1	7,8	12,0	13,3	0,0
UBA D	3,8	5,0	5,9	6,4	3,1	3,9	8,8	3,0	9,2	7,1	6,9	11,1	11,9	0,0
	3,0	3,3	3,6	4,5	2,0	2,3	5,7	2,7	6,2	5,1	5,5	8,9	9,7	0,0
VMM/UGent	3,3	3,6	3,1	4,3	2,4	2,6	6,5	2,8	6,2	5,2	5,0	9,6	19,8	0,0
ERLAP	5,3	5,1	6,0	7,2	2,8	3,2	7,7	3,6	7,5	6,5	6,8	10,6	10,4	0,0
	5,3	5,1	6,7	6,9	2,6	3,4	7,5	3,5	7,2	6,4	6,9	10,2	10,3	0,2
	5,1	5,4	6,8	7,7	2,8	3,3	7,8	3,6	7,5	6,8	6,9	10,6	11,3	0,2
	5,7	4,7	6,6	7,0	3,0	3,3	7,5	3,8	7,2	6,9	6,8	10,6	10,7	0,1
NPL	3,0	3,3	3,8	4,3	2,3	3,0	6,0	3,0	7,7	5,5	5,0	9,1	8,7	0,0
	3,9	3,3	3,9	4,4	2,4	3,1	6,3	3,0	6,1	5,9	5,8	9,4	9,8	0,0
LCSQA / INERIS	6,6	7,2	8,1	8,8	4,0	6,0	11,4	6,1	11,5	8,8	9,2	13,9	14,2	0,0
	6,9	6,9	9,0	8,7	4,0	5,9	11,6	6,1		9,0	8,8	14,3	14,8	0,0
IMI	3,9	3,8	4,5	5,0	2,9	3,9	5,6	4,3	9,0	6,9	7,6	9,4	8,8	0,0
	4,0	5,1	5,1	5,9	2,9	3,8	8,4	3,7	7,4	7,5	8,0	10,1	9,1	0,1
CHMI	6,4	7,1	7,3	7,9	3,9	5,8	11,8	5,8	11,7	9,3	10,1	13,5	14,7	0,4
GGD	3,6	4,4	4,0	4,3	2,4	2,8	5,6	3,3	6,1	5,0	5,2	7,8	6,6	0,0
NCSR-D	4,2	3,2	4,9	5,3	2,9	3,4	8,4	3,1	9,6	8,5	8,6	12,9	12,6	0,7
ISCIII	3,5	3,5	3,8	4,5	2,6	3,0	6,4	3,3	6,6	6,5	6,8	9,7	9,4	
	3,4	3,5	4,2	4,5	2,7	3,4	6,9	3,2	7,2	6,9	6,7	10,0	9,6	
UNIMIB	3,6	4,0	3,8	4,1	2,9	2,9	6,9	3,3	7,0	6,0	5,7	9,6	9,4	
	3,6	4,1	3,9	4,2	3,0	3,0	6,7	3,3	7,4	6,4	5,9	8,8	9,8	
	3,9	4,0	4,6	3,6	2,9		7,3	3,0		5,6	6,1	10,1		
	3,8	4,2	3,8	5,0	3,0		6,7	3,0		5,7	5,7	10,1		

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Abstract
The JRC's European Reference Laboratory for Air Pollution (ERLAP) has organized in 2009 an inter-laboratory comparison for the measurement of elemental carbon (EC) and organic carbon (OC) in particulate matter sampled on filters. The objectives of this comparison have been to evaluate the performances of participants but also to study the effects of the use of different thermal analysis protocols currently used for analysis.
It has been shown that all participants using laboratory analyzers are able to meet a 25% expanded uncertainty as a "fitness-for-purpose" criterion for total carbon (TC, as the sum of OC and EC) and OC. For EC this criterion is only met when results are evaluated by specific protocols (NIOSH or EUSAAR2) separately. Ratios of repeatability and reproducibility standard deviations indicate that the thermal-optical method used is quite robust.

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