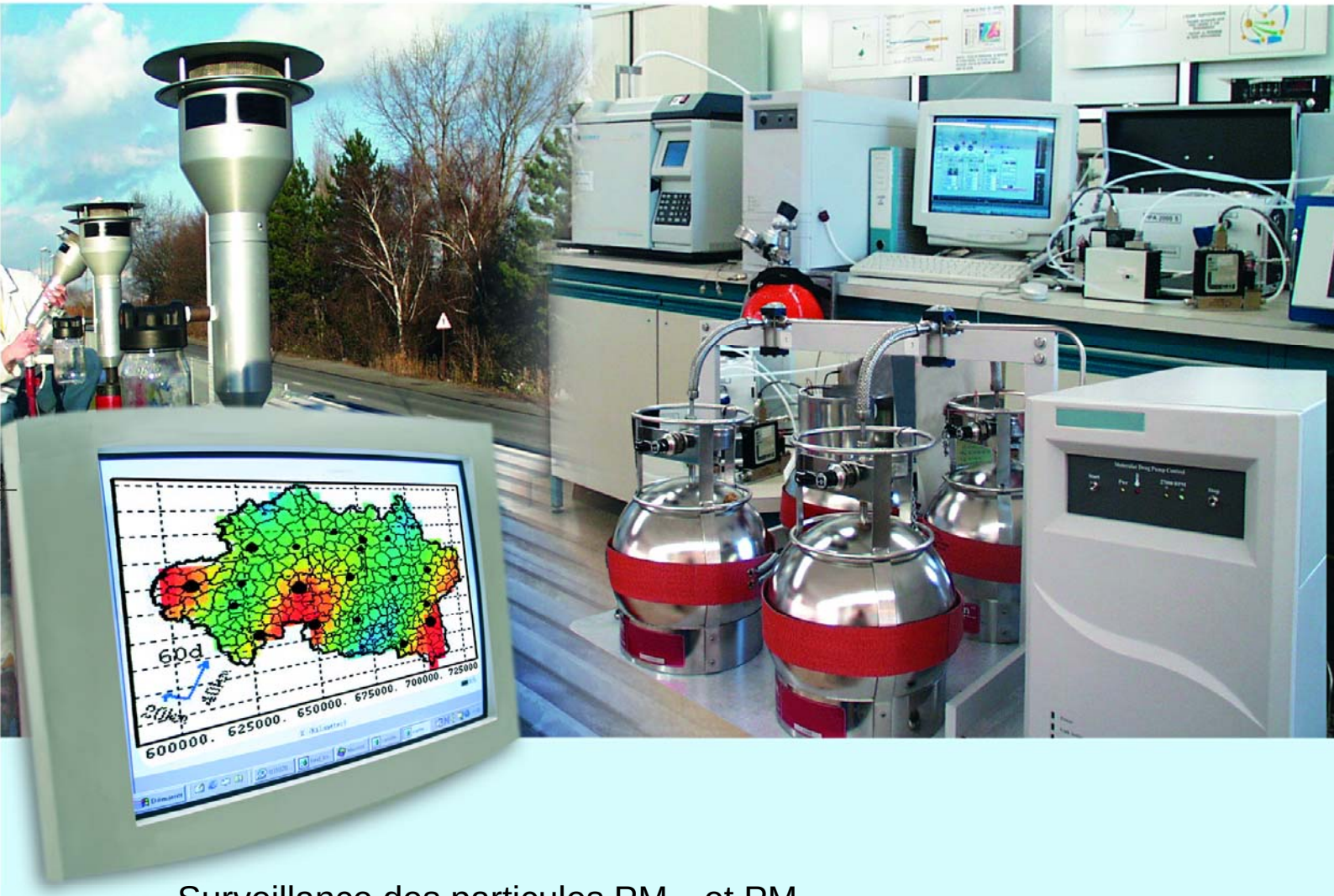
LCSQA

Laboratoire Central
de Surveillance de la Qualité de l'Air



Surveillance des particules PM_{10} et $PM_{2,5}$

Comparaison inter laboratoires organisée pour les laboratoires européens impliqués dans l'analyse du lévoglucosan et de ses isomères

Décembre 2013

Programme 2013

S. VERLHAC

INERIS

PREAMBULE

Le Laboratoire Central de Surveillance de la Qualité de l'Air

Le Laboratoire Central de Surveillance de la Qualité de l'Air est constitué de laboratoires de l'Ecole des Mines de Douai, de l'INERIS et du LNE. Il mène depuis 1991 des études et des recherches finalisées à la demande du Ministère chargé de l'environnement, et en concertation avec les Associations Agréées de Surveillance de la Qualité de l'Air (AASQA). Ces travaux en matière de pollution atmosphérique ont été financés par la Direction Générale de l'Energie et du Climat (bureau de la qualité de l'air) du Ministère de l'Ecologie, du Développement durable, des Transports et du Logement. Ils sont réalisés avec le souci constant d'améliorer le dispositif de surveillance de la qualité de l'air en France en apportant un appui scientifique et technique au MEDDE et aux AASQA.

L'objectif principal du LCSQA est de participer à l'amélioration de la qualité des mesures effectuées dans l'air ambiant, depuis le prélèvement des échantillons jusqu'au traitement des données issues des mesures. Cette action est menée dans le cadre des réglementations nationales et européennes mais aussi dans un cadre plus prospectif destiné à fournir aux AASQA de nouveaux outils permettant d'anticiper les évolutions futures.

Comparaison inter laboratoires organisée pour les laboratoires européens impliqués dans l'analyse du lévoglucosan et de ses isomères

Laboratoire Central de Surveillance
de la Qualité de l'Air

Surveillance des particules PM_{10} et $PM_{2,5}$

Programme financé par la
Direction Générale de l'Energie et du Climat (DGEC)

2013

Stéphane VERLHAC

Ce document comporte 32 pages (hors couverture et annexes)

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RESUME

Depuis 2011, l'INERIS est partenaire associé du réseau européen ACTRIS (**A**erosols, **C**louds, and **T**race gases **R**esearch **I**nfra**S**tructure Network) du programme de recherche « FP7-Infrastructures ». Ce projet vise notamment l'harmonisation des techniques d'observation des particules atmosphériques, des espèces gazeuses à courte durée de vie et des nuages à l'échelle européenne.

Dans ce cadre et à travers le pilotage du programme CARA (Caractérisation chimique des particules) pour le LCSQA (Laboratoire central de surveillance de la qualité de l'air), l'INERIS a organisé une comparaison inter laboratoires analytique (CIL) au premier semestre 2013. Cet essai portait sur l'analyse du lévoglucosan et de ses isomères (mannosan et galactosan) reconnus pour être des composés organiques majeurs dans l'étude des sources de particules, notamment pour identifier la source combustion de biomasse (chauffage au bois).

La comparaison inter laboratoire a été ouverte prioritairement aux membres du réseau ACTRIS puis à tous les laboratoires européens. Sur 15 inscrits, dont 3 français (tous sont impliqués dans l'analyse du levoglucosan pour les AASQA), 13 laboratoires ont rendus des résultats.

Les participants ont reçu les matériaux d'essais suivants à analyser:

- un matériau de référence commercialisé par le NIST (National Institut of Standards and Technology) (SRM 1649b, urban dust).
- trois matériaux solides (poinçons de filtre) préparés par l'INERIS et issus de prélèvements d'air ambiant pour deux d'entre eux, le troisième étant un blanc de terrain. Les prélèvements ont été effectués sur filtre en quartz à l'aide d'un préleveur grand volume de type ANDERSEN, équipé d'une tête PM_{10}, à un débit de 70 m^3/h. Chaque filtre était découpé avec un emporte-pièce en 16 poinçons de 47 mm de diamètre.

Aucune norme n'encadre actuellement l'analyse du lévoglucosan et de ses isomères. Les laboratoires ont mis en œuvre leurs propres méthodes analytiques. Ceci a permis d'obtenir des informations sur les performances analytiques des laboratoires ainsi que sur la comparabilité des données au niveau européen.

La plupart des laboratoires ont obtenu des Z-scores (indicateur statistique de performance) satisfaisants. Seuls deux laboratoires présentent des valeurs aberrantes (13320 et 13373) sur le lévoglucosan et un seul (13312) sur le mannosan et/ou le galactosan. De plus, trois laboratoires (13320, 13373 et 13337) présentent des écart-types de répétabilité supérieurs à 10 %. Les écart-types de reproductibilité sont de l'ordre de 20-25% pour le lévoglucosan et le mannosan mais de 30 à 60 % pour le galactosan.

Un laboratoire (13358) a obtenu un résultat d'analyse sur le filtre blanc très élevé.

Les limites de quantification évaluées par les participants semblent globalement être plus faibles pour les utilisateurs de chaînes analytiques de type GC/MS que ceux utilisant la HPLC.

Aucun impact de la procédure analytique mise en œuvre n'a été détecté lors des traitements statistiques dans les résultats obtenus dans le cadre de cette CIL.

Les incertitudes élargies calculées dans le cadre de cette CIL pour le lévoglucosan et le mannosan sont satisfaisantes et par exemple, cohérentes avec celles requises pour l'analyse du benzo[a]pyrene dans l'air ambiant (Directive européenne 2004/107/CE) (< 50 %).

Les AASQA collaborant avec des laboratoires français impliqués dans l'analyse du levoglucosan et ses isomères sont invités à se rapprocher de ces derniers afin de prendre connaissance de leurs résultats.

Interlaboratory comparison organized for the European laboratories involved in the analysis of levoglucosan and its isomers.

FINAL REPORT – 2ND DRAFT

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FOREWORD

This report was drawn up on the basis of the information provided to INERIS and the objective (scientific or technical) data available and applicable regulations.

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1 GLOSSARY

ILC	An Interlaboratory Comparison is defined and implemented to allow the laboratories to assess and demonstrate their performance in particular test, calibration or measuring sectors, NOTE: Three terms may be used: “interlaboratory tests” or “inter-comparison tests” or “aptitude tests,”
LoQ	Limit of quantification,
Test material	Matrix of interest containing the compounds subject to the interlaboratory comparison, potentially added using a spiking solution.

2 DEFINITIONS

CV_r	:	standard deviation of the x measurements divided by the average of those x measurements by % [(Standard deviation / average) by %],
CV_R	:	reproducibility variation coefficient equal to the standard deviation of the averages of the measurements divided by the average of the averages of the measurements by %,
CV_{rep}	:	mean repeatability variation coefficient, average of the CV_r of the participants,
Standard deviation	:	standard deviation of x measurements,
Population standard deviation	:	standard deviation of the measurement averages,
IC_R	:	reproducibility confidence interval,
IC_r	:	repeatability confidence interval,
Average	:	average of x measurements,
Population average	:	average of the measurement averages,
Number of decimals	:	number imposed in the instruction formula,
σ	:	robust standard deviation for assessing the aptitude (stipulated, perceived or s*: robust standard deviation for evaluating the aptitude obtained using the algorithm A of ISO 13528),
z score	:	performance criteria provided to each participant making it possible to measure its deviation relative to the assigned value. The assigned value is the robust average,
s*	:	robust standard deviation for assessing the aptitude obtained using the algorithm A of ISO 13528,
S_L	:	interlaboratory standard deviation,
S_R	:	reproducibility standard deviation,
S_r	:	repeatability standard deviation,
w*	:	robust standard deviation obtained using algorithm S of ISO 13528,
x*	:	robust average obtained using algorithm A of ISO 13528,
X_{MRC}	:	reference value resulting from the certificate for the certified reference material.

3 INTRODUCTION

Within the European ACTRIS project, WP3 decided to organize in 2013 an interlaboratory comparison (ILC) for the analysis of levoglucosan and its isomers. This ILC was led by INERIS with the help of LGGE for the quality control analysis.

The purpose of this ILC was to evaluate the analytical repeatability and reproducibility standard deviations obtained by the participants using their own analytical methods and to highlight any bias or influencing factor on the measurement quality of the levoglucosan and its isomers.

4 PARTICIPANTS

According to ISO 5725-1 (§ 6.3.3), for each test material, a minimum number of p participants with n measurements such as $p \times n \geq 30$, allows to get a low level of uncertainty on the estimations of the standard deviations of repeatability and reproducibility. A minimum of 10 participants is usually required and a maximum of 16 participants would have been ideal in the present case (limitation due to the number of possible punches made on the field sample filter available).

Participation to the ILC was first opened to European groups involved in the ACTRIS project, and second to any other European laboratory.

13 participants submitted their results (15 registered listed below). 2 laboratories were considered as two independent participants because they provided results using two different analytical procedures. Thus, this ILC respects the instructions of ISO 5725-1 presented above. ACTRIS laboratories are flagged with "*".

- * LGGE – Laboratoire de Glaciologie et Géophysique de l'Environnement (France)
- Helmholtz Zentrum München, Comprehensive Molecular Analytics (× 2) (Germany)
- Vienna University of Technology, Institut of Chemical Technologies and Analytics (Austria)
- * LSCE (× 2) – Laboratoire des Sciences du Climat et l'Environnement (France)
- * IDÆA-CSIC - Institute for Environmental Assessment and Water Research (Spain)
- * TROPOS - Leibniz-Institue für Troposphärenforschung (Germany)
- * NILU - Norwegian Institue fir Air Research (Norway)
- * University of Pannonia (Hungary)
- University of Antwerp (Belgium)
- LCME – Laboratoire Chimie Moléculaire et Environnement (France)
- * FMI - Finnish Meteorological Institute (Finland)
- * Lund University (Sweden)
- University of Milan, Department of Chemistry (Italy)

The instrumentation used by the participants as well as the analytical procedures applied and the results obtained are presented in this report anonymously. A confidential code was assigned to each participant when they registered on-line for their participation to the ILC.

5 ORGANIZATION OF THE INTERLABORATORY COMPARISON

The interlaboratory comparison (ILC) was organized and implemented by the authorized personnel cited below:

	First and Last Names	ILCA Function
INERIS Parc Technologique Alata **60550 VERNEUIL-EN-HALATTE** **☎ 03.44.55.66.77** **🗀 03.44.55.66.99**	Eva LEOZ	ILT Steering
	Stéphane VERLHAC	ILT coordinator
	Stéphane VERLHAC Valérie MINGUET	Test material preparer
	José GUARNERI	Website management Design of the statistical processing tool

The present ILC was organized as follows:

- Week 9: INERIS sent the registration form to the participants. They had to return it before the 15 of March

.

- March, the 25th: INERIS sent the different test materials, a confidential code, an identifier and a password to each participant.

- April, the 29th: Opening of the dedicated web page for on-line results transmission.

- May, the 31st: Last day for the participants to transmit their results on the web page.

6 ILC PROGRAM

ILC took place over a period of 3 months (from March to May) including the invoice of the different test materials, their analysis and the delivery of the results by the participants. ILC focused on the quantification of the following compounds:

- Levoglucosan (1,6-anhydro-β-D-glucopyranose)
- Mannosan (1,6-anhydro-β-D-mannopyranose)
- Galactosan (1,6-anhydro-β-D-galactose)

The annual program of this analytical ILC was designed in cooperation with an advisory group (Eva LEOZ, Alexandre ALBINET, Olivier FAVEZ, Stéphane VERLHAC from INERIS, Yoshi IINUMA from TROPOS, Jean-Luc JAFFREZO from LGGE, Erik SWIETLICKI from Lund University and Karl-Espen YTTRI from NILU). This group included scientific experts having special knowledge about the test materials and the analytical procedures and, an expert in statistical data analysis.

The general organization of the interlaboratory comparison and the different statistical processing procedures are presented in the Annex 1 of this report.

7 DESCRIPTION OF THE TEST MATERIALS

All the test materials and their analytical interest are presented below. Participants had to use their routine measurement method for the analysis of the targeted compounds and to respect the number of injection described below.

Matrices	Analytical interest	Number	Number of injections
Standard reference materials (SRM, NIST solid powder 1649b).	Validation of the full analytical procedure [extraction, pre-concentration, purification (if required) and analysis]. Comparison between the consensual and the certified concentration values.	1	4 injections of one sample extract
"Natural" ambient air aerosol sample (Field sample filter, ∅ = 47 mm).	Validation of the full analytical procedure [extraction, pre-concentration, purification (if required) and analysis] and filter matrix effect.	2 field samples (A and C) and 1 field blank filter (B)	Triplicate analysis: 3 punches to be done in the sample filters provided and analysis of each punch (1 single injection for each punch)

Natural ambient air aerosol samples were collected using a HiVol sampler (Graseby-Andersen working at 70 m^3 h^{-1}) in December 2012 at Verneuil-en-Halatte (France, sub-urban). Quartz fiber filters of 20.3 x 25.4 cm were then punched in 16 pieces of 47 mm diameter (Figure 1).

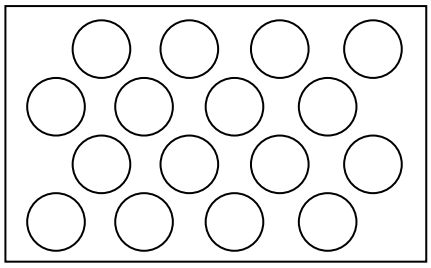


Figure 1 : Example of punched Andersen filter

8 HOMOGENEITY AND STABILITY OF THE AMBIENT AIR AEROSOL SAMPLES

Analyses for quality control on dispatched materials were performed by LGGE (France, Jean-Luc Jaffrezo's group).

8.1 HOMOGENEITY OF THE FILTERS

The homogeneity of the materials was checked before invoice. The analysis of similar samples to the ones sent to the participants was performed using the methodology described in Annex 1. Standard deviations of 5 % were obtained for levoglucosan and galactosan, while mannosan showed slightly higher values (6 to 8 %). These results fully complied with ISO 13528.

8.2 STABILITY OF THE FILTERS

The stability of filters was checked during all the analysis phase conducted by the participants. This quality control was performed on filter samples similar to the ones sent to the participants. One sample (punches from the same filter sample) was analyzed once per week for ten weeks. The stability of the materials was checked according to the methodology described in Annex 1.

Results obtained from the homogeneity and stability experiments indicated that **the test materials can be considered as stable and homogeneous for the entire period of analysis.**

9 RESULTS OF THE INTERLABORATORY COMPARISON

9.1 EXPLOITATION OF THE DATA FROM THE TEST MATERIALS

9.1.1 General information

The details of the statistical analysis are available in **Annex 1**.

In the context of this test, the assigned values were defined as follows :

- the value assigned to the average was taken to be equal to the robust average of the results provided by the participants in the interlaboratory comparison,
- the reference value of the standard deviation for assessing the aptitude was taken to be equal to the robust standard deviation.

The data statistical analysis applied to the data allowed to evaluate::

- the reference value (or assigned value) of each parameter for each test material and its associated uncertainty,
- each participant's performance relative to the reference values using the Z score indicator,
- outliers,
- the repeatability and reproducibility confidence intervals for each compound and each test material.

In the following sections, the results obtained before and after statistical analysis, averages, repeatability standard deviations and performance of each laboratory (Z score) are presented for each test material. A distribution diagram of the Z scores, allowing the comparison of each laboratory to the other ones, is also provided.

The following legend is used:

Legend	
1,4	$\|Z_i\|$ < 2: satisfactory score
2,3	Laboratory having a 2 ≤ $\|Z_i\|$ ≤ 3: score requiring monitoring or preventive action
3,56	Laboratory having a $\|Z_i\|$ ≥ 3 : unsatisfactory score requiring corrective action (the analysis results are not acceptable)

9.1.2 Test material "filter A"

Values observed **before** statistical analysis (raw data)

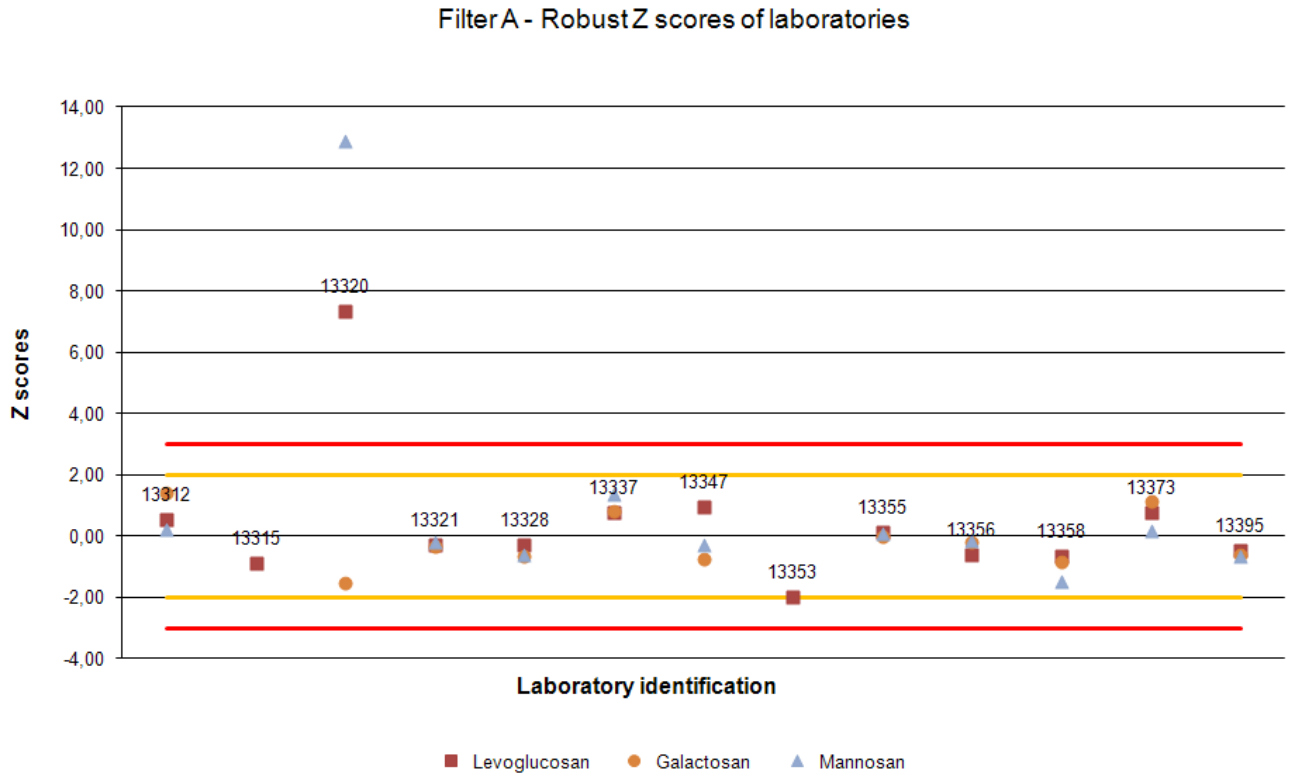
Parameter (ng/cm²)	Levoglucosan	Galactosan	Mannosan
Population average	2624.3	105.6	325.0
Population standard deviation	970.3	61.0	225.7
CVR (%)	37%	58%	69%
CVrep (%)	6%	9%	10%
Population (number)	13	11	11
S_L	957.2	59.3	223.5
S_R	996.0	64.2	230.1
S_r	275.5	24.7	54.7

Values observed **after** statistical analysis.

Parameter (ng/cm²)	Levoglucosan	Galactosan	Mannosan
x*	2445.8	114.8	266.4
s*	409.9	63.0	52.8
u_{X^*}	142.1	24.9	19.9
w*	140.2	8.5	26.5
S_L	401.8	62.8	50.6
S_R	425.6	63.4	57.1
S_r	140.2	8.5	26.5
Relative IC_R (%)	38 %	125 %	48 %
Relative IC_r (%)	12 %	17 %	22 %

Average, standard deviation and Z scores of the different laboratories

Laboratory identification	Levoglucosan				Galactosan				Mannosan			
	x ng/cm²	S_r ng/cm²	S_r %	Z scores	x ng/cm²	S_r ng/cm²	S_r %	Z scores	x ng/cm²	S_r ng/cm²	S_r %	Z scores
13312	2678.7	26.3	1 %	0.54	209.3	5.5	3 %	1.40	280.0	8.2	3 %	0.24
13315	2069.0	22.9	1 %	-0.87	Not analysed				Not analysed			
13320	5631.7	194.2	3 %	7.34	< LoQ				995.0	113.5	11 %	12.90
13321	2322.7	73.4	3 %	-0.28	93.0	2.6	3 %	-0.32	254.7	6.7	3 %	-0.21
13328	2315.7	28.7	1 %	-0.30	69.7	2.5	4 %	-0.67	232.7	19.7	8 %	-0.60
13337	2783.0	288.7	10 %	0.78	171.0	37.6	22 %	0.83	343.7	40.2	12 %	1.37
13347	2859.3	209.2	7 %	0.95	65.7	2.5	4 %	-0.73	251.7	8.3	3 %	-0.26
13353	1579.7	30.9	2 %	-2.00	Not analysed				Not analysed			
13355	2509.7	87.9	4 %	0.15	113.7	3.2	3 %	-0.02	271.3	9.9	4 %	0.09
13356	2184.7	69.6	3 %	-0.60	102.0	5.6	5 %	-0.19	258.0	14.0	5 %	-0.15
13358	2169.7	54.8	3 %	-0.64	59.3	8.5	14 %	-0.82	182.3	10.1	6 %	-1.49
13373	2773.3	892.9	32 %	0.75	191.0	71.4	37 %	1.12	275.3	132.0	48 %	0.16
13395	2238.7	23.4	1 %	-0.48	73.7	6.8	9 %	-0.61	230.0	7.0	3 %	-0.64



Comments

Levoglucosan

- Laboratory 13320 obtained a |Z| score above the admissible value of 3.
- According to the Mandel k test, laboratory 13373 had an intra-laboratory dispersion significantly higher than the rest of the population.

Galactosan

- According to the Mandel k test, laboratory 13373 had an intra-laboratory dispersion significantly higher than the rest of the population.

Mannosan

- Laboratory 13320 obtained a |Z| score above the admissible value of 3
- According to the Mandel k test, laboratories 13320 and 13373 had intra-laboratory dispersions significantly higher than the rest of the population.

9.1.3 Test material “filter C”

Values observed **before** statistical analysis (raw data)

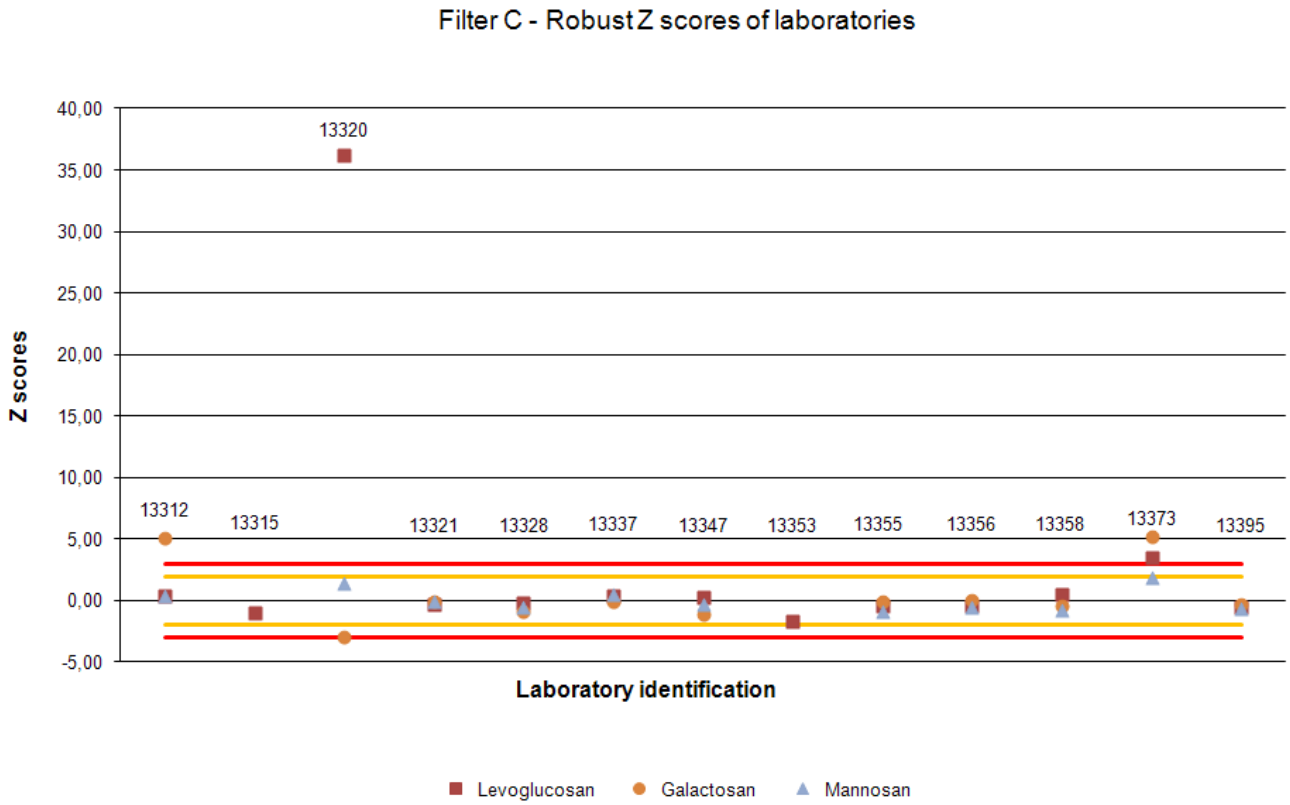
Parameter (ng/cm²)	Levoglucosan	Galactosan	Mannosan
Population average	17949.8	372.8	797.8
Population standard deviation	26805.2	267.7	146.9
CVR (%)	149%	72%	18%
CVrep (%)	7%	10%	8%
Population (number)	13	11	11
S_L	26672.9	258.8	122.6
S_R	27067.9	284.6	186.2
S_r	4607.6	118.4	140.1

Values observed **after** statistical analysis.

Parameter (ng/cm²)	Levoglucosan	Galactosan	Mannosan
x*	10488.1	327.9	790.3
s*	2507.6	100.0	148.9
u_{X^*}	869.4	39.5	56.1
w*	689.3	17.0	49.6
S_L	2475.8	99.5	146.1
S_R	2570.0	100.9	154.3
S_r	689.3	17.0	49.6
Relative IC_R (%)	53 %	70 %	44 %
Relative IC_r (%)	14 %	12 %	14 %

Average, standard deviation and Z scores of the different laboratories

Laboratory identification	Levoglucosan				Galactosan				Mannosan			
	x ng/cm²	S_r ng/cm²	S_r %	Z scores	x ng/cm²	S_r ng/cm²	S_r %	Z scores	x ng/cm²	S_r ng/cm²	S_r %	Z scores
13312	11529.7	216.2	2 %	0.39	871.0	4.4	1 %	5.05	851.7	16.8	2 %	0.39
13315	8011.7	20.8	0 %	-0.93	Not analysed				Not analysed			
13320	106536.0	14743.6	14 %	36.19	< LoQ				1013.7	52.5	5 %	1.40
13321	9583.7	262.9	3 %	-0.34	319.7	13.3	4 %	-0.08	778.3	31.7	4 %	-0.08
13328	9911.7	99.0	1 %	-0.22	236.7	3.2	1 %	-0.85	706.3	11.0	2 %	-0.53
13337	11505.0	1112.0	10 %	0.38	321.0	165.1	51 %	-0.06	872.0	147.6	17 %	0.51
13347	11170.3	491.2	4 %	0.26	212.3	3.1	1 %	-1.08	752.7	21.5	3 %	-0.24
13353	6009.3	194.0	3 %	-1.69	Not analysed				Not analysed			
13355	9288.3	316.7	3 %	-0.45	320.7	13.3	4 %	-0.07	650.7	18.4	3 %	-0.88
13356	9379.0	205.3	2 %	-0.42	333.0	4.6	1 %	0.05	705.0	9.6	1 %	-0.54
13358	11724.3	751.8	6 %	0.47	279.3	15.5	6 %	-0.45	669.3	44.6	7 %	-0.76
13373	19683.3	7486.7	38 %	3.46	893.3	355.3	40 %	5.26	1096.7	430.2	39 %	1.93
13395	9015.7	460.7	5 %	-0.55	300.7	13.7	5 %	-0.25	680.0	46.2	7 %	-0.69



Comments :

Levoglucosan

- Laboratories 13320 and 13373 obtained |Z| scores above the admissible value of 3.
- According to the Mandel k test, laboratory 13320 had an intra-laboratory dispersion significantly higher than the rest of the population.

Galactosan

- Laboratories 13312 and 13373 obtained |Z| scores above the admissible value of 3.
- According to the Mandel k test, laboratory 13373 had an intra-laboratory dispersion significantly higher than the rest of the population.
-

Mannosan

- According to the Mandel k test, laboratory 13373 had an intra-laboratory dispersion significantly higher than the rest of the population.

9.1.4 Test material "NIST SRM 1649b (urban dust)"

This material could not be considered as a certified reference material for the statistical analysis. The NIST does not provide any certified or reference concentration values for levoglucosan, galactosan and mannosan in the certificate of analysis of the SRM 1649b. The concentration values of this SRM are indicated in a scientific paper written by the NIST[1]. Note that, the concentration values reported in this study were determined using only an organic solvent extraction procedure followed by GC/MS analysis with derivatization of the extracts.

Thus, the value assigned to the average was taken to be equal to the robust average of the results provided by the participants.

Values observed **before** statistical analysis (raw data)

Parameter (mg/kg)	Levoglucosan	Galactosan	Mannosan
Population average	172.2	10.9	19.7
Population standard deviation	49.6	12.7	14.4
CVR (%)	29%	117%	74%
CVrep (%)	5%	7%	5%
Population (number)	13	11	11
S_L	49.4	12.6	14.4
S_R	50.3	13.1	14.5
S_r	9.0	3.5	1.1

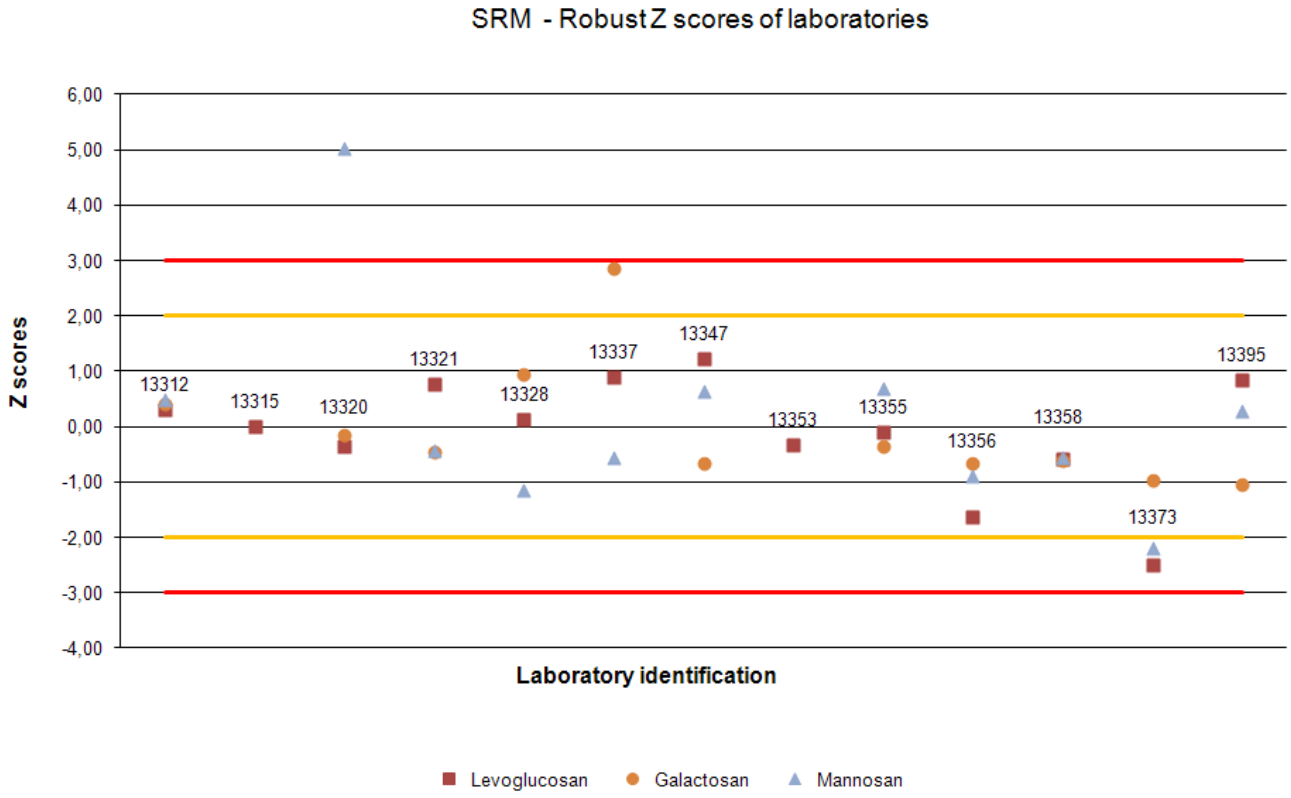
[1] Louchouarn, P., Kuo, L.-J., Wade, T. L. and Schantz, M.: Determination of levoglucosan and its isomers in size fractions of aerosol standard reference materials, Atmospheric Environment, 43(35), 5630–5636, doi:10.1016/j.atmosenv.2009.07.040, 2009

Values observed **after** statistical analysis.

Parameter (mg/kg)	Levoglucosan	Galactosan	Mannosan
NIST values	153.3	4.6	16.0
x*	176.975	11.595	18.665
s*	45.090	10.306	7.308
u_{X^*}	15.632	4.555	2.889
w*	7.846	0.842	1.272
S_L	44.919	10.297	7.280
S_R	45.599	10.332	7.390
S_r	7.846	0.842	1.272
Relative IC_R (%)	56 %	211 %	90 %
Relative IC_r (%)	10 %	17 %	15 %

Average, standard deviation and Z scores of the different laboratories

Laboratory identification	Levoglucosan				Galactosan				Mannosan			
	x mg/kg	S_r mg/kg	S_r %	Z scores	x mg/kg	S_r mg/kg	S_r %	Z scores	x mg/kg	S_r mg/kg	S_r %	Z scores
13312	191.4	10.6	6 %	0.30	16.3	1.2	7 %	0.42	22.5	1,5	7 %	0,49
13315	177.0	5.5	3 %	0.00	Not analysed				Not analysed			
13320	159.9	11.7	7 %	-0.36	< LoQ				58.2	2.0	3 %	5.03
13321	213.2	0.8	0 %	0.76	6.5	0.9	14 %	-0.45	15.3	0,5	3 %	-0,43
13328	183.1	2.2	1 %	0.13	22.3	0.6	3 %	0.95	9.7	1,0	10 %	-1,14
13337	220.0	22.6	10 %	0.90	43.8	11.5	26 %	2.86	14.4	1,9	13 %	-0,55
13347	236.3	1.6	1 %	1.24	4.2	0.2	6 %	-0.66	23.8	0,4	2 %	0,65
13353	161.8	3.6	2 %	-0.32	Not analysed				Not analysed			
13355	172.9	3.6	2 %	-0.09	7.5	0.3	4 %	-0.36	24.2	1,1	5 %	0,71
13356	99.5	2.8	3 %	-1.62	4.1	0.1	4 %	-0.67	11.7	0,4	4 %	-0,88
13358	149.5	3.3	2 %	-0.58	4.7	0.1	3 %	-0.61	14.4	0,3	2 %	-0,55
13373	58.3	14.7	25 %	-2.49	< LoQ				< LoQ			
13395	217.0	1.4	1 %	0.84	< LoQ				21.0	0.8	4 %	0.30



Comments:

Levoglucosan

- Laboratory 13373 obtained a |Z| score between 2 and 3.
- According to the Mandel k test, laboratories 13337 and 13373 had intra-laboratory dispersions significantly higher than the rest of the population

Galactosan

- Laboratory 13337 obtained |Z| score between 2 and 3.
- According to the Mandel k test, laboratory 13337 had an intra-laboratory dispersion significantly higher than the rest of the population.

Mannosan

- Laboratory 13320 obtained |Z| score above the admissible value of 3.
- According to the Mandel k test, laboratory 13373 had an intra-laboratory dispersion significantly higher than the rest of the population.

9.1.5 Test material “filter B” (blank sample filter)

All participants obtained results under their instrumental limits of quantification for galactosan and mannosan.

Similar results were observed for levoglucosan excepted for laboratories 13355, 13356 and 13358. As presented on Figure 2, laboratory 13358 especially obtained an unexplained high concentration value of 76 ng/cm² for levoglucosan.

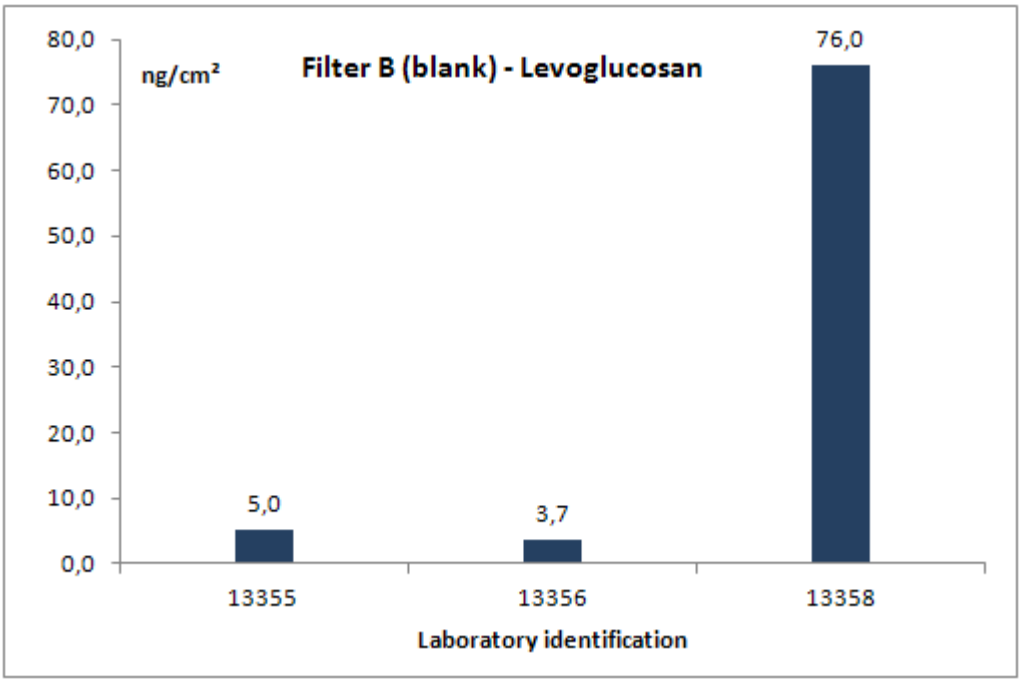


Figure 2 : Results for levoglucosan on filter B

9.2 DISCUSSION OF THE RESULTS

9.2.1 Limits of quantification

Instrumental LoQ and analytical techniques used by each participant are presented below.
Note that, GC/MS users seemed to have significant lower instrumental LoQ values.

Limit of quantification							
Laboratory	Analytical instrumentation	Levoglucosan		Galactosan		Mannosan	
		Filters [ng/cm²]	SRM [mg/kg^{-1}]	Filters [ng/cm²]	SRM [mg/kg^{-1}]	Filters [ng/cm²]	SRM [mg/kg^{-1}]
13355	GC/MS	0.70	0.40	0.20	0.10	0.50	0.20
13356	GC/MS	1.00	0.10	1.00	0.10	1.00	0.10
13347	GC/MS	2.00	0.55	2.00	0.55	2.00	0.55
13321	HPLC-PAD	5.29	1.23	1.76	0.41	4.41	1.02
13315	IC-PAD	10.00	1.00	-			
13320	TD-GC/MS	13.00	9.83	13.00	9.83	13.00	9.83
13373	GC/MS	15.00	1.00	7.00	0.60	20.00	1.50
13337	HPAEC-PAD	23.00	10.00	38.00	17.00	15.00	7.00
13358	GC/MS	28.00	0.01	28.00	0.01	28.00	0.01
13328	HPAEC-PAD	30.00	6.43	11.00	2.33	10.00	2.02
13395	HPAEC-PAD	42.00	13.00	21.00	6.00	21.00	6.00
13312	HPAEC-MS	50.00	4.20	30.00	2.50	30.00	2.50
13353	HPLC-MS	104.00	49.00	-			

9.2.2 Statistical distribution graphs

Distribution graphs show for each substance and test materials the average and the standard deviation of the results obtained by each participant. Results are classified according to the average values obtained by each participant. Scales of the graphs range between x* - 3s* and x* + 3s*. Each graph is bounded on the x-axis by the calculated reference value (robust average). Each participant is represented on the y-axis by its confidential code. The analytical instrumentation used is specified for each participant. This type of representation allows to each participant to visualize its own dispersion relative to the other laboratories. Note that, for the SRM powder, the NIST value is also indicated for each compound and arises from the study of Louchouarn & al[2]. These indicative concentration values were corrected to the moisture content of the SRM 1649b powder sent to each participant was measured (= 4.461 %, NF ISO 11465).

Results obtained showed no significant effect of the analytical procedure used whatever the quantified compound and the test material.

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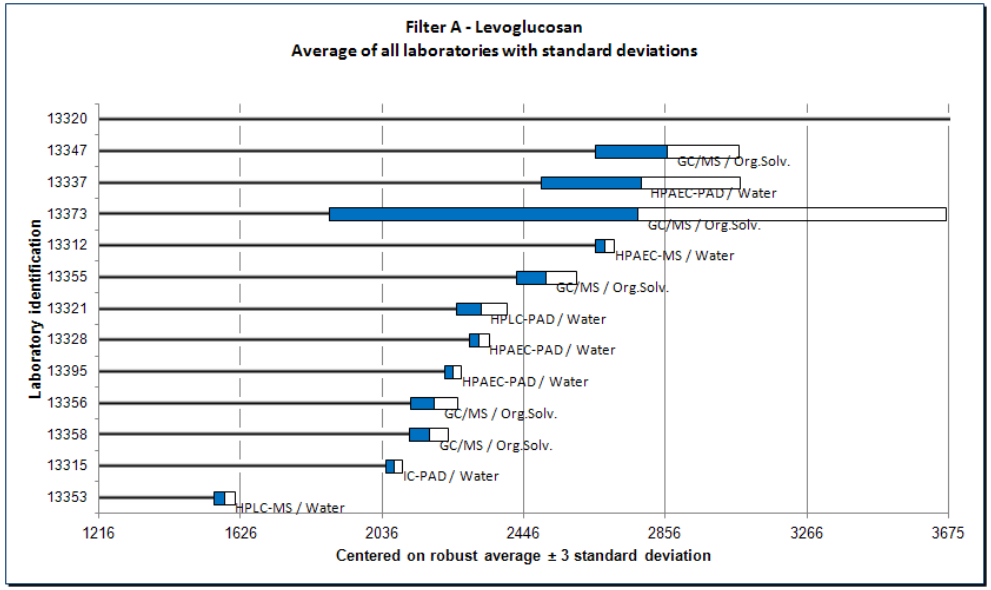
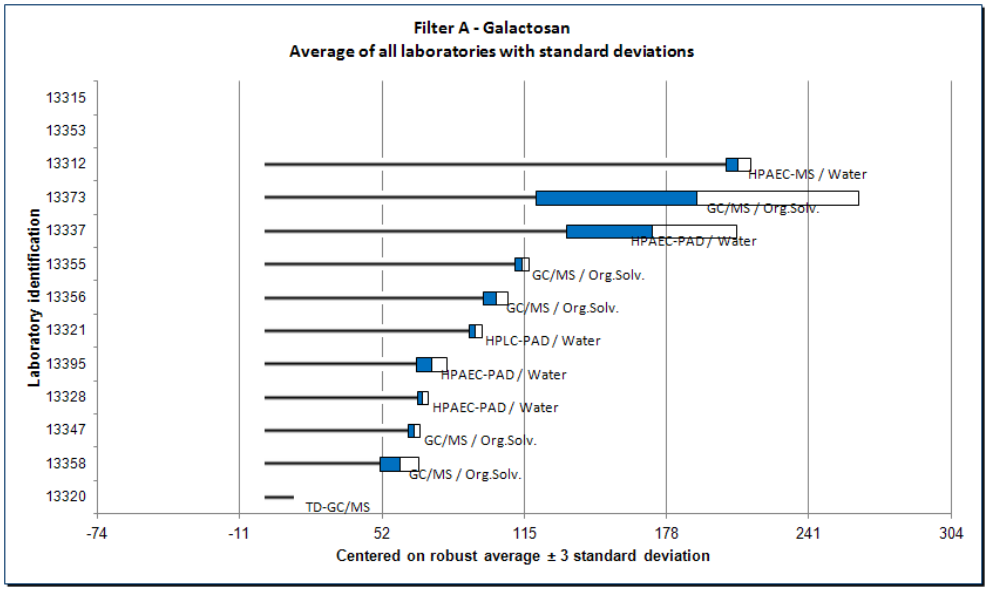
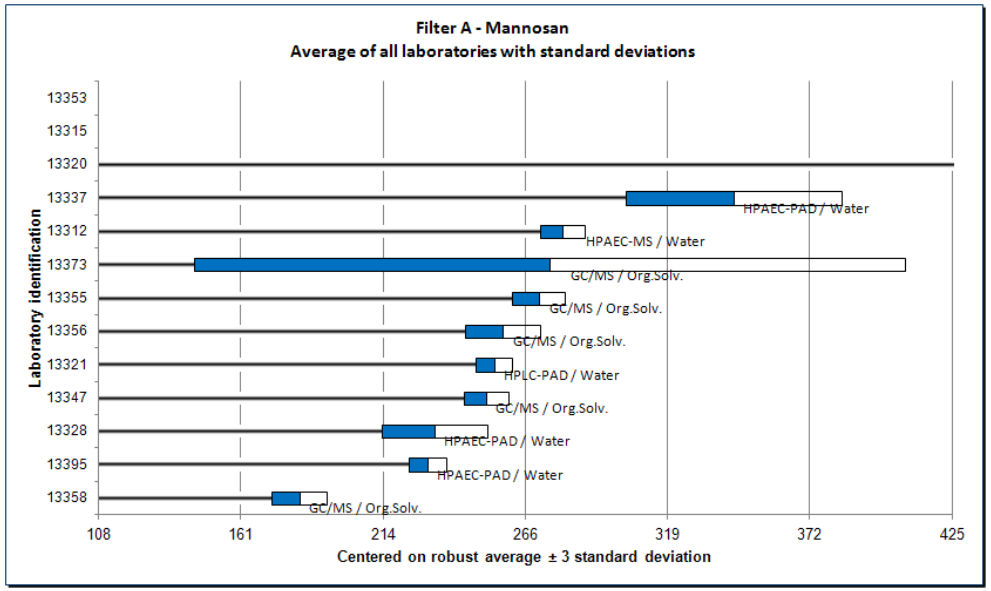
[2] *Louchouarn, P., & al., Determination of levoglucosan and its isomers in size fractions of aerosol standard reference materials, Atmospheric Environment (2009), doi:10.1016/j.atmosenv.2009.07.040*

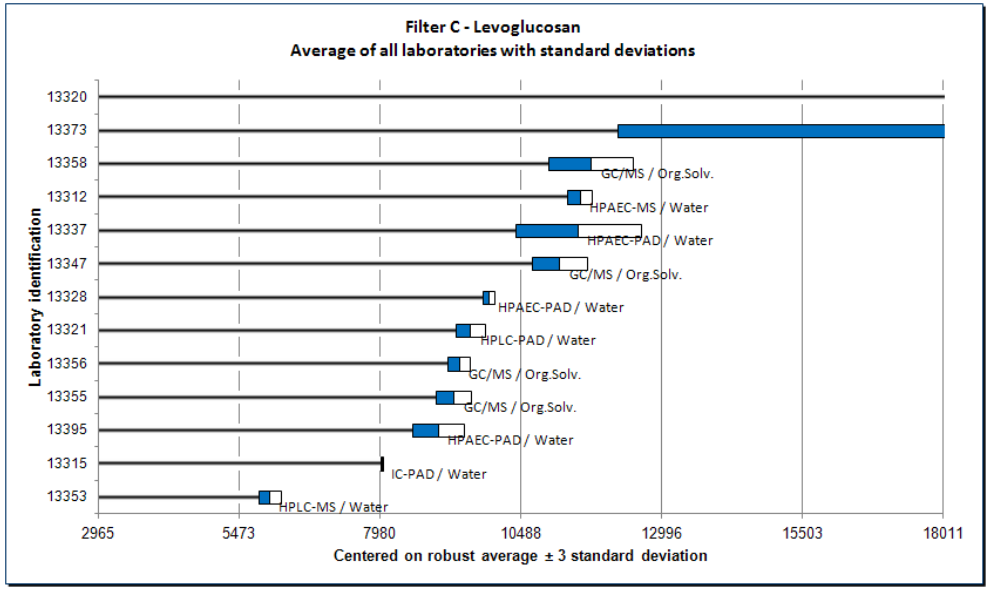
9.2.2.1 Filter A

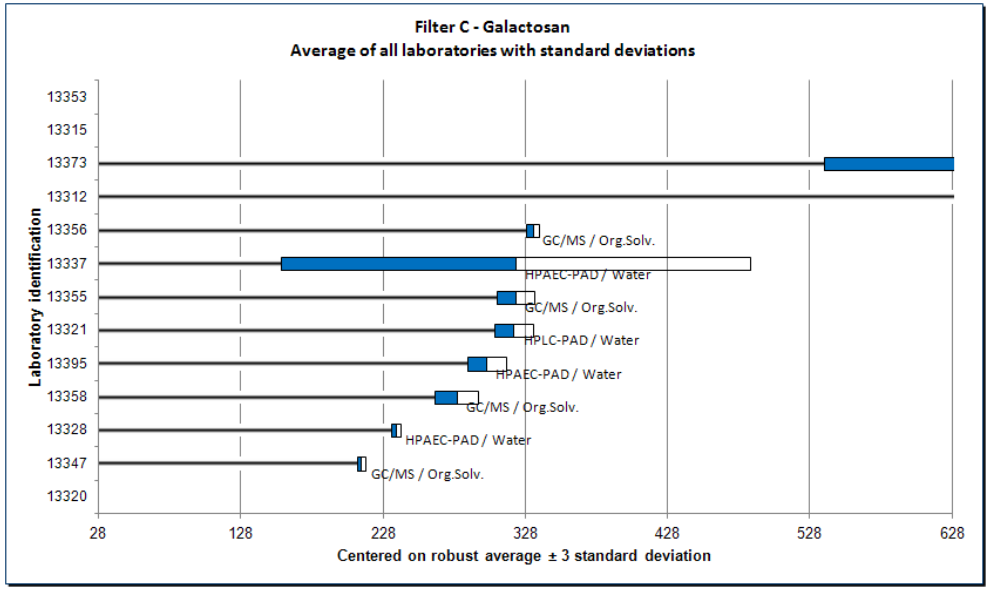


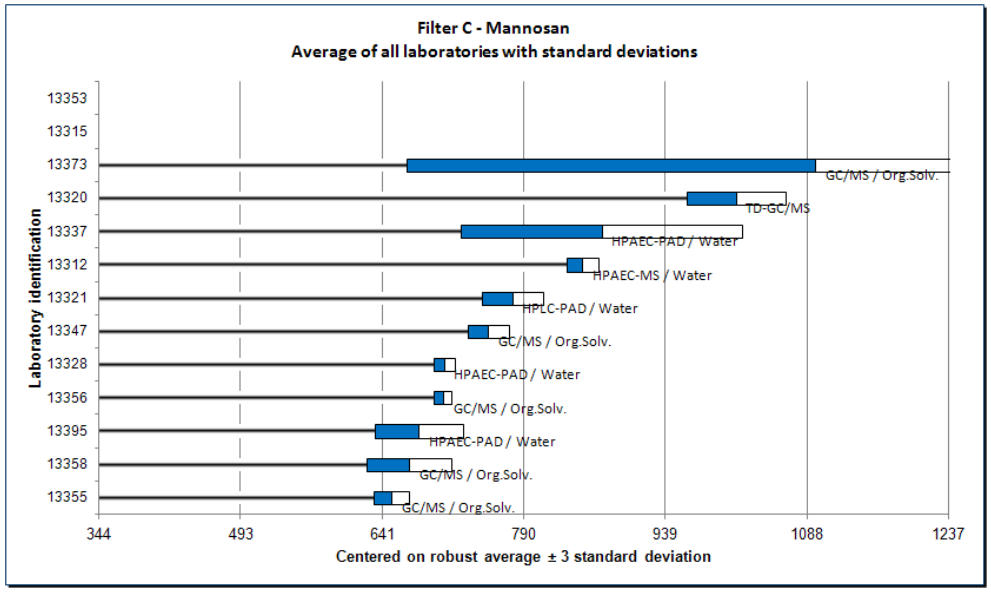




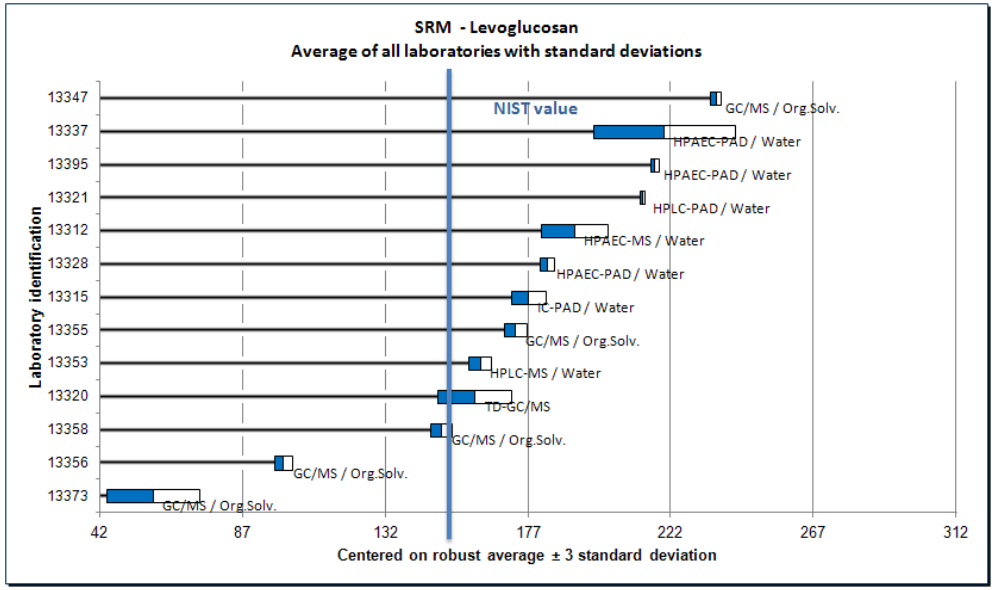
9.2.2.2 Filter C

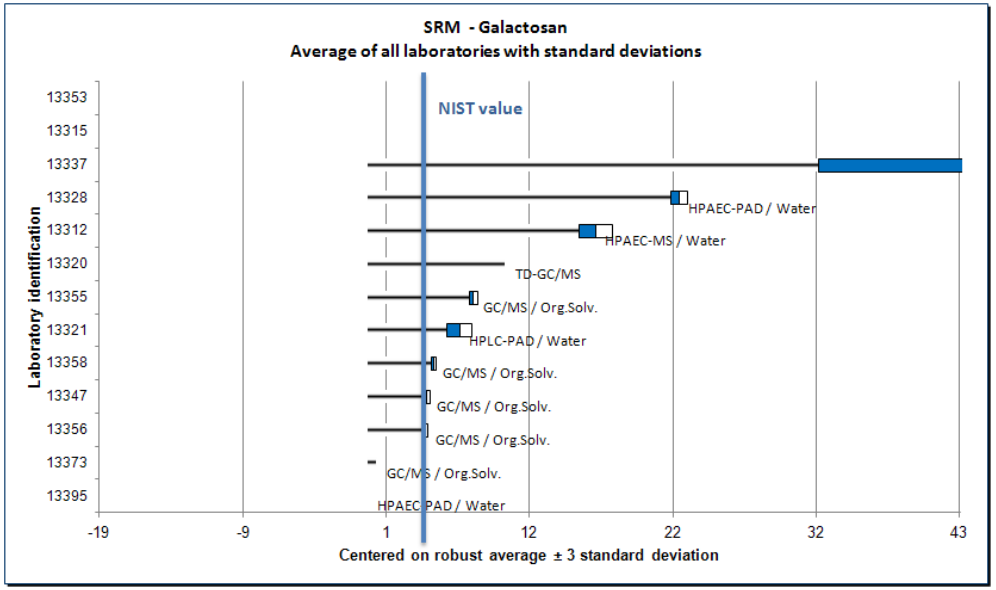


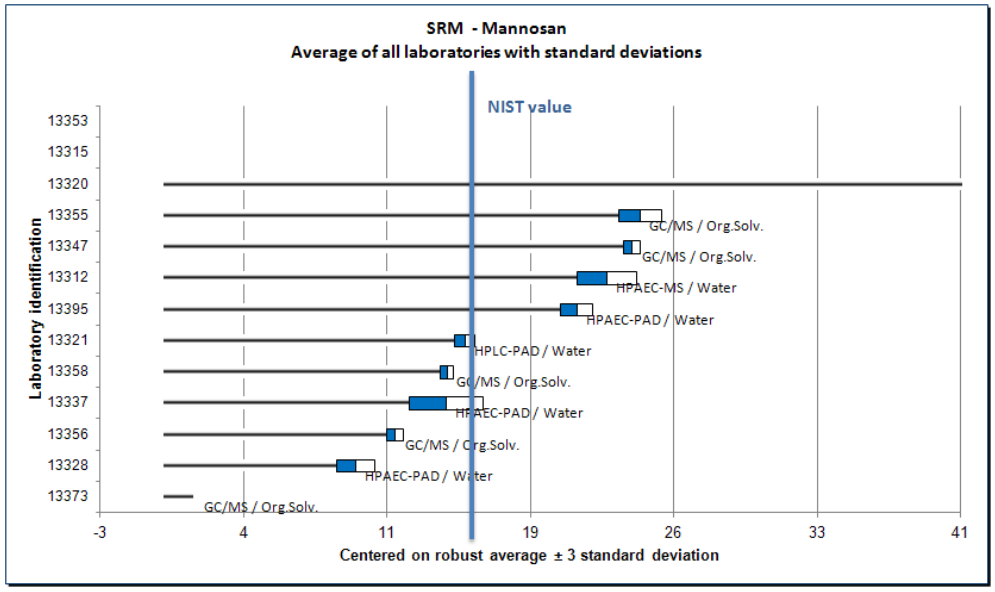




9.2.2.3 SRM Powder







9.2.3 Expanded uncertainties

According to EN 17025, the expanded uncertainty of measurement U could be assessed using the reproducibility standard deviation S_R applying the following equation:

$$U = 2 \times S_R$$

For natural ambient air aerosol samples, the expanded uncertainties determined in the present ILC are reported below. Equivalent ambient air concentration for typical 24 h sampling duration using low and high volume samplers (with flow rates of 1 m^3 h^{-1} and 30 m^3 h^{-1}, respectively) are also specified and correspond to a high winter range.

Filter A - ng/cm²	Robust average x*	**Expanded uncertainty U**	Equivalent concentration for a high volume sampler ng/m^3	Equivalent concentration for a low volume sampler ng/m^3
Galactosan	114.828	**110%**	24.6	57.2
Levoglucosan	2445.848	**35%**	522.9	1217.4
Mannosan	266.37	**43%**	57.0	132.6

Filter C - ng/cm²	Robust average x*	**Expanded uncertainty U**	Equivalent concentration for a high volume sampler ng/m^3	Equivalent concentration for a low volume sampler ng/m^3
Galactosan	327.91	**62%**	70.1	163.2
Levoglucosan	10488.07	**49%**	2242.4	5220.4
Mannosan	790.291	**39%**	169.0	393.4

Low expended uncertainties (< 50 % for levoglucosan and mannosan) for the ambient air samples were observed. For comparison, an expanded uncertainty lower than 50% for the measurement (sampling + analysis - 90% of the global uncertainty is due to the analytical procedure) of benzo[a]pyrene in ambient air on PM_{10} is required by the European Directive 2004/107/CE. The results obtained from the present ILC could be considered as satisfactory.

Uncertainties obtained for the NIST SRM 1649b were similar for levoglucosan and significantly higher for the mannosan and galactosan. Additional sources of uncertainty like weighing of the powder before analysis and sample homogeneity could explain these differences.

SRM - mg/kg^{-1}	Robust average x*	**Expanded uncertainty U**
Galactosan	11.6	**178 %**
Levoglucosan	177.0	**52 %**
Mannosan	18.7	**79 %**

10 CONCLUSIONS

An European interlaboratory comparison (ILC) for the analysis of levoglucosan and its isomers was organized within the European ACTRIS project (WP3). This ILC was led by INERIS with the help of LGGE for the quality control analysis. The test materials concentrations sent to the participants corresponded to a high winter range.

13 Participants submitted their results and most of them obtained satisfactory Z scores for levoglucosan, mannosan and galactosan. Only two laboratories (13320 and 13373) showed outliers for levoglucosan, and only one more (13312) also showed unsatisfactory results for mannosan and/or galactosan.

One laboratory (13358) showed a very high blank value for levoglucosan.

Instrumental limits of quantification evaluated by the participants were significantly lower for most GC/MS users.

One of the main purposes of this ILC was to evaluate the analytical repeatability and reproducibility standard deviations of each participant using their own analytical procedures. Additionally, the objective was to highlight any bias or influencing factor on the measurement quality of levoglucosan and its isomers. Only 3 laboratories (13320, 13373 and 13337) showed standard deviations of repeatability larger than 10 %. Standard deviations of reproducibility were about 20-25 % for levoglucosan and mannosan, while values in the range 30-60 % were obtained for galactosan.

No effect of the analytical procedure was highlighted during this ILC.

Expanded uncertainties obtained during this ILC are satisfactory and, for example, coherent with the one required for the measurement of benzo[a]pyrene in ambient air PM_{10} (European Directive 2004/107/CE).

11 LIST OF ANNEXES

Reference	Title	Number of pages
Annex 1	General organization, description of the tests and statistical analysis	8

ANNEX 1 GENERAL ORGANIZATION, DESCRIPTION OF THE TESTS AND STATISTICAL ANALYSIS

General organization of the test

Number of laboratories participating in the test

A minimum number of 10 participants with 4 results per participant is required, as that number, according to standard NF ISO 5725-1 (§ 6.3.3), makes it possible to obtain a low level of uncertainty in estimates of the repeatability and reproducibility standard deviations. The number of results can be modified during the development of the campaign plan depending on the needs of the interlaboratory tests.

NB: Non-compliance with this minimum number of participants can lead to postponing the interlaboratory tests to a later time so that the minimum number is reached.

Prior checks on the test materials

Before the distribution of the test materials, the organizer must demonstrate that the material being tested is stable and homogenous enough.

These two parameters were verified based on the assessment criteria of Annex B of standard NF ISO 13528.

HOMOGÉNÉITY

The homogeneity of the material was verified before its distribution.

The formulas are those cited in standard ISO 13528, with :

- average standard deviation of the determinations on D+1, S_x,
- intra-sample standard deviation S_w,
- inter-sample standard deviation S_S.

- $S_x = \sqrt{\sum (x_t - X)^2 / (g-1)}$,

  with : x_t = the determination values,

  X = average of the g x_t,

  g = number of samples subject to homogeneity verification

- $Sw = \sqrt{\sum w_t^2 / 2g}$, with $w_t = x_{t1} - x_{t2}$,

- $S_S = \sqrt{S_x^2 - (S_w^2 / 2)}$

After statistical processing of the data sent by the participants, the coordinator introduces, into each spreadsheet, the average *m* and standard deviation □ values for assessing the aptitude of the population.

For each parameter, the coordinator examines the homogeneity criterion. The test material will be considered to have a satisfactory homogeneity if and only if S_s / □ ≤ **0.3**. In the case where S_s^2 is negative, then the ratio S_X / □ is examined.

With :

□ descriptor of the population variability, robust standard deviation or pre-established value.

In the event of an interlaboratory test material that cannot be considered homogenous (S_s / □ **> 0.3),** the coordinator reserves the right, pursuant to chapter B2 c of standard NF ISO 13528, to include the inter-sample standard deviation in the standard deviation of the aptitude tests

$\sigma_n = \sqrt{\sigma^2 + S_s^2}$ with

- Inter-sample standard deviation S_S.
- σ: standard deviation of the aptitude assessment
- σ_n: new standard deviation of the aptitude assessment taking into account the inter-sample dispersion.

STABILITY

The stability of the material is verified at a frequency defined in cooperation with the advisory group, depending on each team's planning possibilities.

Calculation of the averages :

- average of the determinations on D+1, X,
- average of the determinations on D+X, Y.

The assessment starts with a comparison of the values obtained at moment D+1 to the values obtained at moment D+X while taking the intralaboratory dispersion into account. If the average values overlap with plus or minus two standard deviations, then the stability is verified.

If an instability is detected, then the coordinator examines the stability criterion using the assessment criterion of standard NF ISO 13528 according to the following procedure.

After the statistical processing of the data sent by the participants, the coordinator introduces the average *m* and standard deviation *σ* values into each spreadsheet for the population aptitude assessment.

For each parameter, the coordinator examines the stability criterion by using the assessment criterion of standard ISO 13528:

- the general average of the determinations obtained during verification of the homogeneity (at D+1, X) is compared to the general average of the results obtained during verification of the stability (on D+X, Y). The samples are considered stable enough if

  $|X - Y| / \tilde{\sigma} \leq$ □ or, if necessary, $|X - Y| / \tilde{\sigma}_n \leq$ □

Otherwise, the coordinator examines the results with the concerned technical experts and the statistician expert in order to decide how to continue the campaign for the concerned parameter or family of parameters.

EXPLOITATION STATISTICAL OF RÉSULTS

The statistical processing considered to analyze the data obtained from the ILT is done from the recommendations of standards NF ISO 5725. The confirmation of the verification of the hypotheses formulated in the part (NF ISO 5725-1) make it possible to use other parts to analyze the data.

Prior checking of the data before launching statistical calculations

- ***Study of the raw data***

All of the raw data collected at the end of an ILT first undergoes an expert opinion step in order to eliminate, if necessary, certain values during the calculation of the assigned value. This is in particular the case for:

- values returned below the quantification limit ;
- values entered equal to 0 ;
- values for which a dilution or retrieval error in the imposed unit is shown (for example by a factor of 1000).

Methodology:

Retrieval of 4 values

	Data received	Data taken into account
1st case	C, C, C, <LQ	C, C, C
2nd case	C, C, <LQ, <LQ	C, C
3rd case	C, <LQ, C, <LQ	C, C
4th case	C, <LQ, <LQ, <LQ	/

Retrieval of 2 values

	Data received	Data taken into account
1st case	C, <LQ	/
2nd case	<LQ, <LQ	/

The abnormal nature of these values may be viewed by Q-Q plot. These exclusions are presented for approval to the experts from the Advisory Group and drawn in the interlaboratory test report.

- ***Study of the data distribution***

The coordinator verifies, before launching the statistical processing, that all of the data follows a normal distribution. The method used to study the data distribution in order to show unexpected sources of variability is the Q-Q plot.

- ***Abnormal value and coherence tests***

Standard ISO 5725-5 (§6.1.4), making it possible to determine the repeatability and reproducibility of a measuring method, recommends applying the abnormal value test (Grubbs test and Cochran test) and coherence test (Mandel *h* and *k* statistics) to the data, so that the participants and organizer, in a procedure to improve the implementation of the analysis methods, look, in particular based on the comments provided by the laboratories in the results form or the observations, for the origin of the abnormal nature of the values detected as incoherent (for example computation error, or conversion error, etc.).

All of the abnormal value and coherence tests are outlined in the interlaboratory test report.

- ***Cochran test***

The Cochran test consists of comparing the variability within each participant to that of the entire population. The Cochran test is carried out iteratively until no more abnormal or questionable values are detected. Upon each iteration, the population is reduced by one individual.

- ***Grubbs test***

To look for an abnormal observation, the **simple test** is used. This test consists of comparing each extreme value (maximum average X_{max} or minimum average X_{min}) to the average of the entire population. The Grubbs test is carried out iteratively, alternatively at the upper extreme and lower extreme of the population, until no more abnormal or questionable values are detected. Upon each iteration, the population is reduced by one individual.

If the simple test thus carried out does not detect any abnormal values, the **double Grubbs test** is applied.

- ***Coherence tests.***

The *h* and *k* coherence tests lead to a graphic representation by histogram of the data and make it possible to detect the incoherent data visually.

Materials prepared by the INERIS :

The methodology used to determine the assigned value, its associated uncertainty and the standard deviation for the test materials prepared by the INERIS is presented below:

- ***Principle of the robust analysis of the tests***

The basic method for determining the repeatability and reproducibility of a measuring method described in standard ISO 5725-2 requires the use of tests of abnormal values (Cochran and Grubbs tests) in order to identify the data that must be excluded from the statistical calculations.

However, in practice, in applying abnormal value tests, the data analyst may be called upon to exercise judgment to decide what data must actually be excluded (for example if the tests detect an abnormal value and several questionable values for a laboratory: partial or elimination or elimination of all of its data?).

The data analyst's decision may therefore, in certain cases, have a substantial influence on the calculated values of the repeatability and reproducibility standard deviations, as well as the calculation of the average used as reference value and to assess the performance (laboratory score). The interest of the robust analysis of the data as described in standard ISO 5725-5, relative to the basic analysis, is to calculate the assigned value and other statistical parameters from all of the data, including that which may be judged doubful by expert statement or an abnormal value test: the applied data processing minimizes the weight of doubtful values, i.e. "extreme" values, so that the latter do not have a significant impact on the value of that assigned value.

Thus, the calculations of the assigned value (reference value), confidence intervals and performance statistics are not affected by the data analyst's judgment. **The participants' results are processed completely impartially and transparently.**

- ***Determination of the assigned value***

The assigned value for each parameter subject to an inter-comparison test is determined according to standards ISO 13528 and ISO 5725-5.

The assigned value is taken to be equal to the robust average of the results provided by the participants in the inter-comparison test (cf. Annex C of standard ISO 13528).

Even if abnormal values are detected by coherence and abnormal value tests, they are not excluded to calculate the robust average.

The robust average x^* is calculated by applying algorithm A. The iterations are repeated until the convergence is ensured, i.e. the 3rd rounded decimal place of the robust average and of the robust standard deviation no longer changes.

The average $\overline{x_i}$ of each of the p participants is calculated, then the p averages are ranked by increasing order.

- The initial value of the robust average x^* is equal to the median of the p averages.

  $x^* = \text{median of } \overline{x_i} \qquad (i = 1,2,....p)$

  The initial value of the robust standard deviation s^* is equal to:

  $s^* = 1.483 \times \text{median of } \left|\overline{x_i} - x^*\right| \qquad (i = 1,2,....p)$

- The value of x^* is updated as follows:

  $\varphi = 1.5 \times s^*$

  For each value $\overline{x_i}$, one calculates: $x_i^* = \begin{cases} x^* - \varphi & \text{if} \quad \overline{x_i} < x^* - \varphi \\ x^* + \varphi & \text{if} \quad \overline{x_i} > x^* + \varphi \\ x_i^* & \text{if not} \end{cases}$

  The new robust average value is equal to:

$$x^* = \sum_{i=1}^{p} \frac{x_i^*}{p}$$

The new robust standard deviation is equal to:

$$s^* = 1.134\sqrt{\frac{\sum_{i=1}^{p}(x_i - x^*)^2}{p-1}}$$

- ***Determination of the uncertainty associated with the assigned value (robust method)***

The uncertainty of the assigned value u_{x^*} is estimated by:

$$u_{x^*} = 1.25 \times s^* / \sqrt{p}$$

When $u_{x^*} \leq 0.3 \times \hat{\sigma}$, chapter 4.2 of standard NF ISO 13528 recommends neglecting the uncertainty of the assigned value and not including it in the interpretation of the results of the aptitude test, i.e. in the statistical performance test.

For $u_{x^*} \leq 0.3 \times \hat{\sigma}$ i.e. $u_{x^*} \leq 0.3 \times s^*$, the number of participants in the interlaboratory comparisons must be $p \geq 16$. The tests must be organized with at least 10 participants. If the number of participants is between 10 and 15, it is therefore appropriate to take the uncertainty of the assigned value into account in the interpretation of the results of the statistical performance test.

- ***Determination of the standard deviation for the aptitude $\hat{\sigma}$ assessment***

Among the 5 methods proposed by standard NF ISO 13528 to calculate the standard deviation $\hat{\sigma}$ for the aptitude assessment (i.e. to assess the laboratories' performance), the determination from the participants' results is used.

When the interlaboratory test medium does not correspond to a Certified Reference Material, the standard deviation for assessing the aptitude $\hat{\sigma}$ is determined from the participants' results. It is taken to be equal to the robust standard deviation s^* estimated by applying Algorithm A, as previously described.

<u>Particular case : Non-homogenous inter-comparison support</u>

When the homogeneity tests of the test materials find a lack of homogeneity, the coordinator takes the inter-sample standard deviation into account in the standard deviation of the aptitude tests, so as not to impute to the laboratories, during the performance test, the bias related to the variability of the distributed test materials. The standard deviation for assessing the aptitude is recalculated as follows:

$\hat{\sigma} = \sqrt{\hat{\sigma_1}^2 + S_s^2}$ where

$\hat{\sigma}$: standard deviation for assessing the recalculated aptitude;

$\hat{\sigma_1}$: standard deviation for assessing the aptitude, calculated by the robust analysis;

S_s : the inter-sample standard deviation of the distributed test materials.

Statistical performance tests

The laboratories' performance is assessed using the z score.

- ***Z score***

The Z score is calculated as follows:

- Case of a test material prepared by the INERIS: $z_i = \frac{\overline{x_i} - x^*}{\hat{\sigma}}$

Where:

$\hat{\sigma}$ is the estimate of the standard deviation for assessing the aptitude calculated from algorithm A,

$\overline{x_i}$ is the average concentration measured by the laboratory i,

X_{MRC} and x^* correspond to the considered assigned value.

<u>If the standard uncertainty associated with the assigned value is non-negligible</u> :

- In the case of a certified reference material: If $u_{X_{MRC}} > 0.3\hat{\sigma}$,
- In the case of a test material prepared by the INERIS: If p<16

Then the standard uncertainty associated with the assigned value is taken into account and the z score is calculated as follows:

$$z_i = \frac{\overline{x_i} - X_{MRC}}{\sqrt{\hat{\sigma}^2 + u_{X_{MRC}}{}^2}} \text{ or } z_i = \frac{\overline{x_i} - x^*}{\sqrt{\hat{\sigma}^{\,2} + u_{x^*}{}^2}}$$

<u>If the test material prepared by the INERIS is not homogenous</u> :

The inter-sample standard uncertainty S_s should be taken into account :

$$z_i = \frac{\overline{x_i} - x^*}{\sqrt{\hat{\sigma}^{\,2} + S_s^2}}$$

NB: If necessary, both the standard uncertainty associated with the assigned value and the inter-sample standard uncertainty are taken into account.

<u>Assessment of each laboratory's performance</u> :

A laboratory having a z score greater than 3.0 or less than -3.0 causes an "action signal." A z score greater than 2.0 or less than -2.0 causes a warning signal (§7.4.2 standard ISO 13528).