Interlaboratory trial for validation of ISO 16308

FINAL REPORT

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Characterization of the Environment
Department Chronic Risks Division

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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 “proficiency tests,”
Extract	test material elaborated either by extracting real water sample, or by spiking a solvent with some or all of the substances of interest,
LoQ	Limit of Quantification,
Test material	Intended matrix containing the species subject to the interlaboratory comparison, potentially added using a spiking solution. The test matrices are also called, in French referential LAB-CIL REF 02, comparison substrate,
Matrix	Natural element, physical element as well as all of its components other than the species to be analyzed in which the substance subject to the interlaboratory test is placed,
Spiking solution	Concentration solution with known substance(s) dissolved in a solvent,
Assigned value	Value attributed to a particular quantity and accepted, sometimes by convention, as having an uncertainty appropriate for a given purpose (ISO 13528).

2 DEFINITIONS AND SYMBOLS

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,
$\hat{\sigma}$	:	standard deviation for evaluation assessing the aptitude recalculated due to heterogeneity of the test material and / or low population (p <16)
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,
u_{x^*}	:	standard uncertainty u_{x^*},
w*	:	robust standard deviation obtained using algorithm S of ISO 13528,
x*	:	robust average obtained using algorithm A of ISO 13528,

3 REFERENCE DOCUMENTS

EN ISO/CEI 17043 **:** general requirements for proficiency testing – April 2010,

ISO 5725-1 : applications of the statistics – Accuracy (correctness and faithfulness) of the results and measurement methods – Part 1: general principles and definitions – December 1994,

ISO 5725-2 : application of the statistics – Accuracy (correctness and faithfulness) of the measurement results – Part 2: basic method for determining the repeatability and reproducibility of a standardized measurement method – December 1994,

ISO 5725-5 : application of the statistics – Accuracy (correctness and faithfulness) of the measurement results – Part 5: alternative methods for determining the faithfulness of a standardized measurement method – December 1998,

ISO 13528 **:** statistical methods used in aptitude tests by interlaboratory comparisons – December 2005,

ISO 3534-2 **:** vocabulary and symbols Part 2: Applied statistics – December 2006,

NF X06-050 **:** application of the statistics – Study of the normality of a distribution – December 1995.

ISO/DIS 16308 **:** water quality – Determination of glyphosate and AMPA – Method using high performance liquid chromatography (HPLC) with tandem mass spectrometric detection- Complementary element

4 INTRODUCTION

This trial is a validation exercise and not a proficiency testing trial. It is intended to validate the draft standard ISO/DIS 16308 for the determination of glyphosate, AMPA and additionally gluphosinate.

It addresses all European laboratories with proficiency on the analytical protocol. The test materials has been prepared by INERIS and IRSTEA and distributed to participants on April 10th, 2013.

5 PARTICIPANTS

11 participants returned results.

The table 1 describes the distribution of the participants according to their country.

Table 1: Distribution of the participants according to their country

Country	Number of participant
Austria	1
Germany	9
France	1

6 DESCRIPTION OF THE TEST MATERIALS

6.1 DESCRIPTION

The table 2 shows the description of the test materials.

Table 2: Description of the test materials

Flasks	Flasks Reference	Quantity/ Packaging	Comments
1 plastic flask	Drinking water matrix **dechlorinated** (A)	roughly 500 ml	Matrix : Spiked drinking water (A +B)
1 amber glass vial	Spike in methanol for drinking water matrix (B)	exactly 1 ml	
1 plastic flask	Underground water matrix (C)	roughly 500 ml	Matrix : Spiked underground water (C +D)
1 amber glass vial	Spike in methanol for underground water matrix (D)	exactly 1 ml	
1 plastic flask	Surface water matrix (E)	roughly 500 ml	Matrix : Spiked surface water (E +F)
1 amber glass vial	Spike in methanol for surface water matrix (F)	exactly 1 ml	
1 plastic flask	Blank (G)	roughly 500 ml	Quality assurance : Blank (G)

These flasks are conditioned in single-use boxed containers.

The package is accompanied by:

- an acknowledgement of receipt IM-0223 to be filled out and transmitted as soon as the package is received,
- the instruction form IM-1541,
- the ISO/DIS 16308: Water quality – Determination of glyphosate and AMPA – method using high performance liquid chromatography (HPLC) with tandem mass spectrometric detection.

6.2 INSTRUCTIONS

The analyses have to be carried out applying the procedure described in ISO/DIS 16308.

The same operator or team should perform all of the analyses for a given parameter, in a short time interval, specified for each compound below.

These analyses must be considered independent tests: all of the operations must be repeated, from sub-sampling to expression of the final result.

Four independent replicate analyses from each of the 3 samples are required (spiked drinking water, spiked underground water, spiked surface water).

Analysis of test materials

For each test material (except blank), use the following procedure:

- Measure the exact volume of the matrix received before the spiking;
- Open the vial containing the spiking solution and insert (vial + unscrewed cap + solution) in the matrix whose exact volume is know (example spiking solution (B) in Drinking water matrix (A));
- Stir the spiked material for 30 minutes;
- Begin the analytical procedure from § 7 of the ISO 16308;
- Analyze (4 independent analyzes) the following parameters : glyphosate, AMPA, gluphosinate (the later optional);
- Return the result in ng/liter.

6.3 MATRIX CHARACTERIZATION

The table 3 shows the matrix characterization.

Table 3: Matrix characterization

Elements	Blank	Drinking water before spiking	Underground water before spiking	Surface water before spiking
Suspended matters (mg/L)	/	/	<2	31,2
Chlorine (mg/L)	<0,1	<0,1	<0,1	<0,1
TOC (mg/L)	1,74	1,56	1,95	3,03
DOC (mg/L)	0,5	1,23	1,74	2,27
Ca^{2+}	81,2	115	92,9	116
Mg^{2+}	26,2	11,4	27,7	7,0

7 SHIPPING

The shipment was done on April 10th, 2013.

8 HOMOGENEITY AND STABILITY OF THE SPIKING SOLUTION

8.1 HOMOGENEITY OF THE MATERIALS

The homogeneity of the materials was verified at the time of their distribution, according to the methodology explained in annex 1. The results are presented in the table 4.

Table 4: Results of the homogeneity

	Glyphosate					
Variable	**Calibration (50 ppt)**	**Spiked drinking water (60 ppt)**	**Calibration (100 ppt)**	**Spiked underground water (180 ppt)**	**Calibration (1 ppb)**	**Spiked natural water (850 ppt)**
Observations	5	5	5	5	5	5
Obs. with missing data	0	0	0	0	0	0
Obs. without missing data	5	5	5	5	5	5
Minimum	0.0543	0.0382	0.1011	0.128	0.8619	0.663
Maximum	0.0703	0.0499	0.1223	0.156	1.1299	0.744
Average	0.0633	0.0421	0.1121	0.142	1.0083	0.705
Standard deviation	0.0061	0.00456	0.00875	0.01026	0.0958	0.03504
Report (Confidence interval of 95% around the variance ratio] 0.184, 16.975 [)	1.767		0.727		7.477	
F (observed value)	1.767		0.727		7.477	
F (critical value)	9.604		9.604		9.604	
DDL1	4		4		4	
DDL2	4		4		4	
p-value (bilateral)	0.595		0.765		0.07	
alpha	0.05		0.05		0.05	
Conclusion	**Homogeneous**		**Homogeneous**		**Homogeneous**	

The materials are considered homogeneous

8.2 STABILITY OF SPIKING SOLUTIONS

The stability of the materials was verified according to the methodology presented in annex 1. The stability is done during one month at different temperature.

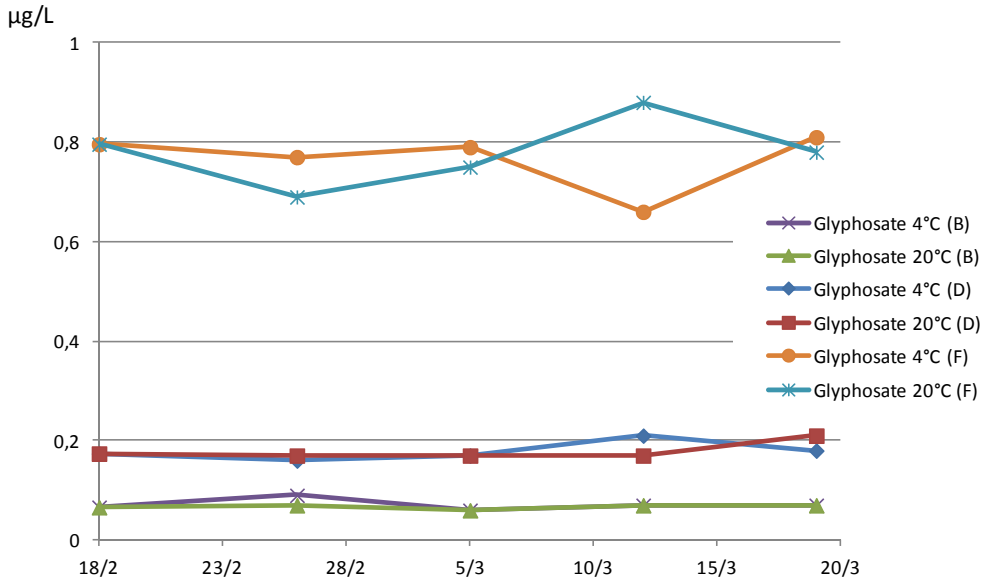


Figure 1: Stability of glyphosate spiking solutions kept at 4 or 20°C for 1 month.

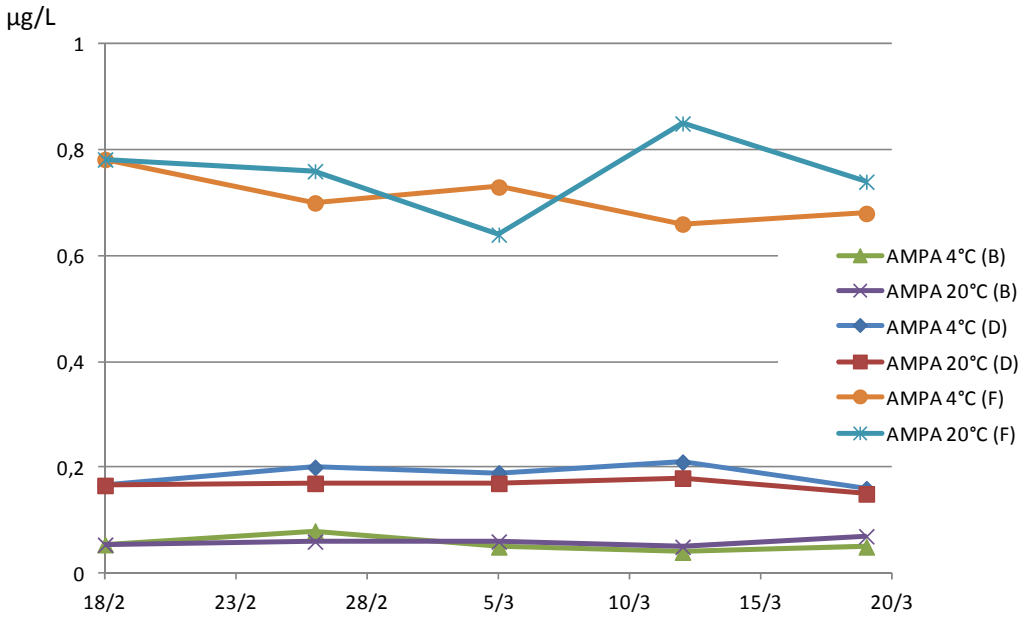


Figure 2: Stability of AMPA spiking solutions kept at 4 or 20°C for 1 month.

The spiking solutions are considered stable for a month

9 METHOD ISO/DIS 16308

During this comparison for the validation of the standard the participants have implemented the following various stages:

Analytical process (% according to the parameter)	*Practices operated by laboratories during the comparison interlaboratories « Validation ISO 16308 »*		
Storage shielded from the light	**Yes**	**No**	**Comments**
	100%	**/**	**/**
Storage temperature	**≤ 6°C**	**≥ 23°C**	**Comments**
	91%	**9%**	**/**
Pretreatment (SPM)	**Yes**	**No**	**Comments**
	54%	**37%**	**1 participant didn't answered (9%)**
Chelate break and derivatisation for direct injection	**Yes**	**No**	**Comments**
	64%	**27%**	**1 participant didn't answered (9%)**
Chelate break and derivatisation prior to pre-concentration	**Yes**	**No**	**Comments**
	27%	**64%**	**1 participant didn't answered (9%)**
Liquid/liquid extraction of analytes derivates	**Yes**	**No**	**Comments**
	27%	**64%**	**1 participant didn't answered (9%)**
Purification	**Yes**	**No**	**Comments**
	27%	**64%**	**1 participant didn't answered (9%)**
Chromatographic determination	**Yes**	**No**	**Comments**
	91%	**/**	**1 participant didn't answered (9%)**
Implemented technique	**HPLC/ESI/MS/MS**		**Comments**
	100%		**Respect of the technique**
Calibration	**External**	**Internal**	**Comments**
	91%	**9%**	**/**
Environment in which is realized the calibration	**Solvent**	**Matrix**	**Comments**
	46%	**54%**	**/**
Correction analytical blank	**Yes**	**No**	**Comments**
	46%	**54%**	**/**
Corrected results	**Yes**	**No**	**Comments**
	27%	**73%**	**Results are corrected :** - **1 : blank** - **1 : exact volume of matrix** - **1 : internal standard**

10 RESULTS OF THE INTERLABORATORY COMPARISON

10.1 DATA FROM THE TEST MATERIALS

10.1.1 General information

The details of the statistical processing are recalled in **annex 1**.

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

- the value assigned to the average is 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 is taken to be equal to the robust standard deviation.

The statistical processing applied to the data made it possible to determine:

- the reference value (or assigned value) of each parameter for each test and its associated uncertainty,
- questionable or outlying results,
- the repeatability and reproducibility confidence intervals for each compound and each test material.

The other results relative to each test material are grouped together in:

- annex 2: raw data for each participant: average, repeatability standard deviation, repeatability variability coefficient, and the values dismissed by expert opinion.
- annex 3: statistical distribution curves: centered on the Averages: Values comprised between $(x^* - 3s^*)$ and $(x^* + 3s^*)$.

10.1.2 Test material "BLANK"

This material allowed the estimation, for each participant, of the mastery of all the following influences: contamination of chemicals, of laboratory glassware, of the measurement system and instrumental drift.

Quantified substances in the material « blank » by certain participants are grouped in the table 5.

Table 5: Quantified substances in the material « blank »

	Parameters		
	Concentrations ng/L		
Participants	AMPA	Additionally Gluphosinate	Glyphosate
13401	<50,00	<50,00	<50,00
13418	<5,00	Not analyzed	<5,00
13425	<20,00	Not analyzed	<20,00
13432	**62,70**	Not analyzed	**32,30**
13439	<20,00	<20,00	<20,00
13440	<10,00	0,00	0,00
13445	**6,00**	**5,00**	**5,00**
13447	<10,00	<10,00	<10,00
13452	**15,80**	**2,50**	10,20
13476	<25,00	Not analyzed	<25,00
13484	0,00	0,00	0,00

10.1.3 Test material "spiked drinking water"

10.1.3.1 Without exclusion

Values observed **before** application of statistical algorithms

Parameters (concentrations ng/liter))	*Population average*	*Population standard deviation*	*CV_R en %*	*$CV_{rép}$ en %*	*Number of decimals*	*Number of measures*	*Interlaboratory Standard deviation S_L*	*Reproducibility Standard deviation S_R*	*Repeatability standard deviation S_r*
AMPA	51,76	21,69	41,90%	6,73%	1	11	21,45	22,38	6,36
Gluphosinate	59,08	10,98	18,58%	10,74%	1	7	9,68	14,17	10,34
Glyphosate	47,86	13,22	27,63%	6,42%	1	11	13,06	13,70	4,12

During the ISO TC 147 in Berlin, the members of the Working Group 55 decided to exclude the data from participant 13432. This participant quantified values in blank.

10.1.3.2 With exclusion of the participant 13432 (quantified values in blank)

Values observed **after** application of statistical algorithms (excluded values of participant 13432)

Parameters (concentrations ng/liter)	*Robust average x**	*Robust standard deviation for assessing the aptitude s**	*Standard deviation for assessing the aptitude recalculated due to low population (p <16) $\hat{\sigma}$*	*Standard uncertainty u_{x^*}*	*Robust standard deviation w**	*Interlaboratory standard deviation S_L*	*Reproducibility standard deviation S_R*	*Repeatability standard deviation S_r*	*Relative reproducibility confidence interval (%)*	*Relative repeatability confidence interval (%)*
AMPA	55,88	19,46	21,27	8,60	4,83	19,30	19,90	4,83	84,21%	20,42%
Gluphosinate	60,60	12,70	14,25	6,48	9,13	11,85	14,96	9,13	63,46%	38,75%
Glyphosate	48,93	12,06	13,07	5,03	4,76	11,82	12,75	4,76	60,08%	22,45%

10.1.4 Test material "spiked underground water"

Values observed **before** application of statistical algorithms

Parameters (concentrations ng/liter)	*Population average*	*Population standard deviation*	*CV_R en %*	*$CV_{rép}$ en %*	*Number of decimals*	*Number of measures*	*Interlaboratory standard deviation S_L*	*Reproducibility standard deviation S_R*	*Repeatability standard deviation S_r*
AMPA	148,74	33,56	22,56%	6,73%	1	11	32,92	35,39	12,97
Gluphosinate	169,73	52,42	30,89%	5,39%	1	7	52,17	53,16	10,17
Glyphosate	151,07	37,98	25,14%	3,78%	1	11	37,86	38,33	5,97

Values observed **after** application of statistical algorithms

Parameters (concentrations ng/liter)	*Robust average x**	*Robust standard deviation for assessing the aptitude s**	*Standard deviation for assessing the aptitude recalculated due to low population (p <16) $\hat{\sigma}$*	*Standard uncertainty u_{x^*}*	*Robust standard deviation w**	*Interlaboratory standard deviation S_L*	*Reproducibility standard deviation S_R*	*Repeatability standard deviation S_r*	*Relative reproducibility confidence interval (%)*	*Relative repeatability confidence interval (%)*
AMPA	148,74	38,05	40,67	14,34	10,46	37,69	39,12	10,46	58,60%	15,68%
Gluphosinate	163,65	44,53	49,25	21,04	10,93	44,20	45,53	10,93	68,07%	16,35%
Glyphosate	150,73	42,32	45,23	15,95	6,55	42,20	42,70	6,55	63,13%	9,69%

10.1.5 Test material "spiked surface water"

Values observed **before** application of statistical algorithms

Parameters (concentrations ng/litre)	*Population average*	*Population standard deviation*	*CV_R en %*	*$CV_{rép}$ en %*	*Number of decimals*	*Number of measures*	*Interlaboratory deviation standard S_L*	*Reproducibility standard deviation S_R*	*Repeatability standard deviation S_r*
AMPA	800,22	111,71	13,96%	4,63%	1	11	109,84	117,14	40,70
Gluphosinate	664,35	232,40	34,98%	7,20%	1	7	230,96	236,67	51,65
Glyphosate	675,16	125,73	18,62%	4,48%	1	11	124,41	129,58	36,21

Values observed **after** application of statistical algorithms

Parameters (concentrations ng/litre)	*Robust average x**	*Robust standard deviation for assessing the aptitude s**	*Standard deviation for assessing the aptitude recalculated due to low population (p <16) $\hat{\sigma}$*	*Standard uncertainty u_{x^*}*	*Robust standard deviation w**	*Interlaboratory standard deviation S_L*	*Reproducibility standard deviation S_R*	*Repeatability standard deviation S_r*	*Relative reproducibility confidence interval (%)*	*Relative repeatability confidence interval (%)*
AMPA	807,42	109,41	116,92	41,24	42,88	107,29	115,54	42,88	31,88%	11,83%
Gluphosinate	664,35	263,55	291,48	124,51	56,66	262,02	268,08	56,66	98,74%	20,87%
Glyphosate	666,23	110,11	117,67	41,50	39,38	108,34	115,27	39,38	38,55%	13,17%

11 CONCLUSION

These results have been presented by France in the Berlin meeting of the ISO/TC 147. The results have been considered highly satisfactory by the members of the working group.

After the Berlin meeting, these results have been integrated in the ISO/FDIS 16308 "Water Quality – Determination of glyphosate and AMPA – Method using high performance liquid chromatography (HPLC) with tandem mass spectrometric detection" in the annex A.

The publication of the standard ISO 16308 is planned for the first semester of 2014.

12 LIST OF ANNEXES

Reference	Title	Number of pages
Annex 1	General organization, description of the tests and algorithms	6
Annex 2	Data received -Averages and Repeatability standard deviations for the laboratories and Values dismissed by expert opinion.	12
Annex 3	Statistical distribution curves: sorted by average values comprised between $(x^* - 3s^*)$ and $(x^* + 3s^*)$.	12

ANNEX 1
GENERAL ORGANIZATION, DESCRIPTION OF THE TESTS AND ALGORITHMS

General organization of the test

The organization can be divided into five distinct phases :

① **January to March, 2013**: administrative phase including contacts, enrollment and transmission of the confidential code;

② **February to March, 2013**: Test material preparation and testing phase;

③ **April 10th to May 31, 2013**: Shipping, participant analysis, and results collection phase;

④ **July to September 2013**: Statistical analysis phase according to the procedures described later in the report,

⑤ **October 2013**: presentation of the results during the meeting of the ISO/TC147

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.

Preliminary checks on the test materials

Before the distribution of the test materials, the organizer must demonstrate that the material being tested is sufficiently stable and homogenous. In certain cases, the homogeneity tests cannot be done before distribution for technical, historical and logistical reasons[1].

In our case, the homogeneity and stability is done.

[1] Organizers of interlaboratory comparisons, requirements for Accreditation – Document LAB-CIL REF02 from the COFRAC.

HOMOGENEITY

The homogeneity of the material is verified during its distribution, i.e. from the analytical results obtained on D+1.

In this trial, the method used is a comparison of variances by Fisher F test between

- variance obtained in the calibration point (same concentration level as the material) and
- variance obtained on the materials.

If F test is less than the appropriate critical value for p = 0.05, then the material may be regarded as sufficiently homogeneous.

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+Z, Y
- with D : date of shipment of test material

The assessment starts with a comparison of the values obtained at time D+1 to the values obtained at time 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 instability is suspected, 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 submitted 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 suitably stable if

  $|X - Y| / \sigma \leq 0.3$ (or, if necessary, $|X - Y| / \sigma_n \leq 0.3$).

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

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

Preliminary checking of the data before launching statistical calculations

- *examination 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 submitted below the quantification limit ;
- values submitted equal to 0 ;
- values for which a dilution or transcription error in the imposed unit is suspected (for example a factor of 1 000).

Methodology:

Set 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	/

Set 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 submitted for approval to the experts from the Advisory Group and highlighted in the interlaboratory test report.

- *Study of the data distribution*

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

Materials prepared by INERIS:

The methodology used to determine the assigned value, its associated uncertainty and the standard deviation for the test materials prepared by 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 ISO 5725-2 requires the use of tests of outlying values (Cochran and Grubbs tests) in order to identify the data that shall be excluded from the statistical calculations.

Excluding outliers can sometimes have a large effect on the repeatability and reproducibility standard deviations, but in practice, when applying the outlier tests, the data analyst may have to use judgment to decide which data to exclude. The interest of the robust is to calculate the assigned value and other statistical parameters from all of the data, including that which may be judged suspicious by expert statement or an abnormal value test: the applied data processing minimizes the weight of suspicious values, i.e. "extreme" values, so that the latter do not have a significant impact on the value of that assigned value.

- *Determination of the assigned value*

The assigned value, for each parameter subject to an inter-comparison test, is determined according to 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 ISO 13528).

Even if outlying values are detected by coherence and outliers detection 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 digit 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, and 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 NF ISO 13528 recommends omitting the uncertainty of the assigned value and not including it in the interpretation of the results of the proficiency 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 NF ISO 13528 to calculate the standard deviation $\hat{\sigma}$ for the proficiency assessment (i.e. to assess the laboratories' performance), the determination from the participants' results is used.

When the interlaboratory test material is not a Certified Reference Material, the standard deviation for assessing the proficiency $\hat{\sigma}$ 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 on the test materials conclude to a lack of homogeneity, the coordinator takes the between-sample standard deviation into account in the standard deviation of the proficiency evaluation, in order not to charge the laboratories, in proficiency assessment, with 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

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

$\hat{\sigma}_1$: is the standard deviation for assessing the aptitude, calculated by the robust analysis;

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

Search outliers

- *Outlying value and coherence tests*

ISO 5725-5 (§6.1.4), usually used to determine the repeatability and reproducibility of a measuring method, recommends applying the outliers 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, investigate, in particular based on the comments provided by the laboratories in the results form or the observations, for the origin of the outliers detected as incoherent (for example computation error, or conversion error, etc.).

All of the outlying value and coherence tests are highlighted in the interlaboratory test report.

- *Cochran test*

The Cochran test consists of comparing the within–lab variability of each participant vs. the entire population. The Cochran test is carried out iteratively until no more outlying or questionable values are detected. At each iteration, the population is reduced by one individual.

- *Grubbs test*

For the detection of outliers, 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 whole population. The Grubbs test is carried out iteratively, alternatively at the upper extreme and lower extreme of the population, until no more outlying or questionable values are detected. At each iteration, the population is reduced by one individual.

If the simple test thus carried out does not detect any outlying value, 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.

ANNEX 2

DATA RECEIVED, AVERAGES AND REPEATABILITY STANDARD DEVIATIONS FOR THE LABORATORIES AND VALUES DISMISSED BY EXPERT OPINION

For each studied matrix, all of the participants' results are presented, including the values excluded from the statistical calculations (expert opinion). For the latter, the reason those values are not taken into account is specified.

Table 1 - Spiked drinking water in ng/l - AMPA - without exclusion

Laboratory identification	Measure 1	Measure 2	Measure 3	Measure 4	Beginning of analysis (day/month/year)	End of analysis (day/month/year)	Standard	Average of measurements	Standard Deviation of Measurements	Repeatability standard deviation by %	Expert opinion	Expert opinion comment
13440	10,00	10,00	10,00	10,00	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	10,000	0,0000	0,0%	Excluded	4 values <LQ
13425	35,60	31,90	33,60	33,90	16/04/2013	17/04/2013	ISO/DIS 16308 (§ 7.2.1 + § 7.4)	33,750	1,5155	4,5%	OK	
13452	29,80	39,10	40,80	31,20	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	35,225	5,5295	15,7%	OK	
13476	45,80	42,40	47,10	45,60	06/05/2013	07/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	45,225	1,9973	4,4%	OK	
13401	50,00	50,00	50,00	50,00	18/04/2013	18/04/2013	Other, to specify (Observations)	50,000	0,0000	0,0%	Excluded	4 values <LQ
13432	49,00	46,10	54,90	59,60	23/04/2013	24/04/2013	ISO/DIS 16308 (§ 7.2.1 + § 7.4)	52,400	6,0371	11,5%	Excluded	High values of Blank
13418	59,20	57,70	58,50	59,70	15/05/2013	15/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	58,775	0,8694	1,5%	OK	
13445	68,20	52,80	62,30	59,50	26/04/2013	29/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	60,700	6,3943	10,5%	OK	
13447	60,20	61,40	63,20	62,30	08/05/2013	08/05/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	61,775	1,2816	2,1%	OK	
13439	66,00	68,00	70,00	62,00	24/04/2013	24/04/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	66,500	3,4157	5,1%	OK	
13484	105,00	110,00	70,00	95,00	16/04/2013	24/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	95,000	17,7951	18,7%	OK	

Table 2 - Spiked drinking water in ng/l - Gluphosinate - without exclusion

Laboratory identification	Measure 1	Measure 2	Measure 3	Measure 4	Beginning of analysis (day/month/year)	End of analysis (day/month/year)	Standard	Average of measurements	Standard Deviation of Measurements	Repeatability standard deviation by %	Expert opinion	Expert opinion comment
13447	41,70	41,90	43,00	43,20	08/05/2013	08/05/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	42,450	0,7594	1,8%	OK	
13401	50,00	50,00	50,00	50,00	18/04/2013	18/04/2013	Other, to specify (Observations)	50,000	0,0000	0,0%	Excluded	4 values <LQ
13440	53,60	52,70	54,80	54,10	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	53,800	0,8832	1,6%	OK	
13439	60,00	74,00	50,00	58,00	24/04/2013	24/04/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	60,500	9,9833	16,5%	OK	
13484	62,00	42,00	98,00	58,00	16/04/2013	24/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	65,000	23,6361	36,4%	OK	
13452	77,10	68,50	64,30	61,40	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	67,825	6,8359	10,1%	OK	
13445	71,60	83,50	72,20	68,70	26/04/2013	29/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	74,000	6,5151	8,8%	OK	
13418							ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	Not analyzed	Not analyzed	Not analyzed	Excluded	
13425							ISO/DIS 16308 (§ 7.2.1 + § 7.4)	Not analyzed	Not analyzed	Not analyzed	Excluded	
13432							ISO/DIS 16308 (§ 7.2.1 + § 7.4)	Not analyzed	Not analyzed	Not analyzed	Excluded	
13476							ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	Not analyzed	Not analyzed	Not analyzed	Excluded	

Table 3 - Spiked drinking water in ng/l - Glyphosate - without exclusion

Laboratory identification	Measure 1	Measure 2	Measure 3	Measure 4	Beginning of analysis (day/month/year)	End of analysis (day/month/year)	Standard	Average of measurements	Standard Deviation of Measurements	Repeatability standard deviation by %	Expert opinion	Expert opinion comment
13440	15,00	15,00	14,70	14,10	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	14,700	0,4243	2,9%	OK	
13425	43,10	36,60	35,30	33,80	16/04/2013	17/04/2013	ISO/DIS 16308 (§ 7.2.1 + § 7.4)	37,200	4,0963	11,0%	OK	
13439	46,00	48,00	48,00	46,00	24/04/2013	24/04/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	47,000	1,1547	2,5%	OK	
13484	47,00	37,00	47,00	58,00	16/04/2013	24/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	47,250	8,5781	18,2%	OK	
13452	56,20	53,30	41,80	42,30	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	48,400	7,4301	15,4%	OK	
13401	50,00	50,00	50,00	50,00	18/04/2013	18/04/2013	Other, to specify (Observations)	50,000	0,0000	0,0%	Excluded	4 values <LQ
13476	47,80	51,50	52,00	50,30	06/05/2013	07/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	50,400	1,8744	3,7%	OK	
13432	52,70	53,70	48,90	53,40	23/04/2013	24/04/2013	ISO/DIS 16308 (§ 7.2.1 + § 7.4)	52,175	2,2232	4,3%	OK	
13447	52,70	52,40	54,10	53,60	08/05/2013	08/05/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	53,200	0,7874	1,5%	OK	
13418	62,60	61,30	57,70	59,90	15/05/2013	15/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	60,375	2,0966	3,5%	OK	
13445	64,10	64,80	73,00	61,00	26/04/2013	29/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	65,725	5,1234	7,8%	OK	

Table 4 - Spiked drinking water in ng/l - AMPA - with exclusion (values of the participant 13432)

Laboratory identification	Measure 1	Measure 2	Measure 3	Measure 4	Beginning of analysis (day/month/year)	End of analysis (day/month/year)	Standard	Average of measurements	Standard Deviation of Measurements	Repeatability standard deviation by %	Expert opinion	Expert opinion comment
13440	10	10	10	10	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	10,000	0,0000	0,0%	Excluded	4 values <LQ
13425	36	32	34	34	16/04/2013	17/04/2013	ISO/DIS 16308 (§ 7.2.1 + § 7.4)	33,750	1,5155	4,5%	OK	
13452	30	39	41	31	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	35,225	5,5295	15,7%	OK	
13476	46	42	47	46	06/05/2013	07/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	45,225	1,9973	4,4%	OK	
13401	50	50	50	50	18/04/2013	18/04/2013	Other, to specify (observations)	50,000	0,0000	0,0%	Excluded	4 values <LQ
13432	49	46	55	60	23/04/2013	24/04/2013	ISO/DIS 16308 (§ 7.2.1 + § 7.4)	52,400	6,0371	11,5%	Excluded	blank value of 62.7ng/L
13418	59	58	59	60	15/05/2013	15/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	58,775	0,8694	1,5%	OK	
13445	68	53	62	60	26/04/2013	29/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	60,700	6,3943	10,5%	OK	
13447	60	61	63	62	08/05/2013	08/05/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	61,775	1,2816	2,1%	OK	
13439	66	68	70	62	24/04/2013	24/04/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	66,500	3,4157	5,1%	OK	
13484	105	110	70	95	16/04/2013	24/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	95,000	17,7951	18,7%	OK	

Table 5 - Spiked drinking water in ng/l - Gluphosinate

Laboratory identification	Measure 1	Measure 2	Measure 3	Measure 4	Beginning of analysis (day/month/year)	End of analysis (day/month/year)	Standard	Average of measurements	Standard Deviation of Measurements	Repeatability standard deviation by %	Expert opinion	Expert opinion comment
13447	42	42	43	43	08/05/2013	08/05/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	42,450	0,7594	1,8%	OK	
13401	50	50	50	50	18/04/2013	18/04/2013	Other, to specify (Observations)	50,000	0,0000	0,0%	Excluded	4 values <LQ
13440	54	53	55	54	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	53,800	0,8832	1,6%	OK	
13439	60	74	50	58	24/04/2013	24/04/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	60,500	9,9833	16,5%	OK	
13484	62	42	98	58	16/04/2013	24/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	65,000	23,6361	36,4%	OK	
13452	77	69	64	61	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	67,825	6,8359	10,1%	OK	
13445	72	84	72	69	26/04/2013	29/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	74,000	6,5151	8,8%	OK	
13418							ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	Not analyzed	Not analyzed	Not analyzed	Excluded	
13425							ISO/DIS 16308 (§ 7.2.1 + § 7.4)	Not analyzed	Not analyzed	Not analyzed	Excluded	
13432							ISO/DIS 16308 (§ 7.2.1 + § 7.4)	Not analyzed	Not analyzed	Not analyzed	Excluded	
13476							ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	Not analyzed	Not analyzed	Not analyzed	Excluded	

Table 6 - Spiked drinking water in ng/l - Glyphosate - with exclusion (values of the participant 13432)

Laboratory identification	Measure 1	Measure 2	Measure 3	Measure 4	Beginning of analysis (day/month/year)	End of analysis (day/month/year)	Standard	Average of measurements	Standard Deviation of Measurements	Repeatability standard deviation by %	Expert opinion	Expert opinion comment
13440	15	15	15	14	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	14,700	0,4243	2,9%	OK	
13425	43	37	35	34	16/04/2013	17/04/2013	ISO/DIS 16308 (§ 7.2.1 + § 7.4)	37,200	4,0963	11,0%	OK	
13439	46	48	48	46	24/04/2013	24/04/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	47,000	1,1547	2,5%	OK	
13484	47	37	47	58	16/04/2013	24/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	47,250	8,5781	18,2%	OK	
13452	56	53	42	42	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	48,400	7,4301	15,4%	OK	
13401	50	50	50	50	18/04/2013	18/04/2013	Other, to specify (Observations)	50,000	0,0000	0,0%	Excluded	4 values <LQ
13476	48	52	52	50	06/05/2013	07/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	50,400	1,8744	3,7%	OK	
13432	53	54	49	53	23/04/2013	24/04/2013	ISO/DIS 16308 (§ 7.2.1 + § 7.4)	52,175	2,2232	4,3%	Excluded	Value of blank in 32,3 ng/L
13447	53	52	54	54	08/05/2013	08/05/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	53,200	0,7874	1,5%	OK	
13418	63	61	58	60	15/05/2013	15/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	60,375	2,0966	3,5%	OK	
13445	64	65	73	61	26/04/2013	29/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	65,725	5,1234	7,8%	OK	

Table 7 - spiked underground water in ng/l - AMPA

Laboratory identification	Measure 1	Measure 2	Measure 3	Measure 4	Beginning of analysis (day/month/year)	End of analysis (day/month/year)	Standard	Average of measurements	Standard Deviation of Measurements	Repeatability standard deviation by %	Expert opinion	Expert opinion comment
13452	94,10	102,20	83,50	91,60	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	92,850	7,7022	8,3%	OK	
13440	104,40	102,90	109,20	99,40	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	103,975	4,0648	3,9%	OK	
13447	119,30	122,70	124,20	107,60	08/05/2013	08/05/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	118,450	7,5182	6,3%	OK	
13432	158,10	126,10	138,80	157,20	23/04/2013	24/04/2013	ISO/DIS 16308 (§ 7.2.1 + § 7.4)	145,050	15,4498	10,7%	OK	
13401	148,00	140,00	137,00	157,00	18/04/2013	18/04/2013	Other, to specify (Observations)	145,500	8,9629	6,2%	OK	
13484	149,00	137,00	152,00	148,00	30/04/2013	24/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	146,500	6,5574	4,5%	OK	
13425	151,10	149,20	159,10	147,50	16/04/2013	17/04/2013	ISO/DIS 16308 (§ 7.2.1 + § 7.4)	151,725	5,1318	3,4%	OK	
13439	188,00	176,00	120,00	194,00	24/04/2013	24/04/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	169,500	33,8378	20,0%	OK	
13418	175,00	183,00	176,00	184,00	15/05/2013	15/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	179,500	4,6547	2,6%	OK	
13476	177,40	186,60	183,20	185,60	06/05/2013	07/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	183,200	4,1215	2,2%	OK	
13445	190,10	188,80	211,30	209,20	26/04/2013	29/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	199,850	12,0511	6,0%	OK	

Table 8 - spiked underground water in ng/l - Gluphosinate

Laboratory identification	Measure 1	Measure 2	Measure 3	Measure 4	Beginning of analysis (day/month/year)	End of analysis (day/month/year)	Standard	Average of measurements	Standard Deviation of Measurements	Repeatability standard deviation by %	Expert opinion	Expert opinion comment
13447	128,00	116,80	115,30	109,10	08/05/2013	08/05/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	117,300	7,8736	6,7%	OK	
13401	124,00	119,00	128,00	135,00	18/04/2013	18/04/2013	Other, to specify (Observations)	126,500	6,7577	5,3%	OK	
13445	145,00	145,20	148,00	151,60	26/04/2013	29/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	147,450	3,0871	2,1%	OK	
13440	159,80	164,10	165,80	154,40	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	161,025	5,0875	3,2%	OK	
13484	185,00	183,00	148,00	156,00	30/04/2013	24/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	168,000	18,7794	11,2%	OK	
13452	192,20	182,80	198,30	206,10	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	194,850	9,8436	5,1%	OK	
13439	270,00	258,00	282,00	282,00	24/04/2013	24/04/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	273,000	11,4891	4,2%	OK	
13418							ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	Not analyzed	Not analyzed	Not analyzed	Excluded	
13425							ISO/DIS 16308 (§ 7.2.1 + § 7.4)	Not analyzed	Not analyzed	Not analyzed	Excluded	
13432							ISO/DIS 16308 (§ 7.2.1 + § 7.4)	Not analyzed	Not analyzed	Not analyzed	Excluded	
13476							ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	Not analyzed	Not analyzed	Not analyzed	Excluded	

Table 9 - spiked underground water in ng/l - Glyphosate

Laboratory identification	Measure 1	Measure 2	Measure 3	Measure 4	Beginning of analysis (day/month/year)	End of analysis (day/month/year)	Standard	Average of measurements	Standard Deviation of Measurements	Repeatability standard deviation by %	Expert opinion	Expert opinion comment
13452	89,60	76,90	88,40	94,70	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	87,400	7,5140	8,6%	OK	
13445	117,20	109,70	102,50	102,20	26/04/2013	29/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	107,900	7,1035	6,6%	OK	
13440	122,60	125,60	125,60	120,70	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	123,625	2,4088	1,9%	OK	
13447	131,70	130,90	127,00	127,50	08/05/2013	08/05/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	129,275	2,3698	1,8%	OK	
13484	156,00	152,00	137,00	153,00	30/04/2013	24/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	149,500	8,5049	5,7%	OK	
13418	150,00	149,00	153,00	150,00	15/05/2013	15/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	150,500	1,7321	1,2%	OK	
13401	143,00	147,00	157,00	163,00	18/04/2013	18/04/2013	Other, to specify (Observations)	152,500	9,1469	6,0%	OK	
13476	174,30	174,50	171,30	174,60	06/05/2013	07/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	173,675	1,5882	0,9%	OK	
13425	178,10	179,20	184,20	184,30	16/04/2013	17/04/2013	ISO/DIS 16308 (§ 7.2.1 + § 7.4)	181,450	3,2645	1,8%	OK	
13432	197,10	191,90	181,90	180,90	23/04/2013	24/04/2013	ISO/DIS 16308 (§ 7.2.1 + § 7.4)	187,950	7,8662	4,2%	Excluded	High values of blank
13439	212,00	220,00	214,00	226,00	24/04/2013	24/04/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	218,000	6,3246	2,9%	OK	

Table 10 - spiked surface water in ng/l - AMPA

Laboratory identification	Measure 1	Measure 2	Measure 3	Measure 4	Beginning of analysis (day/month/year)	End of analysis (day/month/year)	Standard	Average of measurements	Standard Deviation of Measurements	Repeatability standard deviation by %	Expert opinion	Expert opinion comment
13445	502,40	556,80	573,10	624,10	26/04/2013	29/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	564,100	50,1371	8,9%	OK	
13452	678,20	733,60	715,10	637,70	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	691,150	42,4272	6,1%	OK	
13401	762,00	688,00	650,00	720,00	18/04/2013	18/04/2013	Other, to specify (Observations)	705,000	47,5675	6,7%	OK	
13447	716,10	771,50	716,60	750,00	08/05/2013	08/05/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	738,550	27,0962	3,7%	OK	
13425	810,20	822,60	829,40	828,30	16/04/2013	17/04/2013	ISO/DIS 16308 (§ 7.2.1 + § 7.4)	822,625	8,8032	1,1%	OK	
13440	841,50	844,00	860,00	805,60	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	837,775	22,9623	2,7%	OK	
13484	879,00	852,00	837,00	823,00	23/05/2013	24/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	847,750	23,9635	2,8%	OK	
13439	902,00	800,00	890,00	912,00	24/04/2013	24/04/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	876,000	51,4587	5,9%	OK	
13432	980,80	818,80	930,60	825,20	23/04/2013	24/04/2013	ISO/DIS 16308 (§ 7.2.1 + § 7.4)	888,850	79,9087	9,0%	OK	
13418	902,00	931,00	920,00	903,00	15/05/2013	15/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	914,000	14,0238	1,5%	OK	
13476	916,80	936,80	927,50	885,50	06/05/2013	07/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	916,650	22,3166	2,4%	OK	

Table 11 - spiked surface water in ng/l - Gluphosinate

Laboratory identification	Measure 1	Measure 2	Measure 3	Measure 4	Beginning of analysis (day/month/year)	End of analysis (day/month/year)	Standard	Average of measurements	Standard Deviation of Measurements	Repeatability standard deviation by %	Expert opinion	Expert opinion comment
13447	401,70	414,40	424,40	402,30	08/05/2013	08/05/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	410,700	10,8465	2,6%	OK	
13401	551,00	492,00	347,00	408,00	18/04/2013	18/04/2013	Other, to specify (Observations)	449,500	90,0685	20,0%	OK	
13445	470,60	478,10	435,80	422,60	26/04/2013	29/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	451,775	26,7941	5,9%	OK	
13484	854,00	741,00	731,00	676,00	23/05/2013	24/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	750,500	74,6838	10,0%	OK	
13452	712,80	799,30	812,60	745,60	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	767,575	46,6080	6,1%	OK	
13440	772,10	788,60	803,80	791,00	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	788,875	13,0224	1,7%	OK	
13439	1088,00	1038,00	990,00	1010,00	24/04/2013	24/04/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	1031,500	42,5010	4,1%	OK	
13418							ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	Not analyzed	Not analyzed	Not analyzed	Excluded	
13425							ISO/DIS 16308 (§ 7.2.1 + § 7.4)	Not analyzed	Not analyzed	Not analyzed	Excluded	
13432							ISO/DIS 16308 (§ 7.2.1 + § 7.4)	Not analyzed	Not analyzed	Not analyzed	Excluded	
13476							ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	Not analyzed	Not analyzed	Not analyzed	Excluded	

Table 12 - spiked surface water in ng/l - Glyphosate

Identification Laboratoire	Mesure 1	Mesure 2	Mesure 3	Mesure 4	Début d'analyse (day/month/year)	Fin d'analyse (day/month/year)	Norme	Moyenne des mesures	Ecart_type des mesures	CVrép en %	Avis EXPERT	Commentaire Avis Expert
13452	522,80	468,30	396,10	517,50	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	476,175	58,7528	12,3%	OK	
13447	603,70	613,40	596,20	594,10	08/05/2013	08/05/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	601,850	8,7333	1,5%	OK	
13418	602,00	607,00	597,00	605,00	15/05/2013	15/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	602,750	4,3493	0,7%	OK	
13445	685,30	546,40	598,50	612,70	26/04/2013	29/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	610,725	57,3076	9,4%	OK	
13401	658,00	574,00	621,00	593,00	18/04/2013	18/04/2013	Other, to specify (Observations)	611,500	36,5194	6,0%	OK	
13484	656,00	641,00	626,00	668,00	23/05/2013	24/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	647,750	18,2277	2,8%	OK	
13440	669,30	644,60	666,10	662,10	15/04/2013	16/04/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	660,525	11,0177	1,7%	OK	
13476	720,70	711,70	720,70	709,60	06/05/2013	07/05/2013	ISO/DIS 16308 (§ 7 + § 7.2.1 + § 7.4)	715,675	5,8654	0,8%	OK	
13432	787,90	780,70	752,50	760,80	23/04/2013	24/04/2013	ISO/DIS 16308 (§ 7.2.1 + § 7.4)	770,475	16,5820	2,2%	OK	
13425	725,40	719,40	861,40	793,00	16/04/2013	17/04/2013	ISO/DIS 16308 (§ 7.2.1 + § 7.4)	774,800	66,6841	8,6%	OK	
13439	976,00	986,00	940,00	916,00	24/04/2013	24/04/2013	ISO/DIS 16308 (§ 7.2.2 + § 7.3.1 +§ 7.3.5 + § 7.4)	954,500	32,3883	3,4%	OK	

ANNEX 3

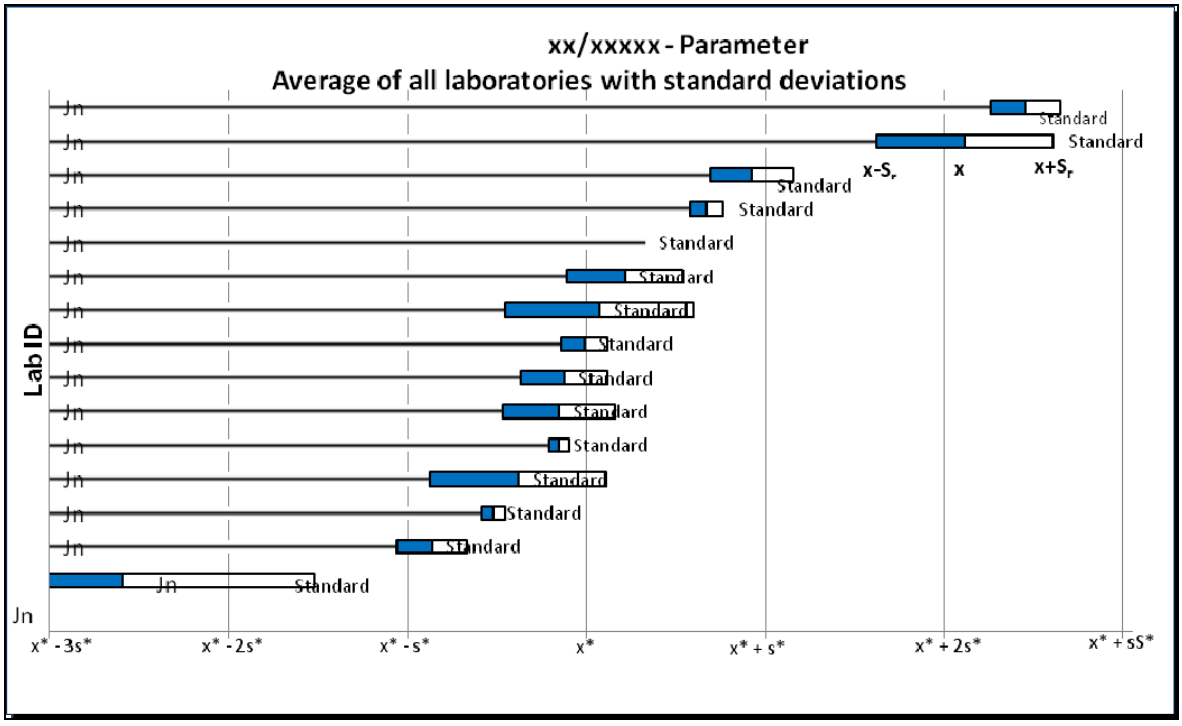
STATISTICAL DISTRIBUTION CURVES: STORTED BY AVERAGE VALUES COMPRISED BETWEEN (X^* - $3S^*$) AND (X^* + $3S^*$).

Distribution curves are shown for each substance. They indicate the average and the standard deviation of the results for each participant. Each curve is limited on the x-axis by the calculated reference values (robust average or reference average of the certified material). The lower limit is given by the reference value of the average minus three times the reference standard deviation, while the upper limit is obtained from the reference value of the average plus three times the reference standard deviation.

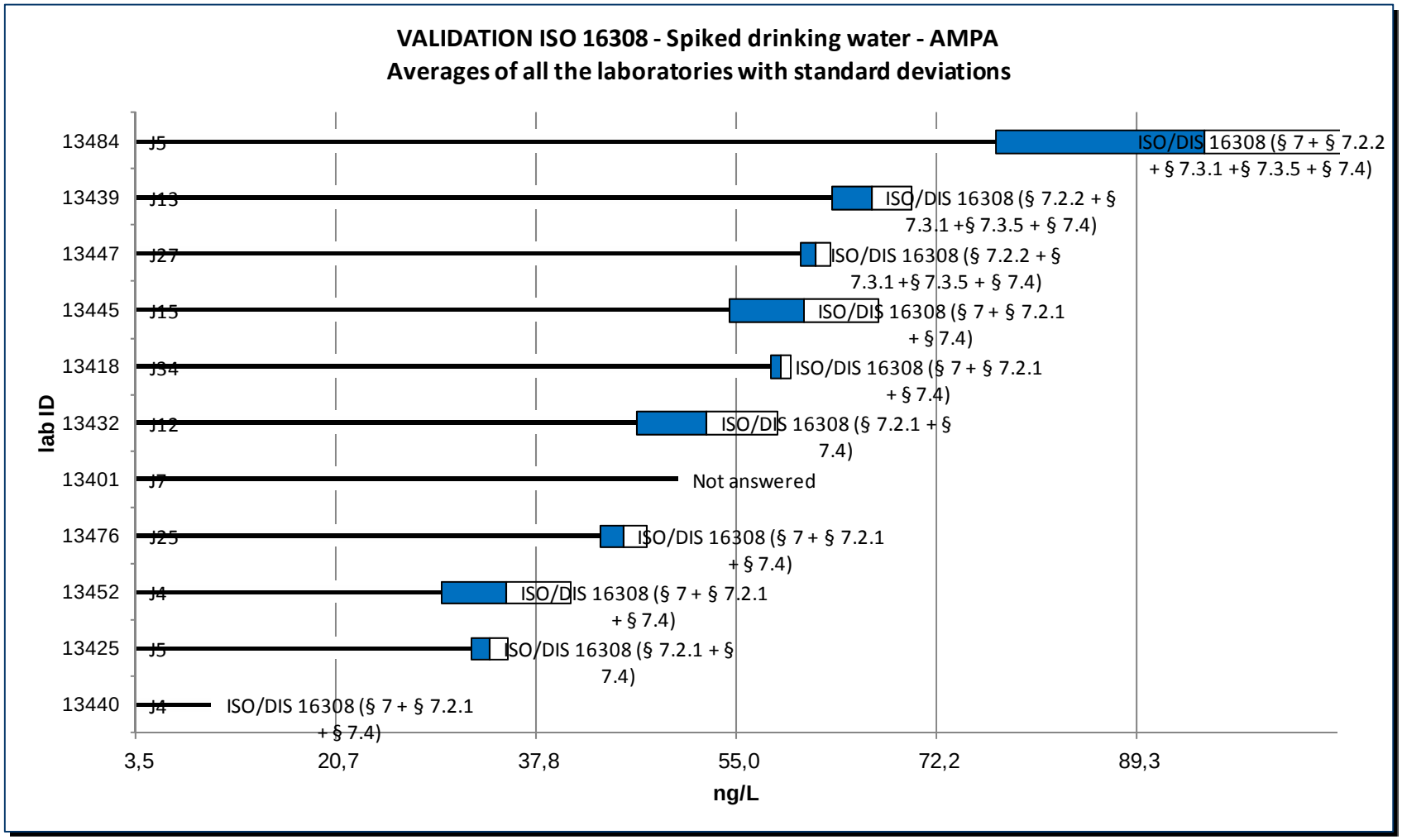
Each participant is represented on the y-axis by its confidential code. The assay method used and the sample withdrawal or analysis date are specified for each participant.

This type of representation allows each participant to view its own dispersion relative to that of the other laboratories.

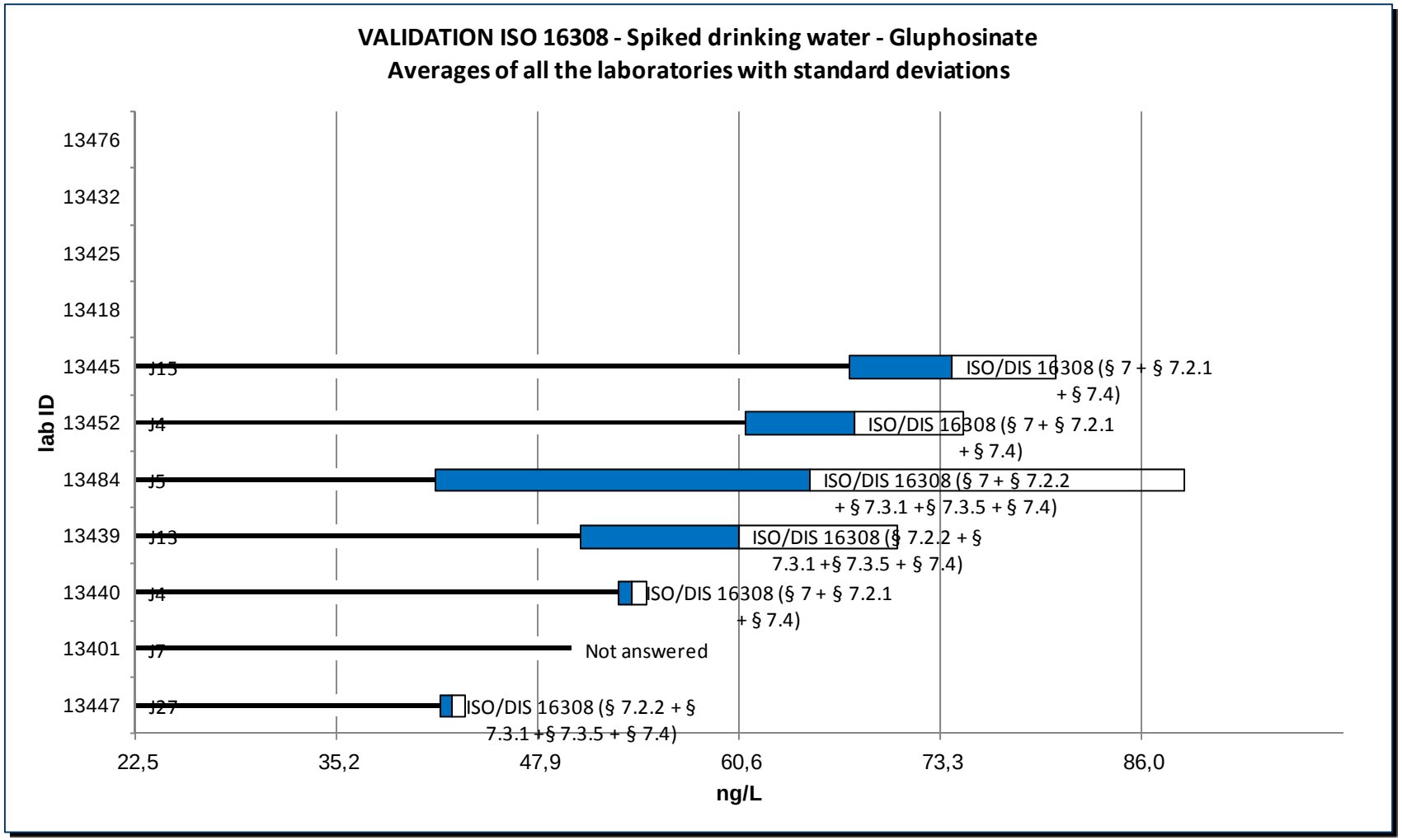
Example:



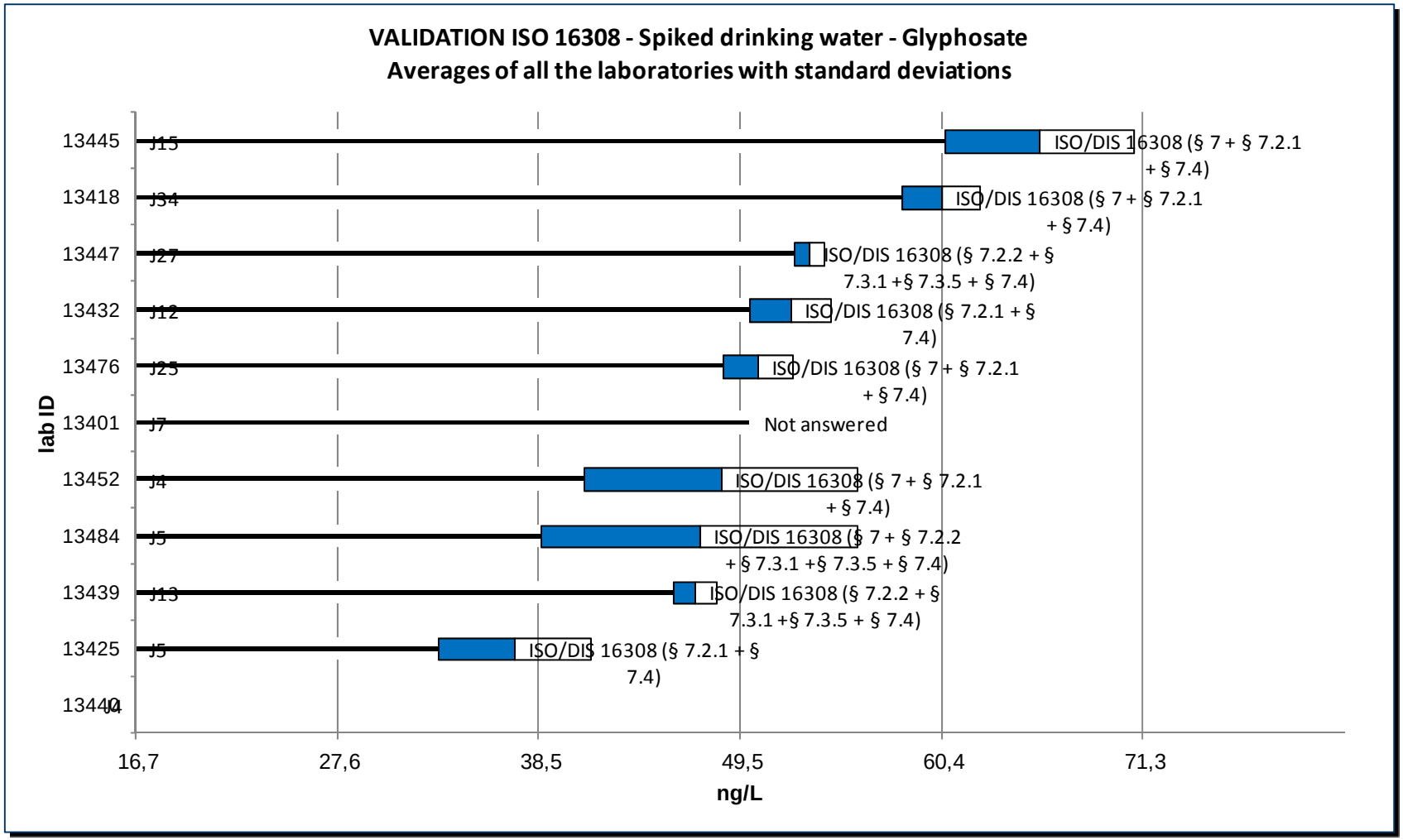
"spiked drinking water" -AMPA



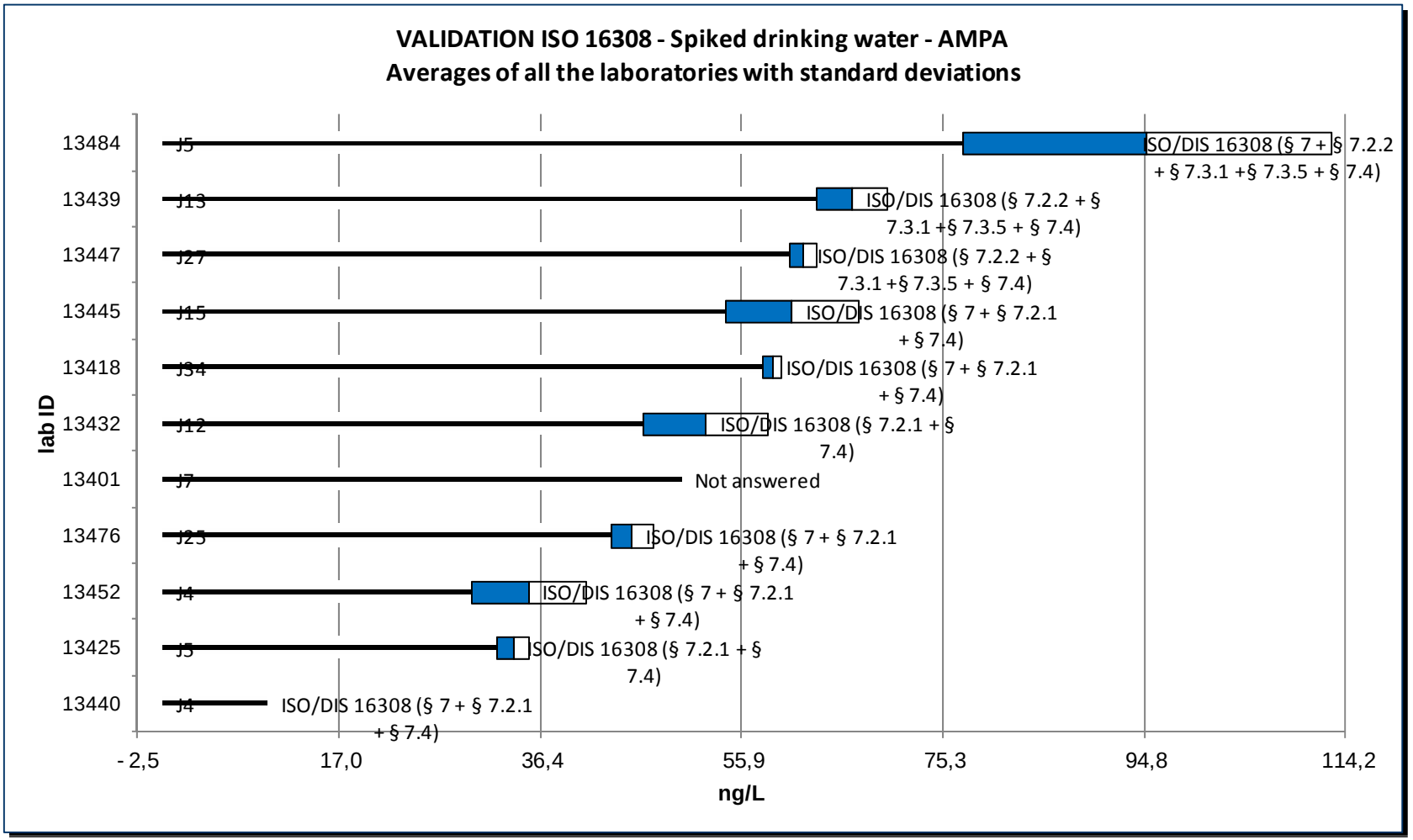
"spiked drinking water" - Gluphosinate



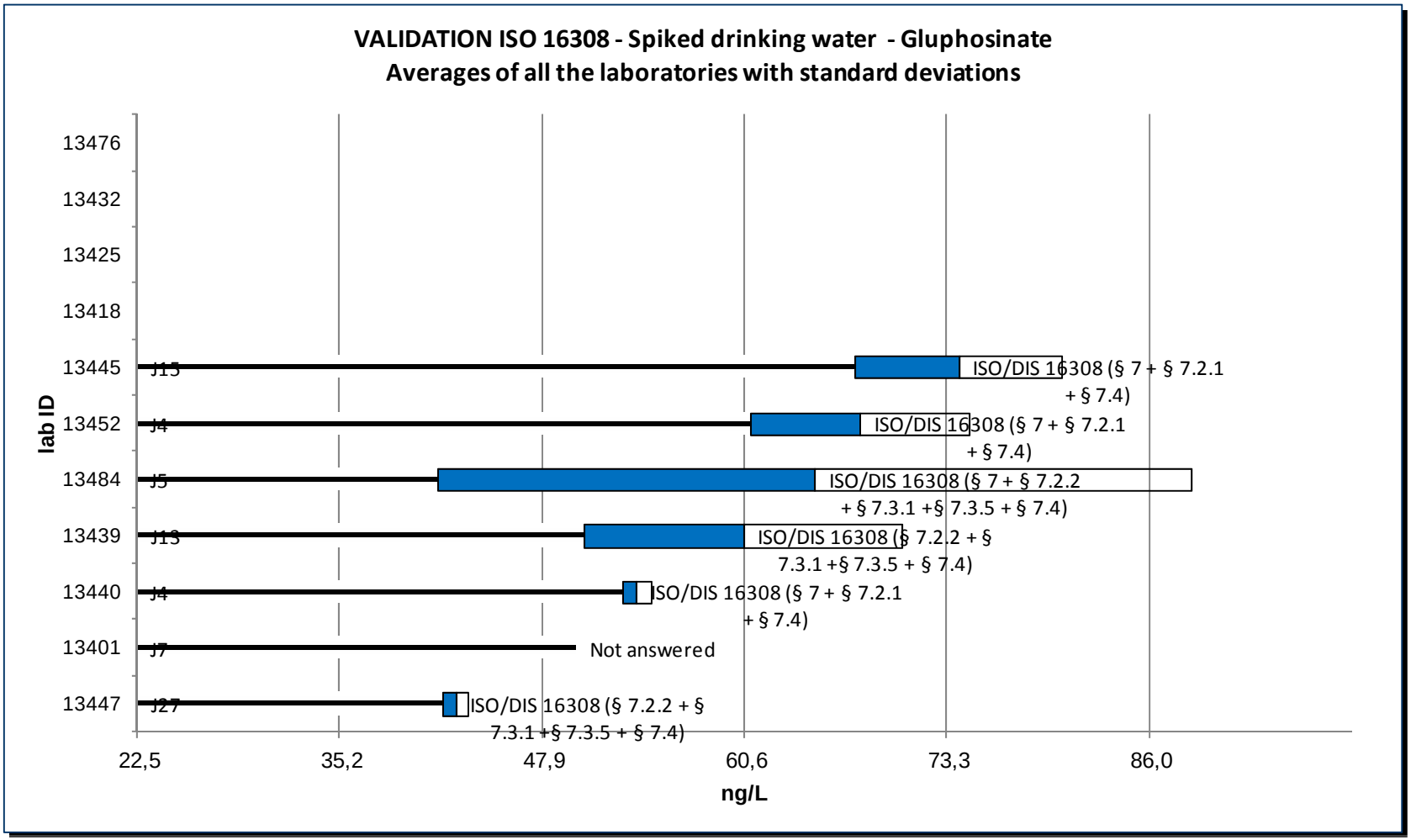
"spiked drinking water" -Glyphosate



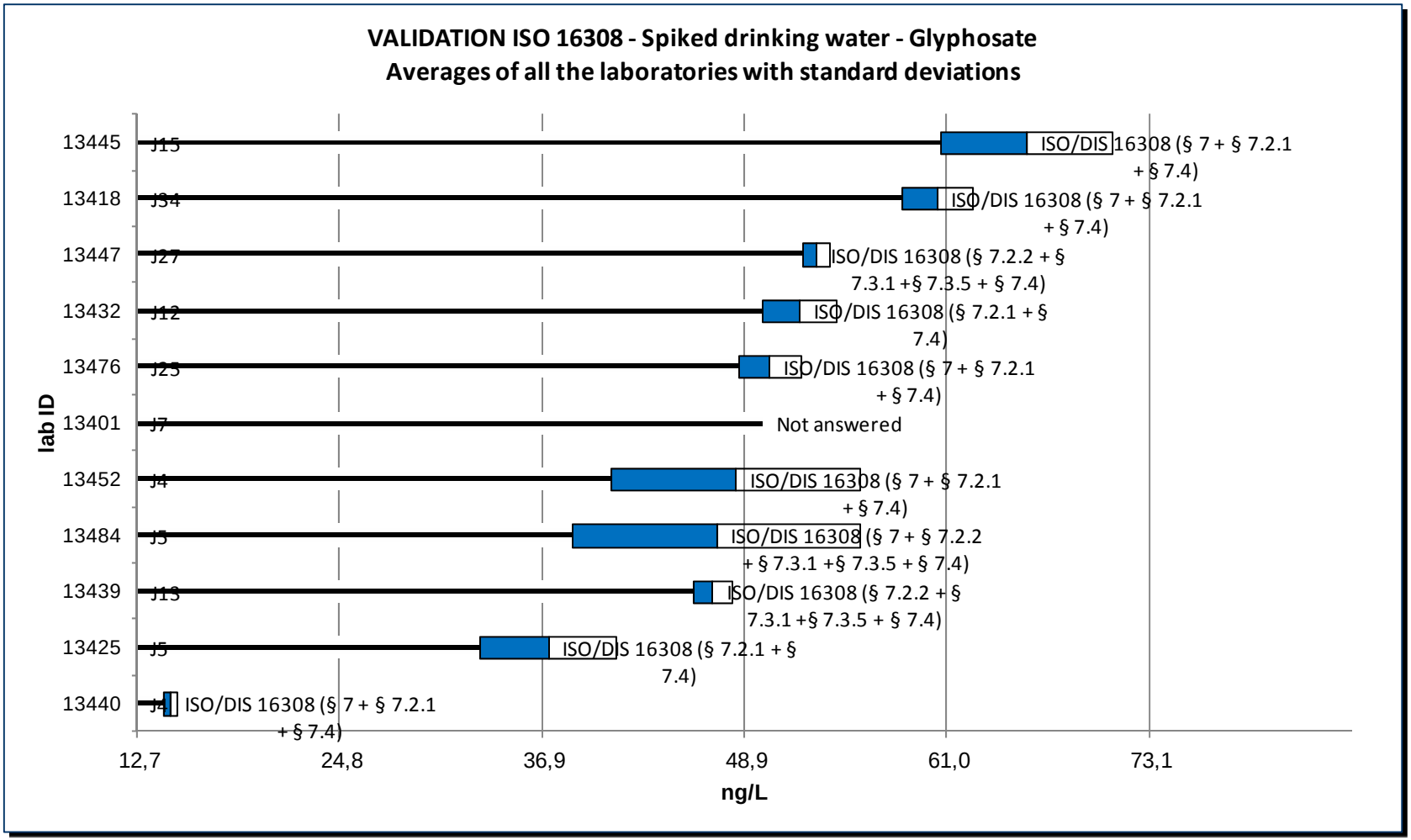
"spiked drinking water" - with exclusion (values of the participant 13432) -AMPA



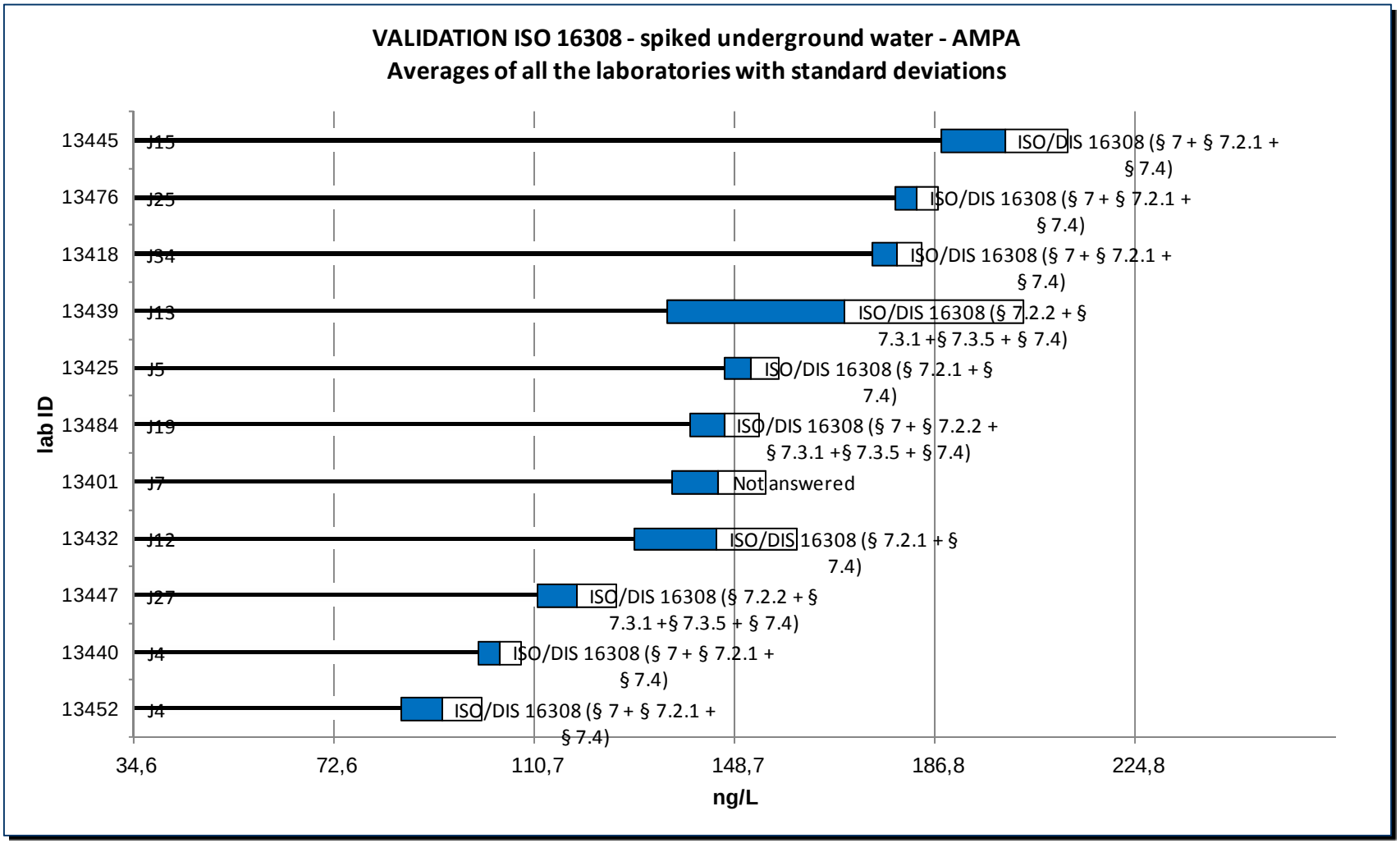
"spiked drinking water" - with exclusion (values of the participant 13432) - Gluphosinate



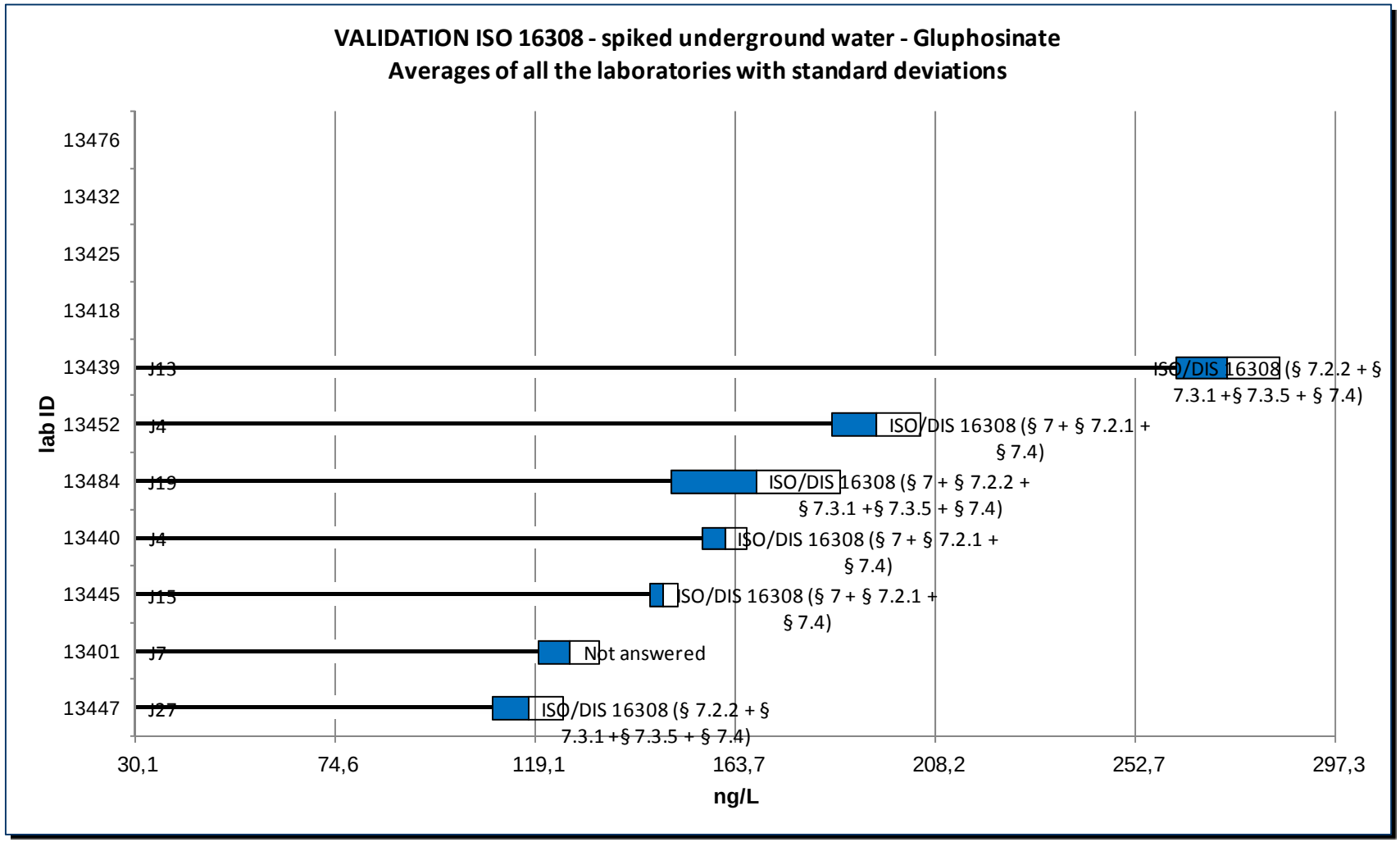
"spiked drinking water" - with exclusion (values of the participant 13432) - Glyphosate



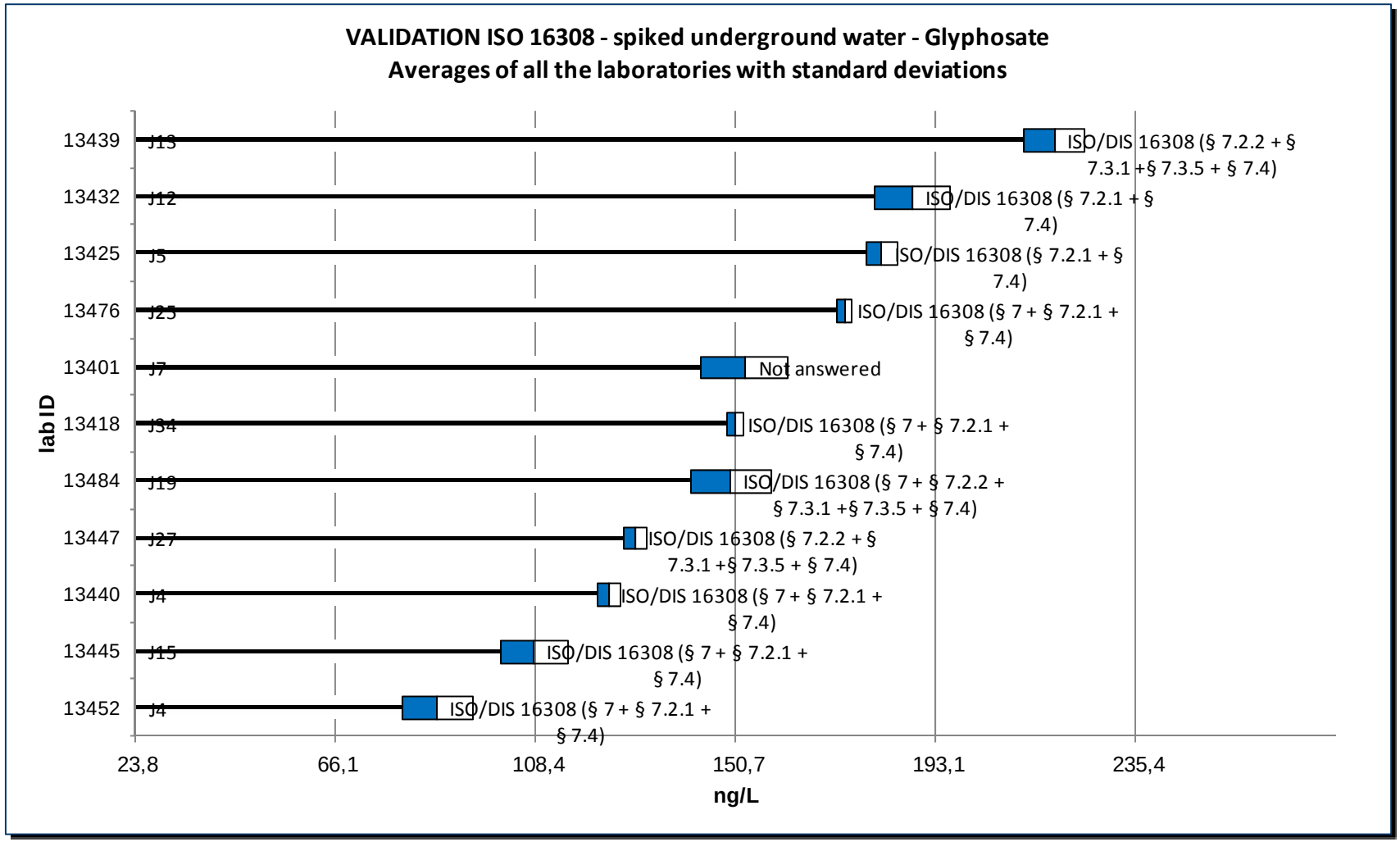
"spiked underground water" - AMPA



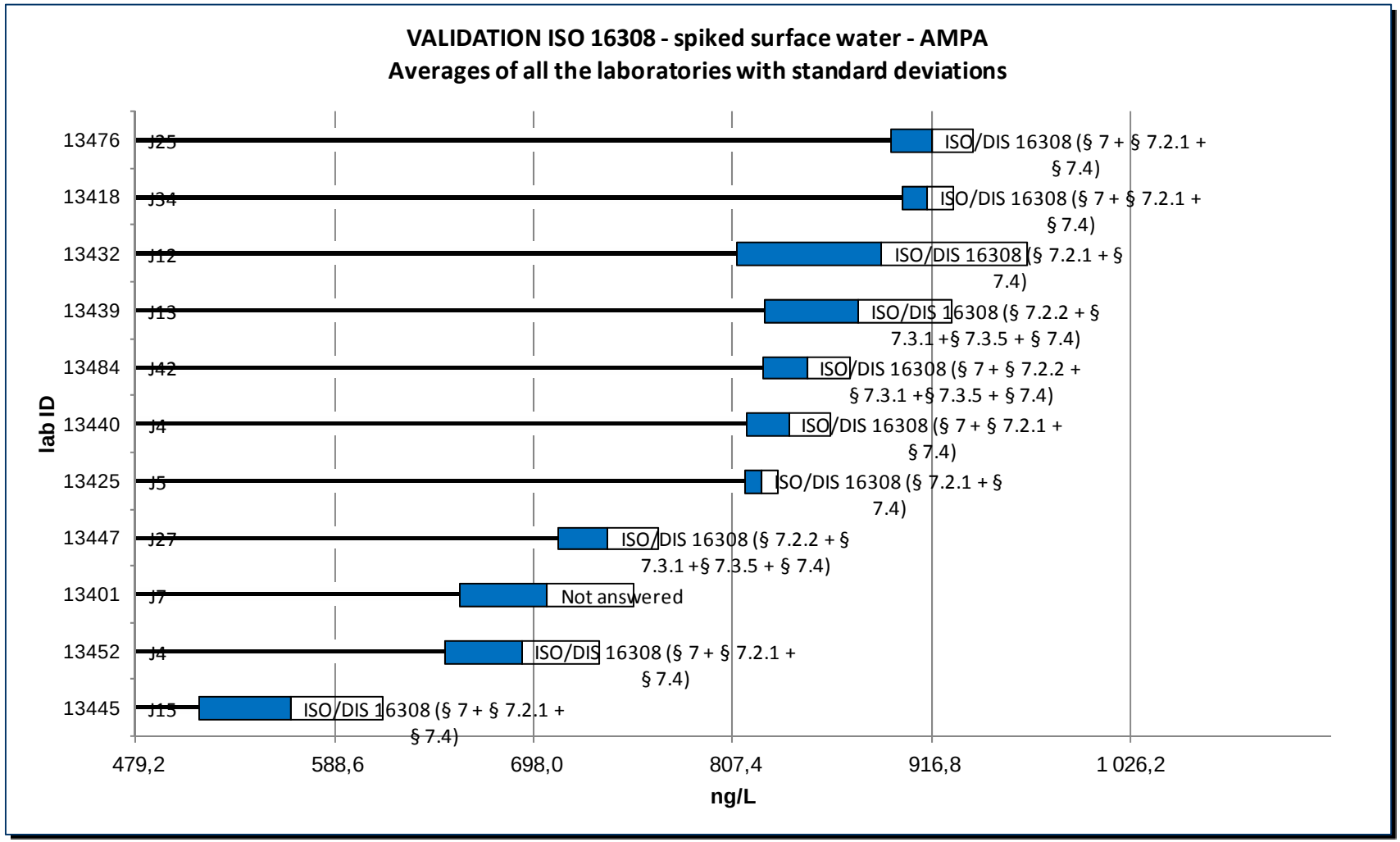
"spiked underground water" - Gluphosinate



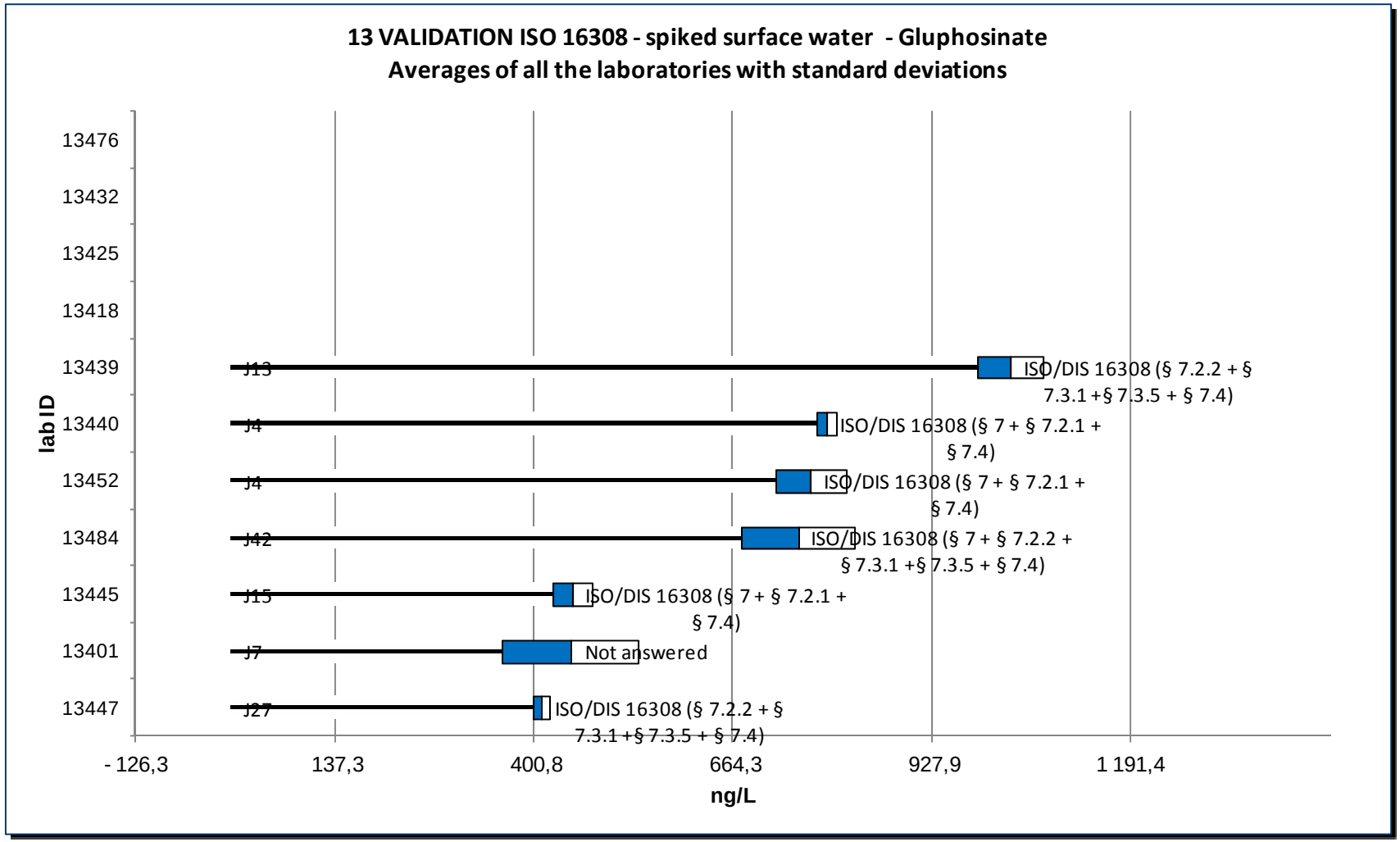
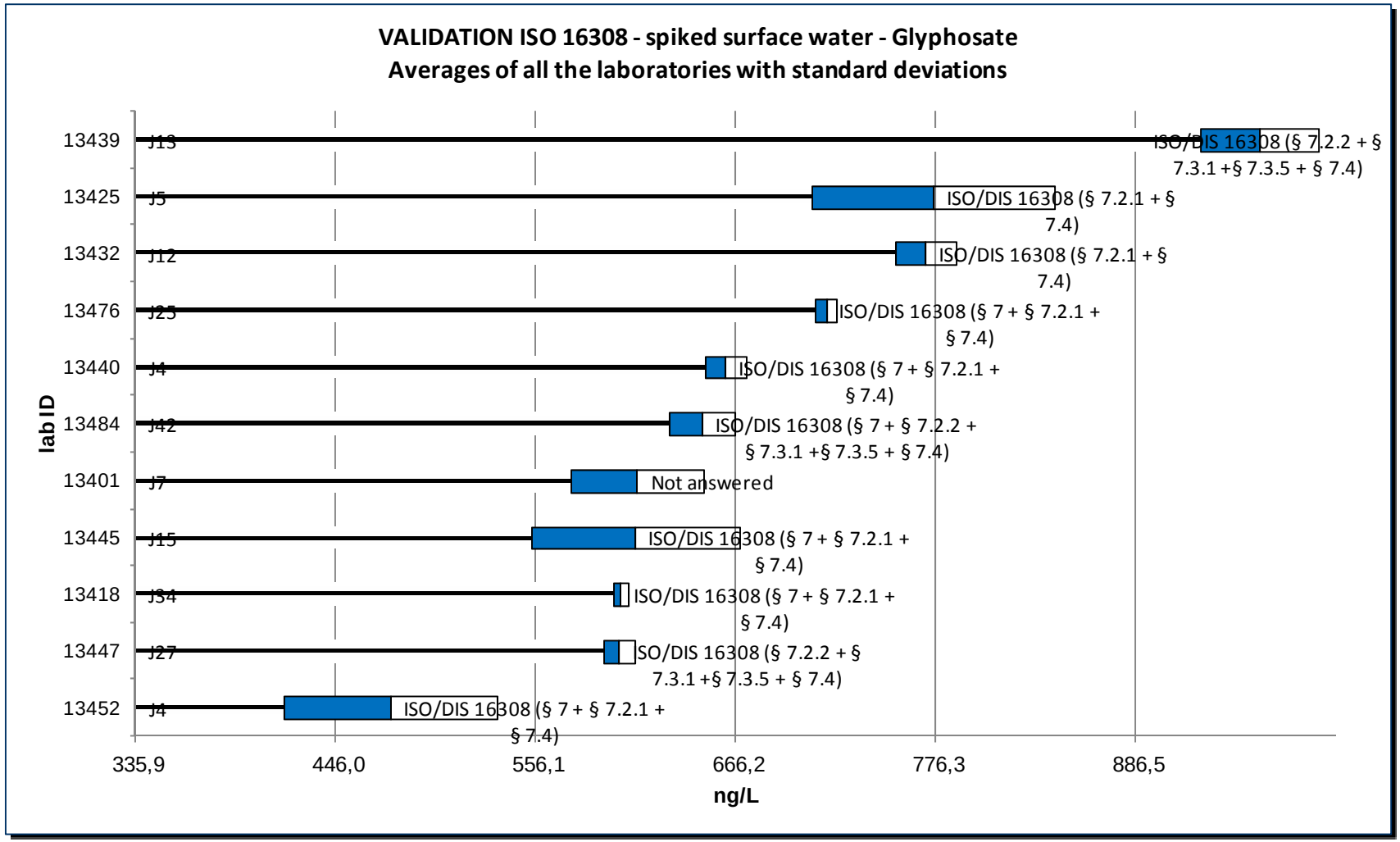
"spiked underground water" - Glyphosate



"spiked surface water" - AMPA



"spiked surface water" - Gluphosinate



"spiked surface water" - Glyphosate