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EMEP Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe

The twenty-first intercomparison of analytical methods within EMEP

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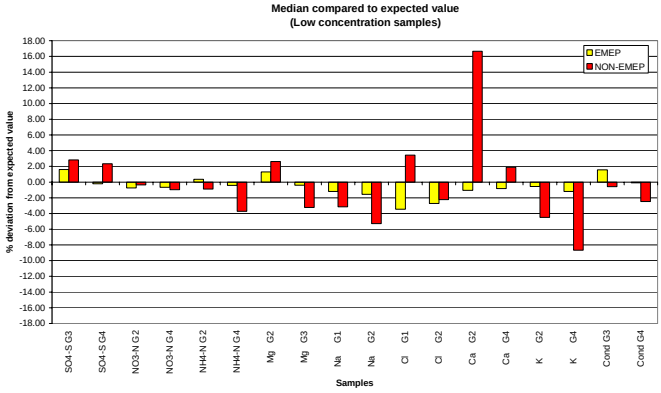

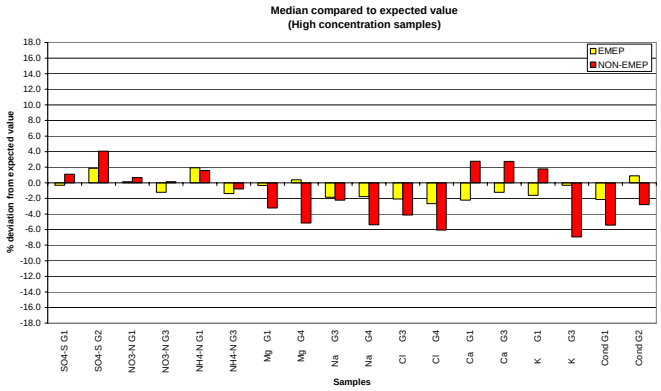

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1. Introduction

36 different laboratories in European countries are performing chemical analysis of air and precipitation samples within EMEP (Co-operative Programme for Monitoring and Evaluation of Long-range Transmission of Air Pollutants in Europe). Since the measurement programme is based on individual national networks, the participating laboratories apply different sampling and analytical methods. Most of the methods used are described in the manual for sampling and chemical analysis (EMEP, 1996).

In order to improve the data comparability and to get a picture of the different laboratories' performance, interlaboratory comparisons are organised by the Chemical Co-ordinating Centre (CCC) at the Norwegian Institute for Air Research (NILU). So far twenty-one intercomparisons have been arranged (Hanssen, 1988, 1990; Hanssen et al., 1983; Hanssen and Ladegård, 1984, 1985, 1987; Hanssen and Skjelmoen, 1992, 1994, 1995, 1996, 1997, 2001; Thrane, 1978, 1980a, 1980b, 1981, Uggerud et al., 2001, 2002, 2003).

Since 2000 the laboratory intercomparisons within EMEP have also been open for participation of laboratories from other networks.

This report gives the results of the twenty-first interlaboratory test.

2. Organisation of the intercomparison

The samples for the twenty-first intercomparison (see Table 2) were prepared and distributed to 68 laboratories in July 2003.

Most of the laboratories had returned their results to the CCC within one month after the deadline given as 15 October 2003. A total of 56 laboratories have returned their results. This includes 32 EMEP-laboratories.

The participating laboratories received the theoretical (expected) values by e-mail 26.11.2003. The laboratories were given the opportunity to compare their results with the expected ones, and give corrected values if obvious mistakes e.g. misprints had occurred. A few corrections were reported. In those cases the corrected values are used in this report. In accordance with the decision of the Steering Body of EMEP, the results are presented in such a way that the different laboratories are identified. Tables 3a and 3b give the names of the participating laboratories together with the numbers used when presenting the results in tables and figures.

Information received on the analytical methods used is given in Tables 4–7.

3. Data handling

The data reported from the participants are presented in Tables 9, 11, 13, 15, 17 and 19–30.

3.1 Data analysis

The reported values are presented in the tables in decreasing order together with the number of the laboratory. The expected (theoretical) value, the number of results, the arithmetic mean value, the median, the standard deviation and the relative standard deviation in percent are also given. After the first statistical run with all results included, the calculation was repeated with the outliers excluded. The outliers (unused) are defined as the results more than two standard deviations from the mean value in the first run.

The ratio between expected values (theoretical) to reported values, the ratio between measured to calculated conductivity and the ratio between equivalent concentrations of anions to equivalent concentrations cations, are presented in tables.

3.2 Bar plots

Bar-plots are used for the graphical presentation of the data. Figures 2–16 are showing the relative deviation from expected value for the different laboratories. There is one plot for each single sample.

Figure 17 gives median compared to expected value for the results reported by EMEP-laboratories and the other participating laboratories, respectively.

3.3 Youden plot

The Youden plot is a graphical method to analyse inter-laboratory data where the samples are ordered in pairs with similar concentrations. One plot is made for each pair of samples and gives results for all participating laboratories. The plots visualize both systematic and random errors.

The plot is draw as a scatter plot where each point represents a pair of concentrations for one laboratory. The expected values for the two samples are drawn as solid blue lines. The arithmetic average of the measured values excluding outliers are drawn as dotted lines. The solid lines divide the plot in four quadrants and a 45° reference line going through the intercept of the solid lines may be added.

If errors are due to random factors, the points will be evenly distributed around the mean value and situated in all four quadrants.

If systematic errors dominate, the results will be close to 45° reference line, and be situated in the upper right quadrant (overestimation) or lower left quadrant (underestimation).

Drawing a line from a given point perpendicular on the 45° reference line gives two line segments, one from the point to the intercept on the reference line (a),

and one continuing from the intercept to the point representing the expected values (b). The lengths of these line segments are measures of the random and systematic errors respectively.

Ellipses with radii corresponding to the data quality objectives (DQO, Table 1) are added in each plot. The data points are colour coded depending on the magnitude of errors as given in Table 1. Arrows indicate point outside the plot area.

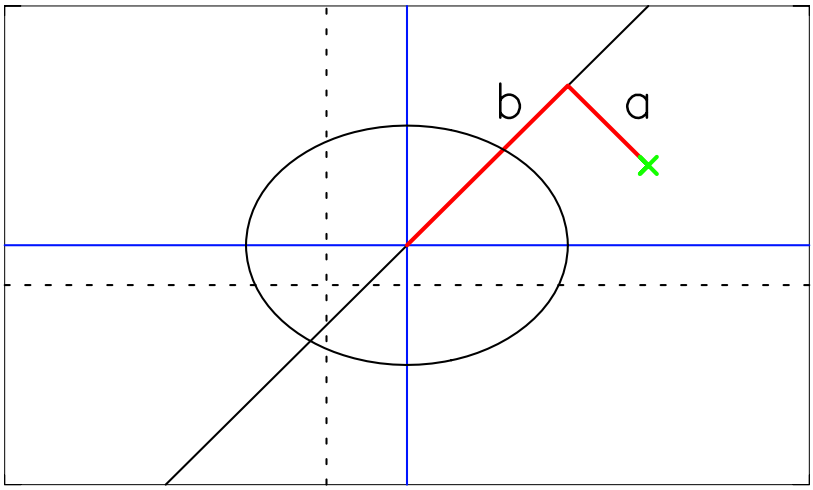


Figure 1: Youden plot showing concentrations for a pair of samples (green), expected values (blue lines), average of measured values (dotted lines) and random and systematic errors (red lines)

In Figures 18–33 the reported data are presented in Youden plots.

Table 1: Youden plot parameters.

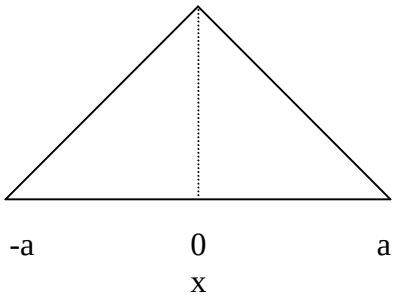
Radii	**Components**
10%	SO_2 in abs.sol, NO_2 in abs.sol.
20%	SO_2, HNO_3 and NH_3 in impregnated filter
Radii = DQO	**Components**
10% accuracy or better	SO_4^{2-}-S , NO_3^--N
15% accuracy or better	NH_4^+, Cl^-, Ca^{2+}, K^+, Mg^{2+}, Na^+ , cond
0.1 units	pH
Criteria	**Colour**
Within 0.5*DQO	Blue
Within DQO	Green
Within 2*DQO	Orange
> 2*DQO	Red

3.4 Estimating random and systematic errors from laboratory comparisons

Table 35 presents relative random and relative systematic errors obtained by the different laboratories in the analysis of each parameter in the precipitation samples. The calculation method and assumptions used are given in Chapter 3.4.1 and Chapter 3.4.2.

3.4.1 Estimating random errors

Systematic errors or bias in the laboratory analyses give a constant shift in the results from the expected ones at a particular concentration level. It is assumed that laboratories taking part in comparisons will obtain results near the expected ones when this bias is removed, and that the differences between expected and obtained results more often will be close to zero than not. A triangular distribution, based upon this assumption, can be used to quantify the random errors in the laboratory results (Eurachem, 2000).



The triangle distribution is symmetric with a baseline 2a. The height in the triangle will be 1/a when the triangle area equals 1. The standard uncertainty is given by

$$u(x) = \frac{a}{\sqrt{6}} \quad (1)$$

and more than 95 % of the data will be within ± 2·u(x). The distance from -a to a (i.e. 2a) is called the range. When applied on the laboratory comparison results, the range equals the distance between the largest and smallest of the four differences between expected and found concentrations. As long as the bias can be assumed to be constant for the samples in the comparison of a specific component, it cannot have an effect on the distance corresponding to 2a. The bias may be dependent upon the concentrations, but can be considered approximate constant for the concentrations used here in the comparison of the main components in precipitation, since the differences between the concentrations are small.

L and T represent the laboratories' and the expected concentrations respectively, and D is the difference. The difference for the lowest concentration is

$$D_1 = L_1 - T_1 \quad (2)$$

and the differences are D_1, D_2, D_3, D_4 in increasing order.

The range is $D_4 - D_1$ and the standard uncertainty for the differences u(D) becomes

$$u(D) = \frac{(D_4 - D_1)}{(2 \cdot \sqrt{6})}. \quad (3)$$

The average expected concentration T for the four samples is given by

$$T = \frac{(T_1 + T_2 + T_3 + T_4)}{4} \quad (4)$$

The relative standard uncertainty, RSD, for 4 samples is given by $\frac{u(D)}{T}$, or

$$RSD = \frac{2 \cdot (D_4 - D_1 \cdot 100)}{\sqrt{6} \cdot (T_1 + T_2 + T_3 + T_4)}\%, \quad (5)$$

and 95 per cent of the laboratory results in this comparison are expected to be within $\pm 2 \cdot RSD$.

If the data quality objectives (DQO) likewise are looked upon as 95 percentiles, then 95 per cent of the laboratory analytical results should not be more than 10 or 15 per cent from the correct values (10 per cent for S and N containing components and 15 per cent for other components).

Correspondingly, the values $2 \cdot RSD$ should therefore be less than 10 or 15 per cent in order to comply with the DQO.

3.4.2 Estimating systematic errors

An estimation of bias in single measurements requires a long data series, and four samples as we normally have in laboratory comparison, are merely able to give an indication of the bias or a very coarse estimate.

Coarse estimates have been performed here in the cases where the four samples had similar concentrations and where all four laboratory results were either higher or lower than the expected concentrations. The median of the differences D_i, as defined above, was taken as a measure of the bias, B, in these cases.

$$B = \text{median}[D_i] \quad (6)$$

A relative bias, RB, was also calculated based upon the average expected concentration T, as defined in (4).

$$RB = \frac{4 \cdot \text{median}[D_i] \cdot 100}{(T_1 + T_2 + T_3 + T_4)}\% \quad (7)$$

4. Results

4.1 Sulphur dioxide in absorbing solution (A-samples)

Four samples and one blank solution were distributed to the laboratories that use the hydrogen peroxide absorption solution method. The results are given in Table 9, Figures 2 and 18. For those laboratories that reported a blank value this has been subtracted from the reported results. The ratios of measured value to expected value are presented in Table 10.

The sulphate concentration in the sample solutions correspond to a SO_2 concentration in air of 2.70–6.79 µg S m^{-3}, when 70 ml absorbing solution and 3.6 m^3 sampling volume is used.

Only 5 laboratories have reported values for SO_2 in absorbing solution.

4.2 Sulphur dioxide and nitric acid on impregnated filter (B-samples)

Five impregnated filter samples (including one blank) for determination of sulphur dioxide were analysed by 19 laboratories. The value reported for the blank filter was subtracted from the other values before the data were used.

The amount of sulphur on the distributed filters corresponds to air concentrations between 0.80-2.56 µg S m^{-3} when 25 m^3 is sampled.

In addition to sulphur dioxide, nitric acid was added to the same impregnated filters for determination of HNO_3-N. The value reported for the blank filter was subtracted from the other values before using the data.

The amount of nitrogen on the distributed filters corresponds to air concentrations between 0.39 µg N m^{-3}–1.37 µg N m^{-3} when 25 m^3 sampling volume is used.

Sulphur dioxide results show prevalence of systematic versus random errors. The systematic error is most clearly for the low concentration samples.

Nitric acid on impregnated filters shows good agreement with expected values. Few outliers are reported and most results are within the 10% of expected value.

The results are presented in Tables 11 and 13 and Figures 3, 4, 19 and 20.

4.3 Nitrogen dioxide in absorbing solution (C-samples)

The four samples distributed were made to represent both absorption solutions and extracts from iodide-impregnated glass filters. The samples contain known amounts of sodium nitrite diluted in water. In order to assure sample stability and to give the laboratories the opportunity to use the matrix they use in their daily routine, the distributed samples were to be diluted 1:10. The results should be reported as the diluted concentrations.

The 10 times diluted samples correspond to air concentrations between 3.4-6.75 µg NO_2-N m^{-3}, when 70 ml absorbing solution and 1.4 m^3 are used. If

4 ml extraction solution and 0.7 m^3 sampling volume are used, the samples correspond to air concentrations between 0.39-0.77 µg NO_2-N m^{-3}.

Nitrogen dioxide in absorbing solution shows good agreement with expected values. Few outliers are reported and most results are within the 10% of expected value. The Youden plots show prevalence of systematic error versus random error.

The results are presented in Table 14 and Figures 5 and 21.

4.4 Ammonia on impregnated filters (J-samples)

For the second time impregnated filters for determination of ammonia were distributed. Six impregnated filters inclusive two unidentified blank filters were sent to 21 laboratories. 19 laboratories have reported their analytical results. The two blank values reported by each laboratory were averaged and subtracted from the other values reported before the data were used. The results are shown in Table 17 and Figures 6 and 22.

The amount of nitrogen on the filters correspond to air concentrations between 0.30-1.52 µg N m^{-3}, if 25 m^3 sampling volume is used.

Several reported values are more than 20% away from expected value. Youden plot shows that for the low concentration filters a considerable number of random errors are present. For the high concentration filters several results are biased low.

4.5 Precipitation (G-samples)

Four precipitation samples were distributed and 2748 single results from 56 laboratories were reported. 109 results were identified as outliers. This is ~4% of the data, which is about the same as obtained last year. It should be noted that 47% of the outliers are caused by only four laboratories, which report more than 10 outliers each. The results are presented in Tables 19–30 and Figures 7–16 and 23–33.

4.5.1 Conductivity and ion balance

In EMEP, conductivity measurements are mainly used for quality control reasons. When all the main ions in the precipitation have been measured, conductivity values are compared with values calculated from the reported results. Table 31 gives the ratios of the measured to the calculated values.

Low concentration ions do not contribute much to the sum of ionic conductivities. By looking at the ratio of measured to calculated conductivity, errors in determination of low concentration ions may not be revealed. To include low concentration ions in the quality control, ion balance control must be used. This ratio should be used as a tool in the quality control system for those laboratories that measure all main components. The ratios of equivalent concentrations of anions versus equivalent concentrations of cations are shown in Table 32.

The Youden plot of conductivity shows manly systematic error, which may be due to bad calibration of the instrument.

5. Conclusions

A total of 56 laboratories participated in the twenty-first intercomparison. 32 of these laboratories are within the EMEP network.

For all the samples analysed, the deviations from theoretical values are calculated. Figure 16 shows the median values compared to the expected values for all the parameters. For the EMEP laboratories the median deviations for both low- and high concentration samples are less than 4%. This is the same as obtained in the last intercomparison. Median deviations except for Ca and K are for other participants less than 7%, which is the same as in earlier intercomparisons. Determination of low concentrations of Ca and K seems to have been more troublesome and median deviations including Ca and K are less than 16%.

As in earlier intercomparisons, outliers are defined as values that deviate more than two standard deviations from the mean value. Outliers occur for all samples and almost all parameters. Out of a total of 2748 single results, 122 are defined as outliers. This is 5% of the reported data, which is a slight increase compared to earlier intercomparisons.

In Table 33 the ratio of the median values to the theoretical values for all the parameters is presented. As can be seen from this table, all parameters have median values that are in good agreement with the theoretical values.

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Appendix 1

Tables

Table 2: Samples distributed for the nineteenth interlaboratory test.

A.	5 synthetic samples for determination of SO_2, consisting of 0.3% H_2O_2 absorbing solution and containing different concentrations of sulphuric acid. One of the samples was an unidentified blank.
B.	6 KOH-impregnated Whatman 40 filters, comprising 1 blank and 8 filters to which different amounts of sulphuric acid have been added.
C.	4 synthetic samples for determination of NO_2 consisting of sodium nitrite diluted in water.
J.	6 Whatman 40 filters impregnated with 3% oxalic acid, comprising 2 blank and 4 filters to which different amounts of ammonium salt solution have been added.
G.	4 synthetic precipitation samples, containing SO_4^{2-}, NO_3^-, NH_4^+, H^+, Na^+, Mg^{2+} and Cl^-, and Ca^{2+} and K^+.

Table 3a: EMEP laboratories participating in the nineteenth laboratory intercomparison. The numbers in front of the names are used in tables and figures.

Austria	(1)	Umweltbundesamt Zweigstelle Sud, Klagenfurt
Canada	(26)	Meteorological Service of Canada, Toronto
Croatia	(35)	Meteorological and Hydrological Service of Croatia
Czech Republic	(3)	Czech Hydrometeorological Institute, Praha
Denmark	(4)	National Environmental Research Institute. Air Pollution Laboratory
Estonia	(38)	Estonian Environmental Research Centre, Tallinn
Finland	(5)	Finnish Meteorological Institute. Air Quality Department
France	(6)	Laboratories Wolff
Germany	(7)	IfE Leipzig GmbH, Umweltlabor
Germany	(8)	Umweltbundesamt, Messtelle Schauinsland
Hungary	(10)	Institute for Atmospheric Physics
Iceland	(11)	Idntæknistofnun Islands (Technological Inst. of Iceland)
Ireland	(12)	Met Eirann, Dublin
Italy	(13)	C.N.R. Istituto Inquinamento Atmosferico
Italy	(30)	Joint Research centre, Ispra
Latvia	(33)	Air Pollution Observation Laboratory
Lithuania	(32)	Atmospheric Pollution Research Laboratory, Institute of Physics, Vilnius
Netherlands	(14)	National Institute of Public Health and Environmental Protection (RIVM)
Norway	(15)	Norwegian Institute for Air Research (NILU)
Macedonia	(40)	Hydrometeorological Institute, Skopje
Poland	(16)	Institute of Meteorology and Water Management, Warsaw
Poland	(39)	Environmental Monitoring Laboratory, Institute of Environmental Protection
Romania	(18)	Research and Engineering Institute for Environment
Russian Federation	(22)	Institute of Global Climate and Ecology
Serbia and Montenegro	(24)	Rep. Hydrometeorological Institute of Serbia
Slovakia	(31)	Slovak Hydrometeorological Institute
Slovenia	(36)	Hydrometeorological Institute of Slovenia
Spain	(19)	Centro Nacional de Sanidad Ambiental
Sweden	(20)	Swedish Environmental Research Institute (IVL), Gothenburg
Switzerland	(21)	Swiss Federal Laboratories for Materials Testing (EMPA)
Turkey	(34)	Refik Saydam Institute, Ankara
United Kingdom	(23)	AEA Technology, National Environmental Technology Centre
United States of America	(27)	Illinois State Water Survey

Table 3b: Participating laboratories outside the EMEP network.

Germany	(104)	Hessige Landwirtschafliche
Sweden	(106)	IVL Svenska Miljöinstitutet AB, Aneboda
Finland	(107)	The Finnish Forest Institute
Germany	(109)	Institut für Bondenkunde und Waldernährung der Universität, Göttingen
Germany	(110)	Thüringer Landesanstalt für Landwirtschaft (TTL), Jena
Finland	(111)	Finnish Forest Research Institute, Vantaa Research Centre
Germany	(112)	Niedersächsische Forstliche Versuchsanstalt (NVF)
Germany	(113)	Landesforstanstalt Eberswalde, abt. Waldökologie
Italy	(114)	C.N.R. Istituto Italiano di Idrobiologia
Germany	(115)	Bayerische Landesanstalt f. Wald- und Forstwirtshaft
Switzerland	(116)	Institute for Applied Plant Biology
Germany	(117)	Sächsische Landesanstalt für Forsten, Graupa
Germany	(118)	Forstliche Versuchs-und Forschungsansta
Germany	(120)	Landwirtschaftliche Untersuchungs- und Forschungsanstalt (LUFA)
Germany	(121)	Landesamt für Natur und Umwelt
Italy	(126)	APPA Laboratorio Biologico Provinciale
Italy	(130)	Universita degli Studi Siena
China	(131)	Chongqing Institute of Environmental Science and Monitoring
Belarus	(133)	Institute for Problems of Natural Resources Use and Ecology
China	(135)	Hunan Research Institute of Environmental Protection Science
China	(136)	Guangzhou Research Institute of Environmental Protection
China	(138)	Guizhou Research Institute of Environmental Protection Science, Guiyang
Italy	(140)	C.N.R. Istituto di Ricerca sulle Acque

Table 4: Analytical methods used at the participating laboratories for the determination of sulphur dioxide in absorbing solution (A).

Method	Laboratory
1. Ion chromatography	6, 15, 17, 19, 21, 23

Table 5: Analytical methods used at the participating laboratories for the determination of sulphur dioxide on impregnated filters (B) .

Method	Laboratory
1. Spectrophotometry	16
2. Ion chromatography	3, 4, 5, 8, 11, 12, 13, 15, 20, 22, 31,32, 33, 34, 36, 38, 116, 131, 135, 138
3. Capillary Ion Analysis	39

Table 6: Analytical methods used at the participating laboratories for determination of nitric acid on impregnated filters (B).

Method	Laboratory
1. Reduction to nitrite	16
2. Ion chromatography	3, 4, 5, 8, 11, 13, 15, 20, 22, 31,32, 33, 34, 36, 116,131, 135, 138
3. Capillary Ion Analysis	39

Table 7: Analytical method for determination of ammonia on impregnated filters (J).

Method	Laboratory
1. Spectrophotometry	3, 4, 8, 10, 19,32, 33,34 39, 116,
2. FIA	11
3 Ion chromatography	5, 13,15, 20, 36, 131, 135, 138

Table 8: Analytical method used for NO_2 in absorbing solution (C).

Method	Laboratory
1. Spectrophotometry	3, 4, 8, 12, 15, 16, 19, 20, 22, 23, 31,32, 33, 34, 35, 38, 39, 131, 135
Ion chromatography	36

Table 9: Analytical results for sulphur dioxide in absorbing solution.

SO2 in absorbing solution
Sample no.: 1
Theoretical value: 0.301
Unit: µg S / ml

Run 1:

Number of laboratories:	5
Arithmetic mean value:	0.272
Median:	0.291
Standard deviation	0.055
Rel. st. deviation (%)	20.268

Run 2:

Number of laboratories:	5
Arithmetic mean value:	0.272
Median:	0.291
Standard deviation	0.055
Rel. st. deviation (%)	20.268

Results in decreasing order:

23	0.319	15	0.264
21	0.304	19	0.180
6	0.291		

SO2 in absorbing solution
Sample no.: 2
Theoretical value: 0.152
Unit: µg S / ml

Run 1:

Number of laboratories:	5
Arithmetic mean value:	0.139
Median:	0.141
Standard deviation	0.021
Rel. st. deviation (%)	15.150

Run 2:

Number of laboratories:	5
Arithmetic mean value:	0.139
Median:	0.141
Standard deviation	0.021
Rel. st. deviation (%)	15.150

Results in decreasing order:

23	0.162	15	0.125
21	0.155	19	0.111
6	0.141		

SO2 in absorbing solution
Sample no.: 3
Theoretical value: 0.341
Unit: µg S / ml

Run 1:

Number of laboratories:	5
Arithmetic mean value:	0.314
Median:	0.330
Standard deviation	0.045
Rel. st. deviation (%)	14.255

Run 2:

Number of laboratories:	5
Arithmetic mean value:	0.314
Median:	0.330
Standard deviation	0.045
Rel. st. deviation (%)	14.255

Results in decreasing order:

23	0.354	15	0.304
21	0.341	19	0.241
6	0.330		

SO2 in absorbing solution
Sample no.: 4
Theoretical value: 0.160
Unit: µg S / ml

Run 1:

Number of laboratories:	5
Arithmetic mean value:	0.150
Median:	0.152
Standard deviation	0.015
Rel. st. deviation (%)	9.991

Run 2:

Number of laboratories:	5
Arithmetic mean value:	0.150
Median:	0.152
Standard deviation	0.015
Rel. st. deviation (%)	9.991

Results in decreasing order:

23	0.168	19	0.136
21	0.161	15	0.134
6	0.152		

Table 10: The ratios of the theoretical values and the results found by the laboratories in the determination of sulphur dioxide in absorbing solutions.

	Measured value / Expected				
	Sample No				
Lab. No	A1	A2	A3	A5	Average
6	0.97	0.93	0.97	0.95	0.95
15	0.88	0.82	0.89	0.84	0.86
19	0.60	0.73	0.71	0.85	0.72
21	1.01	1.02	1.00	1.00	1.01
23	1.06	1.06	1.04	1.05	1.05

Table 11: Analytical results for sulphur dioxide in impregnated filter.

SO2-S on impregnated filter
Sample no.: B1
Theoretical value: 24.048
Unit: µg S / FIL

Run 1:
Number of laboratories: 20
Arithmetic mean value: 23.279
Median: 23.087
Standard deviation 4.021
Rel. st. deviation (%) 17.272

Run 2:
Number of laboratories: 19
Arithmetic mean value: 22.828
Median: 23.003
Standard deviation 3.573
Rel. st. deviation (%) 15.653

Results in decreasing order:

15	31.850 (*)	31	23.003
138	28.699	116	22.900
131	27.110	34	22.619
135	26.870	39	22.000
4	26.500	3	21.390
32	26.220	20	20.980
5	24.910	22	19.100
33	23.721	11	18.860
8	23.633	38	16.800
16	23.170	36	15.240

SO2-S on impregnated filter
Sample no.: B3
Theoretical value: 18.036
Unit: µg S / FIL

Run 1:
Number of laboratories: 20
Arithmetic mean value: 16.473
Median: 16.950
Standard deviation 3.794
Rel. st. deviation (%) 23.034

Run 2:
Number of laboratories: 19
Arithmetic mean value: 16.922
Median: 17.200
Standard deviation 3.307
Rel. st. deviation (%) 19.545

Results in decreasing order:

138	21.958	116	16.700
32	21.930	31	16.547
135	20.120	16	15.900
4	19.900	34	15.536
15	19.350	3	14.990
131	19.060	20	14.930
5	18.350	11	13.370
8	17.691	22	11.800
33	17.281	38	8.900
39	17.200	36	7.940 (*)

SO2-S on impregnated filter
Sample no.: B4
Theoretical value: 56.112
Unit: µg S / FIL

Run 1:
Number of laboratories: 20
Arithmetic mean value: 53.843
Median: 54.138
Standard deviation 4.795
Rel. st. deviation (%) 8.905

Run 2:
Number of laboratories: 19
Arithmetic mean value: 54.387
Median: 54.200
Standard deviation 4.244
Rel. st. deviation (%) 7.804

Results in decreasing order:

131	60.540	8	54.076
32	60.290	16	52.980
15	59.850	22	52.200
135	59.340	33	51.838
138	58.939	20	50.590
4	57.800	3	50.260
31	56.214	116	48.900
5	55.230	36	48.840
34	54.303	11	46.970
39	54.200	38	43.500 (*)

SO2-S on impregnated filter
Sample no.: B5
Theoretical value: 40.080
Unit: µg S / FIL

Run 1:
Number of laboratories: 19
Arithmetic mean value: 38.591
Median: 38.644
Standard deviation 3.905
Rel. st. deviation (%) 10.119

Run 2:
Number of laboratories: 19
Arithmetic mean value: 38.591
Median: 38.644
Standard deviation 3.905
Rel. st. deviation (%) 10.119

Results in decreasing order:

131	45.070	39	38.600
138	43.885	5	38.470
135	43.320	3	37.020
4	42.500	16	36.960
15	42.350	20	36.110
38	41.300	22	35.000
31	39.218	116	33.200
8	39.121	11	32.600
34	38.729	36	31.140
33	38.644		

Table 12: The ratios of the theoretical values and the results found by the laboratories in the determination of sulphur dioxide on impregnated filters. The reported results are corrected for blank value (B1).

	Measured / Expected value				
	Sample No				
Lab. No	B1	B3	B4	B5	Average
3	0.89	0.83	0.90	0.92	0.88
4	1.10	1.10	1.03	1.06	1.06
5	1.04	1.02	0.98	0.96	0.99
8	0.98	0.98	0.96	0.98	0.97
11	0.78	0.74	0.84	0.81	0.80
12	0.00	0.00	0.00	0.00	0.00
13	0.00	0.00	0.00	0.00	0.00
15	1.32	1.07	1.07	1.06	1.07
16	0.96	0.88	0.94	0.92	0.92
19	0.00	0.00	0.00	0.00	0.00
20	0.87	0.83	0.90	0.90	0.88
22	0.79	0.65	0.93	0.87	0.82
31	0.96	0.92	1.00	0.98	0.97
32	1.09	1.22	1.07		1.15
33	0.99	0.96	0.92	0.96	0.95
34	0.94	0.86	0.97	0.97	0.93
36	0.63	0.44	0.87	0.78	0.70
38	0.70	0.49	0.78	1.03	0.77
39	0.91	0.95	0.97	0.96	0.96
116	0.95	0.93	0.87	0.83	0.88
131	1.13	1.06	1.08	1.12	1.09
135	1.12	1.12	1.06	1.08	1.08

Table 13: Analytical results for nitric acid on impregnated filter.

HNO3-N on impregnated filter
Sample no.: B1
Theoretical value: 11.452
Unit: µg N / FIL

Run 1:
Number of laboratories: 18
Arithmetic mean value: 11.221
Median: 11.119
Standard deviation 0.582
Rel. st. deviation (%) 5.187

Run 2:
Number of laboratories: 17
Arithmetic mean value: 11.151
Median: 11.060
Standard deviation 0.515
Rel. st. deviation (%) 4.615

Results in decreasing order:

32	12.420 (*)	16	11.060
15	12.200	34	11.014
135	12.110	3	10.950
39	11.600	36	10.900
5	11.590	31	10.887
8	11.431	33	10.713
131	11.260	116	10.600
4	11.200	22	10.500
138	11.178	20	10.370

HNO3-N on impregnated filter
Sample no.: B3
Theoretical value: 32.720
Unit: µg N / FIL

Run 1:
Number of laboratories: 19
Arithmetic mean value: 32.708
Median: 32.144
Standard deviation 3.035
Rel. st. deviation (%) 9.279

Run 2:
Number of laboratories: 18
Arithmetic mean value: 32.130
Median: 32.122
Standard deviation 1.739
Rel. st. deviation (%) 5.412

Results in decreasing order:

138	43.118 (*)	116	32.100
22	35.300	15	32.100
39	34.300	8	31.987
135	34.120	33	31.694
32	33.150	34	31.500
4	33.100	16	31.320
131	32.600	3	31.010
5	32.600	20	29.600
36	32.200	11	27.510
31	32.144		

HNO3-N on impregnated filter
Sample no.: B4
Theoretical value: 39.264
Unit: µg N / FIL

Run 1:
Number of laboratories: 19
Arithmetic mean value: 38.493
Median: 39.000
Standard deviation 2.413
Rel. st. deviation (%) 6.269

Run 2:
Number of laboratories: 18
Arithmetic mean value: 38.891
Median: 39.050
Standard deviation 1.726
Rel. st. deviation (%) 4.438

Results in decreasing order:

138	41.505	5	38.800
131	41.420	8	38.584
135	41.010	16	38.220
39	40.200	34	38.096
31	40.052	3	37.080
32	39.930	116	36.300
4	39.500	20	36.010
36	39.300	33	35.938
22	39.100	11	31.330 (*)
15	39.000		

HNO3-N on impregnated filter
Sample no.: B5
Theoretical value: 14.724
Unit: µg N / FIL

Run 1:
Number of laboratories: 18
Arithmetic mean value: 14.193
Median: 14.312
Standard deviation 1.578
Rel. st. deviation (%) 11.119

Run 2:
Number of laboratories: 17
Arithmetic mean value: 14.520
Median: 14.323
Standard deviation 0.774
Rel. st. deviation (%) 5.328

Results in decreasing order:

138	15.995	36	14.300
135	15.590	16	14.220
39	15.300	3	14.210
8	15.271	31	14.008
131	15.230	20	13.800
15	14.900	33	13.511
5	14.780	22	13.500
4	14.500	116	13.400
34	14.323	11	8.630 (*)

Table 14: The ratios of the theoretical values and the results found by the laboratories in the determination of nitric acid on impregnated filters. The reported results are corrected for blank value (B1).

	Measured / Expected value				
	Sample No				
Lab.No	B1	B3	B4	B5	Average
3	0.96	0.95	0.94	0.97	0.95
4	0.98	1.01	1.01	0.98	1.00
5	1.01	1.00	0.99	1.00	1.00
8	1.00	0.98	0.98	1.04	1.00
11	0.00	0.84	0.80	0.59	0.56
15	1.07	0.98	0.99	1.01	1.01
16	0.97	0.96	0.97	0.97	0.97
20	0.91	0.90	0.92	0.94	0.92
22	0.92	1.08	1.00	0.92	0.98
31	0.95	0.98	1.02	0.95	0.98
32	1.08	1.01	1.02	0.00	0.78
33	0.94	0.97	0.92	0.92	0.93
34	0.96	0.96	0.97	0.97	0.97
36	0.95	0.98	1.00	0.97	0.98
39	1.01	1.05	1.02	1.04	1.03
116	0.93	0.98	0.92	0.91	0.94
131	0.98	1.00	1.05	1.03	1.02
135	1.06	1.04	1.04	1.06	1.05

Table 15: Analytical results for nitrogen dioxide in absorbing solution.

NO2-N in absorbing solution
Sample no.: C1
Theoretical value: 0.102
Unit: µg N / ml

Run 1:

Number of laboratories:	20
Arithmetic mean value:	0.101
Median:	0.102
Standard deviation	0.005
Rel. st. deviation (%)	5.234

Run 2:

Number of laboratories:	19
Arithmetic mean value:	0.102
Median:	0.102
Standard deviation	0.005
Rel. st. deviation (%)	4.517

Results in decreasing order:

32	0.109	22	0.101
33	0.109	20	0.101
34	0.107	38	0.100
135	0.106	131	0.100
39	0.105	12	0.100
4	0.104	35	0.098
8	0.102	23	0.097
36	0.102	19	0.094
3	0.102	31	0.092
16	0.102	15	0.089 (*)

NO2-N in absorbing solution
Sample no.: C2
Theoretical value: 0.074
Unit: µg N / ml

Run 1:

Number of laboratories:	20
Arithmetic mean value:	0.072
Median:	0.073
Standard deviation	0.008
Rel. st. deviation (%)	10.880

Run 2:

Number of laboratories:	19
Arithmetic mean value:	0.074
Median:	0.074
Standard deviation	0.005
Rel. st. deviation (%)	6.324

Results in decreasing order:

33	0.083	34	0.073
39	0.078	38	0.073
32	0.078	8	0.072
20	0.077	35	0.071
36	0.077	31	0.070
131	0.077	23	0.070
4	0.076	19	0.068
16	0.076	12	0.067
135	0.076	15	0.064
22	0.074	3	0.045 (*)

NO2-N in absorbing solution
Sample no.: C3
Theoretical value: 0.125
Unit: µg N / ml

Run 1:

Number of laboratories:	20
Arithmetic mean value:	0.124
Median:	0.124
Standard deviation	0.007
Rel. st. deviation (%)	5.424

Run 2:

Number of laboratories:	20
Arithmetic mean value:	0.124
Median:	0.124
Standard deviation	0.007
Rel. st. deviation (%)	5.424

Results in decreasing order:

20	0.137	34	0.124
4	0.133	39	0.124
33	0.133	16	0.122
32	0.131	22	0.122
135	0.130	38	0.121
23	0.128	35	0.120
8	0.125	19	0.116
36	0.125	31	0.115
131	0.125	12	0.114
3	0.125	15	0.112

NO2-N in absorbing solution
Sample no.: C4
Theoretical value: 0.135
Unit: µg N / ml

Run 1:

Number of laboratories:	20
Arithmetic mean value:	0.135
Median:	0.135
Standard deviation	0.007
Rel. st. deviation (%)	5.127

Run 2:

Number of laboratories:	19
Arithmetic mean value:	0.134
Median:	0.135
Standard deviation	0.006
Rel. st. deviation (%)	4.494

Results in decreasing order:

33	0.150 (*)	34	0.135
32	0.145	131	0.135
23	0.143	20	0.135
135	0.140	38	0.133
4	0.139	35	0.131
16	0.137	22	0.129
39	0.137	19	0.127
3	0.136	12	0.126
8	0.136	31	0.126
36	0.135	15	0.122

Table 16: The ratios of the theoretical values and the results found by the laboratories in the determination of nitrogen dioxide in absorbing solutions.

	Measured / Expected				
	Sample No.				
Lab.No	C1	C2	C3	C4	Average
3	1.00	0.60	1.00	1.00	0.90
4	1.02	1.02	1.06	1.03	1.03
8	1.01	0.97	1.11	1.00	1.02
9	0.00	0.00	0.00	0.00	0.00
10	0.00	0.00	0.00	0.00	0.00
12	0.98	0.90	0.91	0.93	0.93
15	0.88	0.86	0.89	0.90	0.88
16	1.00	1.02	0.97	1.01	1.00
19	0.92	0.91	0.92	0.94	0.92
20	0.99	1.03	1.09	1.00	1.03
22	0.99	0.99	0.97	0.95	0.98
23	0.96	0.94	1.02	1.06	0.99
24	0.00	0.00	0.00	0.00	0.00
31	0.91	0.94	0.92	0.93	0.92
32	1.07	1.05	1.05	1.07	1.06
33	1.08	1.12	1.06	1.11	1.09
34	1.05	0.98	0.99	1.00	1.01
35	0.97	0.95	0.96	0.97	0.96
36	1.00	1.03	1.00	1.00	1.01
38	0.98	0.98	0.97	0.98	0.98
39	1.03	1.05	0.99	1.01	1.02
131	0.98	1.03	1.00	1.00	1.00
135	1.04	1.02	1.04	1.03	1.03

Table 17: Analytical results for ammonia on impregnated filter.

NH3-N on impregnated filter
Sample no.: J1
Theoretical value: 8.020
Unit: µg N / FIL

Run 1:

Number of laboratories:	19
Arithmetic mean value:	8.121
Median:	7.960
Standard deviation	0.876
Rel. st. deviation (%)	10.790

Run 2:

Number of laboratories:	18
Arithmetic mean value:	7.985
Median:	7.938
Standard deviation	0.662
Rel. st. deviation (%)	8.285

Results in decreasing order:

135	10.580 (*)	3	7.915
8	9.178	32	7.900
33	8.935	11	7.835
138	8.810	5	7.610
131	8.630	4	7.575
39	8.386	19	7.431
116	8.300	15	7.345
13	8.150	20	6.968
34	8.088	10	6.710
36	7.960		

NH3-N on impregnated filter
Sample no.: J3
Theoretical value: 36.090
Unit: µg N / FIL

Run 1:

Number of laboratories:	19
Arithmetic mean value:	34.354
Median:	34.820
Standard deviation	3.709
Rel. st. deviation (%)	10.796

Run 2:

Number of laboratories:	19
Arithmetic mean value:	34.354
Median:	34.820
Standard deviation	3.709
Rel. st. deviation (%)	10.796

Results in decreasing order:

33	41.535	138	34.750
32	39.200	3	34.545
8	38.111	4	33.675
116	37.300	36	33.300
13	36.100	15	33.145
135	35.890	20	29.460
131	35.630	10	28.986
19	35.467	39	27.965
11	35.115	34	27.732
5	34.820		

NH3-N on impregnated filter
Sample no.: J4
Theoretical value: 20.050
Unit: µg N / FIL

Run 1:

Number of laboratories:	19
Arithmetic mean value:	19.383
Median:	19.400
Standard deviation	1.594
Rel. st. deviation (%)	8.226

Run 2:

Number of laboratories:	18
Arithmetic mean value:	19.574
Median:	19.557
Standard deviation	1.399
Rel. st. deviation (%)	7.148

Results in decreasing order:

8	22.400	34	19.308
33	21.935	15	19.245
13	20.800	4	19.175
116	20.500	36	19.100
138	20.350	3	18.635
131	19.940	5	18.320
19	19.789	20	17.256
135	19.740	10	16.726
11	19.715	39	15.945 (*)
32	19.400		

NH3-N on impregnated filter
Sample no.: J6
Theoretical value: 12.030
Unit: µg N / FIL

Run 1:

Number of laboratories:	19
Arithmetic mean value:	11.387
Median:	11.575
Standard deviation	1.519
Rel. st. deviation (%)	13.341

Run 2:

Number of laboratories:	18
Arithmetic mean value:	11.599
Median:	11.617
Standard deviation	1.240
Rel. st. deviation (%)	10.695

Results in decreasing order:

33	13.535	15	11.545
8	13.378	19	11.352
131	13.110	36	11.200
138	12.880	20	10.984
116	12.400	3	10.865
11	12.015	34	10.306
13	11.800	39	9.206
32	11.800	10	9.174
135	11.660	5	7.570 (*)
4	11.575		

Table 18: The ratios of the theoretical values and the results found by the laboratories in the determination of ammonia on impregnated filters. The reported results are corrected for an average blank value (J1 and J6).

	Measured / Expected				
	Sample No.				
Lab. no.	J1	J3	J4	J6	Average
3	0.99	0.96	0.93	0.90	0.94
4	0.94	0.93	0.96	0.96	0.95
5	0.95	0.96	0.91	0.63	0.86
8	1.14	1.06	1.12	1.11	1.11
10	0.84	0.80	0.83	0.76	0.81
11	0.98	0.97	0.98	1.00	0.98
13	1.02	1.00	1.04	0.98	1.01
15	0.92	0.92	0.96	0.96	0.94
19	0.93	0.98	0.99	0.94	0.96
20	0.87	0.82	0.86	0.91	0.86
32	0.99	1.09	0.97	0.98	1.00
33	1.11	1.15	1.09	1.13	1.12
34	1.01	0.77	0.96	0.86	0.90
36	0.99	0.92	0.95	0.93	0.95
39	1.05	0.77	0.80	0.77	0.85
116	1.03	1.03	1.02	1.03	1.03
131	1.08	0.99	0.99	1.09	1.04
135	1.32	0.99	0.98	0.97	1.07
138	1.10	0.96	1.01	1.07	1.04

Table 19: Analytical results for sulphate in precipitations samples.

SO42--S
Sample no.: G1
Theoretical value: 1.637
Unit: µg/l

Run 1:
Number of laboratories: 54
Arithmetic mean value: 1.744
Median: 1.639
Standard deviation 0.595
Rel. st. deviation (%) 34.093

Run 2:
Number of laboratories: 52
Arithmetic mean value: 1.630
Median: 1.635
Standard deviation 0.095
Rel. st. deviation (%) 5.843

Results in decreasing order:

130	5.000 (*)	36	1.638
126	4.390 (*)	21	1.632
133	2.094	6	1.627
38	1.730	26	1.623
121	1.730	104	1.620
14	1.720	7	1.618
111	1.710	20	1.611
138	1.704	112	1.610
13	1.700	23	1.610
107	1.697	30	1.609
114	1.690	34	1.608
33	1.683	110	1.600
118	1.680	1	1.600
35	1.675	11	1.596
32	1.672	136	1.596
131	1.664	116	1.587
27	1.661	15	1.580
8	1.660	10	1.566
120	1.660	109	1.560
5	1.657	24	1.550
115	1.650	16	1.542
31	1.648	117	1.540
4	1.648	140	1.520
135	1.647	19	1.517
3	1.646	22	1.472
39	1.643	18	1.423
12	1.640	113	1.420

SO42--S
Sample no.: G2
Theoretical value: 1.618
Unit: µg/l

Run 1:
Number of laboratories: 54
Arithmetic mean value: 1.773
Median: 1.660
Standard deviation 0.614
Rel. st. deviation (%) 34.658

Run 2:
Number of laboratories: 52
Arithmetic mean value: 1.656
Median: 1.658
Standard deviation 0.125
Rel. st. deviation (%) 7.537

Results in decreasing order:

130	5.040 (*)	135	1.660
126	4.570 (*)	36	1.656
133	2.238	31	1.648
121	1.830	6	1.646
118	1.810	26	1.642
39	1.764	23	1.637
14	1.743	7	1.636
38	1.740	34	1.634
114	1.740	1	1.630
35	1.739	112	1.630
138	1.731	30	1.626
13	1.730	20	1.621
115	1.730	116	1.615
107	1.725	15	1.600
120	1.710	10	1.596
32	1.701	11	1.595
33	1.699	16	1.590
111	1.690	136	1.580
5	1.683	109	1.580
4	1.682	104	1.560
27	1.681	117	1.560
8	1.680	19	1.555
131	1.677	140	1.540
3	1.673	24	1.530
110	1.670	22	1.467
21	1.661	113	1.410
12	1.660	18	1.280

SO42--S
Sample no.: G3
Theoretical value: 0.864
Unit: µg/l

Run 1:
Number of laboratories: 54
Arithmetic mean value: 0.933
Median: 0.880
Standard deviation 0.328
Rel. st. deviation (%) 35.207

Run 2:
Number of laboratories: 52
Arithmetic mean value: 0.870
Median: 0.880
Standard deviation 0.070
Rel. st. deviation (%) 8.043

Results in decreasing order:

130	2.580 (*)	109	0.880
126	2.530 (*)	1	0.880
120	0.980	3	0.878
133	0.966	21	0.878
118	0.960	26	0.875
38	0.940	6	0.872
32	0.940	36	0.872
14	0.937	117	0.870
138	0.932	20	0.868
111	0.920	34	0.861
135	0.918	116	0.861
33	0.914	112	0.860
131	0.910	16	0.856
5	0.900	39	0.852
114	0.900	110	0.850
35	0.897	15	0.848
13	0.895	23	0.844
27	0.894	30	0.840
8	0.891	19	0.833
12	0.890	104	0.830
121	0.890	115	0.820
4	0.889	140	0.820
7	0.887	11	0.816
107	0.887	24	0.810
31	0.884	22	0.766
136	0.881	113	0.750
10	0.880	18	0.490

SO42--S
Sample no.: G4
Theoretical value: 0.946
Unit: µg/l

Run 1:
Number of laboratories: 54
Arithmetic mean value: 0.997
Median: 0.948
Standard deviation 0.345
Rel. st. deviation (%) 34.620

Run 2:
Number of laboratories: 52
Arithmetic mean value: 0.933
Median: 0.946
Standard deviation 0.097
Rel. st. deviation (%) 10.418

Results in decreasing order:

130	2.830 (*)	21	0.947
126	2.500 (*)	36	0.945
133	1.086	31	0.944
121	1.050	3	0.941
120	1.040	1	0.940
118	1.030	26	0.936
14	1.009	6	0.934
38	1.000	20	0.932
115	1.000	34	0.929
138	0.996	117	0.920
136	0.991	112	0.920
131	0.977	104	0.920
33	0.977	16	0.916
4	0.972	15	0.916
114	0.970	32	0.911
39	0.969	23	0.908
5	0.968	30	0.903
135	0.966	140	0.890
13	0.966	110	0.890
116	0.963	109	0.880
7	0.961	11	0.876
27	0.961	19	0.873
8	0.960	10	0.870
111	0.960	24	0.850
107	0.958	22	0.821
12	0.950	113	0.810
35	0.948	18	0.359

Table 20: Analytical results for nitrate in precipitations samples.

NO3-N
Sample no.: G1
Theoretical value: 0.607
Unit: µg/l

Run 1:
Number of laboratories: 54
Arithmetic mean value: 0.687
Median: 0.690
Standard deviation 0.098
Rel. st. deviation (%) 14.294

Run 2:
Number of laboratories: 51
Arithmetic mean value: 0.695
Median: 0.691
Standard deviation 0.033
Rel. st. deviation (%) 4.719

Results in decreasing order:

133	1.031 (*)	126	0.690
40	0.865	118	0.690
113	0.740	6	0.690
12	0.730	110	0.690
38	0.730	14	0.690
135	0.727	26	0.690
104	0.720	21	0.689
114	0.715	7	0.688
33	0.715	32	0.688
39	0.714	130	0.686
120	0.710	4	0.685
13	0.710	1	0.680
35	0.708	34	0.673
27	0.707	140	0.670
20	0.705	15	0.669
8	0.704	19	0.668
5	0.704	10	0.667
138	0.703	24	0.660
31	0.702	117	0.660
115	0.700	112	0.660
23	0.698	30	0.658
107	0.698	22	0.657
131	0.696	16	0.656
116	0.696	11	0.650
36	0.692	111	0.647
121	0.691	109	0.470 (*)
3	0.691	136	0.150 (*)

NO3-N
Sample no.: G2
Theoretical value: 0.546
Unit: µg/l

Run 1:
Number of laboratories: 54
Arithmetic mean value: 0.528
Median: 0.537
Standard deviation 0.076
Rel. st. deviation (%) 14.459

Run 2:
Number of laboratories: 51
Arithmetic mean value: 0.536
Median: 0.537
Standard deviation 0.022
Rel. st. deviation (%) 4.040

Results in decreasing order:

133	0.773 (*)	6	0.537
40	0.585	23	0.537
114	0.565	131	0.537
39	0.561	14	0.536
104	0.560	4	0.535
38	0.560	107	0.534
113	0.560	10	0.534
118	0.560	21	0.534
12	0.560	7	0.532
13	0.559	140	0.530
35	0.556	3	0.527
33	0.556	34	0.524
116	0.553	126	0.520
1	0.550	112	0.520
120	0.550	15	0.517
121	0.548	19	0.514
8	0.547	110	0.510
20	0.546	115	0.510
27	0.546	117	0.510
138	0.546	16	0.508
135	0.544	30	0.503
5	0.544	11	0.502
32	0.542	24	0.500
130	0.541	22	0.492
31	0.539	111	0.473
26	0.537	109	0.290 (*)
36	0.537	136	0.121 (*)

NO3-N
Sample no.: G3
Theoretical value: 0.738
Unit: µg/l

Run 1:
Number of laboratories: 54
Arithmetic mean value: 0.722
Median: 0.730
Standard deviation 0.090
Rel. st. deviation (%) 12.408

Run 2:
Number of laboratories: 52
Arithmetic mean value: 0.736
Median: 0.730
Standard deviation 0.039
Rel. st. deviation (%) 5.325

Results in decreasing order:

133	0.874	6	0.730
40	0.865	1	0.730
126	0.830	7	0.728
113	0.780	4	0.728
135	0.771	21	0.727
12	0.770	26	0.726
130	0.761	14	0.725
115	0.760	131	0.723
33	0.757	121	0.721
32	0.752	39	0.720
35	0.752	3	0.716
13	0.751	34	0.712
38	0.750	10	0.711
104	0.750	140	0.710
114	0.748	19	0.707
27	0.746	16	0.703
116	0.746	110	0.700
31	0.746	112	0.700
138	0.744	30	0.698
5	0.743	15	0.696
20	0.742	111	0.692
8	0.741	22	0.690
118	0.740	117	0.690
107	0.738	24	0.670
23	0.737	11	0.669
120	0.730	109	0.540 (*)
36	0.730	136	0.171 (*)

NO3-N
Sample no.: G4
Theoretical value: 0.521
Unit: µg/l

Run 1:
Number of laboratories: 54
Arithmetic mean value: 0.500
Median: 0.510
Standard deviation 0.067
Rel. st. deviation (%) 13.433

Run 2:
Number of laboratories: 51
Arithmetic mean value: 0.510
Median: 0.511
Standard deviation 0.019
Rel. st. deviation (%) 3.762

Results in decreasing order:

133	0.638 (*)	112	0.510
35	0.543	140	0.510
38	0.540	26	0.510
118	0.540	126	0.510
33	0.534	23	0.509
116	0.531	107	0.508
113	0.530	21	0.508
115	0.530	138	0.507
40	0.530	7	0.506
12	0.530	36	0.503
39	0.527	120	0.500
135	0.524	131	0.499
13	0.523	3	0.498
8	0.522	34	0.497
114	0.521	16	0.496
1	0.520	15	0.494
5	0.520	117	0.490
104	0.520	19	0.488
121	0.519	10	0.485
27	0.519	111	0.484
20	0.518	30	0.479
130	0.517	11	0.478
32	0.516	24	0.470
31	0.513	110	0.470
14	0.513	22	0.456
4	0.512	109	0.270 (*)
6	0.511	136	0.120 (*)

Table 21: Analytical results for ammonium in precipitations sample.

NH4-N
Sample no.: G1
Theoretical value: 0.441
Unit: µg/l

Run 1:
Number of laboratories: 54
Arithmetic mean value: 0.456
Median: 0.450
Standard deviation 0.068
Rel. st. deviation (%) 14.838

Run 2:
Number of laboratories: 51
Arithmetic mean value: 0.447
Median: 0.449
Standard deviation 0.021
Rel. st. deviation (%) 4.768

Results in decreasing order:

109	0.770 (*)	31	0.449		
40	0.760 (*)	131	0.446		
138	0.499	4	0.444		
30	0.497	21	0.443		
33	0.490	8	0.443		
116	0.485	130	0.442		
34	0.473	7	0.442		
104	0.470	14	0.441		
23	0.468	24	0.440		
114	0.464	117	0.440		
35	0.464	118	0.439		
20	0.461	135	0.437		
112	0.460	39	0.436		
107	0.460	5	0.436		
140	0.460	36	0.436		
19	0.458	16	0.435		
6	0.457	126	0.435		
13	0.457	32	0.431		
3	0.456	12	0.430		
27	0.453	15	0.430		
121	0.451	18	0.428		
26	0.451	115	0.420		
10	0.451	133	0.412		
22	0.451	1	0.400		
120	0.450	113	0.400		
38	0.450	110	0.400		
111	0.450	136	0.296 (*)		

NH4-N
Sample no.: G2
Theoretical value: 0.281
Unit: µg/l

Run 1:
Number of laboratories: 54
Arithmetic mean value: 0.287
Median: 0.280
Standard deviation 0.063
Rel. st. deviation (%) 21.811

Run 2:
Number of laboratories: 51
Arithmetic mean value: 0.274
Median: 0.280
Standard deviation 0.023
Rel. st. deviation (%) 8.563

Results in decreasing order:

109	0.590 (*)	117	0.280		
40	0.530 (*)	21	0.280		
116	0.429 (*)	135	0.280		
30	0.312	4	0.278		
34	0.299	5	0.277		
22	0.298	130	0.277		
35	0.292	36	0.276		
121	0.291	8	0.274		
107	0.291	10	0.273		
33	0.290	111	0.273		
104	0.290	120	0.270		
23	0.290	12	0.270		
6	0.290	15	0.270		
112	0.290	24	0.270		
38	0.290	39	0.269		
131	0.286	16	0.266		
31	0.285	118	0.262		
3	0.285	115	0.260		
19	0.285	1	0.260		
114	0.285	126	0.260		
13	0.284	113	0.260		
27	0.283	138	0.257		
18	0.283	32	0.250		
20	0.283	14	0.248		
7	0.281	136	0.203		
140	0.280	133	0.194		
26	0.280	110	0.190		

NH4-N
Sample no.: G3
Theoretical value: 0.521
Unit: µg/l

Run 1:
Number of laboratories: 54
Arithmetic mean value: 0.517
Median: 0.515
Standard deviation 0.069
Rel. st. deviation (%) 13.322

Run 2:
Number of laboratories: 51
Arithmetic mean value: 0.512
Median: 0.515
Standard deviation 0.027
Rel. st. deviation (%) 5.240

Results in decreasing order:

40	0.800 (*)	126	0.515		
109	0.770 (*)	7	0.514		
33	0.570	8	0.514		
116	0.563	34	0.513		
120	0.540	117	0.510		
35	0.540	5	0.509		
104	0.540	36	0.509		
23	0.539	135	0.509		
20	0.538	16	0.507		
114	0.536	3	0.507		
31	0.534	118	0.506		
140	0.530	138	0.505		
6	0.528	22	0.502		
19	0.527	39	0.500		
131	0.526	32	0.500		
111	0.525	133	0.497		
107	0.524	14	0.495		
13	0.523	12	0.490		
30	0.522	38	0.490		
27	0.521	15	0.490		
26	0.521	1	0.480		
112	0.520	115	0.480		
121	0.519	110	0.480		
21	0.518	24	0.470		
10	0.517	113	0.470		
4	0.517	18	0.393		
130	0.515	136	0.252 (*)		

NH4-N
Sample no.: G4
Theoretical value: 0.241
Unit: µg/l

Run 1:
Number of laboratories: 54
Arithmetic mean value: 0.254
Median: 0.237
Standard deviation 0.086
Rel. st. deviation (%) 33.711

Run 2:
Number of laboratories: 51
Arithmetic mean value: 0.235
Median: 0.236
Standard deviation 0.024
Rel. st. deviation (%) 10.046

Results in decreasing order:

18	0.703 (*)	35	0.237		
109	0.540 (*)	131	0.236		
40	0.500 (*)	23	0.236		
116	0.299	15	0.236		
31	0.297	111	0.236		
22	0.281	135	0.234		
112	0.260	121	0.233		
30	0.259	8	0.233		
34	0.257	130	0.232		
3	0.254	120	0.230		
107	0.249	12	0.230		
114	0.246	113	0.230		
21	0.245	117	0.230		
6	0.245	38	0.230		
36	0.244	24	0.230		
5	0.244	10	0.229		
20	0.243	13	0.223		
7	0.242	126	0.222		
19	0.242	1	0.220		
16	0.241	118	0.219		
32	0.240	39	0.217		
33	0.240	136	0.214		
104	0.240	115	0.200		
140	0.240	14	0.195		
27	0.240	138	0.193		
26	0.239	110	0.190		
4	0.238	133	0.155		

Table 22: Analytical results for pH in precipitations samples.

pH
Sample no.: G1
Theoretical value: 4.120
Unit: pH-unit

Run 1:
Number of laboratories: 56
Arithmetic mean value: 4.189
Median: 4.178
Standard deviation 0.101
Rel. st. deviation (%) 2.407

Run 2:
Number of laboratories: 53
Arithmetic mean value: 4.184
Median: 4.176
Standard deviation 0.058
Rel. st. deviation (%) 1.381

Results in decreasing order:

38	4.610 (*)	3	4.176
126	4.440 (*)	107	4.170
40	4.390	27	4.170
104	4.340	121	4.170
19	4.310	7	4.170
133	4.290	8	4.170
113	4.270	36	4.170
115	4.260	4	4.166
35	4.240	5	4.160
109	4.230	21	4.160
117	4.220	31	4.160
14	4.210	15	4.160
1	4.210	33	4.160
136	4.210	118	4.150
140	4.200	130	4.150
34	4.195	135	4.150
24	4.190	11	4.140
106	4.190	39	4.140
111	4.190	138	4.140
20	4.190	116	4.130
114	4.190	23	4.130
112	4.180	10	4.130
110	4.180	12	4.130
22	4.180	6	4.110
13	4.180	131	4.110
32	4.180	18	4.110
16	4.180	30	4.060
26	4.180	120	3.810 (*)

pH
Sample no.: G2
Theoretical value: 4.070
Unit: pH-unit

Run 1:
Number of laboratories: 56
Arithmetic mean value: 4.115
Median: 4.100
Standard deviation 0.085
Rel. st. deviation (%) 2.070

Run 2:
Number of laboratories: 53
Arithmetic mean value: 4.098
Median: 4.100
Standard deviation 0.041
Rel. st. deviation (%) 1.011

Results in decreasing order:

38	4.500 (*)	36	4.100
40	4.400 (*)	107	4.100
126	4.370 (*)	1	4.100
19	4.230	8	4.100
115	4.210	4	4.098
133	4.190	110	4.090
113	4.170	130	4.090
109	4.150	106	4.090
34	4.142	22	4.090
14	4.140	135	4.080
20	4.120	10	4.080
114	4.120	33	4.080
111	4.120	21	4.080
136	4.120	11	4.080
140	4.120	39	4.080
3	4.111	116	4.070
112	4.110	118	4.070
26	4.110	121	4.070
117	4.110	5	4.070
24	4.110	104	4.070
7	4.110	23	4.050
13	4.100	138	4.050
15	4.100	131	4.050
16	4.100	18	4.050
27	4.100	120	4.040
31	4.100	12	4.040
32	4.100	6	4.020
35	4.100	30	4.010

pH
Sample no.: G3
Theoretical value: 4.520
Unit: pH-unit

Run 1:
Number of laboratories: 56
Arithmetic mean value: 4.559
Median: 4.540
Standard deviation 0.129
Rel. st. deviation (%) 2.836

Run 2:
Number of laboratories: 55
Arithmetic mean value: 4.544
Median: 4.540
Standard deviation 0.072
Rel. st. deviation (%) 1.589

Results in decreasing order:

40	5.350 (*)	106	4.540
126	4.770	140	4.540
38	4.750	21	4.530
19	4.750	27	4.530
133	4.690	33	4.530
113	4.660	39	4.530
109	4.610	7	4.530
14	4.600	4	4.527
16	4.590	11	4.520
136	4.580	13	4.520
34	4.571	135	4.510
35	4.570	5	4.500
110	4.570	130	4.500
111	4.570	121	4.500
117	4.570	104	4.500
22	4.560	116	4.500
114	4.560	118	4.500
32	4.560	138	4.500
20	4.560	23	4.490
115	4.560	120	4.490
15	4.550	10	4.480
107	4.550	131	4.480
112	4.550	36	4.460
24	4.550	12	4.460
26	4.550	1	4.460
3	4.548	6	4.450
31	4.540	18	4.430
8	4.540	30	4.400

pH
Sample no.: G4
Theoretical value: 4.430
Unit: pH-unit

Run 1:
Number of laboratories: 56
Arithmetic mean value: 4.474
Median: 4.460
Standard deviation 0.108
Rel. st. deviation (%) 2.414

Run 2:
Number of laboratories: 53
Arithmetic mean value: 4.454
Median: 4.460
Standard deviation 0.054
Rel. st. deviation (%) 1.222

Results in decreasing order:

40	5.070 (*)	106	4.460
38	4.710 (*)	107	4.460
126	4.710 (*)	4	4.460
19	4.640	3	4.456
14	4.580	15	4.450
113	4.550	21	4.450
133	4.540	33	4.440
111	4.530	120	4.440
140	4.510	11	4.440
115	4.510	135	4.440
109	4.500	116	4.430
16	4.490	121	4.430
34	4.485	39	4.430
136	4.480	32	4.430
117	4.480	138	4.420
22	4.480	104	4.420
24	4.480	12	4.410
110	4.470	118	4.410
112	4.470	130	4.400
31	4.470	131	4.400
114	4.470	18	4.400
20	4.470	10	4.400
7	4.460	23	4.400
8	4.460	5	4.400
13	4.460	1	4.380
26	4.460	36	4.370
27	4.460	6	4.360
35	4.460	30	4.320

Table 23: Analytical results for strong acid calculated from pH.

Strong acid calculated from pH
Sample no.: 1
Theoretical value: 75.000
Unit: µeq/l

Run 1:

Number of laboratories:	56
Arithmetic mean value:	66.390
Median:	66.375
Standard deviation	15.934
Rel. st. deviation (%)	24.000

Run 2:

Number of laboratories:	54
Arithmetic mean value:	65.526
Median:	66.375
Standard deviation	9.051
Rel. st. deviation (%)	13.812

Results in decreasing order:

120	154.882 (*)	13	66.069	
30	87.767	32	66.069	
18	77.625	16	66.069	
131	77.625	22	66.069	
6	77.625	110	66.069	
23	74.131	112	66.069	
10	74.131	26	66.069	
116	74.131	106	64.565	
12	74.131	114	64.565	
39	72.444	24	64.565	
138	72.444	20	64.565	
11	72.444	111	64.565	
118	70.795	34	63.826	
135	70.795	140	63.096	
130	70.795	14	61.660	
21	69.183	136	61.660	
5	69.183	1	61.660	
31	69.183	117	60.256	
33	69.183	109	58.884	
15	69.183	35	57.544	
4	68.234	115	54.954	
27	67.608	113	53.703	
36	67.608	133	51.286	
121	67.608	19	48.978	
107	67.608	104	45.709	
7	67.608	40	40.738	
8	67.104	126	36.308	
3	66.681	38	24.547 (*)	

Strong acid calculated from pH
Sample no.: 2
Theoretical value: 85.000
Unit: µeq/l

Run 1:

Number of laboratories:	56
Arithmetic mean value:	77.880
Median:	79.433
Standard deviation	11.993
Rel. st. deviation (%)	15.400

Run 2:

Number of laboratories:	53
Arithmetic mean value:	80.135
Median:	79.433
Standard deviation	7.354
Rel. st. deviation (%)	9.177

Results in decreasing order:

30	96.977	36	79.433	
6	95.499	107	79.433	
12	91.201	1	79.433	
120	91.201	13	79.433	
18	89.125	15	79.433	
23	89.125	16	79.433	
131	89.125	8	78.977	
138	89.125	112	77.625	
116	85.114	7	77.625	
118	85.114	26	77.625	
104	85.114	24	77.625	
121	85.114	117	77.625	
5	85.114	3	77.446	
10	83.176	20	75.858	
21	83.176	136	75.858	
11	83.176	140	75.858	
39	83.176	111	75.858	
135	83.176	114	75.858	
33	83.176	14	72.444	
110	81.283	34	72.111	
130	81.283	109	70.795	
106	81.283	113	67.608	
22	81.283	133	64.565	
4	79.799	115	61.660	
27	79.433	19	58.884	
31	79.433	126	42.658 (*)	
32	79.433	40	39.811 (*)	
35	79.433	38	31.623 (*)	

Strong acid calculated from pH
Sample no.: 3
Theoretical value: 30.000
Unit: µeq/l

Run 1:

Number of laboratories:	56
Arithmetic mean value:	28.475
Median:	28.840
Standard deviation	5.435
Rel. st. deviation (%)	19.088

Run 2:

Number of laboratories:	53
Arithmetic mean value:	28.937
Median:	28.840
Standard deviation	3.882
Rel. st. deviation (%)	13.414

Results in decreasing order:

30	39.506 (*)	140	28.840	
18	37.154	8	28.609	
6	35.481	3	28.314	
1	34.674	112	28.184	
36	34.674	15	28.184	
12	34.674	24	28.184	
131	33.113	26	28.184	
10	33.113	107	28.184	
120	32.359	115	27.542	
23	32.359	22	27.542	
118	31.623	32	27.542	
104	31.623	20	27.542	
5	31.623	114	27.542	
121	31.623	110	26.915	
130	31.623	111	26.915	
116	31.623	35	26.915	
138	31.623	117	26.915	
135	30.903	34	26.853	
13	30.200	136	26.303	
11	30.200	16	25.704	
4	29.717	14	25.119	
39	29.512	109	24.547	
21	29.512	113	21.878	
27	29.512	133	20.417	
33	29.512	19	17.783	
7	29.512	38	17.783	
31	28.840	126	16.982 (*)	
106	28.840	40	4.467 (*)	

Strong acid calculated from pH
Sample no.: 4
Theoretical value: 37.500
Unit: µeq/l

Run 1:

Number of laboratories:	56
Arithmetic mean value:	34.354
Median:	34.674
Standard deviation	6.225
Rel. st. deviation (%)	18.119

Run 2:

Number of laboratories:	52
Arithmetic mean value:	35.163
Median:	34.674
Standard deviation	3.974
Rel. st. deviation (%)	11.301

Results in decreasing order:

30	47.863 (*)	106	34.674	
6	43.652	107	34.674	
36	42.658	4	34.674	
1	41.687	7	34.674	
18	39.811	13	34.674	
5	39.811	8	34.415	
130	39.811	112	33.884	
10	39.811	20	33.884	
23	39.811	31	33.884	
131	39.811	114	33.884	
12	38.905	110	33.884	
118	38.905	22	33.113	
104	38.019	136	33.113	
138	38.019	117	33.113	
121	37.154	24	33.113	
39	37.154	34	32.734	
32	37.154	16	32.359	
116	37.154	109	31.623	
120	36.308	115	30.903	
33	36.308	140	30.903	
135	36.308	111	29.512	
11	36.308	133	28.840	
21	35.481	113	28.184	
15	35.481	14	26.303	
3	34.995	19	22.909	
26	34.674	126	19.498 (*)	
27	34.674	38	19.498 (*)	
35	34.674	40	8.511 (*)	

Table 24: Analytical results for strong acid in precipitations samples.

H
Sample no.: G1
Theoretical value: 75.000
Unit: µeq

Run 1:
Number of laboratories: 3
Arithmetic mean value: 79.067
Median: 79.000
Standard deviation 3.900
Rel. st. deviation (%) 4.933

Run 2:
Number of laboratories: 3
Arithmetic mean value: 79.067
Median: 79.000
Standard deviation 3.900
Rel. st. deviation (%) 4.933

Results in decreasing order:
6 83.000 14 75.200
126 79.000

H
Sample no.: G2
Theoretical value: 85.000
Unit: µeq

Run 1:
Number of laboratories: 3
Arithmetic mean value: 94.167
Median: 94.000
Standard deviation 6.752
Rel. st. deviation (%) 7.170

Run 2:
Number of laboratories: 3
Arithmetic mean value: 94.167
Median: 94.000
Standard deviation 6.752
Rel. st. deviation (%) 7.170

Results in decreasing order:
126 101.000 14 87.500
6 94.000

H
Sample no.: G3
Theoretical value: 30.000
Unit: µeq

Run 1:
Number of laboratories: 3
Arithmetic mean value: 41.267
Median: 39.000
Standard deviation 10.780
Rel. st. deviation (%) 26.123

Run 2:
Number of laboratories: 3
Arithmetic mean value: 41.267
Median: 39.000
Standard deviation 10.780
Rel. st. deviation (%) 26.123

Results in decreasing order:
126 53.000 14 31.800
6 39.000

H
Sample no.: G4
Theoretical value: 37.500
Unit: µeq

Run 1:
Number of laboratories: 3
Arithmetic mean value: 44.500
Median: 47.000
Standard deviation 9.014
Rel. st. deviation (%) 20.256

Run 2:
Number of laboratories: 3
Arithmetic mean value: 44.500
Median: 47.000
Standard deviation 9.014
Rel. st. deviation (%) 20.256

Results in decreasing order:
126 52.000 14 34.500
6 47.000

Table 25: Analytical results for chloride in precipitations samples.

Cl
Sample no.: G1
Theoretical value: 0.145
Unit: µg/l

Run 1:
Number of laboratories: 49
Arithmetic mean value: 0.148
Median: 0.140
Standard deviation 0.067
Rel. st. deviation (%) 45.459

Run 2:
Number of laboratories: 48
Arithmetic mean value: 0.140
Median: 0.140
Standard deviation 0.039
Rel. st. deviation (%) 27.833

Results in decreasing order:

133	0.526 (*)	26	0.140
110	0.250	38	0.140
115	0.220	32	0.139
40	0.219	34	0.138
120	0.200	39	0.136
113	0.190	14	0.136
118	0.190	35	0.135
33	0.187	16	0.133
140	0.170	24	0.130
5	0.160	126	0.130
31	0.156	104	0.130
136	0.153	15	0.129
1	0.150	6	0.121
7	0.150	130	0.120
114	0.150	23	0.115
21	0.148	11	0.106
3	0.147	116	0.105
30	0.147	22	0.105
13	0.146	20	0.101
27	0.145	131	0.099
107	0.144	138	0.092
4	0.141	135	0.075
36	0.141	18	0.045
12	0.140	10	0.043
8	0.140		

Cl
Sample no.: G2
Theoretical value: 0.203
Unit: µg/l

Run 1:
Number of laboratories: 49
Arithmetic mean value: 0.209
Median: 0.198
Standard deviation 0.075
Rel. st. deviation (%) 36.100

Run 2:
Number of laboratories: 48
Arithmetic mean value: 0.200
Median: 0.198
Standard deviation 0.042
Rel. st. deviation (%) 21.243

Results in decreasing order:

133	0.638 (*)	26	0.197
32	0.298	36	0.195
118	0.290	7	0.195
115	0.290	4	0.193
40	0.283	14	0.193
110	0.280	15	0.191
120	0.260	104	0.190
140	0.250	16	0.188
33	0.250	34	0.187
113	0.230	6	0.183
114	0.220	18	0.180
5	0.212	126	0.180
3	0.210	24	0.180
38	0.210	136	0.176
39	0.210	116	0.165
107	0.207	130	0.160
27	0.206	11	0.157
30	0.205	23	0.156
21	0.203	20	0.152
13	0.203	22	0.142
31	0.201	131	0.138
12	0.200	138	0.135
1	0.200	135	0.129
8	0.200	10	0.116
35	0.198		

Cl
Sample no.: G3
Theoretical value: 0.579
Unit: µg/l

Run 1:
Number of laboratories: 55
Arithmetic mean value: 0.558
Median: 0.565
Standard deviation 0.051
Rel. st. deviation (%) 9.142

Run 2:
Number of laboratories: 53
Arithmetic mean value: 0.558
Median: 0.565
Standard deviation 0.044
Rel. st. deviation (%) 7.870

Results in decreasing order:

40	0.704 (*)	15	0.561
33	0.657	126	0.560
140	0.650	14	0.551
113	0.640	130	0.550
32	0.640	30	0.550
18	0.629	4	0.548
115	0.620	6	0.547
118	0.600	107	0.546
111	0.596	19	0.546
114	0.590	131	0.540
12	0.590	34	0.539
38	0.590	20	0.532
26	0.585	104	0.530
1	0.580	109	0.530
110	0.580	135	0.525
31	0.578	24	0.520
21	0.575	16	0.515
27	0.575	112	0.510
5	0.574	11	0.508
13	0.573	117	0.499
3	0.572	121	0.497
116	0.572	23	0.494
120	0.570	39	0.486
136	0.570	138	0.486
8	0.569	10	0.477
35	0.567	133	0.467
7	0.567	22	0.420 (*)
36	0.565		

Cl
Sample no.: G4
Theoretical value: 0.637
Unit: µg/l

Run 1:
Number of laboratories: 55
Arithmetic mean value: 0.616
Median: 0.613
Standard deviation 0.050
Rel. st. deviation (%) 8.138

Run 2:
Number of laboratories: 52
Arithmetic mean value: 0.612
Median: 0.612
Standard deviation 0.035
Rel. st. deviation (%) 5.652

Results in decreasing order:

40	0.825 (*)	32	0.611
113	0.740 (*)	130	0.610
115	0.700	39	0.610
140	0.690	4	0.603
18	0.674	14	0.603
33	0.666	107	0.602
110	0.660	20	0.602
31	0.647	104	0.600
27	0.640	116	0.597
12	0.640	138	0.597
114	0.640	34	0.595
118	0.640	131	0.593
26	0.640	120	0.590
5	0.635	135	0.588
15	0.634	19	0.588
3	0.632	109	0.580
8	0.632	126	0.580
21	0.631	24	0.580
13	0.627	133	0.576
35	0.626	11	0.568
111	0.624	117	0.565
136	0.623	121	0.561
7	0.622	112	0.560
1	0.620	16	0.558
38	0.620	10	0.544
36	0.619	23	0.540
6	0.614	22	0.495 (*)
30	0.613		

Table 26: Analytical results for sodium in precipitations samples.

Na
Sample no.: G1
Theoretical value: 0.336
Unit: µg/l

Run 1:
Number of laboratories: 53
Arithmetic mean value: 0.326
Median: 0.330
Standard deviation 0.042
Rel. st. deviation (%) 12.765

Run 2:
Number of laboratories: 49
Arithmetic mean value: 0.326
Median: 0.330
Standard deviation 0.026
Rel. st. deviation (%) 7.965

Results in decreasing order:

140	0.460 (*)	110	0.330
118	0.420 (*)	130	0.330
32	0.400	138	0.321
109	0.390	1	0.320
4	0.379	21	0.319
22	0.370	35	0.319
126	0.360	135	0.317
112	0.350	131	0.314
30	0.343	10	0.314
14	0.343	117	0.312
26	0.342	34	0.311
104	0.340	12	0.310
7	0.340	33	0.310
39	0.338	120	0.308
36	0.337	38	0.307
5	0.336	3	0.307
6	0.335	31	0.306
13	0.335	133	0.300
27	0.334	11	0.296
107	0.334	23	0.292
20	0.333	40	0.288
8	0.332	111	0.282
19	0.331	113	0.280
114	0.330	115	0.270
16	0.330	116	0.204 (*)
15	0.330	136	0.200 (*)
121	0.330		

Na
Sample no.: G2
Theoretical value: 0.454
Unit: µg/l

Run 1:
Number of laboratories: 53
Arithmetic mean value: 0.438
Median: 0.444
Standard deviation 0.039
Rel. st. deviation (%) 8.962

Run 2:
Number of laboratories: 48
Arithmetic mean value: 0.439
Median: 0.444
Standard deviation 0.028
Rel. st. deviation (%) 6.376

Results in decreasing order:

32	0.550 (*)	114	0.440
109	0.530 (*)	19	0.439
121	0.510	20	0.439
118	0.490	104	0.430
22	0.490	138	0.430
1	0.480	35	0.429
4	0.479	135	0.423
126	0.470	34	0.422
112	0.460	12	0.420
131	0.460	110	0.420
36	0.458	33	0.420
26	0.457	140	0.420
5	0.456	120	0.420
39	0.456	10	0.419
13	0.455	23	0.415
107	0.454	11	0.415
30	0.453	31	0.415
7	0.453	117	0.410
15	0.450	3	0.407
130	0.450	38	0.397
16	0.450	40	0.385
8	0.449	113	0.380
27	0.448	111	0.377
116	0.448	136	0.356 (*)
6	0.447	133	0.350 (*)
21	0.444	115	0.350 (*)
14	0.444		

Na
Sample no.: G3
Theoretical value: 0.537
Unit: µg/l

Run 1:
Number of laboratories: 53
Arithmetic mean value: 0.523
Median: 0.527
Standard deviation 0.060
Rel. st. deviation (%) 11.535

Run 2:
Number of laboratories: 48
Arithmetic mean value: 0.512
Median: 0.524
Standard deviation 0.038
Rel. st. deviation (%) 7.379

Results in decreasing order:

22	0.718 (*)	6	0.526
116	0.683 (*)	30	0.523
32	0.670 (*)	110	0.520
109	0.650 (*)	16	0.520
118	0.580	35	0.518
140	0.580	104	0.510
1	0.570	12	0.510
4	0.567	120	0.502
126	0.560	14	0.500
39	0.543	34	0.496
7	0.540	10	0.494
5	0.540	3	0.492
112	0.540	135	0.491
36	0.539	31	0.488
107	0.537	11	0.487
26	0.536	23	0.486
21	0.535	138	0.476
20	0.535	117	0.471
8	0.532	113	0.460
131	0.531	33	0.460
15	0.530	40	0.451
114	0.530	111	0.448
121	0.530	38	0.447
130	0.530	136	0.427
19	0.529	115	0.420
13	0.527	133	0.400 (*)
27	0.527		

Na
Sample no.: G4
Theoretical value: 0.789
Unit: µg/l

Run 1:
Number of laboratories: 53
Arithmetic mean value: 0.749
Median: 0.760
Standard deviation 0.075
Rel. st. deviation (%) 9.977

Run 2:
Number of laboratories: 50
Arithmetic mean value: 0.754
Median: 0.760
Standard deviation 0.051
Rel. st. deviation (%) 6.703

Results in decreasing order:

22	0.994 (*)	109	0.760
32	0.870	110	0.760
1	0.840	34	0.759
4	0.823	131	0.756
118	0.820	12	0.750
126	0.800	135	0.750
36	0.798	120	0.743
7	0.795	11	0.743
5	0.795	3	0.742
107	0.793	140	0.740
112	0.790	10	0.736
39	0.787	23	0.734
26	0.785	14	0.733
21	0.785	138	0.719
20	0.781	113	0.710
8	0.781	31	0.706
114	0.780	33	0.700
130	0.780	121	0.680
35	0.779	117	0.677
30	0.778	136	0.664
27	0.775	111	0.654
16	0.770	38	0.651
19	0.769	40	0.651
13	0.769	115	0.630
6	0.767	133	0.550 (*)
104	0.760	116	0.494 (*)
15	0.760		

Table 27: Analytical results for magnesium in precipitations samples.

Mg
Sample no.: G1
Theoretical value: 0.155
Unit: µg/l

Run 1:

Number of laboratories:	52
Arithmetic mean value:	0.151
Median:	0.151
Standard deviation	0.020
Rel. st. deviation (%)	13.083

Run 2:

Number of laboratories:	47
Arithmetic mean value:	0.152
Median:	0.152
Standard deviation	0.010
Rel. st. deviation (%)	6.551

Results in decreasing order:

20	0.213 (*)	107	0.151		
126	0.210 (*)	14	0.151		
118	0.171	114	0.150		
112	0.170	115	0.150		
138	0.169	117	0.150		
135	0.163	23	0.150		
34	0.162	16	0.150		
3	0.161	121	0.150		
33	0.160	110	0.150		
104	0.160	130	0.150		
7	0.160	27	0.150		
15	0.160	8	0.149		
22	0.159	30	0.149		
31	0.159	111	0.147		
13	0.159	6	0.147		
131	0.158	12	0.147		
21	0.157	40	0.143		
5	0.156	1	0.140		
11	0.156	113	0.140		
26	0.155	4	0.136		
19	0.155	38	0.133		
10	0.154	133	0.127		
120	0.154	140	0.120		
35	0.153	136	0.108 (*)		
39	0.153	109	0.100 (*)		
36	0.152	116	0.091 (*)		

Mg
Sample no.: G2
Theoretical value: 0.077
Unit: µg/l

Run 1:

Number of laboratories:	52
Arithmetic mean value:	0.079
Median:	0.078
Standard deviation	0.014
Rel. st. deviation (%)	17.992

Run 2:

Number of laboratories:	50
Arithmetic mean value:	0.077
Median:	0.078
Standard deviation	0.008
Rel. st. deviation (%)	10.053

Results in decreasing order:

126	0.150 (*)	5	0.078		
20	0.125 (*)	14	0.077		
136	0.101	120	0.077		
112	0.090	39	0.077		
30	0.088	12	0.076		
138	0.088	117	0.076		
22	0.084	36	0.076		
118	0.083	11	0.076		
135	0.083	16	0.076		
3	0.081	40	0.076		
13	0.080	27	0.075		
1	0.080	35	0.075		
15	0.080	8	0.075		
31	0.080	116	0.074		
104	0.080	34	0.074		
130	0.080	111	0.073		
33	0.080	23	0.073		
114	0.080	140	0.070		
113	0.080	109	0.070		
121	0.079	115	0.070		
131	0.079	4	0.068		
10	0.079	133	0.068		
21	0.079	6	0.067		
26	0.079	110	0.060		
7	0.078	107	0.056		
19	0.078	38	0.055		

Mg
Sample no.: G3
Theoretical value: 0.093
Unit: µg/l

Run 1:

Number of laboratories:	52
Arithmetic mean value:	0.092
Median:	0.090
Standard deviation	0.016
Rel. st. deviation (%)	17.044

Run 2:

Number of laboratories:	50
Arithmetic mean value:	0.092
Median:	0.090
Standard deviation	0.009
Rel. st. deviation (%)	9.734

Results in decreasing order:

126	0.160 (*)	1	0.090		
20	0.123	114	0.090		
22	0.112	115	0.090		
35	0.108	8	0.090		
116	0.104	27	0.090		
138	0.104	16	0.090		
135	0.100	104	0.090		
112	0.100	15	0.090		
118	0.099	109	0.090		
3	0.098	33	0.090		
7	0.097	113	0.090		
131	0.097	12	0.089		
121	0.095	111	0.088		
13	0.095	30	0.087		
21	0.095	117	0.087		
26	0.094	23	0.085		
5	0.094	6	0.084		
10	0.093	133	0.082		
36	0.093	4	0.081		
19	0.093	40	0.081		
31	0.093	107	0.081		
34	0.092	110	0.080		
120	0.092	130	0.080		
39	0.092	140	0.080		
14	0.091	38	0.068		
11	0.091	136	0.029 (*)		

Mg
Sample no.: G4
Theoretical value: 0.116
Unit: µg/l

Run 1:

Number of laboratories:	52
Arithmetic mean value:	0.114
Median:	0.116
Standard deviation	0.016
Rel. st. deviation (%)	14.136

Run 2:

Number of laboratories:	50
Arithmetic mean value:	0.114
Median:	0.116
Standard deviation	0.010
Rel. st. deviation (%)	8.634

Results in decreasing order:

126	0.180 (*)	19	0.115		
20	0.142	8	0.114		
112	0.130	135	0.114		
35	0.129	120	0.113		
138	0.126	16	0.113		
22	0.125	27	0.112		
118	0.123	12	0.111		
7	0.123	11	0.111		
1	0.120	121	0.110		
33	0.120	130	0.110		
3	0.120	113	0.110		
104	0.120	114	0.110		
131	0.119	115	0.110		
21	0.119	6	0.109		
13	0.118	23	0.109		
10	0.118	111	0.109		
30	0.118	117	0.108		
26	0.118	40	0.101		
5	0.117	140	0.100		
14	0.117	110	0.100		
36	0.116	109	0.100		
39	0.116	4	0.098		
107	0.116	133	0.097		
15	0.116	38	0.092		
31	0.116	116	0.087		
34	0.116	136	0.050 (*)		

Table 28: Analytical results for calcium in precipitations samples.

Ca
Sample no.: G1
Theoretical value: 0.287
Unit: µg/l

Run 1:
Number of laboratories: 53
Arithmetic mean value: 0.288
Median: 0.283
Standard deviation 0.063
Rel. st. deviation (%) 21.760

Run 2:
Number of laboratories: 49
Arithmetic mean value: 0.288
Median: 0.283
Standard deviation 0.032
Rel. st. deviation (%) 11.054

Results in decreasing order:

104	0.510 (*)	21	0.283
118	0.450 (*)	30	0.281
22	0.386	34	0.280
107	0.359	13	0.280
20	0.358	19	0.280
117	0.331	140	0.280
126	0.330	8	0.279
109	0.330	131	0.278
138	0.322	7	0.278
10	0.310	31	0.277
115	0.310	111	0.275
33	0.310	27	0.273
32	0.300	3	0.273
110	0.300	135	0.271
112	0.300	4	0.270
1	0.300	35	0.270
130	0.300	38	0.266
15	0.300	23	0.262
26	0.292	12	0.260
114	0.290	113	0.260
36	0.290	6	0.260
5	0.290	40	0.242
39	0.288	121	0.220
16	0.288	136	0.200
14	0.283	133	0.136 (*)
120	0.283	116	0.049 (*)
11	0.283		

Ca
Sample no.: G2
Theoretical value: 0.192
Unit: µg/l

Run 1:
Number of laboratories: 53
Arithmetic mean value: 0.203
Median: 0.192
Standard deviation 0.045
Rel. st. deviation (%) 22.266

Run 2:
Number of laboratories: 50
Arithmetic mean value: 0.199
Median: 0.192
Standard deviation 0.028
Rel. st. deviation (%) 14.253

Results in decreasing order:

104	0.410 (*)	14	0.192
114	0.300 (*)	19	0.191
118	0.290	15	0.190
20	0.252	33	0.190
130	0.250	38	0.190
107	0.242	13	0.190
109	0.240	110	0.190
126	0.240	21	0.188
135	0.236	11	0.188
133	0.236	120	0.187
136	0.229	7	0.187
138	0.228	111	0.185
140	0.220	35	0.184
10	0.214	27	0.183
131	0.212	8	0.182
22	0.209	32	0.180
1	0.200	12	0.180
3	0.200	4	0.180
115	0.200	30	0.178
112	0.200	34	0.175
5	0.198	23	0.164
31	0.197	6	0.164
117	0.196	113	0.160
36	0.195	40	0.153
26	0.195	121	0.130
39	0.195	116	0.087 (*)
16	0.192		

Ca
Sample no.: G3
Theoretical value: 0.326
Unit: µg/l

Run 1:
Number of laboratories: 53
Arithmetic mean value: 0.318
Median: 0.322
Standard deviation 0.065
Rel. st. deviation (%) 20.330

Run 2:
Number of laboratories: 49
Arithmetic mean value: 0.320
Median: 0.322
Standard deviation 0.035
Rel. st. deviation (%) 10.801

Results in decreasing order:

107	0.520 (*)	14	0.322
104	0.470 (*)	16	0.320
118	0.400	34	0.320
22	0.390	117	0.319
35	0.363	19	0.317
138	0.362	8	0.314
1	0.360	120	0.314
131	0.351	111	0.312
126	0.350	30	0.308
10	0.350	133	0.308
140	0.350	4	0.307
7	0.342	6	0.306
135	0.341	38	0.304
115	0.340	27	0.304
15	0.340	12	0.300
112	0.340	33	0.290
110	0.340	20	0.290
3	0.332	23	0.286
36	0.332	130	0.280
31	0.332	40	0.270
26	0.330	109	0.260
114	0.330	113	0.250
5	0.329	121	0.240
21	0.329	32	0.220
39	0.328	136	0.123 (*)
11	0.322	116	0.077 (*)
13	0.322		

Ca
Sample no.: G4
Theoretical value: 0.239
Unit: µg/l

Run 1:
Number of laboratories: 53
Arithmetic mean value: 0.241
Median: 0.239
Standard deviation 0.044
Rel. st. deviation (%) 18.260

Run 2:
Number of laboratories: 48
Arithmetic mean value: 0.234
Median: 0.238
Standard deviation 0.028
Rel. st. deviation (%) 11.984

Results in decreasing order:

109	0.380 (*)	21	0.239
107	0.370 (*)	26	0.237
104	0.340 (*)	19	0.236
118	0.330 (*)	31	0.236
126	0.300	120	0.235
140	0.290	34	0.235
10	0.288	30	0.235
35	0.259	8	0.234
138	0.258	13	0.231
7	0.251	111	0.229
1	0.250	27	0.227
115	0.250	135	0.226
15	0.250	131	0.225
112	0.250	11	0.223
130	0.250	12	0.220
32	0.250	4	0.220
38	0.250	20	0.218
117	0.247	23	0.217
3	0.244	6	0.214
36	0.244	40	0.192
39	0.242	113	0.190
5	0.241	22	0.189
33	0.240	136	0.175
16	0.240	121	0.160
114	0.240	133	0.156
110	0.240	116	0.153 (*)
14	0.239		

Table 29: Analytical results for potassium in precipitations samples.

K
Sample no.: G1
Theoretical value: 0.280
Unit: µg/l

Run 1:
Number of laboratories: 52
Arithmetic mean value: 0.278
Median: 0.272
Standard deviation 0.073
Rel. st. deviation (%) 26.327

Run 2:
Number of laboratories: 50
Arithmetic mean value: 0.266
Median: 0.271
Standard deviation 0.035
Rel. st. deviation (%) 13.027

Results in decreasing order:

133	0.700 (*)	22	0.272
109	0.450 (*)	114	0.270
118	0.360	126	0.270
32	0.320	130	0.270
30	0.314	12	0.270
112	0.310	27	0.270
35	0.290	36	0.269
104	0.290	117	0.266
6	0.288	21	0.264
5	0.287	111	0.261
14	0.286	1	0.260
20	0.286	4	0.260
3	0.285	31	0.255
19	0.285	131	0.254
26	0.284	138	0.254
107	0.283	34	0.251
38	0.282	33	0.250
15	0.280	110	0.250
121	0.280	120	0.245
13	0.280	140	0.240
39	0.278	113	0.240
16	0.275	10	0.226
135	0.275	40	0.209
7	0.273	115	0.180
23	0.273	116	0.164
8	0.272	136	0.158

K
Sample no.: G2
Theoretical value: 0.178
Unit: µg/l

Run 1:
Number of laboratories: 52
Arithmetic mean value: 0.180
Median: 0.176
Standard deviation 0.045
Rel. st. deviation (%) 25.239

Run 2:
Number of laboratories: 50
Arithmetic mean value: 0.172
Median: 0.176
Standard deviation 0.024
Rel. st. deviation (%) 13.776

Results in decreasing order:

109	0.390 (*)	7	0.176
116	0.355 (*)	31	0.176
22	0.213	21	0.174
117	0.211	5	0.174
112	0.210	8	0.171
32	0.210	23	0.171
38	0.206	130	0.170
118	0.200	114	0.170
133	0.200	36	0.169
131	0.195	135	0.168
14	0.191	4	0.167
12	0.190	16	0.166
3	0.184	138	0.161
26	0.182	30	0.160
19	0.182	111	0.160
6	0.182	104	0.160
15	0.180	33	0.160
1	0.180	140	0.160
110	0.180	120	0.155
126	0.180	136	0.152
35	0.180	113	0.150
13	0.180	10	0.135
20	0.179	34	0.133
107	0.178	121	0.120
27	0.177	115	0.110
39	0.177	40	0.101

K
Sample no.: G3
Theoretical value: 0.331
Unit: µg/l

Run 1:
Number of laboratories: 52
Arithmetic mean value: 0.313
Median: 0.322
Standard deviation 0.065
Rel. st. deviation (%) 20.879

Run 2:
Number of laboratories: 49
Arithmetic mean value: 0.315
Median: 0.324
Standard deviation 0.038
Rel. st. deviation (%) 12.156

Results in decreasing order:

109	0.590 (*)	104	0.320
32	0.400	114	0.320
22	0.394	12	0.320
20	0.363	36	0.319
118	0.360	131	0.316
112	0.360	14	0.316
35	0.345	21	0.310
5	0.344	4	0.307
126	0.340	130	0.300
38	0.336	1	0.300
3	0.335	111	0.299
6	0.334	23	0.297
19	0.333	34	0.295
26	0.333	30	0.291
107	0.332	33	0.290
39	0.331	120	0.289
7	0.331	113	0.280
31	0.331	140	0.280
110	0.330	138	0.279
15	0.330	10	0.264
27	0.330	121	0.260
117	0.328	40	0.238
16	0.325	136	0.206
13	0.325	115	0.200
135	0.325	116	0.155 (*)
8	0.324	133	0.100 (*)

K
Sample no.: G4
Theoretical value: 0.127
Unit: µg/l

Run 1:
Number of laboratories: 52
Arithmetic mean value: 0.125
Median: 0.124
Standard deviation 0.034
Rel. st. deviation (%) 27.346

Run 2:
Number of laboratories: 50
Arithmetic mean value: 0.120
Median: 0.123
Standard deviation 0.020
Rel. st. deviation (%) 16.884

Results in decreasing order:

116	0.307 (*)	7	0.124
133	0.200 (*)	14	0.123
118	0.160	5	0.122
112	0.160	8	0.121
22	0.157	130	0.120
31	0.141	33	0.120
126	0.140	114	0.120
109	0.140	13	0.120
12	0.140	135	0.119
32	0.140	36	0.119
140	0.140	30	0.118
3	0.133	4	0.117
38	0.132	111	0.113
19	0.131	136	0.111
1	0.130	131	0.111
34	0.130	120	0.111
15	0.129	113	0.110
26	0.129	23	0.104
6	0.129	104	0.100
35	0.129	110	0.100
21	0.127	138	0.092
27	0.126	10	0.091
16	0.125	40	0.077
39	0.125	121	0.076
107	0.124	115	0.070
20	0.124	117	0.068

Table 30: Analytical results for conductivity in precipitations samples.

Cond.
Sample no.: G1
Theoretical value: 43.300
Unit: µS/cm

Run 1:
Number of laboratories: 54
Arithmetic mean value: 40.653
Median: 41.700
Standard deviation 3.525
Rel. st. deviation (%) 8.671

Run 2:
Number of laboratories: 51
Arithmetic mean value: 41.277
Median: 42.000
Standard deviation 2.392
Rel. st. deviation (%) 5.795

Results in decreasing order:

12	45.700	126	41.700
14	45.000	111	41.500
23	45.000	106	41.400
31	44.570	15	41.400
115	44.000	117	41.300
36	43.900	118	41.000
21	43.730	140	40.900
19	43.200	138	40.900
30	43.100	131	40.600
20	43.020	22	40.300
3	42.950	1	40.300
32	42.800	16	39.700
114	42.700	7	39.300
27	42.600	136	39.200
112	42.500	113	38.900
10	42.500	34	38.700
35	42.500	11	38.700
39	42.400	18	38.600
33	42.250	130	37.800
107	42.200	38	37.500
8	42.200	110	37.000
13	42.200	121	37.000
109	42.200	135	35.400
5	42.100	104	35.000
4	42.000	116	33.120 (*)
120	42.000	40	29.000 (*)
6	41.700	24	28.000 (*)

Cond.
Sample no.: G2
Theoretical value: 44.600
Unit: µS/cm

Run 1:
Number of laboratories: 54
Arithmetic mean value: 43.369
Median: 44.450
Standard deviation 3.473
Rel. st. deviation (%) 8.009

Run 2:
Number of laboratories: 51
Arithmetic mean value: 44.059
Median: 44.600
Standard deviation 1.929
Rel. st. deviation (%) 4.379

Results in decreasing order:

12	47.700	107	44.400
31	46.700	32	44.400
36	46.300	33	44.400
3	46.200	6	44.200
21	46.200	5	44.200
23	46.100	117	43.900
20	46.030	106	43.800
115	46.000	138	43.500
18	45.800	15	43.400
19	45.500	140	43.200
114	45.400	131	43.000
30	45.300	118	43.000
10	45.200	111	42.800
104	45.000	121	42.800
38	45.000	34	42.700
35	45.000	22	42.600
120	45.000	11	42.300
27	44.900	16	42.300
39	44.800	7	41.600
14	44.800	136	40.800
109	44.700	113	40.600
112	44.700	130	40.500
13	44.700	110	40.000
126	44.700	135	37.200
4	44.600	116	34.910 (*)
1	44.600	24	30.000 (*)
8	44.500	40	30.000 (*)

Cond.
Sample no.: G3
Theoretical value: 25.700
Unit: µS/cm

Run 1:
Number of laboratories: 54
Arithmetic mean value: 25.472
Median: 25.800
Standard deviation 1.840
Rel. st. deviation (%) 7.225

Run 2:
Number of laboratories: 52
Arithmetic mean value: 25.760
Median: 25.800
Standard deviation 1.116
Rel. st. deviation (%) 4.334

Results in decreasing order:

130	28.500	13	25.800
31	28.030	126	25.700
12	27.600	6	25.700
104	27.000	117	25.700
18	26.880	8	25.700
34	26.800	15	25.700
14	26.600	10	25.630
3	26.500	138	25.600
30	26.500	5	25.600
36	26.500	140	25.500
21	26.430	38	25.500
4	26.300	111	25.500
121	26.300	106	25.400
32	26.300	107	25.300
114	26.300	7	25.200
1	26.300	11	25.200
20	26.240	131	25.200
19	26.200	118	25.000
27	26.100	22	24.500
39	26.100	113	24.500
23	26.100	110	24.000
115	26.000	136	24.000
120	26.000	16	23.700
35	26.000	116	22.600
109	25.900	135	22.200
112	25.800	24	18.000 (*)
33	25.800	40	18.000 (*)

Cond.
Sample no.: G4
Theoretical value: 26.200
Unit: µS/cm

Run 1:
Number of laboratories: 54
Arithmetic mean value: 25.489
Median: 25.900
Standard deviation 1.883
Rel. st. deviation (%) 7.386

Run 2:
Number of laboratories: 52
Arithmetic mean value: 25.777
Median: 25.950
Standard deviation 1.166
Rel. st. deviation (%) 4.524

Results in decreasing order:

114	28.400	34	25.900
31	28.130	138	25.900
12	27.900	5	25.800
104	27.000	6	25.700
23	26.900	112	25.700
18	26.830	107	25.600
36	26.800	140	25.500
39	26.760	131	25.400
3	26.660	11	25.400
21	26.650	15	25.400
14	26.600	111	25.400
30	26.600	106	25.300
20	26.400	7	25.100
27	26.400	32	25.100
1	26.400	22	25.100
19	26.400	110	25.000
121	26.300	118	25.000
4	26.300	13	24.800
10	26.200	38	24.600
8	26.200	113	24.500
35	26.130	16	23.800
33	26.000	136	23.700
109	26.000	130	23.500
115	26.000	116	23.250
117	26.000	135	22.100
120	26.000	24	19.000 (*)
126	25.900	40	17.000 (*)

Table 31: Ratio of the measured to the calculated conductivity in synthetic precipitation samples (G1-G4).

Lab.No.	Measured value / calculated value				Remarks
	G1	G2	G3	G4	
1	1.06	1.04	0.96	0.95	
3	1.06	1.10	1.06	1.06	
4	1.03	1.04	1.03	1.04	
5	1.02	0.98	0.97	0.95	
6	0.95	0.91	0.94	0.91	
7	0.97	0.99	0.98	0.99	
8	1.04	1.04	1.02	1.04	
10	1.01	1.04	0.97	1.00	
11	0.99	1.02	1.17	1.08	$NH4^+$ and K^+ are missing
12	1.06	1.02	1.01	1.05	
13	1.01	1.03	0.99	0.98	
14	1.15	1.10	1.11	1.20	
15	1.01	1.02	1.05	1.01	
16	1.01	1.00	1.00	0.99	
18					Reports only NH_4^+, Cl^-, pH and cond
19	1.30	1.31	1.25	1.29	Cl^- values < LOD
20	1.07	1.10	1.05	1.06	
21	1.06	1.05	1.04	1.04	
22	1.02	1.00	1.00	1.04	
23	1.05	1.00	1.00	1.02	
24	0.77	0.77	0.86	0.92	K^+, Ca^{2+}, Na^+ and Mg^{2+} are missing
26					Cond. is missing
27	1.04	1.04	1.02	1.05	
30	0.90	0.93	0.93	0.90	
31	1.08	1.09	1.10	1.12	
32	1.07	1.03	1.05	0.98	
33	1.01	1.00	1.00	1.00	
34	0.99	1.07	1.11	1.06	
35	1.13	1.04	1.04	1.03	
36	1.08	1.08	0.97	0.96	
38	1.44	1.69	1.19	1.24	
39	1.00	1.00	1.04	1.02	
40					SO_4^{2-} is missing
104	1.03	1.00	1.02	1.02	
107	1.02	1.03	0.99	1.00	
109	1.11	1.11	1.05	1.07	Cl^- values < LOD
110	0.93	0.93	1.00	1.04	
111	1.06	1.05	1.05	1.11	Cl^- values < LOD
112	1.07	1.07	1.04	1.03	Cl^- values < LOD
113	1.13	1.09	1.12	1.11	
114	1.06	1.07	1.05	1.13	
115	1.22	1.26	1.08	1.10	
116	0.80	0.77	0.88	0.90	
117	1.11	1.06	1.07	1.09	Cl^- value missing
118	0.95	0.93	0.92	0.91	
120	0.59	0.95	0.97	1.00	
121	0.91	0.95	1.02	1.02	
126	0.95	1.00	0.85	0.93	
130	0.65	0.67	0.83	0.65	
131	0.92	0.93	0.94	0.95	
133					Cond. is missing
135	0.85	0.84	0.85	0.86	
136	1.16	1.06	1.28	1.08	
138	0.95	0.94	0.97	0.99	
140	1.06	1.05	1.01	1.07	

Table 32: Ratio of equivalent concentration of anions to the equivalent concentration of cation measured in synthetic precipitation samples.

Lab.No.	Measured value / calculated value					Remarks
	G1	G2	G3	G4	Average	
1	1.11	1.05	0.97	0.95	1.02	
3	1.07	1.08	1.03	1.01	1.05	
4	1.06	1.07	1.02	1.04	1.05	
5	1.06	1.03	1.01	0.99	1.02	
6	0.98	0.95	0.96	0.96	0.96	
7	1.04	1.06	1.00	1.01	1.03	
8	1.08	1.09	1.04	1.05	1.06	
10	0.95	1.00	0.97	0.91	0.96	
11	1.33	1.20	1.51	1.18	1.30	$NH4^+$ and K^+ are missing
12	1.06	1.00	1.04	1.03	1.03	
13	0.97	1.10	1.02	1.07	1.04	
14	1.13	1.17	1.11	1.21	1.15	
15	1.00	1.02	1.00	1.00	1.01	
16	1.01	1.02	1.02	1.01	1.01	
17						
18	0.83	0.78	0.74	0.46	0.70	Reports only NH_4^+, Cl^-, pH and cond
19	1.10	1.13	1.07	1.08	1.09	Cl^- values < LOD
20	1.00	1.01	0.99	1.01	1.00	
21	1.05	1.03	1.01	1.01	1.02	
22	0.92	0.89	0.82	0.81	0.86	
23	1.01	0.99	0.99	0.98	0.99	
24	1.54	1.41	1.83	2.08	1.71	K^+, Ca^{2+}, Na^+ and Mg^{2+} are missing
26	1.05	1.06	1.01	1.02	1.03	
27	1.08	1.08	1.04	1.05	1.06	
30	0.88	0.90	0.91	0.87	0.89	
31	1.06	1.06	1.03	1.03	1.05	
32	1.15	1.13	1.15	1.03	1.11	
33	1.06	1.07	1.09	1.08	1.08	
34	1.05	1.11	1.03	1.02	1.05	
35	1.15	1.11	1.02	1.03	1.08	
36	1.06	1.06	0.97	0.94	1.01	
38	1.62	1.74	1.27	1.35	1.50	
39	1.03	1.11	0.91	0.96	1.00	
40						SO_4^{2-} is missing
104	1.17	0.98	0.89	0.92	0.99	
107	1.02	1.11	0.88	0.94	0.99	
109	0.83	0.79	0.70	0.61	0.73	Cl^- values < LOD
110	1.09	1.13	0.94	0.96	1.03	
111	1.13	1.12	0.98	1.05	1.07	Cl^- values < LOD
112	1.00	1.05	0.89	0.91	0.96	Cl^- values < LOD
113	1.19	1.12	1.04	0.99	1.08	
114	1.10	1.11	0.98	0.98	1.04	
115	1.24	1.34	1.01	1.15	1.19	
116	1.08	0.92	0.93	0.98	0.98	
117	1.08	1.05	0.95	1.00	1.02	Cl^- value missing
118	1.00	1.09	0.93	0.94	0.99	
120	0.69	1.04	0.96	1.01	0.93	
121	1.14	1.11	0.94	1.07	1.06	
126	2.46	3.00	1.91	1.96	2.33	
130	2.31	2.51	1.86	1.93	2.15	
131	1.01	1.00	0.90	0.94	0.96	
133	1.73	1.71	1.32	1.44	1.55	
135	1.06	1.04	0.97	0.98	1.01	
136	0.97	0.87	0.96	0.80	0.90	
138	1.03	1.05	0.96	1.00	1.01	
140	1.04	1.05	0.88	0.96	0.98	

Table 33: The ratio of the median values to the theoretical values for all parameters and samples.

Parameter	Sample No.	Median / Expected
SO4-S	G1	1.00
	G2	1.03
	G3	1.02
	G4	1.00
NO3-N	G1	1.00
	G2	0.99
	G3	0.99
	G4	0.99
NH4-N	G1	1.02
	G2	1.00
	G3	0.99
	G4	0.99
pH (calc.From H+)	G1	0.89
	G2	0.93
	G3	0.96
	G4	0.92
H	G1	1.05
	G2	1.11
	G3	1.30
	G4	1.25
Mg	G1	0.98
	G2	1.01
	G3	0.98
	G4	1.00
Na	G1	0.98
	G2	0.97
	G3	0.98
	G4	0.96
Cl	G1	0.97
	G2	0.98
	G3	0.98
	G4	0.96
Ca	G1	0.99
	G2	1.01
	G3	0.99
	G4	1.00
K	G1	0.97
	G2	0.99
	G3	0.97
	G4	0.98
Cond	G1	0.96
	G2	1.00
	G3	1.00
	G4	0.99

Table 34: Analytical methods used for the determination of chemical constituents in precipitation samples.

Constituents	Methods	Laboratory
SO_4	1. Thorin	18
	2. Ion chromatography	1, 3, 4, 5, 6, 7, 8, 10, 11, 12, 13, 14, 15, 16, 19, 20, 21, 22, 23, 24, 26, 27, 31,32, 33, 34, 35, 36, 38, 104, 107,110, 111, 114, 115, 116, 118, 126, 130, 131, 133, 135, 136, 138, 140
	3. Capillary electrophoresis	39
	4. ICP-AES	109, 112, 113, 117
	5. FIA	121
NO_3	1 Griess after Cd-red.	112,117
	2 Ion chromatography	1, 3, 4, 5, 6, 7, 8, 10, 11, 12, 13, 14, 15, 16, 19, 20, 21, 22, 23, 24, 26, 27, 31,32, 33, 34, 35, 36, 38, 107,110, 113, 114, 115, 116, 118, 126,130, 131, 133, 135, 136, 138, 140
	3 UV-method/Photometric	40, 104,
	4 Capillary electrophoresis	39
	5 FIA	109, 111, 121
NH_4	1 Indophenol	10, 19, 20, 32, 33, 34, 39, 40, 112, 114, 116, 117, 126, 140
	2 Berthelot reaction, salycilate	26, 118,
	3 Ion chromatography	1, 5, 6, 7, 8, 12, 13, 15, 21, 22, 23, 24, 31, 35, 36, 107,113, 115, 131,135,136
	4 Flow injection analysis (FIA)	14, 27, 109, 111, 121
	5 Chloramin T	16
	6 Nessler method	18,
	7 Kjeldahl	
	8 Photometry	3, 4, 104, 110,114, 133
H^+	1 Acidimetric titration	14, 126
	2 Alkali titration to spec. pH	6,
Mg	1 Atomic absorption (AAS)	3, 4, 10, 16, 19, 22, 26, 27, 33, 34, 38, 39, 40, 116, 133
	2 Ion chromatography	1, 5, 6, 7, 8, 12, 13, 15, 20, 21, 23, 31, 35, 36, 107,113, 114, 126, 130, 131, 135, 136, 138, 140
	3 ICP-AES	11, 104, 109, 111, 112, 115, 117, 118, 121
	4 ICP-MS	14,
Na	1 AES	32, 33, 38, 39, 116, 133
	2 AAS	3, 4, 10, 16, 19, 26, 27, 34, 40,
	3 ICP-AES	11, 104, 109, 110,111, 112, 115, 117,118, 121
	5 Ion chromatography	1, 5, 6, 7, 8, 12, 13, 15, 20, 21, 22, 23, 31, 35, 36, 107, 113, 114, 126, 130, 131, 135, 136, 138, 140
	6 ICP-MS	14
Cl	1 Mercury thiocyanate-iron	18, 117, 40
	2 Ion chromatography	1, 3, 4, 5, 6, 7, 8, 10, 11, 12, 13, 14, 15, 16, 19, 20, 21, 22, 23, 24, 26, 27, 31,32, 33, 34, 35, 36, 38, 104, 107,110, 111, 113, 114, 115, 116, 118, 126,130, 131, 133, 135, 136, 138, 140
	3 Capillary electrophoresis	39
	4 Potensiometric method	109, 112
	5 FIA	121
Ca	1 AAS	3, 4, 10, 16, 19, 22, 26, 27, 33, 34, 38, 39, 40, 116, 133
	2 ICP-AES	11, 104, 109,110, 111, 112, 115,117, 118, 121
	3 Ion chromatography	1, 5, 6, 7, 8, 12, 15, 20,21, 23, 31, 35, 36, 107, 113, 114, 126, 130, 131, 135, 136, 138, 140
	6 AES	32,
	7 ICP-MS	14
K	1 AAS	3, 4, 10, 16, 19, 26, 27, 33, 34, 35, 40,
	2 Ion chromatography	1, 5, 6, 7, 8, 12, 13, 15, 20, 21, 22, 23, 31, 35, 36, 107, 113, 114, 126,130, 131, 135, 136, 138, 140
	3 AES	32, 39, 116, 133
	4 ICP-AES	11, 104, 109, 110,111, 112, 115, 117, 118, 121,
	5 ICP-MS	14

Table 35: Relative random and systematic errors obtained by the different laboratories in the analysis of each parameter in the precipitation samples.

Lab. no.	SO_4^{2-}		NO^{3-}		NH_4^+		Mg^{2+}		H^+ calc	
	Random error %	Systematic error %	Random error %	Systematic error %	Random error %	Systematic error %	Random error %	Systematic error %	Random error %	Systematic error %
1	2	0	1	0	2	-8	8	0	13	-1
3	2	1	2	-2	3	2	1	4	5	-9
4	2	2	0	-1	1	-1	4	-14	5	-7
5	1	2	1	1	2	-1	0	1	6	2
6	1	0	1	-1	1	2	1	-8	6	0
7	1	1	1	-1	1	0	2	4	5	-9
8	1	2	1	1	1	-2	1	-2	5	-8
10	3	-4	1	-4	2	-2	1	1	4	1
11	2	-4	2	-6			2	-1	2	-3
12	1	1	2	4	2	-3	3	-4	5	5
13	3	4	1	2	4	1	1	2	7	-7
14	2	6	1	-1	5	-8	2	-1	6	-21
15	1	-2	1	-4	0	-3	3	3	3	-7
16	3	-2	1	-5	2	-3	1	-3	3	0
18	12	-28			65	-1			3	6
19	3	-5	1	-4	2	1	1	0	10	-36
20	1	0	1	1	2	3	12	35	6	-11
21	2	1	1	-1	1	0	0	2	4	-3
22	2	-11	2	-8	6	4	6	7	5	-7
23	2	-2	1	0	4	4	1	-5	4	4
24	1	-7	3	-7	6	-3			6	-10
26	1	0	1	-1	1	0	1	1	5	-9
27	2	2	1	1	1	0	1	-3	5	-7
30	2	-2	1	-6	6	7	6	-2	2	20
31	1	1	1	0	6	3	1	1	3	-8
32	4	4	1	0	3	-4			6	-7
33	2	4	1	3	6	8	3	3	4	-3
34	1	-1	1	-3	4	5	4	0	7	-14
35	4	3	1	3	3	4	6	5	11	-8
36	1	0	1	-1	2	-1	1	0	9	-1
38	2	7	2	4	4	0	1	-21	30	-60
39	5	1			2	-4	1	0	2	-2
40			11	14	8	73	5	-11	14	-56
104	1	-2			3	4	3	3	22	1
106									7	-6
107	3	3	1	-1	2	2	8	-7	4	-7
109	3	-4	3	-37	9	82	19	-10	8	-18
110	3	-2	3	-6	6	-12	4	-13	4	-6
111	2	5	2	-7	2	0	1	-5	5	-15
112	1	-1	2	-4	2	4	3	12	5	-10
113	3	-14	2	5	4	-8	7	-4	9	-23
114	3	4	1	3	2	3	3	-4	6	-11
115	5	3	3	2	2	-8	1	-5	15	-23
116	2	0	1	2	12	14	28	-15	2	0
117	3	-3	2	-5	1	-2	3	-5	8	-10
118	5	7	2	2	2	-5	4	6	4	1
120	3	7	2	0	3	0	1	-1	58	8
121	6	8	2	0	2	1	3	-1	6	0
126	45	174	7	0	2	-3	7	59	21	-50
130	55	207	2	0	1	-1	6	-5	5	-2
131	1	3	2	-2	1	1	1	3	1	5
133	17	24	14	30	7	-15	7	-14	11	-26
135	1	2			1	-1	4	6	4	-3
136	3	-1	11	-77	27	-30	33	-50	7	-12
138	2	5	1	1	12	-5	1	10	5	2
140	2	-5	2	-2	2	1	10	-13	8	-14

Table 35, cont.

Lab. no.	Na^+		Cl^-		Ca^{2+}		K^+		Cond.	
	Random error %	Systematic error %	Random error %	Systematic error %	Random error %	Systematic error %	Random error %	Systematic error %	Random error %	Systematic error %
1	5	6	2	0	5	5	5	-5	4	0
3	1	-9	1	0	3	2	0	2	2	2
4	1	6	3	-5	1	-7	2	-7	2	0
5	0	0	2	1	1	1	3	1	1	-1
6	2	-2	1	-6	1	-10	1	2	2	-1
7	1	1	2	-3	4	1	1	-1	4	-6
8	0	-1	1	-1	1	-3	0	-3	1	0
10	2	-7	2	-25	4	9	6	-21	2	0
11	1	-8	3	-15	2	-2	36	0	5	-5
12	1	-6	2	0	2	-9	4	0	2	6
13	2	-1	1	-1	1	-2	2	-1	2	-1
14	5	-4	3	-5	1	-1	5	0	2	2
15	2	-1	2	-4	3	5	1	0	2	-3
16	1	-2	7	-10	1	0	2	-2	2	-7
18			16	2					7	2
19	1	-2	6	-10	1	-2	1	2	1	1
20	1	-1	2	-12	17	7	6	2	2	1
21	1	-1	1	-1	1	-1	4	-4	1	2
22	13	21	12	-26	23	16	13	14	2	-5
23	1	-9	7	-17	3	-10	5	-7	2	3
24			5	-10					9	0
26	1	0	1	0	1	1	0	1		
27	1	-2	1	0	2	-5	2	0	1	1
30	2	-1	3	-3	2	-4	13	-6	1	2
31	4	-8	1	1	3	0	7	0	1	6
32	5	17	13	7	19	0	10	16		
33	5	-10	5	11	9	0	6	-10	1	-1
34	1	0	4	-7	2	-2	9	-14	7	-3
35	1	-3	1	-3	8	2	2	3	1	0
36	1	1	1	-3	0	2	1	-4	1	2
38	8	-14	3	0	5	-4	5	2	7	
39	1	0	10	-5	0	1	0	-1	2	1
40	7	-15	12	26	3	-18	8	-32	8	-34
104	3	-5	4	-7	19	69	7	-6	11	2
106									2	-3
107	0	0	4	-4	23	39	1	0	1	-1
109	11	12	6	-14	32	17	44	83	1	0
110	2	-4	11	13	3	3	6	-6	6	-9
111	6	-16	13	-7	1	-4	3	-8	2	-4
112	1	1	11	-12	1	5	1	14		
113	2	-14	8	14	8	-16	6	-15	4	-8
114	1	-2	1	2	17	1	1	-4	3	2
115	7	-21	5	18	2	5	13	-37	2	1
116	34	-13	3	-10	25	-66	63	13	8	-18
117	7	-10	4	-19	8	2	16	-4	2	-1
118	4	7	9	8	14	36	10	14	2	-4
120	1	-7	11	6	1	-2	5	-13	2	0
121	13	-1	8	-23	4	-28	13	-24	8	-3
126	1	4	4	-5	6	17	4	2	2	0
130	0	-1	2	-7	16	5	4	-4	10	-10
131	3	-3	3	-12	6	2	8	-7	3	-4
133	16	-23	57	41	31	-19	116	21		
135	2	-7	3	-16	9	0	1	-3	5	-17
136	3	-22	4	-3	38	-29	19	-32	3	-9
138	4	-8	6	-15	3	14	6	-13	3	-2
140	13	1	5	13	9	10	11	-13	3	-3

Appendix 2

Figures

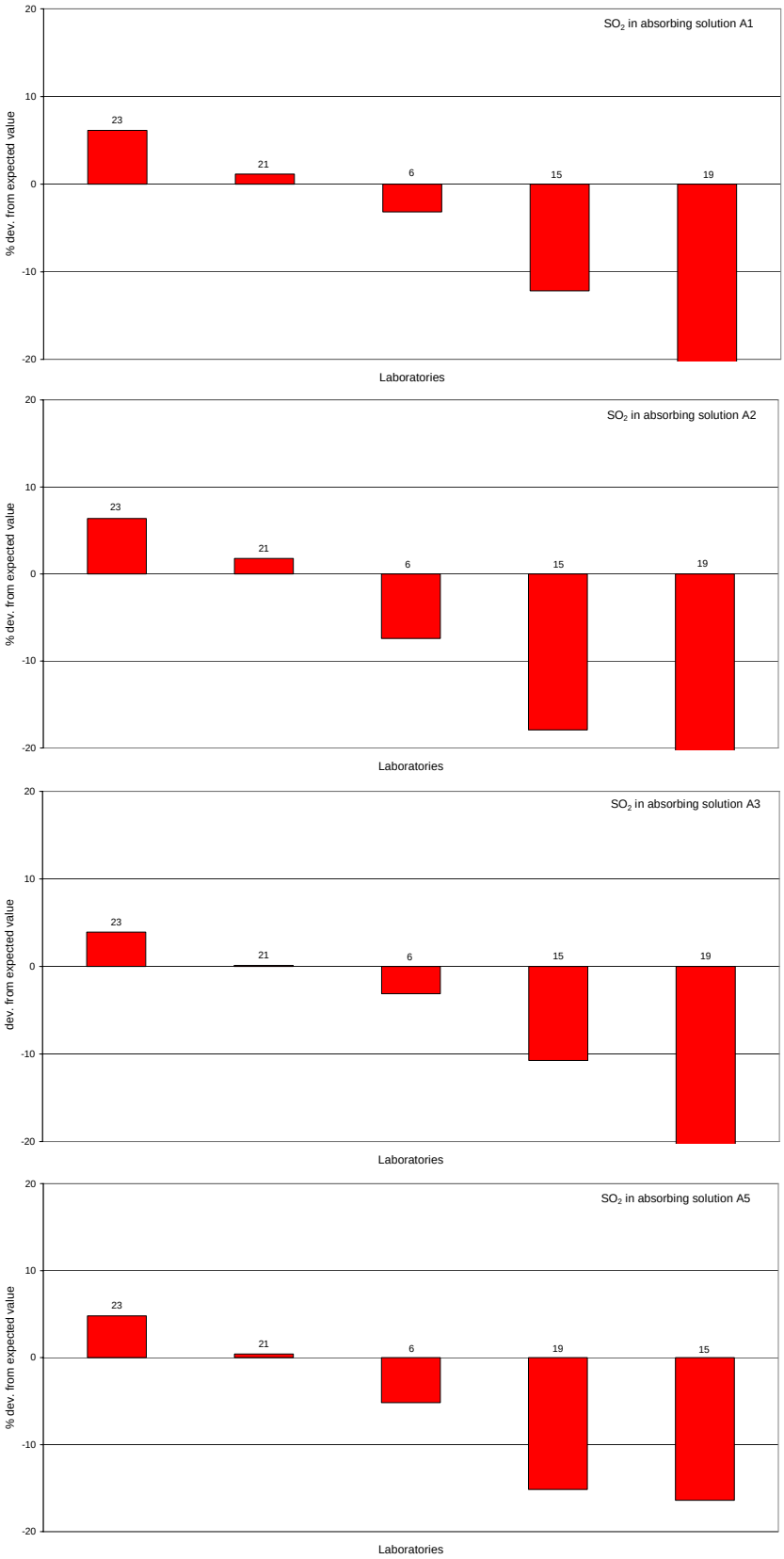

Figure 2: SO_2 in absorbing solution.

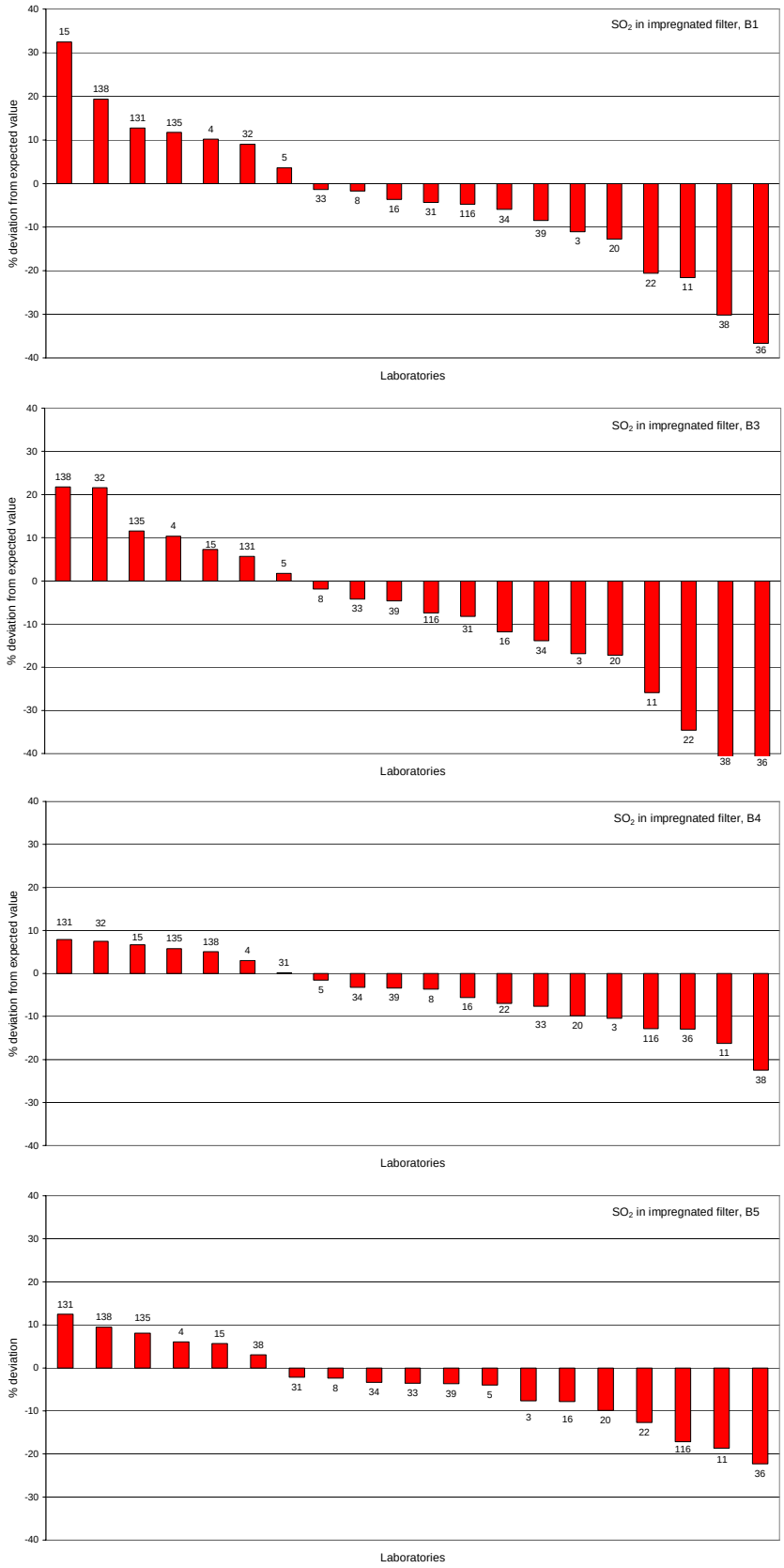

Figure 3: SO_2 in impregnated filter.

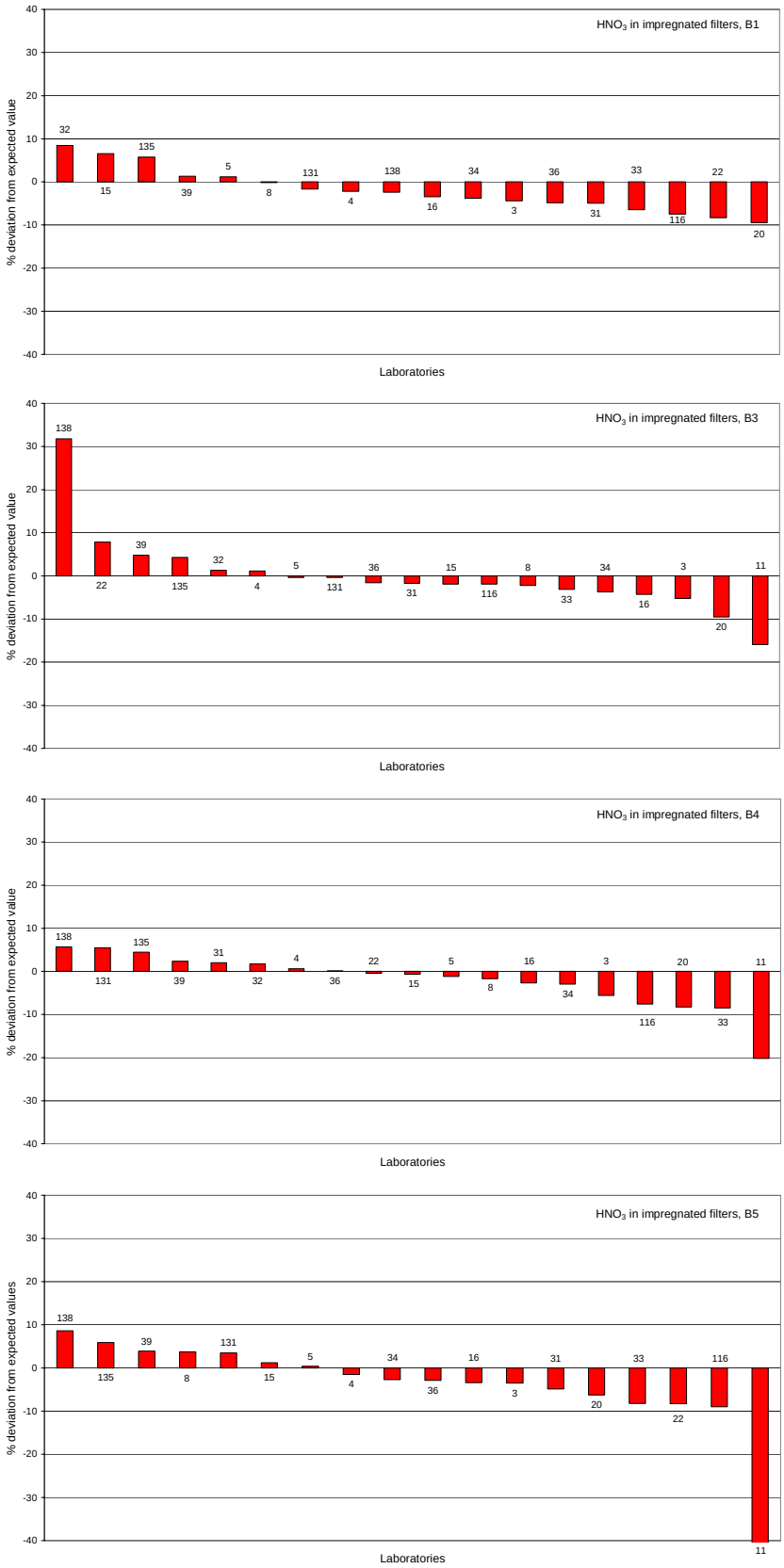

Figure 4: HNO_3 in impregnated filter.

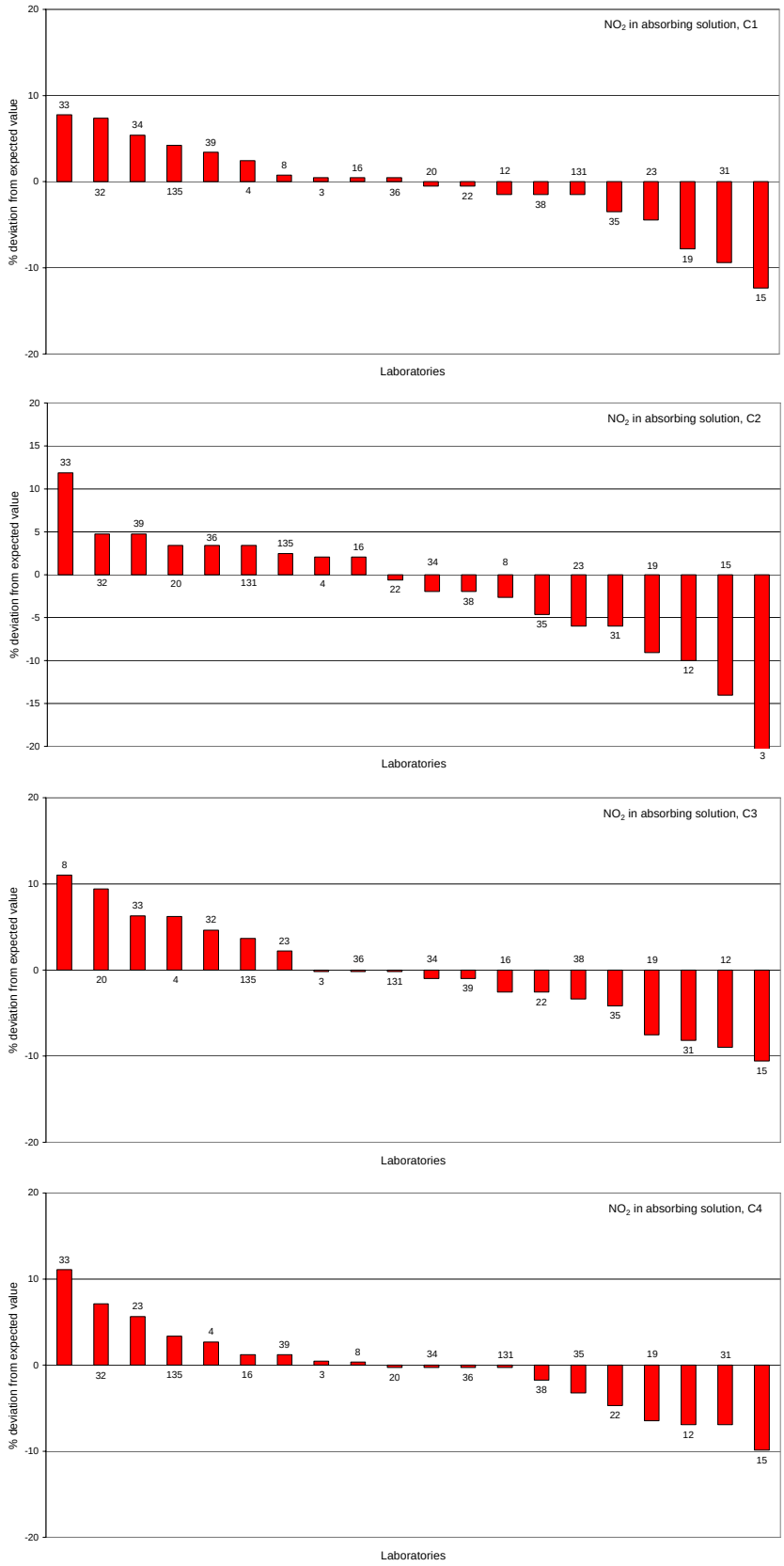

Figure 5: NO_2 in absorbing solution.

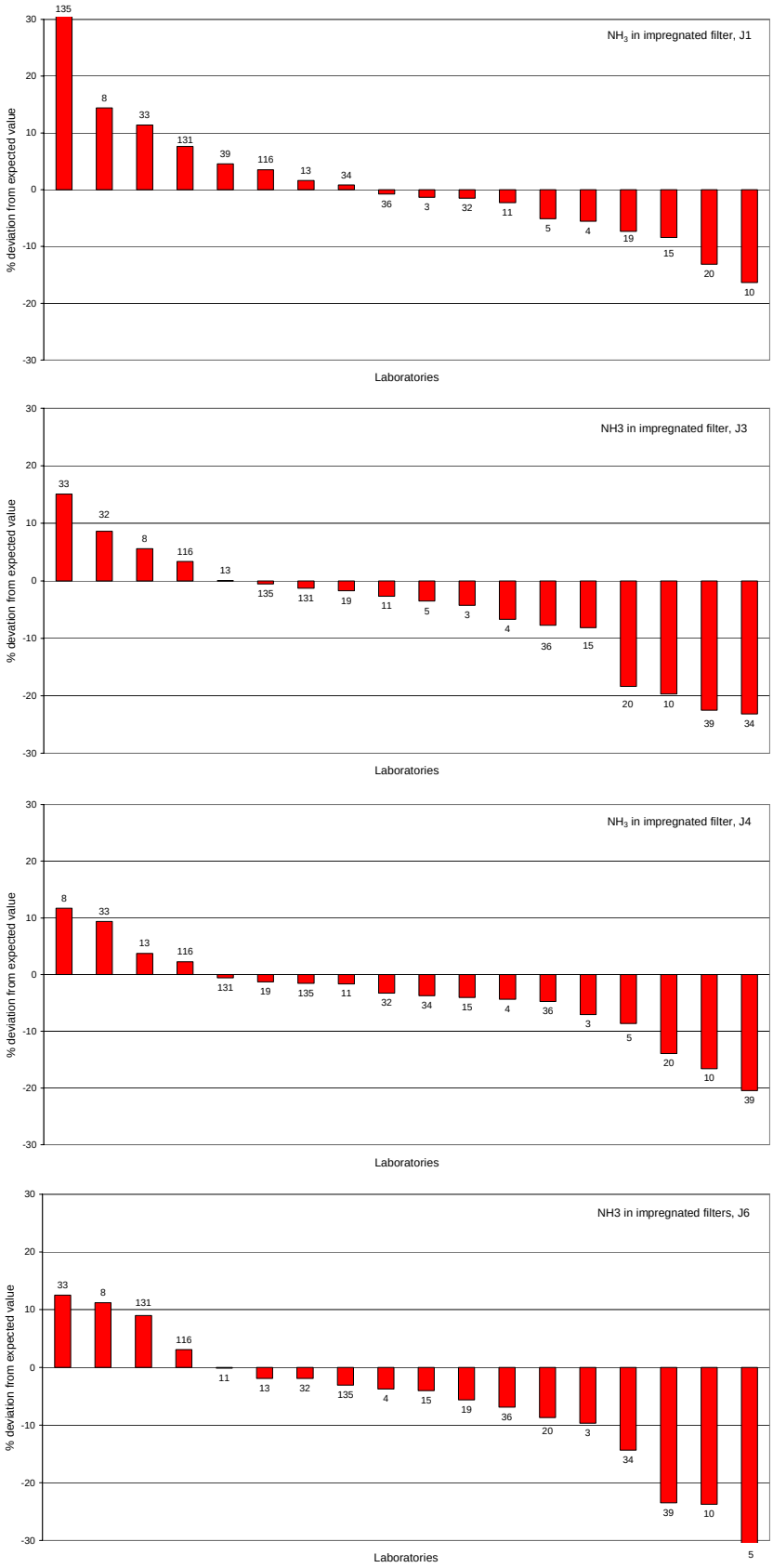

Figure 6: NH_3 in impregnated filter.

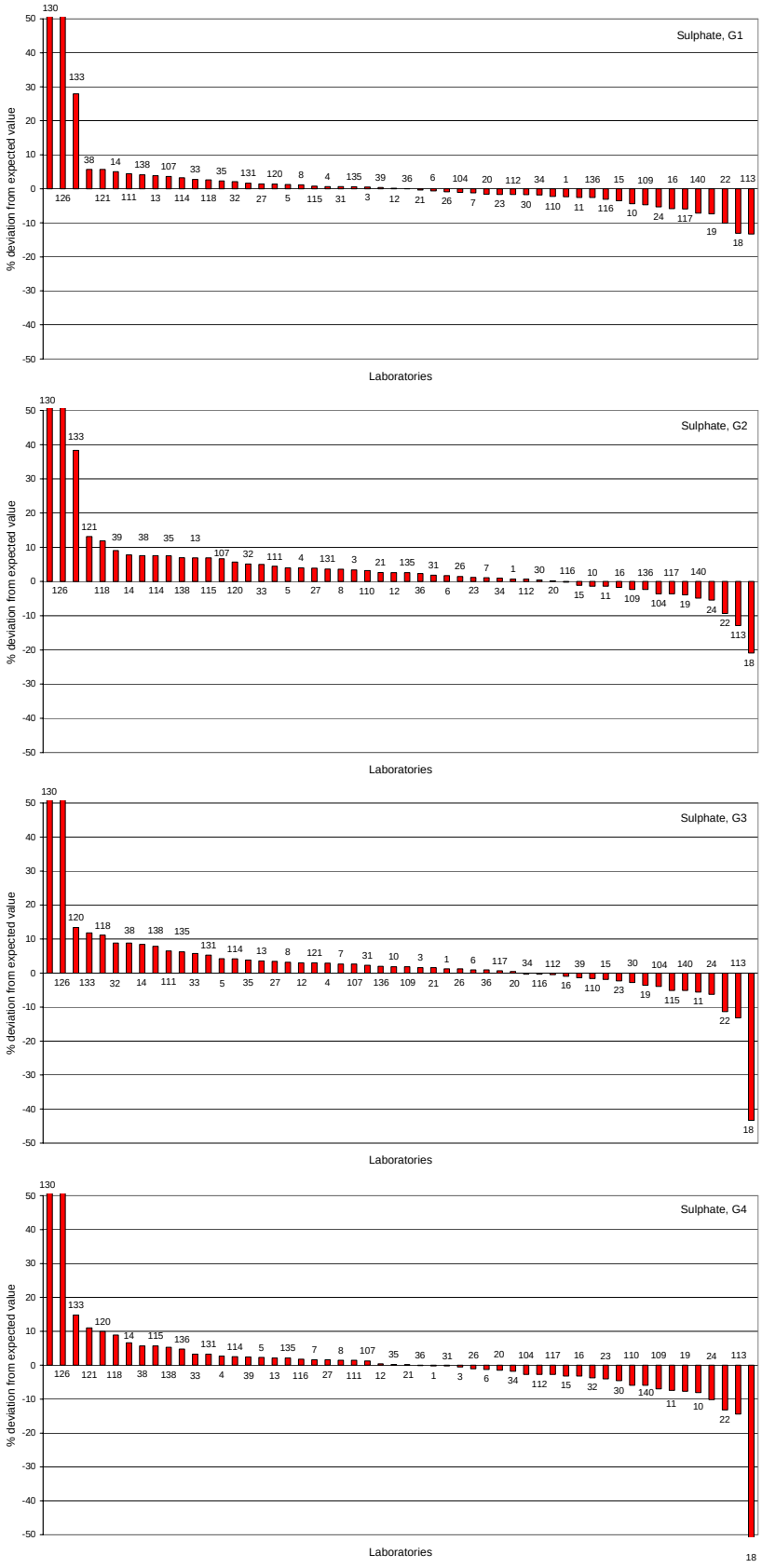

Figure 7: Percent deviation from theoretical value for sulphate.

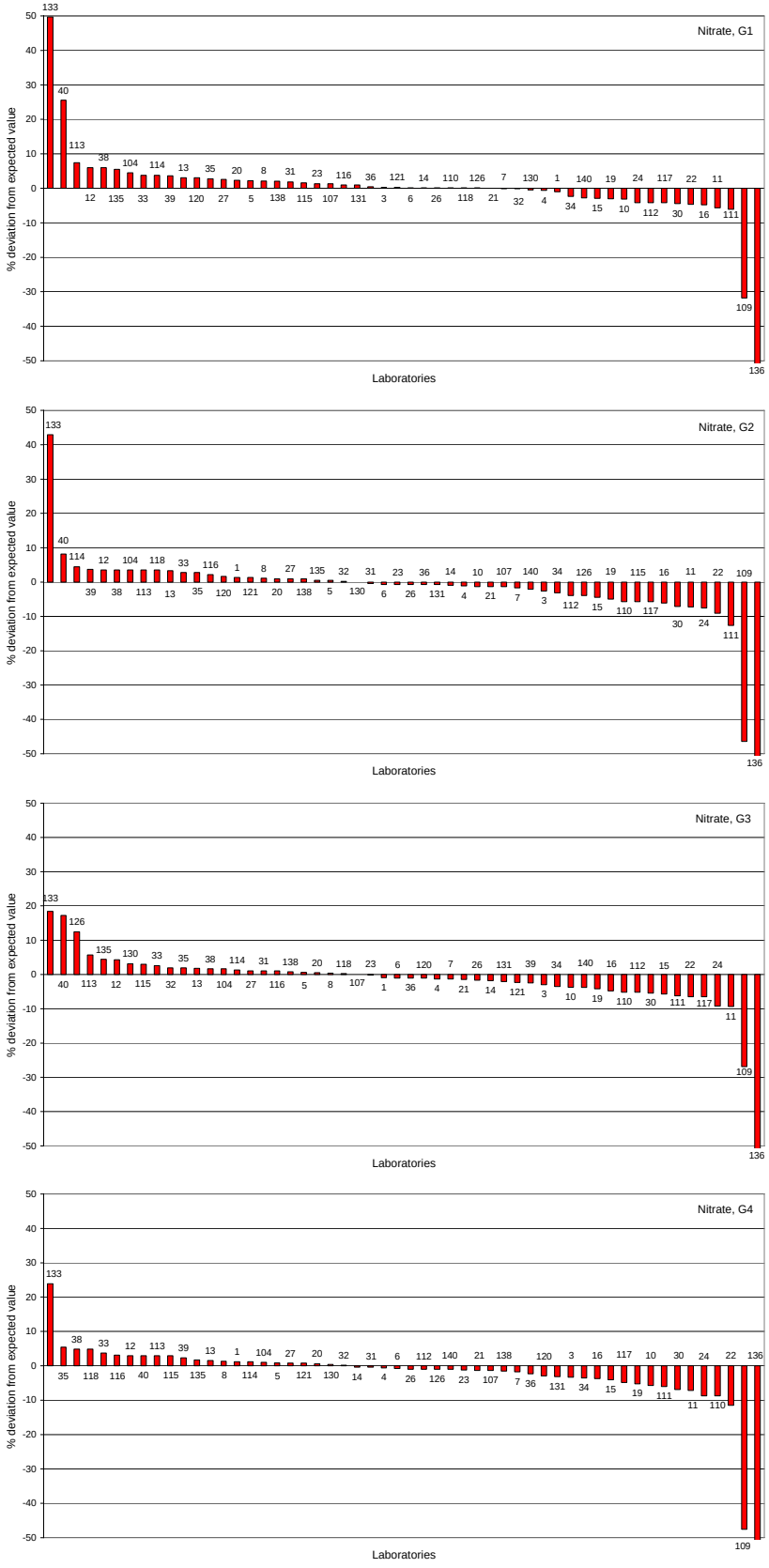

Figure 8: Percent deviation from theoretical value for nitrate.

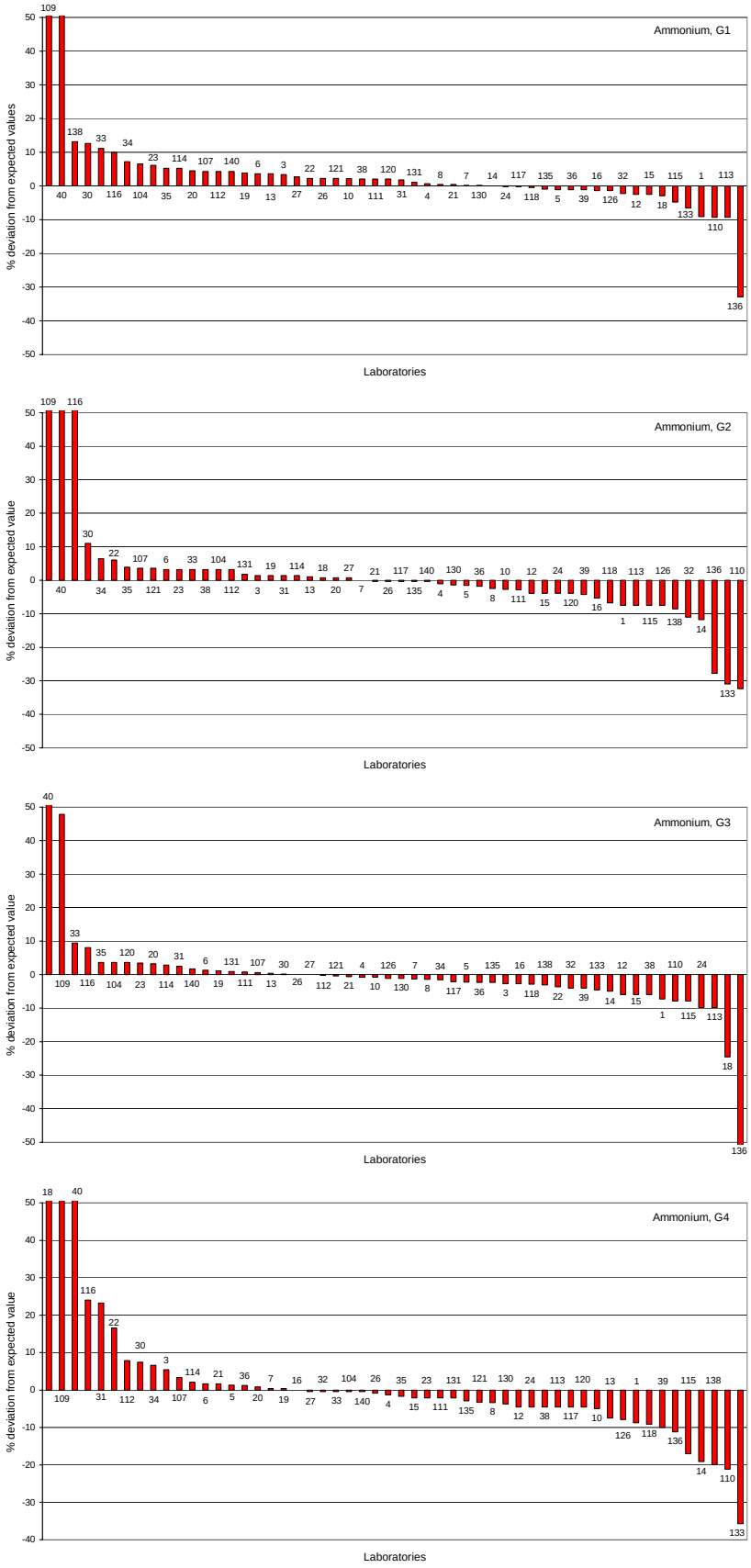

Figure 9: Percent deviation from theoretical value for ammonium.

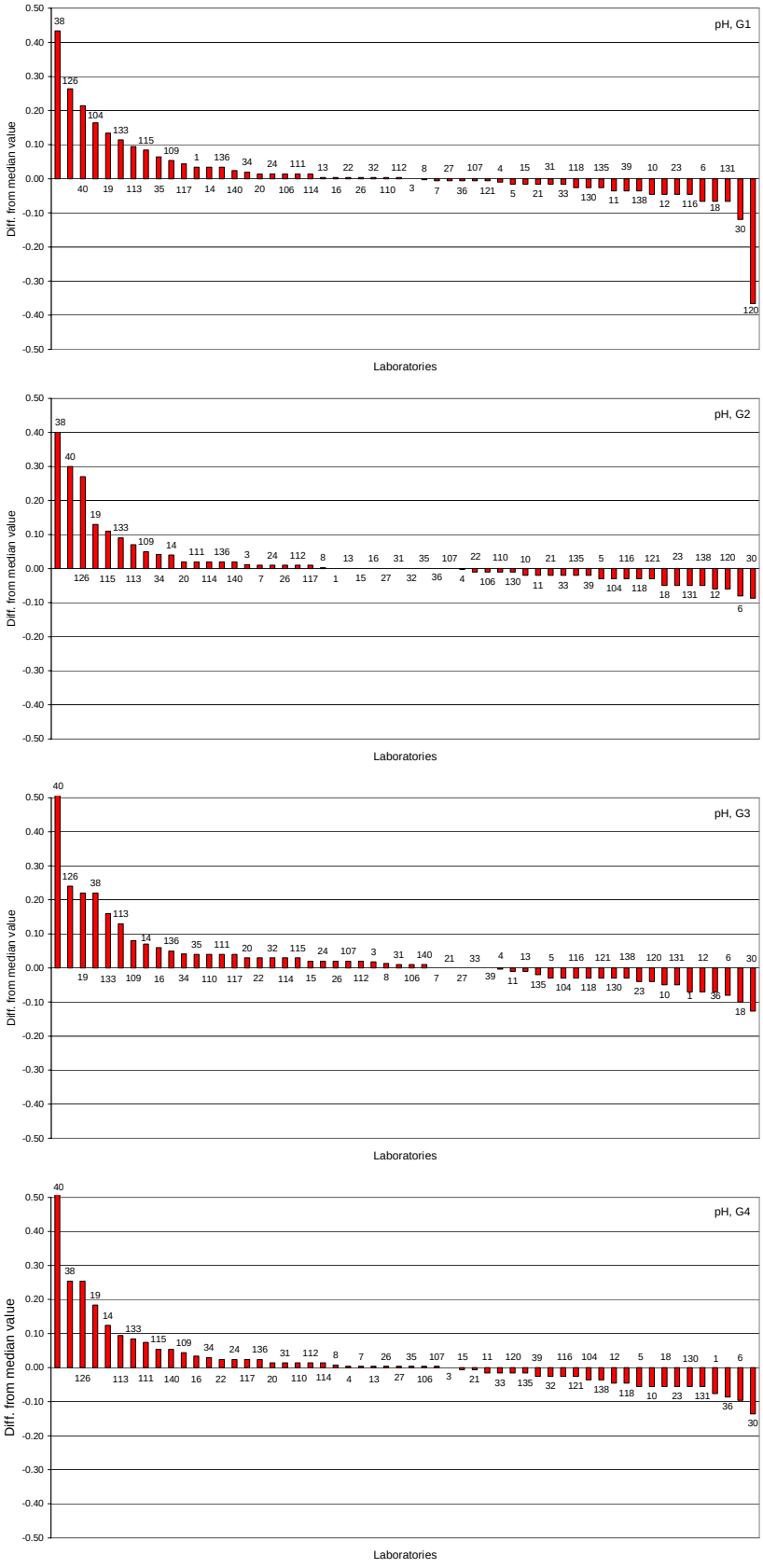

Figure 10: Percent deviation from theoretical value for pH.

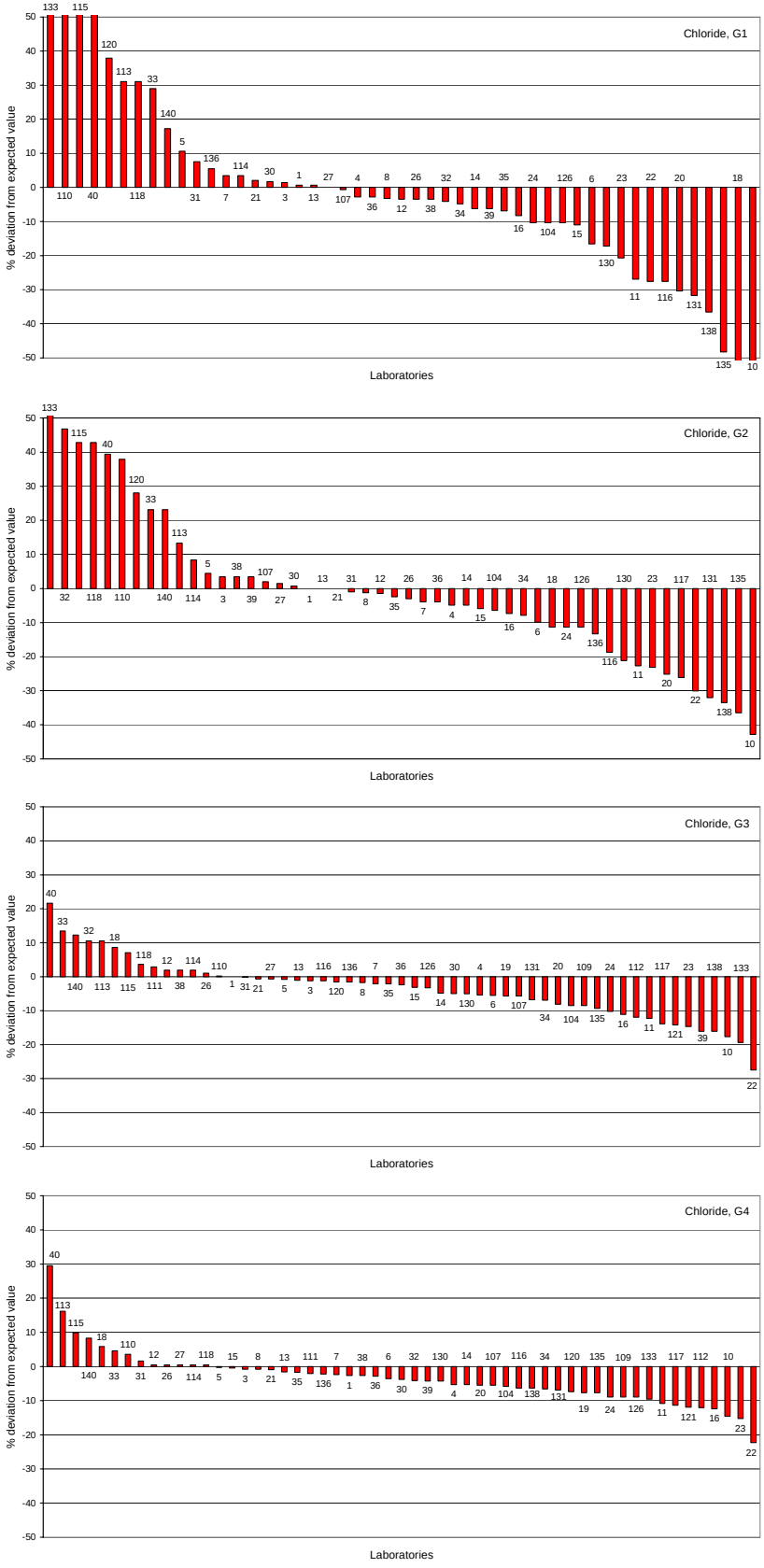

Figure 11: Percent deviation from theoretical value for chloride.

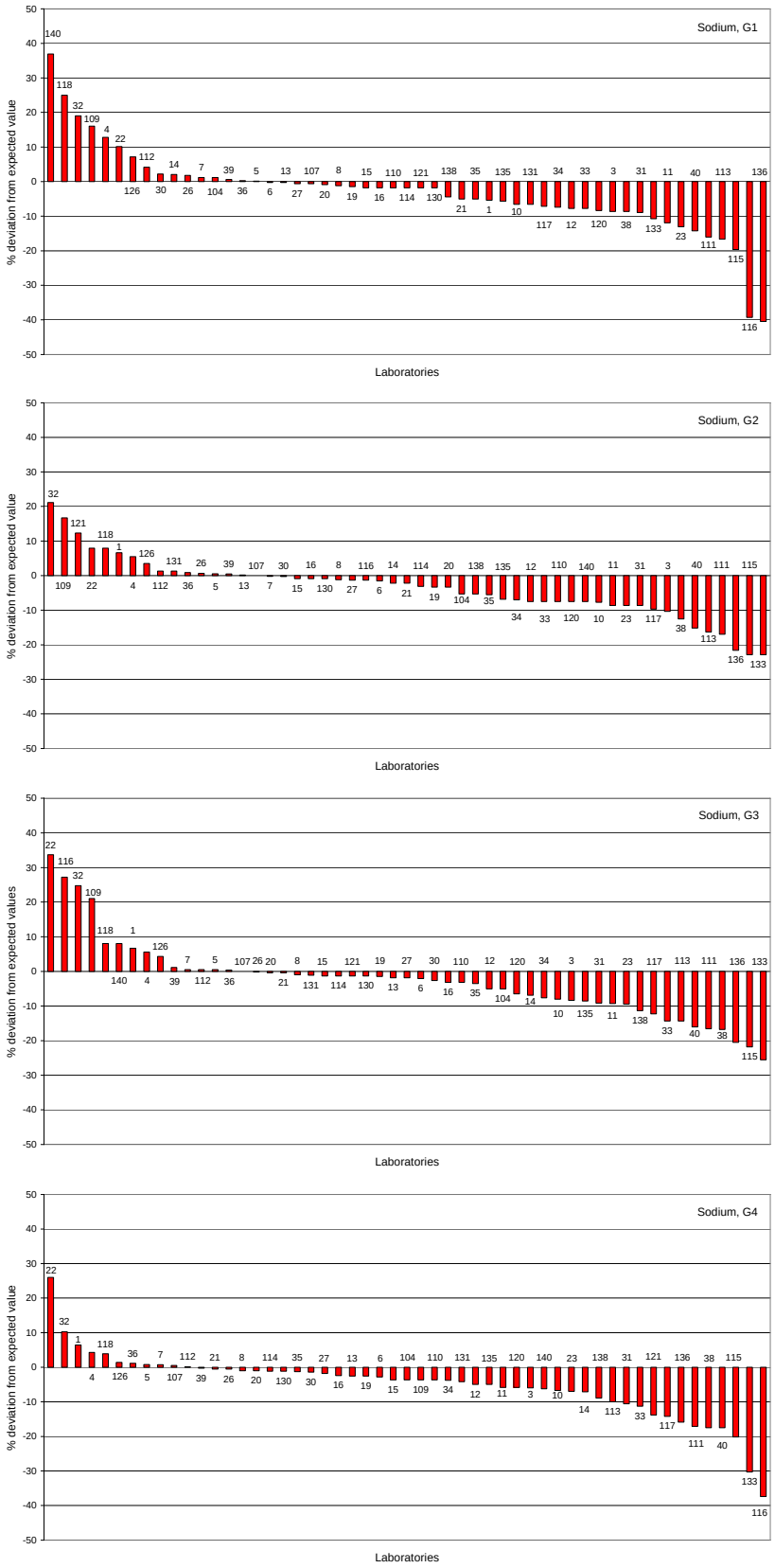

Figure 12: Percent deviation from theoretical value for sodium.

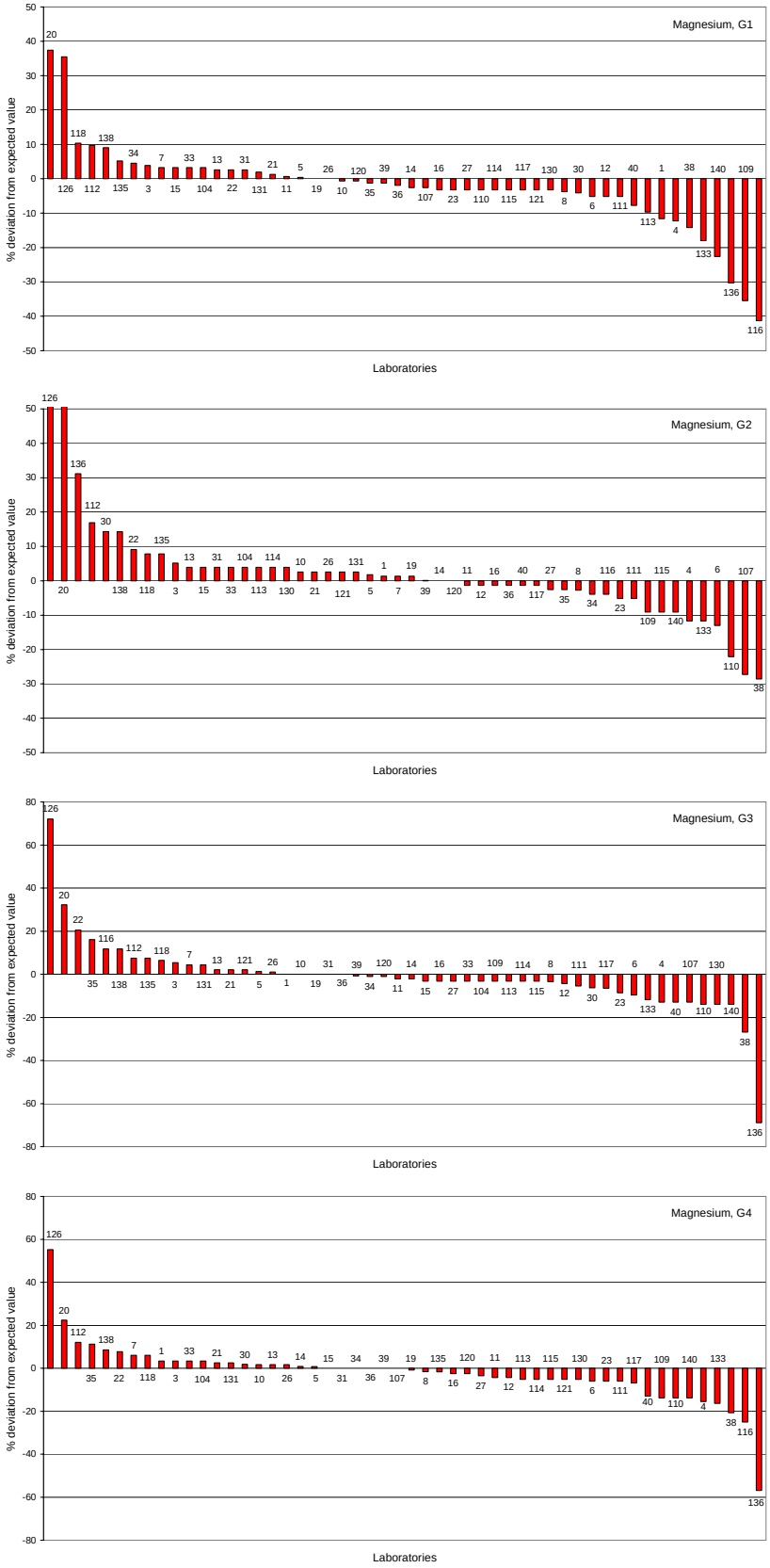

Figure 13: Percent deviation from theoretical value for magnesium.

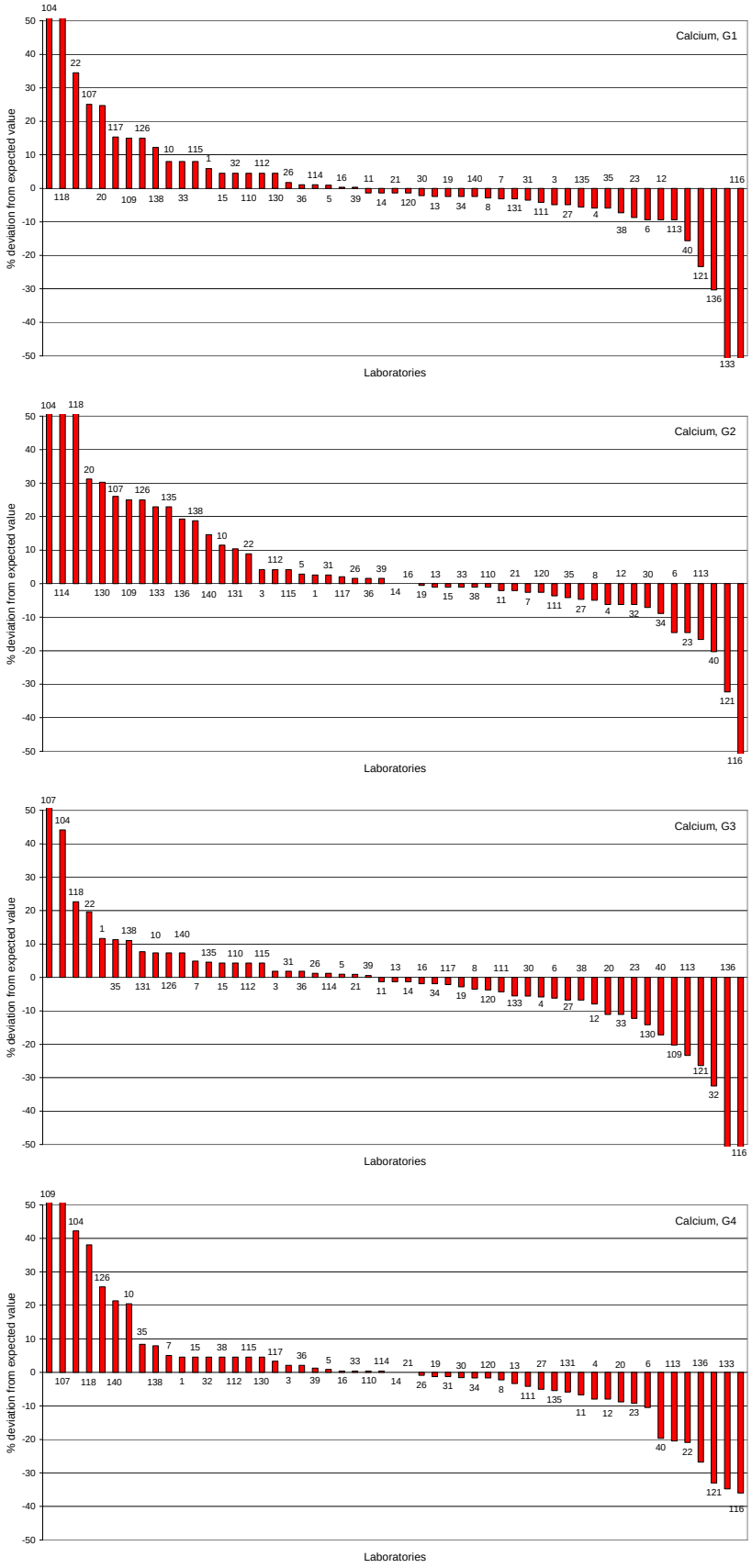

Figure 14: Percent deviation from theoretical value for calcium.

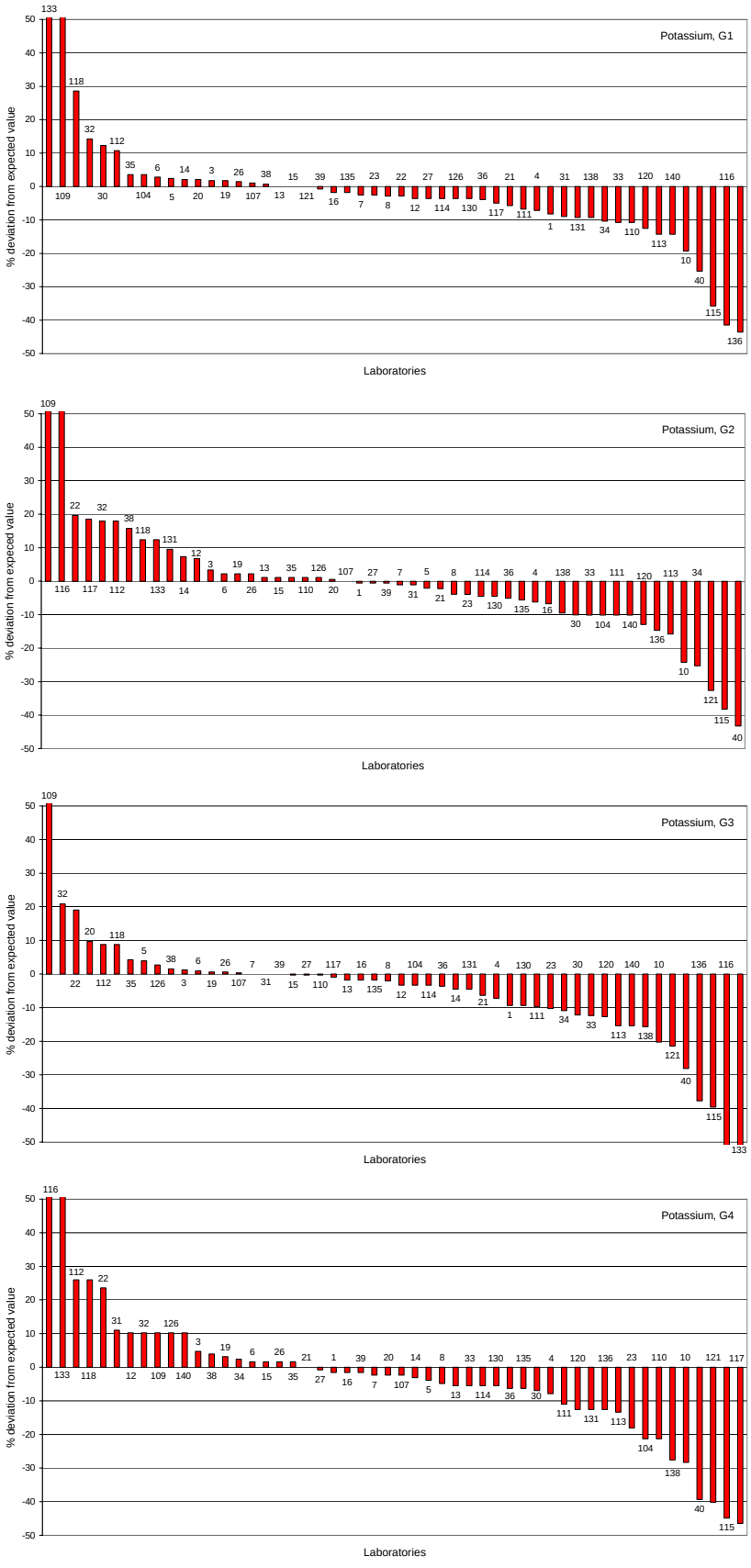

Figure 15: Percent deviation from theoretical value for potassium.

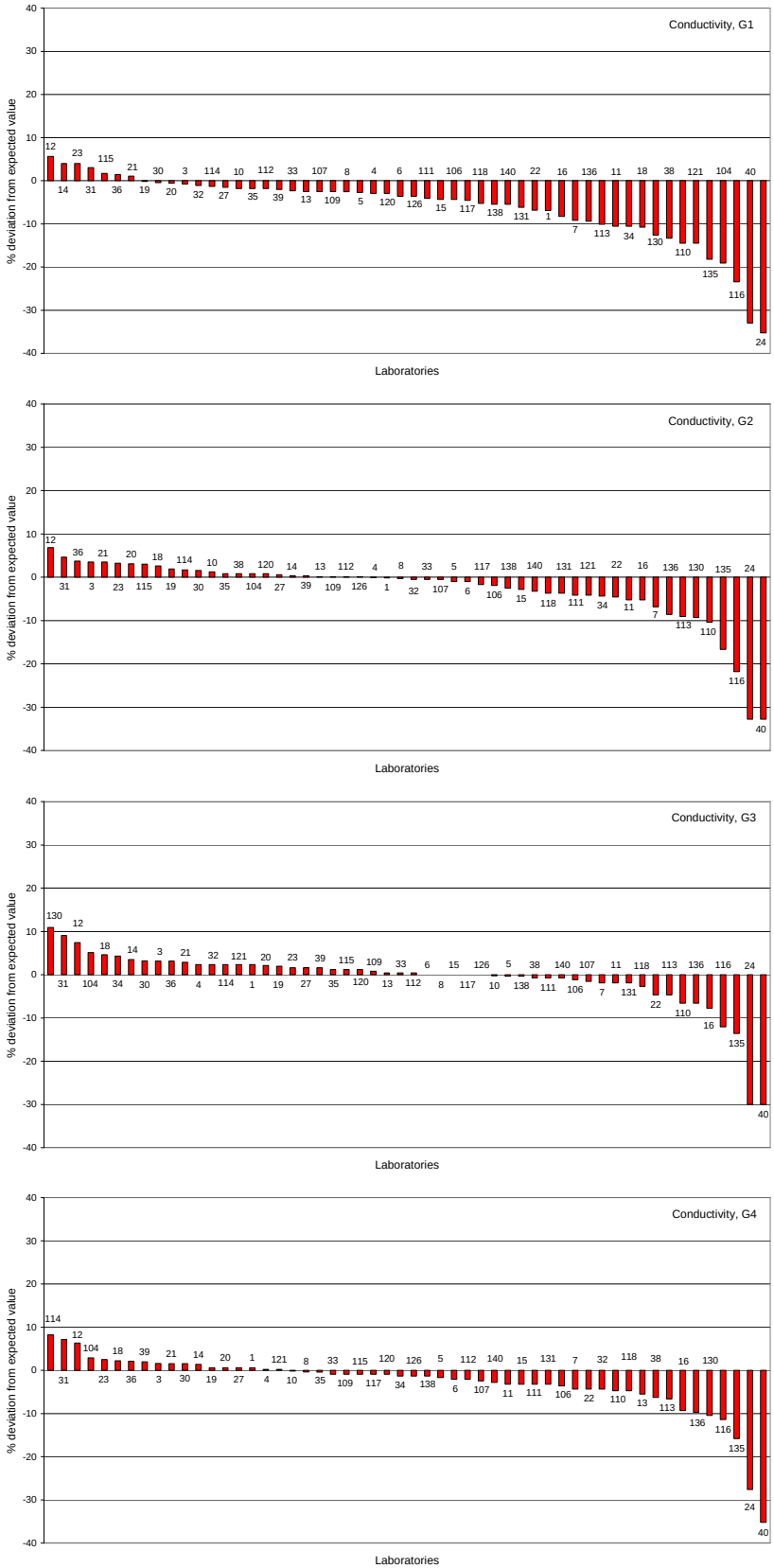

Figure 16: Percent deviation from theoretical value for conductivity.

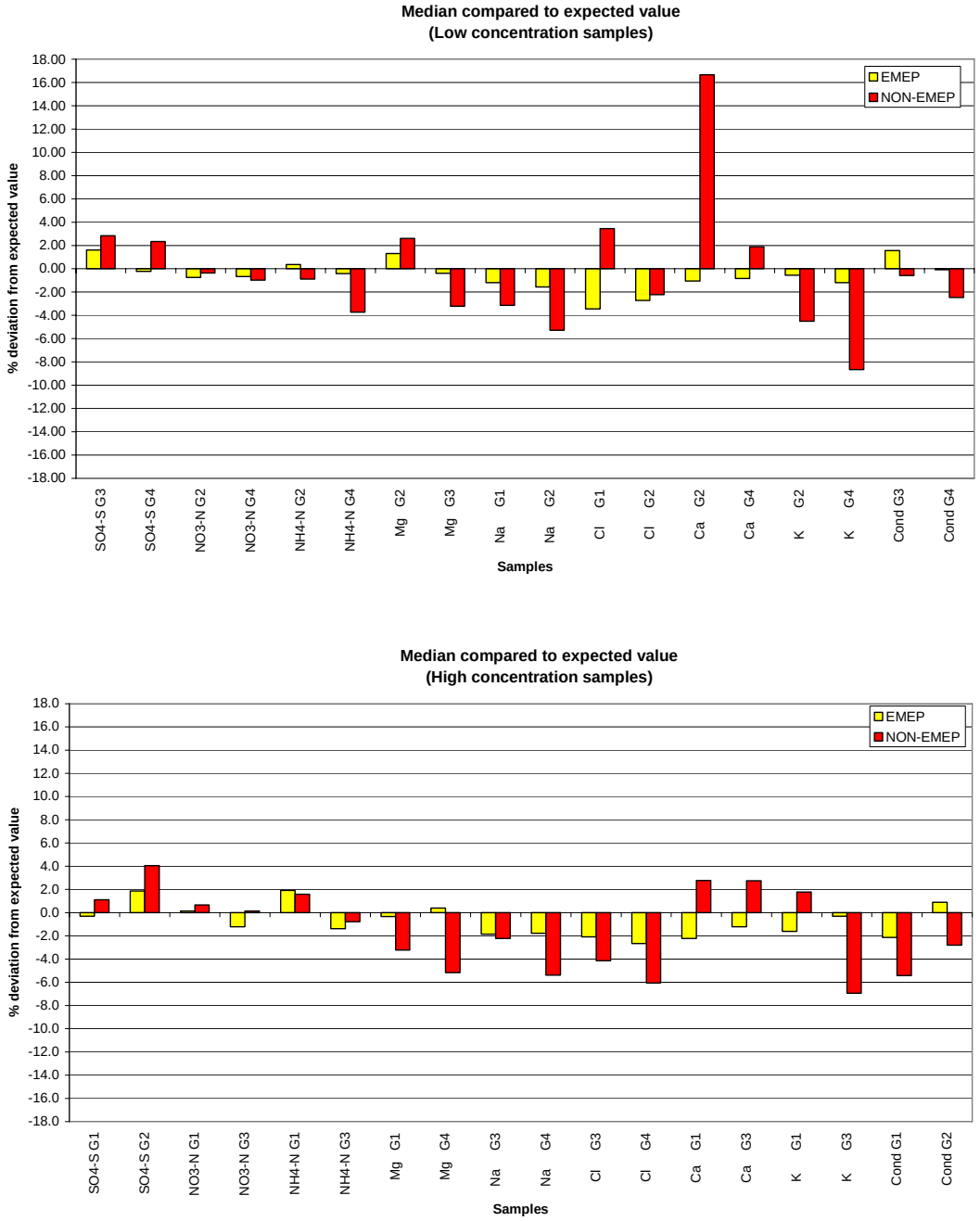

Figure 17: The median compared to theoretical value.

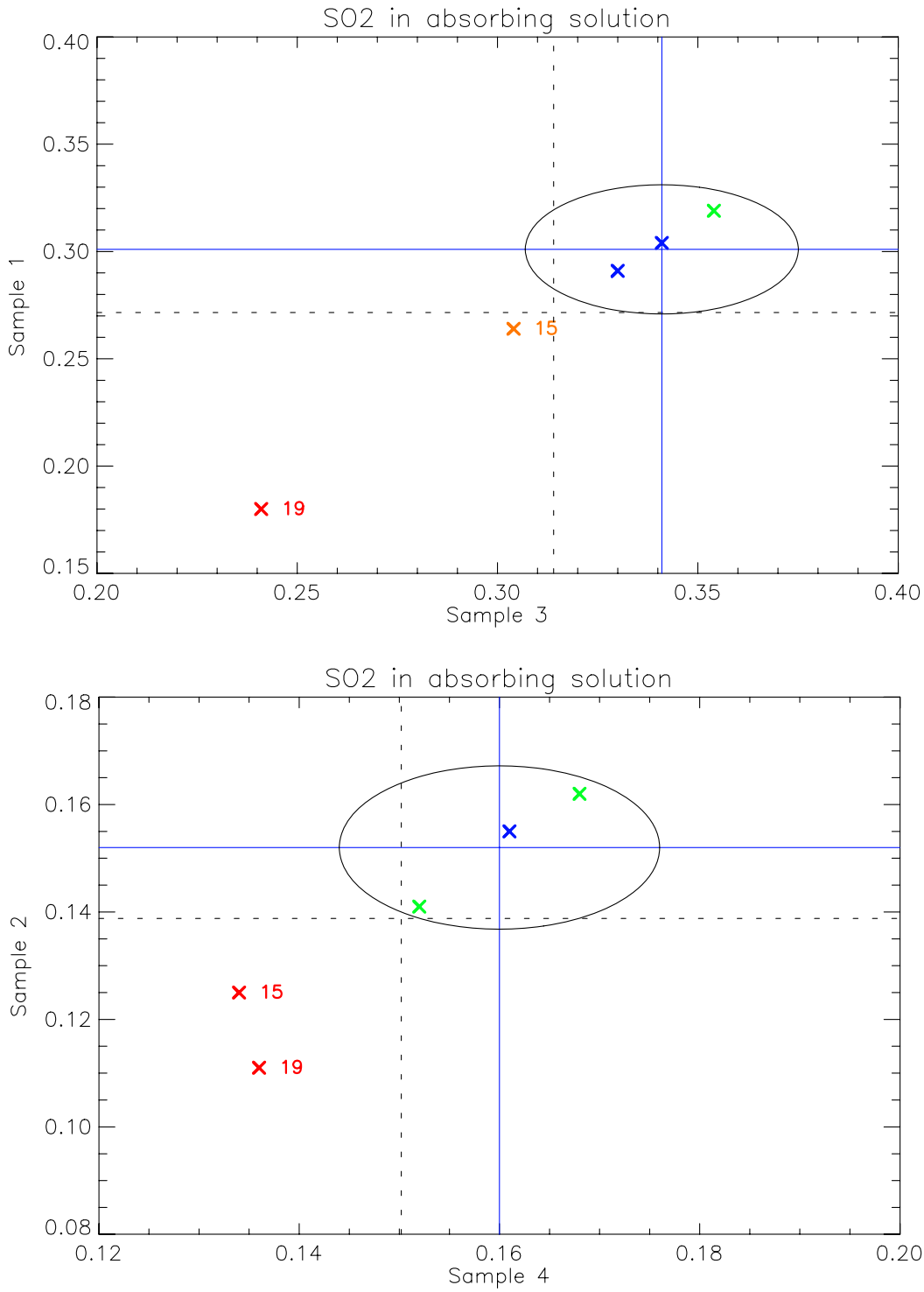

Figure 18: Youden plot of SO_2-S in absorbing solution.

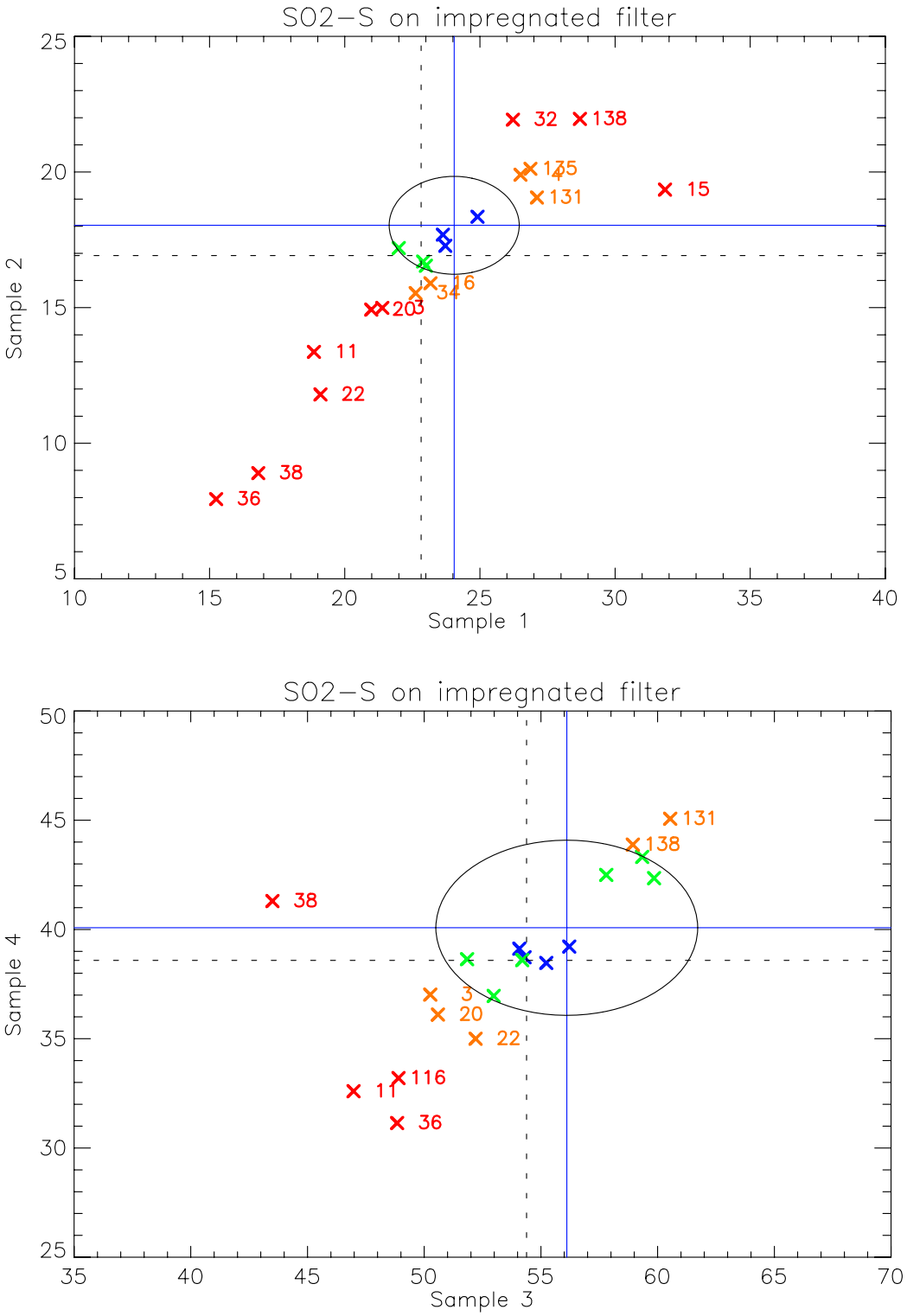

Figure 19: Youden plot of SO_2-S on impregnated filter.

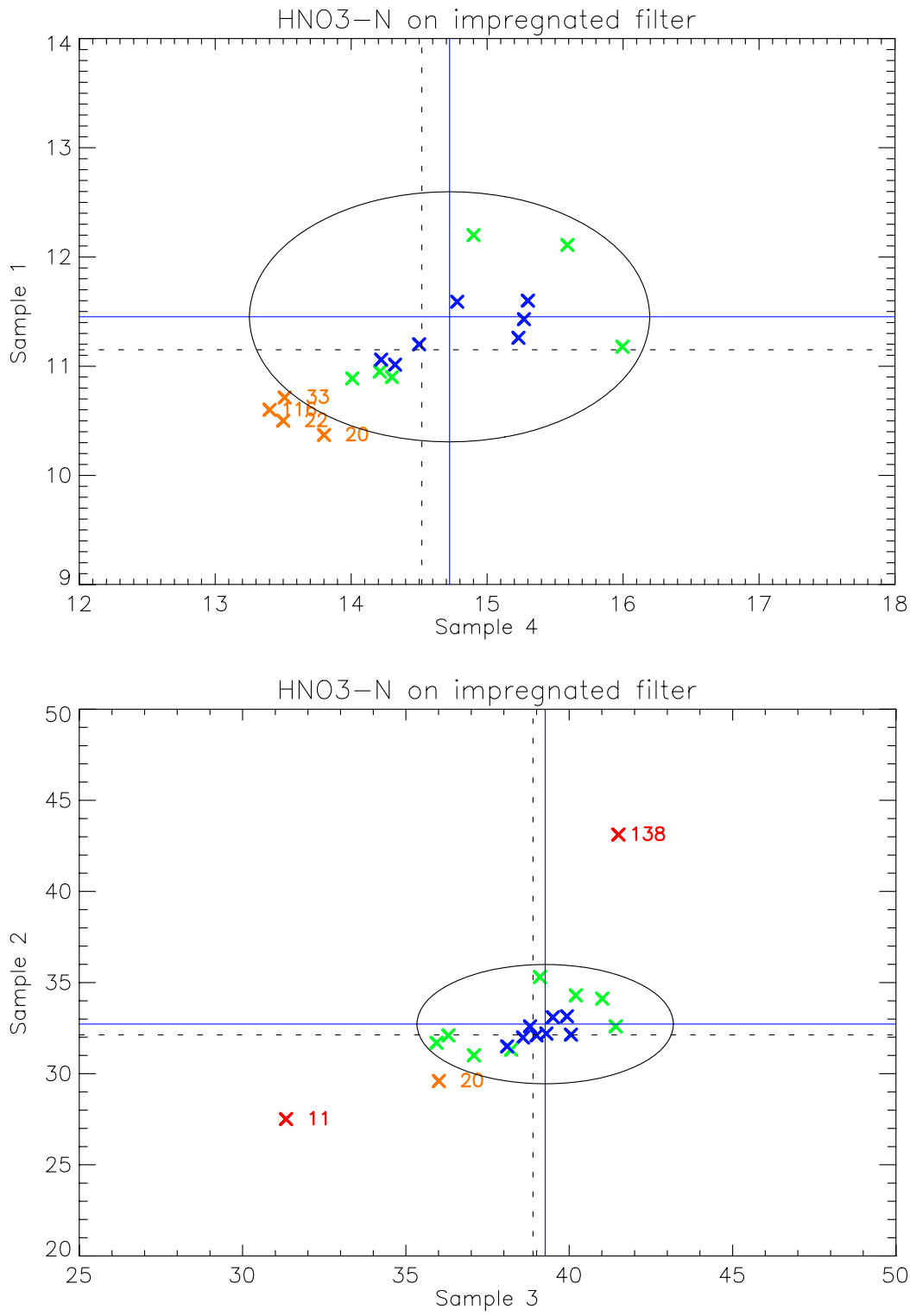

Figure 20: Youden plot of HNO_3-N on impregnated filter.

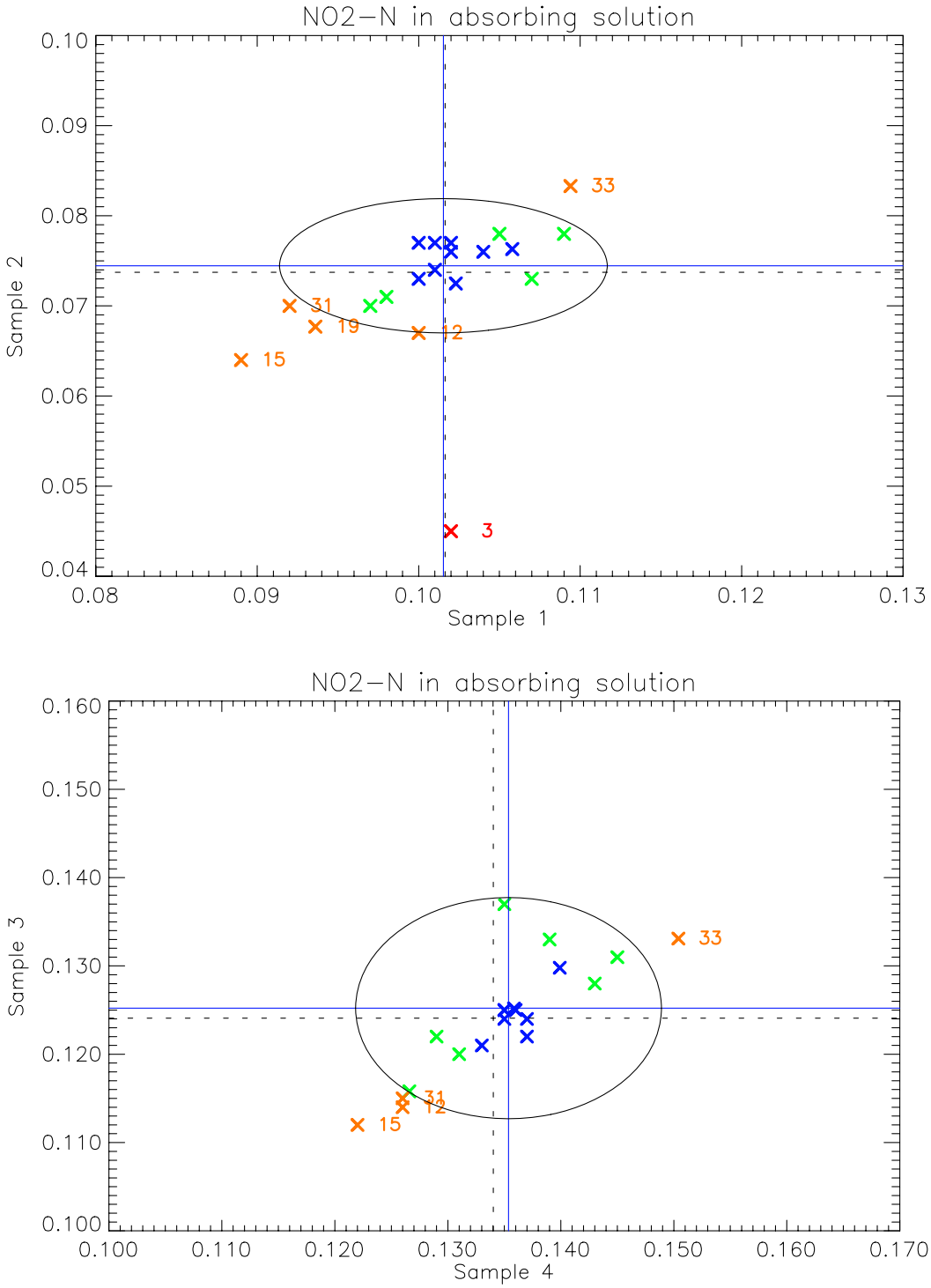

Figure 21: Youden plot of NO_2-N in absorbing solution.

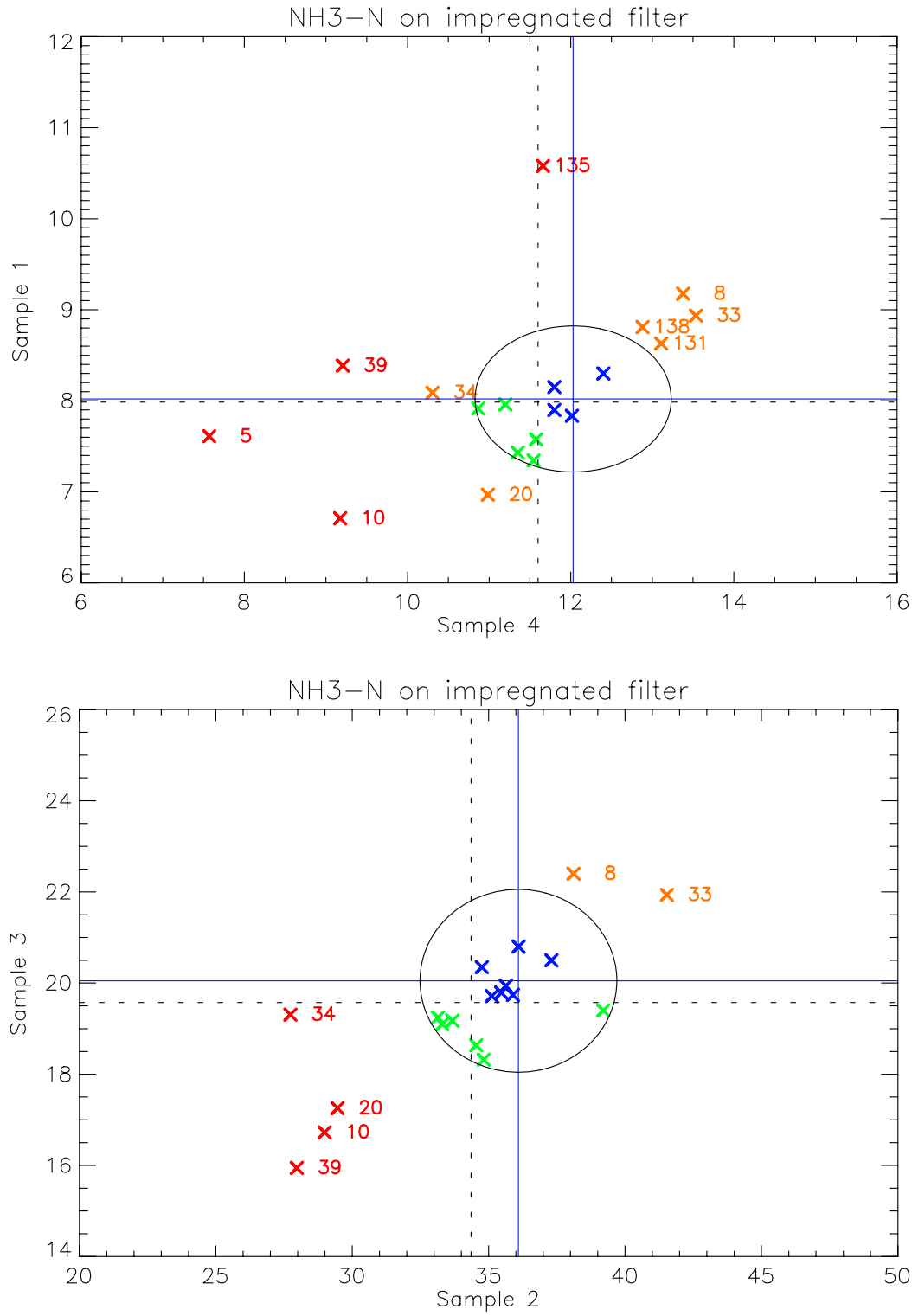

Figure 22: Youden plot of NH_3-N on impregnated filter.

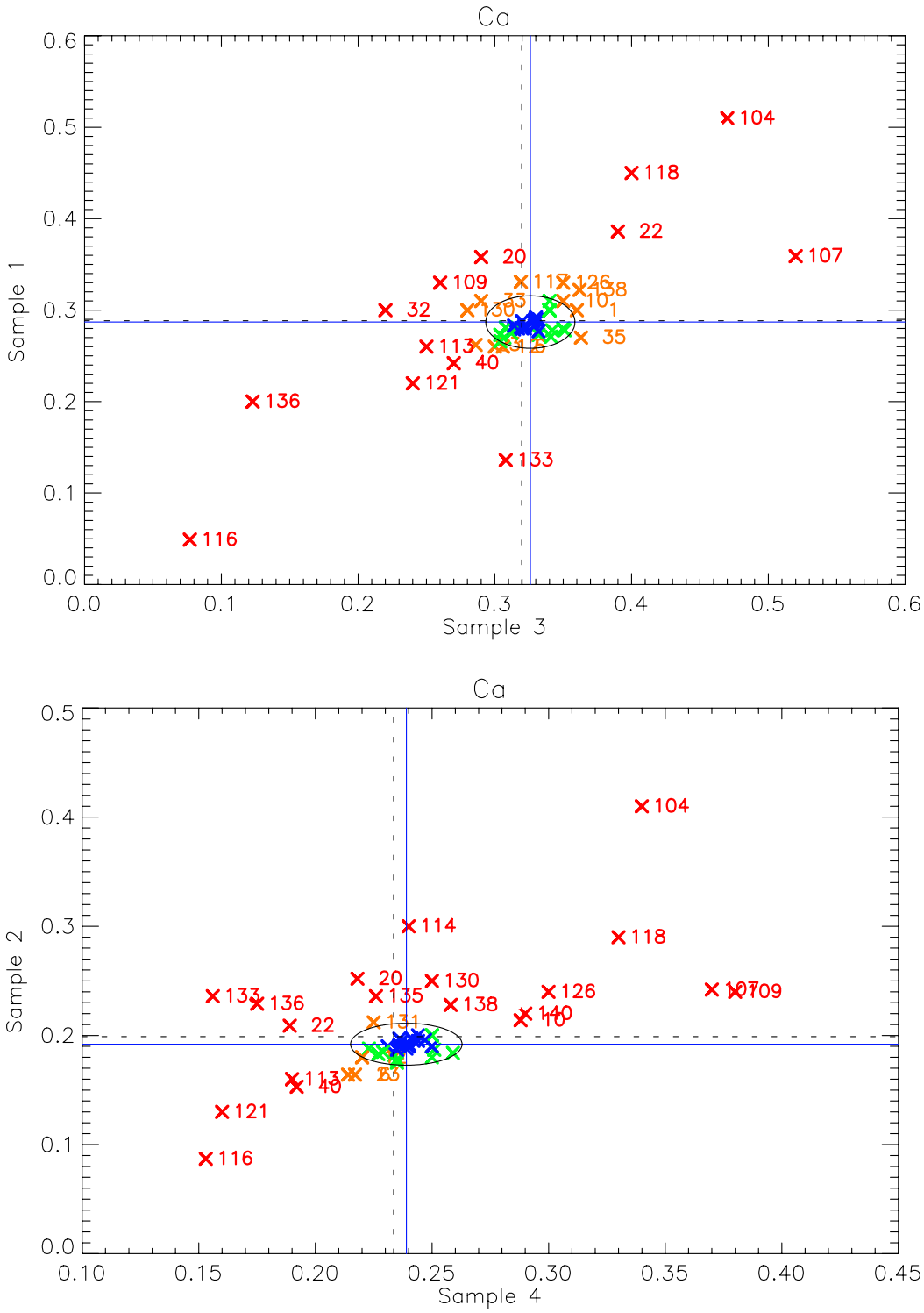

Figure 23: Youden plot of Ca in precipitation.

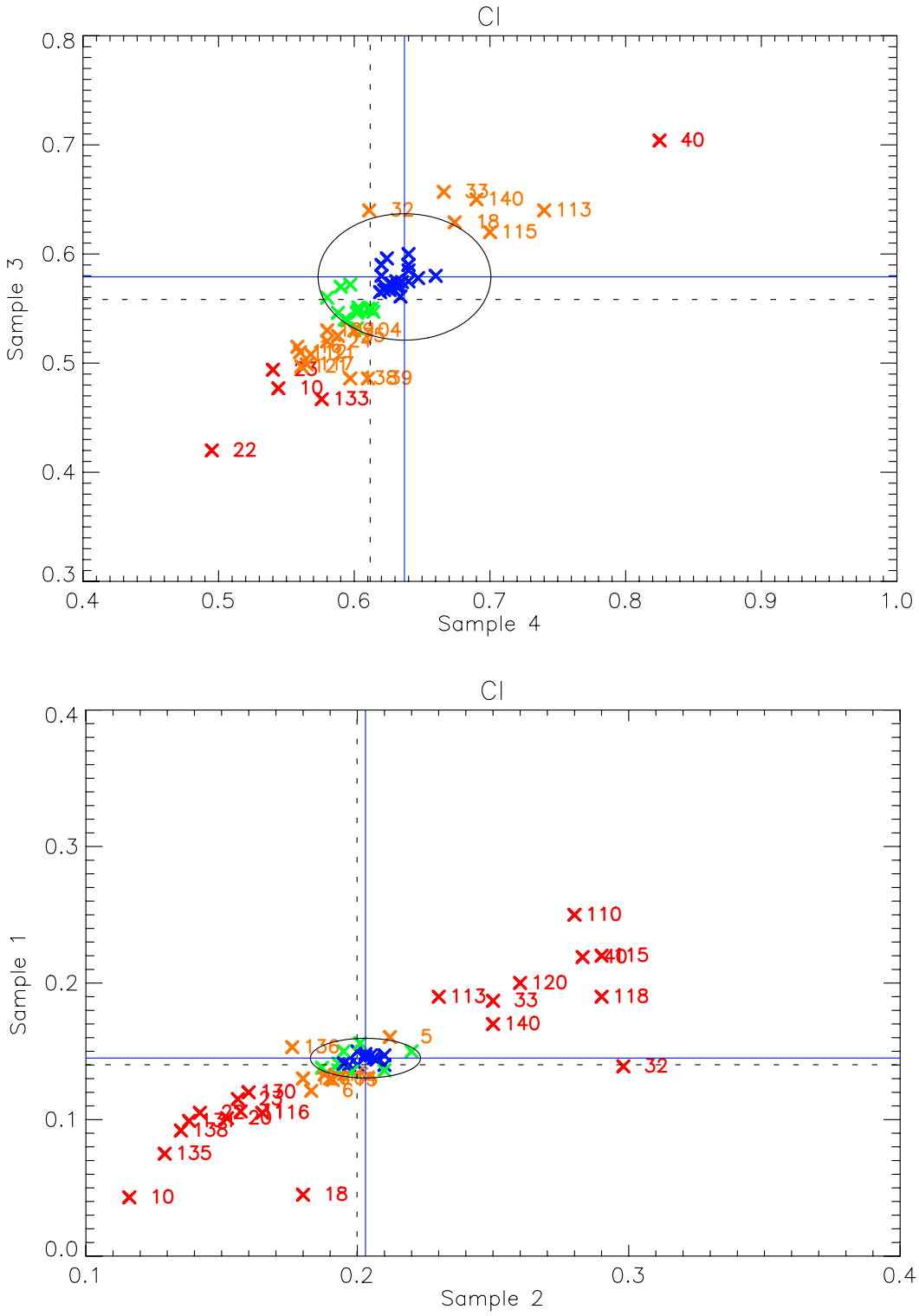

Figure 24: Youden plot of Cl in precipitation.

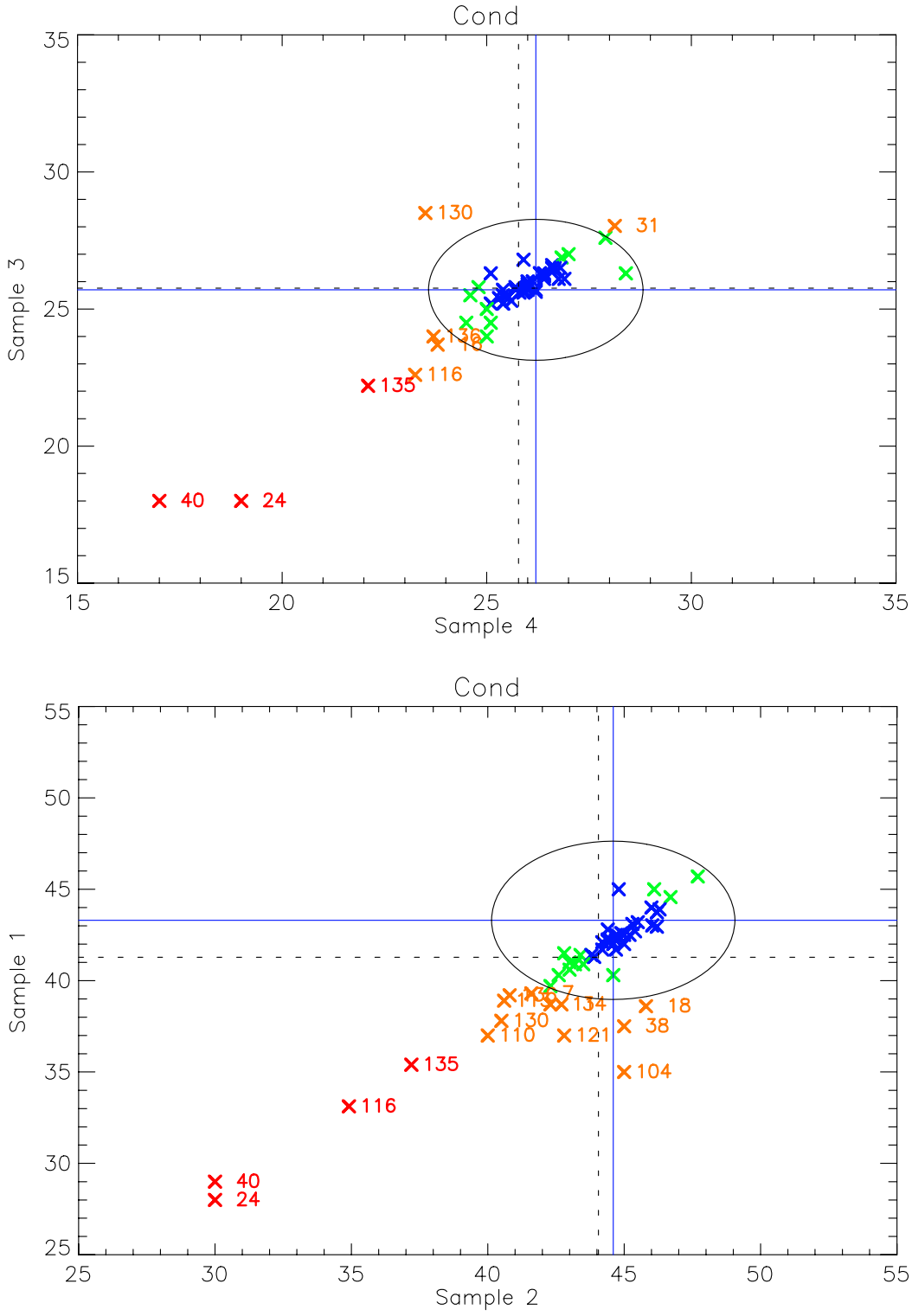

Figure 25: Youden plot of conductivity in precipitation.

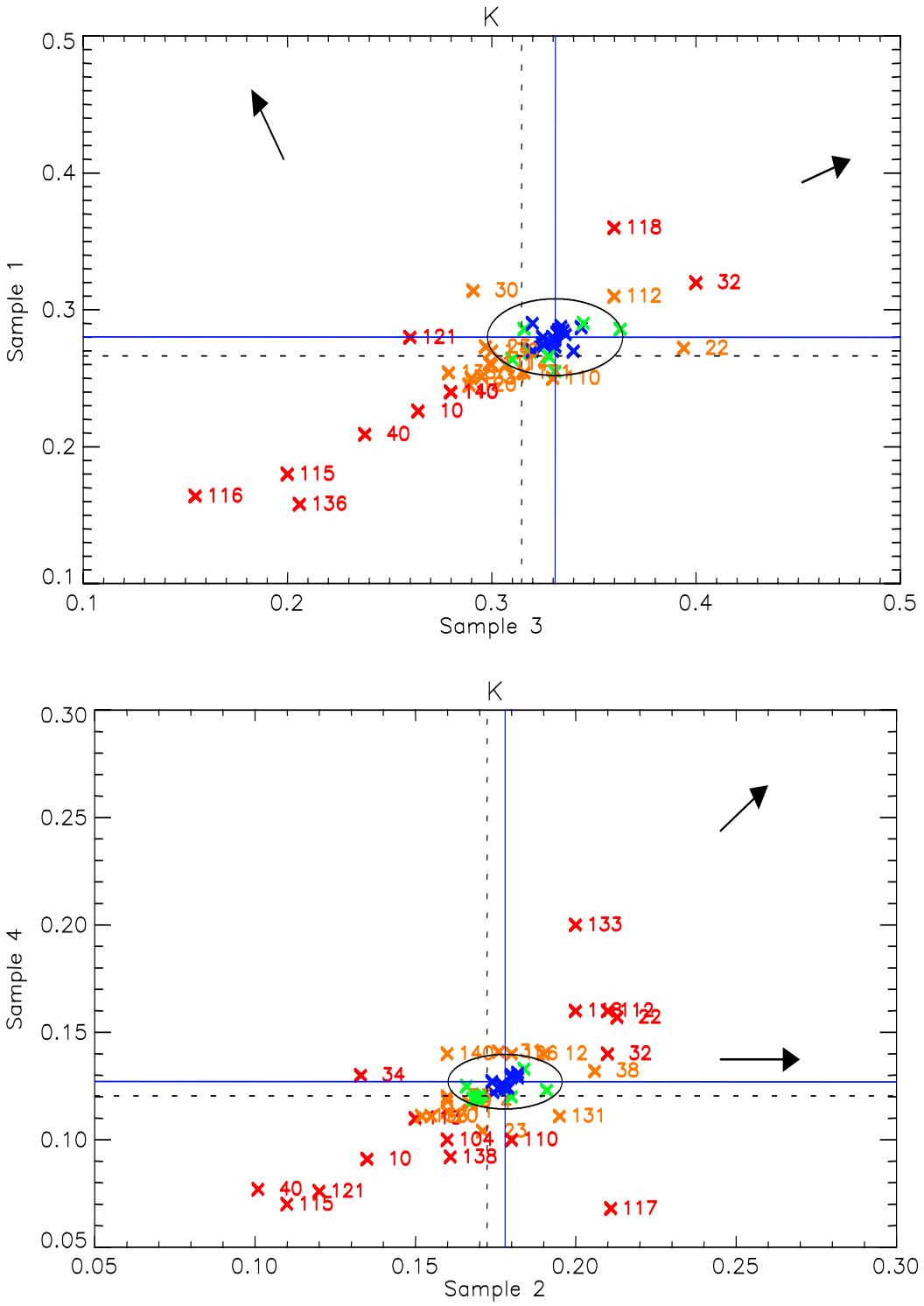

Figure 26: Youden plot of K in precipitation.

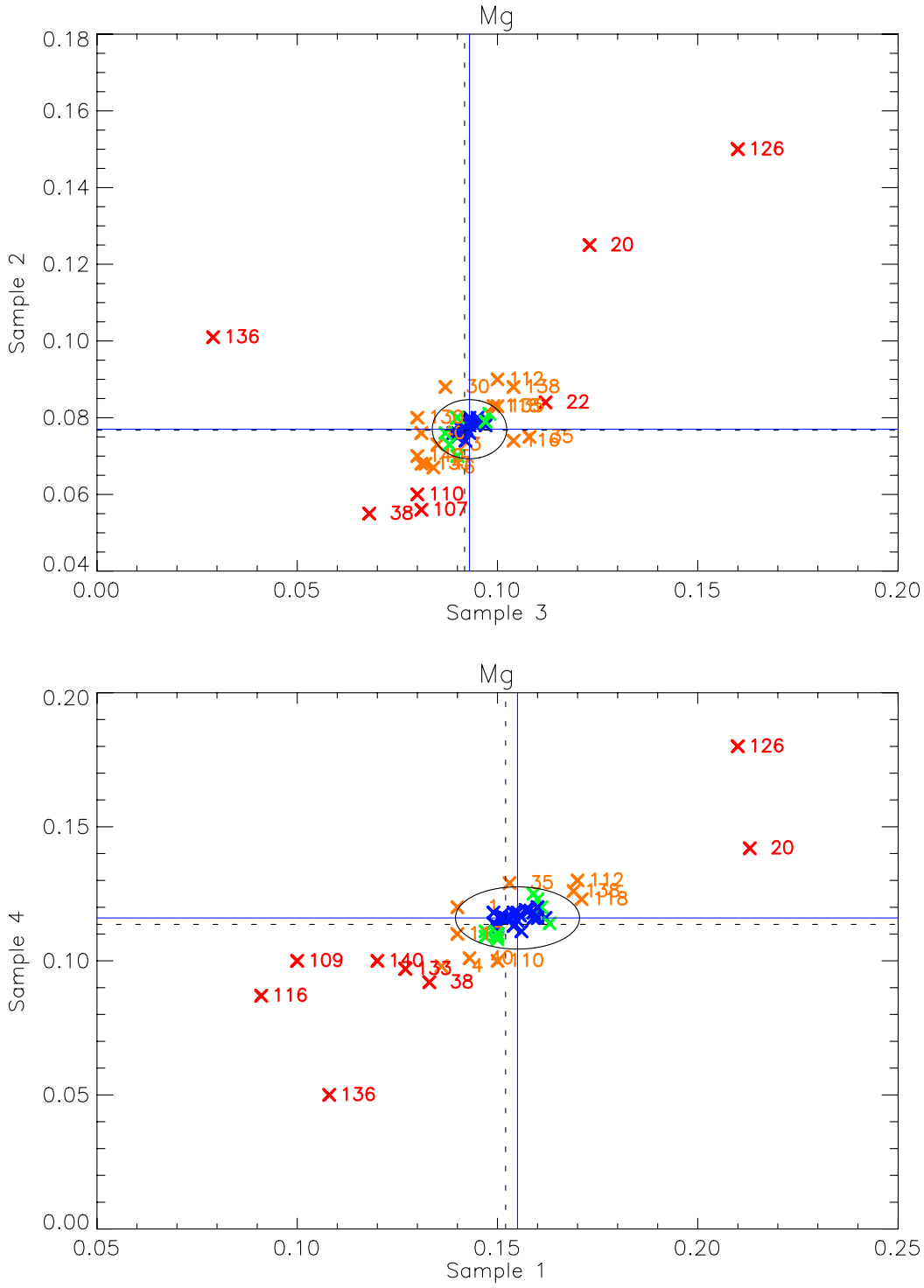

Figure 27: Youden plot of Mg in precipitation.

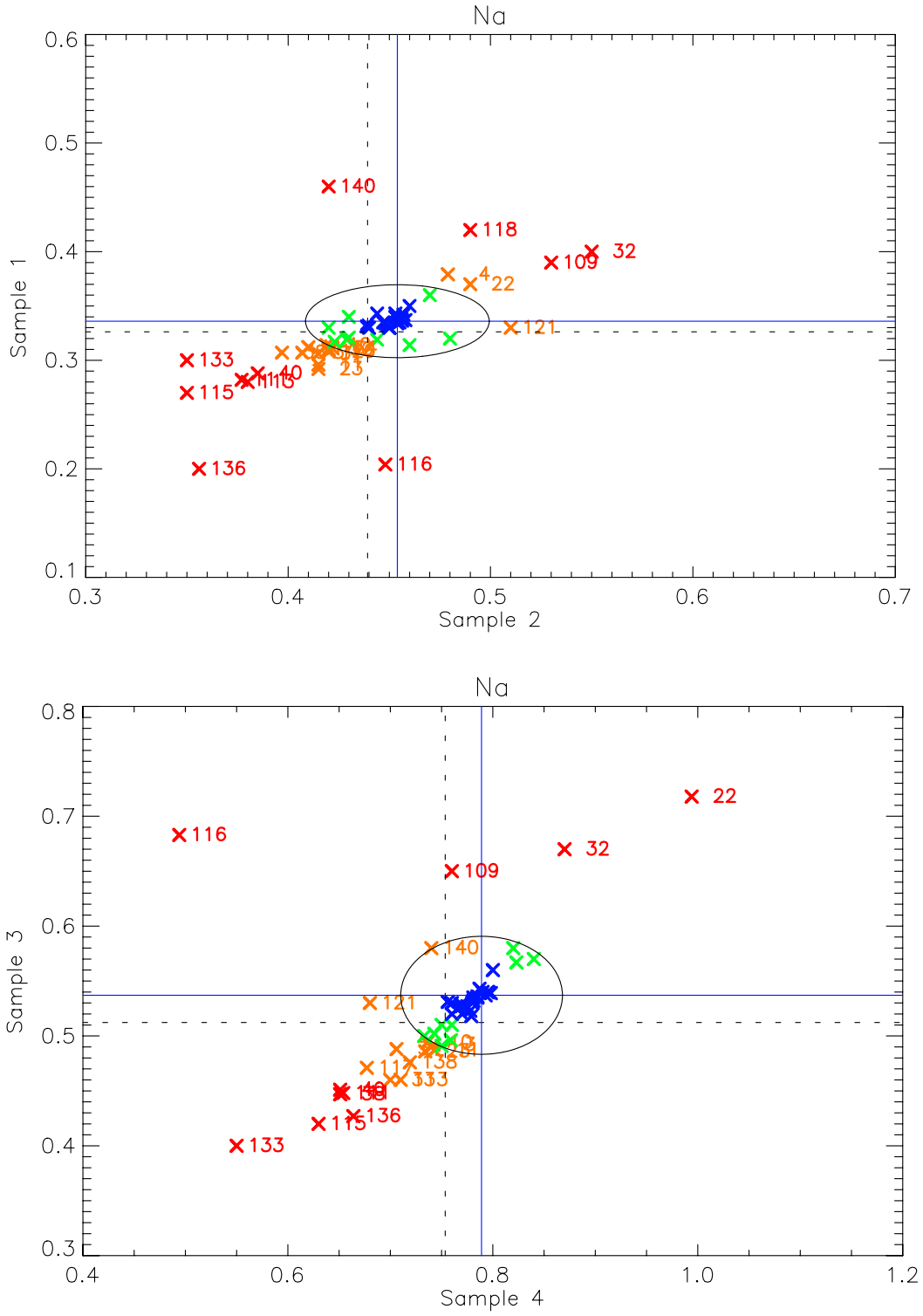

Figure 28: Youden plot of Na in precipitation.

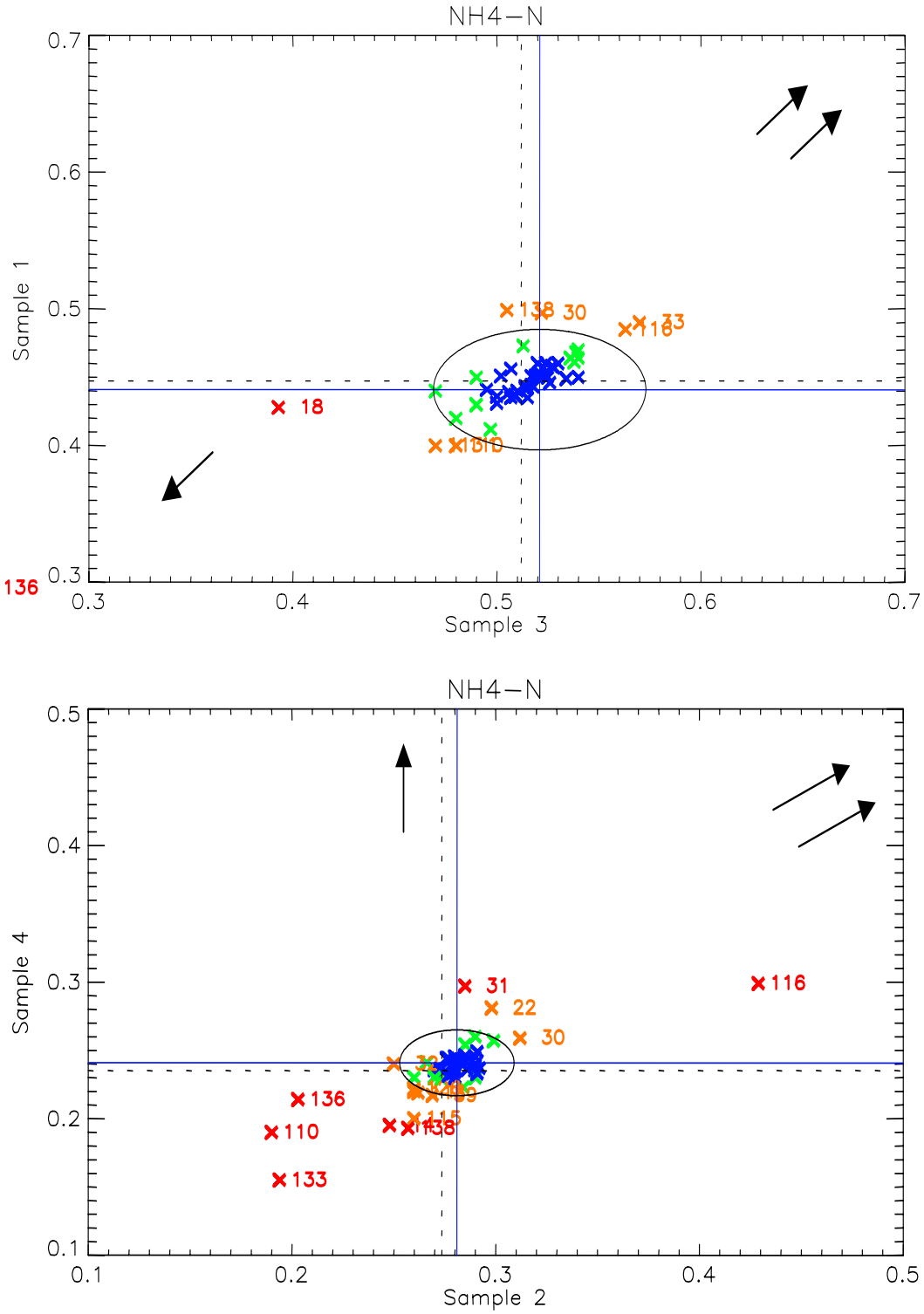

Figure 29: Youden plot of NH_4-N in precipitation.

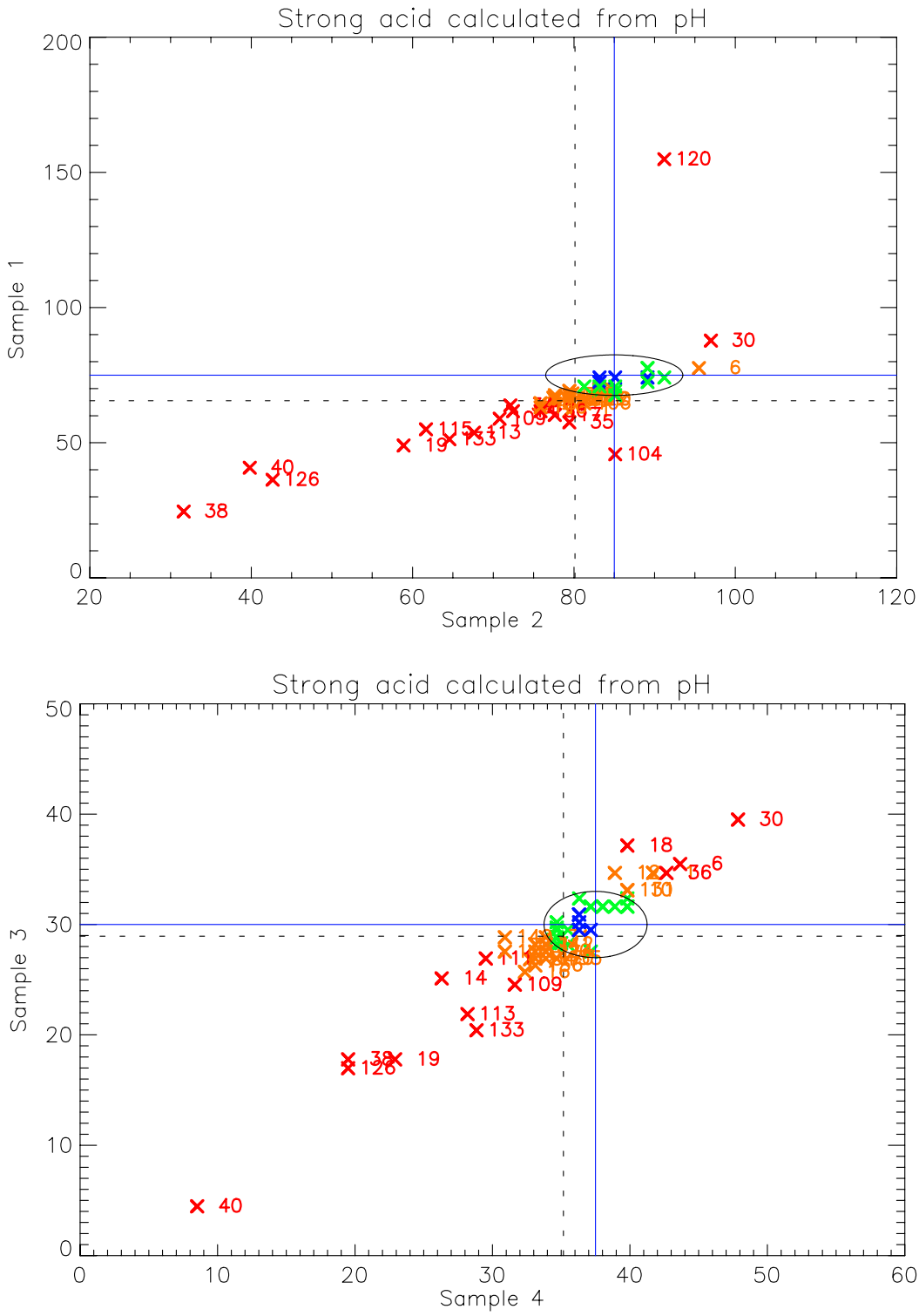

Figure 30: Youden plot of strong acid in precipitation.

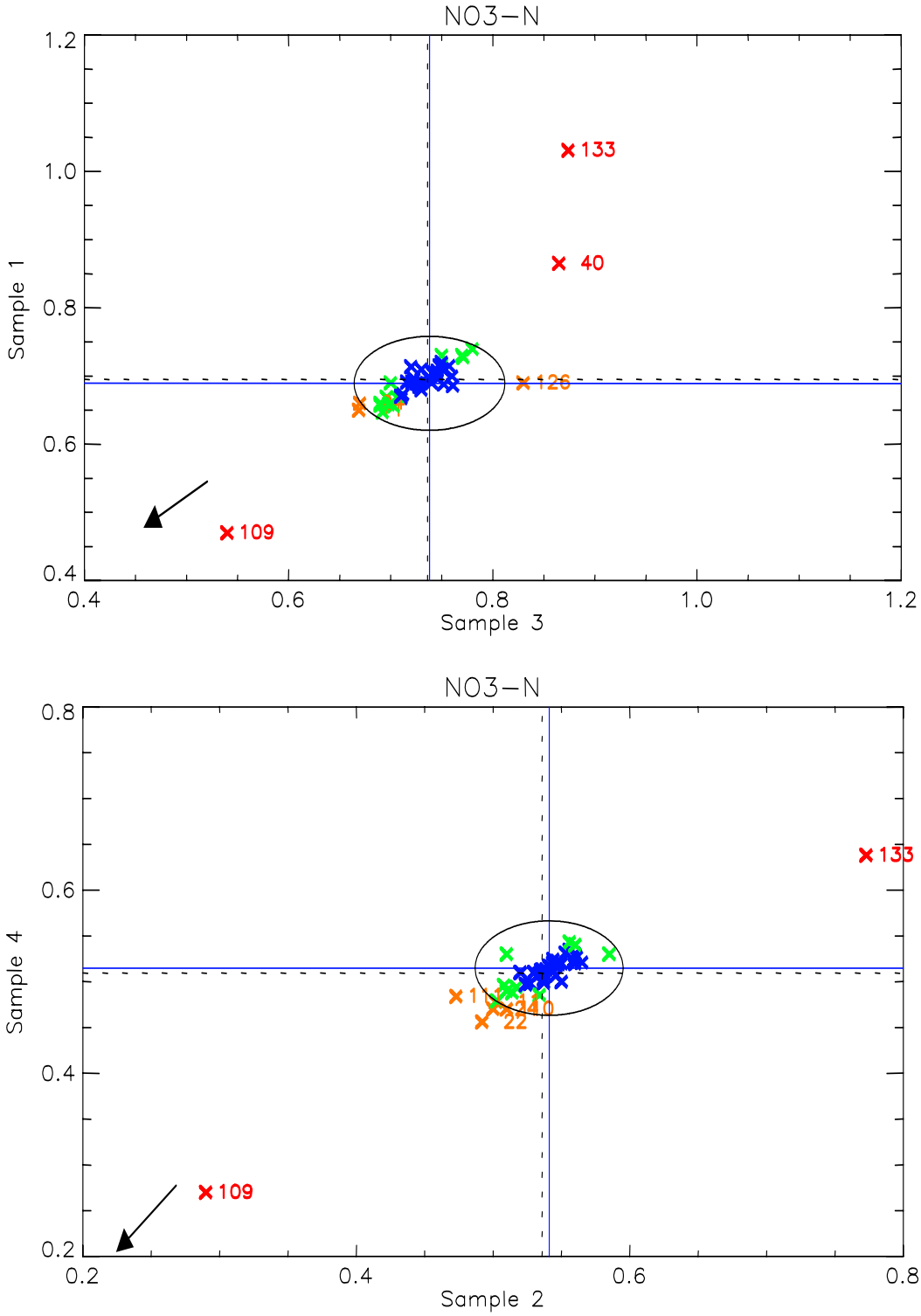

Figure 31: Youden plot of NO_3-N in precipitation.

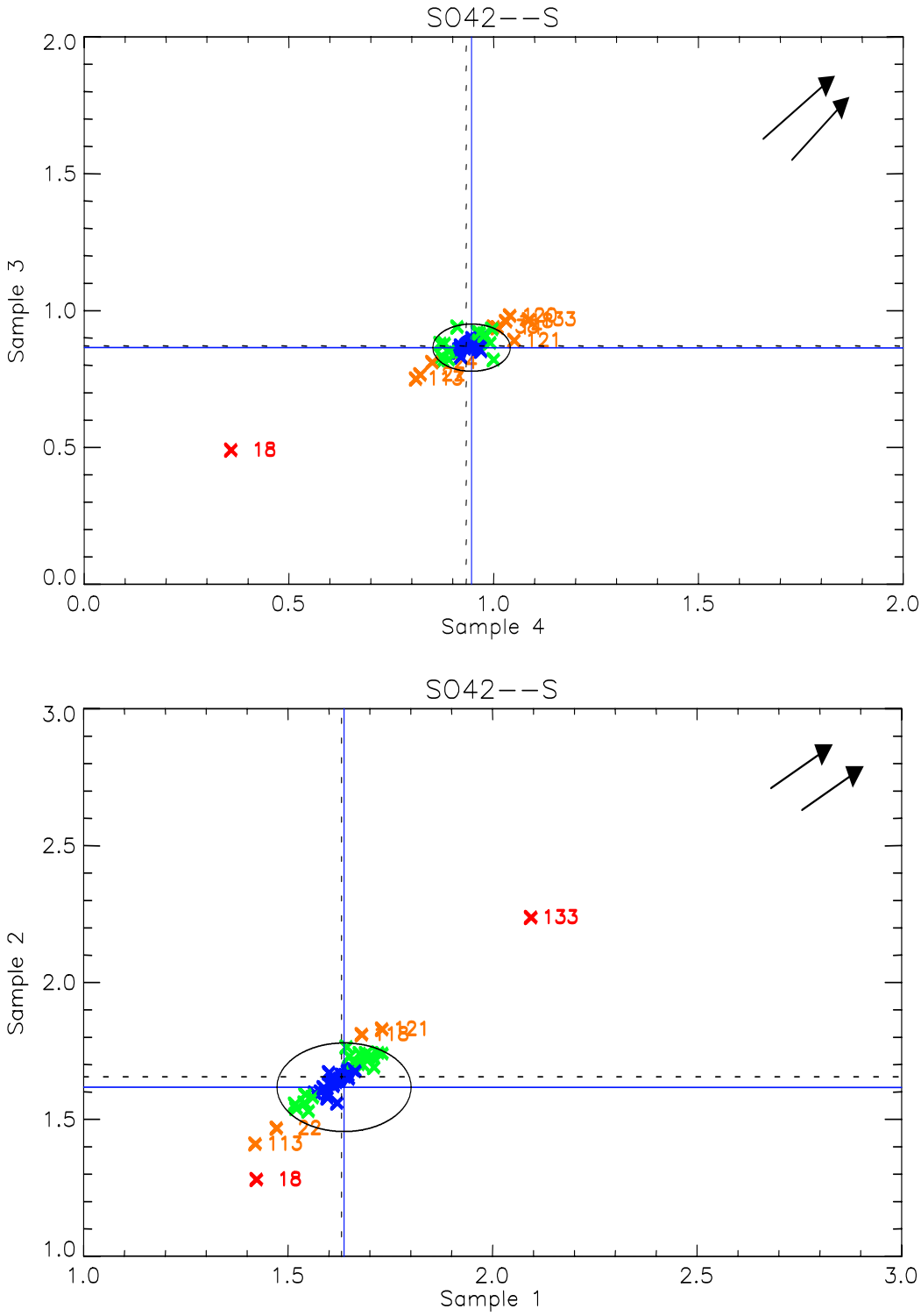

Figure 32: Youden plot of SO_4-S in precipitation.

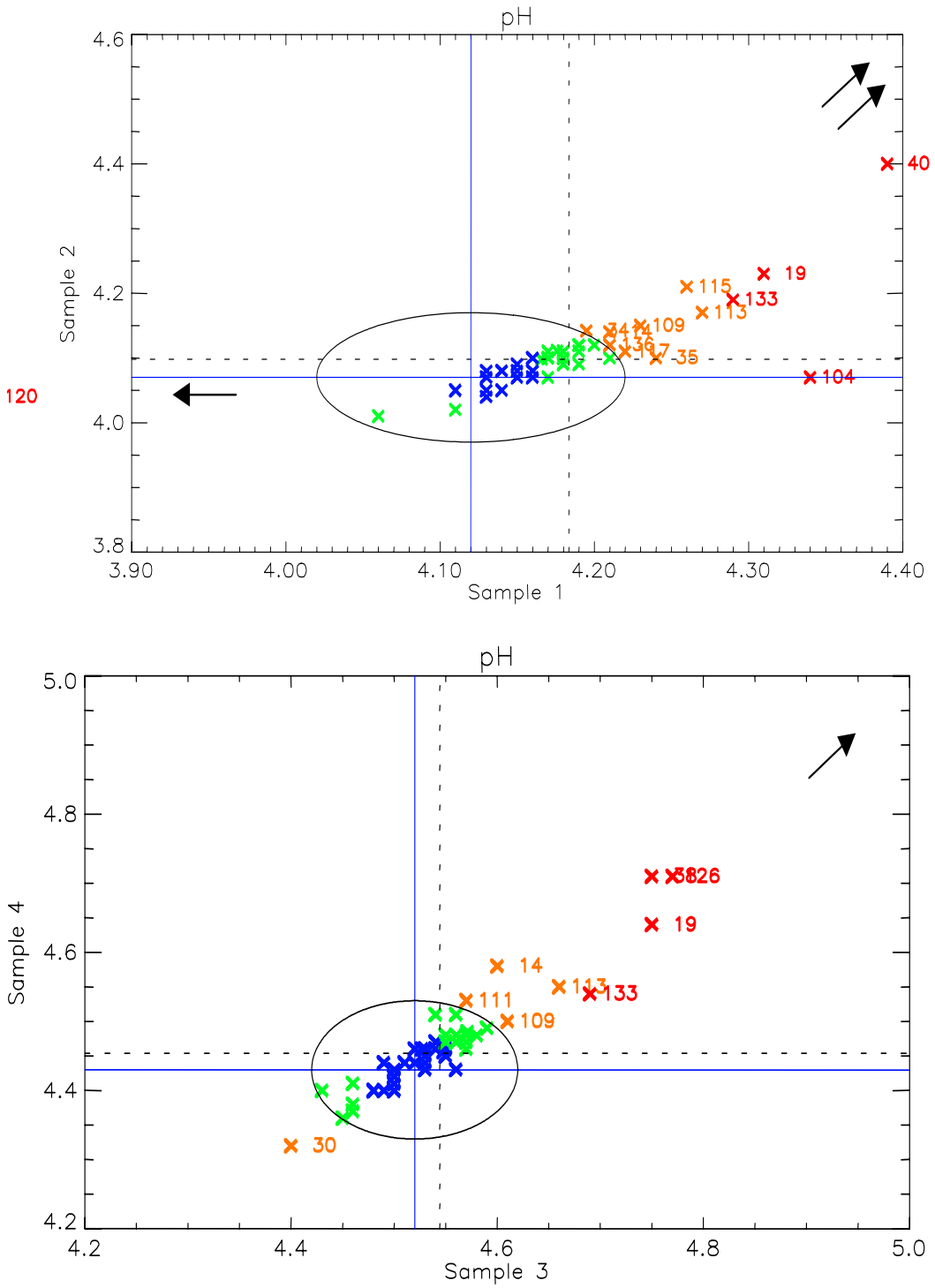

Figure 33: Youden plot of pH in precipitation.