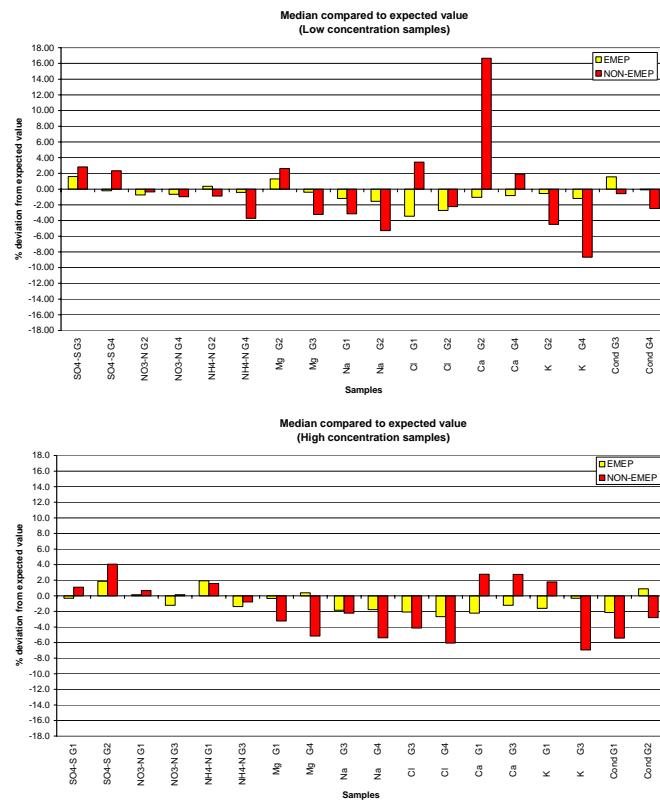


The twenty-first intercomparison of analytical methods within EMEP

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

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The twenty-first intercomparison of analytical methods within EMEP

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.

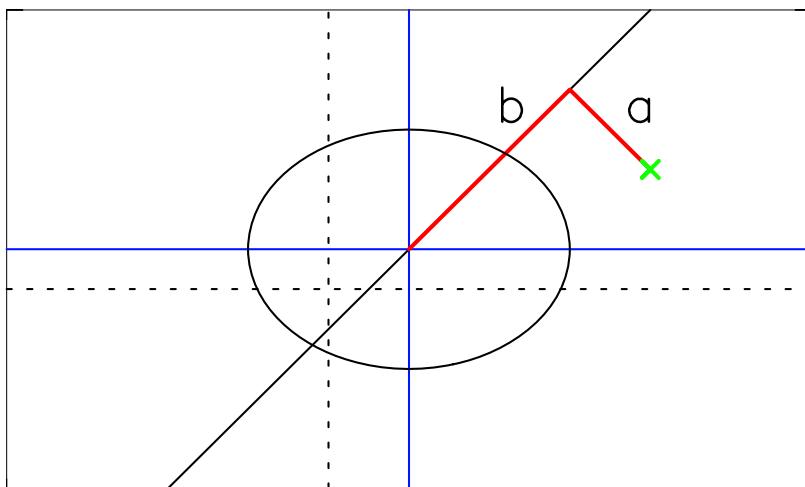


Figure 1: Youden plot showing concentrations for a pair of samples (green), expected values (blue lines), average of measured values (dotted lines) and random and systematic errors (red lines)

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

Table 1: Youden plot parameters.

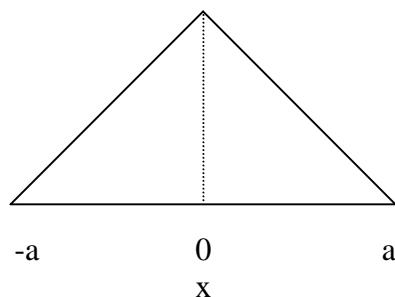
Radii	Components
10%	SO ₂ in abs.sol, NO ₂ in abs.sol.
20%	SO ₂ , HNO ₃ and NH ₃ in impregnated filter
Radii = DQO	Components
10% accuracy or better	SO ₄ ²⁻ -S , NO ₃ ⁻ -N
15% accuracy or better	NH ₄ ⁺ , Cl ⁻ , Ca ²⁺ , K ⁺ , Mg ²⁺ , Na ⁺ , cond
0.1 units	pH
Criteria	Colour
Within 0.5*DQO	Blue
Within 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 $\pm 2 \cdot u(x)$. 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

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

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 SO₂ concentration in air of 2.70–6.79 µg S m⁻³, when 70 ml absorbing solution and 3.6 m³ sampling volume is used.

Only 5 laboratories have reported values for SO₂ 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 m³ is sampled.

In addition to sulphur dioxide, nitric acid was added to the same impregnated filters for determination of HNO₃-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 m³ 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 NO₂-N m⁻³, when 70 ml absorbing solution and 1.4 m³ are used. If

4 ml extraction solution and 0.7 m³ sampling volume are used, the samples correspond to air concentrations between 0.39-0.77 µg NO₂-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 m³ 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 mainly 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 ₂ O 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, Messstelle 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 Landwirtschaftliche
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 Forstwirtschaft
Switzerland	(116)	Institute for Applied Plant Biology
Germany	(117)	Sächsische Landesanstalt für Forsten, Graupa
Germany	(118)	Forstliche Versuchs-und Forschungsanstalt
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 NO₂ 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.

SO ₂ in absorbing solution	SO ₂ in absorbing solution
Sample no.: 1	Sample no.: 2
Theoretical value: 0.301	Theoretical value: 0.152
Unit: µg S / ml	Unit: µg S / ml
Run 1:	Run 1:
Number of laboratories: 5	Number of laboratories: 5
Arithmetric mean value: 0.272	Arithmetric mean value: 0.139
Median: 0.291	Median: 0.141
Standard deviation 0.055	Standard deviation 0.021
Rel. st. deviation (%) 20.268	Rel. st. deviation (%) 15.150
Run 2:	Run 2:
Number of laboratories: 5	Number of laboratories: 5
Arithmetric mean value: 0.272	Arithmetric mean value: 0.139
Median: 0.291	Median: 0.141
Standard deviation 0.055	Standard deviation 0.021
Rel. st. deviation (%) 20.268	Rel. st. deviation (%) 15.150
Results in decreasing order:	Results in decreasing order:
23 0.319 15 0.264	23 0.162 15 0.125
21 0.304 19 0.180	21 0.155 19 0.111
6 0.291	6 0.141
SO ₂ in absorbing solution	SO ₂ in absorbing solution
Sample no.: 3	Sample no.: 4
Theoretical value: 0.341	Theoretical value: 0.160
Unit: µg S / ml	Unit: µg S / ml
Run 1:	Run 1:
Number of laboratories: 5	Number of laboratories: 5
Arithmetric mean value: 0.314	Arithmetric mean value: 0.150
Median: 0.330	Median: 0.152
Standard deviation 0.045	Standard deviation 0.015
Rel. st. deviation (%) 14.255	Rel. st. deviation (%) 9.991
Run 2:	Run 2:
Number of laboratories: 5	Number of laboratories: 5
Arithmetric mean value: 0.314	Arithmetric mean value: 0.150
Median: 0.330	Median: 0.152
Standard deviation 0.045	Standard deviation 0.015
Rel. st. deviation (%) 14.255	Rel. st. deviation (%) 9.991
Results in decreasing order:	Results in decreasing order:
23 0.354 15 0.304	23 0.168 19 0.136
21 0.341 19 0.241	21 0.161 15 0.134
6 0.330	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).

Lab. No	Measured / Expected value				Average	
	Sample No					
	B1	B3	B4	B5		
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).

Lab.No	Measured / Expected value				Average	
	Sample No					
	B1	B3	B4	B5		
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.

NO ₂ -N in absorbing solution Sample no.: C1 Theoretical value: 0.102 Unit: µg N / ml	NO ₂ -N in absorbing solution Sample no.: C2 Theoretical value: 0.074 Unit: µg N / ml
Run 1: Number of laboratories: 20 Arithmetric mean value: 0.101 Median: 0.102 Standard deviation 0.005 Rel. st. deviation (%) 5.234	Run 1: Number of laboratories: 20 Arithmetric mean value: 0.072 Median: 0.073 Standard deviation 0.008 Rel. st. deviation (%) 10.880
Run 2: Number of laboratories: 19 Arithmetric mean value: 0.102 Median: 0.102 Standard deviation 0.005 Rel. st. deviation (%) 4.517	Run 2: Number of laboratories: 19 Arithmetric mean value: 0.074 Median: 0.074 Standard deviation 0.005 Rel. st. deviation (%) 6.324
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 (*)	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 (*)
NO ₂ -N in absorbing solution Sample no.: C3 Theoretical value: 0.125 Unit: µg N / ml	NO ₂ -N in absorbing solution Sample no.: C4 Theoretical value: 0.135 Unit: µg N / ml
Run 1: Number of laboratories: 20 Arithmetric mean value: 0.124 Median: 0.124 Standard deviation 0.007 Rel. st. deviation (%) 5.424	Run 1: Number of laboratories: 20 Arithmetric mean value: 0.135 Median: 0.135 Standard deviation 0.007 Rel. st. deviation (%) 5.127
Run 2: Number of laboratories: 20 Arithmetric mean value: 0.124 Median: 0.124 Standard deviation 0.007 Rel. st. deviation (%) 5.424	Run 2: Number of laboratories: 19 Arithmetric mean value: 0.134 Median: 0.135 Standard deviation 0.006 Rel. st. deviation (%) 4.494
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	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.

Lab.No	Measured / Expected				Average	
	Sample No.					
	C1	C2	C3	C4		
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.: 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.: 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.: 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).

Lab. no.	Measured / Expected				Average	
	Sample No.					
	J1	J3	J4	J6		
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				SO42--S			
Sample no.: G1		Sample no.: G2					
Theoretical value:		1.637		Theoretical value:		1.618	
Unit: µg/l							
Run 1:		Run 1:		Run 1:		Run 1:	
Number of laboratories:		54		Number of laboratories:		54	
Arithmettic mean value:		1.744		Arithmettic mean value:		1.773	
Median:		1.639		Median:		1.660	
Standard deviation		0.595		Standard deviation		0.614	
Rel. st. deviation (%)		34.093		Rel. st. deviation (%)		34.658	
Run 2:		Run 2:		Run 2:		Run 2:	
Number of laboratories:		52		Number of laboratories:		52	
Arithmettic mean value:		1.630		Arithmettic mean value:		1.656	
Median:		1.635		Median:		1.658	
Standard deviation		0.095		Standard deviation		0.125	
Rel. st. deviation (%)		5.843		Rel. st. deviation (%)		7.537	
Results in decreasing order:				Results in decreasing order:			
130	5.000 (*)	36	1.638	130	5.040 (*)	135	1.660
126	4.390 (*)	21	1.632	126	4.570 (*)	36	1.656
133	2.094	6	1.627	133	2.238	31	1.648
38	1.730	26	1.623	121	1.830	6	1.646
121	1.730	104	1.620	118	1.810	26	1.642
14	1.720	7	1.618	39	1.764	23	1.637
111	1.710	20	1.611	14	1.743	7	1.636
138	1.704	112	1.610	38	1.740	34	1.634
13	1.700	23	1.610	114	1.740	1	1.630
107	1.697	30	1.609	35	1.739	112	1.630
114	1.690	34	1.608	138	1.731	30	1.626
33	1.683	110	1.600	13	1.730	20	1.621
118	1.680	1	1.600	115	1.730	116	1.615
35	1.675	11	1.596	107	1.725	15	1.600
32	1.672	136	1.596	120	1.710	10	1.596
131	1.664	116	1.587	32	1.701	11	1.595
27	1.661	15	1.580	33	1.699	16	1.590
8	1.660	10	1.566	111	1.690	136	1.580
120	1.660	109	1.560	5	1.683	109	1.580
5	1.657	24	1.550	4	1.682	104	1.560
115	1.650	16	1.542	27	1.681	117	1.560
31	1.648	117	1.540	8	1.680	19	1.555
4	1.648	140	1.520	131	1.677	140	1.540
135	1.647	19	1.517	3	1.673	24	1.530
3	1.646	22	1.472	110	1.670	22	1.467
39	1.643	18	1.423	21	1.661	113	1.410
12	1.640	113	1.420	12	1.660	18	1.280
SO42--S				SO42--S			
Sample no.: G3		Sample no.: G4		Sample no.: G3		Sample no.: G4	
Theoretical value:		0.864		Theoretical value:		0.946	
Unit: µg/l							
Run 1:		Run 1:		Run 1:		Run 1:	
Number of laboratories:		54		Number of laboratories:		54	
Arithmettic mean value:		0.933		Arithmettic mean value:		0.997	
Median:		0.880		Median:		0.948	
Standard deviation		0.328		Standard deviation		0.345	
Rel. st. deviation (%)		35.207		Rel. st. deviation (%)		34.620	
Run 2:		Run 2:		Run 2:		Run 2:	
Number of laboratories:		52		Number of laboratories:		52	
Arithmettic mean value:		0.870		Arithmettic mean value:		0.933	
Median:		0.880		Median:		0.946	
Standard deviation		0.070		Standard deviation		0.097	
Rel. st. deviation (%)		8.043		Rel. st. deviation (%)		10.418	
Results in decreasing order:				Results in decreasing order:			
130	2.580 (*)	109	0.880	130	2.830 (*)	21	0.947
126	2.530 (*)	1	0.880	126	2.500 (*)	36	0.945
120	0.980	3	0.878	133	1.086	31	0.944
133	0.966	21	0.878	121	1.050	3	0.941
118	0.960	26	0.875	120	1.040	1	0.940
38	0.940	6	0.872	118	1.030	26	0.936
32	0.940	36	0.872	14	1.009	6	0.934
14	0.937	117	0.870	38	1.000	20	0.932
138	0.932	20	0.868	115	1.000	34	0.929
111	0.920	34	0.861	138	0.996	117	0.920
135	0.918	116	0.861	136	0.991	112	0.920
33	0.914	112	0.860	131	0.977	104	0.920
131	0.910	16	0.856	33	0.977	16	0.916
5	0.900	39	0.852	4	0.972	15	0.916
114	0.900	110	0.850	114	0.970	32	0.911
35	0.897	15	0.848	39	0.969	23	0.908
13	0.895	23	0.844	5	0.968	30	0.903
27	0.894	30	0.840	135	0.966	140	0.890
8	0.891	19	0.833	13	0.966	110	0.890
12	0.890	104	0.830	116	0.963	109	0.880
121	0.890	115	0.820	7	0.961	11	0.876
4	0.889	140	0.820	27	0.961	19	0.873
7	0.887	11	0.816	8	0.960	10	0.870
107	0.887	24	0.810	111	0.960	24	0.850
31	0.884	22	0.766	107	0.958	22	0.821
136	0.881	113	0.750	12	0.950	113	0.810
10	0.880	18	0.490	35	0.948	18	0.359

Table 20: Analytical results for nitrate in precipitations samples.

NO3-N			
Sample no.: G1		Sample no.: G2	
Theoretical value:	0.607	Theoretical value:	0.546
Unit: µg/l		Unit: µg/l	
Run 1:		Run 1:	
Number of laboratories:	54	Number of laboratories:	54
Arithmetic mean value:	0.687	Arithmetic mean value:	0.528
Median:	0.690	Median:	0.537
Standard deviation	0.098	Standard deviation	0.076
Rel. st. deviation (%)	14.294	Rel. st. deviation (%)	14.459
Run 2:		Run 2:	
Number of laboratories:	51	Number of laboratories:	51
Arithmetic mean value:	0.695	Arithmetic mean value:	0.536
Median:	0.691	Median:	0.537
Standard deviation	0.033	Standard deviation	0.022
Rel. st. deviation (%)	4.719	Rel. st. deviation (%)	4.040
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 (*)
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		Sample no.: G4	
Theoretical value:	0.738	Theoretical value:	0.521
Unit: µg/l		Unit: µg/l	
Run 1:		Run 1:	
Number of laboratories:	54	Number of laboratories:	54
Arithmetic mean value:	0.722	Arithmetic mean value:	0.500
Median:	0.730	Median:	0.510
Standard deviation	0.090	Standard deviation	0.067
Rel. st. deviation (%)	12.408	Rel. st. deviation (%)	13.433
Run 2:		Run 2:	
Number of laboratories:	52	Number of laboratories:	51
Arithmetic mean value:	0.736	Arithmetic mean value:	0.510
Median:	0.730	Median:	0.511
Standard deviation	0.039	Standard deviation	0.019
Rel. st. deviation (%)	5.325	Rel. st. deviation (%)	3.762
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 (*)
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
114	0.521	16	0.496
114	0.521	11	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: Unit: $\mu\text{g/l}$	NH4-N Sample no.: G2 Theoretical value: Unit: $\mu\text{g/l}$
Run 1: Number of laboratories: 54 Arithmmetic mean value: 0.456 Median: 0.450 Standard deviation 0.068 Rel. st. deviation (%) 14.838	Run 1: Number of laboratories: 54 Arithmmetic mean value: 0.287 Median: 0.280 Standard deviation 0.063 Rel. st. deviation (%) 21.811
Run 2: Number of laboratories: 51 Arithmmetic mean value: 0.447 Median: 0.449 Standard deviation 0.021 Rel. st. deviation (%) 4.768	Run 2: Number of laboratories: 51 Arithmmetic mean value: 0.274 Median: 0.280 Standard deviation 0.023 Rel. st. deviation (%) 8.563
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 (*)	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: Unit: $\mu\text{g/l}$	NH4-N Sample no.: G4 Theoretical value: Unit: $\mu\text{g/l}$
Run 1: Number of laboratories: 54 Arithmmetic mean value: 0.517 Median: 0.515 Standard deviation 0.069 Rel. st. deviation (%) 13.322	Run 1: Number of laboratories: 54 Arithmmetic mean value: 0.254 Median: 0.237 Standard deviation 0.086 Rel. st. deviation (%) 33.711
Run 2: Number of laboratories: 51 Arithmmetic mean value: 0.512 Median: 0.515 Standard deviation 0.027 Rel. st. deviation (%) 5.240	Run 2: Number of laboratories: 51 Arithmmetic mean value: 0.235 Median: 0.236 Standard deviation 0.024 Rel. st. deviation (%) 10.046
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 (*)	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 0.236 112 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: Unit: pH-unit	4.120	pH Sample no.: G2 Theoretical value: Unit: pH-unit	4.070
Run 1:		Run 1:	
Number of laboratories: 56		Number of laboratories: 56	
Arithmetic mean value: 4.189		Arithmetic mean value: 4.115	
Median: 4.178		Median: 4.100	
Standard deviation 0.101		Standard deviation 0.085	
Rel. st. deviation (%) 2.407		Rel. st. deviation (%) 2.070	
Run 2:		Run 2:	
Number of laboratories: 53		Number of laboratories: 53	
Arithmetic mean value: 4.184		Arithmetic mean value: 4.098	
Median: 4.176		Median: 4.100	
Standard deviation 0.058		Standard deviation 0.041	
Rel. st. deviation (%) 1.381		Rel. st. deviation (%) 1.011	
Results in decreasing order:		Results in decreasing order:	
38 4.610 (*) 3 4.176		38 4.500 (*) 36 4.100	
126 4.440 (*) 107 4.170		40 4.400 (*) 107 4.100	
40 4.390 27 4.170		126 4.370 (*) 1 4.100	
104 4.340 121 4.170		19 4.230 8 4.100	
19 4.310 7 4.170		115 4.210 4 4.098	
133 4.290 8 4.170		133 4.190 110 4.090	
113 4.270 36 4.170		113 4.170 130 4.090	
115 4.260 4 4.166		109 4.150 106 4.090	
35 4.240 5 4.160		34 4.142 22 4.090	
109 4.230 21 4.160		14 4.140 135 4.080	
117 4.220 31 4.160		20 4.120 10 4.080	
14 4.210 15 4.160		114 4.120 33 4.080	
1 4.210 33 4.160		111 4.120 21 4.080	
136 4.210 118 4.150		136 4.120 11 4.080	
140 4.200 130 4.150		140 4.120 39 4.080	
34 4.195 135 4.150		3 4.111 116 4.070	
24 4.190 11 4.140		112 4.110 118 4.070	
106 4.190 39 4.140		26 4.110 121 4.070	
111 4.190 138 4.140		117 4.110 5 4.070	
20 4.190 116 4.130		24 4.110 104 4.070	
114 4.190 23 4.130		7 4.110 23 4.050	
112 4.180 10 4.130		13 4.100 138 4.050	
110 4.180 12 4.130		15 4.100 131 4.050	
22 4.180 6 4.110		16 4.100 18 4.050	
13 4.180 131 4.110		27 4.100 120 4.040	
32 4.180 18 4.110		31 4.100 12 4.040	
16 4.180 30 4.060		32 4.100 6 4.020	
26 4.180 120 3.810 (*)		35 4.100 30 4.010	
pH Sample no.: G3 Theoretical value: Unit: pH-unit	4.520	pH Sample no.: G4 Theoretical value: Unit: pH-unit	4.430
Run 1:		Run 1:	
Number of laboratories: 56		Number of laboratories: 56	
Arithmetic mean value: 4.559		Arithmetic mean value: 4.474	
Median: 4.540		Median: 4.460	
Standard deviation 0.129		Standard deviation 0.108	
Rel. st. deviation (%) 2.836		Rel. st. deviation (%) 2.414	
Run 2:		Run 2:	
Number of laboratories: 55		Number of laboratories: 53	
Arithmetic mean value: 4.544		Arithmetic mean value: 4.454	
Median: 4.540		Median: 4.460	
Standard deviation 0.072		Standard deviation 0.054	
Rel. st. deviation (%) 1.589		Rel. st. deviation (%) 1.222	
Results in decreasing order:		Results in decreasing order:	
40 5.350 (*) 106 4.540		40 5.070 (*) 106 4.460	
126 4.770 140 4.540		38 4.710 (*) 107 4.460	
38 4.750 21 4.530		126 4.710 (*) 4 4.460	
19 4.750 27 4.530		19 4.640 3 4.456	
133 4.690 33 4.530		14 4.580 15 4.450	
113 4.660 39 4.530		113 4.550 21 4.450	
109 4.610 7 4.530		133 4.540 33 4.440	
14 4.600 4 4.527		111 4.530 120 4.440	
16 4.590 11 4.520		140 4.510 11 4.440	
136 4.580 13 4.520		115 4.510 135 4.440	
34 4.571 135 4.510		109 4.500 116 4.430	
35 4.570 5 4.500		16 4.490 121 4.430	
110 4.570 130 4.500		34 4.485 39 4.430	
111 4.570 121 4.500		136 4.480 32 4.430	
117 4.570 104 4.500		117 4.480 138 4.420	
22 4.560 116 4.500		22 4.480 104 4.420	
114 4.560 118 4.500		24 4.480 12 4.410	
32 4.560 138 4.500		110 4.470 118 4.410	
20 4.560 23 4.490		112 4.470 130 4.400	
115 4.560 120 4.490		31 4.470 131 4.400	
15 4.550 10 4.480		114 4.470 18 4.400	
107 4.550 131 4.480		20 4.470 10 4.400	
112 4.550 36 4.460		7 4.460 23 4.400	
24 4.550 12 4.460		8 4.460 5 4.400	
26 4.550 1 4.460		13 4.460 1 4.380	
3 4.548 6 4.450		26 4.460 36 4.370	
31 4.540 18 4.430		27 4.460 6 4.360	
8 4.540 30 4.400		35 4.460 30 4.320	

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

Strong acid calculated from pH			
Sample no.: 1		Sample no.: 2	
Theoretical value:	75.000	Theoretical value:	85.000
Unit: $\mu\text{eq/l}$		Unit: $\mu\text{eq/l}$	
Run 1:		Run 1:	
Number of laboratories:	56	Number of laboratories:	56
Arithmetical mean value:	66.390	Arithmetical mean value:	77.880
Median:	66.375	Median:	79.433
Standard deviation	15.934	Standard deviation	11.993
Rel. st. deviation (%)	24.000	Rel. st. deviation (%)	15.400
Run 2:		Run 2:	
Number of laboratories:	54	Number of laboratories:	53
Arithmetical mean value:	65.526	Arithmetical mean value:	80.135
Median:	66.375	Median:	79.433
Standard deviation	9.051	Standard deviation	7.354
Rel. st. deviation (%)	13.812	Rel. st. deviation (%)	9.177
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 (*)
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		Sample no.: 4	
Theoretical value:	30.000	Theoretical value:	37.500
Unit: $\mu\text{eq/l}$		Unit: $\mu\text{eq/l}$	
Run 1:		Run 1:	
Number of laboratories:	56	Number of laboratories:	56
Arithmetical mean value:	28.475	Arithmetical mean value:	34.354
Median:	28.840	Median:	34.674
Standard deviation	5.435	Standard deviation	6.225
Rel. st. deviation (%)	19.088	Rel. st. deviation (%)	18.119
Run 2:		Run 2:	
Number of laboratories:	53	Number of laboratories:	52
Arithmetical mean value:	28.937	Arithmetical mean value:	35.163
Median:	28.840	Median:	34.674
Standard deviation	3.882	Standard deviation	3.974
Rel. st. deviation (%)	13.414	Rel. st. deviation (%)	11.301
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 (*)
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	Sample no.:	G2
Theoretical value:	75.000	Theoretical value:	85.000
Unit:	μeq	Unit:	μeq
Run 1:		Run 1:	
Number of laboratories:	3	Number of laboratories:	3
Arithmetic mean value:	79.067	Arithmetic mean value:	94.167
Median:	79.000	Median:	94.000
Standard deviation	3.900	Standard deviation	6.752
Rel. st. deviation (%)	4.933	Rel. st. deviation (%)	7.170
Run 2:		Run 2:	
Number of laboratories:	3	Number of laboratories:	3
Arithmetic mean value:	79.067	Arithmetic mean value:	94.167
Median:	79.000	Median:	94.000
Standard deviation	3.900	Standard deviation	6.752
Rel. st. deviation (%)	4.933	Rel. st. deviation (%)	7.170
Results in decreasing order:		Results in decreasing order:	
6	83.000	14	75.200
126	79.000	6	94.000
H			
Sample no.:	G3	Sample no.:	G4
Theoretical value:	30.000	Theoretical value:	37.500
Unit:	μeq	Unit:	μeq
Run 1:		Run 1:	
Number of laboratories:	3	Number of laboratories:	3
Arithmetic mean value:	41.267	Arithmetic mean value:	44.500
Median:	39.000	Median:	47.000
Standard deviation	10.780	Standard deviation	9.014
Rel. st. deviation (%)	26.123	Rel. st. deviation (%)	20.256
Run 2:		Run 2:	
Number of laboratories:	3	Number of laboratories:	3
Arithmetic mean value:	41.267	Arithmetic mean value:	44.500
Median:	39.000	Median:	47.000
Standard deviation	10.780	Standard deviation	9.014
Rel. st. deviation (%)	26.123	Rel. st. deviation (%)	20.256
Results in decreasing order:		Results in decreasing order:	
126	53.000	14	31.800
6	39.000	6	47.000

Table 25: Analytical results for chloride in precipitations samples.

Cl				Cl			
Sample no.: G1				Sample no.: G2			
Theoretical value: 0.145				Theoretical value: 0.203			
Unit: µg/l				Unit: µg/l			
Run 1:				Run 1:			
Number of laboratories:	49	Number of laboratories:	49	Arithmmetic mean value:	0.148	Arithmmetic mean value:	0.209
Median:	0.140	Median:	0.140	Standard deviation	0.067	Standard deviation	0.075
Standard deviation	0.067	Rel. st. deviation (%)	45.459	Rel. st. deviation (%)	36.100		
Rel. st. deviation (%)	45.459						
Run 2:				Run 2:			
Number of laboratories:	48	Number of laboratories:	48	Arithmmetic mean value:	0.140	Arithmmetic mean value:	0.200
Median:	0.140	Median:	0.140	Standard deviation	0.039	Standard deviation	0.042
Standard deviation	0.039	Rel. st. deviation (%)	27.833	Rel. st. deviation (%)	21.243		
Rel. st. deviation (%)	27.833						
Results in decreasing order:				Results in decreasing order:			
133	0.526 (*)	26	0.140	133	0.638 (*)	26	0.197
110	0.250	38	0.140	32	0.298	36	0.195
115	0.220	32	0.139	118	0.290	7	0.195
40	0.219	34	0.138	115	0.290	4	0.193
120	0.200	39	0.136	40	0.283	14	0.193
113	0.190	14	0.136	110	0.280	15	0.191
118	0.190	35	0.135	120	0.260	104	0.190
33	0.187	16	0.133	140	0.250	16	0.188
140	0.170	24	0.130	33	0.250	34	0.187
5	0.160	126	0.130	113	0.230	6	0.183
31	0.156	104	0.130	114	0.220	18	0.180
136	0.153	15	0.129	5	0.212	126	0.180
1	0.150	6	0.121	3	0.210	24	0.180
7	0.150	130	0.120	38	0.210	136	0.176
114	0.150	23	0.115	39	0.210	116	0.165
21	0.148	11	0.106	107	0.207	130	0.160
3	0.147	116	0.105	27	0.206	11	0.157
30	0.147	22	0.105	30	0.205	23	0.156
13	0.146	20	0.101	21	0.203	20	0.152
27	0.145	131	0.099	13	0.203	22	0.142
107	0.144	138	0.092	31	0.201	131	0.138
4	0.141	135	0.075	12	0.200	138	0.135
36	0.141	18	0.045	1	0.200	135	0.129
12	0.140	10	0.043	8	0.200	10	0.116
8	0.140			35	0.198		
Results in decreasing order:				Results in decreasing order:			
40	0.704 (*)	15	0.561	40	0.825 (*)	32	0.611
33	0.657	126	0.560	113	0.740 (*)	130	0.610
140	0.650	14	0.551	115	0.700	39	0.610
113	0.640	130	0.550	140	0.690	4	0.603
32	0.640	30	0.550	18	0.674	14	0.603
18	0.629	4	0.548	33	0.666	107	0.602
115	0.620	6	0.547	110	0.660	20	0.602
118	0.600	107	0.546	31	0.647	104	0.600
111	0.596	19	0.546	27	0.640	116	0.597
114	0.590	131	0.540	12	0.640	138	0.597
12	0.590	34	0.539	114	0.640	34	0.595
38	0.590	20	0.532	118	0.640	131	0.593
26	0.585	104	0.530	26	0.640	120	0.590
1	0.580	109	0.530	5	0.635	135	0.588
110	0.580	135	0.525	15	0.634	19	0.588
31	0.578	24	0.520	3	0.632	109	0.580
21	0.575	16	0.515	8	0.632	126	0.580
27	0.575	112	0.510	21	0.631	24	0.580
5	0.574	11	0.508	13	0.627	133	0.576
13	0.573	117	0.499	35	0.626	11	0.568
3	0.572	121	0.497	111	0.624	117	0.565
116	0.572	23	0.494	136	0.623	121	0.561
120	0.570	39	0.486	7	0.622	112	0.560
136	0.570	138	0.486	1	0.620	16	0.558
8	0.569	10	0.477	38	0.620	10	0.544
35	0.567	133	0.467	36	0.619	23	0.540
7	0.567	22	0.420 (*)	6	0.614	22	0.495 (*)
36	0.565			30	0.613		

Table 26: Analytical results for sodium in precipitations samples.

Na		Na	
Sample no.: G1		Sample no.: G2	
Theoretical value:	0.336	Theoretical value:	0.454
Unit: µg/l		Unit: µg/l	
Run 1:		Run 1:	
Number of laboratories:	53	Number of laboratories:	53
Arithmetic mean value:	0.326	Arithmetic mean value:	0.438
Median:	0.330	Median:	0.444
Standard deviation	0.042	Standard deviation	0.039
Rel. st. deviation (%)	12.765	Rel. st. deviation (%)	8.962
Run 2:		Run 2:	
Number of laboratories:	49	Number of laboratories:	48
Arithmetic mean value:	0.326	Arithmetic mean value:	0.439
Median:	0.330	Median:	0.444
Standard deviation	0.026	Standard deviation	0.028
Rel. st. deviation (%)	7.965	Rel. st. deviation (%)	6.376
Results in decreasing order:		Results in decreasing order:	
140 0.460 (*) 110 0.330		32 0.550 (*) 114 0.440	
118 0.420 (*) 130 0.330		109 0.530 (*) 19 0.439	
32 0.400 138 0.321		121 0.510 20 0.439	
109 0.390 1 0.320		118 0.490 104 0.430	
4 0.379 21 0.319		22 0.490 138 0.430	
22 0.370 35 0.319		1 0.480 35 0.429	
126 0.360 135 0.317		4 0.479 135 0.423	
112 0.350 131 0.314		126 0.470 34 0.422	
30 0.343 10 0.314		112 0.460 12 0.420	
14 0.343 117 0.312		131 0.460 110 0.420	
26 0.342 34 0.311		36 0.458 33 0.420	
104 0.340 12 0.310		26 0.457 140 0.420	
7 0.340 33 0.310		5 0.456 120 0.420	
39 0.338 120 0.308		39 0.456 10 0.419	
36 0.337 38 0.307		13 0.455 23 0.415	
5 0.336 3 0.307		107 0.454 11 0.415	
6 0.335 31 0.306		30 0.453 31 0.415	
13 0.335 133 0.300		7 0.453 117 0.410	
27 0.334 11 0.296		15 0.450 3 0.407	
107 0.334 23 0.292		130 0.450 38 0.397	
20 0.333 40 0.288		16 0.450 40 0.385	
8 0.332 111 0.282		8 0.449 113 0.380	
19 0.331 113 0.280		27 0.448 111 0.377	
114 0.330 115 0.270		116 0.448 136 0.356 (*)	
16 0.330 116 0.204 (*)		6 0.447 133 0.350 (*)	
15 0.330 136 0.200 (*)		21 0.444 115 0.350 (*)	
121 0.330		14 0.444	
Na		Na	
Sample no.: G3		Sample no.: G4	
Theoretical value:	0.537	Theoretical value:	0.789
Unit: µg/l		Unit: µg/l	
Run 1:		Run 1:	
Number of laboratories:	53	Number of laboratories:	53
Arithmetic mean value:	0.523	Arithmetic mean value:	0.749
Median:	0.527	Median:	0.760
Standard deviation	0.060	Standard deviation	0.075
Rel. st. deviation (%)	11.535	Rel. st. deviation (%)	9.977
Run 2:		Run 2:	
Number of laboratories:	48	Number of laboratories:	50
Arithmetic mean value:	0.512	Arithmetic mean value:	0.754
Median:	0.524	Median:	0.760
Standard deviation	0.038	Standard deviation	0.051
Rel. st. deviation (%)	7.379	Rel. st. deviation (%)	6.703
Results in decreasing order:		Results in decreasing order:	
22 0.718 (*) 6 0.526		22 0.994 (*) 109 0.760	
116 0.683 (*) 30 0.523		32 0.870 110 0.760	
32 0.670 (*) 110 0.520		1 0.840 34 0.759	
109 0.650 (*) 16 0.520		4 0.823 131 0.756	
118 0.580 35 0.518		118 0.820 12 0.750	
140 0.580 104 0.510		126 0.800 135 0.750	
1 0.570 12 0.510		36 0.798 120 0.743	
4 0.567 120 0.502		7 0.795 11 0.743	
126 0.560 14 0.500		5 0.795 3 0.742	
39 0.543 34 0.496		107 0.793 140 0.740	
7 0.540 10 0.494		112 0.790 10 0.736	
5 0.540 3 0.492		39 0.787 23 0.734	
112 0.540 135 0.491		26 0.785 14 0.733	
36 0.539 31 0.488		21 0.785 138 0.719	
107 0.537 11 0.487		20 0.781 113 0.710	
26 0.536 23 0.486		8 0.781 31 0.706	
21 0.535 138 0.476		114 0.780 33 0.700	
20 0.535 117 0.471		130 0.780 121 0.680	
8 0.532 113 0.460		35 0.779 117 0.677	
131 0.531 33 0.460		30 0.778 136 0.664	
15 0.530 40 0.451		27 0.775 111 0.654	
114 0.530 111 0.448		16 0.770 38 0.651	
121 0.530 38 0.447		19 0.769 40 0.651	
130 0.530 136 0.427		13 0.769 115 0.630	
19 0.529 115 0.420		6 0.767 133 0.550 (*)	
13 0.527 133 0.400 (*)		104 0.760 116 0.494 (*)	
27 0.527		15 0.760	

Table 27: Analytical results for magnesium in precipitations samples.

Mg			
Sample no.: G1		Sample no.: G2	
Theoretical value:	0.155	Theoretical value:	0.077
Unit: µg/l		Unit: µg/l	
Run 1:		Run 1:	
Number of laboratories:	52	Number of laboratories:	52
Arithmmetic mean value:	0.151	Arithmmetic mean value:	0.079
Median:	0.151	Median:	0.078
Standard deviation	0.020	Standard deviation	0.014
Rel. st. deviation (%)	13.083	Rel. st. deviation (%)	17.992
Run 2:		Run 2:	
Number of laboratories:	47	Number of laboratories:	50
Arithmmetic mean value:	0.152	Arithmmetic mean value:	0.077
Median:	0.152	Median:	0.078
Standard deviation	0.010	Standard deviation	0.008
Rel. st. deviation (%)	6.551	Rel. st. deviation (%)	10.053
Results in decreasing order:		Results in decreasing order:	
20 0.213 (*) 107 0.151		126 0.150 (*) 5 0.078	
126 0.210 (*) 14 0.151		20 0.125 (*) 14 0.077	
118 0.171 114 0.150		136 0.101 120 0.077	
112 0.170 115 0.150		112 0.090 39 0.077	
138 0.169 117 0.150		30 0.088 12 0.076	
135 0.163 23 0.150		138 0.088 117 0.076	
34 0.162 16 0.150		22 0.084 36 0.076	
3 0.161 121 0.150		118 0.083 11 0.076	
33 0.160 110 0.150		135 0.083 16 0.076	
104 0.160 130 0.150		3 0.081 40 0.076	
7 0.160 27 0.150		13 0.080 27 0.075	
15 0.160 8 0.149		1 0.080 35 0.075	
22 0.159 30 0.149		15 0.080 8 0.075	
31 0.159 111 0.147		31 0.080 116 0.074	
13 0.159 6 0.147		104 0.080 34 0.074	
131 0.158 12 0.147		130 0.080 111 0.073	
21 0.157 40 0.143		33 0.080 23 0.073	
5 0.156 1 0.140		114 0.080 140 0.070	
11 0.156 113 0.140		113 0.080 109 0.070	
26 0.155 4 0.136		121 0.079 115 0.070	
19 0.155 38 0.133		131 0.079 4 0.068	
10 0.154 133 0.127		10 0.079 133 0.068	
120 0.154 140 0.120		21 0.079 6 0.067	
35 0.153 136 0.108 (*)		26 0.079 110 0.060	
39 0.153 109 0.100 (*)		7 0.078 107 0.056	
36 0.152 116 0.091 (*)		19 0.078 38 0.055	
Results in decreasing order:		Results in decreasing order:	
126 0.160 (*) 1 0.090		126 0.180 (*) 19 0.115	
20 0.123 114 0.090		20 0.142 8 0.114	
22 0.112 115 0.090		112 0.130 135 0.114	
35 0.108 8 0.090		35 0.129 120 0.113	
116 0.104 27 0.090		138 0.126 16 0.113	
138 0.104 16 0.090		22 0.125 27 0.112	
135 0.100 104 0.090		118 0.123 12 0.111	
112 0.100 15 0.090		7 0.123 11 0.111	
118 0.099 109 0.090		1 0.120 121 0.110	
3 0.098 33 0.090		33 0.120 130 0.110	
7 0.097 113 0.090		3 0.120 113 0.110	
131 0.097 12 0.089		104 0.120 114 0.110	
121 0.095 111 0.088		131 0.119 115 0.110	
13 0.095 30 0.087		21 0.119 6 0.109	
21 0.095 117 0.087		13 0.118 23 0.109	
26 0.094 23 0.085		10 0.118 111 0.109	
5 0.094 6 0.084		30 0.118 117 0.108	
10 0.093 133 0.082		26 0.118 40 0.101	
36 0.093 4 0.081		5 0.117 140 0.100	
19 0.093 40 0.081		14 0.117 110 0.100	
31 0.093 107 0.081		36 0.116 109 0.100	
34 0.092 110 0.080		39 0.116 4 0.098	
120 0.092 130 0.080		107 0.116 133 0.097	
39 0.092 140 0.080		15 0.116 38 0.092	
14 0.091 38 0.068		31 0.116 116 0.087	
11 0.091 136 0.029 (*)		34 0.116 136 0.050 (*)	

Table 28: Analytical results for calcium in precipitations samples.

Ca			
Sample no.: G1		Sample no.: G2	
Theoretical value:	0.287	Theoretical value:	0.192
Unit: µg/l		Unit: µg/l	
Run 1:		Run 1:	
Number of laboratories:	53	Number of laboratories:	53
Arithmetic mean value:	0.288	Arithmetic mean value:	0.203
Median:	0.283	Median:	0.192
Standard deviation	0.063	Standard deviation	0.045
Rel. st. deviation (%)	21.760	Rel. st. deviation (%)	22.266
Run 2:		Run 2:	
Number of laboratories:	49	Number of laboratories:	50
Arithmetic mean value:	0.288	Arithmetic mean value:	0.199
Median:	0.283	Median:	0.192
Standard deviation	0.032	Standard deviation	0.028
Rel. st. deviation (%)	11.054	Rel. st. deviation (%)	14.253
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		
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		Sample no.: G4	
Theoretical value:	0.326	Theoretical value:	0.239
Unit: µg/l		Unit: µg/l	
Run 1:		Run 1:	
Number of laboratories:	53	Number of laboratories:	53
Arithmetic mean value:	0.318	Arithmetic mean value:	0.241
Median:	0.322	Median:	0.239
Standard deviation	0.065	Standard deviation	0.044
Rel. st. deviation (%)	20.330	Rel. st. deviation (%)	18.260
Run 2:		Run 2:	
Number of laboratories:	49	Number of laboratories:	48
Arithmetic mean value:	0.320	Arithmetic mean value:	0.234
Median:	0.322	Median:	0.238
Standard deviation	0.035	Standard deviation	0.028
Rel. st. deviation (%)	10.801	Rel. st. deviation (%)	11.984
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		
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		Sample no.: G2	
Theoretical value:	0.280	Theoretical value:	0.178
Unit: µg/l		Unit: µg/l	
Run 1:		Run 1:	
Number of laboratories:	52	Number of laboratories:	52
Arithmmetic mean value:	0.278	Arithmmetic mean value:	0.180
Median:	0.272	Median:	0.176
Standard deviation	0.073	Standard deviation	0.045
Rel. st. deviation (%)	26.327	Rel. st. deviation (%)	25.239
Run 2:		Run 2:	
Number of laboratories:	50	Number of laboratories:	50
Arithmmetic mean value:	0.266	Arithmmetic mean value:	0.172
Median:	0.271	Median:	0.176
Standard deviation	0.035	Standard deviation	0.024
Rel. st. deviation (%)	13.027	Rel. st. deviation (%)	13.776
Results in decreasing order:		Results in decreasing order:	
133 0.700 (*) 22 0.272		109 0.390 (*) 7 0.176	
109 0.450 (*) 114 0.270		116 0.355 (*) 31 0.176	
118 0.360 126 0.270		22 0.213 21 0.174	
32 0.320 130 0.270		117 0.211 5 0.174	
30 0.314 12 0.270		112 0.210 8 0.171	
112 0.310 27 0.270		32 0.210 23 0.171	
35 0.290 36 0.269		38 0.206 130 0.170	
104 0.290 117 0.266		118 0.200 114 0.170	
6 0.288 21 0.264		133 0.200 36 0.169	
5 0.287 111 0.261		131 0.195 135 0.168	
14 0.286 1 0.260		14 0.191 4 0.167	
20 0.286 4 0.260		12 0.190 16 0.166	
3 0.285 31 0.255		3 0.184 138 0.161	
19 0.285 131 0.254		26 0.182 30 0.160	
26 0.284 138 0.254		19 0.182 111 0.160	
107 0.283 34 0.251		6 0.182 104 0.160	
38 0.282 33 0.250		15 0.180 33 0.160	
15 0.280 110 0.250		1 0.180 140 0.160	
121 0.280 120 0.245		110 0.180 120 0.155	
13 0.280 140 0.240		126 0.180 136 0.152	
39 0.278 113 0.240		35 0.180 113 0.150	
16 0.275 10 0.226		13 0.180 10 0.135	
135 0.275 40 0.209		20 0.179 34 0.133	
7 0.273 115 0.180		107 0.178 121 0.120	
23 0.273 116 0.164		27 0.177 115 0.110	
8 0.272 136 0.158		39 0.177 40 0.101	
Results in decreasing order:		Results in decreasing order:	
109 0.590 (*) 104 0.320		116 0.307 (*) 7 0.124	
32 0.400 114 0.320		133 0.200 (*) 14 0.123	
22 0.394 12 0.320		118 0.160 5 0.122	
20 0.363 36 0.319		112 0.160 8 0.121	
118 0.360 131 0.316		22 0.157 130 0.120	
112 0.360 14 0.316		31 0.141 33 0.120	
35 0.345 21 0.310		126 0.140 114 0.120	
5 0.344 4 0.307		109 0.140 13 0.120	
126 0.340 130 0.300		12 0.140 135 0.119	
38 0.336 1 0.300		32 0.140 36 0.119	
3 0.335 111 0.299		140 0.140 30 0.118	
6 0.334 23 0.297		3 0.133 4 0.117	
19 0.333 34 0.295		38 0.132 111 0.113	
26 0.333 30 0.291		19 0.131 136 0.111	
107 0.332 33 0.290		1 0.130 131 0.111	
39 0.331 120 0.289		34 0.130 120 0.111	
7 0.331 113 0.280		15 0.129 113 0.110	
31 0.331 140 0.280		26 0.129 23 0.104	
110 0.330 138 0.279		6 0.129 104 0.100	
15 0.330 10 0.264		35 0.129 110 0.100	
27 0.330 121 0.260		21 0.127 138 0.092	
117 0.328 40 0.238		27 0.126 10 0.091	
16 0.325 136 0.206		16 0.125 40 0.077	
13 0.325 115 0.200		39 0.125 121 0.076	
135 0.325 116 0.155 (*)		107 0.124 115 0.070	
8 0.324 133 0.100 (*)		20 0.124 117 0.068	

Table 30: Analytical results for conductivity in precipitations samples.

Cond. Sample no.: G1 Theoretical value: Unit: $\mu\text{S}/\text{cm}$	Cond. Sample no.: G2 Theoretical value: Unit: $\mu\text{S}/\text{cm}$
43.300	44.600
Run 1: Number of laboratories: 54 Arithmetic mean value: 40.653 Median: 41.700 Standard deviation 3.525 Rel. st. deviation (%) 8.671	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: 41.277 Median: 42.000 Standard deviation 2.392 Rel. st. deviation (%) 5.795	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 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 (*)	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: Unit: $\mu\text{S}/\text{cm}$	Cond. Sample no.: G4 Theoretical value: Unit: $\mu\text{S}/\text{cm}$
25.700	26.200
Run 1: Number of laboratories: 54 Arithmetic mean value: 25.472 Median: 25.800 Standard deviation 1.840 Rel. st. deviation (%) 7.225	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: 25.760 Median: 25.800 Standard deviation 1.116 Rel. st. deviation (%) 4.334	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: 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 (*)	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	NH ₄ ⁺ 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 Cond. is missing
26					
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	NH ₄ ⁺ 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 Cl ⁻ values < LOD
19	1.10	1.13	1.07	1.08	1.09	
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	
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 2. Ion chromatography 3. Capillary electrophoresis 4. ICP-AES 5. FIA	18 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 39 109, 112, 113, 117 121
NO ₃	1 Griess after Cd-red. 2 Ion chromatography 3 UV-method/Photometric 4 Capillary electrophoresis 5 FIA	112, 117 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 40, 104, 39 109, 111, 121
NH ₄	1 Indophenol 2 Berthelot reaction, salicylate 3 Ion chromatography 4 Flow injection analysis (FIA) 5 Chloramin T 6 Nessler method 7 Kjeldahl 8 Photometry	10, 19, 20, 32, 33, 34, 39, 40, 112, 114, 116, 117, 126, 140 26, 118, 1, 5, 6, 7, 8, 12, 13, 15, 21, 22, 23, 24, 31, 35, 36, 107, 113, 115, 131, 135, 136 14, 27, 109, 111, 121 16 18, 3, 4, 104, 110, 114, 133
H ⁺	1 Acidimetric titration 2 Alkali titration to spec. pH	14, 126 6,
Mg	1 Atomic absorption (AAS) 2 Ion chromatography 3 ICP-AES 4 ICP-MS	3, 4, 10, 16, 19, 22, 26, 27, 33, 34, 38, 39, 40, 116, 133 1, 5, 6, 7, 8, 12, 13, 15, 20, 21, 23, 31, 35, 36, 107, 113, 114, 126, 130, 131, 135, 136, 138, 140 11, 104, 109, 111, 112, 115, 117, 118, 121 14,
Na	1 AES 2 AAS 3 ICP-AES 5 Ion chromatography 6 ICP-MS	32, 33, 38, 39, 116, 133 3, 4, 10, 16, 19, 26, 27, 34, 40, 11, 104, 109, 110, 111, 112, 115, 117, 118, 121 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 14
Cl	1 Mercury thiocyanate-iron 2 Ion chromatography 3 Capillary electrophoresis 4 Potentiometric method 5 FIA	18, 117, 40 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 39 109, 112 121
Ca	1 AAS 2 ICP-AES 3 Ion chromatography 6 AES 7 ICP-MS	3, 4, 10, 16, 19, 22, 26, 27, 33, 34, 38, 39, 40, 116, 133 11, 104, 109, 110, 111, 112, 115, 117, 118, 121 1, 5, 6, 7, 8, 12, 15, 20, 21, 23, 31, 35, 36, 107, 113, 114, 126, 130, 131, 135, 136, 138, 140 32, 14
K	1 AAS 2 Ion chromatography 3 AES 4 ICP-AES 5 ICP-MS	3, 4, 10, 16, 19, 26, 27, 33, 34, 35, 40, 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 32, 39, 116, 133 11, 104, 109, 110, 111, 112, 115, 117, 118, 121, 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 %								
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

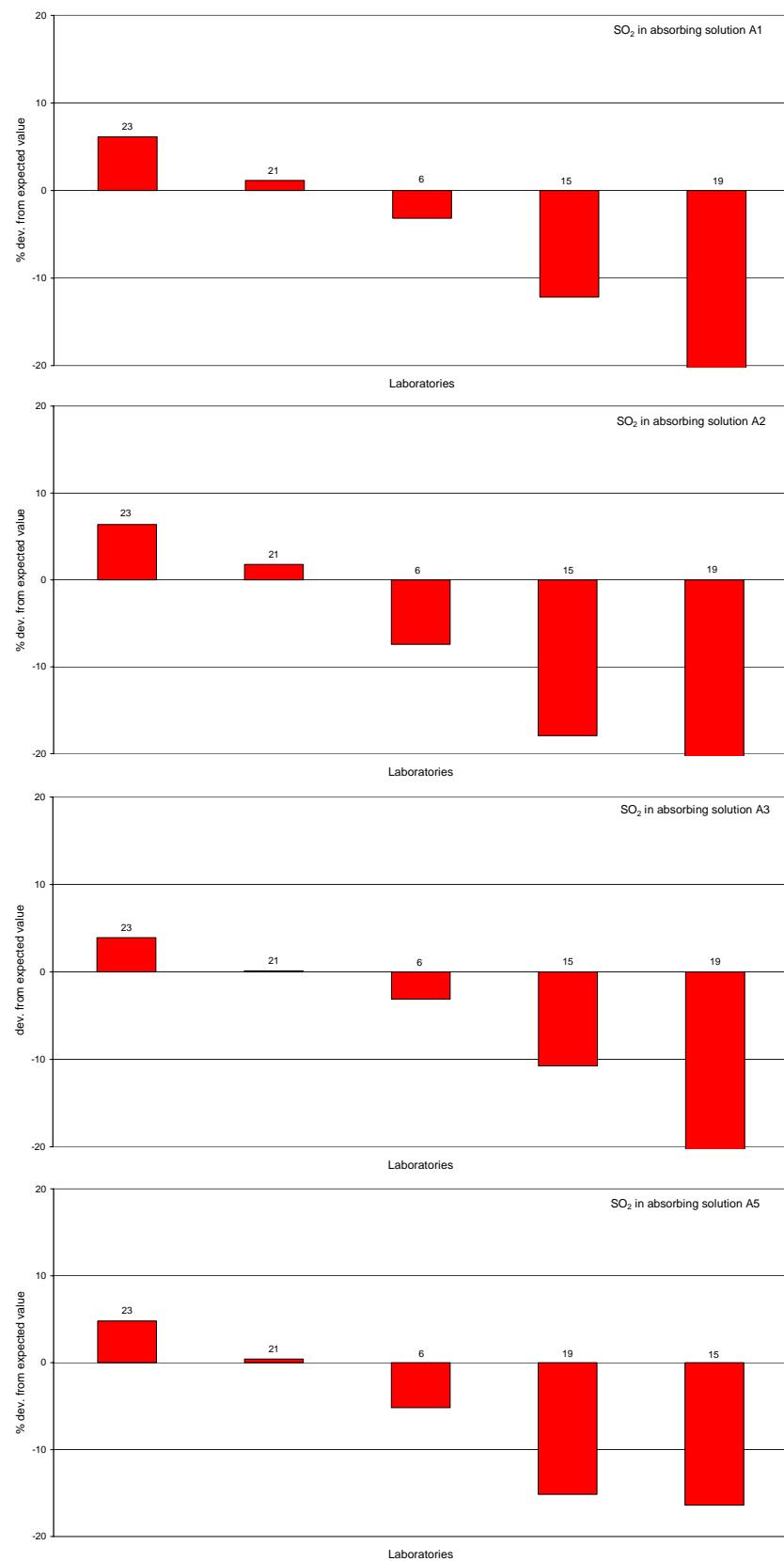


Figure 2: SO_2 in absorbing solution.

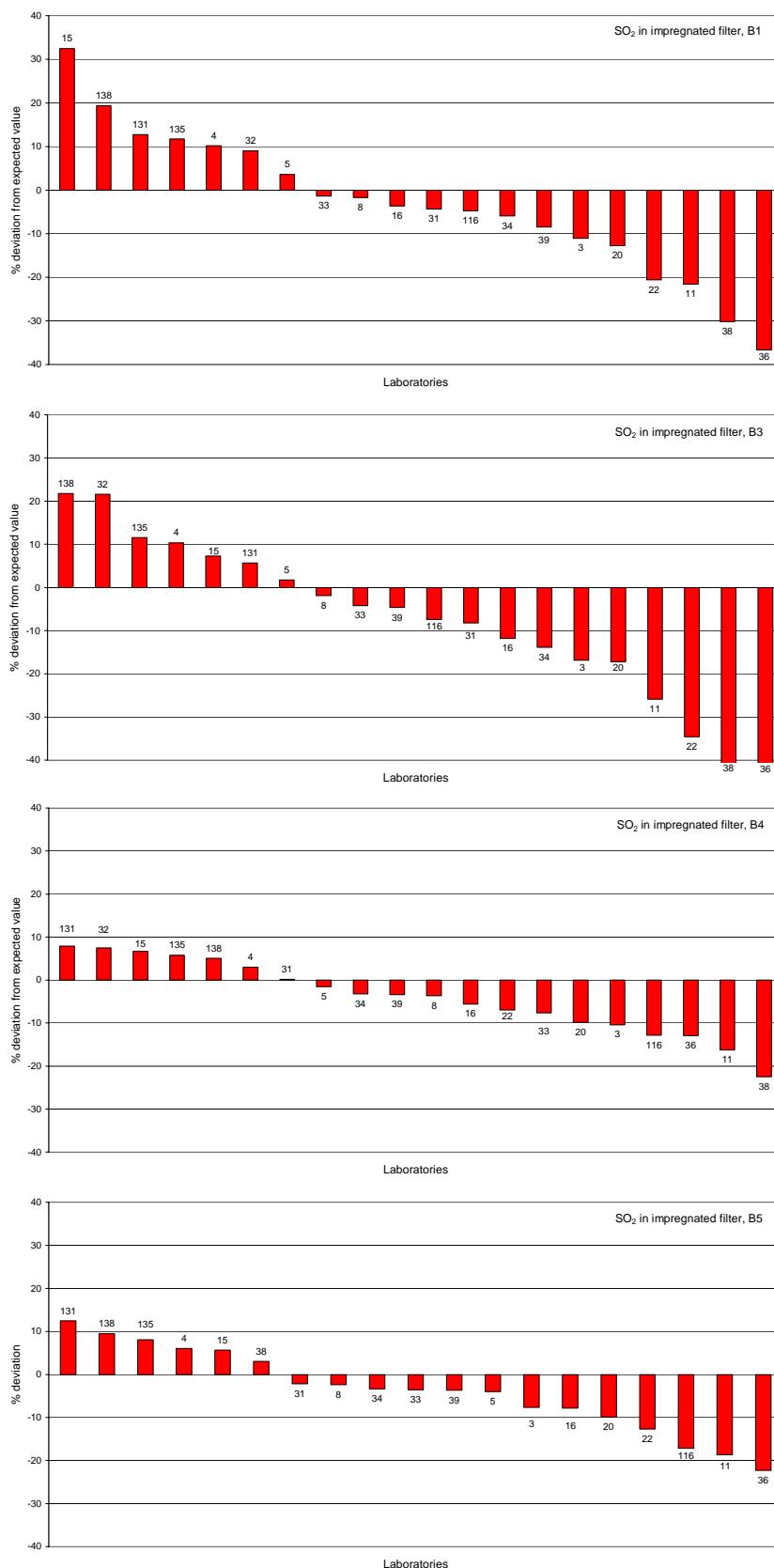


Figure 3: SO₂ in impregnated filter.

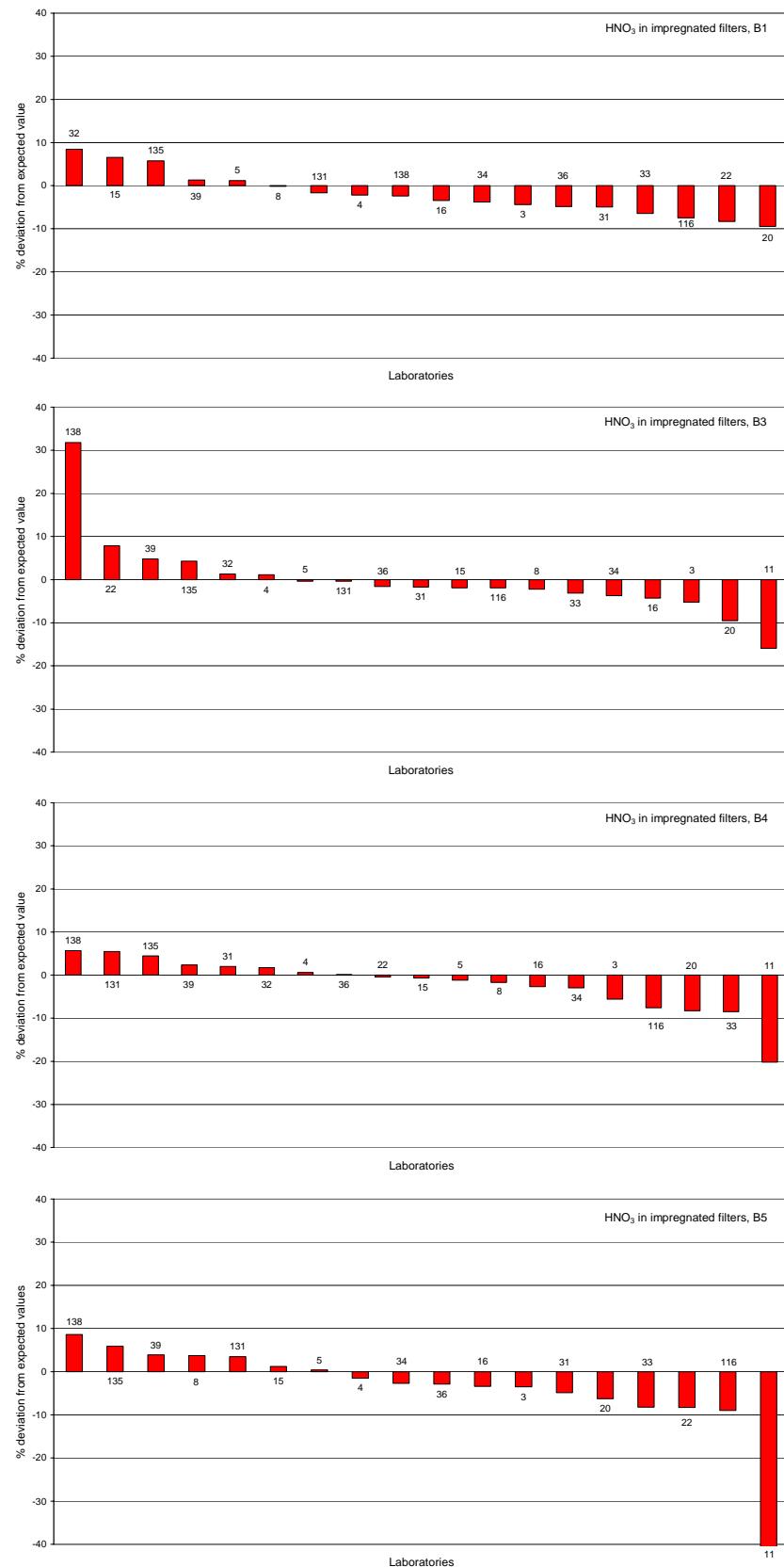


Figure 4: HNO_3 in impregnated filter.

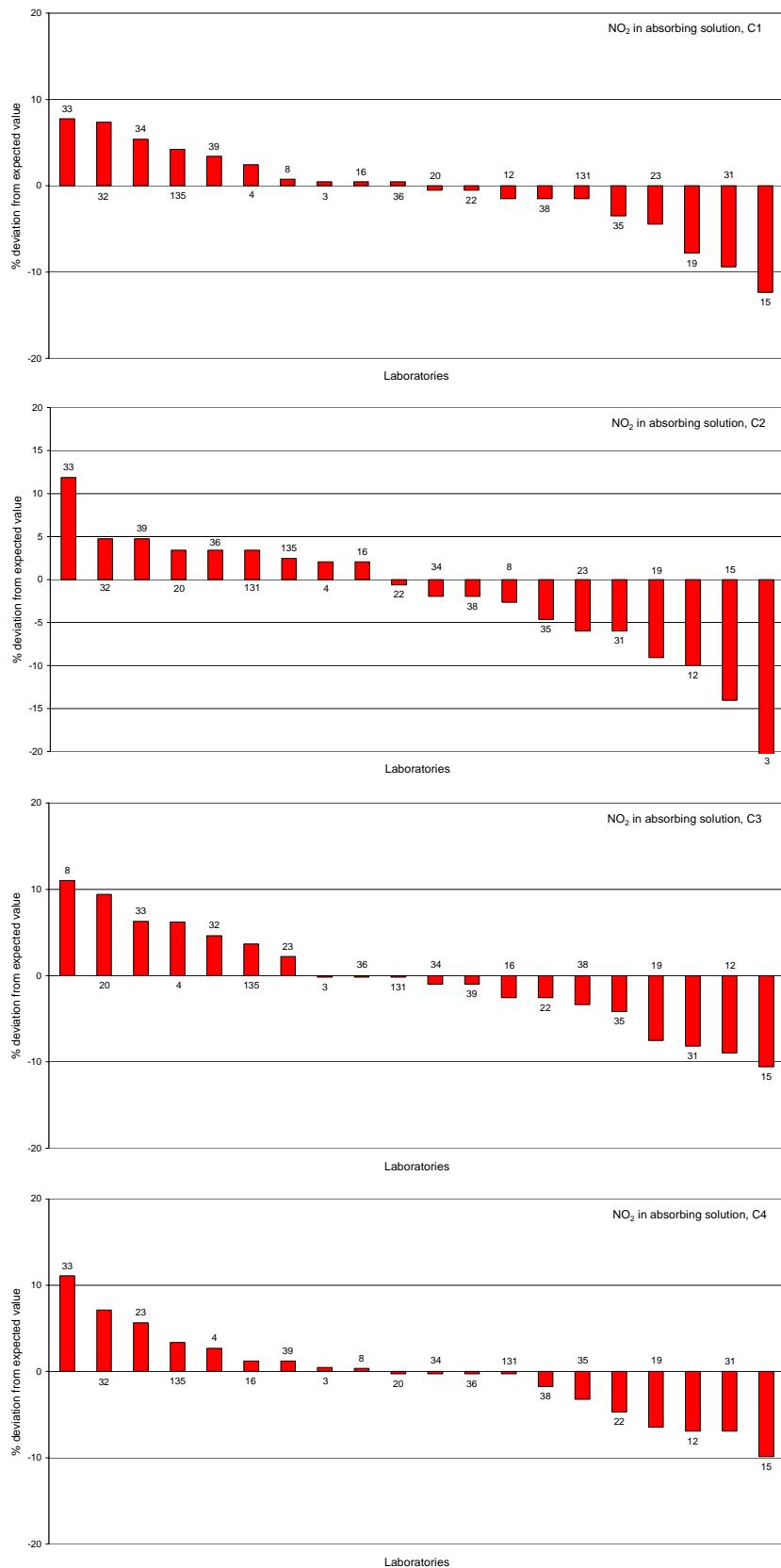


Figure 5: NO_2 in absorbing solution.

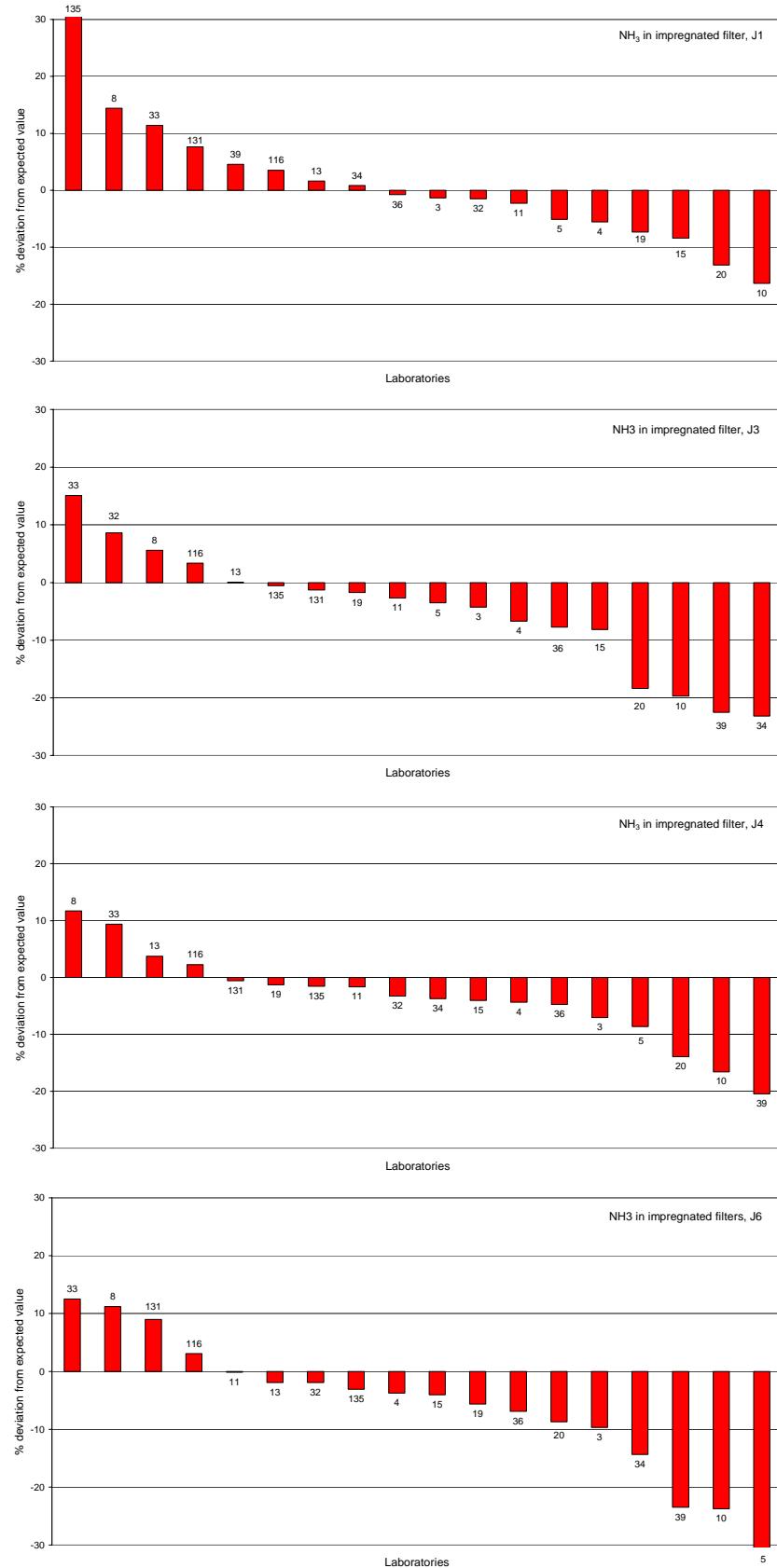


Figure 6: NH_3 in impregnated filter.

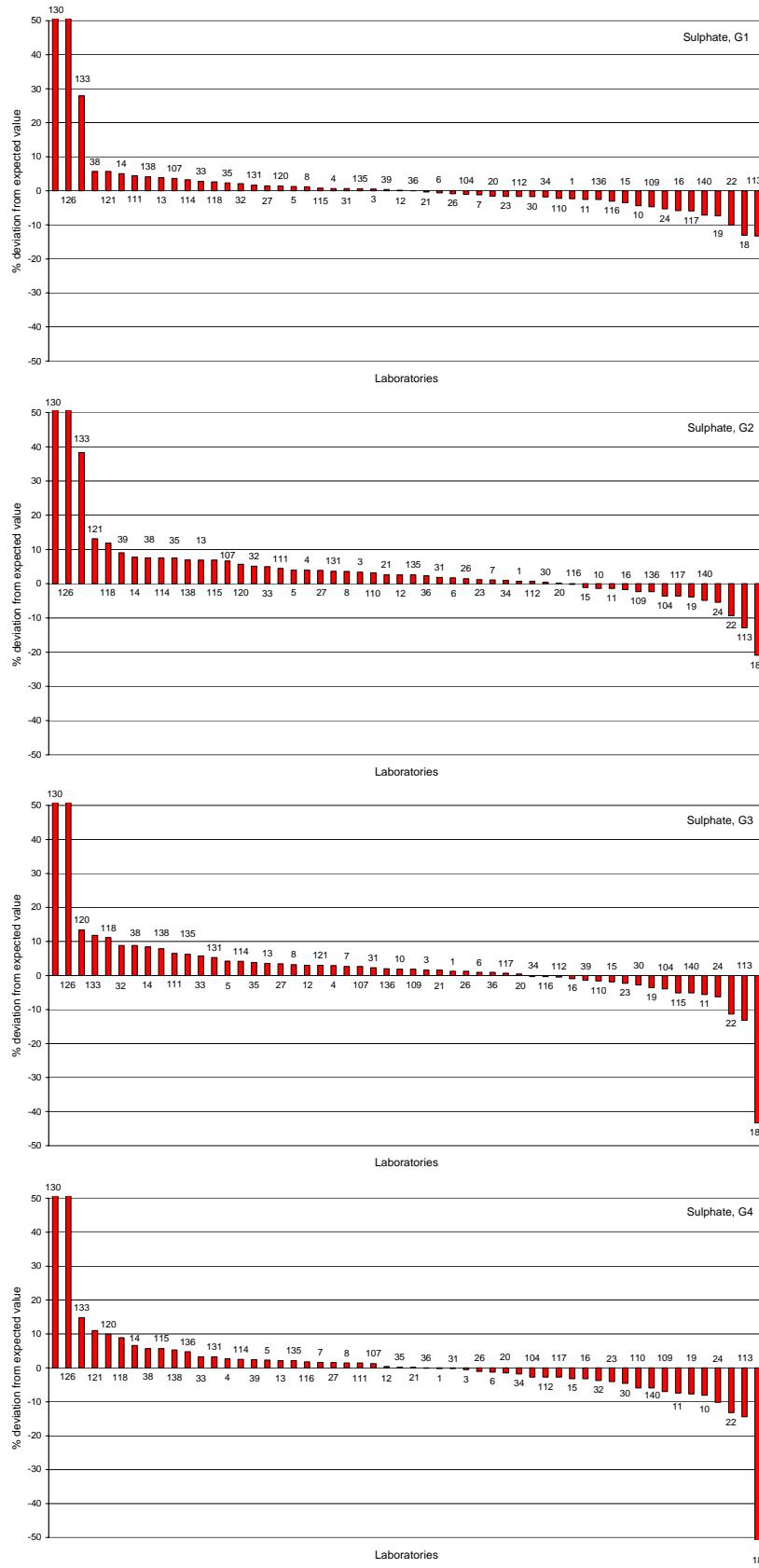


Figure 7: Percent deviation from theoretical value for sulphate.

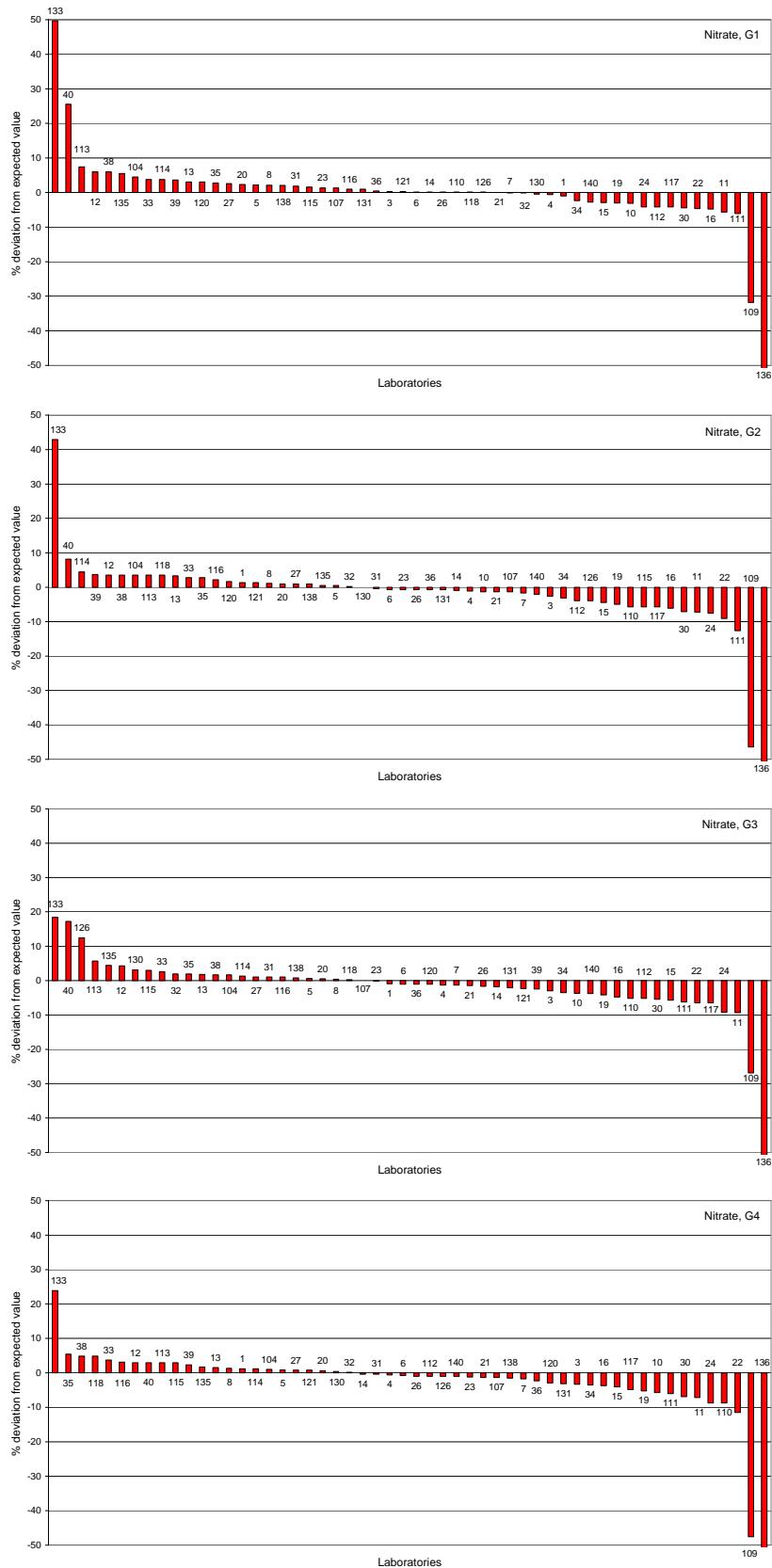


Figure 8: Percent deviation from theoretical value for nitrate.

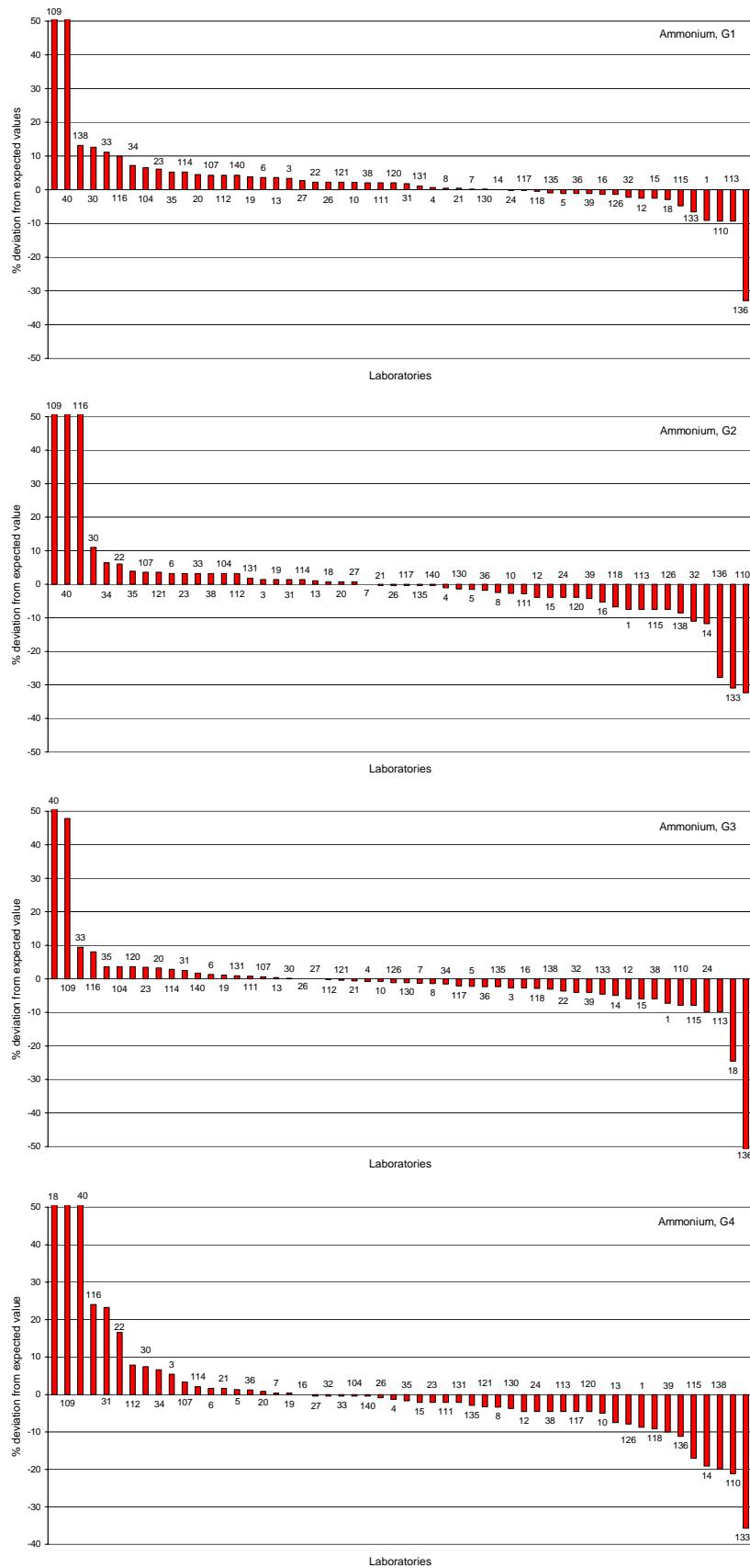


Figure 9: Percent deviation from theoretical value for ammonium.

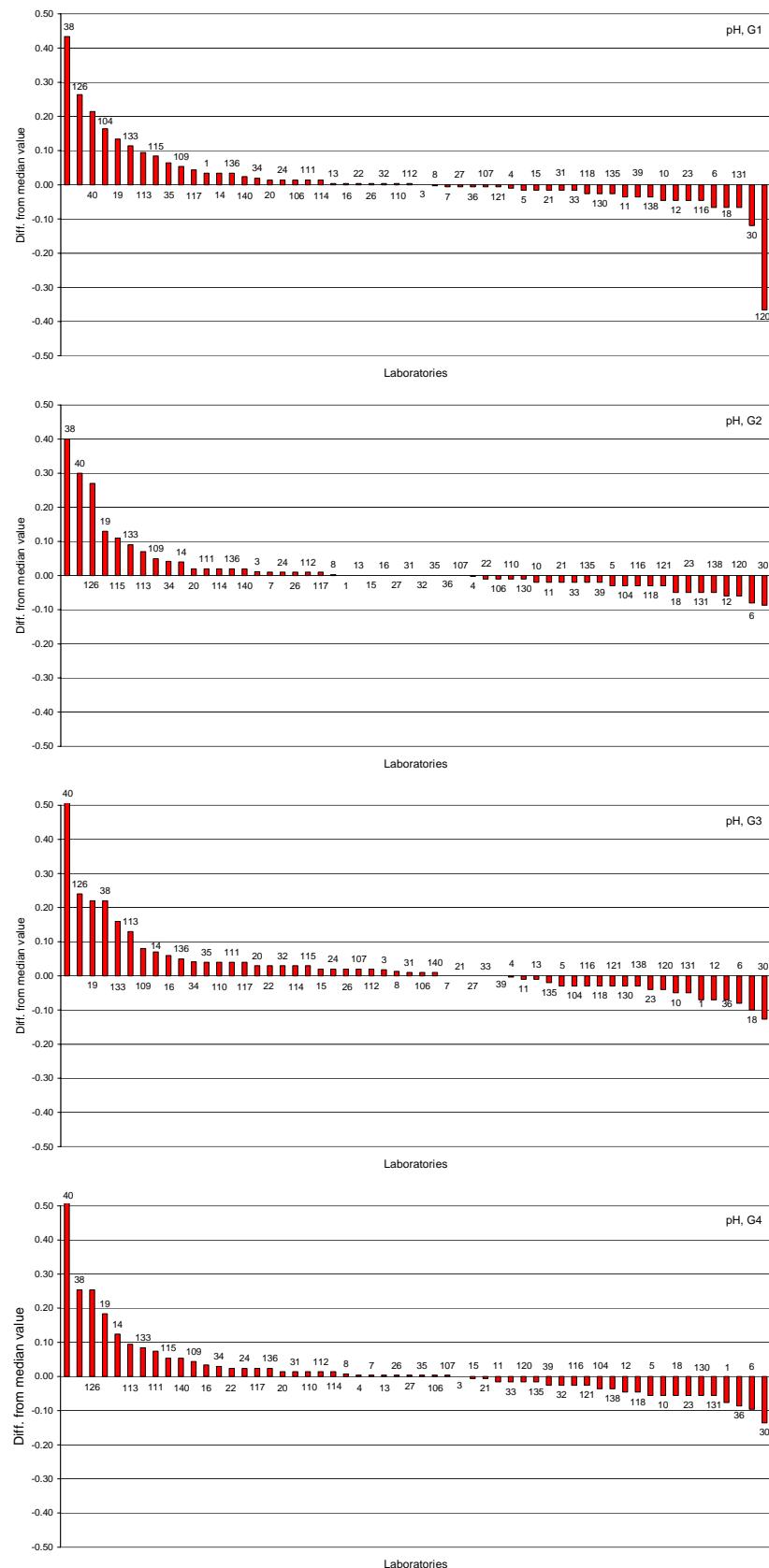


Figure 10: Percent deviation from theoretical value for pH.

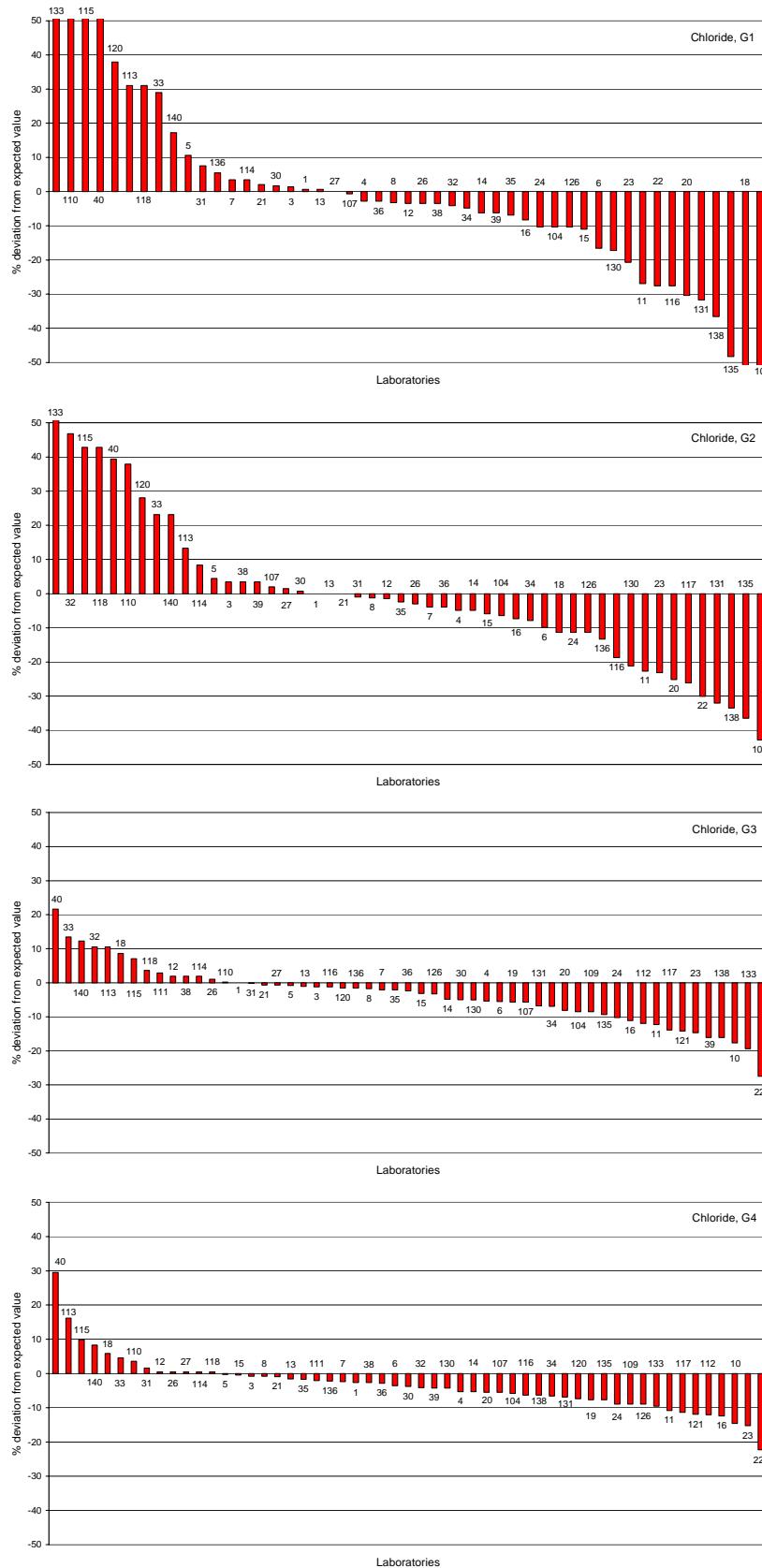


Figure 11: Percent deviation from theoretical value for chloride.

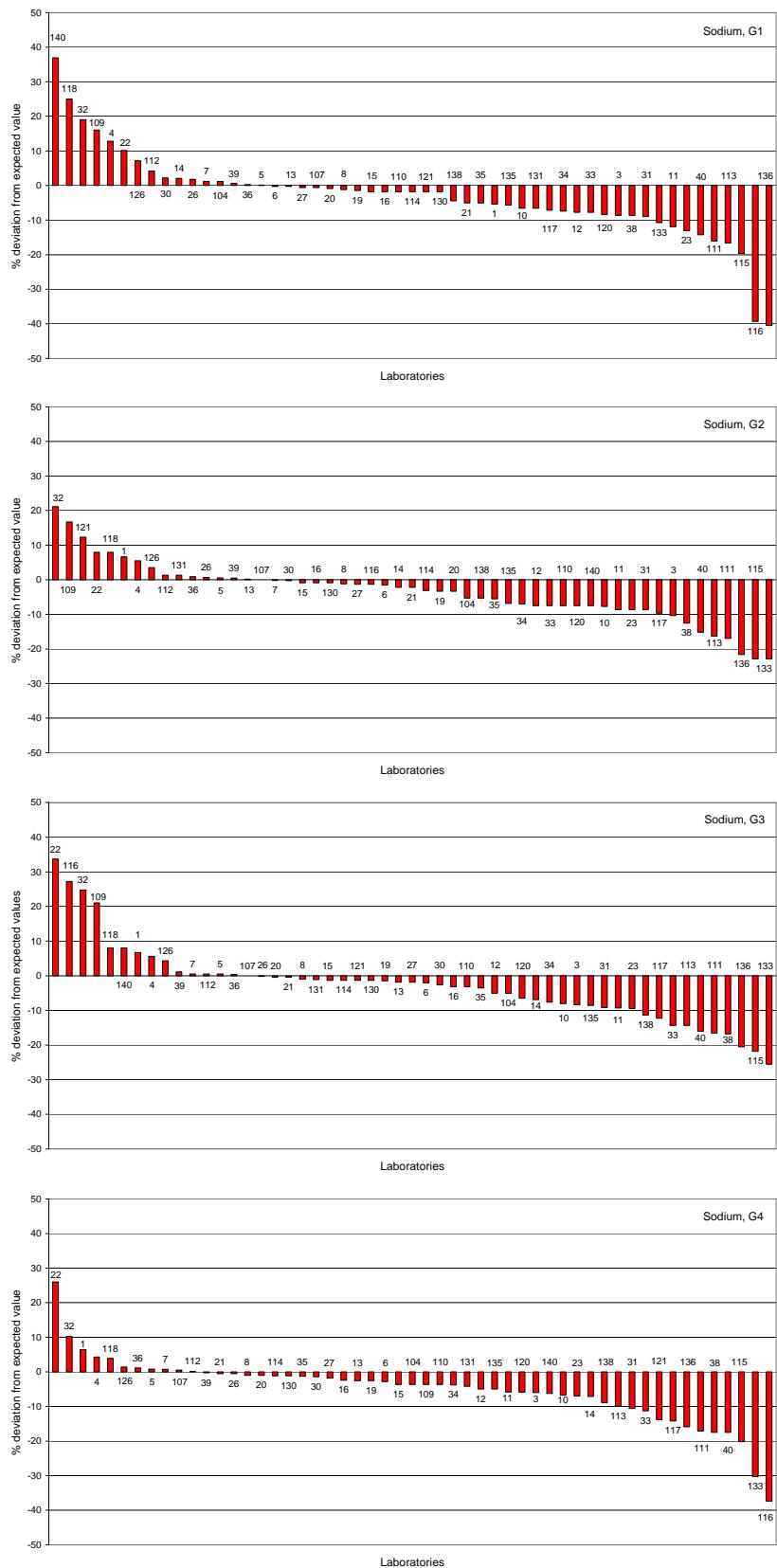


Figure 12: Percent deviation from theoretical value for sodium.

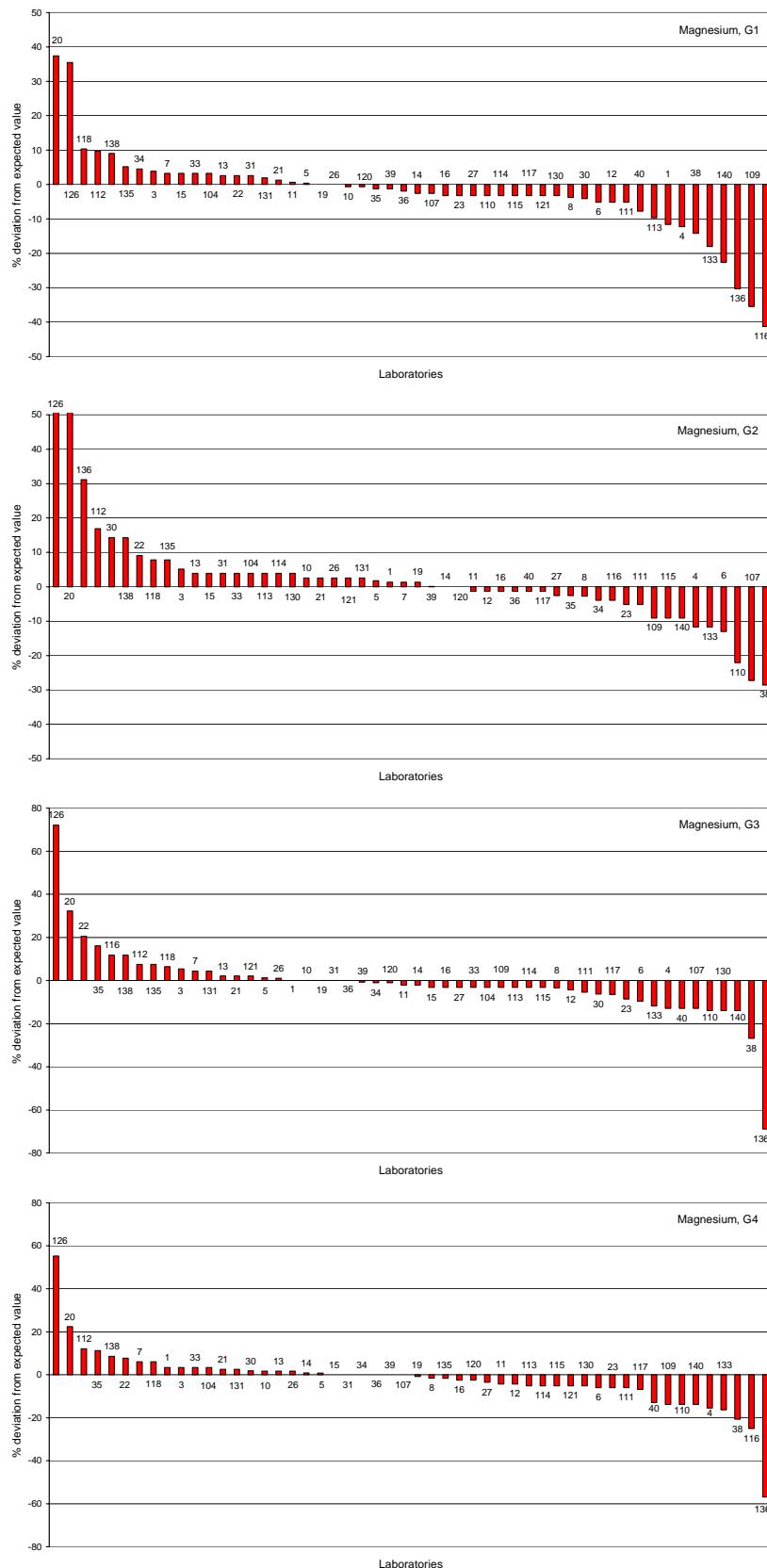


Figure 13: Percent deviation from theoretical value for magnesium.

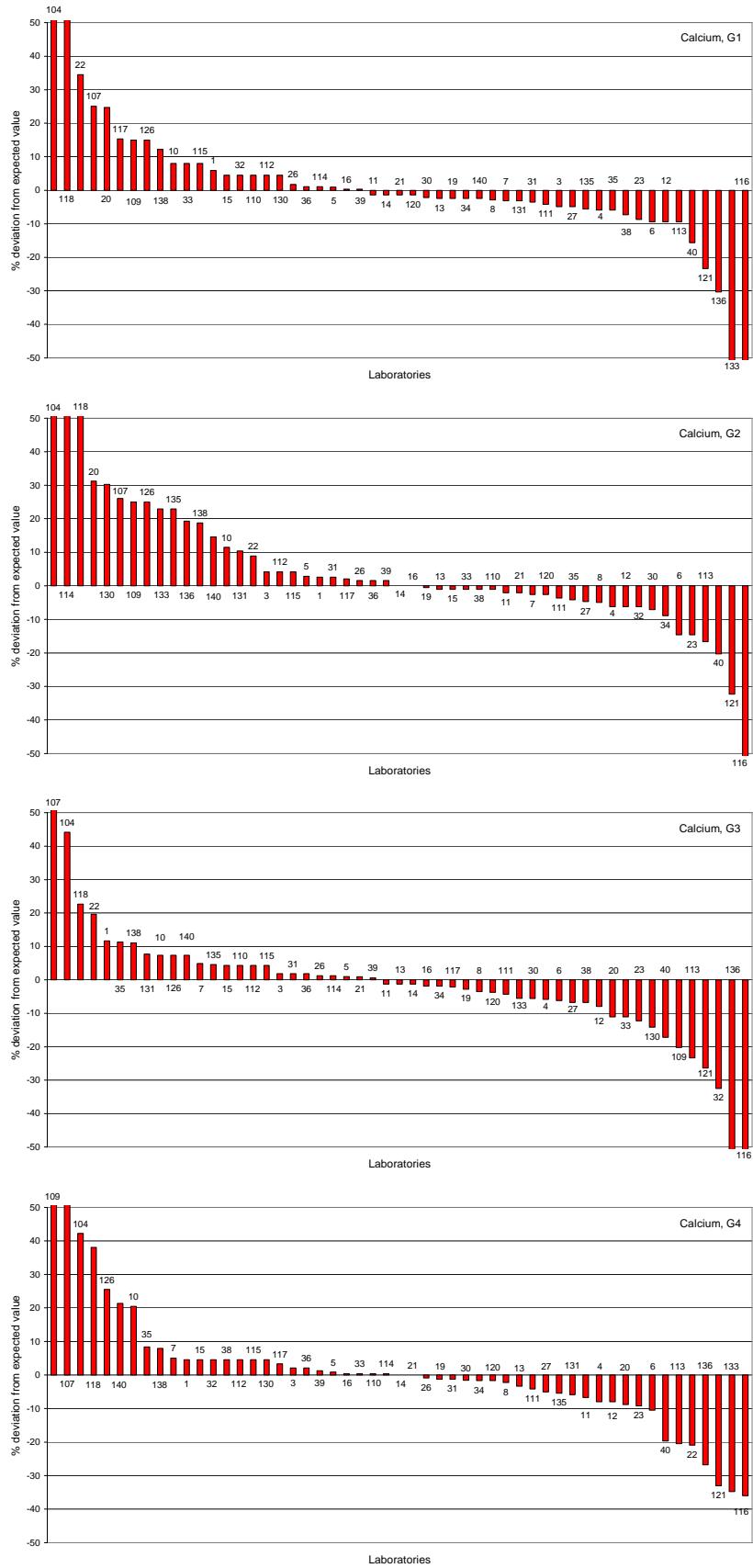


Figure 14: Percent deviation from theoretical value for calcium.

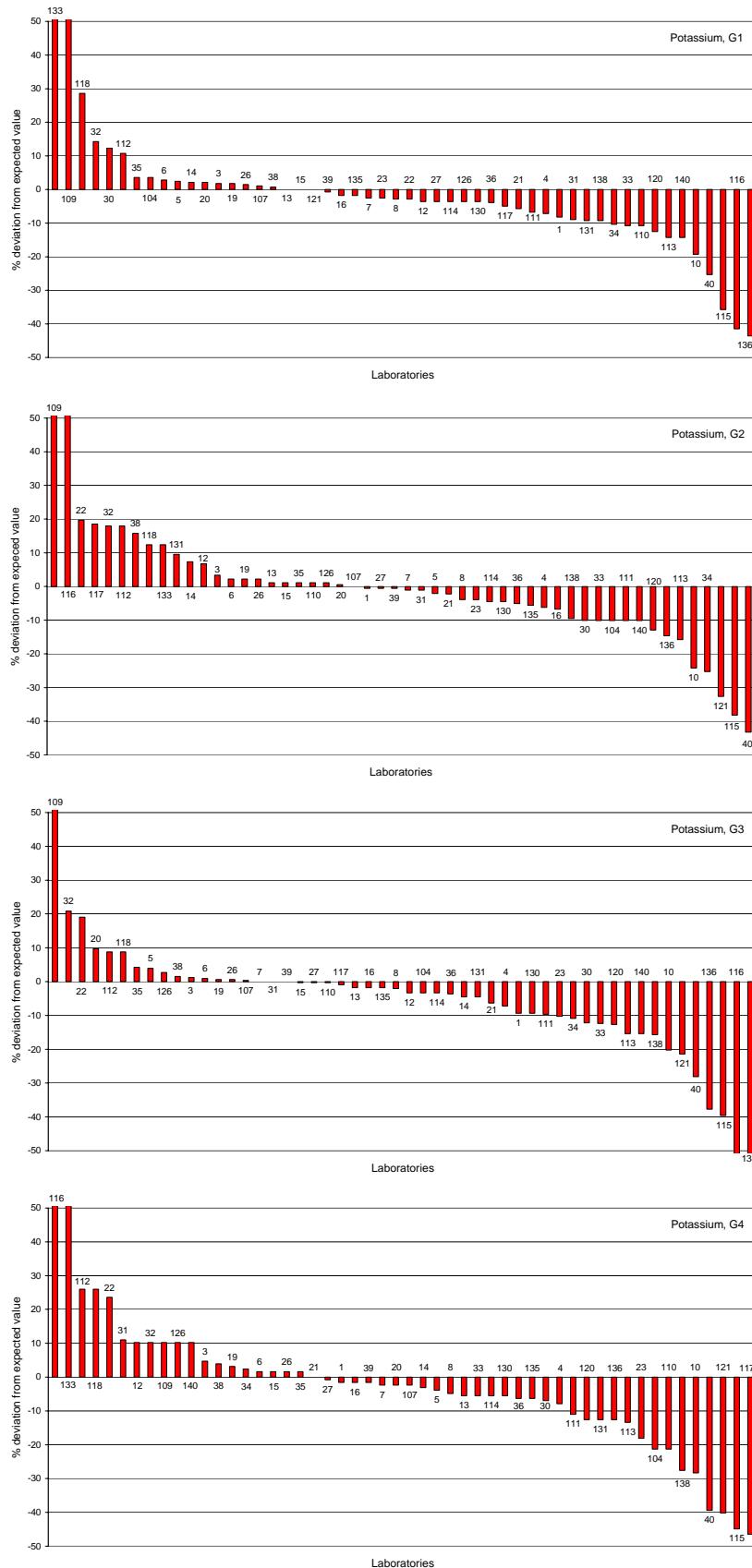


Figure 15: Percent deviation from theoretical value for potassium.

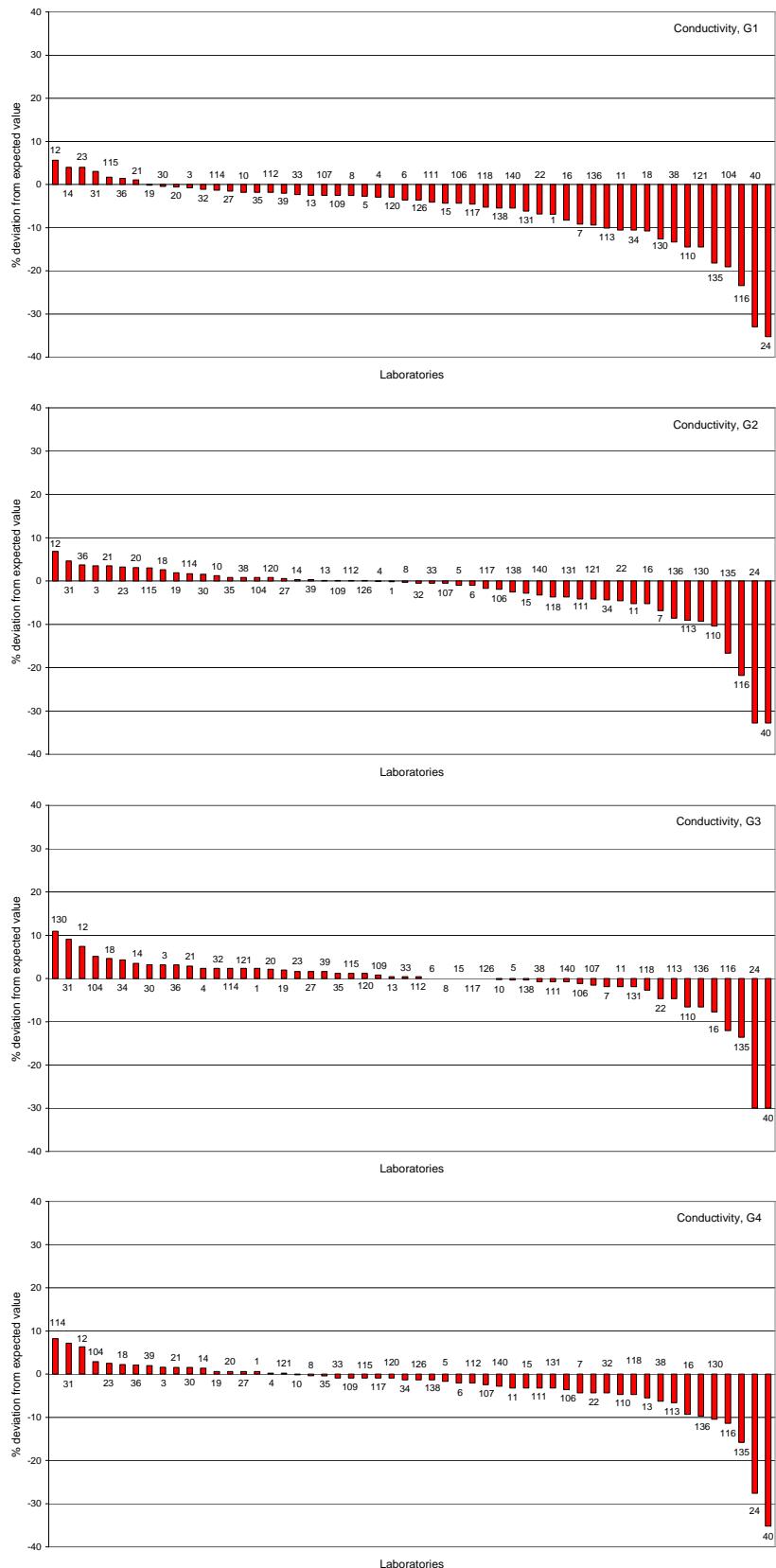


Figure 16: Percent deviation from theoretical value for conductivity.

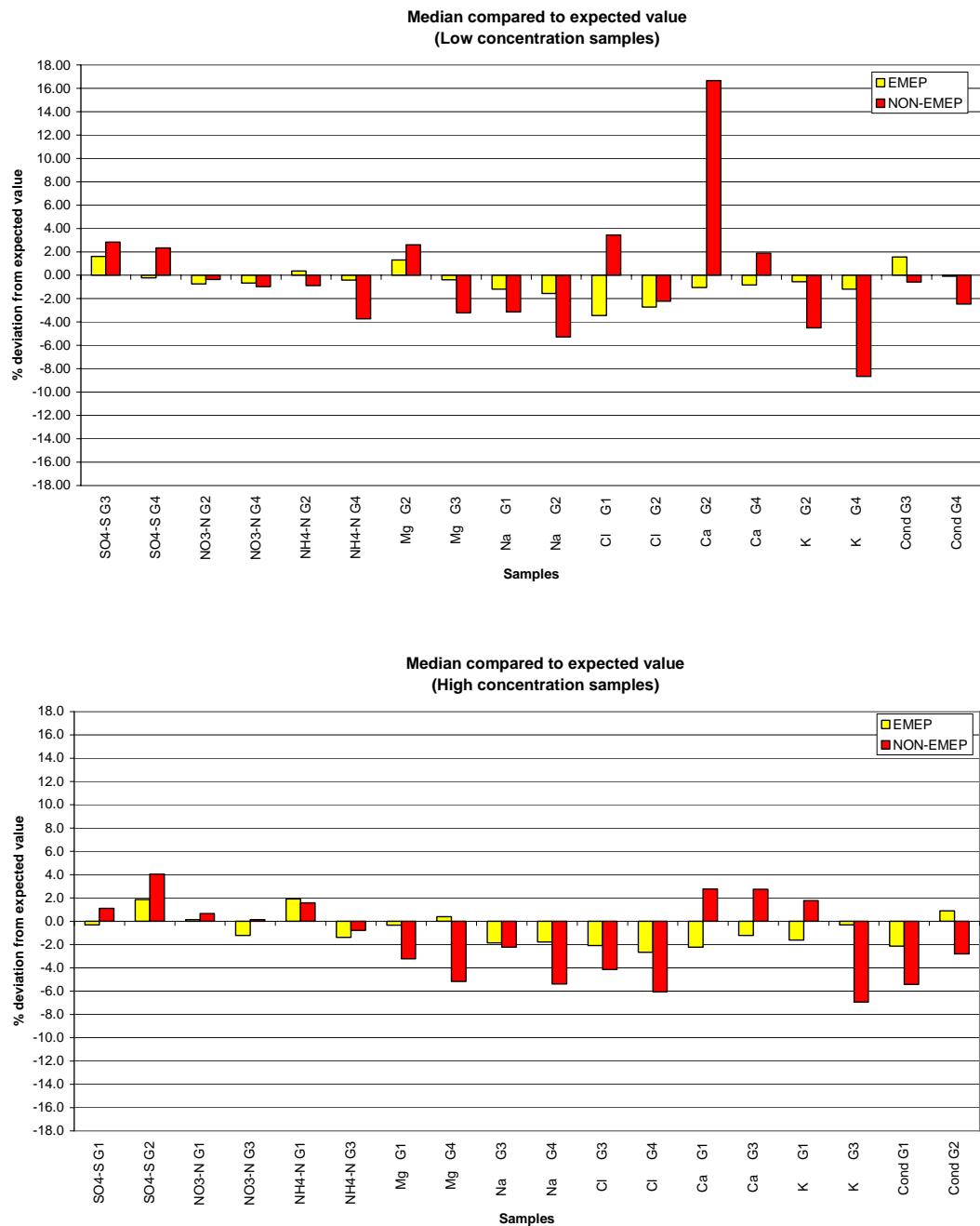


Figure 17: The median compared to theoretical value.

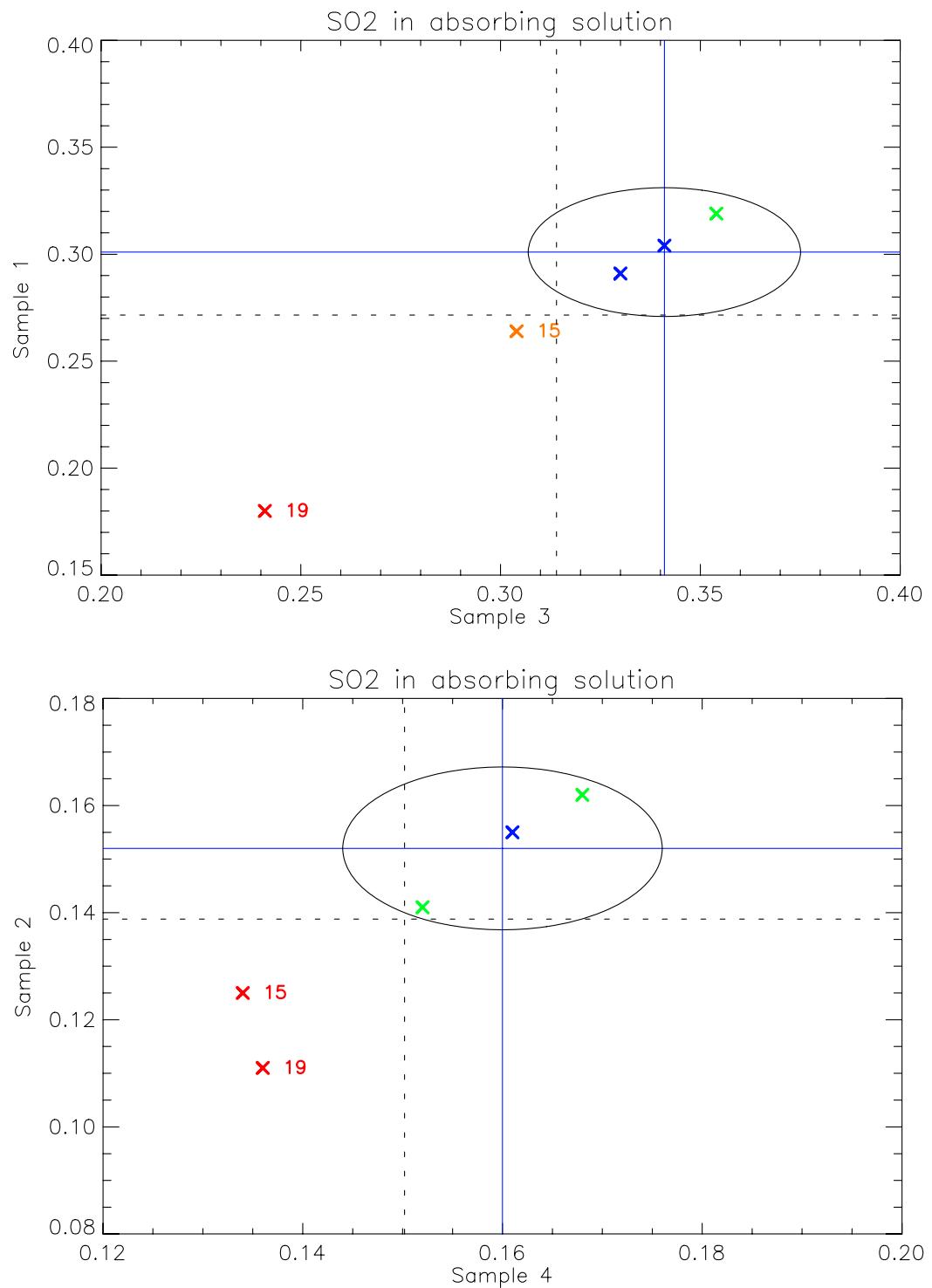


Figure 18: Youden plot of SO₂-S in absorbing solution.

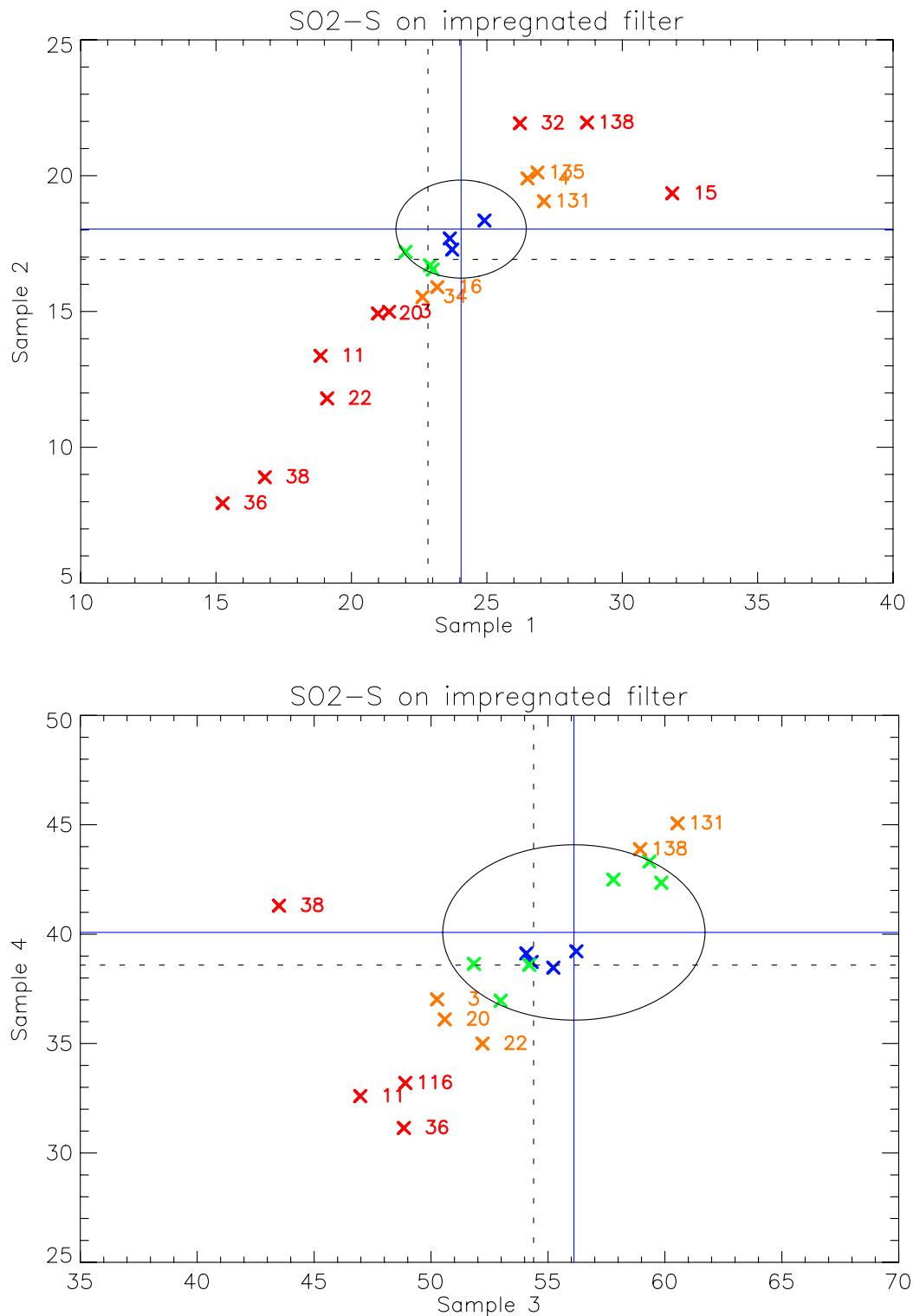


Figure 19: Youden plot of SO₂-S on impregnated filter.

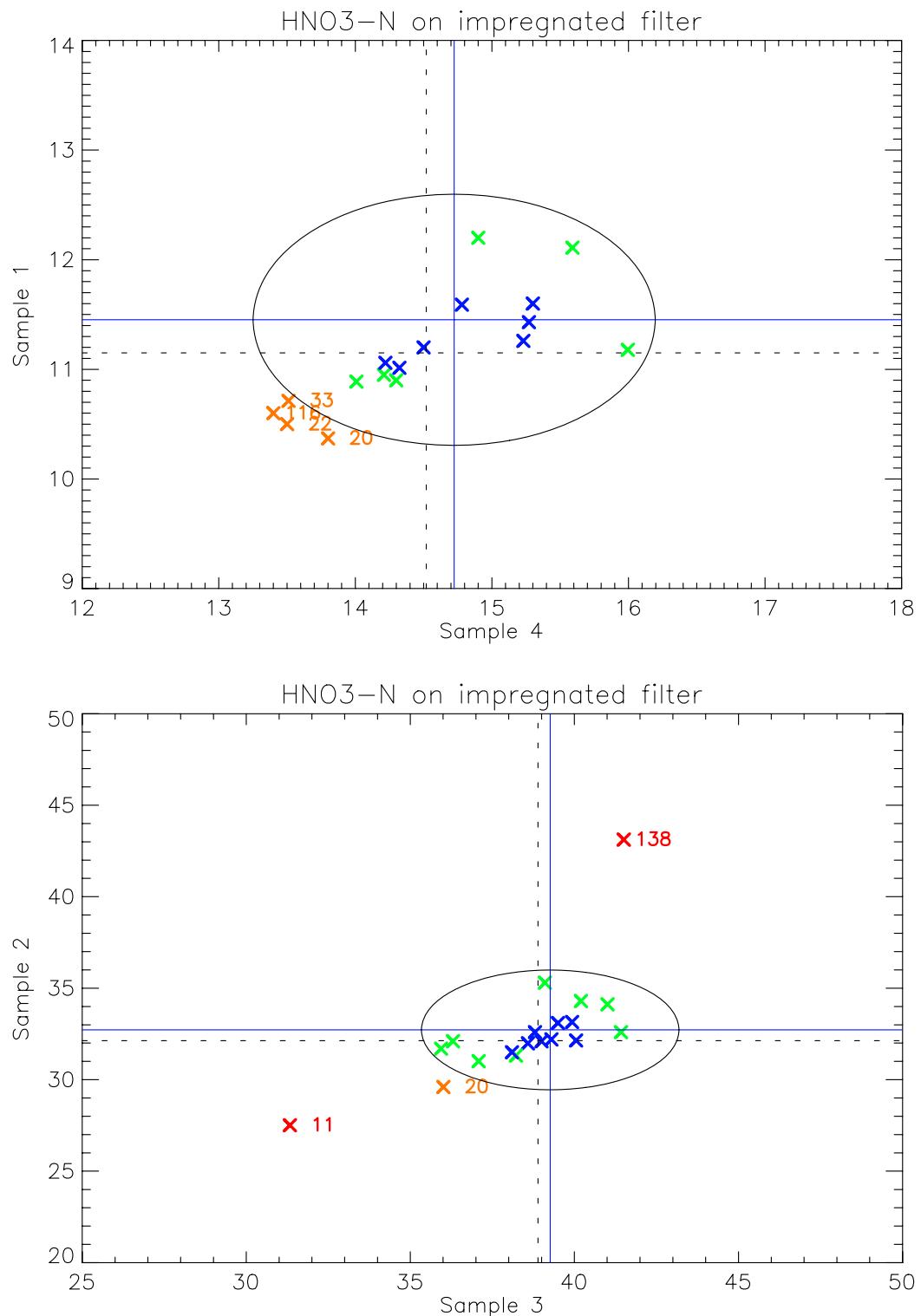


Figure 20: Youden plot of HNO₃-N on impregnated filter.

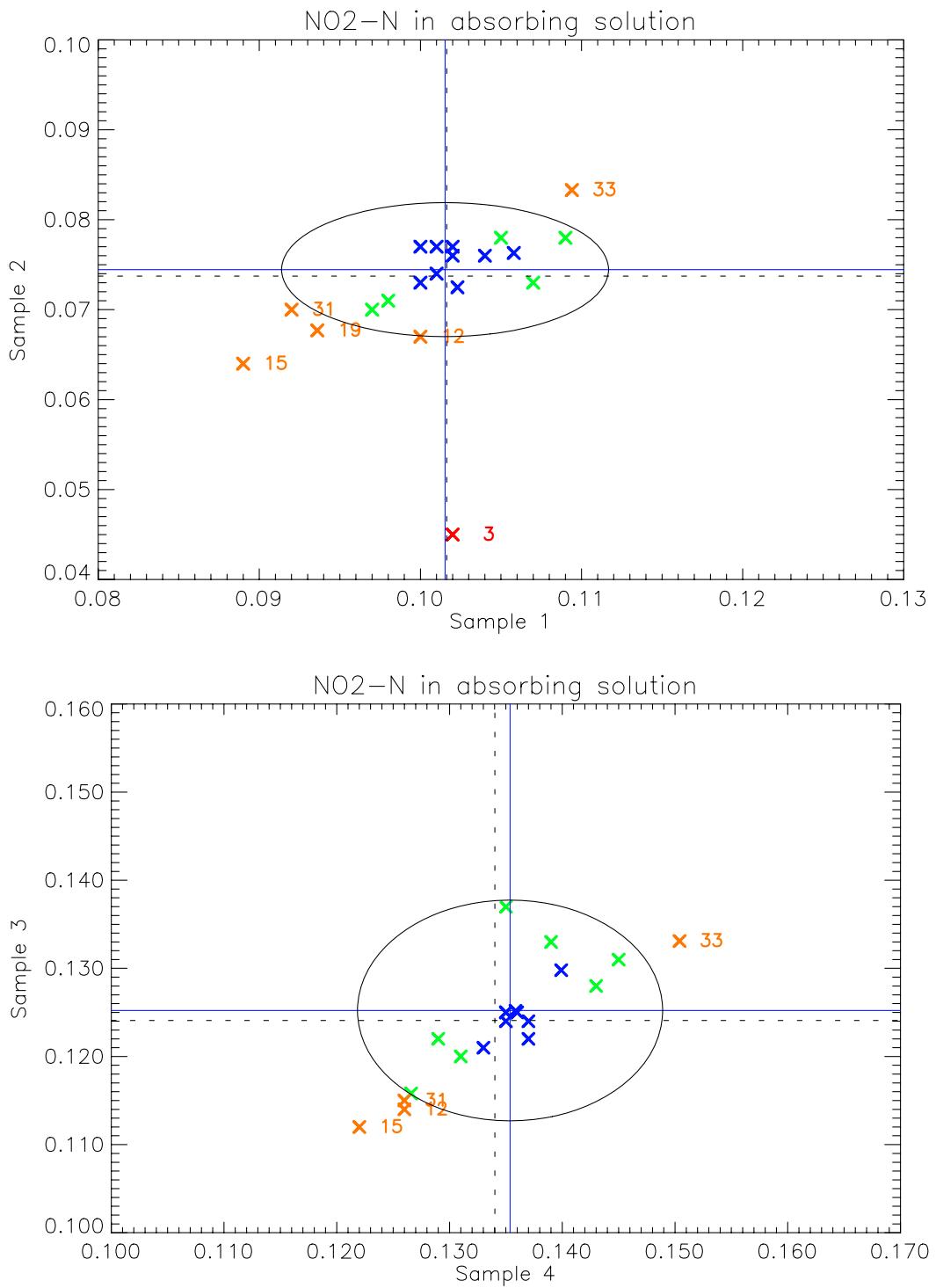


Figure 21: Youden plot of NO₂-N in absorbing solution.

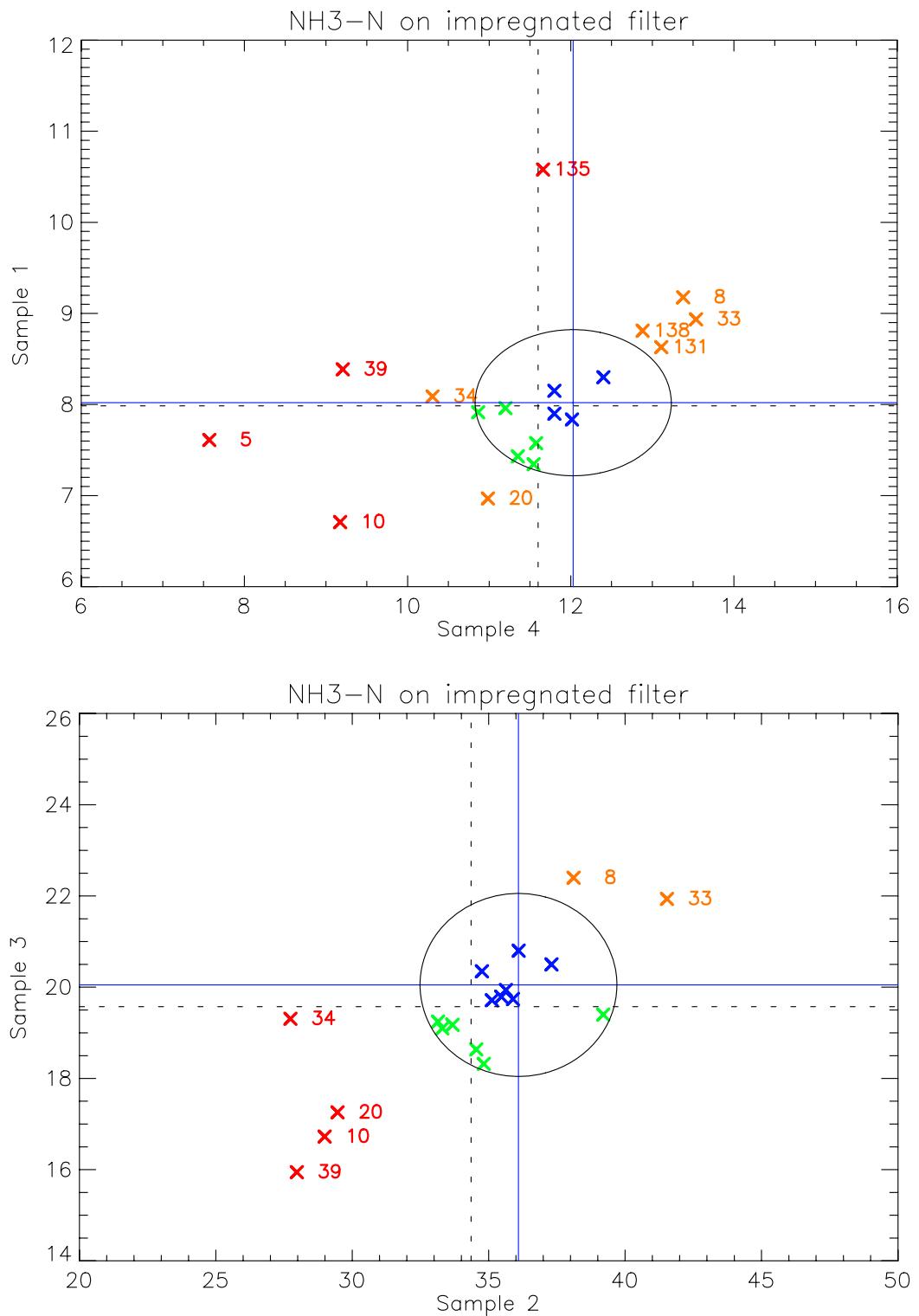


Figure 22: Youden plot of NH₃-N on impregnated filter.

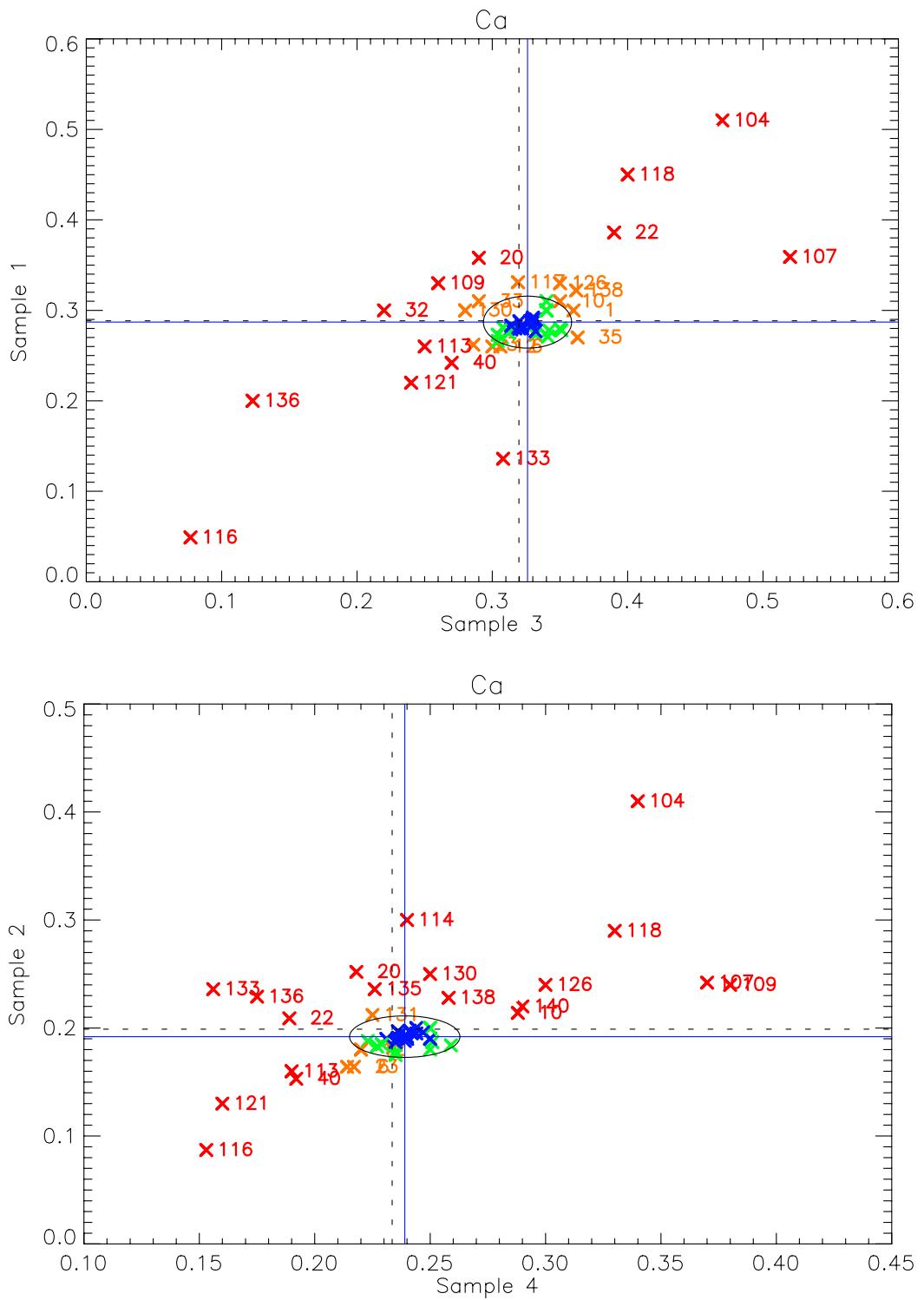


Figure 23: Youden plot of Ca in precipitation.

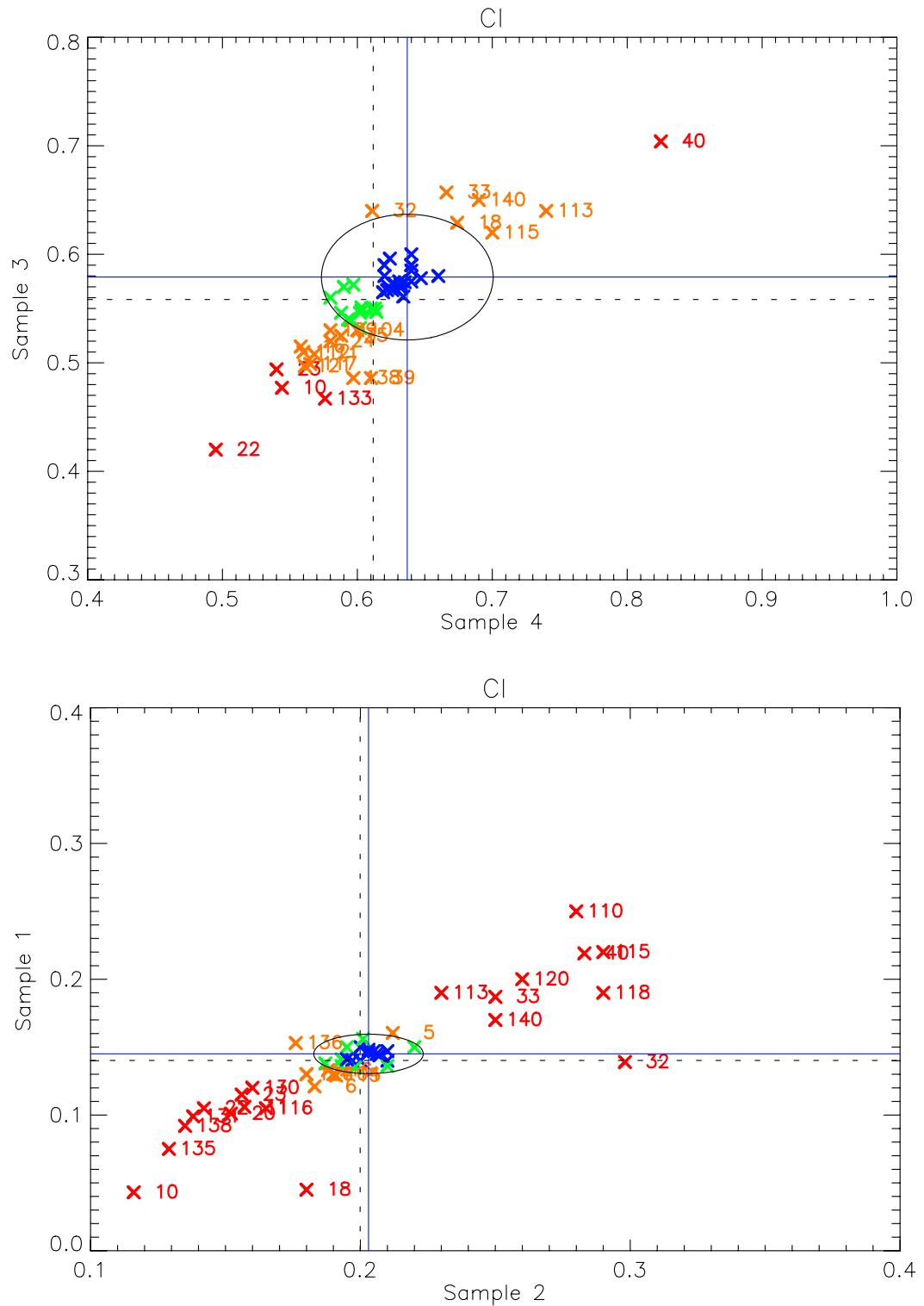


Figure 24: Youden plot of Cl in precipitation.

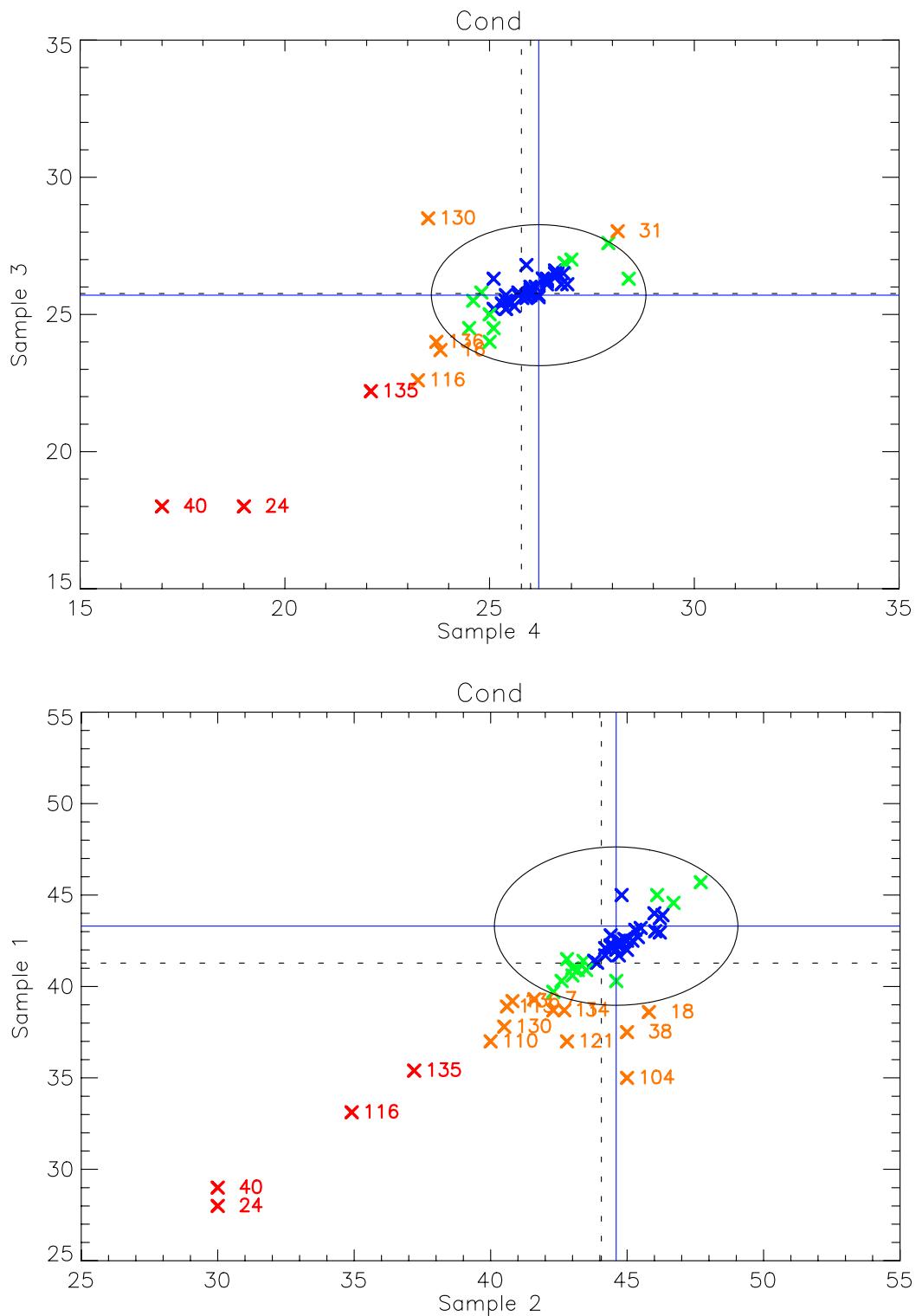


Figure 25: Youden plot of conductivity in precipitation.

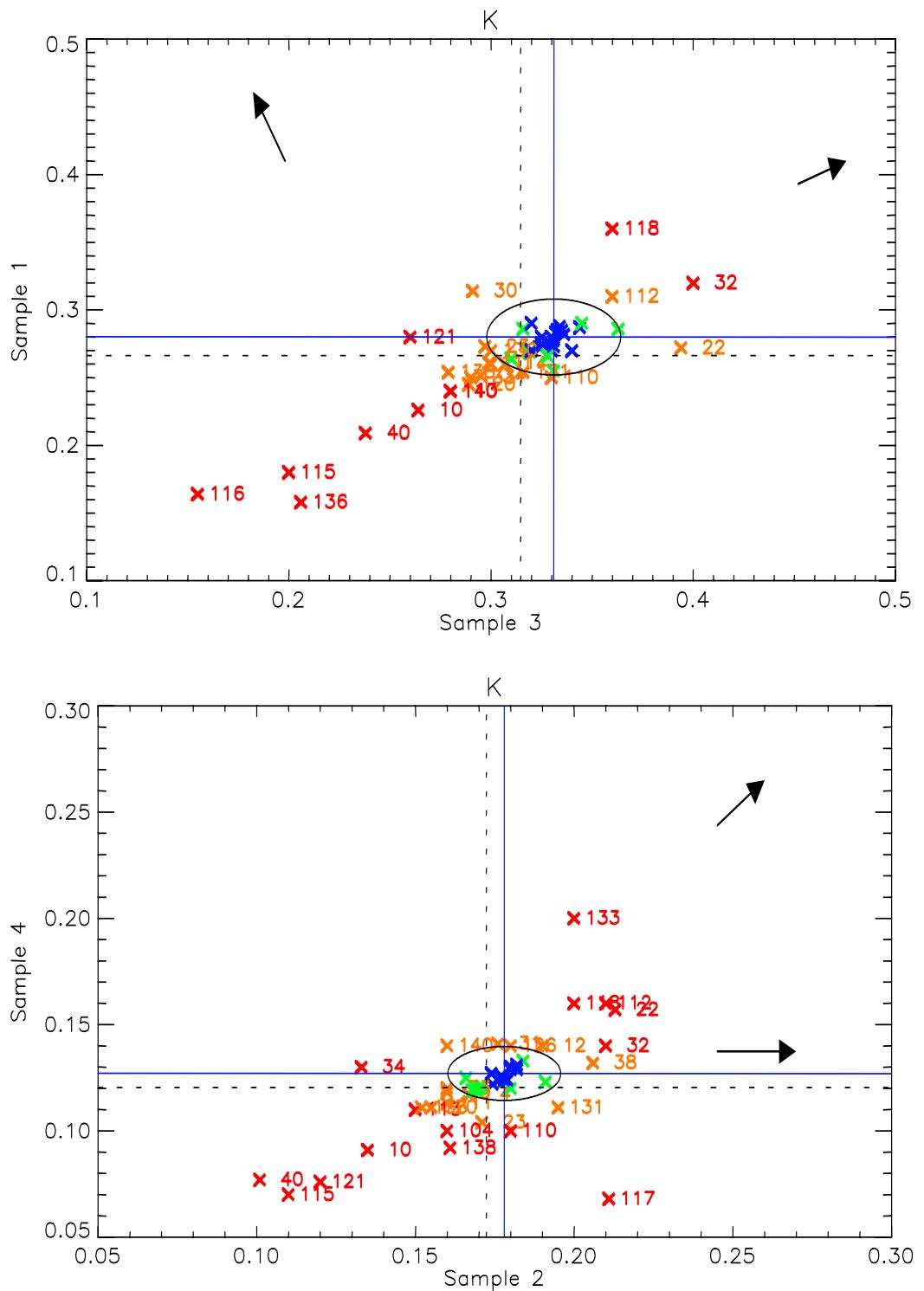


Figure 26: Youden plot of K in precipitation.

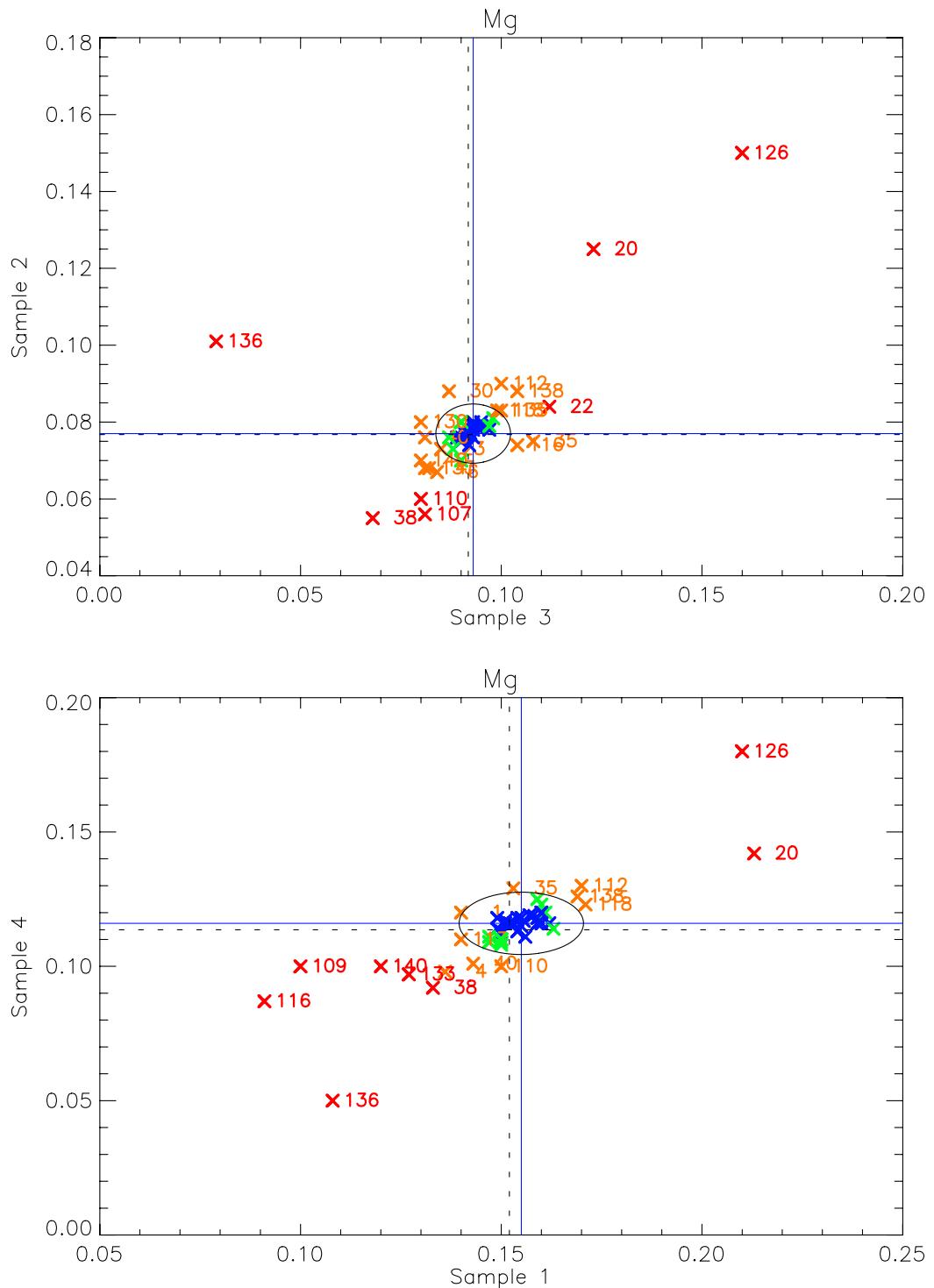


Figure 27: Youden plot of Mg in precipitation.

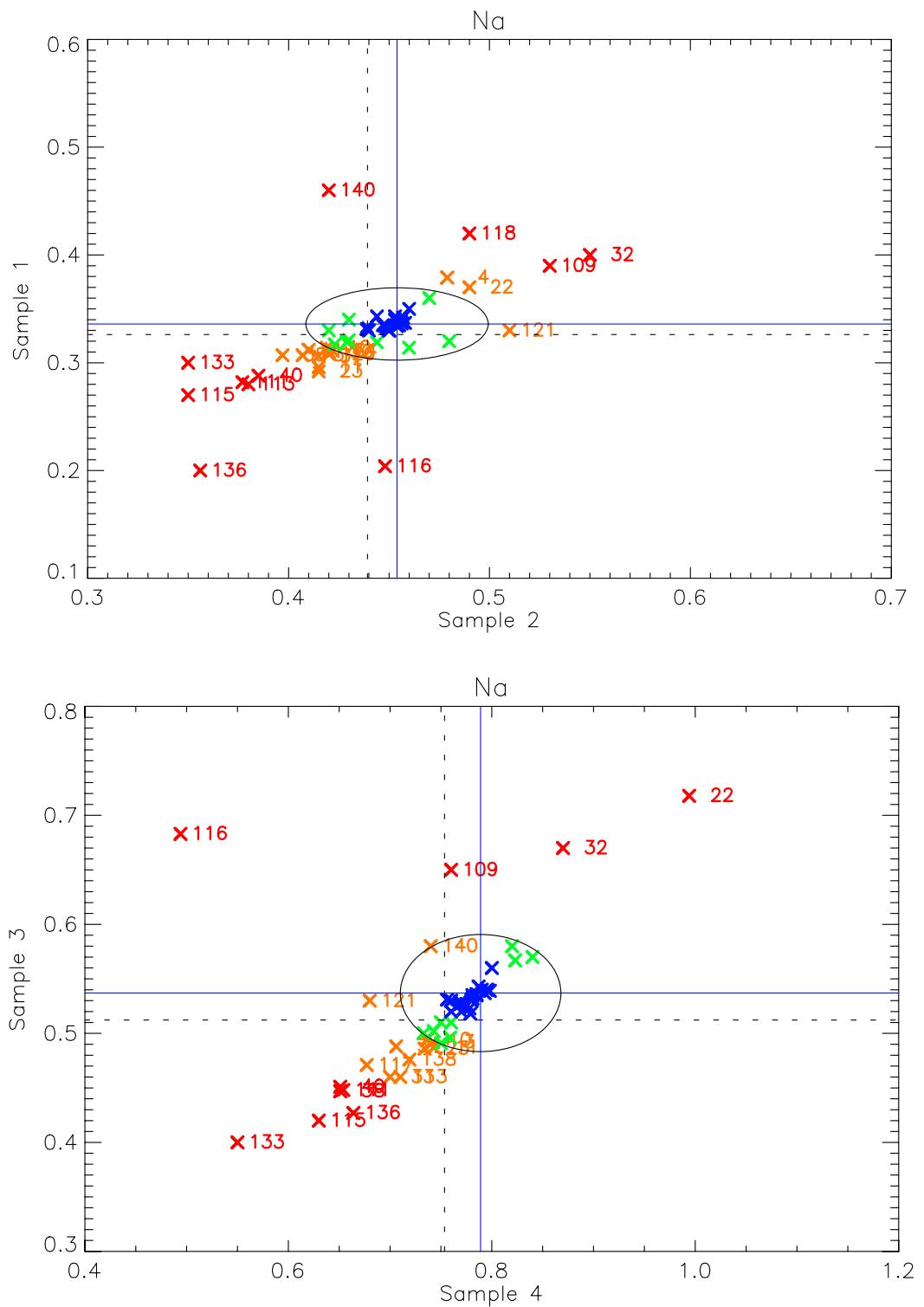


Figure 28: Youden plot of Na in precipitation.

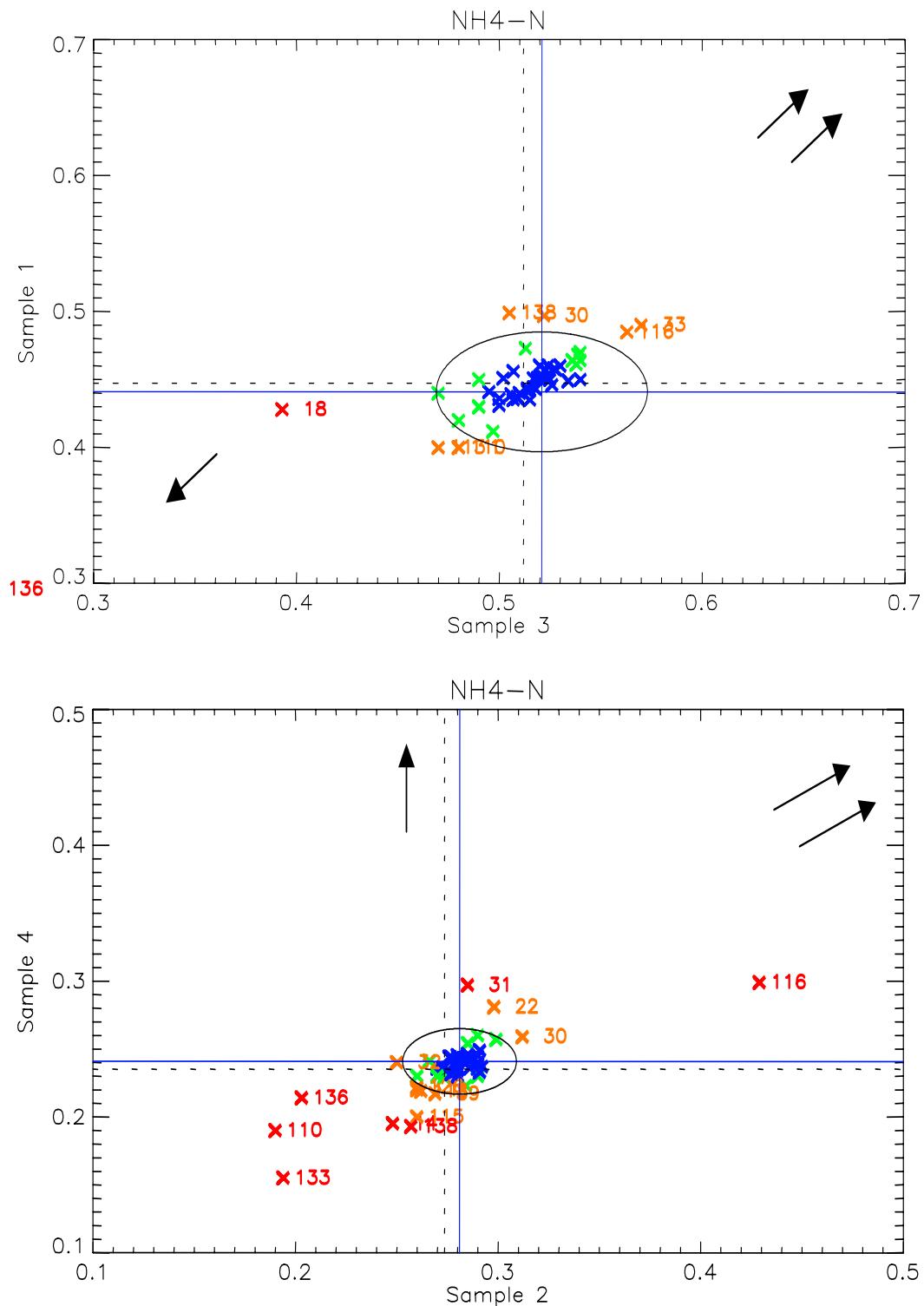


Figure 29: Youden plot of NH₄-N in precipitation.

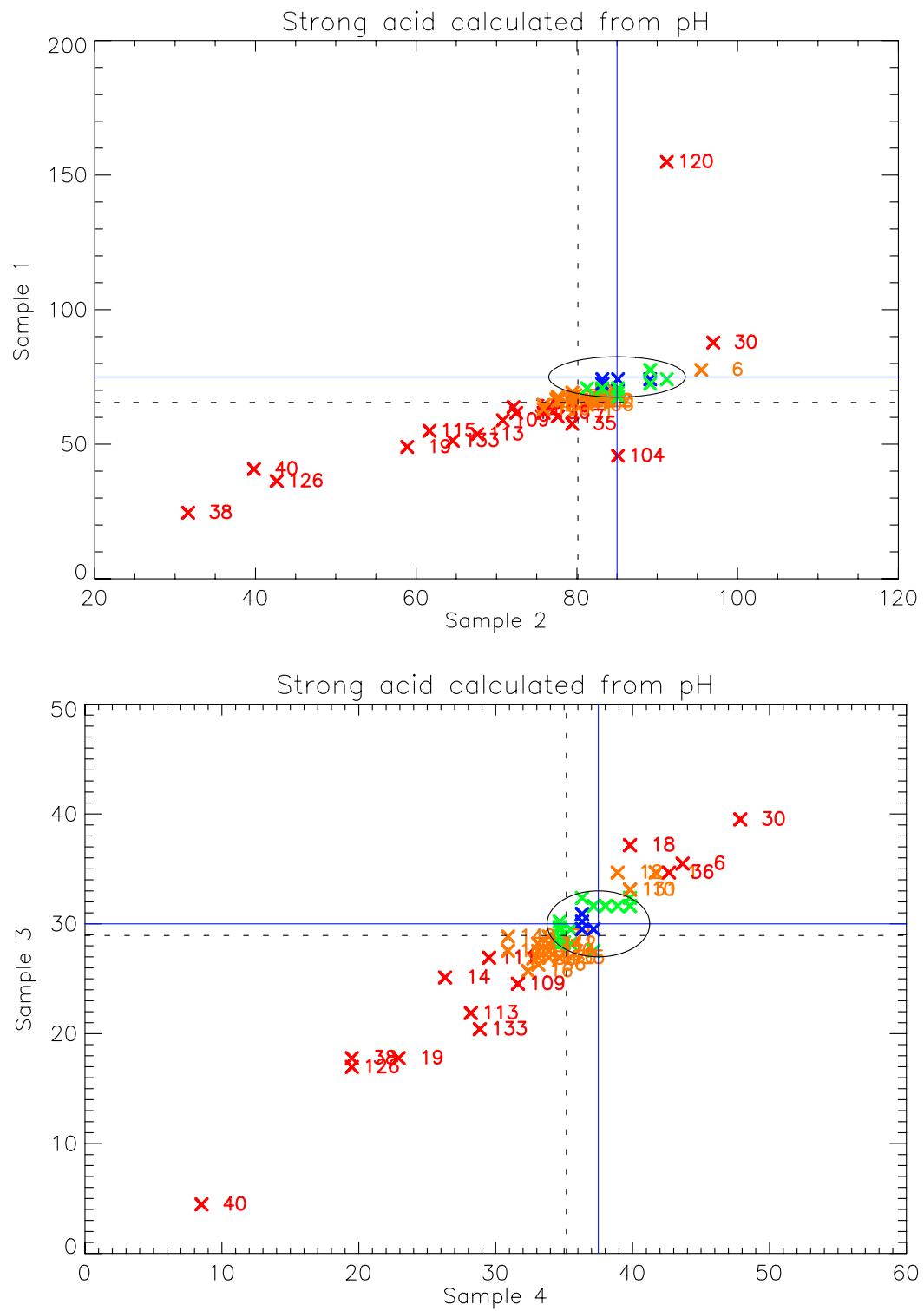


Figure 30: Youden plot of strong acid in precipitation.

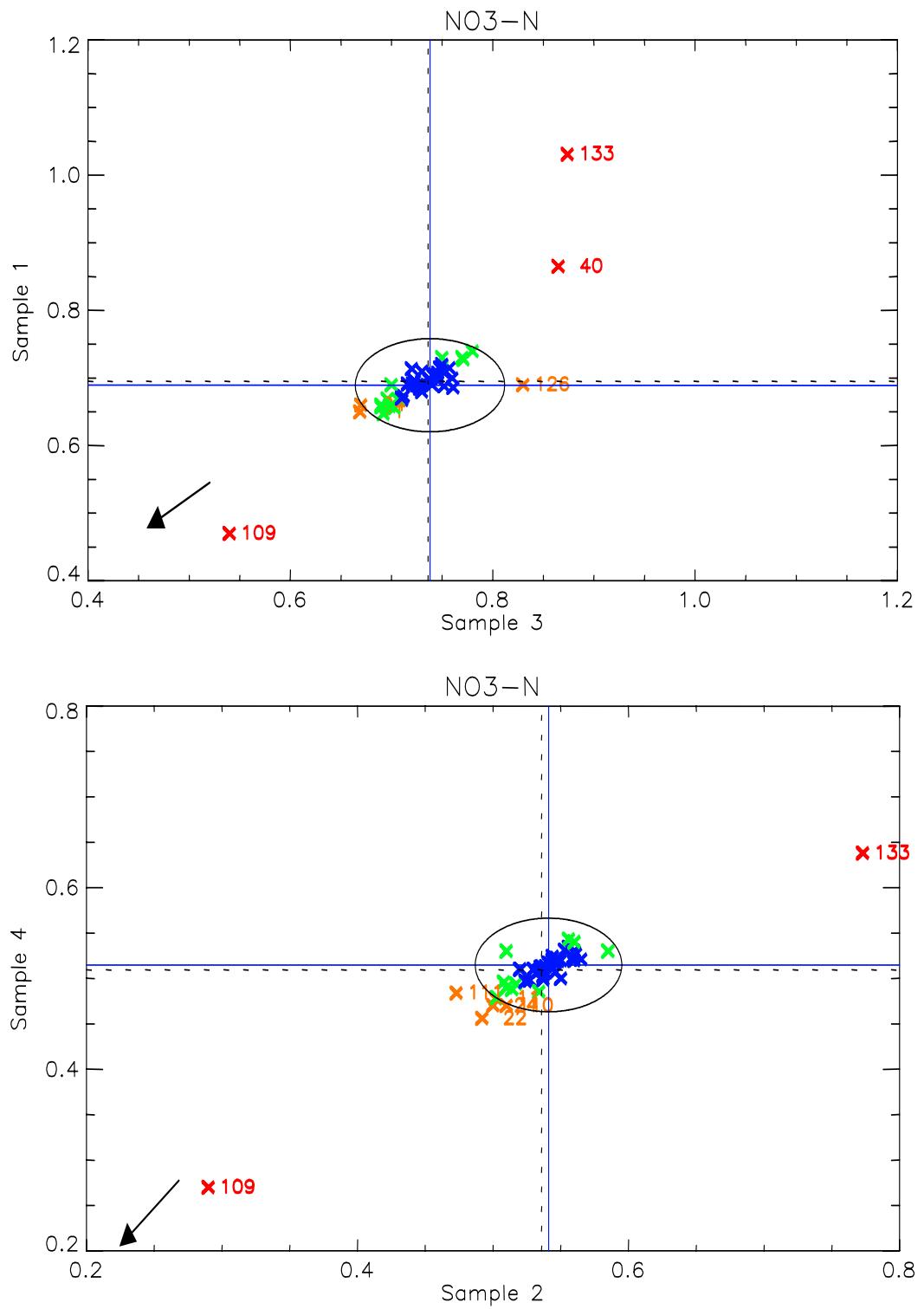


Figure 31: Youden plot of $\text{NO}_3\text{-N}$ in precipitation.

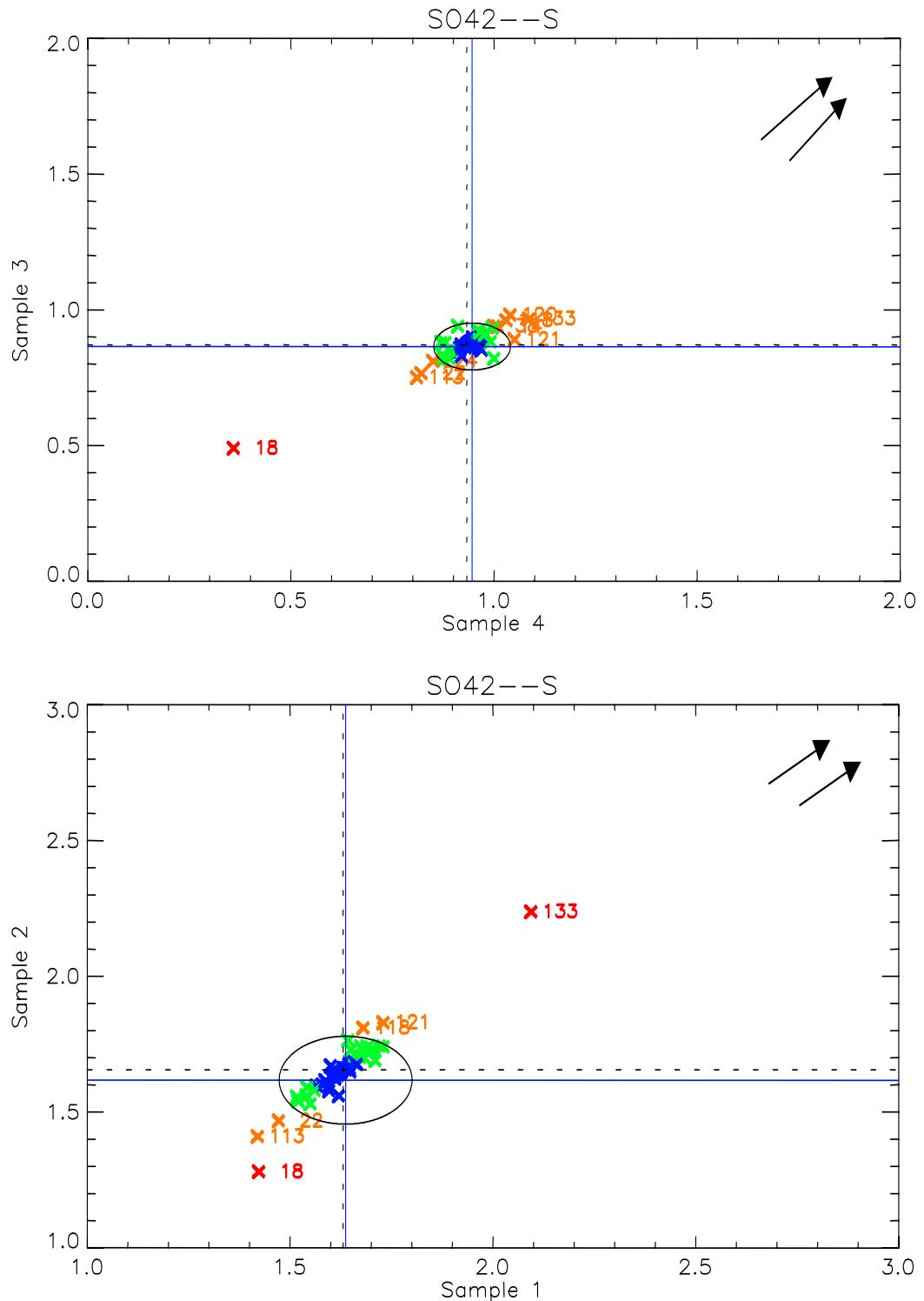


Figure 32: Youden plot of SO₄-S in precipitation.

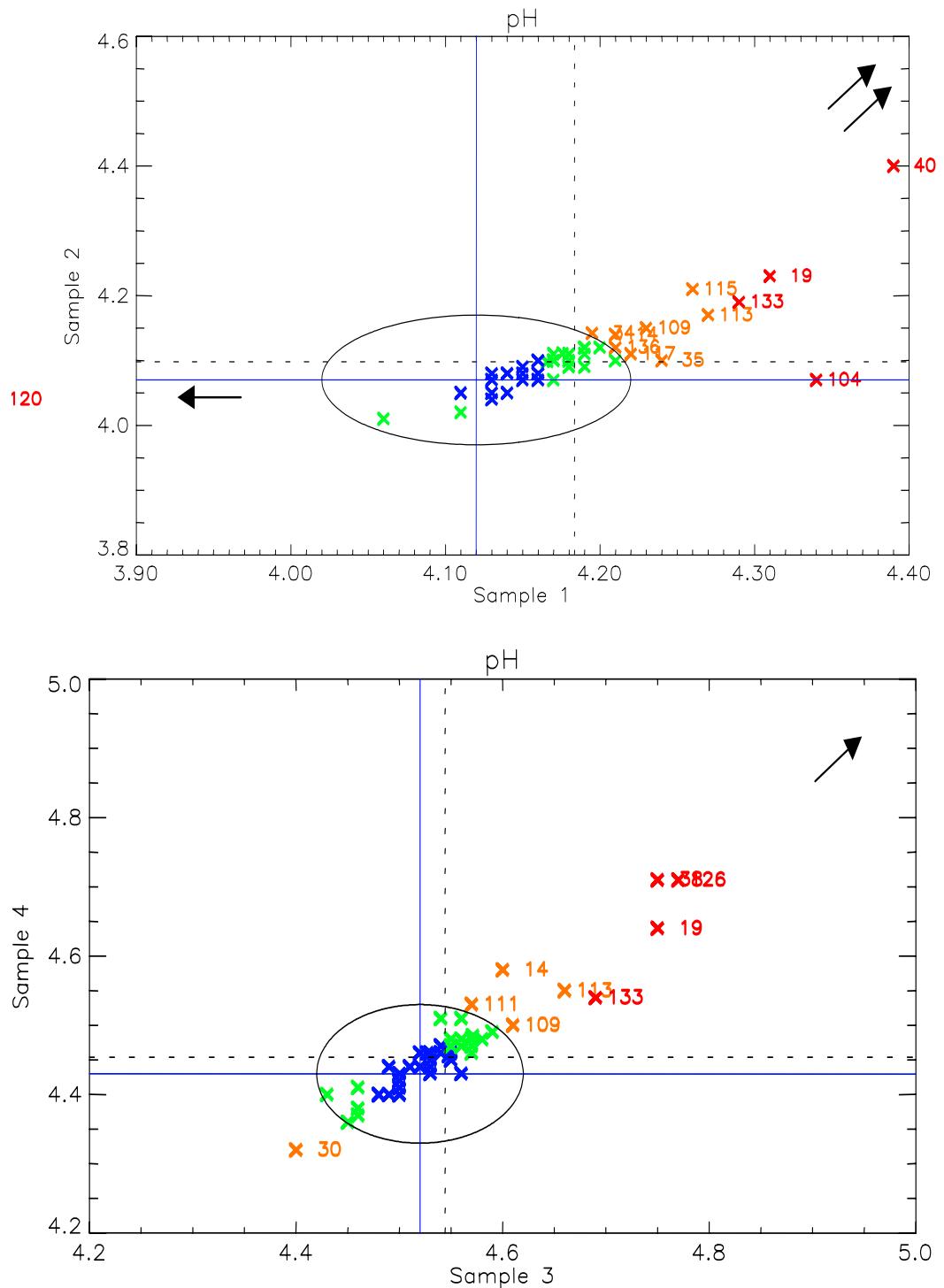


Figure 33: Youden plot of pH in precipitation.