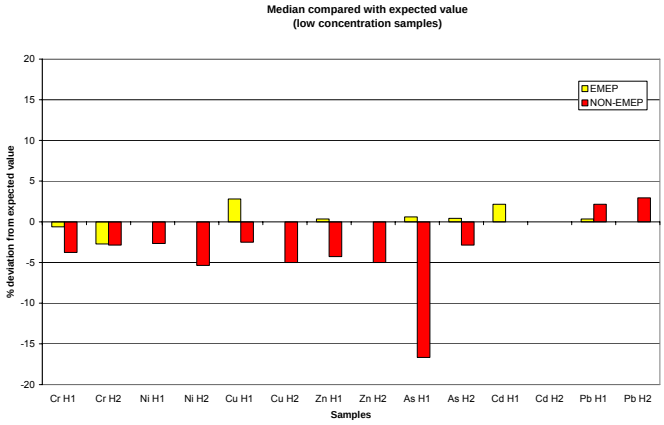
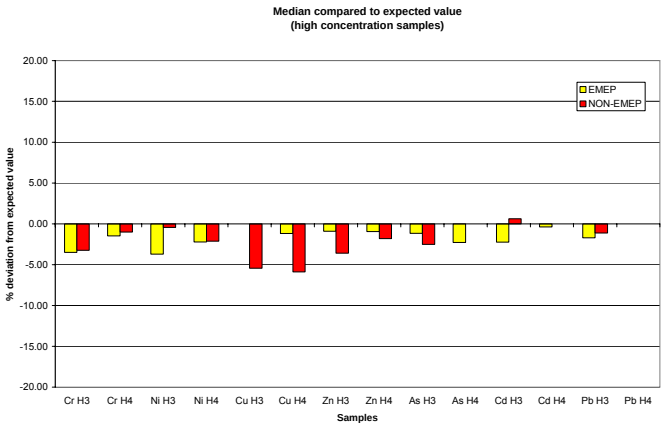
EMEP/CCC-Report 7/2005

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

Analytical intercomparison of heavy metals in precipitation, 2003 and 2004

Hilde Thelle Uggerud and Anne-Gunn Hjellbrekke





Norwegian Institute for Air Research
PO Box 100, NO-2027 Kjeller, Norway
Chemical Co-ordinating Centre of EMEP (CCC)

NILU : EMEP/CCC-Report 7/2005
REFERENCE : O-7729
DATE : SEPTEMBER 2005

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

Analytical intercomparison of heavy metals in precipitation, 2003 and 2004

Hilde Thelle Uggerud and Anne-Gunn Hjellbrekke

Norwegian Institute for Air Research
P.O. Box 100, N-2027 Kjeller, Norway

Contents

Page

Analytical intercomparison of heavy metals in precipitation, 2003 and 2004

1. Analytical intercomparison of heavy metals in precipitation, 2003

1.1 Introduction

Heavy metals were included in the EMEP's monitoring programme in 1999. 20 countries are reporting data to the heavy metal database. Since EMEP's measurement programme is based on individual national networks, different sampling and analytical methods are applied by the participating laboratories. In order to ensure data comparability, interlaboratory tests are organized by the Chemical Co-ordinating Centre (CCC) at the Norwegian Institute for Air Research. So far five intercomparisons have been arranged (Berg and Semb, 1995; Berg and Aas, 2000; Uggerud and Skjelmoen, 2001; Uggerud and Skjelmoen, 2002; Uggerud and Skjelmoen, 2003).

This report presents results from the sixth analytical intercomparison of heavy metals in precipitation, which was carried out during 2003. Seven heavy metals were included: Pb, Cd, Cu, Zn, As, Cr, and Ni.

1.2 Organization of the intercomparison

The samples for the sixth intercomparison were prepared and distributed to 43 laboratories in July 2003.

A total of 32 laboratories, 15 from the EMEP network, reported results within the end of October 2003. 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 A.1.1a and A1.1b give the names of the participating laboratories together with the number used when presenting the results in tables and figures.

Information received on the analytical methods used is given in Table A1.9.

1.3 Intercomparison samples

The four synthetic precipitation samples distributed were made from multi-element standards traceable to NIST-standards. The multi-element standards were conserved with 2.5% HNO_3. The distributed synthetic precipitation samples contained Pb, Cd, Cu, Zn, As, Cr, and Ni in 0.5% HNO_3. Sample H1 and H2 contained concentrations similar to what is normally found in Southern Scandinavia. Sample H3 and H4 contained the elements in concentrations normally found in Central Europe.

All equipment in contact with the samples were soaked in 3% HNO_3 for 4 days. Preparation of the intercomparison samples was carried out in a clean room area.

1.4 Data handling

The data reported from the participants are presented in Tables A1.2-A1.8 and Figures A2.1-A2.15.

1.4.1 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.

1.4.2 Bar-plots

Bar-plots are used for the graphical presentation of the data. Figure A2.1-A2.7 the relative deviation from expected value for the different laboratories. There is one plot for each single sample.

Figure A2.8 shows medians compared to expected value for the results reported by EMEP-laboratories and the other participating laboratories, respectively.

1.4.3 Youden plot

Youden plot is a graphical technique, which allows for analysing inter laboratory data, where 2 samples of equal or similar concentrations have been analysed. The Youden plot visualises systematic errors as well as random errors.

The precipitation samples are made in pairs with similar concentrations and the reported value for one sample is plotted on the x-axis and the reported value of the other sample is plotted on the y-axis. Thus, each point in the plot is representing a pair of results from a single laboratory. Two fully drawn lines represent the expected values of the two samples. Two dotted lines represent the arithmetic mean values in the second statistical run. The lines divide the plot in four quadrants. A 45º-reference line may be drawn through the intercept of the lines representing the expected values.

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

If the errors are due to systematic factors, the results will be close to the 45º-reference line, but situated in the upper right or lower left quadrant.

Ellipses with radii corresponding to the data quality objectives within EMEP are drawn in each plot (see table 1). The data points are colour coded as given in Table 1. Drawn arrows indicate points outside the plot area.

The length of the perpendicular from an individual point and to the reference line gives a measure of the random error. The perpendicular intercepts the 45º-

reference line at a distance from the origin of the fully drawn lines. This distance is a measure of the systematic error.

Youden plots are presented in Figures A2.9–A2.15.

Table 1: Youden-plot parameters.

Radii = DQO	**Concentration**
25% accuracy or better	Pb, Ni, Cr, As <1 μg/l, Cd <0.5 μg/l, Zn< 10 μg/l, Cu <2 μg/l
15% accuracy or better	Pb, Ni, Cr, As >1 μg/l, Cd >0.5 μg/l, Zn >10 μg/l, Cu >2 μg/l
Criteria	Colour
Within 0.5*DQO	Blue
Within DQO	Green
Within 2*DQO	Orange
> 2*DQO	Red

1.5 Summary

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 760 single results, 38 are defined as outliers. This is about 5% of the reported data, which is comparable to earlier intercomparisons.

For all the samples analysed the deviation from the theoretical value was calculated. The median deviations for the EMEP laboratories were below 5% and below 3% for the low- and high concentration samples, respectively. This is an improvement compared to earlier intercomparisons. The median deviations for the other participating laboratories were below 9% for high concentration samples. The median deviations for low concentration samples were (exclusive the median value for As in sample H1), below 20%.

2. Analytical intercomparison of heavy metals in precipitation, 2004

2.1 Introduction

Heavy metals were included in the EMEP's monitoring programme in 1999. 20 countries are reporting data to the heavy metal database. Since EMEP's measurement programme is based on individual national networks, different sampling and analytical methods are applied by the participating laboratories. In order to ensure data comparability, interlaboratory tests are organized by the Chemical Co-ordinating Centre (CCC) at the Norwegian Institute for Air Research. So far six intercomparisons have been arranged (Berg and Semb, 1995; Berg and Aas, 2000; Uggerud and Skjelmoen, 2001; Uggerud and Skjelmoen, 2002; Uggerud and Skjelmoen, 2003; Uggerud and Hjellbrekke, this report).

This report presents results from the seventh analytical intercomparison of heavy metals in precipitation, which was carried out during 2004. Seven heavy metals were included: Pb, Cd, Cu, Zn, As, Cr, and Ni.

2.2 Organization of the intercomparison

The samples for the seventh intercomparison were prepared and distributed to 46 laboratories in July 2004.

A total of 33 laboratories, 16 from the EMEP network, reported results within the end of October 2004. 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 A3.1a and A3.1b give the names of the participating laboratories together with the number used when presenting the results in tables and figures.

Information received on the analytical methods used is given in Table A3.9.

2.3 Intercomparison samples

The four synthetic precipitation samples distributed were made from multi-element standards traceable to NIST-standards. The multi-element standards were conserved with 2.5% HNO_3. The distributed synthetic precipitation samples contained Pb, Cd, Cu, Zn, As, Cr, and Ni in 0.5% HNO_3. Sample H1 and H2 contained concentrations similar to what is normally found in Southern Scandinavia. Sample H3 and H4 contained the elements in concentrations normally found in Central Europe.

All equipment in contact with the samples were soaked in 3% HNO_3 for 4 days. Preparation of the intercomparison samples was carried out in a clean room area.

2.4 Data handling

The data reported from the participants are presented in Tables A3.2-A3.8 and Figures A4.1-A4.15

2.4.1 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.

2.4.2 Bar-plots

Bar-plots are used for the graphical presentation of the data. Figure A4.1-A4.7 the relative deviation from expected value for the different laboratories. There is one plot for each single sample.

Figure A2.8 shows medians compared to expected value for the results reported by EMEP-laboratories and the other participating laboratories, respectively.

2.4.3 Youden plot

Youden plot is a graphical technique, which allows for analysing inter laboratory data, where 2 samples of equal or similar concentrations have been analysed. The Youden plot visualises systematic errors as well as random errors.

The precipitation samples are made in pairs with similar concentrations and the reported value for one sample is plotted on the x-axis and the reported value of the other sample is plotted on the y-axis. Thus, each point in the plot is representing a pair of results from a single laboratory. Two fully drawn lines represent the expected values of the two samples. Two dotted lines represent the arithmetic mean values in the second statistical run. The lines divide the plot in four quadrants. A 45º-reference line may be drawn through the intercept of the lines representing the expected values.

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

If the errors are due to systematic factors, the results will be close to the 45º-reference line, but situated in the upper right or lower left quadrant.

Ellipses with radii corresponding to the data quality objectives within EMEP are drawn in each plot (see table 1). The data points are colour coded as given in Table 1. Drawn arrows indicate points outside the plot area.

The length of the perpendicular from an individual point and to the reference line gives a measure of the random error. The perpendicular intercepts the 45^{o} - reference line at a distance from the origin of the fully drawn lines. This distance is a measure of the systematic error.

Youden plots are presented in Figures A4.9-A4.15.

Table 2: Youden-plot parameters.

Radii = DQO	**Concentration**
25% accuracy or better	Pb, Ni, Cr, As <1 μg/l, Cd <0.5 μg/l, Zn< 10 μg/l, Cu <2 μg/l
15% accuracy or better	Pb, Ni, Cr, As >1 μg/l, Cd >0.5 μg/l, Zn >10 μg/l, Cu >2 μg/l
Criteria	Colour
Within 0.5*DQO	Blue
Within DQO	Green
Within 2*DQO	Orange
> 2*DQO	Red

2.5 Summary

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 787 single results, 48 are defined as outliers. This is about 6% of the reported data, which is comparable to earlier intercomparisons.

For all the samples analysed the deviation from the theoretical value was calculated. The median deviations for the EMEP laboratories were below 3% and 4% for the low- and high concentration samples, respectively. The median deviations for the other participating laboratories were below 6% for both high and low concentration samples (exclusive the median value for As in sample H1).

3. References

Berg, T. and Aas, W. (2000) Analytical intercomparison of heavy metals in precipitation 1999. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 8/2000).

Berg, T. and Semb, A. (1995) Preliminary results from HELCOM-EMEP-PARCOM-AMAP analytical intercomparison of heavy metals in precipitation. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Note 1/95).

Uggerud, H.Th. and Skjelmoen, J.E. (2001) Analytical intercomparison of heavy metals in precipitation 2000. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 12/2001).

Uggerud, H.Th. and Skjelmoen, J.E. (2002) Analytical intercomparison of heavy metals in precipitation 2001. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 2/2002).

Uggerud, H.Th. and Skjelmoen, J.E. (2003) Analytical intercomparison of heavy metals in precipitation 2002. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 7/2003).

Appendix 1

Tables, 2003

Table A1.1a: Participating laboratories in the EMEP network, 2003. The numbers in front are used in tables.

No	Laboratory identification
1	Federal Environmental Agency, Austria
3	Czech Hydrometeorological Institute, Czech Republic
4	National Environmental Research Institute. Air Pollution Laboratory, Denmark
5	Finnish Meteorological Institute, Finland
6	Laboratories Wollf, France
8	Umweltbundesamt, Germany
14	RIVM Laboratory of Inorganic Analytical Chemistry, The Netherlands
15	The Norwegian Institute for Air Research, Norway
16	Inst. Of Meteorology and Water Management, Poland
23	AEA Technology, National Environmental Techn. Centre, United Kingdom
26	Ontario Ministry of Environment, Canada
31	Slovak Hydrometeorological Institute, Slovakia
32	Atmospheric Pollution Research Laboratory, Institute of Physics, Lithuania
33	Latvian Hydrometeorological Agency, Latvia
36	Hydrometeorological Institute of Slovenia, Slovenia
38	Estonian Environmental Research Centre, Estonia
39	Environmental Monitoring Laboratory, Institute of Environmental Protection, Poland

Table A1.1b: Participating laboratories outside the EMEP network, 2003. The number in front of the names is used in tables and figures.

No	Laboratory identification
107	The Finnish Forest Institute, Finland
109	Institut f. Bondenkunde und Waldernährung der Universität, Germany
110	Thüringer Landesanstalt für Landwirtschaft (TTL), Germany
112	Niedersächsische Forstliche Versuchsanstalt (NVF), Germany
114	C.N.R. Istituto Italiano di Idrobiologia, Italy
115	Bayerishe Landesanstalt f. Wald- und Forstwirtschaft, Germany
117	Sächsische Landesanstalt für Forsten, Germany
118	Forstliche Versuchs- und Forschungsanstalt Baden-Württemberg, Germany
120	Landwirtschaftliche Untersuchungs- und Forschungsanstalt (LUFA), Germany
121	Landesamt für Natur und Umwelt, Germany
125	Bayerisches Landesamt für Umweltschutz, Germany
127	Department of Chemistry, Jalan Sultan, Malaysia
128	Dubai Central Laboratory, United Arab Emirates
129	Ecole Nationale d'Ingenieurs de Sfax, Tunisie
132	Comision Chilena De Energia Nuclear, Chile
141	Pollutants Chemical Analysis Centre, Marine Division, Japan
142	EPLD, Lagor, France
143	Department of Mines, Air division, Botswana

Table A1.2: Analytical results for Cr in synthetic precipitation samples, 2003.

Chromium
Sample no.: 1
Theoretical value: 0.700
Unit: µg/l

Run 1:
Number of laboratories: 27
Arithmetic mean value: 0.717
Median: 0.700
Standard deviation 0.099
Rel. st. deviation (%) 13.808

Run 2:
Number of laboratories: 26
Arithmetic mean value: 0.706
Median: 0.700
Standard deviation 0.083
Rel. st. deviation (%) 11.726

Results in decreasing order:

114	1.000 (*)	14	0.700
118	0.900	39	0.700
120	0.820	31	0.690
142	0.820	32	0.680
109	0.800	23	0.680
127	0.800	15	0.670
5	0.780	125	0.640
3	0.770	36	0.620
112	0.750	26	0.620
115	0.740	6	0.600
117	0.710	110	0.600
8	0.700	4	0.600
1	0.700	33	0.560
121	0.700	38	<1.000
		107	<37.000
		129	<15.000
		132	<1.400

Chromium
Sample no.: 2
Theoretical value: 0.900
Unit: µg/l

Run 1:
Number of laboratories: 27
Arithmetic mean value: 0.914
Median: 0.900
Standard deviation 0.143
Rel. st. deviation (%) 15.676

Run 2:
Number of laboratories: 26
Arithmetic mean value: 0.892
Median: 0.900
Standard deviation 0.084
Rel. st. deviation (%) 9.466

Results in decreasing order:

118	1.500 (*)	15	0.900
142	1.100	32	0.900
120	1.010	8	0.890
127	1.000	1	0.890
114	1.000	31	0.870
115	0.960	36	0.820
112	0.940	125	0.820
5	0.930	23	0.820
109	0.930	26	0.820
39	0.900	6	0.800
117	0.900	110	0.800
3	0.900	4	0.800
14	0.900	33	0.690
121	0.900	38	<1.000
		107	<37.000
		129	<15.000
		132	<1.400

Chromium
Sample no.: 3
Theoretical value: 9.000
Unit: µg/l

Run 1:
Number of laboratories: 30
Arithmetic mean value: 8.746
Median: 8.840
Standard deviation 1.421
Rel. st. deviation (%) 16.242

Run 2:
Number of laboratories: 29
Arithmetic mean value: 8.979
Median: 8.880
Standard deviation 0.639
Rel. st. deviation (%) 7.119

Results in decreasing order:

38	10.600	1	8.800
142	10.100	109	8.770
120	10.100	32	8.680
115	9.760	39	8.600
5	9.730	110	8.600
127	9.500	6	8.500
14	9.400	3	8.500
4	9.400	23	8.500
112	9.240	31	8.460
15	9.100	125	8.400
36	9.100	118	8.400
114	9.000	121	8.400
117	8.960	33	8.220
26	8.880	132	7.800
8	8.880	129	2.000 (*)
		107	<37.000

Chromium
Sample no.: 4
Theoretical value: 6.000
Unit: µg/l

Run 1:
Number of laboratories: 30
Arithmetic mean value: 6.097
Median: 6.000
Standard deviation 0.539
Rel. st. deviation (%) 8.835

Run 2:
Number of laboratories: 29
Arithmetic mean value: 6.031
Median: 6.000
Standard deviation 0.408
Rel. st. deviation (%) 6.771

Results in decreasing order:

129	8.000 (*)	39	6.000
38	7.000	114	6.000
115	6.730	8	5.990
120	6.670	26	5.980
142	6.600	15	5.900
127	6.400	109	5.900
4	6.400	31	5.870
112	6.360	110	5.800
14	6.300	118	5.700
117	6.100	6	5.700
5	6.080	125	5.630
32	6.080	3	5.600
1	6.000	132	5.550
121	6.000	33	5.370
36	6.000	23	5.200
		107	<37.000

* Data unused in run 2.

Table A1.3: Analytical results for Ni in synthetic precipitation samples, 2003.

Nickel
Sample no.: 1
Theoretical value: 0.500
Unit: µg/l

Run 1:
Number of laboratories: 22
Arithmetic mean value: 0.579
Median: 0.535
Standard deviation 0.201
Rel. st. deviation (%) 34.705

Run 2:
Number of laboratories: 20
Arithmetic mean value: 0.573
Median: 0.535
Standard deviation 0.105
Rel. st. deviation (%) 18.424

Results in decreasing order:

4	1.200 (*)	15	0.520	
142	0.800	32	0.520	
120	0.770	115	0.520	
31	0.710	1	0.510	
118	0.700	8	0.510	
3	0.650	39	0.500	
110	0.600	14	0.500	
121	0.600	117	0.490	
33	0.580	26	0.470	
23	0.560	125	0.390	
5	0.550	36	0.080	(*)
		6	<0.500	
		38	<1.000	
		107	<58.000	
		109	<0.100	
		112	<0.480	
		114	<0.800	
		127	<2.000	
		129	<88.000	
		132	<2.000	

Nickel
Sample no.: 2
Theoretical value: 0.600
Unit: µg/l

Run 1:
Number of laboratories: 22
Arithmetic mean value: 0.706
Median: 0.600
Standard deviation 0.363
Rel. st. deviation (%) 51.384

Run 2:
Number of laboratories: 21
Arithmetic mean value: 0.640
Median: 0.600
Standard deviation 0.191
Rel. st. deviation (%) 29.810

Results in decreasing order:

118	2.100 (*)	14	0.600	
120	1.110	39	0.600	
3	0.970	15	0.600	
31	0.930	23	0.590	
142	0.700	8	0.590	
110	0.700	117	0.580	
115	0.690	112	0.540	
33	0.670	26	0.540	
32	0.660	4	0.500	
5	0.610	125	0.480	
1	0.600	36	0.170	
		6	<0.500	
		38	<1.000	
		107	<58.000	
		109	<0.100	
		114	<0.800	
		121	<0.500	
		127	<2.000	
		129	<88.000	
		132	<2.000	

Nickel
Sample no.: 3
Theoretical value: 7.000
Unit: µg/l

Run 1:
Number of laboratories: 29
Arithmetic mean value: 6.803
Median: 6.900
Standard deviation 0.581
Rel. st. deviation (%) 8.535

Run 2:
Number of laboratories: 28
Arithmetic mean value: 6.891
Median: 6.930
Standard deviation 0.339
Rel. st. deviation (%) 4.922

Results in decreasing order:

115	7.730	1	6.800	
4	7.500	26	6.790	
117	7.210	31	6.780	
14	7.200	5	6.770	
127	7.200	132	6.750	
112	7.150	3	6.730	
38	7.100	8	6.720	
39	7.100	121	6.700	
23	7.000	120	6.450	
32	7.000	36	6.400	
114	7.000	118	6.400	
142	7.000	33	6.310	
15	7.000	6	6.300	
125	6.960	109	4.330	(*)
110	6.900	107	<58.000	
		129	<88.000	

Nickel
Sample no.: 4
Theoretical value: 8.500
Unit: µg/l

Run 1:
Number of laboratories: 29
Arithmetic mean value: 8.549
Median: 8.510
Standard deviation 0.872
Rel. st. deviation (%) 10.202

Run 2:
Number of laboratories: 27
Arithmetic mean value: 8.544
Median: 8.510
Standard deviation 0.423
Rel. st. deviation (%) 4.946

Results in decreasing order:

118	11.500 (*)	110	8.500	
115	9.800	125	8.460	
4	9.100	1	8.400	
142	9.000	32	8.400	
117	8.950	26	8.340	
5	8.930	132	8.340	
14	8.900	8	8.310	
127	8.800	39	8.200	
112	8.790	33	8.100	
15	8.700	23	8.000	
38	8.620	114	8.000	
121	8.600	36	8.000	
120	8.590	6	7.800	
3	8.540	109	5.730	(*)
31	8.510	107	<58.000	
		129	<88.000	

Table A1.4: Analytical results for Cu in synthetic precipitation samples, 2003.

Copper
Sample no.: 1
Theoretical value: 1.200
Unit: µg/l

Run 1:

Number of laboratories:	29
Arithmetic mean value:	1.262
Median:	1.200
Standard deviation	0.388
Rel. st. deviation (%)	30.716

Run 2:

Number of laboratories:	27
Arithmetic mean value:	1.170
Median:	1.200
Standard deviation	0.147
Rel. st. deviation (%)	12.526

Results in decreasing order:

118	2.900 (*)	14	1.200
120	2.120 (*)	8	1.200
5	1.400	31	1.190
142	1.400	1	1.160
112	1.330	33	1.150
132	1.310	26	1.120
4	1.300	121	1.100
23	1.300	109	1.100
125	1.250	127	1.100
32	1.250	6	1.050
115	1.230	16	1.000
3	1.200	114	1.000
110	1.200	117	0.910
39	1.200	36	0.730
15	1.200	38	<1.000
		107	<32.000
		129	<10.000

Copper
Sample no.: 2
Theoretical value: 1.000
Unit: µg/l

Run 1:

Number of laboratories:	29
Arithmetic mean value:	1.019
Median:	0.970
Standard deviation	0.373
Rel. st. deviation (%)	36.598

Run 2:

Number of laboratories:	28
Arithmetic mean value:	0.959
Median:	0.965
Standard deviation	0.189
Rel. st. deviation (%)	19.705

Results in decreasing order:

118	2.700 (*)	1	0.960
142	1.500	23	0.960
132	1.260	3	0.950
5	1.160	26	0.930
112	1.140	127	0.900
32	1.100	4	0.900
125	1.060	16	0.900
115	1.050	6	0.820
39	1.000	33	0.800
114	1.000	121	0.800
15	1.000	109	0.800
14	1.000	117	0.750
110	1.000	120	0.660
8	0.980	36	0.490
31	0.970	38	<1.000
		107	<32.000
		129	<10.000

Copper
Sample no.: 3
Theoretical value: 6.500
Unit: µg/l

Run 1:

Number of laboratories:	30
Arithmetic mean value:	6.515
Median:	6.445
Standard deviation	0.538
Rel. st. deviation (%)	8.263

Run 2:

Number of laboratories:	28
Arithmetic mean value:	6.486
Median:	6.445
Standard deviation	0.338
Rel. st. deviation (%)	5.211

Results in decreasing order:

142	8.500 (*)	110	6.400
118	7.400	39	6.400
115	7.060	14	6.400
114	7.000	31	6.370
38	6.990	26	6.370
32	6.850	8	6.360
125	6.730	117	6.350
5	6.540	112	6.320
3	6.500	120	6.300
15	6.500	1	6.300
16	6.500	4	6.100
23	6.500	36	6.100
109	6.500	6	5.980
127	6.500	121	5.800
132	6.490	33	5.350 (*)
		107	<32.000
		129	<10.000

Copper
Sample no.: 4
Theoretical value: 9.000
Unit: µg/l

Run 1:

Number of laboratories:	30
Arithmetic mean value:	9.041
Median:	8.995
Standard deviation	0.626
Rel. st. deviation (%)	6.921

Run 2:

Number of laboratories:	28
Arithmetic mean value:	9.046
Median:	8.995
Standard deviation	0.497
Rel. st. deviation (%)	5.491

Results in decreasing order:

142	10.500 (*)	8	8.990
115	10.200	117	8.970
118	10.100	120	8.960
38	10.000	26	8.910
5	9.820	3	8.900
32	9.250	1	8.800
4	9.200	16	8.800
125	9.190	36	8.800
14	9.100	110	8.800
15	9.100	109	8.770
132	9.060	39	8.700
112	9.030	23	8.600
31	9.010	6	8.440
114	9.000	121	7.800
127	9.000	33	7.440 (*)
		107	<32.000
		129	<10.000

Table A1.5: Analytical results for Zn in synthetic precipitation samples, 2003.

Zinc
Sample no.: 1
Theoretical value: 6.000
Unit: µg/l

Run 1:
Number of laboratories: 26
Arithmetic mean value: 7.300
Median: 6.680
Standard deviation 3.978
Rel. st. deviation (%) 54.496

Run 2:
Number of laboratories: 25
Arithmetic mean value: 6.552
Median: 6.600
Standard deviation 1.154
Rel. st. deviation (%) 17.616

Results in decreasing order:

129	26.000 (*)	121	6.600	
32	9.400	112	6.350	
118	9.000	3	6.000	
115	7.820	16	6.000	
6	7.500	1	5.900	
26	7.220	117	5.860	
127	7.100	132	5.820	
125	7.040	23	5.800	
114	7.000	8	5.710	
15	7.000	39	5.500	
14	7.000	33	5.320	
120	6.900	110	4.600	
5	6.760	36	4.600	
		38	<10.000	
		107	<10.000	
		109	<10.000	
		142	<10.000	

Zinc
Sample no.: 2
Theoretical value: 5.000
Unit: µg/l

Run 1:
Number of laboratories: 26
Arithmetic mean value: 6.755
Median: 5.475
Standard deviation 6.466
Rel. st. deviation (%) 95.721

Run 2:
Number of laboratories: 25
Arithmetic mean value: 5.505
Median: 5.360
Standard deviation 1.114
Rel. st. deviation (%) 20.234

Results in decreasing order:

129	38.000 (*)	117	5.360	
32	8.400	15	5.100	
125	7.240	23	5.000	
115	6.800	14	5.000	
118	6.700	1	4.900	
127	6.500	3	4.900	
6	6.400	132	4.880	
26	6.040	8	4.810	
114	6.000	16	4.800	
121	5.800	39	4.500	
5	5.790	112	4.210	
120	5.700	110	3.600	
33	5.590	36	3.600	
38	<10.000			
		107	<10.000	
		109	<10.000	
		142	<10.000	

Zinc
Sample no.: 3
Theoretical value: 103.000
Unit: µg/l

Run 1:
Number of laboratories: 30
Arithmetic mean value: 104.599
Median: 104.000
Standard deviation 10.498
Rel. st. deviation (%) 10.036

Run 2:
Number of laboratories: 28
Arithmetic mean value: 103.992
Median: 104.000
Standard deviation 6.858
Rel. st. deviation (%) 6.595

Results in decreasing order:

6	142.850 (*)	39	104.000	
125	117.950	33	103.920	
115	117.000	26	103.560	
129	116.000	15	103.000	
5	112.000	8	101.740	
110	109.000	121	99.900	
114	108.000	1	98.100	
142	107.900	118	98.000	
112	107.300	23	98.000	
14	107.000	36	98.000	
127	106.800	38	96.000	
3	106.000	107	95.000	
120	105.000	117	92.010	
16	105.000	132	91.600	
32	104.000	109	83.330	(*)

Zinc
Sample no.: 4
Theoretical value: 115.000
Unit: µg/l

Run 1:
Number of laboratories: 30
Arithmetic mean value: 117.087
Median: 116.275
Standard deviation 11.272
Rel. st. deviation (%) 9.627

Run 2:
Number of laboratories: 27
Arithmetic mean value: 116.504
Median: 116.000
Standard deviation 7.086
Rel. st. deviation (%) 6.082

Results in decreasing order:

6	143.650 (*)	15	116.000	
5	140.000 (*)	3	116.000	
115	136.000	121	115.000	
125	131.680	16	115.000	
112	122.800	32	115.000	
110	121.000	142	114.900	
114	121.000	33	114.690	
14	121.000	1	112.000	
118	119.900	36	111.000	
120	119.000	38	110.000	
26	118.800	23	110.000	
127	118.500	132	107.000	
129	118.000	107	106.000	
39	117.000	117	101.800	
8	116.550	109	83.330	(*)

Table A1.6: Analytical results for As in synthetic precipitation samples, 2003.

Arsenic
Sample no.: 1
Theoretical value: 0.500
Unit: µg/l

Run 1:
Number of laboratories: 21
Arithmetic mean value: 0.541
Median: 0.500
Standard deviation 0.198
Rel. st. deviation (%) 36.623

Run 2:
Number of laboratories: 20
Arithmetic mean value: 0.514
Median: 0.500
Standard deviation 0.157
Rel. st. deviation (%) 30.602

Results in decreasing order:

115	1.090 (*)	6	0.500
142	0.930	8	0.500
132	0.910	26	0.490
5	0.557	23	0.480
14	0.530	15	0.480
36	0.520	3	0.450
125	0.510	31	0.420
1	0.500	118	0.400
121	0.500	33	0.390
4	0.500	32	0.210
127	0.500	38	<1.000
		110	<0.500
		114	<3.000
		120	<0.500

Arsenic
Sample no.: 2
Theoretical value: 0.700
Unit: µg/l

Run 1:
Number of laboratories: 22
Arithmetic mean value: 0.741
Median: 0.685
Standard deviation 0.228
Rel. st. deviation (%) 30.717

Run 2:
Number of laboratories: 19
Arithmetic mean value: 0.659
Median: 0.670
Standard deviation 0.093
Rel. st. deviation (%) 14.152

Results in decreasing order:

132	1.300 (*)	8	0.680
115	1.270 (*)	3	0.670
142	1.200 (*)	14	0.670
118	0.800	33	0.660
125	0.770	15	0.660
5	0.744	31	0.660
36	0.710	23	0.610
26	0.710	127	0.600
121	0.700	6	0.600
4	0.700	110	0.500
1	0.690	32	0.390
		38	<1.000
		114	<3.000
		120	<0.500

Arsenic
Sample no.: 3
Theoretical value: 3.500
Unit: µg/l

Run 1:
Number of laboratories: 25
Arithmetic mean value: 3.694
Median: 3.450
Standard deviation 0.926
Rel. st. deviation (%) 25.063

Run 2:
Number of laboratories: 24
Arithmetic mean value: 3.533
Median: 3.425
Standard deviation 0.470
Rel. st. deviation (%) 13.305

Results in decreasing order:

132	7.550 (*)	23	3.400
114	5.000	15	3.400
115	4.250	3	3.400
142	4.200	4	3.400
125	3.750	6	3.400
127	3.700	33	3.390
120	3.700	31	3.390
26	3.660	1	3.340
14	3.580	110	3.300
121	3.500	118	3.300
36	3.500	32	2.700
8	3.490	38	2.600
5	3.450		

Arsenic
Sample no.: 4
Theoretical value: 5.000
Unit: µg/l

Run 1:
Number of laboratories: 25
Arithmetic mean value: 5.172
Median: 5.000
Standard deviation 0.710
Rel. st. deviation (%) 13.719

Run 2:
Number of laboratories: 24
Arithmetic mean value: 5.065
Median: 5.000
Standard deviation 0.474
Rel. st. deviation (%) 9.353

Results in decreasing order:

132	7.750 (*)	127	5.000
115	6.040	23	5.000
120	5.900	36	5.000
142	5.720	31	4.970
5	5.630	6	4.900
125	5.410	15	4.900
4	5.400	1	4.820
14	5.250	110	4.800
26	5.140	118	4.800
121	5.100	33	4.460
8	5.090	32	4.200
114	5.000	38	4.020
3	5.000		

Table A1.7: Analytical results for Cd in synthetic precipitation samples, 2003.

Cadmium
Sample no.: 1
Theoretical value: 0.060
Unit: µg/l

Run 1:
Number of laboratories: 23
Arithmetic mean value: 0.106
Median: 0.060
Standard deviation 0.118
Rel. st. deviation (%) 110.774

Run 2:
Number of laboratories: 22
Arithmetic mean value: 0.088
Median: 0.060
Standard deviation 0.080
Rel. st. deviation (%) 91.006

Results in decreasing order:

23	0.510 (*)	33	0.060
4	0.340	39	0.060
142	0.320	121	0.060
3	0.101	125	0.060
114	0.100	1	0.060
115	0.100	15	0.057
5	0.066	16	0.055
14	0.062	117	0.050
8	0.060	118	0.050
26	0.060	141	0.050
31	0.060	38	0.043
32	0.060	6	<0.100
		36	<0.040
		107	<24.000
		109	<0.100
		110	<0.200
		112	<0.320
		120	<0.100
		127	<0.200
		128	<0.500
		129	<4.000
		132	<0.200

Cadmium
Sample no.: 2
Theoretical value: 0.080
Unit: µg/l

Run 1:
Number of laboratories: 24
Arithmetic mean value: 0.128
Median: 0.080
Standard deviation 0.180
Rel. st. deviation (%) 140.567

Run 2:
Number of laboratories: 23
Arithmetic mean value: 0.095
Median: 0.080
Standard deviation 0.079
Rel. st. deviation (%) 83.565

Results in decreasing order:

23	0.890 (*)	39	0.080
142	0.450	121	0.080
115	0.120	125	0.080
4	0.110	14	0.079
114	0.100	15	0.077
3	0.091	16	0.075
5	0.084	118	0.070
1	0.080	141	0.070
8	0.080	32	0.060
26	0.080	117	0.060
31	0.080	38	0.055
33	0.080	36	0.040
		6	<0.100
		107	<24.000
		109	<0.100
		110	<0.200
		112	<0.320
		120	<0.100
		127	<0.200
		128	<0.500
		129	<4.000
		132	<0.200

Cadmium
Sample no.: 3
Theoretical value: 0.800
Unit: µg/l

Run 1:
Number of laboratories: 32
Arithmetic mean value: 1.043
Median: 0.800
Standard deviation 1.363
Rel. st. deviation (%) 130.622

Run 2:
Number of laboratories: 31
Arithmetic mean value: 0.803
Median: 0.800
Standard deviation 0.077
Rel. st. deviation (%) 9.593

Results in decreasing order:

23	8.500 (*)	114	0.800
120	1.070	125	0.800
115	0.930	14	0.798
39	0.900	1	0.790
142	0.860	33	0.790
141	0.860	36	0.780
117	0.850	8	0.780
4	0.850	5	0.765
118	0.840	3	0.765
112	0.830	128	0.760
32	0.820	26	0.760
121	0.810	38	0.728
127	0.800	16	0.700
31	0.800	110	0.700
6	0.800	132	0.680
15	0.800	109	0.670
		107	<24.000
		129	<4.000

Cadmium
Sample no.: 4
Theoretical value: 0.700
Unit: µg/l

Run 1:
Number of laboratories: 32
Arithmetic mean value: 0.954
Median: 0.710
Standard deviation 1.342
Rel. st. deviation (%) 140.651

Run 2:
Number of laboratories: 31
Arithmetic mean value: 0.717
Median: 0.710
Standard deviation 0.069
Rel. st. deviation (%) 9.615

Results in decreasing order:

23	8.300 (*)	1	0.710
142	0.940	31	0.710
115	0.850	15	0.700
16	0.800	39	0.700
117	0.780	114	0.700
4	0.780	127	0.700
5	0.773	8	0.700
121	0.740	6	0.700
141	0.740	36	0.680
26	0.730	118	0.680
125	0.730	132	0.670
33	0.730	38	0.661
120	0.730	112	0.650
14	0.725	110	0.600
3	0.717	128	0.600
32	0.710	109	0.600
		107	<24.000
		129	<4.000

Table A1.8: Analytical results for Pb in synthetic precipitation samples, 2003.

Lead
Sample no.: 1
Theoretical value: 1.300
Unit: µg/l

Run 1:
Number of laboratories: 24
Arithmetic mean value: 1.362
Median: 1.300
Standard deviation 0.389
Rel. st. deviation (%) 28.565

Run 2:
Number of laboratories: 23
Arithmetic mean value: 1.286
Median: 1.300
Standard deviation 0.122
Rel. st. deviation (%) 9.473

Results in decreasing order:

142	3.100 (*)	6	1.300	
115	1.450	15	1.300	
5	1.440	127	1.300	
110	1.400	14	1.300	
118	1.400	32	1.270	
121	1.400	8	1.260	
33	1.360	38	1.250	
16	1.350	112	1.230	
125	1.320	23	1.200	
1	1.300	26	1.200	
31	1.300	117	1.050	
3	1.300	4	0.900	
		36	<0.040	
		107	<319.000	
		109	<1.000	
		114	<4.000	
		120	<1.000	
		128	<5.000	
		129	<41.000	
		132	<5.000	

Lead
Sample no.: 2
Theoretical value: 1.600
Unit: µg/l

Run 1:
Number of laboratories: 25
Arithmetic mean value: 1.770
Median: 1.600
Standard deviation 1.111
Rel. st. deviation (%) 62.756

Run 2:
Number of laboratories: 24
Arithmetic mean value: 1.550
Median: 1.600
Standard deviation 0.160
Rel. st. deviation (%) 10.331

Results in decreasing order:

142	7.050 (*)	127	1.600	
112	1.840	33	1.550	
115	1.790	8	1.540	
110	1.700	31	1.510	
16	1.700	23	1.500	
5	1.680	3	1.500	
38	1.630	6	1.500	
15	1.620	26	1.490	
125	1.620	32	1.310	
1	1.600	120	1.300	
118	1.600	117	1.230	
14	1.600	4	1.200	
		121	1.600	
		36	<0.040	
		107	<319.000	
		109	<1.000	
		114	<4.000	
		128	<5.000	
		129	<41.000	
		132	<5.000	

Lead
Sample no.: 3
Theoretical value: 48.000
Unit: µg/l

Run 1:
Number of laboratories: 31
Arithmetic mean value: 46.724
Median: 47.400
Standard deviation 7.635
Rel. st. deviation (%) 16.341

Run 2:
Number of laboratories: 30
Arithmetic mean value: 48.014
Median: 47.400
Standard deviation 2.621
Rel. st. deviation (%) 5.460

Results in decreasing order:

120	54.500	1	47.400	
128	53.300	33	47.020	
115	52.800	32	47.000	
5	51.800	36	47.000	
112	50.700	31	46.980	
16	50.000	4	46.600	
109	49.670	142	46.200	
117	49.180	23	46.000	
114	49.000	26	45.800	
14	48.900	8	45.700	
125	48.280	38	45.600	
118	47.900	121	45.000	
110	47.800	6	44.300	
127	47.800	132	43.400	
15	47.400	129	8.000 (*)	
3	47.400	107	<319.000	

Lead
Sample no.: 4
Theoretical value: 27.000
Unit: µg/l

Run 1:
Number of laboratories: 31
Arithmetic mean value: 27.659
Median: 27.300
Standard deviation 1.797
Rel. st. deviation (%) 6.498

Run 2:
Number of laboratories: 30
Arithmetic mean value: 27.505
Median: 27.200
Standard deviation 1.604
Rel. st. deviation (%) 5.833

Results in decreasing order:

5	32.300 (*)	4	27.100	
120	31.200	31	27.080	
129	31.000	15	27.000	
115	30.900	114	27.000	
128	29.200	1	27.000	
142	29.000	125	26.930	
112	28.900	8	26.480	
16	28.800	33	26.010	
117	28.210	38	26.000	
32	28.000	23	26.000	
110	27.700	26	26.000	
118	27.700	36	26.000	
14	27.700	121	26.000	
127	27.400	109	25.330	
6	27.300	132	24.900	
3	27.300	107	<319.000	

Table A1.9: Analytical techniques used at the participating laboratories for the different elements, 2003.

Lab. no.	Elements	Technique
1	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
3	Ni, Cd, Cu, Pb,	GF-AAS
	Cr, As	ICP-MS
	Zn	F-AAS
4	Cr, Ni, Cu, Zn, As, Cd, Pb	GF-AAS
5	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
6	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
8	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
14	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
15	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
16	Cr, Ni, Cu, Cd, Pb	GF-AAS
	Zn	F-AAS
23	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
26	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
31	Cr, Ni, Cu, Cd, Pb	GF-AAS
	As	HG-GF-AAS
	Zn	F-AAS
32	Cr, Ni, Cu, Zn, As, Cd, Pb	GF-AAS
33	Cu, Cd, Pb	GF-AAS
	Zn	F-AAS
	As	HG-AAS
36	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
38	Cr, Ni, Cu, , Cd, Pb	GF-AAS
	Zn	F-AAS
39	Cr, Ni, Cu, Cd,	GF-AAS
	Zn	F-AAS
107	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-OES
109	Cr, Ni, Cu, Zn, Cd, Pb	GF-AAS
110	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
112	Cr, Ni, Cu, Zn, As, Cd, Pb	USN-ICP-MS
114	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-OES
115	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
117	Cr, Ni, Cu , Zn	USN-ICP-OES
	As, Cd, Pb	GF-AAS
118	Cu, Cd, Pb	GF-AAS
	As ,Zn Cr, Ni	ICP-OES
120	Cr, Ni, Cu, Zn, As, Cd, Pb	GF-AAS
121	Cr, Ni, Cu, Cd, Pb	GF-AAS
	Zn	Voltametry
	As	HG-AAS
125	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
127	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
128	Cu, Cd, Pb	GF-AAS
	As	HG-AAS
	Zn	F-AAS
129	Cr, Ni, Cu, Zn, Cd, Pb	F-AAS (Polarized Zeeman)
132	Cr, Ni, Cu, Zn , Cd	USN-ICP-OES
	Pb	GF-AAS
	As	HG-AAS
141	Cr, Ni, Cu, As, Cd, Pb	ICP-MS
142	Zn	ICP-OES
143	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS

Appendix 2

Figures, 2003

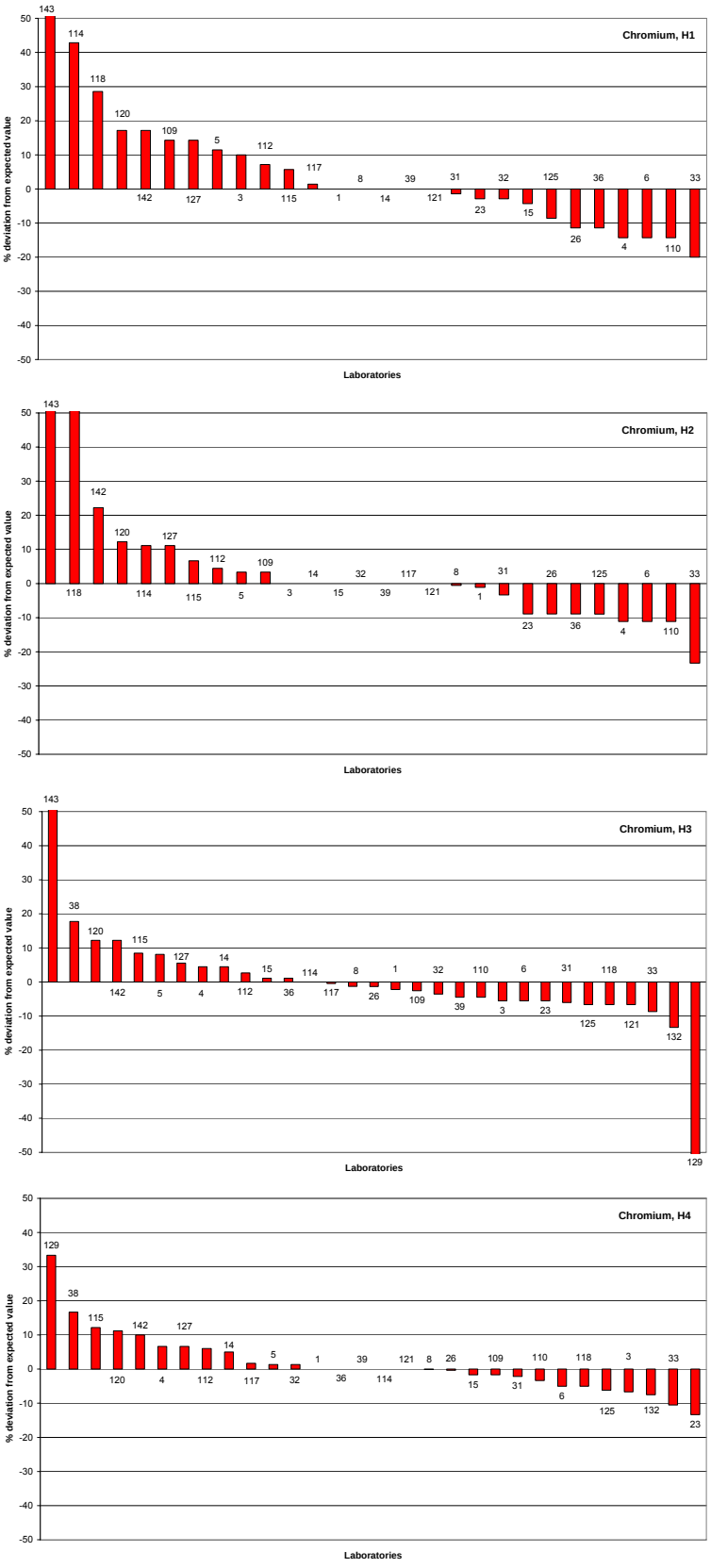


Figure A2.1: Results from determination of Cr, 2003.

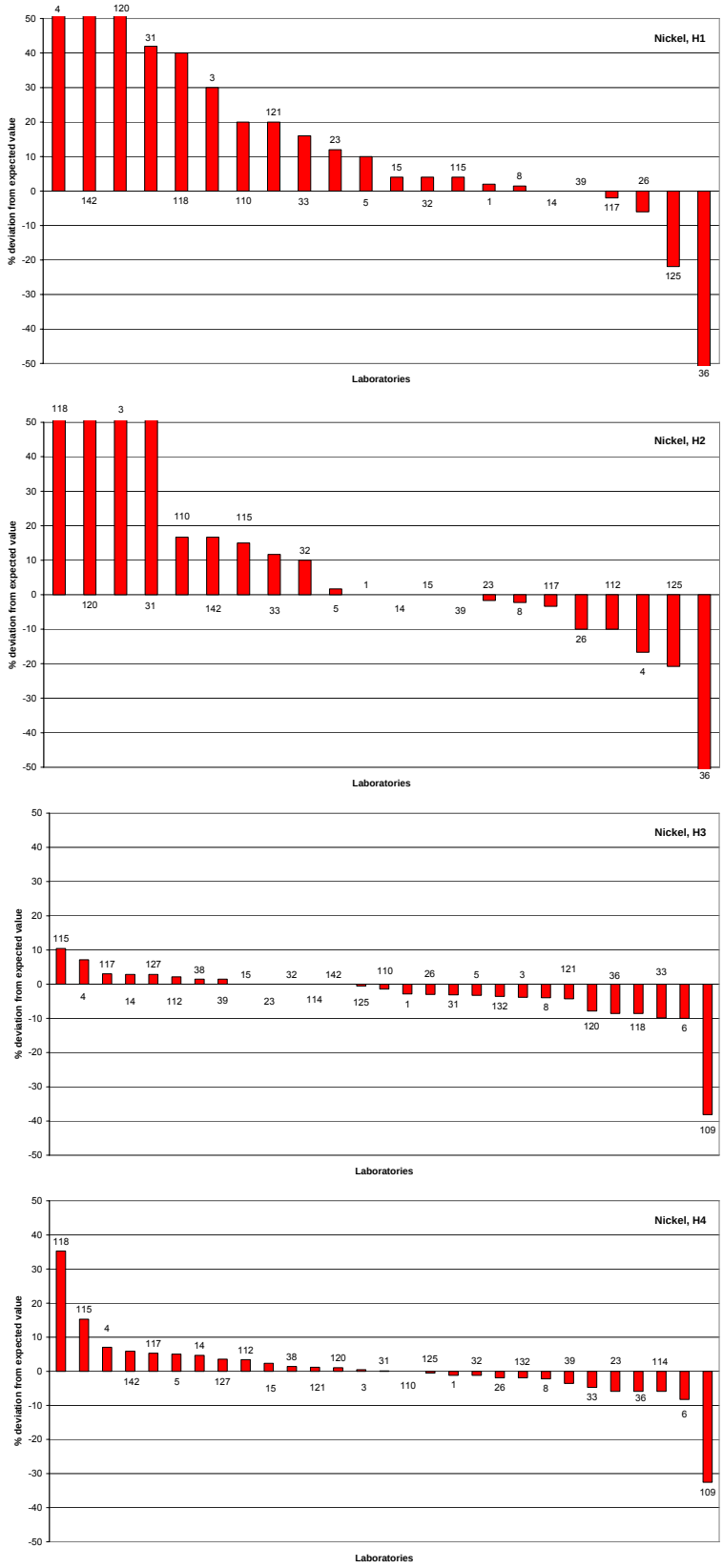


Figure A2.2: Results from determination of Ni, 2003.

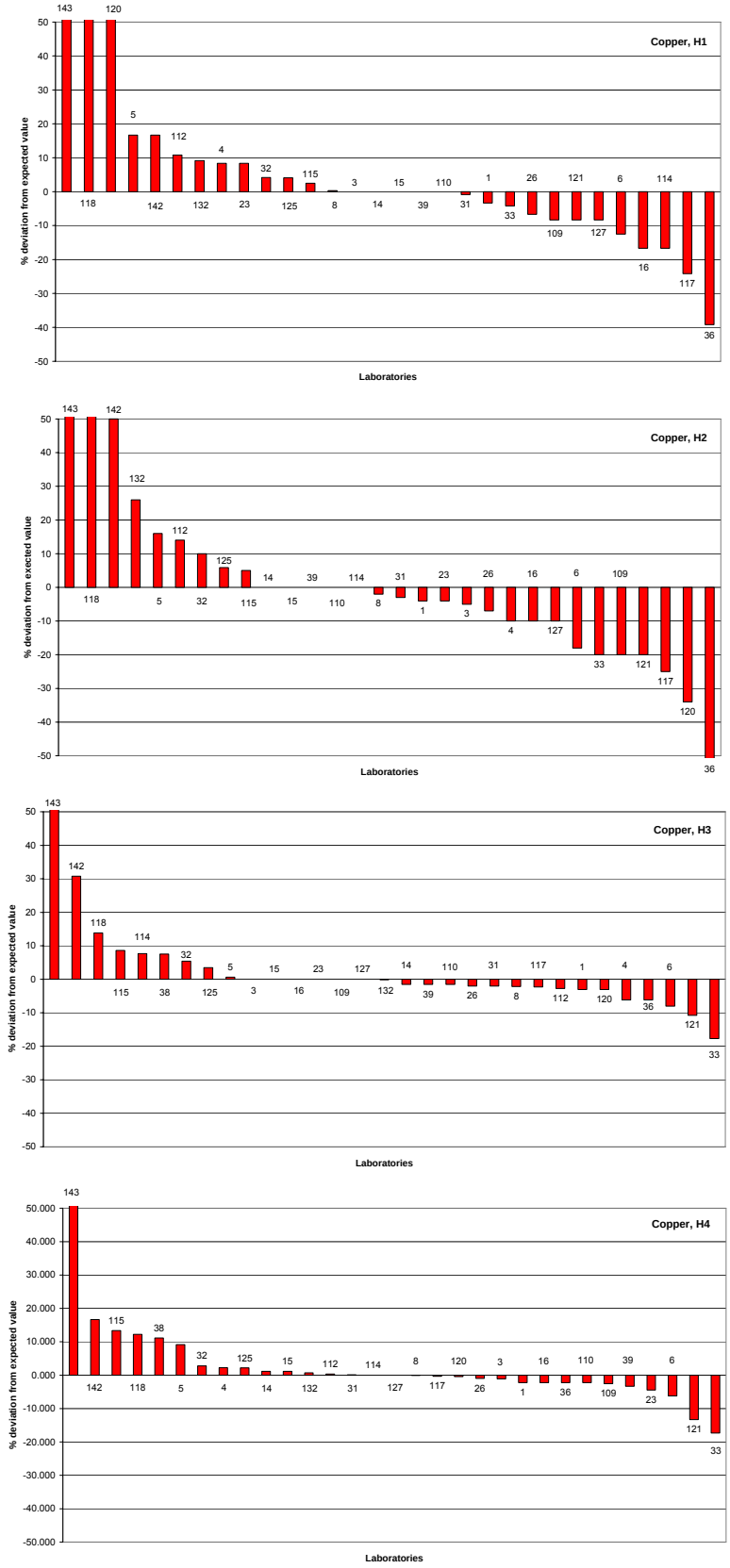


Figure A2.3: Results from determination of Cu, 2003.

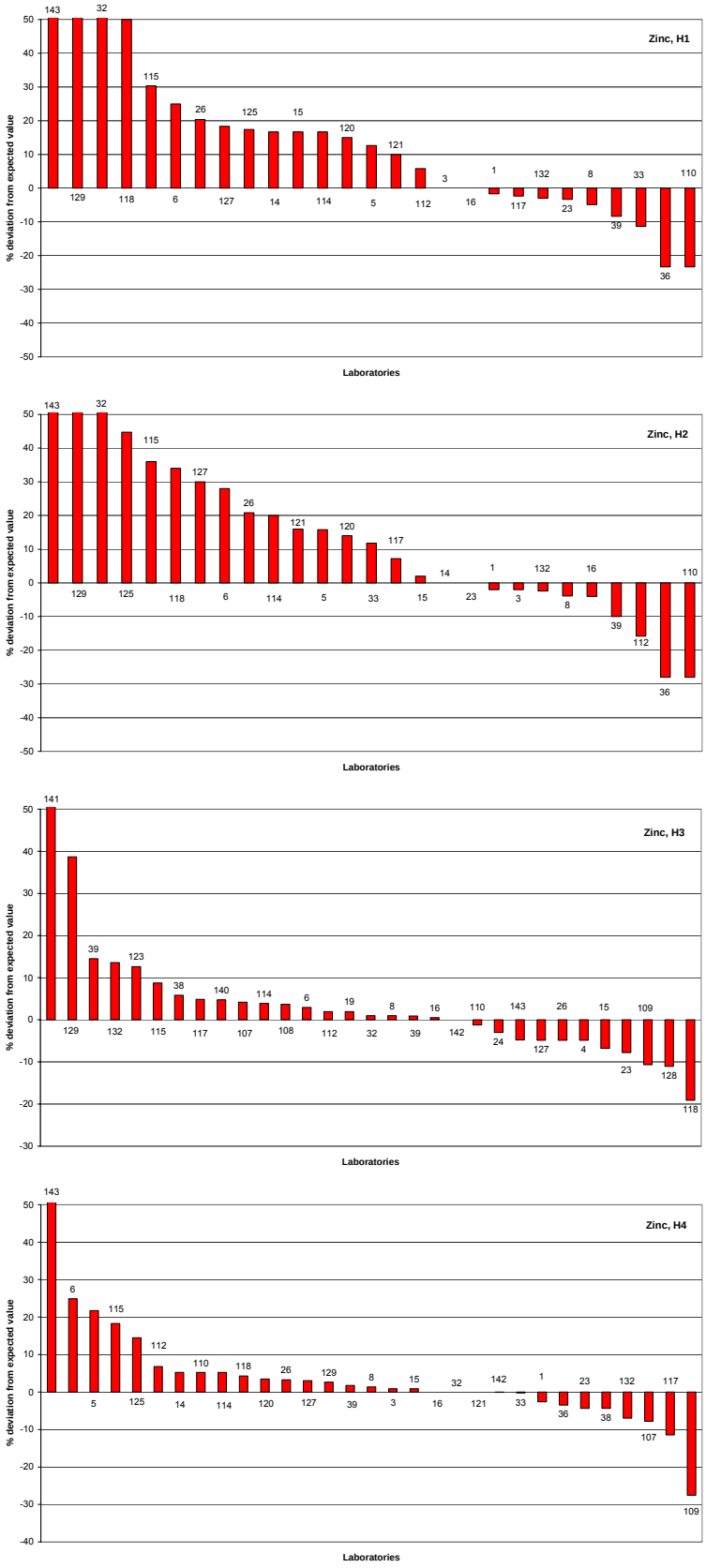


Figure A2.4: Results from determination of Zn, 2003.

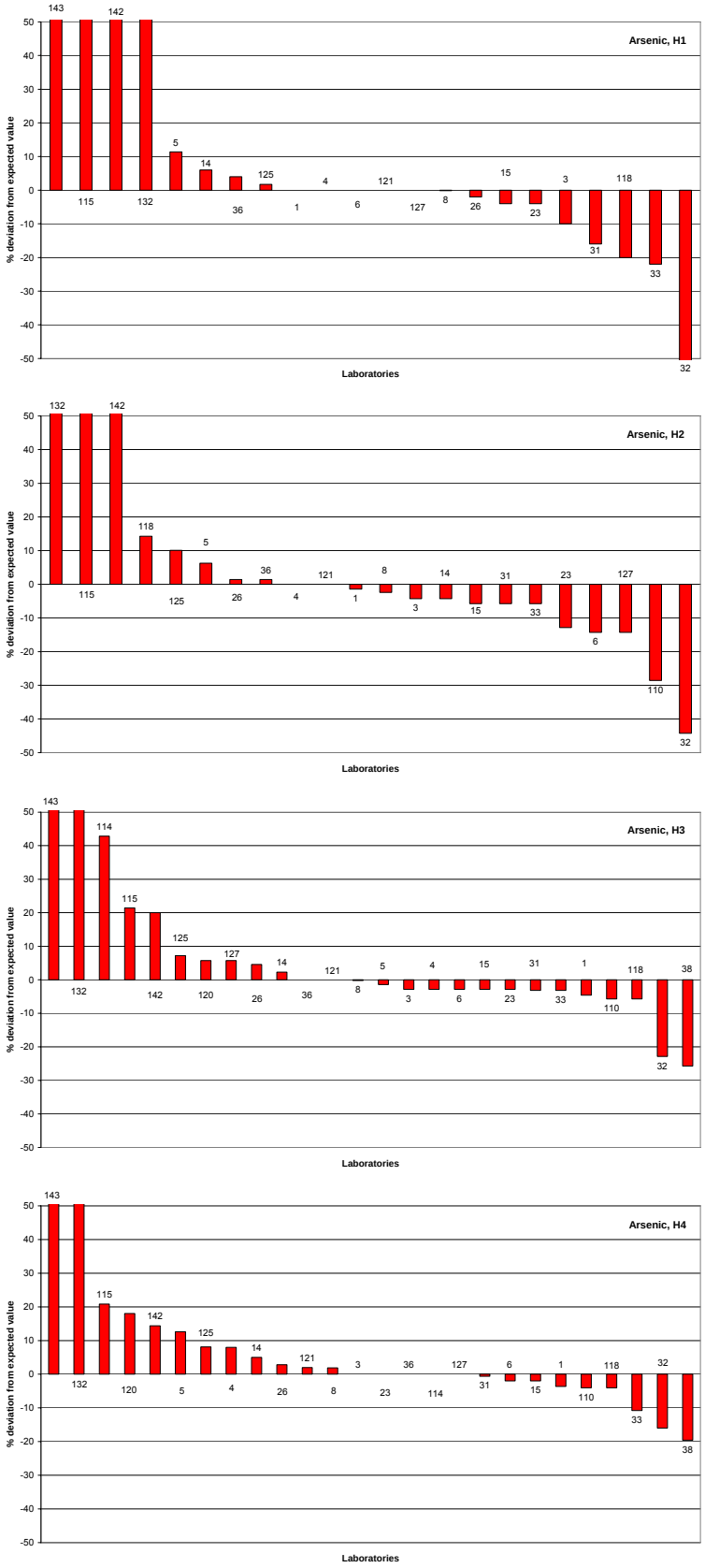


Figure A2.5: Results from determination of As, 2003.

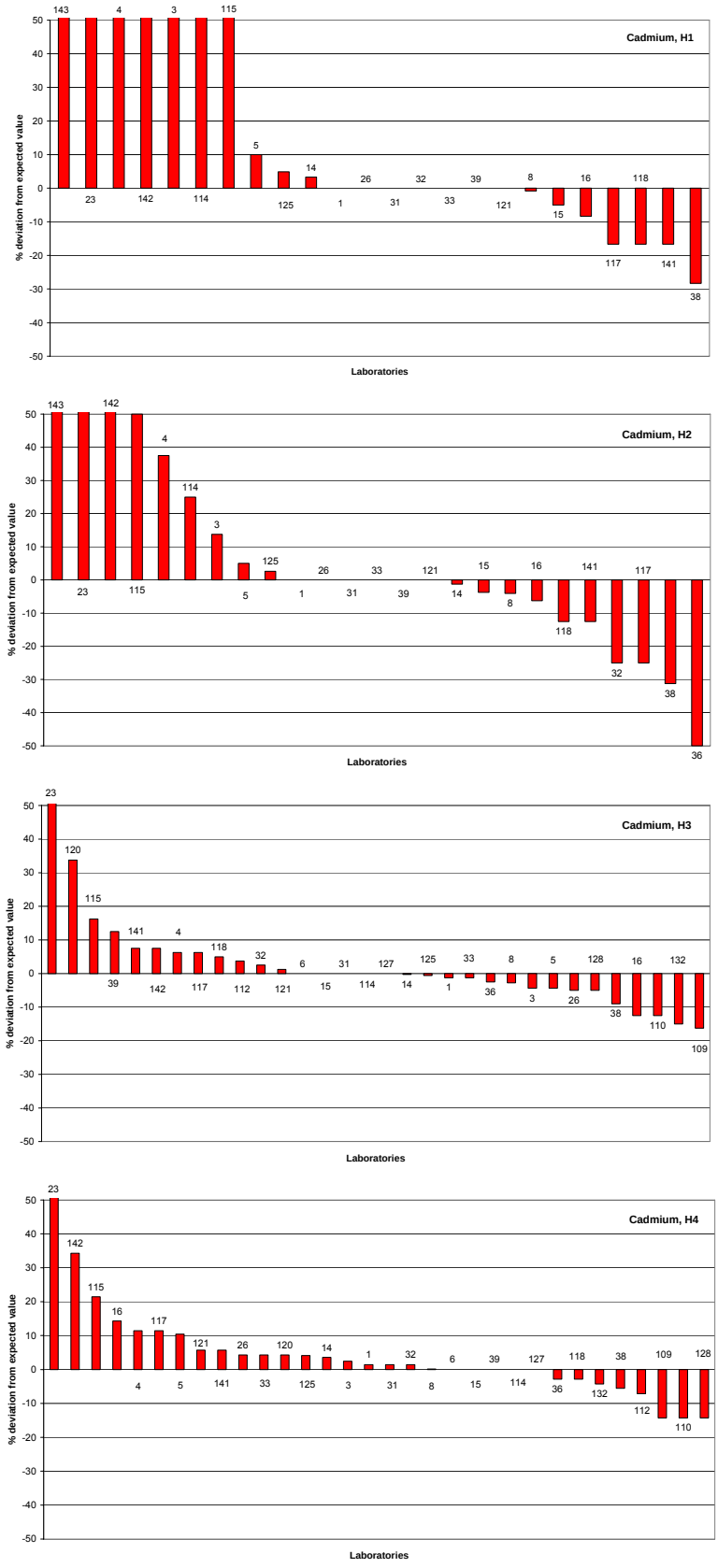


Figure A2.6: Results from determination of Cd, 2003.

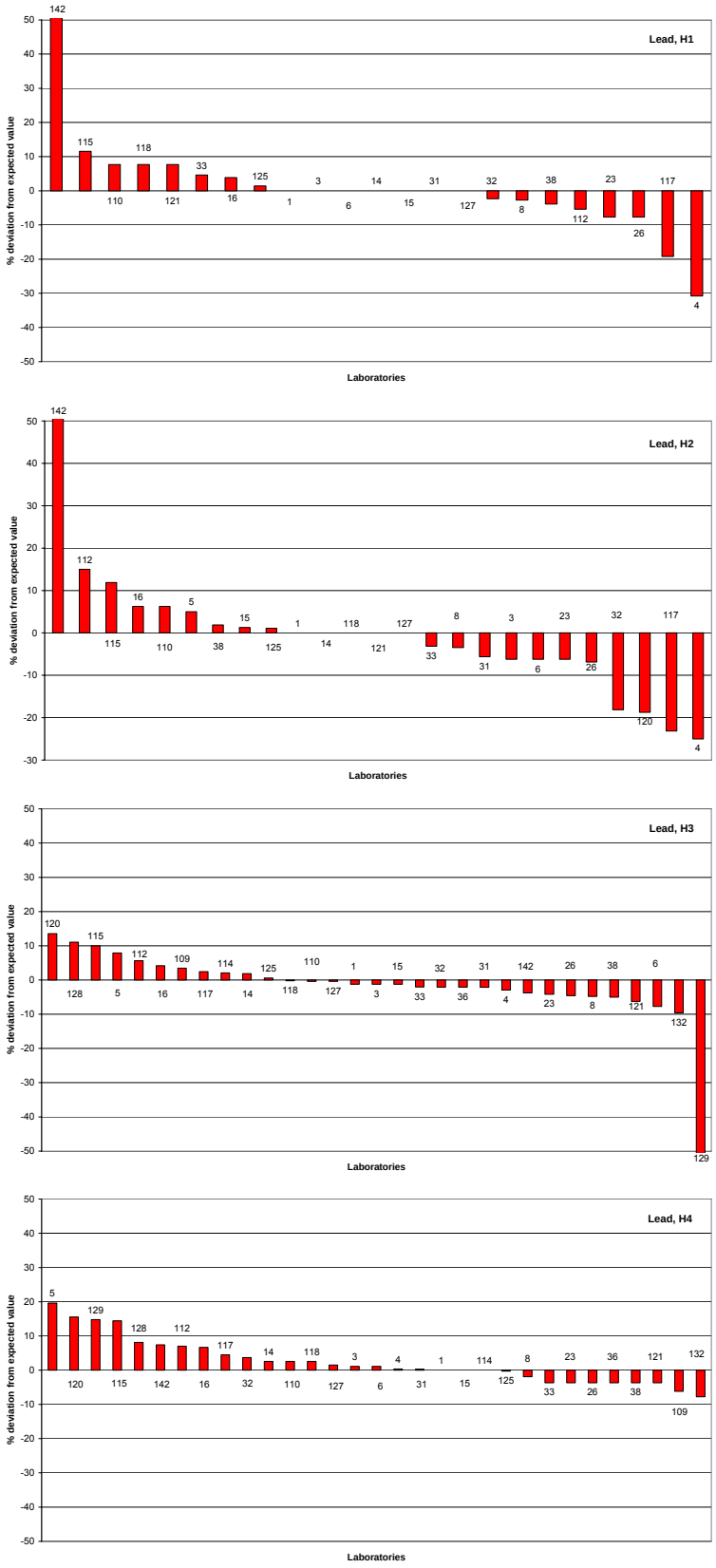


Figure A2.7: Results from determination of Pb, 2003.

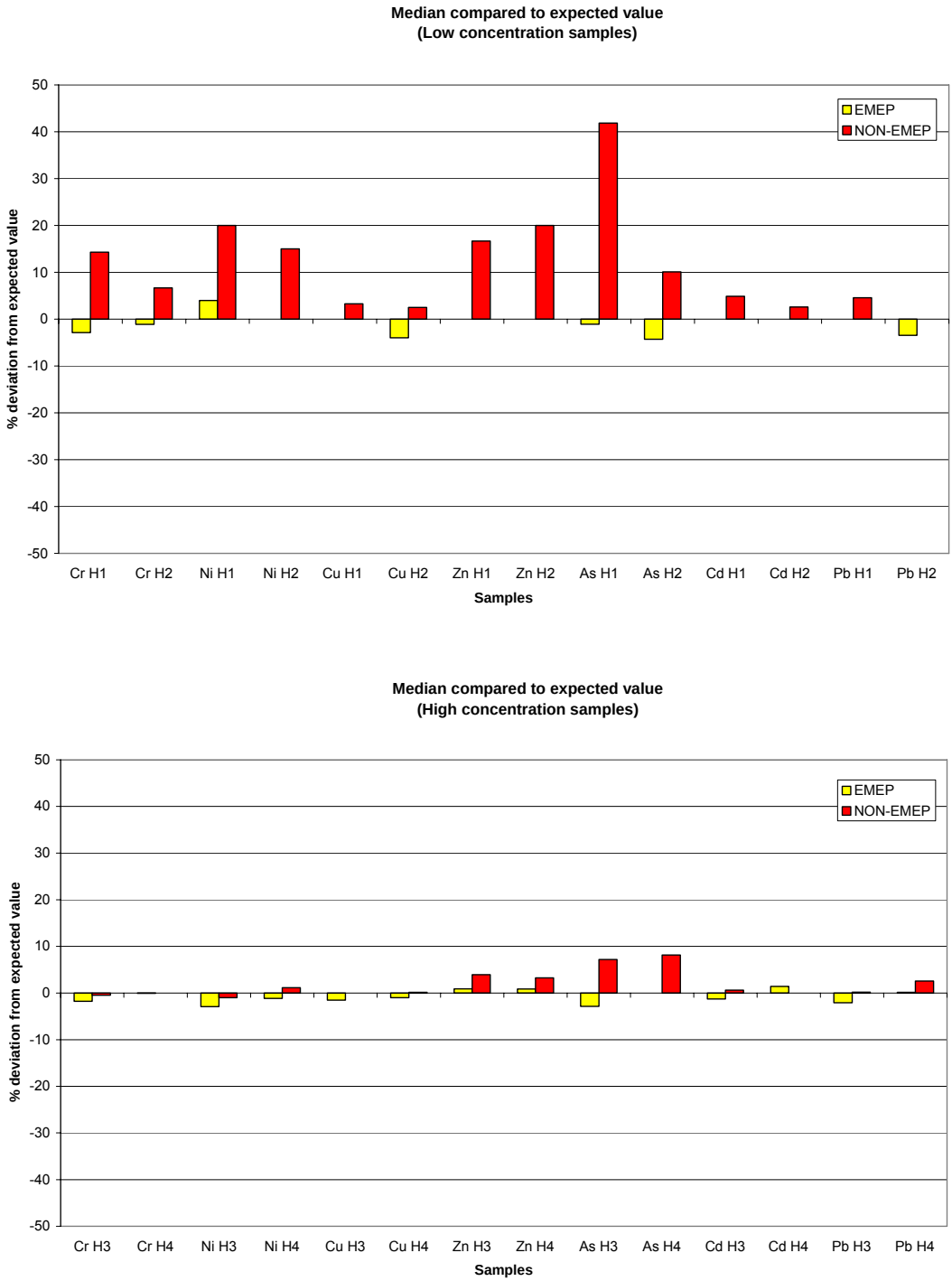


Figure A2.8: The median compared to theoretical value for low and high concentration samples in 2003, respectively.

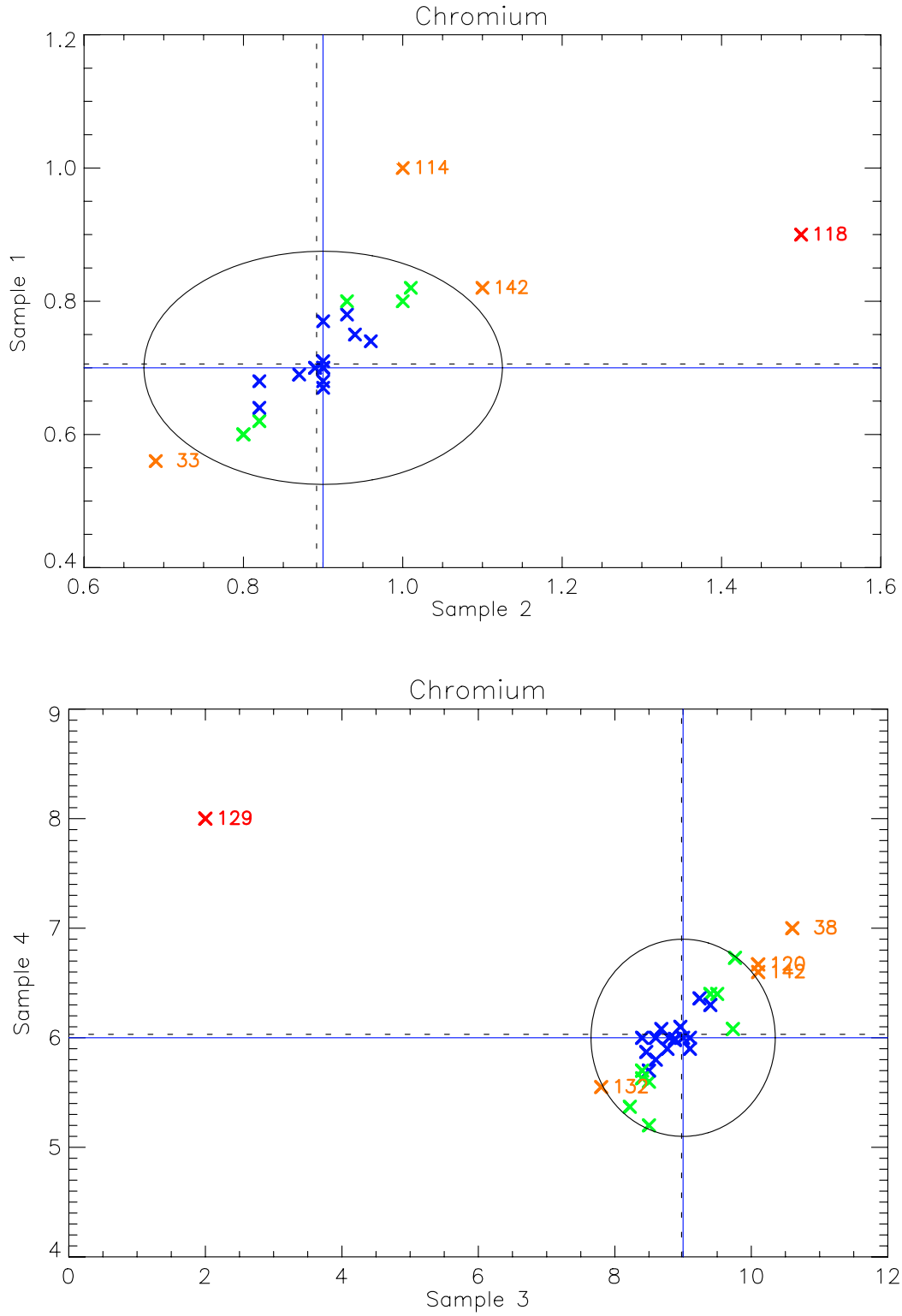


Figure A2.9: Youden plot of chromium, 2003.

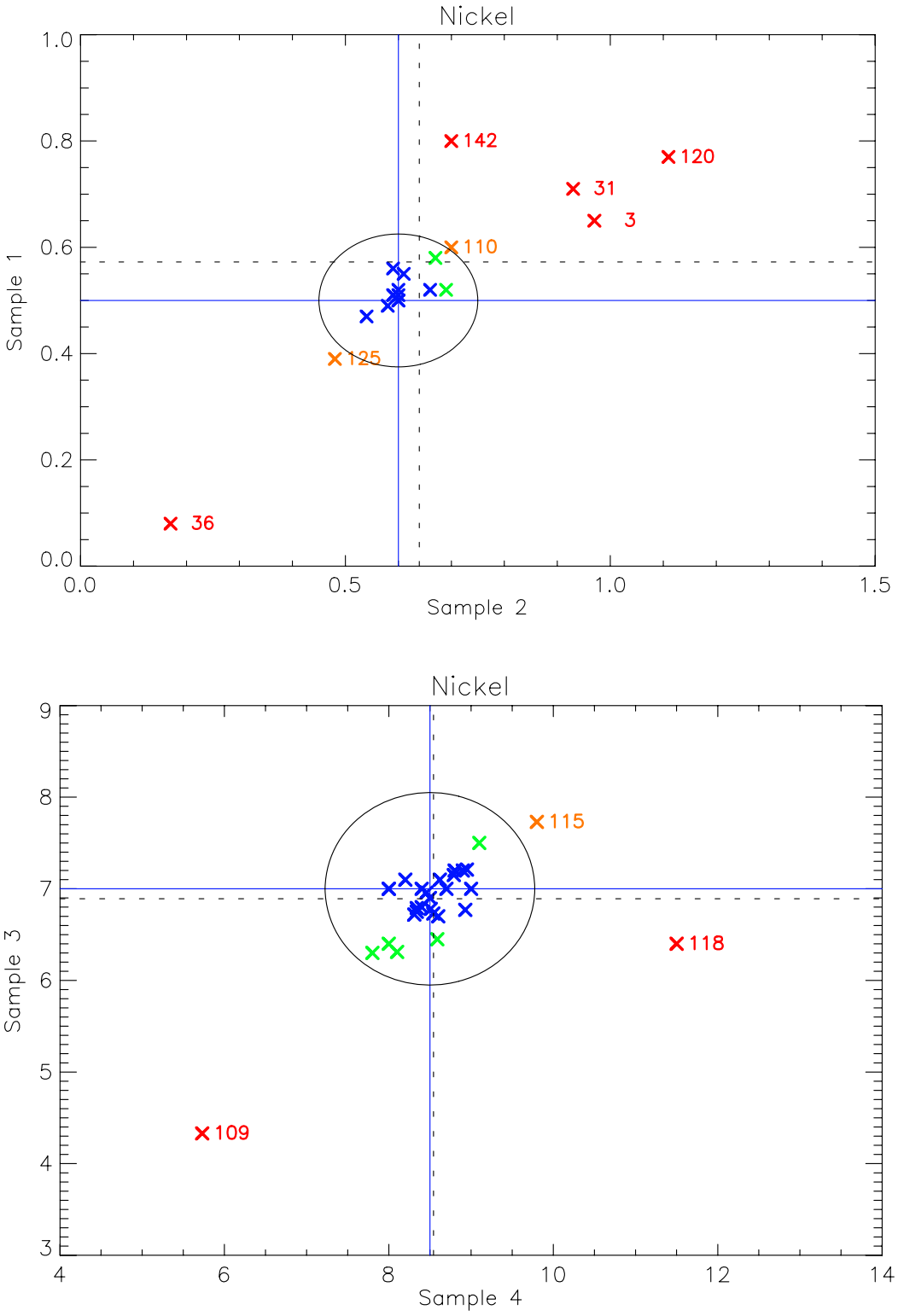


Figure A2.10: Youden plot of nickel, 2003.

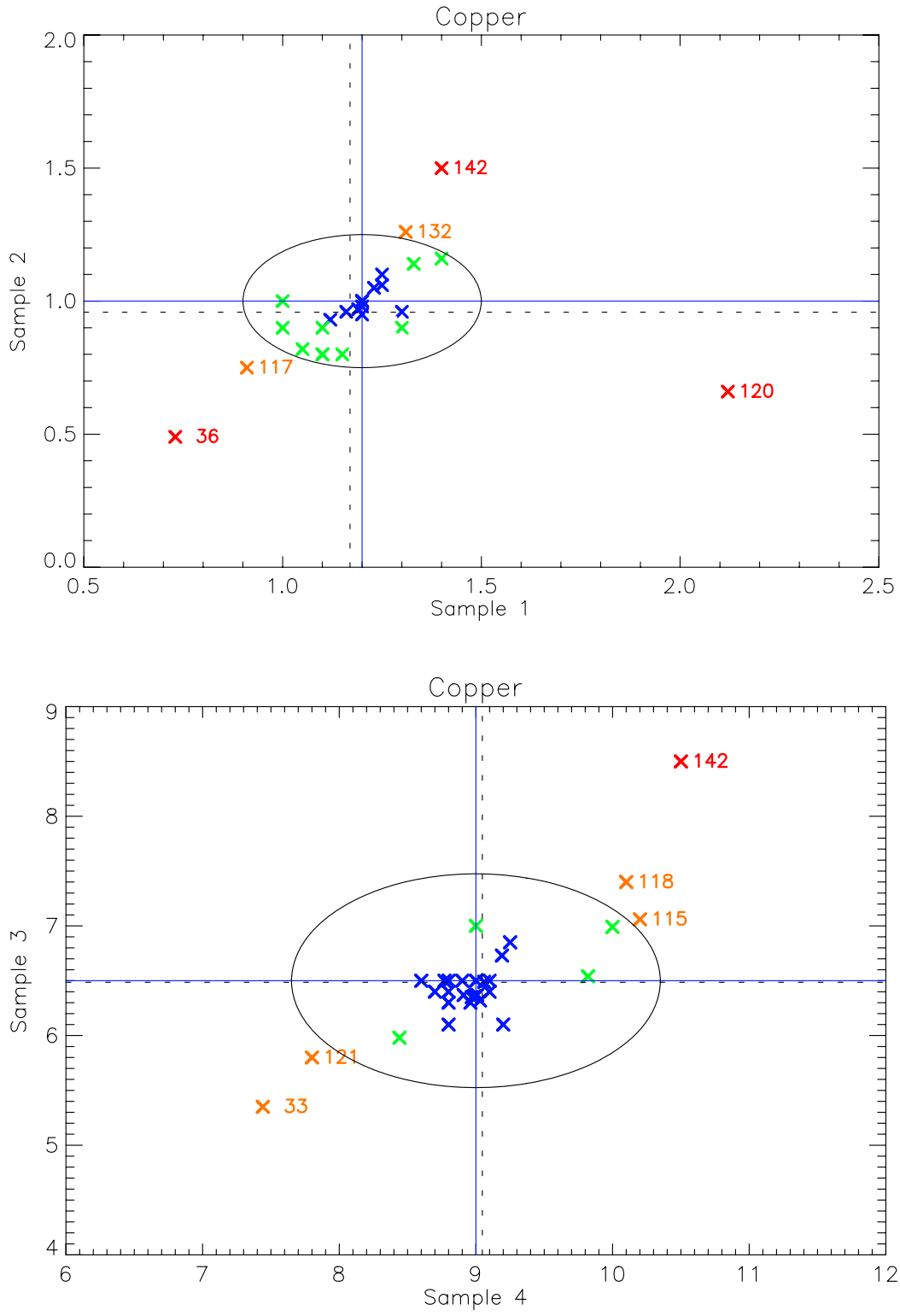


Figure A2.11: Youden plot of copper, 2003.

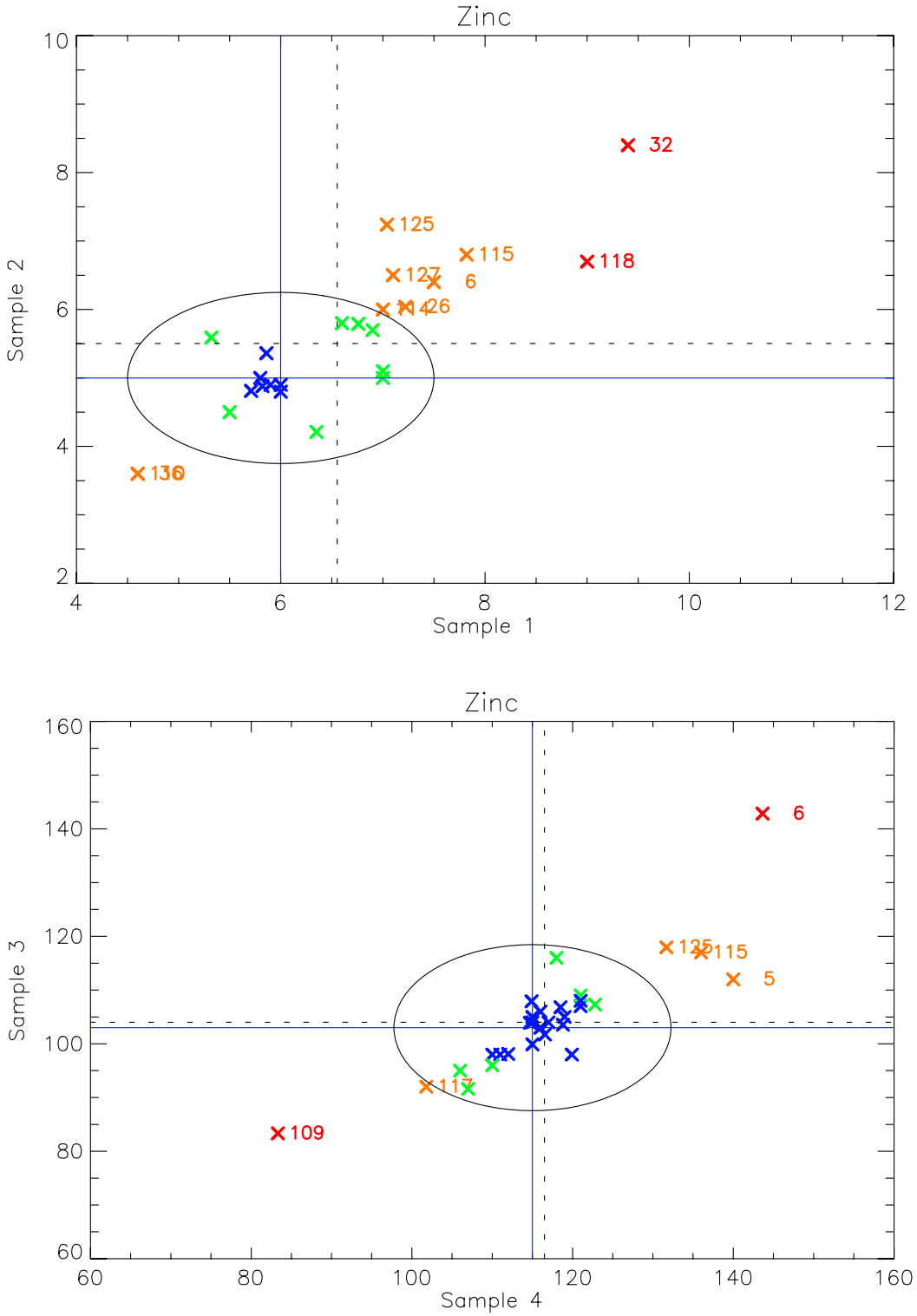


Figure A2.12: Youden plot of zinc, 2003.

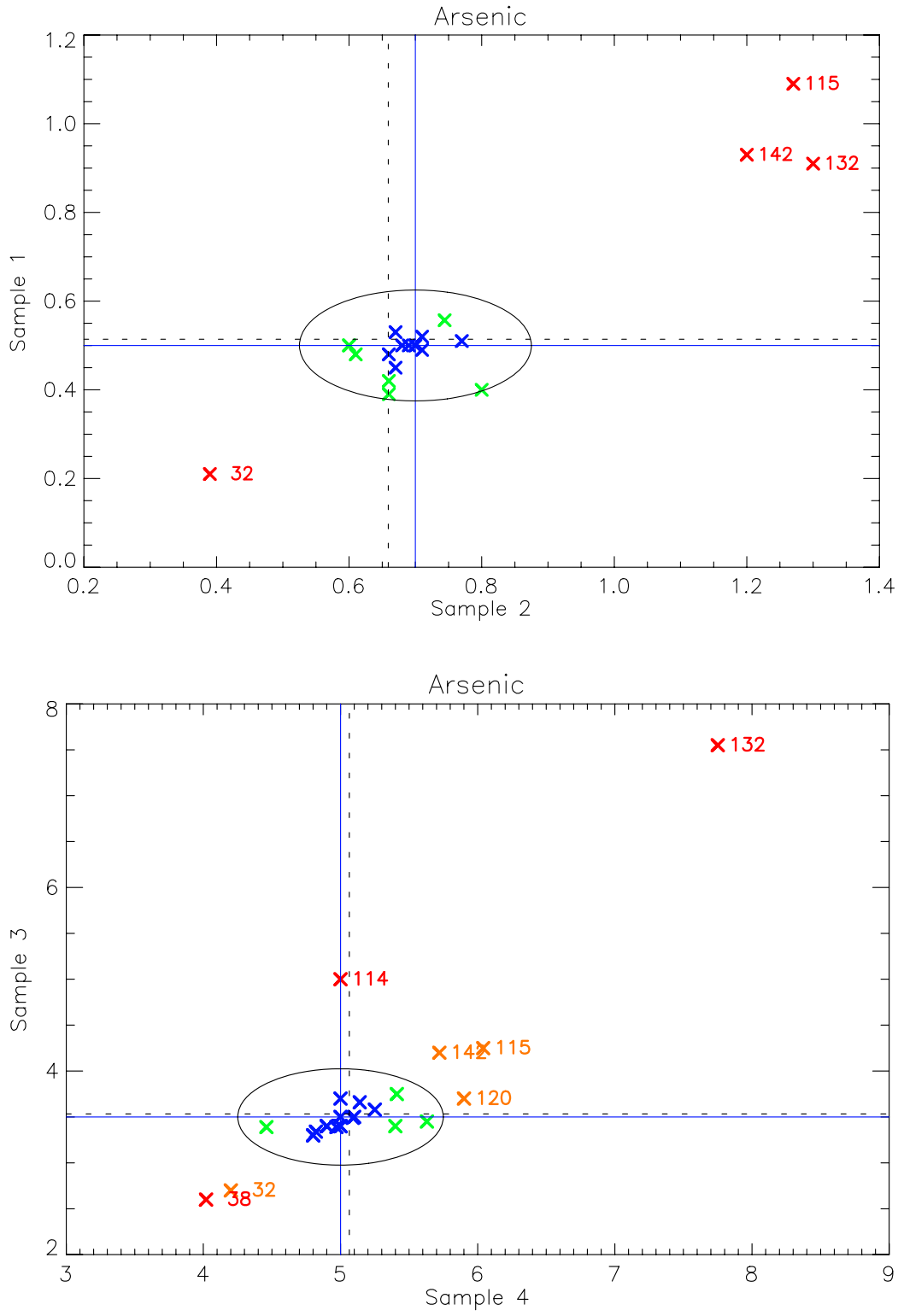


Figure A2.13: Youden plot of arsenic, 2003.

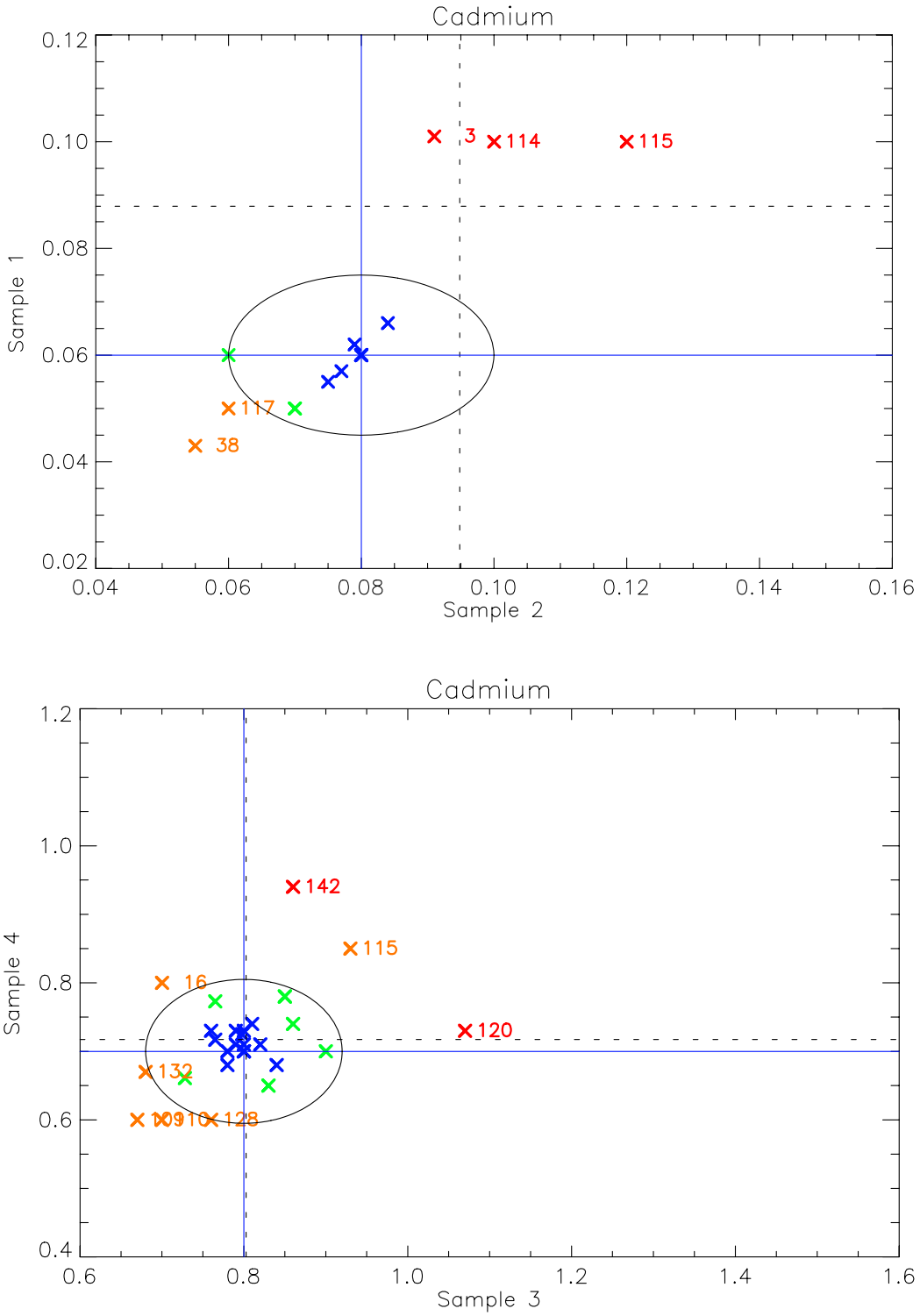


Figure A2.14: Youden plot of cadmium, 2003.

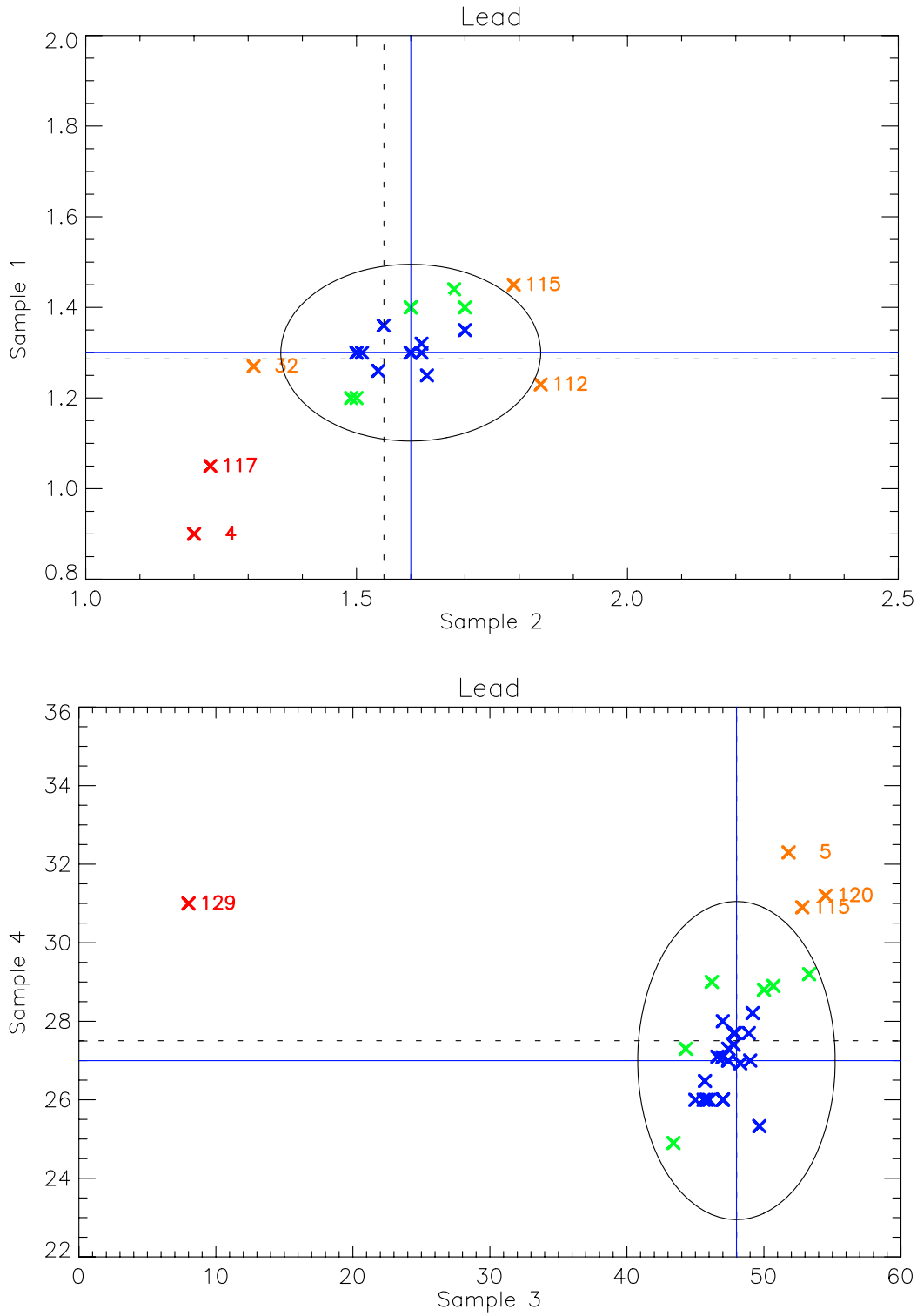


Figure A2.15: Youden plot of lead, 2003.

Appendix 3

Tables, 2004

Table A3.1a: Participating laboratories in the EMEP network, 2004. The numbers in front are used in tables.

No	Laboratory identification
1	Federal Environmental Agency, Austria
2	Flemish Environment Agency, Belgium
3	Czech Hydrometeorological Institute, Czech Republic
4	National Environmental Research Institute. Air Pollution Laboratory, Denmark
5	Finnish Meteorological Institute, Finland
6	Laboratories Wollf, France
7	IfE Leipzig GmbH, Umweltlabor, Germany
8	Umweltbundesamt, Germany
13	C.N.R. Istituto Inquinamento Atmosferico
14	RIVM Laboratory of Inorganic Analytical Chemistry, The Netherlands
15	The Norwegian Institute for Air Research, Norway
16	Inst. Of Meteorology and Water Management, Poland
23	AEA Technology, National Environmental Techn. Centre, United Kingdom
26	Ontario Ministry of Environment, Canada
31	Slovak Hydrometeorological Institute, Slovakia
32	Atmospheric Pollution Research Laboratory, Institute of Physics, Lithuania
36	Hydrometeorological Institute of Slovenia, Slovenia
38	Estonian Environmental Research Centre, Estonia

Table A3.1b: Participating laboratories outside the EMEP network, 2004. The number in front of the names is used in tables and figures.

No	Laboratory identification
108	Technishe Universität Dresden, Germany
112	Niedersächsische Forstliche Versuchsanstalt (NVF), Germany
114	C.N.R. Istituto Italiano di Idrobiologia, Italy
115	Bayerishe Landesanstalt f. Wald- und Forstwirtschaft, Germany
117	Sächsische Landesanstalt für Forsten, Germany
118	Forstliche Versuchs- und Forschungsanstalt Baden-Württemberg, Germany
120	Landwirtschaftliche Untersuchungs- und Forschungsanstalt (LUFA), Germany
121	Landesamt für Natur und Umwelt, Germany
125	Bayerisches Landesamt für Umweltschutz, Germany
127	Department of Chemistry, Jalan Sultan, Malaysia
129	Ecole Nationale d'Ingenieurs de Sfax, Tunisie
132	Comision Chilena De Energia Nuclear, Chile
141	Pollutants Chemical Analysis Centre, Marine Division, Japan
142	EPLD, Lagor, France
154	Laboratorio de Analise Instrumental, Portugal
159	CARSO, CEDEX, France

Table A3.2: Analytical results for Cr in synthetic precipitation samples, 2004.

Chromium
Sample no.: 1
Theoretical value: 0.800
Unit: µg/l

Run 1:
Number of laboratories: 30
Arithmetic mean value: 0.776
Median: 0.790
Standard deviation 0.185
Rel. st. deviation (%) 23.797

Run 2:
Number of laboratories: 29
Arithmetic mean value: 0.748
Median: 0.790
Standard deviation 0.110
Rel. st. deviation (%) 14.637

Results in decreasing order:

142	1.570 (*)	159	0.790	
117	1.060	5	0.773	
36	0.850	15	0.770	
8	0.813	121	0.770	
125	0.811	26	0.760	
112	0.810	32	0.700	
1	0.810	23	0.700	
7	0.803	114	0.700	
14	0.800	31	0.690	
16	0.800	2	0.664	
110	0.800	115	0.600	
4	0.800	118	0.600	
127	0.800	120	0.600	
6	0.800	154	0.540	
3	0.790	129	0.500	
		38	<1.000	

Chromium
Sample no.: 2
Theoretical value: 0.700
Unit: µg/l

Run 1:
Number of laboratories: 30
Arithmetic mean value: 1.057
Median: 0.681
Standard deviation 2.072
Rel. st. deviation (%) 196.032

Run 2:
Number of laboratories: 29
Arithmetic mean value: 0.679
Median: 0.680
Standard deviation 0.143
Rel. st. deviation (%) 21.085

Results in decreasing order:

129	12.000 (*)	15	0.680	
142	1.050	121	0.680	
14	1.000	159	0.670	
117	0.920	3	0.660	
31	0.870	36	0.650	
110	0.800	26	0.640	
112	0.730	23	0.600	
125	0.715	32	0.600	
8	0.704	2	0.546	
16	0.700	115	0.520	
127	0.700	118	0.500	
4	0.700	120	0.500	
7	0.697	114	0.500	
1	0.690	154	0.500	
5	0.682	6	0.500	
		38	<1.000	

Chromium
Sample no.: 3
Theoretical value: 8.000
Unit: µg/l

Run 1:
Number of laboratories: 33
Arithmetic mean value: 7.691
Median: 7.740
Standard deviation 0.898
Rel. st. deviation (%) 11.680

Run 2:
Number of laboratories: 32
Arithmetic mean value: 7.817
Median: 7.770
Standard deviation 0.536
Rel. st. deviation (%) 6.853

Results in decreasing order:

108	9.400	1	7.720	
129	8.920	132	7.700	
31	8.460	3	7.640	
36	8.420	15	7.600	
127	8.300	26	7.600	
6	8.100	23	7.600	
125	8.100	5	7.595	
142	8.090	118	7.500	
7	8.000	14	7.400	
16	8.000	114	7.400	
121	8.000	120	7.300	
2	7.965	38	7.300	
117	7.900	159	7.300	
110	7.900	115	7.070	
8	7.837	32	6.500	
4	7.800	154	3.640 (*)	
112	7.740			

Chromium
Sample no.: 4
Theoretical value: 5.000
Unit: µg/l

Run 1:
Number of laboratories: 32
Arithmetic mean value: 4.840
Median: 4.951
Standard deviation 0.651
Rel. st. deviation (%) 13.456

Run 2:
Number of laboratories: 30
Arithmetic mean value: 4.886
Median: 4.951
Standard deviation 0.353
Rel. st. deviation (%) 7.226

Results in decreasing order:

108	6.200 (*)	117	4.950	
31	5.870	6	4.900	
129	5.500	1	4.890	
127	5.300	5	4.850	
36	5.260	23	4.800	
121	5.100	15	4.800	
142	5.090	3	4.760	
125	5.040	120	4.600	
110	5.000	114	4.600	
7	5.000	118	4.600	
16	5.000	115	4.510	
14	5.000	132	4.500	
26	4.980	38	4.400	
112	4.970	159	4.300	
2	4.962	32	4.100	
8	4.952	154	2.080 (*)	

Table A3.3: Analytical results for Ni in synthetic precipitation samples, 2004.

Nickel
Sample no.: 1
Theoretical value: 0.600
Unit: µg/l

Run 1:
Number of laboratories: 23
Arithmetic mean value: 0.728
Median: 0.600
Standard deviation 0.528
Rel. st. deviation (%) 72.497

Run 2:
Number of laboratories: 22
Arithmetic mean value: 0.625
Median: 0.600
Standard deviation 0.188
Rel. st. deviation (%) 30.028

Results in decreasing order:

6	3.000 (*)	32	0.600
142	1.390	125	0.584
2	0.720	5	0.583
31	0.710	3	0.570
121	0.700	15	0.570
110	0.700	117	0.560
159	0.630	115	0.510
8	0.616	14	0.500
1	0.610	23	0.500
36	0.600	4	0.500
16	0.600	118	0.400
26	0.600		
112	<0.490	114	<1.000
120	<1.000	127	<2.000
129	<88.000	38	<1.000
154	<0.300		

Nickel
Sample no.: 2
Theoretical value: 0.700
Unit: µg/l

Run 1:
Number of laboratories: 23
Arithmetic mean value: 0.705
Median: 0.700
Standard deviation 0.116
Rel. st. deviation (%) 16.427

Run 2:
Number of laboratories: 22
Arithmetic mean value: 0.692
Median: 0.700
Standard deviation 0.099
Rel. st. deviation (%) 14.267

Results in decreasing order:

142	1.000 (*)	2	0.699
31	0.930	125	0.685
121	0.820	15	0.680
110	0.800	8	0.679
4	0.800	26	0.670
3	0.750	117	0.640
159	0.750	115	0.610
5	0.712	23	0.600
1	0.700	14	0.600
36	0.700	112	0.500
16	0.700	118	0.500
32	0.700		
38	<1.000	114	<1.000
120	<1.000	127	<2.000
129	<88.000	6	<0.500
154	<0.300		

Nickel
Sample no.: 3
Theoretical value: 8.000
Unit: µg/l

Run 1:
Number of laboratories: 32
Arithmetic mean value: 7.793
Median: 7.850
Standard deviation 0.539
Rel. st. deviation (%) 6.916

Run 2:
Number of laboratories: 31
Arithmetic mean value: 7.828
Median: 7.900
Standard deviation 0.509
Rel. st. deviation (%) 6.502

Results in decreasing order:

2	8.716	16	7.800
127	8.700	23	7.800
108	8.700	8	7.702
159	8.500	3	7.700
4	8.400	14	7.600
36	8.270	7	7.510
117	8.230	15	7.500
1	8.130	118	7.500
121	8.100	38	7.400
142	8.050	112	7.330
110	8.000	32	7.300
120	8.000	115	7.240
26	7.980	6	7.200
125	7.930	154	6.800
5	7.911	31	6.780
114	7.900	132	6.700 (*)
		129	<88.000

Nickel
Sample no.: 4
Theoretical value: 9.000
Unit: µg/l

Run 1:
Number of laboratories: 32
Arithmetic mean value: 8.883
Median: 8.810
Standard deviation 0.746
Rel. st. deviation (%) 8.399

Run 2:
Number of laboratories: 29
Arithmetic mean value: 8.857
Median: 8.800
Standard deviation 0.515
Rel. st. deviation (%) 5.813

Results in decreasing order:

127	10.400 (*)	16	8.800
117	10.400 (*)	23	8.800
2	10.080	114	8.800
4	9.900	3	8.600
159	9.700	15	8.600
142	9.530	108	8.600
121	9.400	7	8.550
36	9.260	31	8.510
1	9.210	118	8.500
120	9.000	132	8.400
14	9.000	112	8.350
110	9.000	115	8.340
26	8.950	38	8.300
8	8.893	32	8.300
5	8.857	6	7.800
125	8.820	154	6.600 (*)
		129	<88.000

Table A3.4: Analytical results for Cu in synthetic precipitation samples, 2004.

Copper
Sample no.: 1
Theoretical value: 1.000
Unit: µg/l

Run 1:
Number of laboratories: 30
Arithmetic mean value: 1.167
Median: 1.000
Standard deviation 0.647
Rel. st. deviation (%) 55.425

Run 2:
Number of laboratories: 29
Arithmetic mean value: 1.062
Median: 1.000
Standard deviation 0.306
Rel. st. deviation (%) 28.776

Results in decreasing order:

6	4.200 (*)	16	1.000
120	2.000	26	1.000
154	1.910	3	1.000
13	1.437	14	1.000
23	1.200	117	0.990
38	1.200	7	0.985
31	1.190	132	0.960
1	1.110	121	0.930
125	1.080	142	0.930
2	1.057	159	0.910
36	1.050	32	0.900
8	1.028	110	0.900
5	1.014	115	0.880
112	1.010	15	0.840
127	1.000	118	0.300
114	<2.200	129	<10.000

Copper
Sample no.: 2
Theoretical value: 1.400
Unit: µg/l

Run 1:
Number of laboratories: 30
Arithmetic mean value: 1.422
Median: 1.365
Standard deviation 0.346
Rel. st. deviation (%) 24.346

Run 2:
Number of laboratories: 27
Arithmetic mean value: 1.375
Median: 1.360
Standard deviation 0.176
Rel. st. deviation (%) 12.824

Results in decreasing order:

154	2.640 (*)	142	1.360
120	2.200 (*)	8	1.358
13	1.767	7	1.350
38	1.700	3	1.350
14	1.700	121	1.300
125	1.510	6	1.300
1	1.480	132	1.300
2	1.473	112	1.300
117	1.460	159	1.300
5	1.444	15	1.280
36	1.410	115	1.250
16	1.400	32	1.200
23	1.400	110	1.000
127	1.400	31	0.970
26	1.370	118	0.700 (*)
114	<2.200	129	<10.000

Copper
Sample no.: 3
Theoretical value: 7.000
Unit: µg/l

Run 1:
Number of laboratories: 33
Arithmetic mean value: 6.814
Median: 6.900
Standard deviation 0.468
Rel. st. deviation (%) 6.866

Run 2:
Number of laboratories: 32
Arithmetic mean value: 6.780
Median: 6.852
Standard deviation 0.432
Rel. st. deviation (%) 6.372

Results in decreasing order:

6	7.900 (*)	8	6.803
13	7.543	3	6.800
36	7.360	114	6.700
129	7.340	142	6.680
38	7.300	154	6.620
1	7.220	117	6.600
120	7.200	110	6.500
159	7.200	115	6.460
16	7.100	132	6.400
108	7.100	31	6.370
26	7.040	15	6.300
5	7.016	127	6.200
7	7.000	121	6.200
14	7.000	32	6.100
2	6.974	112	6.060
125	6.960	118	5.900
23	6.900		

Copper
Sample no.: 4
Theoretical value: 8.500
Unit: µg/l

Run 1:
Number of laboratories: 33
Arithmetic mean value: 8.168
Median: 8.200
Standard deviation 0.726
Rel. st. deviation (%) 8.888

Run 2:
Number of laboratories: 31
Arithmetic mean value: 8.190
Median: 8.200
Standard deviation 0.568
Rel. st. deviation (%) 6.934

Results in decreasing order:

108	9.700 (*)	7	8.190
13	9.530	117	8.050
31	9.010	115	8.000
1	9.000	129	8.000
38	9.000	114	8.000
159	8.900	3	7.900
36	8.890	127	7.800
5	8.547	110	7.800
8	8.500	15	7.600
125	8.460	132	7.600
2	8.426	121	7.500
23	8.400	32	7.500
14	8.300	112	7.460
16	8.300	118	7.300
26	8.270	120	7.200
142	8.250	154	5.970 (*)
6	8.200		

Table A3.5: Analytical results for Zn in synthetic precipitation samples, 2004.

Zinc
Sample no.: 1
Theoretical value: 7.000
Unit: µg/l

Run 1:

Number of laboratories:	30
Arithmetic mean value:	8.274
Median:	6.785
Standard deviation	5.589
Rel. st. deviation (%)	67.556

Run 2:

Number of laboratories:	29
Arithmetic mean value:	7.311
Median:	6.770
Standard deviation	1.883
Rel. st. deviation (%)	25.751

Results in decreasing order:

6	36.200 (*)	125	6.770
2	13.150	3	6.700
38	12.000	115	6.700
117	10.740	16	6.700
159	9.300	121	6.700
23	8.600	15	6.600
142	8.500	108	6.500
26	7.740	13	6.344
1	7.220	118	6.200
8	7.166	132	6.200
114	7.100	112	5.620
7	7.050	110	5.600
14	7.000	120	5.500
5	6.914	32	5.400
127	6.800	36	5.200
		129	<3.000
		154	<8.000

Zinc
Sample no.: 2
Theoretical value: 6.000
Unit: µg/l

Run 1:

Number of laboratories:	29
Arithmetic mean value:	6.163
Median:	5.930
Standard deviation	1.423
Rel. st. deviation (%)	23.095

Run 2:

Number of laboratories:	27
Arithmetic mean value:	5.875
Median:	5.900
Standard deviation	0.966
Rel. st. deviation (%)	16.443

Results in decreasing order:

2	10.100 (*)	16	5.900
38	10.000 (*)	115	5.700
159	8.100	121	5.700
117	7.800	15	5.600
142	7.600	13	5.549
23	7.000	3	5.500
1	6.630	127	5.500
5	6.275	118	5.400
8	6.196	132	5.300
26	6.050	120	5.300
14	6.000	32	4.800
108	6.000	112	4.650
114	6.000	110	4.300
7	5.950	36	3.900
125	5.930	129	<6.000
		154	<8.000

Zinc
Sample no.: 3
Theoretical value: 100.000
Unit: µg/l

Run 1:

Number of laboratories:	32
Arithmetic mean value:	97.898
Median:	98.000
Standard deviation	7.308
Rel. st. deviation (%)	7.465

Run 2:

Number of laboratories:	30
Arithmetic mean value:	98.117
Median:	98.000
Standard deviation	5.508
Rel. st. deviation (%)	5.614

Results in decreasing order:

159	114.000 (*)	14	98.000
110	110.000	16	98.000
2	108.400	114	98.000
129	107.600	127	97.000
38	107.000	112	96.700
6	103.000	108	96.400
26	102.200	115	94.300
3	101.600	118	94.000
1	100.000	132	93.200
23	100.000	120	93.000
117	99.940	125	92.500
5	99.470	121	91.000
8	98.723	13	90.290
142	98.700	154	89.500
7	98.500	36	88.500
15	98.000	32	75.200 (*)

Zinc
Sample no.: 4
Theoretical value: 110.000
Unit: µg/l

Run 1:

Number of laboratories:	32
Arithmetic mean value:	107.815
Median:	108.065
Standard deviation	8.400
Rel. st. deviation (%)	7.791

Run 2:

Number of laboratories:	30
Arithmetic mean value:	107.957
Median:	108.065
Standard deviation	6.618
Rel. st. deviation (%)	6.130

Results in decreasing order:

159	127.000 (*)	5	108.030
110	120.000	7	108.000
38	119.000	15	108.000
2	118.800	114	108.000
129	116.000	16	108.000
6	113.000	14	107.000
26	112.800	115	105.400
108	112.400	118	103.700
3	112.200	120	103.000
142	110.700	125	101.000
1	110.300	13	100.040
23	110.000	121	100.000
8	109.896	36	96.800
117	109.830	132	95.500
127	109.500	154	93.700
112	108.100	32	84.400 (*)

Table A3.6: Analytical results for As in synthetic precipitation samples, 2004.

Arsenic
Sample no.: 1
Theoretical value: 0.600
Unit: µg/l

Run 1:
Number of laboratories: 22
Arithmetic mean value: 0.589
Median: 0.597
Standard deviation 0.150
Rel. st. deviation (%) 25.449

Run 2:
Number of laboratories: 20
Arithmetic mean value: 0.584
Median: 0.597
Standard deviation 0.104
Rel. st. deviation (%) 17.879

Results in decreasing order:

6	1.000 (*)	5	0.595	
118	0.800	26	0.590	
4	0.800	1	0.570	
23	0.650	2	0.567	
159	0.650	32	0.510	
3	0.640	110	0.500	
14	0.620	121	0.500	
15	0.610	115	0.450	
8	0.607	31	0.420	
125	0.602	127	0.400	
36	0.600	142	0.280	(*)
38	<0.100	114	<3.300	
120	<0.500	154	<1.000	

Arsenic
Sample no.: 2
Theoretical value: 0.700
Unit: µg/l

Run 1:
Number of laboratories: 24
Arithmetic mean value: 0.807
Median: 0.695
Standard deviation 0.547
Rel. st. deviation (%) 67.853

Run 2:
Number of laboratories: 23
Arithmetic mean value: 0.698
Median: 0.690
Standard deviation 0.136
Rel. st. deviation (%) 19.501

Results in decreasing order:

114	3.300 (*)	15	0.690
154	1.200	26	0.690
6	0.900	142	0.680
159	0.770	31	0.660
2	0.735	121	0.650
125	0.732	23	0.640
14	0.720	32	0.620
5	0.712	127	0.600
3	0.710	118	0.600
1	0.710	110	0.600
8	0.706	115	0.540
36	0.700	4	0.500
38	< 0.100	120	<0.500

Arsenic
Sample no.: 3
Theoretical value: 4.000
Unit: µg/l

Run 1:
Number of laboratories: 28
Arithmetic mean value: 4.126
Median: 3.950
Standard deviation 0.822
Rel. st. deviation (%) 19.921

Run 2:
Number of laboratories: 25
Arithmetic mean value: 3.905
Median: 3.900
Standard deviation 0.533
Rel. st. deviation (%) 13.647

Results in decreasing order:

132	6.100 (*)	15	3.900	
154	6.000 (*)	118	3.900	
6	5.800 (*)	26	3.880	
4	5.400	7	3.750	
159	4.900	2	3.718	
114	4.800	23	3.700	
3	4.140	121	3.700	
14	4.100	142	3.620	
8	4.091	32	3.550	
36	4.090	115	3.420	
1	4.040	127	3.400	
125	4.040	31	3.390	
5	4.008	120	3.100	
110	4.000	38	3.000	

Arsenic
Sample no.: 4
Theoretical value: 5.500
Unit: µg/l

Run 1:
Number of laboratories: 28
Arithmetic mean value: 5.365
Median: 5.420
Standard deviation 0.900
Rel. st. deviation (%) 16.776

Run 2:
Number of laboratories: 26
Arithmetic mean value: 5.186
Median: 5.410
Standard deviation 0.626
Rel. st. deviation (%) 12.081

Results in decreasing order:

6	8.100 (*)	1	5.420
154	7.300 (*)	118	5.400
159	6.300	7	5.330
8	5.727	15	5.300
3	5.720	23	5.300
142	5.630	2	5.104
36	5.630	31	4.970
132	5.600	32	4.870
5	5.552	115	4.830
125	5.530	127	4.800
110	5.500	114	4.500
121	5.500	38	3.900
14	5.490	4	3.800
26	5.420	120	3.700

Table A3.7: Analytical results for Cd in synthetic precipitation samples, 2004.

Cadmium
Sample no.: 1
Theoretical value: 0.070
Unit: µg/l

Run 1:

Number of laboratories:	24
Arithmetic mean value:	0.111
Median:	0.072
Standard deviation	0.152
Rel. st. deviation (%)	137.412

Run 2:

Number of laboratories:	23
Arithmetic mean value:	0.081
Median:	0.070
Standard deviation	0.042
Rel. st. deviation (%)	52.226

Results in decreasing order:

4	0.800 (*)	7	0.070
142	0.220	159	0.070
114	0.200	125	0.068
6	0.100	2	0.067
118	0.080	121	0.065
36	0.080	26	0.061
117	0.080	23	0.060
5	0.076	31	0.060
1	0.074	14	0.058
15	0.073	115	0.055
3	0.073	32	0.050
8	0.073	13	0.050
38	<0.100	110	<0.200
112	<0.330	120	<0.100
127	<0.200	129	<4.000
154	<0.050		

Cadmium
Sample no.: 2
Theoretical value: 0.090
Unit: µg/l

Run 1:

Number of laboratories:	27
Arithmetic mean value:	0.142
Median:	0.090
Standard deviation	0.193
Rel. st. deviation (%)	136.006

Run 2:

Number of laboratories:	25
Arithmetic mean value:	0.089
Median:	0.090
Standard deviation	0.019
Rel. st. deviation (%)	20.904

Results in decreasing order:

6	0.900 (*)	7	0.090
4	0.700 (*)	159	0.090
142	0.160	8	0.088
117	0.110	1	0.086
120	0.100	14	0.083
114	0.100	121	0.080
15	0.100	31	0.080
3	0.092	115	0.077
5	0.092	16	0.070
125	0.091	23	0.070
2	0.091	154	0.070
36	0.090	32	0.070
26	0.090	13	0.064
118	<0.090	38	<0.100
110	<0.200	112	<0.330
127	<0.200	129	<4.000

Cadmium
Sample no.: 3
Theoretical value: 0.800
Unit: µg/l

Run 1:

Number of laboratories:	34
Arithmetic mean value:	1.030
Median:	0.791
Standard deviation	1.246
Rel. st. deviation (%)	120.963

Run 2:

Number of laboratories:	33
Arithmetic mean value:	0.825
Median:	0.790
Standard deviation	0.356
Rel. st. deviation (%)	43.151

Results in decreasing order:

4	7.800 (*)	26	0.790
132	2.600	121	0.790
6	1.100	5	0.787
129	1.050	8	0.784
142	0.960	15	0.780
159	0.920	14	0.773
36	0.830	3	0.765
108	0.820	115	0.745
117	0.810	23	0.740
118	0.810	1	0.740
2	0.810	38	0.700
31	0.800	112	0.690
7	0.800	13	0.680
110	0.800	32	0.660
114	0.800	154	0.620
127	0.800	120	0.600
125	0.792	16	0.090

Cadmium
Sample no.: 4
Theoretical value: 0.600
Unit: µg/l

Run 1:

Number of laboratories:	33
Arithmetic mean value:	0.840
Median:	0.600
Standard deviation	0.943
Rel. st. deviation (%)	112.265

Run 2:

Number of laboratories:	31
Arithmetic mean value:	0.614
Median:	0.599
Standard deviation	0.122
Rel. st. deviation (%)	19.929

Results in decreasing order:

4	5.300 (*)	8	0.599
132	3.400 (*)	14	0.597
142	1.080	5	0.593
16	0.800	121	0.590
6	0.800	125	0.589
108	0.800	26	0.580
31	0.710	3	0.579
159	0.650	115	0.551
36	0.630	1	0.550
15	0.610	38	0.540
117	0.610	112	0.540
2	0.606	23	0.530
114	0.600	13	0.507
118	0.600	32	0.500
127	0.600	154	0.490
7	0.600	120	0.400
110	0.600	129	<4.000

Table A3.8: Analytical results for Pb in synthetic precipitation samples, 2004.

Lead
Sample no.: 1
Theoretical value: 1.400
Unit: µg/l

Run 1:
Number of laboratories: 30
Arithmetic mean value: 1.448
Median: 1.405
Standard deviation 0.385
Rel. st. deviation (%) 26.599

Run 2:
Number of laboratories: 28
Arithmetic mean value: 1.440
Median: 1.405
Standard deviation 0.300
Rel. st. deviation (%) 20.839

Results in decreasing order:

142	2.520 (*)	110	1.400	
114	2.200	121	1.400	
154	2.000	23	1.400	
127	1.900	32	1.400	
26	1.800	159	1.400	
3	1.530	125	1.380	
36	1.530	117	1.370	
112	1.510	15	1.360	
14	1.500	5	1.351	
6	1.500	31	1.300	
1	1.490	13	1.234	
8	1.462	38	1.100	
2	1.457	118	0.800	
115	1.430	4	0.700	
7	1.410	16	0.600	(*)
		120	<1.000	
		129	<41.000	

Lead
Sample no.: 2
Theoretical value: 1.700
Unit: µg/l

Run 1:
Number of laboratories: 31
Arithmetic mean value: 4.400
Median: 1.708
Standard deviation 15.147
Rel. st. deviation (%) 344.267

Run 2:
Number of laboratories: 30
Arithmetic mean value: 1.680
Median: 1.704
Standard deviation 0.294
Rel. st. deviation (%) 17.507

Results in decreasing order:

129	86.000 (*)	23	1.700	
127	2.400	121	1.700	
154	2.300	110	1.700	
6	1.900	14	1.700	
7	1.860	2	1.695	
112	1.830	15	1.690	
1	1.800	26	1.680	
32	1.800	117	1.620	
159	1.800	13	1.582	
8	1.779	31	1.510	
142	1.770	16	1.400	
36	1.770	38	1.300	
3	1.760	118	1.200	
115	1.730	4	1.000	
125	1.710	120	1.000	
5	1.708	114	<2.100	

Lead
Sample no.: 3
Theoretical value: 45.000
Unit: µg/l

Run 1:
Number of laboratories: 34
Arithmetic mean value: 43.063
Median: 44.330
Standard deviation 11.671
Rel. st. deviation (%) 27.101

Run 2:
Number of laboratories: 31
Arithmetic mean value: 44.840
Median: 44.460
Standard deviation 4.264
Rel. st. deviation (%) 9.509

Results in decreasing order:

129	68.200 (*)	125	44.200	
127	54.900	23	44.000	
132	53.700	5	43.610	
120	51.000	1	43.430	
6	49.800	15	42.700	
121	49.000	118	42.700	
159	49.000	32	42.500	
31	46.980	108	42.400	
36	46.800	14	42.400	
4	46.700	114	42.000	
3	46.400	13	41.940	
2	46.150	154	41.900	
115	45.300	117	41.620	
7	45.000	142	35.650	
112	44.500	38	34.800	
8	44.487	110	4.220	(*)
26	44.460	16	1.700	(*)

Lead
Sample no.: 4
Theoretical value: 25.000
Unit: µg/l

Run 1:
Number of laboratories: 34
Arithmetic mean value: 26.108
Median: 25.000
Standard deviation 4.127
Rel. st. deviation (%) 15.809

Run 2:
Number of laboratories: 31
Arithmetic mean value: 25.035
Median: 24.800
Standard deviation 2.173
Rel. st. deviation (%) 8.681

Results in decreasing order:

16	40.000 (*)	23	25.000	
127	37.200 (*)	3	24.800	
132	34.400 (*)	112	24.800	
129	31.000	32	24.500	
120	30.000	14	24.500	
6	28.400	13	24.430	
31	27.080	125	24.400	
2	26.410	1	24.030	
118	26.400	117	23.980	
36	26.200	15	23.900	
159	26.000	5	23.850	
4	25.700	110	23.700	
8	25.592	154	23.500	
26	25.350	114	23.000	
115	25.100	108	22.800	
121	25.000	142	22.250	
7	25.000	38	19.400	

Table A3.9: Analytical techniques used at the participating laboratories for the different elements, 2004.

Lab. no.	Elements	Technique
1	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
2	Cr, Ni, Cu, As, Cd, Pb	GF-AAS
	Zn	F-AAS
3	Ni, Cd, Cu, Pb,	GF-AAS
	Cr, As	ICP-MS
	Zn	F-AAS
4	Cr, Ni, Cu, Zn, As, Cd, Pb	GF-AAS
5	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
6	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
7	Cr, Ni, Cu, Zn, As, Cd, Pb	GF-AAS and ICP-OES
8	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
13	Cu, Zn, , Cd, Pb	Anodic Stripping Voltammetry
14	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
15	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
16	Cr, Ni, Cu, Cd, Pb	GF-AAS
	Zn	F-AAS
23	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
26	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
31	Cr, Ni, Cu, Cd, Pb	GF-AAS
	As	HG-GF-AAS
	Zn	F-AAS
32	Cr, Ni, Cu, Zn, As, Cd, Pb	GF-AAS
36	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
38	Cr, Ni, Cu, Cd, Pb	GF-AAS
	Zn	F-AAS
108	Cr, Ni, Cu, Zn, Cd, Pb	ICP-OES
112	Cr, Ni, Cu, Zn, As, Cd, Pb	USN-ICP-MS
114	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-OES
115	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
117	Cr, Ni, Cu , Zn	USN-ICP-OES
	As, Cd, Pb	GF-AAS
118	Cu, Cd, Pb	GF-AAS
	As ,Zn Cr, Ni	ICP-OES
120	Cr, Ni, Cu, Zn, As, Cd, Pb	GF-AAS
121	Cr, Ni, Cu, Cd, Pb	GF-AAS
	Zn	Voltametry
	As	HG-AAS
125	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
127	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
129	Cr, Ni, Cu, Zn, Cd, Pb	F-AAS (Polarized Zeeman)
132	Cr, Ni, Cu, Zn , Cd	USN-ICP-OES
	Pb	GF-AAS
	As	HG-AAS
141	Cr, Ni, Cu, As, Cd, Pb	ICP-MS
142	Zn	ICP-OES
154	Cr, Ni, Cu, Cd, Pb	GF-AAS
	Zn	F-AAS
	As	HG-AAS
159	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS

Appendix 4

Figures, 2004

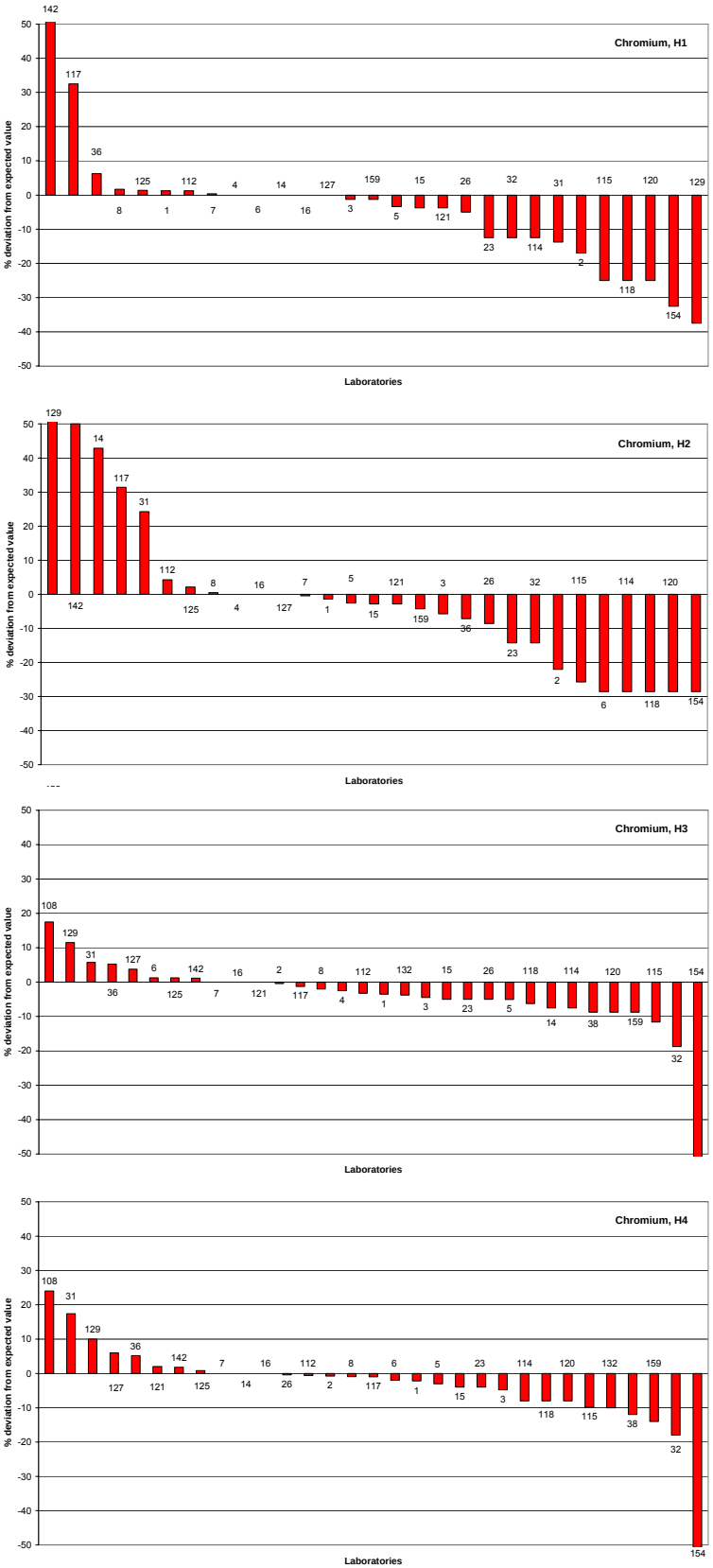


Figure A4.1: Results from determination of Cr, 2004.

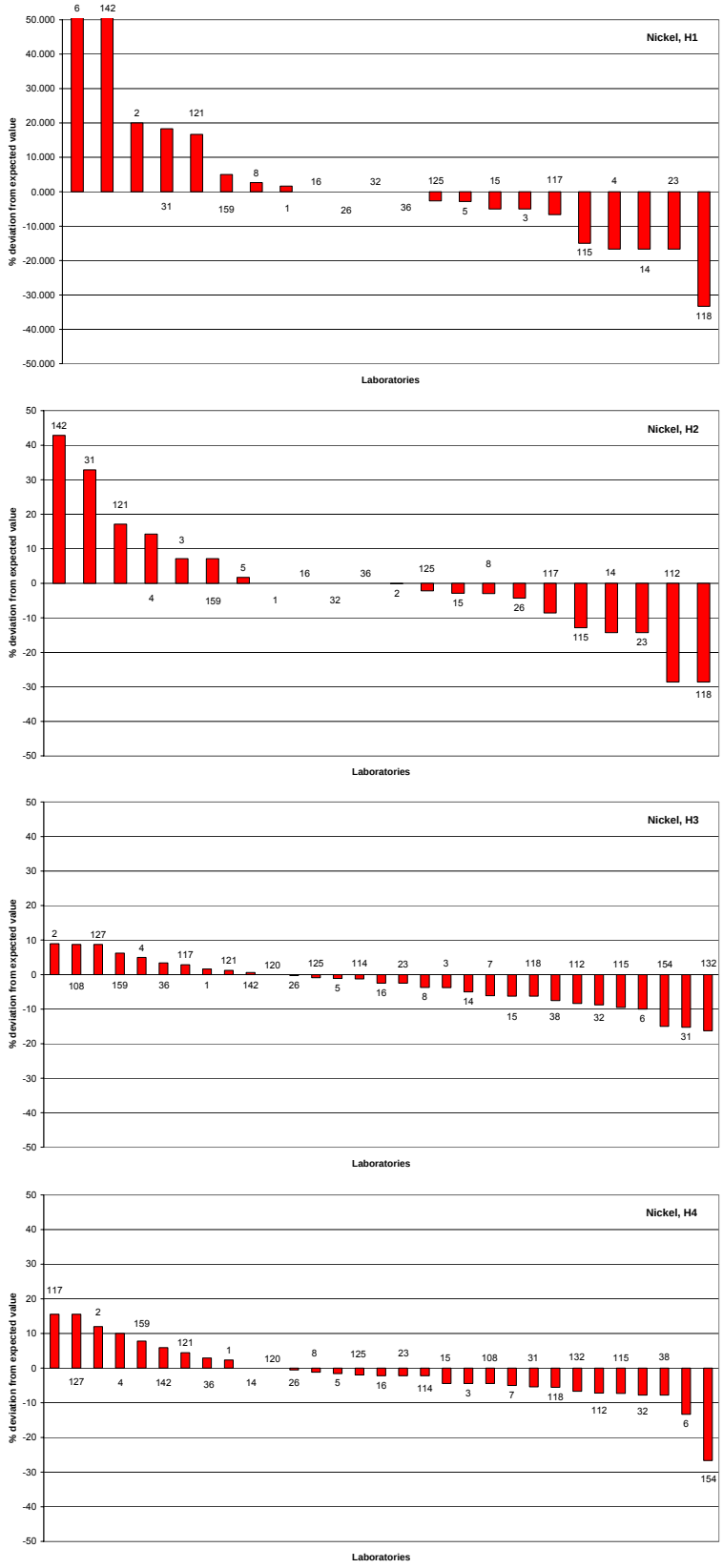


Figure A4.2: Results from determination of Ni, 2004.

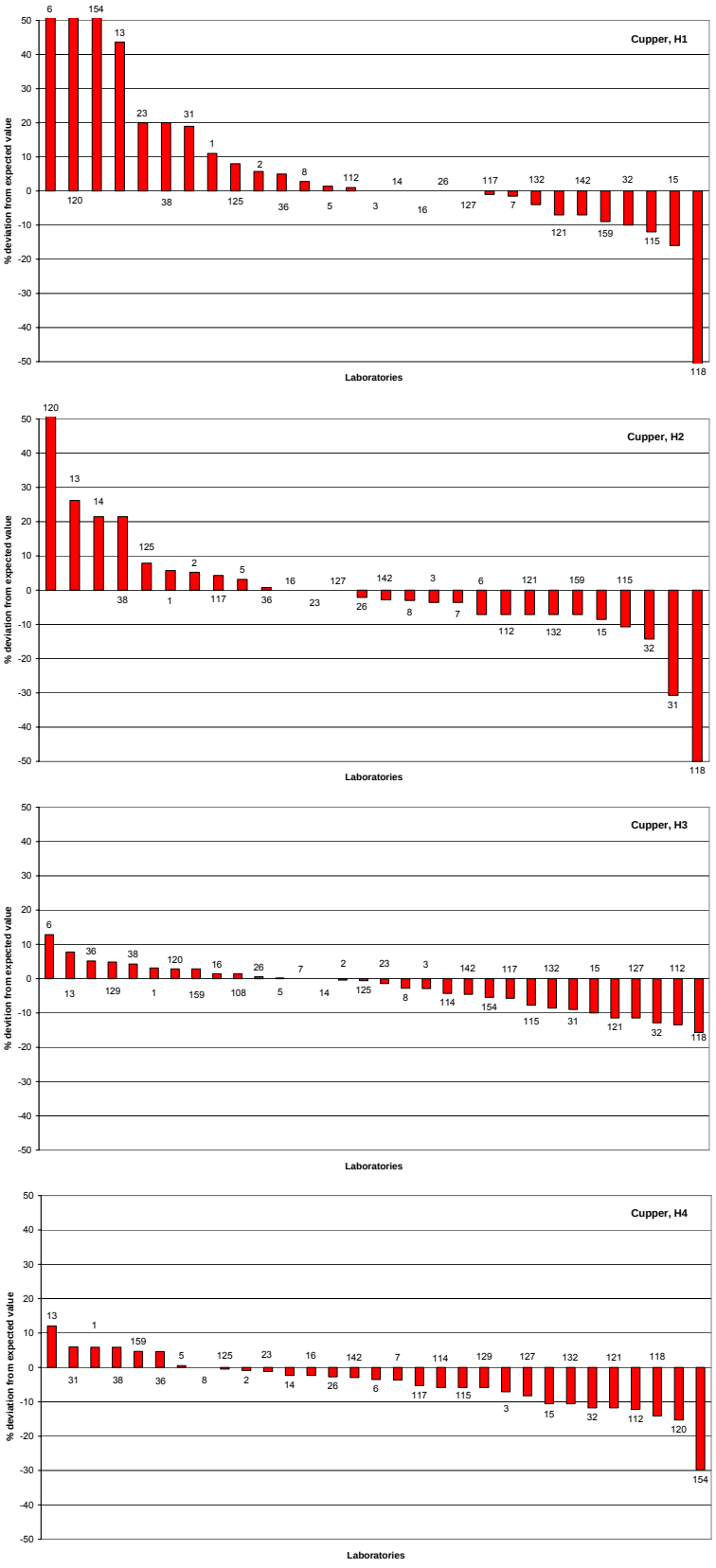


Figure A4.3: Results from determination of Cu, 2004.

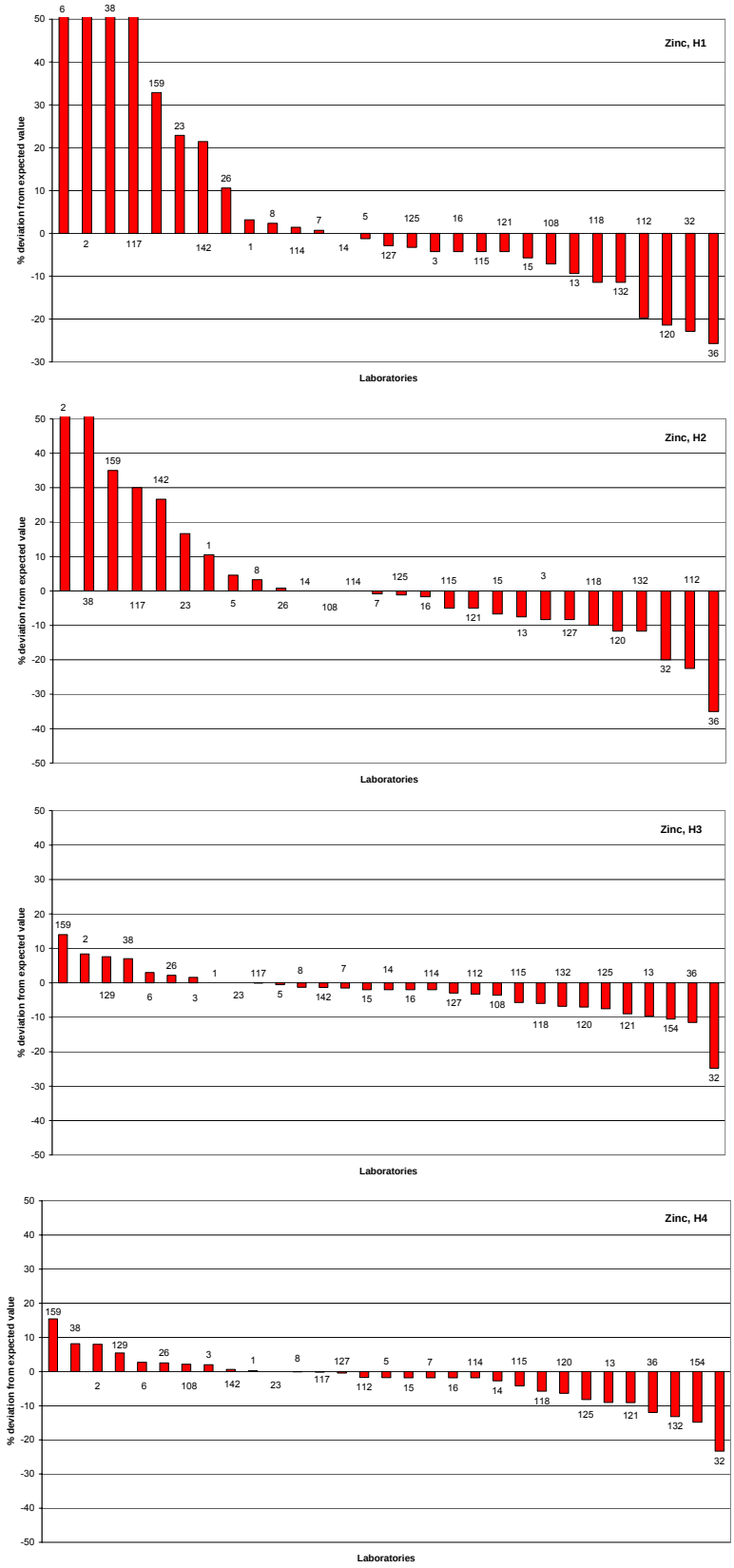


Figure A4.4: Results from determination of Zn, 2004.

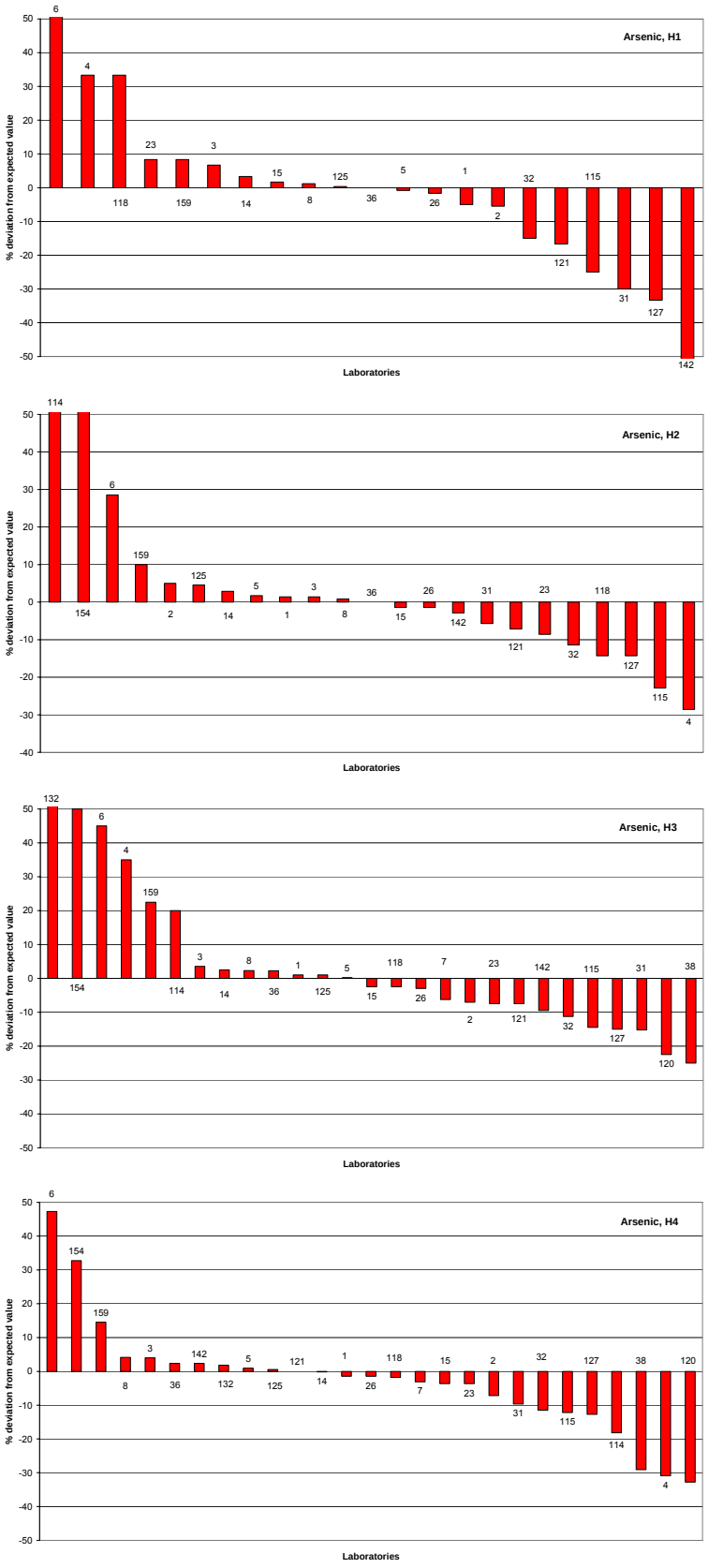


Figure A4.5: Results from determination of As, 2004.

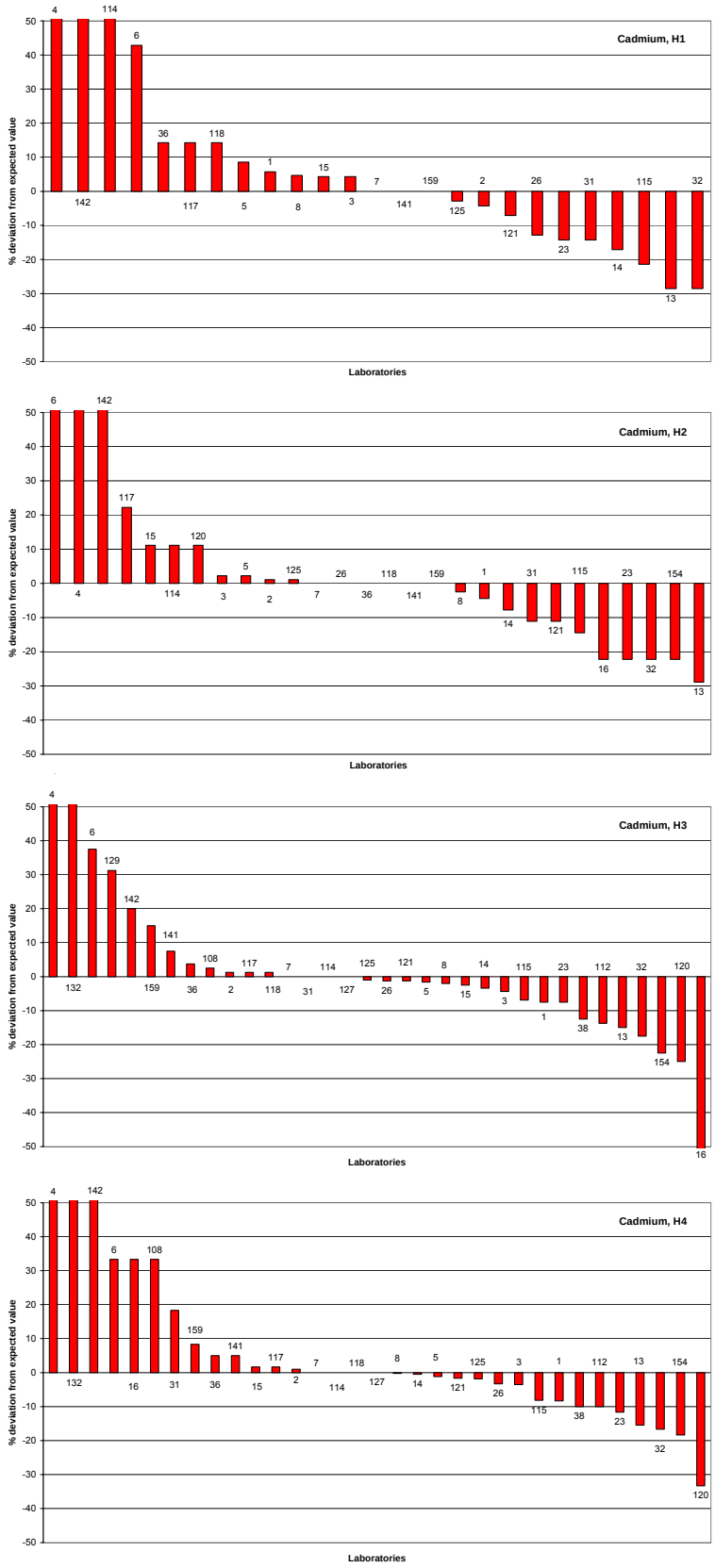


Figure A4.6: Results from determination of Cd, 2004.

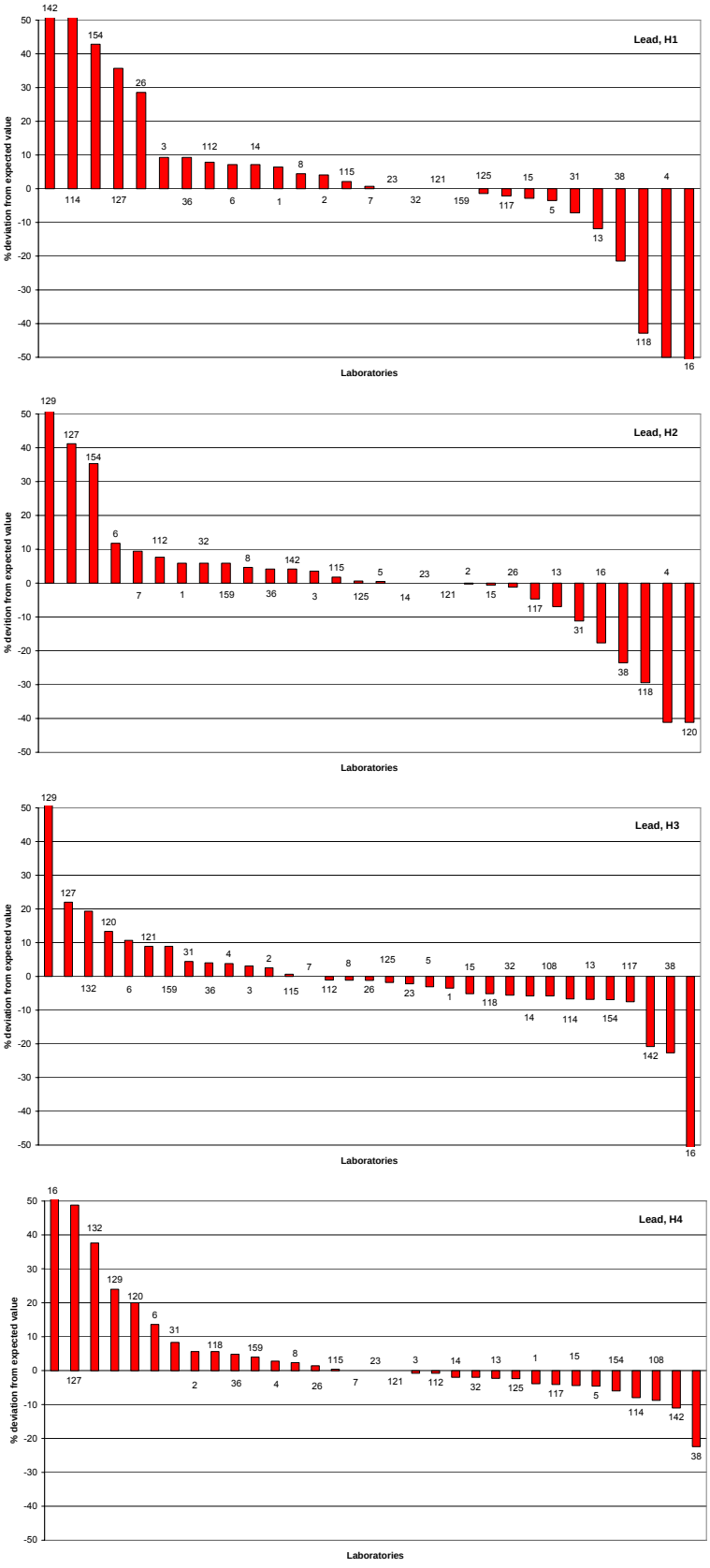


Figure A4.7: Results from determination of Pb, 2004.

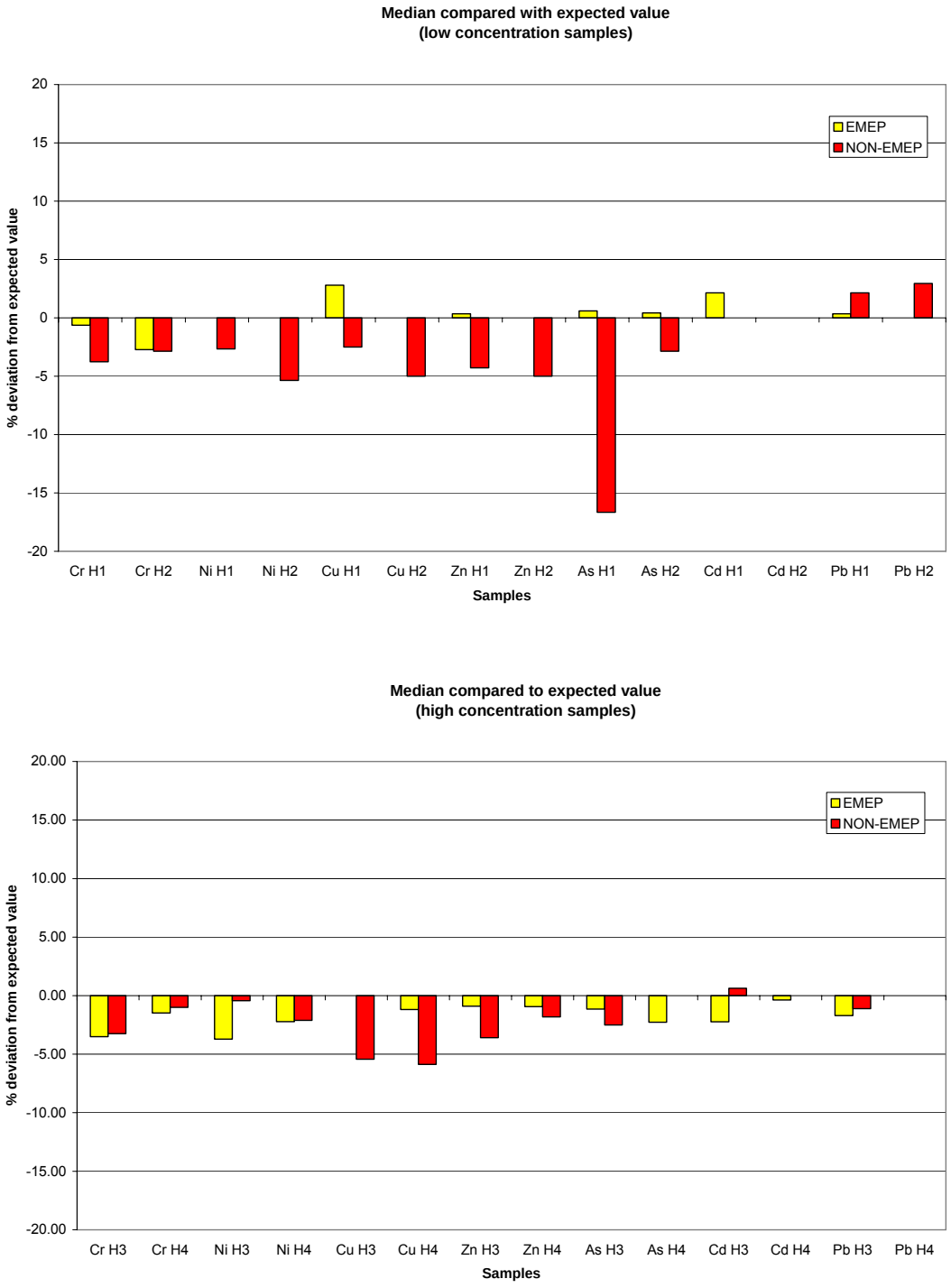


Figure A4.8: The median compared to theoretical value for low and high concentration samples in 2004, respectively.

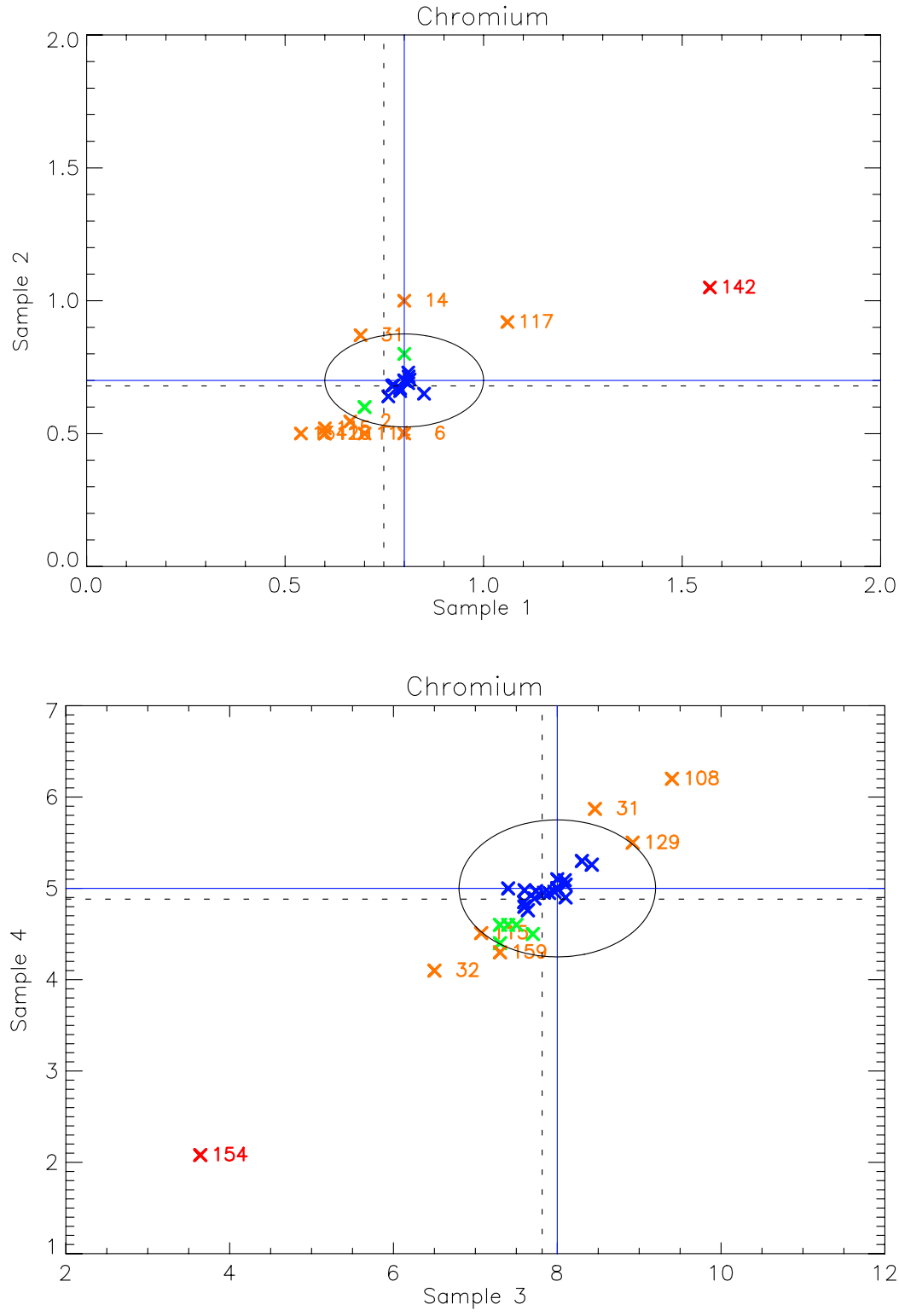


Figure A4.9: Youden plot of chromium, 2004.

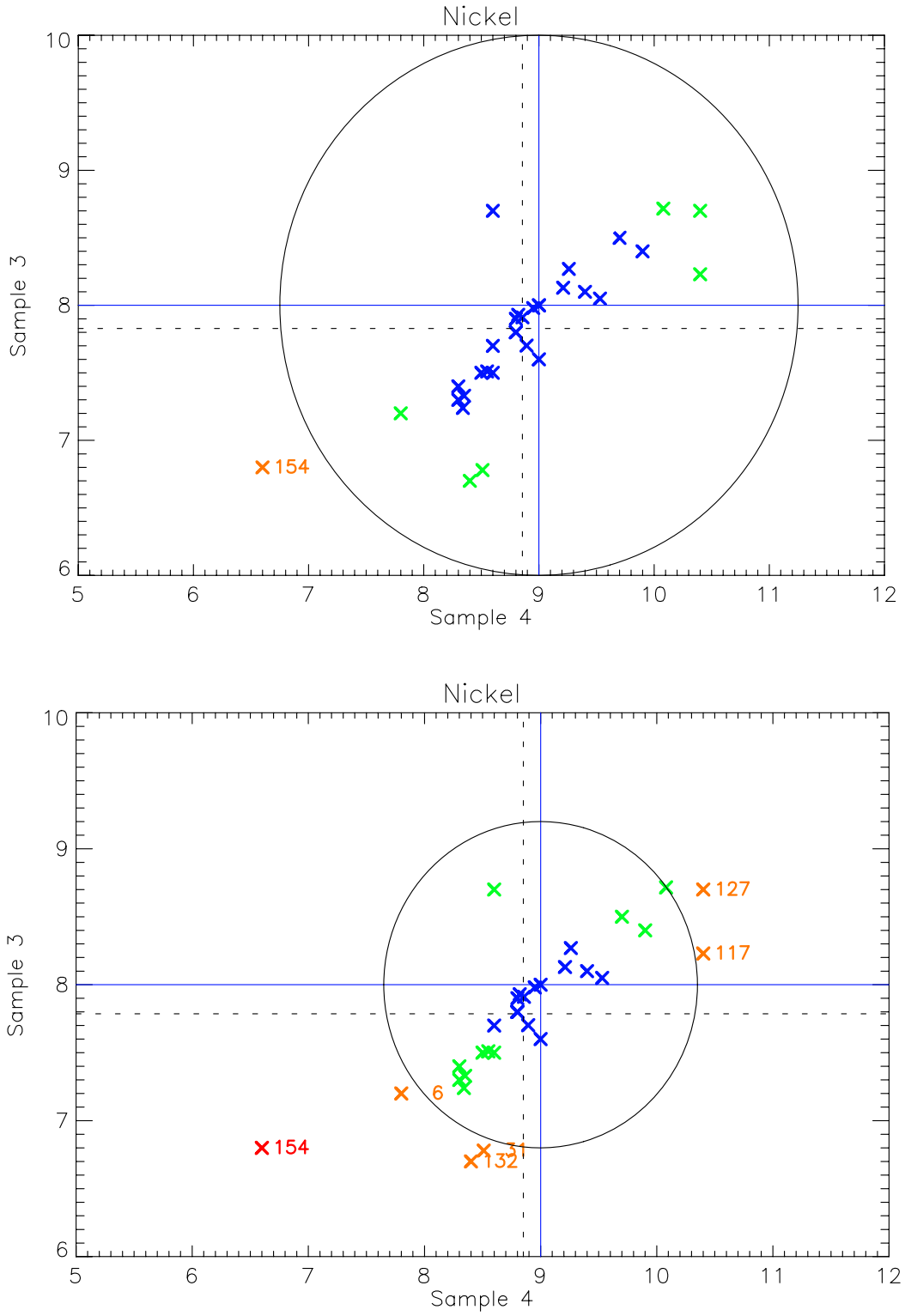


Figure A4.10: Youden plot of nickel, 2004.

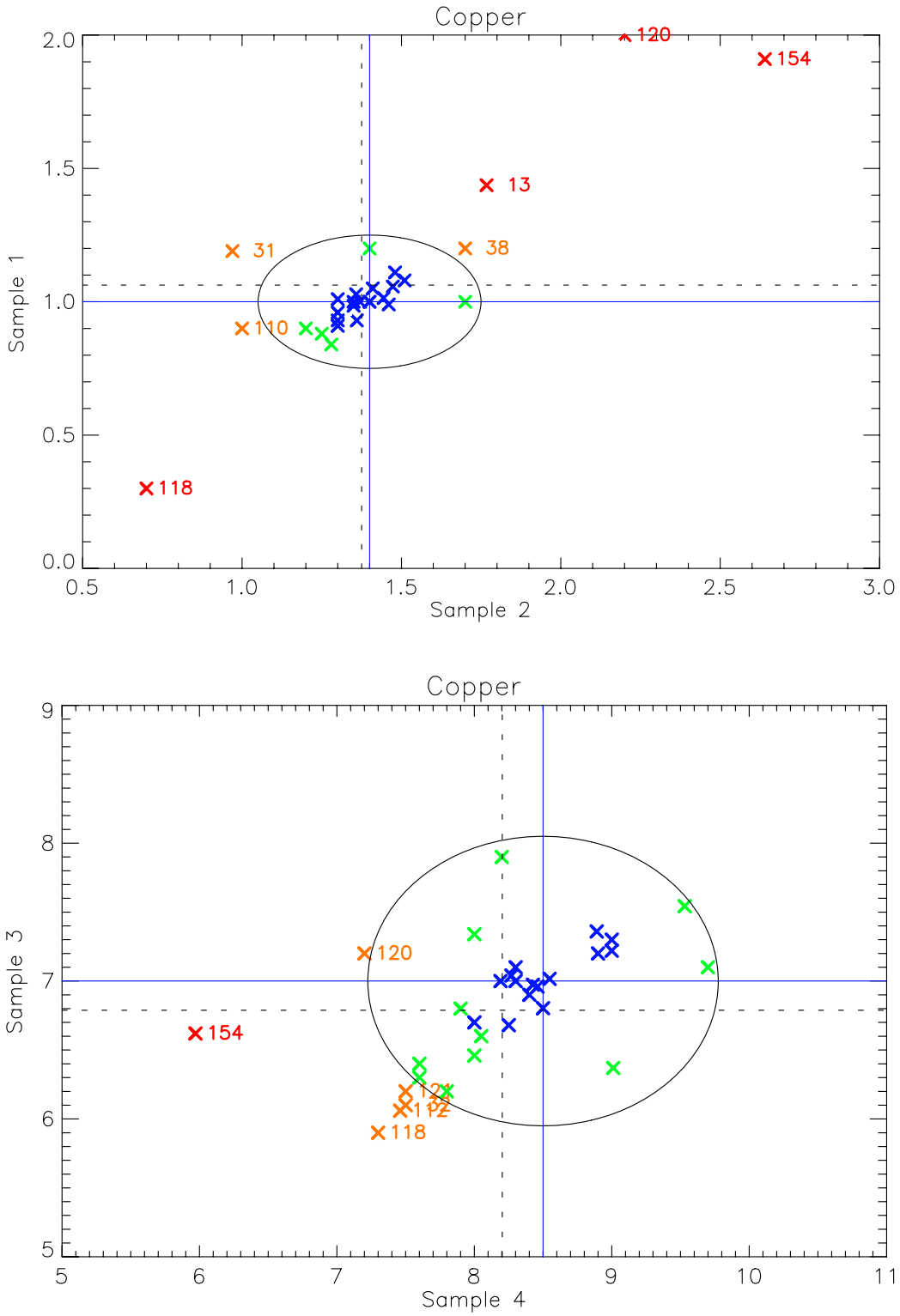


Figure A4.11: Youden plot of copper, 2004.

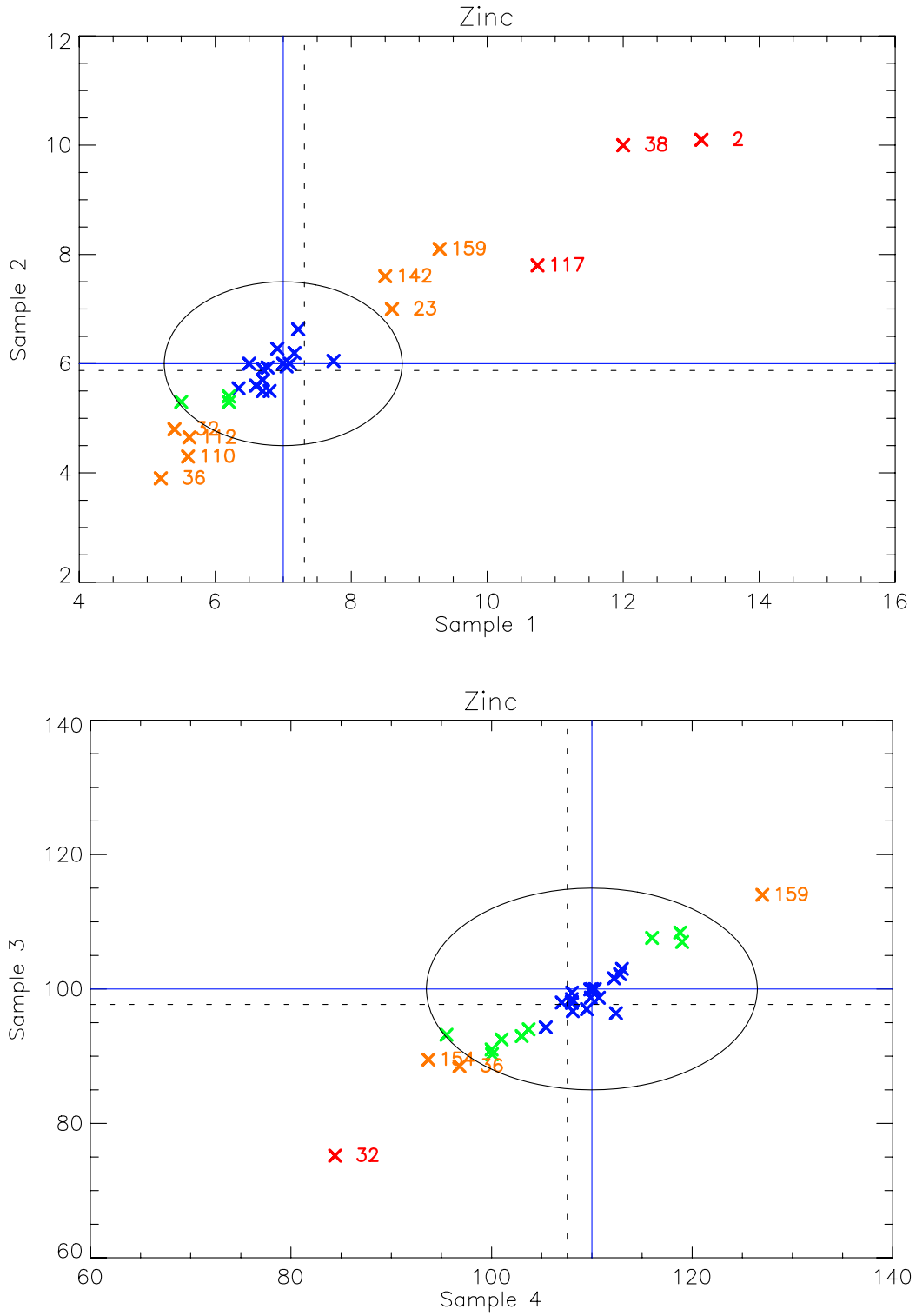


Figure A4.12: Youden plot of zinc, 2004.

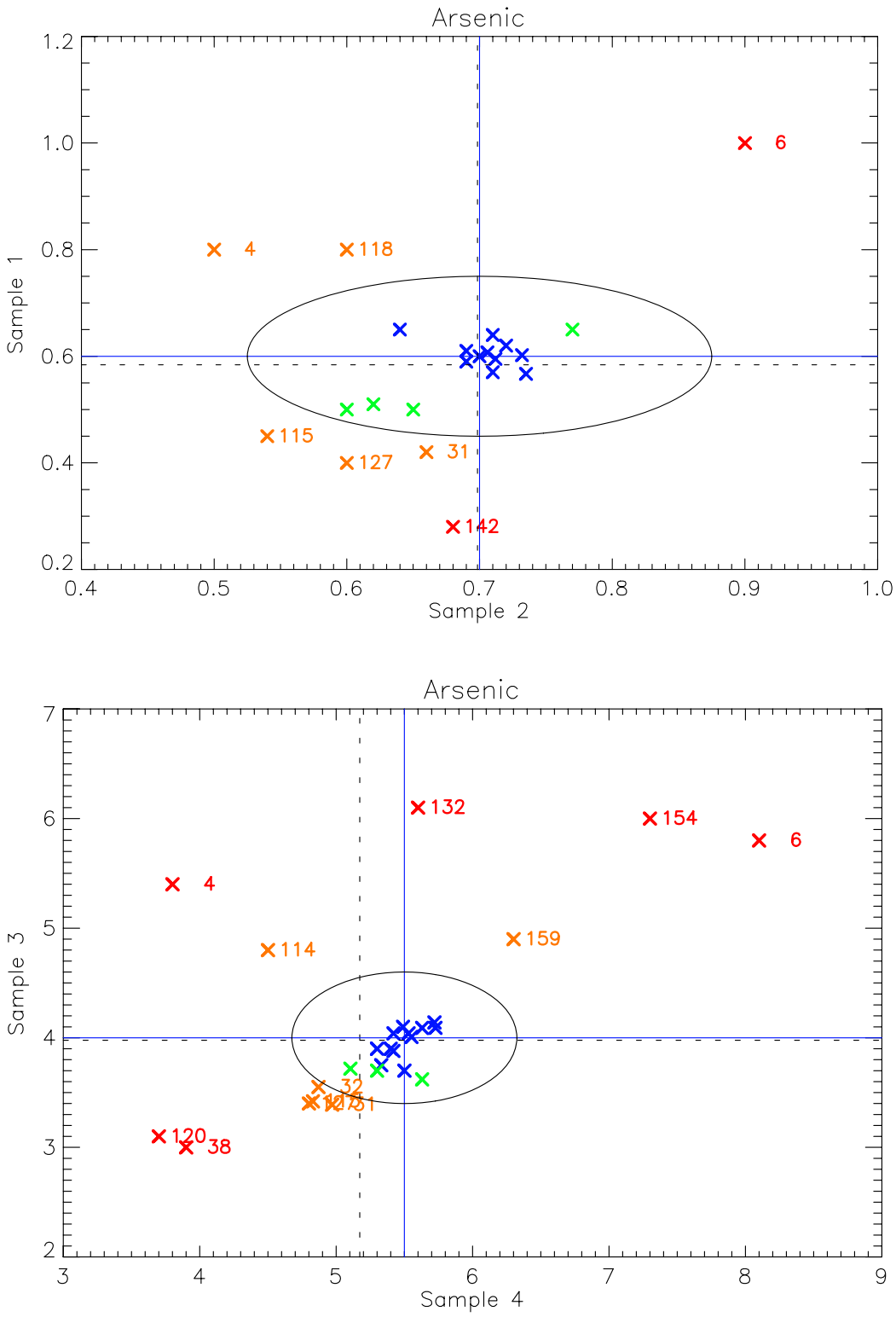


Figure A4.13: Youden plot of arsenic, 2004.

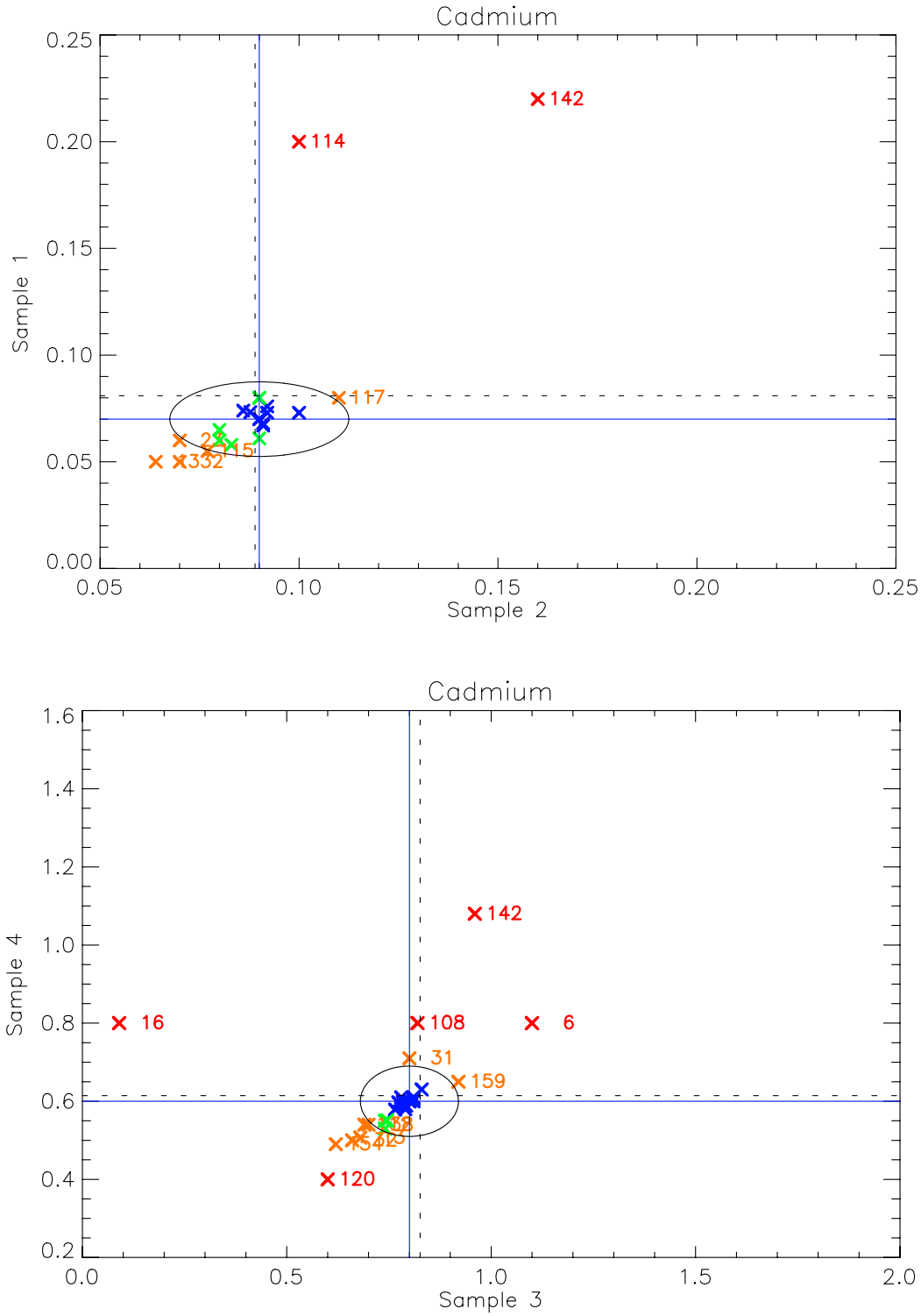


Figure A4.14: Youden plot of cadmium, 2004.

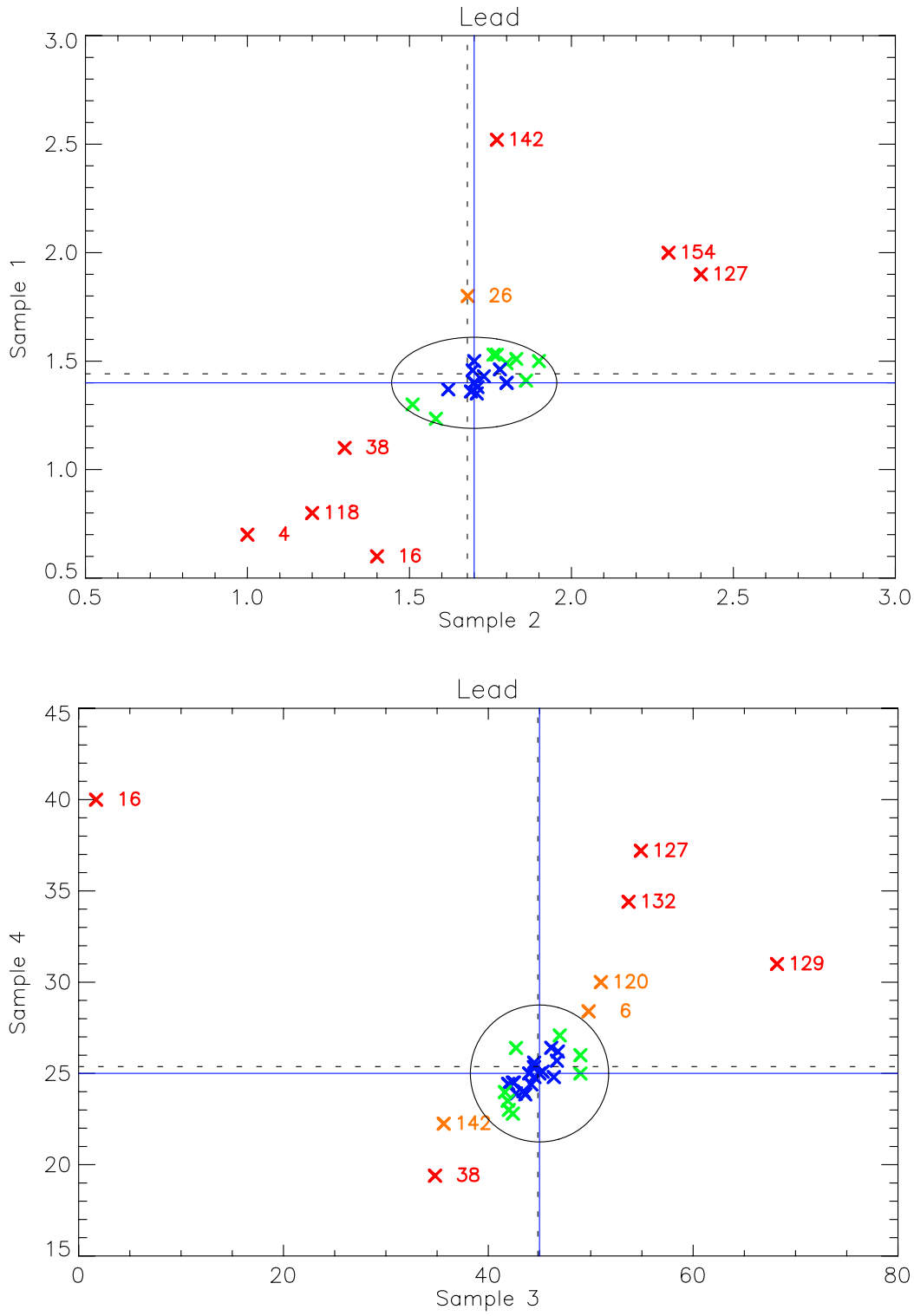


Figure A4.15: Youden plot of lead, 2004.