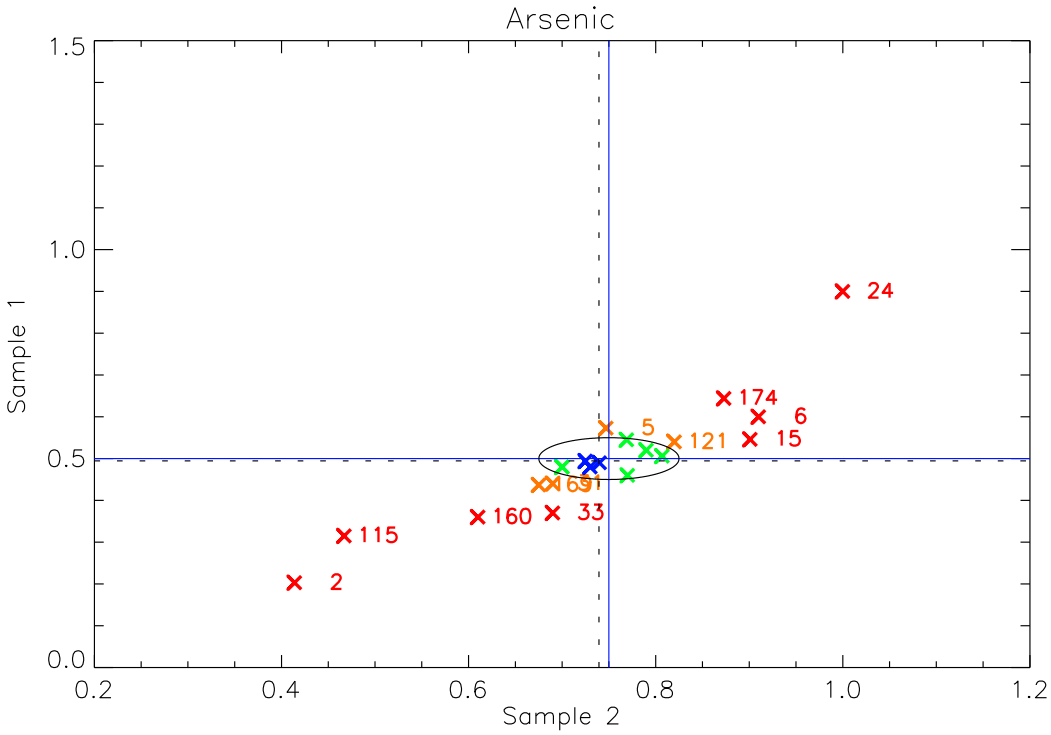
EMEP/CCC-Report 6/2008

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, 2007

Hilde Thelle Uggerud and Anne-Gunn Hjellbrekke



Youden plot of arsenic, 2007

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NILU : EMEP/CCC-Report 6/2008
REFERENCE : O-7729
DATE : DECEMBER 2008

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Analytical intercomparison of heavy metals in precipitation, 2007

1. Analytical intercomparison of heavy metals in precipitation, 2007

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 seven 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, 2005; Uggerud and Hjellbrekke, 2007).

This report presents results from the tenth analytical intercomparison of heavy metals in precipitation, which was carried out during 2007. Seven heavy metals were included: Pb, Cd, Cu, Zn, As, Cr, and Ni.

1.2 Organization of the intercomparison

The samples for the tenth intercomparison were prepared and distributed to 55 laboratories in October 2007.

A total of 39 laboratories, 19 from the EMEP network, reported results within the end of December 2007. 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 2 a and b 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 3.

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. Samples H1 and H2 contained concentrations similar to what is normally found in Southern Scandinavia. Samples H3 and H4 contained the elements in concentrations normally found in Central Europe.

All equipment in contact with the samples was 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 5–11 and Figures 1–7. An overview of all results is presented in Table 4.

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 Youden plot

Youden plot is a graphical technique, which allows for analysing interlaboratory data, where two 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.

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

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 1–7.

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 796 single results, 42 are defined as outliers. This is about 5% of the reported data, which is comparable to earlier intercomparisons.

2. 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).

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Uggerud, H.T. and Hjellbrekke, A.-G. (2007) Analytical intercomparison of heavy metals in precipitation, 2005 and 2006. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 4/2007).

Appendix 1

Tables and figures, 2007

Table 2a: Participating laboratories in the EMEP network, 2007. 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
8	Umweltbundesamt, Germany
10	Hungarian Meteorological Service, Hungary
13	C.N.R. Istituto Inquinamento Atmosferico, Italy
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
24	Hydrometeorological Institute of Serbia, Serbia
31	Slovak Hydrometeorological Institute, Slovakia
33	Environmental Pollution Observ. Centre, Latvia
36	Hydrometeorological Institute of Slovenia, Slovenia
38	Estonian Environmental Research Centre, Estonia
39	Environmental Monitoring Laboratory, Institute of Environmental Protection, Poland

Table 2b: Participating laboratories outside the EMEP network, 2007. The number in front of the names is used in tables and figures.

No	Laboratory identification
108	Institut f. Bondenkunde und Standortlehre der TU Dresden, Germany
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
132	Comision Chilena De Energia Nuclear, Chile
141	Pollutants Chemical Analysis Centre, Marine Division, Japan
144	National Institute of Chemistry, Slovenia
146	Cellule de Recherche en Environment et Biotechnologies Public Research Center-Gabriel Lippman, Luxembourg
159	CARSO, France
160	Coillte, Newtownmountkennedy, Ireland
161	National Institute of Chemistry, Slovenia
169	Lancaster Environment Centre, Centre for Ecology &Hydrology, UK
174	Laboratories des Pyrénéés, France

Table 3: Analytical techniques used at the participating laboratories for the different elements, 2007.

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, As, Cd, Pb	GF-AAS
5	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
6	Cr, Ni, Cu, Zn, Cd, Pb	ICP-AES
	As	GF-AAS
8	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
10	As, Pb	GF-AAS
13	As, Cd, Cr, Cu	Polarography
14	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
15	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
16	Cr, Ni, Cu, Zn, Cd, Pb	GF-AAS
23	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
24	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
31	As ,Cr, Ni, Cu, Cd, Pb	GF-AAS
	Zn	F-AAS
33	As, Cu, Cd, Cr, Ni, Pb	GF-AAS
	Zn	F-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
108	Cr, Ni, Cu, Zn, Cd, Pb	ICP-AES
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	Zn	ICP-OES
	As, Cd, Cr, Cu, Ni, Pb	GF-AAS
118	Cu, Cd, Pb	GF-AAS
	As ,Zn Cr, Ni	ICP-OES
120	Cr, Ni, Cu, As, Cd, Pb	GF-AAS
	Zn	F-AAS
121	Cr, Ni, Cu, Cd, Pb	GF-AAS
	Zn	Voltametry
	As	HG-AAS
125	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
132	Cr, Ni, Cu, Zn , Cd	USN-ICP-OES
	Pb	GF-AAS
	As	HG-AAS
141	Cd,	GF-AAS
144	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
146	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
159		
160	Cr, Ni, Cu, Zn, As, Cd, Pb	F-AAS
161	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
169	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
174	Cr, Ni, Cu, As, Cd, Pb	ICP-MS
	Zn,	ICP-OES

Table 4: Reported results for metal determination in precipitation samples, expressed as % deviation from expected value.

Lab no.	Arsenic				Cadmium				Chromium				Copper				Lead				Nickel				Zinc			
	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4
1	4	5	-4	0	60	25	3	2	-2	1	-5	-3	4	9	3	4	0	0	0	0	1	5	0	0	-5	-4	-2	-2
2	-59.4	-45	-4	-2	0	0	3	4	-90	-67	-2	-1	-4	-2	0	0	12	10	7	5	18	9	12	14	24	23	-3	2
3					4	8	-3	-3									-14	6	16	5	< 0.8	< 0.8	-3	0	33	6	0	0
4	< 1.5	< 1.5	-11	-9	< 0.35	< 0.35	-11	-13	< 2	< 2	0	-3	< 2.5	< 2.5	0	-3	< 3	< 3	-4	-5	< 3	< 3	-9	-5				
5	14.6	0	-5	-1	20	3	-4	0	53	1	-3	1	25	10	0	3	13	0	-5	-7	23	1	-2	2	14	3	-4	-6
6	20	21	26	26	< 0.1	25	20	20	-22	-19	-9	-9	0	5	3	3	-16	-14	-16	-13	-24	-24	-4	-4	58	41	11	11
8	-4	-3	-2	-2	-4	0	-3	-3	0	0	-3	-3	0	1	-2	-2	-4	-6	-8	-8	-3	-4	-3	-3	2	2	0	0
10					2	13	26	24									-11	-12	10	21								
13	1440	-96	-69	-84	17700	-48	129	75	16233	-25	290	-8	14838	-36	466	0												
14	-8	3	-2	2	4	-5	2	4	0	7	1	-3	11	5	1	2	4	-1	-1	-2	3	9	-1	4	-3	-1	-3	-1
15	9.2	20	-1	-6	0	4	4	1	2	1	1	-7	1	3	-1	-2	-1	1	-3	-1	-4	-4	-4	-4	13	21	1	-3
16					0	13	14	13	0	0	0	-3	-13	-18	-5	-1	0	6	0	0	-14	-13	-6	-3	-8	0	0	-4
23	< 3	< 3	-27	-33	100		-29	0	< 2	< 2	-50	-60	-13	-36	-23	50	0	-6	-12	-10	-14	-38	-14	-8	< 20	< 20	-10	-20
24	80	33	-9	-11	100	25	0	13	< 1	38	-2	15	463	545	45	78	-7	50	6	2	< 1	< 1	-21	62	47	79	-10	-9
31	-12	-8	-7	-7	-2	0	-1	-1	-5	-4	-3	-6	4	35	2	3	0	1	4	0	0	5	-2	1	27	9	-5	-6
33	-26	-8	0	-1	-20	-13	0	4	-7	-4	2	2	-3	4	2	2	-5	-3	0	0	-27	-21	2	3	-3	0	3	3
36	-2	-1	-2	0	< 0.1	< 0.1	-4	-4	< 1	< 1	0	0	< 1	-1	-1	0	-6	-6	-3	-11	< 1	< 1	0	0	-2	1	11	4
38	< 1	73	-27	-19	< 0.1	< 0.1	-4	-9	< 1	< 1	15	17	< 1	0	2	2	< 1	< 1	-8	-9	43	38	-6	-3	< 10	29	-5	-5
39			0	-7			0	0			0	7			-3	0			-12	0			14	8	8	0	0	0
108					< 0.5	< 0.5	14	25	< 1	< 1	7	0	0.82	< 0.82	2	-1	< 2.7	< 2.7	-12	-4	< 0.4	< 0.4	0	2	60	41	-1	-1
109					< 1	< 1			2733	< 109	17	33	125	45	9	8	< 10	< 10	< 10	-20	1471	< 5	43	69	0	-6	0	4
110	< 0.5	< 0.5	-4	0	< 0.2	< 0.2	-41	-38	-8	-9	-6	-7	< 0.5	-7	-16	-15	2	-1	-8	-9	-14	-15	-7	-7	< 1.0	< 1.0	1	4
112					-20	0	-90	-90	2	1	0	0	-1	-1	-8	-7	-4	-1	-3	-2	0	0	-1	0	-4	-8	-6	-4
114	< 5	< 5	-5	-1	100	150	0	0	17	13	-3	-1	-13	-9	3	-3	14	63	-2	-3	0	13	-1	2	18	0	-3	-2
115	-37	-38	-9	-7	-12	-8	-3	-1	-37	-28	-8	-7	-11	-8	-4	-3	9	4	1	1	16	5	-6	-5	-8	-8	-6	-4
117	< 1	< 1	0	-1	0	0	16	16	0	-12	-5	-5	16	6	-4	-2	-1	-2	-4	-9	22	26	-4	-2	5	1	-2	0
118		< 2.5	-24	-20	120	-25	-6	-4	< 0.6	0	-5	-4	< 2.3	< 2.3	-5	-5	< 2	< 2	-7	-6	< 0.7	< 0.7	-10	-9	7	-1	-7	-6
120					< 0.1	< 0.1	14	13	0	13	13	16	-38	-27	-14	-19	-29	-38	-8	-5	< 1	< 1	0	8	3	0	24	1482
121	8	9	0	-3	0	0	0	1	3	-4	-3	-7	1	8	8	4	-11	525	8	-18	10	2	11	17	-5	-2	0	5
125	9	3	4	3	8	8	9	7	-5	-3	-2	-3	8	7	4	2	-2	-3	2	4	0	-2	3	2	21	19	23	22
132					< 1.4	< 1.4	-13	-2	< 1.4	< 1.4	-1	1	114	39	-3	10	< 10	< 10	15	6	< 2.1	< 2.1	3	8	-20	-15	-6	-90
141					0	6	4	5																				
144	-4	-7	-1	-1	-60	-75	-16	-9	0	0	-3	-1	0	0	-2	-1	4	1	0	4	0	0	-1	1392	5	-1	-3	-3
146	1.2	8	5	3	6	13	3	4	40	11	7	9	71	16	10	11	6	13	5	4	6	9	8	5	-19	-2	11	11
159	-1.2	-3	-1	-1	-2	3	-2	-4	0	-4	-1	0	-10	-9	-4	-4	-1	-1	-4	-3	-8	-11	-2	1	2	0	0	-1
160	-28	-19	-2	-1	-20	-25	-3	-1	-23	-20	-9	-8	-23	-15	-1	0	4	0	6	12	-3	-5	-1	-1	21	18	12	11
161	-4	-7	-1	-1	-60	-75	-16	-9	0	0	-3	-1	0	0	-2	-1	4	1	0	4	0	0	-1	1392	5	-1	-3	-3
169	-12.6	-10	-10	-12	-10.6	-7	-11	-11	-18	-11	-10	-12	-8	-5	-10	-12	-17	-16	-17	-17	-11	-11	-11	-11	-3	-1	-8	-10
174	28.8	16	11	-2	-50	-4	-1	-3	-18	-8	-2	0	-17	-10	-3	-6	-25	-21	-9	-6	-18	-22	-11	-11	-7	-5	8	8

Pb, Ni, Cr and As (< 1 µg/l), Cd < 0.5 µg/l, Zn< 10 µg/l, Cu < 2 g/l between ± 25 and 50%

Pb, Ni, Cr and As (< 1 µg/l), Cd < 0.5 µg/l, Zn < 10 µg/l, Cu < 2 g/l more than 50%

Pb, Ni, Cr and As (> 1 µg/l), Cd > 0.5 µg/l, Zn> 10 µg/l, Cu >2 g/l between ± 15 and 30%

Pb, Ni, Cr and As (> 1 µg/l), Cd > 0.5 µg/l, Zn> 10 µg/l, Cu >2 g/l more than ± 30%

Table 5: Analytical results for Cr in synthetic precipitation samples, 2007.

Chromium
Sample no.: H1
Theoretical value: 0.600
Unit: µg/l

Run 1:
Number of laboratories: 27
Arithmetic mean value: 4.788
Median: 0.600
Standard deviation 18.895
Rel. st. deviation (%) 394.607

Run 2:
Number of laboratories: 26
Arithmetic mean value: 1.203
Median: 0.599
Standard deviation 3.225
Rel. st. deviation (%) 268.049

Results in decreasing order:

13	98.000 (*)	159	0.599
109	17.000	117	0.598
5	0.915	1	0.590
146	0.837	31	0.570
114	0.700	125	0.570
121	0.620	33	0.560
15	0.613	110	0.550
112	0.610	169	0.495
8	0.600	174	0.492
120	0.600	6	0.470
144	0.600	160	0.460
14	0.600	115	0.378
161	0.600	2	0.058
16	0.600	118 <	0.6
		24 <	1.0
		108 <	1.0
		36 <	1
		38 <	1
		132 <	1.4
		4 <	2
		23 <	2

Chromium
Sample no.: H2
Theoretical value: 0.800
Unit: µg/l

Run 1:
Number of laboratories: 28
Arithmetic mean value: 0.763
Median: 0.786
Standard deviation 0.141
Rel. st. deviation (%) 18.477

Run 2:
Number of laboratories: 26
Arithmetic mean value: 0.769
Median: 0.786
Standard deviation 0.083
Rel. st. deviation (%) 10.839

Results in decreasing order:

24	1.100 (*)	125	0.773
114	0.900	31	0.770
120	0.900	33	0.770
146	0.889	121	0.770
14	0.860	159	0.770
112	0.810	174	0.735
1	0.810	110	0.730
15	0.808	169	0.715
5	0.805	117	0.702
16	0.800	6	0.650
8	0.800	160	0.640
118	0.800	13	0.600
144	0.800	115	0.579
161	0.800	2	0.265 (*)
		36 <	1
		38 <	1
		108 <	1
		132 <	1.4
		4 <	2
		23 <	2
		109 <	2

Chromium
Sample no.: H3
Theoretical value: 6.000
Unit: µg/l

Run 1:
Number of laboratories: 36
Arithmetic mean value: 6.356
Median: 5.900
Standard deviation 2.985
Rel. st. deviation (%) 46.966

Run 2:
Number of laboratories: 35
Arithmetic mean value: 5.869
Median: 5.900
Standard deviation 0.619
Rel. st. deviation (%) 10.548

Results in decreasing order:

13	23.400 (*)	174	5.900
109	7.000	2	5.877
38	6.900	31	5.830
120	6.800	5	5.818
108	6.400	8	5.800
146	6.400	161	5.800
33	6.090	144	5.800
15	6.050	121	5.800
14	6.030	114	5.800
4	6.000	117	5.702
36	6.000	118	5.700
39	6.000	1	5.700
16	6.000	110	5.660
112	5.980	115	5.520
159	5.970	160	5.490
132	5.923	6	5.460
125	5.910	169	5.390
24	5.900	23	3.000

Chromium
Sample no.: H4
Theoretical value: 7.500
Unit: µg/l

Run 1:
Number of laboratories: 36
Arithmetic mean value: 7.371
Median: 7.355
Standard deviation 0.996
Rel. st. deviation (%) 13.520

Run 2:
Number of laboratories: 34
Arithmetic mean value: 7.422
Median: 7.355
Standard deviation 0.512
Rel. st. deviation (%) 6.899

Results in decreasing order:

109	10.000 (*)	125	7.310
38	8.800	4	7.300
120	8.700	1	7.300
24	8.600	16	7.300
146	8.156	14	7.270
39	8.000	8	7.250
33	7.620	118	7.200
5	7.590	117	7.126
132	7.556	31	7.030
108	7.500	121	7.000
36	7.490	115	6.980
174	7.490	110	6.960
112	7.480	15	6.960
159	7.470	13	6.900
2	7.461	160	6.870
114	7.400	6	6.850
161	7.400	169	6.620
144	7.400	23	3.000 (*)

Table 6: Analytical results for Ni in synthetic precipitation samples, 2007.

Nickel
Sample no.: H1
Theoretical value: 0.700
Unit: µg/l

Run 1:
Number of laboratories: 27
Arithmetic mean value: 1.082
Median: 0.700
Standard deviation 1.985
Rel. st. deviation (%) 183.519

Run 2:
Number of laboratories: 26
Arithmetic mean value: 0.700
Median: 0.700
Standard deviation 0.109
Rel. st. deviation (%) 15.533

Results in decreasing order:

109	11.000 (*)	31	0.700
38	1.000	125	0.699
5	0.863	8	0.680
117	0.852	160	0.680
2	0.824	15	0.670
115	0.809	159	0.646
121	0.770	169	0.626
146	0.744	16	0.600
14	0.720	110	0.600
1	0.710	23	0.600
112	0.700	174	0.572
114	0.700	6	0.530
161	0.700	33	0.510
144	0.700	108 <	0.4
		118 <	0.7
		3 <	0.8
		24 <	1
		36 <	1
		120 <	1
		132 <	2.1
		4 <	3

Nickel
Sample no.: H2
Theoretical value: 0.800
Unit: µg/l

Run 1:
Number of laboratories: 26
Arithmetic mean value: 0.785
Median: 0.800
Standard deviation 0.124
Rel. st. deviation (%) 15.834

Run 2:
Number of laboratories: 24
Arithmetic mean value: 0.784
Median: 0.800
Standard deviation 0.095
Rel. st. deviation (%) 12.073

Results in decreasing order:

38	1.100 (*)	144	0.800
117	1.005	125	0.785
114	0.900	15	0.770
146	0.876	8	0.770
14	0.870	160	0.760
2	0.869	169	0.714
115	0.840	159	0.712
1	0.840	16	0.700
31	0.840	110	0.680
121	0.820	33	0.630
5	0.805	174	0.623
161	0.800	6	0.610
112	0.800	23	0.500 (*)
		108 <	0.4
		118 <	0.7
		3 <	0.8
		36 <	1
		24 <	1
		120 <	1
		132 <	2.1
		4 <	3
		109 <	5

Nickel
Sample no.: H3
Theoretical value: 7.000
Unit: µg/l

Run 1:
Number of laboratories: 36
Arithmetic mean value: 6.930
Median: 6.895
Standard deviation 0.717
Rel. st. deviation (%) 10.340

Run 2:
Number of laboratories: 35
Arithmetic mean value: 6.842
Median: 6.890
Standard deviation 0.493
Rel. st. deviation (%) 7.211

Results in decreasing order:

109	10.000 (*)	31	6.890
39	8.000	5	6.857
2	7.827	159	6.850
121	7.800	3	6.800
146	7.527	8	6.800
125	7.240	117	6.740
132	7.176	15	6.740
33	7.110	6	6.720
36	7.020	16	6.600
108	7.000	38	6.600
1	7.000	115	6.550
120	7.000	110	6.480
112	6.950	4	6.400
14	6.920	118	6.300
160	6.910	169	6.250
161	6.900	174	6.230
144	6.900	23	6.000
114	6.900	24	5.500

Nickel
Sample no.: H4
Theoretical value: 6.500
Unit: µg/l

Run 1:
Number of laboratories: 36
Arithmetic mean value: 11.764
Median: 6.545
Standard deviation 20.993
Rel. st. deviation (%) 178.452

Run 2:
Number of laboratories: 34
Arithmetic mean value: 6.750
Median: 6.530
Standard deviation 1.095
Rel. st. deviation (%) 16.219

Results in decreasing order:

161	97.000 (*)	112	6.530
144	97.000 (*)	36	6.530
109	11.000	1	6.500
24	10.500	3	6.500
121	7.600	160	6.420
2	7.409	117	6.360
120	7.000	38	6.300
39	7.000	8	6.300
132	6.997	16	6.300
146	6.856	6	6.220
14	6.750	15	6.220
33	6.680	115	6.200
5	6.650	4	6.200
125	6.640	110	6.060
114	6.600	23	6.000
108	6.600	118	5.900
31	6.580	174	5.780
159	6.560	169	5.760

Table 7: Analytical results for Cu in synthetic precipitation samples, 2007.

Copper
Sample no.: H1
Theoretical value: 0.800
Unit: µg/l

Run 1:
Number of laboratories: 29
Arithmetic mean value: 5.084
Median: 0.800
Standard deviation 22.018
Rel. st. deviation (%) 433.096

Run 2:
Number of laboratories: 28
Arithmetic mean value: 0.997
Median: 0.800
Standard deviation 0.746
Rel. st. deviation (%) 74.758

Results in decreasing order:

13	119.500 (*)	161	0.800
24	4.500	8	0.800
109	1.800	112	0.790
132	1.715	33	0.780
146	1.364	2	0.771
5	0.999	169	0.740
117	0.925	159	0.719
14	0.890	115	0.711
125	0.861	23	0.700
31	0.830	114	0.700
1	0.830	16	0.700
15	0.811	174	0.663
121	0.810	160	0.620
6	0.800	120	0.500
144	0.800	110	< 0.5
		108	< 0.82
		36	< 1
		38	< 1
		118	< 2.3
		4	< 2.5

Copper
Sample no.: H2
Theoretical value: 1.100
Unit: µg/l

Run 1:
Number of laboratories: 32
Arithmetic mean value: 1.291
Median: 1.100
Standard deviation 1.078
Rel. st. deviation (%) 83.491

Run 2:
Number of laboratories: 31
Arithmetic mean value: 1.104
Median: 1.100
Standard deviation 0.200
Rel. st. deviation (%) 18.103

Results in decreasing order:

24	7.100 (*)	161	1.100
109	1.600	38	1.100
132	1.531	112	1.090
31	1.490	36	1.090
146	1.280	2	1.083
5	1.213	169	1.040
1	1.200	110	1.020
121	1.190	115	1.010
125	1.180	114	1.000
117	1.171	159	0.996
6	1.160	174	0.995
14	1.160	160	0.940
33	1.140	16	0.900
15	1.130	120	0.800
8	1.110	23	0.700
144	1.100	13	0.700
		108	< 0.82
		118	< 2.3
		4	< 2.5

Copper
Sample no.: H3
Theoretical value: 6.500
Unit: µg/l

Run 1:
Number of laboratories: 36
Arithmetic mean value: 7.315
Median: 6.460
Standard deviation 5.097
Rel. st. deviation (%) 69.677

Run 2:
Number of laboratories: 35
Arithmetic mean value: 6.472
Median: 6.460
Standard deviation 0.663
Rel. st. deviation (%) 10.247

Results in decreasing order:

13	36.800 (*)	36	6.460
24	9.400	160	6.450
146	7.122	161	6.400
109	7.100	8	6.400
121	7.000	144	6.400
125	6.770	132	6.328
1	6.700	174	6.310
6	6.700	39	6.300
114	6.700	117	6.248
33	6.620	115	6.240
108	6.600	159	6.220
31	6.600	118	6.200
38	6.600	16	6.200
14	6.590	112	5.980
2	6.514	169	5.830
5	6.500	120	5.600
4	6.500	110	5.490
15	6.460	23	5.000

Copper
Sample no.: H4
Theoretical value: 8.000
Unit: µg/l

Run 1:
Number of laboratories: 36
Arithmetic mean value: 8.211
Median: 8.000
Standard deviation 1.318
Rel. st. deviation (%) 16.059

Run 2:
Number of laboratories: 34
Arithmetic mean value: 7.923
Median: 7.950
Standard deviation 0.486
Rel. st. deviation (%) 6.136

Results in decreasing order:

24	14.200 (*)	13	8.000
23	12.000 (*)	108	7.900
146	8.865	16	7.900
132	8.810	144	7.900
109	8.600	161	7.900
121	8.360	117	7.857
1	8.300	15	7.840
31	8.260	8	7.830
6	8.250	114	7.800
5	8.235	4	7.800
38	8.200	115	7.740
33	8.170	159	7.690
14	8.140	118	7.600
125	8.140	174	7.550
2	8.014	112	7.410
36	8.000	169	7.030
39	8.000	110	6.790
160	8.000	120	6.500

Table 8: Analytical results for Zn in synthetic precipitation samples, 2007.

Zinc
Sample no.: H1
Theoretical value: 6.000
Unit: µg/l

Run 1:
Number of laboratories: 32
Arithmetic mean value: 6.537
Median: 6.239
Standard deviation 1.172
Rel. st. deviation (%) 17.924

Run 2:
Number of laboratories: 30
Arithmetic mean value: 6.336
Median: 6.150
Standard deviation 0.894
Rel. st. deviation (%) 14.110

Results in decreasing order:

108	9.600 (*)	120	6.200
6	9.500 (*)	8	6.100
24	8.800	159	6.100
3	8.000	109	6.000
31	7.600	36	5.880
2	7.468	33	5.850
160	7.270	169	5.820
125	7.240	14	5.800
114	7.100	112	5.760
5	6.816	1	5.700
15	6.770	121	5.700
39	6.500	174	5.600
118	6.400	115	5.540
144	6.300	16	5.500
161	6.300	146	4.858
117	6.279	132	4.823
		110 <	1.0
		38 <	10
		23 <	20

Zinc
Sample no.: H2
Theoretical value: 8.500
Unit: µg/l

Run 1:
Number of laboratories: 33
Arithmetic mean value: 9.120
Median: 8.500
Standard deviation 1.574
Rel. st. deviation (%) 17.263

Run 2:
Number of laboratories: 32
Arithmetic mean value: 8.930
Median: 8.500
Standard deviation 1.153
Rel. st. deviation (%) 12.909

Results in decreasing order:

24	15.200 (*)	39	8.500
108	12.000	16	8.500
6	12.000	120	8.500
38	11.000	144	8.400
2	10.490	118	8.400
15	10.300	161	8.400
125	10.100	14	8.400
160	10.070	169	8.400
31	9.300	146	8.364
3	9.000	121	8.300
5	8.717	1	8.200
8	8.700	174	8.100
117	8.611	109	8.000
36	8.560	112	7.860
159	8.530	115	7.860
33	8.510	132	7.190
114	8.500	110 <	1.0
		23 <	20

Zinc
Sample no.: H3
Theoretical value: 100.000
Unit: µg/l

Run 1:
Number of laboratories: 35
Arithmetic mean value: 100.524
Median: 99.400
Standard deviation 8.018
Rel. st. deviation (%) 7.976

Run 2:
Number of laboratories: 33
Arithmetic mean value: 99.131
Median: 98.000
Standard deviation 5.770
Rel. st. deviation (%) 5.821

Results in decreasing order:

120	124.000 (*)	1	98.000
125	123.000 (*)	117	97.900
160	111.700	161	97.000
146	111.247	144	97.000
36	111.100	114	97.000
6	110.500	2	96.970
174	107.700	14	96.700
33	103.000	5	95.650
15	101.000	31	95.000
110	101.000	38	95.000
121	100.000	112	94.470
8	100.000	115	94.400
3	100.000	132	94.090
109	100.000	118	93.000
39	100.000	169	92.100
16	100.000	24	90.500
159	99.900	23	90.000
108	99.400		

Zinc
Sample no.: H4
Theoretical value: 125.000
Unit: µg/l

Run 1:
Number of laboratories: 35
Arithmetic mean value: 174.458
Median: 123.500
Standard deviation 314.526
Rel. st. deviation (%) 180.288

Run 2:
Number of laboratories: 34
Arithmetic mean value: 121.413
Median: 123.450
Standard deviation 21.376
Rel. st. deviation (%) 17.606

Results in decreasing order:

120	1978.000 (*)	14	123.400
125	152.000	1	123.000
6	139.000	114	122.000
160	138.400	144	121.000
146	138.149	161	121.000
174	134.500	15	121.000
121	131.000	16	120.000
36	130.100	112	119.900
110	130.000	115	119.400
109	130.000	38	119.000
33	129.000	31	118.000
2	128.000	118	117.300
3	125.000	5	117.000
39	125.000	24	113.400
8	125.000	169	113.000
117	124.900	23	100.000
159	124.000	132	12.080
108	123.500		

Table 9: Analytical results for As in synthetic precipitation samples, 2007.

Arsenic
Sample no.: H1
Theoretical value: 0.500
Unit: µg/l

Run 1:
Number of laboratories: 22
Arithmetic mean value: 0.822
Median: 0.492
Standard deviation 1.542
Rel. st. deviation (%) 187.598

Run 2:
Number of laboratories: 21
Arithmetic mean value: 0.494
Median: 0.490
Standard deviation 0.136
Rel. st. deviation (%) 27.548

Results in decreasing order:

13	7.700 (*)	36	0.490
24	0.900	161	0.480
174	0.644	144	0.480
6	0.600	8	0.480
5	0.573	14	0.460
15	0.546	31	0.440
125	0.545	169	0.437
121	0.540	33	0.370
1	0.520	160	0.360
146	0.506	115	0.315
159	0.494	2	0.203
		110 <	0.5
		38 <	1
		117 <	1
		4 <	1.5
		23 <	3
		114 <	5

Arsenic
Sample no.: H2
Theoretical value: 0.750
Unit: µg/l

Run 1:
Number of laboratories: 24
Arithmetic mean value: 0.727
Median: 0.735
Standard deviation 0.229
Rel. st. deviation (%) 31.499

Run 2:
Number of laboratories: 22
Arithmetic mean value: 0.732
Median: 0.735
Standard deviation 0.136
Rel. st. deviation (%) 18.612

Results in decreasing order:

38	1.300 (*)	8	0.730
24	1.000	159	0.725
6	0.910	161	0.700
15	0.901	144	0.700
174	0.873	31	0.690
121	0.820	33	0.690
146	0.807	169	0.675
1	0.790	160	0.610
14	0.770	110	0.580
125	0.769	115	0.467
5	0.747	2	0.414
36	0.740	13	0.030 (*)
		117 <	1
		4 <	1.5
		118 <	2.5
		23 <	3
		114 <	5

Arsenic
Sample no.: H3
Theoretical value: 5.500
Unit: µg/l

Run 1:
Number of laboratories: 30
Arithmetic mean value: 5.168
Median: 5.390
Standard deviation 0.862
Rel. st. deviation (%) 16.673

Run 2:
Number of laboratories: 28
Arithmetic mean value: 5.230
Median: 5.390
Standard deviation 0.485
Rel. st. deviation (%) 9.283

Results in decreasing order:

6	6.910 (*)	160	5.390
174	6.130	1	5.300
146	5.778	110	5.280
125	5.740	2	5.259
39	5.500	5	5.249
33	5.500	114	5.200
117	5.497	31	5.090
121	5.490	115	5.010
15	5.470	24	5.000
161	5.440	169	4.940
144	5.440	4	4.900
159	5.430	118	4.200
14	5.410	38	4.000
8	5.400	23	4.000
36	5.390	13	1.700 (*)

Arsenic
Sample no.: H4
Theoretical value: 7.500
Unit: µg/l

Run 1:
Number of laboratories: 30
Arithmetic mean value: 7.003
Median: 7.370
Standard deviation 1.310
Rel. st. deviation (%) 18.708

Run 2:
Number of laboratories: 29
Arithmetic mean value: 7.203
Median: 7.390
Standard deviation 0.731
Rel. st. deviation (%) 10.142

Results in decreasing order:

6	9.470	8	7.350
146	7.726	174	7.350
125	7.690	2	7.318
14	7.620	121	7.310
1	7.500	15	7.070
36	7.500	39	7.000
110	7.470	31	6.990
5	7.449	115	6.950
117	7.437	4	6.800
160	7.430	24	6.700
144	7.420	169	6.630
161	7.420	38	6.100
33	7.400	118	6.000
114	7.400	23	5.000
159	7.390	13	1.200 (*)

Table10: Analytical results for Cd in synthetic precipitation samples, 2007.

Cadmium
Sample no.: H1
Theoretical value: 0.050
Unit: µg/l

Run 1:
Number of laboratories: 29
Arithmetic mean value: 0.360
Median: 0.050
Standard deviation 1.643
Rel. st. deviation (%) 456.665

Run 2:
Number of laboratories: 28
Arithmetic mean value: 0.055
Median: 0.050
Standard deviation 0.023
Rel. st. deviation (%) 42.084

Results in decreasing order:

13	8.900 (*)	117	0.050
118	0.110	141	0.050
114	0.100	121	0.050
24	0.100	31	0.049
23	0.100	159	0.049
1	0.080	8	0.048
5	0.060	169	0.045
125	0.054	115	0.044
146	0.053	112	0.040
14	0.052	160	0.040
3	0.052	33	0.040
10	0.051	174	0.025
15	0.050	161	0.020
16	0.050	144	0.020
2	0.050	6 <	0.1
		36 <	0.1
		38 <	0.1
		120 <	0.1
		110 <	0.2
		4 <	0.35
		108 <	0.5
		109 <	1
		132 <	1.4

Cadmium
Sample no.: H2
Theoretical value: 0.080
Unit: µg/l

Run 1:
Number of laboratories: 29
Arithmetic mean value: 0.080
Median: 0.080
Standard deviation 0.030
Rel. st. deviation (%) 37.722

Run 2:
Number of laboratories: 28
Arithmetic mean value: 0.076
Median: 0.080
Standard deviation 0.020
Rel. st. deviation (%) 26.327

Results in decreasing order:

114	0.200 (*)	31	0.080
24	0.100	8	0.080
6	0.100	112	0.080
1	0.100	117	0.080
10	0.090	174	0.077
16	0.090	14	0.076
146	0.090	115	0.074
125	0.086	169	0.074
3	0.086	33	0.070
141	0.085	118	0.060
15	0.083	160	0.060
5	0.082	13	0.042
159	0.082	161	0.020
2	0.080	144	0.020
121	0.080	23 <	0.1
		36 <	0.1
		38 <	0.1
		120 <	0.1
		110 <	0.2
		108 <	0.5
		132 <	1.4

Cadmium
Sample no.: H3
Theoretical value: 0.700
Unit: µg/l

Run 1:
Number of laboratories: 38
Arithmetic mean value: 0.700
Median: 0.696
Standard deviation 0.200
Rel. st. deviation (%) 28.606

Run 2:
Number of laboratories: 36
Arithmetic mean value: 0.693
Median: 0.696
Standard deviation 0.088
Rel. st. deviation (%) 12.773

Results in decreasing order:

13	1.600 (*)	174	0.693	
10	0.879	31	0.690	
6	0.840	159	0.684	
117	0.810	8	0.680	
108	0.800	160	0.680	
16	0.800	3	0.678	
120	0.800	115	0.678	
125	0.766	5	0.672	
15	0.730	38	0.670	
141	0.730	36	0.670	
146	0.722	118	0.660	
2	0.721	169	0.626	
1	0.720	4	0.620	
14	0.715	132	0.611	
24	0.700	144	0.590	
114	0.700	161	0.590	
33	0.700	23	0.500	
39	0.700	110	0.410	
121	0.700	112	0.069	(*)

Cadmium
Sample no.: H4
Theoretical value: 0.800
Unit: µg/l

Run 1:
Number of laboratories: 38
Arithmetic mean value: 0.806
Median: 0.800
Standard deviation 0.177
Rel. st. deviation (%) 21.966

Run 2:
Number of laboratories: 36
Arithmetic mean value: 0.810
Median: 0.800
Standard deviation 0.090
Rel. st. deviation (%) 11.070

Results in decreasing order:

13	1.400 (*)	39	0.800	
108	1.000	5	0.797	
10	0.988	115	0.796	
6	0.960	160	0.790	
117	0.930	31	0.790	
24	0.900	132	0.788	
16	0.900	8	0.780	
120	0.900	3	0.777	
125	0.860	174	0.775	
141	0.840	159	0.772	
14	0.836	36	0.770	
2	0.833	118	0.770	
33	0.830	161	0.730	
146	0.829	38	0.730	
1	0.820	144	0.730	
15	0.810	169	0.712	
121	0.810	4	0.700	
23	0.800	110	0.500	
114	0.800	112	0.081	(*)

Table 11: Analytical results for Pb in synthetic precipitation samples, 2007.

Lead
Sample no.: H1
Theoretical value: 1.400
Unit: µg/l

Run 1:
Number of laboratories: 30
Arithmetic mean value: 1.362
Median: 1.385
Standard deviation 0.144
Rel. st. deviation (%) 10.545

Run 2:
Number of laboratories: 28
Arithmetic mean value: 1.386
Median: 1.395
Standard deviation 0.115
Rel. st. deviation (%) 8.291

Results in decreasing order:

114	1.600	159	1.380	
5	1.586	117	1.380	
2	1.564	125	1.370	
115	1.530	8	1.350	
146	1.479	112	1.350	
161	1.460	33	1.330	
160	1.460	36	1.320	
144	1.460	24	1.300	
14	1.450	10	1.247	
110	1.430	121	1.240	
16	1.400	3	1.200	
31	1.400	6	1.180	
23	1.400	169	1.160	
1	1.400	174	1.055	(*)
15	1.390	120	1.000	(*)
		38 <	1	
		118 <	2	
		108 <	2.7	
		4 <	3	
		109 <	10	
		132 <	10	

Lead
Sample no.: H2
Theoretical value: 1.600
Unit: µg/l

Run 1:
Number of laboratories: 30
Arithmetic mean value: 1.894
Median: 1.595
Standard deviation 1.557
Rel. st. deviation (%) 82.233

Run 2:
Number of laboratories: 29
Arithmetic mean value: 1.614
Median: 1.590
Standard deviation 0.291
Rel. st. deviation (%) 18.041

Results in decreasing order:

121	10.000	(*)	14	1.590
114	2.600		159	1.580
24	2.400		112	1.580
146	1.800		110	1.580
2	1.757		117	1.570
16	1.700		125	1.550
3	1.700		33	1.550
115	1.660		36	1.510
144	1.620		23	1.500
31	1.620		8	1.500
15	1.620		10	1.409
161	1.620		6	1.380
5	1.604		169	1.350
160	1.600		174	1.270
1	1.600		120	1.000
			38 <	1
			118 <	2
			108 <	2.7
			4 <	3
			109 <	10
			132 <	10

Lead
Sample no.: H3
Theoretical value: 25.000
Unit: µg/l

Run 1:
Number of laboratories: 36
Arithmetic mean value: 24.552
Median: 24.450
Standard deviation 1.964
Rel. st. deviation (%) 8.000

Run 2:
Number of laboratories: 34
Arithmetic mean value: 24.301
Median: 24.300
Standard deviation 1.708
Rel. st. deviation (%) 7.030

Results in decreasing order:

3	29.000	(*)	36	24.300
132	28.650	(*)	15	24.300
10	27.420		112	24.240
121	27.000		159	24.100
2	26.850		117	24.030
160	26.580		4	24.000
24	26.500		5	23.730
146	26.364		118	23.300
31	25.940		8	23.000
125	25.400		120	23.000
115	25.300		38	23.000
144	25.100		110	22.900
161	25.100		174	22.650
33	25.000		108	22.100
1	25.000		23	22.000
16	25.000		39	22.000
14	24.720		6	21.000
114	24.600		169	20.700
			109 <	10

Lead
Sample no.: H4
Theoretical value: 40.000
Unit: µg/l

Run 1:
Number of laboratories: 37
Arithmetic mean value: 38.940
Median: 39.130
Standard deviation 3.238
Rel. st. deviation (%) 8.315

Run 2:
Number of laboratories: 35
Arithmetic mean value: 38.870
Median: 39.130
Standard deviation 2.662
Rel. st. deviation (%) 6.848

Results in decreasing order:

10	48.330	(*)	114	38.800
160	44.960		159	38.700
132	42.550		108	38.600
3	42.000		120	38.000
2	41.920		4	38.000
146	41.775		174	37.800
125	41.600		118	37.700
161	41.400		5	37.080
144	41.400		8	37.000
24	40.600		38	36.600
115	40.500		110	36.400
33	40.000		117	36.220
39	40.000		23	36.000
16	40.000		36	35.800
1	40.000		6	34.970
31	39.900		169	33.100
15	39.700		121	33.000
14	39.240		109	32.000 (*)
112	39.130			

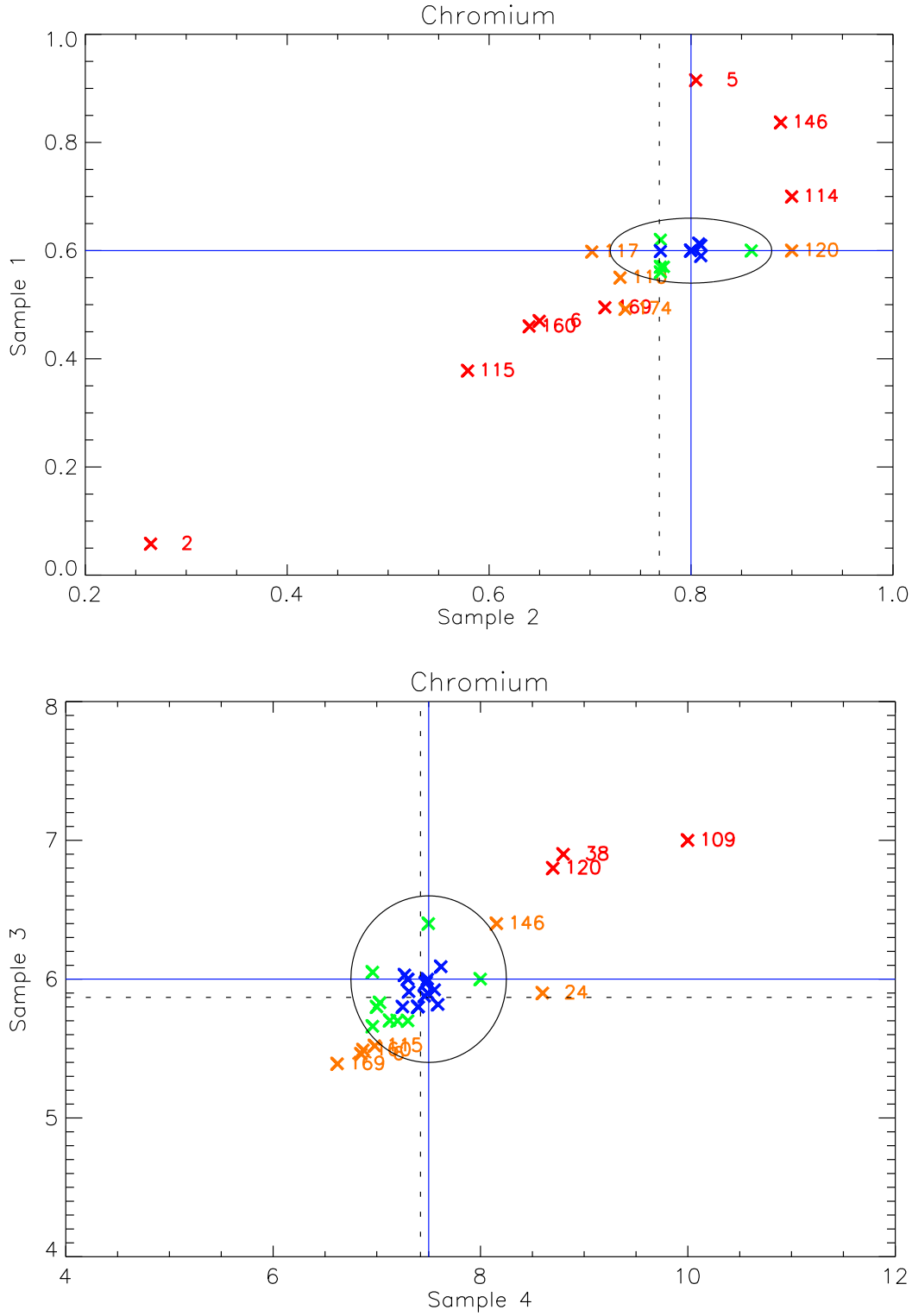

Figure 1: Youden plot of chromium, 2007.

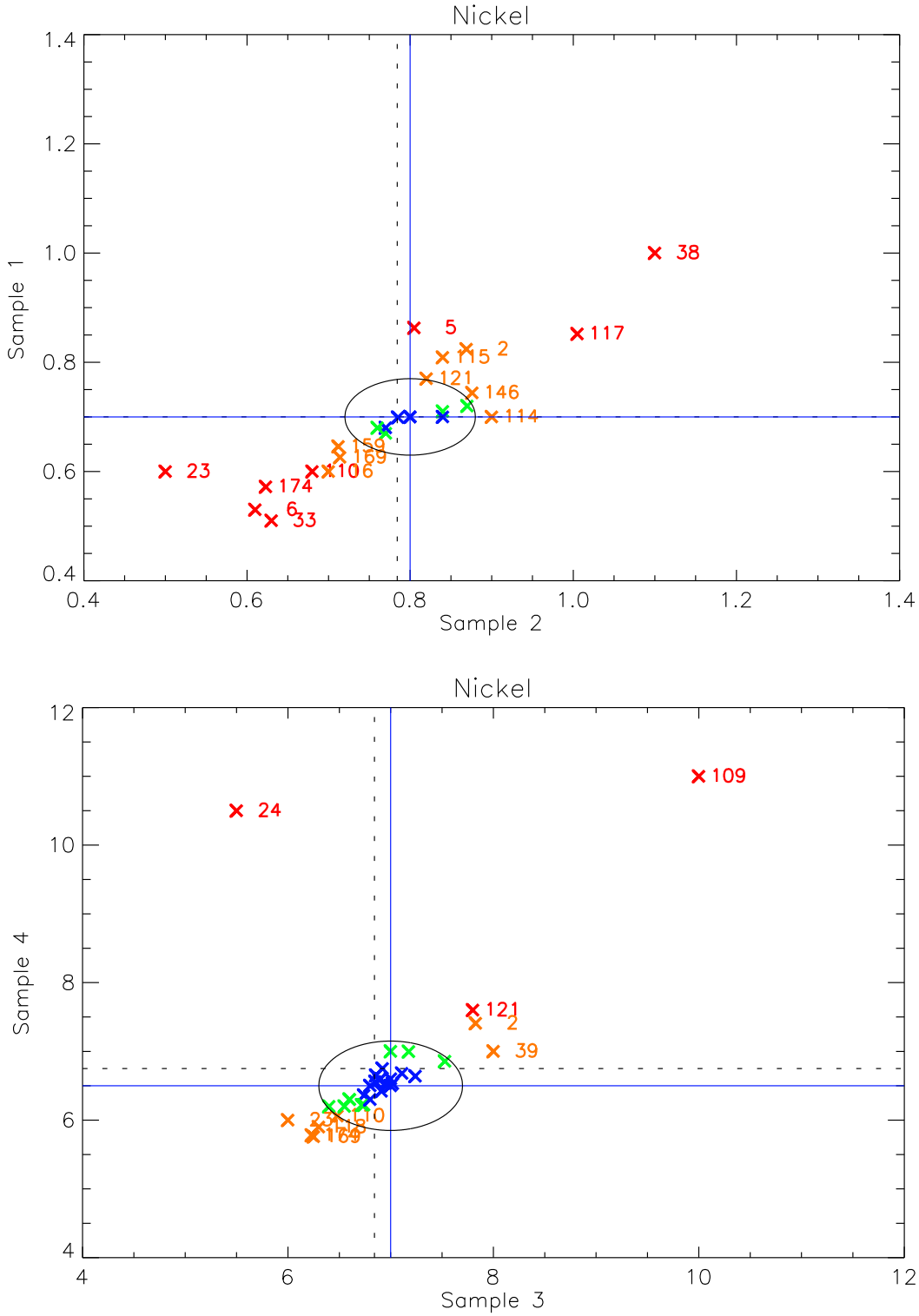

Figure.2: Youden plot of nickel, 2007.

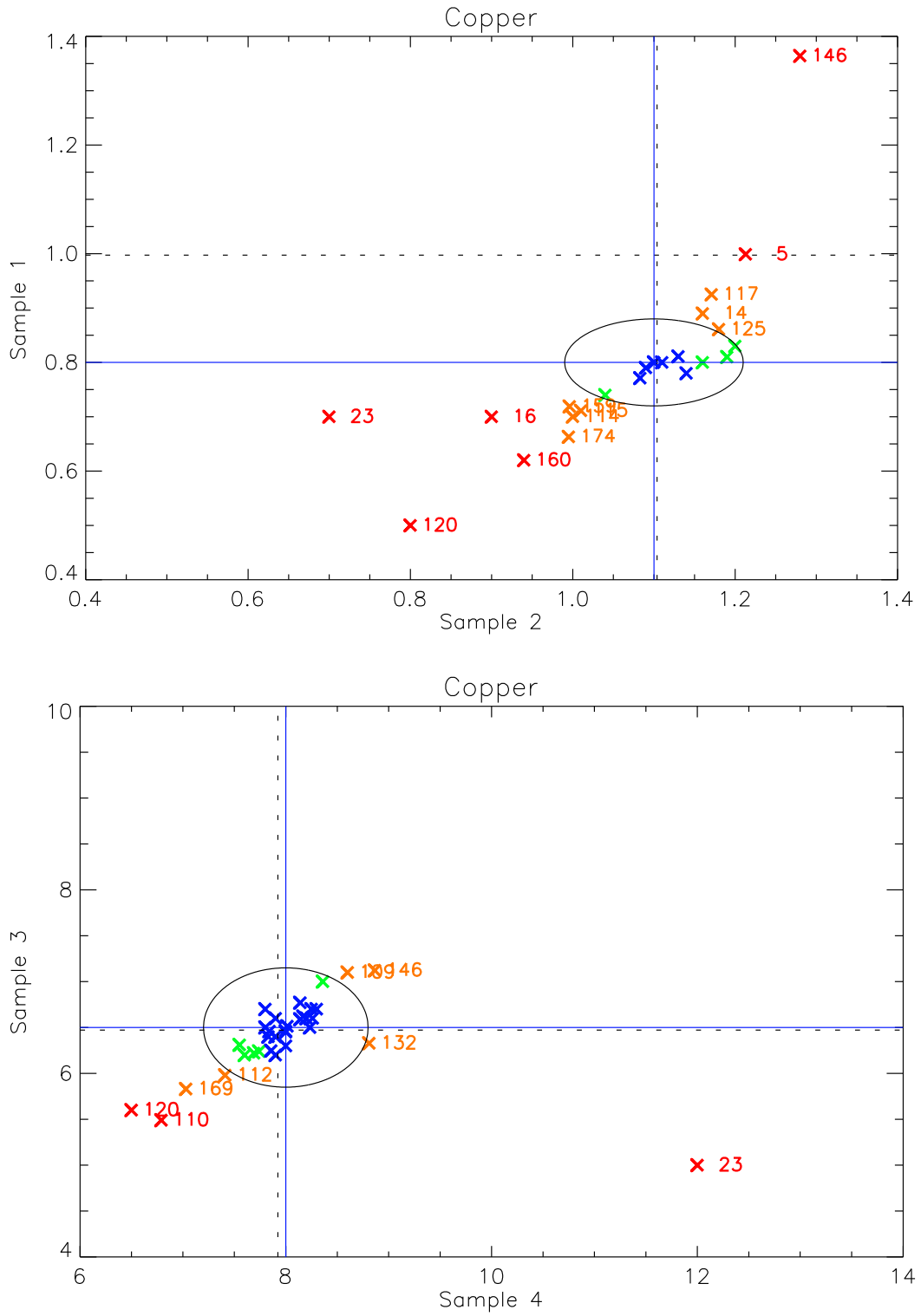

Figure.3: Youden plot of copper, 2007.

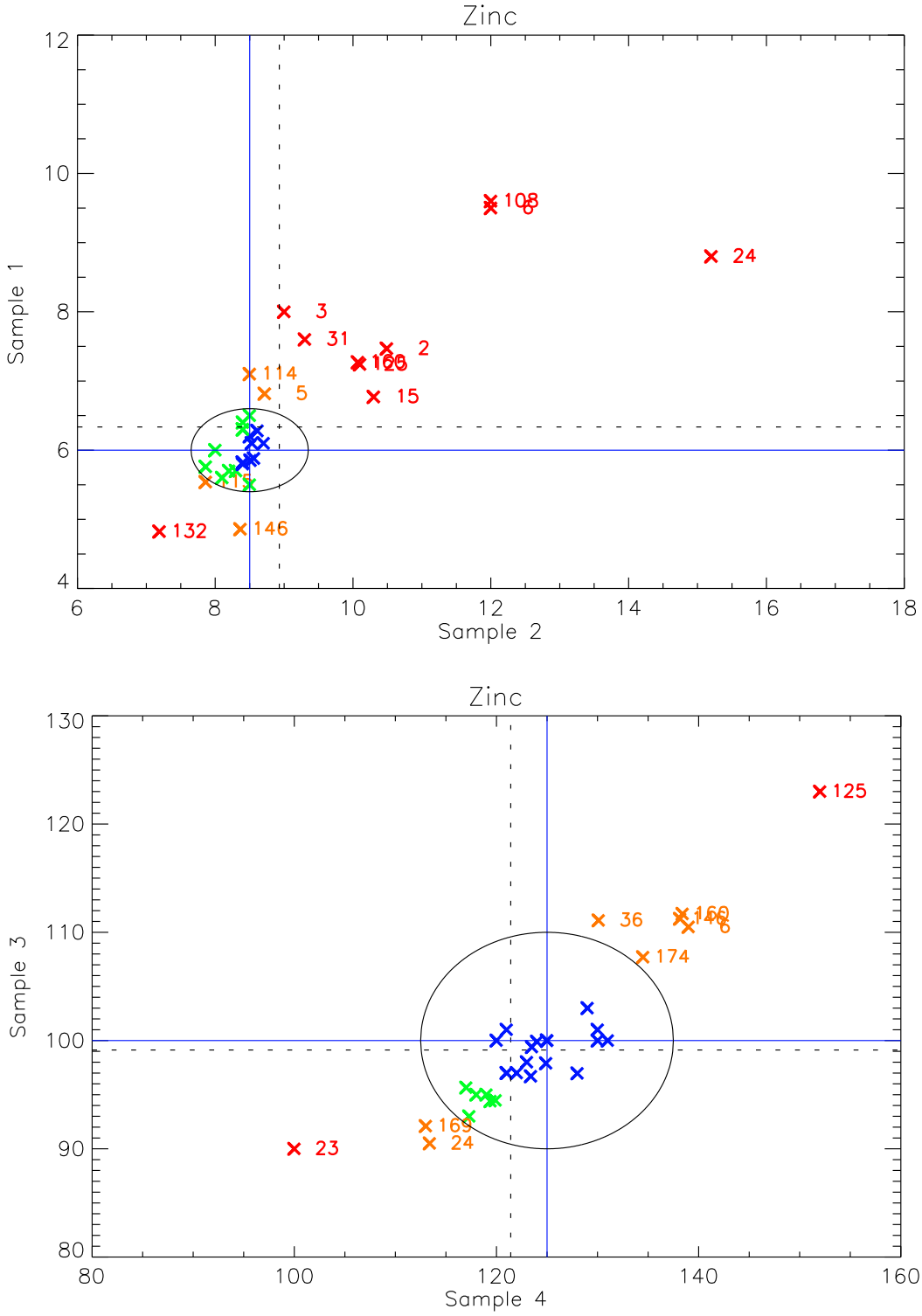

Figure.4: Youden plot of zinc, 2007.

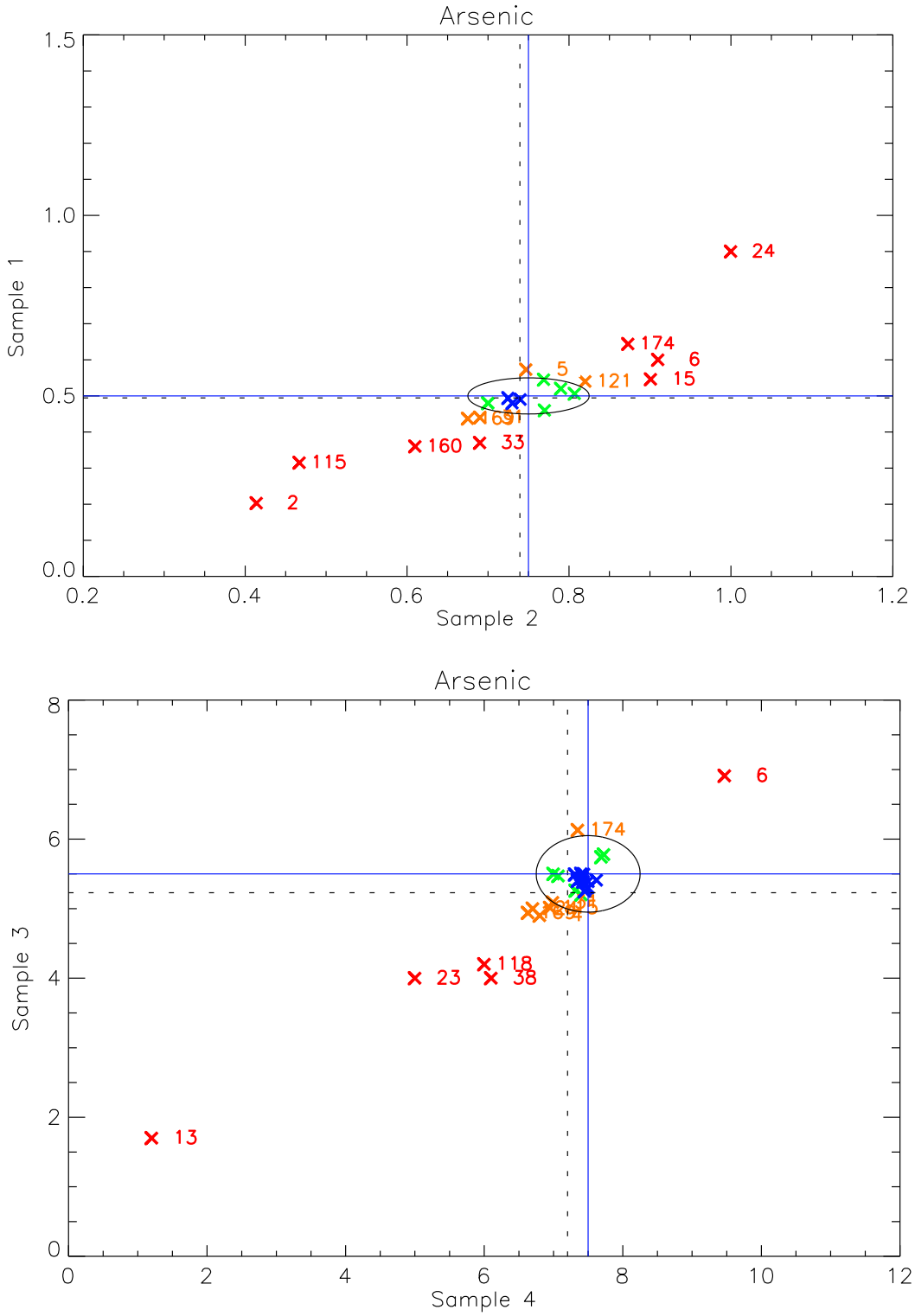

Figure.5: Youden plot of arsenic, 2007.

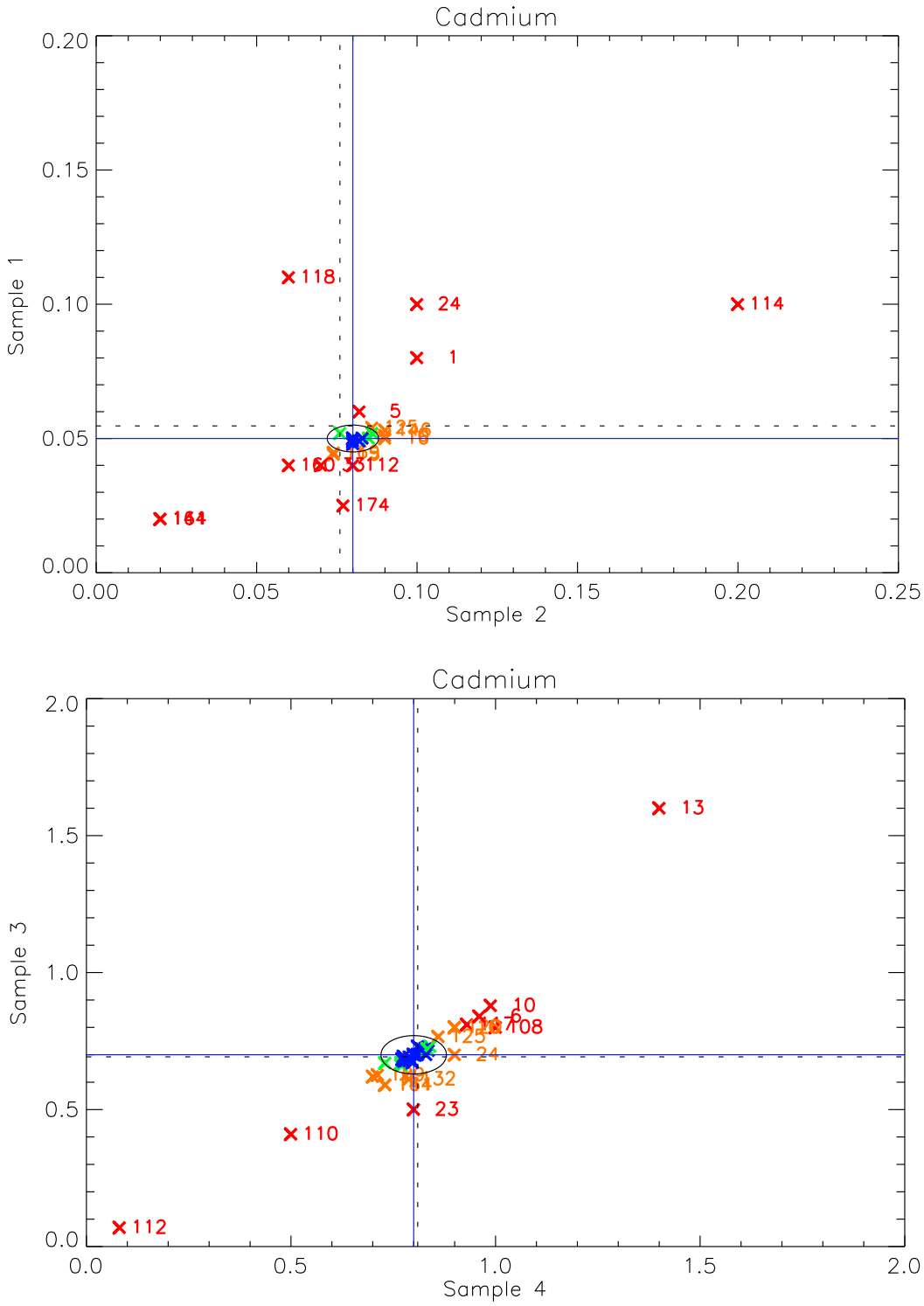

Figure 6: Youden plot of cadmium, 2007.

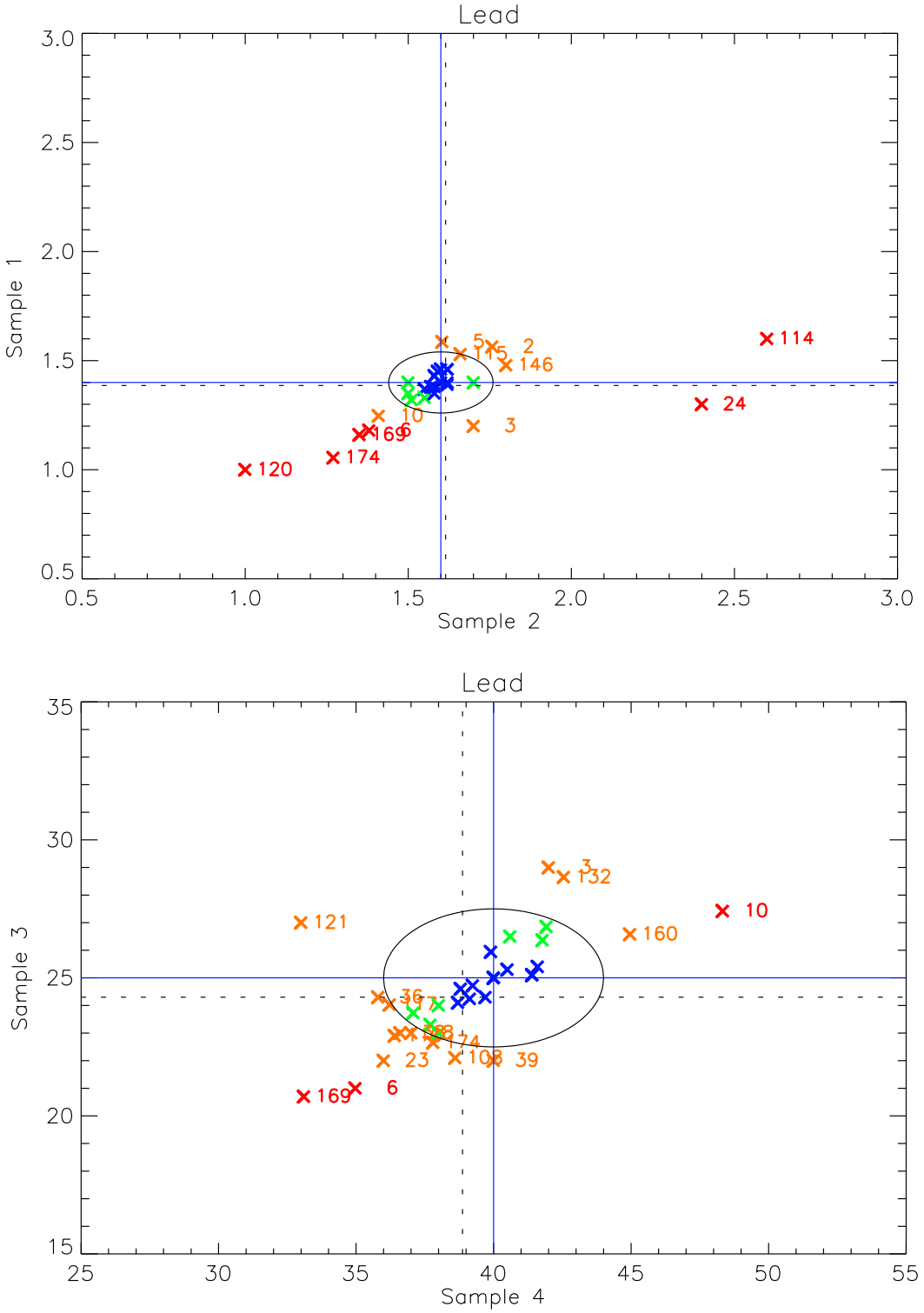

Figure 7: Youden plot of lead, 2007.