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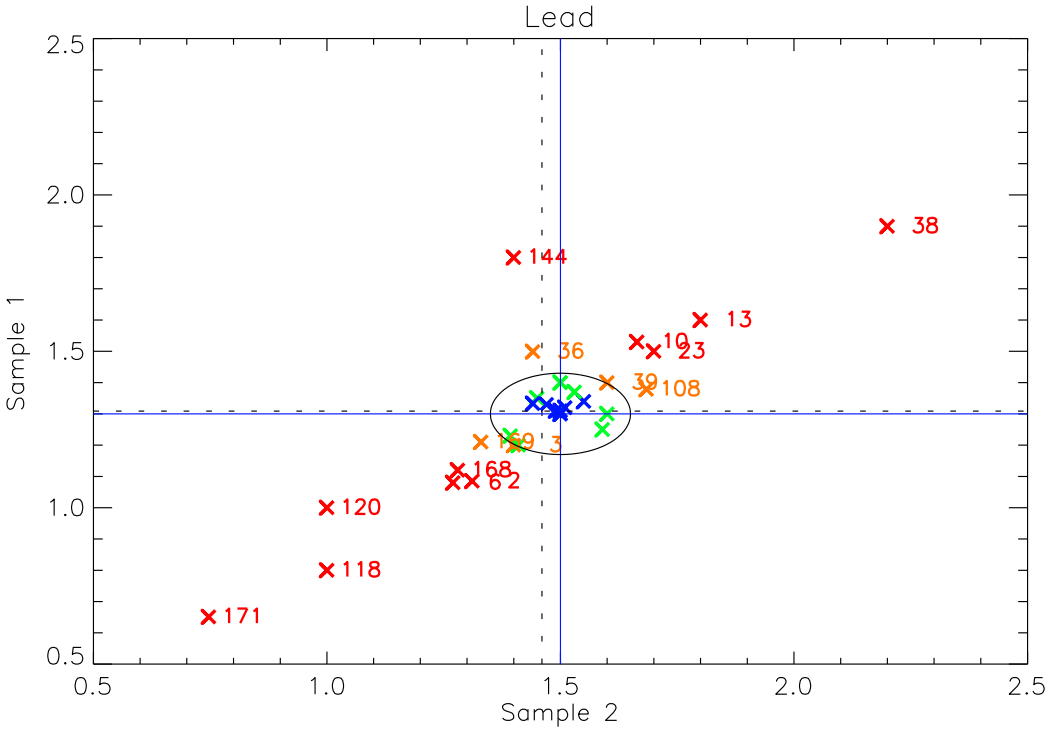
EMEP Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe

Analytical intercomparison of heavy metals in precipitation, 2008

Hilde Thelle Uggerud and Anne-Gunn Hjellbrekke



Youden plot of lead, 2008

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1. Analytical intercomparison of heavy metals in precipitation, 2008

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 ten intercomparisons have been arranged (Berg and Semb, 1995; Berg and Aas, 2000; Uggerud and Skjelmoen, 2001, 2002, 2003; Uggerud and Hjellbrekke, 2005,2006, 2007, 2008).

The present report presents results from the eleventh analytical intercomparison of heavy metals in precipitation, which was carried out during 2008. Seven heavy metals were included: Pb, Cd, Cu, Zn, As, Cr, and Ni.

1.2 Organization of the intercomparison

The samples for the eleventh intercomparison were prepared and distributed to 51 laboratories in July 2008.

A total of 36 laboratories, 19 from the EMEP network, reported results within the end of November 2008. 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. 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 equipments 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 5-11 and Figures1-7. 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 deviates more than two standard deviations from the mean value. Outliers occur for all samples and all parameters. Even so, more than 93% of the results reported for each parameter were acceptable. Out of a total of 880 single results, 46 are defined as outliers. This is about 5% of the reported data, which is comparable to earlier intercomparisons.

2. References

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Appendix 1

Tables and figures, 2008

Table 2a: Participating laboratories in the EMEP network, 2008. 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, 2008. 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
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	Dept. Of Chemistry, Environmental Health Division, Malaysia
132	Comision Chilena De Energia Nuclear, Chile
141	Pollutants Chemical Analysis Centre, Marine Division, Japan
144	National Institute of Chemistry, Slovenia
157	Ecological laboratory of Forest Research Institute, Hungary
159	CARSO, France
168	Universite de Bretagne Occidentale, France
169	Lancaster Environment Centre, Centre for Ecology &Hydrology, UK
171	Ecole de Mines de Douai, Departement Chimie et Environment, France

Table 3: Analytical techniques used at the participating laboratories for the different elements, 2008.

Lab no.	As	Cd	Cr	Cu	Pb	Ni	Zn
1	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
2	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	ICP-MS
3	ICP-MS	GF-AAS	ICP-MS	ICP-MS	GF-AAS	GF-AAS	F-AAS
4	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	
5	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
6	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
8	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
10		GF-AAS			GF-AAS		
13		AS voltammetry		AS voltammetry	AS voltammetry		AS voltammetry
14	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
15	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
16		GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS, H3, H4 – F-AAS
23	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
24	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
31	HG-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	F-AAS
33	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
36	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
38	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	F-AAS
39	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	F-AAS
108	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
109		ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES
110	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
112		GF-AAS	ICP-AES	ICP-AES	GF-AAS	ICP-AES	ICP-AES
114	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES
115	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
118	ICP-AES	GF-AAS	ICP-AES	ICP-AES	GF-AAS	GF-AAS	ICP-AES
120		GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	ICP-AES
125		ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
127	Hydrid-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	ICP-AES, Voltammetrie (H1, H2)
132	ICP-MS	ICP-MS	ICP-MS		ICP-MS	ICP-MS	ICP-MS
141		GF-AAS					
144	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
157		ICP-AES		ICP-AES	ICP-AES	ICP-AES	ICP-AES
159	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
168	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS
169	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
171	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS

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

	Arsenic				Cadmium				Chromium				Copper				Lead				Nickel				Zinc			
Lab no	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	3	0	8	8	0	-16	3	1	4	5	2	0	1	0	-1	-1	1	0	2	1	-3	-6	1	1	2	1	2	1
2	-7	-18	-5	-6	42	4	3	4	-5	-10	0	-1	< 1	< 1	-8	-8	-17	-13	9	5	-15	-5	-1	1	-9	-12	-15	-13
3	0	0	-4	-5	-8	0	-3	-4	0	0	-8	-8	0	-8	-7	-7	-8	-7	4	0	< 1	< 1	0	0	< 9	< 9	0	0
4	< 1.5	< 1.5	-14	-20	< 0.35	< 0.35	-10	-1	< 2.0	< 2.0	4	3	< 2.5	< 2.5	-8	-7	< 3	< 3	-4	-3	< 3	< 3	-4	-7				
5	-10	-13	-14	-14	-7	-10	-10	-10	-27	-40	-14	-15	0	-5	-7	-8	-5	-7	-10	-11	-7	-9	-8	-8	0	-3	-8	-8
6	10	10	9	10	167	157	22	19	-3	-3	-1	-2	-4	-3	0	0	-17	-15	-31	-28	-7	-4	-1	-2	30	25	5	5
8	-4	-2	-2	-3	-8	-7	-5	-4	-3	-2	-4	-4	-10	-1	-5	-5	-8	-6	-8	-9	-7	-7	-5	-6	-4	-1	-3	-3
10					-20	-40	1	4									18	11	-10	-13								
13					-17	0	-33	-19					14	-4	36	28	23	20	-13	-7					29	17	-4	-8
14	5	16	2	-1	8	39	7	0	-10	-10	6	-6	11	-1	0	-6	3	3	1	2	3	3	3	-3	11	10	2	-2
15	7	-2	0	-2	0	7	2	3	0	-2	-1	-9	-1	-7	2	-2	1	-1	7	1	-15	7	-6	-11	-7	-7	1	2
16					0	-7	-8	-7	0	0	0	0	0	-50	0	0	0	0	-13	-14	0	0	0	0	0	0	0	-3
23	-17	-20	-2	-3	17	29	18	0			0	-17			7	11	15	13	-4	-3			0	-22				
24	17	20	26	22	0	0	8	7	-43	-50	10	10	43	17	33	58	0	7	7	8	33	29	28	24	24	24	26	24
31	0	0	0	-1	0	-7	2	1	3	3	-1	-1	1	-2	-7	-3	4	-3	-5	-6	12	13	0	2	9	14	-5	-12
33	3	4	5	3	0	0	7	4	0	-3	6	5	0	0	5	3	0	0	5	3	3	0	5	4	-2	-3	0	-1
36	2	6	3	3	3	-10	-2	0	-10	-11	-3	-3	2	-3	-2	-2	15	-4	-6	-6	-11	-14	-2	-1	15	6	14	14
38	< 1	< 1	-28	-33	< 1	< 1	0	0	< 1	< 1	-6	-2	< 1	17	4	4	46	47	-1	3	< 1	< 1	-23	-28	< 10	< 10	-5	-8
39					17	14	0	0	0	0	0	0	14	-8	0	0	8	7	0	0	17	14	0	0			1	-1
108	-99	-99	-99	-99	-3	1	-6	-10	-8	-7	-10	-12	0	37	-2	-10	6	12	5	0	-6	12	-4	-8	-12	4	-9	-13
109					< 0.1	< 0.1	< 0.1	-39	49	< 0.1	-10	-8	701	423	73	51	< 1	< 1	-2	1	< 0.1	< 0.1	-16	-7	16	10	3	3
110	-12	< 0.5	-5	-6	< 0.2	< 0.2	-22	-16	-14	-18	-10	-11	20	-11	-8	-10	2	-2	-4	-4	-7	-9	-2	-3	-6	-8	-1	-2
112					3	-6	0	1	1	0	1	1	-5	4	-5	-6	3	-4	-1	0	-15	-13	1	2	5	2	0	1
114	233	300	0	-67	67	43	-17	-14	0	0	-10	-17	-14	-17	-7	-11			0	3	0	0	-10	-14	27	26	-3	-4
115	-16	-18	-2	-2	-12	-7	2	3	-11	-11	-5	-5	-2	0	-2	-3	5	2	5	5	-3	-3	-3	-3	4	7	6	4
118	0	20	0	-12	-33	-14	3	0	-29	-50	-12	-12	-43	-33	-16	-14	-38	-33	-5	-6	-67	-57	-13	-12	-11	-11	-7	-8
120	17	-20	8	3	-267	-243	-17	0	-29	-67	-4	-2	-43	-33	-19	-17	-23	-33	-4	-6			-13	0	27	14	1	1
121	17	20	-4	-3	0	0	-5	-11	0	0	-2	3	-14	-8	-12	-11	8	0	0	3			6	10	-4	-1	10	11
125	5	3	4	0	10	6	4	3	0	-6	4	4	4	9	2	-1	2	1	1	-1	15	1	3	1	5	3	0	1
127	17	20	-4	-3	0	0	-5	-11	0	0	-2	3	-14	-8	-12	-11	8	0	0	3	< 0.5	< 0.5	6	10	-4	-1	10	11
132	< 1	< 1	20	18	< 1	<1	1833	< 1	< 1	< 1	32	10					< 1	< 1	15	5	< 1	< 1	18	3	< 10	< 10	81	4
141					-10	-10	0	-1																				
144	50	-40	-2	-2	< 0.3	< 0.3	-50	-43	43	< 0.3	-18	-10	71	-17	-8	-6	38	-7	-4	-5	67	-29	-10	-8	15	0	-1	-3
157																												
159	5	3	-4	-7	-28	-30	-11	-11	-15	-18	-3	-6	-7	-5	-2	-5	-4	6	2	0	-20	-4	-4	-6	2	2	0	-12
168	-22	-32	-43	-43	-17	0	-2	-4	-7	-15	-21	-21	-9	-13	-12	-13	-14	-15	-5	-8	35	49	-6	-7	-20	-18	5	-2
169	-10	-12	-9	-10	-7	-10	-9	-9	-23	-24	-6	-6	-7	-8	-8	-8	-7	-11	-8	-9	-10	-11	-9	-10	-3	-7	-7	-8
171	-49	-50	-50	-50	-47	-47	-48	-49	-50	-49	-49	-49	-46	-48	-48	-46	-50	-50	-51	-50	-48	-49	-49	-48	-47	-48	-49	-47

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, 2008.

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

Run 1:
Number of laboratories: 30
Arithmetic mean value: 0.656
Median: 0.680
Standard deviation 0.137
Rel. st. deviation (%) 20.944

Run 2:
Number of laboratories: 27
Arithmetic mean value: 0.641
Median: 0.680
Standard deviation 0.084
Rel. st. deviation (%) 13.116

Results in decreasing order:

109	1.040 (*)	8	0.680	
144	1.000 (*)	2	0.663	
1	0.730	168	0.650	
31	0.720	108	0.646	
112	0.706	36	0.630	
125	0.703	14	0.630	
39	0.700	115	0.620	
3	0.700	110	0.600	
114	0.700	159	0.592	
121	0.700	169	0.539	
127	0.700	5	0.511	
15	0.700	118	0.500	
16	0.700	120	0.500	
33	0.700	24	0.400	
6	0.680	171	0.352	(*)

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

Run 1:
Number of laboratories: 28
Arithmetic mean value: 0.517
Median: 0.560
Standard deviation 0.116
Rel. st. deviation (%) 22.454

Run 2:
Number of laboratories: 27
Arithmetic mean value: 0.529
Median: 0.563
Standard deviation 0.100
Rel. st. deviation (%) 18.901

Results in decreasing order:

1	0.630	108	0.558	
31	0.620	14	0.540	
3	0.600	2	0.539	
121	0.600	36	0.537	
16	0.600	115	0.535	
114	0.600	168	0.510	
39	0.600	159	0.493	
127	0.600	110	0.490	
112	0.598	169	0.455	
15	0.590	5	0.358	
8	0.590	171	0.309	
33	0.580	24	0.300	
6	0.580	118	0.300	
125	0.563	120	0.200	(*)

Chromium
Sample no.: 3
Theoretical value: 5.000
Unit: µg/l

Run 1:
Number of laboratories: 34
Arithmetic mean value: 4.804
Median: 4.880
Standard deviation 0.599
Rel. st. deviation (%) 12.480

Run 2:
Number of laboratories: 32
Arithmetic mean value: 4.818
Median: 4.880
Standard deviation 0.346
Rel. st. deviation (%) 7.178

Results in decreasing order:

132	6.580 (*)	159	4.860	
24	5.500	36	4.826	
14	5.320	8	4.820	
33	5.290	120	4.800	
125	5.200	115	4.760	
4	5.200	38	4.700	
1	5.100	169	4.700	
112	5.038	3	4.600	
16	5.000	110	4.520	
39	5.000	109	4.510	
23	5.000	108	4.509	
2	4.996	114	4.500	
15	4.960	118	4.400	
31	4.950	5	4.291	
6	4.950	144	4.100	
127	4.900	168	3.970	
121	4.900	171	2.570	(*)

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

Run 1:
Number of laboratories: 34
Arithmetic mean value: 5.672
Median: 5.789
Standard deviation 0.635
Rel. st. deviation (%) 11.195

Run 2:
Number of laboratories: 33
Arithmetic mean value: 5.750
Median: 5.838
Standard deviation 0.449
Rel. st. deviation (%) 7.800

Results in decreasing order:

24	6.600	8	5.740	
132	6.580	115	5.710	
33	6.290	159	5.650	
125	6.220	14	5.620	
121	6.200	169	5.610	
4	6.200	109	5.520	
127	6.200	3	5.500	
112	6.054	15	5.450	
1	6.000	144	5.400	
16	6.000	110	5.320	
39	6.000	118	5.300	
31	5.960	108	5.265	
2	5.958	5	5.130	
120	5.900	114	5.000	
38	5.900	23	5.000	
6	5.880	168	4.770	
36	5.838	171	3.090	(*)

Table 6: Analytical results for Ni in synthetic precipitation samples, 2008.

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

Run 1:
Number of laboratories: 26
Arithmetic mean value: 12.065
Median: 0.572
Standard deviation 58.524
Rel. st. deviation (%) 485.090

Run 2:
Number of laboratories: 25
Arithmetic mean value: 0.587
Median: 0.564
Standard deviation 0.153
Rel. st. deviation (%) 26.044

Results in decreasing order:

157	299.000 (*)	108	0.564
144	1.000	110	0.560
168	0.810	5	0.560
24	0.800	6	0.560
39	0.700	8	0.560
125	0.690	169	0.538
31	0.670	36	0.535
33	0.620	112	0.511
14	0.620	15	0.510
16	0.600	2	0.510
114	0.600	159	0.482
115	0.585	171	0.312
1	0.580	118	0.200

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

Run 1:
Number of laboratories: 26
Arithmetic mean value: 18.956
Median: 0.673
Standard deviation 93.219
Rel. st. deviation (%) 491.767

Run 2:
Number of laboratories: 25
Arithmetic mean value: 0.674
Median: 0.670
Standard deviation 0.147
Rel. st. deviation (%) 21.857

Results in decreasing order:

157	476.000 (*)	159	0.670
168	1.040	6	0.670
24	0.900	2	0.662
39	0.800	1	0.660
31	0.790	8	0.650
108	0.783	110	0.640
15	0.750	5	0.638
14	0.720	169	0.620
125	0.709	112	0.611
33	0.700	36	0.605
114	0.700	144	0.500
16	0.700	171	0.360
115	0.677	118	0.300

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

Run 1:
Number of laboratories: 35
Arithmetic mean value: 16.363
Median: 7.877
Standard deviation 51.102
Rel. st. deviation (%) 312.310

Run 2:
Number of laboratories: 34
Arithmetic mean value: 7.726
Median: 7.854
Standard deviation 0.959
Rel. st. deviation (%) 12.417

Results in decreasing order:

157	310.000 (*)	110	7.830
24	10.200	115	7.760
132	9.430	159	7.720
127	8.500	4	7.700
121	8.500	108	7.643
33	8.400	8	7.590
14	8.230	15	7.500
125	8.220	168	7.490
112	8.109	5	7.381
1	8.100	169	7.290
23	8.000	144	7.200
16	8.000	114	7.200
31	8.000	120	7.000
39	8.000	118	7.000
3	8.000	109	6.730
6	7.900	38	6.200
2	7.884	171	4.110
36	7.877		

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

Run 1:
Number of laboratories: 35
Arithmetic mean value: 20.514
Median: 8.730
Standard deviation 70.563
Rel. st. deviation (%) 343.979

Run 2:
Number of laboratories: 34
Arithmetic mean value: 8.588
Median: 8.730
Standard deviation 1.074
Rel. st. deviation (%) 12.510

Results in decreasing order:

157	426.000 (*)	115	8.730
24	11.200	14	8.700
127	9.900	8	8.470
121	9.900	159	8.470
33	9.350	4	8.400
132	9.290	168	8.380
112	9.166	109	8.330
31	9.150	144	8.300
2	9.130	108	8.299
1	9.100	5	8.255
125	9.070	169	8.140
3	9.000	15	8.000
120	9.000	118	7.900
16	9.000	114	7.700
39	9.000	23	7.000
36	8.907	38	6.500
6	8.840	171	4.680
110	8.730		

Table 7: Analytical results for Cu in synthetic precipitation samples, 2008.

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

Run 1:
Number of laboratories: 30
Arithmetic mean value: 0.855
Median: 0.700
Standard deviation 0.912
Rel. st. deviation (%) 106.631

Run 2:
Number of laboratories: 29
Arithmetic mean value: 0.691
Median: 0.699
Standard deviation 0.160
Rel. st. deviation (%) 23.128

Results in decreasing order:

109	5.610 (*)	108	0.699	
144	1.200	15	0.690	
24	1.000	115	0.685	
110	0.840	6	0.670	
39	0.800	112	0.664	
13	0.800	169	0.654	
14	0.774	159	0.651	
125	0.728	168	0.640	
36	0.717	8	0.630	
1	0.710	127	0.600	
31	0.710	114	0.600	
5	0.703	121	0.600	
16	0.700	118	0.400	
3	0.700	120	0.400	
33	0.700	171	0.375	

Copper
Sample no.: 2
Theoretical value: 1.200
Unit: µg/l

Run 1:
Number of laboratories: 31
Arithmetic mean value: 1.282
Median: 1.145
Standard deviation 0.949
Rel. st. deviation (%) 73.966

Run 2:
Number of laboratories: 30
Arithmetic mean value: 1.116
Median: 1.143
Standard deviation 0.210
Rel. st. deviation (%) 18.859

Results in decreasing order:

109	6.270 (*)	159	1.140	
108	1.649	15	1.110	
38	1.400	121	1.100	
24	1.400	39	1.100	
125	1.310	127	1.100	
112	1.250	3	1.100	
1	1.200	169	1.100	
115	1.200	110	1.070	
33	1.200	168	1.050	
8	1.190	114	1.000	
14	1.184	144	1.000	
31	1.180	118	0.800	
36	1.169	120	0.800	
6	1.160	171	0.626	
13	1.150	16	0.600	
5	1.145			

Copper
Sample no.: 3
Theoretical value: 7.500
Unit: µg/l

Run 1:
Number of laboratories: 34
Arithmetic mean value: 7.405
Median: 7.229
Standard deviation 1.415
Rel. st. deviation (%) 19.107

Run 2:
Number of laboratories: 32
Arithmetic mean value: 7.340
Median: 7.229
Standard deviation 0.849
Rel. st. deviation (%) 11.565

Results in decreasing order:

109	13.000 (*)	8	7.120	
13	10.200	112	7.110	
24	10.000	114	7.000	
23	8.000	3	7.000	
33	7.900	31	6.980	
38	7.800	5	6.969	
15	7.650	110	6.910	
125	7.650	169	6.910	
6	7.510	144	6.900	
16	7.500	4	6.900	
39	7.500	2	6.883	
14	7.473	121	6.600	
1	7.400	168	6.600	
115	7.380	127	6.600	
159	7.350	118	6.300	
108	7.341	120	6.100	
36	7.339	171	3.900 (*)	

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

Run 1:
Number of laboratories: 34
Arithmetic mean value: 8.831
Median: 8.515
Standard deviation 1.611
Rel. st. deviation (%) 18.239

Run 2:
Number of laboratories: 31
Arithmetic mean value: 8.631
Median: 8.500
Standard deviation 0.751
Rel. st. deviation (%) 8.699

Results in decreasing order:

24	14.200 (*)	144	8.500	
109	13.620 (*)	112	8.491	
13	11.500	14	8.484	
23	10.000	3	8.400	
38	9.400	4	8.400	
33	9.300	5	8.287	
39	9.000	2	8.266	
16	9.000	169	8.240	
6	8.980	110	8.120	
125	8.950	108	8.106	
1	8.900	127	8.000	
36	8.859	114	8.000	
15	8.810	121	8.000	
115	8.760	168	7.840	
31	8.700	118	7.700	
8	8.530	120	7.500	
159	8.530	171	4.870 (*)	

Table 8: Analytical results for Zn in synthetic precipitation samples, 2008.

Zinc
Sample no.: 1
Theoretical value: 5.500
Unit: µg/l

Run 1:
Number of laboratories: 29
Arithmetic mean value: 5.675
Median: 5.600
Standard deviation 0.905
Rel. st. deviation (%) 15.947

Run 2:
Number of laboratories: 28
Arithmetic mean value: 5.775
Median: 5.615
Standard deviation 0.744
Rel. st. deviation (%) 12.876

Results in decreasing order:

6	7.170	16	5.500	
13	7.100	5	5.476	
114	7.000	33	5.400	
120	7.000	169	5.350	
24	6.800	121	5.300	
109	6.360	8	5.300	
144	6.300	127	5.300	
36	6.298	110	5.170	
14	6.100	15	5.110	
31	6.000	2	4.999	
125	5.790	118	4.900	
112	5.775	108	4.843	
115	5.710	168	4.410	
159	5.630	171	2.895	(*)
1	5.600			

Zinc
Sample no.: 2
Theoretical value: 7.000
Unit: µg/l

Run 1:
Number of laboratories: 29
Arithmetic mean value: 7.107
Median: 7.100
Standard deviation 1.013
Rel. st. deviation (%) 14.246

Run 2:
Number of laboratories: 28
Arithmetic mean value: 7.230
Median: 7.105
Standard deviation 0.780
Rel. st. deviation (%) 10.785

Results in decreasing order:

114	8.800	16	7.000	
6	8.730	144	7.000	
24	8.700	127	6.900	
13	8.200	8	6.900	
31	8.000	121	6.900	
120	8.000	33	6.800	
14	7.700	5	6.774	
109	7.670	15	6.530	
115	7.490	169	6.510	
36	7.413	110	6.450	
108	7.304	118	6.200	
125	7.210	2	6.180	
112	7.147	168	5.730	
159	7.110	171	3.663	(*)
1	7.100			

Zinc
Sample no.: 3
Theoretical value: 110.000
Unit: µg/l

Run 1:
Number of laboratories: 33
Arithmetic mean value: 111.699
Median: 110.000
Standard deviation 19.957
Rel. st. deviation (%) 17.867

Run 2:
Number of laboratories: 31
Arithmetic mean value: 110.666
Median: 110.000
Standard deviation 8.236
Rel. st. deviation (%) 7.442

Results in decreasing order:

132	199.000	125	110.000	
24	138.500	16	110.000	
36	124.900	159	110.000	
127	121.000	144	109.000	
121	121.000	110	109.000	
115	116.100	114	107.000	
6	116.000	8	107.000	
168	115.100	13	106.000	
109	113.530	31	105.000	
14	112.200	38	104.000	
1	112.000	118	102.000	
120	111.000	169	102.000	
15	111.000	5	101.607	
39	111.000	108	100.472	
112	110.448	2	93.800	
33	110.000	171	56.420	(*)
3	110.000			

Zinc
Sample no.: 4
Theoretical value: 120.000
Unit: µg/l

Run 1:
Number of laboratories: 33
Arithmetic mean value: 117.289
Median: 118.200
Standard deviation 13.456
Rel. st. deviation (%) 11.473

Run 2:
Number of laboratories: 31
Arithmetic mean value: 118.006
Median: 118.200
Standard deviation 8.127
Rel. st. deviation (%) 6.887

Results in decreasing order:

24	148.300	110	118.000	
36	136.500	14	117.900	
121	133.000	144	117.000	
127	133.000	16	117.000	
6	125.500	8	116.000	
132	125.000	114	115.000	
115	124.800	169	111.000	
109	123.570	13	111.000	
15	122.000	38	111.000	
120	121.000	5	110.062	
1	121.000	118	110.000	
125	121.000	31	106.000	
112	120.928	159	106.000	
3	120.000	108	104.636	
39	119.000	2	104.100	
33	119.000	171	64.040	(*)
168	118.200			

Table 9: Analytical results for As in synthetic precipitation samples, 2008.

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

Run 1:
Number of laboratories: 27
Arithmetic mean value: 0.632
Median: 0.613
Standard deviation 0.314
Rel. st. deviation (%) 49.614

Run 2:
Number of laboratories: 26
Arithmetic mean value: 0.580
Median: 0.607
Standard deviation 0.157
Rel. st. deviation (%) 27.108

Results in decreasing order:

114	2.000 (*)	118	0.600
144	0.900	3	0.600
24	0.700	31	0.600
127	0.700	8	0.577
121	0.700	2	0.558
120	0.700	5	0.542
6	0.660	169	0.539
15	0.640	110	0.530
14	0.630	115	0.507
125	0.629	23	0.500
159	0.629	168	0.470
1	0.620	171	0.306
33	0.620	108	0.006
36	0.613		

Arsenic
Sample no.: H2
Theoretical value: 0.500
Unit: µg/l

Run 1:
Number of laboratories: 26
Arithmetic mean value: 0.518
Median: 0.500
Standard deviation 0.329
Rel. st. deviation (%) 63.535

Run 2:
Number of laboratories: 25
Arithmetic mean value: 0.459
Median: 0.500
Standard deviation 0.133
Rel. st. deviation (%) 29.081

Results in decreasing order:

114	2.000 (*)	3	0.500
118	0.600	8	0.491
24	0.600	15	0.490
127	0.600	169	0.439
121	0.600	5	0.437
14	0.580	115	0.409
6	0.550	2	0.408
36	0.529	23	0.400
33	0.520	120	0.400
159	0.517	168	0.340
125	0.513	144	0.300
1	0.500	171	0.248
31	0.500	108	0.005

Arsenic
Sample no.: H3
Theoretical value: 5.000
Unit: µg/l

Run 1:
Number of laboratories: 30
Arithmetic mean value: 4.658
Median: 4.905
Standard deviation 1.153
Rel. st. deviation (%) 24.761

Run 2:
Number of laboratories: 29
Arithmetic mean value: 4.817
Median: 4.910
Standard deviation 0.770
Rel. st. deviation (%) 15.988

Results in decreasing order:

24	6.300	23	4.900	
132	5.980	144	4.900	
6	5.430	159	4.810	
120	5.400	3	4.800	
1	5.400	121	4.800	
33	5.240	127	4.800	
125	5.190	2	4.773	
36	5.156	110	4.750	
14	5.100	169	4.550	
15	5.010	5	4.312	
118	5.000	4	4.300	
31	5.000	38	3.600	
114	5.000	168	2.840	
115	4.920	171	2.510	
8	4.910	108	0.050	(*)

Arsenic
Sample no.: H4
Theoretical value: 6.000
Unit: µg/l

Run 1:
Number of laboratories: 30
Arithmetic mean value: 5.351
Median: 5.800
Standard deviation 1.500
Rel. st. deviation (%) 28.038

Run 2:
Number of laboratories: 28
Arithmetic mean value: 5.659
Median: 5.815
Standard deviation 0.930
Rel. st. deviation (%) 16.433

Results in decreasing order:

24	7.300	127	5.800	
132	7.070	121	5.800	
6	6.570	3	5.700	
1	6.500	2	5.660	
120	6.200	110	5.630	
33	6.180	159	5.600	
36	6.169	169	5.420	
125	5.980	118	5.300	
31	5.970	5	5.133	
14	5.930	4	4.800	
144	5.900	38	4.000	
15	5.890	168	3.440	
115	5.860	171	3.030	
8	5.830	114	2.000	(*)
23	5.800	108	0.057	(*)

Table10: Analytical results for Cd in synthetic precipitation samples, 2008.

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

Run 1:
Number of laboratories: 31
Arithmetic mean value: 0.057
Median: 0.060
Standard deviation 0.036
Rel. st. deviation (%) 63.806

Run 2:
Number of laboratories: 29
Arithmetic mean value: 0.059
Median: 0.060
Standard deviation 0.013
Rel. st. deviation (%) 21.380

Results in decreasing order:

6	0.160 (*)	16	0.060	
114	0.100	108	0.058	
2	0.085	5	0.056	
39	0.070	169	0.056	
23	0.070	3	0.055	
125	0.066	8	0.055	
14	0.065	141	0.054	
36	0.062	115	0.053	
112	0.062	13	0.050	
1	0.060	168	0.050	
127	0.060	10	0.048	
33	0.060	159	0.043	
31	0.060	118	0.040	
121	0.060	171	0.032	
24	0.060	120	-0.100	(*)
15	0.060			

Cadmium
Sample no.: 2
Theoretical value: 0.070
Unit: µg/l

Run 1:
Number of laboratories: 31
Arithmetic mean value: 0.066
Median: 0.070
Standard deviation 0.039
Rel. st. deviation (%) 58.824

Run 2:
Number of laboratories: 29
Arithmetic mean value: 0.068
Median: 0.070
Standard deviation 0.013
Rel. st. deviation (%) 19.469

Results in decreasing order:

6	0.180 (*)	112	0.066	
114	0.100	16	0.065	
14	0.097	8	0.065	
23	0.090	31	0.065	
39	0.080	115	0.065	
15	0.075	169	0.063	
125	0.074	5	0.063	
2	0.073	36	0.063	
108	0.070	141	0.063	
3	0.070	118	0.060	
121	0.070	1	0.059	
127	0.070	159	0.049	
168	0.070	10	0.042	
13	0.070	171	0.037	
24	0.070	120	-0.100	(*)
33	0.070			

Cadmium
Sample no.: 3
Theoretical value: 0.600
Unit: µg/l

Run 1:
Number of laboratories: 36
Arithmetic mean value: 0.876
Median: 0.595
Standard deviation 1.841
Rel. st. deviation (%) 210.190

Run 2:
Number of laboratories: 35
Arithmetic mean value: 0.569
Median: 0.590
Standard deviation 0.090
Rel. st. deviation (%) 15.835

Results in decreasing order:

132	11.600 (*)	168	0.590	
6	0.730	36	0.589	
23	0.710	3	0.580	
24	0.650	8	0.570	
14	0.643	121	0.570	
33	0.640	127	0.570	
125	0.626	108	0.566	
2	0.620	16	0.550	
1	0.620	169	0.547	
118	0.620	4	0.540	
115	0.614	5	0.539	
15	0.610	159	0.537	
31	0.610	114	0.500	
10	0.603	120	0.500	
112	0.602	110	0.470	
38	0.600	13	0.400	
39	0.600	171	0.310	
141	0.599	144	0.300	

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

Run 1:
Number of laboratories: 36
Arithmetic mean value: 0.658
Median: 0.694
Standard deviation 0.095
Rel. st. deviation (%) 14.453

Run 2:
Number of laboratories: 33
Arithmetic mean value: 0.682
Median: 0.700
Standard deviation 0.053
Rel. st. deviation (%) 7.793

Results in decreasing order:

6	0.830	141	0.692	
24	0.750	4	0.690	
33	0.730	3	0.670	
2	0.730	8	0.670	
10	0.727	168	0.670	
115	0.720	16	0.650	
15	0.720	169	0.637	
125	0.719	108	0.628	
1	0.710	5	0.627	
31	0.710	159	0.622	
112	0.707	121	0.620	
38	0.700	127	0.620	
39	0.700	114	0.600	
118	0.700	110	0.590	
120	0.700	13	0.570	
23	0.700	109	0.430	(*)
36	0.700	144	0.400	(*)
14	0.697	171	0.360	(*)

Table 11: Analytical results for Pb in synthetic precipitation samples, 2008.

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

Run 1:
Number of laboratories: 32
Arithmetic mean value: 1.306
Median: 1.315
Standard deviation 0.241
Rel. st. deviation (%) 18.463

Run 2:
Number of laboratories: 28
Arithmetic mean value: 1.309
Median: 1.315
Standard deviation 0.139
Rel. st. deviation (%) 10.611

Results in decreasing order:

38	1.900	(*)	1	1.310
144	1.800	(*)	15	1.310
13	1.600		16	1.300
10	1.530		33	1.300
23	1.500		24	1.300
36	1.499		159	1.250
127	1.400		5	1.230
121	1.400		169	1.210
39	1.400		8	1.200
108	1.379		3	1.200
115	1.370		168	1.120
31	1.350		2	1.085
14	1.340		6	1.080
112	1.333		120	1.000
110	1.330		118	0.800 (*)
125	1.320		171	0.651 (*)

Lead
Sample no.: 2
Theoretical value: 1.500
Unit: µg/l

Run 1:
Number of laboratories: 32
Arithmetic mean value: 1.461
Median: 1.495
Standard deviation 0.251
Rel. st. deviation (%) 17.152

Run 2:
Number of laboratories: 30
Arithmetic mean value: 1.460
Median: 1.495
Standard deviation 0.175
Rel. st. deviation (%) 12.005

Results in decreasing order:

38	2.200	(*)	15	1.490
13	1.800		110	1.470
23	1.700		31	1.450
108	1.684		36	1.441
10	1.664		112	1.441
39	1.600		8	1.410
24	1.600		3	1.400
159	1.590		144	1.400
14	1.550		5	1.393
115	1.530		169	1.330
125	1.510		2	1.311
1	1.500		168	1.280
121	1.500		6	1.270
127	1.500		120	1.000
16	1.500		118	1.000
33	1.500		171	0.747 (*)

Lead
Sample no.: 3
Theoretical value: 23.000
Unit: µg/l

Run 1:
Number of laboratories: 36
Arithmetic mean value: 22.198
Median: 22.575
Standard deviation 2.600
Rel. st. deviation (%) 11.711

Run 2:
Number of laboratories: 34
Arithmetic mean value: 22.702
Median: 22.720
Standard deviation 1.467
Rel. st. deviation (%) 6.460

Results in decreasing order:

132	26.500	109	22.450	
2	24.980	144	22.000	
24	24.700	120	22.000	
15	24.700	110	22.000	
108	24.208	23	22.000	
33	24.200	4	22.000	
115	24.100	118	21.900	
3	24.000	31	21.900	
1	23.500	168	21.800	
159	23.500	36	21.690	
125	23.300	169	21.200	
14	23.230	8	21.100	
121	23.000	5	20.794	
127	23.000	10	20.780	
114	23.000	16	20.000	
39	23.000	13	19.900	
112	22.740	6	15.900	(*)
38	22.700	171	11.370	(*)

Lead
Sample no.: 4
Theoretical value: 35.000
Unit: µg/l

Run 1:
Number of laboratories: 36
Arithmetic mean value: 33.575
Median: 34.670
Standard deviation 3.675
Rel. st. deviation (%) 10.946

Run 2:
Number of laboratories: 34
Arithmetic mean value: 34.294
Median: 34.856
Standard deviation 1.955
Rel. st. deviation (%) 5.702

Results in decreasing order:

24	37.700	125	34.500	
115	36.900	4	34.000	
132	36.900	23	34.000	
2	36.810	110	33.700	
38	36.200	144	33.200	
33	36.000	118	33.000	
114	36.000	120	33.000	
127	36.000	36	32.959	
121	36.000	31	32.800	
14	35.660	13	32.600	
1	35.400	168	32.100	
109	35.340	169	32.000	
15	35.200	8	31.900	
3	35.000	5	31.085	
159	35.000	10	30.330	
39	35.000	16	30.000	
108	34.871	6	25.230	(*)
112	34.840	171	17.470	(*)

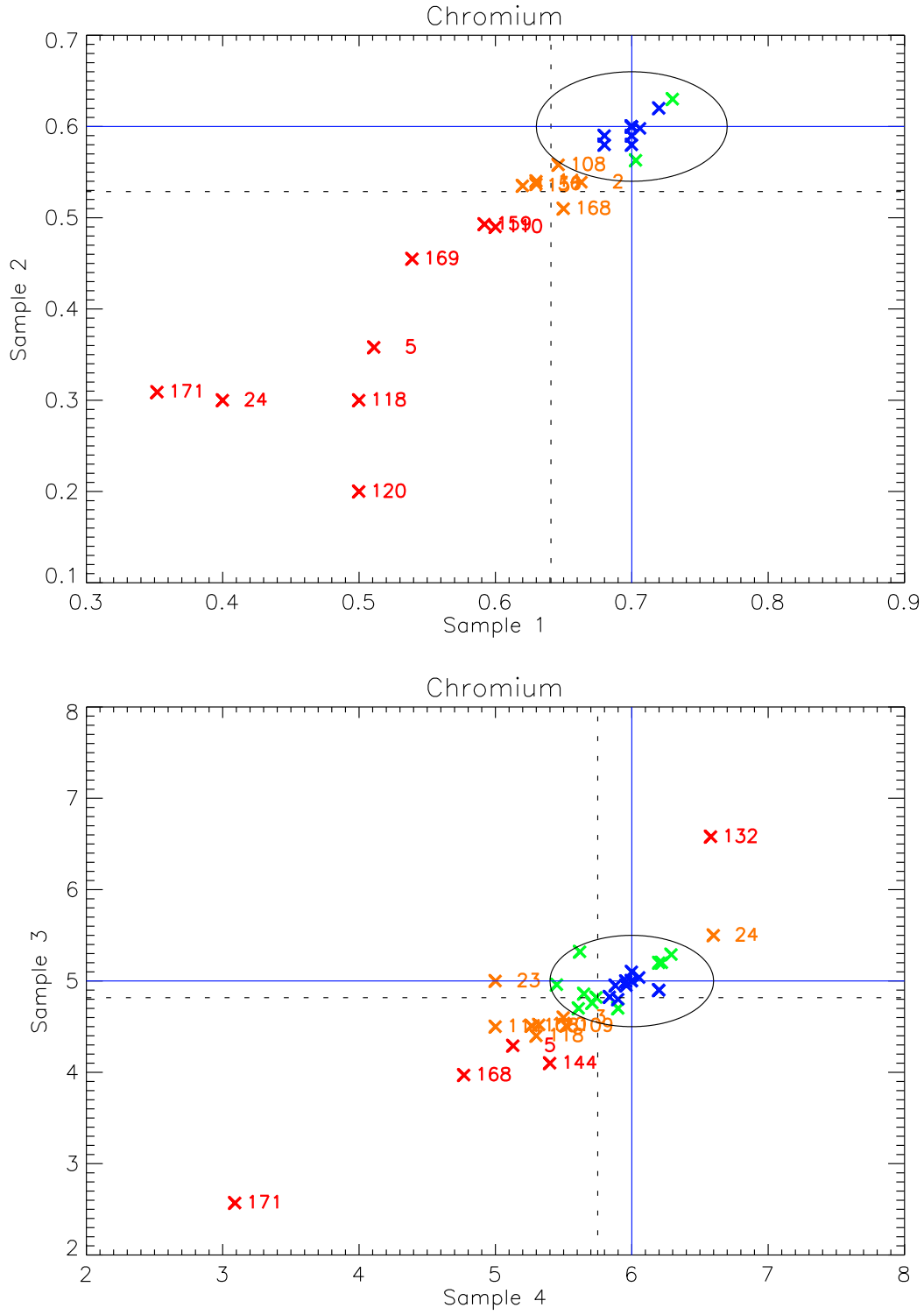

Figure 1: Youden plot of chromium, 2008.

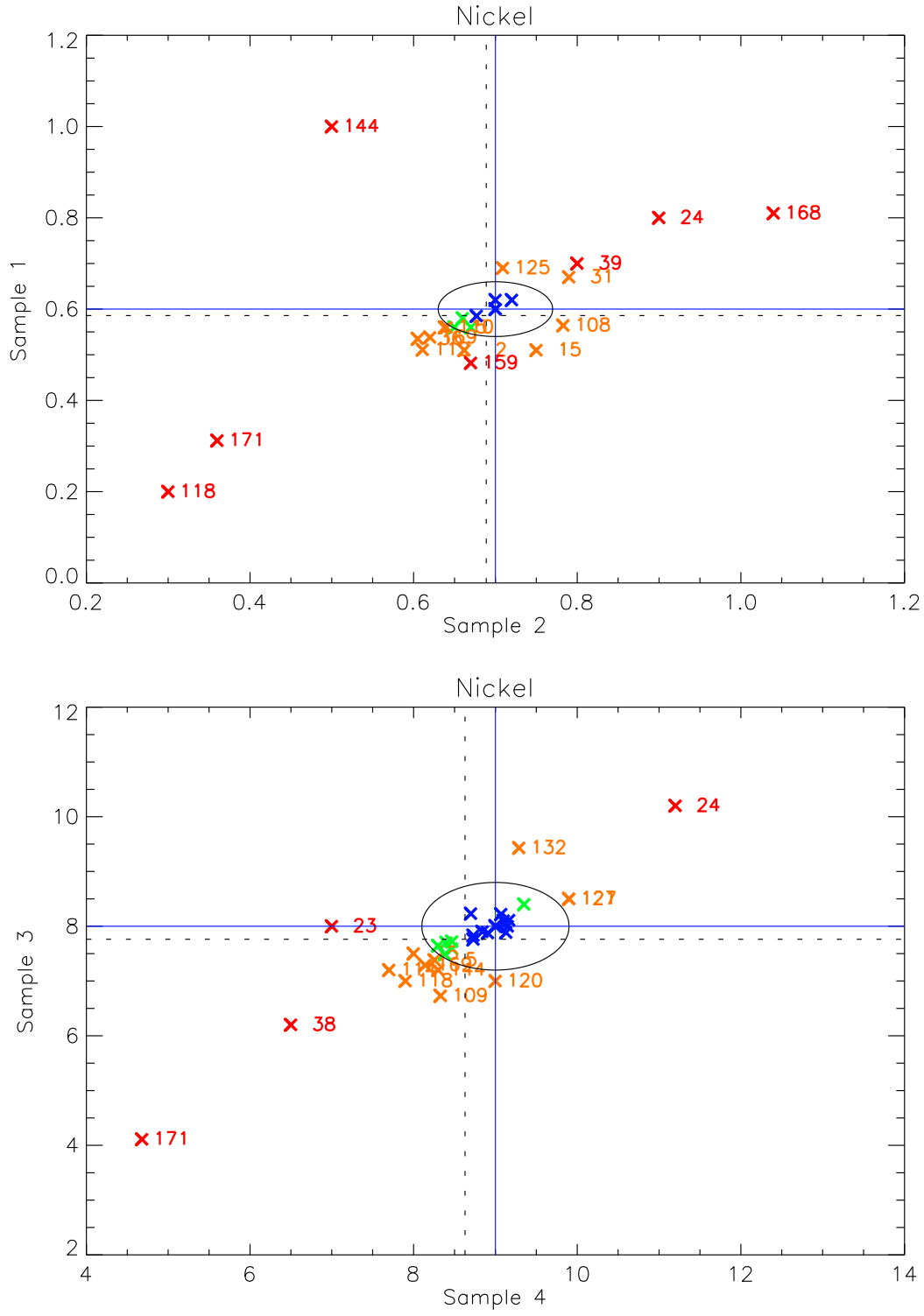

Figure.2: Youden plot of nickel, 2008.

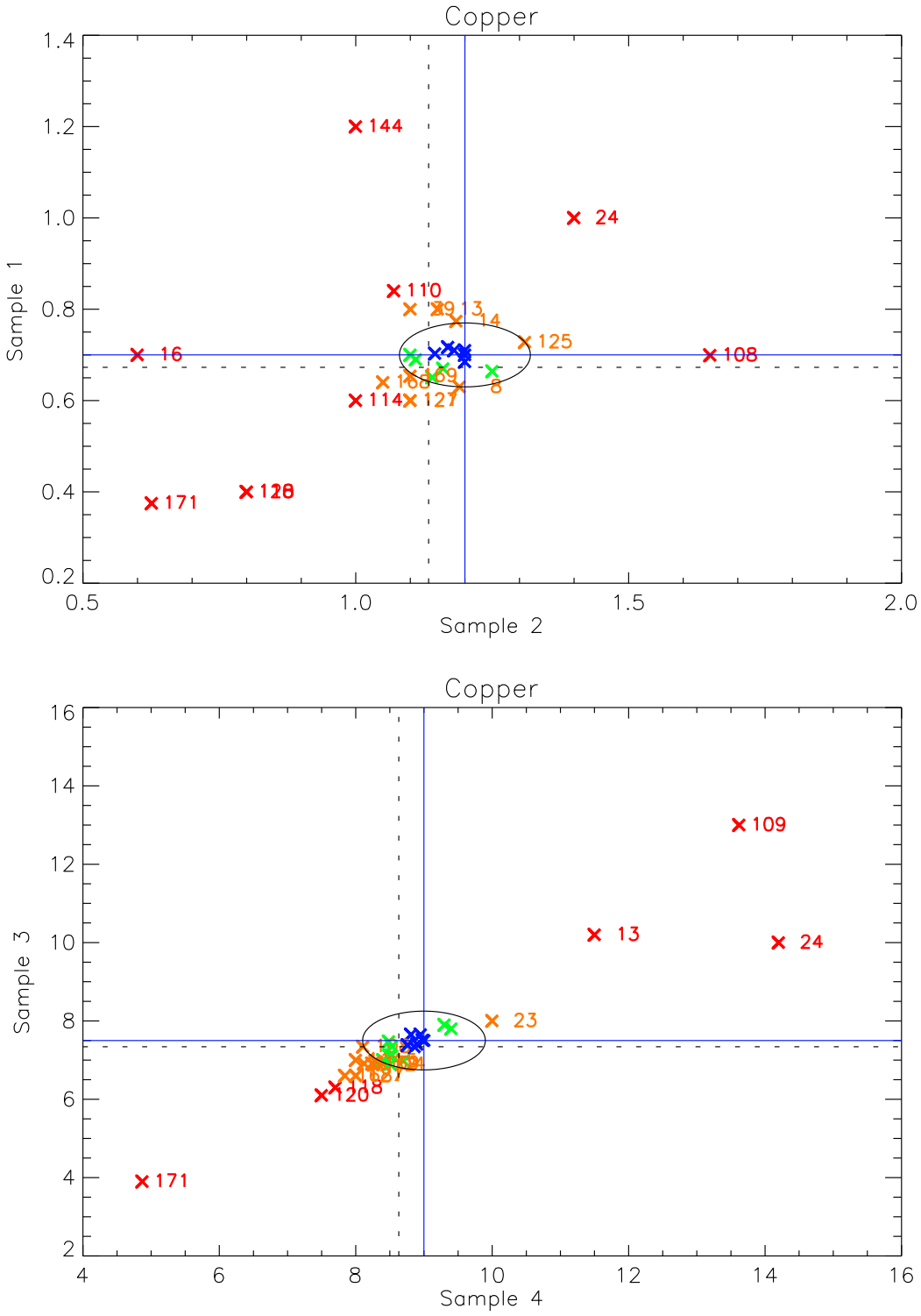

Figure.3: Youden plot of copper, 2008.

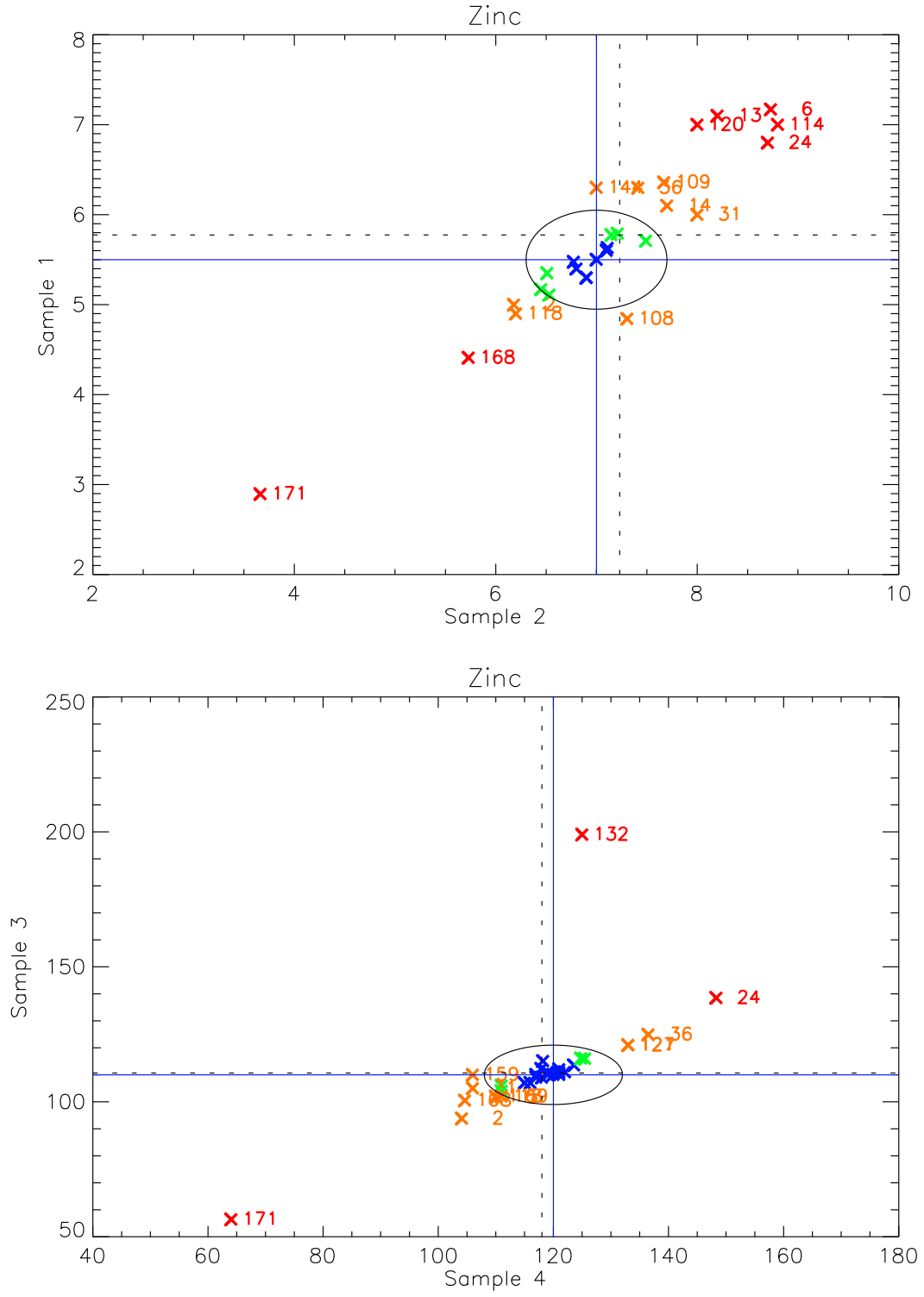

Figure.4: Youden plot of zinc, 2008.

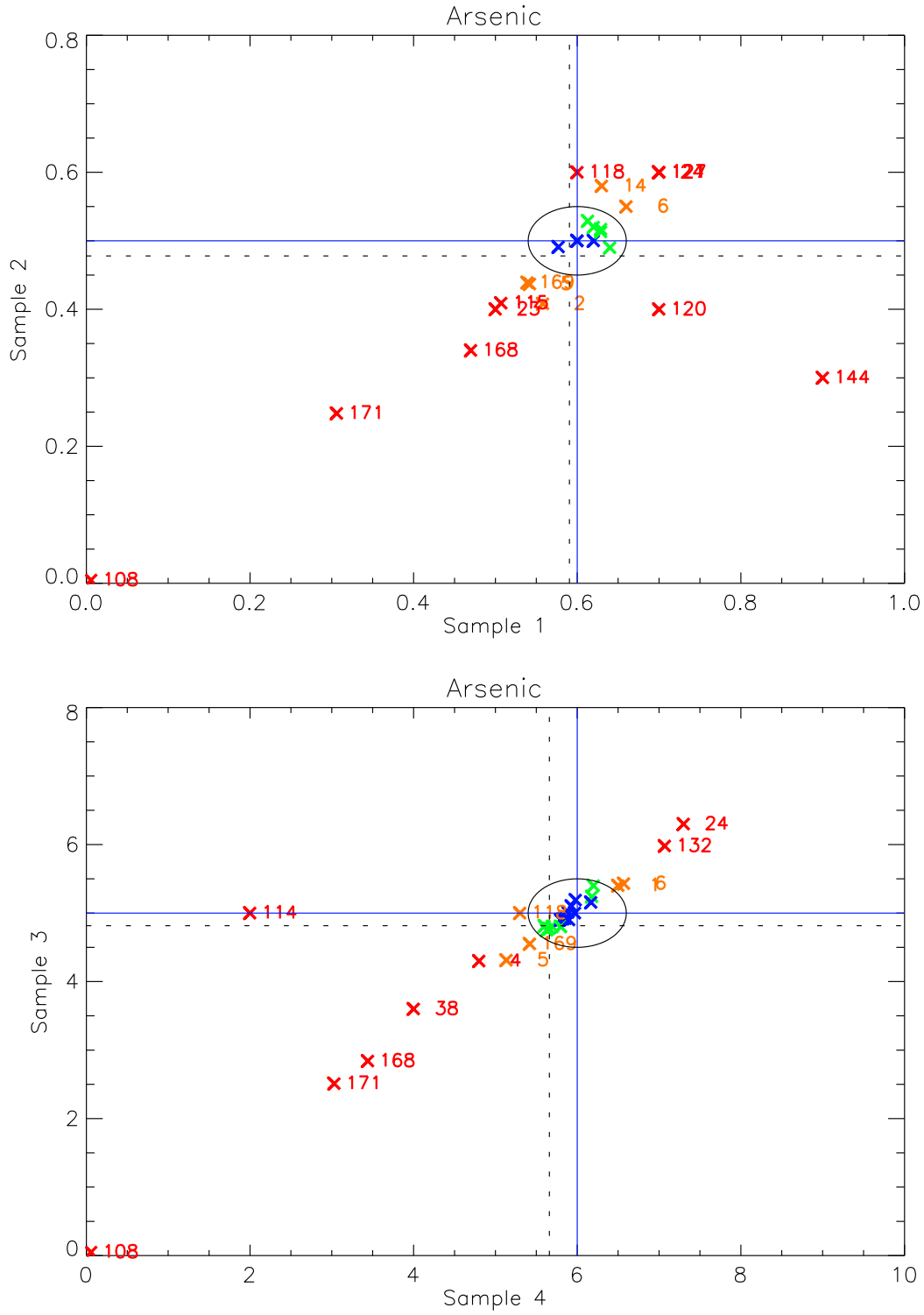

Figure.5: Youden plot of arsenic, 2008.

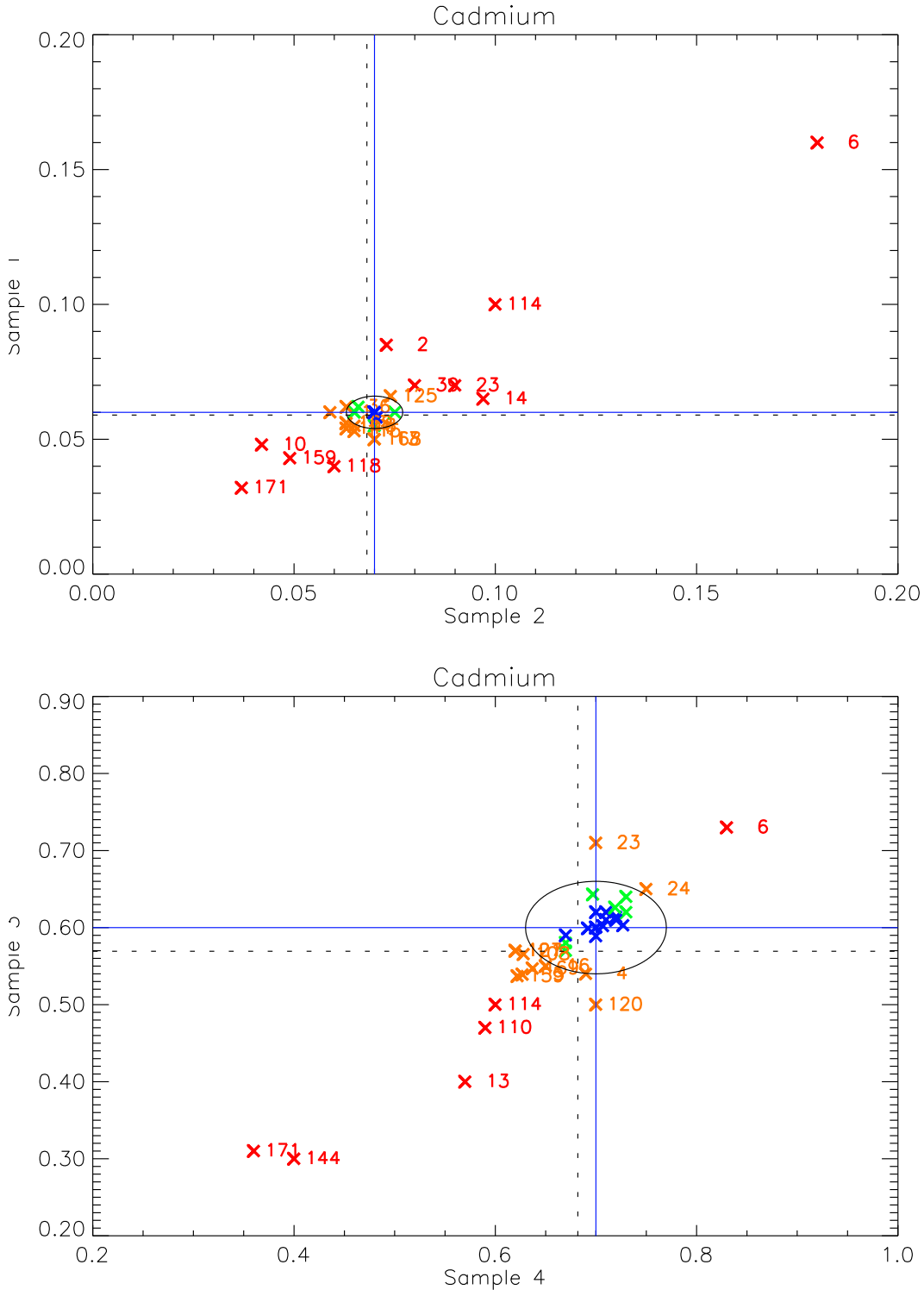

Figure 6: Youden plot of cadmium, 2008.

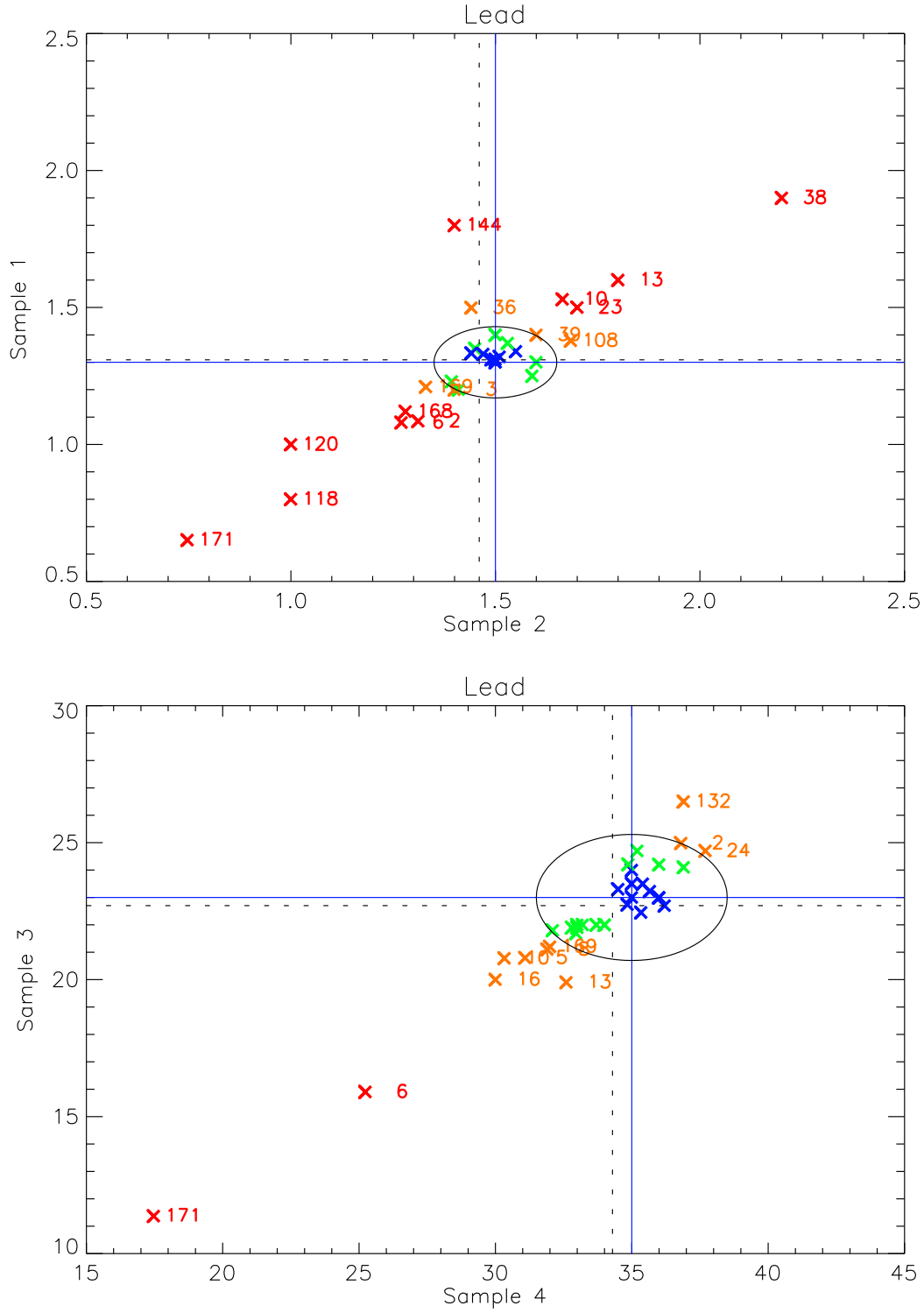

Figure 7: Youden plot of lead, 2008.