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Analytical intercomparison of heavy metals in precipitation 1999

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Contents

Page

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1. Introduction

Heavy metals were included in the EMEP's monitoring programme in 1999. 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 important to carry out.

During the 1990s EMEP started collecting available heavy metal data from the participants (Berg et al., 2000) and was actively involved in an intercomparison which was carried out in the framework of HELCOM-EMEP-PARCOM-AMAP (Berg and Semb, 1995; Winkler and Roider, 1997). The exercise was divided in an analytical and a field intercomparison part and included: Pb, Cd, Cu, Zn, As, Cr, and Ni. The results from the analytical part of the intercomparison showed that a majority of the participating laboratories reported data within 25% of the theoretical values. In general, the intercomparison results for Pb were best. The field intercomparison part of the exercise was carried out at the German EMEP station Deuselbach (DE0004R). The results for Pb, Cd and eventually Zn were acceptable, but problems still remained to be solved for the other heavy metals considered.

This report presents results from the second analytical intercomparison of heavy metals in precipitation which was carried out during 1999. Seven heavy metals were included: Pb, Cd, Cu, Zn, As, Cr, and Ni. Interlaboratory tests will be organized on annual basis by the Chemical Coordination Centre (CCC) from 1999.

2. Intercomparison samples

The four synthetic precipitation samples distributed to the laboratories were made on basis of four multi-element standards traceable to NIST-standards. The multi-element standards were conserved in 2.5% HNO_3. The intercomparison samples contained 0.5% HNO_3 in addition to Cr, Ni, Cu, Zn, As, Cd and Pb. Sample 1 and 2 contained trace element concentrations typical of precipitation in Southern Scandinavia, whereas samples 3 and 4 contained concentrations typical of Central Europe.

All equipment coming in contact with the samples was soaked in 10% HNO_3 (v/v) for four days before use, and the preparation of the intercomparison samples were carried out in a clean room.

3. Presentation of the data

The names of the participating laboratories together with the identification numbers used when presenting the results are given in Table A.1.1.

Table A.1.2 presents the results for the intercomparison samples in decreasing order together with the laboratory numbers. The theoretical value, the number of results, the arithmetic mean value, the median, the standard deviation and the relative standard deviation are also given. In the first statistical run only values below the detection limit were excluded. In the second run also outliers were excluded. The outliers were defined as values more than two standard deviations from the mean value in the first run.

Figure 1 and Table A.1.3 give summaries of the results, showing the relative percentage deviation from the theoretical results for the different laboratories, and for the low and the high concentration ranges, respectively. Two results have been reported for each element and concentration range, and the average of the two low and the two high concentration ranges have been used for this table.

Table A.1.4 gives information on the analytical methods used.

4. Results

The analytical results from the intercomparison are presented in Figure 1, and in Tables A.1.2 and A.1.3. The results reported from the laboratories were generally in accordance with the expected values with a quite good correspondence between median results from the second runs and theoretical results. The relative standard deviations are below 5% for all high concentration samples and somewhat higher for the low concentration samples. Zn differ most with 13.7% and 18.3% for the two low concentration samples.

4.1 Cr

A total of 15 laboratories have reported results for Cr, which include one value below the detection limit for the low concentration samples and two for the high concentration samples. Two laboratories reported values which were more than 25% from the theoretical value. The relative standard deviations are 10.9% and 13.9% for the low concentration samples and 9.3% and 13.5% for the high concentration samples, when outliers are excluded.

4.2 Ni

Fifteen laboratories have reported results for Ni, but the low concentration samples include three values below the detection limit. Three laboratories reported values which were more than 25% from the theoretical value for the low concentration samples, whereas one laboratory deviated more than 25% for the high concentration samples. The relative standard deviations were 12.3% and 31.8% for the low concentration samples and 9.2% and 13.2% for the high concentration samples, excluding outliers.

4.3 Cu

For Cu, 16 laboratories reported results, which include one value below the detection limit for the low concentration samples. Three laboratories reported values which were more than 25% from the theoretical value. The relative standard deviations are 34.0% and 52.6% for the low concentration samples and 13.0% for the high concentration samples, when outliers are excluded.

4.4 Zn

A total of 15 laboratories have reported results for Zn, which include two values below the detection limit for the low concentration samples. Four and three laboratories reported values which deviated more than 25% from the theoretical value for, respectively the low concentration samples and the high concentration samples. The relative standard deviations are 15.4% and 17.1% for the low concentration samples and 13.4% and 17.0 % for the high concentration samples, when outliers are excluded.

4.5 As

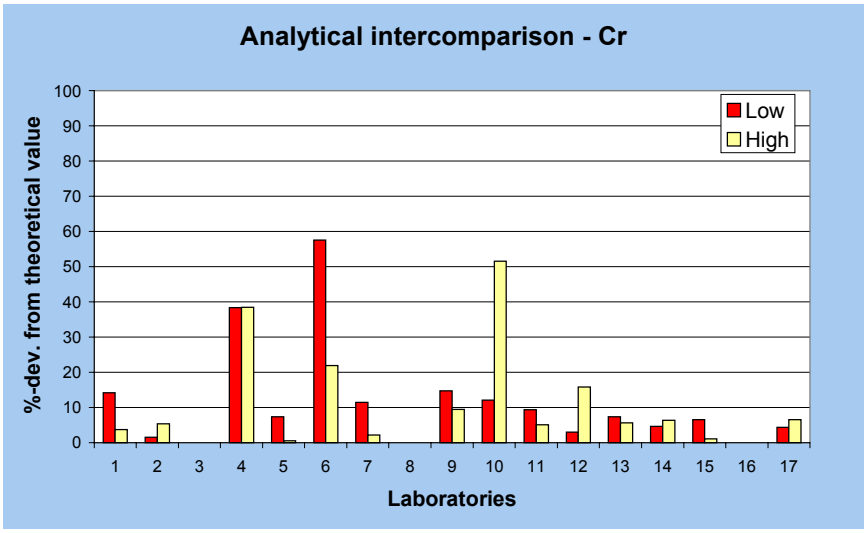
Thirteen laboratories have reported data for As, but the low concentration samples include five and three values below the detection limit. One and three laboratories reported values which deviated more than 25% from the theoretical value for, respectively the low concentration samples and the high concentration samples. The relative standard deviations are 11.1% and 11.6% for the low concentration samples and 8.4% and 13% for the high concentration samples, when outliers are excluded

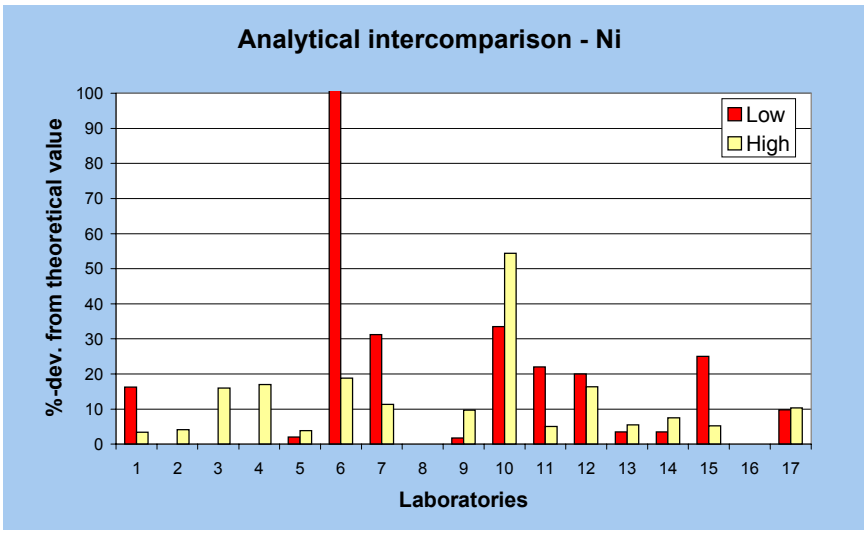
4.6 Cd

All participants (17) reported results for Cd, but the low concentration samples include one value below the detection limit. Eight and five laboratories reported values which were more than 25% from the theoretical value for, respectively the low concentration samples and the high concentration samples. The relative standard deviations are 34.2% and 38.5% for the low concentration samples and 21.4% and 28.0% for the high concentration samples, when outliers are excluded.

4.7 Pb

All participants (17) reported results for Pb, which includes one value below the detection limit for the low concentration samples. Five and two laboratories reported values which were more than 25% from the theoretical value for, respectively the low concentration samples and the high concentration samples. The relative standard deviations are 16.0% and 16.4% for the low concentration samples and 9.7% and 18.3% for the high concentration samples, when outliers are excluded.





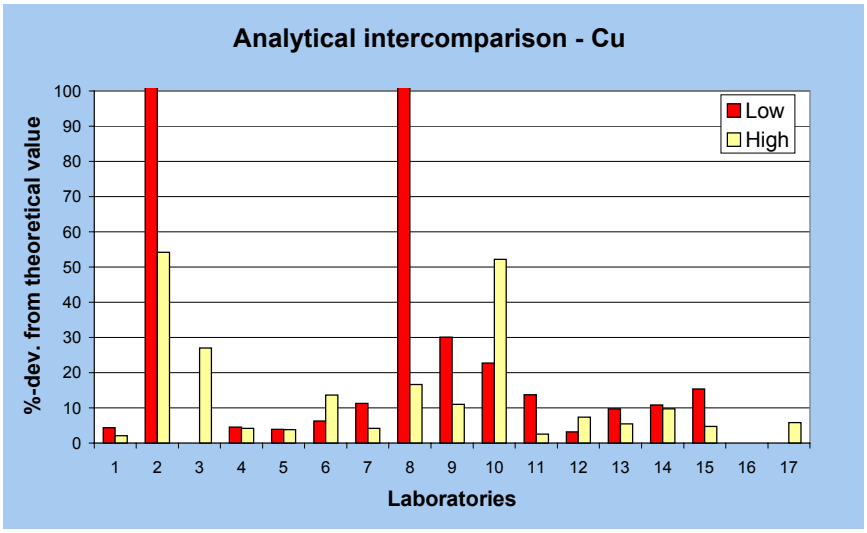
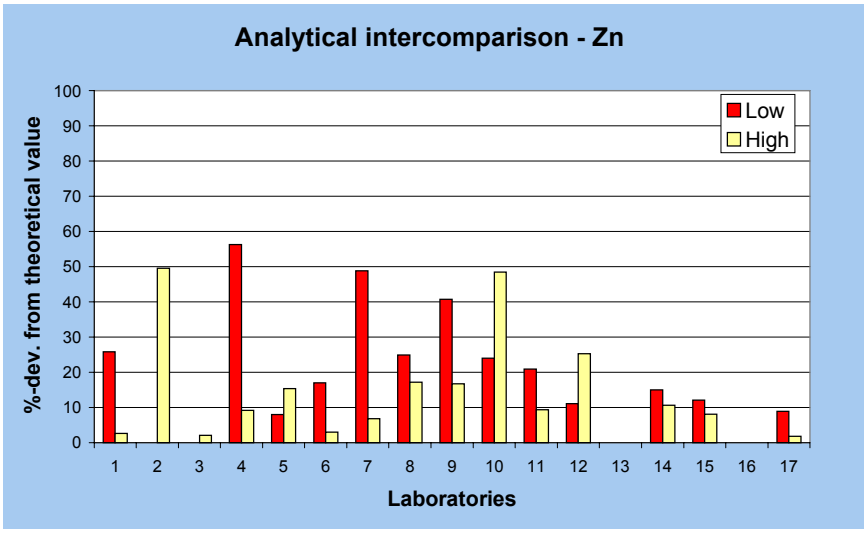
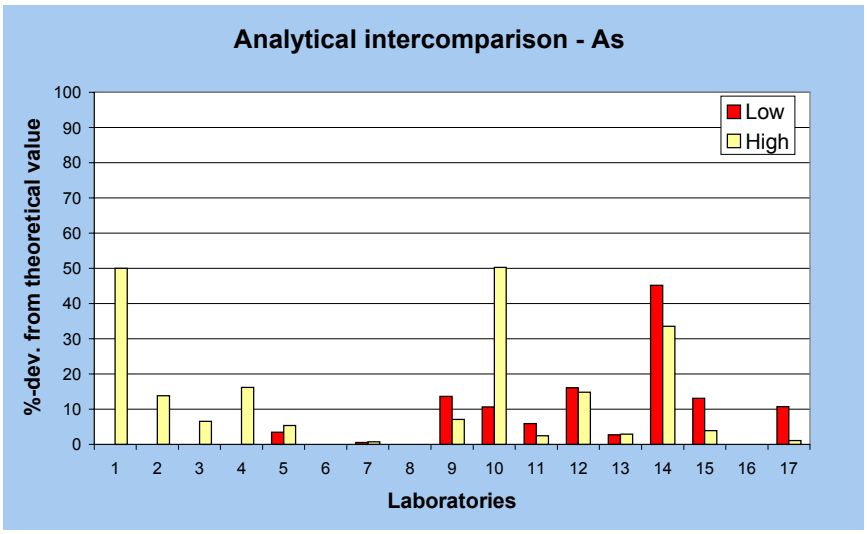


Figure 1: Percent deviation from the theoretical values for the different elements.





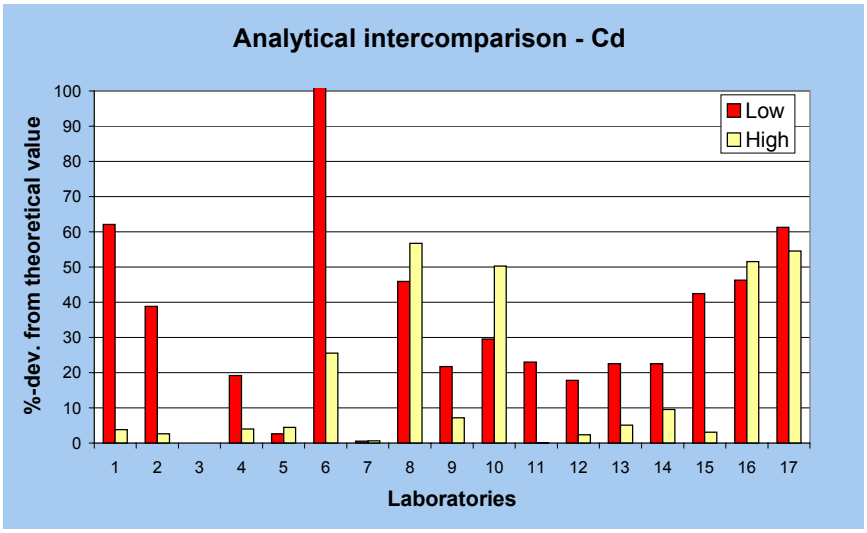


Figure 1, cont.

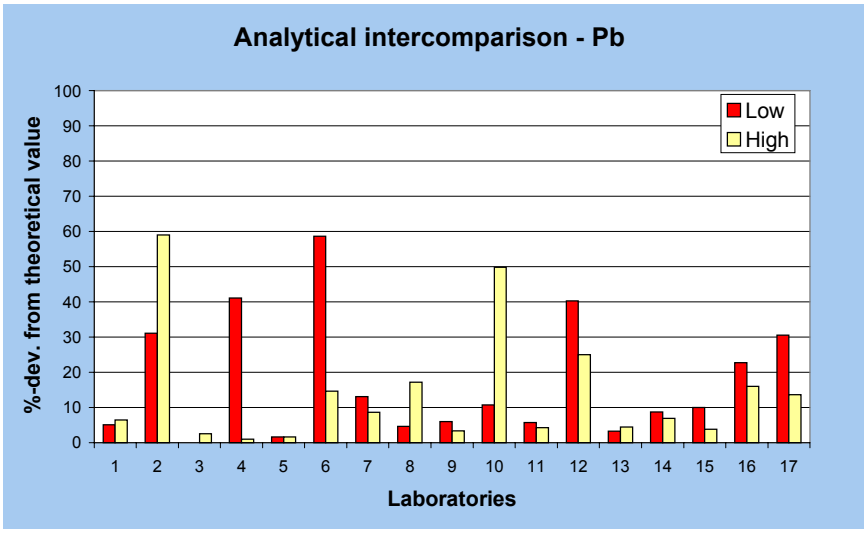


Figure 1, cont.

5. Conclusions and further work

A total of 17 laboratories participated in the analytical intercomparison on heavy metals in precipitation. Two samples contained trace element concentrations typical of precipitation in Southern Scandinavia, and two samples contained concentrations typical of Central Europe.

The elements showed the following order of success: Cr > Pb > As > Cu > Cd > Ni > Zn. For all the samples analysed the deviations from the theoretical values were calculated. The median deviations for all the laboratories were below 27% for all elements and concentration levels (Figure 2). For the high concentration samples the average deviations were below 10%. It should be emphasised that most laboratories involved measure mainly concentrations similar to the high concentration samples in their monitoring networks, and therefore have less experience than others with low concentration samples.

From 1999 heavy metals have been a part of EMEP's measurement programme, and as a part of the quality assurance, analytical intercomparisons will be carried out on annual basis.

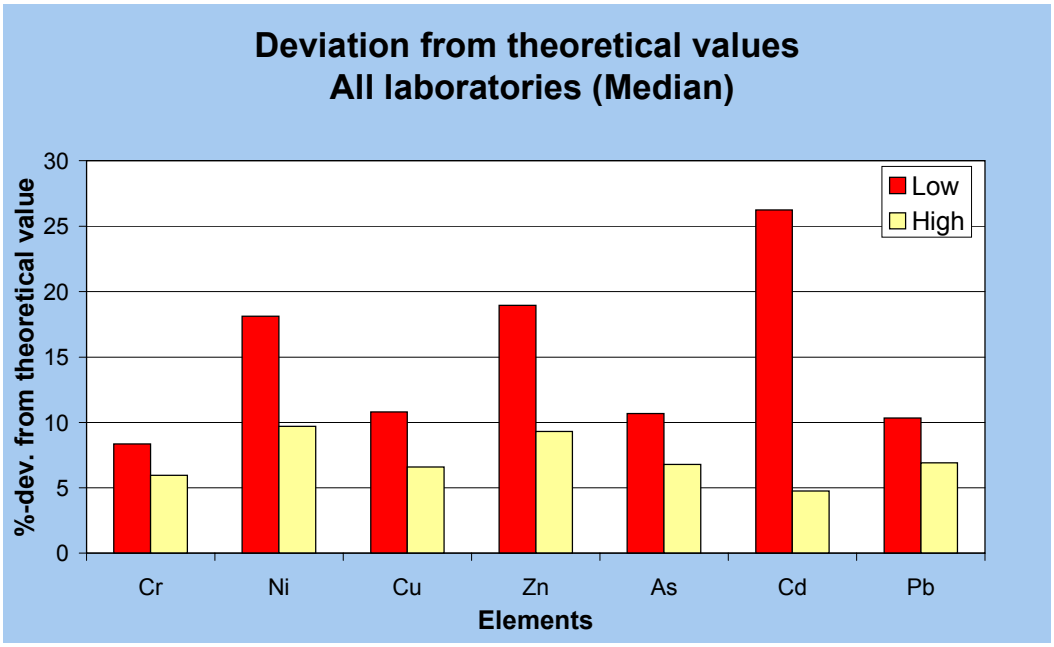


Figure 2: The median deviations for all the laboratories.

6. Literature

Berg, T., Hjellbrekke, A.-G. and Larsen, R. (2000) Heavy metals and POPs within Europe - 1998. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 2/2000).

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

Winkler, P. and Roider, G. (1997) HELCOM-EMEP-PARCOM-AMAP field intercomparison of heavy metals in precipitation 1995. Offenbach (Umweltbundesamt, Luftreinhaltung, Forschungbericht 104 08 540).

Annex 1

Tables

Table 1.1: Participating laboratories in the EMEP-intercomparison of heavy metals in precipitation. The numbers in front are used in tables.

1.	Institute of Meteorology and Water Management, Poland
2.	Estonian Environmental Research Centre, Estonia
3.	Laboratories Wolff, France
4.	Federal Hydrometeorological Institute of Yugoslavia, Yugoslavia
5.	Finnish Meteorological Institute, Finland
6.	Hydrometeorological Institute of Slovenia, Slovenia
7.	Environmental Protection Agency, Ireland
8.	Latvian Hydrometeorological Agency, Latvia
9.	National Institute of Public Health and Environmental Protection, The Netherlands
10.	Ontario Ministry of Environment, Canada
11.	Slovak Hydrometeorological Institute, Slovakia
12.	Institute of Physics, Lithuania
13.	Umweltbundesamt, Offenbach, Germany
14.	Norwegian Institute for Air Research, Norway
15.	Czech Hydrometeorological Institute, Czech Republic
16.	Laboratory of integrated monitoring, Institute of Geography, Russia
17.	Institute of Environmental Protection, Poland

Table 1.2: Analytical results for Cr in synthetic precipitation samples.

Cr
SAMPLE NO.: 1
THEORETICAL VALUE 1.500
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	15
ARITHMETIC MEAN VALUE:	1.588
MEDIAN:	1.580
STANDARD DEVIATON:	0.271
REL. ST. DEVIATION (%):	17.067

RUN 2:

NUMBER OF LABORATORIES:	13
ARITHMETIC MEAN VALUE:	1.540
MEDIAN:	1.570
STANDARD DEVIATON:	0.214
REL. ST. DEVIATION (%):	13.904

RESULTS IN DECREASING ORDER:

3	<10.0		
4	2.20*	13	1.57
6	2.10	1	1.55
11	1.63	2	1.50
14	1.60	12	1.41
15	1.60	7	1.40
5	1.59	9	1.266
17	1.59	10	1.22

<: DATA UNUSED IN RUN 1 AND 2
*: DATA UNUSED IN RUN 2

Cr
SAMPLE NO.: 2
THEORETICAL VALUE 0.800
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	15
ARITHMETIC MEAN VALUE:	0.906
MEDIAN:	0.870
STANDARD DEVIATON:	0.174
REL. ST. DEVIATION (%):	19.166

RUN 2:

NUMBER OF LABORATORIES:	12
ARITHMETIC MEAN VALUE:	0.865
MEDIAN:	0.860
STANDARD DEVIATON:	0.095
REL. ST. DEVIATION (%):	10.925

RESULTS IN DECREASING ORDER:

3	<10.0		
2	< 1.0	5	0.87
6	1.40*	15	0.85
4	1.04	10	0.844
1	1.00	14	0.82
9	0.91	17	0.82
11	0.88	12	0.80
13	0.88	7	0.67

<: DATA UNUSED IN RUN 1 AND 2
*: DATA UNUSED IN RUN 2

Cr
SAMPLE NO.: 3
THEORETICAL VALUE 4.500
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	15
ARITHMETIC MEAN VALUE:	4.343
MEDIAN:	4.560
STANDARD DEVIATON:	1.335
REL. ST. DEVIATION (%):	30.736

RUN 2:

NUMBER OF LABORATORIES:	13
ARITHMETIC MEAN VALUE:	4.661
MEDIAN:	4.620
STANDARD DEVIATON:	0.629
REL. ST. DEVIATION (%):	13.487

RESULTS IN DECREASING ORDER:

3	<20.0		
4	6.25	5	4.50
6	5.30	15	4.40
13	4.84	7	4.39
17	4.83	11	4.05
2	4.80	9	4.009
14	4.80	12	3.80
1	4.62	10	0.207*

<: DATA UNUSED IN RUN 1 AND 2
*: DATA UNUSED IN RUN 2

Cr
SAMPLE NO.: 4
THEORETICAL VALUE 5.000
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	15
ARITHMETIC MEAN VALUE:	5.255
MEDIAN:	5.190
STANDARD DEVIATON:	0.658
REL. ST. DEVIATION (%):	12.529

RUN 2:

NUMBER OF LABORATORIES:	13
ARITHMETIC MEAN VALUE:	5.129
MEDIAN:	5.180
STANDARD DEVIATON:	0.476
REL. ST. DEVIATION (%):	9.288

RESULTS IN DECREASING ORDER:

3	<10.0		
4	6.90*	13	5.18
6	6.30	5	5.05
9	5.394	11	5.00
14	5.30	15	5.00
17	5.28	7	4.91
1	5.24	10	4.62
2	5.20	12	4.20

<: DATA UNUSED IN RUN 1 AND 2
*: DATA UNUSED IN RUN 2

Table 1.2: Analytical results for Ni in synthetic precipitation samples.

Ni
SAMPLE NO.: 1
THEORETICAL VALUE 0.400
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	15
ARITHMETIC MEAN VALUE:	0.824
MEDIAN:	0.385
STANDARD DEVIATON:	1.540
REL. ST. DEVIATION (%):	186.856

RUN 2:

NUMBER OF LABORATORIES:	11
ARITHMETIC MEAN VALUE:	0.381
MEDIAN:	0.380
STANDARD DEVIATON:	0.121
REL. ST. DEVIATION (%):	31.785

RESULTS IN DECREASING ORDER:

3	<10.0	9	0.39
2	< 1.0	14	0.38
4	< 1.0	1	0.35
6	5.70*	17	0.33
15	0.60	12	0.32
11	0.56	7	0.27
13	0.42	10	0.169
5	0.40		

<: DATA UNUSED IN RUN 1 AND 2
*: DATA UNUSED IN RUN 2

Ni
SAMPLE NO.: 2
THEORETICAL VALUE 0.500
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	15
ARITHMETIC MEAN VALUE:	0.935
MEDIAN:	0.495
STANDARD DEVIATON:	1.627
REL. ST. DEVIATION (%):	174.078

RUN 2:

NUMBER OF LABORATORIES:	11
ARITHMETIC MEAN VALUE:	0.465
MEDIAN:	0.490
STANDARD DEVIATON:	0.057
REL. ST. DEVIATION (%):	12.259

RESULTS IN DECREASING ORDER:

3	<10.0		
2	<1.0		
4	<1.0		
6	6.100*	14	0.490
5	0.520	11	0.480
13	0.510	10	0.454
17	0.510	1	0.400
9	0.505	12	0.400
15	0.500	7	0.350

<: DATA UNUSED IN RUN 1 AND 2
*: DATA UNUSED IN RUN 2

Ni
SAMPLE NO.: 3
THEORETICAL VALUE 8.500
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	15
ARITHMETIC MEAN VALUE:	8.218
MEDIAN:	8.697
STANDARD DEVIATON:	2.436
REL. ST. DEVIATION (%):	29.639

RUN 2:

NUMBER OF LABORATORIES:	14
ARITHMETIC MEAN VALUE:	8.777
MEDIAN:	8.729
STANDARD DEVIATON:	1.162
REL. ST. DEVIATION (%):	13.241

RESULTS IN DECREASING ORDER:

6	11.700	1	8.570
3	10.000	2	8.200
17	9.280	11	7.810
4	9.200	15	7.700
14	9.200	7	7.550
13	9.110	12	7.100
5	8.760	10	0.399*
9	8.697		

*: DATA UNUSED IN RUN 2

Ni
SAMPLE NO.: 4
THEORETICAL VALUE 10.500
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	15
ARITHMETIC MEAN VALUE:	10.801
MEDIAN:	10.990
STANDARD DEVIATON:	1.152
REL. ST. DEVIATION (%):	10.662

RUN 2:

NUMBER OF LABORATORIES:	14
ARITHMETIC MEAN VALUE:	10.630
MEDIAN:	10.945
STANDARD DEVIATON:	0.977
REL. ST. DEVIATION (%):	9.188

RESULTS IN DECREASING ORDER:

4	13.200*	13	10.900
3	12.000	6	10.500
17	11.700	15	10.400
9	11.519	11	10.290
14	11.200	7	9.300
1	11.130	10	9.090
2	11.000	12	8.800
5	10.990		

*: DATA UNUSED IN RUN 2

Table 1.2: Analytical results for Cu in synthetic precipitation samples.

Cu
SAMPLE NO.: 1
THEORETICAL VALUE 1.600
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	16
ARITHMETIC MEAN VALUE:	2.883
MEDIAN:	1.740
STANDARD DEVIATON:	4.197
REL. ST. DEVIATION (%):	145.587

RUN 2:

NUMBER OF LABORATORIES:	14
ARITHMETIC MEAN VALUE:	1.810
MEDIAN:	1.725
STANDARD DEVIATON:	0.617
REL. ST. DEVIATION (%):	34.062

RESULTS IN DECREASING ORDER:

3	<10.0		
2	17.90*	9	1.711
8	3.848	12	1.700
11	1.82	5	1.65
14	1.80	4	1.60
15	1.80	17	1.60
13	1.78	6	1.40
7	1.77	10	1.12
1	1.74		

<: DATA UNUSED IN RUN 1 AND 2
*: DATA UNUSED IN RUN 2

Cu
SAMPLE NO.: 2
THEORETICAL VALUE 1.100
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	16
ARITHMETIC MEAN VALUE:	2.459
MEDIAN:	1.200
STANDARD DEVIATON:	4.220
REL. ST. DEVIATION (%):	171.610

RUN 2:

NUMBER OF LABORATORIES:	14
ARITHMETIC MEAN VALUE:	1.385
MEDIAN:	1.195
STANDARD DEVIATON:	0.728
REL. ST. DEVIATION (%):	52.613

RESULTS IN DECREASING ORDER:

3	<10.0		
2	17.50*	13	1.19
8	3.848	5	1.15
9	1.685	1	1.10
15	1.30	6	1.10
11	1.25	12	1.10
7	1.23	17	1.10
4	1.20	10	0.931
14	1.20		

<: DATA UNUSED IN RUN 1 AND 2
*: DATA UNUSED IN RUN 2

Cu
SAMPLE NO.: 3
THEORETICAL VALUE 18.000
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	16
ARITHMETIC MEAN VALUE:	17.664
MEDIAN:	18.775
STANDARD DEVIATON:	5.064
REL. ST. DEVIATION (%):	28.667

RUN 2:

NUMBER OF LABORATORIES:	15
ARITHMETIC MEAN VALUE:	18.783
MEDIAN:	18.800
STANDARD DEVIATON:	2.450
REL. ST. DEVIATION (%):	13.044

RESULTS IN DECREASING ORDER:

2	25.800	5	18.750
3	20.000	11	18.610
9	19.826	4	17.800
14	19.700	1	17.250
13	19.300	6	16.700
17	19.300	12	16.500
7	18.870	8	14.546
15	18.800	10	0.877*

*: DATA UNUSED IN RUN 2

Cu
SAMPLE NO.: 4
THEORETICAL VALUE 14.000
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	16
ARITHMETIC MEAN VALUE:	15.194
MEDIAN:	14.550
STANDARD DEVIATON:	2.799
REL. ST. DEVIATION (%):	18.422

RUN 2:

NUMBER OF LABORATORIES:	15
ARITHMETIC MEAN VALUE:	14.667
MEDIAN:	14.500
STANDARD DEVIATON:	1.906
REL. ST. DEVIATION (%):	12.994

RESULTS IN DECREASING ORDER:

2	23.100*	13	14.500
3	20.000	7	14.480
8	15.970	5	14.470
9	15.657	11	14.230
14	15.400	1	14.000
4	15.000	12	13.100
15	14.700	10	12.700
17	14.600	6	11.200

*: DATA UNUSED IN RUN 2

Table 1.2: Analytical results for Zn in synthetic precipitation samples.

Zn
SAMPLE NO.: 1
THEORETICAL VALUE 6.000
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	15
ARITHMETIC MEAN VALUE:	7.036
MEDIAN:	7.100
STANDARD DEVIATON:	1.205
REL. ST. DEVIATION (%):	17.125

RUN 2:

NUMBER OF LABORATORIES:	13
ARITHMETIC MEAN VALUE:	7.036
MEDIAN:	7.100
STANDARD DEVIATON:	1.205
REL. ST. DEVIATION (%):	17.125

RESULTS IN DECREASING ORDER:

3	<10.0		
2	<10.0		
7	8.81	15	7.10
8	8.393	14	6.50
4	8.05	5	6.31
9	8.043	12	5.50
11	7.80	17	5.40
1	7.38	10	5.079
6	7.10		

<: DATA UNUSED IN RUN 1 AND 2
*: DATA UNUSED IN RUN 2

Zn
SAMPLE NO.: 2
THEORETICAL VALUE 5.100
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	15
ARITHMETIC MEAN VALUE:	6.307
MEDIAN:	5.900
STANDARD DEVIATON:	1.226
REL. ST. DEVIATION (%):	19.437

RUN 2:

NUMBER OF LABORATORIES:	12
ARITHMETIC MEAN VALUE:	6.074
MEDIAN:	5.800
STANDARD DEVIATON:	0.933
REL. ST. DEVIATION (%):	15.364

RESULTS IN DECREASING ORDER:

3	<10.0		
2	<10.0		
4	9.10*	11	5.70
7	7.69	5	5.65
9	7.52	8	5.607
10	6.76	17	5.50
1	6.56	15	5.40
14	6.20	12	4.40
6	5.90		

<: DATA UNUSED IN RUN 1 AND 2
*: DATA UNUSED IN RUN 2

Zn
SAMPLE NO.: 3
THEORETICAL VALUE110.000
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	15
ARITHMETIC MEAN VALUE:	105.756
MEDIAN:	108.000
STANDARD DEVIATON:	33.236
REL. ST. DEVIATION (%):	31.427

RUN 2:

NUMBER OF LABORATORIES:	14
ARITHMETIC MEAN VALUE:	112.886
MEDIAN:	109.000
STANDARD DEVIATON:	19.195
REL. ST. DEVIATION (%):	17.004

RESULTS IN DECREASING ORDER:

2	164.00	17	108.00
9	127.118	15	101.00
5	126.80	11	100.40
14	123.00	4	100.00
7	118.35	8	98.53
1	112.70	12	82.50
3	110.00	10	5.94*
6	108.00		

*: DATA UNUSED IN RUN 2

Zn
SAMPLE NO.: 4
THEORETICAL VALUE 96.000
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	14
ARITHMETIC MEAN VALUE:	98.386
MEDIAN:	98.500
STANDARD DEVIATON:	17.907
REL. ST. DEVIATION (%):	18.201

RUN 2:

NUMBER OF LABORATORIES:	13
ARITHMETIC MEAN VALUE:	94.877
MEDIAN:	98.300
STANDARD DEVIATON:	12.675
REL. ST. DEVIATION (%):	13.359

RESULTS IN DECREASING ORDER:

2	144.00*	10	98.30
9	113.19	17	94.30
5	110.70	6	92.00
14	105.00	15	88.40
7	101.69	11	86.50
3	100.00	8	73.12
1	98.70	12	71.50

*: DATA UNUSED IN RUN 2

Table 1.2: Analytical results for As in synthetic precipitation samples.

As
SAMPLE NO.: 1
THEORETICAL VALUE 0.400
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	13
ARITHMETIC MEAN VALUE:	0.434
MEDIAN:	0.410
STANDARD DEVIATON:	0.076
REL. ST. DEVIATION (%):	17.518

RUN 2:

NUMBER OF LABORATORIES:	7
ARITHMETIC MEAN VALUE:	0.412
MEDIAN:	0.410
STANDARD DEVIATON:	0.046
REL. ST. DEVIATION (%):	11.127

RESULTS IN DECREASING ORDER:

3	<5.0	15	0.43
4	<2.0	5	0.41
2	<1.0	13	0.41
14	0.59*	7	0.40
17	<0.5	11	0.37
12	0.50	10	0.361
9	<0.45		

<: DATA UNUSED IN RUN 1 AND 2
*: DATA UNUSED IN RUN 2

As
SAMPLE NO.: 2
THEORETICAL VALUE 0.700
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	13
ARITHMETIC MEAN VALUE:	0.749
MEDIAN:	0.730
STANDARD DEVIATON:	0.118
REL. ST. DEVIATION (%):	15.810

RUN 2:

NUMBER OF LABORATORIES:	9
ARITHMETIC MEAN VALUE:	0.721
MEDIAN:	0.730
STANDARD DEVIATON:	0.084
REL. ST. DEVIATION (%):	11.593

RESULTS IN DECREASING ORDER:

3	<5.0		
4	<2.0		
2	<1.0		
14	1.000*	11	0.730
15	0.830	13	0.720
9	0.795	7	0.700
10	0.781	12	0.650
5	0.730	17	0.550

<: DATA UNUSED IN RUN 1 AND 2
*: DATA UNUSED IN RUN 2

As
SAMPLE NO.: 3
THEORETICAL VALUE 5.700
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	13
ARITHMETIC MEAN VALUE:	5.491
MEDIAN:	5.700
STANDARD DEVIATON:	1.725
REL. ST. DEVIATION (%):	31.407

RUN 2:

NUMBER OF LABORATORIES:	12
ARITHMETIC MEAN VALUE:	5.924
MEDIAN:	5.855
STANDARD DEVIATON:	0.769
REL. ST. DEVIATION (%):	12.975

RESULTS IN DECREASING ORDER:

14	7.700	17	5.700
12	6.700	7	5.670
9	6.197	15	5.600
3	6.100	4	5.000
5	6.010	2	4.700
13	6.010	10	0.300*
11	5.700		

*: DATA UNUSED IN RUN 2

As
SAMPLE NO.: 4
THEORETICAL VALUE 5.000
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	13
ARITHMETIC MEAN VALUE:	5.204
MEDIAN:	5.240
STANDARD DEVIATON:	0.585
REL. ST. DEVIATION (%):	11.238

RUN 2:

NUMBER OF LABORATORIES:	12
ARITHMETIC MEAN VALUE:	5.088
MEDIAN:	5.170
STANDARD DEVIATON:	0.426
REL. ST. DEVIATION (%):	8.367

RESULTS IN DECREASING ORDER:

14	6.600*	17	5.100
4	6.000	13	5.010
3	5.300	7	4.960
15	5.300	10	4.710
9	5.273	2	4.500
5	5.260	12	4.400
11	5.240		

*: DATA UNUSED IN RUN 2

Table 1.2: Analytical results for Cd in synthetic precipitation samples.

Cd
SAMPLE NO.: 1
THEORETICAL VALUE 0.050
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	17
ARITHMETIC MEAN VALUE:	0.064
MEDIAN:	0.055
STANDARD DEVIATON:	0.044
REL. ST. DEVIATION (%):	68.506

RUN 2:

NUMBER OF LABORATORIES:	15
ARITHMETIC MEAN VALUE:	0.054
MEDIAN:	0.050
STANDARD DEVIATON:	0.021
REL. ST. DEVIATION (%):	38.456

RESULTS IN DECREASING ORDER:

3	<2.0		
6	0.210*	7	0.050
1	0.099	5	0.048
15	0.080	4	0.044
17	0.080	12	0.041
8	0.064	9	0.037
11	0.063	10	0.033
13	0.060	2	0.030
14	0.060	16	0.025

<: DATA UNUSED IN RUN 1 AND 2
*: DATA UNUSED IN RUN 2

Cd
SAMPLE NO.: 2
THEORETICAL VALUE 0.080
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	17
ARITHMETIC MEAN VALUE:	0.086
MEDIAN:	0.087
STANDARD DEVIATON:	0.038
REL. ST. DEVIATION (%):	44.163

RUN 2:

NUMBER OF LABORATORIES:	15
ARITHMETIC MEAN VALUE:	0.079
MEDIAN:	0.080
STANDARD DEVIATON:	0.027
REL. ST. DEVIATION (%):	34.159

RESULTS IN DECREASING ORDER:

3	<2.0		
6	0.190*	7	0.080
17	0.130	5	0.079
1	0.101	12	0.066
13	0.100	10	0.060
14	0.100	4	0.059
15	0.100	2	0.050
11	0.096	16	0.046
9	0.094	8	0.029

<: DATA UNUSED IN RUN 1 AND 2
*: DATA UNUSED IN RUN 2

Cd
SAMPLE NO.: 3
THEORETICAL VALUE 0.800
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	17
ARITHMETIC MEAN VALUE:	0.720
MEDIAN:	0.785
STANDARD DEVIATON:	0.276
REL. ST. DEVIATION (%):	38.279

RUN 2:

NUMBER OF LABORATORIES:	15
ARITHMETIC MEAN VALUE:	0.765
MEDIAN:	0.790
STANDARD DEVIATON:	0.215
REL. ST. DEVIATION (%):	28.038

RESULTS IN DECREASING ORDER:

3	<2.0		
17	1.230	2	0.780
14	0.900	9	0.780
13	0.860	15	0.780
1	0.855	12	0.770
5	0.820	6	0.610
4	0.819	16	0.390
11	0.801	8	0.296
7	0.790	10	0.039*

<: DATA UNUSED IN RUN 1 AND 2
*: DATA UNUSED IN RUN 2

Cd
SAMPLE NO.: 4
THEORETICAL VALUE 1.100
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	17
ARITHMETIC MEAN VALUE:	1.061
MEDIAN:	1.097
STANDARD DEVIATON:	0.272
REL. ST. DEVIATION (%):	25.665

RUN 2:

NUMBER OF LABORATORIES:	15
ARITHMETIC MEAN VALUE:	1.017
MEDIAN:	1.093
STANDARD DEVIATON:	0.217
REL. ST. DEVIATION (%):	21.366

RESULTS IN DECREASING ORDER:

3	<2.0		
17	1.710*	1	1.093
9	1.229	12	1.090
14	1.200	15	1.060
5	1.170	4	1.040
2	1.130	10	1.040
13	1.130	6	0.800
7	1.100	8	0.546
11	1.100	16	0.530

<: DATA UNUSED IN RUN 1 AND 2
*: DATA UNUSED IN RUN 2

Table 1.2: Analytical results for Pb in synthetic precipitation samples.

Pb
SAMPLE NO.: 1
THEORETICAL VALUE 2.200
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	17
ARITHMETIC MEAN VALUE:	2.384
MEDIAN:	2.375
STANDARD DEVIATON:	0.657
REL. ST. DEVIATION (%):	27.553

RUN 2:

NUMBER OF LABORATORIES:	15
ARITHMETIC MEAN VALUE:	2.516
MEDIAN:	2.400
STANDARD DEVIATON:	0.403
REL. ST. DEVIATION (%):	16.015

RESULTS IN DECREASING ORDER:

3	<10.0		
2	3.110	11	2.350
12	3.100	9	2.316
4	3.000	13	2.260
16	2.970	5	2.220
17	2.900	1	2.160
15	2.500	8	2.154
7	2.490	10	1.810
14	2.400	6	0.400*

<: DATA UNUSED IN RUN 1 AND 2
*: DATA UNUSED IN RUN 2

Pb
SAMPLE NO.: 2
THEORETICAL VALUE 4.800
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	17
ARITHMETIC MEAN VALUE:	5.083
MEDIAN:	5.060
STANDARD DEVIATON:	0.980
REL. ST. DEVIATION (%):	19.277

RUN 2:

NUMBER OF LABORATORIES:	15
ARITHMETIC MEAN VALUE:	5.215
MEDIAN:	5.100
STANDARD DEVIATON:	0.854
REL. ST. DEVIATION (%):	16.372

RESULTS IN DECREASING ORDER:

3	<10.0		
4	7.000	11	5.020
12	6.700	13	4.980
17	6.200	5	4.910
7	5.420	10	4.620
16	5.300	8	4.462
14	5.200	1	4.400
9	5.118	2	3.800
15	5.100	6	3.100*

<: DATA UNUSED IN RUN 1 AND 2
*: DATA UNUSED IN RUN 2

Pb
SAMPLE NO.: 3
THEORETICAL VALUE 54.000
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	17
ARITHMETIC MEAN VALUE:	51.277
MEDIAN:	55.100
STANDARD DEVIATON:	15.804
REL. ST. DEVIATION (%):	30.821

RUN 2:

NUMBER OF LABORATORIES:	16
ARITHMETIC MEAN VALUE:	54.317
MEDIAN:	55.668
STANDARD DEVIATON:	9.943
REL. ST. DEVIATION (%):	18.305

RESULTS IN DECREASING ORDER:

12	67.200	4	55.000
17	63.200	11	54.980
8	60.231	5	54.620
1	58.200	3	54.000
7	58.010	16	51.300
14	57.400	6	45.000
13	56.800	2	21.800
9	56.236	10	2.640*
15	55.100		

*: DATA UNUSED IN RUN 2

Pb
SAMPLE NO.: 4
THEORETICAL VALUE 40.000
UNIT: UG/ML

RUN 1:

NUMBER OF LABORATORIES:	17
ARITHMETIC MEAN VALUE:	41.357
MEDIAN:	42.000
STANDARD DEVIATON:	7.552
REL. ST. DEVIATION (%):	18.260

RUN 2:

NUMBER OF LABORATORIES:	16
ARITHMETIC MEAN VALUE:	42.904
MEDIAN:	42.100
STANDARD DEVIATON:	4.173
REL. ST. DEVIATION (%):	9.726

RESULTS IN DECREASING ORDER:

16	50.800	3	42.000
12	50.200	13	41.500
8	49.077	9	41.026
17	44.100	5	40.800
7	43.880	4	40.000
14	43.000	10	38.200
11	42.680	6	35.000
15	42.200	2	16.600*
1	42.000		

*: DATA UNUSED IN RUN 2

Table 1.3: Percentage deviation from theoretical concentration values (see text for explanation).

Element	No. of laboratories	Lab. Identification
Cr (low)		
0-10%	8	2, 5, 11, 12, 13, 14, 15, 17
10-25%	4	1, 7, 9, 10
>25%	2	4, 6
Cr (high)		
0-10%	10	1, 2, 5, 7, 9, 11, 13, 14, 15, 17
10-25%	2	6, 12
>25%	2	4, 10
Ni (low)		
0-10%	5	5, 9, 13, 14, 17
10-25%	4	1, 11, 12, 15
>25%	3	6, 7, 10
Ni (high)		
0-10%	8	1, 2, 5, 9, 11, 13, 14, 15
10-25%	6	3, 4, 6, 7, 12, 17
>25%	1	10
Cu (low)		
0-10%	7	1, 4, 5, 6, 12, 13, 17
10-25%	5	7, 10, 11, 14, 15
>25%	3	2, 8, 9
Cu (high)		
0-10%	10	1, 4, 5, 7, 11, 12, 13, 14, 15, 17
10-25%	3	6, 8, 9
>25%	3	2, 3, 10
Zn (low)		
0-10%	2	5, 17
10-25%	7	6, 8, 10, 11, 12, 14, 15
>25%	4	1, 4, 7, 9
Zn (high)		
0-10%	8	1, 3, 4, 6, 7, 11, 15, 17
10-25%	4	5, 8, 9, 14
>25%	3	2, 10, 12
As (low)		
0-10%	4	5, 7, 11, 13
10-25%	5	9, 10, 12, 15, 17
>25%	1	14
As (high)		
0-10%	8	3, 5, 7, 9, 11, 13, 15, 17
10-25%	3	2, 4, 12
>25%	3	1, 10, 14
Cd (low)		
0-10%	2	5, 7
10-25%	6	4, 9, 11, 12, 13, 14
>25%	8	1, 2, 6, 8, 10, 15, 16, 17
Cd (high)		
0-10%	11	1, 2, 4, 5, 7, 9, 11, 12, 13, 14, 15
10-25%	1	17
>25%	5	6, 8, 10, 16, 17

Table 1.3, cont.

Element	No. of laboratories	Lab. Identification
Pb (low)		
0-10%	8	1, 5, 8, 9, 11, 13, 14, 15
10-25%	3	7, 10, 16
>25%	5	2, 4, 6, 12, 17
Pb (high)		
0-10%	10	1, 3, 4, 5, 7, 9, 11, 13, 14, 15
10-25%	5	6, 8, 12, 16, 17
>25%	2	2, 10

Table 1.4: Analytical methods used at the participating laboratories for the different elements.

Lab. No.	Elements	Technique
1.	Cr, Ni, Cu, Cd, Pb Zn	GF-AAS F-AAS
2.	Cr, Ni, Cu, As, Cd, Pb Zn	GF-AAS F-AAS
3.	Cr, Ni, Cu, Zn, Cd, Pb As	ICP-OES (+ ultrasonic nebulizer) GF-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, Cd, Pb Zn	GF-AAS F-AAS
7.	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
8.	Cu, Zn, Cd, Pb	GF-AAS
9.	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
10.	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
11.	Cr, Ni, Cu, Cd, Pb Zn As	GF-AAS F-AAS HS
12	Cr, Ni, Cu, Zn, As, Cd, Pb	GF-AAS
13.	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
14.	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
15.	Ni, Cu, Cd, Pb Zn Cr As	GF-AAS F-AAS ICP-MS CV/ICP-MS
16.	Cd, Pb	GF-AAS
17.	Cr, Ni, Cu, As, Cd, Pb Zn	GF-AAS F-AAS

F-AAS: Flame Atomic Absorption Spectroscopy
GF-AAS: Graphite Furnace Atomic Absorption Spectroscopy
ICP-MS: Inductively Coupled Plasma – Mass Spectrometry
ICP-OES: Inductively Coupled Plasma – Optical Emission Spectrometry
HS: Hydride System
CV: Cold Vapour