EMEP/CCC-Report 2/2002

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 2001

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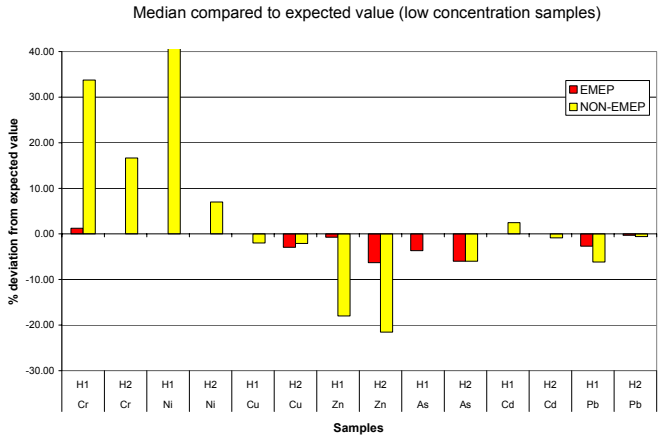


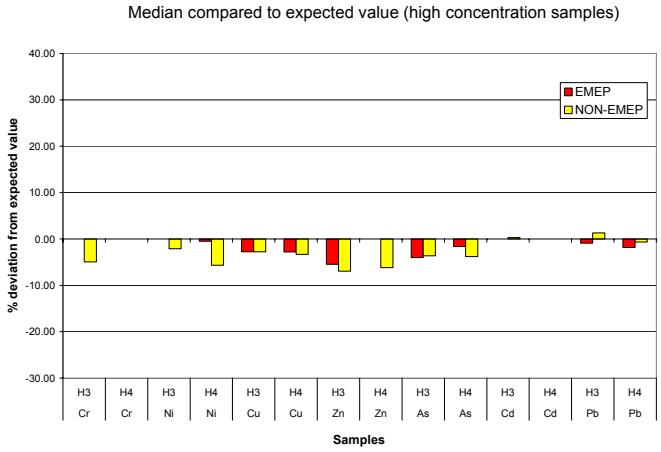


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# Analytical intercomparison of heavy metals in precipitation 2001

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# Analytical intercomparison of heavy metals in precipitation 2001

## 1. Introduction

Heavy metals were included in the EMEP's monitoring programme in 1999. 21 laboratories 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 three intercomparisons have been arranged (Berg and Semb, 1995; Berg and Aas, 1999; Uggerud and Skjelmoen, 2000).

This report presents results from the fourth analytical intercomparison of heavy metals in precipitation, which was carried out during 2001. Seven heavy metals were included: Pb, Cd, Cu, Zn, As, Cr, and Ni.

## 2. Organization of the intercomparison

The samples for the fourth intercomparison were prepared and distributed to 45 laboratories. In addition to 16 EMEP laboratories, 13 laboratories connected to the ICP-forest measurement programme, 13 laboratories connected to WMO and 3 other laboratories also received samples. A total of 29 laboratories, 15 from the EMEP network, reported results within the end of October 2001. In accordance with the decision of the Steering Body of EMEP, the results are presented in such a way that the different laboratories are identified. Tables A.1.1a and A1.1b give the names of the participating laboratories together with the number used when presenting the results in tables and figures.

## 3. Intercomparison samples

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

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

## 4. Presentation of data

Tables A1.2-A1.8 present the reported results 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 statistic run only values below 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.

In Figures A2.1-A2.7 the results are presented in plots showing the relative percentage deviation from expected value for each participating laboratory. There is one plot for every single sample.

The median calculated from the results reported from EMEP laboratories and other participating laboratories respectively, are compared to expected value in Figure A2.8.

A summary of the results is presented in Table A1.9. The results reported from each laboratory are divided in four percent intervals. The number of results reported by the laboratories in each per cent interval is also shown.

Table A1.10 gives information of the analytical techniques used by each laboratory.

## 5. Results

The analytical results from the intercomparison are presented in Figures A2.1-A2.8, Tables A1.2-A1.8 and Table A1.9. The results that were reported by the participating laboratories were generally in accordance with the theoretical values, with good agreement between the median from the second runs and the expected values.

### 5.1 Chromium (Cr)

A total of 25 laboratories reported values for Cr. Four laboratories reported eight values below detection limit for the low concentration samples. Seven laboratories reported results from the low concentration samples that deviated more than 25% from expected value, whereas ten laboratories reported results more than 15% away from expected value for the high concentration samples. The relative standard deviations for the low concentration samples were 23.2% and 32.2%, outliers excluded. For the high concentration samples the relative standard deviation were 10.6% and 12.7%, when outliers were excluded. This is the same as last year's results.

### 5.2 Nickel (Ni)

26 laboratories reported results for Ni. Six laboratories reported values below detection limit for the low concentration samples, whereas no such results were reported for the high concentration samples. For low concentration samples, results that deviated more than 25% from expected value, were reported by nine

laboratories. For high concentration samples, three laboratories reported results that deviated more than 15% from expected value. The relative standard deviations, for the two low concentration samples, were 103.8% and 48.1% when outliers were excluded. Compared to last year's result this might seem bad, but the concentrations in the samples distributed this year were lower than in last year's samples. For the high concentration samples, the relative standard deviations were 11% and 7.3%, which is an improvement compared to earlier intercomparisons.

### 5.3 Copper (Cu)

A total of 28 laboratories reported values for the determination of Cu. Three laboratories reported results from analysis of low concentration samples to be below detection limit. No such results were reported for the high concentration samples. Six laboratories reported values, for the low concentration samples, that deviated more than 25% from expected value. For the high concentration samples, six laboratories reported results that deviated more than 15%. The relative standard deviations for the to low concentration samples were 13.2% and 21.9%, when outliers were excluded. For the high concentration samples the standard deviations were 7.8% and 10.8% when outliers were excluded.

### 5.4 Zinc (Zn)

Results were obtained from 29 laboratories. For the low concentration samples, three laboratories reported values below detection limits. For both low and high concentration samples, eight laboratories reported values more than 25% and 15% away from expected value, respectively. The relative standard deviations were for the two low concentration samples 28.6% and 23.7%, and for the high concentration samples 18.6% and 18%, when outliers were excluded. For both sample groups, these results are not as good as those obtained in the last intercomparison.

### 5.5 Arsenic (As)

A total of 23 laboratories reported values for the determination of As. Five laboratories reported values below detection limit. For low concentration samples four laboratories reported values that deviated more than 25% from expected value, while six laboratories reported values that deviated more than 15% from expected value for the high concentration samples. The relative standard deviations for the two low concentration samples were 16.8% and 8.5%, when outliers were excluded. For the high concentration samples the relative standard deviations were 8.2% and 8.3%, when outliers were excluded. For both sample groups, this is an improvement compared to last year's results.

### 5.6 Cadmium (Cd)

Results for the determination of Cd were obtained from 27 laboratories. 11 laboratories reported values below detection limit. Six laboratories reported results for low concentration samples that deviated more than 25% from expected value. For the high concentration samples seven laboratories reported results that deviated more than 15%. Relative standard deviation for the two low concentration samples were 27.2% and 29.3%, outliers excluded. For the high

concentration samples, the relative standard deviations were 8.3% and 7.5%, outliers excluded. This is an improvement compared to last intercomparison.

### 5.7 Lead (Pb)

A total of 28 laboratories reported values for the determination of Pb. Two laboratories reported values to be below detection limit. Four laboratories reported results for the low concentration samples that deviated more than 25% from expected value. For high concentration samples six laboratories reported values that deviated more than 15%. Relative standard deviations for low concentration samples were 12% and 9.4%, when outliers were excluded. This is an improvement compared to last year. For the two high concentration samples, the relative standard deviations were 9.2% and 8.2%, when outliers were excluded. This is slightly worse than last year.

## 6. Conclusions and further work

The elements showed the following order of success: Pb>As>Cu>Cd>Cr>Zn>Ni.

For all the samples analysed the deviation from the theoretical value was calculated. The median deviations for the EMEP laboratories were below 6.3% and below 5.45% for the low- and high concentration samples, respectively. For low concentration samples this is a marked improvement. The median deviations for the other participating laboratories were below 6.9% for high concentration samples. This is about the same as last year. The median deviations for low concentration samples were (exclusive the median value for Ni in sample H1), below 34%. This is not as good as last year's result.

The field intercomparison on Hg in precipitation and air planned to be arranged in Germany during 2002, is postponed to spring 2003.

A new data flag system is in progress. For heavy metal data, the new data quality objectives differentiate between high and low concentrations, the accuracy in the laboratory should be better than 15% and 25% for high and low concentrations, respectively.

## 7. References

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 HELCOM-EMEP-PARCOM-AMAP analytical intercomparison of heavy metals in precipitation. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Note 1/95).

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

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

# Appendix 1

# Tables

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

| No | Laboratory identification |
|---|---|
| 1 | Federal Environmental Agency, Austria |
| 3 | Czech Hydrometeorological Institute, Czech Republic |
| 5 | Finnish Meteorological Institute, Finland |
| 6 | Laboratories Wollf, France |
| 8 | Umweltbundesamt, Germany |
| 14 | RIVM Laboratory of Inorganic Analytical Chemistry, The Netherlands |
| 15 | The Norwegian Institute for Air Research, Norway |
| 16 | Inst. Of Meteorology and Water Management, Poland |
| 23 | AEA Technology, National Environmental Techn. Centre, United Kingdom |
| 26 | Ontario Ministry of Environment, Canada |
| 31 | Slovak Hydrometeorological Institute, Slovakia |
| 33 | Latvian Hydrometeorological Agency, Latvia |
| 34 | Ministry of Health, Refit Saydam Hygiene Center, Turkey |
| 36 | Hydrometeorological Institute of Slovenia, Slovenia |
| 38 | Estonian Environmental Research Centre, Estonia |

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

| No | Laboratory identification |
|---|---|
| 105 | Universität des Saarlandes Umweltforsuchungszentrum, Germany |
| 109 | Institut f. Bondenkunde und Waldernährung der Universität, Germany |
| 112 | Niedersächsische Forstliche Versuchsanstalt (NVF), Germany |
| 115 | Bayerishe Landesanstalt f. Wald- und Forstwirtschaft, Germany |
| 117 | Sächsische Landesanstalt für Forsten, Germany |
| 118 | Forstliche Versuchs- und Forschungsanstalt Baden-Württemberg, Germany |
| 119 | Landesumweltamt (LUA) |
| 121 | Landesamt für Natur und Umwelt, Germany |
| 125 | Bayerisches Landesamt für Umweltschutz, Germany |
| 127 | Department of Chemistry, Jalan Sultan, Malaysia |
| 128 | Dubai Central Laboratory, United Arab Emirates |
| 129 | Ecole Nationale d'Ingenieurs de Sfax, Tunisie |
| 132 | Comision Chilena De Energia Nuclear, Chile |
| 134 | Wissenschaftszentrum für Ernaehrung, Landnutzung und Umwelt, Germany |

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

Cr
SAMPLE NO.: H1
THEORETICAL VALUE 0.400
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 23
ARITHMETIC MEAN VALUE: 0.665
MEDIAN: 0.410
STANDARD DEVIATON: 0.845
REL. ST. DEVIATION (%): 127.006

RUN 2:
NUMBER OF LABORATORIES: 18
ARITHMETIC MEAN VALUE: 0.474
MEDIAN: 0.410
STANDARD DEVIATON: 0.153
REL. ST. DEVIATION (%): 32.222

RESULTS IN DECREASING ORDER:

| | | | |
|---|---|---|---|
| 125 | 4.100 UNUSED | | |
| 132 | < 1.05 | | |
| 6 | < 1.0 | | |
| 38 | < 1.0 | | |
| 117 | < 1.0 | 121 | 0.410 |
| 112 | 0.820 | 23 | 0.405 |
| 115 | 0.770 | 16 | 0.400 |
| 3 | 0.730 | 36 | 0.400 |
| 109 | 0.570 | 105 | 0.400 |
| 14 | 0.500 | 26 | 0.390 |
| 127 | 0.500 | 119 | 0.390 |
| 8 | 0.430 | 31 | 0.355 |
| 1 | 0.410 | 5 | 0.250 |
| 15 | 0.410 | | |

"UNUSED": DATA UNUSED IN RUN 2

Cr
SAMPLE NO.: H2
THEORETICAL VALUE 0.600
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 24
ARITHMETIC MEAN VALUE: 0.726
MEDIAN: 0.610
STANDARD DEVIATON: 0.335
REL. ST. DEVIATION (%): 46.125

RUN 2:
NUMBER OF LABORATORIES: 19
ARITHMETIC MEAN VALUE: 0.659
MEDIAN: 0.610
STANDARD DEVIATON: 0.153
REL. ST. DEVIATION (%): 23.188

RESULTS IN DECREASING ORDER:

| | | | |
|---|---|---|---|
| 129 | 2.000 UNUSED | | |
| 132 | < 1.05 | | |
| 6 | < 1.0 | | |
| 38 | < 1.0 | | |
| 117 | < 1.0 | 119 | 0.610 |
| 3 | 1.000 | 125 | 0.609 |
| 112 | 0.960 | 14 | 0.600 |
| 115 | 0.940 | 16 | 0.600 |
| 105 | 0.700 | 36 | 0.600 |
| 127 | 0.700 | 1 | 0.590 |
| 109 | 0.670 | 26 | 0.590 |
| 15 | 0.620 | 121 | 0.590 |
| 23 | 0.620 | 31 | 0.526 |
| 8 | 0.610 | 5 | 0.380 |

"UNUSED": DATA UNUSED IN RUN 2

Cr
SAMPLE NO.: H3
THEORETICAL VALUE 8.500
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 25
ARITHMETIC MEAN VALUE: 8.200
MEDIAN: 8.450
STANDARD DEVIATON: 1.461
REL. ST. DEVIATION (%): 17.819

RUN 2:
NUMBER OF LABORATORIES: 23
ARITHMETIC MEAN VALUE: 8.229
MEDIAN: 8.450
STANDARD DEVIATON: 0.876
REL. ST. DEVIATION (%): 10.649

RESULTS IN DECREASING ORDER:

| | | | | |
|---|---|---|---|---|
| 129 | 12.000 UNUSED | 26 | 8.390 | |
| 38 | 10.200 | 125 | 8.360 | |
| 3 | 9.200 | 15 | 8.300 | |
| 23 | 9.110 | 36 | 8.100 | |
| 112 | 8.980 | 118 | 7.800 | |
| 115 | 8.960 | 6 | 7.570 | |
| 8 | 8.530 | 109 | 7.500 | |
| 14 | 8.500 | 127 | 7.500 | |
| 16 | 8.500 | 132 | 7.050 | |
| 31 | 8.499 | 5 | 6.430 | |
| 119 | 8.490 | 105 | 6.400 | |
| 1 | 8.450 | 117 | 3.740 | UNUSED |
| 121 | 8.450 | | | |

"UNUSED": DATA UNUSED IN RUN 2

Cr
SAMPLE NO.: H4
THEORETICAL VALUE 1.500
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 25
ARITHMETIC MEAN VALUE: 1.695
MEDIAN: 1.500
STANDARD DEVIATON: 0.916
REL. ST. DEVIATION (%): 54.072

RUN 2:
NUMBER OF LABORATORIES: 24
ARITHMETIC MEAN VALUE: 1.516
MEDIAN: 1.500
STANDARD DEVIATON: 0.193
REL. ST. DEVIATION (%): 12.704

RESULTS IN DECREASING ORDER:

| | | | |
|---|---|---|---|
| 129 | 6.000 UNUSED | 16 | 1.500 |
| 115 | 1.900 | 105 | 1.500 |
| 112 | 1.830 | 121 | 1.500 |
| 117 | 1.830 | 132 | 1.480 |
| 3 | 1.800 | 26 | 1.440 |
| 14 | 1.700 | 36 | 1.400 |
| 23 | 1.610 | 109 | 1.400 |
| 119 | 1.560 | 125 | 1.400 |
| 38 | 1.550 | 118 | 1.300 |
| 31 | 1.523 | 127 | 1.300 |
| 8 | 1.510 | 5 | 1.170 |
| 1 | 1.500 | 6 | 1.170 |
| 15 | 1.500 | | |

"UNUSED": DATA UNUSED IN RUN 2

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

Ni
SAMPLE NO.: H1
THEORETICAL VALUE 0.300
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 24
ARITHMETIC MEAN VALUE: 0.747
MEDIAN: 0.314
STANDARD DEVIATON: 0.998
REL. ST. DEVIATION (%): 133.623

RUN 2:
NUMBER OF LABORATORIES: 17
ARITHMETIC MEAN VALUE: 0.551
MEDIAN: 0.310
STANDARD DEVIATON: 0.572
REL. ST. DEVIATION (%): 103.806

RESULTS IN DECREASING ORDER:

| | | | |
|---|---|---|---|
| 125 | 4.070 UNUSED | 1 | 0.310 |
| 105 | 2.400 | 121 | 0.310 |
| 127 < 2 | | | |
| 132 < 1.35 | | | |
| 115 | 1.290 | 14 | 0.300 |
| 38 | 1.100 | 26 | 0.300 |
| 117 < 1 | | | |
| 119 < 0.9 | | | |
| 31 | 0.567 | 36 | 0.300 |
| 3 | 0.550 | 8 | 0.280 |
| 112 | 0.530 | 5 | 0.250 |
| 6 < 0.5 | | | |
| 16 | 0.350 | 15 | 0.220 |
| 23 | 0.318 | 109 < 0.1 | |

"UNUSED": DATA UNUSED IN RUN 2

Ni
SAMPLE NO.: H2
THEORETICAL VALUE 0.500
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 24
ARITHMETIC MEAN VALUE: 0.664
MEDIAN: 0.500
STANDARD DEVIATON: 0.452
REL. ST. DEVIATION (%): 68.057

RUN 2:
NUMBER OF LABORATORIES: 18
ARITHMETIC MEAN VALUE: 0.579
MEDIAN: 0.500
STANDARD DEVIATON: 0.278
REL. ST. DEVIATION (%): 48.061

RESULTS IN DECREASING ORDER:

| | | | |
|---|---|---|---|
| 105 | 2.200 UNUSED | 26 | 0.500 |
| 127 < 2 | | | |
| 115 | 1.490 | 36 | 0.500 |
| 132 < 1.35 | | | |
| 38 | 1.150 | 16 | 0.480 |
| 117 < 1 | | | |
| 119 < 0.9 | | | |
| 31 | 0.649 | 8 | 0.460 |
| 3 | 0.590 | 125 | 0.447 |
| 112 | 0.560 | 15 | 0.430 |
| 23 | 0.535 | 5 | 0.410 |
| 1 | 0.510 | 34 | 0.400 |
| 121 | 0.510 | 109 | 0.300 |
| 6 < 0.5 | | | |
| 14 | 0.500 | | |

"UNUSED": DATA UNUSED IN RUN 2

Ni
SAMPLE NO.: H3
THEORETICAL VALUE 6.700
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 26
ARITHMETIC MEAN VALUE: 7.548
MEDIAN: 6.630
STANDARD DEVIATON: 4.154
REL. ST. DEVIATION (%): 55.380

RUN 2:
NUMBER OF LABORATORIES: 25
ARITHMETIC MEAN VALUE: 6.729
MEDIAN: 6.600
STANDARD DEVIATON: 0.738
REL. ST. DEVIATION (%): 10.966

RESULTS IN DECREASING ORDER:

| | | | |
|---|---|---|---|
| 129 | 28.000 UNUSED | 1 | 6.600 |
| 105 | 9.800 | 121 | 6.600 |
| 38 | 7.420 | 132 | 6.520 |
| 115 | 7.290 | 36 | 6.500 |
| 31 | 7.245 | 109 | 6.500 |
| 112 | 6.990 | 125 | 6.410 |
| 16 | 6.900 | 127 | 6.400 |
| 23 | 6.820 | 6 | 6.350 |
| 14 | 6.800 | 15 | 6.200 |
| 3 | 6.770 | 34 | 6.200 |
| 8 | 6.740 | 118 | 6.000 |
| 119 | 6.720 | 117 | 5.960 |
| 26 | 6.660 | 5 | 5.840 |

"UNUSED": DATA UNUSED IN RUN 2

Ni
SAMPLE NO.: H4
THEORETICAL VALUE 8.500
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 26
ARITHMETIC MEAN VALUE: 8.251
MEDIAN: 8.320
STANDARD DEVIATON: 0.751
REL. ST. DEVIATION (%): 9.097

RUN 2:
NUMBER OF LABORATORIES: 25
ARITHMETIC MEAN VALUE: 8.324
MEDIAN: 8.340
STANDARD DEVIATON: 0.612
REL. ST. DEVIATION (%): 7.342

RESULTS IN DECREASING ORDER:

| | | | | |
|---|---|---|---|---|
| 38 | 9.570 | 132 | 8.300 | |
| 34 | 9.400 | 26 | 8.280 | |
| 23 | 9.100 | 6 | 8.200 | |
| 115 | 9.050 | 15 | 8.100 | |
| 31 | 8.808 | 36 | 8.100 | |
| 3 | 8.740 | 109 | 8.100 | |
| 112 | 8.680 | 117 | 7.940 | |
| 14 | 8.600 | 125 | 7.900 | |
| 119 | 8.540 | 127 | 7.800 | |
| 16 | 8.470 | 118 | 7.600 | |
| 1 | 8.450 | 5 | 7.220 | |
| 121 | 8.450 | 105 | 6.800 | |
| 8 | 8.340 | 129 | 6.000 | UNUSED |

"UNUSED": DATA UNUSED IN RUN 2

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

Cu
SAMPLE NO.: H1
THEORETICAL VALUE 1.500
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 27
ARITHMETIC MEAN VALUE: 1.500
MEDIAN: 1.500
STANDARD DEVIATON: 0.433
REL. ST. DEVIATION (%): 28.891

RUN 2:
NUMBER OF LABORATORIES: 21
ARITHMETIC MEAN VALUE: 1.426
MEDIAN: 1.450
STANDARD DEVIATON: 0.188
REL. ST. DEVIATION (%): 13.211

RESULTS IN DECREASING ORDER:

| | | | | |
|---|---|---|---|---|
| 33 | 2.900 UNUSED | 26 | 1.450 | |
| 118 | 2.400 UNUSED | 31 | 1.440 | |
| 128 < 2 | | | | |
| 117 | 1.760 UNUSED | 112 | 1.430 | |
| 115 | 1.730 | 14 | 1.400 | |
| 38 | 1.700 | 15 | 1.400 | |
| 125 | 1.690 | 132 | 1.340 | |
| 119 < 1.68 | | | | |
| 3 | 1.550 | 5 | 1.320 | |
| 8 | 1.540 | 6 | 1.240 | |
| 1 | 1.510 | 34 | 1.100 | |
| 121 | 1.510 | 109 | 1.100 | |
| 16 | 1.500 | 127 | 1.000 | |
| 23 | 1.500 | 105 | 0.500 | UNUSED |
| 36 | 1.500 | | | |

"UNUSED": DATA UNUSED IN RUN 2

Cu
SAMPLE NO.: H2
THEORETICAL VALUE 1.200
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 27
ARITHMETIC MEAN VALUE: 1.140
MEDIAN: 1.170
STANDARD DEVIATON: 0.250
REL. ST. DEVIATION (%): 21.943

RUN 2:
NUMBER OF LABORATORIES: 24
ARITHMETIC MEAN VALUE: 1.140
MEDIAN: 1.170
STANDARD DEVIATON: 0.250
REL. ST. DEVIATION (%): 21.943

RESULTS IN DECREASING ORDER:

| | | | |
|---|---|---|---|
| 128 < 2 | | | |
| 119 < 1.68 | | | |
| 33 | 1.500 | 121 | 1.170 |
| 118 | 1.500 | 26 | 1.160 |
| 112 | 1.350 | 117 | 1.150 |
| 115 | 1.350 | 15 | 1.100 |
| 3 | 1.300 | 16 | 1.100 |
| 14 | 1.300 | 36 | 1.100 |
| 38 | 1.300 | 105 | 1.100 |
| 23 | 1.280 | 31 | 1.060 |
| 125 | 1.210 | 6 < 1.0 | |
| | | 5 | 1.000 |
| 132 | 1.180 | 109 | 0.800 |
| 1 | 1.170 | 127 | 0.700 |
| 8 | 1.170 | 34 | 0.300 |

"UNUSED": DATA UNUSED IN RUN 2

Cu
SAMPLE NO.: H3
THEORETICAL VALUE 7.200
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 28
ARITHMETIC MEAN VALUE: 6.868
MEDIAN: 7.000
STANDARD DEVIATON: 0.983
REL. ST. DEVIATION (%): 14.310

RUN 2:
NUMBER OF LABORATORIES: 25
ARITHMETIC MEAN VALUE: 7.004
MEDIAN: 7.000
STANDARD DEVIATON: 0.553
REL. ST. DEVIATION (%): 7.890

RESULTS IN DECREASING ORDER:

| | | | | |
|---|---|---|---|---|
| 33 | 8.900 UNUSED | 36 | 7.000 | |
| 117 | 8.600 | 121 | 7.000 | |
| 3 | 7.700 | 26 | 6.920 | |
| 23 | 7.600 | 15 | 6.800 | |
| 118 | 7.500 | 38 | 6.700 | |
| 115 | 7.490 | 128 | 6.650 | |
| 125 | 7.380 | 109 | 6.500 | |
| 8 | 7.330 | 132 | 6.440 | |
| 14 | 7.300 | 5 | 6.280 | |
| 31 | 7.180 | 6 | 6.260 | |
| 119 | 7.140 | 34 | 6.200 | |
| 112 | 7.030 | 127 | 6.100 | |
| 1 | 7.000 | 105 | 4.300 | UNUSED |
| 16 | 7.000 | 129 | 4.000 | UNUSED |

"UNUSED": DATA UNUSED IN RUN 2

Cu
SAMPLE NO.: H4
THEORETICAL VALUE 10.000
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 28
ARITHMETIC MEAN VALUE: 9.180
MEDIAN: 9.710
STANDARD DEVIATON: 1.846
REL. ST. DEVIATION (%): 20.108

RUN 2:
NUMBER OF LABORATORIES: 27
ARITHMETIC MEAN VALUE: 9.477
MEDIAN: 9.720
STANDARD DEVIATON: 1.028
REL. ST. DEVIATION (%): 10.848

RESULTS IN DECREASING ORDER:

| | | | | |
|---|---|---|---|---|
| 23 | 10.700 | 36 | 9.700 | |
| 117 | 10.550 | 112 | 9.670 | |
| 14 | 10.400 | 128 | 9.590 | |
| 115 | 10.400 | 8 | 9.540 | |
| 118 | 10.400 | 26 | 9.540 | |
| 3 | 10.100 | 132 | 9.350 | |
| 31 | 10.020 | 38 | 9.200 | |
| 16 | 10.000 | 109 | 9.200 | |
| 119 | 9.970 | 127 | 8.800 | |
| 125 | 9.810 | 6 | 8.610 | |
| 15 | 9.800 | 5 | 8.500 | |
| 33 | 9.800 | 105 | 6.800 | |
| 1 | 9.720 | 129 | 6.000 | |
| 121 | 9.720 | 34 | 1.150 | UNUSED |

"UNUSED": DATA UNUSED IN RUN 2

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

Zn
SAMPLE NO.: H1
THEORETICAL VALUE 7.000
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 28
ARITHMETIC MEAN VALUE: 6.895
MEDIAN: 6.680
STANDARD DEVIATON: 3.193
REL. ST. DEVIATION (%): 46.313

RUN 2:
NUMBER OF LABORATORIES: 23
ARITHMETIC MEAN VALUE: 6.708
MEDIAN: 6.680
STANDARD DEVIATON: 1.918
REL. ST. DEVIATION (%): 28.600

RESULTS IN DECREASING ORDER:

| | | | | |
|---|---|---|---|---|
| 119 | < 30 | 15 | 6.700 | |
| 127 | < 25 | 1 | 6.680 | |
| 129 | 18.000 | UNUSED | 121 | 6.680 |
| 125 | 12.900 | | 36 | 6.500 |
| 38 | < 10 | | 5 | 6.290 |
| 33 | 8.700 | | 14 | 6.000 |
| 8 | 8.300 | | 118 | 5.900 |
| 23 | 7.980 | | 132 | 5.740 |
| 34 | 7.800 | | 117 | 5.510 |
| 115 | 7.700 | | 112 | 5.310 |
| 26 | 7.240 | | 127 | 4.800 |
| 3 | 7.100 | | 105 | 4.400 |
| 31 | 7.000 | | 6 | 2.150 |
| 16 | 6.900 | | 109 | 0.100 UNUSED |

"UNUSED": DATA UNUSED IN RUN 2

Zn
SAMPLE NO.: H2
THEORETICAL VALUE 6.500
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 28
ARITHMETIC MEAN VALUE: 7.040
MEDIAN: 6.000
STANDARD DEVIATON: 7.344
REL. ST. DEVIATION (%): 104.325

RUN 2:
NUMBER OF LABORATORIES: 23
ARITHMETIC MEAN VALUE: 5.820
MEDIAN: 6.000
STANDARD DEVIATON: 1.381
REL. ST. DEVIATION (%): 23.720

RESULTS IN DECREASING ORDER:

| | | | | |
|---|---|---|---|---|
| 129 | 42.000 | UNUSED | 14 | 6.000 |
| 119 | < 30 | | 31 | 6.000 |
| 127 | < 25 | | 34 | 5.800 |
| 38 | < 10 | | 5 | 5.600 |
| 23 | 8.700 | | 36 | 5.400 |
| 33 | 7.500 | | 132 | 5.330 |
| 8 | 7.100 | | 118 | 5.100 |
| 26 | 7.080 | | 117 | 5.080 |
| 125 | 6.990 | | 112 | 4.930 |
| 115 | 6.870 | | 105 | 4.800 |
| 3 | 6.800 | | 127 | 4.300 |
| 15 | 6.400 | | 16 | 3.970 |
| 1 | 6.180 | | 6 | 1.780 |
| 121 | 6.180 | | 109 | 0.100 UNUSED |

"UNUSED": DATA UNUSED IN RUN 2

Zn
SAMPLE NO.: H3
THEORETICAL VALUE 110.000
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 29
ARITHMETIC MEAN VALUE: 94.855
MEDIAN: 104.000
STANDARD DEVIATON: 30.364
REL. ST. DEVIATION (%): 32.011

RUN 2:
NUMBER OF LABORATORIES: 27
ARITHMETIC MEAN VALUE: 101.446
MEDIAN: 104.000
STANDARD DEVIATON: 18.918
REL. ST. DEVIATION (%): 18.648

RESULTS IN DECREASING ORDER:

| | | | | |
|---|---|---|---|---|
| 8 | 123.000 | | 23 | 103.000 |
| 129 | 122.000 | | 33 | 102.000 |
| 125 | 115.000 | | 5 | 101.000 |
| 3 | 113.000 | | 118 | 100.800 |
| 112 | 112.000 | | 16 | 100.400 |
| 119 | 112.000 | | 134 | 100.000 |
| 6 | 110.500 | | 132 | 97.600 |
| 14 | 110.000 | | 36 | 97.000 |
| 31 | 110.000 | | 127 | 94.800 |
| 115 | 110.000 | | 117 | 92.240 |
| 128 | 110.000 | | 38 | 42.700 |
| 26 | 108.000 | | 105 | 37.000 |
| 15 | 107.000 | | 34 | 11.650 UNUSED |
| 1 | 104.000 | | 109 | 0.100 UNUSED |
| 121 | 104.000 | | | |

"UNUSED": DATA UNUSED IN RUN 2

Zn
SAMPLE NO.: H4
THEORETICAL VALUE 130.000
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 29
ARITHMETIC MEAN VALUE: 114.021
MEDIAN: 123.000
STANDARD DEVIATON: 36.081
REL. ST. DEVIATION (%): 31.644

RUN 2:
NUMBER OF LABORATORIES: 27
ARITHMETIC MEAN VALUE: 121.956
MEDIAN: 128.000
STANDARD DEVIATON: 21.956
REL. ST. DEVIATION (%): 18.003

RESULTS IN DECREASING ORDER:

| | | | | |
|---|---|---|---|---|
| 8 | 156.000 | | 121 | 123.000 |
| 23 | 154.000 | | 118 | 120.900 |
| 119 | 134.000 | | 16 | 120.200 |
| 3 | 133.000 | | 134 | 120.000 |
| 112 | 133.000 | | 5 | 120.000 |
| 14 | 132.000 | | 33 | 119.000 |
| 6 | 131.500 | | 36 | 116.000 |
| 15 | 131.000 | | 132 | 114.000 |
| 115 | 131.000 | | 127 | 113.800 |
| 125 | 131.000 | | 117 | 110.100 |
| 26 | 130.000 | | 38 | 65.300 |
| 31 | 130.000 | | 105 | 43.000 |
| 128 | 130.000 | | 34 | 13.710 UNUSED |
| 129 | 128.000 | | 109 | 0.110 UNUSED |
| 1 | 123.000 | | | |

"UNUSED": DATA UNUSED IN RUN 2

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

As
SAMPLE NO.: H1
THEORETICAL VALUE 0.300
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 22
ARITHMETIC MEAN VALUE: 0.302
MEDIAN: 0.300
STANDARD DEVIATON: 0.060
REL. ST. DEVIATION (%): 19.945

RUN 2:
NUMBER OF LABORATORIES: 16
ARITHMETIC MEAN VALUE: 0.292
MEDIAN: 0.299
STANDARD DEVIATON: 0.048
REL. ST. DEVIATION (%): 16.423

RESULTS IN DECREASING ORDER:

| | | | |
|---|---|---|---|
| 128 | < 5 | | |
| 119 | < 1.05 | | |
| 38 | < 1 | | |
| 117 | < 1 | | |
| 112 | < 0.6 | | |
| 6 | 0.450 UNUSED | 125 | 0.299 |
| 33 | 0.400 | 31 | 0.278 |
| 115 | 0.380 | 23 | 0.273 |
| 3 | 0.320 | 15 | 0.270 |
| 1 | 0.300 | 8 | 0.260 |
| 26 | 0.300 | 5 | 0.250 |
| 36 | 0.300 | 14 | 0.250 |
| 121 | 0.300 | 132 | 0.200 |
| 127 | 0.300 | | |

"UNUSED": DATA UNUSED IN RUN 2

As
SAMPLE NO.: H2
THEORETICAL VALUE 0.500
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 22
ARITHMETIC MEAN VALUE: 0.466
MEDIAN: 0.470
STANDARD DEVIATON: 0.072
REL. ST. DEVIATION (%): 15.466

RUN 2:
NUMBER OF LABORATORIES: 15
ARITHMETIC MEAN VALUE: 0.465
MEDIAN: 0.470
STANDARD DEVIATON: 0.039
REL. ST. DEVIATION (%): 8.476

RESULTS IN DECREASING ORDER:

| | | | |
|---|---|---|---|
| 128 | < 5 | | |
| 119 | < 1.05 | | |
| 38 | < 1 | | |
| 117 | < 1 | | |
| 6 | 0.650 UNUSED | 121 | 0.470 |
| 112 | < 0.6 | | |
| 23 | 0.530 | 31 | 0.460 |
| 115 | 0.530 | 26 | 0.450 |
| 36 | 0.500 | 132 | 0.450 |
| 125 | 0.485 | 14 | 0.430 |
| 1 | 0.470 | 127 | 0.400 |
| 3 | 0.470 | 5 | 0.390 |
| 8 | 0.470 | 33 | 0.300 UNUSED |
| 15 | 0.470 | | |

"UNUSED": DATA UNUSED IN RUN 2

As
SAMPLE NO.: H3
THEORETICAL VALUE 2.500
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 23
ARITHMETIC MEAN VALUE: 2.412
MEDIAN: 2.405
STANDARD DEVIATON: 0.293
REL. ST. DEVIATION (%): 12.155

RUN 2:
NUMBER OF LABORATORIES: 20
ARITHMETIC MEAN VALUE: 2.411
MEDIAN: 2.405
STANDARD DEVIATON: 0.199
REL. ST. DEVIATION (%): 8.262

RESULTS IN DECREASING ORDER:

| | | | |
|---|---|---|---|
| 128 | <5 | 8 | 2.400 |
| 6 | 3.150 UNUSED | 1 | 2.390 |
| 112 | 2.780 | 121 | 2.390 |
| 3 | 2.700 | 14 | 2.370 |
| 132 | 2.640 | 15 | 2.300 |
| 23 | 2.570 | 118 | 2.300 |
| 31 | 2.550 | 127 | 2.200 |
| 119 | 2.540 | 117 | 2.150 |
| 36 | 2.500 | 5 | 2.100 |
| 125 | 2.490 | 33 | 2.000 |
| 26 | 2.440 | 38 | 1.700 UNUSED |
| 115 | 2.410 | | |

"UNUSED": DATA UNUSED IN RUN 2

As
SAMPLE NO.: H4
THEORETICAL VALUE 5.000
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 23
ARITHMETIC MEAN VALUE: 4.910
MEDIAN: 4.850
STANDARD DEVIATON: 0.596
REL. ST. DEVIATION (%): 12.142

RUN 2:
NUMBER OF LABORATORIES: 20
ARITHMETIC MEAN VALUE: 4.926
MEDIAN: 4.850
STANDARD DEVIATON: 0.411
REL. ST. DEVIATION (%): 8.334

RESULTS IN DECREASING ORDER:

| | | | |
|---|---|---|---|
| 6 | 6.200 UNUSED | 121 | 4.850 |
| 23 | 5.780 | 115 | 4.830 |
| 33 | 5.700 | 125 | 4.810 |
| 117 | 5.500 | 15 | 4.800 |
| 3 | 5.300 | 118 | 4.800 |
| 31 | 5.050 | 112 | 4.780 |
| 119 | 5.000 | 8 | 4.760 |
| 128 | <5 | 132 | 4.600 |
| 14 | 4.960 | 127 | 4.200 |
| 26 | 4.920 | 5 | 4.130 |
| 36 | 4.900 | 38 | 3.300 UNUSED |
| 1 | 4.850 | | |

"UNUSED": DATA UNUSED IN RUN 2

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

Cd
SAMPLE NO.: H1
THEORETICAL VALUE 0.040
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 26
ARITHMETIC MEAN VALUE: 0.053
MEDIAN: 0.040
STANDARD DEVIATON: 0.040
REL. ST. DEVIATION (%): 74.600

RUN 2:
NUMBER OF LABORATORIES: 15
ARITHMETIC MEAN VALUE: 0.043
MEDIAN: 0.040
STANDARD DEVIATON: 0.012
REL. ST. DEVIATION (%): 27.158

RESULTS IN DECREASING ORDER:

| | | | |
|---|---|---|---|
| 128 < 1 | | 125 | 0.042 |
| 132 < 0.6 | | 1 | 0.040 |
| 112 < 0.32 | | 31 | 0.040 |
| 34 | 0.200 | 33 | 0.040 |
| 36 < 0.2 | | 121 | 0.040 |
| 127 < 0.2 | | 119 < 0.035 | |
| 6 < 0.1 | | 23 | 0.039 |
| 109 < 0.1 | | 16 | 0.038 |
| 38 | 0.080 | 8 | 0.037 |
| 115 | 0.060 | 14 | 0.037 |
| 26 < 0.05 | | 5 | 0.034 |
| 15 | 0.047 | 117 | 0.030 |
| 3 | 0.045 | 105 < 0.01 | |

"UNUSED": DATA UNUSED IN RUN 2

Cd
SAMPLE NO.: H2
THEORETICAL VALUE 0.060
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 27
ARITHMETIC MEAN VALUE: 0.091
MEDIAN: 0.060
STANDARD DEVIATON: 0.092
REL. ST. DEVIATION (%): 101.063

RUN 2:
NUMBER OF LABORATORIES: 17
ARITHMETIC MEAN VALUE: 0.060
MEDIAN: 0.059
STANDARD DEVIATON: 0.018
REL. ST. DEVIATION (%): 29.252

RESULTS IN DECREASING ORDER:

| | | | |
|---|---|---|---|
| 128 < 1 | | 16 | 0.060 |
| 132 < 0.6 | | 26 | 0.060 |
| 112 < 0.32 | | 121 | 0.060 |
| 105 | 0.300 UNUSED | 8 | 0.059 |
| 34 | 0.300 UNUSED | 125 | 0.059 |
| 36 < 0.2 | | 31 | 0.058 |
| 127 < 0.2 | | 33 | 0.054 |
| 38 | 0.120 | 14 | 0.052 |
| 6 < 0.1 | | 26 < 0.05 | |
| 109 < 0.1 | | 5 | 0.048 |
| 115 | 0.080 | 119 | 0.046 |
| 23 | 0.067 | 15 | 0.040 |
| 3 | 0.064 | 117 | 0.040 |
| 1 | 0.060 | | |

"UNUSED": DATA UNUSED IN RUN 2

Cd
SAMPLE NO.: H3
THEORETICAL VALUE 0.600
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 27
ARITHMETIC MEAN VALUE: 0.604
MEDIAN: 0.600
STANDARD DEVIATON: 0.063
REL. ST. DEVIATION (%): 10.443

RUN 2:
NUMBER OF LABORATORIES: 26
ARITHMETIC MEAN VALUE: 0.595
MEDIAN: 0.600
STANDARD DEVIATON: 0.050
REL. ST. DEVIATION (%): 8.336

RESULTS IN DECREASING ORDER:

| | | | |
|---|---|---|---|
| 128 < 1 | | 109 | 0.600 |
| 34 | 0.800 UNUSED | 118 | 0.600 |
| 112 | 0.720 | 8 | 0.594 |
| 132 | 0.670 | 6 | 0.590 |
| 38 | 0.640 | 1 | 0.580 |
| 3 | 0.634 | 121 | 0.580 |
| 23 | 0.633 | 14 | 0.567 |
| 31 | 0.625 | 117 | 0.540 |
| 26 | 0.620 | 33 | 0.532 |
| 15 | 0.610 | 5 | 0.530 |
| 115 | 0.610 | 36 | 0.500 |
| 119 | 0.610 | 127 | 0.500 |
| 125 | 0.604 | 105 < 0.01 | |
| 16 | 0.600 | | |

"UNUSED": DATA UNUSED IN RUN 2

Cd
SAMPLE NO.: H4
THEORETICAL VALUE 0.900
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 27
ARITHMETIC MEAN VALUE: 0.875
MEDIAN: 0.900
STANDARD DEVIATON: 0.162
REL. ST. DEVIATION (%): 18.532

RUN 2:
NUMBER OF LABORATORIES: 24
ARITHMETIC MEAN VALUE: 0.899
MEDIAN: 0.900
STANDARD DEVIATON: 0.067
REL. ST. DEVIATION (%): 7.484

RESULTS IN DECREASING ORDER:

| | | | | |
|---|---|---|---|---|
| 128 < 1 | | 16 | 0.900 | |
| 34 | 1.100 | 26 | 0.900 | |
| 118 | 1.100 | 109 | 0.900 | |
| 23 | 1.010 | 1 | 0.880 | |
| 132 | 1.010 | 121 | 0.880 | |
| 8 | 0.989 | 125 | 0.866 | |
| 3 | 0.979 | 117 | 0.830 | |
| 31 | 0.953 | 36 | 0.800 | |
| 112 | 0.950 | 127 | 0.800 | |
| 119 | 0.930 | 33 | 0.785 | |
| 115 | 0.920 | 5 | 0.780 | |
| 15 | 0.910 | 105 | 0.400 | UNUSED |
| 38 | 0.910 | 14 | 0.380 | UNUSED |
| 6 | 0.900 | | | |

"UNUSED": DATA UNUSED IN RUN 2

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

Pb
SAMPLE NO.: H1
THEORETICAL VALUE 1.300
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 27
ARITHMETIC MEAN VALUE: 1.250
MEDIAN: 1.240
STANDARD DEVIATON: 0.330
REL. ST. DEVIATION (%): 26.409

RUN 2:
NUMBER OF LABORATORIES: 22
ARITHMETIC MEAN VALUE: 1.279
MEDIAN: 1.265
STANDARD DEVIATON: 0.153
REL. ST. DEVIATION (%): 11.978

RESULTS IN DECREASING ORDER:

| | | | | |
|---|---|---|---|---|
| 128 | < 20 | 119 | 1.220 | |
| 118 | 2.200 | UNUSED | 15 | 1.200 |
| 115 | 1.630 | | 16 | 1.200 |
| 112 | 1.560 | | 33 | 1.200 |
| 34 | 1.500 | | 36 | 1.200 |
| 3 | 1.450 | | 23 | 1.180 |
| 31 | 1.399 | | 5 | 1.150 |
| 125 | 1.360 | | 132 | 1.130 |
| 6 | 1.300 | | 117 | 1.040 |
| 8 | 1.300 | | 38 | < 1 |
| 14 | 1.300 | | 109 | 1.000 |
| 1 | 1.290 | | 127 | 0.500 UNUSED |
| 121 | 1.290 | | 105 | 0.400 UNUSED |
| 26 | 1.240 | | | |

"UNUSED": DATA UNUSED IN RUN 2

Pb
SAMPLE NO.: H2
THEORETICAL VALUE 1.700
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 25
ARITHMETIC MEAN VALUE: 1.636
MEDIAN: 1.690
STANDARD DEVIATON: 0.279
REL. ST. DEVIATION (%): 17.034

RUN 2:
NUMBER OF LABORATORIES: 23
ARITHMETIC MEAN VALUE: 1.704
MEDIAN: 1.700
STANDARD DEVIATON: 0.161
REL. ST. DEVIATION (%): 9.430

RESULTS IN DECREASING ORDER:

| | | | | |
|---|---|---|---|---|
| 128 | < 20 | 121 | 1.690 | |
| 31 | 2.032 | 26 | 1.610 | |
| 109 | 2.000 | 15 | 1.600 | |
| 112 | 1.940 | 118 | 1.600 | |
| 3 | 1.920 | 117 | 1.570 | |
| 125 | 1.810 | 132 | 1.570 | |
| 34 | 1.800 | 16 | 1.500 | |
| 115 | 1.790 | 33 | 1.500 | |
| 8 | 1.780 | 36 | 1.500 | |
| 119 | 1.740 | 5 | 1.440 | |
| 23 | 1.710 | 38 | < 1 | |
| 6 | 1.700 | 127 | 0.900 | UNUSED |
| 14 | 1.700 | 105 | 0.800 | UNUSED |
| 1 | 1.690 | | | |

"UNUSED": DATA UNUSED IN RUN 2

Pb
SAMPLE NO.: H3
THEORETICAL VALUE 45.000
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 28
ARITHMETIC MEAN VALUE: 43.617
MEDIAN: 44.750
STANDARD DEVIATON: 9.909
REL. ST. DEVIATION (%): 22.718

RUN 2:
NUMBER OF LABORATORIES: 26
ARITHMETIC MEAN VALUE: 44.026
MEDIAN: 44.750
STANDARD DEVIATON: 4.096
REL. ST. DEVIATION (%): 9.241

RESULTS IN DECREASING ORDER:

| | | | | |
|---|---|---|---|---|
| 132 | 71.900 | UNUSED | 8 | 44.700 |
| 128 | 52.850 | | 1 | 44.600 |
| 117 | 48.200 | | 121 | 44.600 |
| 112 | 47.300 | | 3 | 43.540 |
| 6 | 47.200 | | 26 | 43.200 |
| 115 | 47.200 | | 15 | 43.000 |
| 23 | 46.100 | | 16 | 42.600 |
| 119 | 45.900 | | 36 | 42.500 |
| 31 | 45.680 | | 127 | 41.600 |
| 118 | 45.600 | | 5 | 41.000 |
| 125 | 45.400 | | 105 | 40.500 |
| 14 | 45.100 | | 38 | 36.600 |
| 33 | 44.900 | | 129 | 30.000 |
| 34 | 44.800 | | 109 | 4.700 UNUSED |

"UNUSED": DATA UNUSED IN RUN 2

Pb
SAMPLE NO.: H4
THEORETICAL VALUE 30.000
UNIT: ng /ml

RUN 1:
NUMBER OF LABORATORIES: 28
ARITHMETIC MEAN VALUE: 28.634
MEDIAN: 29.650
STANDARD DEVIATON: 6.067
REL. ST. DEVIATION (%): 21.187

RUN 2:
NUMBER OF LABORATORIES: 26
ARITHMETIC MEAN VALUE: 30.106
MEDIAN: 29.700
STANDARD DEVIATON: 2.461
REL. ST. DEVIATION (%): 8.175

RESULTS IN DECREASING ORDER:

| | | | | |
|---|---|---|---|---|
| 128 | 35.690 | | 8 | 29.600 |
| 132 | 35.200 | | 3 | 29.450 |
| 34 | 35.200 | | 26 | 29.400 |
| 23 | 32.100 | | 125 | 29.200 |
| 118 | 31.900 | | 16 | 28.500 |
| 115 | 31.800 | | 36 | 28.400 |
| 117 | 31.700 | | 6 | 28.150 |
| 112 | 31.600 | | 15 | 28.000 |
| 31 | 30.370 | | 127 | 28.000 |
| 1 | 29.800 | | 105 | 27.000 |
| 14 | 29.800 | | 5 | 27.000 |
| 121 | 29.800 | | 38 | 25.700 |
| 33 | 29.700 | | 129 | 16.000 UNUSED |
| 119 | 29.700 | | 109 | 3.000 UNUSED |

"UNUSED": DATA UNUSED IN RUN 2

*Table A1.9: Percentage deviation from theoretical concentration value.*

| **Element and percent interval** | **Lab. Identification** *The number in brackets are number of results reported in the particular percent interval by the laboratory* | | |
|---|---|---|---|
| | EMEP | Other | |
| **Cr** | | | |
| 0-5% | 9 | 5 | 1(4), 8(3), 14(2), 15(4),16(4), 23(2), 26(4), 32(2), 36(3), 105(2), 119(4), 121(4), 125(2), 132(1) |
| 5-15% | 7 | 6 | 3(1), 6(1), 8(1), 14(1), 23(2), 31(2), 36(1), 109(3), 112(1), 115(1), 118(2), 125(1), 127(2), |
| 15-25% | 5 | 4 | 3(1), 5(2), 6(1), 14(1), 10(1), 112(1), 117(1), 127(2), 132(1) |
| >25% | 2 | 7 | 3(2), 5(2), 105(1), 109(1), 112(2), 115(3), 117(1), 125(1), 129(3) |
| **Ni** | | | |
| 0-5% | 12 | 7 | 1(4), 3(2), 6(1), 8(2), 14(4), 5(1), 16(3), 23(1), 26(4), 31(1), 34(1), 36(4), 109(2), 112(2), 119(2), 121(4), 125(1), 127(1), 132(2) |
| 5-15% | 8 | 6 | 5(1), 6(1), 8(2), 15(2), 23(3), 31(1), 34(2), 38(2), 112(1), 115(2), 117(2), 118(2), 125(2), 127(1), |
| 15-25% | 3 | 1 | 5(3), 16(1), 34(1), 105(1) |
| >25% | 3 | 6 | 3(1), 31(2), 38(2), 105(3), 109(1), 112(1), 115(2), 125(1), 129(2) |
| **Cu** | | | |
| 0-5% | 11 | 8 | 1(4), 3(2), 8(4),14(2), 15(1), 16(3), 23(1), 26(4), 31(3), 33(1), 36(3), 112(3), 115(2), 117(2), 118(2), 119(2), 121(4), 125(3), 132(2) |
| 5-15% | 10 | 7 | 3(2), 5(3), 6(2), 14(2), 15(3), 16(1), 23(3), 31(1), 36(1), 38(4), 105(1), 109(2), 112(1), 115(2), 125(1), 127(1), 132(2) |
| 15-25% | 4 | 3 | 5(1), 6(1), 33(2), 34(1), 117(2), 118(1), 127(1), |
| >25% | 2 | 5 | 33(1), 34(3), 105(3), 109(2), 117(1), 127(2), 129(2) |
| **Zn** | | | |
| 0-5% | 8 | 6 | 1(2), 3(4), 6(2), 14(2), 15(4), 16(1), 26(3), 31(3), 112(2), 115(2), 119(2), 121(2), 125(2), 129(1) |
| 5-15% | 11 | 7 | 1(2), 5(4), 8(2), 14(2), 16(2), 23(2), 26(1), 31(1), 33(2), 34(2), 36(3), 115(2), 118(2), 121(2), 125(1), 129(1), 132(2), 134(2) |
| 15-25% | 4 | 5 | 8(2), 23(1), 33(2), 36(1), 112(2), 117(4), 118(2), 127(2), 132(2) |
| >25% | 5 | 5 | 6(2), 16(1), 23(1), 34(2), 38(2), 105(4), 109(4), 125(1), 127(2), 129(2) |
| **As** | | | |
| 0-5% | 8 | 7 | 1(3), 8(2), 14(1), 15(1), 23(1), 26(3), 31(2), 36(4), 112(1), 115(2), 118(1), 119(2), 121(3), 125(4), 127(1) |
| 5-15% | 9 | 7 | 1(1), 3(4), 8(2), 14(2), 15(3), 23(2), 26(1), 31(2), 33(1), 112(1), 115(1), 117(2), 118(1), 121(1), 127(1), 132(3) |
| 15-25% | 5 | 1 | 5(4), 6(1), 14(1), 23(1), 33(1), 127(2) |
| >25% | 3 | 2 | 6(3), 33(2), 38(2), 115(1), 132(1) |
| **Cd** | | | |
| 0-5% | 10 | 6 | 1(4), 6(2), 8(2), 15(2), 16(4), 23(1), 26(3), 31(3), 33(1), 38(1), 109(2), 115(2), 118(1), 119(2), 121(4), 125(4) |
| 5-15% | 9 | 4 | 3(4), 5(3), 8(2), 14(3), 23(3), 31(1), 33(3), 36(1), 38(1), 112(1), 117(2), 127(1), 133(1) |
| 15-25% | 4 | 5 | 5(1), 15(1), 34(1), 36(1), 112(1), 117(1), 118(1), 119(1), 127(1) |
| >25% | 2 | 3 | 14(1), 15(1), 34(3), 105(2), 115(2), 117(1) |
| **Pb** | | | |
| 0-5% | 12 | 5 | 1(4), 3(2), 6(3), 8(4), 14(4), 15(2), 16(1), 23(2), 26(3), 31(2), 33(2), 34(1), 115(1), 118(1), 119(3), 121(4), 125(3) |
| 5-15% | 12 | 9 | 3(2), 5(3), 6(1), 15(2), 16(3), 23(2), 26(1), 31(1), 33(2), 34(1), 36(4), 38(1), 105(2), 112(3), 115(2), 117(3), 118(2), 119(1), 125(1), 127(2), 132(2) |
| 15-25% | 4 | 5 | 5(1), 31(1), 34(2), 38(1), 109(2), 112(1), 117(1), 128(2), 132(1) |
| >25% | 0 | 7 | 105(2), 109(2), 115(1), 118(1), 127(2), 129(2), 132(1) |

*Table A1.10: Analytical techniques used at the participating laboratories for the different elements.*

| Lab. no. | Elements | Technique |
|---|---|---|
| 1 | Cr, Ni, Cu, Zn, As, Cd, Pb | ICP-MS |
| 3 | Ni, Cd, Cu, Pb,<br>Cr, As<br>Zn | GF-AAS<br>ICP-MS<br>F-AAS |
| 5 | Cr, Ni, Cu, Zn, As, Cd, Pb | ICP-MS |
| 6 | Cr, Ni, Cu, Zn, As, Cd, Pb | ICP-MS |
| 8 | Cr, Ni, Cu, Zn, As, Cd, Pb | ICP-MS |
| 14 | Cr, Ni, Cu, Zn, As, Cd, Pb | ICP-MS |
| 15 | Cr, Ni, Cu, Zn, As, Cd, Pb | ICP-MS |
| 16 | Cr, Ni, Cu, Cd, Pb<br>Zn | GF-AAS<br>F-AAS |
| 23 | Cr, Ni, Cu, Zn, As, Cd, Pb | ICP-MS |
| 26 | Cr, Ni, Cu, Zn, As, Cd, Pb | ICP-MS |
| 31 | Cr, Ni, Cu, Cd, Pb<br>As<br>Zn | GF-AAS<br>HG-GF-AAS<br>F-AAS |
| 33 | Cu, Cd, Pb<br>Zn<br>As | GF-AAS<br>F-AAS<br>HG-AAS |
| 34 | Ni, Cu | AAS |
| 36 | Cr, Ni, Cu, Zn, As, Cd, Pb | ICP-MS |
| 38 | Cr, Ni, Cu, , Cd, Pb<br>Zn | GF-AAS<br>F-AAS |
| 105 | Cr, NI, Cu, Zn, Cd, Pb | GF-AAS |
| 109 | Cr, Ni, Cu, Zn, Cd, Pb | GF-AAS |
| 112 | Cr, Ni, Cu, Zn, As, Cd, Pb | USN-ICP-MS |
| 115 | Cr, Ni, Cu, Zn, As, Cd, Pb | ICP-MS |
| 117 | Cr, Ni, Cu , Zn<br>As, Cd, Pb | USN-ICP-OES<br>GF-AAS |
| 118 | Cu, Cd, Pb<br>As ,Zn Cr, Ni | GF-AAS<br>ICP-OES |
| 119 | Cr, Ni, Cu, As, Cd, Pb<br>Zn | GF-AAS<br>F-AAS |
| 121 | Cr, Ni, Cu, Cd, Pb<br>Zn<br>As | GF-AAS<br>Voltametry<br>HG-AAS |
| 125 | Cr, Ni, Cu, Zn, As, Cd, Pb | ICP-MS |
| 127 | Cr, Ni, Cu, Zn, As, Cd, Pb | ICP-MS |
| 128 | Cu, Cd, Pb<br>As<br>Zn | GF-AAS<br>HG-AAS<br>F-AAS |
| 129 | Cr, Ni, Cu, Zn, Cd, Pb | F-AAS (Polarized Zeeman) |
| 132 | Cr, Ni, Cu, Zn , Cd<br>Pb<br>As | USN-ICP-OES<br>GF-AAS<br>HG-AAS |
| 134 | Zn | ICP-OES |

# Appendix 2

# Figures

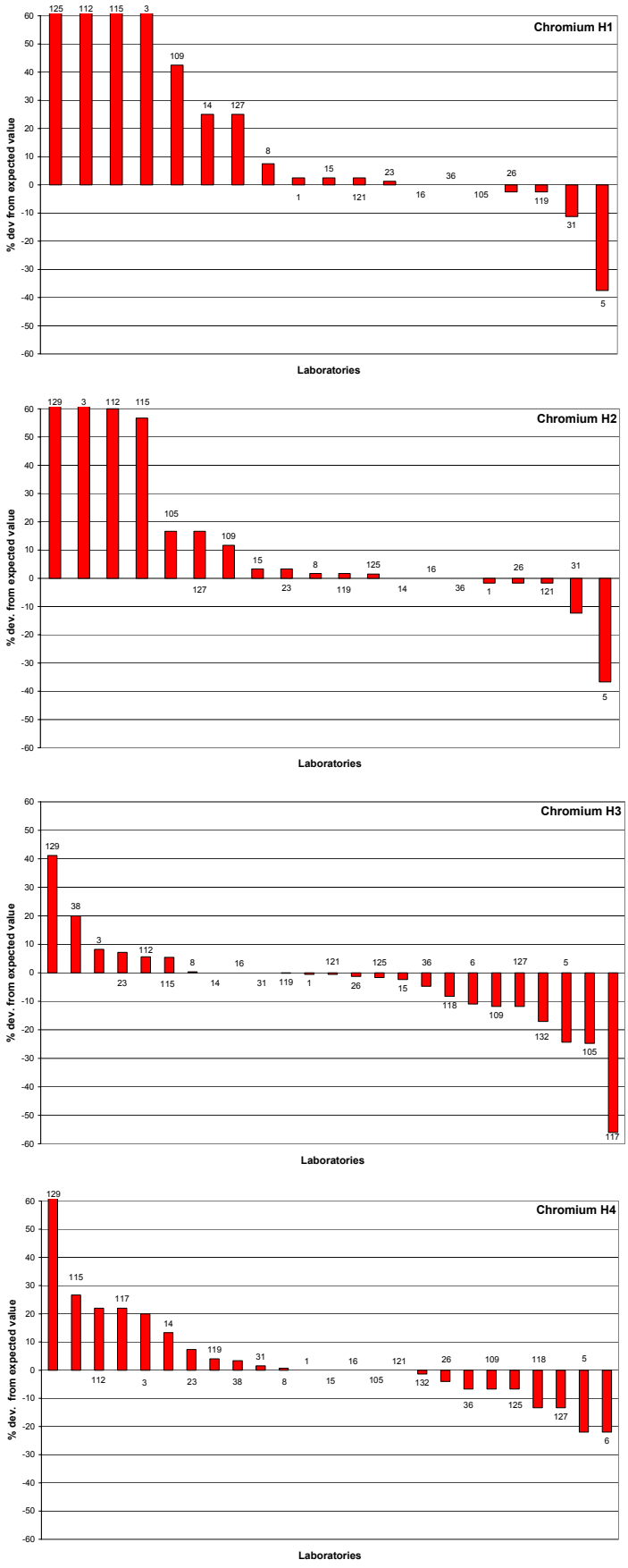



*Figure A2.1: Results from determination of Cr.*

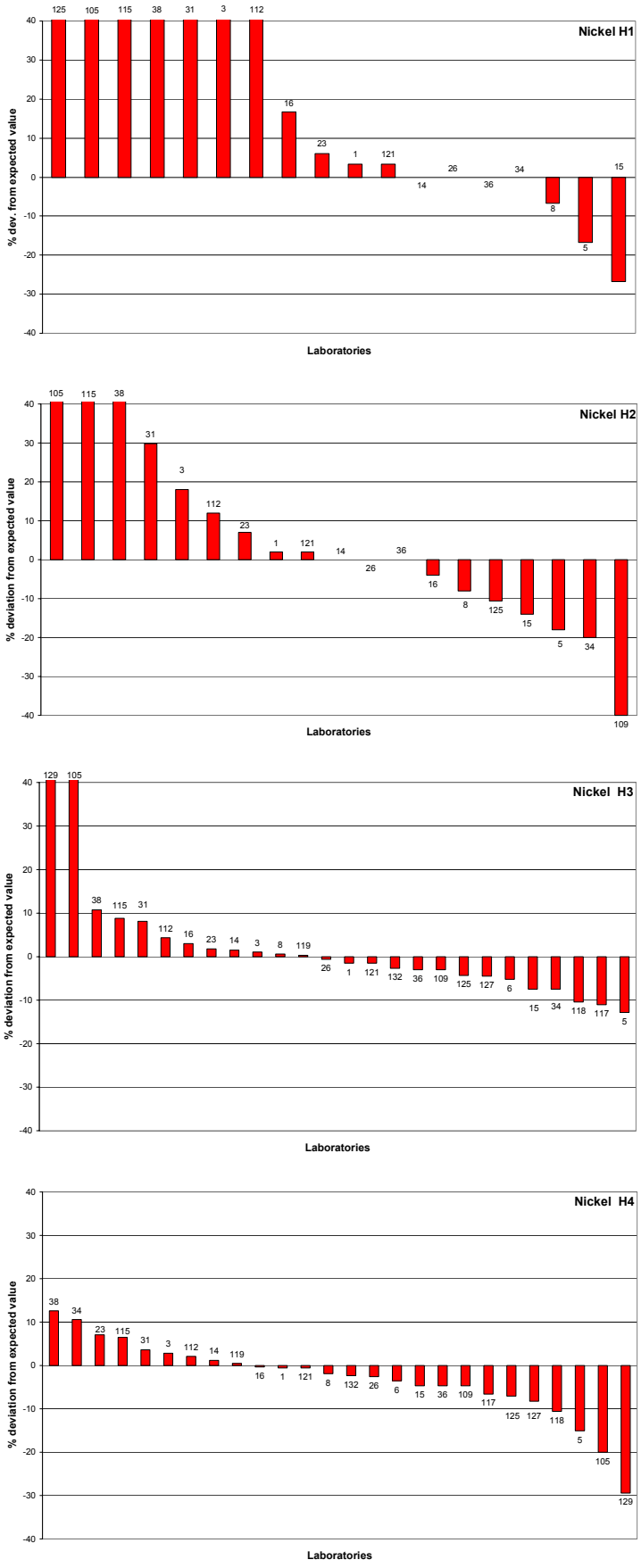



*Figure A2.2: Results from determination of Ni.*

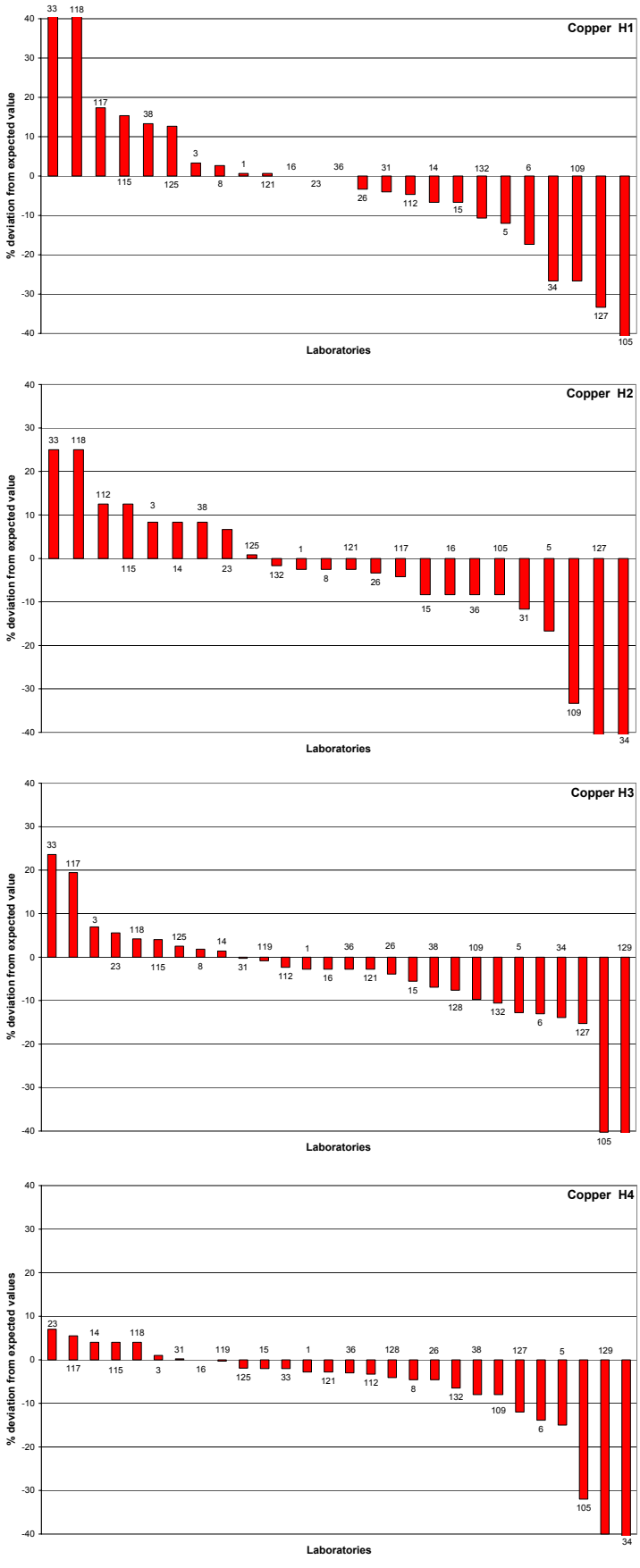



*Figure A2.3: Results from determination of Cu.*

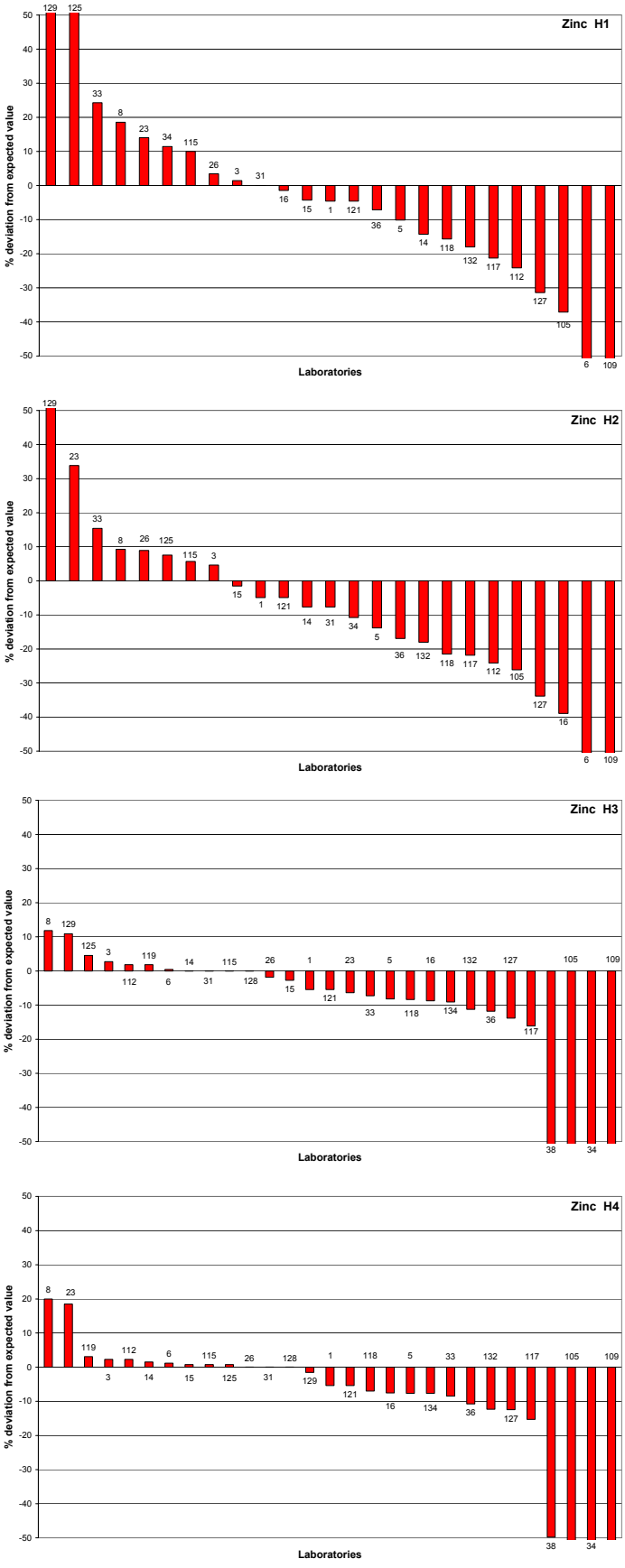
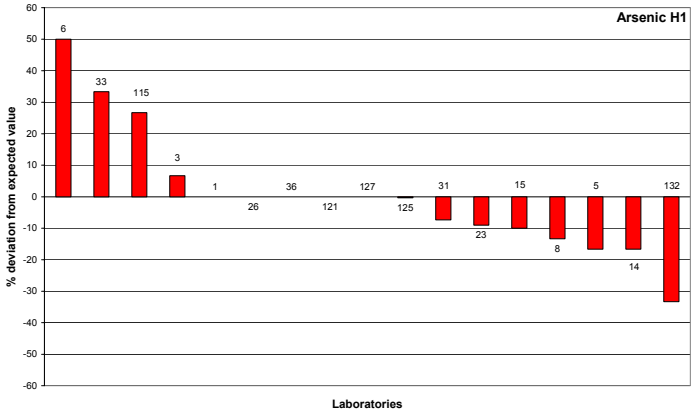
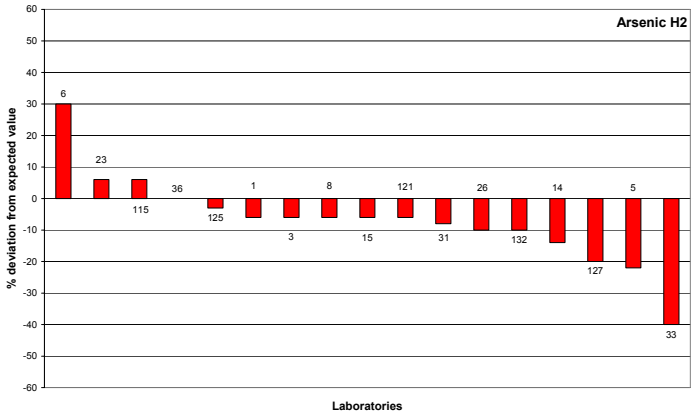
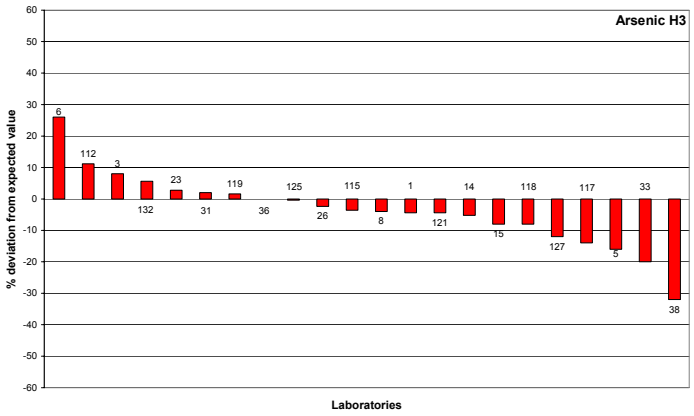



*Figure A2.4: Results from determination of Zn.*



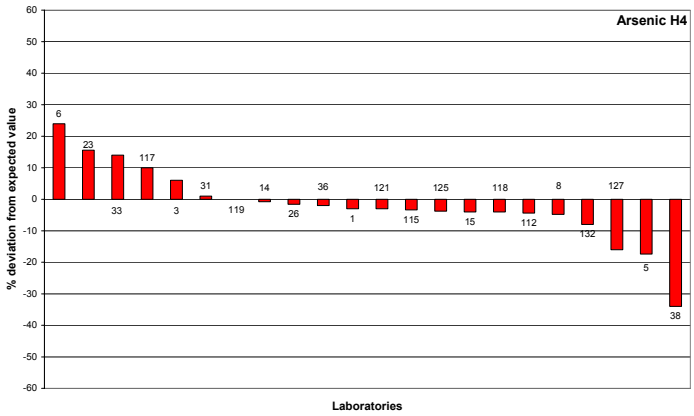




*Figure A2.5: Results from determination of As.*

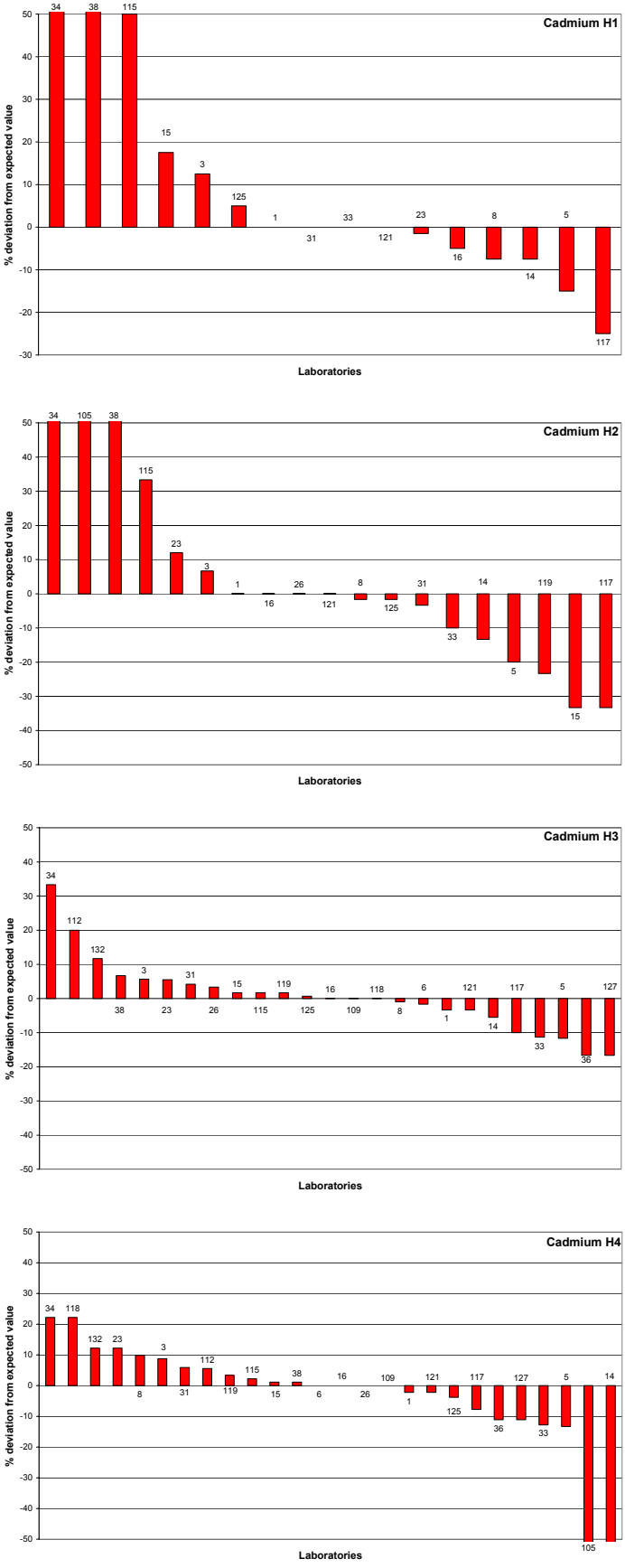



*Figure A2.6: Results from determination of Cd.*

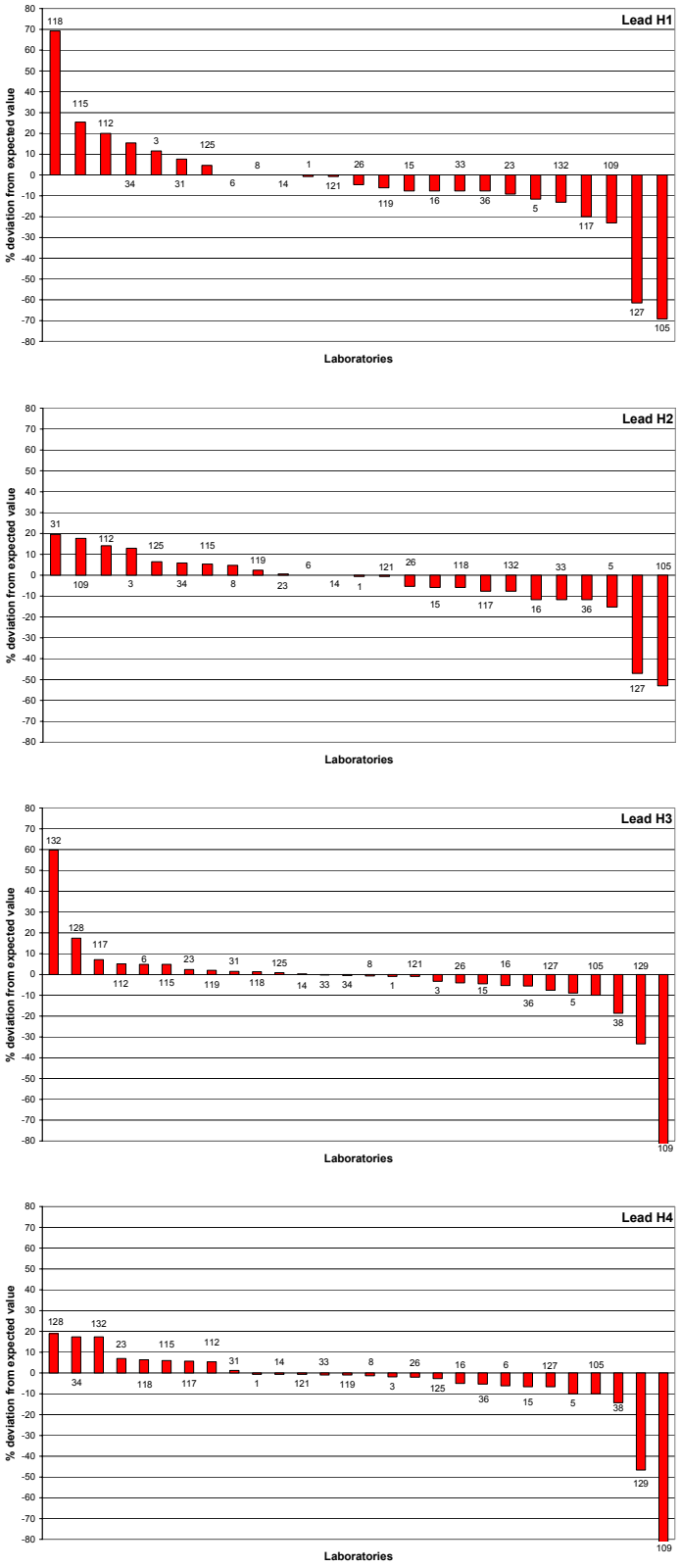



*Figure A2.7: Results from determination of Pb.*

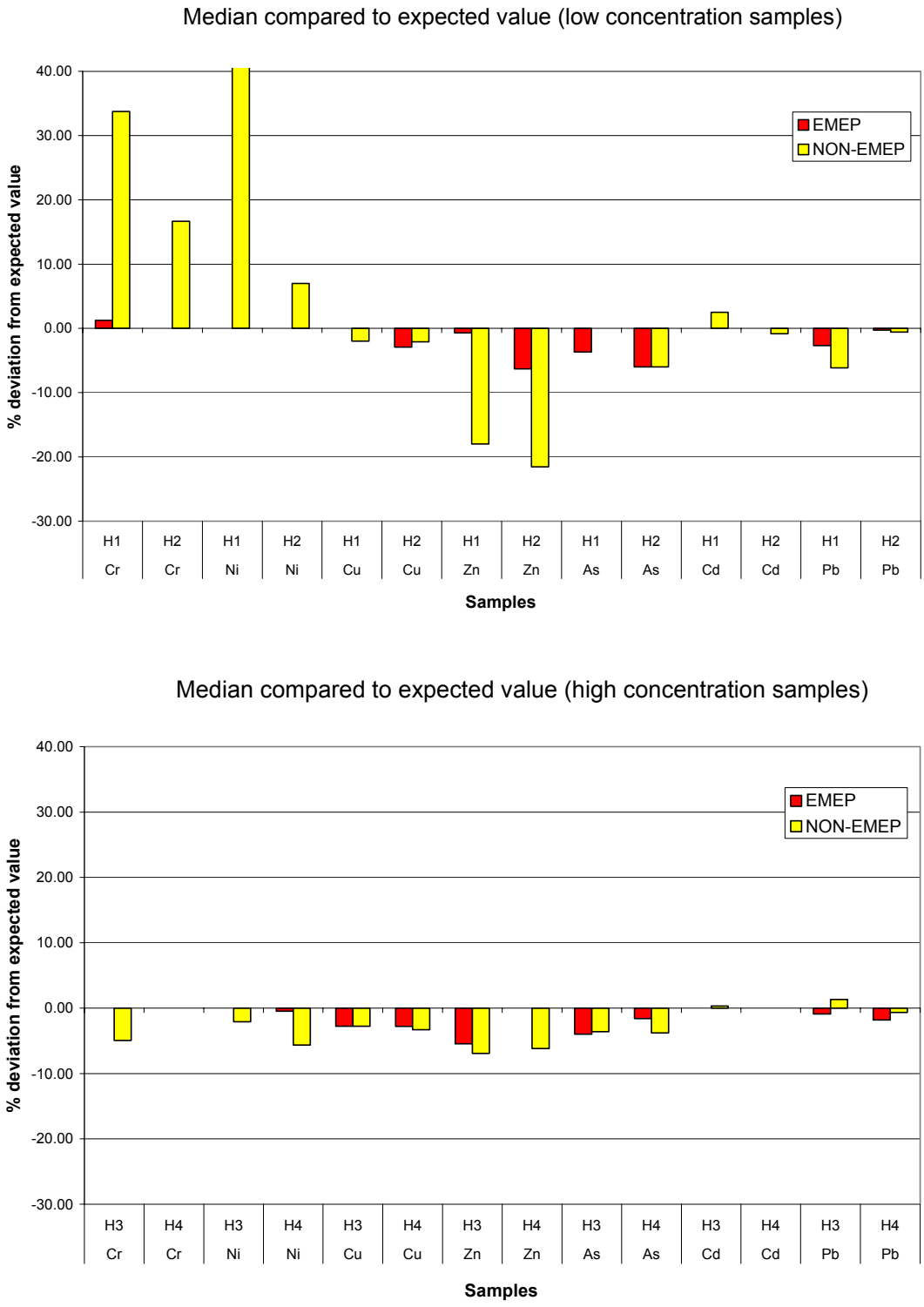



*Figure A2.8: The median compared to theoretical value for low and high concentration samples, respectively.*