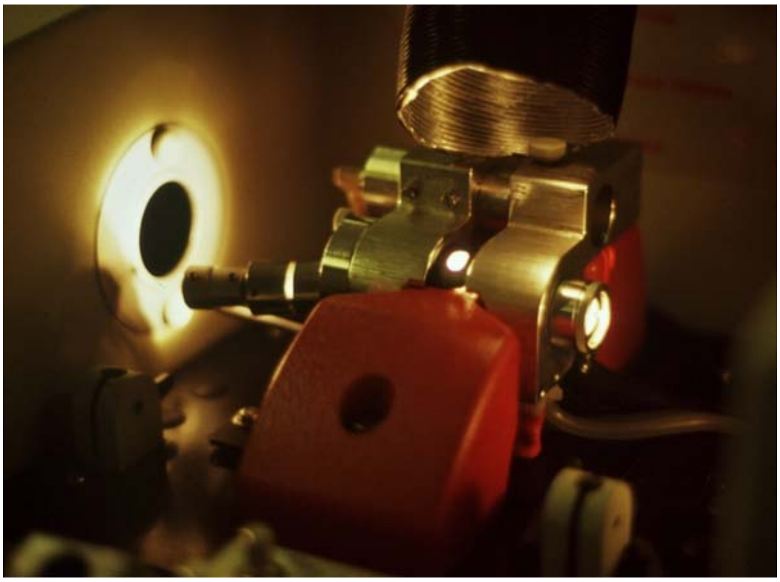
ITM report 106

# Interlaboratory trial for validation of ISO/DIS 15586



## Water quality – Determination of trace elements by atomic absorption spectrometry with graphite furnace

Karin Holm
Hans Borg

Institutet för tillämpad miljöforskning
Institute of Applied Environmental Research

# Interlaboratory trial for validation of ISO/DIS 15586

## Water quality – Determination of trace elements by atomic absorption spectrometry with graphite furnace

**Karin Holm**
**Hans Borg**

Institute of Applied Environmental Research
Stockholm university
SE-106 91 Stockholm, Sweden

ISSN 1103-341
Printer: ITM, 2003-02-27
ISRN SU-ITM-R-106-SE

# Contents

# 1. Background

The purpose with this interlaboratory trial was to validate the draft international standard ”Water quality - Determination of trace elements by atomic absorption spectrometry with graphite furnace” (ISO / DIS 15586). The standard was also subject for ISO / CEN parallel voting.

It was decided by the ISO working group (ISO / TC 147 / SC 2 / WG 41) to send out all the different sample types that are included in the standard.

- Synthetic samples, high and low level
- Fresh water samples, high and low level
- Waste water sample to be digested by the participants
- A nitric acid digest of a sediment
- A dry sample of the same sediment to be digested by the participants

All samples should be sent in duplicates. 17 elements are included in the standard, but the participants were asked to analyse As, Cd, Cr, Pb and Tl with the highest priority and thereafter as many of the other elements as possible.

# 2. Introduction

38 laboratories from 11 different countries were participating in the trial with graphite furnace analyses.

The samples were distributed at the end of February 2002, and the participants were asked for results by the beginning of April. At the end of August a preliminary statistical evaluation of the results was distributed to the members of the ISO working group, and it was thereafter included in the draft standard.

As the purpose of the trial was to evaluate the proposed standard, the laboratories were required to follow the procedures that are given in the draft. References are also given to ISO 15587-1 and 2; Digestion for the determination of selected elements in water – Aqua regia digestion (part 1), Nitric acid digestion (part 2). Full texts of ISO / DIS 15586 and ISO / FDIS 15587 were sent along with the samples.

Many thanks to Pia Kärrhage for help with preparation of the samples, to Jörgen Ek for help with taking the samples, to Bo Lagerman for help with test design and statistical advice and to Leif Gunnarsson at Hallstavik paper mill for providing waste water. The interlaboratory trial was financially supported by the Swedish EPA.

# 3. Sample containers

The sample containers for the liquid samples were 125 ml polypropylene bottles (60 ml for the sediment digest), cleaned according to the standard. They were first washed in a laboratory dish washing machine and rinsed with water. Then they were soaked in 6 M HCl at 45 °C for 24 hours, rinsed with water, and thereafter soaked in 0.1 M $HNO_3$ for one week. Before use they were rinsed with Milli-Q water several times. 10 ml polystyrene containers were used for the dry sediment samples.

# 4. Samples

The total of 14 samples as 7 pairs of duplicates were sent out to each participating laboratory, with the exception that some laboratories did not participate in the analyses of all the different sample types.

Samples A-D were **synthetic solutions**, A and B low concentrations, C and D higher concentrations. The samples were preserved with concentrated nitric acid ($HNO_3$), 0.5 ml per 100 ml of sample.

Samples E-H were **fresh water**, E and F low concentrations, G and H higher concentrations. The samples were preserved with concentrated nitric acid ($HNO_3$), 0.5 ml per 100 ml of sample. The water was from Lake Mälaren, the third largest lake in Sweden. To achieve suitable concentrations for measurement, it was spiked with many of the elements. A typical conductivity value for Lake Mälaren is 20-25 mS/m.

Samples J and K were **waste water** from a Swedish paper mill that produces mechanical printing paper. The samples were preserved with concentrated nitric acid ($HNO_3$), 0.5 ml per 100 ml of sample. To achieve suitable concentrations for measurement, it was spiked with many of the elements. Samples J and K were supposed to be digested by the participants according to ISO 15587-1 (aqua regia) and/or 15587-2 (nitric acid). Some characteristics of the water were: Suspended material – 15 mg/l, COD – 220 mg/l, total phosphorous – 0.10 mg/l.

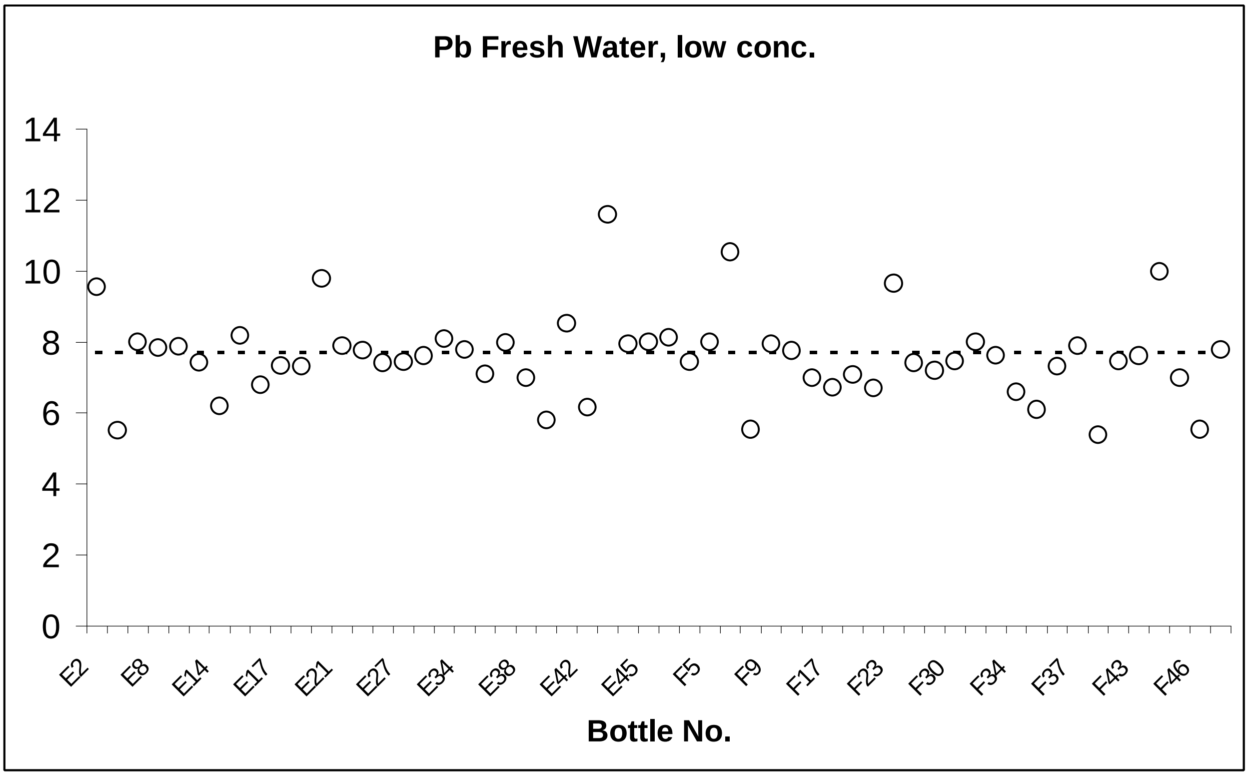
Samples L and M were **nitric acid digests of a sediment** from a Swedish lake. The samples were mixed from 33 digestions made according to Annex B in ISO/DIS 15586. 1.5 g of dried samples were weighed into digestion flasks. 60 ml of nitric acid, 7 mol/l, was added and the samples were heated in an autoclave at 120 °C. After cooling they were diluted with water to 300 ml each. The digests were filtrated through membrane filter with a pore size of 0.45 µm.

Samples N and O were **dried sediment samples** (about 3 g of each), of the same origin as the digests for samples L and M. Samples N and O were supposed to be digested by the participants according to ISO/DIS 15586, Annex B. The results should be expressed as mg/kg dry weight. As the samples were freeze dried and contained a few percent of water, the total residue (dry weight) at 105 ºC had to be determined to calculate the correct amount of sample weighed for digestion.

As all the samples except the synthetic solutions were natural samples, the concentrations of some elements were higher than the optimum working range for graphite furnace determination and had to be diluted before analysis. As guidance, for each sample group and element, the order of magnitude of the concentration was given in a table.

All sample containers were numbered in the same order as they were filled with sample, and then randomly choosen for each laboratory. The participants were asked to report their numbers. Therefore it was possible to evaluate if there was any drift in the concentration of the analytes caused by suspended matter. This was not expected as the samples were stirred during filling the sample containers, and it was also concluded that there was not any such drift. An example is shown in Figure 1 for Pb in fresh water.

Figure 1. Results for Pb (µg/l) in the fresh water sample with lower concentration, ordered after bottle number. The dotted line is the mean value after the statistical evaluation.



# 5. Test analyses

ICP-MS analyses were made on test samples of bottle blanks (Milli-Q water preserved with concentrated nitric acid ($HNO_3$), 0.5 ml per 100 ml of sample), synthetic solutions (low and high concentrations), fresh water samples (low and high concentrations) and undigested waste water samples, 5 of each. The results on the bottle blanks were under the detection limits for all elements except Al and Zn, where some results were a bit enhanced. One result for Al on the synthetic solutions with low concentrations was significantly higher than the rest. Table 1 shows results for Al and Zn on the test analyses.

Table 1. Results for Al and Zn with ICP-MS analyses on test samples, µg/l.

| | Al | Zn | | Al | Zn |
|---|---|---|---|---|---|
| **Bottle blanks** | <0.1 | 1.8 | **Fresh water sample** | 80.9 | 1.2 |
| | 0.1 | <0.1 | **lower conc.** | 80.5 | 1.1 |
| | <0.1 | <0.1 | | 83.5 | 1.1 |
| | 0.8 | 0.5 | | 83.2 | 1.7 |
| | 1.0 | <0.1 | | 82.5 | 1.4 |
| **Synthetic solution** | 4.8 | 0.8 | **Fresh water sample** | 102 | 5.8 |
| **lower conc.** | 5.0 | 0.6 | **higher conc.** | 104 | 6.9 |
| | 16.6 | 0.6 | | 100 | 9.8 |
| | 4.7 | 0.7 | | 101 | 5.9 |
| | 7.1 | 0.4 | | 103 | 6.0 |
| **Synthetic solution** | 44.6 | 4.4 | **Waste water sample** | 64.9 | 73.8 |
| **higher conc.** | 44.3 | 4.3 | **undigested** | 64.4 | 71.3 |
| | 43.9 | 4.4 | | 64.9 | 72.8 |
| | 44.2 | 4.4 | | 65.2 | 72.1 |
| | 43.6 | 5.1 | | 66.9 | 73.2 |

Two laboratories had big differences in Al results between the duplicates for the synthetic solution with low concentration and one for the synthetic solution with higher concentration. It is not out of the question that this depends on Al contamination from the bottle containers. Since a random enhanced value is likely to give a Cochran outlier (see chapter 6), it might not however influence the final results for repeatability and reproducibility.

# 6. Statistical evaluation

The statistical evaluation was made according to ISO 5725-2 and Iglewicz & Hoaglin (1993). The repeatability and reproducibility was calculated for each sample type and concentration level.

The data set was first searched for **Cochran outliers**. Cochran's test is a test of the **within-laboratory** variabilities.

$\mathbf{C} = \max d_i^2 / \sum d_i^2$

where

$\mathbf{d_i}$ = dupl. 2 – dupl. 1 (for each laboratory)
**dupl. 1** and **dupl. 2** = the concentrations of the analyte for a duplicate pair (sample A and B etc.)

Critical values for C are given in tables, at 5% level (identification of stragglers), and at 1% level (identification of outliers). Stragglers are included in the further evaluation, but shall be checked for inconsistencies. Outliers are excluded from further statistical evaluation.

After Cochran outliers were excluded, the material was searched for **Grubb outliers**. Grubb's test is a test of **between-laboratory** variability.

$\mathbf{G_i} = (m_i - M) / s$ (for each laboratory)

where

$\mathbf{m_i}$ = (dupl. 1 + dupl. 2) / 2
$\mathbf{M} = \sum m_i / n$
**n** = the number of duplicate pairs
**s** = the standard deviation for M

Critical values for G are given in tables, at 5% level (identification of stragglers), and at 1% level (identification of outliers). Stragglers are included in the further evaluation, but shall be checked for inconsistencies. Outliers are excluded. Calculations were also made to test whether the three largest or the three smallest observations together were Grubb outliers. No such cases were however observed. If there were any Grubb outliers, they were excluded from the whole material, which then was searched for Cochran outliers once more.

The final statistical evaluation was then made.

$\mathbf{s^2_r} = \sum d_i^2 / 2n$
$\mathbf{s^2_L} = s^2 - s^2_r / 2$

(For $d_i$, n and s, see above.)

$$s^2_R = s^2_L + s^2_r$$

where

$s^2_R$ is the estimate of the **reproducibility** variance,

$s^2_L$ is the estimate of the between-laboratory variance, and

$s^2_r$ is the estimate of the **repeatability** (within-laboratory) variance.

# 7. Results

A summary of the statistical evaluation is given in Appendix I. Detailed lists and Youden plots for all results are given in Appendix III. Five of the participating laboratories had in addition to graphite furnace measurements used other analytical techniques (ICP-MS, ICP-OES, flame AAS and hydride generation AAS) for some element or some samples. Two laboratories had made only ICP-MS analyses. Those results are presented in this report as well, but with no statistical evaluation. Four laboratories that received samples were not able to leave any results at all. All participants are listed in Appendix IV.

# 8. The significance of options in the method

For many steps in the analytical procedures the standard describes various possibilities. The analyte can be atomized from the **wall** of the graphite tube, or from a **platform**. Different techniques for background correction can be used, e.g. **Zeeman** background correction or a **deuterium lamp**. A number of different **matrix modifiers** are listed (i.e. Pd, $Mg(NO_3)_2$, $NH_4H_2PO_4$, Ni and some combinations of these), and if proved to give correct results, it is allowed to use other alternatives. Calibration by **standard addition** technique is recommended if it is necessary. Otherwise a calibration curve is used. For waste water and sediment, where the samples have to be digested, reference is made to ISO 15587-1, 15587-2 and to Annex B in ISO/DIS 15586, where it is possible to use either **aqua regia** or **nitric acid**. It is also possible to use various **digestion systems**, as microwave oven, autoclave, open systems etc.

The participants were asked to give detailed information about what options they had used, and it was possible to see if any of them had any significant influence on the results. It was shown for As and Pb that this was not the case, and the statistical evaluation is therefore exclusively made on the whole data material. Youden plots, where the results using different options in the method are shown for As and Pb in some of the material, are presented in Appendix II.

# 9. Conclusions

The mean value of all reproducibility variation coefficients (for all elements and sample types) is 24 %, and the median value is 18 %. The mean and median values of all repeatability variation coefficients are 4.4 and 3.5 % respectively. In Table 2 some figures are listed for each sample type. As expected the variation is lower for repeatability (within-laboratory variation) than for reproducibility, and both repeatability and reproducibility is lower for samples with higher concentration.

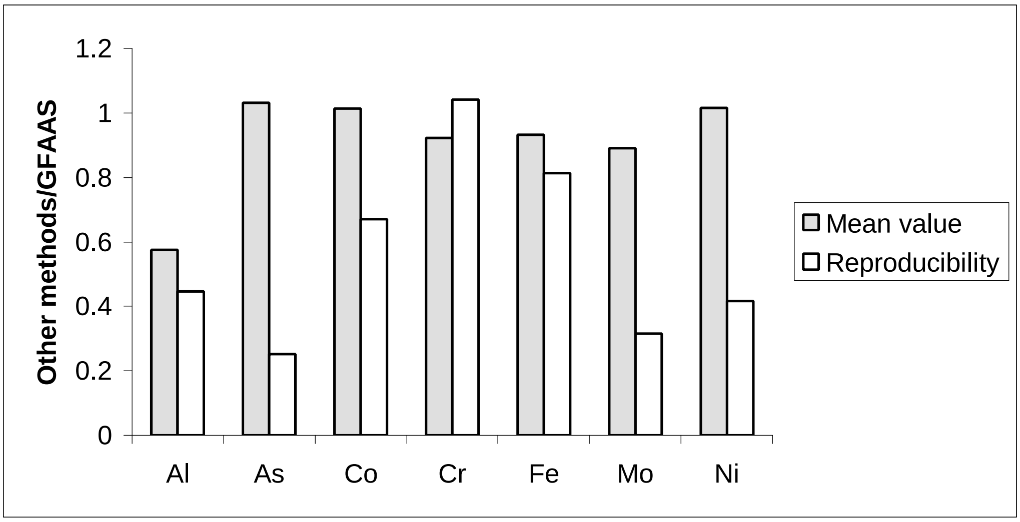
Table 2. Repeatability (CVr) and reproducibility ($CV_R$) variation coefficients for the different sample types. Mean, median, maximum and minimum values of all elements.

| | **$CV_r$, %** | | | | **$CV_R$, %** | | | |
|---|---|---|---|---|---|---|---|---|
| | Mean | Med. | Max. | Min. | Mean | Med. | Max. | Min. |
| Synthetic, low | 5.8 | 4.5 | 14.2 | 1.2 | 23.9 | 17.5 | 53.1 | 8.5 |
| Synthetic, high | 2.7 | 2.4 | 6.6 | 1.0 | 14.5 | 13.8 | 35.9 | 5.6 |
| Fresh water, low | 6.8 | 7.4 | 11.7 | 2.4 | 24.2 | 21.2 | 56.9 | 9.9 |
| Fresh water, high | 3.2 | 2.9 | 6.5 | 1.6 | 17.9 | 13.1 | 44.0 | 6.6 |
| Waste water | 5.0 | 4.2 | 10.0 | 1.1 | 34.0 | 32.5 | 60.2 | 7.0 |
| $HNO_3$ digest | 4.1 | 2.7 | 14.0 | 0.2 | 30.3 | 16.0 | 88.4 | 6.8 |
| Sediment | 3.1 | 2.6 | 6.9 | 0.7 | 27.1 | 21.7 | 73.7 | 7.1 |

The synthetic solutions had a “true” concentration, and the recovery was calculated (see Appendix I). For the low concentration the mean recovery of all elements was 109 % and the median value was 101 %. For the higher concentration the mean and median recovery was 100 and 102 % respectively. For 10 of the 17 elements in the trial the recovery was within 95-105 % for both concentrations.

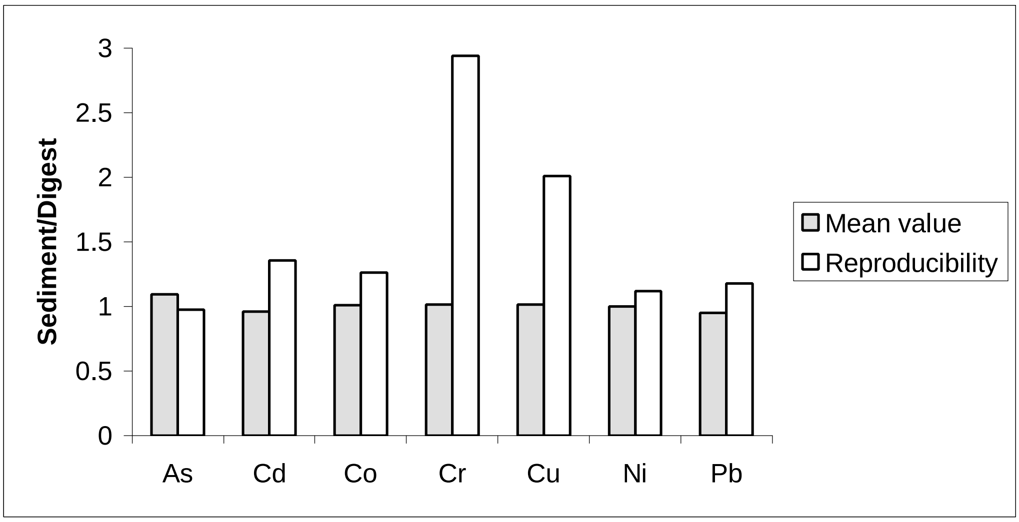
Some laboratories participated with other techniques (mostly ICP-OES and ICP-MS) than graphite furnace. These results are presented in tables and Youden plots in Appendix III, but are not included in any statistical evaluation. It seems though, that the variation with these techniques is smaller than with graphite furnace. Figure 2 shows an example of the relation between “other techniques” and graphite furnace for some elements in the fresh water sample with higher concentration. The ratio for the mean value is close to 1 (except for Al), but for the reproducibility the ratio is often much lower. The figures are rather uncertain, since there are only 4 or 5 results for “other methods”, but the tendency has also been observed in interlaboratory comparisons for Swedish laboratories, that the Institute for Applied Environmental Research has organized (http://enviropro.itm.su.se).

Figure 2. Fresh water with higher concentration. The ratio between results for "other methods" and graphite furnace.




It is not possible to see any differences in the results whether $HNO_3$ or aqua regia is used for digestion, but it is obvious that the reproducibility increases when the participants have digested the sediment sample themselves, compared to the results for the sediment $HNO_3$ digest. Figure 3 shows the relation between the results for the sediment and the sediment digest. The ratio between sediment and digest is close to 1 for the mean value, but is increased, especially for Cr and Cu, for the reproducibility ratio.

Figure 3. The ratio between results for the dry sediment sample and the sediment $HNO_3$ digest. (The mean values in µg/l for the digest have been recalculated to give the results in µg/g.) Only elements where there are 5 or more results are included.



# 10. References

ISO 5725-2:1994. Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.

ISO / DIS 15586. Water quality – Determination of trace elements by atomic absorption spectrometry with graphite furnace.

ISO 15587-1:2002. Water quality – Digestion for the determination of selected elements in water – Part 1: Aqua regia digestion.

ISO 15587-2:2002. Water quality – Digestion for the determination of selected elements in water – Part 2: Nitric acid digestion.

Iglewicz, B. and Hoaglin, D. C. (1993). How to detect and handle outliers. The ASQ basic references in quality control: Statistical techniques (Edward F. Mykytka, Ph.D., editor). Volume 16. ISBN 0-87389-247-X.

# Appendix I.
# Summary of the statistical evaluation

N = number of laboratories after outlier elimination, M = missing values (< values or only one result for a duplicate pair), O = number of outliers.
$s_r$ = repeatability variation, $CV_r$ = repeatability variation coefficient, $s_R$ = reproducibility variation, $CV_R$ = reproducibility variation coefficient.
S L = synthetic solution lower concentration, S H = synthetic solution higher concentration, F W L = fresh water lower concentration, F W H = fresh water higher concentration, W W = waste water digested by the participants, Dig = sediment digested in $HNO_3$, Sed = sediment sample digested by the participants.
Results in µg/l, for the dried sediment sample in µg/g.

| | N | M | O | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|---|---|---|
| **Ag** | | | | | | | | | | |
| S L | 9 | 1 | | 0.8 | 1.00 | 126 | 0.083 | 8.2 | 0.53 | 53.1 |
| S H | 9 | 1 | | 7.2 | 8.13 | 113 | 0.30 | 3.6 | 1.9 | 22.9 |
| F W L | 5 | 4 | 1 | | 0.774 | | 0.064 | 8.2 | 0.440 | 56.9 |
| F W H | 9 | 1 | | | 5.92 | | 0.30 | 5.0 | 1.95 | 33.0 |
| W W | 7 | 1 | 1 | | 3.43 | | 0.30 | 8.8 | 1.10 | 32.0 |
| Dig | 9 | 3 | | | 1.00 | | 0.14 | 14.0 | 0.69 | 69.0 |
| Sed | 4 | 3 | 1 | | 0.172 | | 0.011 | 6.5 | 0.047 | 27.1 |
| **Al** | | | | | | | | | | |
| S L | 6 | 5 | 2 | 5 | 5.85 | 117 | 0.83 | 14.2 | 2.59 | 44.3 |
| S H | 10 | 1 | 2 | 45 | 38.6 | 86 | 0.93 | 2.4 | 6.3 | 16.4 |
| F W L | 11 | | | | 170 | | 11 | 6.6 | 79 | 46.2 |
| F W H | 11 | | | | 193 | | 10 | 5.4 | 85 | 44.0 |
| W W | 4 | | 2 | | 147 | | 5.7 | 3.9 | 59 | 40.3 |
| Dig | 3 | | | | 111150 | | 1966 | 1.8 | 93999 | 84.6 |
| Sed | 3 | | | | 37628 | | 729 | 1.9 | 17561 | 46.7 |
| **As** | | | | | | | | | | |
| S L | 17 | 2 | 2 | 9 | 9.00 | 100 | 0.25 | 2.8 | 1.27 | 14.1 |
| S H | 19 | | 2 | 81 | 77.5 | 96 | 2.1 | 2.7 | 8.1 | 10.5 |
| F W L | 19 | 2 | | | 8.74 | | 0.64 | 7.4 | 2.20 | 25.2 |
| F W H | 21 | | | | 68.6 | | 2.4 | 3.6 | 12.2 | 17.8 |
| W W | 14 | 3 | 1 | | 11.6 | | 0.47 | 4.0 | 4.2 | 35.9 |
| Dig | 18 | | 1 | | 74.4 | | 3.1 | 4.2 | 20.0 | 26.9 |
| Sed | 17 | | 1 | | 16.3 | | 0.62 | 3.8 | 4.3 | 26.2 |
| **Cd** | | | | | | | | | | |
| S L | 33 | 3 | 1 | 0.3 | 0.303 | 101 | 0.011 | 3.5 | 0.052 | 17.0 |
| S H | 34 | 1 | 2 | 2.7 | 2.81 | 104 | 0.05 | 1.9 | 0.30 | 10.7 |
| F W L | 31 | 3 | 2 | | 0.572 | | 0.016 | 2.9 | 0.085 | 14.9 |
| F W H | 31 | 2 | 3 | | 3.07 | | 0.065 | 2.1 | 0.32 | 10.4 |
| W W | 27 | 3 | 2 | | 0.989 | | 0.028 | 2.8 | 0.297 | 30.0 |
| Dig | 29 | | 2 | | 48.7 | | 1.1 | 2.2 | 7.2 | 14.8 |
| Sed | 27 | | 3 | | 9.36 | | 0.34 | 3.6 | 1.88 | 20.1 |

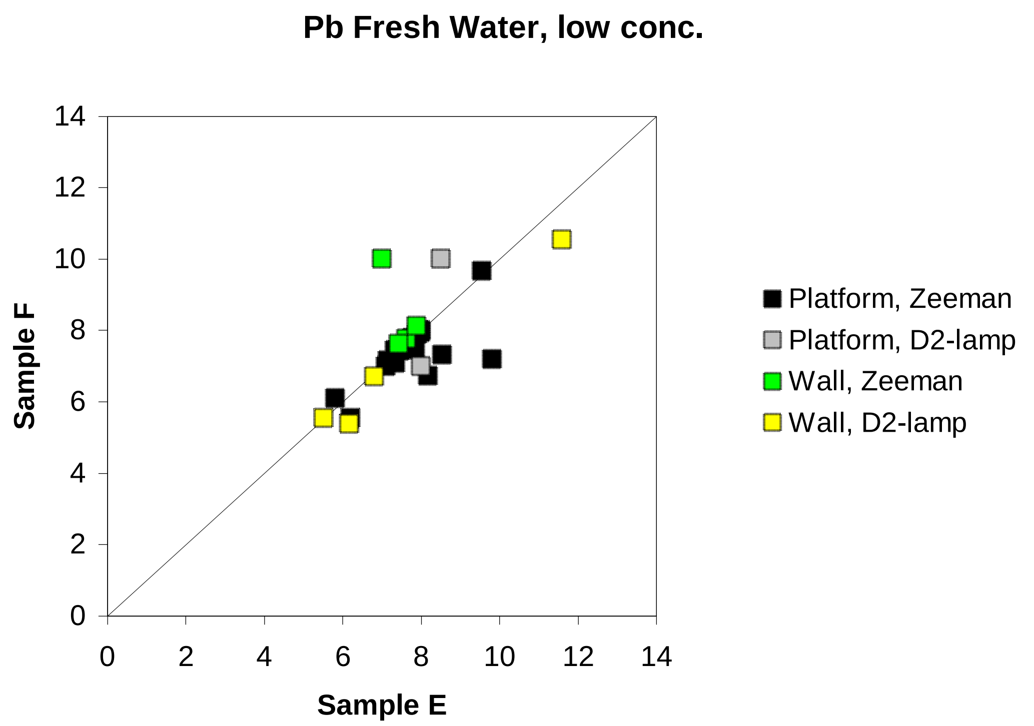
| | N | M | O | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|---|---|---|
| **Co** | | | | | | | | | | |
| S L | 13 | 1 | | 5.5 | 5.71 | 104 | 0.18 | 3.1 | 0.49 | 8.5 |
| S H | 12 | | 2 | 49.5 | 50.6 | 102 | 0.5 | 1.0 | 4.0 | 7.9 |
| F W L | 13 | 1 | | | 4.23 | | 0.38 | 9.0 | 0.63 | 14.8 |
| F W H | 13 | | 1 | | 40.5 | | 1.1 | 2.6 | 4.3 | 10.6 |
| W W | 10 | | | | 11.6 | | 0.82 | 7.0 | 3.8 | 32.9 |
| Dig | 11 | | | | 337 | | 5.4 | 1.6 | 41 | 12.2 |
| Sed | 10 | | | | 68.0 | | 1.2 | 1.8 | 10.5 | 15.4 |
| **Cr** | | | | | | | | | | |
| S L | 21 | 2 | 3 | 1.9 | 1.91 | 101 | 0.14 | 7.5 | 0.24 | 12.4 |
| S H | 24 | 1 | 1 | 17.1 | 17.5 | 102 | 0.4 | 2.0 | 1.4 | 7.9 |
| F W L | 23 | 2 | 1 | | 1.95 | | 0.15 | 7.7 | 0.48 | 24.7 |
| F W H | 23 | 1 | 2 | | 14.0 | | 0.28 | 2.0 | 1.0 | 7.3 |
| W W | 17 | 1 | 4 | | 3.80 | | 0.16 | 4.3 | 1.66 | 43.6 |
| Dig | 19 | | | | 246 | | 9.1 | 3.7 | 21 | 8.7 |
| Sed | 18 | | 3 | | 49.9 | | 0.61 | 1.2 | 12.8 | 25.6 |
| **Cu** | | | | | | | | | | |
| S L | 18 | 2 | 1 | 2.5 | 2.60 | 104 | 0.21 | 8.1 | 0.34 | 13.2 |
| S H | 19 | 1 | 1 | 22.5 | 23.0 | 102 | 0.9 | 3.8 | 1.3 | 5.6 |
| F W L | 19 | 2 | | | 2.37 | | 0.15 | 6.4 | 0.36 | 15.4 |
| F W H | 20 | | 1 | | 29.8 | | 0.69 | 2.3 | 2.2 | 7.2 |
| W W | 11 | 2 | 1 | | 5.08 | | 0.51 | 10.0 | 1.54 | 30.3 |
| Dig | 10 | | 2 | | 216 | | 4.6 | 2.1 | 19 | 9.0 |
| Sed | 12 | | 1 | | 43.9 | | 1.7 | 4.0 | 7.9 | 18.1 |
| **Fe** | | | | | | | | | | |
| S L | 5 | 1 | 1 | 3 | 4.43 | 148 | 0.40 | 9.0 | 1.46 | 33.0 |
| S H | 7 | | | 27 | 27.0 | 100 | 0.9 | 3.4 | 3.7 | 13.8 |
| F W L | 7 | | | | 98.3 | | 2.3 | 2.4 | 9.7 | 9.9 |
| F W H | 6 | 1 | | | 116 | | 1.9 | 1.6 | 13 | 11.2 |
| W W | 2 | | | | 592 | | - | - | - | - |
| Dig | 2 | | | | 257013 | | - | - | - | - |
| Sed | 2 | | | | 56128 | | - | - | - | - |
| **Mn** | | | | | | | | | | |
| S L | 8 | 2 | | 1.5 | 1.71 | 114 | 0.075 | 4.4 | 0.51 | 30.0 |
| S H | 10 | | | 13.5 | 14.5 | 108 | 0.3 | 2.0 | 2.2 | 15.3 |
| F W L | 8 | 1 | 1 | | 5.47 | | 0.15 | 2.7 | 1.23 | 22.5 |
| F W H | 10 | | | | 17.7 | | 0.57 | 3.2 | 2.6 | 14.6 |
| W W | 5 | | | | 100 | | 4.3 | 4.3 | 14 | 13.8 |
| Dig | 3 | | 1 | | 10540 | | 21 | 0.2 | 809 | 7.7 |
| Sed | 4 | | | | 2093 | | 27 | 1.3 | 149 | 7.1 |
| **Mo** | | | | | | | | | | |
| S L | 6 | 1 | | 4.5 | 5.69 | 126 | 0.26 | 4.6 | 1.36 | 23.8 |
| S H | 7 | | | 40.5 | 44.3 | 109 | 1.2 | 2.8 | 6.2 | 14.0 |
| F W L | 4 | 2 | | | 5.76 | | 0.66 | 11.5 | 0.79 | 13.7 |
| F W H | 6 | | | | 29.4 | | 1.2 | 3.9 | 3.7 | 12.7 |
| W W | 5 | | | | 10.8 | | 0.61 | 5.6 | 6.5 | 60.2 |
| Dig | 6 | | | | 12.0 | | 1.1 | 9.5 | 10.6 | 88.4 |
| Sed | 4 | 1 | | | 2.84 | | 0.074 | 2.6 | 2.09 | 73.7 |

| | N | M | O | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|---|---|---|
| **Ni** | | | | | | | | | | |
| S L | 20 | | | 6 | 5.92 | 99 | 0.21 | 3.5 | 0.89 | 15.0 |
| S H | 20 | | | 54 | 53.6 | 99 | 1.1 | 2.0 | 4.7 | 8.8 |
| F W L | 17 | 1 | 1 | | 3.11 | | 0.36 | 11.7 | 0.75 | 24.0 |
| F W H | 19 | | | | 33.2 | | 0.84 | 2.5 | 3.0 | 9.1 |
| W W | 15 | | 1 | | 11.4 | | 0.47 | 4.1 | 3.1 | 27.5 |
| Dig | 14 | | 2 | | 294 | | 7.2 | 2.4 | 20 | 6.8 |
| Sed | 12 | | 3 | | 58.9 | | 0.93 | 1.6 | 4.5 | 7.6 |
| **Pb** | | | | | | | | | | |
| S L | 30 | 5 | 2 | 5 | 5.07 | 101 | 0.16 | 3.1 | 0.65 | 12.8 |
| S H | 34 | | 3 | 45 | 46.5 | 103 | 0.8 | 1.8 | 4.1 | 8.8 |
| F W L | 32 | 3 | | | 7.76 | | 0.66 | 8.5 | 1.34 | 17.2 |
| F W H | 33 | 1 | 1 | | 68.2 | | 1.9 | 2.8 | 10.2 | 15.0 |
| W W | 22 | 1 | 5 | | 14.2 | | 0.34 | 2.4 | 5.6 | 39.8 |
| Dig | 29 | | | | 541 | | 17 | 3.1 | 80 | 14.7 |
| Sed | 29 | | 1 | | 103 | | 3.6 | 3.5 | 18 | 17.3 |
| **Sb** | | | | | | | | | | |
| S L | 5 | 2 | | 8 | 7.39 | 92 | 0.25 | 3.3 | 1.32 | 17.9 |
| S H | 7 | | | 72 | 66.9 | 93 | 2.3 | 3.4 | 9.2 | 13.8 |
| F W L | 5 | 2 | | | 5.78 | | 0.28 | 4.9 | 1.22 | 21.2 |
| F W H | 7 | | | | 52.7 | | 1.6 | 3.1 | 3.5 | 6.6 |
| W W | 2 | 2 | 1 | | 11.5 | | - | - | - | - |
| Dig | 2 | 4 | | | 7.25 | | - | - | - | - |
| Sed | 1 | 4 | | | 1.70 | | - | - | - | - |
| **Se** | | | | | | | | | | |
| S L | 10 | 1 | | 12 | 11.9 | 99 | 0.68 | 5.7 | 2.7 | 23.0 |
| S H | 11 | | | 108 | 109 | 101 | 4 | 3.7 | 24 | 21.9 |
| F W L | 10 | | 1 | | 10.2 | | 0.61 | 5.9 | 1.4 | 13.4 |
| F W H | 11 | | | | 85.2 | | 2.5 | 2.9 | 17.7 | 20.8 |
| W W | 8 | 1 | | | 16.0 | | 1.6 | 9.8 | 4.1 | 25.6 |
| Dig | 4 | 5 | 1 | | 4.94 | | 0.38 | 7.7 | 1.95 | 39.5 |
| Sed | 3 | 4 | 1 | | 0.887 | | 0.006 | 0.7 | 0.193 | 21.7 |
| **Tl** | | | | | | | | | | |
| S L | 2 | 3 | | 4 | 3.96 | 99 | - | - | - | - |
| S H | 5 | | | 36 | 37.0 | 103 | 2.4 | 6.6 | 7.4 | 19.9 |
| F W L | 3 | 2 | | | 4.20 | | 0.14 | 3.4 | 1.70 | 40.6 |
| F W H | 5 | | | | 27.7 | | 0.84 | 3.0 | 11.3 | 40.7 |
| W W | 2 | 2 | 1 | | 8.31 | | - | - | - | - |
| Dig | 2 | 3 | | | 5.03 | | - | - | - | - |
| Sed | 3 | 2 | | | 0.834 | | 0.057 | 6.9 | 0.480 | 57.5 |
| **V** | | | | | | | | | | |
| S L | 5 | | | 15 | 15.1 | 101 | 0.2 | 1.2 | 2.4 | 15.9 |
| S H | 5 | | | 135 | 138 | 102 | 2 | 1.4 | 17 | 12.4 |
| F W L | 3 | 2 | | | 12.3 | | 1.0 | 8.4 | 1.4 | 11.1 |
| F W H | 5 | | | | 83.8 | | 1.9 | 2.3 | 11.0 | 13.1 |
| W W | 3 | 1 | | | 50.0 | | 0.57 | 1.1 | 28.2 | 56.4 |
| Dig | 5 | | | | 330 | | 5.2 | 1.6 | 57 | 17.3 |
| Sed | 4 | | | | 63.0 | | 3.8 | 6.0 | 12.1 | 19.2 |

| | N | M | O | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|---|---|---|
| **Zn** | | | | | | | | | | |
| S L | 5 | 1 | 1 | 0.5 | 0.579 | 116 | 0.062 | 10.8 | 0.275 | 47.6 |
| S H | 5 | 1 | 1 | 4.5 | 3.71 | 82 | 0.079 | 2.1 | 1.33 | 35.9 |
| F W L | 6 | 1 | 1 | | 1.17 | | 0.10 | 8.8 | 0.47 | 40.3 |
| F W H | 7 | 1 | | | 5.99 | | 0.39 | 6.5 | 1.82 | 30.4 |
| W W | 4 | | | | 120 | | 2.4 | 2.0 | 8.4 | 7.0 |
| Dig | 3 | | | | 1373 | | 42 | 3.0 | 344 | 25.0 |
| Sed | 4 | | | | 233 | | 3.6 | 1.6 | 54 | 23.4 |

# Appendix II.
# Options in the method - Examples for Pb and As

Figure II:1. Pb in fresh water. Different types of tube and background correction.



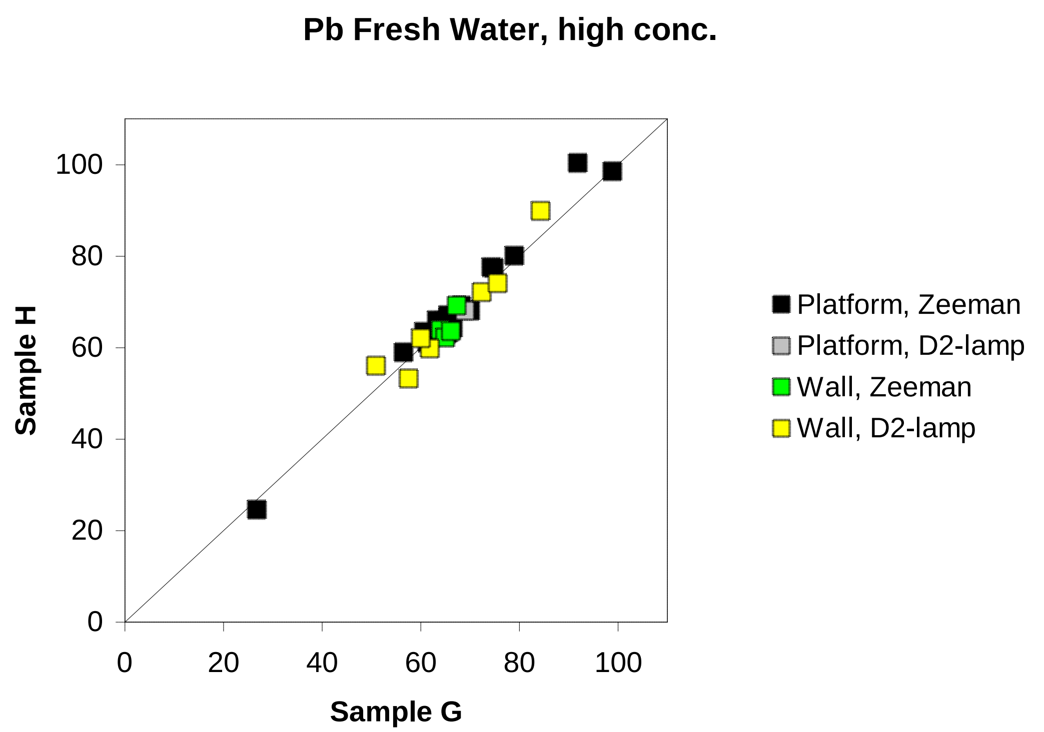
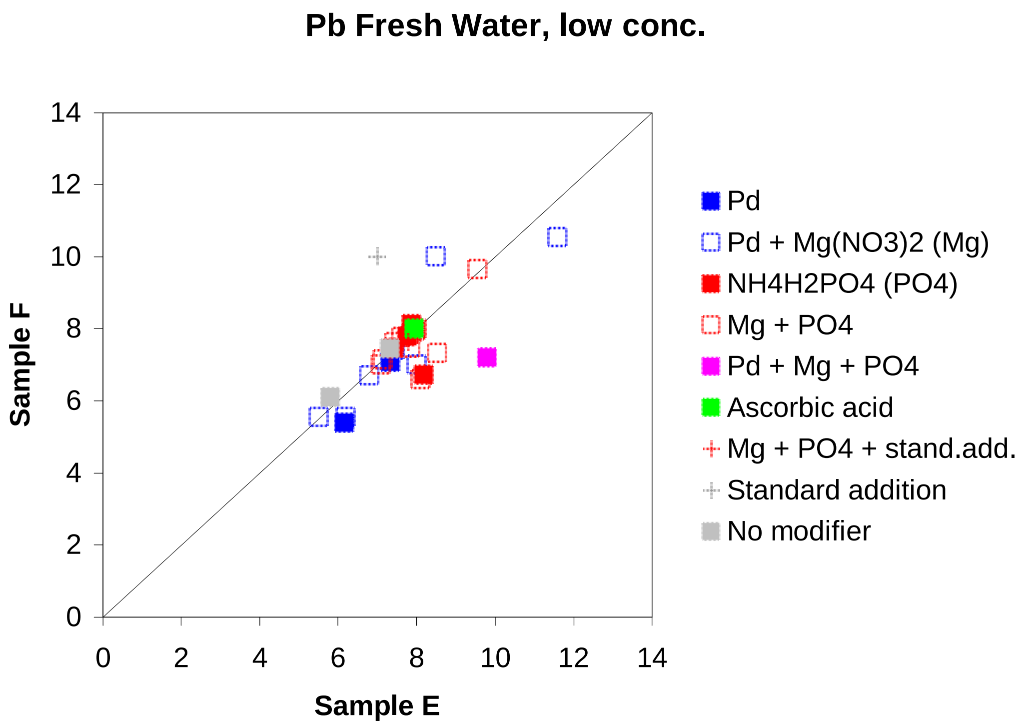



Figure II:2. Pb in fresh water. Different matrix modifiers.



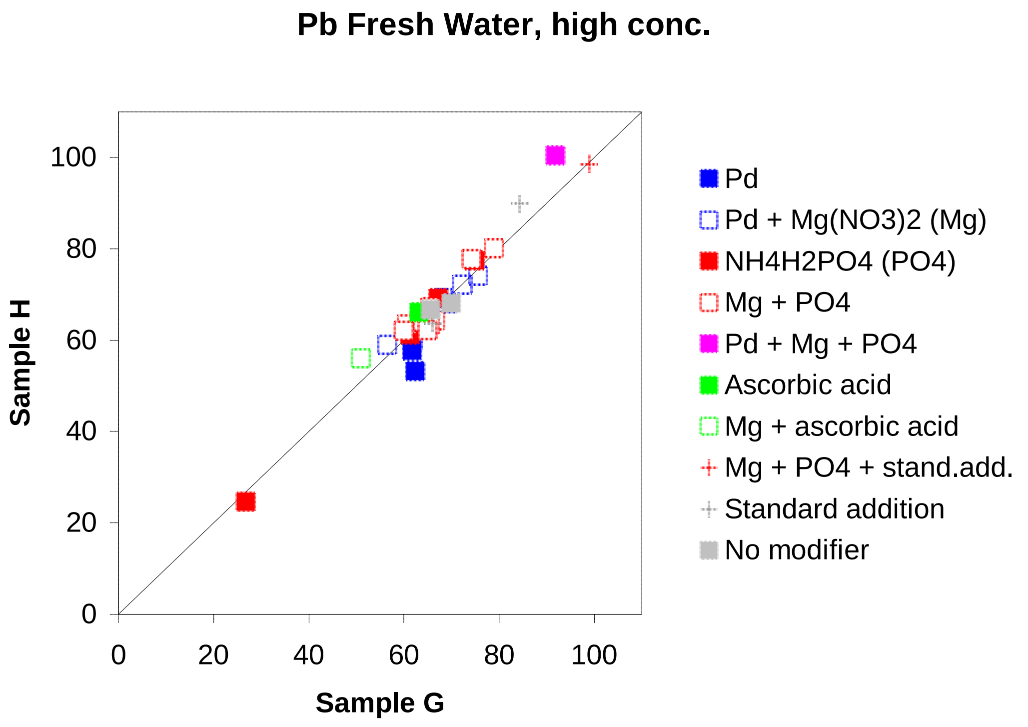
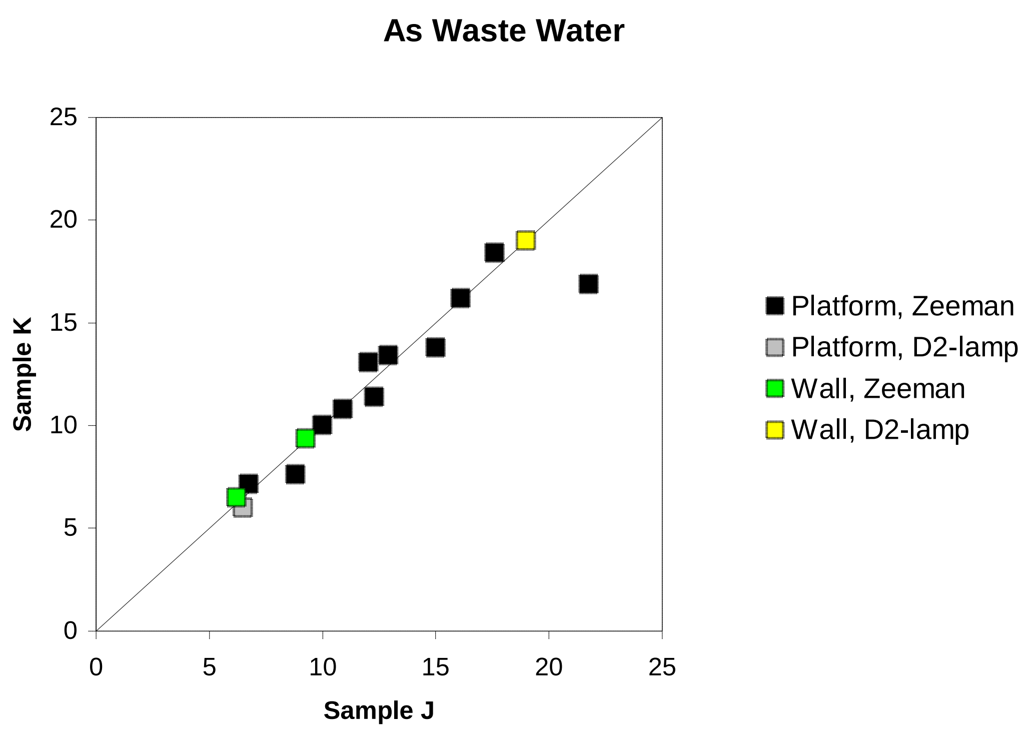



Figure II:3. As and Pb in waste water. Different types of tubes and background correction.



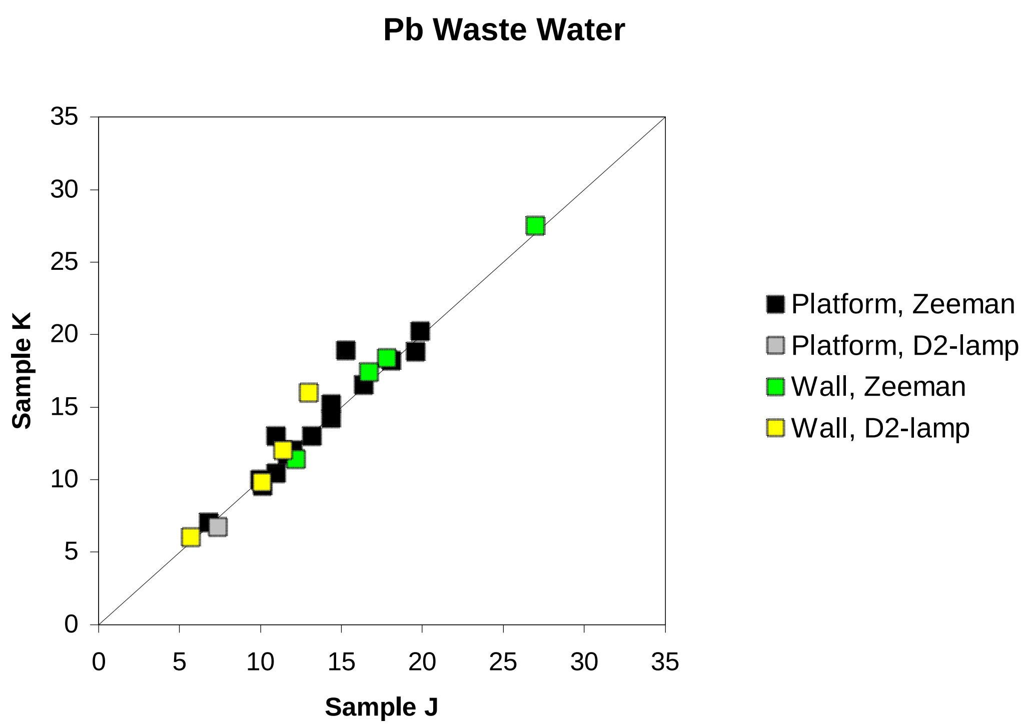
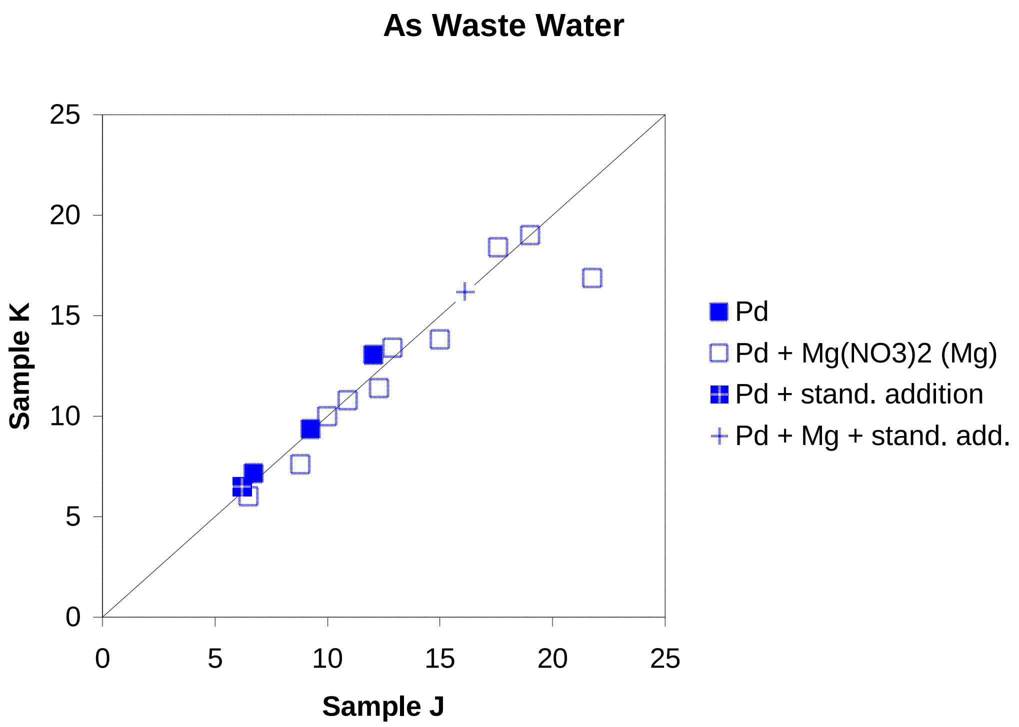



Figure II:4. As and Pb in waste water. Different matrix modifiers.



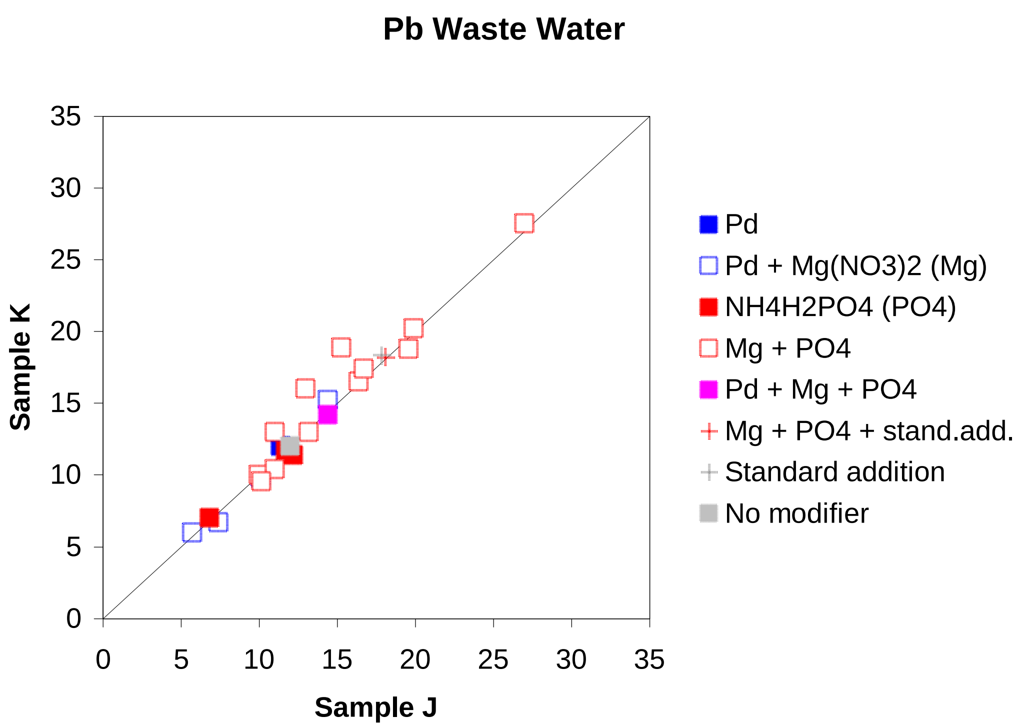
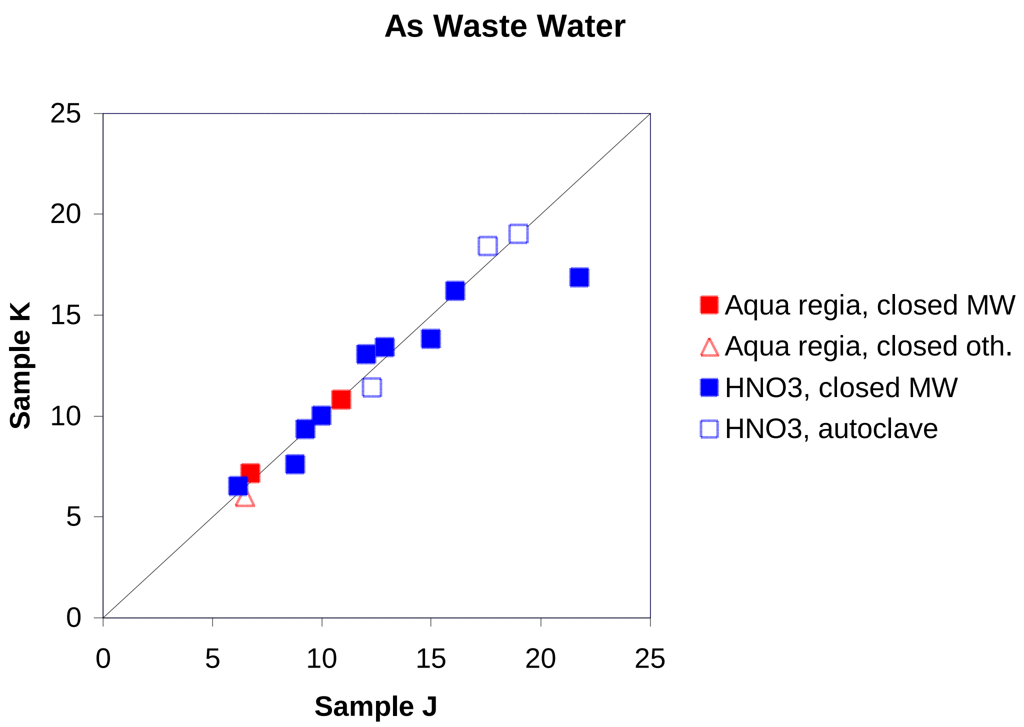



Figure II:5. As and Pb in waste water. Different digestion acids and digestion systems.



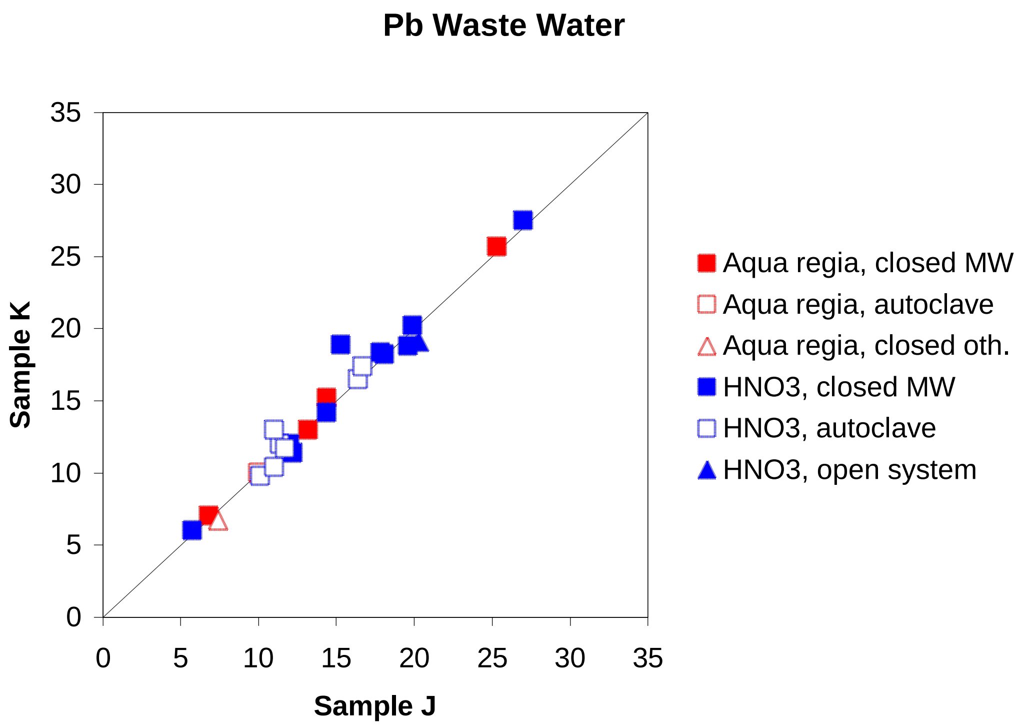
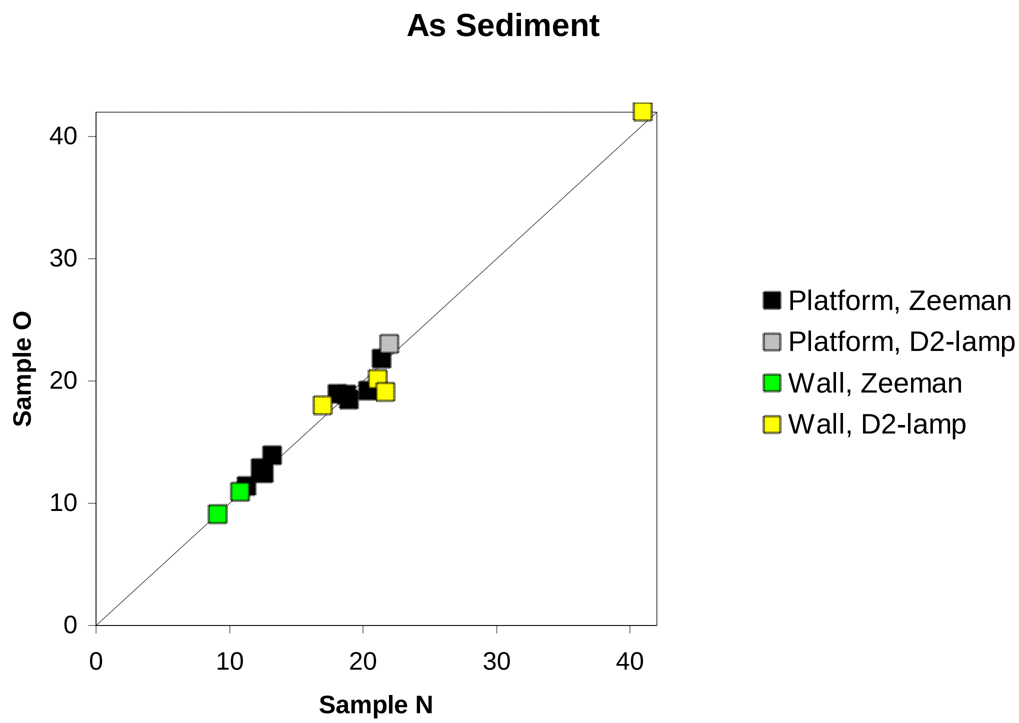



Figure II:6. As and Pb in sediment. Different tubes and background correction.



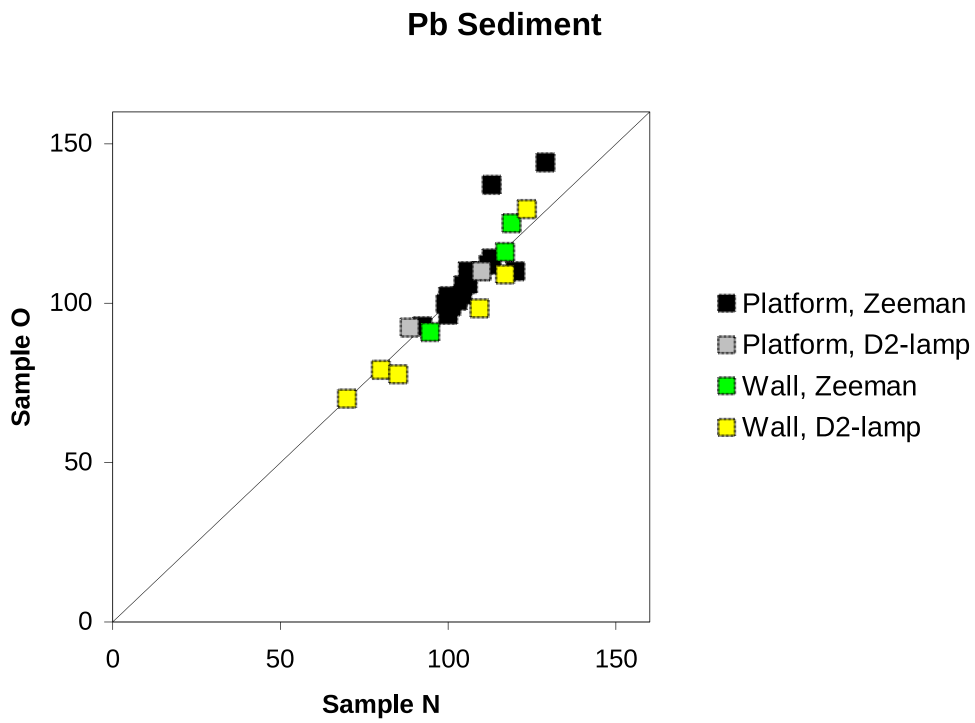
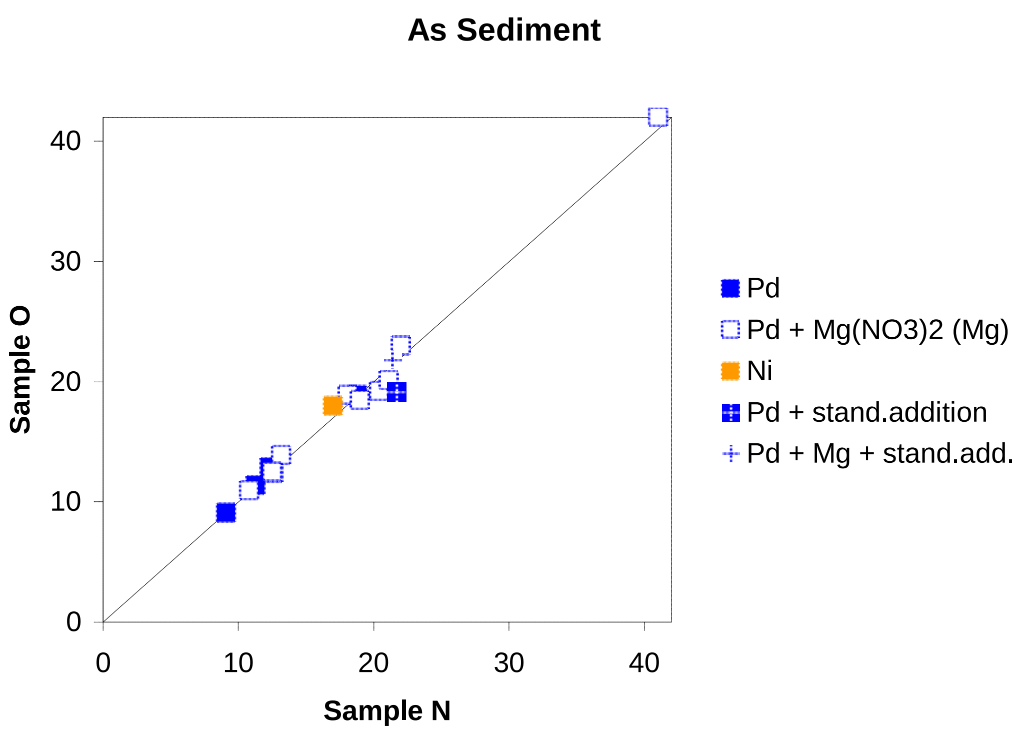



Figure II:7. As and Pb in sediment. Different matrix modifiers.



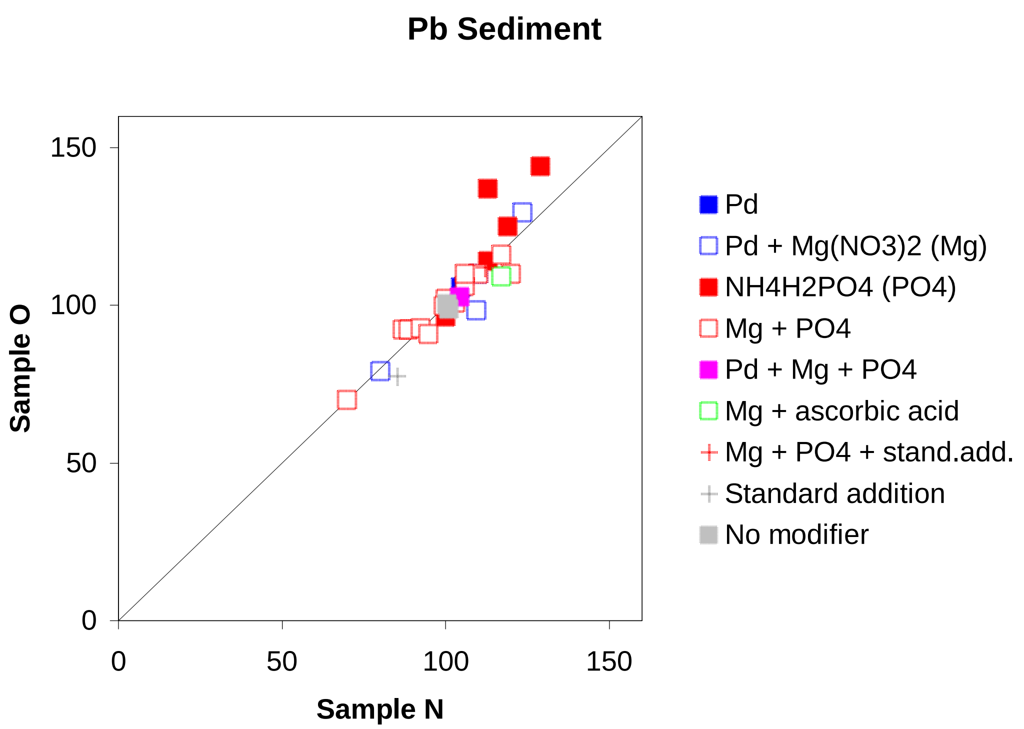
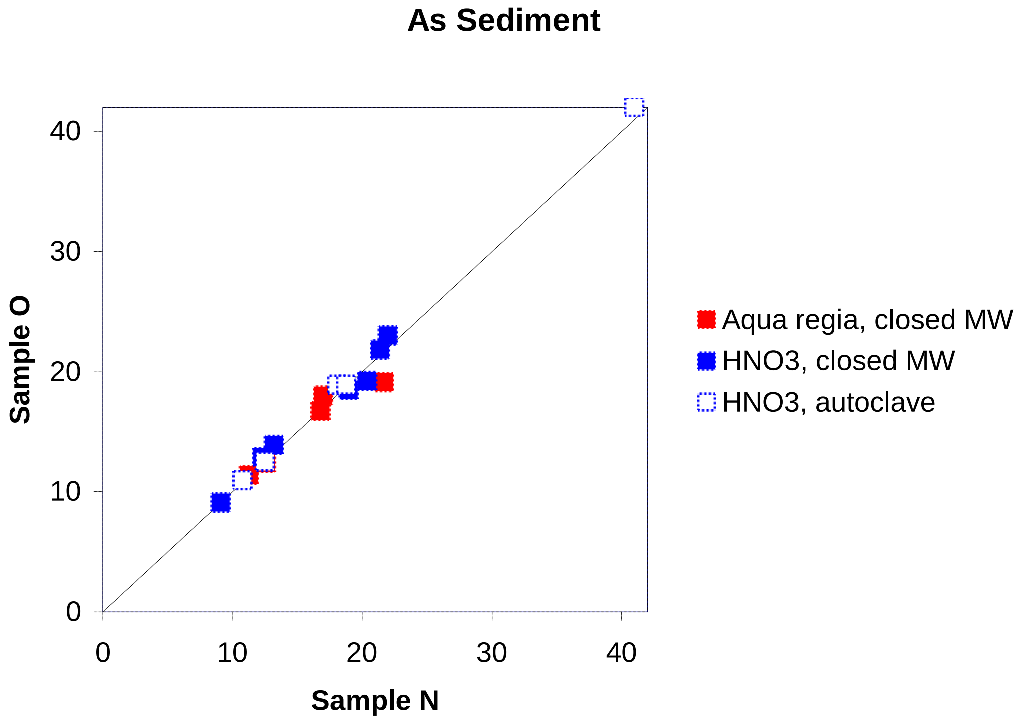
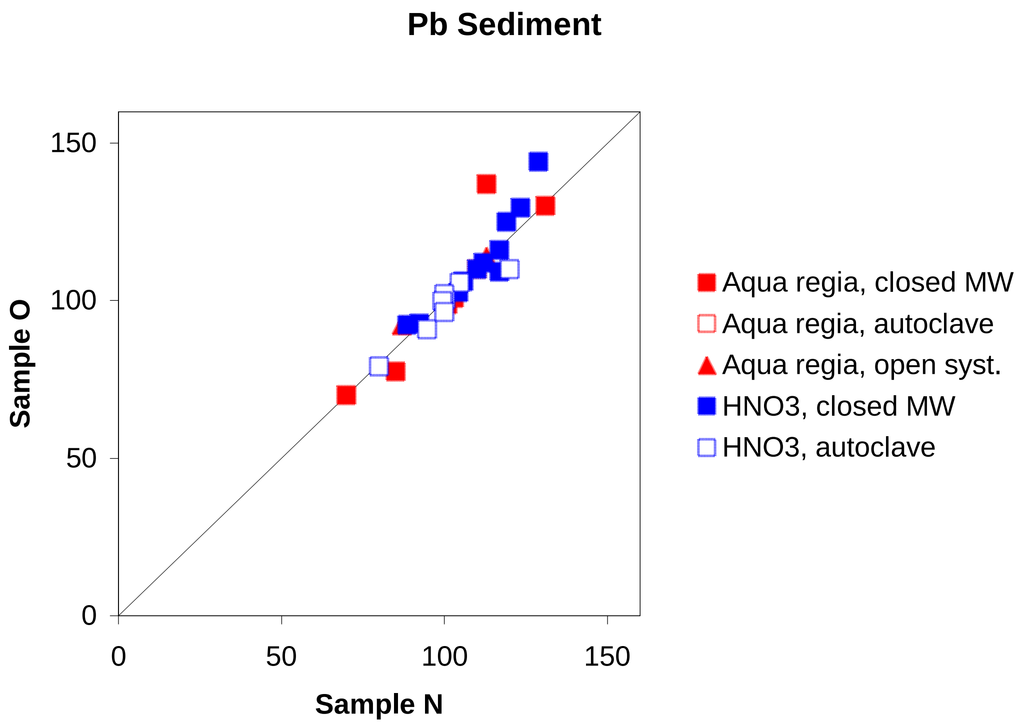



Figure II:8. As and Pb in sediment. Different digestion acids and digestion systems.



# Appendix III.
# Tables and Youden plots for all results

The data material was first searched for Cochran outliers and those were excluded from further statistical evaluation. Therefore a Cochran outlier could also is be a Grubb outlier, but Grubb's test has not been necessary to make. For statistical evaluation, see chapter 6.

Outliers are not included in the final statistical evaluation for repeatability and reproducibility. Stragglers are included. The results in the tables are ordered in ascending concentration after the first sample in a duplicate pair.

In the tables all results are followed by a code, that identifies the specific technique used. A key to the codes is given in the table below.

| **Digestion acid** | **Code** | **Digestion system** | **Code** |
|---|---|---|---|
| Aqua regia | A | Open system | o |
| Nitric acid | N | Closed system Microwave oven | m |
| | | Closed system Autoclave | a |
| | | Closed system, other | c |
| | | Evaporation | e |
| | | | |
| **Matrix modifier** | **Code** | **Graphite tube** | **Code** |
| No modifier | 0 | Wall | W |
| Pd | 1 | Platform | P |
| $Mg(NO_3)_2$ | 2 | | |
| $NH_4H_2PO_4$ | 3 | **Background correction** | **Code** |
| Ni | 4 | Zeeman | Z |
| Ascorbic acid | 5 | Deuterium lamp | D |
| $(NH_4)_2SO_4$ | 6 | | |
| Standard addition | + | | |
| | | | |
| **Other methods** | **Code** | | |
| ICP-OES | I | | |
| ICP-MS | K | | |
| Flame AAS | F | | |
| Hydride generation AAS | H | Not reported | ? |

Other abbreviations: C = Cochran outlier, G = Grubb outlier, C 5% = Cochran straggler, G 5% = Grubb straggler, $s_r$ = repeatability variation, $CV_r$ = repeatability variation coefficient, $s_R$ = reproducibility variation, $CV_R$ = reproducibility variation coefficient.

# Synthetic solutions

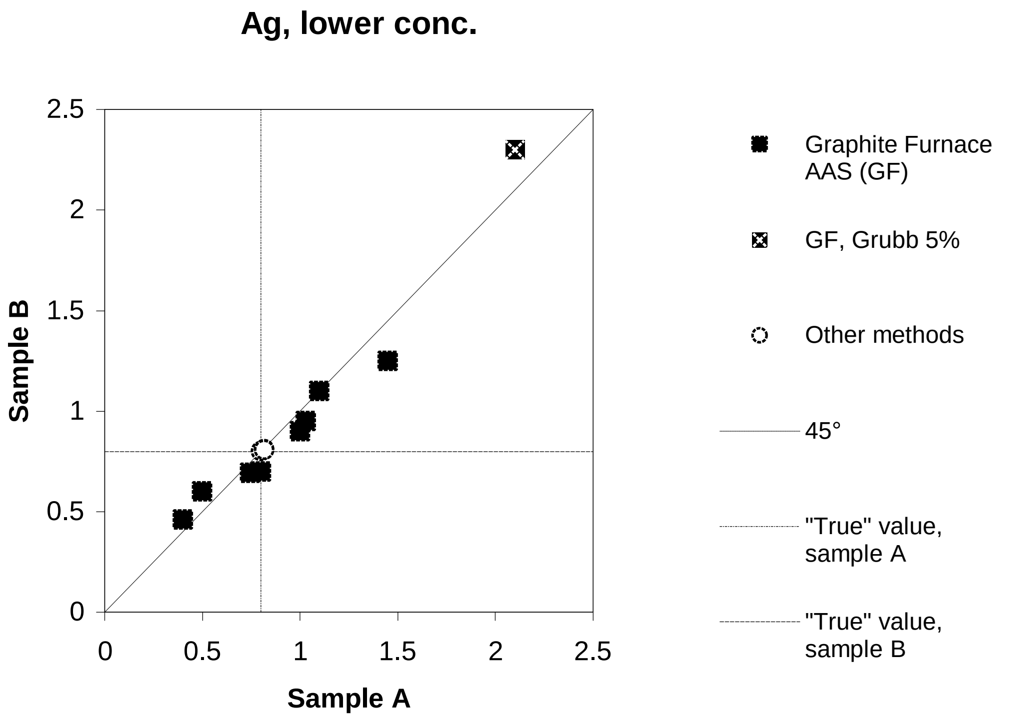
## Ag, synthetic solutions (µg/l)

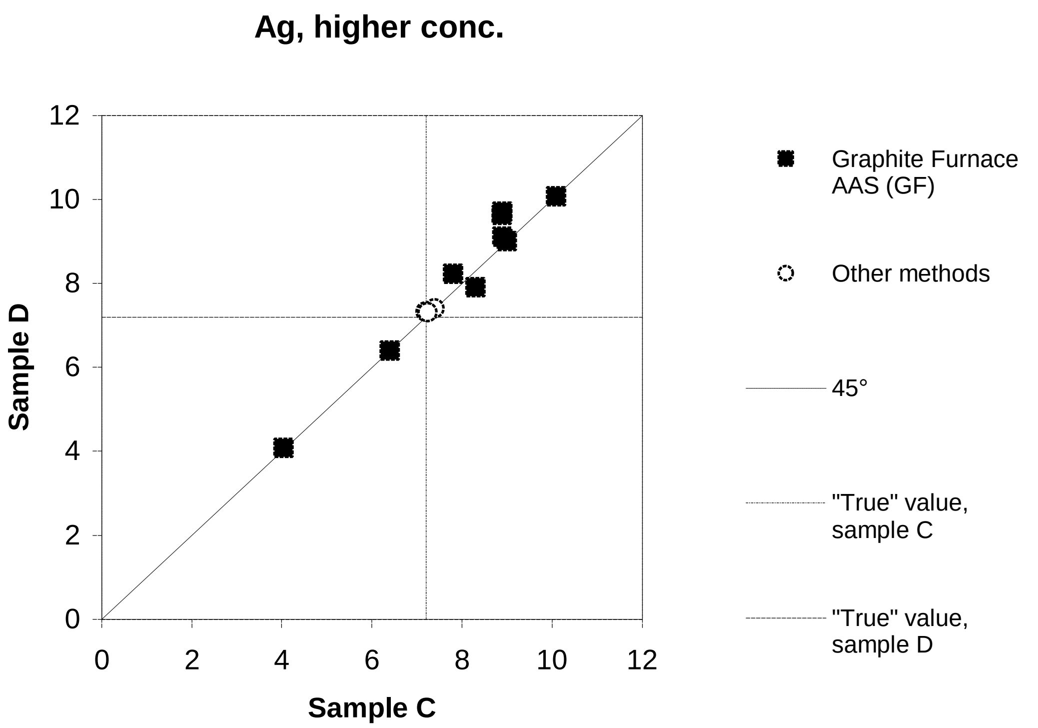
| Lab No. | A | B | Code | Outl./Str. | Lab No. | C | D | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 32 | 0.40 | 0.46 | 1,2WZ | | 32 | 4.05 | 4.08 | 1,2WZ | |
| 12 | 0.5 | 0.6 | 1,2PZ | | 12 | 6.4 | 6.4 | 1,2PZ | |
| 5 | 0.744 | 0.693 | 1,2WZ | | 5 | 7.808 | 8.22 | 1,2WZ | |
| 37 | 0.8 | 0.7 | 0WD | | 37 | 8.3 | 7.9 | 0WD | |
| 40 | 1 | 0.9 | 1,2PZ | | 42 | 8.88 | 9.63 | 0PZ | |
| 42 | 1.03 | 0.95 | 0PZ | | 1 | 8.9 | 9.7 | 0+WD | |
| 29 | 1.1 | 1.1 | 0W | | 29 | 8.9 | 9.1 | 0W | |
| 10 | 1.45 | 1.25 | 2PZ | | 40 | 9 | 9 | 1,2PZ | |
| 1 | 2.1 | 2.3 | 0+WD | G 5% | 10 | 10.09 | 10.07 | 2PZ | |
| 15 | <10 | <10 | ? | | 15 | <10 | <10 | ? | |

| | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|
| **A,B** | 0.8 | 1.00 | 126 | 0.083 | 8.2 | 0.53 | 53.1 |
| **C,D** | 7.2 | 8.13 | 113 | 0.30 | 3.6 | 1.9 | 22.9 |

## Ag, other methods

| Lab No. | A | B | Code | | Lab No. | C | D | Code |
|---|---|---|---|---|---|---|---|---|
| 19 | 0.8 | 0.8 | K | | 38 | 7.19 | 7.32 | K |
| 44 | 0.816 | 0.806 | K | | 44 | 7.24 | 7.31 | K |
| 38 | 0.818 | 0.811 | K | | 19 | 7.4 | 7.4 | K |
| 2 | <10 | <10 | I | | 2 | <10 | <10 | I |


Ag, lower conc.
Sample B
Sample A
2.5
2
1.5
1
0.5
0
0
0.5
1
1.5
2
2.5
Graphite Furnace AAS (GF)
GF, Grubb 5%
Other methods
45°
"True" value, sample A
"True" value, sample B


Ag, higher conc.
Sample D
Sample C
12
10
8
6
4
2
0
0
2
4
6
8
10
12
Graphite Furnace AAS (GF)
Other methods
45°
"True" value, sample C
"True" value, sample D

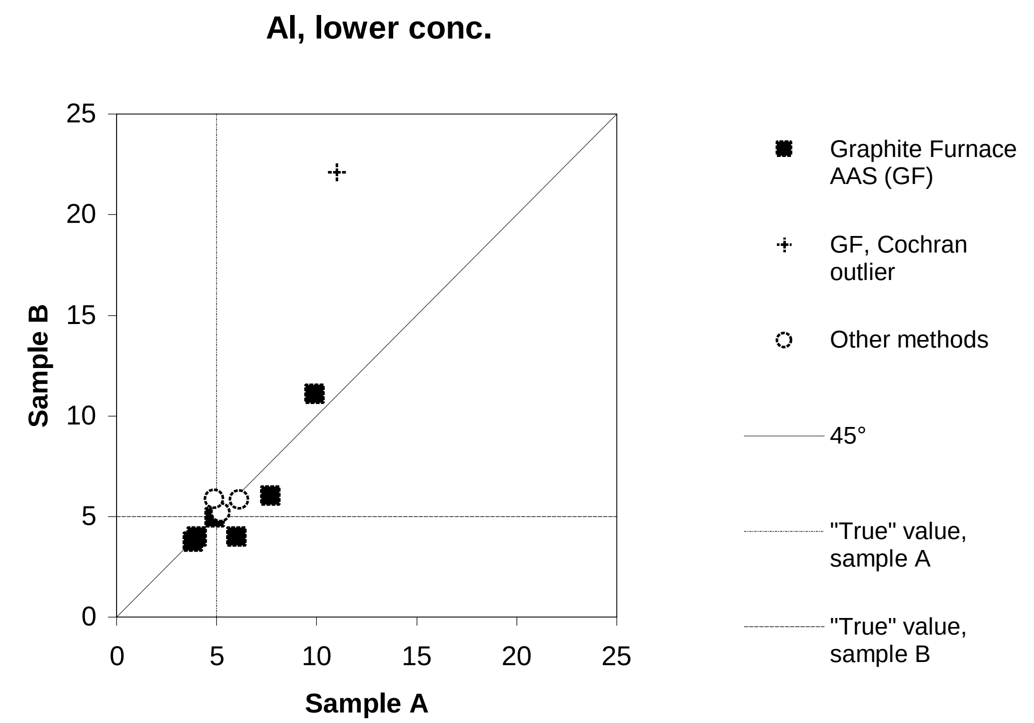
## Al, synthetic solutions (µg/l)

| Lab No. | A | B | Code | Outl./Str. | Lab No. | C | D | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 5 | 3.82 | 3.75 | 0WZ | | 1 | 25.6 | 26.5 | 0+WD | |
| 29 | 4 | 4 | 0W | | 37 | 32.1 | 34.2 | 0WD | |
| 6 | 4.9 | 5.0 | 2PZ | | 42 | 33.7 | 34.5 | 2PZ | |
| 21 | 5 | 87 | 0P | C | 5 | 35.8 | 37.2 | 0WZ | |
| 14 | 6 | 4 | 1,2?Z | | 8 | 38.3 | 38.29 | 2W | |
| 42 | 7.71 | 6.02 | 2PZ | | 15 | 41 | 43 | ? | |
| 32 | 9.91 | 11.09 | 0WZ | | 14 | 42 | 43 | 1,2?Z | |
| 10 | 11 | 22.1 | 2PZ | C | 21 | 43 | 42 | 0P | |
| 1 | 10.9 | <8 | 0+WD | | 6 | 45 | 43 | 2PZ | |
| 15 | <10 | <10 | ? | | 10 | 47 | 47.4 | 2PZ | |
| 8 | <3 | <3 | 2W | | 29 | 48 | 40 | 0W | C |
| 31 | <50 | <50 | 1,2PD | | 32 | 94.03 | 99.84 | 0WZ | G |
| 37 | M | M | | | 31 | <50 | <50 | 1,2PD | |

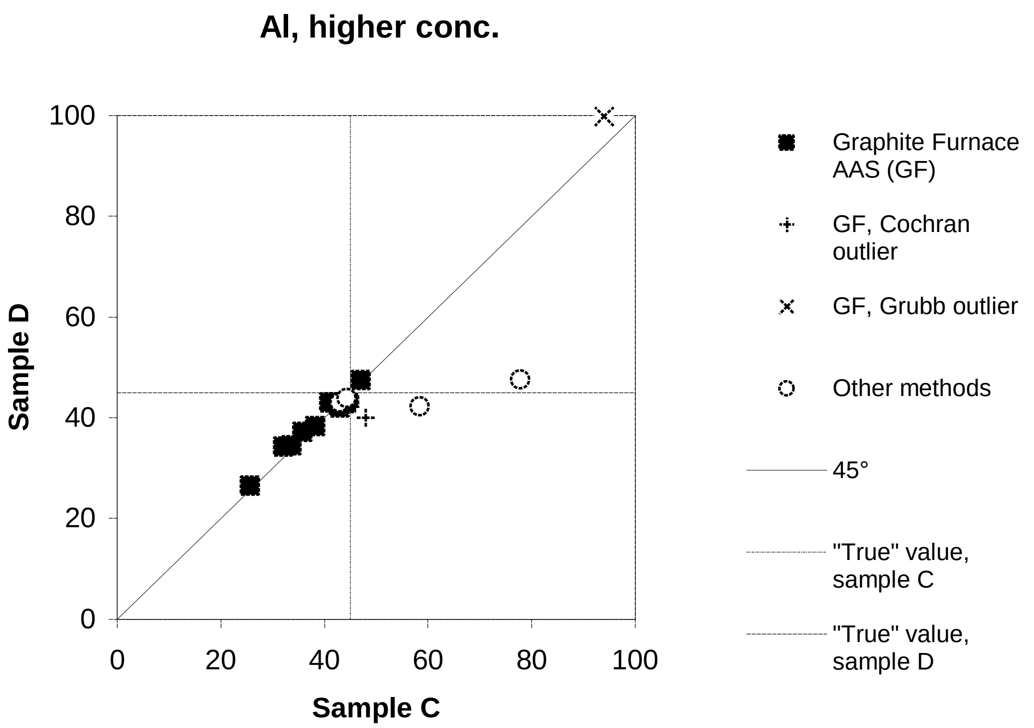
| | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|
| **A,B** | 5 | 5.85 | 117 | 0.83 | 14.2 | 2.59 | 44.3 |
| **C,D** | 45 | 38.6 | 86 | 0.93 | 2.4 | 6.3 | 16.4 |

## Al, other methods

| Lab No. | A | B | Code | | Lab No. | C | D | Code |
|---|---|---|---|---|---|---|---|---|
| 44 | 4.89 | 5.89 | K | | 3 | 43 | 43 | I |
| 19 | 5.2 | 5.2 | K | | 44 | 44.3 | 43.9 | K |
| 38 | 6.11 | 5.83 | K | | 19 | 58.4 | 42.2 | K |
| 3 | <10 | <10 | I | | 38 | 77.8 | 47.5 | K |
| 2 | <100 | <100 | I | | 2 | <100 | <100 | I |



Al, lower conc.
25
20
15
10
5
0
Sample B
0
5
10
15
20
25
Sample A
Graphite Furnace AAS (GF)
GF, Cochran outlier
Other methods
45°
"True" value, sample A
"True" value, sample B

Al, higher conc.
100
80
60
40
20
0
Sample D
0
20
40
60
80
100
Sample C
Graphite Furnace AAS (GF)
GF, Cochran outlier
GF, Grubb outlier
Other methods
45°
"True" value, sample C
"True" value, sample D

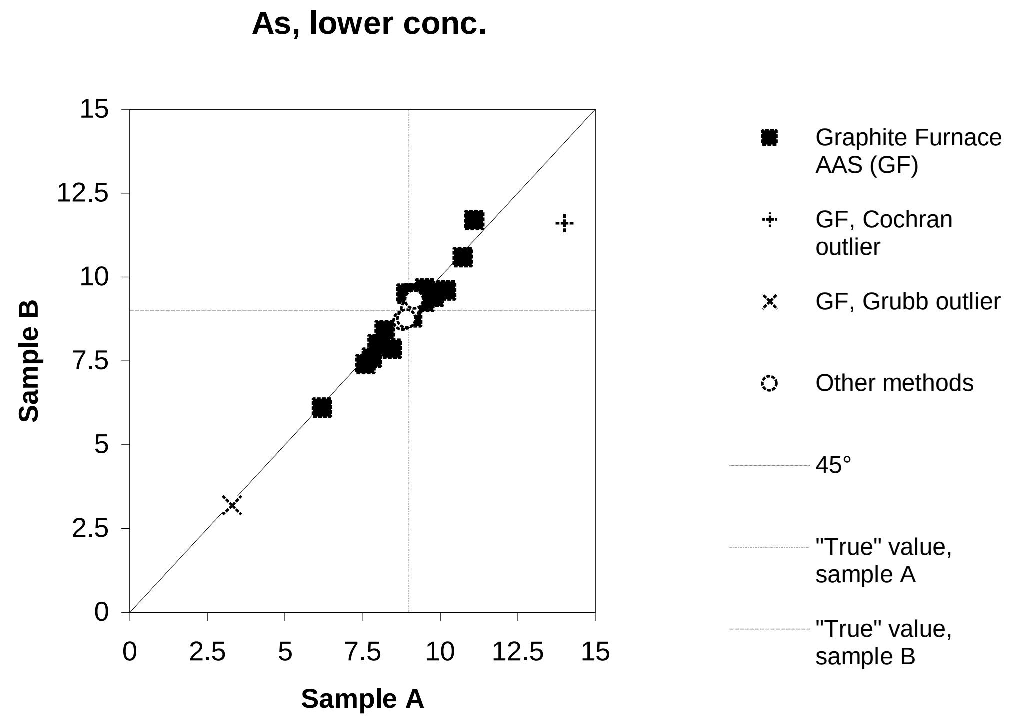
## As, synthetic solutions (µg/l)

| Lab No. | A | B | Code | Outl./Str. | Lab No. | C | D | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 7 | 3.3 | 3.2 | 1,2PD | G | 1 | 49.8 | 63.3 | 1+WD | C |
| 24 | 6.2 | 6.1 | 1+WZ | | 2 | 54 | 61 | 4WD | |
| 42 | 7.6 | 7.4 | 1,2PZ | | 42 | 61.7 | 62.6 | 1,2PZ | |
| 19 | 7.8 | 7.6 | 1,2PZ | | 19 | 70 | 69 | 1,2PZ | |
| 9 | 8 | 8 | 1,2WD | | 24 | 71 | 71 | 1+WZ | |
| 3 | 8.22 | 8.41 | 2PZ | | 9 | 74 | 76 | 1,2WD | |
| 5 | 8.45 | 7.86 | 1WZ | | 5 | 74.4 | 76.7 | 1WZ | |
| 32 | 8.92 | 9.5 | 1,2WZ | | 12 | 75.9 | 81 | 1,2PZ | |
| 12 | 9.1 | 8.8 | 1,2PZ | | 34 | 76.05 | 80.64 | 1PZ | |
| 41 | 9.16 | 9.51 | 1,2PZ | | 3 | 76.7 | 79.5 | 2PZ | |
| 35 | 9.5 | 9.25 | 1,2PZ | | 10 | 77.4 | 79.5 | 1,2PZ | |
| 16 | 9.52 | 9.66 | 1PZ | | 15 | 78.5 | 78.7 | ? | |
| 22 | 9.6 | 9.5 | 1,2WD | | 27 | 80 | 80.1 | 1,2PZ | |
| 11 | 9.8 | 9.4 | 1,2PZ | | 32 | 80.1 | 83.3 | 1,2WZ | |
| 27 | 9.81 | 9.52 | 1,2PZ | | 35 | 80.6 | 81.2 | 1,2PZ | |
| 10 | 10.2 | 9.59 | 1,2PZ | | 16 | 82.29 | 83.15 | 1PZ | |
| 34 | 10.73 | 10.58 | 1PZ | | 41 | 83.02 | 78.54 | 1,2PZ | |
| 2 | 11 | <10 | 4WD | | 7 | 85 | 88 | 1,2PD | |
| 26 | 11.1 | 11.7 | 1,2+PZ | | 11 | 86.0 | 86.2 | 1,2PZ | |
| 1 | 14.0 | 11.6 | 1+WD | C | 22 | 89.1 | 91.7 | 1,2WD | |
| 15 | <10 | <10 | ? | | 26 | 123 | 125 | 1,2+PZ | G |

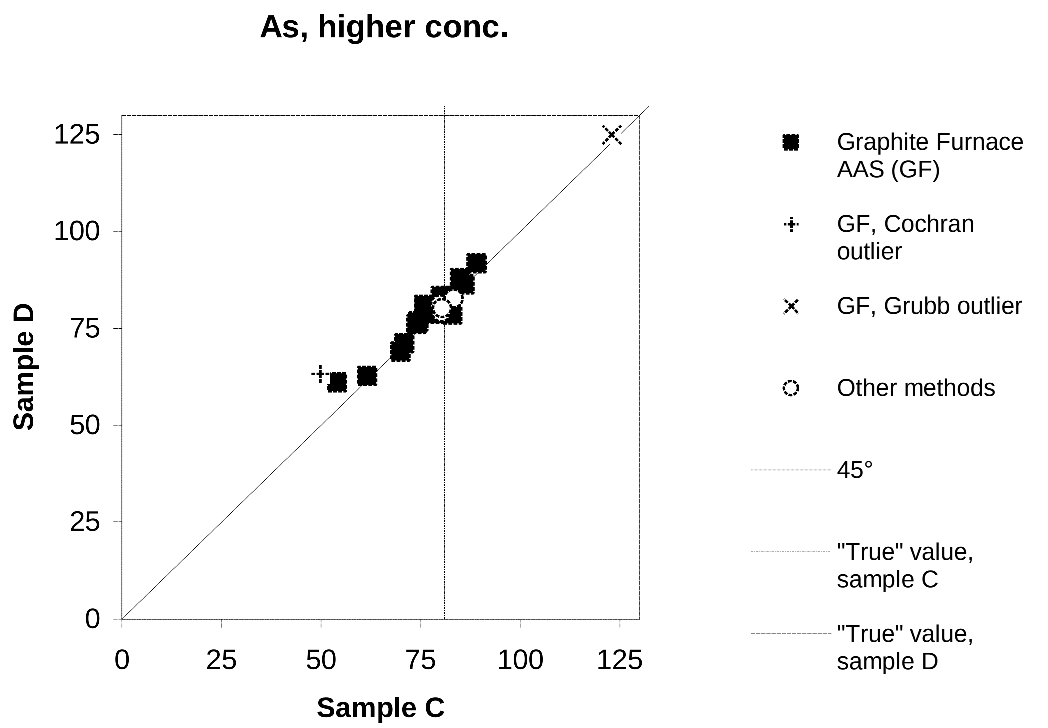
| | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|
| **A,B** | 9 | 9.00 | 100 | 0.25 | 2.8 | 1.27 | 14.1 |
| **C,D** | 81 | 77.5 | 96 | 2.1 | 2.7 | 8.1 | 10.5 |

## As, other methods

| Lab No. | A | B | Code | | Lab No. | C | D | Code |
|---|---|---|---|---|---|---|---|---|
| 19 | 8.8 | 8.7 | K | | 23 | 80 | 81.2 | H |
| 44 | 8.93 | 8.75 | K | | 19 | 80.3 | 79 | K |
| 23 | 9.05 | 9.05 | H | | 44 | 80.4 | 80.2 | K |
| 38 | 9.16 | 9.33 | K | | 38 | 83.4 | 82.6 | K |



As, lower conc.
15
12.5
10
7.5
5
2.5
0
Sample B
0
2.5
5
7.5
10
12.5
15
Sample A
Graphite Furnace AAS (GF)
GF, Cochran outlier
GF, Grubb outlier
Other methods
45°
"True" value, sample A
"True" value, sample B

As, higher conc.
125
100
75
50
25
0
Sample D
0
25
50
75
100
125
Sample C
Graphite Furnace AAS (GF)
GF, Cochran outlier
GF, Grubb outlier
Other methods
45°
"True" value, sample C
"True" value, sample D

Cd, synthetic solutions (µg/l)

| Lab No. | A | B | Code | Outl./Str. | Lab No. | C | D | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 8 | 0.196 | 0.188 | 1,2WD | | 14 | 2.3 | 2.4 | 0?Z | |
| 31 | 0.21 | 0.21 | 3PD | | 37 | 2.3 | 3 | 0WD | C |
| 37 | 0.24 | 0.27 | 0WD | | 8 | 2.36 | 2.33 | 1,2WD | |
| 13 | 0.25 | 0.25 | 2,3PZ | | 31 | 2.45 | 2.37 | 3PD | |
| 24 | 0.25 | 0.25 | 1+WZ | | 26 | 2.51 | 2.51 | 2,3+PZ | |
| 34 | 0.26 | 0.27 | 1PZ | | 35 | 2.51 | 2.42 | 3PZ | |
| 4 | 0.268 | 0.252 | 2,3PZ | | 32 | 2.56 | 2.55 | 0PZ | |
| 35 | 0.271 | 0.278 | 3PZ | | 20 | 2.57 | 2.56 | 1,2WZ | |
| 3 | 0.28 | 0.28 | 2,3PZ | | 7 | 2.6 | 2.6 | 1,2PD | |
| 26 | 0.28 | 0.28 | 2,3+PZ | | 9 | 2.6 | 2.5 | 1,2WD | |
| 32 | 0.28 | 0.27 | 0PZ | | 13 | 2.6 | 2.6 | 2,3PZ | |
| 20 | 0.283 | 0.286 | 1,2WZ | | 21 | 2.6 | 2.5 | 1,2PD | |
| 17 | 0.286 | 0.297 | 2,3PZ | | 34 | 2.65 | 2.68 | 1PZ | |
| 6 | 0.29 | 0.26 | 2,3PZ | | 41 | 2.68 | 2.68 | 2,3PZ | |
| 9 | 0.29 | 0.3 | 1,2WD | | 4 | 2.71 | 2.71 | 2,3PZ | |
| 5 | 0.298 | 0.305 | 3WZ | | 6 | 2.71 | 2.70 | 2,3PZ | |
| 7 | 0.3 | 0.3 | 1,2PD | | 39 | 2.78 | 2.8 | 2,3WZ | |
| 11 | 0.30 | 0.31 | 2,3PZ | | 29 | 2.79 | 2.83 | 2,3PZ | |
| 12 | 0.3 | 0.3 | 1,2,3PZ | | 5 | 2.80 | 2.72 | 3WZ | |
| 21 | 0.3 | 0.3 | 1,2PD | | 42 | 2.8 | 2.6 | 0PZ | |
| 41 | 0.3 | 0.32 | 2,3PZ | | 11 | 2.88 | 2.91 | 2,3PZ | |
| 42 | 0.3 | 0.3 | 0PZ | | 22 | 2.88 | 2.98 | 1,2WD | |
| 29 | 0.31 | 0.31 | 2,3PZ | | 3 | 2.89 | 2.78 | 2,3PZ | |
| 30 | 0.316 | 0.293 | 1WD | | 30 | 2.89 | 2.89 | 1WD | |
| 16 | 0.32 | 0.36 | 3PZ | | 24 | 2.9 | 2.9 | 1+WZ | |
| 22 | 0.33 | 0.35 | 1,2WD | | 17 | 2.943 | 2.959 | 2,3PZ | |
| 27 | 0.33 | 0.34 | 2,3PZ | | 12 | 3 | 2.9 | 1,2,3PZ | |
| 23 | 0.369 | 0.257 | 0+WZ | C | 40 | 3 | 3 | 2,3PZ | |
| 19 | 0.37 | 0.36 | 0PZ | | 27 | 3.03 | 3.03 | 2,3PZ | |
| 39 | 0.379 | 0.364 | 2,3WZ | | 2 | 3.1 | 3.1 | 1,2WD | |
| 33 | 0.39 | 0.4 | 0WD | | 19 | 3.1 | 3 | 0PZ | |
| 14 | 0.4 | 0.4 | 0?Z | | 1 | 3.3 | 3.4 | 0+WD | |
| 40 | 0.4 | 0.4 | 2,3PZ | | 10 | 3.32 | 3.27 | 2,3PZ | |
| 10 | 0.41 | 0.37 | 2,3PZ | | 33 | 3.38 | 3.36 | 0WD | |
| 1 | <1 | <1 | 0+WD | | 23 | 3.46 | 3.69 | 0+WZ | |
| 2 | <2 | <2 | 1,2WD | | 16 | 4.65 | 4.36 | 3PZ | C 5%, G |
| 15 | <2 | <2 | ? | | 15 | <2 | <2 | ? | |

| | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|
| **A,B** | 0.3 | 0.303 | 101 | 0.011 | 3.5 | 0.052 | 17.0 |
| **C,D** | 2.7 | 2.81 | 104 | 0.05 | 1.9 | 0.30 | 10.7 |

Cd, other methods

| Lab No. | A | B | Code | | Lab No. | C | D | Code |
|---|---|---|---|---|---|---|---|---|
| 38 | 0.316 | 0.319 | K | | 44 | 2.83 | 2.83 | K |
| 44 | 0.316 | 0.303 | K | | 38 | 2.91 | 3 | K |
| 19 | 0.4 | 0.4 | K | | 19 | 3.2 | 3.2 | K |

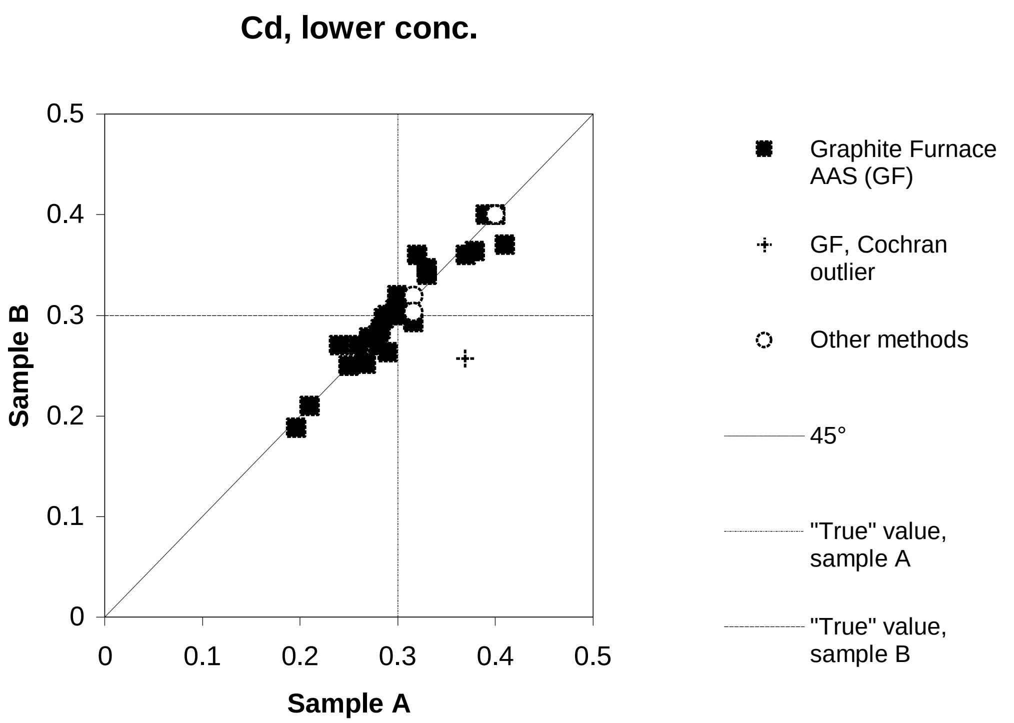
Co, synthetic solutions (µg/l)

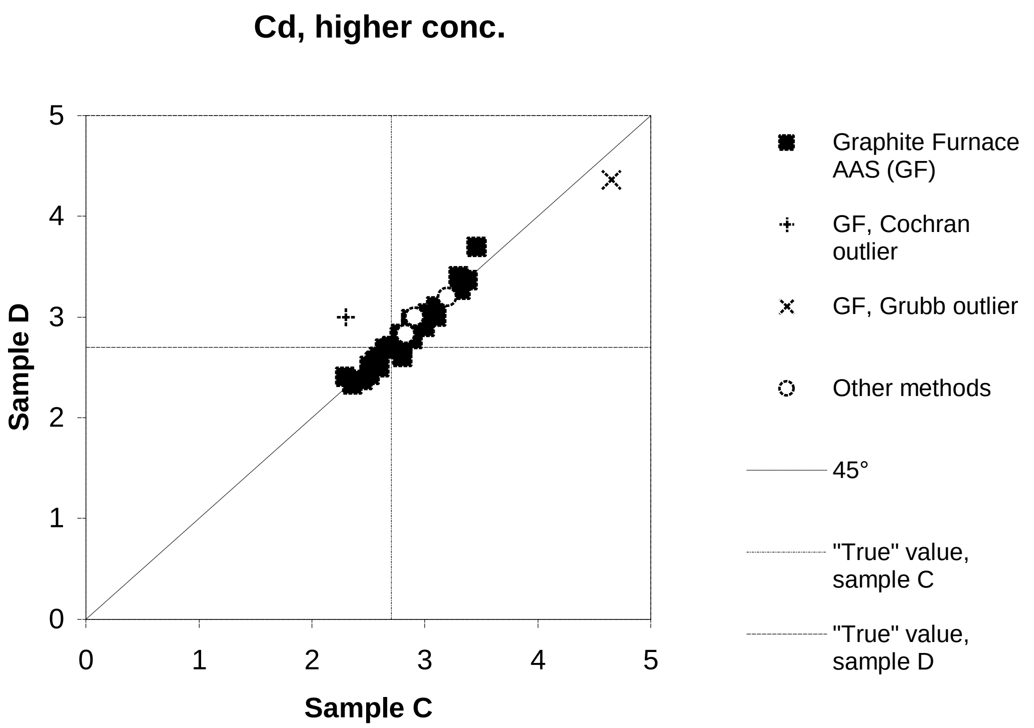
| Lab No. | A | B | Code | Outl./Str. | Lab No. | C | D | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 3 | 4.73 | 4.83 | 0PZ | | 1 | 26.3 | 25.6 | 0+WD | G |
| 42 | 5.2 | 5.1 | 0PZ | | 8 | 45.36 | 44.52 | 2WD | |
| 8 | 5.41 | 5.11 | 2WD | | 3 | 47.2 | 47.2 | 0PZ | |
| 17 | 5.638 | 5.115 | 2PZ | | 21 | 48 | 48 | 2WD | |
| 10 | 5.65 | 5.45 | 2WZ | | 29 | 48.2 | 48.3 | 0WD | |
| 29 | 5.8 | 5.5 | 0WD | | 10 | 49.4 | 50.4 | 2WZ | |
| 1 | 5.9 | 5.6 | 0+WD | | 17 | 49.68 | 50.09 | 2PZ | |
| 21 | 6 | 6 | 2WD | | 15 | 49.7 | 50 | ? | |
| 40 | 6 | 6 | 2PZ | | 5 | 49.7 | 50.9 | 2WZ | |
| 5 | 6.05 | 5.93 | 2WZ | | 32 | 50.9 | 50.4 | 0PZ | |
| 32 | 6.13 | 6.24 | 0PZ | | 19 | 54 | 55 | 0PZ | |
| 19 | 6.2 | 6.1 | 0PZ | | 42 | 54.2 | 53.2 | 0PZ | |
| 37 | 6.6 | 6.2 | 0WD | | 40 | 55 | 60 | 2PZ | C |
| 15 | <5 | <5 | ? | | 37 | 60.2 | 60 | 0WD | |

| | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|
| **A,B** | 5.5 | 5.71 | 104 | 0.18 | 3.1 | 0.49 | 8.5 |
| **C,D** | 49.5 | 50.6 | 102 | 0.5 | 1.0 | 4.0 | 7.9 |

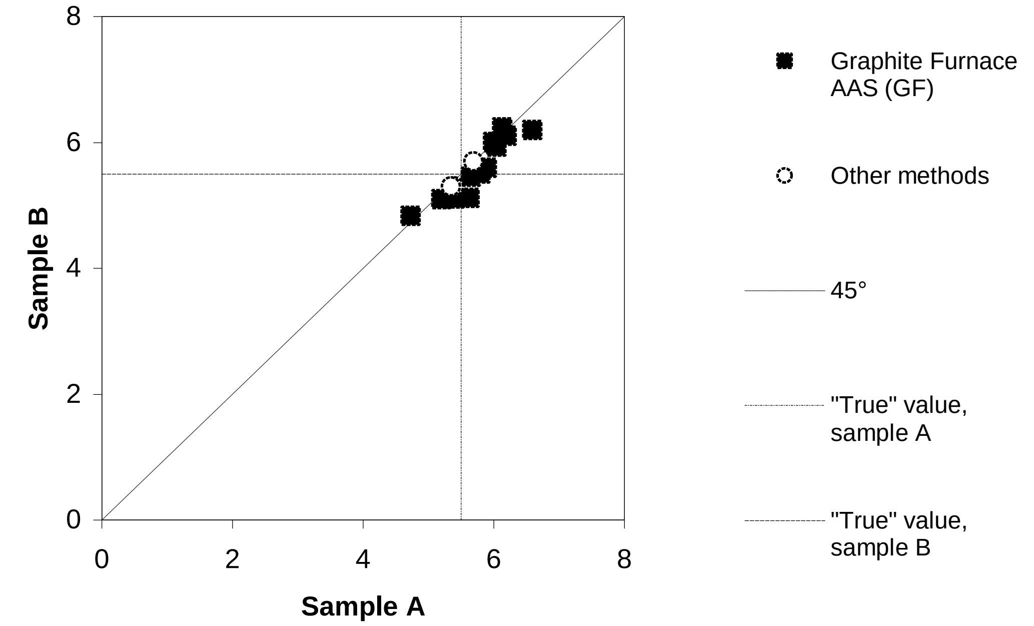
Co, other methods

| Lab No. | A | B | Code | | Lab No. | C | D | Code |
|---|---|---|---|---|---|---|---|---|
| 44 | 5.35 | 5.3 | K | | 19 | 47.2 | 47.2 | K |
| 19 | 5.4 | 5.3 | K | | 44 | 49 | 49.1 | K |
| 38 | 5.69 | 5.7 | K | | 38 | 50.6 | 50.3 | K |
| 2 | <10 | <10 | I | | 3 | 56 | 56 | I |
| 3 | <50 | <50 | I | | 2 | <50 | <50 | I |

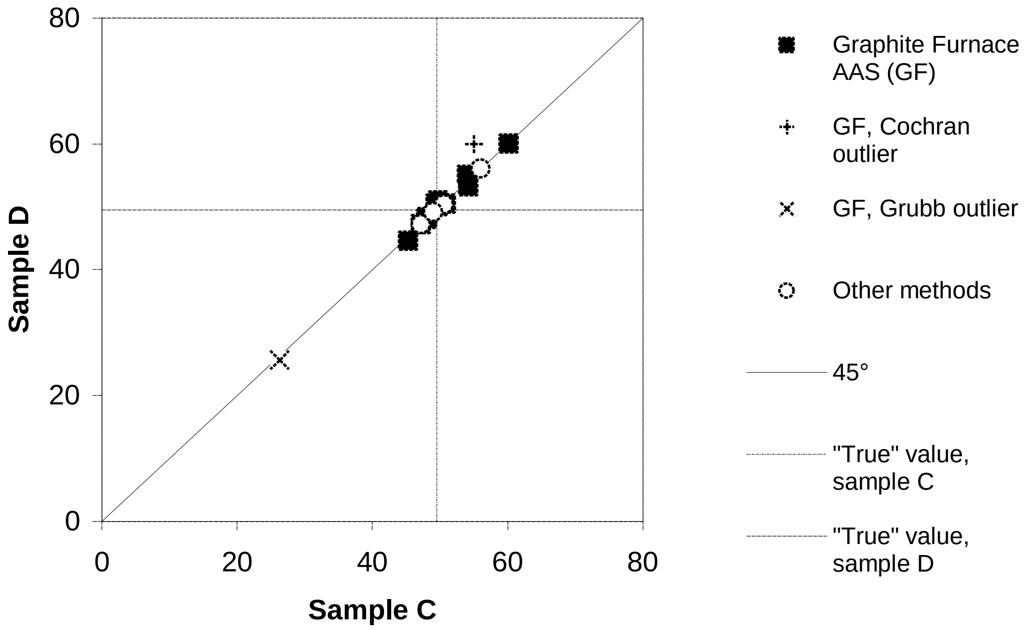

Cd, lower conc.
0.5
0.4
0.3
0.2
0.1
0
Sample B
0
0.1
0.2
0.3
0.4
0.5
Sample A
Graphite Furnace AAS (GF)
GF, Cochran outlier
Other methods
45°
"True" value, sample A
"True" value, sample B


Cd, higher conc.
5
4
3
2
1
0
Sample D
0
1
2
3
4
5
Sample C
Graphite Furnace AAS (GF)
GF, Cochran outlier
GF, Grubb outlier
Other methods
45°
"True" value, sample C
"True" value, sample D

**Co, lower conc.**




**Co, higher conc.**



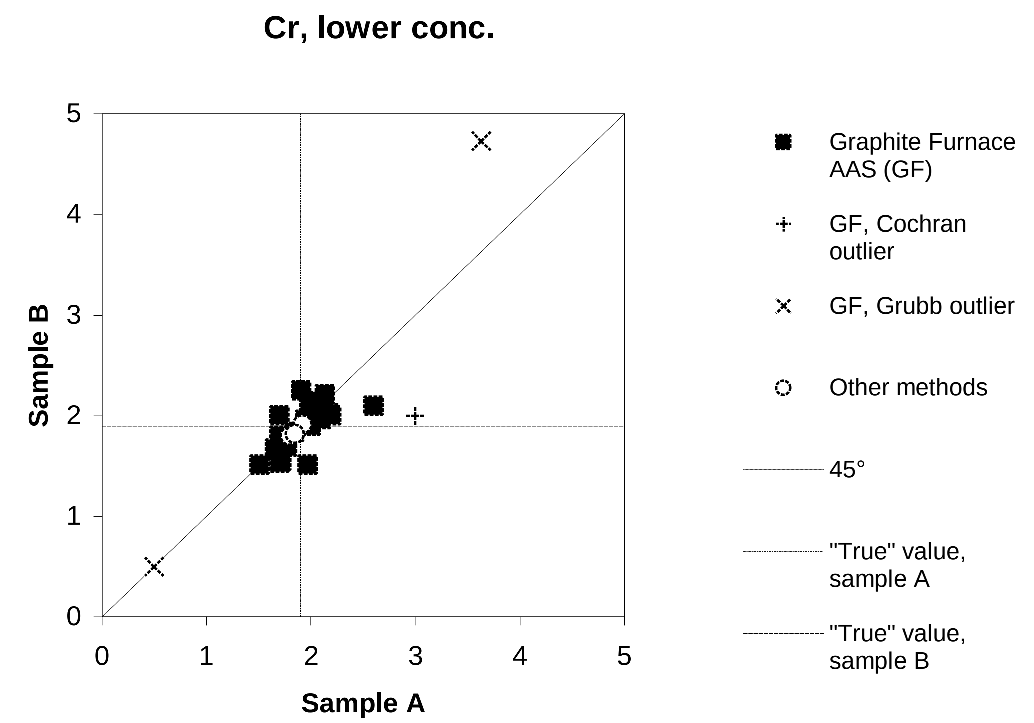
Cr, synthetic solutions (µg/l)

| Lab No. | A | B | Code | Outl./Str. | Lab No. | C | D | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 12 | 0.5 | 0.5 | 2PZ | G | 1 | 13.6 | 13.6 | 3+WD | G 5% |
| 32 | 1.51 | 1.51 | 0PZ | | 23 | 13.6 | 19.7 | 0+WZ | C |
| 31 | 1.66 | 1.67 | 2P | | 15 | 15.1 | 15.1 | ? | |
| 11 | 1.7 | 1.8 | 2PZ | | 11 | 16.4 | 17.0 | 2PZ | |
| 22 | 1.70 | 1.53 | 2WD | | 35 | 16.5 | 16.6 | 2PZ | |
| 29 | 1.7 | 2 | 0W | | 17 | 16.52 | 16.19 | 2PZ | |
| 30 | 1.72 | 1.55 | 2W | | 36 | 16.6 | 16.9 | 2,5WD | |
| 17 | 1.777 | 1.693 | 2PZ | | 8 | 16.63 | 16.2 | 2W | |
| 26 | 1.84 | 1.84 | 0+PZ | | 26 | 17 | 16.6 | 0+PZ | |
| 41 | 1.91 | 2.25 | 2PZ | | 3 | 17.5 | 18.2 | 2,3PZ | |
| 35 | 1.95 | 1.96 | 2PZ | | 10 | 17.5 | 17.9 | 2WZ | |
| 3 | 1.97 | 1.51 | 2,3PZ | | 22 | 17.6 | 16.2 | 2WD | |
| 23 | 1.99 | 2.11 | 0+WZ | | 9 | 17.7 | 17.2 | 2W | |
| 9 | 2 | 1.9 | 2W | | 6 | 17.8 | 17.9 | 2PZ | |
| 21 | 2 | 2 | 0W | | 29 | 17.8 | 17.8 | 0W | |
| 36 | 2 | 1.9 | 2,5WD | | 41 | 17.81 | 17.96 | 2PZ | |
| 10 | 2.09 | 2.14 | 2WZ | | 19 | 18 | 18 | 0PZ | |
| 6 | 2.1 | 2.0 | 2PZ | | 21 | 18 | 19 | 0W | |
| 5 | 2.14 | 2.21 | 2WZ | | 40 | 18 | 18 | 2PZ | |
| 27 | 2.18 | 2.02 | 2PZ | | 30 | 18.2 | 18 | 2W | |
| 19 | 2.2 | 2 | 0PZ | | 12 | 18.4 | 18 | 2PZ | |
| 1 | 2.6 | 2.1 | 3+WD | | 5 | 19.0 | 19.4 | 2WZ | |
| 40 | 3 | 2 | 2PZ | C | 31 | 19.2 | 19.5 | 2P | |
| 16 | 3.63 | 4.73 | 1WZ | C 5%, G | 27 | 19.6 | 19 | 2PZ | |
| 8 | <1 | <1 | 2W | | 32 | 19.8 | 19.2 | 0PZ | |
| 15 | <5 | <5 | ? | | 16 | M | 21.28 | 1WZ | |

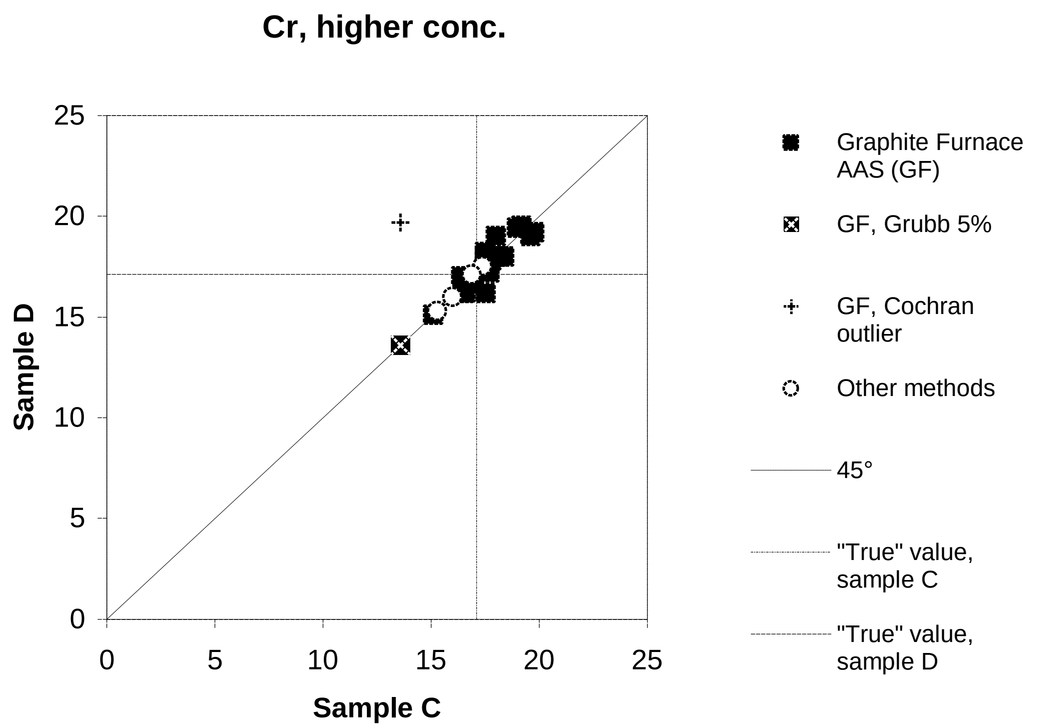
| | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|
| **A,B** | 1.9 | 1.91 | 101 | 0.14 | 7.5 | 0.24 | 12.4 |
| **C,D** | 17.1 | 17.5 | 102 | 0.4 | 2.0 | 1.4 | 7.9 |

Cr, other methods

| Lab No. | A | B | Code | | Lab No. | C | D | Code |
|---|---|---|---|---|---|---|---|---|
| 19 | 1.8 | 1.8 | K | | 19 | 15.3 | 15.3 | K |
| 44 | 1.85 | 1.82 | K | | 2 | 16 | 16 | I |
| 38 | 1.92 | 1.91 | K | | 44 | 16.9 | 17.1 | K |
| 2 | <10 | <10 | I | | 38 | 17.4 | 17.5 | K |



Cr, lower conc.
Sample B
Sample A
0
1
2
3
4
5
Graphite Furnace AAS (GF)
GF, Cochran outlier
GF, Grubb outlier
Other methods
45°
"True" value, sample A
"True" value, sample B

Cr, higher conc.
Sample D
Sample C
0
5
10
15
20
25
Graphite Furnace AAS (GF)
GF, Grubb 5%
GF, Cochran outlier
Other methods
45°
"True" value, sample C
"True" value, sample D

## Cu, synthetic solutions (µg/l)

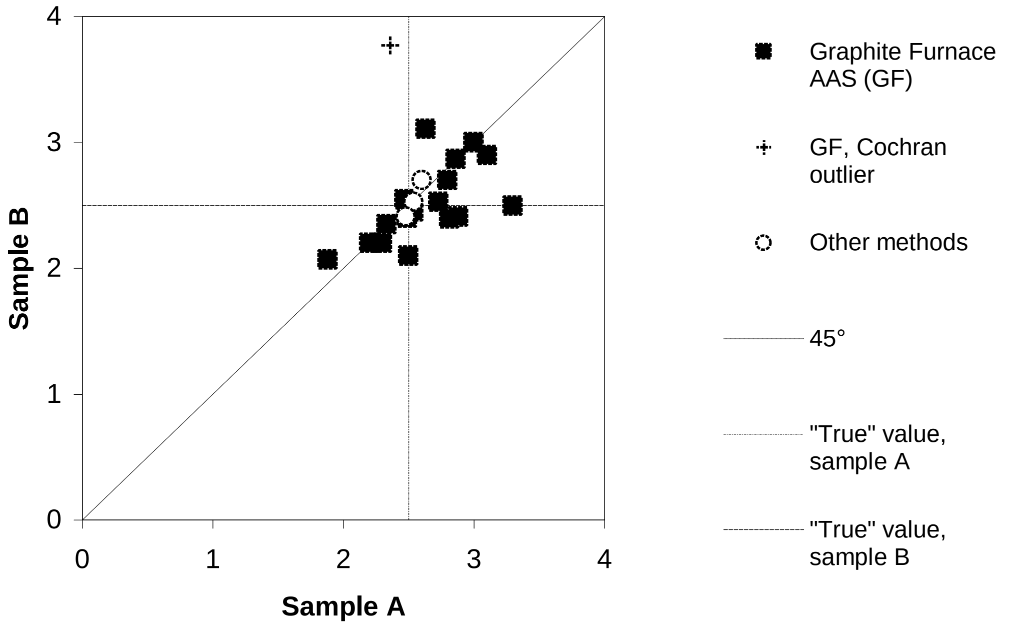
| Lab No. | A | B | Code | Outl./Str. | Lab No. | C | D | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 32 | 1.88 | 2.07 | 0WZ | | 42 | 16.9 | 16.8 | 0PZ | G |
| 42 | 2.2 | 2.2 | 0PZ | | 16 | 20.55 | 20.41 | 1WZ | |
| 11 | 2.3 | 2.2 | 0PZ | | 5 | 21.0 | 21.7 | 0WZ | |
| 22 | 2.33 | 2.35 | 0WD | | 1 | 21.4 | 21.1 | 0+WD | |
| 16 | 2.36 | 3.77 | 1WZ | C | 6 | 21.6 | 21.7 | 2PZ | |
| 3 | 2.47 | 2.55 | 1,2PZ | | 41 | 21.62 | 25.33 | 1,2PZ | C 5% |
| 33 | 2.49 | 2.4 | 0WD | | 11 | 22.2 | 22.1 | 0PZ | |
| 37 | 2.5 | 2.1 | 0WD | | 29 | 22.5 | 22.9 | 0PZ | |
| 5 | 2.54 | 2.45 | 0WZ | | 21 | 23 | 23 | 0WD | |
| 27 | 2.63 | 3.11 | 1,2PZ | | 31 | 23.1 | 23.7 | 0PD | |
| 10 | 2.73 | 2.53 | 1,2WZ | | 22 | 23.2 | 22.5 | 0WD | |
| 29 | 2.8 | 2.7 | 0PZ | | 32 | 23.4 | 23.7 | 0WZ | |
| 6 | 2.8 | 2.4 | 2PZ | | 3 | 23.5 | 23.9 | 1,2PZ | |
| 41 | 2.86 | 2.87 | 1,2PZ | | 10 | 23.7 | 23.9 | 1,2WZ | |
| 17 | 2.879 | 2.409 | 0PZ | | 19 | 24 | 23 | 0PZ | |
| 21 | 3 | 3 | 0WD | | 37 | 24 | 25.1 | 0WD | |
| 40 | 3 | 3 | 1,2PZ | | 17 | 24.11 | 23.13 | 0PZ | |
| 19 | 3.1 | 2.9 | 0PZ | | 33 | 24.3 | 23.2 | 0WD | |
| 31 | 3.3 | 2.5 | 0PD | | 27 | 24.6 | 21.8 | 1,2PZ | |
| 1 | <8 | <8 | 0+WD | | 40 | 25 | 24 | 1,2PZ | |
| 15 | <20 | <20 | ? | | 15 | <20 | 21 | ? | |

| | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|
| **A,B** | 2.5 | 2.60 | 104 | 0.21 | 8.1 | 0.34 | 13.2 |
| **C,D** | 22.5 | 23.0 | 102 | 0.9 | 3.8 | 1.3 | 5.6 |

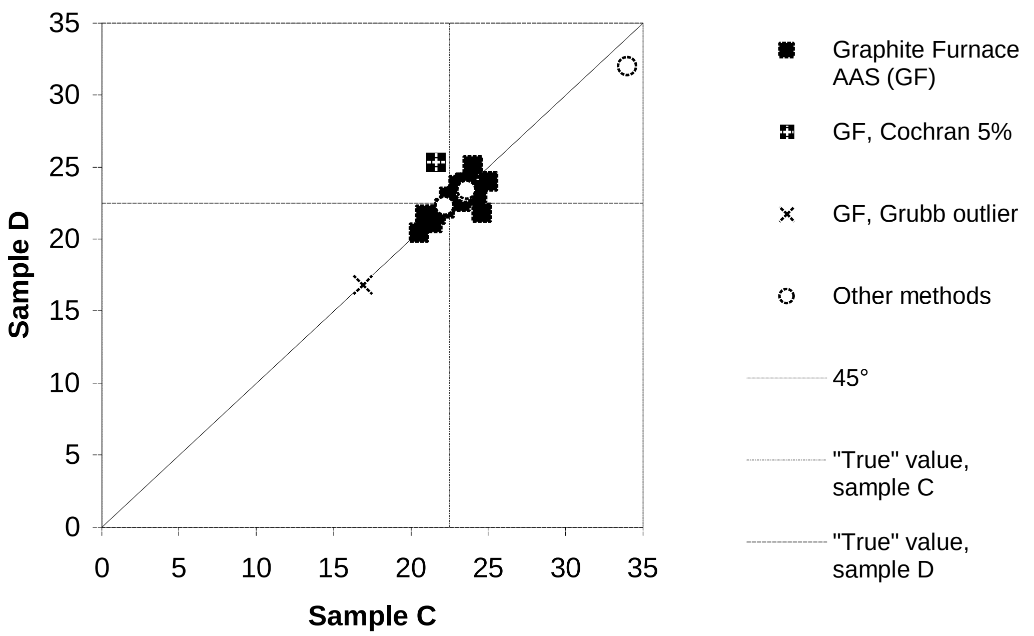
## Cu, other methods

| Lab No. | A | B | Code | | Lab No. | C | D | Code |
|---|---|---|---|---|---|---|---|---|
| 44 | 2.48 | 2.41 | K | | 44 | 22.2 | 22.3 | K |
| 38 | 2.54 | 2.53 | K | | 19 | 23.5 | 23.2 | K |
| 19 | 2.6 | 2.7 | K | | 38 | 23.6 | 23.4 | K |
| 2 | <10 | <10 | I | | 2 | 34 | 32 | I |

**Cu, lower conc.**




**Cu, higher conc.**



Fe, synthetic solutions (µg/l)

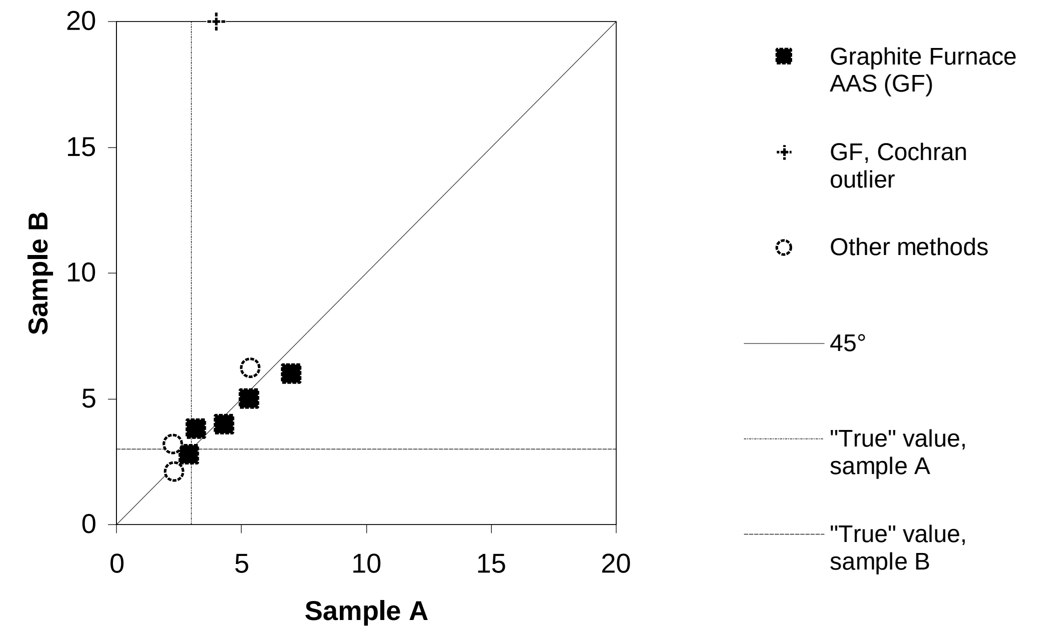
| Lab No. | A | B | Code | Outl./Str. | Lab No. | C | D | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 29 | 2.9 | 2.8 | 0WD | | 42 | 19.2 | 20.3 | 0PZ | |
| 5 | 3.18 | 3.82 | 0WZ | | 15 | 26.4 | 26.7 | ? | |
| 21 | 4 | 20 | 0WD | C | 5 | 26.5 | 25.6 | 0WZ | |
| 6 | 4.3 | 4.0 | 2PZ | | 21 | 27 | 27 | 0WD | |
| 42 | 5.3 | 5.0 | 0PZ | | 29 | 28.7 | 28 | 0WD | |
| 32 | 7 | 6 | 0WZ | | 32 | 29 | 32 | 0WZ | C 5% |
| 15 | <20 | <20 | ? | | 6 | 30.7 | 30.6 | 2PZ | |

| | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|
| **A,B** | 3 | 4.43 | 148 | 0.40 | 9.0 | 1.46 | 33.0 |
| **C,D** | 27 | 27.0 | 100 | 0.9 | 3.4 | 3.7 | 13.8 |

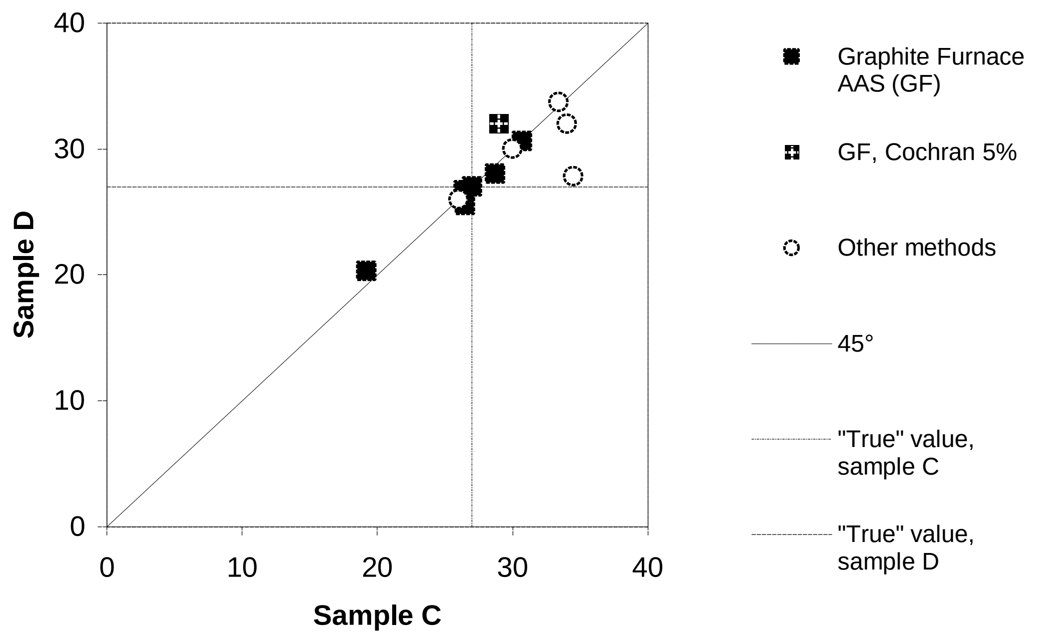
Fe, other methods

| Lab No. | A | B | Code | | Lab No. | C | D | Code |
|---|---|---|---|---|---|---|---|---|
| 38 | 2.26 | 3.2 | K | | 3 | 26 | 26 | I |
| 19 | 2.3 | 2.1 | K | | 2 | 30 | 30 | I |
| 44 | 5.35 | 6.22 | K | | 44 | 33.4 | 33.7 | K |
| 2 | <10 | <10 | I | | 19 | 34 | 32 | K |
| 3 | <10 | <10 | I | | 38 | 34.5 | 27.8 | K |

**Fe, lower conc.**




**Fe, higher conc.**



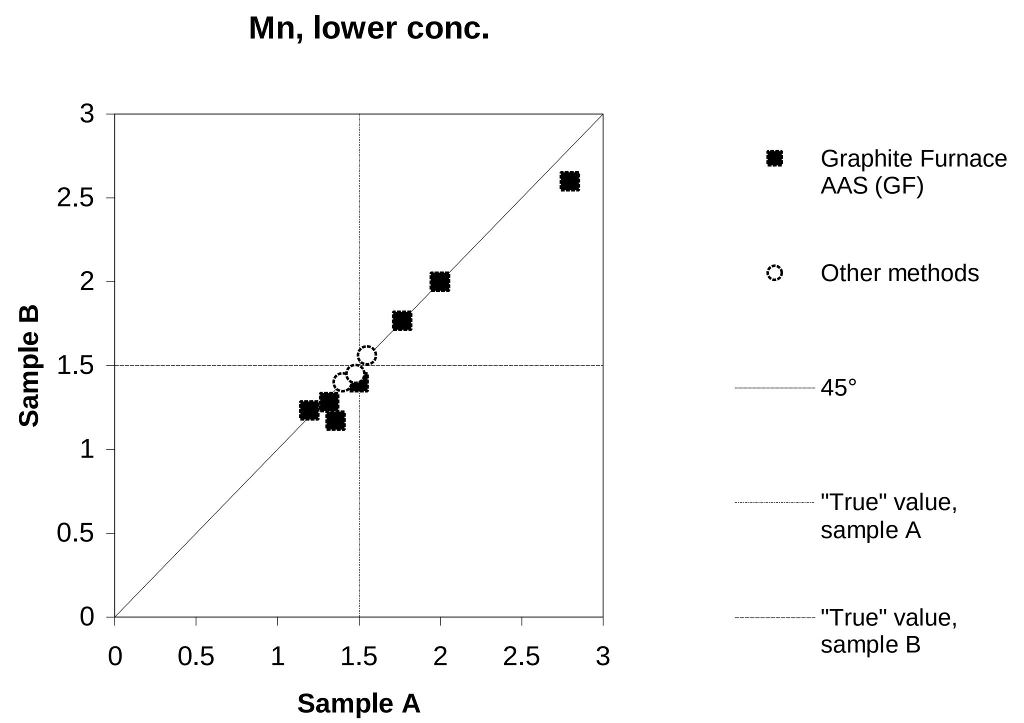
## Mn, synthetic solutions (µg/l)

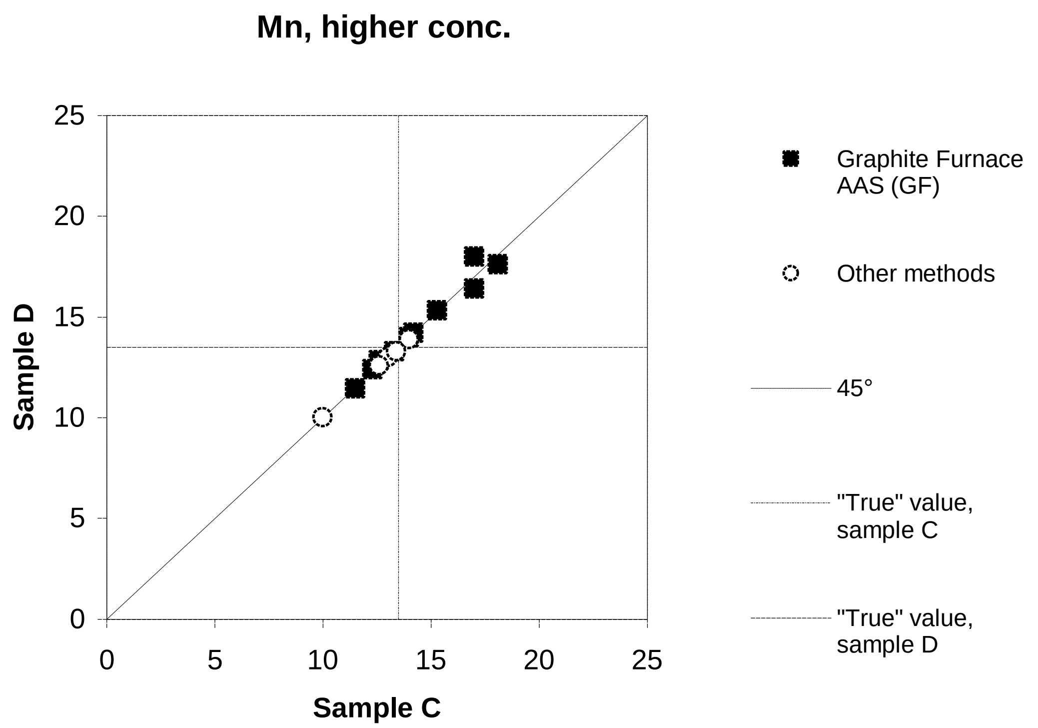
| Lab No. | A | B | Code | Outl./Str. | Lab No. | C | D | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 17 | 1.199 | 1.233 | 2PZ | | 17 | 11.51 | 11.45 | 2PZ | |
| 5 | 1.32 | 1.28 | 0WZ | | 15 | 12.3 | 12.4 | ? | |
| 32 | 1.36 | 1.17 | 1,2WZ | | 5 | 12.6 | 12.9 | 0WZ | |
| 29 | 1.5 | 1.4 | 0WD | | 29 | 13.3 | 13.3 | 0WD | |
| 6 | 1.8 | 1.8 | 2PZ | | 21 | 14 | 14 | 0W | |
| 21 | 2 | 2 | 0W | | 31 | 14.2 | 14.2 | 1,2PD | |
| 40 | 2 | 2 | 1,2PZ | | 6 | 15.3 | 15.3 | 2PZ | |
| 42 | 2.8 | 2.6 | 0PZ | | 40 | 17 | 18 | 1,2PZ | |
| 31 | <2 | <2 | 1,2PD | | 32 | 17.01 | 16.39 | 1,2WZ | |
| 15 | <5 | <5 | ? | | 42 | 18.1 | 17.6 | 0PZ | |

| | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|
| **A,B** | 1.5 | 1.71 | 114 | 0.075 | 4.4 | 0.51 | 30.0 |
| **C,D** | 13.5 | 14.5 | 108 | 0.3 | 2.0 | 2.2 | 15.3 |

## Mn, other methods

| Lab No. | A | B | Code | | Lab No. | C | D | Code |
|---|---|---|---|---|---|---|---|---|
| 19 | 1.4 | 1.4 | K | | 2 | 10 | 10 | I |
| 44 | 1.48 | 1.45 | K | | 19 | 12.6 | 12.6 | K |
| 38 | 1.55 | 1.56 | K | | 3 | 13 | 13 | I |
| 2 | <10 | <10 | I | | 44 | 13.4 | 13.3 | K |
| 3 | <10 | <10 | I | | 38 | 14 | 13.9 | K |


Mn, lower conc.
Sample B
Sample A
3
2.5
2
1.5
1
0.5
0
0
0.5
1
1.5
2
2.5
3
Graphite Furnace AAS (GF)
Other methods
45°
"True" value, sample A
"True" value, sample B


Mn, higher conc.
Sample D
Sample C
25
20
15
10
5
0
0
5
10
15
20
25
Graphite Furnace AAS (GF)
Other methods
45°
"True" value, sample C
"True" value, sample D

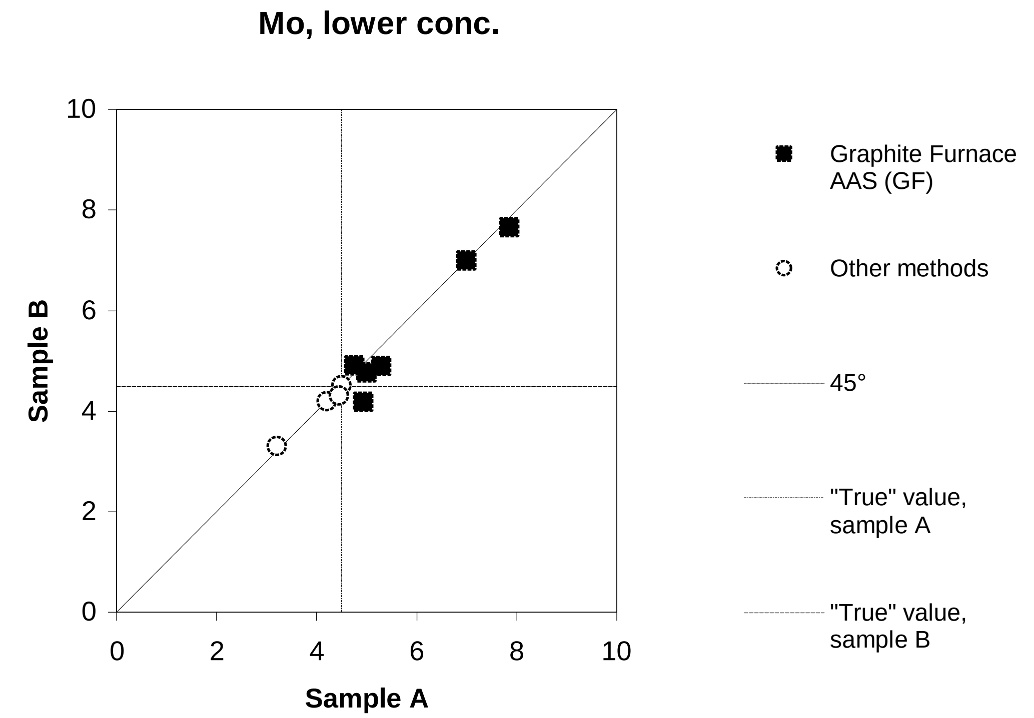
Mo, synthetic solutions (µg/l)

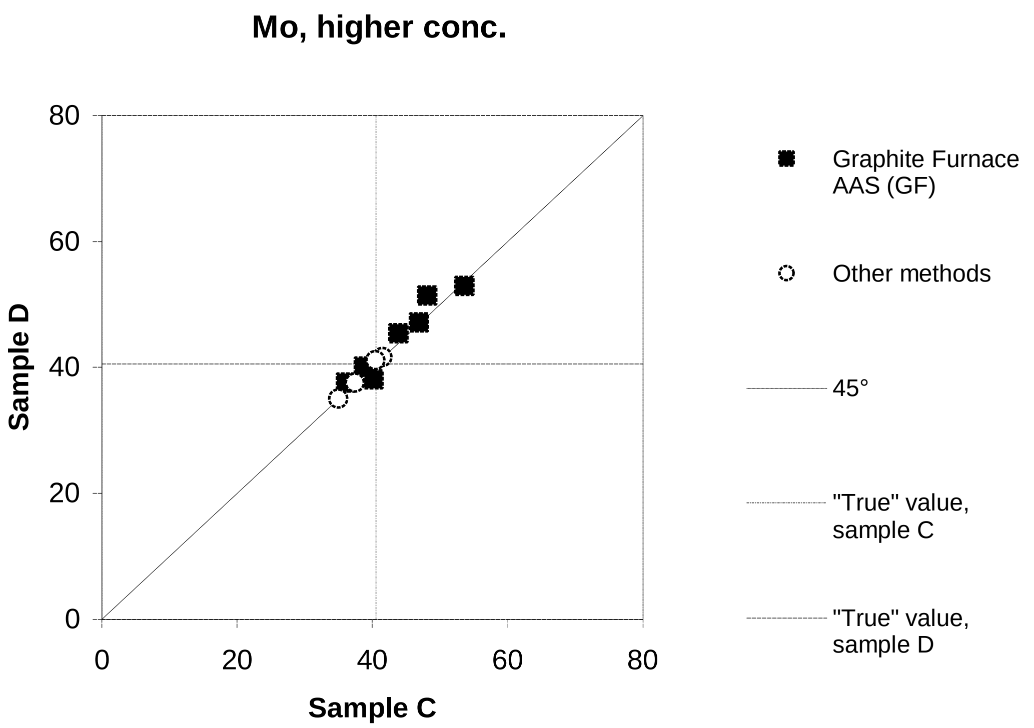
| Lab No. | A | B | Code | Outl./Str. | Lab No. | C | D | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 5 | 4.76 | 4.91 | 0WZ | | 37 | 36.1 | 37.5 | 0WD | |
| 3 | 4.93 | 4.18 | 0PZ | | 5 | 38.8 | 40.1 | 0WZ | |
| 8 | 5 | 4.77 | 0W | | 3 | 40.2 | 38 | 0PZ | |
| 37 | 5.3 | 4.9 | 0WD | | 8 | 43.9 | 45.39 | 0W | |
| 15 | 7 | 7 | ? | | 15 | 46.9 | 47.1 | ? | |
| 10 | 7.86 | 7.66 | 0WZ | | 32 | 48.2 | 51.4 | 0WZ | |
| 32 | <1 | <1 | 0WZ | | 10 | 53.7 | 52.9 | 0WZ | |

| | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|
| **A,B** | 4.5 | 5.69 | 126 | 0.26 | 4.6 | 1.36 | 23.8 |
| **C,D** | 40.5 | 44.3 | 109 | 1.2 | 2.8 | 6.2 | 14.0 |

Mo, other methods

| Lab No. | A | B | Code | | Lab No. | C | D | Code |
|---|---|---|---|---|---|---|---|---|
| 24 | 3.2 | 3.3 | I | | 24 | 35 | 35 | I |
| 19 | 4.2 | 4.2 | K | | 19 | 37.5 | 37.5 | K |
| 44 | 4.45 | 4.31 | K | | 44 | 40.5 | 41.1 | K |
| 38 | 4.5 | 4.51 | K | | 38 | 41.5 | 41.6 | K |
| 2 | <50 | <50 | I | | 2 | <50 | <50 | I |
| 3 | <50 | <50 | I | | 3 | <50 | <50 | I |


Mo, lower conc.
10
8
6
4
2
0
0
2
4
6
8
10
Sample A
Sample B
Graphite Furnace AAS (GF)
Other methods
45°
"True" value, sample A
"True" value, sample B


Mo, higher conc.
80
60
40
20
0
0
20
40
60
80
Sample C
Sample D
Graphite Furnace AAS (GF)
Other methods
45°
"True" value, sample C
"True" value, sample D

## Ni, synthetic solutions (µg/l)

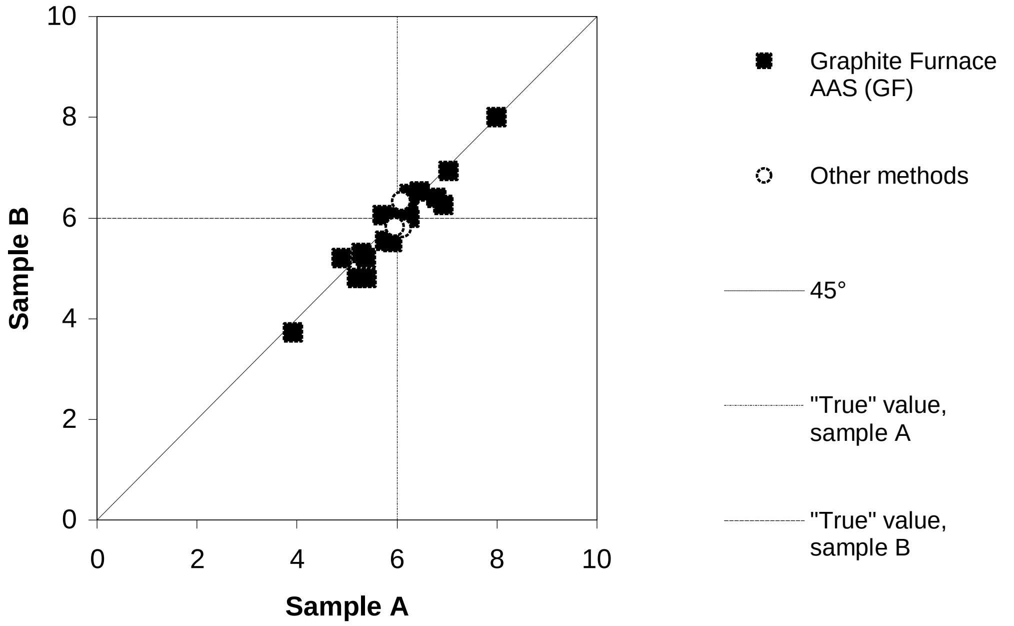
| Lab No. | A | B | Code | Outl./Str. | Lab No. | C | D | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 8 | 3.93 | 3.73 | 2WD | | 8 | 43.41 | 43.23 | 2WD | |
| 14 | 4.9 | 5.2 | 0?Z | | 41 | 46.83 | 47.1 | 2PZ | |
| 12 | 5.2 | 4.8 | 2PZ | | 5 | 47.3 | 47.8 | 0WZ | |
| 42 | 5.3 | 5.3 | 0PZ | | 14 | 48.5 | 47.3 | 0?Z | |
| 22 | 5.39 | 5.20 | 1,2WD | | 6 | 51 | 50 | 2PZ | |
| 29 | 5.4 | 4.8 | 0PD | | 31 | 51.57 | 47.87 | 0PD | |
| 10 | 5.72 | 6.05 | 2WZ | | 21 | 52 | 54 | 0WD | |
| 5 | 5.77 | 5.55 | 0WZ | | 10 | 52.7 | 55.5 | 2WZ | |
| 17 | 5.909 | 5.522 | 0PZ | | 29 | 54.2 | 55.2 | 0PD | |
| 15 | 6 | 6 | ? | | 27 | 54.3 | 55.6 | 0PZ | |
| 21 | 6 | 6 | 0WD | | 17 | 54.73 | 53.68 | 0PZ | |
| 27 | 6.2 | 6.18 | 0PZ | | 15 | 55 | 55 | ? | |
| 31 | 6.23 | 6.28 | 0PD | | 32 | 55.43 | 55.74 | 0PZ | |
| 3 | 6.25 | 6.47 | 1,2PZ | | 22 | 55.7 | 54.9 | 1,2WD | |
| 41 | 6.26 | 6 | 2PZ | | 19 | 56 | 56 | 0PZ | |
| 35 | 6.46 | 6.52 | 2PZ | | 35 | 56.4 | 54.8 | 2PZ | |
| 19 | 6.8 | 6.4 | 0PZ | | 42 | 56.8 | 56.8 | 0PZ | |
| 32 | 6.94 | 6.26 | 0PZ | | 12 | 58.4 | 56.6 | 2PZ | |
| 6 | 7.0 | 6.9 | 2PZ | | 3 | 58.8 | 60.3 | 1,2PZ | |
| 40 | 8 | 8 | 0PZ | | 40 | 62 | 64 | 0PZ | |

| | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|
| **A,B** | 6 | 5.92 | 99 | 0.21 | 3.5 | 0.89 | 15.0 |
| **C,D** | 54 | 53.6 | 99 | 1.1 | 2.0 | 4.7 | 8.8 |

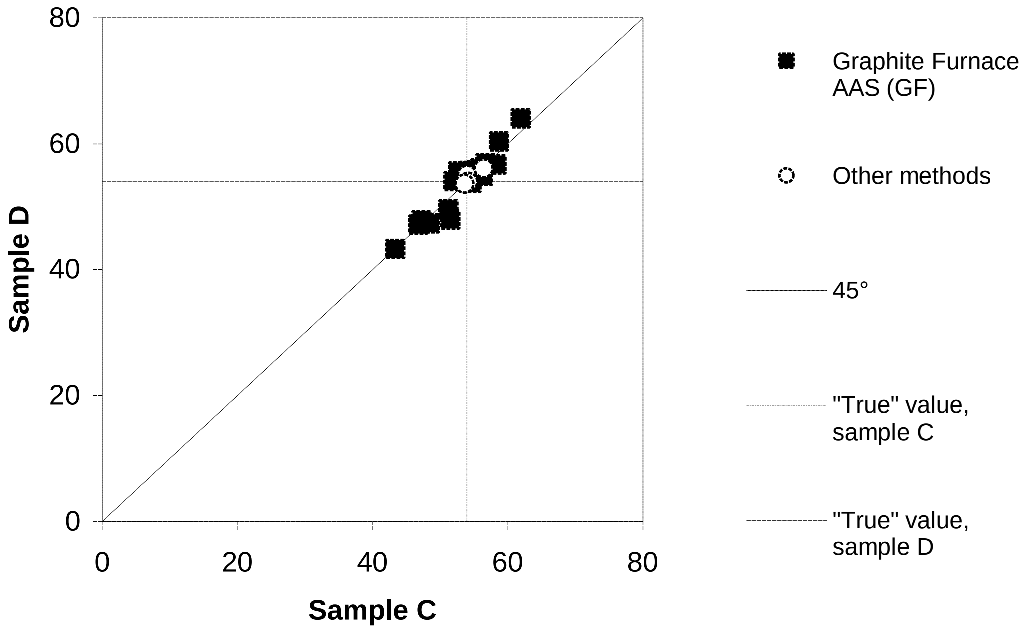
## Ni, other methods

| Lab No. | A | B | Code | | Lab No. | C | D | Code |
|---|---|---|---|---|---|---|---|---|
| 44 | 5.96 | 5.82 | K | | 44 | 53.7 | 53.6 | K |
| 38 | 6.09 | 6.33 | K | | 2 | 54 | 55 | I |
| 19 | 6.1 | 5.8 | K | | 19 | 54.2 | 53.9 | K |
| 2 | <10 | <10 | I | | 38 | 56.5 | 56 | K |

**Ni, lower conc.**




**Ni, higher conc.**



Pb, synthetic solutions (µg/l)

| Lab No. | A | B | Code | Outl./Str. | Lab No. | C | D | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 42 | 3.36 | 3.26 | 1,2PZ | | 16 | 22.85 | 33.4 | 3PZ | C |
| 16 | 3.78 | 4.96 | 3PZ | C | 30 | 38.5 | 40.1 | 1WD | |
| 22 | 4.11 | 4.18 | 1,2WD | | 14 | 40.6 | 40.6 | 2,3?Z | |
| 30 | 4.38 | 4.19 | 1WD | | 42 | 41.7 | 39.6 | 1,2PZ | |
| 12 | 4.4 | 4.3 | 1,2,3PZ | | 32 | 41.75 | 44.53 | 0PZ | |
| 26 | 4.61 | 4.73 | 2,3+PZ | | 39 | 43 | 43.8 | 2,3WZ | |
| 34 | 4.66 | 4.73 | 1PZ | | 35 | 43.5 | 44.2 | 3PZ | |
| 9 | 4.7 | 4.7 | 1,2WD | | 41 | 43.59 | 43.37 | 2,3PZ | |
| 4 | 4.79 | 4.89 | 2,3PZ | | 6 | 44 | 45 | 2,3PZ | |
| 32 | 4.84 | 5.3 | 0PZ | | 34 | 43.96 | 44.17 | 1PZ | |
| 5 | 4.87 | 4.90 | 3WZ | | 13 | 44 | 44.9 | 5PZ | |
| 23 | 4.88 | 5.33 | 0+WZ | | 5 | 44.0 | 44.9 | 3WZ | |
| 39 | 4.89 | 4.96 | 2,3WZ | | 27 | 44.1 | 44.6 | 2,3PZ | |
| 29 | 4.9 | 4.9 | 2,3PZ | | 20 | 44.3 | 44.4 | 2,3WZ | |
| 6 | 4.9 | 4.8 | 2,3PZ | | 11 | 44.5 | 44.6 | 2,3PZ | |
| 3 | 4.97 | 5.02 | 1,2PZ | | 31 | 44.9 | 45.7 | 3PD | |
| 21 | 5 | 5 | 1,2PD | | 22 | 45.5 | 45.2 | 1,2WD | |
| 35 | 5.06 | 4.99 | 3PZ | | 37 | 45.5 | 44 | 0WD | |
| 37 | 5.1 | 4.7 | 0WD | | 8 | 45.83 | 47.12 | 1,2WD | |
| 17 | 5.131 | 5.054 | 3PZ | | 21 | 46 | 46 | 1,2PD | |
| 27 | 5.17 | 5.34 | 2,3PZ | | 15 | 46.5 | 49.4 | ? | |
| 19 | 5.2 | 5.1 | 0PZ | | 29 | 46.5 | 46.9 | 2,3PZ | |
| 31 | 5.39 | 9.17 | 3PD | C | 36 | 46.7 | 49 | 2,5WD | |
| 7 | 5.4 | 5.5 | 1,2PD | | 2 | 47 | 46 | 2,3WD | |
| 11 | 5.4 | 5.3 | 2,3PZ | | 19 | 47 | 46 | 0PZ | |
| 41 | 5.56 | 5.01 | 2,3PZ | | 3 | 47.9 | 48 | 1,2PZ | |
| 20 | 5.59 | 5.71 | 2,3WZ | | 23 | 47.9 | 42.7 | 0+WZ | C |
| 13 | 5.6 | 5.2 | 5PZ | | 4 | 48.1 | 48.3 | 2,3PZ | |
| 40 | 6 | 6 | 2,3PZ | | 1 | 48.9 | 47.3 | 0+WD | |
| 8 | 6.17 | 5.94 | 1,2WD | | 7 | 49 | 50 | 1,2PD | |
| 33 | 6.2 | 6.25 | 0WD | | 33 | 49.8 | 50 | 0WD | |
| 10 | 6.77 | 6.3 | 2,3PZ | | 17 | 49.88 | 50.68 | 3PZ | |
| 1 | <10 | <10 | 0+WD | | 9 | 50.1 | 49.9 | 1,2WD | |
| 2 | <10 | <10 | 2,3WD | | 40 | 53 | 54 | 2,3PZ | |
| 15 | <10 | <10 | ? | | 10 | 57.7 | 57.5 | 2,3PZ | |
| 14 | <2 | <2 | 2,3?Z | | 12 | 57.7 | 57.3 | 1,2,3PZ | |
| 36 | M | M | | | 26 | 67.4 | 68.9 | 2,3+PZ | G |

| | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|
| **A,B** | 5 | 5.07 | 101 | 0.16 | 3.1 | 0.65 | 12.8 |
| **C,D** | 45 | 46.5 | 103 | 0.8 | 1.8 | 4.1 | 8.8 |

Pb, other methods

| Lab No. | A | B | Code | | Lab No. | C | D | Code |
|---|---|---|---|---|---|---|---|---|
| 44 | 5.18 | 5.26 | K | | 38 | 45.5 | 45.7 | K |
| 38 | 5.29 | 5.21 | K | | 44 | 45.6 | 46.2 | K |
| 19 | 5.5 | 5.5 | K | | 19 | 47.9 | 48.2 | K |

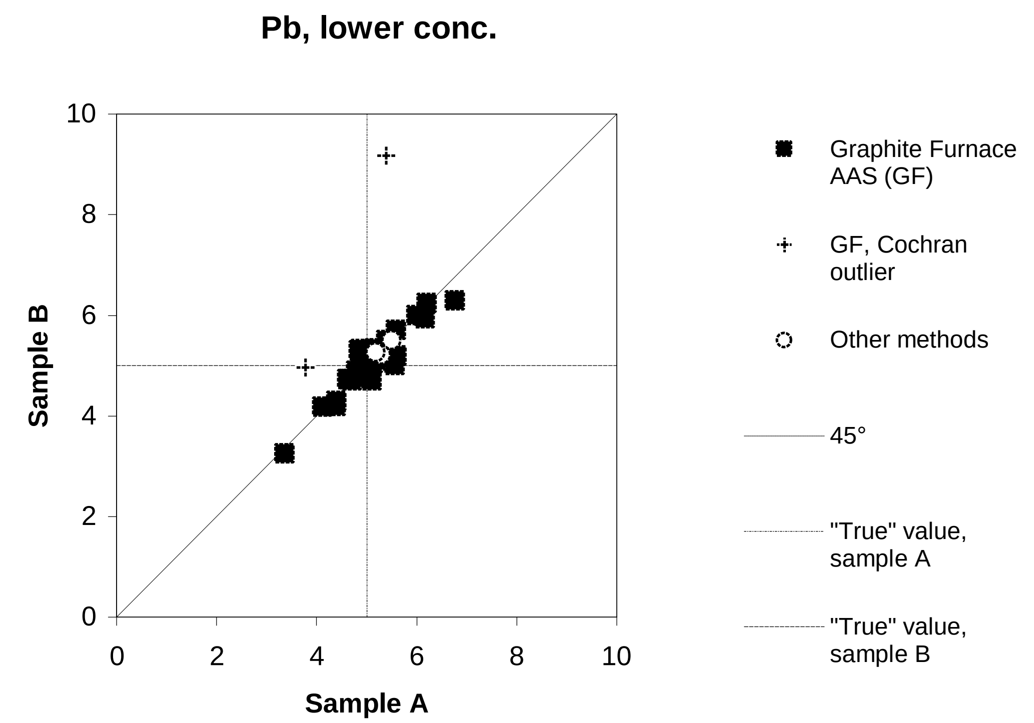
Sb, synthetic solutions (µg/l)

| Lab No. | A | B | Code | Outl./Str. | Lab No. | C | D | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 24 | 6.1 | 6.1 | 1+WZ | | 1 | 54.7 | 52.2 | 0+WD | |
| 42 | 6.63 | 6.88 | 1,2PZ | | 24 | 58 | 57 | 1+WZ | |
| 19 | 7.2 | 7.1 | 1,2PZ | | 19 | 60 | 65 | 1,2PZ | |
| 5 | 7.51 | 7.23 | 1,2WZ | | 2 | 68 | 74 | 4WD | |
| 32 | 9.91 | 9.23 | 1,2PZ | | 5 | 72.9 | 73.9 | 1,2WZ | |
| 1 | <20 | <20 | 0+WD | | 42 | 74.6 | 73.0 | 1,2PZ | |
| 2 | <10 | <10 | 4WD | | 32 | 76.74 | 77.02 | 1,2PZ | |

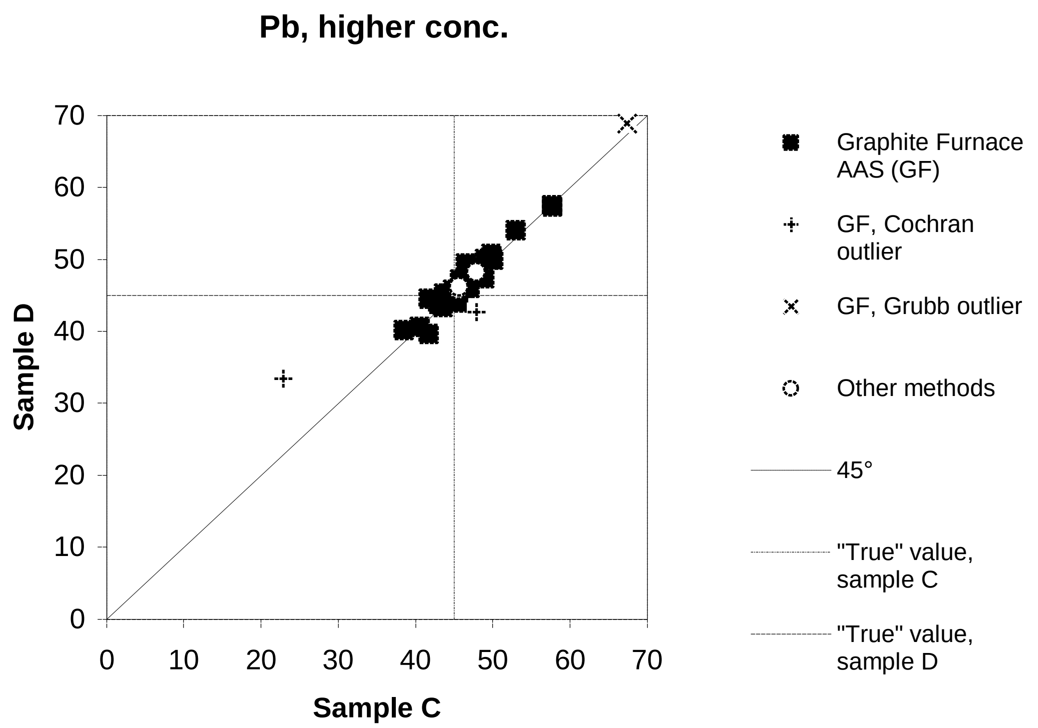
| | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|
| **A,B** | 8 | 7.39 | 92 | 0.25 | 3.3 | 1.32 | 17.9 |
| **C,D** | 72 | 66.9 | 93 | 2.3 | 3.4 | 9.2 | 13.8 |

Sb, other methods

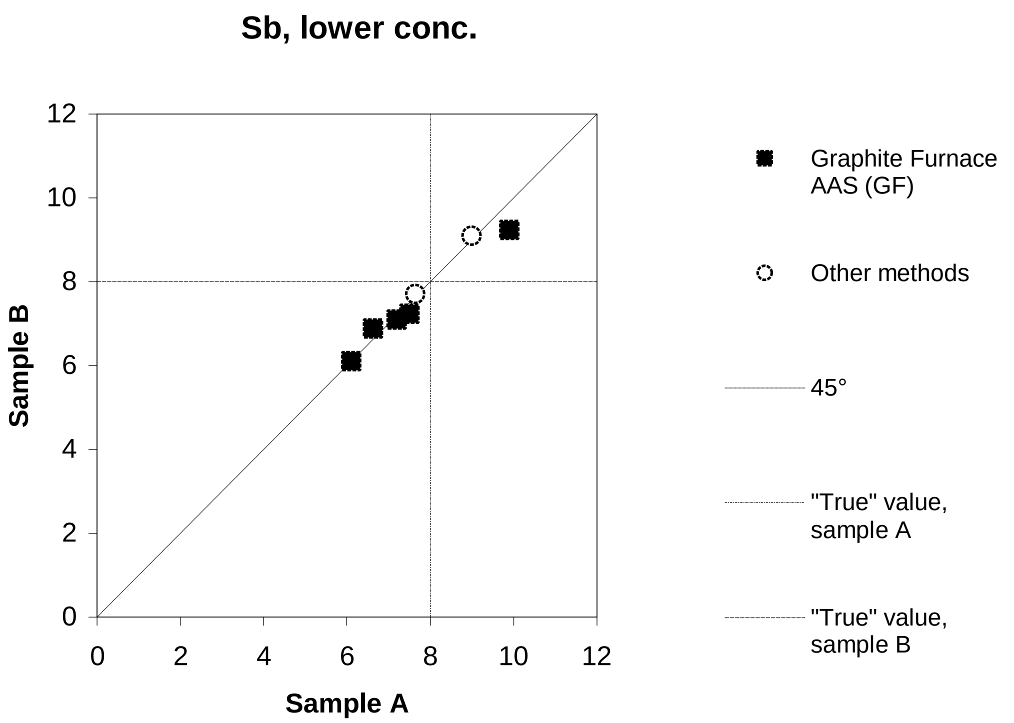
| Lab No. | A | B | Code | | Lab No. | C | D | Code |
|---|---|---|---|---|---|---|---|---|
| 44 | 7.64 | 7.71 | K | | 44 | 72.2 | 72.9 | K |
| 19 | 9.0 | 9.1 | K | | 19 | 78 | 82 | K |
| 3 | <200 | <200 | I | | 3 | <200 | <200 | I |

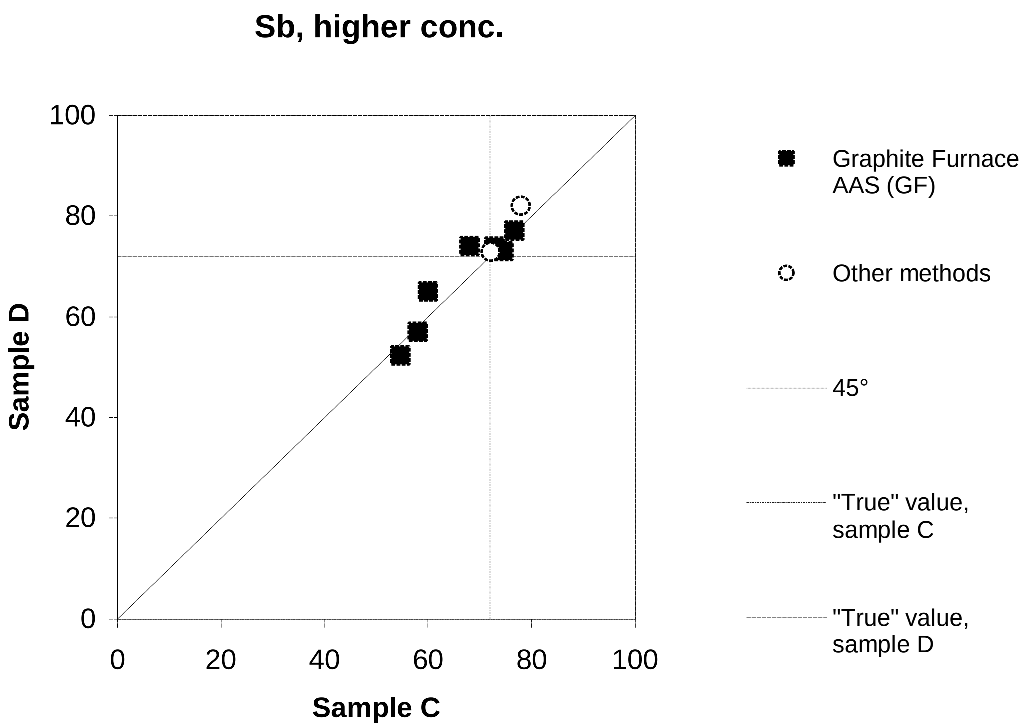


Pb, lower conc.
Sample B
Sample A
0
2
4
6
8
10
Graphite Furnace AAS (GF)
GF, Cochran outlier
Other methods
45°
"True" value, sample A
"True" value, sample B

Pb, higher conc.
Sample D
Sample C
0
10
20
30
40
50
60
70
Graphite Furnace AAS (GF)
GF, Cochran outlier
GF, Grubb outlier
Other methods
45°
"True" value, sample C
"True" value, sample D


Sb, lower conc.
12
10
8
6
4
2
0
0
2
4
6
8
10
12
Sample B
Sample A
Graphite Furnace AAS (GF)
Other methods
45°
"True" value, sample A
"True" value, sample B


Sb, higher conc.
100
80
60
40
20
0
0
20
40
60
80
100
Sample D
Sample C
Graphite Furnace AAS (GF)
Other methods
45°
"True" value, sample C
"True" value, sample D

Se, synthetic solutions (µg/l)

| Lab No. | A | B | Code | Outl./Str. | Lab No. | C | D | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 24 | 6.1 | 6.2 | 1+WZ | | 24 | 57 | 60 | 1+WZ | |
| 42 | 9.7 | 10.5 | 1,2PZ | | 42 | 93.4 | 96.8 | 1,2PZ | |
| 15 | 10 | <5 | ? | | 19 | 95 | 96 | 1,2PZ | |
| 19 | 10 | 10 | 1,2PZ | | 15 | 98.5 | 102 | ? | |
| 12 | 10.7 | 11.3 | 1,2PZ | | 5 | 105.5 | 108.5 | 1,2WZ | |
| 5 | 11.6 | 12.2 | 1,2WZ | | 12 | 108.7 | 107.3 | 1,2PZ | |
| 26 | 12.2 | 12.6 | 1,2+PZ | | 2 | 110 | 110 | 1,2WD | |
| 10 | 13.5 | 13.4 | 1,2PZ | | 10 | 113.2 | 115.5 | 1,2PZ | |
| 1 | 14.9 | 15.2 | 1+WD | | 1 | 131 | 135 | 1+WD | |
| 2 | 15 | 14 | 1,2WD | | 32 | 143.1 | 126.2 | 1,2PZ | |
| 32 | 15.32 | 12.76 | 1,2PZ | C 5% | 26 | 147 | 146 | 1,2+PZ | |

| | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|
| **A,B** | 12 | 11.9 | 99 | 0.68 | 5.7 | 2.7 | 23.0 |
| **C,D** | 108 | 109 | 101 | 4 | 3.7 | 24 | 21.9 |

Se, other methods

| Lab No. | A | B | Code | | Lab No. | C | D | Code |
|---|---|---|---|---|---|---|---|---|
| 19 | 12 | 11.9 | K | | 19 | 101 | 100 | K |
| 38 | 12.3 | 12.3 | K | | 38 | 113 | 112 | K |

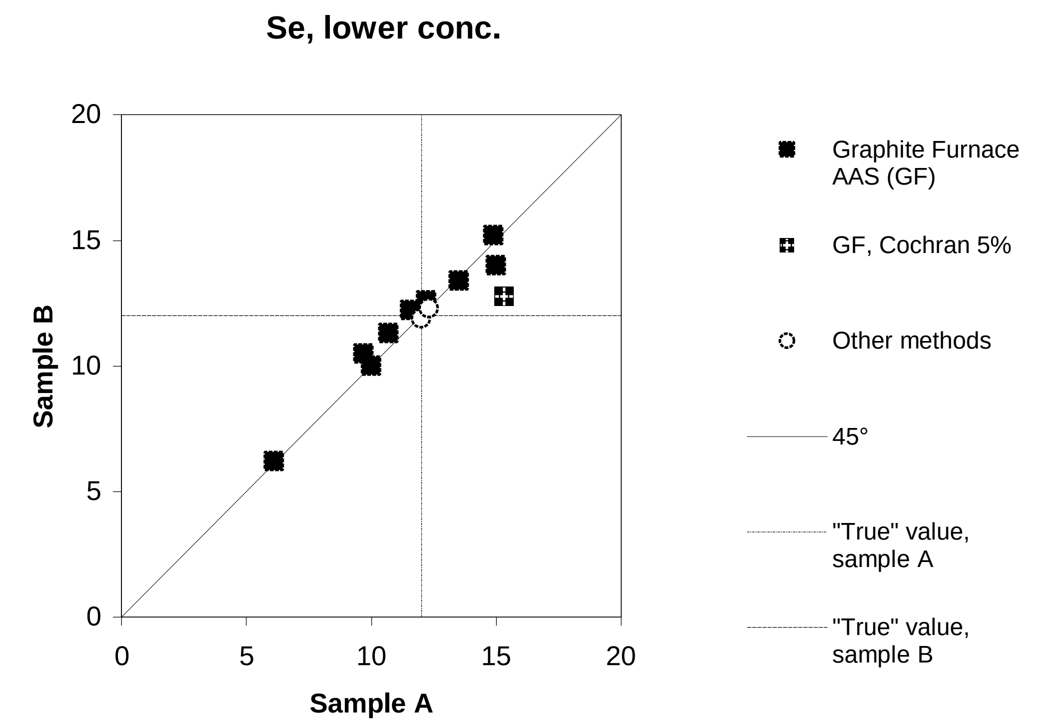
Tl, synthetic solutions (µg/l)

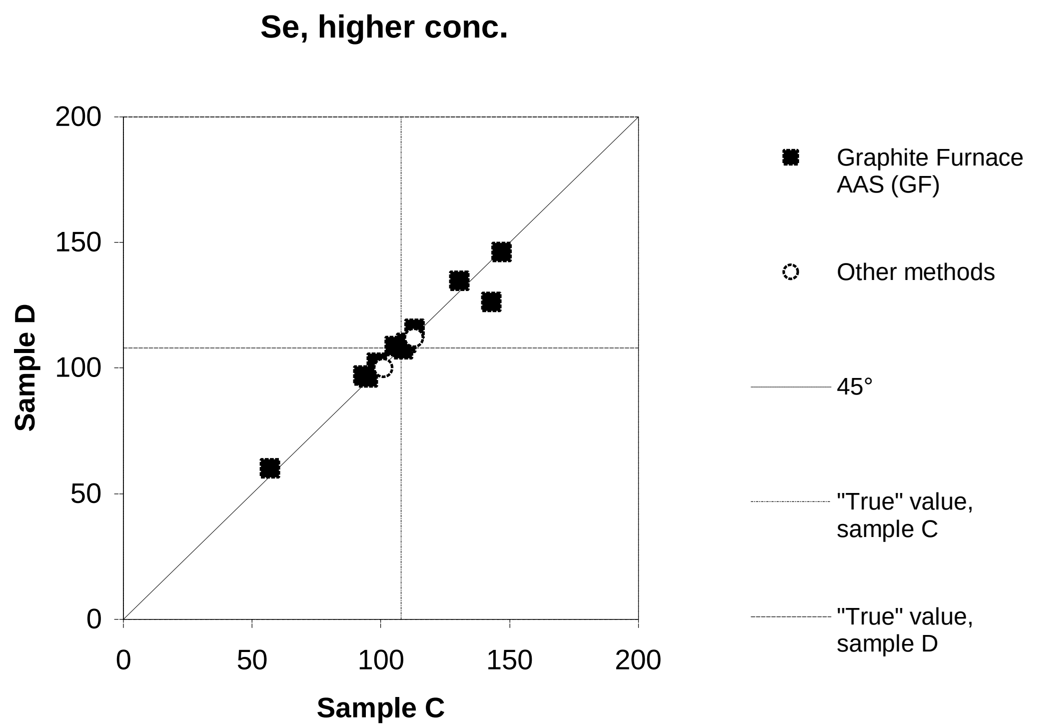
| Lab No. | A | B | Code | Outl./Str. | Lab No. | C | D | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 19 | 3.8 | 3.8 | 1,2PZ | | 1 | 30.9 | 24.0 | 0+PD | |
| 5 | 3.91 | 4.33 | 0WZ | | 19 | 35 | 34 | 1,2PZ | |
| 1 | <4 | 4.3 | 0+PD | | 6 | 35 | 38 | 1,2PZ | |
| 6 | <5 | <5 | 1,2PZ | | 5 | 39.5 | 40.1 | 0WZ | |
| 2 | <10 | <10 | 0WD | | 2 | 48 | 46 | 0WD | |

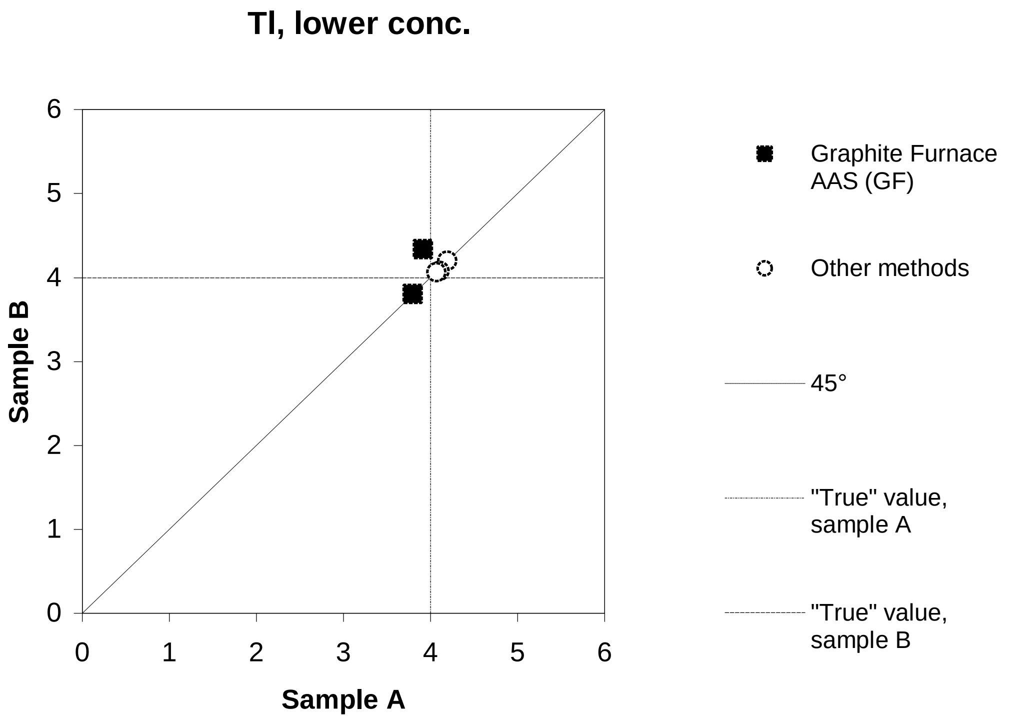
| | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|
| **A,B** | 4 | 3.96 | 99 | - | - | - | - |
| **C,D** | 36 | 37.0 | 103 | 2.4 | 6.6 | 7.4 | 19.9 |

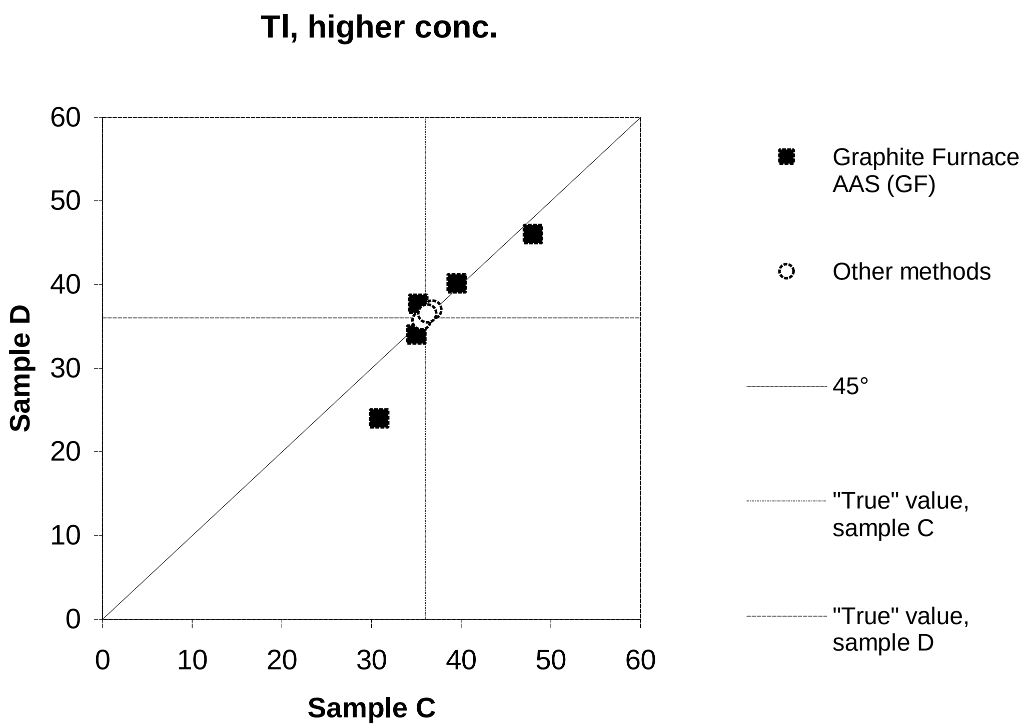
Tl, other methods

| Lab No. | A | B | Code | | Lab No. | C | D | Code |
|---|---|---|---|---|---|---|---|---|
| 44 | 4.07 | 4.06 | K | | 38 | 35.6 | 35.7 | K |
| 38 | 4.11 | 4.08 | K | | 44 | 36.2 | 36.5 | K |
| 19 | 4.2 | 4.2 | K | | 19 | 36.8 | 37 | K |


Se, lower conc.
Sample B
Sample A
20
15
10
5
0
0
5
10
15
20
Graphite Furnace AAS (GF)
GF, Cochran 5%
Other methods
45°
"True" value, sample A
"True" value, sample B


Se, higher conc.
Sample D
Sample C
200
150
100
50
0
0
50
100
150
200
Graphite Furnace AAS (GF)
Other methods
45°
"True" value, sample C
"True" value, sample D


Tl, lower conc.
Sample B
Sample A
0
1
2
3
4
5
6
Graphite Furnace AAS (GF)
Other methods
45°
"True" value, sample A
"True" value, sample B


Tl, higher conc.
Sample D
Sample C
0
10
20
30
40
50
60
Graphite Furnace AAS (GF)
Other methods
45°
"True" value, sample C
"True" value, sample D

V, synthetic solutions (µg/l)

| Lab No. | A | B | Code | Outl./Str. | Lab No. | C | D | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 12.0 | 11.6 | 0+WD | | 1 | 117 | 118 | 0+WD | |
| 8 | 14 | 14.1 | 0W | | 8 | 127.1 | 122.5 | 0W | |
| 5 | 14.9 | 14.7 | 0WZ | | 5 | 135.8 | 138.5 | 0WZ | |
| 10 | 17.3 | 17.5 | 0WZ | | 10 | 151 | 154 | 0WZ | |
| 32 | 17.59 | 17.37 | 0WZ | | 32 | 157.47 | 156.36 | 0WZ | |

| | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|
| **A,B** | 15 | 15.1 | 101 | 0.2 | 1.2 | 2.4 | 15.9 |
| **C,D** | 135 | 138 | 102 | 2 | 1.4 | 17 | 12.4 |

V, other methods

| Lab No. | A | B | Code | | Lab No. | C | D | Code |
|---|---|---|---|---|---|---|---|---|
| 19 | 14.4 | 14.2 | K | | 19 | 125 | 124 | K |
| 44 | 14.6 | 14.4 | K | | 38 | 126 | 126 | K |
| 38 | 15.3 | 15.2 | K | | 2 | 130 | 130 | I |
| 2 | <50 | <50 | I | | 44 | 134 | 134 | K |

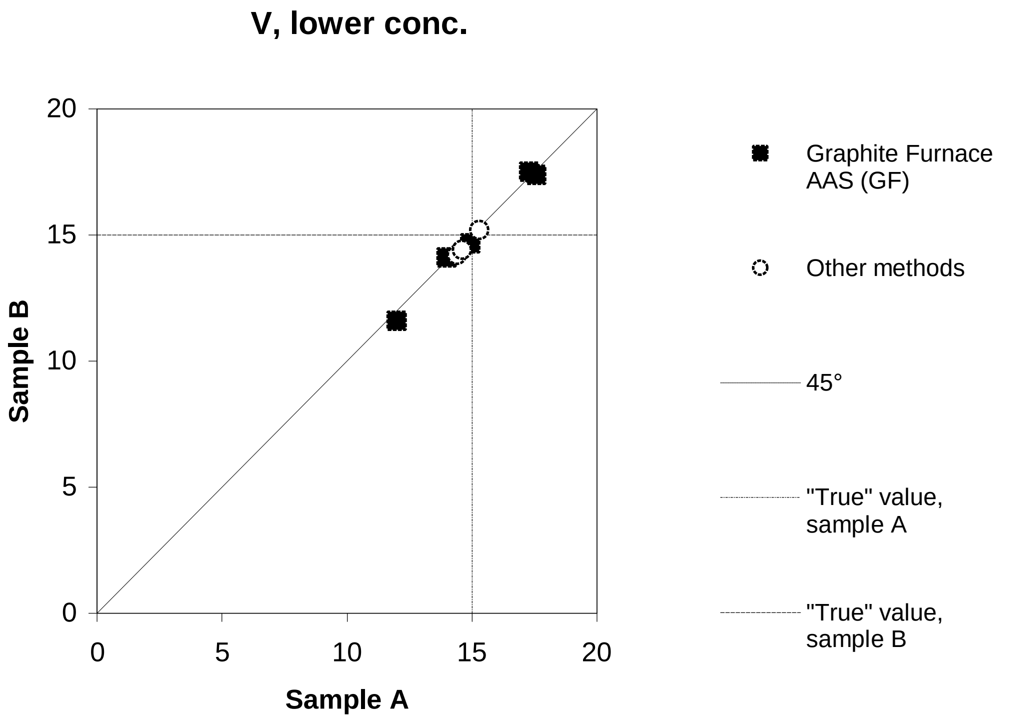
Zn, synthetic solutions (µg/l)

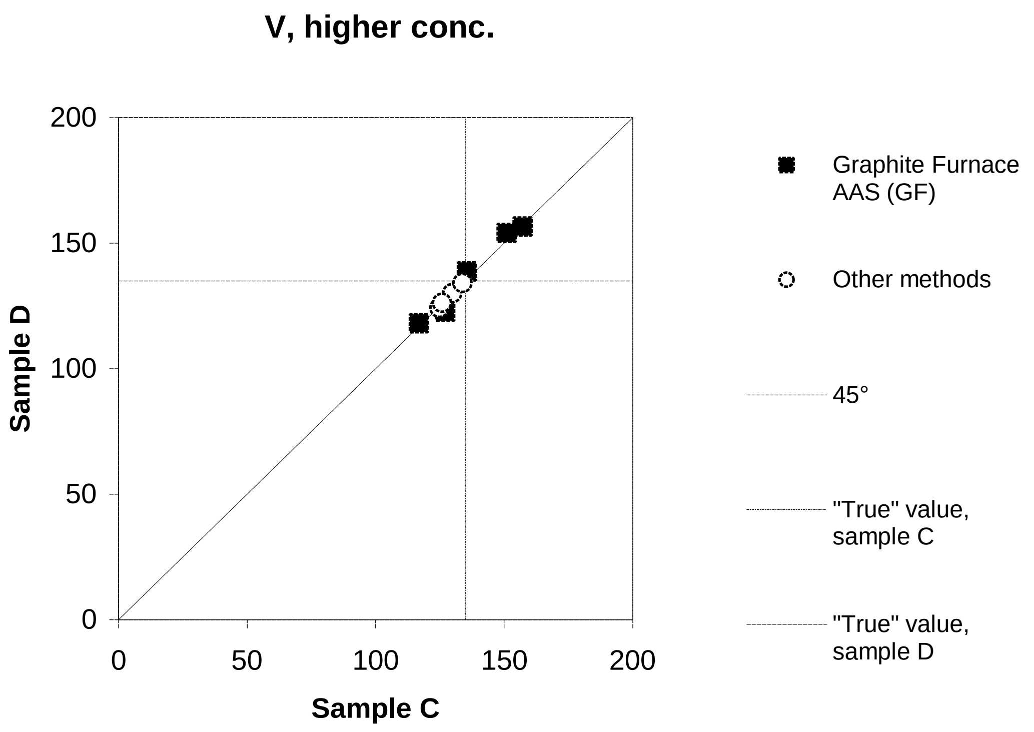
| Lab No. | A | B | Code | Outl./Str. | Lab No. | C | D | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 29 | 0.3 | 0.4 | 0WD | | 42 | 1.53 | 1.53 | 2PZ | |
| 42 | 0.403 | 0.252 | 2PZ | | 5 | 3.45 | 3.68 | 0WZ | |
| 5 | 0.618 | 0.552 | 0WZ | | 32 | 3.99 | 3.98 | 0WZ | |
| 32 | 0.65 | 0.61 | 0WZ | | 29 | 4.5 | 4.4 | 0WD | |
| 40 | 1 | 1 | 0PZ | | 40 | 5 | 5 | 0PZ | |
| 17 | 1.934 | 4.213 | 0PZ | C | 17 | 11.73 | 5.876 | 0PZ | C |
| 15 | <10 | <10 | ? | | 15 | <10 | <10 | ? | |

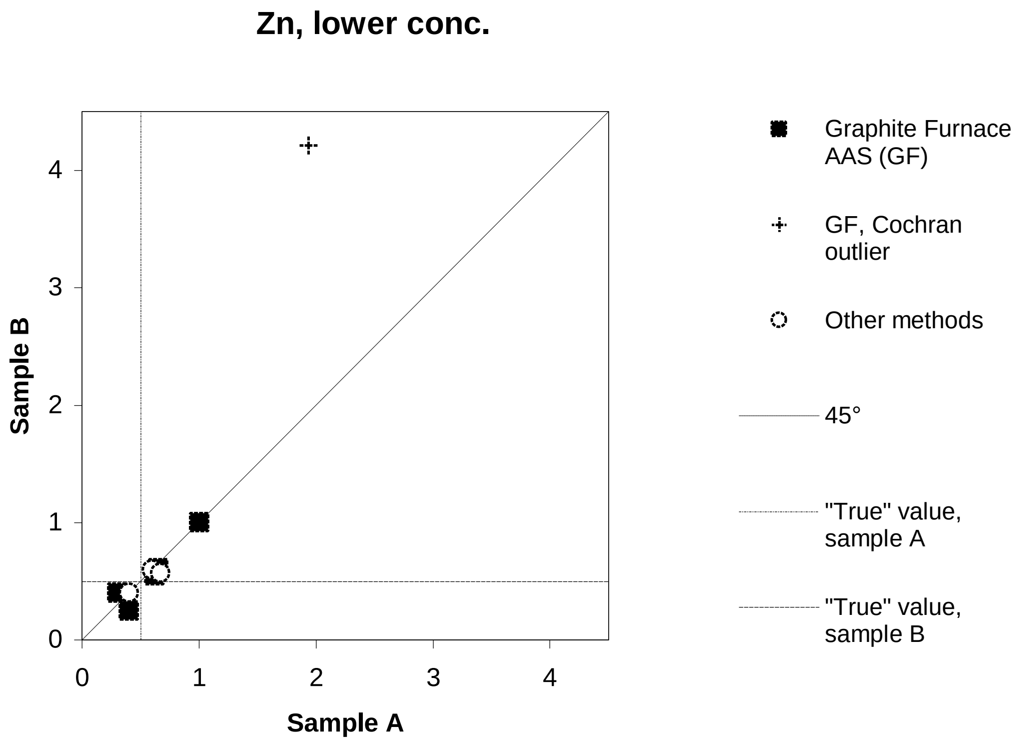
| | "True" value | General mean | Reco-very, % | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|---|---|
| **A,B** | 0.5 | 0.579 | 116 | 0.062 | 10.8 | 0.275 | 47.6 |
| **C,D** | 4.5 | 3.71 | 82 | 0.079 | 2.1 | 1.33 | 35.9 |

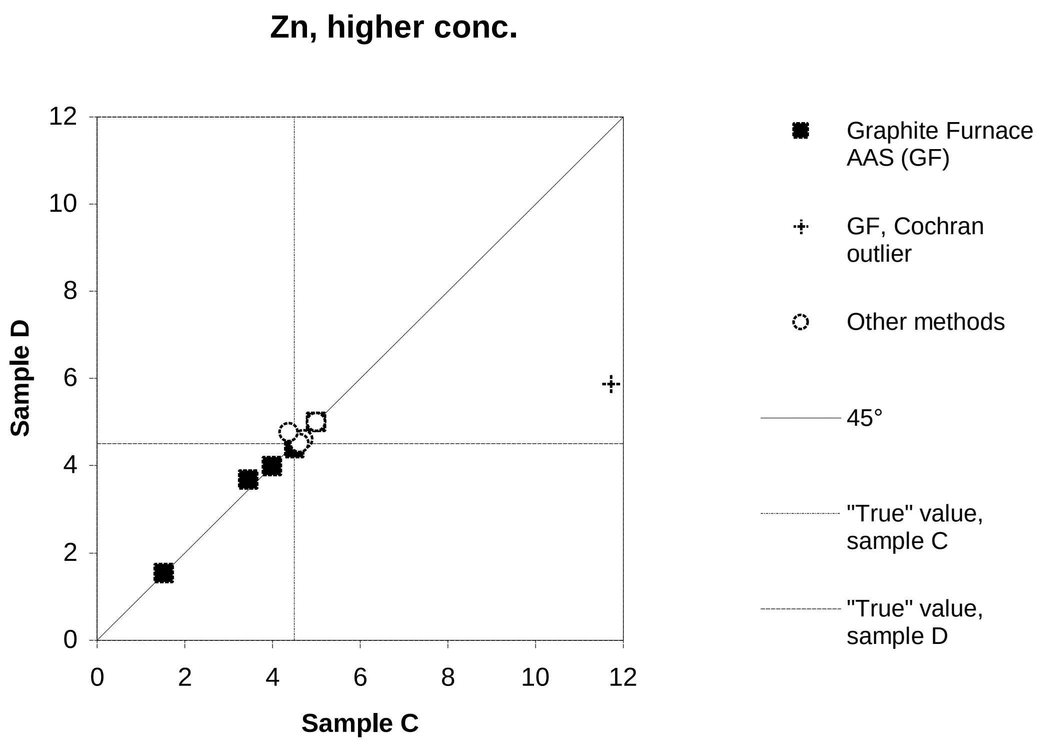
Zn, other methods

| Lab No. | A | B | Code | | Lab No. | C | D | Code |
|---|---|---|---|---|---|---|---|---|
| 38 | 0.4 | 0.4 | K | | 44 | 4.37 | 4.76 | K |
| 19 | 0.6 | 0.6 | K | | 38 | 4.62 | 4.51 | K |
| 44 | 0.67 | 0.57 | K | | 3 | 4.7 | 4.6 | I |
| 3 | <1 | <1 | I | | 19 | 5 | 5 | K |
| 2 | <10 | <10 | I | | 2 | <10 | <10 | I |


V, lower conc.
Sample B
Sample A
0
5
10
15
20
Graphite Furnace AAS (GF)
Other methods
45°
"True" value, sample A
"True" value, sample B


V, higher conc.
Sample D
Sample C
0
50
100
150
200
Graphite Furnace AAS (GF)
Other methods
45°
"True" value, sample C
"True" value, sample D


Zn, lower conc.
Sample B
Sample A
0
1
2
3
4
Graphite Furnace AAS (GF)
GF, Cochran outlier
Other methods
45°
"True" value, sample A
"True" value, sample B


Zn, higher conc.
Sample D
Sample C
0
2
4
6
8
10
12
Graphite Furnace AAS (GF)
GF, Cochran outlier
Other methods
45°
"True" value, sample C
"True" value, sample D

# Fresh water samples

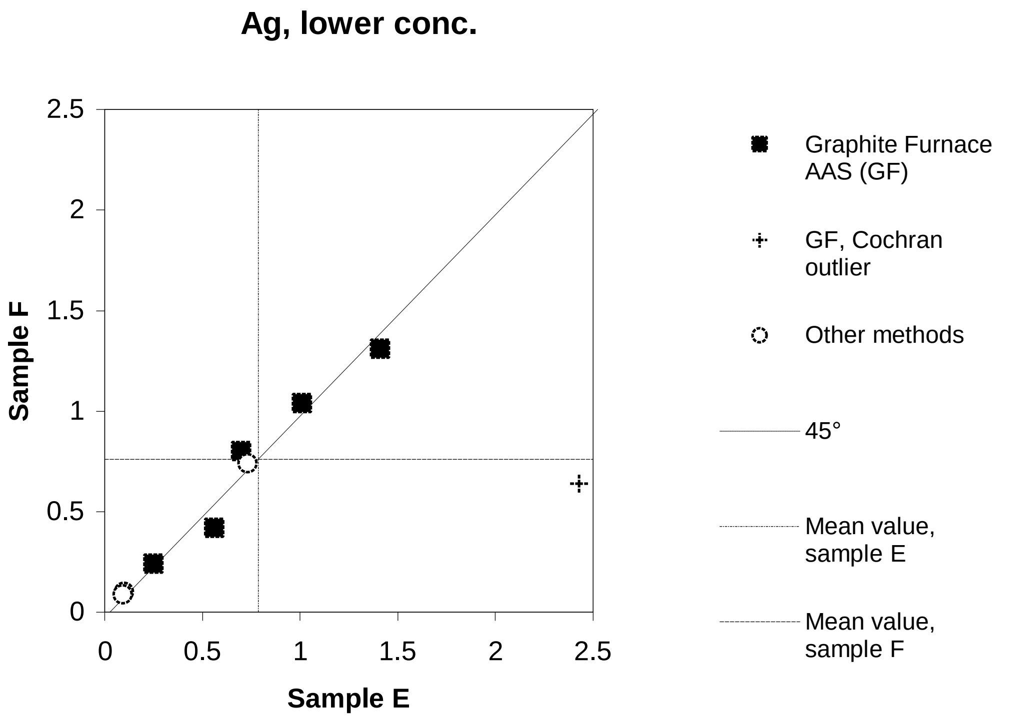
## Ag, fresh water (µg/l)

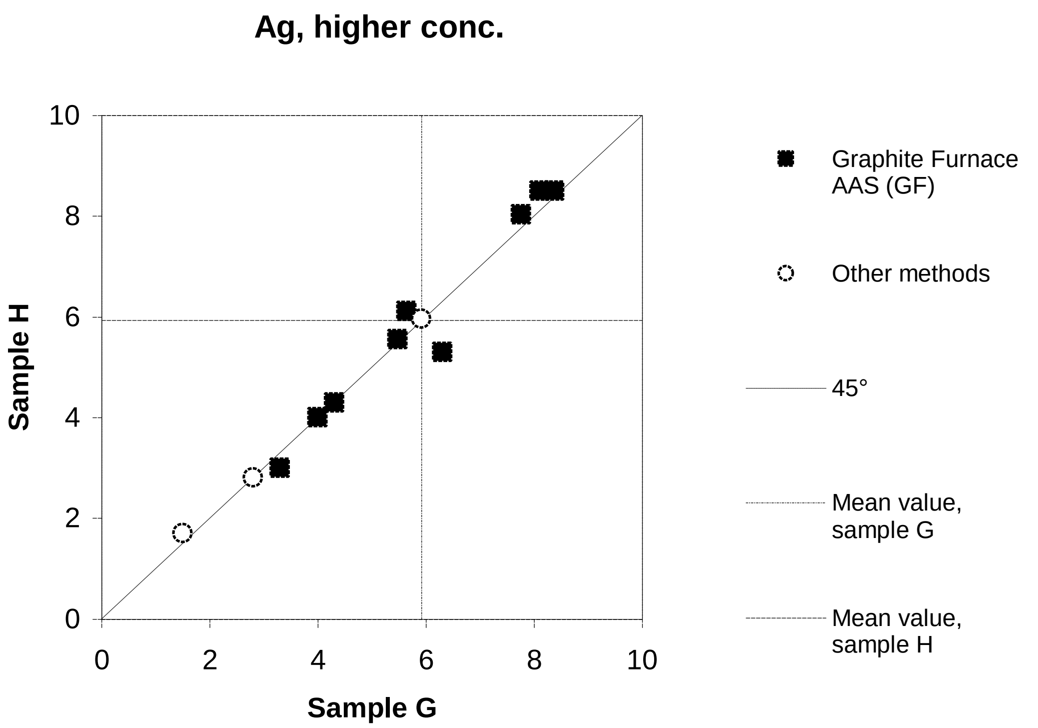
| Lab No. | E | F | Code | Outl./Str. | Lab No. | G | H | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 32 | 0.25 | 0.24 | 1,2WZ | | 32 | 3.3 | 3.0 | 1,2WZ | |
| 5 | 0.56 | 0.42 | 1,2WZ | | 40 | 4 | 4 | 1,2PZ | |
| 37 | 0.7 | 0.8 | 0WD | | 12 | 4.3 | 4.3 | 1,2PZ | |
| 10 | 1.01 | 1.04 | 2PZ | | 5 | 5.47 | 5.56 | 1,2WZ | |
| 42 | 1.41 | 1.31 | 0PZ | | 42 | 5.64 | 6.12 | 0PZ | |
| 1 | 2.43 | 0.64 | 0+WD | C | 29 | 6.3 | 5.3 | 0W | |
| 29 | <0,5 | <0,5 | 0W | | 10 | 7.76 | 8.04 | 2PZ | |
| 40 | <1 | <1 | 1,2PZ | | 37 | 8.1 | 8.5 | 0WD | |
| 15 | <10 | <10 | ? | | 1 | 8.38 | 8.51 | 0+WD | |
| 12 | M | M | | | 15 | <10 | <10 | ? | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **E,F** | 0.774 | 0.064 | 8.2 | 0.440 | 56.9 |
| **G,H** | 5.92 | 0.30 | 5.0 | 1.95 | 33.0 |

## Ag, other methods

| Lab No. | E | F | Code | | Lab No. | G | H | Code |
|---|---|---|---|---|---|---|---|---|
| 44 | 0.093 | 0.089 | K | | 19 | 1.5 | 1.7 | K |
| 19 | 0.1 | 0.1 | K | | 44 | 2.8 | 2.81 | K |
| 38 | 0.732 | 0.74 | K | | 38 | 5.92 | 5.96 | K |
| 2 | <10 | <10 | I | | 2 | <10 | <10 | I |


Ag, lower conc.
2.5
2
1.5
1
0.5
0
Sample F
0
0.5
1
1.5
2
2.5
Sample E
Graphite Furnace AAS (GF)
GF, Cochran outlier
Other methods
45°
Mean value, sample E
Mean value, sample F


Ag, higher conc.
10
8
6
4
2
0
Sample H
0
2
4
6
8
10
Sample G
Graphite Furnace AAS (GF)
Other methods
45°
Mean value, sample G
Mean value, sample H

## Al, fresh water (µg/l)

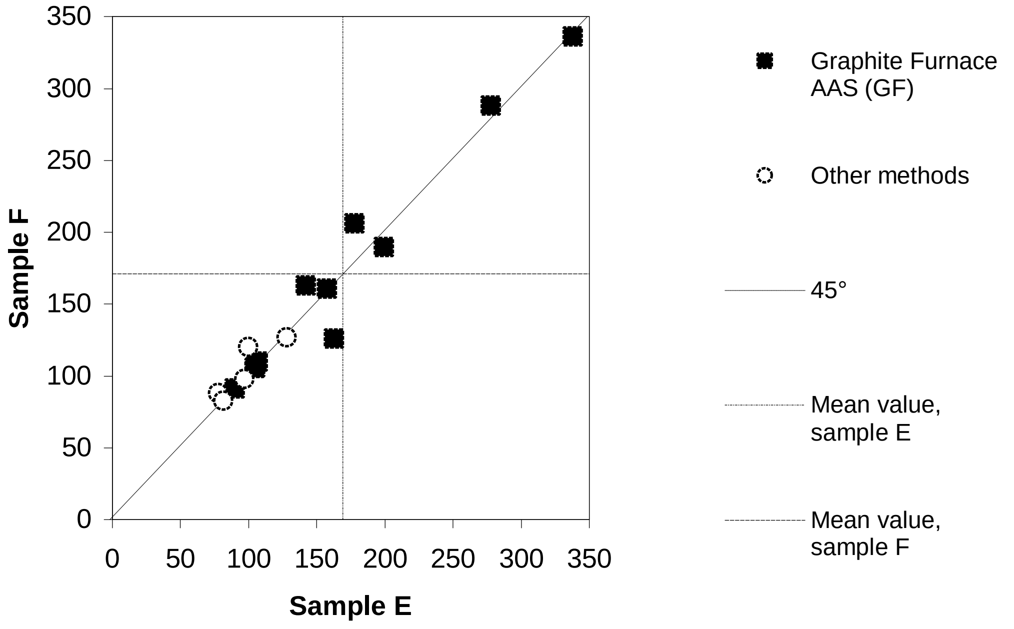
| Lab No. | E | F | Code | Outl./Str. | Lab No. | G | H | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 6 | 90 | 91 | 2PZ | | 6 | 83 | 84 | 2PZ | |
| 5 | 104 | 106 | 0WZ | | 8 | 103.3 | 103.2 | 2W | |
| 8 | 105.2 | 105.9 | 2W | | 15 | 124 | 122 | ? | |
| 15 | 107 | 110 | ? | | 5 | 129 | 139 | 0WZ | |
| 42 | 142 | 163 | 2PZ | | 42 | 148 | 144 | 2PZ | |
| 32 | 158 | 160 | 0WZ | | 1 | 176 | 194 | 0+WD | |
| 29 | 163 | 126 | 0W | | 29 | 206 | 179 | 0W | |
| 10 | 178 | 206 | 2PZ | | 10 | 226 | 259 | 2PZ | |
| 1 | 200 | 190 | 0+WD | | 32 | 288 | 280 | 0WZ | |
| 21 | 278 | 288 | 0P | | 21 | 315 | 313 | 0P | |
| 31 | 338 | 336 | 1,2PD | | 31 | 316 | 322 | 1,2PD | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **E,F** | 170 | 11 | 6.6 | 79 | 46.2 |
| **G,H** | 193 | 10 | 5.4 | 85 | 44.0 |

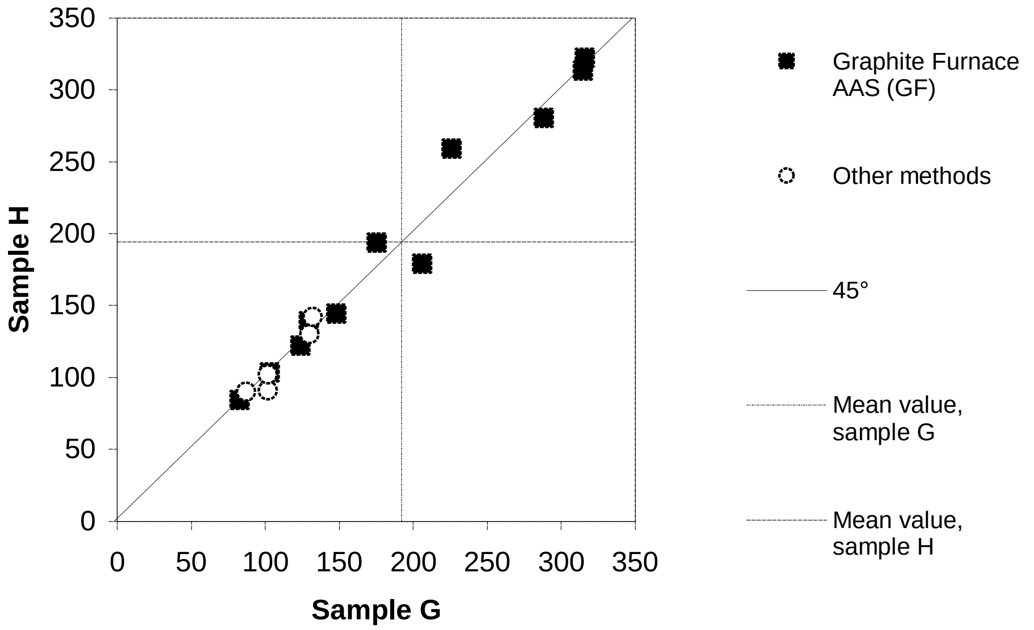
## Al, other methods

| Lab No. | E | F | Code | | Lab No. | G | H | Code |
|---|---|---|---|---|---|---|---|---|
| 19 | 78 | 88 | K | | 19 | 87 | 90 | K |
| 44 | 81.6 | 82.8 | K | | 3 | 102 | 91 | I |
| 3 | 97 | 98 | I | | 44 | 102 | 102 | K |
| 2 | 100 | 120 | I | | 2 | 130 | 130 | I |
| 38 | 128 | 127 | K | | 38 | 132 | 142 | K |

## Al, lower conc.




## Al, higher conc.



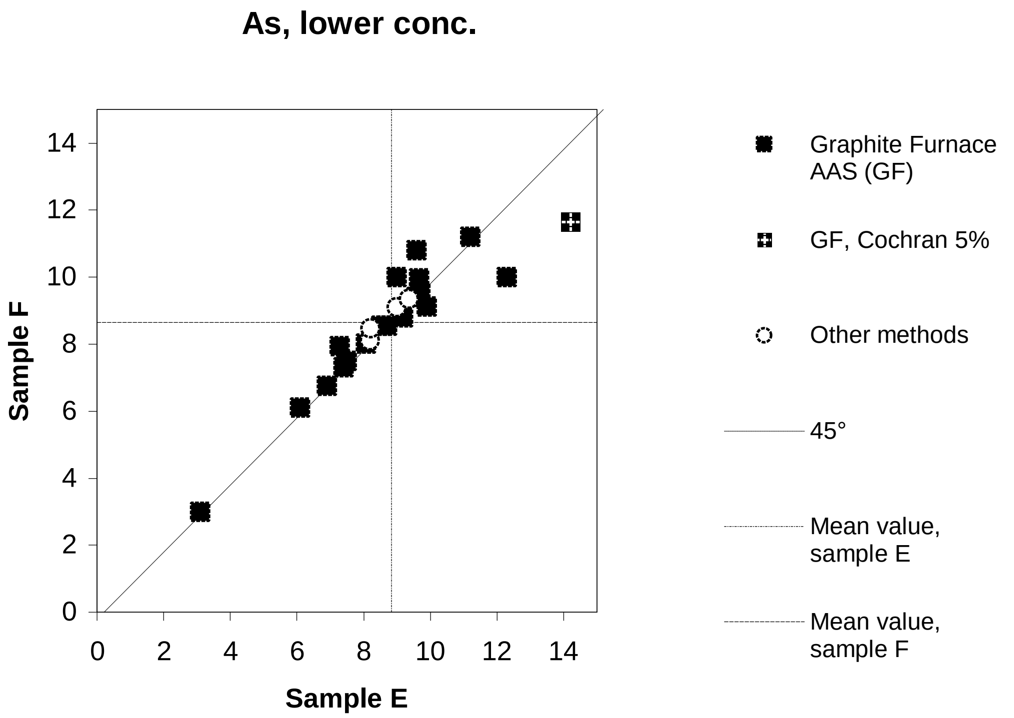
## As, fresh water (µg/l)

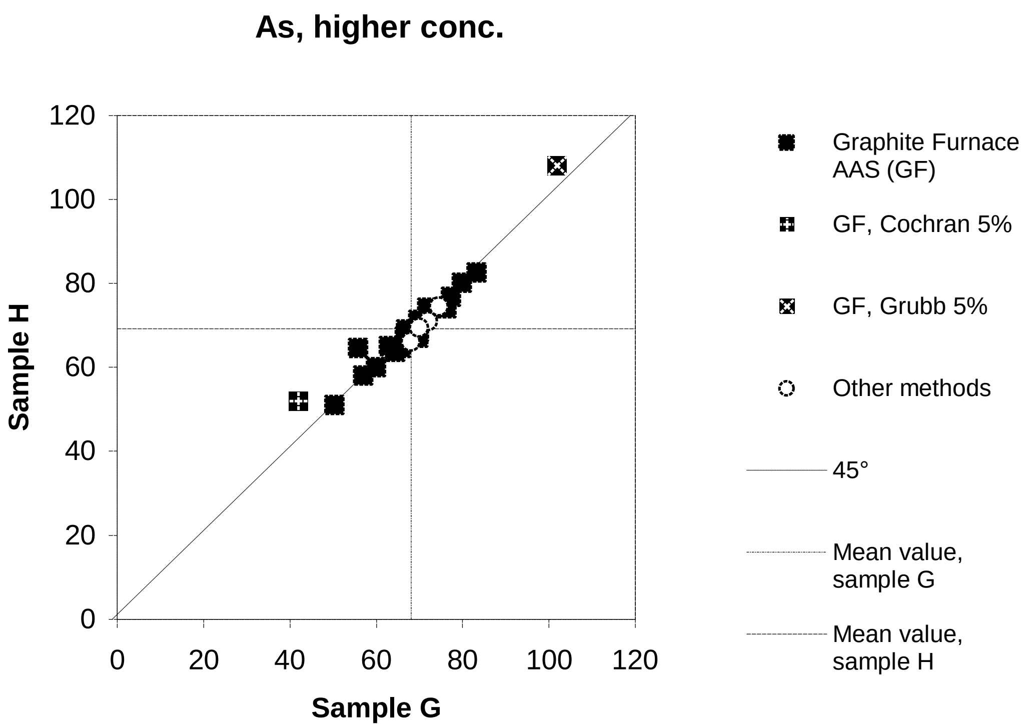
| Lab No. | E | F | Code | Outl./Str. | Lab No. | G | H | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 7 | 3.1 | 3 | 1,2PD | | 2 | 42 | 52 | 4WD | C 5% |
| 42 | 6.1 | 6.1 | 1,2PZ | | 42 | 50.3 | 51.0 | 1,2PZ | |
| 22 | 6.90 | 6.75 | 1,2WD | | 1 | 55.8 | 64.6 | 1+WD | |
| 5 | 7.29 | 7.94 | 1WZ | | 7 | 57 | 58 | 1,2PD | |
| 19 | 7.4 | 7.3 | 1,2PZ | | 19 | 60 | 60 | 1,2PZ | |
| 24 | 7.5 | 7.5 | 1+WZ | | 24 | 63 | 65 | 1+WZ | |
| 16 | 8.08 | 8.01 | 1PZ | | 5 | 64.5 | 63.7 | 1WZ | |
| 32 | 8.53 | 8.54 | 1,2WZ | | 10 | 65.8 | 64.6 | 1,2PZ | |
| 3 | 8.72 | 8.55 | 1,2PZ | | 15 | 66.7 | 67.3 | ? | |
| 9 | 9 | 10 | 1,2WD | | 9 | 67 | 69 | 1,2WD | |
| 35 | 9.19 | 8.79 | 1,2PZ | | 16 | 68.14 | 67.83 | 1PZ | |
| 1 | 9.6 | 10.8 | 1+WD | | 3 | 68.4 | 68.7 | 1,2PZ | |
| 11 | 9.6 | 9.4 | 1,2PZ | | 12 | 69.8 | 66.9 | 1,2PZ | |
| 41 | 9.68 | 9.96 | 1,2PZ | | 27 | 69.8 | 71.3 | 1,2PZ | |
| 27 | 9.71 | 9.56 | 1,2PZ | | 35 | 69.9 | 68.3 | 1,2PZ | |
| 10 | 9.91 | 9.12 | 1,2PZ | | 32 | 71.92 | 74.21 | 1,2WZ | |
| 26 | 11.2 | 11.2 | 1,2+PZ | | 41 | 76.35 | 74.04 | 1,2PZ | |
| 12 | 12.3 | 10 | 1,2PZ | | 22 | 77.4 | 76.8 | 1,2WD | |
| 34 | 14.21 | 11.65 | 1PZ | C 5% | 11 | 79.9 | 80.1 | 1,2PZ | |
| 2 | <10 | 10 | 4WD | | 34 | 83.23 | 82.48 | 1PZ | |
| 15 | <10 | <10 | ? | | 26 | 102 | 108 | 1,2+PZ | G 5% |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **E,F** | 8.74 | 0.64 | 7.4 | 2.20 | 25.2 |
| **G,H** | 68.6 | 2.4 | 3.6 | 12.2 | 17.8 |

## As, other methods

| Lab No. | E | F | Code | | Lab No. | G | H | Code |
|---|---|---|---|---|---|---|---|---|
| 23 | 8.2 | 8.1 | H | | 23 | 68 | 66 | H |
| 44 | 8.21 | 8.46 | K | | 44 | 69.9 | 69.4 | K |
| 19 | 9.0 | 9.1 | K | | 19 | 72 | 71 | K |
| 38 | 9.36 | 9.35 | K | | 38 | 74.5 | 74.5 | K |


As, lower conc.
Sample F
Sample E
0
2
4
6
8
10
12
14
Graphite Furnace AAS (GF)
GF, Cochran 5%
Other methods
45°
Mean value, sample E
Mean value, sample F


As, higher conc.
Sample H
Sample G
0
20
40
60
80
100
120
Graphite Furnace AAS (GF)
GF, Cochran 5%
GF, Grubb 5%
Other methods
45°
Mean value, sample G
Mean value, sample H

Cd, fresh water (µg/l)

| Lab No. | E | F | Code | Outl./Str. | Lab No. | G | H | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 31 | 0.38 | 0.39 | 3PD | | 37 | 2.2 | 2 | 0WD | G 5% |
| 8 | 0.386 | 0.413 | 1,2WD | | 8 | 2.48 | 2.49 | 1,2WD | |
| 37 | 0.4 | 0.36 | 0WD | | 9 | 2.7 | 2.8 | 1,2WD | |
| 9 | 0.44 | 0.45 | 1,2WD | | 35 | 2.7 | 2.77 | 3PZ | |
| 21 | 0.5 | 0.5 | 1,2PD | | 31 | 2.81 | 2.75 | 3PD | |
| 35 | 0.527 | 0.527 | 3PZ | | 26 | 2.83 | 2.79 | 2,3+PZ | |
| 32 | 0.53 | 0.53 | 0PZ | | 24 | 2.9 | 2.9 | 1+WZ | |
| 4 | 0.545 | 0.541 | 2,3PZ | | 20 | 2.94 | 2.94 | 1,2WZ | |
| 13 | 0.55 | 0.5 | 2,3PZ | | 7 | 3 | 3 | 1,2PD | |
| 26 | 0.55 | 0.54 | 2,3+PZ | | 13 | 3 | 3 | 2,3PZ | |
| 20 | 0.557 | 0.552 | 1,2WZ | | 21 | 3 | 2.9 | 1,2PD | |
| 3 | 0.56 | 0.58 | 2,3PZ | | 40 | 3 | 3 | 2,3PZ | |
| 22 | 0.58 | 0.60 | 1,2WD | | 41 | 3 | 2.98 | 2,3PZ | |
| 30 | 0.581 | 0.519 | 1WD | | 32 | 3.05 | 3.00 | 0PZ | |
| 34 | 0.59 | 0.59 | 1PZ | | 6 | 3.1 | 3.0 | 2,3PZ | |
| 17 | 0.592 | 0.585 | 2,3PZ | | 34 | 3.12 | 3.13 | 1PZ | |
| 7 | 0.6 | 0.6 | 1,2PD | | 3 | 3.13 | 3.17 | 2,3PZ | |
| 24 | 0.6 | 0.6 | 1+WZ | | 5 | 3.13 | 3.09 | 3WZ | |
| 40 | 0.6 | 0.6 | 2,3PZ | | 29 | 3.13 | 3.14 | 2,3PZ | |
| 41 | 0.6 | 0.6 | 2,3PZ | | 30 | 3.14 | 3.31 | 1WD | |
| 42 | 0.6 | 0.6 | 0PZ | | 4 | 3.16 | 3.2 | 2,3PZ | |
| 29 | 0.61 | 0.58 | 2,3PZ | | 14 | 3.2 | 3.1 | 0?Z | |
| 6 | 0.61 | 0.60 | 2,3PZ | | 42 | 3.2 | 2.9 | 0PZ | C 5% |
| 23 | 0.632 | 0.641 | 0+WZ | | 22 | 3.26 | 3.24 | 1,2WD | |
| 5 | 0.64 | 0.63 | 3WZ | | 39 | 3.28 | 3.21 | 2,3WZ | |
| 11 | 0.65 | 0.63 | 2,3PZ | | 17 | 3.325 | 3.278 | 2,3PZ | |
| 27 | 0.65 | 0.65 | 2,3PZ | | 11 | 3.43 | 3.48 | 2,3PZ | |
| 19 | 0.67 | 0.6 | 0PZ | C 5% | 10 | 3.49 | 3.52 | 2,3PZ | |
| 12 | 0.7 | 0.6 | 1,2,3PZ | C | 12 | 3.5 | 3.7 | 1,2,3PZ | |
| 14 | 0.7 | 0.7 | 0?Z | | 19 | 3.5 | 4.5 | 0PZ | C |
| 39 | 0.706 | 0.695 | 2,3WZ | | 27 | 3.53 | 3.49 | 2,3PZ | |
| 10 | 0.72 | 0.71 | 2,3PZ | | 1 | 3.6 | 3.6 | 0+WD | |
| 16 | 0.87 | 0.66 | 3PZ | C | 23 | 3.69 | 4.24 | 0+WZ | C |
| 1 | < 1 | < 1 | 0+WD | | 16 | 4.63 | 4.21 | 3PZ | C |
| 2 | <2 | <2 | 1,2WD | | 2 | <2 | <2 | 1,2WD | |
| 15 | <2 | <2 | ? | | 15 | <2 | <2 | ? | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **E,F** | 0.572 | 0.016 | 2.9 | 0.085 | 14.9 |
| **G,H** | 3.07 | 0.065 | 2.1 | 0.32 | 10.4 |

## Cd, other methods

| Lab No. | E | F | Code | | Lab No. | G | H | Code |
|---|---|---|---|---|---|---|---|---|
| 44 | 0.592 | 0.571 | K | | 44 | 3.09 | 3.08 | K |
| 38 | 0.643 | 0.651 | K | | 19 | 3.3 | 3.3 | K |
| 19 | 0.7 | 0.6 | K | | 38 | 3.37 | 3.36 | K |

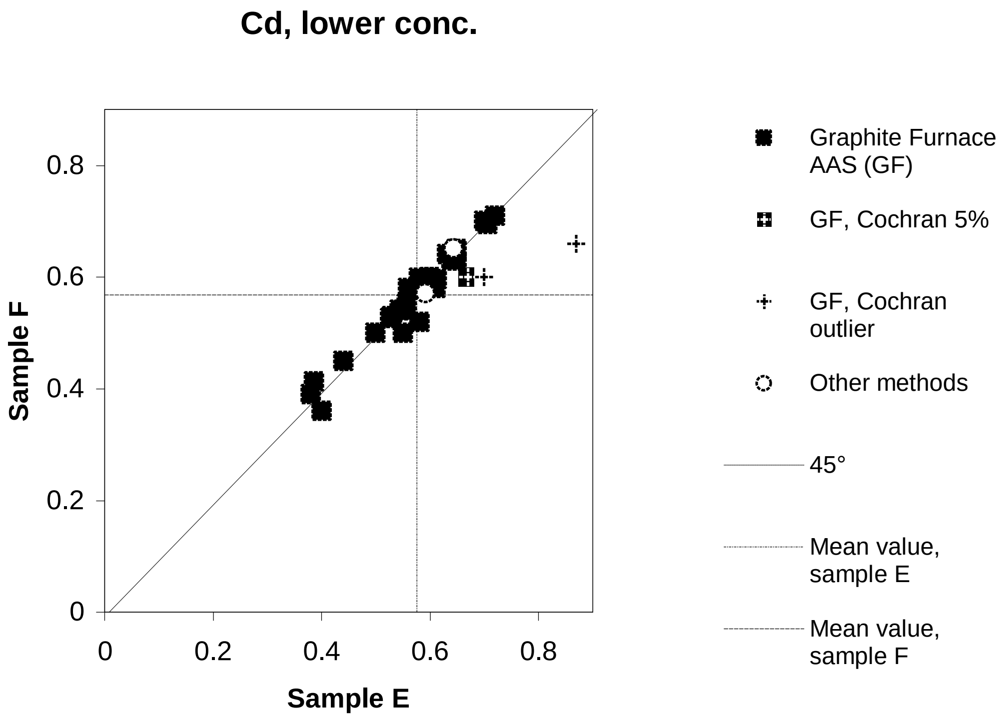
## Co, fresh water (µg/l)

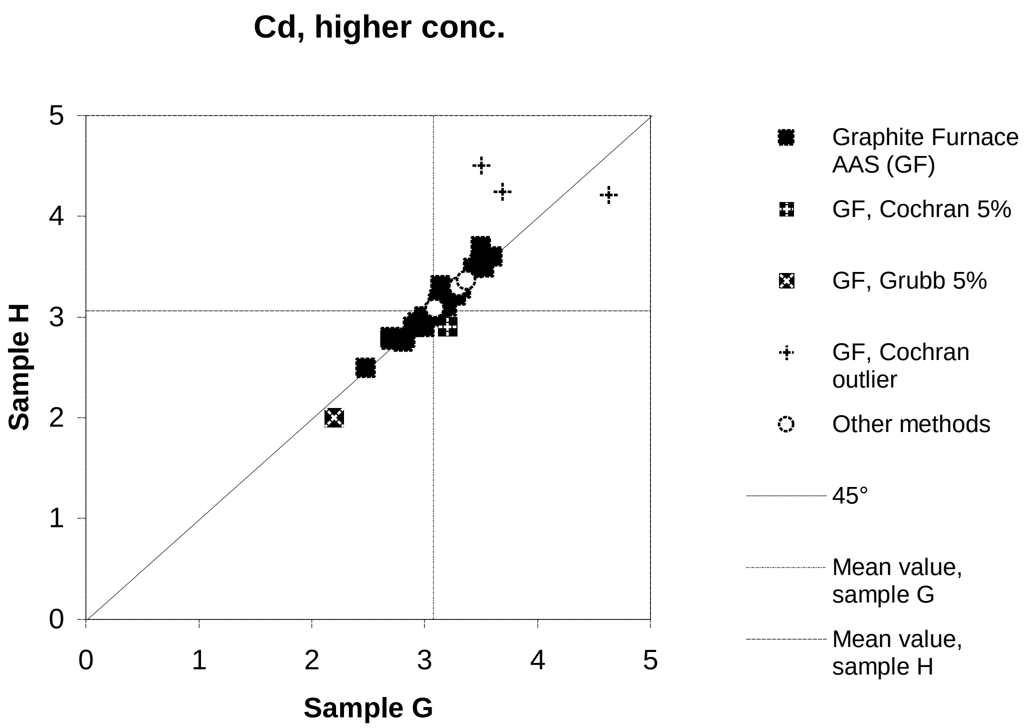
| Lab No. | E | F | Code | Outl./Str. | Lab No. | G | H | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 17 | 3.518 | 3.747 | 2PZ | | 1 | 20.7 | 19.4 | 0+WD | G |
| 8 | 3.57 | 2.97 | 2WD | | 8 | 31.41 | 31.19 | 2WD | |
| 37 | 3.7 | 3.4 | 0WD | | 32 | 36.3 | 36.6 | 0PZ | |
| 3 | 3.77 | 3.48 | 0PZ | | 3 | 37.1 | 37.1 | 0PZ | |
| 21 | 4 | 5 | 2WD | | 10 | 37.9 | 39.2 | 2WZ | |
| 40 | 4 | 4 | 2PZ | | 21 | 39 | 42 | 2WD | |
| 1 | 4.4 | 4.4 | 0+WD | | 17 | 39.88 | 40.21 | 2PZ | |
| 29 | 4.5 | 4.5 | 0WD | | 29 | 40.1 | 39.6 | 0WD | |
| 5 | 4.68 | 4.20 | 2WZ | | 42 | 40.2 | 40.3 | 0PZ | |
| 19 | 4.8 | 4.8 | 0PZ | | 15 | 42 | 43 | ? | |
| 10 | 4.98 | 3.93 | 2WZ | | 5 | 43.7 | 42.2 | 2WZ | |
| 42 | 5.0 | 4.1 | 0PZ | | 37 | 44.9 | 41.1 | 0WD | |
| 32 | 5.22 | 5.22 | 0PZ | | 19 | 45 | 46 | 0PZ | |
| 15 | <5 | <5 | ? | | 40 | 48 | 48 | 2PZ | |

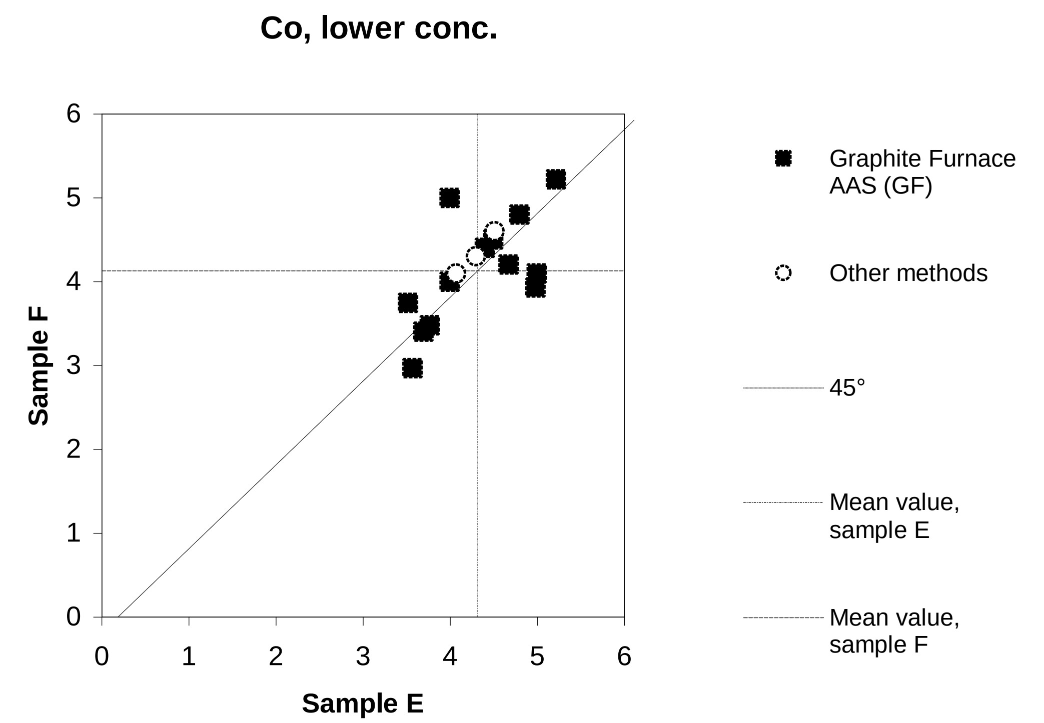
| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **E,F** | 4.23 | 0.38 | 9.0 | 0.63 | 14.8 |
| **G,H** | 40.5 | 1.1 | 2.6 | 4.3 | 10.6 |

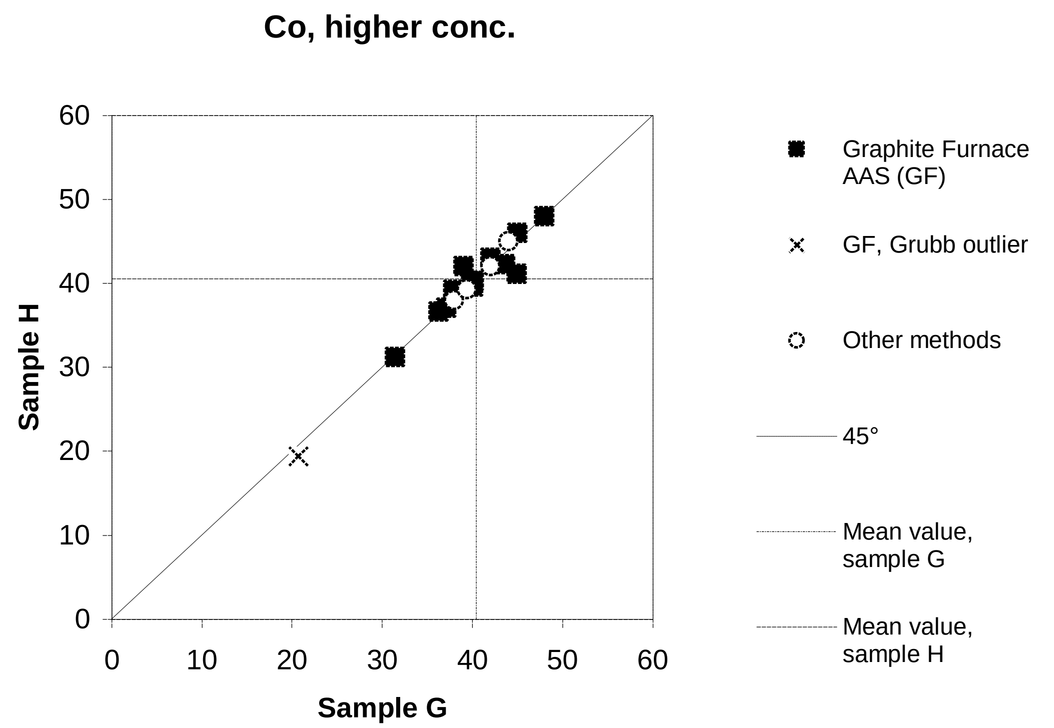
## Co, other methods

| Lab No. | E | F | Code | | Lab No. | G | H | Code |
|---|---|---|---|---|---|---|---|---|
| 44 | 4.07 | 4.1 | K | | 19 | 38 | 38 | K |
| 19 | 4.3 | 4.3 | K | | 44 | 39.4 | 39.3 | K |
| 38 | 4.51 | 4.6 | K | | 38 | 42 | 42 | K |
| 2 | <10 | <10 | I | | 3 | 44 | 45 | I |
| 3 | <50 | <50 | I | | 2 | <50 | <50 | I |


Cd, lower conc.
0.8
0.6
0.4
0.2
0
0
0.2
0.4
0.6
0.8
Sample F
Sample E
Graphite Furnace AAS (GF)
GF, Cochran 5%
GF, Cochran outlier
Other methods
45°
Mean value, sample E
Mean value, sample F


Cd, higher conc.
5
4
3
2
1
0
0
1
2
3
4
5
Sample H
Sample G
Graphite Furnace AAS (GF)
GF, Cochran 5%
GF, Grubb 5%
GF, Cochran outlier
Other methods
45°
Mean value, sample G
Mean value, sample H


Co, lower conc.
Sample F
Sample E
0
1
2
3
4
5
6
Graphite Furnace AAS (GF)
Other methods
45°
Mean value, sample E
Mean value, sample F


Co, higher conc.
Sample H
Sample G
0
10
20
30
40
50
60
Graphite Furnace AAS (GF)
GF, Grubb outlier
Other methods
45°
Mean value, sample G
Mean value, sample H

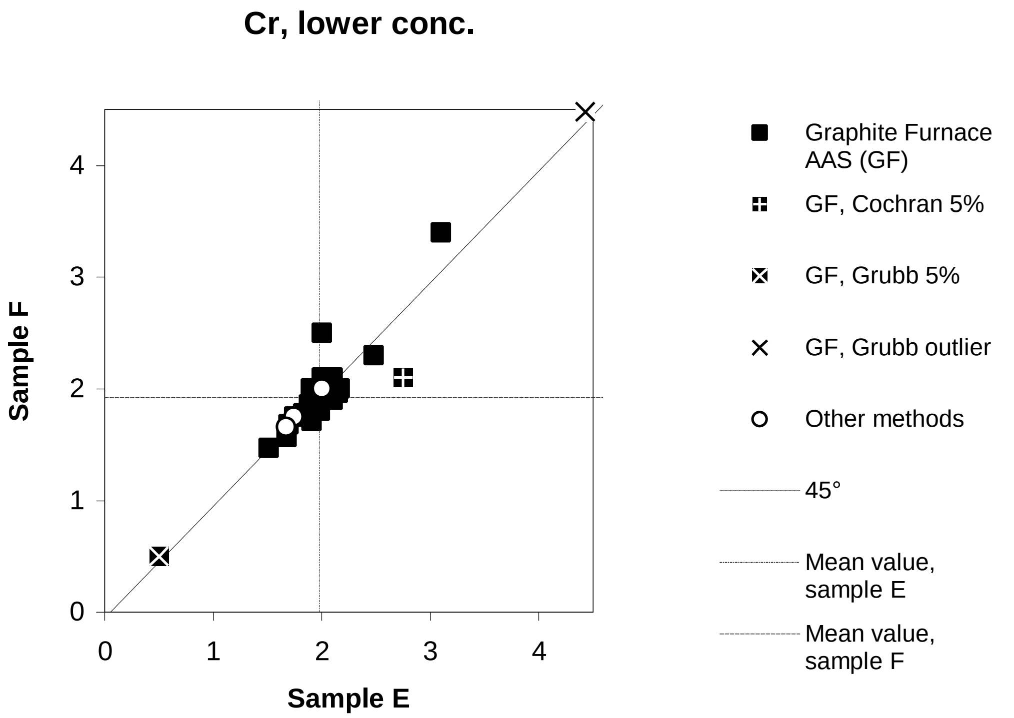
## Cr, fresh water (µg/l)

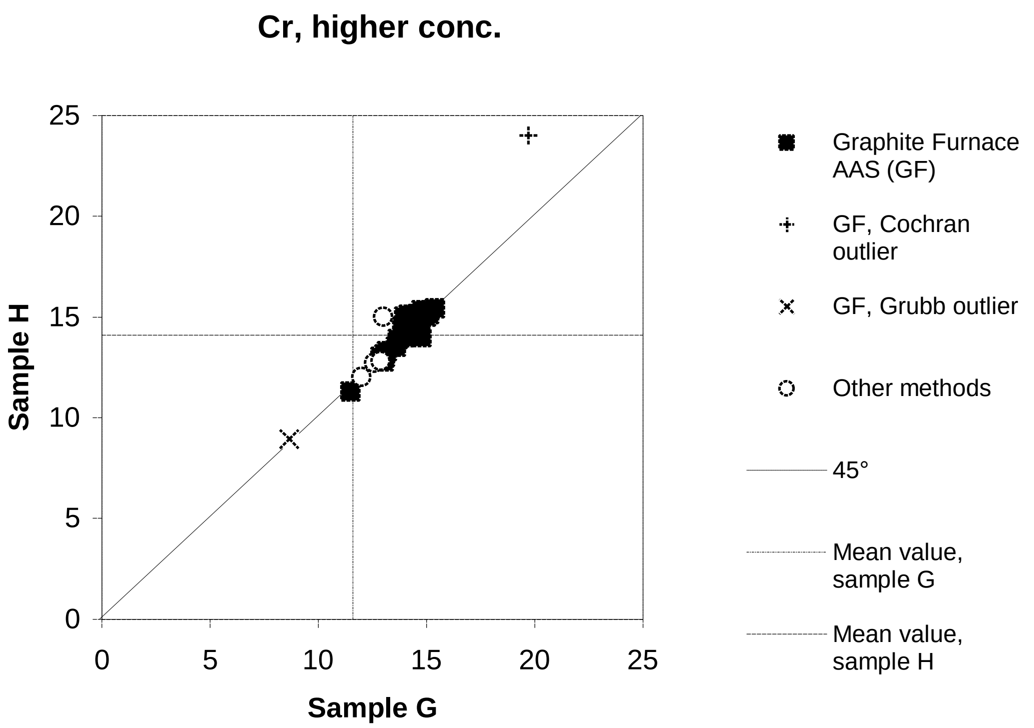
| Lab No. | E | F | Code | Outl./Str. | Lab No. | G | H | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 12 | 0.5 | 0.5 | 2PZ | G 5% | 8 | 8.67 | 8.94 | 2W | G |
| 3 | 1.51 | 1.47 | 2,3PZ | | 15 | 11.5 | 11.3 | ? | |
| 30 | 1.68 | 1.57 | 2W | | 3 | 12.9 | 13 | 2,3PZ | |
| 17 | 1.693 | 1.681 | 2PZ | | 12 | 12.9 | 13 | 2PZ | |
| 26 | 1.75 | 1.75 | 0+PZ | | 5 | 13.0 | 12.8 | 2WZ | |
| 27 | 1.83 | 1.78 | 2PZ | | 17 | 13.07 | 13.12 | 2PZ | |
| 22 | 1.88 | 1.86 | 2WD | | 26 | 13.1 | 13 | 0+PZ | |
| 9 | 1.9 | 2 | 2W | | 35 | 13.2 | 13.3 | 2PZ | |
| 31 | 1.91 | 1.71 | 2P | | 9 | 13.6 | 13.5 | 2W | |
| 32 | 1.95 | 1.88 | 0PZ | | 31 | 13.68 | 13.88 | 2P | |
| 35 | 1.97 | 1.87 | 2PZ | | 30 | 13.9 | 14.5 | 2W | |
| 5 | 1.98 | 1.80 | 2WZ | | 19 | 14 | 14 | 0PZ | |
| 19 | 2 | 2.1 | 0PZ | | 21 | 14 | 15 | 0W | |
| 21 | 2 | 2 | 0W | | 40 | 14 | 14 | 2PZ | |
| 36 | 2 | 2.5 | 2,5WD | | 10 | 14.2 | 15.1 | 2WZ | |
| 40 | 2 | 2 | 2PZ | | 32 | 14.6 | 15.1 | 0PZ | |
| 11 | 2.1 | 1.9 | 2PZ | | 6 | 14.6 | 14.6 | 2PZ | |
| 29 | 2.1 | 2.1 | 0W | | 11 | 14.7 | 14.7 | 2PZ | |
| 23 | 2.15 | 1.96 | 0+WZ | | 22 | 14.8 | 15.3 | 2WD | |
| 6 | 2.2 | 2.0 | 2PZ | | 23 | 14.8 | 14 | 0+WZ | |
| 10 | 2.48 | 2.3 | 2WZ | | 36 | 15 | 15 | 2,5WD | |
| 41 | 2.75 | 2.1 | 2PZ | C 5% | 27 | 15.1 | 15.3 | 2PZ | |
| 1 | 3.1 | 3.4 | 3+WD | | 41 | 15.15 | 15.14 | 2PZ | |
| 16 | 4.43 | 4.48 | 1WZ | G | 29 | 15.4 | 15.4 | 0W | |
| 8 | <1 | <1 | 2W | | 1 | 19.7 | 24 | 3+WD | C |
| 15 | <5 | <5 | ? | | 16 | M | 38.4 | 1WZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **E,F** | 1.95 | 0.15 | 7.7 | 0.48 | 24.7 |
| **G,H** | 14.0 | 0.28 | 2.0 | 1.0 | 7.3 |

## Cr, other methods

| Lab No. | E | F | Code | | Lab No. | G | H | Code |
|---|---|---|---|---|---|---|---|---|
| 44 | 1.67 | 1.66 | K | | 19 | 12 | 12 | K |
| 38 | 1.74 | 1.75 | K | | 38 | 12.6 | 12.7 | K |
| 19 | 2.0 | 2.0 | K | | 44 | 12.9 | 12.8 | K |
| 2 | <10 | <10 | I | | 2 | 13 | 15 | I |


Cr, lower conc.
Sample F
Sample E
0
1
2
3
4
Graphite Furnace AAS (GF)
GF, Cochran 5%
GF, Grubb 5%
GF, Grubb outlier
Other methods
45°
Mean value, sample E
Mean value, sample F


Cr, higher conc.
Sample H
Sample G
0
5
10
15
20
25
Graphite Furnace AAS (GF)
GF, Cochran outlier
GF, Grubb outlier
Other methods
45°
Mean value, sample G
Mean value, sample H

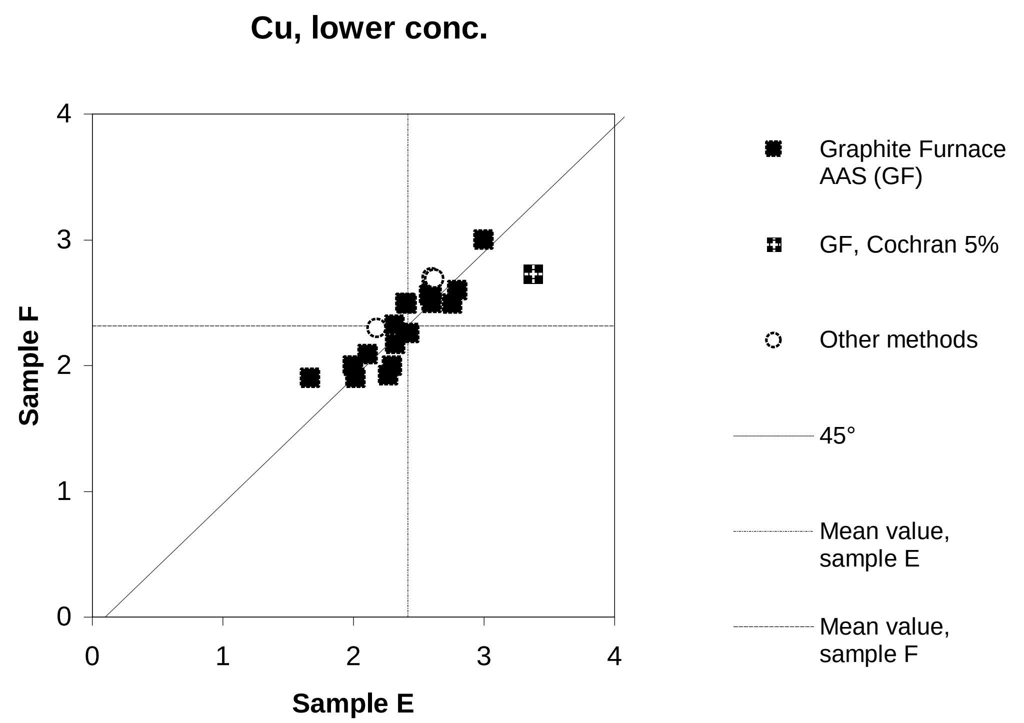
## Cu, fresh water (µg/l)

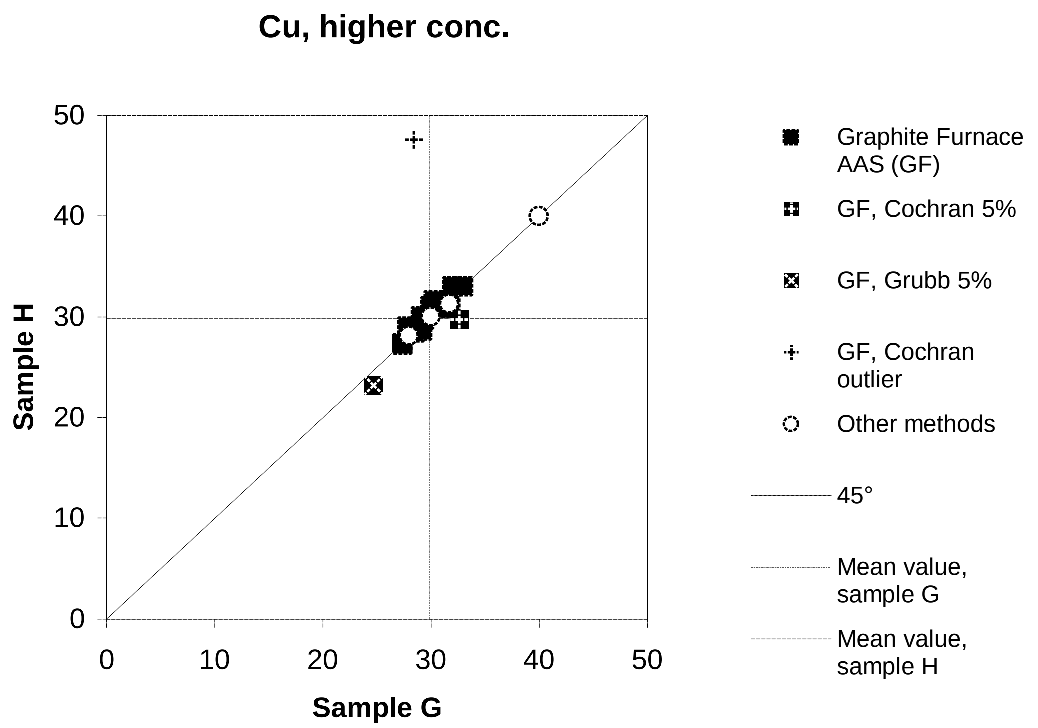
| Lab No. | E | F | Code | Outl./Str. | Lab No. | G | H | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 30 | 1.67 | 1.9 | 0W | | 42 | 24.7 | 23.2 | 0PZ | G 5% |
| 40 | 2 | 2 | 1,2PZ | | 1 | 27.4 | 27.2 | 0+WD | |
| 42 | 2 | 2 | 0PZ | | 16 | 27.4 | 27.31 | 1WZ | |
| 17 | 2.018 | 1.903 | 0PZ | | 5 | 27.9 | 29.0 | 0WZ | |
| 32 | 2.11 | 2.09 | 0WZ | | 27 | 28.4 | 47.6 | 1,2PZ | C |
| 5 | 2.27 | 1.92 | 0WZ | | 10 | 28.5 | 28.4 | 1,2WZ | |
| 37 | 2.3 | 2 | 0WD | | 41 | 28.68 | 28.91 | 1,2PZ | |
| 22 | 2.32 | 2.32 | 0WD | | 6 | 29.1 | 30.0 | 2PZ | |
| 27 | 2.32 | 2.17 | 1,2PZ | | 30 | 29.2 | 28.6 | 0W | |
| 11 | 2.4 | 2.5 | 0PZ | | 11 | 29.4 | 29.7 | 0PZ | |
| 10 | 2.41 | 2.49 | 1,2WZ | | 19 | 30 | 31 | 0PZ | |
| 16 | 2.43 | 2.26 | 1WZ | | 21 | 30 | 31 | 0WD | |
| 3 | 2.58 | 2.56 | 1,2PZ | | 22 | 30.3 | 31.6 | 0WD | |
| 29 | 2.6 | 2.5 | 0PZ | | 29 | 30.9 | 30.8 | 0PZ | |
| 31 | 2.6 | 2.6 | 0PD | | 37 | 31.2 | 30.9 | 0WD | |
| 6 | 2.8 | 2.5 | 2PZ | | 32 | 31.3 | 31.3 | 0WZ | |
| 19 | 2.8 | 2.6 | 0PZ | | 3 | 31.7 | 31.3 | 1,2PZ | |
| 21 | 3 | 3 | 0WD | | 31 | 31.8 | 31 | 0PD | |
| 41 | 3.38 | 2.73 | 1,2PZ | C 5% | 40 | 32 | 33 | 1,2PZ | |
| 1 | < 8 | < 8 | 0+WD | | 17 | 32.60 | 29.71 | 0PZ | C 5% |
| 15 | <20 | <20 | ? | | 15 | 33 | 33 | ? | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **E,F** | 2.37 | 0.15 | 6.4 | 0.36 | 15.4 |
| **G,H** | 29.8 | 0.69 | 2.3 | 2.2 | 7.2 |

## Cu, other methods

| Lab No. | E | F | Code | | Lab No. | G | H | Code |
|---|---|---|---|---|---|---|---|---|
| 44 | 2.18 | 2.30 | K | | 44 | 28 | 28.1 | K |
| 19 | 2.6 | 2.7 | K | | 19 | 30 | 30 | K |
| 38 | 2.62 | 2.69 | K | | 38 | 31.7 | 31.3 | K |
| 2 | <10 | <10 | I | | 2 | 40 | 40 | I |


Cu, lower conc.
Sample F
Sample E
0
1
2
3
4
Graphite Furnace AAS (GF)
GF, Cochran 5%
Other methods
45°
Mean value, sample E
Mean value, sample F


Cu, higher conc.
Sample H
Sample G
0
10
20
30
40
50
Graphite Furnace AAS (GF)
GF, Cochran 5%
GF, Grubb 5%
GF, Cochran outlier
Other methods
45°
Mean value, sample G
Mean value, sample H

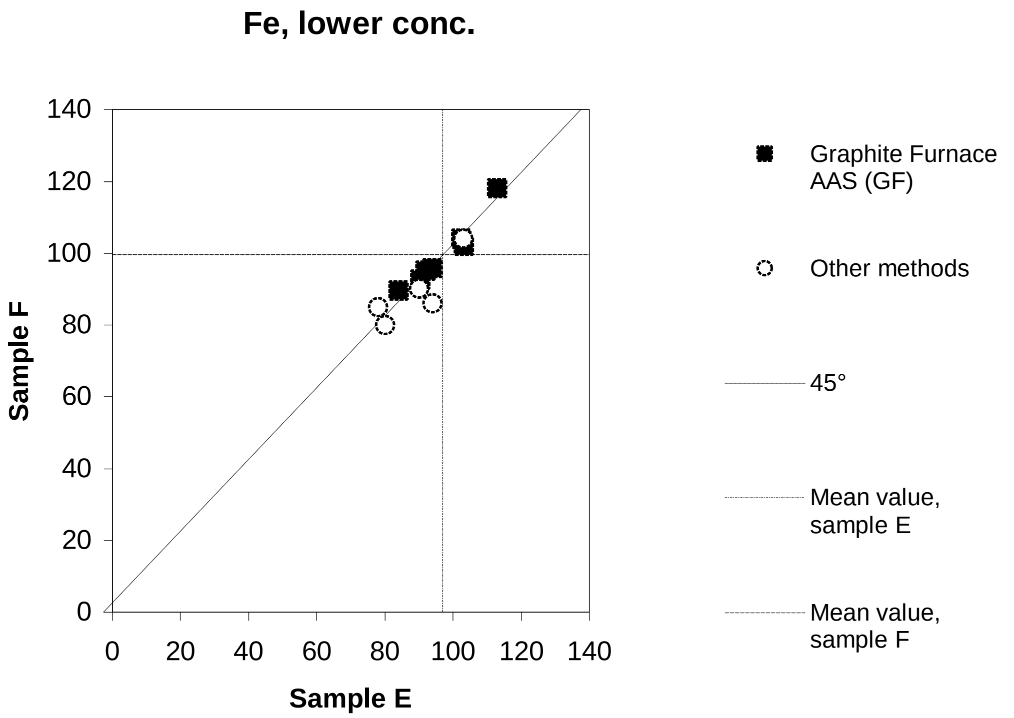
## Fe, fresh water (µg/l)

| Lab No. | E | F | Code | Outl./Str. | Lab No. | G | H | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 42 | 84.0 | 89.5 | 0PZ | | 42 | 98.0 | 100.5 | 0PZ | |
| 5 | 90.4 | 92.5 | 0WZ | | 5 | 109 | 107 | 0WZ | |
| 32 | 92 | 95 | 0WZ | | 32 | 111 | 116 | 0WZ | |
| 15 | 94.1 | 95.7 | ? | | 15 | 115 | 113 | ? | |
| 29 | 102.5 | 104 | 0WD | | 29 | 128.4 | 129.3 | 0WD | |
| 6 | 103 | 102 | 2PZ | | 21 | 135 | 133 | 0WD | |
| 21 | 113 | 118 | 0WD | | 6 | M | M | | |

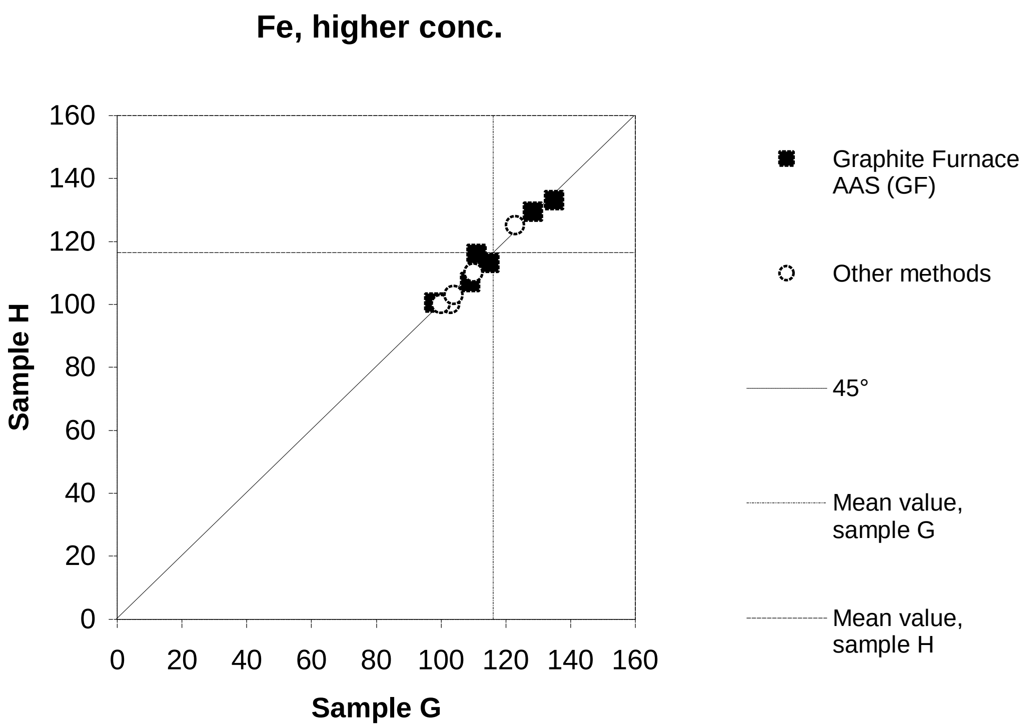
| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **E,F** | 98.3 | 2.3 | 2.4 | 9.7 | 9.9 |
| **G,H** | 116 | 1.9 | 1.6 | 13 | 11.2 |

## Fe, other methods

| Lab No. | E | F | Code | | Lab No. | G | H | Code |
|---|---|---|---|---|---|---|---|---|
| 19 | 78 | 85 | K | | 19 | 100 | 100 | K |
| 44 | 80.2 | 80 | K | | 3 | 103 | 100 | I |
| 2 | 90 | 90 | I | | 44 | 104 | 103 | K |
| 3 | 94.1 | 86 | I | | 2 | 110 | 110 | I |
| 38 | 103 | 104 | K | | 38 | 123 | 125 | K |



Fe, lower conc.
Sample F
Sample E
0
20
40
60
80
100
120
140
Graphite Furnace AAS (GF)
Other methods
45°
Mean value, sample E
Mean value, sample F

Fe, higher conc.
Sample H
Sample G
0
20
40
60
80
100
120
140
160
Graphite Furnace AAS (GF)
Other methods
45°
Mean value, sample G
Mean value, sample H

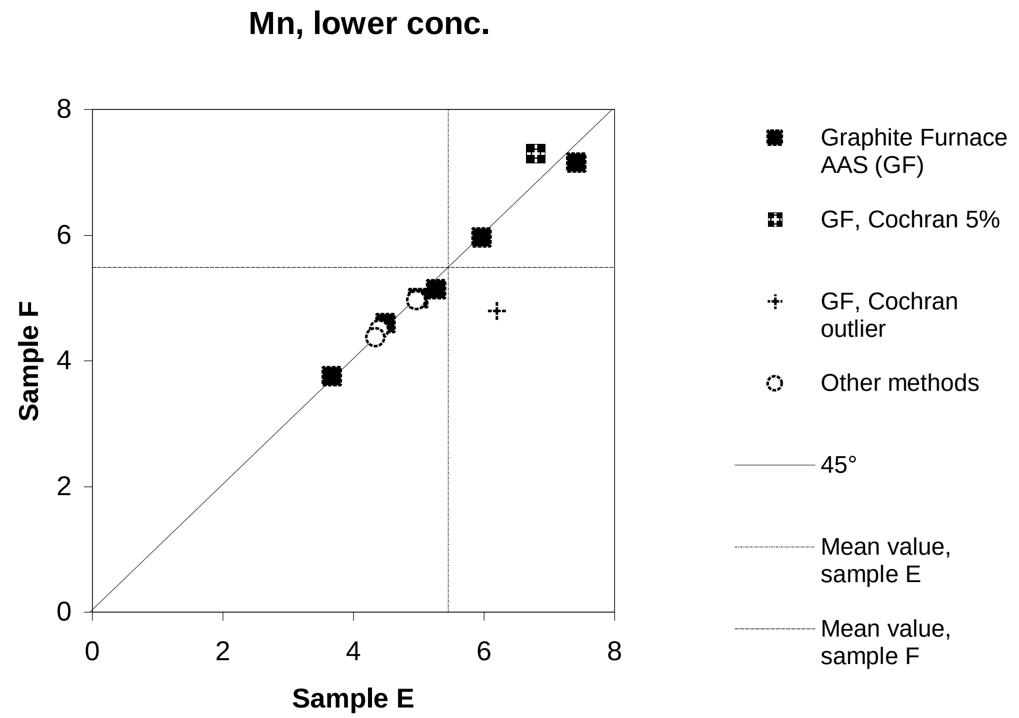
## Mn, fresh water (μg/l)

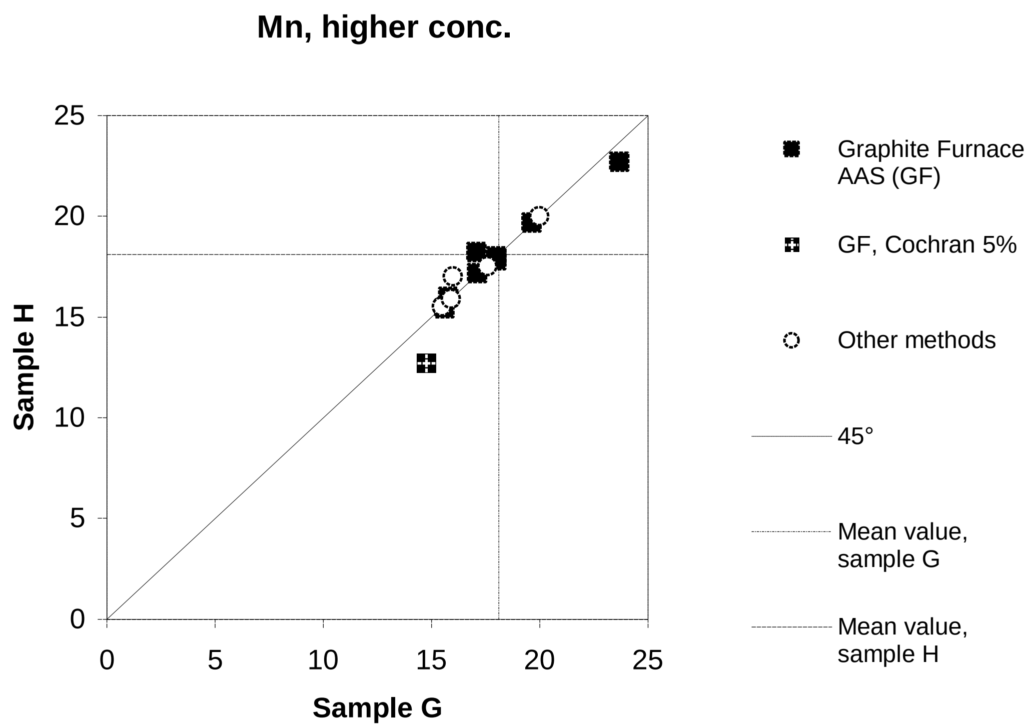
| Lab No. | E | F | Code | Outl./Str. | Lab No. | G | H | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 17 | 3.672 | 3.750 | 2PZ | | 17 | 14.76 | 12.70 | 2PZ | C 5% |
| 29 | 4.5 | 4.6 | 0WD | | 15 | 15.6 | 15.4 | ? | |
| 21 | 5 | 5 | 0W | | 29 | 15.8 | 16 | 0WD | |
| 40 | 5 | 5 | 1,2PZ | | 31 | 17.1 | 18.2 | 1,2PD | |
| 5 | 5.28 | 5.13 | 0WZ | | 5 | 17.1 | 17.2 | 0WZ | |
| 6 | 6.0 | 6.0 | 2PZ | | 21 | 18 | 18 | 0W | |
| 31 | 6.2 | 4.8 | 1,2PD | C | 40 | 18 | 18 | 1,2PZ | |
| 42 | 6.8 | 7.3 | 0PZ | C 5% | 42 | 18.0 | 17.8 | 0PZ | |
| 32 | 7.42 | 7.15 | 0WZ | | 6 | 19.6 | 19.7 | 2PZ | |
| 15 | <5 | <5 | ? | | 32 | 23.7 | 22.7 | 0WZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **E,F** | 5.47 | 0.15 | 2.7 | 1.23 | 22.5 |
| **G,H** | 17.7 | 0.57 | 3.2 | 2.6 | 14.6 |

## Mn, other methods

| Lab No. | E | F | Code | | Lab No. | G | H | Code |
|---|---|---|---|---|---|---|---|---|
| 44 | 4.34 | 4.37 | K | | 19 | 15.5 | 15.5 | K |
| 19 | 4.4 | 4.5 | K | | 44 | 15.9 | 15.9 | K |
| 38 | 4.97 | 4.96 | K | | 3 | 16 | 17 | I |
| 2 | <10 | <10 | I | | 38 | 17.6 | 17.5 | K |
| 3 | <10 | <10 | I | | 2 | 20 | 20 | I |


Mn, lower conc.
Sample F
Sample E
0
2
4
6
8
Graphite Furnace AAS (GF)
GF, Cochran 5%
GF, Cochran outlier
Other methods
45°
Mean value, sample E
Mean value, sample F


Mn, higher conc.
Sample H
Sample G
0
5
10
15
20
25
Graphite Furnace AAS (GF)
GF, Cochran 5%
Other methods
45°
Mean value, sample G
Mean value, sample H

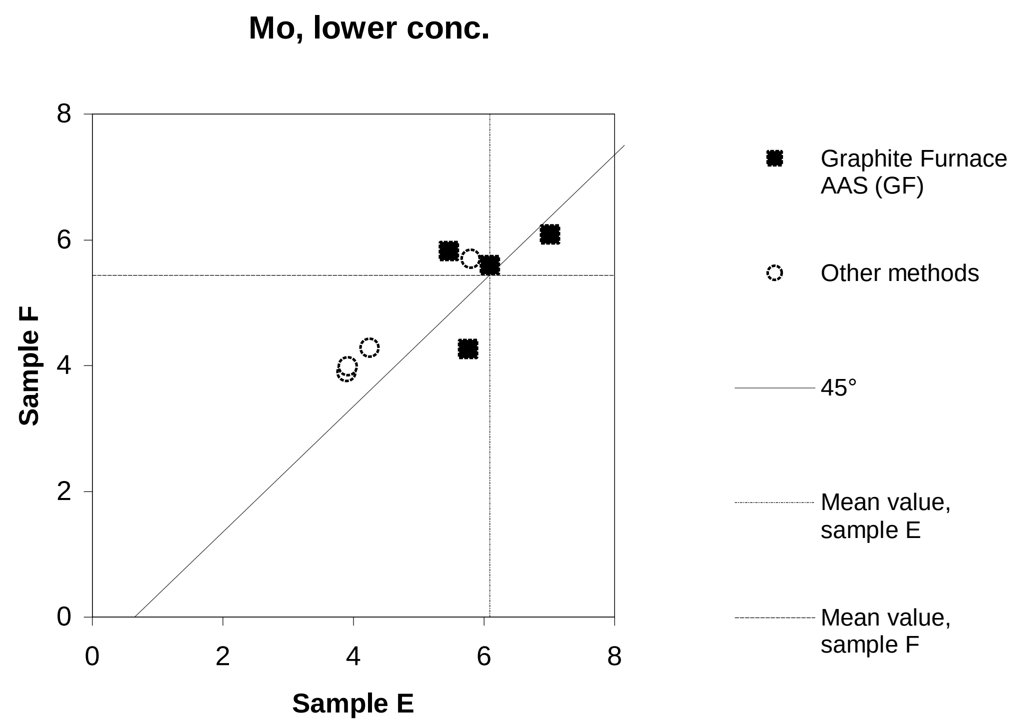
## Mo, fresh water (µg/l)

| Lab No. | E | F | Code | Outl./Str. | Lab No. | G | H | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 5 | 5.47 | 5.82 | 0WZ | | 5 | 26.1 | 27.5 | 0WZ | |
| 8 | 5.76 | 4.26 | 0W | | 8 | 26.08 | 26.55 | 0W | |
| 15 | 6.1 | 5.6 | ? | | 3 | 27.2 | 25.3 | 0PZ | |
| 10 | 7.02 | 6.08 | 0WZ | | 15 | 29.8 | 29.2 | ? | |
| 32 | <1 | <1 | 0WZ | | 32 | 30.73 | 33.84 | 0WZ | |
| 3 | <4 | <4 | 0PZ | | 10 | 34.8 | 35.2 | 0WZ | |

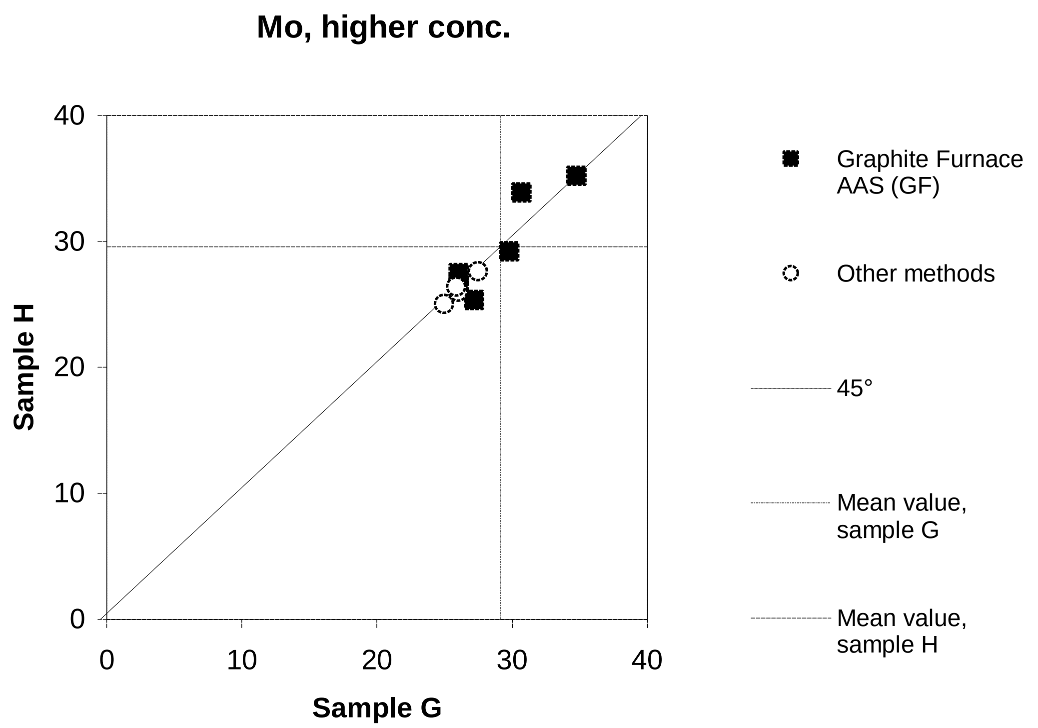
| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **E,F** | 5.76 | 0.66 | 11.5 | 0.79 | 13.7 |
| **G,H** | 29.4 | 1.2 | 3.9 | 3.7 | 12.7 |

## Mo, other methods

| Lab No. | E | F | Code | | Lab No. | G | H | Code |
|---|---|---|---|---|---|---|---|---|
| 19 | 3.9 | 3.9 | K | | 19 | 25 | 25 | K |
| 44 | 3.92 | 3.99 | K | | 44 | 25.9 | 26.4 | K |
| 38 | 4.25 | 4.28 | K | | 24 | 26 | 26 | I |
| 24 | 5.8 | 5.7 | I | | 38 | 27.5 | 27.6 | K |
| 2 | <50 | <50 | I | | 2 | <50 | <50 | I |
| 3 | <50 | <50 | I | | 3 | <50 | <50 | I |



Mo, lower conc.
8
6
4
2
0
0
2
4
6
8
Sample F
Sample E
Graphite Furnace AAS (GF)
Other methods
45°
Mean value, sample E
Mean value, sample F

Mo, higher conc.
40
30
20
10
0
0
10
20
30
40
Sample H
Sample G
Graphite Furnace AAS (GF)
Other methods
45°
Mean value, sample G
Mean value, sample H

## Ni, fresh water (µg/l)

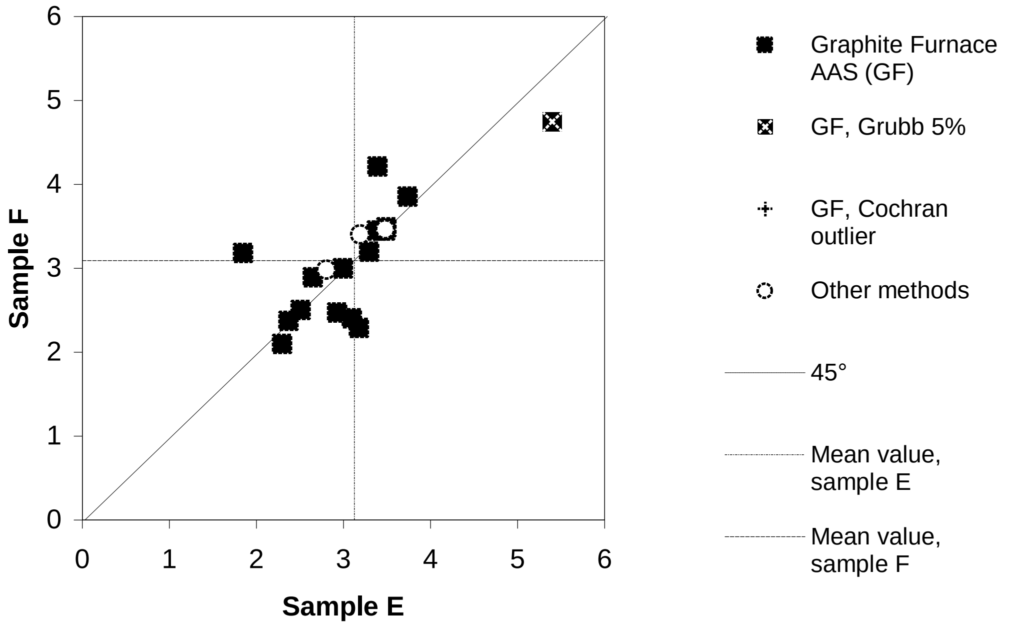
| Lab No. | E | F | Code | Outl./Str. | Lab No. | G | H | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 10 | 1.85 | 3.18 | 2WZ | | 8 | 25.69 | 26.09 | 2WD | |
| 12 | 2.3 | 2.1 | 2PZ | | 5 | 28.1 | 27.8 | 0WZ | |
| 32 | 2.37 | 2.37 | 0PZ | | 41 | 30.36 | 30.37 | 2PZ | |
| 22 | 2.51 | 2.50 | 1,2WD | | 22 | 31.4 | 30.9 | 1,2WD | |
| 5 | 2.65 | 2.89 | 0WZ | | 6 | 32 | 30 | 2PZ | |
| 31 | 2.93 | 2.47 | 0PD | | 32 | 31.83 | 32.57 | 0PZ | |
| 21 | 3 | 3 | 0WD | | 29 | 32.6 | 33.4 | 0PD | |
| 40 | 3 | 3 | 0PZ | | 21 | 33 | 33 | 0WD | |
| 29 | 3.1 | 2.4 | 0PD | | 17 | 33.13 | 33.07 | 0PZ | |
| 42 | 3.12 | 12.6 | 0PZ | C | 31 | 34.36 | 33.5 | 0PD | |
| 8 | 3.18 | 2.29 | 2WD | | 12 | 34.4 | 35.3 | 2PZ | |
| 19 | 3.3 | 3.2 | 0PZ | | 35 | 34.6 | 32.4 | 2PZ | |
| 27 | 3.39 | 3.45 | 0PZ | | 15 | 35 | 34 | ? | |
| 17 | 3.395 | 4.209 | 0PZ | | 19 | 35 | 34 | 0PZ | |
| 35 | 3.48 | 3.45 | 2PZ | | 40 | 35 | 37 | 0PZ | |
| 41 | 3.5 | 3.49 | 2PZ | | 27 | 35.4 | 36.1 | 0PZ | |
| 3 | 3.74 | 3.85 | 1,2PZ | | 10 | 35.8 | 37.3 | 2WZ | |
| 6 | 5.4 | 4.8 | 2PZ | G 5% | 3 | 37.5 | 37.4 | 1,2PZ | |
| 15 | <5 | <5 | ? | | 42 | 37.7 | 34.8 | 0PZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **E,F** | 3.11 | 0.36 | 11.7 | 0.75 | 24.0 |
| **G,H** | 33.2 | 0.84 | 2.5 | 3.0 | 9.1 |

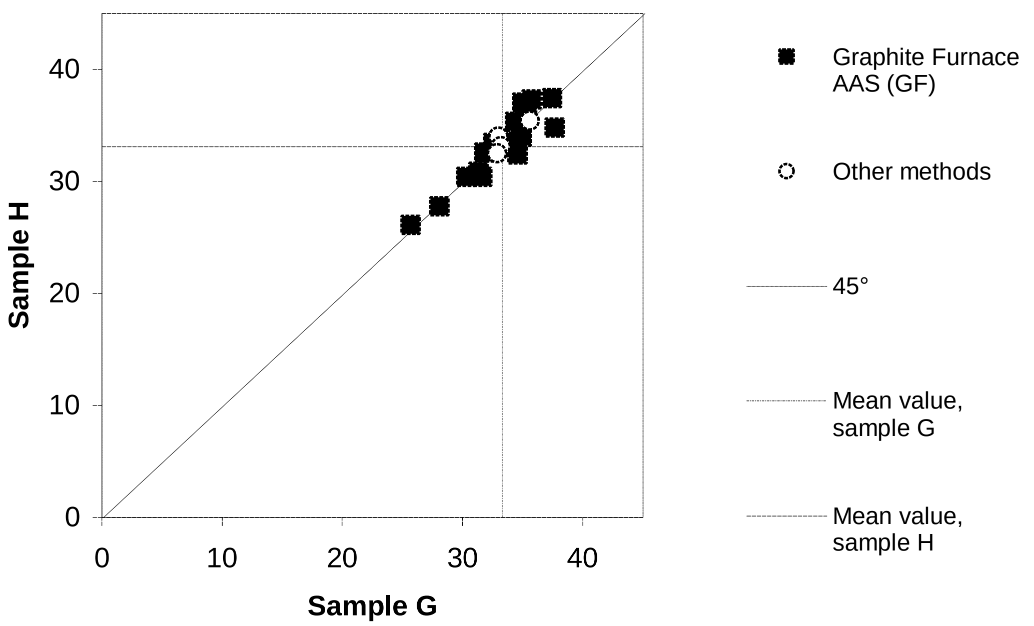
## Ni, other methods

| Lab No. | E | F | Code | | Lab No. | G | H | Code |
|---|---|---|---|---|---|---|---|---|
| 44 | 2.81 | 2.98 | K | | 44 | 32.9 | 32.5 | K |
| 19 | 3.2 | 3.4 | K | | 2 | 33 | 34 | I |
| 38 | 3.48 | 3.46 | K | | 19 | 33.2 | 33.1 | K |
| 2 | <10 | <10 | I | | 38 | 35.6 | 35.4 | K |

**Ni, lower conc.**




**Ni, higher conc.**



Pb, fresh water (µg/l)

| Lab No. | E | F | Code | Outl./Str. | Lab No. | G | H | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 22 | 5.51 | 5.54 | 1,2WD | | 16 | 26.83 | 24.53 | 3PZ | G |
| 19 | 5.8 | 6.1 | 0PZ | | 36 | 51 | 56 | 2,5WD | |
| 30 | 6.16 | 5.38 | 1WD | | 42 | 56.6 | 58.9 | 1,2PZ | |
| 42 | 6.20 | 5.54 | 1,2PZ | | 30 | 57.6 | 53.2 | 1WD | |
| 9 | 6.8 | 6.7 | 1,2WD | | 2 | 60 | 62 | 2,3WD | |
| 23 | 7 | 10 | 0+WZ | C 5% | 41 | 60.69 | 63.37 | 2,3PZ | |
| 29 | 7.1 | 7 | 2,3PZ | | 35 | 61.4 | 61.1 | 3PZ | |
| 41 | 7.15 | 7.15 | 2,3PZ | | 34 | 61.77 | 62.42 | 1PZ | |
| 32 | 7.32 | 7.45 | 0PZ | | 9 | 61.9 | 59.8 | 1,2WD | |
| 34 | 7.34 | 7.08 | 1PZ | | 31 | 62.6 | 61.3 | 3PD | |
| 35 | 7.42 | 7.46 | 3PZ | | 13 | 63.3 | 66 | 5PZ | |
| 39 | 7.43 | 7.63 | 2,3WZ | | 21 | 64 | 64 | 1,2PD | |
| 3 | 7.45 | 7.42 | 1,2PZ | | 20 | 64.1 | 63.9 | 2,3WZ | |
| 20 | 7.62 | 7.76 | 2,3WZ | | 6 | 65 | 66 | 2,3PZ | |
| 17 | 7.763 | 7.790 | 3PZ | | 11 | 64.7 | 64.7 | 2,3PZ | |
| 26 | 7.79 | 7.62 | 2,3+PZ | | 39 | 65 | 62.1 | 2,3WZ | |
| 6 | 7.8 | 7.5 | 2,3PZ | | 29 | 65.5 | 63.2 | 2,3PZ | |
| 5 | 7.88 | 8.13 | 3WZ | | 4 | 65.6 | 67.1 | 2,3PZ | |
| 11 | 7.9 | 7.9 | 2,3PZ | | 32 | 65.68 | 66.6 | 0PZ | |
| 13 | 7.95 | 8 | 5PZ | | 23 | 66.1 | 63.6 | 0+WZ | |
| 27 | 7.98 | 7.95 | 2,3PZ | | 27 | 66.6 | 64.2 | 2,3PZ | |
| 21 | 8 | 7 | 1,2PD | | 15 | 66.8 | 65.1 | ? | |
| 40 | 8 | 8 | 2,3PZ | | 5 | 67.3 | 69.1 | 3WZ | |
| 31 | 8.05 | 8.25 | 3PD | | 3 | 68.3 | 69.1 | 1,2PZ | |
| 14 | 8.1 | 6.6 | 2,3?Z | | 7 | 69 | 68 | 1,2PD | |
| 16 | 8.18 | 6.72 | 3PZ | | 19 | 70 | 68 | 0PZ | |
| 7 | 8.5 | 10 | 1,2PD | | 8 | 72.33 | 72.04 | 1,2WD | |
| 4 | 8.53 | 7.32 | 2,3PZ | | 10 | 74.3 | 77.6 | 2,3PZ | |
| 10 | 9.55 | 9.66 | 2,3PZ | | 17 | 74.88 | 77.35 | 3PZ | |
| 12 | 9.8 | 7.2 | 1,2,3PZ | | 22 | 75.6 | 74.0 | 1,2WD | |
| 15 | 11.5 | 10.9 | ? | | 40 | 79 | 80 | 2,3PZ | |
| 8 | 11.59 | 10.54 | 1,2WD | | 1 | 84.3 | 89.9 | 0+WD | |
| 1 | <10 | <10 | 0+WD | | 12 | 91.9 | 100.3 | 1,2,3PZ | C 5% |
| 2 | <10 | <10 | 2,3WD | | 26 | 98.9 | 98.5 | 2,3+PZ | G 5% |
| 36 | M | M | | | 14 | M | M | | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **E,F** | 7.76 | 0.66 | 8.5 | 1.34 | 17.2 |
| **G,H** | 68.2 | 1.9 | 2.8 | 10.2 | 15.0 |

Pb, other methods

| Lab No. | E | F | Code | | Lab No. | G | H | Code |
|---|---|---|---|---|---|---|---|---|
| 19 | 7.4 | 7.4 | K | | 38 | 62.9 | 62.4 | K |
| 38 | 7.47 | 7.41 | K | | 19 | 63 | 63 | K |
| 44 | 7.54 | 7.64 | K | | 44 | 64.9 | 66.8 | K |

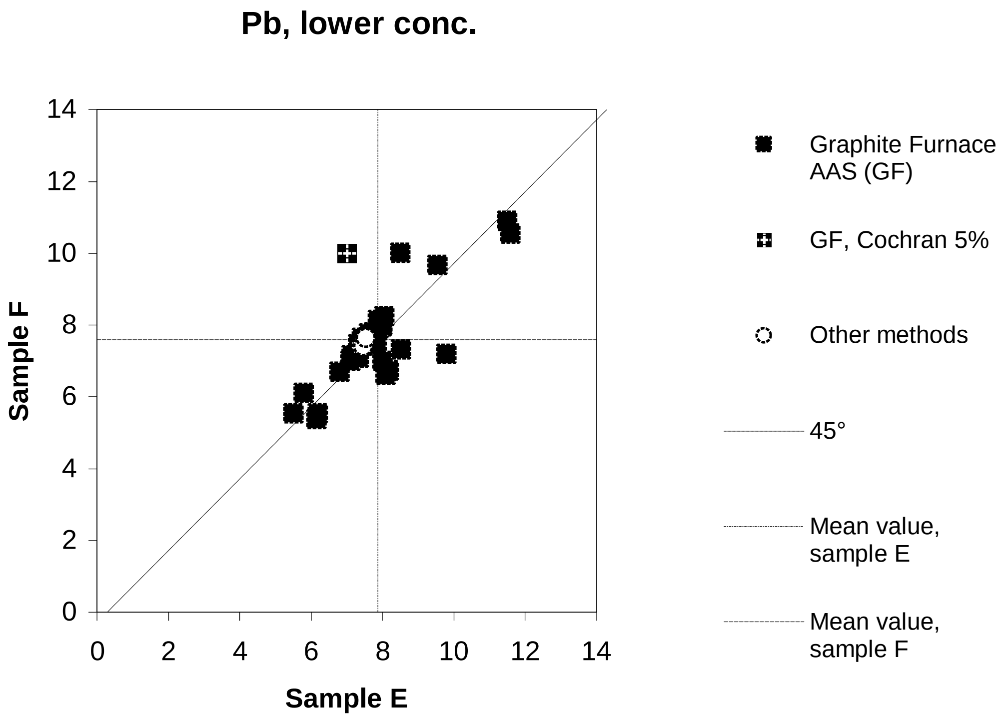
Sb, fresh water (µg/l)

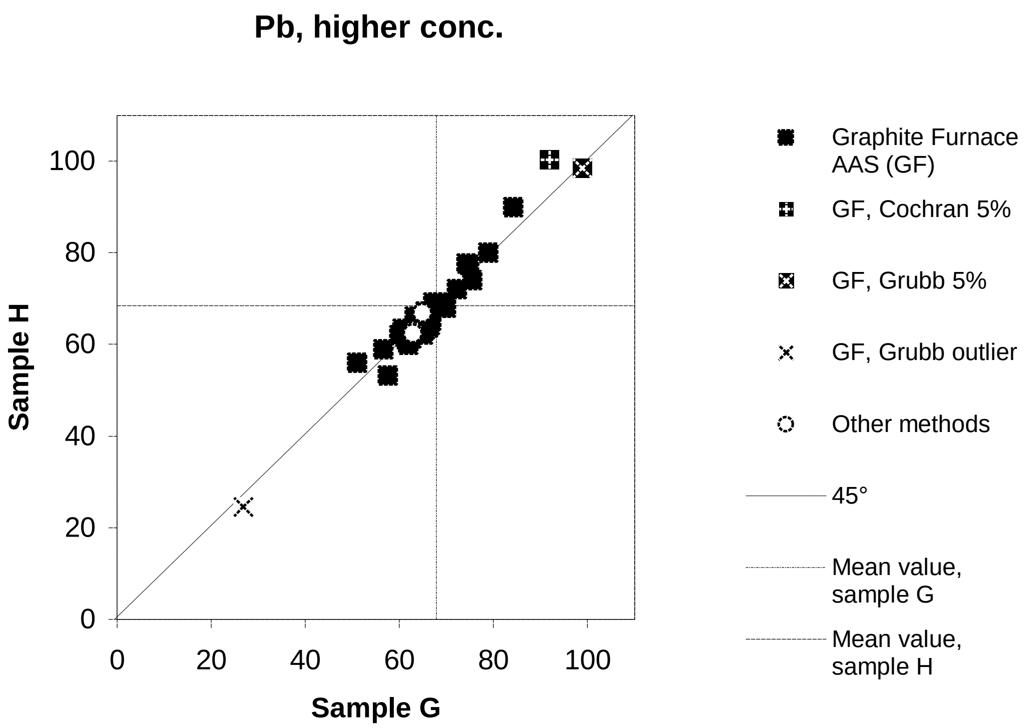
| Lab No. | E | F | Code | Outl./Str. | Lab No. | G | H | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 5 | 4.86 | 5.37 | 1,2WZ | | 42 | 47.3 | 47.8 | 1,2PZ | |
| 42 | 4.9 | 4.24 | 1,2PZ | | 19 | 51 | 53 | 1,2PZ | |
| 19 | 5.2 | 5.3 | 1,2PZ | | 5 | 51.2 | 49.0 | 1,2WZ | |
| 24 | 6.2 | 6.5 | 1+WZ | | 2 | 53 | 54 | 4WD | |
| 32 | 7.6 | 7.6 | 1,2PZ | | 32 | 54.5 | 51.7 | 1,2PZ | |
| 1 | < 20 | < 20 | 0+WD | | 24 | 55 | 55 | 1+WZ | |
| 2 | <10 | <10 | 4WD | | 1 | 55.6 | 59.9 | 0+WD | |

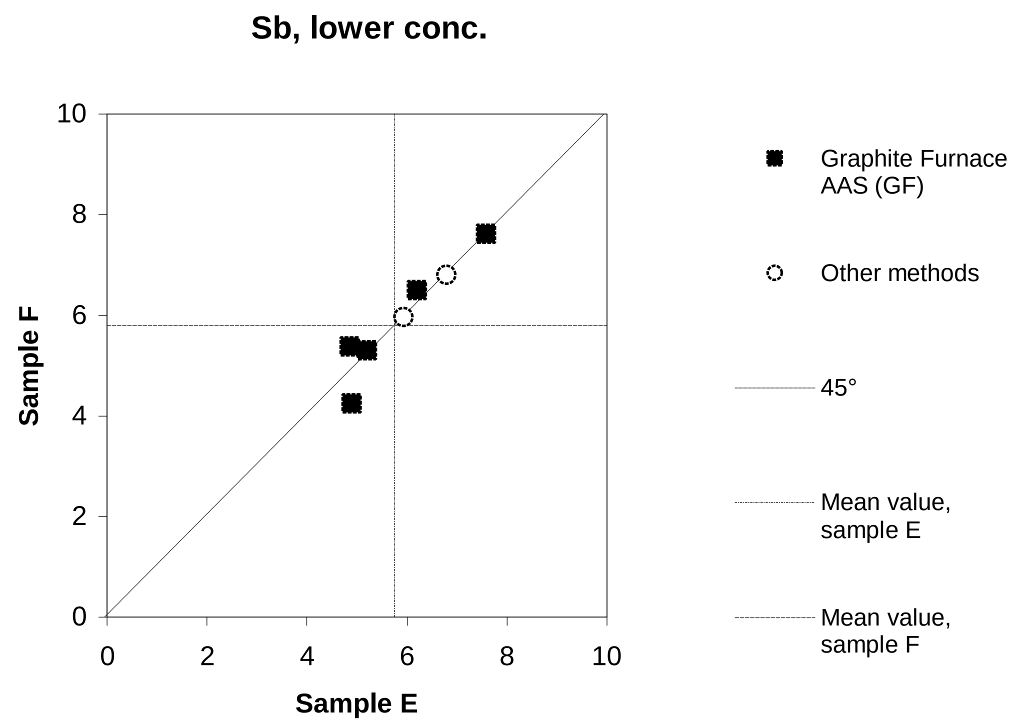
| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **E,F** | 5.78 | 0.28 | 4.9 | 1.22 | 21.2 |
| **G,H** | 52.7 | 1.6 | 3.1 | 3.5 | 6.6 |

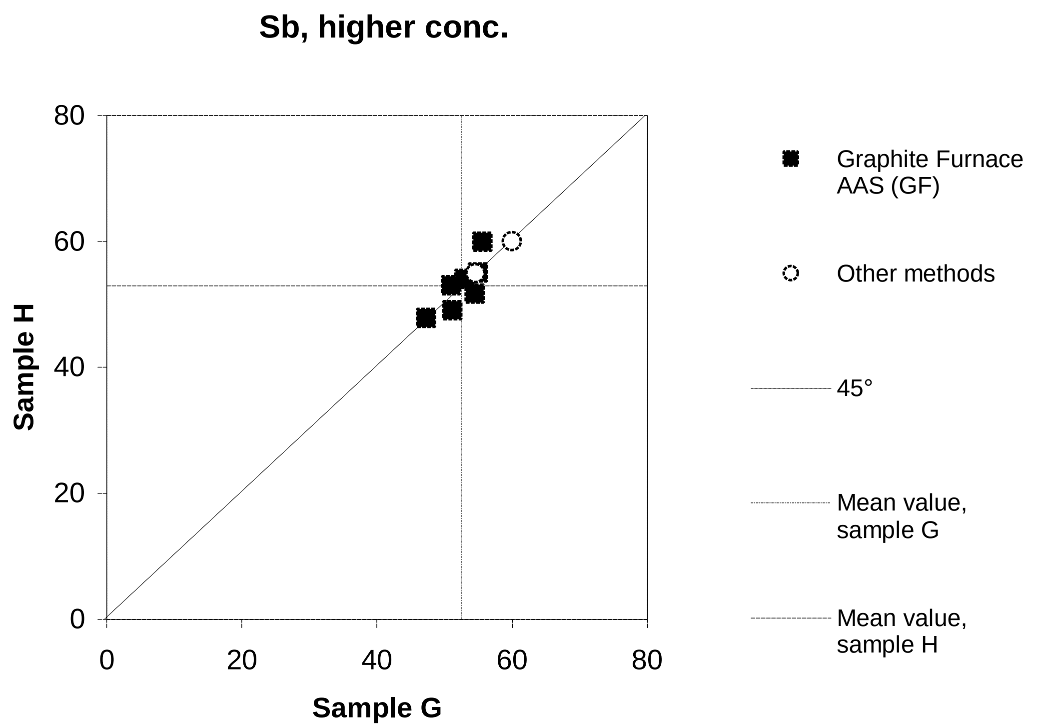
Sb, other methods

| Lab No. | E | F | Code | | Lab No. | G | H | Code |
|---|---|---|---|---|---|---|---|---|
| 44 | 5.93 | 5.96 | K | | 44 | 54.6 | 54.9 | K |
| 19 | 6.8 | 6.8 | K | | 19 | 60 | 60 | K |
| 3 | <200 | <200 | I | | 3 | <200 | <200 | I |


Pb, lower conc.
Sample F
Sample E
0
2
4
6
8
10
12
14
Graphite Furnace AAS (GF)
GF, Cochran 5%
Other methods
45°
Mean value, sample E
Mean value, sample F


Pb, higher conc.
Sample H
Sample G
0
20
40
60
80
100
Graphite Furnace AAS (GF)
GF, Cochran 5%
GF, Grubb 5%
GF, Grubb outlier
Other methods
45°
Mean value, sample G
Mean value, sample H


Sb, lower conc.
10
8
6
4
2
0
0
2
4
6
8
10
Sample F
Sample E
Graphite Furnace AAS (GF)
Other methods
45°
Mean value, sample E
Mean value, sample F


Sb, higher conc.
80
60
40
20
0
0
20
40
60
80
Sample H
Sample G
Graphite Furnace AAS (GF)
Other methods
45°
Mean value, sample G
Mean value, sample H

Se, fresh water (µg/l)

| Lab No. | E | F | Code | Outl./Str. | Lab No. | G | H | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 12 | 8.8 | 8.3 | 1,2PZ | | 19 | 68 | 67 | 1,2PZ | |
| 19 | 8.9 | 8.8 | 1,2PZ | | 42 | 72.3 | 75.2 | 1,2PZ | |
| 1 | 9.2 | 9.6 | 1+WD | | 10 | 74.4 | 74.7 | 1,2PZ | |
| 24 | 9.5 | 9.6 | 1+WZ | | 24 | 77 | 78 | 1+WZ | |
| 10 | 9.61 | 10.04 | 1,2PZ | | 5 | 77.6 | 78.3 | 1,2WZ | |
| 5 | 10.7 | 9.4 | 1,2WZ | | 15 | 79.1 | 80.8 | ? | |
| 2 | 11 | 11 | 1,2WD | | 12 | 80.1 | 80.2 | 1,2PZ | |
| 26 | 11.2 | 10.8 | 1,2+PZ | | 1 | 86.6 | 79.2 | 1+WD | |
| 42 | 11.7 | 9.5 | 1,2PZ | C 5% | 2 | 89 | 81 | 1,2WD | |
| 15 | 13 | 13 | ? | | 26 | 113 | 111 | 1,2+PZ | |
| 32 | 17.7 | 17.1 | 1,2PZ | G | 32 | 126.2 | 125.7 | 1,2PZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **E,F** | 10.2 | 0.61 | 5.9 | 1.4 | 13.4 |
| **G,H** | 85.2 | 2.5 | 2.9 | 17.7 | 20.8 |

Se, other methods

| Lab No. | E | F | Code | | Lab No. | G | H | Code |
|---|---|---|---|---|---|---|---|---|
| 19 | 10 | 10 | K | | 19 | 91 | 91 | K |
| 38 | 11.3 | 11.4 | K | | 38 | 91.2 | 91.5 | K |

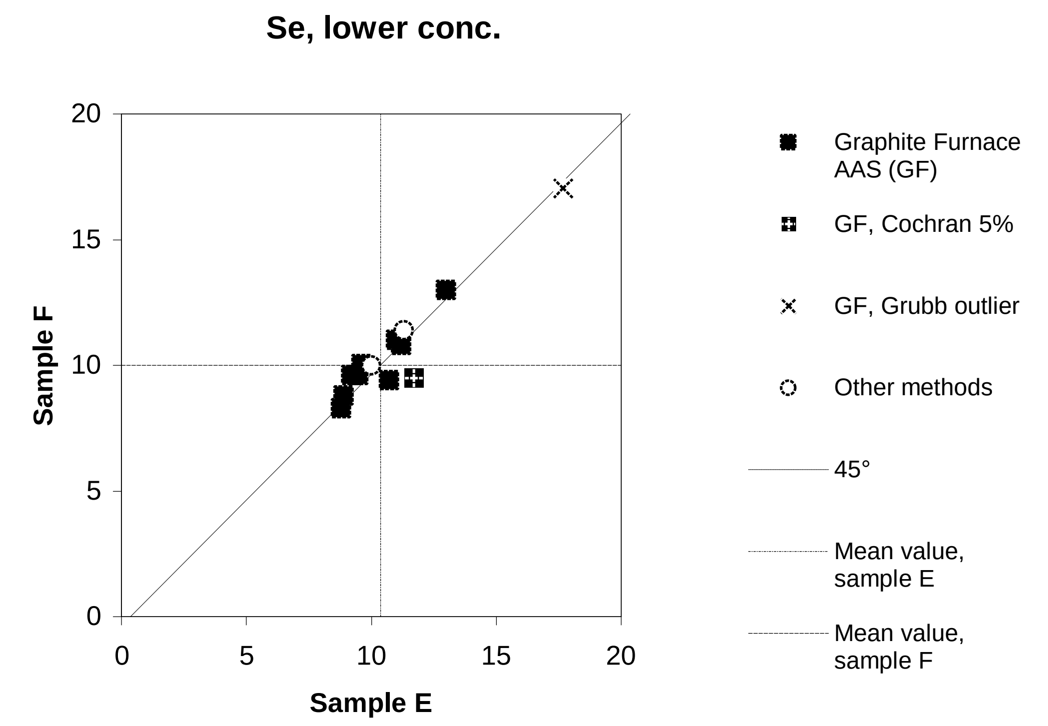
Tl, fresh water (µg/l)

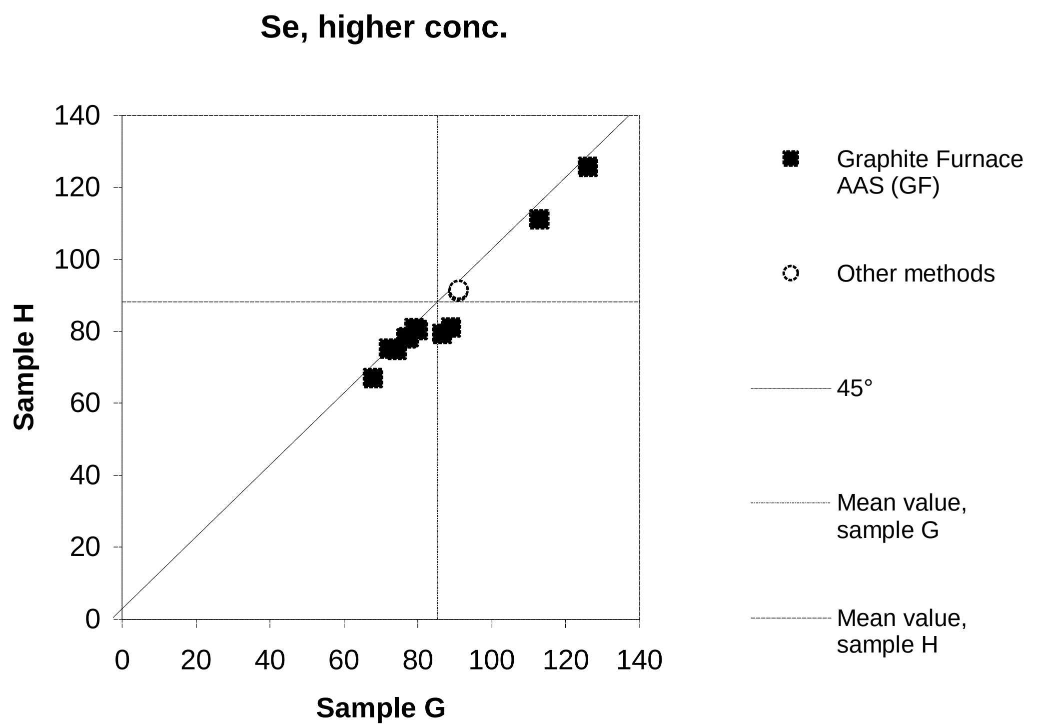
| Lab No. | E | F | Code | Outl./Str. | Lab No. | G | H | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 5 | 2.85 | 3.15 | 0WZ | | 1 | 9.5 | 8.1 | 0+PD | |
| 19 | 3.5 | 3.4 | 1,2PZ | | 5 | 27.3 | 26.7 | 0WZ | |
| 6 | 6.2 | 6.1 | 1,2PZ | | 6 | 32 | 31 | 1,2PZ | |
| 1 | < 4 | < 4 | 0+PD | | 19 | 33 | 33 | 1,2PZ | |
| 2 | <10 | <10 | 0WD | | 2 | 37 | 39 | 0WD | |

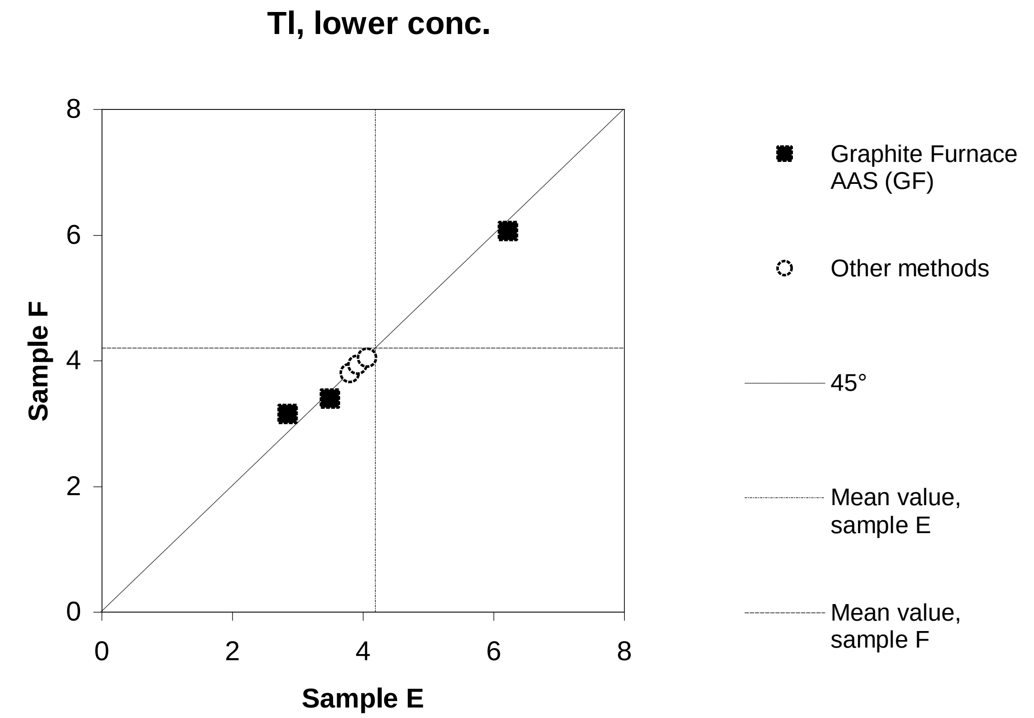
| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **E,F** | 4.20 | 0.14 | 3.4 | 1.70 | 40.6 |
| **G,H** | 27.7 | 0.84 | 3.0 | 11.3 | 40.7 |

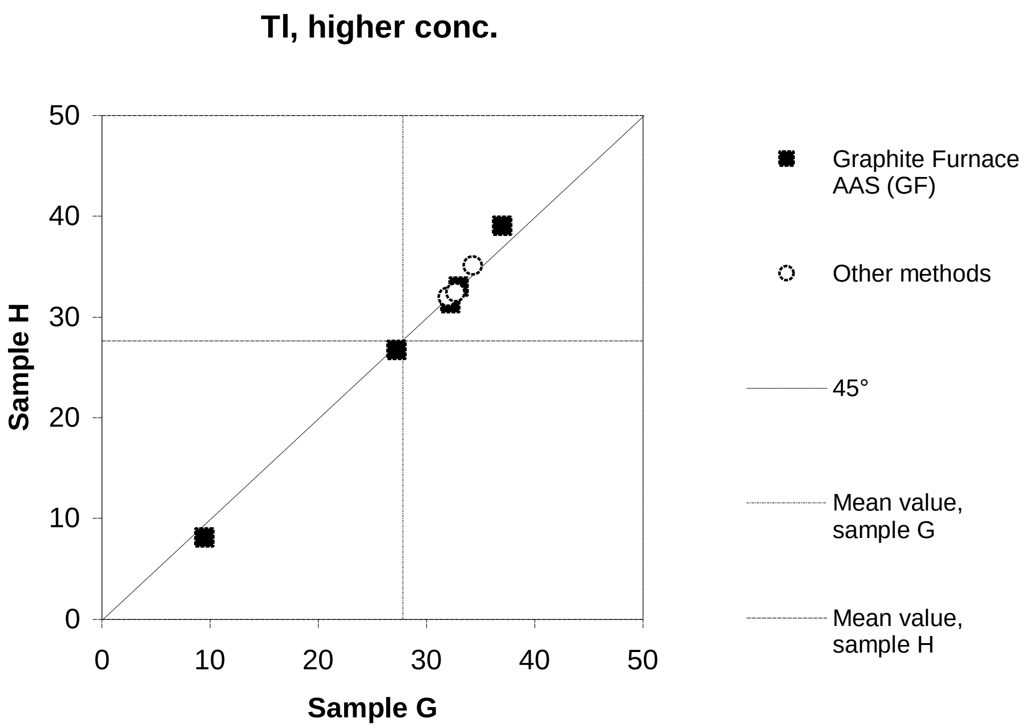
Tl, other methods

| Lab No. | E | F | Code | | Lab No. | G | H | Code |
|---|---|---|---|---|---|---|---|---|
| 19 | 3.8 | 3.8 | K | | 19 | 32 | 32 | K |
| 38 | 3.92 | 3.94 | K | | 38 | 32.7 | 32.4 | K |
| 44 | 4.07 | 4.05 | K | | 44 | 34.3 | 35.1 | K |


Se, lower conc.
Sample F
Sample E
20
15
10
5
0
0
5
10
15
20
Graphite Furnace AAS (GF)
GF, Cochran 5%
GF, Grubb outlier
Other methods
45°
Mean value, sample E
Mean value, sample F


Se, higher conc.
Sample H
Sample G
140
120
100
80
60
40
20
0
0
20
40
60
80
100
120
140
Graphite Furnace AAS (GF)
Other methods
45°
Mean value, sample G
Mean value, sample H


Tl, lower conc.
Sample F
Sample E
0
2
4
6
8
Graphite Furnace AAS (GF)
Other methods
45°
Mean value, sample E
Mean value, sample F


Tl, higher conc.
Sample H
Sample G
0
10
20
30
40
50
Graphite Furnace AAS (GF)
Other methods
45°
Mean value, sample G
Mean value, sample H

V, fresh water (µg/l)

| Lab No. | E | F | Code | Outl./Str. | Lab No. | G | H | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 5 | 11.0 | 11.3 | 0WZ | | 1 | 71.8 | 74.5 | 0+WD | |
| 10 | 13.1 | 13.7 | 0WZ | | 8 | 73.2 | 73.5 | 0W | |
| 32 | 13.5 | 11.0 | 0WZ | | 5 | 81.3 | 84.9 | 0WZ | |
| 1 | <10 | <10 | 0+WD | | 10 | 90.4 | 94.5 | 0WZ | |
| 8 | <10 | <10 | 0W | | 32 | 97.3 | 96.9 | 0WZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **E,F** | 12.3 | 1.0 | 8.4 | 1.4 | 11.1 |
| **G,H** | 83.8 | 1.9 | 2.3 | 11.0 | 13.1 |

V, other methods

| Lab No. | E | F | Code | | Lab No. | G | H | Code |
|---|---|---|---|---|---|---|---|---|
| 19 | 10 | 9.9 | K | | 19 | 80 | 80 | K |
| 44 | 10.03 | 10.05 | K | | 38 | 82.4 | 82.6 | K |
| 38 | 10.2 | 10.3 | K | | 44 | 84.7 | 84.9 | K |
| 2 | <50 | <50 | I | | 2 | 90 | 100 | I |

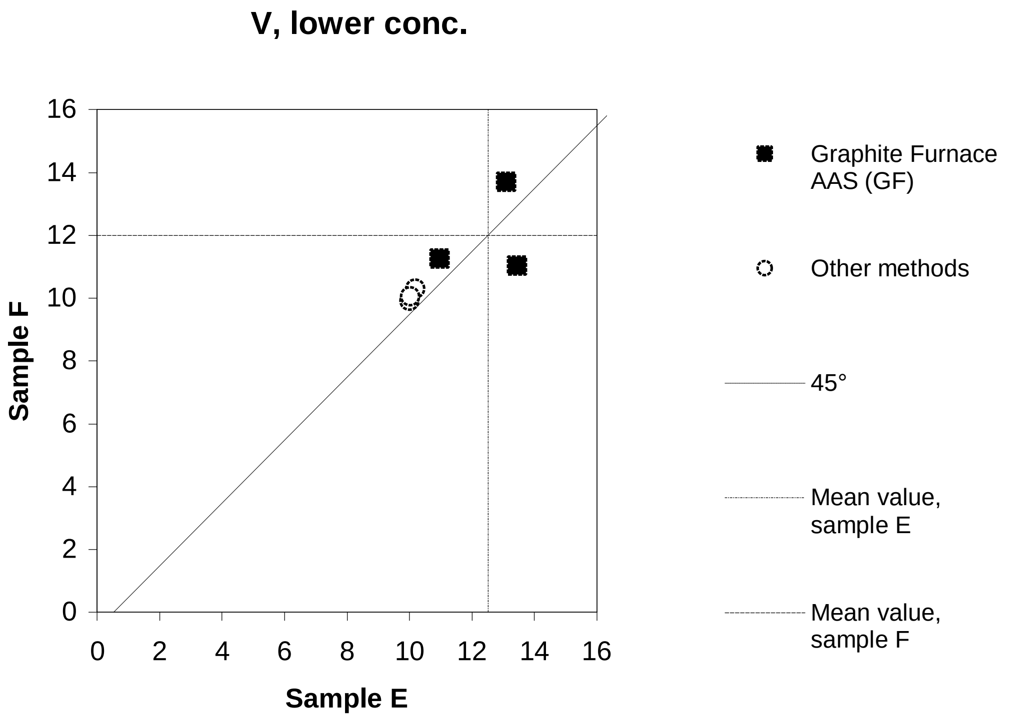
Zn, fresh water (µg/l)

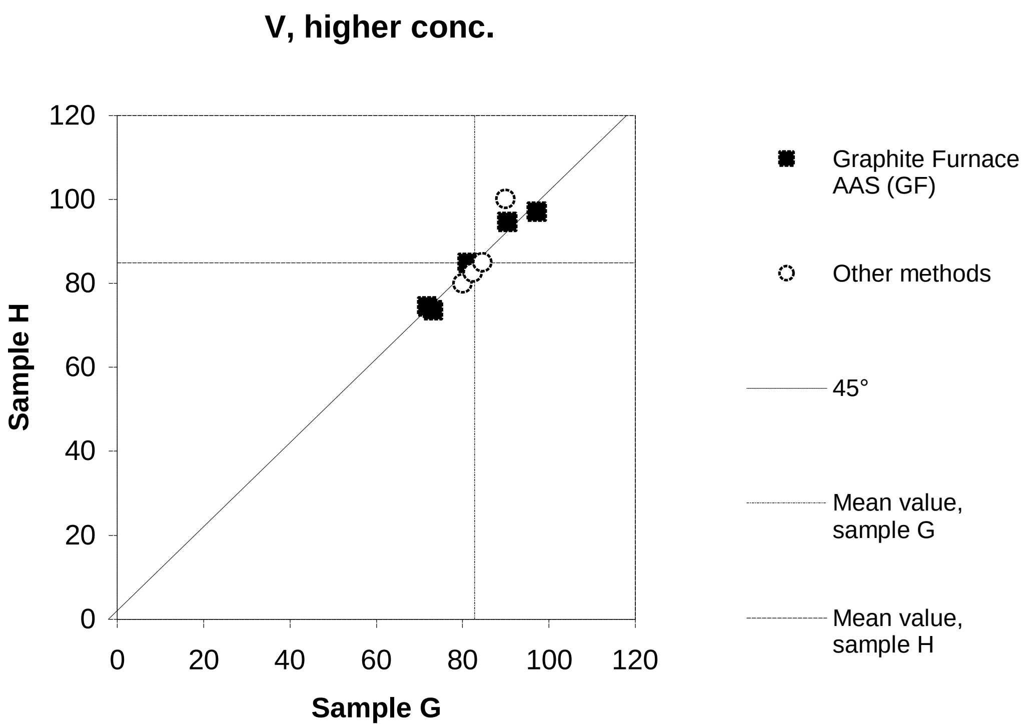
| Lab No. | E | F | Code | Outl./Str. | Lab No. | G | H | Code | Outl./Str. |
|---|---|---|---|---|---|---|---|---|---|
| 42 | 0.643 | 0.556 | 2PZ | | 42 | 3.19 | 2.56 | 2PZ | |
| 29 | 0.8 | 0.7 | 0WD | | 29 | 4.7 | 4.6 | 0WD | |
| 32 | 1.0 | 1.3 | 0WZ | | 5 | 5.39 | 5.95 | 0WZ | |
| 40 | 1 | 2 | 0PZ | C | 32 | 5.8 | 6.0 | 0WZ | |
| 5 | 1.05 | 1.25 | 0WZ | | 40 | 7 | 8 | 0PZ | |
| 17 | 1.584 | 1.666 | 0PZ | | 30 | 7.39 | 7.96 | 0WD | |
| 30 | 1.81 | 1.76 | 0WD | | 17 | 7.526 | 7.742 | 0PZ | |
| 15 | <10 | <10 | ? | | 15 | <10 | <10 | ? | |

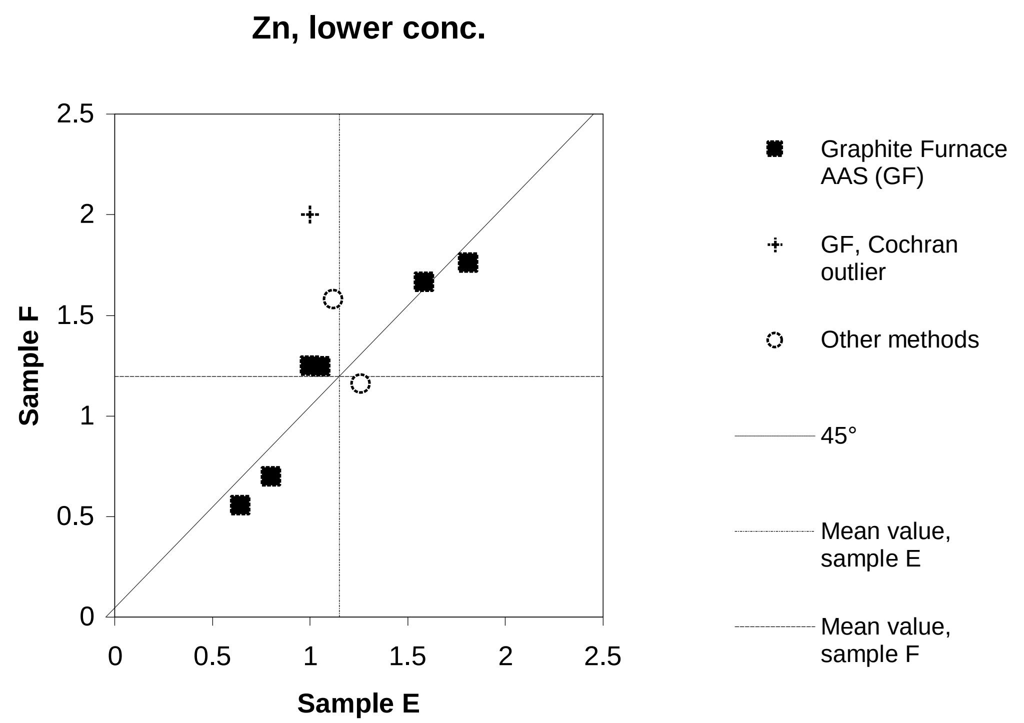
| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **E,F** | 1.17 | 0.10 | 8.8 | 0.47 | 40.3 |
| **G,H** | 5.99 | 0.39 | 6.5 | 1.82 | 30.4 |

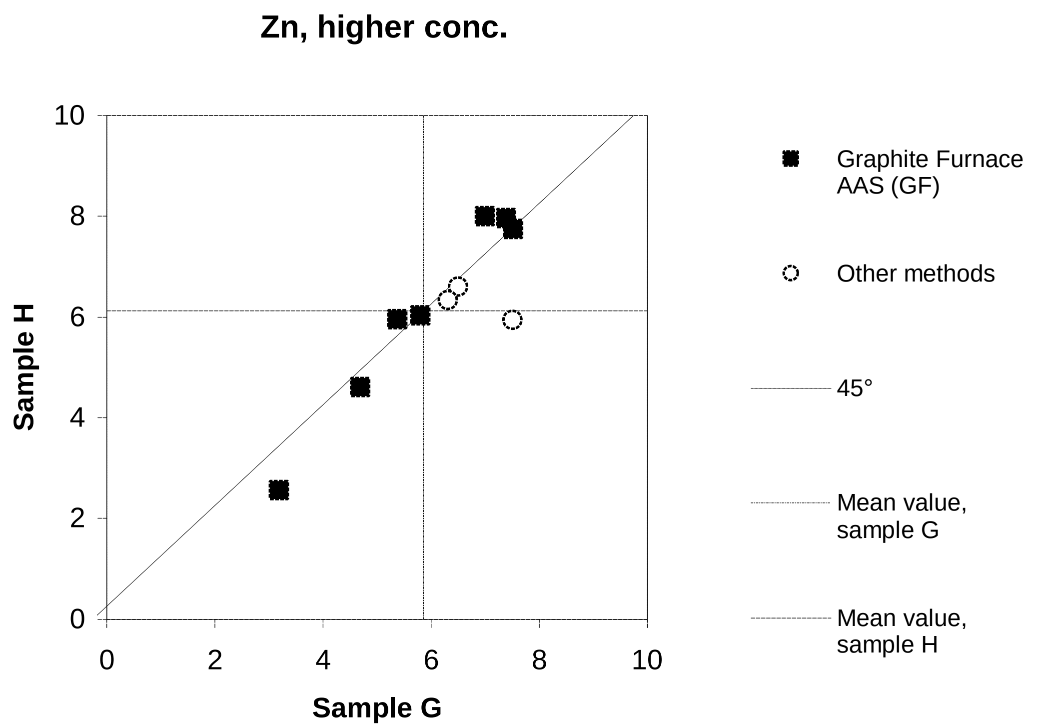
Zn, other methods

| Lab No. | E | F | Code | | Lab No. | G | H | Code |
|---|---|---|---|---|---|---|---|---|
| 19 | 1 | 2 | K | | 38 | 6.32 | 6.33 | K |
| 44 | 1.12 | 1.58 | K | | 19 | 6.5 | 6.6 | K |
| 38 | 1.26 | 1.16 | K | | 44 | 7.51 | 5.94 | K |
| 2 | <10 | <10 | I | | 2 | <10 | <10 | I |


V, lower conc.
16
14
12
10
8
6
4
2
0
Sample F
0
2
4
6
8
10
12
14
16
Sample E
Graphite Furnace AAS (GF)
Other methods
45°
Mean value, sample E
Mean value, sample F


V, higher conc.
120
100
80
60
40
20
0
Sample H
0
20
40
60
80
100
120
Sample G
Graphite Furnace AAS (GF)
Other methods
45°
Mean value, sample G
Mean value, sample H


Zn, lower conc.
Sample F
Sample E
2.5
2
1.5
1
0.5
0
0
0.5
1
1.5
2
2.5
Graphite Furnace AAS (GF)
GF, Cochran outlier
Other methods
45°
Mean value, sample E
Mean value, sample F


Zn, higher conc.
Sample H
Sample G
10
8
6
4
2
0
0
2
4
6
8
10
Graphite Furnace AAS (GF)
Other methods
45°
Mean value, sample G
Mean value, sample H

# Waste water samples

Ag, waste water (µg/l)

| Lab No. | J | K | Code | Outl./Str. |
|---|---|---|---|---|
| 5 | 1.82 | 2.12 | Nm1,2WZ | |
| 40 | 3 | 3 | Na1,2PZ | |
| 40 | 3 | 3 | Aa1,2PZ | |
| 12 | 3.1 | 2.9 | Nm1,2PZ | |
| 10 | 3.44 | 3.31 | Nm2PZ | |
| 29 | 4.8 | 4 | Na0W | |
| 37 | 4.9 | 5.6 | No0WD | |
| 1 | 13.3 | 24.0 | Am0+WD | C |
| 15 | <100 | <100 | Am? | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **J,K** | 3.43 | 0.30 | 8.8 | 1.10 | 32.0 |

Ag, other methods

| Lab No. | J | K | Code |
|---|---|---|---|
| 19 | 2.6 | 2.6 | NmK |
| 2 | 10 | <10 | N?I |

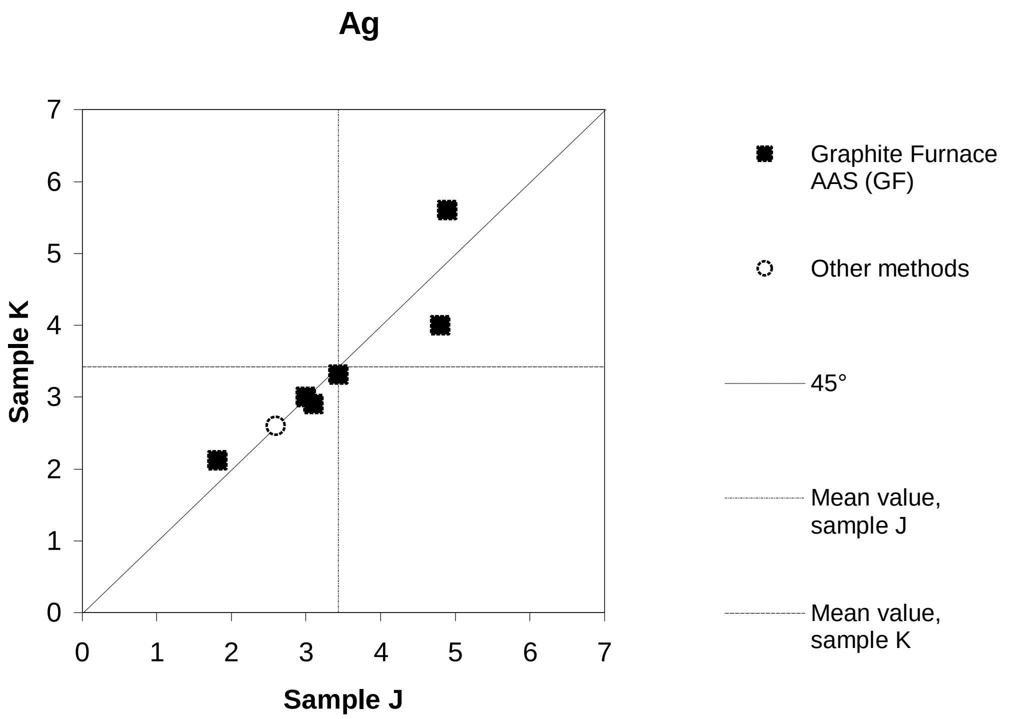
Al, waste water (µg/l)

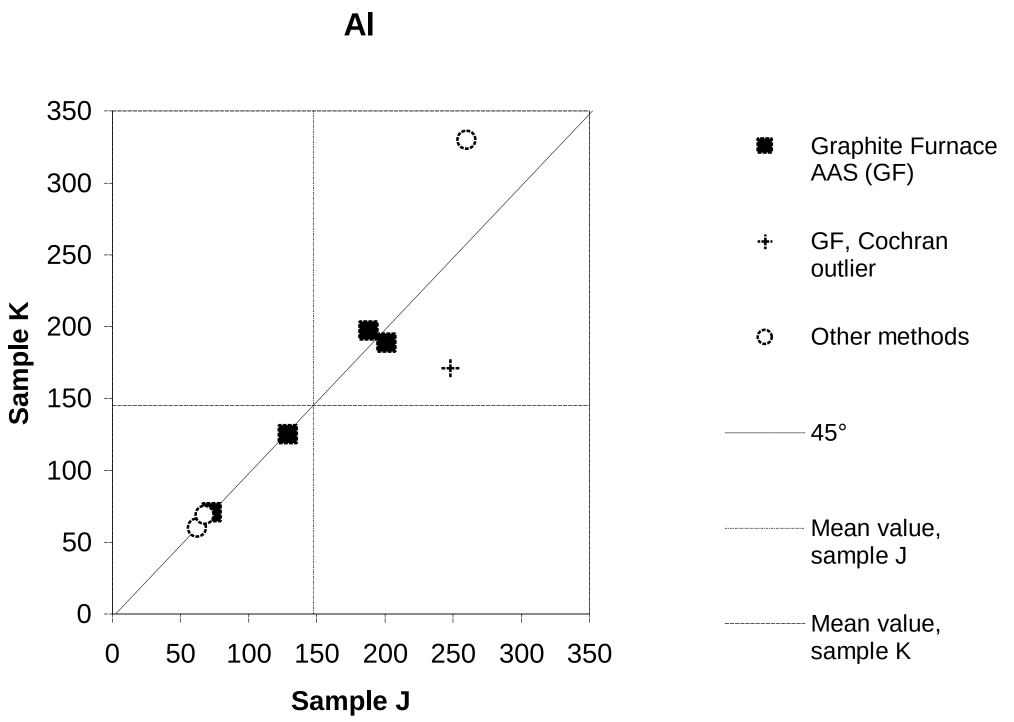
| Lab No. | J | K | Code | Outl./Str. |
|---|---|---|---|---|
| 10 | 72.9 | 70.9 | Nm2PZ | |
| 15 | 129 | 125 | Am? | |
| 5 | 188 | 197 | Nm0WZ | |
| 8 | 201.1 | 188.5 | Nm2W | |
| 29 | 248 | 171 | Na0W | C |
| 1 | 414 | 973 | Am0+WD | C |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **J,K** | 147 | 5.7 | 3.9 | 59 | 40.3 |

Al, other methods

| Lab No. | J | K | Code |
|---|---|---|---|
| 3 | 62.5 | 60 | AmI |
| 19 | 68 | 69 | NmK |
| 2 | 260 | 330 | N?I |


Ag
Sample K
Sample J
0
1
2
3
4
5
6
7
Graphite Furnace AAS (GF)
Other methods
45°
Mean value, sample J
Mean value, sample K


Al
Sample K
Sample J
0
50
100
150
200
250
300
350
Graphite Furnace AAS (GF)
GF, Cochran outlier
Other methods
45°
Mean value, sample J
Mean value, sample K

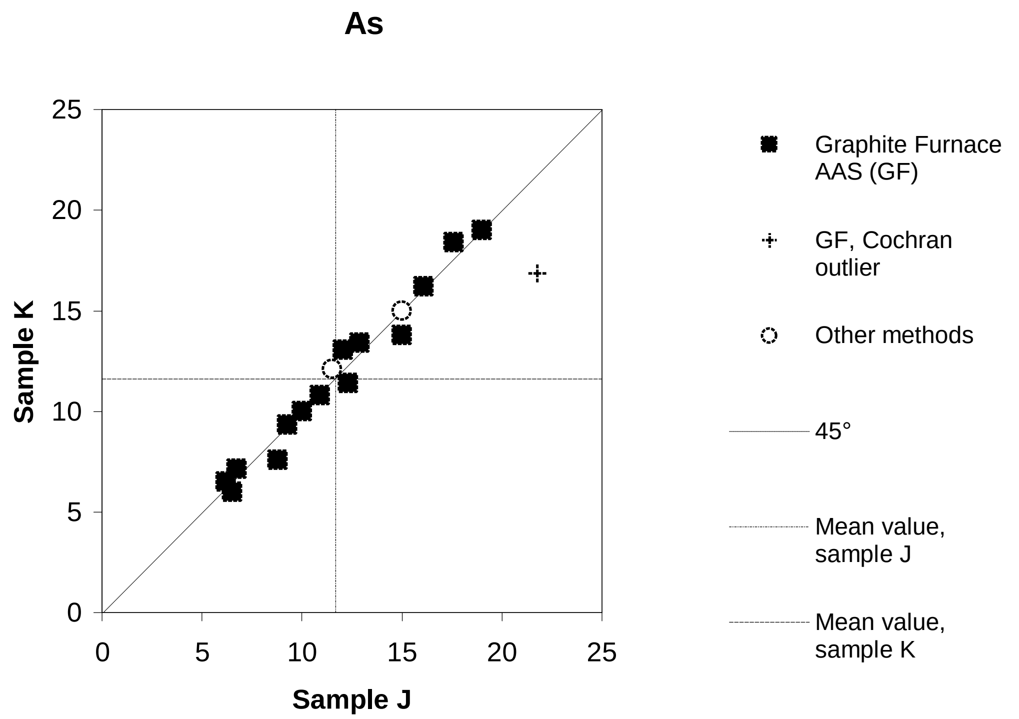
As, waste water (µg/l)

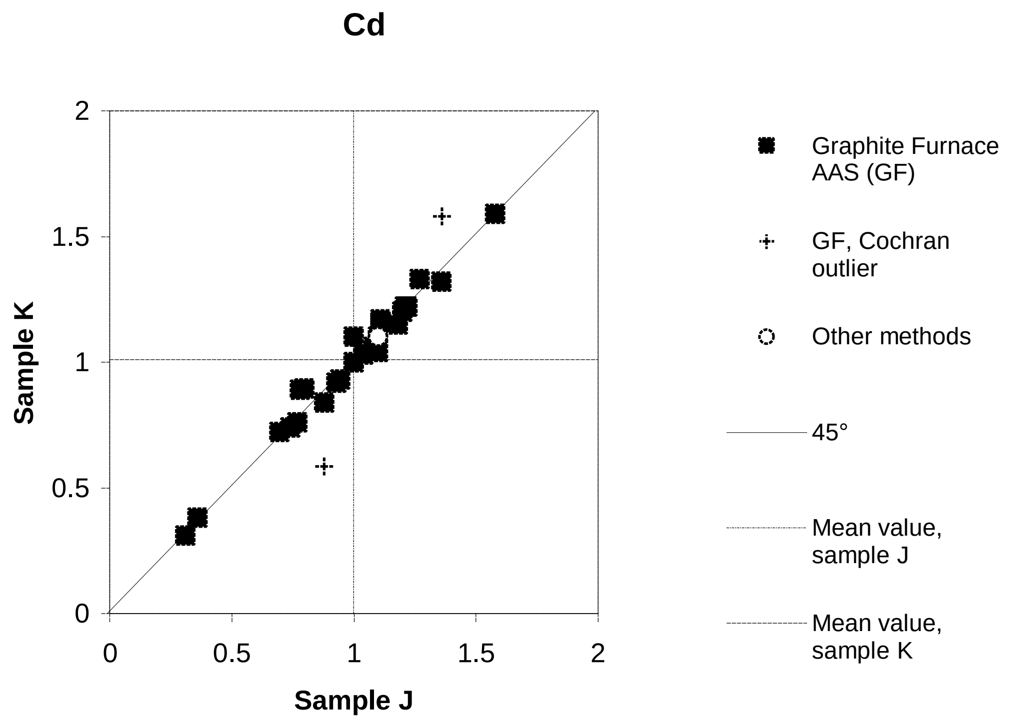
| Lab No. | J | K | Code | Outl./Str. |
|---|---|---|---|---|
| 24 | 6.2 | 6.5 | Nm1+WZ | |
| 7 | 6.5 | 6 | Ac1,2PD | |
| 16 | 6.74 | 7.16 | Am1PZ | |
| 12 | 8.8 | 7.6 | Nm1,2PZ | |
| 5 | 9.27 | 9.35 | Nm1WZ | |
| 2 | 10 | <10 | N4WD | |
| 19 | 10 | 10 | Nm1,2PZ | |
| 3 | 10.9 | 10.8 | Am1,2PZ | |
| 16 | 12.04 | 13.06 | Nm1PZ | |
| 35 | 12.3 | 11.4 | Na1,2PZ | |
| 10 | 12.9 | 13.4 | Nm1,2PZ | |
| 11 | 15.0 | 13.8 | Nm1,2PZ | |
| 26 | 16.1 | 16.2 | Nm1,2+PZ | |
| 27 | 17.6 | 18.4 | Na1,2PZ | |
| 9 | 19 | 19 | Na1,2WD | |
| 41 | 21.78 | 16.87 | Nm1,2PZ | C |
| 1 | <53 | <53 | Am1+WD | |
| 15 | <20 | <20 | Am? | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **J,K** | 11.6 | 0.47 | 4.0 | 4.2 | 35.9 |

As, other methods

| Lab No. | J | K | Code |
|---|---|---|---|
| 23 | 11.5 | 12.1 | NmH |
| 19 | 15 | 15 | NmK |


As
Sample K
Sample J
0
5
10
15
20
25
Graphite Furnace AAS (GF)
GF, Cochran outlier
Other methods
45°
Mean value, sample J
Mean value, sample K


Cd
Sample K
Sample J
0
0.5
1
1.5
2
Graphite Furnace AAS (GF)
GF, Cochran outlier
Other methods
45°
Mean value, sample J
Mean value, sample K

Cd, waste water (µg/l)

| Lab No. | J | K | Code | Outl./Str. |
|---|---|---|---|---|
| 22 | 0.31 | 0.31 | Nm1,2WD | |
| 7 | 0.36 | 0.38 | Ac1,2PD | |
| 35 | 0.697 | 0.721 | Na3PZ | |
| 37 | 0.74 | 0.74 | No0WD | |
| 9 | 0.77 | 0.76 | Na1,2WD | |
| 6 | 0.78 | 0.89 | No2,3PZ | |
| 30 | 0.798 | 0.896 | Na1WD | |
| 8 | 0.879 | 0.587 | Nm1,2WD | C |
| 26 | 0.88 | 0.84 | Nm2,3+PZ | |
| 5 | 0.928 | 0.918 | Nm3WZ | |
| 20 | 0.945 | 0.93 | Nm1,2WZ | |
| 14 | 1 | 1.1 | Ne0?Z | |
| 40 | 1 | 1 | Na2,3PZ | |
| 40 | 1 | 1 | Aa2,3PZ | |
| 3 | 1.04 | 1.03 | Am2,3PZ | |
| 10 | 1.08 | 1.06 | Nm2,3PZ | |
| 24 | 1.1 | 1.1 | Nm1+WZ | |
| 29 | 1.1 | 1.04 | Na2,3PZ | |
| 39 | 1.11 | 1.17 | Na2,3WZ | |
| 41 | 1.11 | 1.16 | Nm2,3PZ | |
| 11 | 1.18 | 1.15 | Nm2,3PZ | |
| 13 | 1.2 | 1.2 | Am6PZ | |
| 19 | 1.2 | 1.2 | Nm0PZ | |
| 36 | 1.21 | 1.22 | N?2,3WD | |
| 12 | 1.22 | 1.22 | Nm1,2,3PZ | |
| 27 | 1.27 | 1.33 | Na2,3PZ | |
| 16 | 1.36 | 1.58 | Nm3PZ | C |
| 23 | 1.36 | 1.32 | Nm0+WZ | |
| 16 | 1.58 | 1.59 | Am3PZ | |
| 1 | <6,7 | <6,7 | Am0+WD | |
| 2 | <2 | <2 | N1,2WD | |
| 15 | <4 | <4 | Am? | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **J,K** | 0.989 | 0.028 | 2.8 | 0.297 | 30.0 |

Cd, other methods

| Lab No. | J | K | Code |
|---|---|---|---|
| 19 | 1.1 | 1.1 | NmK |

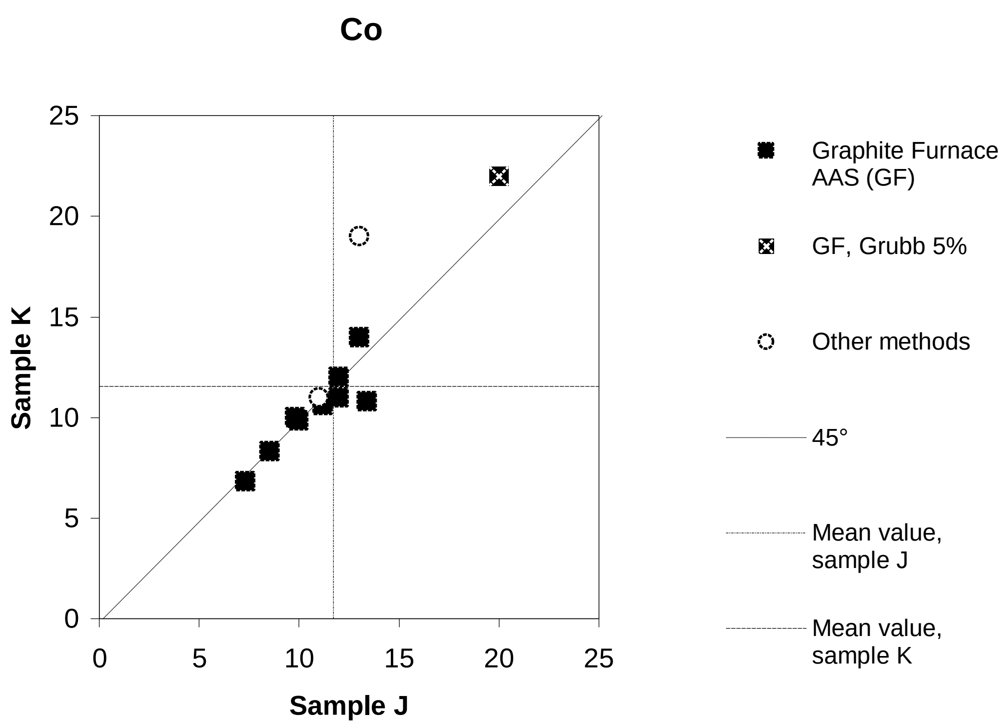
Co, waste water (µg/l)

| Lab No. | J | K | Code | Outl./Str. |
|---|---|---|---|---|
| 8 | 7.32 | 6.84 | Nm2WD | |
| 3 | 8.54 | 8.33 | Am0PZ | |
| 15 | 9.8 | 10 | Am? | |
| 10 | 9.98 | 9.86 | Nm2WZ | |
| 5 | 11.2 | 10.6 | Nm2WZ | |
| 19 | 12 | 12 | Nm0PZ | |
| 40 | 12 | 11 | Aa2PZ | |
| 40 | 13 | 14 | Na2PZ | |
| 29 | 13.4 | 10.8 | Na0WD | |
| 1 | 20.0 | 22.0 | Am0+WD | G 5% |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **J,K** | 11.6 | 0.82 | 7.0 | 3.8 | 32.9 |

Co, other methods

| Lab No. | J | K | Code |
|---|---|---|---|
| 19 | 11 | 11 | NmK |
| 2 | 13 | 19 | N?I |
| 3 | <62,5 | <62,5 | AmI |



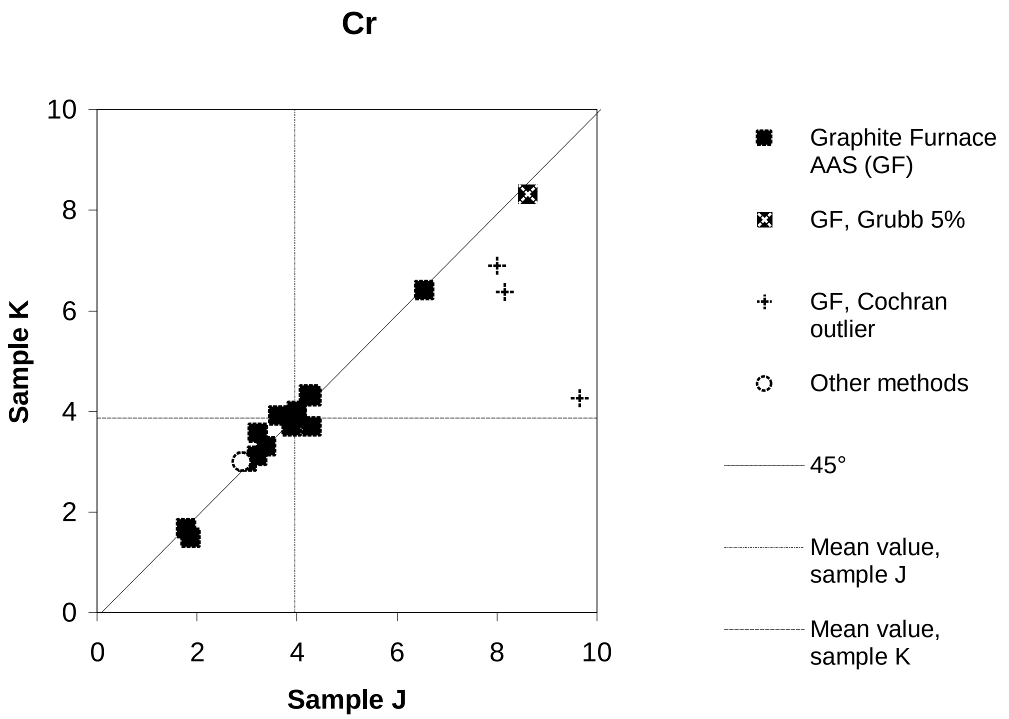
## Cr, waste water (μg/l)

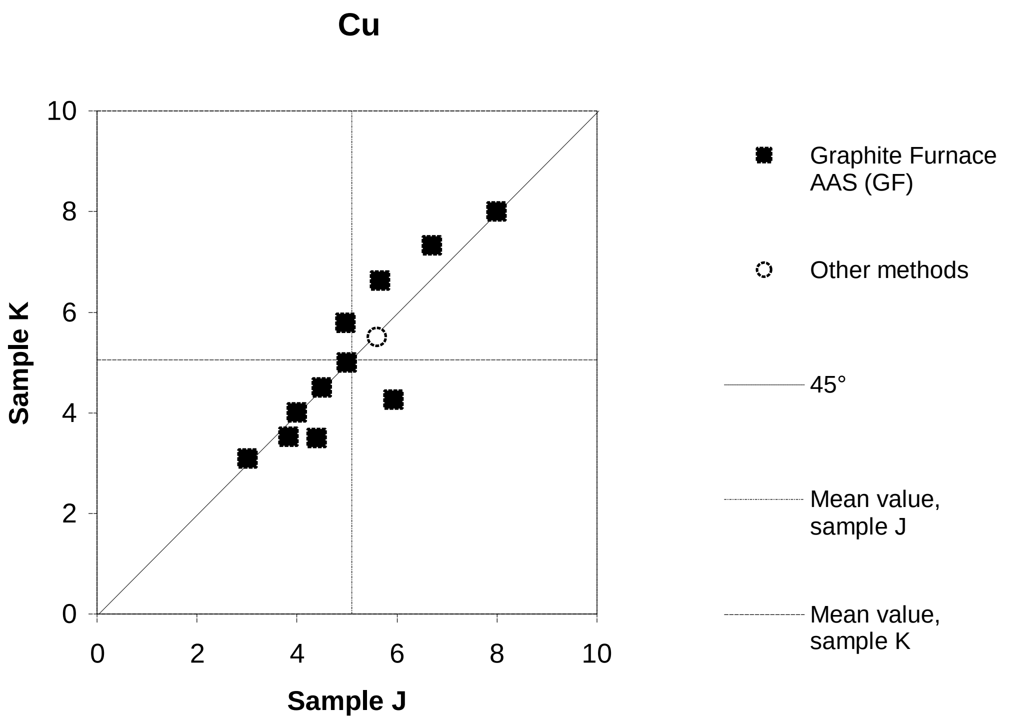
| Lab No. | J | K | Code | Outl./Str. |
|---|---|---|---|---|
| 12 | 1.78 | 1.67 | Nm2PZ | |
| 16 | 1.88 | 1.48 | Am1WZ | |
| 40 | 3 | 3 | Na2PZ | |
| 27 | 3.2 | 3.11 | Na2PZ | |
| 5 | 3.21 | 3.12 | Nm2WZ | |
| 3 | 3.22 | 3.57 | Am2,3PZ | |
| 26 | 3.38 | 3.3 | Nm0+PZ | |
| 35 | 3.63 | 3.91 | Na2PZ | |
| 6 | 3.9 | 3.7 | No2PZ | |
| 11 | 4.0 | 3.9 | Nm2PZ | |
| 19 | 4 | 4 | Nm0PZ | |
| 40 | 4 | 4 | Aa2PZ | |
| 10 | 4.25 | 4.34 | Nm2WZ | |
| 8 | 4.3 | 3.7 | Nm2W | |
| 9 | 4.3 | 4.3 | Na2W | |
| 30 | 6.55 | 6.41 | Na2W | |
| 29 | 8 | 6.9 | Na0W | C |
| 41 | 8.16 | 6.38 | Nm2PZ | C |
| 23 | 8.62 | 8.32 | Nm0+WZ | G 5% |
| 16 | 9.66 | 4.26 | Nm1WZ | C |
| 1 | 55.3 | 45.3 | Am3+WD | C |
| 15 | <10 | <10 | Am? | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **J,K** | 3.80 | 0.16 | 4.3 | 1.66 | 43.6 |

## Cr, other methods

| Lab No. | J | K | Code |
|---|---|---|---|
| 19 | 2.9 | 3.0 | NmK |
| 2 | <10 | <10 | N?I |


Cr
10
8
6
4
2
0
0
2
4
6
8
10
Sample K
Sample J
Graphite Furnace AAS (GF)
GF, Grubb 5%
GF, Cochran outlier
Other methods
45°
Mean value, sample J
Mean value, sample K


Cu
10
8
6
4
2
0
0
2
4
6
8
10
Sample K
Sample J
Graphite Furnace AAS (GF)
Other methods
45°
Mean value, sample J
Mean value, sample K

Cu, waste water (µg/l)

| Lab No. | J | K | Code | Outl./Str. |
|---|---|---|---|---|
| 27 | 3.02 | 3.09 | Na1,2PZ | |
| 10 | 3.84 | 3.52 | Nm1,2WZ | |
| 40 | 4 | 4 | Na1,2PZ | |
| 16 | 4.4 | 3.5 | Am1WZ | |
| 11 | 4.5 | 4.5 | Nm0PZ | |
| 3 | 4.98 | 5.79 | Am1,2PZ | |
| 19 | 5 | 5 | Nm0PZ | |
| 41 | 5.66 | 6.63 | Nm1,2PZ | |
| 16 | 5.94 | 4.26 | Nm1WZ | |
| 5 | 6.71 | 7.32 | Nm0WZ | |
| 40 | 8 | 8 | Aa1,2PZ | |
| 29 | 39.9 | 7.4 | Na0PZ | C |
| 1 | <53 | <53 | Am0+WD | |
| 15 | <40 | <40 | Am? | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **J,K** | 5.08 | 0.51 | 10.0 | 1.54 | 30.3 |

Cu, other methods

| Lab No. | J | K | Code |
|---|---|---|---|
| 19 | 5.6 | 5.5 | NmK |
| 2 | <10 | <10 | N?I |

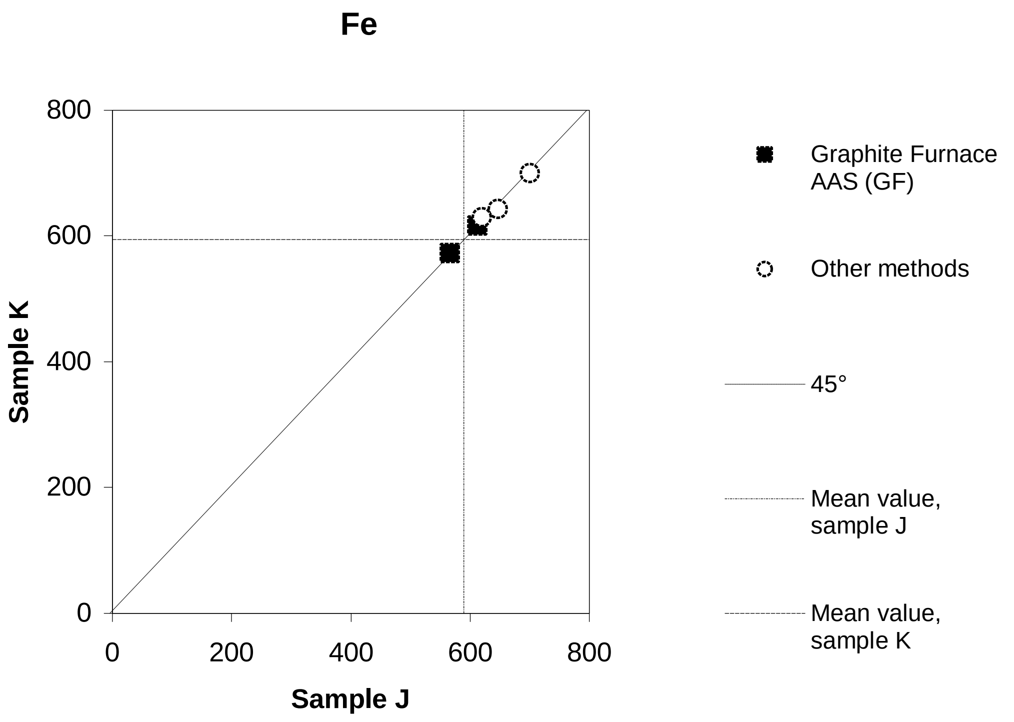
Fe, waste water (µg/l)

| Lab No. | J | K | Code | Outl./Str. |
|---|---|---|---|---|
| 5 | 566 | 572 | Nm0WZ | |
| 15 | 613 | 616 | Am? | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **J,K** | 592 | - | - | - | - |

Fe, other methods

| Lab No. | J | K | Code |
|---|---|---|---|
| 19 | 620 | 629 | NmK |
| 3 | 647 | 643 | AmI |
| 2 | 700 | 700 | N?I |



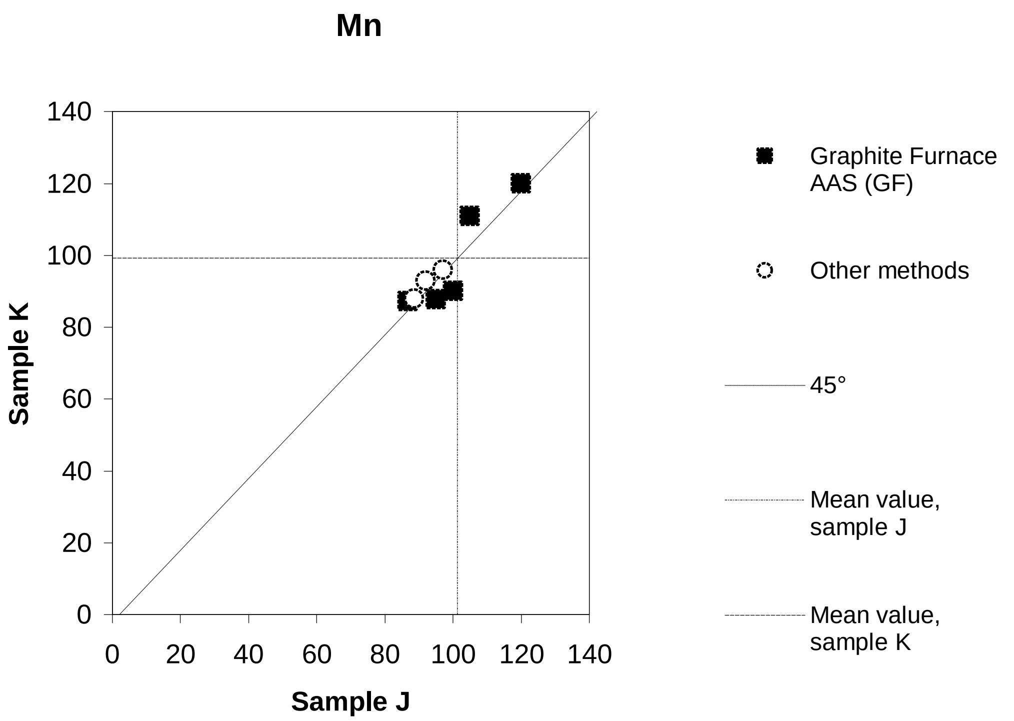
## Mn, waste water (µg/l)

| Lab No. | J | K | Code | Outl./Str. |
|---|---|---|---|---|
| 15 | 86.7 | 87.2 | Am? | |
| 29 | 94.9 | 87.8 | Na0WD | |
| 40 | 100 | 90 | Aa1,2PZ | |
| 5 | 105 | 111 | Nm0WZ | |
| 40 | 120 | 120 | Na1,2PZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **J,K** | 100 | 4.3 | 4.3 | 14 | 13.8 |

## Mn, other methods

| Lab No. | J | K | Code |
|---|---|---|---|
| 3 | 88.5 | 88 | AmI |
| 19 | 92 | 93 | NmK |
| 2 | 97 | 96 | N?I |



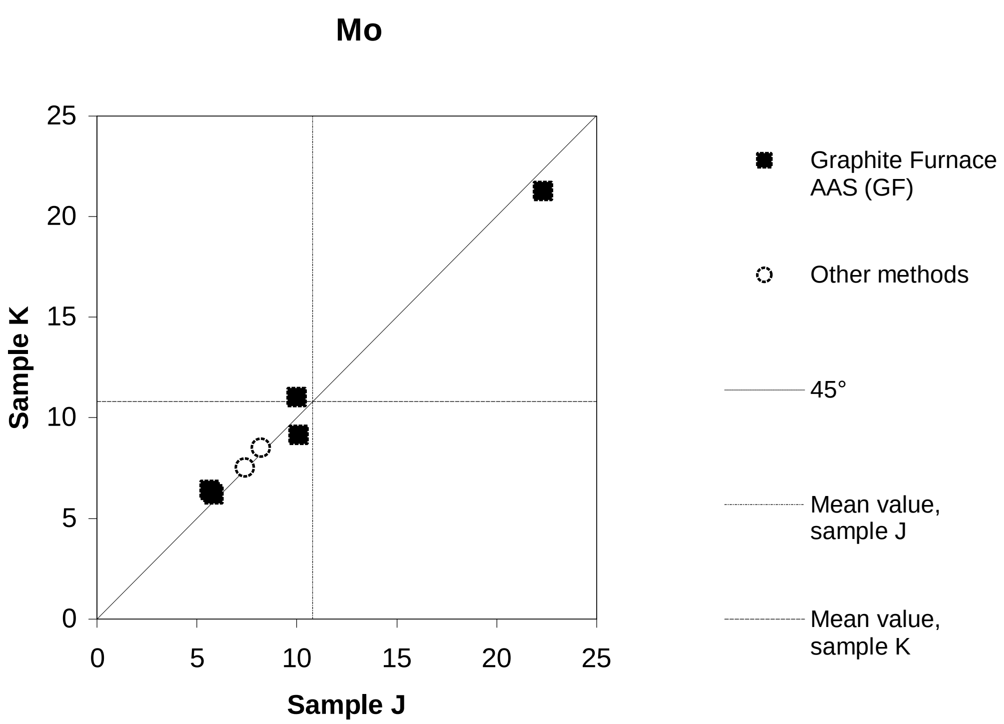
Mo, waste water (µg/l)

| Lab No. | J | K | Code | Outl./Str. |
|---|---|---|---|---|
| 3 | 5.65 | 6.39 | Am0PZ | |
| 5 | 5.85 | 6.17 | Nm0WZ | |
| 15 | 10 | 11 | Am? | |
| 10 | 10.1 | 9.15 | Nm0WZ | |
| 8 | 22.32 | 21.26 | Nm0W | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **J,K** | 10.8 | 0.61 | 5.6 | 6.5 | 60.2 |

Mo, other methods

| Lab No. | J | K | Code |
|---|---|---|---|
| 19 | 7.4 | 7.5 | NmK |
| 24 | 8.2 | 8.5 | NmI |
| 2 | <50 | <50 | N?I |
| 3 | <62,5 | <62,5 | AmI |



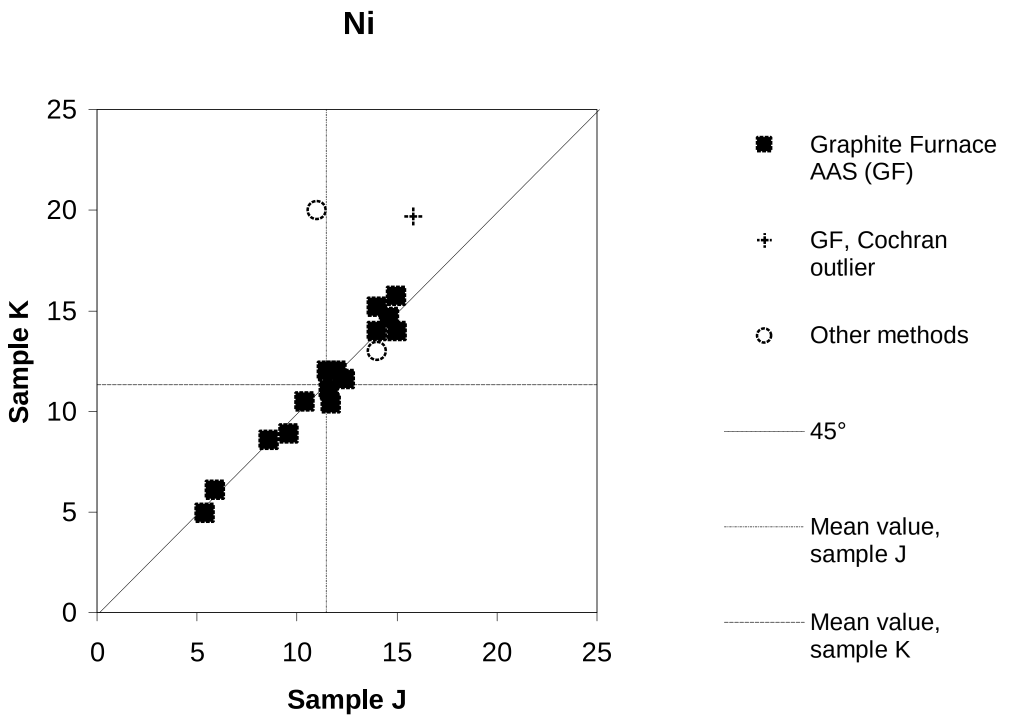
Ni, waste water (µg/l)

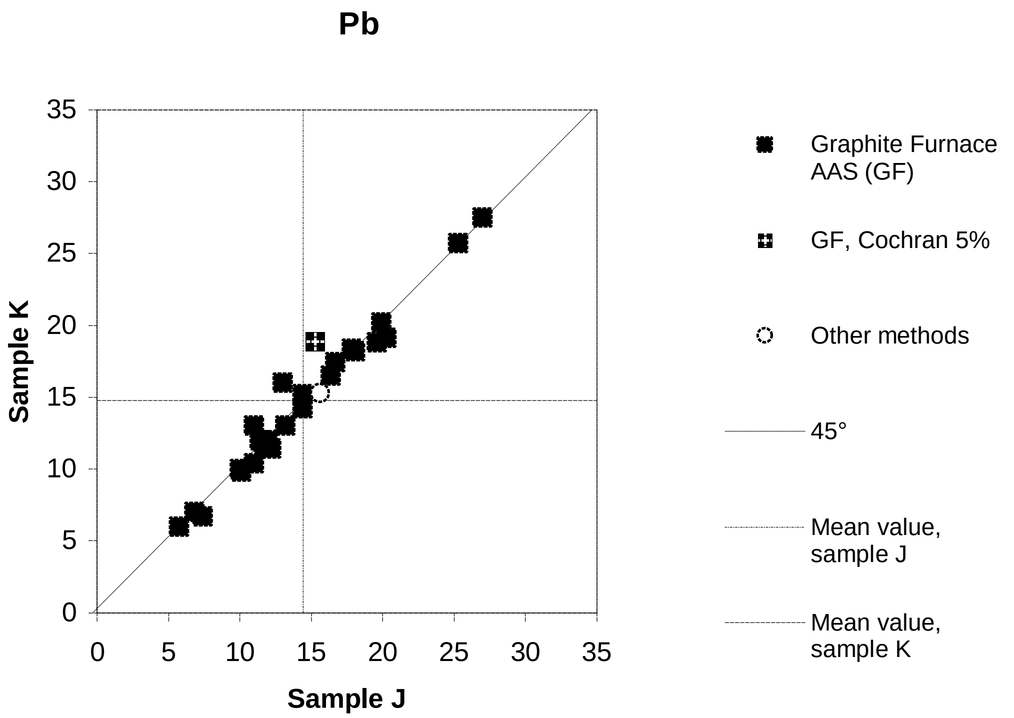
| Lab No. | J | K | Code | Outl./Str. |
|---|---|---|---|---|
| 8 | 5.4 | 4.94 | Nm2WD | |
| 22 | 5.9 | 6.1 | Nm1,2WD | |
| 30 | 8.59 | 8.57 | Na0WD | |
| 29 | 9.6 | 8.9 | Na0PD | |
| 27 | 10.4 | 10.5 | Na0PZ | |
| 15 | 11.5 | 12 | Am? | |
| 12 | 11.6 | 11.1 | Nm2PZ | |
| 31 | 11.7 | 10.4 | Nm0PD | |
| 19 | 12 | 12 | Nm0PZ | |
| 5 | 12.4 | 11.6 | Nm0WZ | |
| 10 | 14 | 15.2 | Nm2WZ | |
| 40 | 14 | 14 | Na0PZ | |
| 3 | 14.6 | 14.7 | Am1,2PZ | |
| 41 | 14.98 | 15.73 | Nm2PZ | |
| 40 | 15 | 14 | Aa0PZ | |
| 35 | 15.8 | 19.7 | Na2PZ | C |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **J,K** | 11.4 | 0.47 | 4.1 | 3.1 | 27.5 |

Ni, other methods

| Lab No. | J | K | Code |
|---|---|---|---|
| 2 | 11 | 20 | N?I |
| 19 | 14 | 13 | NmK |


Ni
Sample K
Sample J
0
5
10
15
20
25
Graphite Furnace AAS (GF)
GF, Cochran outlier
Other methods
45°
Mean value, sample J
Mean value, sample K


Pb
Sample K
Sample J
0
5
10
15
20
25
30
35
Graphite Furnace AAS (GF)
GF, Cochran 5%
Other methods
45°
Mean value, sample J
Mean value, sample K

## Pb, waste water (µg/l)

| Lab No. | J | K | Code | Outl./Str. |
|---|---|---|---|---|
| 22 | 5.7 | 6.0 | Nm1,2WD | |
| 16 | 6.82 | 7.02 | Am3PZ | |
| 7 | 7.4 | 6.7 | Ac1,2PD | |
| 40 | 10 | 10 | Aa2,3PZ | |
| 9 | 10.1 | 9.8 | Na1,2WD | |
| 27 | 11 | 10.4 | Na2,3PZ | |
| 40 | 11 | 13 | Na2,3PZ | |
| 30 | 11.4 | 12 | Na1WD | |
| 35 | 11.7 | 11.7 | Na3PZ | |
| 19 | 12 | 12 | Nm0PZ | |
| 5 | 12.2 | 11.4 | Nm3WZ | |
| 2 | 13 | 16 | N2,3WD | |
| 13 | 13.2 | 13 | Am2,3PZ | |
| 3 | 14.4 | 15.2 | Am1,2PZ | |
| 12 | 14.4 | 14.2 | Nm1,2,3PZ | |
| 41 | 15.28 | 18.89 | Nm2,3PZ | C 5% |
| 29 | 16.4 | 16.5 | Na2,3PZ | |
| 39 | 16.7 | 17.4 | Na2,3WZ | |
| 23 | 17.84 | 18.34 | Nm0+WZ | |
| 26 | 18.1 | 18.2 | Nm2,3+PZ | |
| 10 | 19.6 | 18.8 | Nm2,3PZ | |
| 11 | 19.9 | 20.2 | Nm2,3PZ | |
| 6 | 20.3 | 19.1 | No2,3PZ | |
| 15 | 25.3 | 25.7 | Am? | |
| 20 | 27 | 27.5 | Nm2,3WZ | |
| 8 | 85.24 | 46.83 | Nm1,2WD | C |
| 1 | 116 | 135 | Am0+WD | C |
| 16 | M | 13.42 | Nm3PZ | |

| | **General mean** | $s_r$ | **$CV_r$, %** | $s_R$ | **$CV_R$, %** |
|---|---|---|---|---|---|
| **J,K** | 14.2 | 0.34 | 2.4 | 5.6 | 39.8 |

## Pb, other methods

| Lab No. | J | K | Code |
|---|---|---|---|
| 19 | 15.6 | 15.3 | NmK |

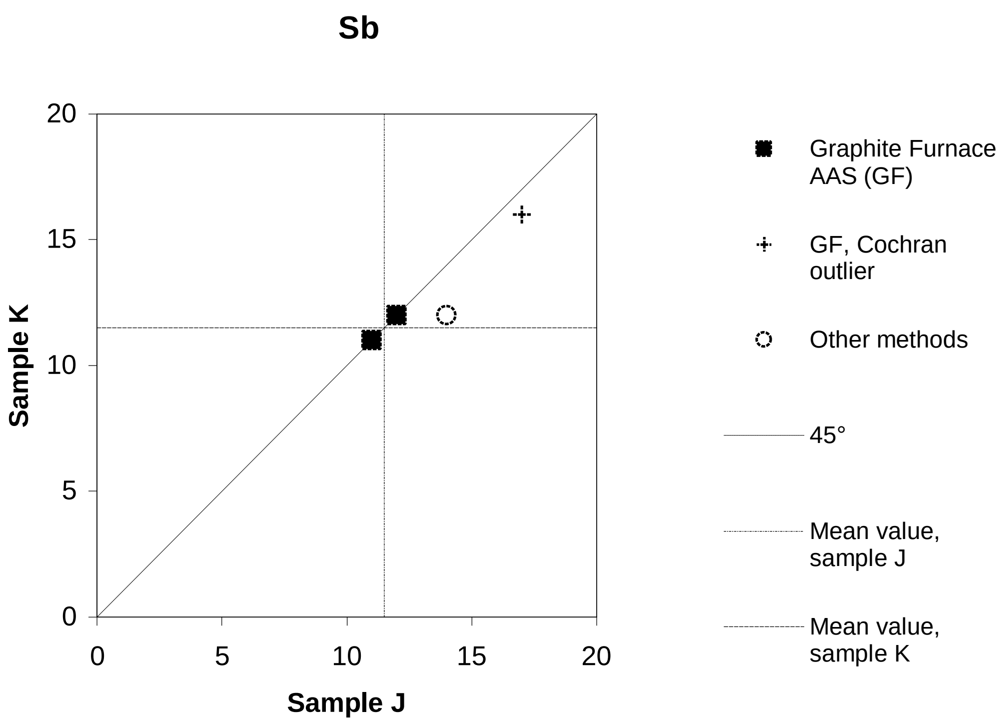
Sb, waste water (µg/l)

| Lab No. | J | K | Code | Outl./Str. |
|---|---|---|---|---|
| 19 | 11 | 11 | Nm1,2PZ | |
| 24 | 12 | 12 | Nm1+WZ | |
| 2 | 17 | 16 | N4WD | C |
| 1 | <133 | <133 | Am0+WD | |
| 5 | <10 | <10 | Nm1,2WZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **J,K** | 11.5 | - | - | - | - |

Sb, other methods

| Lab No. | J | K | Code |
|---|---|---|---|
| 19 | 14 | 12 | NmK |
| 3 | <250 | <250 | AmI |



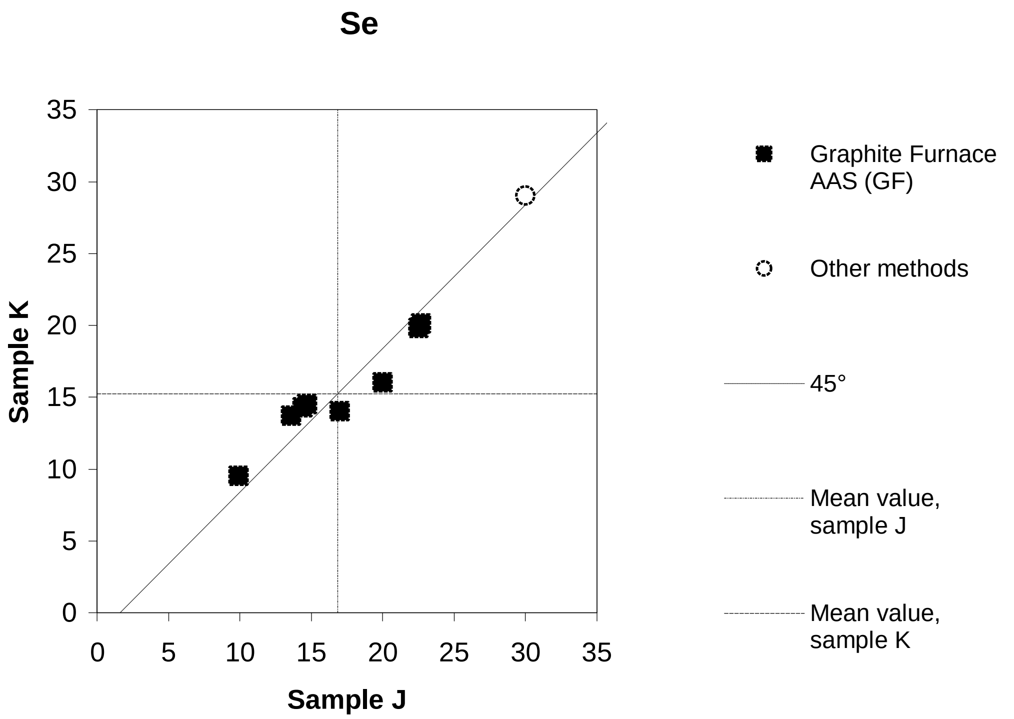
Se, waste water (µg/l)

| Lab No. | J | K | Code | Outl./Str. |
|---|---|---|---|---|
| 24 | 9.9 | 9.5 | Nm1+WZ | |
| 12 | 13.6 | 13.7 | Nm1,2PZ | |
| 26 | 14.4 | 14.3 | Nm1,2+PZ | |
| 10 | 14.7 | 14.5 | Nm1,2PZ | |
| 19 | 17 | 14 | Nm1,2PZ | |
| 2 | 20 | 16 | N1,2WD | |
| 15 | 22.5 | 19.8 | Am? | |
| 5 | 22.7 | 20.1 | Nm1,2WZ | |
| 1 | <67 | <67 | Am1+WD | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **J,K** | 16.0 | 1.6 | 9.8 | 4.1 | 25.6 |

Se, other methods

| Lab No. | J | K | Code |
|---|---|---|---|
| 19 | 30 | 29 | NmK |



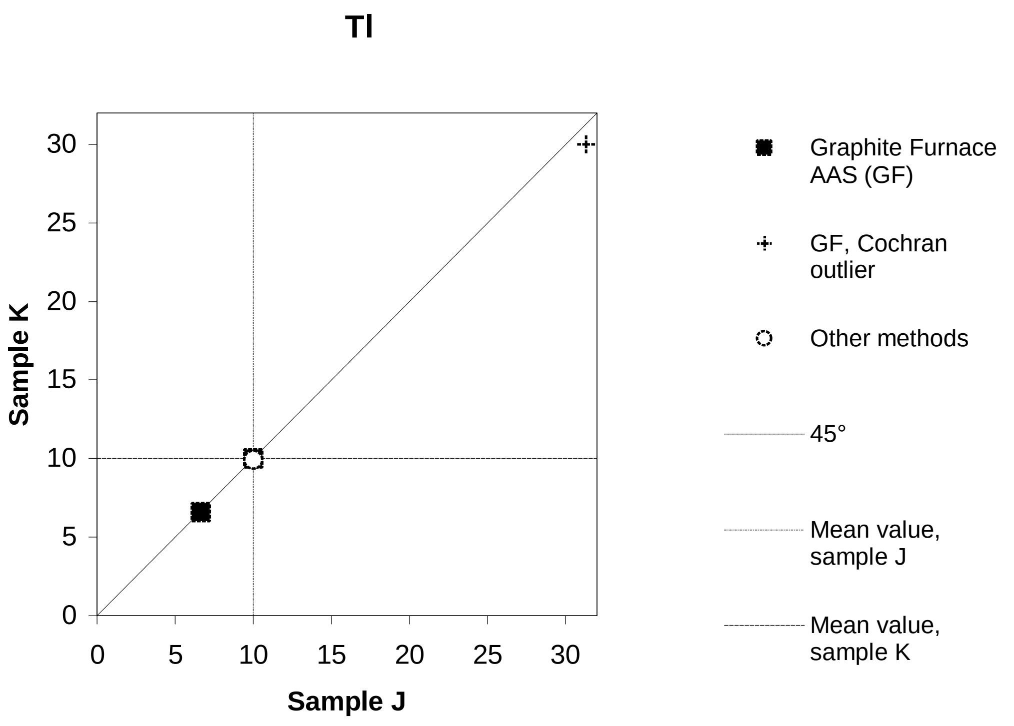
Tl, waste water (µg/l)

| Lab No. | J | K | Code | Outl./Str. |
|---|---|---|---|---|
| 5 | 6.67 | 6.58 | Nm0WZ | |
| 19 | 10 | 10 | Nm1,2PZ | |
| 1 | 31.3 | 30.0 | Am0+PD | C |
| 6 | <10 | <10 | No1,2PZ | |
| 2 | <10 | <10 | N0WD | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **J,K** | 8.31 | - | - | - | - |

Tl, other methods

| Lab No. | J | K | Code |
|---|---|---|---|
| 19 | 10 | 9.9 | NmK |



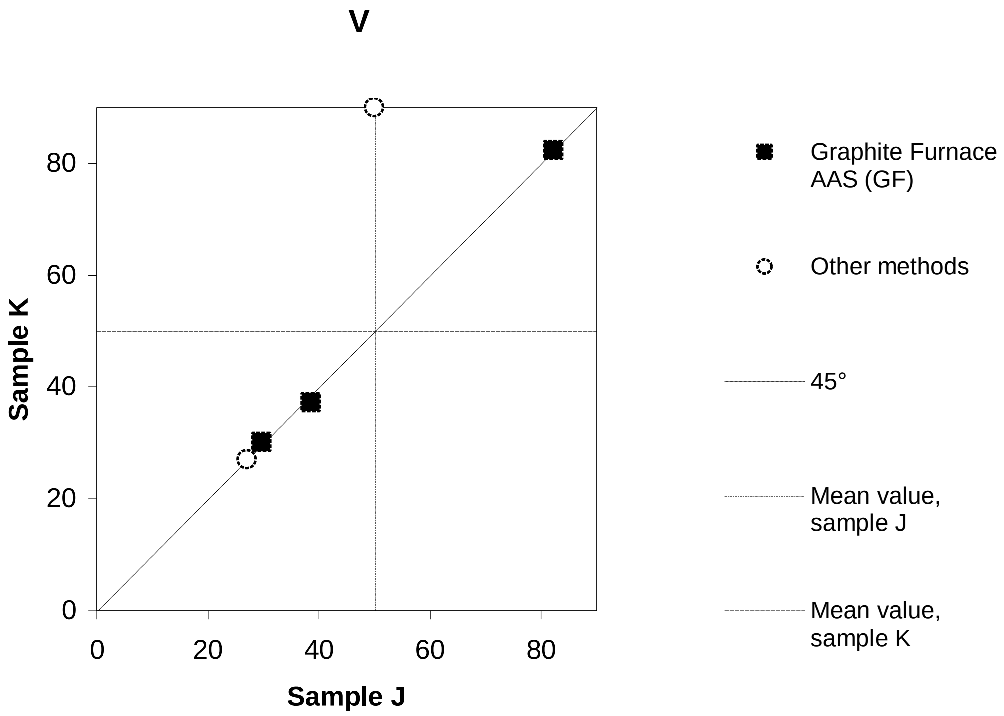
## V, waste water (µg/l)

| Lab No. | J | K | Code | Outl./Str. |
|---|---|---|---|---|
| 5 | 29.7 | 30.2 | Nm0WZ | |
| 10 | 38.5 | 37.2 | Nm0WZ | |
| 8 | 82.2 | 82.4 | Nm0W | |
| 1 | <67 | <67 | Am0+WD | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **J,K** | 50.0 | 0.57 | 1.1 | 28.2 | 56.4 |

## V, other methods

| Lab No. | J | K | Code |
|---|---|---|---|
| 19 | 27 | 27 | NmK |
| 2 | 50 | 90 | N?I |



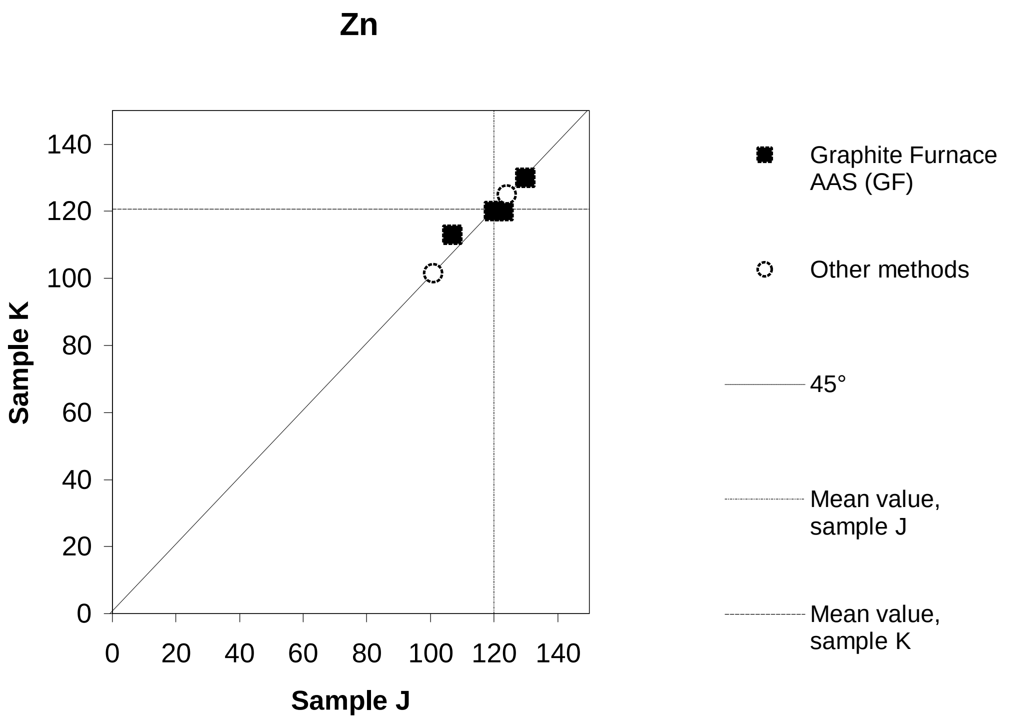
Zn, waste water (µg/l)

| Lab No. | J | K | Code | Outl./Str. |
|---|---|---|---|---|
| 15 | 107 | 113 | Am? | |
| 40 | 120 | 120 | Na0PZ | |
| 5 | 123 | 120 | Nm0WZ | |
| 40 | 130 | 130 | Aa0PZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **J,K** | 120 | 2.4 | 2.0 | 8.4 | 7.0 |

Zn, other methods

| Lab No. | J | K | Code |
|---|---|---|---|
| 3 | 101 | 101.5 | AmI |
| 2 | 120 | 170 | N?I |
| 19 | 124 | 125 | NmK |



# Sediment $HNO_3$ digest

Ag, digest (µg/l)

| Lab No. | L | M | Code | Outlier |
|---|---|---|---|---|
| 12 | 0.5 | 0.5 | 1,2PZ | |
| 32 | 0.59 | 0.48 | 1,2WZ | |
| 10 | 0.66 | 0.50 | 2PZ | |
| 37 | 1 | 1.2 | 0WD | |
| 40 | 1 | 1 | 1,2PZ | |
| 1 | 2.1 | 2.5 | 0+WD | G 5% |
| 5 | <0,5 | <0,5 | 1,2WZ | |
| 29 | <0,5 | <0,5 | 0W | |
| 15 | <100 | <100 | ? | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **L,M** | 1.00 | 0.14 | 14.0 | 0.69 | 69.0 |

Ag, other methods

| Lab No. | L | M | Code |
|---|---|---|---|
| 19 | 12 | 7.5 | K |
| 2 | 20 | 10 | I |

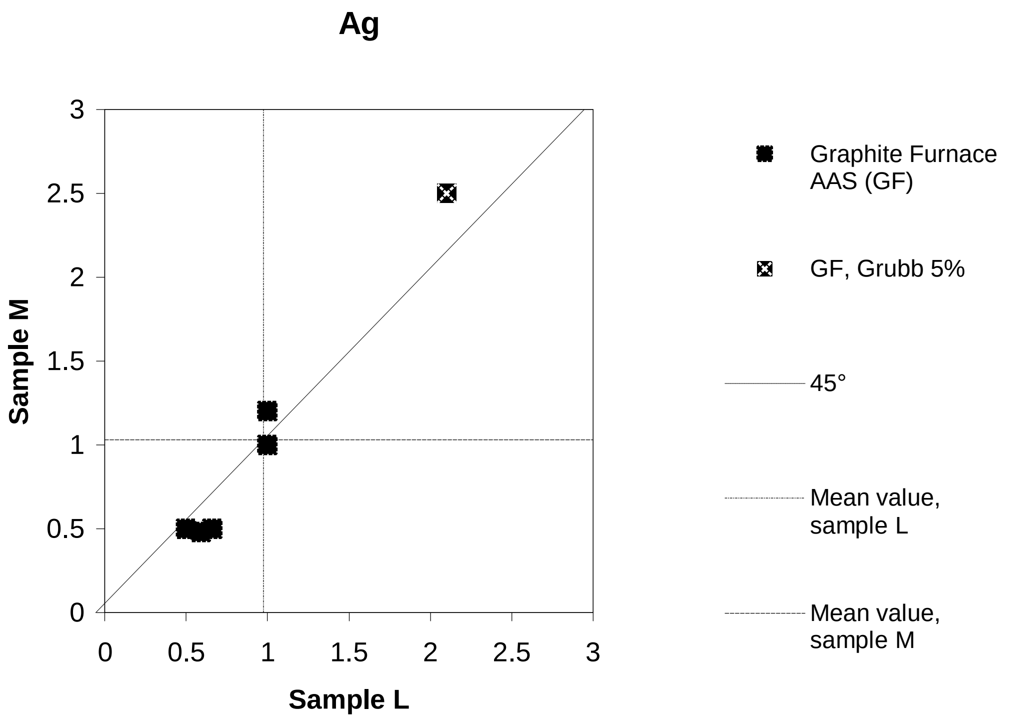
Al, digest (mg/l)

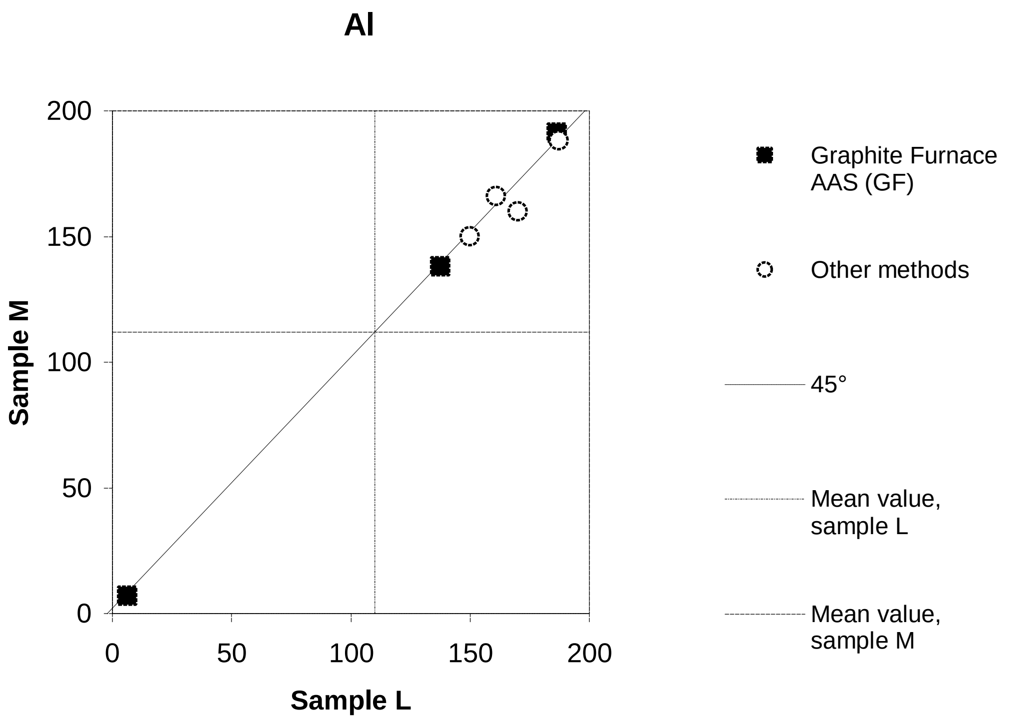
| Lab No. | L | M | Code | Outlier |
|---|---|---|---|---|
| 1 | 6.34 | 7.04 | 0+WD | |
| 15 | 137.6 | 138.17 | ? | |
| 5 | 186.51 | 191.24 | 0WZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **L,M** | 111 | 2 | 1.8 | 94 | 84.6 |

Al, other methods

| Lab No. | L | M | Code |
|---|---|---|---|
| 19 | 150 | 150 | K |
| 3 | 161 | 166 | I |
| 2 | 170 | 160 | I |
| 32 | 187.1 | 188.3 | F |


Ag
Sample M
Sample L
3
2.5
2
1.5
1
0.5
0
0
0.5
1
1.5
2
2.5
3
Graphite Furnace AAS (GF)
GF, Grubb 5%
45°
Mean value, sample L
Mean value, sample M


Al
Sample M
Sample L
200
150
100
50
0
0
50
100
150
200
Graphite Furnace AAS (GF)
Other methods
45°
Mean value, sample L
Mean value, sample M

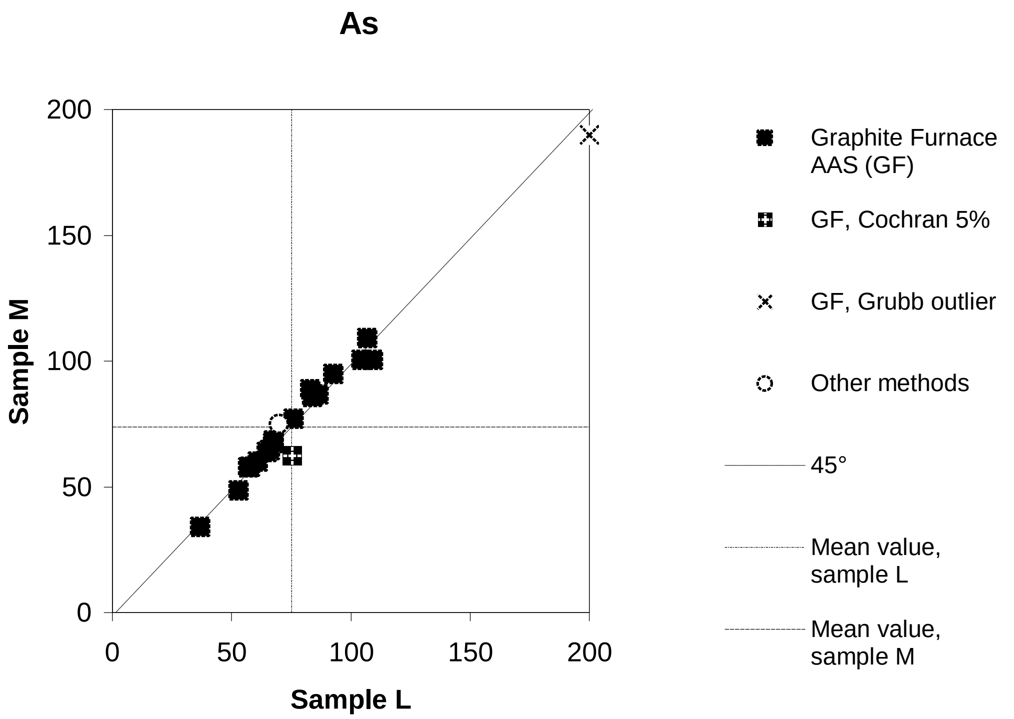
## As, digest (µg/l)

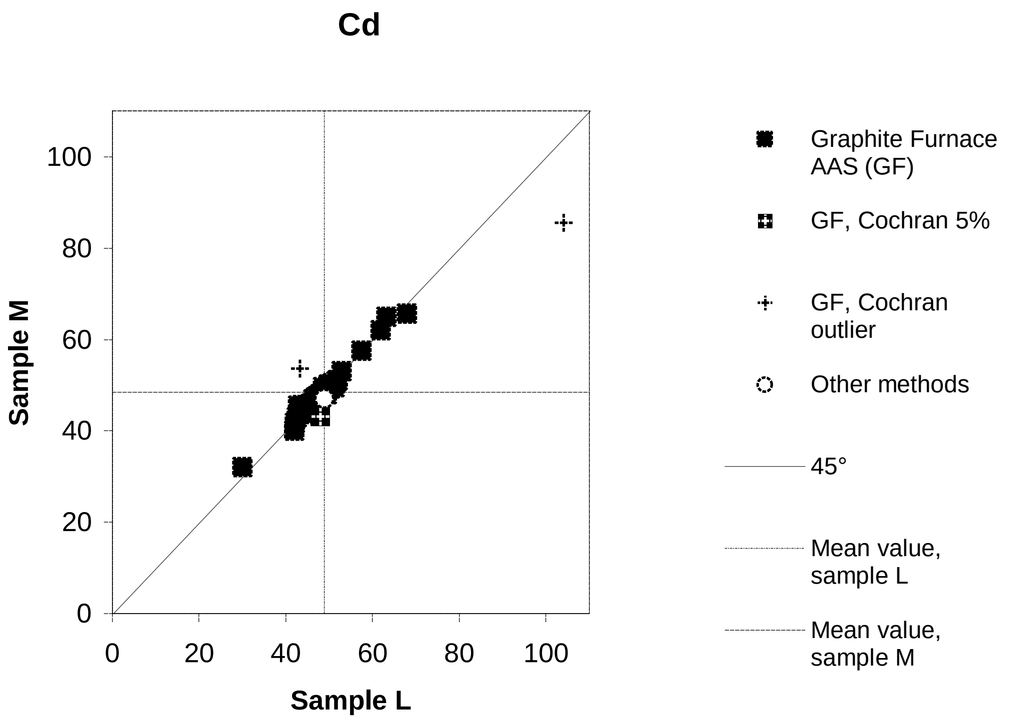
| Lab No. | L | M | Code | Outlier |
|---|---|---|---|---|
| 2 | 37 | 34 | 4WD | |
| 5 | 53.1 | 48.5 | 1WZ | |
| 12 | 57 | 57.7 | 1,2PZ | |
| 32 | 58.0 | 57.8 | 1,2WZ | |
| 19 | 61 | 60 | 1,2PZ | |
| 16 | 64.9 | 63.7 | 1PZ | |
| 10 | 66.2 | 64.6 | 1,2PZ | |
| 24 | 67.5 | 67.3 | 1+WZ | |
| 35 | 67.7 | 68.5 | 1,2PZ | |
| 1 | 75.4 | 62.3 | 1+WD | C 5% |
| 15 | 76 | 77 | ? | |
| 11 | 83.1 | 88.7 | 1,2PZ | |
| 27 | 84 | 85.7 | 1,2PZ | |
| 26 | 86.7 | 86.8 | 1,2+PZ | |
| 41 | 92.68 | 94.89 | 1,2PZ | |
| 22 | 105 | 101 | 1,2WD | |
| 7 | 107 | 109 | 1,2PD | |
| 34 | 109.3 | 100.4 | 1PZ | |
| 9 | 200 | 190 | 1,2WD | G |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **L,M** | 74.4 | 3.1 | 4.2 | 20.0 | 26.9 |

## As, other methods

| Lab No. | L | M | Code |
|---|---|---|---|
| 19 | 70 | 75 | K |


As
200
150
100
50
0
Sample M
0
50
100
150
200
Sample L
Graphite Furnace AAS (GF)
GF, Cochran 5%
GF, Grubb outlier
Other methods
45°
Mean value, sample L
Mean value, sample M


Cd
100
80
60
40
20
0
Sample M
0
20
40
60
80
100
Sample L
Graphite Furnace AAS (GF)
GF, Cochran 5%
GF, Cochran outlier
Other methods
45°
Mean value, sample L
Mean value, sample M

## Cd, digest (µg/l)

| Lab No. | L | M | Code | Outlier |
|---|---|---|---|---|
| 2 | 30 | 32 | 1,2WD | |
| 12 | 42 | 40 | 1,2,3PZ | |
| 35 | 42.2 | 41.6 | 3PZ | |
| 29 | 42.6 | 42.9 | 2,3PZ | |
| 32 | 42.9 | 45.4 | 0PZ | |
| 16 | 43.2 | 53.7 | 3PZ | C |
| 31 | 43.5 | 44.1 | 1PD | |
| 8 | 43.9 | 45.6 | 1,2WD | |
| 41 | 44.29 | 43.58 | 2,3PZ | |
| 3 | 45.8 | 45.8 | 2,3PZ | |
| 4 | 46.4 | 46.9 | 2,3PZ | |
| 13 | 47 | 44.6 | 6PZ | |
| 20 | 47 | 47.1 | 1,2WZ | |
| 36 | 47.1 | 47.2 | 2,3WD | |
| 7 | 47.5 | 47.5 | 1,2PD | |
| 9 | 48 | 48 | 1,2WD | |
| 14 | 48 | 43.2 | 0?Z | C 5% |
| 34 | 48.7 | 49.47 | 1PZ | |
| 6 | 50 | 48 | 2,3PZ | |
| 19 | 50 | 50 | 0PZ | |
| 10 | 50.3 | 49.2 | 2,3PZ | |
| 39 | 50.8 | 50.3 | 2,3WZ | |
| 22 | 51 | 50 | 1,2WD | |
| 26 | 51.8 | 50.7 | 2,3+PZ | |
| 37 | 52 | 51 | 0WD | |
| 40 | 53 | 53 | 2,3PZ | |
| 24 | 57.5 | 57.5 | 1+WZ | |
| 15 | 62 | 62 | ? | |
| 5 | 63.2 | 64.9 | 3WZ | |
| 1 | 68.0 | 65.6 | 0+WD | |
| 11 | 104 | 85.5 | 2,3PZ | C |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **L,M** | 48.7 | 1.1 | 2.2 | 7.2 | 14.8 |

## Cd, other methods

| Lab No. | L | M | Code |
|---|---|---|---|
| 19 | 49 | 47 | K |

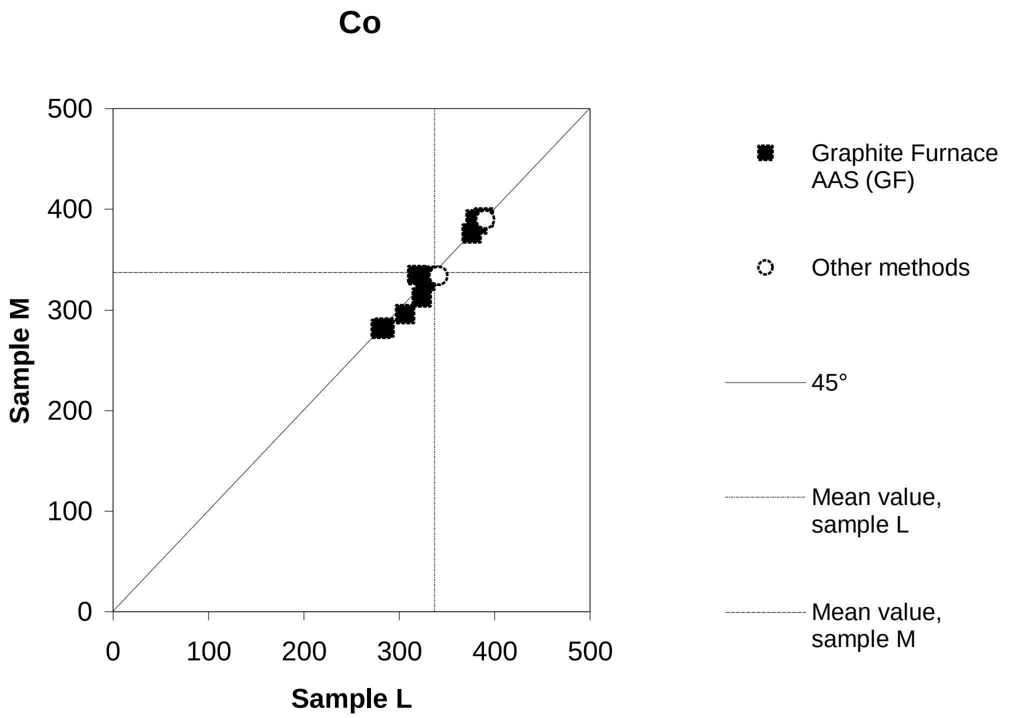
Co, digest (µg/l)

| Lab No. | L | M | Code | Outlier |
|---|---|---|---|---|
| 10 | 281 | 281 | 2WZ | |
| 3 | 285 | 282 | 0PZ | |
| 8 | 306.5 | 295.9 | 2WD | |
| 1 | 319 | 335 | 0+WD | |
| 29 | 324 | 312 | 0WD | |
| 32 | 327.6 | 328.6 | 0PZ | |
| 19 | 334 | 334 | 0PZ | |
| 15 | 376 | 376 | ? | |
| 40 | 380 | 390 | 2PZ | |
| 37 | 382 | 385 | 0WD | |
| 5 | 389 | 392 | 2WZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **L,M** | 337 | 5.4 | 1.6 | 41 | 12.2 |

Co, other methods

| Lab No. | L | M | Code |
|---|---|---|---|
| 19 | 341 | 334 | K |
| 2 | 390 | 390 | I |



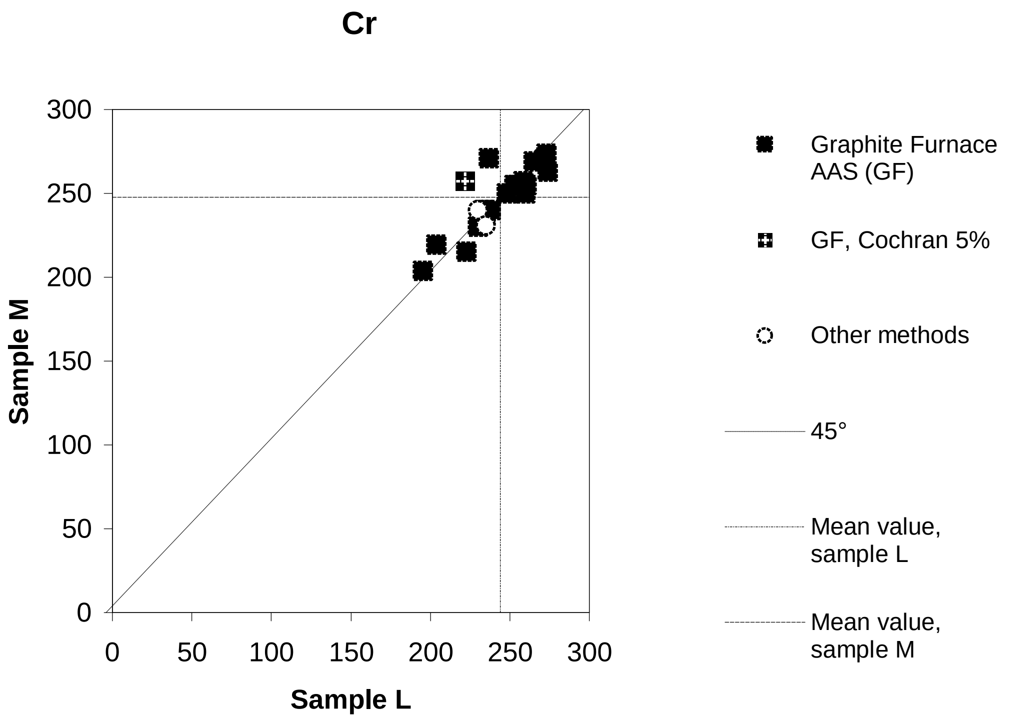
Cr, digest (µg/l)

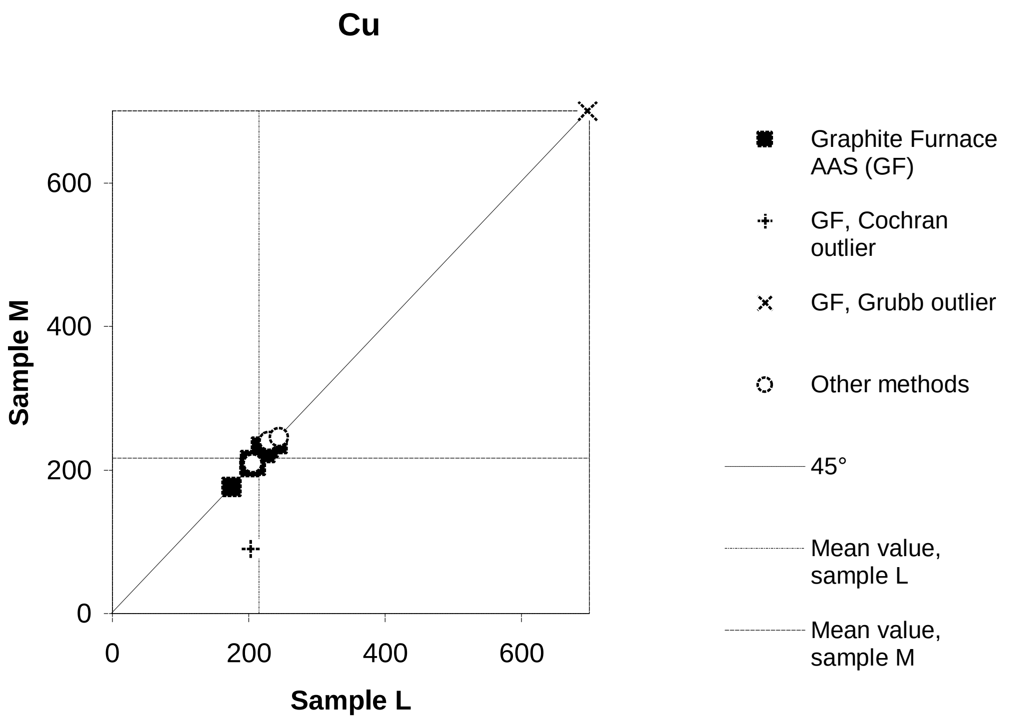
| Lab No. | L | M | Code | Outlier |
|---|---|---|---|---|
| 8 | 195.5 | 203.9 | 2W | |
| 1 | 204 | 219 | 3+WD | |
| 27 | 222 | 257.5 | 2PZ | C 5% |
| 26 | 223 | 215 | 0+PZ | |
| 15 | 230 | 230 | ? | |
| 5 | 234 | 240 | 2WZ | |
| 3 | 235 | 237 | 0PZ | |
| 12 | 237 | 271 | 2PZ | |
| 9 | 238 | 240 | 2W | |
| 35 | 248 | 250 | 2PZ | |
| 36 | 253 | 255 | 2,5WD | |
| 19 | 255 | 255 | 0PZ | |
| 41 | 258.79 | 257.02 | 2PZ | |
| 40 | 260 | 250 | 2PZ | |
| 6 | 261 | 255 | 2PZ | |
| 29 | 265 | 269 | 0W | |
| 11 | 272 | 270 | 2PZ | |
| 32 | 273.2 | 273.4 | 0PZ | |
| 10 | 274 | 263 | 2WZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **L,M** | 246 | 9.1 | 3.7 | 21 | 8.7 |

Cr, other methods

| Lab No. | L | M | Code |
|---|---|---|---|
| 2 | 230 | 240 | I |
| 19 | 235 | 231 | K |


Cr
300
250
200
150
100
50
0
Sample M
0
50
100
150
200
250
300
Sample L
Graphite Furnace AAS (GF)
GF, Cochran 5%
Other methods
45°
Mean value, sample L
Mean value, sample M


Cu
600
400
200
0
Sample M
0
200
400
600
Sample L
Graphite Furnace AAS (GF)
GF, Cochran outlier
GF, Grubb outlier
Other methods
45°
Mean value, sample L
Mean value, sample M

Cu, digest (µg/l)

| Lab No. | L | M | Code | Outlier |
|---|---|---|---|---|
| 29 | 175 | 176 | 0PZ | |
| 19 | 202 | 204 | 0PZ | |
| 16 | 202.2 | 213.8 | 1WZ | |
| 27 | 203.25 | 90.25 | 1,2PZ | C |
| 10 | 208 | 210 | 1,2WZ | |
| 1 | 211 | 205 | 0+WD | |
| 41 | 218.21 | 232.12 | 1,2PZ | |
| 22 | 225 | 223 | 0WD | |
| 40 | 230 | 230 | 1,2PZ | |
| 32 | 235.1 | 238.1 | 0WZ | |
| 5 | 243 | 236 | 0WZ | |
| 15 | 697 | 700 | ? | G |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **L,M** | 216 | 4.6 | 2.1 | 19 | 9.0 |

Cu, other methods

| Lab No. | L | M | Code |
|---|---|---|---|
| 3 | 206 | 209 | I |
| 2 | 230 | 240 | I |
| 19 | 245 | 246 | K |

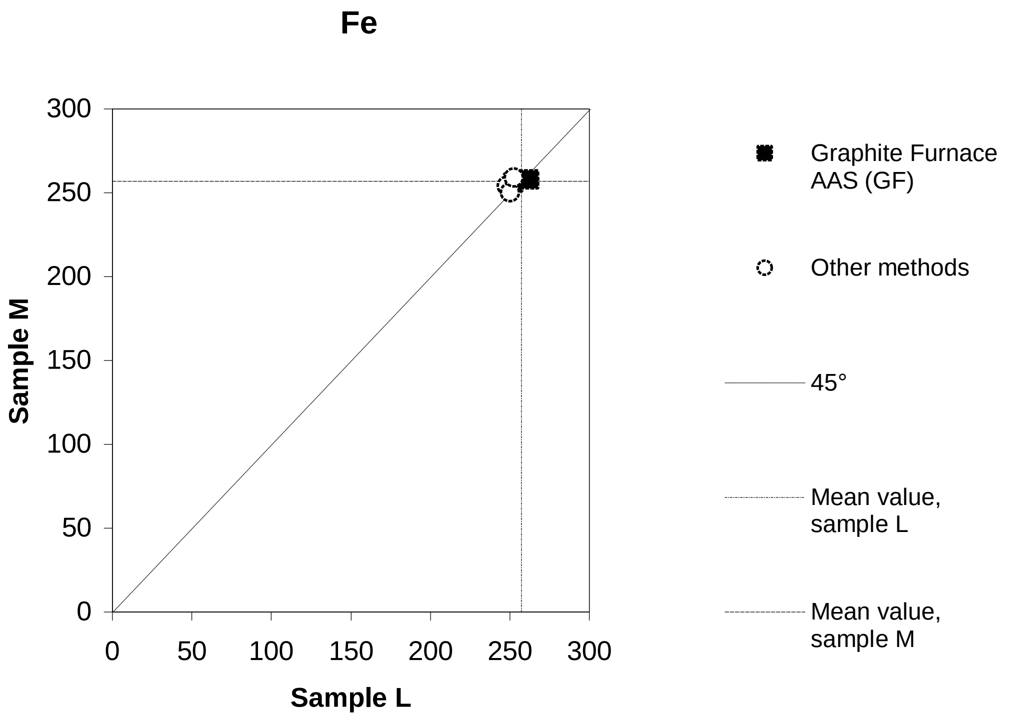
Fe, digest (mg/l)

| Lab No. | L | M | Code | Outlier |
|---|---|---|---|---|
| 15 | 252.11 | 255.73 | ? | |
| 5 | 262.43 | 257.78 | 0WZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **L,M** | 257 | - | - | - | - |

Fe, other methods

| Lab No. | L | M | Code |
|---|---|---|---|
| 3 | 248 | 254 | I |
| 2 | 250 | 250 | I |
| 19 | 250 | 250 | K |
| 32 | 252.5 | 258.97 | F |



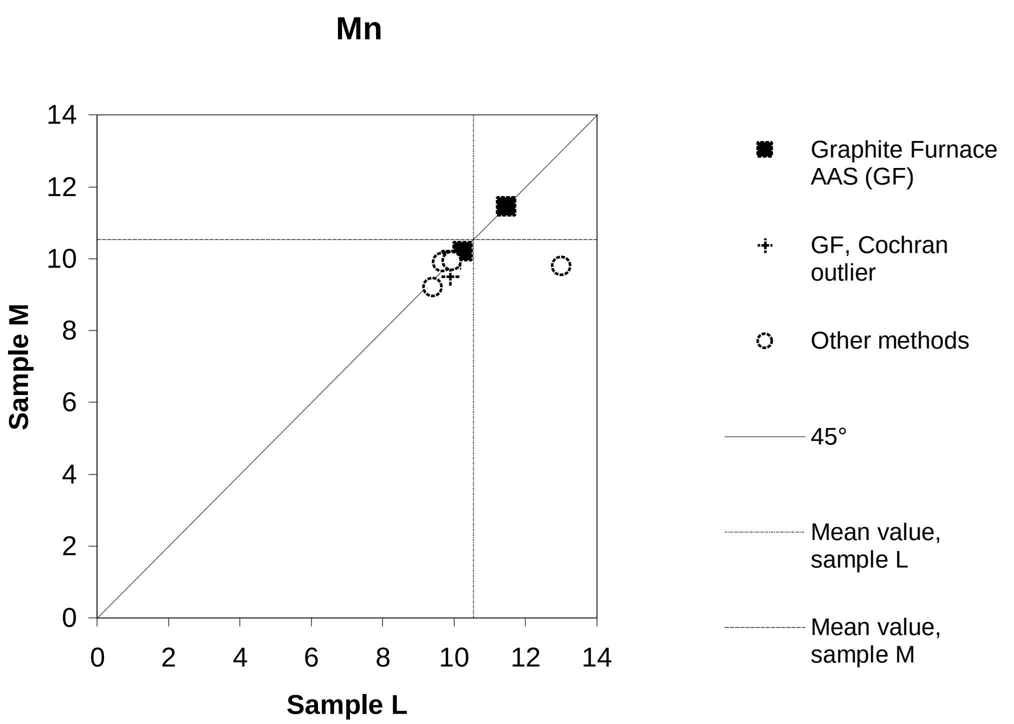
Mn, digest (mg/l)

| Lab No. | L | M | Code | Outlier |
|---|---|---|---|---|
| 40 | 9.9 | 9.5 | 1,2PZ | C |
| 15 | 9.93 | 9.95 | ? | |
| 5 | 10.24 | 10.2 | 0WZ | |
| 6 | 11.472 | 11.447 | 2PZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **L,M** | 10.5 | 0.02 | 0.2 | 0.8 | 7.7 |

Mn, other methods

| Lab No. | L | M | Code |
|---|---|---|---|
| 19 | 9.4 | 9.2 | K |
| 3 | 9.67 | 9.89 | I |
| 32 | 9.935 | 9.927 | F |
| 2 | 13 | 9.8 | I |



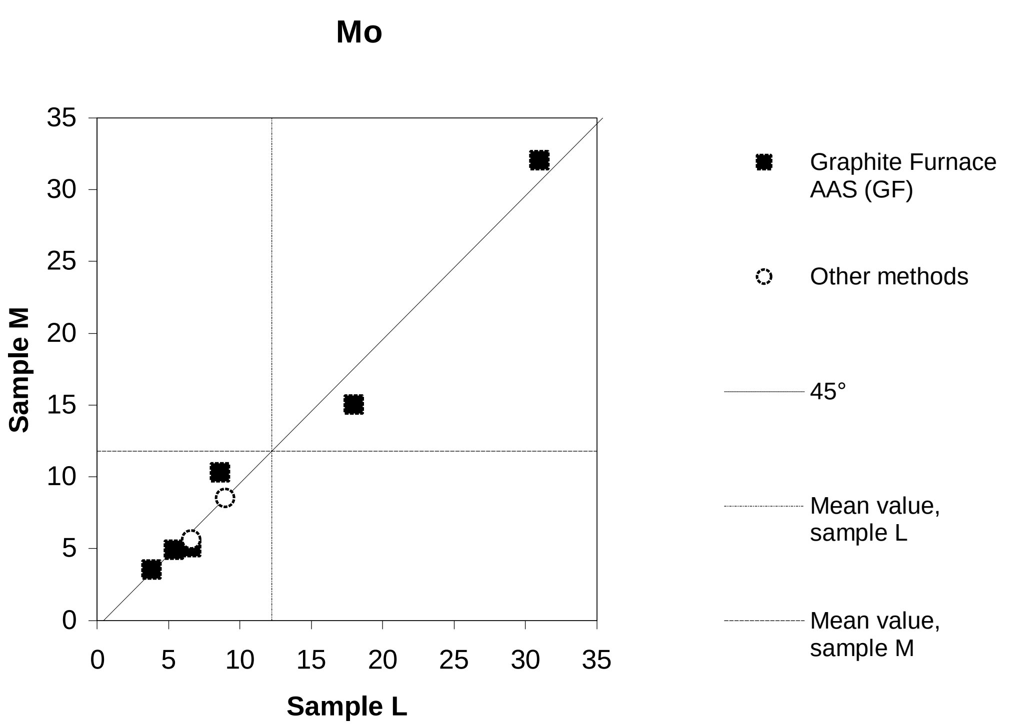
Mo, digest (µg/l)

| Lab No. | L | M | Code | Outlier |
|---|---|---|---|---|
| 32 | 3.83 | 3.53 | 0WZ | |
| 3 | 5.37 | 4.93 | 0PZ | |
| 5 | 6.6 | 5.09 | 0WZ | |
| 10 | 8.60 | 10.3 | 0WZ | |
| 15 | 18 | 15 | ? | |
| 8 | 30.99 | 32.01 | 0W | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **L,M** | 12.0 | 1.1 | 9.5 | 10.6 | 88.4 |

Mo, other methods

| Lab No. | L | M | Code |
|---|---|---|---|
| 19 | 6.6 | 5.6 | K |
| 24 | 9 | 8.5 | I |
| 2 | <50 | <50 | I |



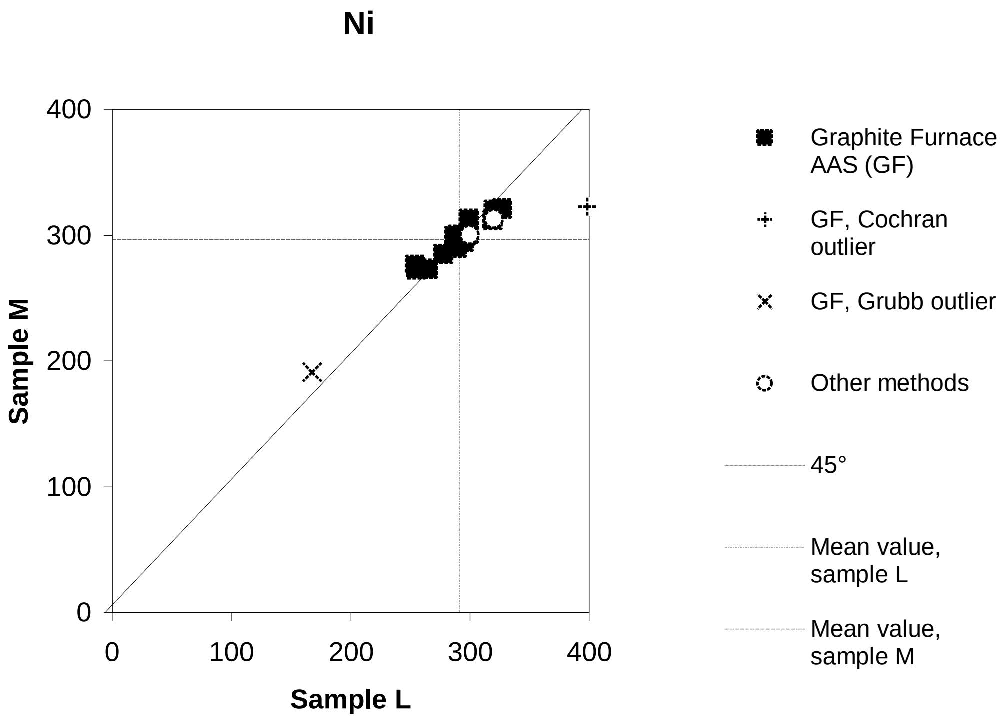
Ni, digest (µg/l)

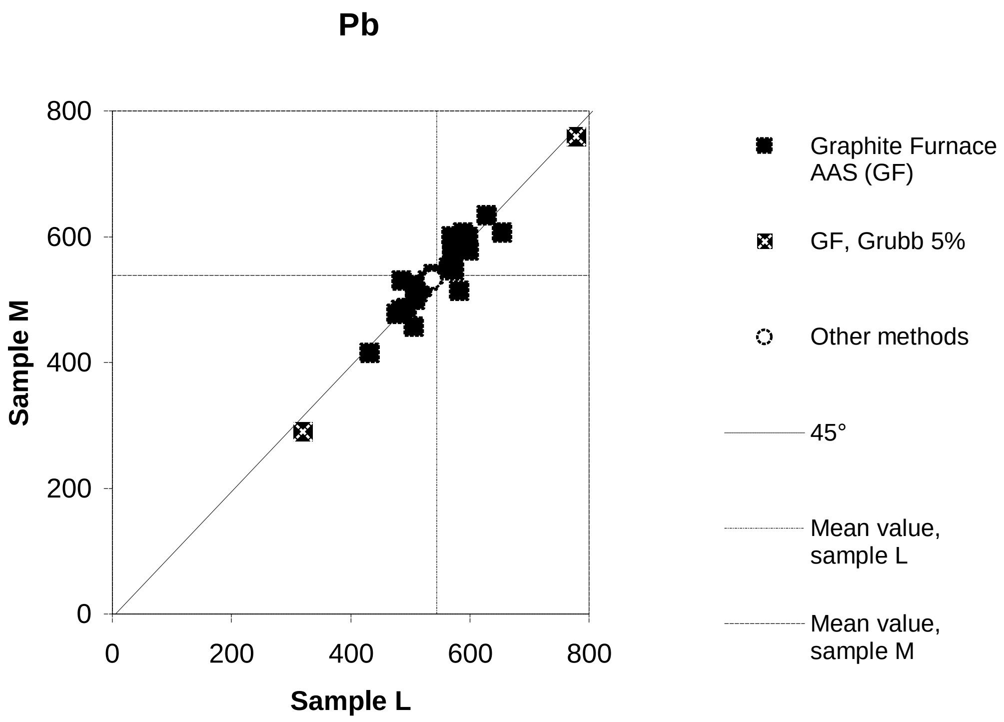
| Lab No. | L | M | Code | Outlier |
|---|---|---|---|---|
| 8 | 167.6 | 191.1 | 2WD | G |
| 41 | 254.21 | 276.1 | 2PZ | |
| 27 | 255 | 272.5 | 0PZ | |
| 5 | 265 | 273 | 0WZ | |
| 32 | 277.6 | 284.7 | 0PZ | |
| 6 | 287 | 299 | 2PZ | |
| 29 | 289 | 290 | 0PD | |
| 19 | 290 | 300 | 0PZ | |
| 22 | 295 | 294 | 1,2WD | |
| 31 | 296.4 | 299.6 | 0PD | |
| 3 | 299 | 313 | 0PZ | |
| 15 | 299 | 301 | ? | |
| 35 | 319 | 312 | 2PZ | |
| 40 | 320 | 320 | 0PZ | |
| 10 | 327 | 321 | 2WZ | |
| 12 | 398 | 323 | 2PZ | C |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **L,M** | 294 | 7.2 | 2.4 | 20 | 6.8 |

Ni, other methods

| Lab No. | L | M | Code |
|---|---|---|---|
| 2 | 300 | 300 | I |
| 19 | 320 | 313 | K |


Ni
Sample M
Sample L
0
100
200
300
400
0
100
200
300
400
Graphite Furnace AAS (GF)
GF, Cochran outlier
GF, Grubb outlier
Other methods
45°
Mean value, sample L
Mean value, sample M


Pb
Sample M
Sample L
0
200
400
600
800
0
200
400
600
800
Graphite Furnace AAS (GF)
GF, Grubb 5%
Other methods
45°
Mean value, sample L
Mean value, sample M

Pb, digest (µg/l)

| Lab No. | L | M | Code | Outlier |
|---|---|---|---|---|
| 2 | 320 | 290 | 2,3WD | G 5% |
| 9 | 432 | 415 | 1,2WD | |
| 41 | 477.37 | 476.8 | 2,3PZ | |
| 13 | 484.6 | 483.6 | 2,3PZ | |
| 27 | 486 | 530 | 2,3PZ | |
| 35 | 494 | 486 | 3PZ | |
| 14 | 506.5 | 456.6 | 2,3?Z | |
| 31 | 507.9 | 522.9 | 2,3PD | |
| 29 | 508 | 500 | 2,3PZ | |
| 32 | 509.2 | 513.2 | 0PZ | |
| 11 | 513 | 512 | 2,3PZ | |
| 34 | 519.4 | 519.4 | 1PZ | |
| 22 | 521 | 521 | 1,2WD | |
| 19 | 530 | 530 | 0PZ | |
| 20 | 540 | 540 | 2,3WZ | |
| 16 | 565 | 550 | 3PZ | |
| 40 | 570 | 600 | 2,3PZ | |
| 39 | 571 | 576 | 2,3WZ | |
| 1 | 572 | 587 | 0+WD | |
| 4 | 572 | 578 | 2,3PZ | |
| 3 | 574 | 546 | 3PZ | |
| 26 | 579 | 582 | 2,3+PZ | |
| 12 | 582 | 514 | 1,2,3PZ | |
| 10 | 589 | 606 | 2,3PZ | |
| 6 | 597 | 599 | 2,3PZ | |
| 7 | 598 | 578 | 1,2PD | |
| 15 | 629 | 634 | ? | |
| 5 | 654 | 606 | 3WZ | |
| 8 | 778 | 760 | 1,2WD | G 5% |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **L,M** | 541 | 17 | 3.1 | 80 | 14.7 |

Pb, other methods

| Lab No. | L | M | Code |
|---|---|---|---|
| 19 | 537 | 532 | K |

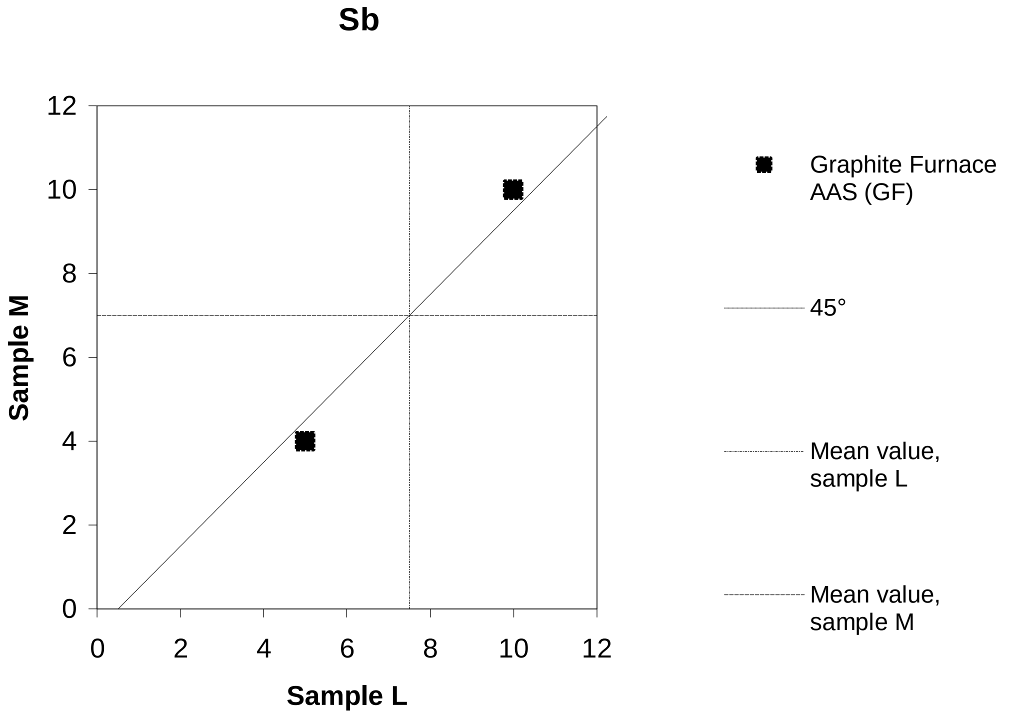
Sb, digest (µg/l)

| Lab No. | L | M | Code | Outlier |
|---|---|---|---|---|
| 19 | 5 | 4 | 1,2PZ | |
| 24 | 10 | 10 | 1+WZ | |
| 1 | < 20 | < 20 | 0+WD | |
| 5 | < 5 | < 5 | 1,2WZ | |
| 32 | <1 | <1 | 1,2PZ | |
| 2 | <10 | <10 | 4WD | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **L,M** | 7.25 | - | - | - | - |

Sb, other methods

| Lab No. | L | M | Code |
|---|---|---|---|
| - | | | |



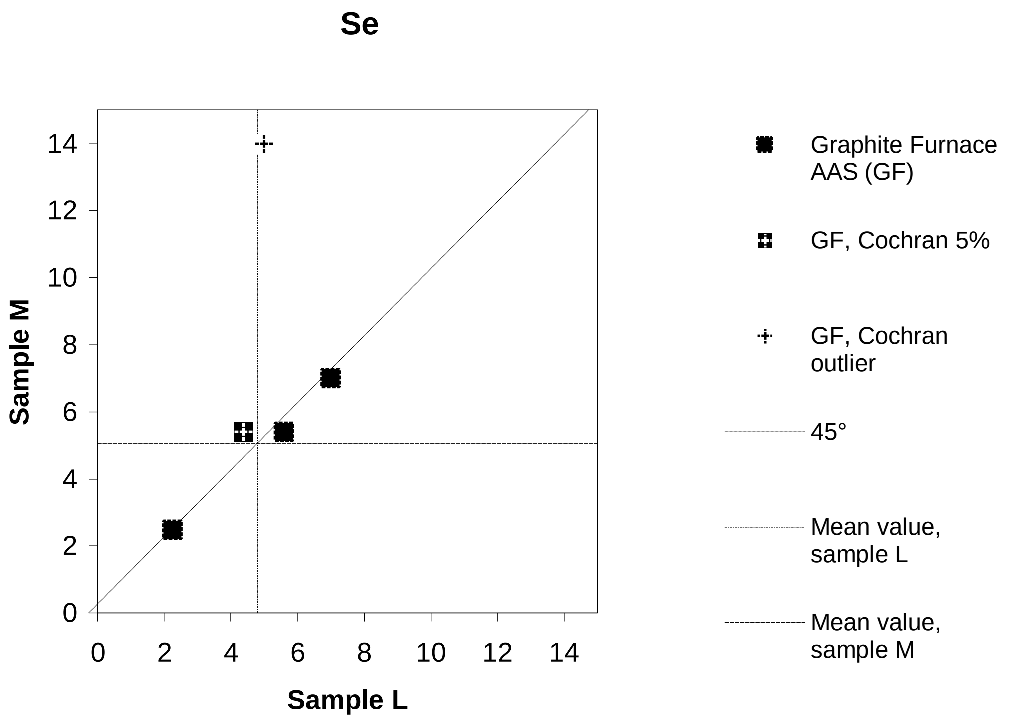
Se, digest (µg/l)

| Lab No. | L | M | Code | Outlier |
|---|---|---|---|---|
| 10 | 2.25 | 2.48 | 1,2PZ | |
| 26 | 4.37 | 5.4 | 1,2+PZ | C 5% |
| 15 | 5 | 14 | ? | C |
| 12 | 5.6 | 5.4 | 1,2PZ | |
| 19 | 7 | 7 | 1,2PZ | |
| 1 | <10 | <10 | 1+WD | |
| 5 | <5 | <5 | 1,2WZ | |
| 32 | <1 | <1 | 1,2PZ | |
| 2 | <10 | <10 | 1,2WD | |
| 24 | <2 | <2 | 1+WZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **L,M** | 4.94 | 0.38 | 7.7 | 1.95 | 39.5 |

Se, other methods

| Lab No. | L | M | Code |
|---|---|---|---|
| - | | | |



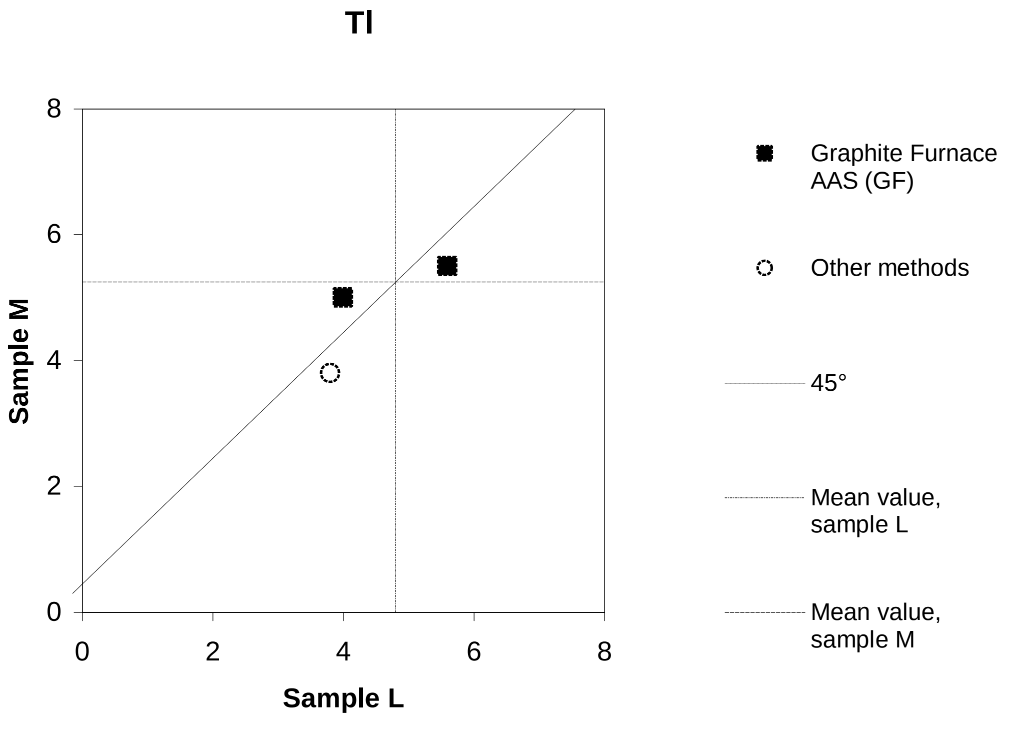
## Tl, digest (µg/l)

| Lab No. | L | M | Code | Outlier |
|---|---|---|---|---|
| 19 | 4 | 5 | 1,2PZ | |
| 1 | 5.6 | 5.5 | 0+PD | |
| 5 | < 5 | < 5 | 0WZ | |
| 6 | < 5 | < 5 | 1,2PZ | |
| 2 | <10 | <10 | 0WD | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **L,M** | 5.03 | - | - | - | - |

## Tl, other methods

| Lab No. | L | M | Code |
|---|---|---|---|
| 19 | 3.8 | 3.8 | K |



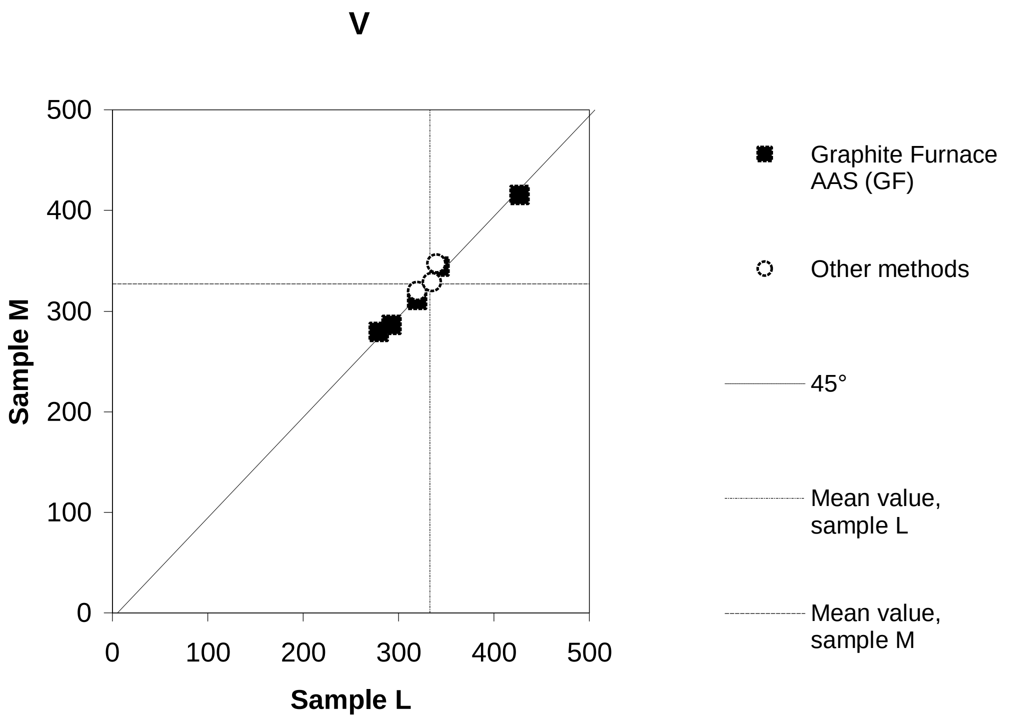
V, digest (µg/l)

| Lab No. | L | M | Code | Outlier |
|---|---|---|---|---|
| 32 | 279 | 279 | 0WZ | |
| 1 | 293 | 286 | 0+WD | |
| 5 | 320 | 311 | 0WZ | |
| 8 | 343.3 | 344.1 | 0W | |
| 10 | 427 | 415 | 0WZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **L,M** | 330 | 5.2 | 1.6 | 57 | 17.3 |

V, other methods

| Lab No. | L | M | Code |
|---|---|---|---|
| 2 | 320 | 320 | I |
| 19 | 335 | 329 | K |
| 3 | 340 | 347 | I |



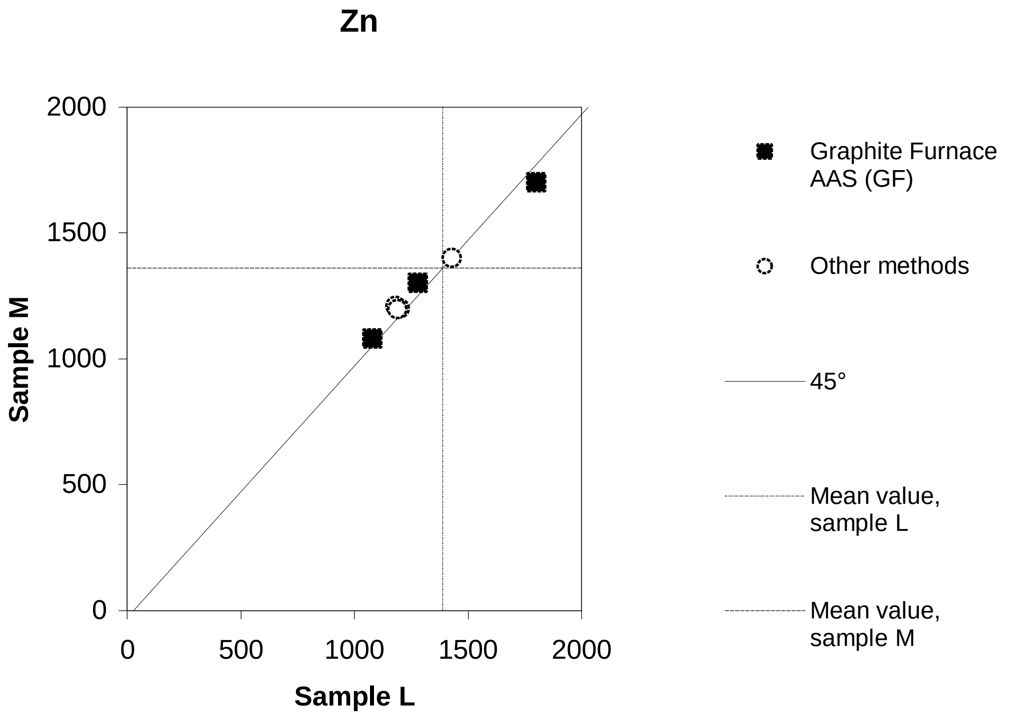
Zn, digest (µg/l)

| Lab No. | L | M | Code | Outlier |
|---|---|---|---|---|
| 15 | 1080 | 1080 | ? | |
| 5 | 1280 | 1300 | 0WZ | |
| 40 | 1800 | 1700 | 0PZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **L,M** | 1373 | 42 | 3.0 | 344 | 25.0 |

Zn, other methods

| Lab No. | L | M | Code |
|---|---|---|---|
| 3 | 1180 | 1210 | I |
| 32 | 1190 | 1196 | F |
| 2 | 1200 | 1200 | I |
| 19 | 1430 | 1400 | K |



# Dry sediment sample

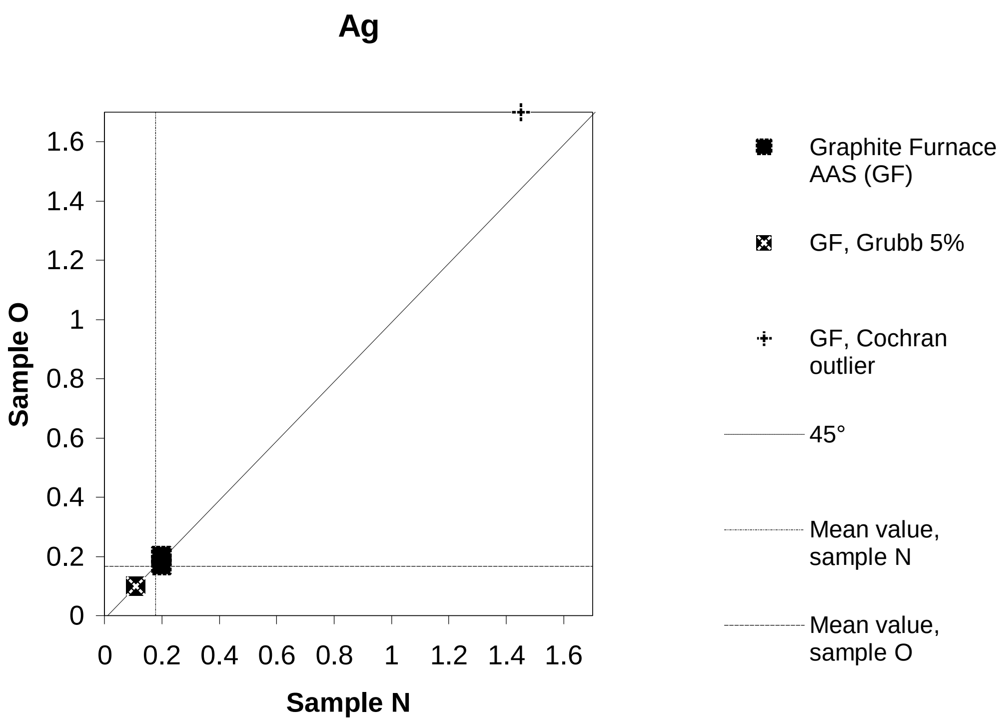
Ag, sediment (µg/g)

| Lab No. | N | O | Code | Outlier |
|---|---|---|---|---|
| 12 | 0.109 | 0.099 | Nm1,2PZ | G 5% |
| 32 | 0.2 | 0.2 | Na1,2WZ | |
| 40 | 0.2 | 0.2 | Na1,2PZ | |
| 40 | 0.2 | 0.2 | Aa1,2PZ | |
| 1 | 1.45 | 1.7 | Am0+WD | C |
| 5 | <0,2 | <0,2 | Nm1,2WZ | |
| 29 | <0,5 | <0,5 | Na0W | |
| 15 | <5 | <5 | Am? | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **N,O** | 0.172 | 0.011 | 6.5 | 0.047 | 27.1 |

Ag, other methods

| Lab No. | N | O | Code |
|---|---|---|---|
| 2 | 7.7 | 6.5 | AmI |



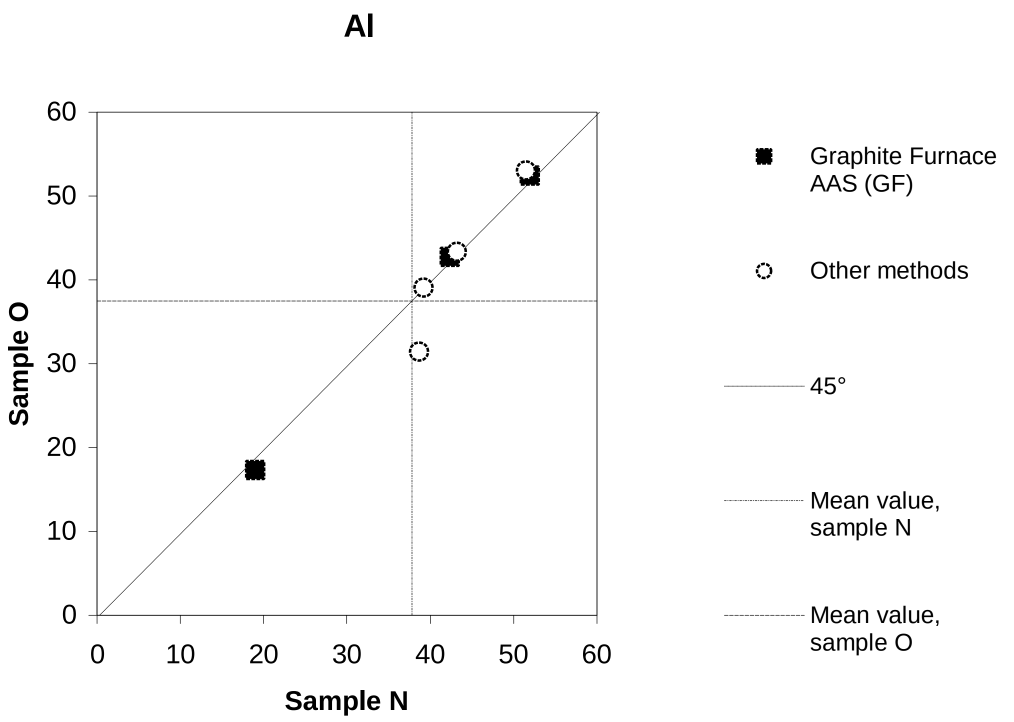
## Al, sediment (mg/g)

| Lab No. | N | O | Code | Outlier |
|---|---|---|---|---|
| 1 | 18.99 | 17.29 | Am0+WD | |
| 15 | 42.365 | 42.72 | Am? | |
| 5 | 51.99 | 52.41 | Nm0WZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **N,O** | 37.6 | 0.7 | 1.9 | 17.6 | 46.7 |

## Al, other methods

| Lab No. | N | O | Code |
|---|---|---|---|
| 2 | 38.7 | 31.4 | AmI |
| 3 | 39.2 | 39.0 | AoI |
| 32 | 43.260 | 43.272 | NaF |
| 19 | 51.5 | 53.0 | AmI |



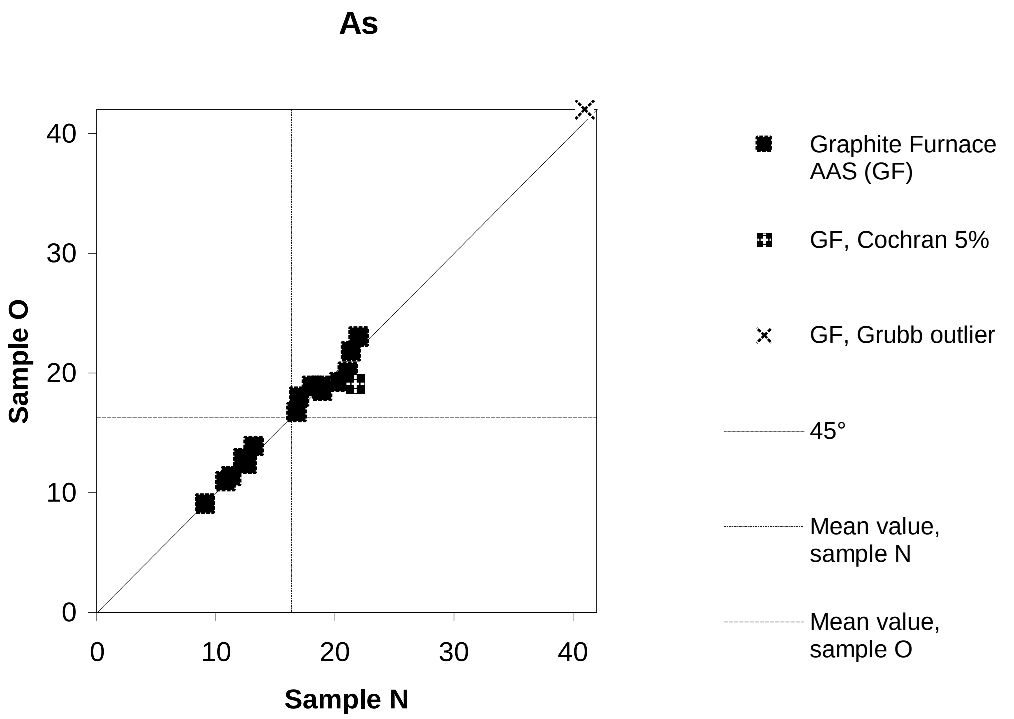
As, sediment (µg/g)

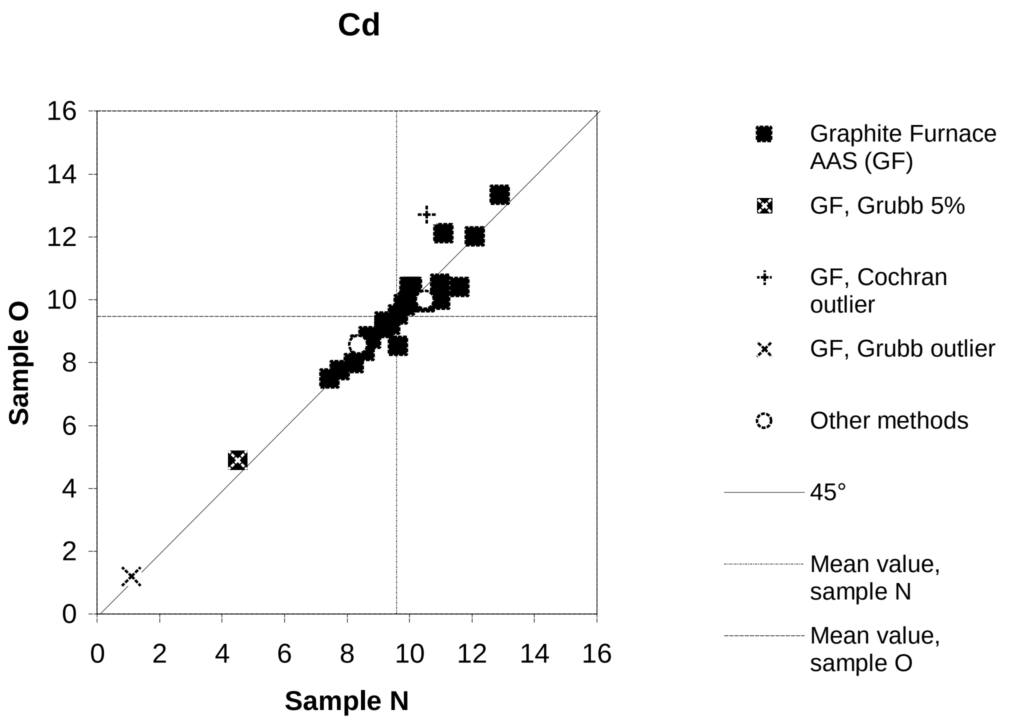
| Lab No. | N | O | Code | Outlier |
|---|---|---|---|---|
| 5 | 9.13 | 9.07 | Nm1WZ | |
| 32 | 10.82 | 10.93 | Na1,2WZ | |
| 16 | 11.29 | 11.38 | Am1PZ | |
| 16 | 12.34 | 12.84 | Nm1PZ | |
| 35 | 12.5 | 12.5 | Na1,2PZ | |
| 19 | 12.6 | 12.4 | Am1,2PZ | |
| 12 | 13.2 | 13.88 | Nm1,2PZ | |
| 15 | 16.8 | 16.7 | Am? | |
| 2 | 17 | 18 | Am4WD | |
| 27 | 18.1 | 18.9 | Na1,2PZ | |
| 34 | 18.79 | 18.89 | Na1PZ | |
| 41 | 18.98 | 18.47 | Nm1,2PZ | |
| 11 | 20.4 | 19.2 | Nm1,2PZ | |
| 22 | 21.1 | 20.1 | N?1,2WD | |
| 26 | 21.4 | 21.8 | Nm1,2+PZ | |
| 1 | 21.7 | 19.1 | Am1+WD | C 5% |
| 7 | 22 | 23 | Nm1,2PD | |
| 9 | 41 | 42 | Na1,2WD | G |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **N,O** | 16.3 | 0.6 | 3.8 | 4.3 | 26.2 |

As, other methods

| Lab No. | N | O | Code |
|---|---|---|---|
| - | | | |


As
Sample O
Sample N
0
10
20
30
40
0
10
20
30
40
Graphite Furnace AAS (GF)
GF, Cochran 5%
GF, Grubb outlier
45°
Mean value, sample N
Mean value, sample O


Cd
Sample O
Sample N
0
2
4
6
8
10
12
14
16
0
2
4
6
8
10
12
14
16
Graphite Furnace AAS (GF)
GF, Grubb 5%
GF, Cochran outlier
GF, Grubb outlier
Other methods
45°
Mean value, sample N
Mean value, sample O

Cd, sediment (µg/g)

| Lab No. | N | O | Code | Outlier |
|---|---|---|---|---|
| 2 | 1.1 | 1.2 | Am1,2WD | G |
| 1 | 4.5 | 4.9 | Am0+WD | G 5% |
| 31 | 7.44 | 7.48 | Nm1PD | |
| 8 | 7.78 | 7.76 | Nm1,2WD | |
| 35 | 8.23 | 7.97 | Na3PZ | |
| 29 | 8.43 | 8.57 | Na2,3PZ | |
| 13 | 8.58 | 8.37 | Am6PZ | |
| 41 | 8.7 | 8.83 | Nm2,3PZ | |
| 14 | 8.77 | 8.75 | Ao0?Z | |
| 3 | 9.2 | 9.1 | Ao2,3PZ | |
| 6 | 9.2 | 9.3 | Nc2,3PZ | |
| 36 | 9.2 | 9.1 | Nm2,3WD | |
| 9 | 9.4 | 9.2 | Na1,2WD | |
| 12 | 9.63 | 8.53 | Nm1,2,3PZ | |
| 20 | 9.65 | 9.52 | Nm1,2WZ | |
| 39 | 9.83 | 9.84 | Na2,3WZ | |
| 11 | 9.87 | 9.8 | Nm2,3PZ | |
| 34 | 9.95 | 9.9 | Na1PZ | |
| 27 | 10 | 10.4 | Na2,3PZ | |
| 40 | 10 | 10 | Aa2,3PZ | |
| 32 | 10.1 | 10.4 | Na0PZ | |
| 19 | 10.5 | 9.9 | Am0PZ | |
| 16 | 10.56 | 12.7 | Nm3PZ | C |
| 26 | 11 | 10.5 | Nm2,3+PZ | |
| 40 | 11 | 10 | Na2,3PZ | |
| 16 | 11.1 | 12.1 | Am3PZ | |
| 22 | 11.6 | 10.4 | N?1,2WD | |
| 15 | 12.1 | 12 | Am? | |
| 5 | 12.9 | 13.32 | Nm3WZ | |
| 7 | 86 | 86 | Nm1,2PD | G |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **N,O** | 9.36 | 0.34 | 3.6 | 1.88 | 20.1 |

Cd, other methods

| Lab No. | N | O | Code |
|---|---|---|---|
| 37 | 8.37 | 8.57 | NoF |
| 19 | 10.5 | 10.0 | AmI |

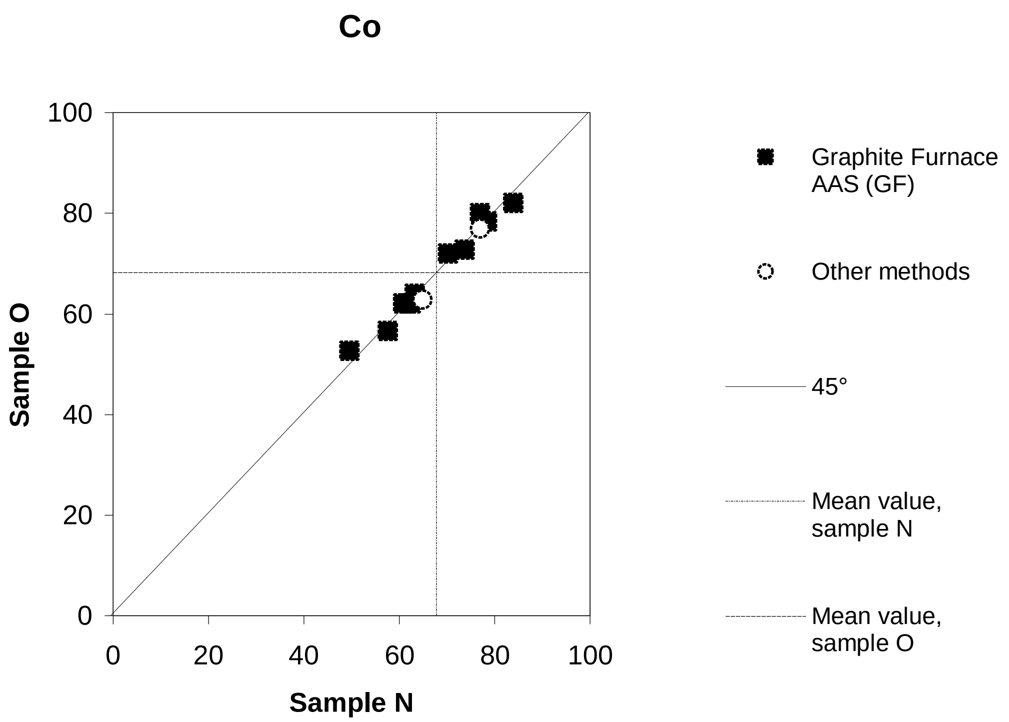
Co, sediment (µg/g)

| Lab No. | N | O | Code | Outlier |
|---|---|---|---|---|
| 8 | 49.55 | 52.64 | Nm2WD | |
| 3 | 57.6 | 56.6 | Ao0PZ | |
| 29 | 60.8 | 62 | Na0WD | |
| 1 | 62.5 | 62.0 | Am0+WD | |
| 32 | 63.3 | 63.9 | Na0PZ | |
| 19 | 70.3 | 72 | Am0PZ | |
| 15 | 73.8 | 72.7 | Am? | |
| 40 | 77 | 80 | Aa2PZ | |
| 5 | 78.5 | 78.3 | Nm2WZ | |
| 40 | 84 | 82 | Na2PZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **N,O** | 68.0 | 1.2 | 1.8 | 10.5 | 15.4 |

Co, other methods

| Lab No. | N | O | Code |
|---|---|---|---|
| 37 | 64.85 | 62.8 | NoF |
| 2 | 77 | 77 | AmI |



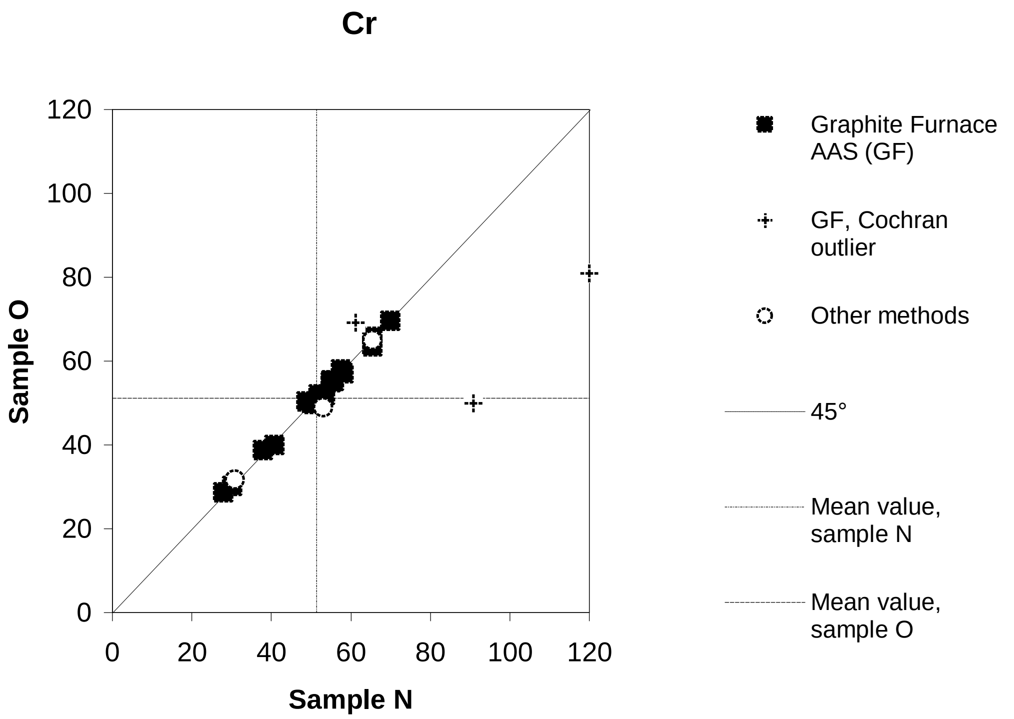
## Cr, sediment (µg/g)

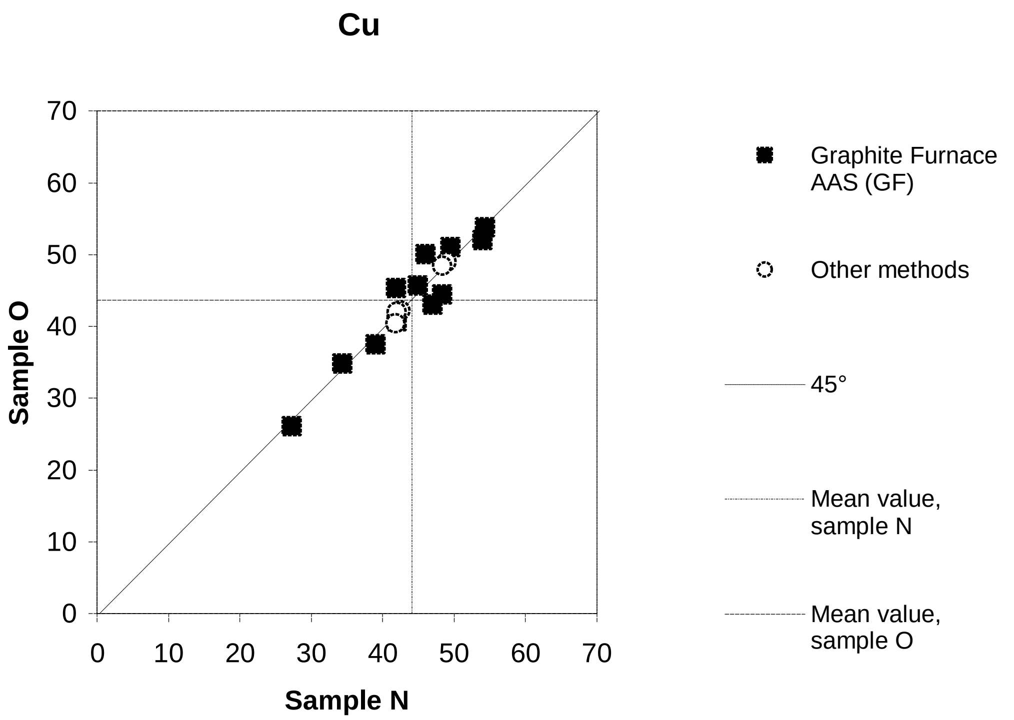
| Lab No. | N | O | Code | Outlier |
|---|---|---|---|---|
| 5 | 28.0 | 28.7 | Nm2WZ | |
| 8 | 30.18 | 30.19 | Nm2W | |
| 1 | 38.0 | 38.7 | Am3+WD | |
| 26 | 40.9 | 40 | Nm0+PZ | |
| 6 | 48.9 | 50.4 | Nc2PZ | |
| 40 | 50 | 50 | Na2PZ | |
| 29 | 50.7 | 49.8 | Na0W | |
| 35 | 51.2 | 50.2 | Na2PZ | |
| 9 | 52 | 52 | Na2W | |
| 27 | 53.6 | 51.9 | Na2PZ | |
| 40 | 55 | 55 | Aa2PZ | |
| 15 | 55.1 | 55.4 | Am? | |
| 3 | 55.8 | 55.3 | Ao0PZ | |
| 11 | 57.6 | 58.0 | Nm2PZ | |
| 41 | 58.24 | 57.13 | Nm2PZ | |
| 36 | 61.2 | 69.2 | Nm2,5WD | C |
| 19 | 65.5 | 63.4 | Am0PZ | |
| 32 | 65.5 | 65.7 | Na0PZ | |
| 12 | 69.96 | 69.52 | Nm2PZ | |
| 16 | 90.8 | 50 | Am1WZ | C |
| 16 | 120 | 81 | Nm1WZ | C |

| | **General mean** | **$s_r$** | **$CV_r$, %** | **$s_R$** | **$CV_R$, %** |
|---|---|---|---|---|---|
| **N,O** | 49.9 | 0.61 | 1.2 | 12.8 | 25.6 |

## Cr, other methods

| Lab No. | N | O | Code |
|---|---|---|---|
| 37 | 30.9 | 31.7 | NoF |
| 2 | 53 | 49 | AmI |
| 19 | 65.5 | 65.0 | AmI |


Cr
120
100
80
60
40
20
0
Sample O
0
20
40
60
80
100
120
Sample N
Graphite Furnace AAS (GF)
GF, Cochran outlier
Other methods
45°
Mean value, sample N
Mean value, sample O


Cu
70
60
50
40
30
20
10
0
Sample O
0
10
20
30
40
50
60
70
Sample N
Graphite Furnace AAS (GF)
Other methods
45°
Mean value, sample N
Mean value, sample O

Cu, sediment (μg/g)

| Lab No. | N | O | Code | Outlier |
|---|---|---|---|---|
| 16 | 27.3 | 26.1 | Am1WZ | |
| 29 | 34.4 | 34.8 | Na0PZ | |
| 16 | 39 | 37.5 | Nm1WZ | |
| 19 | 41.9 | 45.3 | Am0PZ | |
| 11 | 42.0 | 40.7 | Nm0PZ | |
| 41 | 44.96 | 45.7 | Nm1,2PZ | |
| 40 | 46 | 50 | Aa1,2PZ | |
| 22 | 47 | 43 | N?0WD | |
| 27 | 48.4 | 44.4 | Na1,2PZ | |
| 5 | 49.5 | 51 | Nm0WZ | |
| 40 | 54 | 52 | Na1,2PZ | |
| 1 | 54.4 | 53.8 | Am0+WD | |
| 15 | 137 | 135 | Am? | G |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **N,O** | 43.9 | 1.7 | 4.0 | 7.9 | 18.1 |

Cu, other methods

| Lab No. | N | O | Code |
|---|---|---|---|
| 37 | 41.8 | 40.4 | NoF |
| 19 | 42.0 | 42.0 | AmI |
| 3 | 42.5 | 42.2 | AoI |
| 32 | 48.4 | 48.4 | NaF |
| 2 | 49 | 49 | AmI |

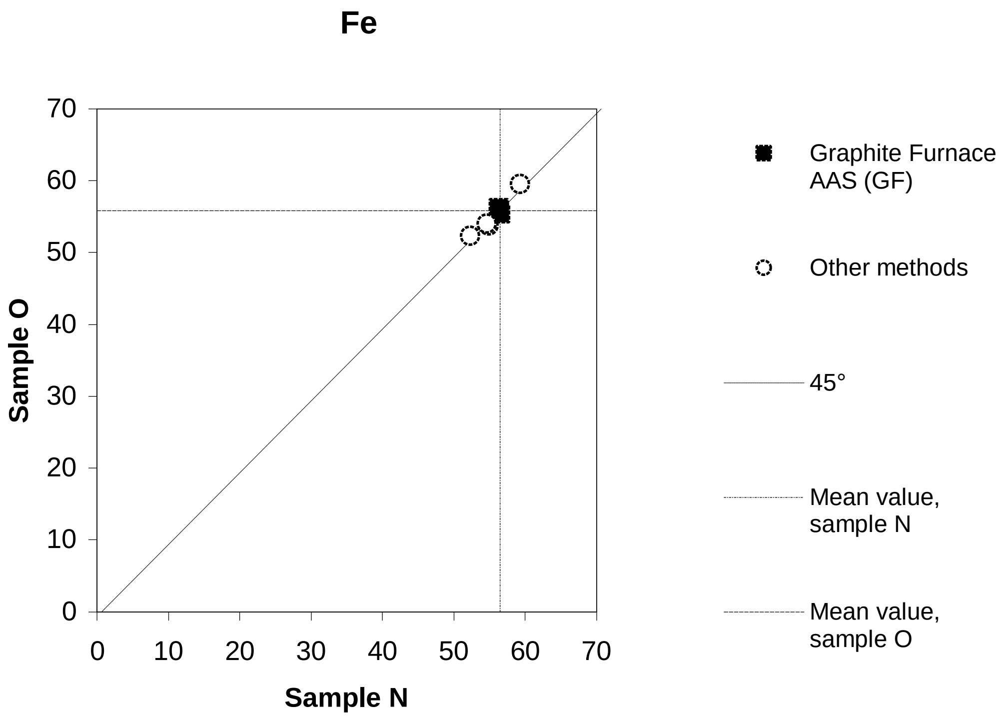
Fe, sediment (mg/g)

| Lab No. | N | O | Code | Outlier |
|---|---|---|---|---|
| 5 | 56.38 | 56.17 | Nm0WZ | |
| 15 | 56.523 | 55.438 | Am? | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| N,O | 56.1 | - | - | - | - |

Fe, other methods

| Lab No. | N | O | Code |
|---|---|---|---|
| 32 | 52.345 | 52.313 | NaF |
| 3 | 54.6 | 54.0 | AoI |
| 2 | 54.9 | 53.7 | AmI |
| 19 | 59.3 | 59.5 | AmI |



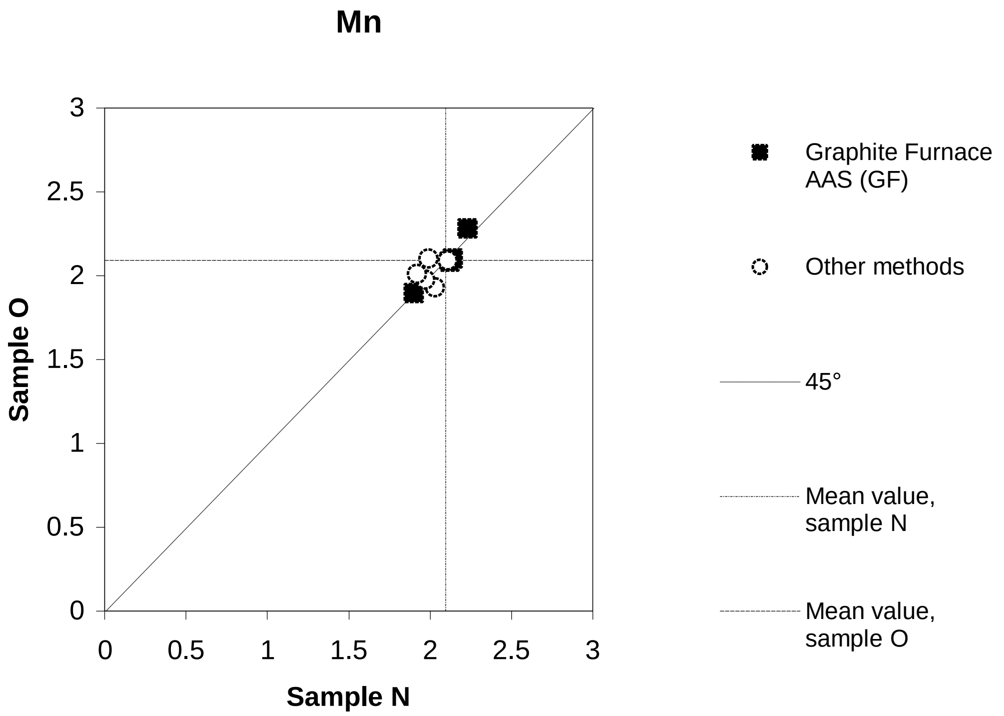
Mn, sediment (mg/g)

| Lab No. | N | O | Code | Outlier |
|---|---|---|---|---|
| 15 | 1.9 | 1.895 | Am? | |
| 40 | 2.12 | 2.08 | Na1,2PZ | |
| 5 | 2.14 | 2.1 | Nm0WZ | |
| 40 | 2.23 | 2.28 | Aa1,2PZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **N,O** | 2.09 | 0.027 | 1.3 | 0.15 | 7.1 |

Mn, other methods

| Lab No. | N | O | Code |
|---|---|---|---|
| 37 | 1.921 | 2.009 | NoF |
| 32 | 1.9729 | 1.9754 | NaF |
| 19 | 1.99 | 2.10 | AmI |
| 2 | 2.03 | 1.93 | AmI |
| 3 | 2.11 | 2.09 | AoI |



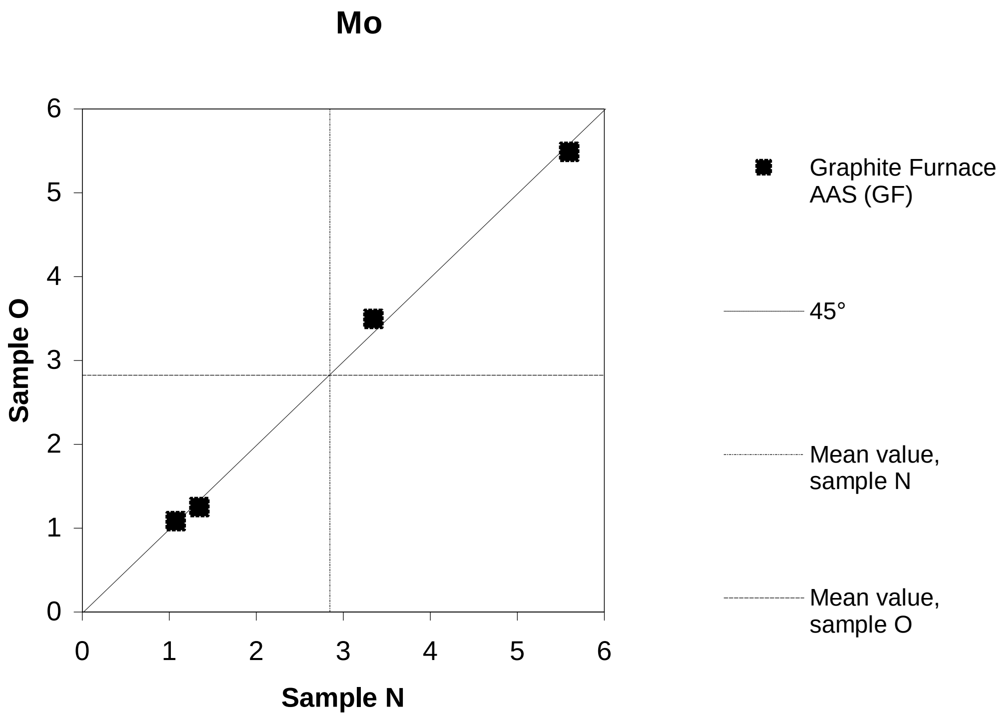
Mo, sediment (µg/g)

| Lab No. | N | O | Code | Outlier |
|---|---|---|---|---|
| 32 | 1.08 | 1.08 | Na0WZ | |
| 3 | 1.35 | 1.25 | Ao0PZ | |
| 15 | 3.35 | 3.49 | Am? | |
| 8 | 5.6 | 5.48 | Nm0W | |
| 5 | <0,5 | <0,5 | Nm0WZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **N,O** | 2.84 | 0.074 | 2.6 | 2.09 | 73.7 |

Mo, other methods

| Lab No. | N | O | Code |
|---|---|---|---|
| 2 | <20 | <20 | AmI |



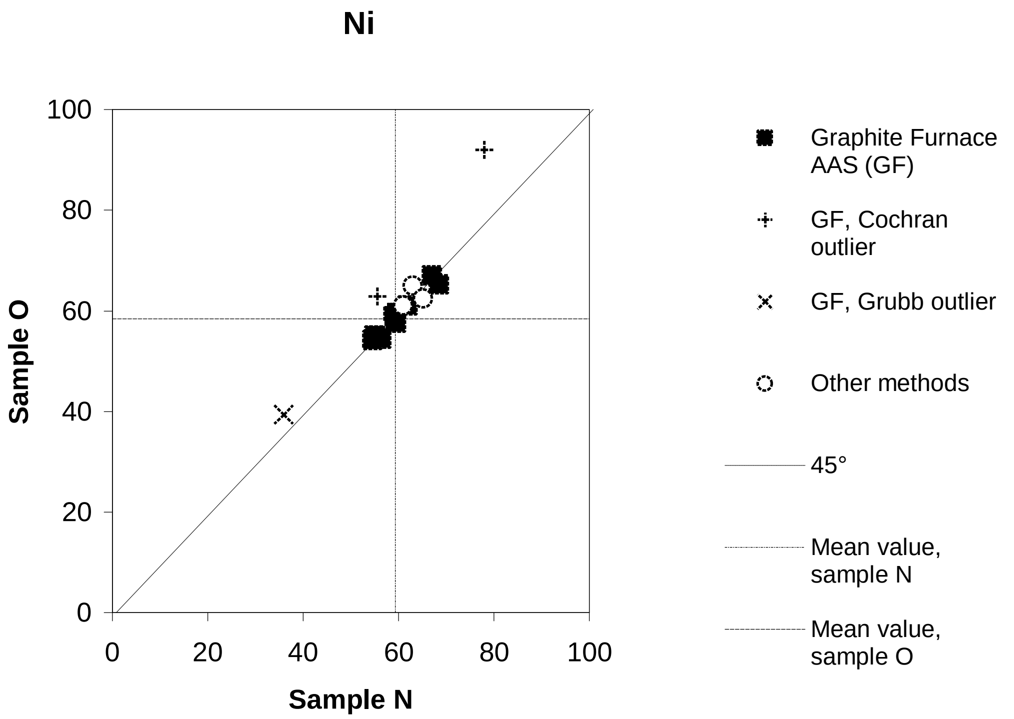
Ni, sediment (µg/g)

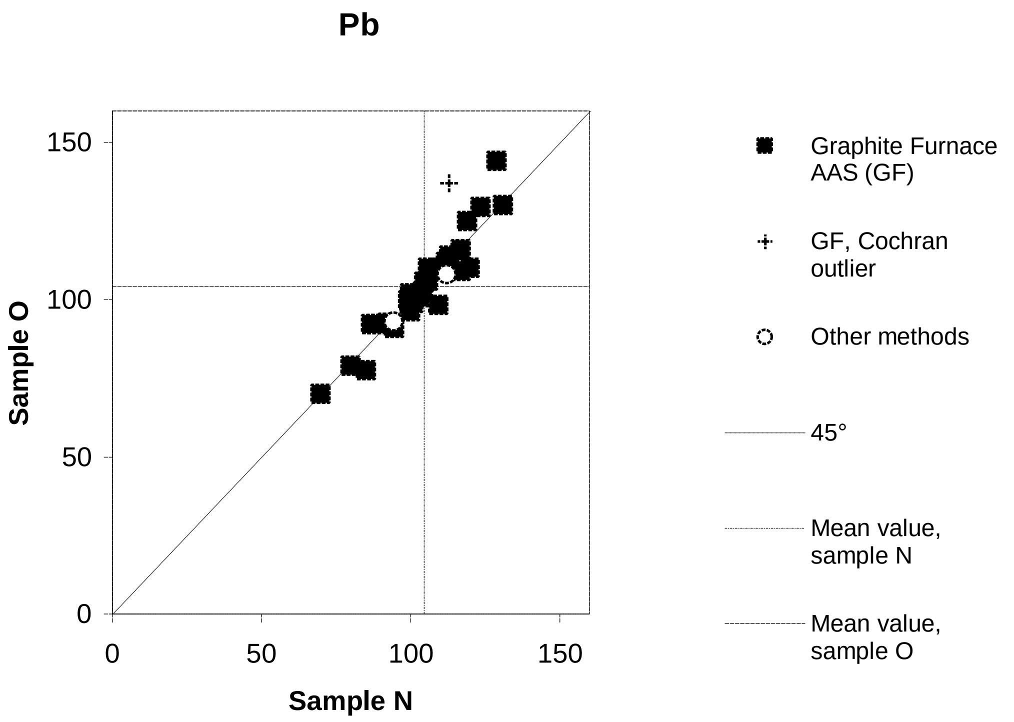
| Lab No. | N | O | Code | Outlier |
|---|---|---|---|---|
| 8 | 35.98 | 39.35 | Nm2WD | G |
| 15 | 54.6 | 54.2 | Am? | |
| 29 | 55 | 55 | Na0PD | |
| 5 | 55.2 | 54.7 | Nm0WZ | |
| 27 | 55.4 | 54.9 | Na0PZ | |
| 41 | 55.51 | 62.93 | Nm2PZ | C |
| 31 | 56.49 | 54.38 | Nm0PD | |
| 35 | 59 | 59.5 | Na2PZ | |
| 3 | 59.2 | 58.5 | Ao0PZ | |
| 32 | 59.4 | 59.5 | Na0PZ | |
| 22 | 59.5 | 57.6 | N?1,2WD | |
| 19 | 62.0 | 61.0 | Am0PZ | |
| 40 | 67 | 67 | Na0PZ | |
| 12 | 68.47 | 65.25 | Nm2PZ | |
| 40 | 78 | 92 | Aa0PZ | C |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **N,O** | 58.9 | 0.93 | 1.6 | 4.5 | 7.6 |

Ni, other methods

| Lab No. | N | O | Code |
|---|---|---|---|
| 2 | 61 | 61 | AmI |
| 19 | 63.0 | 65.0 | AmI |
| 37 | 65.1 | 62.4 | NoF |


Ni
Sample O
Sample N
0
20
40
60
80
100
Graphite Furnace AAS (GF)
GF, Cochran outlier
GF, Grubb outlier
Other methods
45°
Mean value, sample N
Mean value, sample O


Pb
Sample O
Sample N
0
50
100
150
Graphite Furnace AAS (GF)
GF, Cochran outlier
Other methods
45°
Mean value, sample N
Mean value, sample O

Pb, sediment (µg/g)

| Lab No. | N | O | Code | Outlier |
|---|---|---|---|---|
| 2 | 70 | 70 | Am2,3WD | |
| 9 | 80 | 79 | Na1,2WD | |
| 1 | 85.2 | 77.5 | Am0+WD | |
| 14 | 86.9 | 92.2 | Ao2,3?Z | |
| 31 | 88.67 | 92.23 | Nm2,3PD | |
| 41 | 92.47 | 92.67 | Nm2,3PZ | |
| 39 | 94.7 | 90.9 | Na2,3WZ | |
| 29 | 99.4 | 99.7 | Na2,3PZ | |
| 27 | 100 | 102 | Na2,3PZ | |
| 35 | 100 | 96.3 | Na3PZ | |
| 32 | 100.4 | 100.4 | Na0PZ | |
| 19 | 101 | 98.8 | Am0PZ | |
| 13 | 102.9 | 100.7 | Am2,3PZ | |
| 12 | 104.3 | 102.54 | Nm1,2,3PZ | |
| 34 | 104.7 | 105.6 | Na1PZ | |
| 6 | 106 | 110 | Nc2,3PZ | |
| 11 | 106 | 106 | Nm2,3PZ | |
| 22 | 109.5 | 98.3 | N?1,2WD | |
| 7 | 110 | 110 | Nm1,2PD | |
| 40 | 110 | 110 | Aa2,3PZ | |
| 26 | 112 | 112 | Nm2,3+PZ | |
| 3 | 113 | 114 | Ao3PZ | |
| 16 | 113 | 137 | Am3PZ | C |
| 20 | 117 | 116 | Nm2,3WZ | |
| 36 | 117 | 109 | Nm2,5WD | |
| 5 | 119 | 125 | Nm3WZ | |
| 40 | 120 | 110 | Na2,3PZ | |
| 8 | 123.5 | 129.4 | Nm1,2WD | |
| 16 | 129 | 144 | Nm3PZ | |
| 15 | 131 | 130 | Am? | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **N,O** | 103 | 3.6 | 3.5 | 18 | 17.3 |

Pb, other methods

| Lab No. | N | O | Code |
|---|---|---|---|
| 19 | 94.4 | 93 | AmI |
| 37 | 112.2 | 108 | NoF |

Sb, sediment (µg/g)

| Lab No. | N | O | Code | Outlier |
|---|---|---|---|---|
| 19 | 1.75 | 1.65 | Am1,2PZ | |
| 5 | <1 | <1 | Nm1,2WZ | |
| 1 | <10 | <10 | Am0+WD | |
| 32 | <1 | <1 | Na1,2PZ | |
| 2 | <5 | <5 | Am4WD | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **N,O** | 1.70 | - | - | - | - |

Sb, other methods

| Lab No. | N | O | Code |
|---|---|---|---|
| - | | | |

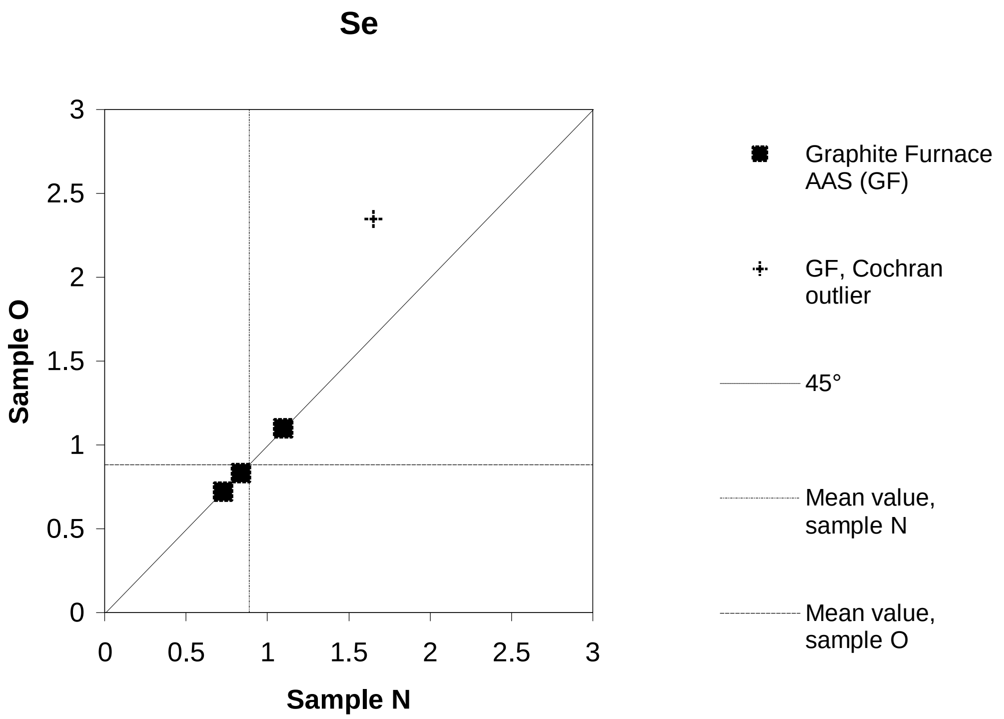
Se, sediment (µg/g)

| Lab No. | N | O | Code | Outlier |
|---|---|---|---|---|
| 12 | 0.73 | 0.72 | Nm1,2PZ | |
| 26 | 0.84 | 0.83 | Nm1,2+PZ | |
| 19 | 1.1 | 1.1 | Nm1,2PZ | |
| 15 | 1.65 | 2.35 | Am? | C |
| 5 | <1 | <1 | Nm1,2WZ | |
| 1 | <5 | <5 | Am1+WD | |
| 32 | <1 | <1 | Na1,2PZ | |
| 2 | <5 | <5 | Am1,2WD | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **N,O** | 0.887 | 0.006 | 0.7 | 0.193 | 21.7 |

Se, other methods

| Lab No. | N | O | Code |
|---|---|---|---|
| - | | | |



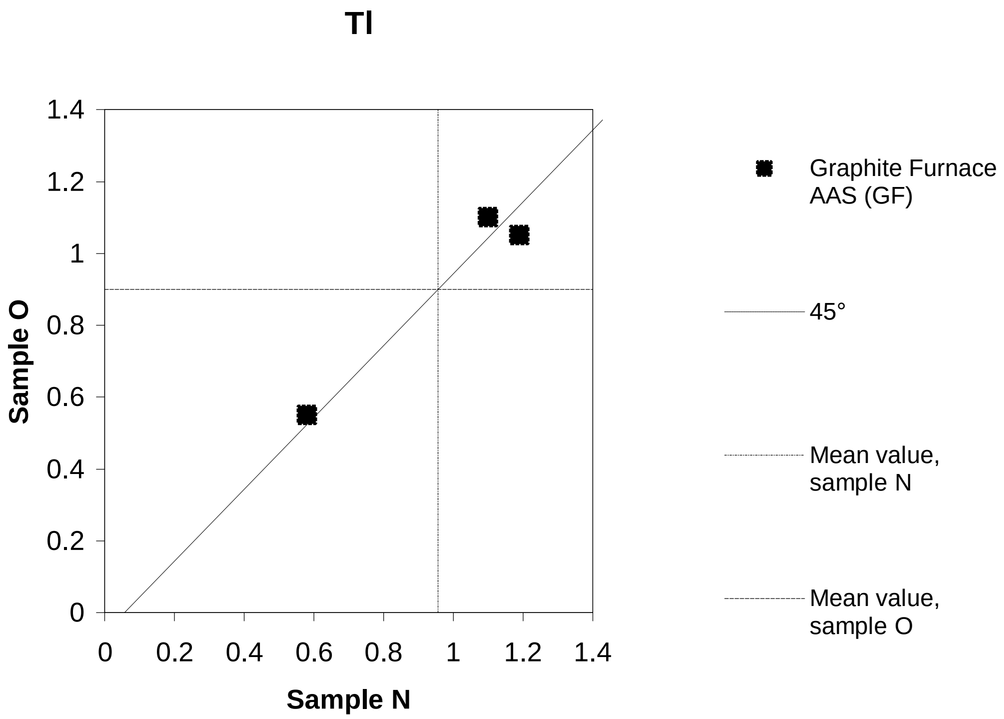

Tl, sediment (µg/g)

| Lab No. | N | O | Code | Outlier |
|---|---|---|---|---|
| 6 | 0.58 | 0.55 | Nc1,2PZ | |
| 19 | 1.1 | 1.1 | Nm1,2PZ | |
| 5 | 1.19 | 1.05 | Nm0WZ | |
| 1 | <2 | <2 | Am0+PD | |
| 2 | <5 | <5 | Am0WD | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **N,O** | 0.834 | 0.057 | 6.9 | 0.480 | 57.5 |

Tl, other methods

| Lab No. | N | O | Code |
|---|---|---|---|
| - | | | |



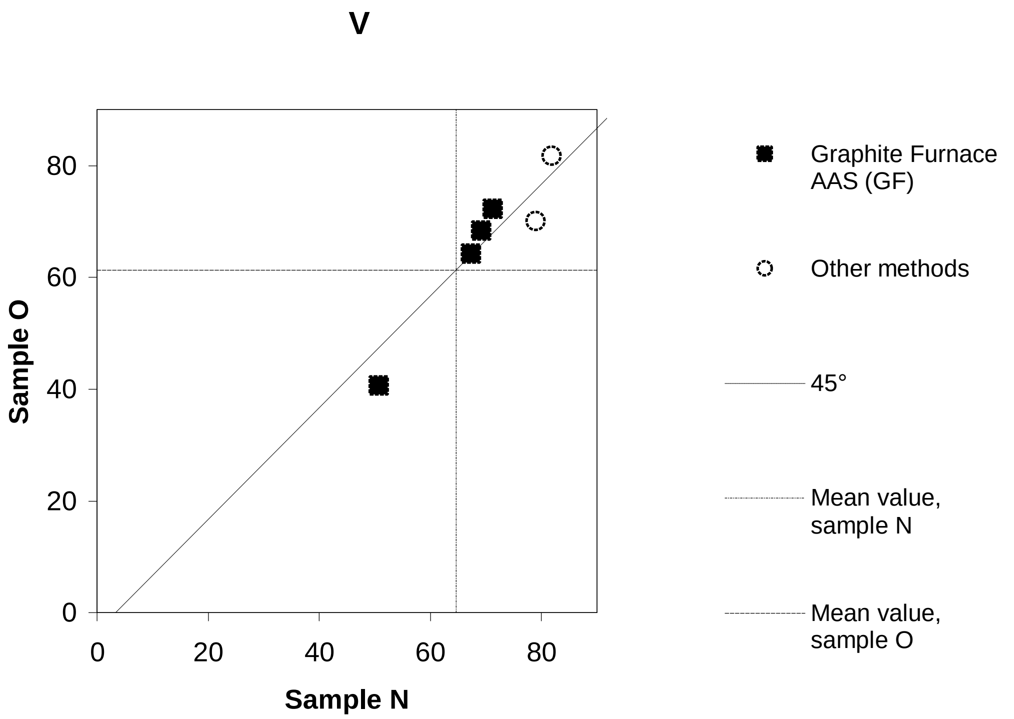

V, sediment (µg/g)

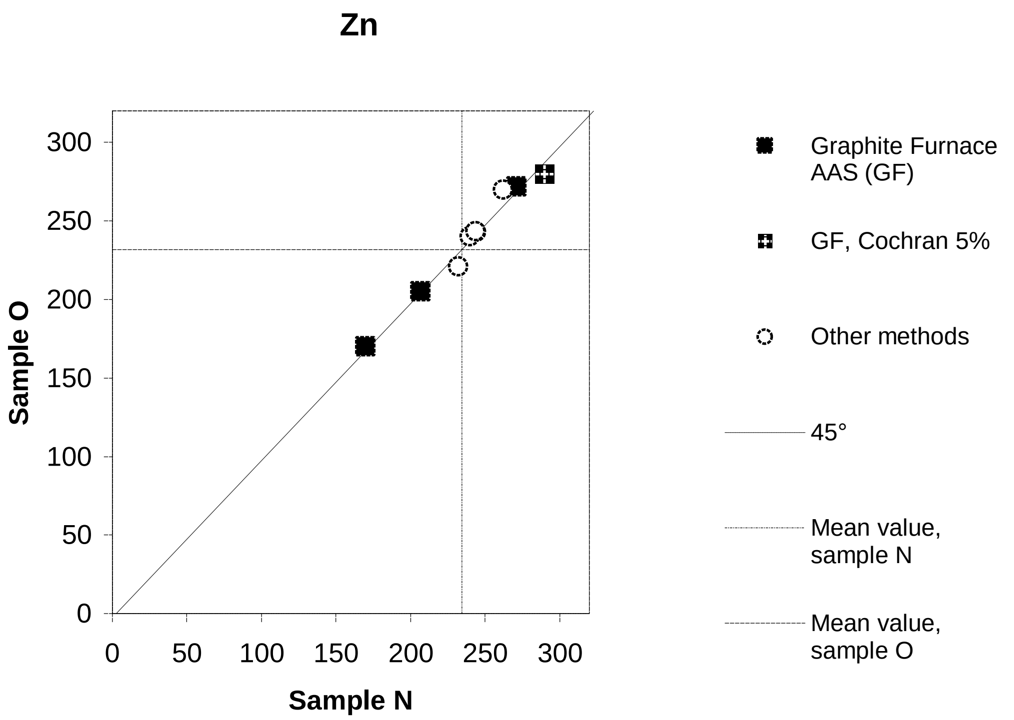
| Lab No. | N | O | Code | Outlier |
|---|---|---|---|---|
| 8 | 50.81 | 40.64 | Nm0W | |
| 1 | 67.4 | 64.2 | Am0+WD | |
| 5 | 69.2 | 68.3 | Nm0WZ | |
| 32 | 71.3 | 72.2 | Na0WZ | |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **N,O** | 63.0 | 3.8 | 6.0 | 12.1 | 19.2 |

V, other methods

| Lab No. | N | O | Code |
|---|---|---|---|
| 2 | 79 | 70 | AmI |
| 3 | 81.9 | 81.7 | AoI |


V
Sample O
80
60
40
20
0
0
20
40
60
80
Sample N
Graphite Furnace AAS (GF)
Other methods
45°
Mean value, sample N
Mean value, sample O


Zn
Sample O
300
250
200
150
100
50
0
0
50
100
150
200
250
300
Sample N
Graphite Furnace AAS (GF)
GF, Cochran 5%
Other methods
45°
Mean value, sample N
Mean value, sample O

Zn, sediment (µg/g)

| Lab No. | N | O | Code | Outlier |
|---|---|---|---|---|
| 40 | 170 | 170 | Aa0PZ | |
| 15 | 207 | 205 | Am? | |
| 5 | 271 | 272 | Nm0WZ | |
| 40 | 290 | 280 | Na0PZ | C 5% |

| | General mean | $s_r$ | $CV_r$, % | $s_R$ | $CV_R$, % |
|---|---|---|---|---|---|
| **N,O** | 233 | 3.6 | 1.6 | 54 | 23.4 |

Zn, other methods

| Lab No. | N | O | Code |
|---|---|---|---|
| 37 | 232 | 221 | NoF |
| 3 | 240 | 240 | AoI |
| 32 | 244 | 243 | NaF |
| 2 | 244 | 243 | AmI |
| 19 | 262 | 270 | AmI |

Total residue (%)

| Lab No. | N | O |
|---|---|---|
| 5 | 92.9 | 92.9 |
| 15 | 97.5 | |
| 11 | 97.8 | |
| 20 | 97.8 | 98.5 |
| 9 | 97.9 | 97.7 |
| 27 | 98 | |
| 19 | 98.1 | |
| 26 | 98.1 | 97.5 |
| 35 | 98.1 | 98.3 |
| 37 | 98.22 | 98.21 |
| 16 | 98.28 | 97.13 |
| 2 | 98.3 | 98.7 |
| 8 | 98.3 | 98.2 |
| 6 | 98.6 | |
| 12 | 98.82 | |
| 34 | 98.9 | 99.3 |
| 22 | 99.16 | 99.46 |

# Appendix IV.
# Participants

AUSTRIA

Amt der Salzburger Landesregierung
Abteilung 16, Landeslabor
Ulrich-Schreier-Strasse 18
A-5020 Salzburg

Amt der Tiroler Landesregierung
Chemisch-Technische Umweltschutzanstalt
A-6200 Rotholz Nr. 46

IFA-Tulln, Analytikzentrum
Konrad-Lorenz-Straße 20
A-3430 Tulln

Montanuniversität Leoben
Institut für Entsorgungs- und Deponietechnik
Peter-Tunner-Straße 15
A-8700 Leoben

Rumpold AG
Dellachergasse 8
A-8783 Trofaiach

Umweltlabor
Dr. Axel Begert GmbH.
Ringstrasse 11
A-4672 Bachmanning

BRAZIL

Departamento de Quimica
Universidade Federal de Santa Catarina
88040-900 Florianopolis

ESTONIA

Estonian Environ Research Lab
Marja 4D
EE-10617 Tallinn

Tartu Environmental Research Ltd
Akadeemia 4
EE-51003 Tarttu

FINLAND

Pirkanmaa Regional Environment Centre
Kokkolankatu 4
FIN-33300 Tampere

Water and Env. Res. of South-West Finland
Telekatu 16
FIN-20360 Turku

FRANCE

C.A.R. Dpt Hydrologie et Environnement
76 route du Rhin, BP 321
F-67411 Illkirch

INERIS
Parc Technologique ALATA, BP 2
F-60550 Verneuil en Halatte

Institut Pasteur de Lille
Water and Environment Department
1, rue Calmette, BP 245
F-59019 Lille Cedex

Laboratoire Departemente d'Hydrologie et d'Hygiene
18, Bd Lavoisier, BP 943
F-49009 Angers Cedex 01

Laboratoire LARA
75 voie du TOEC
F-31300 Toulouse

GERMANY

Bayer. Landesamt für Wasserwirtschaft
Lazarettstraße 67
D-80636 München

Bundesanstalt für Gewässerkunde
Schnellerstraße 140
D-12439 Berlin

IWW GmbH
Moritzstraße 26
D-45476 Mülheim an der Ruhr

Landesamt für Wasserwirtschaft Rheinland-Pfalz
Am Zollhafen 9
D-55118 Mainz

Ruhrverband
Kronprinzenstraße 37
D-45128 Essen

Stadtwerke Essen AG
Rüttenscheider Straße 27-37
D-45128 Essen

## HUNGARY

Directorat of Environmental Protection
Central Laboratory
H-1113 Budapest, AGA U. 4

National Center for Public Health
Centr. Labor for Chemical Analysis
Nagyvárad tér 2
H-1450 Budapest, Pf.: 22

National Institute of Environmental Health
Gyáli út 2-6
H-1097 Budapest, Pf. 26

## THE NETHERLANDS

RIVM, Dept. LAC
P.O. Box 1
3720 Ba Bilthoven

## NORWAY

Alex Stewart Environmental Services A/S
Tyssedalsvn. 16
N-5750 Odda

ANØ miljøkompetanse
Hvamstubben 14, Postboks 38
N-2027 Kjeller

Lab Nett Lillehammer
Vormstuguveien 40, Fakkelgården
N-2624 Lillehammer

Nasjonalt Folkehelseinstitutt
Postboks 4404 Nydalen
N-0403 Oslo

NIVA
Brekkevejen 19, P.O. Box 173 Kjelsås
N-0411 Oslo

Norges geologiske undersøkelse
NGU-Lab
Leif Erikssons vei 39
N-7491 Trondheim

Oslo kommune, vann- og avløpsetaten
Herslebsgate 5, 7.etg
Postboks 4704 Sofienberg
N-0506 Oslo

Planteforsk
Kjemisk analyselaboratorium Holt
N-9292 Tromsø

Vestfold interkommunale
nœ ringsmiddellaboratorium
Postboks 2009 Postterminalen
N-3103 Tønsberg

## SLOVAK REPUBLIC

Water Research Institute
Nábr. Arm. Gen. L. Svobudu 5
SK-81249 Bratislava

## SWEDEN

Göteborgs VA-verk
Box 123
SE-424 23 Angered

Institute of Applied Environmental Research
(ITM)
Stockholm university
SE-106 91 Stockholm

IVL Svenska Miljöinstitutet AB
Box 210 60
SE-100 31 Stockholm

Stockholm Vatten AB, Vattenvård
Torsgatan 26
SE-106 36 Stockholm