# 5th Workshop

# Proficiency Testing for Water Testing Laboratories Evaluation of 4th PT round

Dar es Salaam
4 – 6 December 2007

# Report on the Workshop Proficiency Testing for Water Testing Laboratories with Training Course on Method Validation and Measurement Uncertainty

## *Dar es Salaam, Tanzania, 4 – 6 December 2007*

Prepared by Dr.-Ing. Michael Koch

## *Summary*


The workshop covered the evaluation of the 4th SADCMET Water PT round and all aspects that could be derived from the results. The results showed that there is - generally seen - not really an improvement over the 4 PT rounds. Most probably this is due to the absence of adequate corrective actions after failures in the PT.

Therefore one of the topics in the training session was the information how to do corrective actions as part of a method validation procedure.

Most of the participants are still very enthusiastic. It is highly recommended to continue the PT system for chemical analyses and to extend it to microbiology as discussed in 2006. The structure of local coordinators turned out to be very useful and should be further strengthened to minimize logistical problems and to increase the number of participants. The assessment procedure using limited standard deviations has again proven to be very effective, the statistical methods are in accordance with the internationally recommended procedures.

The SADC ASSOCIATION OF WATER TESTING LABORATORIES (SADCWATERLAB) had its general assembly meeting during the workshop. This association is the responsible body for the PT system and an opportunity for collaboration and information exchange between its members. The role of SADCWATERLAB should be strengthened by an officially memorandum of understanding. This MoU will be finalised within the next months.


## *Introduction*

The workshop reported here followed previous workshops held in Windhoek, Namibia (February 2004), Pretoria, South Africa (November 2004), Dar es Salaam, Tanzania (November 2005) and Gaborone, Botswana (November 2006). The reports are available from http://www.sadcmet.org. As a result of these workshop the first and second proficiency tests for water testing laboratories were organised by Umgeni Water (Pietermaritzburg, South Africa), the following rounds after a training in Germany by Namwater (Windhoek, Namibia). One of the aims of this workshop in Dar es Salaam was the evaluation of the fourth PT round on chemical parameters.
Besides this the opportunity of the workshop was used to provide training courses on method validation and measurement uncertainty.
The cooperation of laboratories within he SADCWaterLab Association was also discussed during the workshop.

## *Participants and Organisation*

The workshop was attended by 32 participants from the following countries:

- Botswana 1
- Ethiopia 1
- Kenya 2
- Madagascar 1
- Malawi 1
- Mauritius 1
- Namibia 3
- South Africa 2
- Swaziland 1
- Tanzania 14
- Uganda 2
- Zambia 1
- Zimbabwe 2

A complete list of participants is given in annex 1.

## *PT Workshop Programme*

### Tuesday, 04 December 2007:

Welcome, Opening of $4^{th}$ PT evaluation and assessment

### Wednesday, 05 December 2007:

Training course on Corrective Actions, Method Validation and Measurement Uncertainty

### Thursday, 06 December 2007:

Lab visit at Tanzania Bureau of Standards
SADCWaterLab general assembly

## *Tuesday, 04 December 2007*

### *Opening and Evaluation of and experiences from the 4th SADCMET Water PT*

- Opening
- ***All Participants***: Introduction
- ***M. Conradie***: Experiences of the PT provider
- **Local coordinators:** Report
- **All participants:** Working group discussions 1
- ***M. Koch***: Assigned values for the 4th SADCMET Water PT
- ***M. Koch***: Presentation on the content of the workshop CD
- ***M. Koch***: Evaluation of the 4th SADCMET WATER PT
- ***M. Koch***: Development of standard deviations over the 4 PT rounds
- **All participants:** Working group discussions 2

### Opening

The Workshop was officially opened by Charles Ekelege, acting director for the Tanzania Bureau of Standards.
The PTB representative Stefan Wallerath, the new SADCMET regional coordinator Donald Masuku and Mrs.Kezia Mbwambo as chair of SADC Water Lab also welcomed the participants.
All participants shortly introduced themselves.

### M. Conradie: Experiences of the PT provider

Merylinda Conradie reported about her experiences with this 4th PT round. She listed the changes in participation from the member countries (table 1).

Table 1: Number of labs participating in the PT rounds

| country | 2004 | 2005 | 2006 | 2007 |
|---|---|---|---|---|
| Angola | 1 | 1 | 1 | 0 |
| Botswana | 2 | 2 | 2 | 4 |
| Ethiopia | 1 | 1 | 1 | 0 |
| Kenya | 2 | 2 | 4 | 3 |
| Lesotho | 1 | 1 | 0 | 1 |
| Madagascar | 0 | 0 | 2 | 2 |
| Malawi | 2 | 2 | 2 | 3 |
| Mauritius | 1 | 3 | 4 | 3 |
| Mozambique | 2 | 3 | 2 | 0 |
| Namibia | 2 | 2 | 3 | 3 |
| Seychelles | 1 | 2 | 2 | 1 |
| Swaziland | 1 | 1 | 0 | 1 |
| Tanzania | 2 | 8 | 5 | 12 |
| Uganda | 1 | 3 | 6 | 5 |
| Zambia | 1 | 4 | 2 | 3 |
| Zimbabwe | 2 | 3 | 3 | 5 |
| total number | 22 | 44 | 39 | 46 |

She listed the parameters to be analysed in this PT round (table 2). There was no change compared to 2006

Table 2: List of parameters in the 3rd PT round

| | |
|---|---|
| Sulphate | Manganese |
| Chloride | Aluminium |
| Fluoride | Lead |
| Nitrate | Copper |
| Phosphate | Zink |
| Calcium | Chromium |
| Magnesium | Nickel |
| Sodium | Arsenic |
| Potassium | Cadmium |
| Iron | |

She described the planning including the chemicals used for spiking, the necessary materials for sample preparation and packaging, choice of courier and necessary balances.
In detail she explained the preparation of the samples including

- Cleaning of bottles
- Weighing of chemicals
- Traceability of the weighings by taking pictures with a digital camera
- Digestion of metals
- Preparation of stock solutions
- Labelling of bottles
- Preparation of final batches
- pH adjustment
- Ensuring homogeneity
- Sample dispensing
- Storage
- Preparation of documentation
- Packaging
- Information to courier
- Shipment

The participants from Angola and Lesotho reported customs problems.
Results were received by fax or e-mail. The deadline had to be extended because of courier problems.
The results were typed into an EXCEL spreadsheet. Evaluation was done using the programme developed especially for the SADCMET PT scheme.
Payments were made using bank drafts, transfers and cheques. Some payments were made, but the money is still outstanding. Namwater still experiences problems to identify the payments within Namwater due to insufficient informationfrom bank/participant. Some payments were not yet made at all.
Local coordinators were very helpful especially with the courier problems.
Details of the evaluation were explained by M. Koch in the following presentations.
The following challenges for 2008 were identified:

- The results should be used as a motivation to improve performance and apply corrective actions if necessary

- Strive to improve the success
- Increase the number of analysed parameters
- Reporting of results again caused problems with incorrect units (e.g as N and not $NO_3$ and as P and not $PO_4$
- Try and rectify the analyses not determined due to a lack of chemicals or problems with equipment
- Instrumentation or method should be stipulated clearly
- Once again very high standard deviations in the 2007 PT scheme to be improved in 2008

The PT provider experienced the following problems:

- Interruptions of sample preparation and evaluation by routine tasks in the laboratory
- Limited number of staff
- Late confirmations and requests of participation caused problems and unnecessary rearrangements with the courier
- The initial return date for the results was set as the 31st of August 2007 with an extension of three weeks for some of the laboratories due to transportation problems. Five laboratories did not submit results at all.
- Follow-up of participation where people did not respond on e-mails
- Late submitting of results due to courier problems delayed the submitting of the evaluation report
- Receipt of results by fax – unclear and difficult to get hold of the participant
- Three labs did not take part due to courier problems

M. Conradie expressed her thanks to PTB for the financial support, especially for the new balances, to SADCMET secretariat, to M. Koch, to the Namwater colleagues, the local distributors and all participants.
The full presentation is included in annex 2.

## Local coordinators: Report

The local coordinators were asked to fill out a questionnaire (annex 3) for the report about their activities and to give a short oral report.
The completed questionnaires of the local coordinators from Madagascar, Zimbabwe, Uganda, Swaziland, Tanzania, Namibia, Mauritius, Kenya, Malawi and Zambia may be found in annex 4.
It was agreed that it is the local coordinators most important task to promote the PT system as much as possible. The activities of the local coordinator in Tanzania who succeeded in mobilising 12 participants could serve as an example for others. The use of personal contacts seems to be the most efficient way.

## All participants: Working group discussions

The experiences of the participants were discussed in three working groups answering seven questions. The results can be summarized as follows:

1. **Announcement of the scheme – did you receive enough information in good time?**
    - Enough time
    - E-mail communication problems
    - Try to use fax if e-mail does not work
    - receipt of communication
    - clear and enough

2. **Registering – did you have any problems?**
    - see above

3. **Local coordinators – did it work?  - have all interested/relevant laboratories got all the information from local coordinators?**
    - little problems
    - resources for communication
    - need of support from institutions
    - change from persons to institutions
    - letter to institution, not to persons
    - need of awareness creation
    - need to use national associations
    - not very effective, letter to be improved
    - coordination should be a task of the institutions

4. **Shipment – did you encounter any courier problems? - did everybody get the samples in time?**
    - no problem
    - some customs problems
    - delay in picking up the samples from LC

5. **Reporting of results – any problems?**
    - no problem
    - need for acknowledgement

6. **Payment / costs? – Is the fee affordable? – Problems with money transfer?**
    - Fee is affordable
    - no problem with transfer
    - need for proforma invoice
    - bank charges problems

7. **Are you, as a customer, satisfied with the organisation?**
    - very much satisfied
    - work very much appreciated

    Need to expand to other areas

## M. Koch: Assigned values for the 4th SADCMET Water PT

M. Koch explained the different possibilities for the determination of the assigned values as stated in ISO 13528. Since there no CRM and no reference measurements were  available and the consensus means of the participants were not reliable enough, reference values from sample preparation were chosen as assigned values. The procedure for the sample preparation was explained in detail including the formula for the calculation of the assigned value from the different weighings, the molar masses, the purity of the chemicals, the density and the buoyancy correction factor. With this formula a measurement uncertainty budget was calculated according to the Guide to the Expression of Uncertainty in Measurement. The estimation of the uncertainty of the weighings from precision experiments and from manufacturers trueness information was explained. The estimation of all the other uncertainties as shown resulting in the low expanded relative uncertainties (k=2) shown in figure 1.

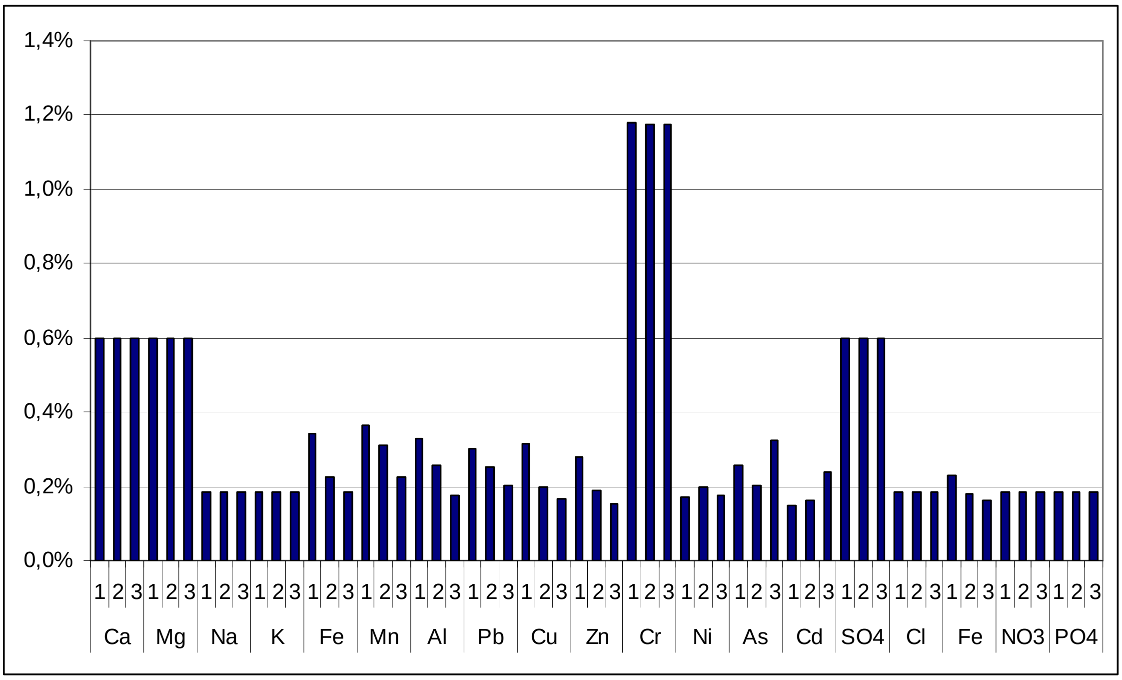


Figure 1: Expanded relative uncertainties of the reference values

## M. Koch: Evaluation of the 4th SADCMET Water PT

M. Koch explained in detail the result of the evaluation of the PT round. As in the last round the assigned values were derived from the weighings made for the preparation of the samples. the standard deviations were calculated using Algorithm A from ISO 13528. These standard deviations were used for the calculation of z-scores, if they were below the limits for the standard deviations agreed upon during the previous workshops (table 3).

Table 3: Limits for standard deviations

| Parameter | limit in % |
|---|---|
| Sulphate | 10 |
| Chloride | 10 |
| Fluoride | 12 |
| Nitrate | 15 |
| Phosphate | 10 |
| Calcium | 10 |
| Magnesium | 10 |
| Sodium | 10 |
| Potassium | 10 |
| Iron | <1 mg/l: 20, >1 mg/l: 12 |
| Manganese | <1 mg/l: 20, >1 mg/l: 12 |
| Aluminium | 30 |
| Lead | < 0,5 mg/l: 40, > 0,5 mg/l: 25 |
| Copper | 20 |
| Zinc | 20 |
| Chrome | 25 |
| Nickel | 25 |
| Cadmium | 30 |
| Arsenic | 30 |

In order not to affect the statistical calculations by gross outliers all values outside the range ref.-value/8 to ref.-value*8 were excluded prior to these calculations.
The detailed presentation is included in annex 5.
For the individual parameters the following conclusions could be derived from the data:

- Sulphate: The means of the data were higher than the reference value, showing positive bias. The standard deviations were higher than the limits. The gravimetrically determined values showed a high portion of too high values
- Chloride: There was a quite good agreement between the data means and the reference values. The standard deviations were around the limit. As in the previous round it was not clear, what was meant with the statement "titrimetric" as method. So the method specific evaluation was not very clear. Nevertheless the data showed many outliers (with too high values) for the colorimetric and potentiometric method
- Fluoride: The mean values were around the reference values. For low concentrations the standard deviations were higher than the limit. The colorimetrically determined values had a very high portion of non-reliable values.
- Nitrate: As in the previous rounds some values obviously were reported in wrong units. Therefore the mean values were quite low and the standard deviations high. The average quality of the data is very bad. The parameter needs more emphasis. Harmonization of methods could help.
- Phosphate: Some values also were reported with wrong units. Generally the standard deviation and the number of outliers were high. The data set of colorimetrically determined values contained a high number outlying values, which partially was due to reporting in wrong units.
- Calcium: The mean of the values were close to the reference values. The standard deviations were above the limit. A tendency to lower values could be recognised for AAS-values, a tendency to higher values for titrimetric values

- Magnesium: The mean values were around the reference values, but the standard deviations were too high. Titrimetrically determined values in general were not reliable.
- Sodium: The means were close to the reference values. The standard deviations were too high. Many values determined with FEP were too high, many of the AAS-values were not reliable.
- Potassium: The means of the values were close to the reference values, the standard deviations a bit higher than the limit. AAS values contained many non-reliable data.
- Iron: The means were lower than the reference values and the standard deviations were higher than the limit. The colorimetric method delivered many outlying values.
- Manganese: The means were about 4% below the reference values, the standard deviation around the limit. AAS values showed a broad statistical distribution
- Aluminium: Only few participants analysed this parameter. Therefore the number of values was small. The mean were a bit below the reference values. Lead: The means of the datasets were only a bit below the reference values. Compared with the limit the standard deviations of the datasets were quite low.
- Copper: For this parameter the data means also were in good agreement with the reference values and the standard deviations also were low.
- Zinc/Chromium/Nickel: The data means also showed no bias for the determination of zinc and the standard deviations were around the limit.
- Arsenic: Only a few laboratories analysed for arsenic. So the number of values was very low. The means of the dataset were close to the reference values and the standard deviations were around the limit
- Cadmium: The mean values of the data sets were slightly below the reference values.

Only 4 participants analysed all parameters. The  percentage of participation per laboratory is shown in fig. 2.

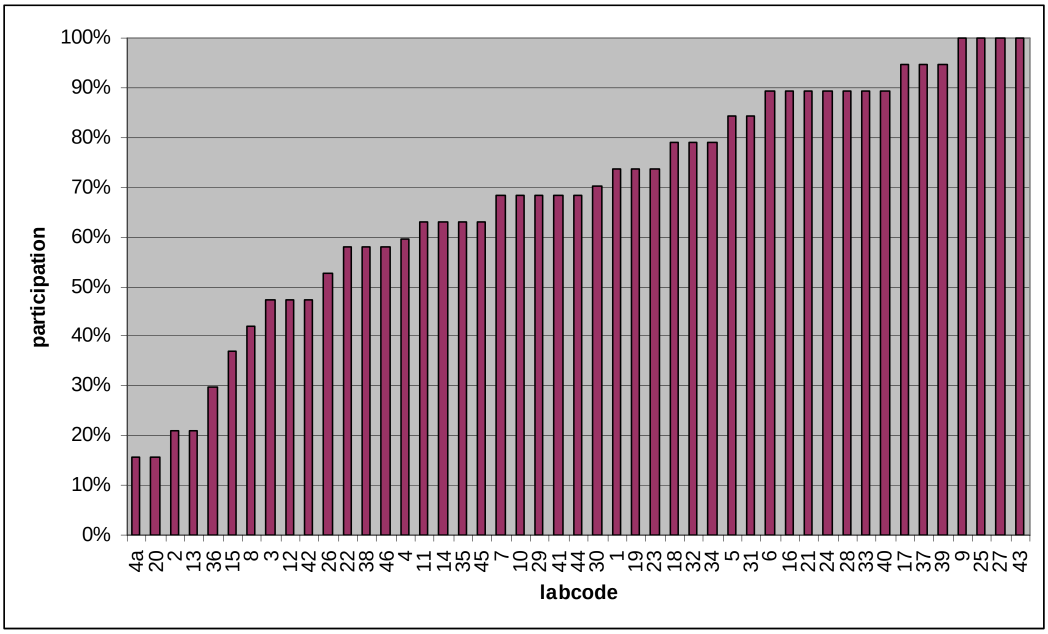


Figure 2: Percentage of participation for each participant

17 participants managed to analyse more than 80% of their values within the tolerance limits (compared to 10 labs in 2006). Fig. 3 shows the proportion of successfully analysed parameters for each participant.
For the laboratories with more than 80% successfully analysed values the number of values delivered is also shown in the diagram.

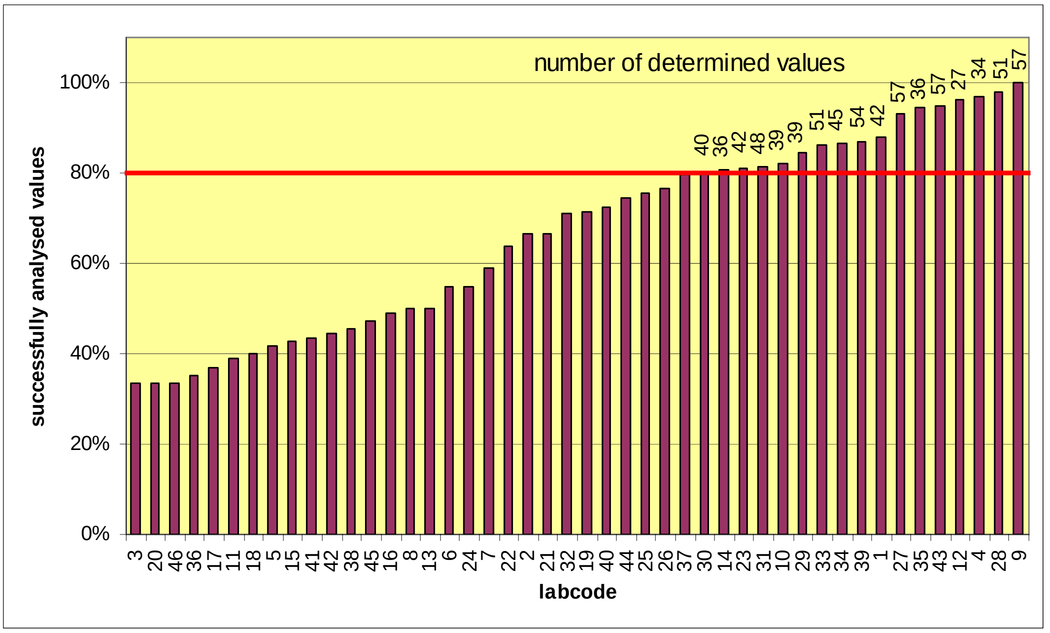


Figure 3: Percentage of successfully analysed values for each participant

The definition of fitness-for-purpose criteria (in the form of limits for the standard deviation) resulted in a higher proportion of values outside the tolerance limits. Experience from Germany shows that normally up to 20% of non-successfully analysed values can be expected for each parameter.
Fig. 4 shows for each parameter the percentage of values outside the tolerance limits. The figure shows that – on the basis of the current fitness-for-purpose-criteria - improvement is still necessary for most of the parameters.

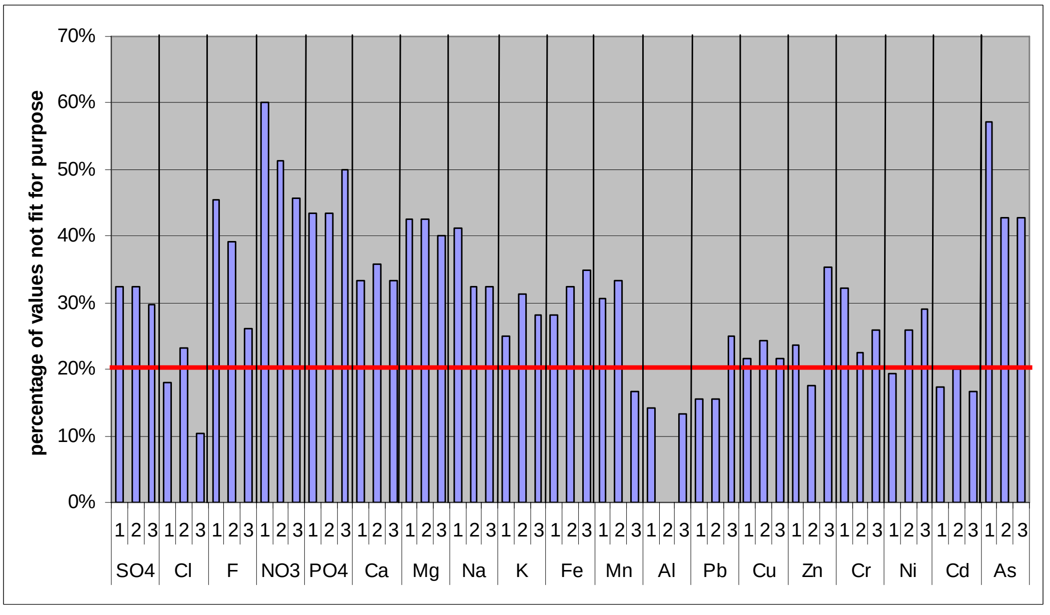


Figure 4: Percentage of values outside the tolerance limits for all samples

Michael Koch came to the following conclusions:

- The PT Provider did a very good job
- The evaluation and assessment procedure is fit for the purpose
- The SADCMET Water PT is a good possibility for the participants to compare with peers and with stated fitness-for-purpose criteria
- The results of many laboratories are still not satisfactory and need improvement
- Special emphasis should be put on corrective actions after unsatisfactory participation

## M. Koch: Development of Standard Deviations over the 4 PT rounds

M. Koch showed in his presentation (annex 6) the development of the standard deviations over the four SADCMET PT rounds for all parameters. The comparison of the standard deviations of the 4th round with the previous rounds is summarized in table 4:

Table 4: Assessment of the standard deviations of the 3rd round from a comparison with the previous rounds

| | |
|---|---|
| better | potassium, arsenic |
| no change | sulphate, chloride, fluoride, phosphate, sodium, iron, manganese, aluminium, lead, copper, zinc |
| worse | nitrate, calcium magnesium |

During the previous workshops the participants agreed on quality standards (limits for the standard deviation) for all parameters. The comparison of the standard deviations calculated from the data sets with these quality standards gives the results shown in table 5.

Table 5: Comparison of calculated standard deviations with the quality standards set during the previous workshops.

| | |
|---|---|
| good | aluminium, lead, copper, zinc |
| still acceptable | chloride, potassium, iron, manganese, chromium, nickel, cadmium |
| not acceptable | fluoride, arsenic |
| bad | sulphate, nitrate, phosphate, calcium, magnesium, sodium |

The main question remaining from these data is, why we can't see a clear improvement after 4 PT rounds. This was also discussed during the following working group discussions.

**All Participants: Working group discussions - PT evaluation**
Five questions were discussed in three working groups.
Results of the discussion:

### 1. How do you judge the outcome of the PT round?

- some parameters (Ca, Mg) good, bad for some others (Nitrate)
- quality of results should be improved
- standard deviations quite high
- general commitment observed (increased number of labs)
- not that good

2. **Is the evaluation procedure ok?**
   - yes
   - more sample volume for re-testing?
   - no doubt

3. **How can we help national coordinators to better promote the PT scheme?**
   - need to support
   - national workshops
   - creation of awareness
   - participants to be ambassadors
   - collect samples at LC instead of national transport
   - talk to other people
   - dissemination of information by participants

4. **What has to be changed in the system? (fee, time schedule, …)**
   - appointment of LC more official
   - announcements earlier
   - nothing

5. **Why can't we see a clear improvement after 4 PT rounds?**
   - corrective actions were not taken
   - no appropriate quality management system in the labs
   - training of trainers need
   - problems not properly recognized
   - procedure to find the proper corrective action is not clear
   - improve equipment
   - proper storage procedures needed
   - update methods regularly – harmonize
   - takes long time to get chemicals
   - bad quality of chemicals
   - high level of staff fluctuation

Further discussions and agreements were made during the SADCWaterLab General Assembly (see below).

## *Wednesday, 05 December 2007*

### *Training*

- ***C. Modika***: SABS Proficiency Testing Scheme
- ***M. Koch***: Content of the Workshop CD
- ***M. Koch***: Types of errors / corrective actions
- ***M. Koch***: Method validation
- ***M. Koch***: Explanation of EXCELKONTROL 2.0 – software for control charts
- ***M. Koch***: Measurement uncertainty revisited

## C. Modika: SABS Proficiency Testing Scheme

C. Modika presented the SABS proficiency testing programme with special emphasis on the water check scheme. The complete presentation may be found in annex 7.

## M. Koch: Content of the workshop CD

A CD was distributed to all participants by M. Koch with the following content:

- European Union - COUNCIL DIRECTIVE 98/83/EC of 3 November 1998 on the quality of water intended for human consumption
- Accreditation
    - CITAC_EURACHEM Guide to Quality in Analytical Chemistry 2002
    - EA-4-09rev01Accreditation for Sensory Testing Laboratories
    - EA-4-10rev02Accreditation for Microbiological Laboratories
    - EA-4-15rev00Accreditation for Bodies Performing non-Destructive Testing
    - EURACHEM_EA Accreditation for Microbiological Laboratories 2002
    - Ilac-g4 Guidelines on Scopes of Accreditation
    - Ilac-g10 Harmonised Procedures for Surveillance & Reassessment of Accredited Laboratories
    - Ilac-g14 Guidelines for the Use of Accreditation Body Logos and for Claims of Accreditation Status
    - Ilac-g15 Guidance for Accreditation to ISO-IEC 17025
    - Ilac-g18 The Scope of Accreditation and Consideration of Methods and Criteria for the Assessment
    - Ilac-g19 Guidelines for Forensic Science Laboratories
- Control charts
    - NORDTEST TR 569 Internal Quality Control
    - ***new:*** EXCELKONTROL 2.0 – Software for Quality Control Charts
    - Manual for EXCELKONTROL
- General
    - Harmonised Guidelines for the Use of Recovery Information in Analytical Measurements 1998
    - Quality Assurance for Research and Development and Non-routine Analysis
- Measurement uncertainty
    - A2LA Guide for the Estimation of Measurement Uncertainty In Testing
    - VAM Project 3.2.1 Development and Harmonisation of Measurement Uncertainty Principles - Part (d): Protocol for uncertainty evaluation from validation data
    - EA-4-16rev00EA Guidelines on the Expression of Uncertainty in Quantitative Testing
    - Ilac-g17 Introducing the Concept of Uncertainty of Measurement in Testing
    - NORDTEST - Uncertainty of quantitative determinations derived by cultivation of microorganisms
    - NORDTEST – Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories
    - EURACHEM/CITAC Quantifying Uncertainty in Analytical Measurement, 2nd Edition 2000
    - ***new:*** Eurachem/EUROLAB/CITAC/Nordtest Guide (Draft 2007): Estimation of measurement uncertainty arising from sampling

    - ***new:*** EUROLAB Technical report No. 1/2007: Measurement uncertainty revisited: Alternative approaches to uncertainty evaluation
    - ***new:*** EURACHEM/CITAC Guide: Use of uncertainty information in compliance assessment. First edition 2007
- Proficiency Testing
    - EA-3-04-rev01Use of Proficiency Testing as a Tool for Accreditation in Testing
    - ***new:*** Ilac-g13 Guidelines for the Requirements for the Competence of Providers of Proficiency Testing Schemes 8/2007
    - Ilac-g22 Use of Proficiency Testing as a Tool for Accreditation in Testing
    - IUPAC - The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories 2006
    - Selection, Use and Interpretation of Proficiency Testing (PT) Schemes by Laboratories 2000
- Reference Materials
    - EA-4-14rev00The Selection and Use of Reference Materials
    - Ilac-g9 Guidelines for the Selection and Use of Certified Reference Materials
    - Ilac-g12 Guidelines for the Requirements for the Competence of Reference Materials Producers
    - The Selection and use of Reference Materials 2002
- Traceability
    - EA-4-07 Traceability of Measuring and Test Equipment to National Standards
    - Ilac-g2 Traceability of Measurements
    - EURACHEM/CITAC - Traceability in Chemical Measurement 2003
- Validation
    - EURACHEM - The Fitness for Purpose of Analytical Methods - A Laboratory Guide to Method Validation and Related Topics 1998

**M. Koch: Types of errors / corrective actions**
M. Koch explained how the graphical displays of lab results vs. assigned values provided with the evaluation report of the PT may be used to get hints for the type of errors in the case of non-satisfactory participation (annex 8).
According to M. Koch the following corrective actions should be applied:

- If you found a proportional systematic error: Check calibration
- Check for precision using internal quality control data (Control Charts)
- Check for bias using a certified or in-house reference material
- If you can't find the problem, carry out full method validation

**M. Koch: Method validation**
M. Koch explained the principals of method validation and what is necessary under given circumstances. After a definition and introduction he put special emphasis on the calibration including linearity, residual analysis, homogeneity of variances and outlier tests. He described methods for the determination of l.o.d. and l.o.q. Selectivity and robustness of methods were also described. Finally the standard addition procedure – a calibration in the real sample – was explained. The full presentation is attached in annex 9.

**M. Koch: Explanation of EXCELKONTROL 2.0 – software for control charts**
M. Koch explained the new version of EXCELKONTROL 2.0 – a freeware tool for control charts programmed by Michael Gluschke and Michael Koch. The programme is included in the workshop CD.

**M. Koch: Measurement uncertainty revisited**
Based on the EUROLAB Technical Report No. 1/2007 "Measurement Uncertainty Revisited" M. Koch described alternative approaches to uncertainty evaluation. These approaches can be grouped into

- two intralaboratory approaches
    - Modelling approach (often called the "GUM approach")
    - Single laboratory validation approach
- two interlaboratory approaches
    - Interlaboratory validation approach
    - PT approach

The full presentation is included in annex 10.

## *Thursday, 06 December 2006*

| |
|---|
| ***Lab visit*** <br><br> ***SADCWaterLab General Assembly*** |

### Lab visit

In the morning the participants could visit the laboratory facilities of the Tanzania Bureau of Standards.

### SADCWaterLab General Assembly

Kezia Mbwambo welcomed all members as chair of SADCWaterLab and gave a short introduction for new participants. Donald Masuku, the secretary, presented the agenda, which was adopted by the participants.
Kezia Mbwambo gave a short **report about the PMC meeting** on Monday. All subjects discussed at the PMC meeting were also on the agenda for the general assembly.
Some discussion points **remained from the previous meeting in Gaborone**. D. Masuku stated, that due to SADC regulations it is not possible to have voting rights for associate members.
The **Memorandum of Understanding (MoU)** could not yet be finalised. But this will be done during the next months.
D. Masuku reported about the status of the **new SADC standard on drinking water**. The draft at present is on the committee stage. There it goes to all members for 6 months for comments. Those will be collected by the secretary. A 3 months approval stage will follow. So the new standard is expected to be ready in September 2008.
Discussion of **parameters** in the Water PT resulted in Cobalt to be added in 2008.
**Standard deviation limits** were also discussed. It was agreed, that the limits for parameters where the calculated standard deviations were significantly lower than the limits should be adjusted. M. Koch will make proposals.

Patricia Ejalu sent a **status report for the microbiology PT**. This report is attached as annex 11. The Uganda National Bureau of Standards received all necessary equipment except sterile plastic bottles for sample distribution, which will be provided by PTB, staff is trained, some trial runs are in progress.

A brainstorming on possible mutual help within SADCWaterLab resulted in the following ideas:

- **exchange test methods for harmonization**
- help is needed for laboratories **how to write a quality manual**
- **training through SADCAS on quality management** issues is proposed for the next evaluation workshop
- **staff exchange** (especially visits in accredited labs for about 2 weeks) would be helpful. This could promote exchange of information on accreditation issues and technical know-how as well as harmonization of methods. Sponsorship of such staff exchange through PTB might be possible.

The **next evaluation workshop** should be held in Kampala (Uganda) together with the evaluation workshop for the microbiology PT. If this is not possible, Windhoek could be a suitable venue.

**Sustainability** of the PT system (without sponsoring in future) can only be achieved by **increasing the number of participants**. Therefore **national workshops** could be a good tool to raise awareness. Promotion of the PT scheme within the **SADC structures** also could be helpful.

Under the topic "any other business" the following was discussed:

- focus for next years training:
  - quality management
  - basic statistics
  - if possible there should be basic as well as advanced training to fulfil all requirements
- it was recommended to extend the EAC PT systems (with other matrices) also to SADC countries.

The discussions were summarized in the work programme 2008 for SADCWaterLab (table 6).

Table 6: SADCWaterLab work programme 2008

| | | |
|---|---|---|
| Put presentations on the web and inform participants | Dec 07 | Michael |
| MoU to be finalised | Jan 08 | Donald |
| recirculate questionnaire on used instrumentation | Feb 08 | Donald |
| search for useful used instrumentation | ongoing | Michael/Stefan |
| clarify local coordinators | Jan 08 | Donald |
| write new letter for nomination of local coordinators directly to institutions | Jan 08 | Donald |
| redesign PT leaflet | Feb 08 | Donald |
| microbiology PT according to work plan in report | announcement Jan 08 | Patricia |
| install mailing list | Jan 08 | Donald |
| PT provider to contact well performing labs in nitrate and phosphate to precisely describe their methods in the mailing list | Feb 08 | Merylinda |
| next chemistry PT | according to decided schedule announcement Feb 08 | Merylinda |
| evaluation workshop in Kampala (if not possible: Windhoek) | Nov/Dec 08 | all |
| promote the PT scheme | ongoing | all |
| raise awareness through national workshops | ongoing | all |

## Evaluation questionnaire

M. Koch distributed an evaluation questionnaire (annex 12) for the workshop to be filled out by all participants.
The results of this questionnaire were as follows:

The judgement of the participants regarding

- **The venue of the workshop:**
  Very good 9
  Good 15
  Mean: 1.63 (1 for very good, 2 for good)
- **The content of the presentations:**
  Very good 9
  Good 14
  Fair 1
  Mean: 1.67 (1 for very good, 2 for good, 3 for fair)
- **The material distributed:**
  Very good 8
  Good 12
  Fair 3
  Mean: 1.78 (1 for very good, 2 for good, 3 for fair)

- **The working group discussions:**
  Very good 8
  Good 14
  Mean: 1.64 (1 for very good, 2 for good)

The judgement of the participants regarding the different parts of the workshop on a scale from 1 (very useful) to 5 not useful):

- **Evaluation of the chemistry PT**
  1: 20
  2: 3
  3: 0
  4: 0
  5: 0
  Mean: 1.13
- **Training**
  1: 12
  2: 7
  3: 4
  4: 1
  5: 0
  Mean: 1.75
- **Lab Visit**
  1: 12
  2: 11
  3: 1
  4: 0
  5: 0
  Mean: 1.54
- **SADCWaterLab Meeting**
  1: 14
  2: 9
  3: 1
  4: 0
  5: 0
  Mean: 1.46

**The most important topics (in brackets the number of participants mentioning this point):**

- Measurement uncertainty training (21)
- Method validation training(20)
- Evaluation of Chemistry PT (12)
- Control charts (6)
- Experience of the PT provider (5)
- Lab visit (5)
- Quality Assurance (3)
- SADCWATERLAB meeting (3)
- PT sample preparation (3)
- Limit of quantitation (2)
- Corrective actions (2)
- Comparison of PTs (2)

- Sampling (2)
- Method performance (1)
- Calibrations (1)
- Internal auditing (1)
- Discussion of colleagues (1)
- Discussions on the way forward (1)
- Sustainability of PT (1)

**Did the workshop fulfil your expectations?**

Yes: 21
No: 2
Partly: 1
reasons for no or partly:

- no answer
- Time for training was too short (twice)

**What benefits did you draw from the workshop?**

- The training on method validation and uncertainty
- PT sample preparation, modelling approach, purity of chemicals from manufacturer, evaluation of x-charts
- It helped me to correct my mistakes; to identify the method best for the parameter; to know how provider take trouble to prepare the sample; to exchange ideas with other participants; GUM approach of measurement uncertainty
- to make sure the instrument is fully calibrated and all equipment used are rinsed properly and reporting in correct units
- ExcelKontrol software; CD on the whole workshop
- How to draw and use the control chart and how to do method validation
- Good analytical results can be obtained by proper analytical methods, good reagents etc.
- PT is a vital tool to our lab to met the national requirements; to go home and arise awareness to other labs to participate in the PT scheme; GUM approach
- too much to mention; much I expect to gain
- I learnt more about the process involved in PT preparation and dispatch; I learnt more about the various methods that give better results.; I gathered helpful suggestions from the discussions
- I learnt enough on method validation
- Better understanding of measurement uncertainty to be used in full implementation of the ISO/IEC 17025 system
- None
- General ideas in labs performance in the SADC region. But I recommend, the SADCMET to extend the testing parameters including PESTICIDE RESIDUES in water (drinking water?)
- Uncertainty
- The PT evaluation assisted me to continue improving our laboratory performance by identifying the corrective actions to be undertaken
- Exchange of ideas and knowledge. Opportunities of acquiring donated equipment. Sponsored forum which may not have ben possible, if countries were self sponsored. Training materials which are very useful. The PT is being used as a yardstick for improvement in the performance of the lab

- Knowledge and continuous improvement
- Exposure and communication establishment with the different participants
- Training on different approaches for measurement uncertainties
- Enrichment of my knowledge in method validation, calculation of uncertainties, control charts, information derived from the evaluation of the PT results
- An idea on how to go about correcting unsatisfactory results

**Any other comments:**

- The one week (or so) training has been so intensive, which is a good thing. However the organisation of the future evaluation workshops should leave some time at the end (say half a day) for the participants to visit some sites in the country and also to relax.
- The time schedule for technical trainings should be extended; the time for lab visits should also be increased to provide more time for healthy information exchange and discussions

## Closure of the meeting

Kezia Mbwambo, Donald Masuku, Stefan Wallerath and Michael Koch closed the workshop and thanked all participants for their cooperation.

Report prepared by Dr.-Ing Michael Koch
Stuttgart, 10.1.2008

**Annex I - List of Participants and Lecturers**

| Name | | | Institution | City | country | e-mail | | |
|---|---|---|---|---|---|---|---|---|
| Mr. | Teddy | Ditsabatho | Water Utilities Corporation | Gaborone | Botswana | tditsabatho@wuc.bw | | |
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| Mr. | John | Bomani | SWAMIC | Dar es Salaam | Tanzania | | | |
| Mr. | Phillipo | Chandi | Water Central Lab | Dar es Salaam | Tanzania | | | |
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# Experiences of the PT Provider

Merylinda Conradie Pr.Sci.Nat
NamWater

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# Namibia Water Corporation (NamWater)

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# Introduction

- Changes and Progress of participation
- Planning for the PT 2007 in Windhoek for the first time
- Sample preparation
- Sample distribution
- Evaluation

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# Changes and Progress in the number of participants

| Country | 2004 | 2005 | 2006 | 2007 |
|---|---|---|---|---|
| Angola | 1 | 1 | 1 | 0 |
| Botswana | 2 | 2 | 2 | 4 |
| Ethiopia | 1 | 1 | 1 | 0 |
| Kenya | 2 | 2 | 4 | 3 |
| Lesotho | 1 | 1 | 0 | 1 |
| Madagascar | 0 | 0 | 2 | 2 |
| Malawi | 2 | 2 | 2 | 3 |
| Mauritius | 1 | 3 | 4 | 3 |
| Mozambique | 2 | 3 | 2 | 0 |

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# Changes and Progress in the number of participants

| Country | 2004 | 2005 | 2006 | 2007 |
|---|---|---|---|---|
| Namibia | 2 | 2 | 3 | 3 |
| Republic of Seychelles | 1 | 2 | 2 | 1 |
| Swaziland | 1 | 1 | 0 | 1 |
| Tanzania | 2 | 8 | 5 | 12 |
| Uganda | 1 | 3 | 6 | 5 |
| Zambia | 1 | 4 | 2 | 3 |
| Zimbabwe | 2 | 3 | 3 | 5 |
| Number of labs participating | **22** | **44** | **39** | **46** |

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# Changes and Progress Parameters

| 2004 | | 2005 | | 2006 | | 2007 | |
|---|---|---|---|---|---|---|---|
| **Anions** | **Cations** | **Anions** | **Cations** | **Anions** | **Cations** | **Anions** | **Cations** |
| SO4 | Ca | SO4 | Ca | SO4 | Ca | **SO4** | **Ca** |
| Cl | Mg | Cl | Mg | Cl | Mg | **Cl** | **Mg** |
| F | Na | F | Na | F | Na | **F** | **Na** |
| NO3 | K | NO3 | K | NO3 | K | **NO3** | **K** |
| | Fe | **PO4** | Fe | PO4 | Fe | **PO4** | **Fe** |
| | Mn | | Mn | | Mn | | **Mn** |
| | Al | | Al | | Al | | **Al** |
| | | | **Pb** | | Pb | | **Pb** |
| | | | **Cu** | | Cu | | **Cu** |
| | | | **Zn** | | Zn | | **Zn** |
| | | | **Cr** | | Cr | | **Cr** |
| | | | **Ni** | | Ni | | **Ni** |
| | | | | | **As** | | **As** |
| | | | | | **Cd** | | **Cd** |
| **Total** | **11** | | **17** | | **19** | | **19** |

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# Planning

- Calculation of the target values (masses and volumes)
- Ensure the timorously delivering of requires chemicals ( 8 weeks ) AR / GR grade chemicals, supplied by Merck, Sigma-Aldrich and Strem chemicals were used. Copies of the certificate of analysis are available.
- Ensure enough samples one liter bottles, crates, enough 50 ml beakers, 200 ml beakers and 500ml volumetric flasks,
- 100 liter containers with tap
- Ensure availability of packaging material (boxes, shredded paper, packaging tape, labels, envelopes, paper )

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# Planning

- Quotations and choice of courier
- Availability and suitability of balances for the different weighings
  - Analytical balance : wires and the salts
  - Top loader : Stock solutions and the 200g weighing
  - 50 kg top loader : Weighing of the final batches - Problem

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# Sample bottle preparation I

- Bottles were first to arrive
- Wash all 300 bottles which was ordered
- Planned for 50 participants
- Bottles were rinse twice with deionised water
- Bottles & caps were put in the oven @ 60 °C overnight

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# Sample bottle preparation II

- Next day – check completely dry
- Closed bottles immediately to prevent them from dust
- Store them in the crates until needed

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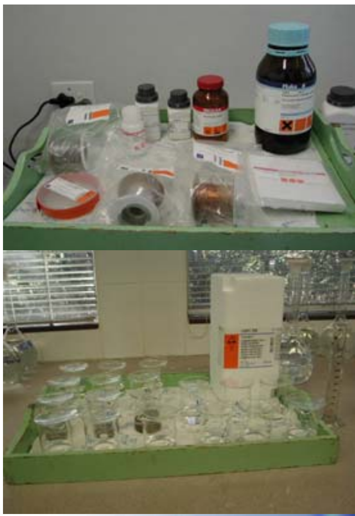
# Weighings of wires

- Start of by weighing the different target masses for the 3 levels of each parameter
- Continue with the weighings of the metals where different wires were used



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# Calculated Sample mass - cations

| Parameter | Chemical | Purity % | Level 1 | Level 2 | Level 3 |
|---|---|---|---|---|---|
| Calcium | $CaCl_2.2H_2O$ | 99.5 | 7.2911 | 13.7358 | 23.0648 |
| Magnesium | $Mg(NO_3)_2.6\ H_2O$ | 99.5 | 27.006 | 41.4963 | 72.8506 |
| Sodium | NaCl | 99.6 | 8.0412 | 12.6016 | 18.5693 |
| Potassium | KCl | 99.6 | 2.2736 | 2.9922 | 4.4514 |
| Iron | Fe-Wire | 99.95 | 0.1100 | 0.2034 | 0.3156 |
| Manganese | Mn-Powder | 99.4 | 0.1061 | 0.1328 | 0.2637 |
| Aluminium | Al-wire | 99.9995 | 0.1134 | 0.1560 | 0.3222 |
| Lead | $Pb(NO_3)_2$ | 99.7 | 0.1409 | 0.1905 | 0.3811 |
| Copper | Cu-wire | 99.999 | 0.1188 | 0.2380 | 0.3947 |
| Zinc | Zn-wire | 99.99995 | 0.138 | 0.2694 | 0.5663 |
| Chromium | $CrCl_3.6\ H_2O$ | 99 | 0.2688 | 0.5554 | 0.9795 |
| Nickel | Ni-wire | 99.9975 | 0.3649 | 0.2428 | 0.3244 |
| Arsenic | $As_2O_3$ | 99.50 | 0.1853 | 0.3834 | 0.1256 |
| Cadmium | $CdCl_2$ | 99.995 | 1.1845 | 0.4688 | 0.1728 |

Sample 4, 5 and 6 were constituted as follows with $HNO_3$ acid preservation to a pH 2.1. The samples matrix was pure water. The final weight for the cation samples was 57.08g with the Density (Deionised water) = 0.998g/ml and the temperature 24 ºC.

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# Traceability of the weighings

- Since traceability is very important in a PT scheme
- Biggest problem for 2007 - Balances had no possibility for a printer connection
- Tried various option to borrow a balance – without success

# Documentation of wires

- Solution for the problem - Pictures were taken of all the weighings with a digital camera
- Pictures were downloaded, printed and cut out
- Paste it next to the written weighing for proof of the traceability

# Digestion of metals

- Digestion of the pure metals e.g.
- Water and HNO3 acid was added for digestion / As  32 % NaOH
- Left on a hot plate  at very low temperature setting until the metals were completely dissolved

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# Weighing of the salts

- Continue with weighing of the salts
- Weigh the substances for three levels
- Continue to prepare the stock solution

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# Calculated Sample mass - Anions

| Parameter | Chemical | Purity % | Level 1 | Level 2 | Level 3 |
|---|---|---|---|---|---|
| Sulphate | K2SO4 | 99.5 | 7.0676 | 10.3072 | 13.6371 |
| Chloride | KCl | 99.6 | 11.0492 | 13.5912 | 17.365 |
| Fluoride | KF | 100 | 0.2000 | 0.3404 | 0.5938 |
| Nitrate | KNO3 | 99.3 | 3.1201 | 7.2868 | 12.3361 |
| Phosphate | KH2PO4 | 99.9 | 1.5061 | 2.9053 | 3.6030 |

Sample 1, 2 and 3 were constituted as follows without acid preservation. The sample matrix was pure water. The final weight for the cation samples was 57.08g with the Density (Deionised water) = 0.998 g/ml and the temperature 24 ºC.

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# Preparation of stock solutions

- Fill the 500 ml volumetric flask by weight
- Wash accurately into a 500ml volumetric flask
- Repeat for all the parameters

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## Documentation of Stock solutions

- Pictures were again taken of all the weighings with a digital camera
- Downloaded, printed and cut out
- Paste next to the written weighing for proof of the traceability


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## Labeling of the bottles

- Prepare labels for each sample bottle with a short description of the information
- Print labels
- Stick on the samples bottles for identification of the samples
- Put sellotape over the labels – to protect the labels
- Bottles were ready for the filling process

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# Preparation of final batches

- Obtain a suitable balance
- Find a suitable container
- Made special rack for the stirrer in order to mix the samples properly

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# Preparations for the 200g weighings

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# Preparation of the 200g weighings

- Weigh the empty container
- Weigh the calculated amount of the different stock solutions with the density taken into consideration
- Add some water into the big container
- Add the calculated amount of the stock solution (by weight)
- Rinse over in the 100 l container
- Fill by weight

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# Preparation of final batch

- 50 liters of each sample were prepared
- Pure water spiked with parameter of interest
- Nitric acid was added to the cations for preservation (pH 2)

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# pH adjustment

- Stirring took place for continuously during the process
- Filled by weight
- Final stirring for 15 minutes
- Document the pH

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# Homogeneity

- All analytes were physically dissolved
- Proper stirring ensure the homogeneity of the samples
- Conductivity check on the first samples and the last samples – basically NO difference
- Documentation

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# Documentation of information of batch

- All the readings of the balance were once again downloaded, cut out and pasted next to the weighings
- The weigings of the final batch was also documented
- pH and temperature were documented

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# Samples dispensing

- Samples bottles were filled after each batch
- Put in the crate
- Tank was washed properly in between the batches
- Start to prepare for the next batch

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## Storing

- Space was limited in the fridge
- Crates were very handy – stacked all the samples
- All samples were stored at 4 ° C until all six batches were prepared

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## Packaging

- Strong packaging was once again a requirement
- Flat cartons needed to be fold into boxes
- Staple it together

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# Preparation of the documentation

- Hard copies of the forms for the results and the method information were included in each box
- Labels of all the participants were prepared

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# Packaging of the samples

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# Packaging of the samples

- Packed six polyethylene bottles into each box
- Shredded paper was used for the packaging material
- sealed with packaging tape



# Packaging of the samples

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# Packaging of the samples

# Packaging

# Ready for pick up

- Samples ready to be picked up by the courier for distribution to the local coordinators

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# Loading

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# Information to courier

- Supplied the correct address list of the local distributors to the courier with the total weight of one parcel
  - Determine the weight of bottle filled with deionised water
  - Determine the weight of empty box
  - Determine the weight of envelope filled with documentation

# Loading completed

# Shipment

- The courier was Kuehne & Nagel in Namibia
- Participants were notified by e-mail to inform them that the samples are on their way


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# Shipment

- All samples were shipped to the address of the local distributor.
- Samples were delivered with a lot of frustration and problems  and the PT deadline needed to be change for some of the laboratories
- No leakage problems were reported

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# Evaluation

- Results were received by fax or e-mail
- Deadline was extended on request because of courier problems
- The last results were received on the 04th October 2007
- Angola informed that they experience problems with the samples and the customs clearance.
- Lesotho also informed me that they experince customs problems.

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# Evaluation

- Results were typed into a spreadsheet
- Copied and paste into different parameter files
- All the files were created for the different laboratories in Excel
- Excel files were converted to a pdf format to reduce the size of the file and to ensure all the participants will be able to read the file.
- Precision tests were run on the balances
- Measurement uncertainty was taken in consideration according to the method told by Angelique in the 2005 workshop

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## Payment

- Payments were made by bank drafts, transfers and cheques
- Some payments were made, but the money is still outstanding
- NamWater still experiences problems to identify the payments within NamWater due to insufficient information from bank/participant
- Some payments were not yet made at all

## Successes of 4rd PT

- Increased and continued enthusiasm - Tanzania was the country with most participants !
- Local distributors are very important and I very helpful and reliable specially with the courier problems
- Five form 51 laboratories did not submit results ( 3 due to courier problems)

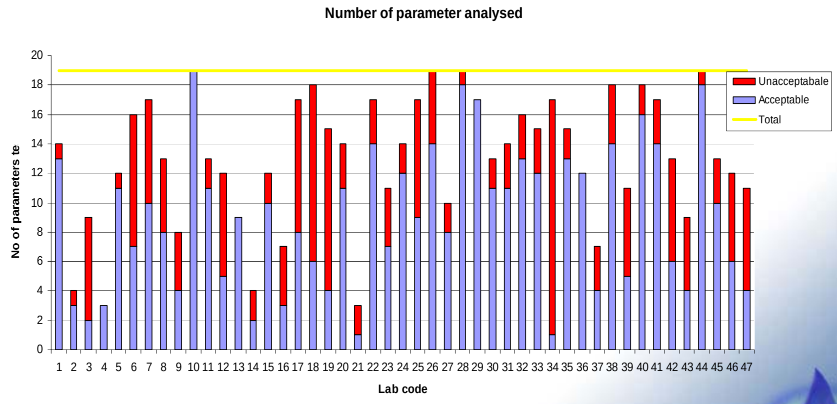
# Confidentiality

- Confidentiality was once again very important
- PT round require a high degree of confidentiality from the provider
- Lab codes were changed
- It is also the responsibility of everybody involved to keep all the data and items of information relating to inter-laboratory confidential

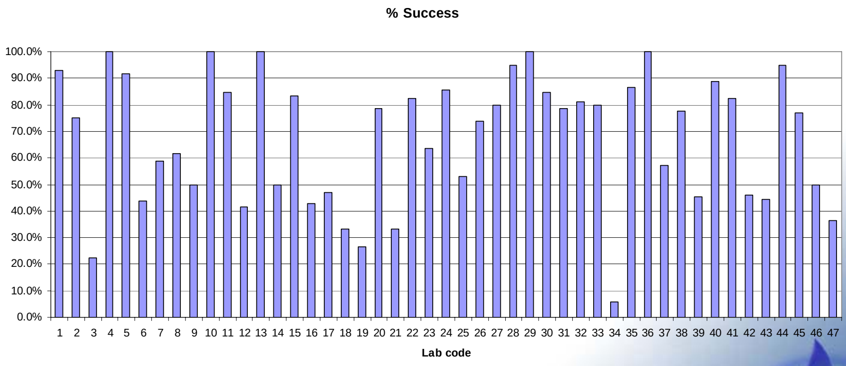
# Conclusions

- Participation is an important and a valuable tool for a laboratory to uncover errors and improve on their performance
- Valuable method of quality control where suitable reference materials are not available
- The performance certificate can be used to proof competence in in the testing field
- It is a regular, external and independent check on the data quality of the laboratory

# Number of parameters analyzed




# % Success



# Challenges for 2008

- The results should be used as a motivation to improve performance and apply corrective actions if necessary
- Strive to improve the success
- Increase the number of analyzed parameters
- Reporting of results again caused problems with incorrect units (e.g as N and not NO3 and as P and not PO4
- Try and rectify the analyses not determined due to a lack of chemicals or problems with equipment
- Instrumentation or method should be stipulated clearly
- Once again very high standard deviations in the 2007 PT scheme

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# Problems experienced

- Dedicated time for the preparation and evaluation period without interruptions
- The PT provider had a limited number of staff
- Contract with local electricity supplier - results to be reported by 12h00 every day
- Accreditation requirement for NamWater laboratory was delayed
- Late confirmations and requests of participation caused problems and unnecessary rearrangements with the courier
- The initial return date for the results was set as the 31st of August 2007 with an extension of three weeks for some of the laboratories due to transportation problems. Five laboratories did not submit results at all.
- Follow-up of participation where people did not respond on e-mails

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# Problems

- Late submitting of results due to courier problems delay the submitting of the evaluation report
- Receipt of results by fax – unclear and difficult to get hold of the participant
- Five labs did submit results at all for unknown reasons
- Three labs did not take part due to courier problems

# PTB Donation

# Thank you

- **PTB**
- Stefan Wallerath
- Annedore Heinichen
- **SADCMET**
- Margaret Ngobeni
- **University of Stuttgart**
- Dr Michael Koch
- **NamWater colleagues**
- **Assistance of Local distributors**
- **Participants**

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| | |
|---|---|
| SADCMET | Physikalisch-Technische Bundesanstalt<br>Braunschweig und Berlin |

# Evaluation Workshop of 4th SADCMET Water PT scheme
# 04.-06.12.2007, Dar es Salaam, Tanzania

## Local Coordinator's report on PT promotion

***Guiding Questions:***

1. For which country are you the local PT coordinator?

2. How many laboratories doing water testing (amongst other duties) do approximately exist in your country?

3. Which are the most important ones? Which mandate/background do they have? (private, public, under which ministry, water utility company ….)

4. How did you promote the PT scheme?

5. How was the feedback from the laboratories?

6. How many labs did participate in your country? (did they all submit results?)

7. What are the reasons for non-participation?

8. How did you arrange for the payments? (commonly, individually?)

9. Did you encounter customs problems during reception of the samples? (if yes, during which year/round?)

10. Did you pro-actively inform customs authorities in your country?

11. Do you feel you required additional support/guidance? (from whom? In order to address which issue/challenge?)

12. Feel free to give us additional comments (use the back of the form, if required):

**THANKS FOR YOUR COOPERATION!!**

**Local Coordinator's report on PT promotion**

# Madagascar

### How many laboratories doing water testing(amongst other duties) do approximately exist in your country?

3 labs, but  participating to the PT

### Which are the most important ones? Which mandate/background do they have?

TIRAMA's water testing laboratory under Mining & Energy Ministry, which is not participating in the PT for financial rehabilitation

### How did you promote the PT scheme?

As the local coordinator I am due to make the existence of PT known by all laboratories while working with standards bureau and through workshops

### How was the feedback from the laboratories?

Laboratories are interested, but only 3 labs are working in the water testing field

### How many labs did participate in your country?

2 for the time being, but still lobbying to get all 3 labs participating. Both labs submitted results

### What are the reasons for non-participating?

Tirama's water lab would participate after financial restructuration.
Following are the main reasons for non-participation:

- Ability to pay participation fee
- lower awareness regarding the importance of PT schemes
- problems with old equipment and standards

### How did you arrange for the payments?

The payments were made individually

### Did you encounter customs problems during reception of the samples?

No, although customs duties are supported by my institution (CNRE)

### Did you pro-actively inform customs authorities in your country?

I have to address the issue at the level of Standards Bureau much more in charge of SADC affairs

### Do you feel you required additional support/guidance?

Probably a letter to be addressed to Standard Bureau for the issue above-mentioned

### Additional comments:

Promotional meeting also has been carried out with the National Water and Sanitation Authority (ANDEA) of Madagascar

**Local Coordinator's report on PT promotion**

## Zimbabwe

### How many laboratories doing water testing(amongst other duties) do approximately exist in your country?

about 20

### Which are the most important ones? Which mandate/background do they have?

Ministry of Health, SA2 for regulation and standardization, WLA2

### How did you promote the PT scheme?

### How was the feedback from the laboratories?

Good on PTS scheme

### How many labs did participate in your country?

5, all reporting results

### What are the reasons for non-participating?

- Lack of awareness
- General apathy
- foreign currency
- lack of capitalisation
- no equipment
- no calibration of equipment

### How did you arrange for the payments?

bank transferfor BARC

### Did you encounter customs problems during reception of the samples?

No

### Did you pro-actively inform customs authorities in your country?

### Do you feel you required additional support/guidance?

### Additional comments:

Zimbabwe is a country … siege. Capitalisation of labs has suffered a lot under such an environment. Huge inflation gave rise to unaffordable costs of equipment, calibration and chemicals

**Local Coordinator's report on PT promotion**

# Uganda

### How many laboratories doing water testing(amongst other duties) do approximately exist in your country?

15

### Which are the most important ones? Which mandate/background do they have?

8

- Private
- Water utility company
- Labs for the water processing industry
- Regulatory agencies
- Academia

### How did you promote the PT scheme?

Through

- meetings
- personal contacts, i.e. telephones, e-mails

### How was the feedback from the laboratories?

Not highly responsive, waiting for the PT from university, waiting for the EAC-scheme, that was free

### How many labs did participate in your country?

5

### What are the reasons for non-participating?

- Fees
- Willing
- Long procurement systems in some organisations

### How did you arrange for the payments?

Individual payments

### Did you encounter customs problems during reception of the samples?

No

### Did you pro-actively inform customs authorities in your country?

No

### Do you feel you required additional support/guidance?

Yes, on issues concerning resources for awareness and communication

### Additional comments:

**Local Coordinator’s report on PT promotion**

# Swaziland

### How many laboratories doing water testing(amongst other duties) do approximately exist in your country?

About 8 laboratories and some from the private companies. They all shown interests but fear of their bosses

### Which are the most important ones? Which mandate/background do they have?

All important water analysis is under the ministry of natural resources and energy

### How did you promote the PT scheme?

Arranging meetings trying to explain what is the PT, but their hands were full, they couldn’t participate

### How was the feedback from the laboratories?

Their supervisors wouldn’t allow them to participate the brochure will be useful

### How many labs did participate in your country?

None – but laboratories doing microbiology, they are interested. So they want to know when is it

### What are the reasons for non-participating?

see above

### How did you arrange for the payments?

inividual

### Did you encounter customs problems during reception of the samples?

No. Samples were delivered from the airport and phoned. When I went to collect the samples they told me it has to be picked by the courier and they charged

### Did you pro-actively inform customs authorities in your country?

No

### Do you feel you required additional support/guidance?

Yes

### Additional comments:

The brochure I think will be more useful to our colleagues

**Local Coordinator's report on PT promotion**

# Tanzania

### How many laboratories doing water testing(amongst other duties) do approximately exist in your country?

about 55

### Which are the most important ones? Which mandate/background do they have?

- Private
- Public
- Water utility companies
- Academia

### How did you promote the PT scheme?

- Leaflet
- Letter of invitation
- Calls to the lab managers
- e-mails
- Informed during national PT meeting

### How was the feedback from the laboratories?

Very slow, I had to follow it up by visiting/calling.
I invited  labs, but only 13 confirmed participation

### How many labs did participate in your country?

13 confirmed participation and received samples; 1 lab did not submit results

### What are the reasons for non-participating?

- lack of awareness of PT
- they think PT is not adding any value to them

### How did you arrange for the payments?

Those who submitted in time, the payment was done commonly. Otherwise individual payment was also done

### Did you encounter customs problems during reception of the samples?

Only this round samples were not delivered to TBS, but we had to clear the samples from the airport, after some clarification

### Did you pro-actively inform customs authorities in your country?

No, because there was nor problem faced in previous rounds

### Do you feel you required additional support/guidance?

letter for coordination was addressed to me, not to the CEO of the institution.
Provider to ensure samples are delivered to the coordinator.

### Additional comments:

1. I would suggest more awareness workshops be conducted at national levels

# Local Coordinator's report on PT promotion

2. Payment shall be individually
3. Letters to Local Coordinators to be resent

**Local Coordinator's report on PT promotion**

# Namibia

### How many laboratories doing water testing(amongst other duties) do approximately exist in your country?

3

### Which are the most important ones? Which mandate/background do they have?

Namwater, City of Windhoek

### How did you promote the PT scheme?

E-mailed "flyer" to other labs and Trade & Industry

### How was the feedback from the laboratories?

3 interested labs – good
others - poor

### How many labs did participate in your country?

3, all submitted results

### What are the reasons for non-participating?

Water related parameters carried out too little

### How did you arrange for the payments?

Send out a temporariliy invoice

### Did you encounter customs problems during reception of the samples?

No

### Did you pro-actively inform customs authorities in your country?

No

### Do you feel you required additional support/guidance?

### Additional comments:

- Angola is a problem
- List countries who paid money for the customs
- Local coordinators should be proactively involved with customs
- Fax proof of payment

**Local Coordinator’s report on PT promotion**

# Mauritius

### How many laboratories doing water testing(amongst other duties) do approximately exist in your country?

8

### Which are the most important ones? Which mandate/background do they have?

All of them are important.
They fall under various ministries:

1. Ministry of Public Utilities
2. Ministry of Agro Industry & Fisheries
3. Ministry of Industry

### How did you promote the PT scheme?

By talking with the heads of labs about the importance of the PT scheme

### How was the feedback from the laboratories?

main problem was the approval for payment

### How many labs did participate in your country?

3

### What are the reasons for non-participating?

People must be encouraged
Decision amking problem

### How did you arrange for the payments?

Individually

### Did you encounter customs problems during reception of the samples?

No

### Did you pro-actively inform customs authorities in your country?

The Water samples were brought by the courier company to the Bureau without any problems

### Do you feel you required additional support/guidance?

Yes, we need a brochure to be given to potential participants

### Additional comments:

### Local Coordinator's report on PT promotion

## Kenya

### How many laboratories doing water testing(amongst other duties) do approximately exist in your country?

- National irrigation board labs
- KEBS
- National Water Control Laboratories
- Government Chemist
- Public Health Laboratories
- Nairobi National Water
- Mines & geology labs
- SGS laboratories
- Universities

### Which are the most important ones? Which mandate/background do they have?

- National Water Control Laboratories
- Nairobi National Water
- KEBS

### How did you promote the PT scheme?

- Testing open days
- Customer education / information sessions

### How was the feedback from the laboratories?

positive

### How many labs did participate in your country?

3

### What are the reasons for non-participating?

- New into market
- Payment problems

### How did you arrange for the payments?

### Did you encounter customs problems during reception of the samples?

No

### Did you pro-actively inform customs authorities in your country?

Yes

### Do you feel you required additional support/guidance?

### Additional comments:

**Local Coordinator's report on PT promotion**

# Malawi

### How many laboratories doing water testing(amongst other duties) do approximately exist in your country?

9

### Which are the most important ones? Which mandate/background do they have?

- MBS (public)
- NRWB (public)
- Polytechnic (university)
- BWB (public)
- SRWB (public)
- all water boards under the Ministry of water development and irrigation

### How did you promote the PT scheme?

- Through publicity and correspondences
- plans are underway early next year to hold workshops

### How was the feedback from the laboratories?

Feedback was quite encouraging although there were late responses

### How many labs did participate in your country?

4 labs registered
MBS, Poly, NRWB failed to communicate with the forth city assembly

### What are the reasons for non-participating?

Most other labs do not have enough equipment although the have expertism

### How did you arrange for the payments?

Individually, however they were given the other option as well

### Did you encounter customs problems during reception of the samples?

We were charged handling and clearing charges. There were no problems with customs, but the problems were with the office to effect handling and clearing payment

### Did you pro-actively inform customs authorities in your country?

We have had no problems with them therefore here was no need to inform them in advance

### Do you feel you required additional support/guidance?

Yes, support on capacity building in terms of equipment such as AAS. Main challenges are to meet customer demands. In that not all required parameters are analysed

### Additional comments:

MBS – Statutory Cooperation – under Ministry of Trade
Northern Region Water Board – Ministry of Water Development and Irrigation

## Local Coordinator's report on PT promotion

Southern Region Water Board – Ministry of Water Development and Irrigation
Central Region Water Board – Ministry of Water Development and Irrigation
Blantyre Water Board – Ministry of Water Development and Irrigation
Lilongwe Water Board – Ministry of Water Development and Irrigation
Polytechnic – University of Malawi  Statutory Cooperations
Chancellor College– University of Malawi  Statutory Cooperations
Mzuzu University

**Challenges:**

- melting the customers expectations in terms of the parameters in question as well as residence time due to lack of equipment and adequate personel
- Top management commitments to support and equip the labs due to financial hardships
- choice of appropriate method

**Other isues:**
Organise other training workshops for all participating labs other than National Coordinators alone, or support the National coordinators to organise internal training workshop

**Local Coordinator's report on PT promotion**

# Zambia

### How many laboratories doing water testing(amongst other duties) do approximately exist in your country?

10

### Which are the most important ones? Which mandate/background do they have?

FOCL – Ministry of Health
NISIP – Research Laboratory
F+Kwight – Private (accredited)
NicawaWater Utilities company

### How did you promote the PT scheme?

- communication through mail, telephone, fax, e-mail
- PT brochure

### How was the feedback from the laboratories?

positive
F+Kwight, accredited lab – did not respond

### How many labs did participate in your country?

3

### What are the reasons for non-participating?

- lack of interest
- inadequate capacity in the laboratories

### How did you arrange for the payments?

individually
need a quotation for payment and receipts

### Did you encounter customs problems during reception of the samples?

007 had to pay customs duty and handling charges as local coordinator
about 100 US-$

### Did you pro-actively inform customs authorities in your country?

Customs informed, but could not waiver the duty and handling charges

### Do you feel you required additional support/guidance?

Awareness of the PT scheme in the country
Workshop, IEC materials

### Additional comments:

- More support in form of IEC materials
- Better arrangements for transportation of samples
- Better communication system (Tel, Fax, e-mail)
- enlist a courier company which the receiver does not pay duty & handling charges

# Evaluation of the
# $4^{th}$ SADCMET Water PT

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## Evaluation and Assessment

- according to same procedure as in the last rounds
  - assigned value from the weighings at sample preparation (with an uncertainty budget)
  - calculation of standard deviation using Algorithm A from ISO 13528
  - but! – limitation of the standard deviation (as ‘fitness for purpose’ requirement)

## Limits for standard deviation

| parameter | std limit |
|---|---|
| sulphate | 10 % |
| chloride | 10 % |
| fluoride | 12 % |
| nitrate | 15 % |
| phosphate | 10 % |
| calcium | 10 % |
| magnesium | 10 % |
| sodium | 10 % |
| potassium | 10 % |

| parameter | std limit |
|---|---|
| iron | 20 % / 12 % |
| manganese | 20 % / 12 % |
| aluminium | 30 % |
| lead | 40 % / 25 % |
| copper | 20 % |
| zinc | 20 % |
| chromium | 25 % |
| nickel | 25 % |
| cadmium | 30 % |
| arsenic | 30 % |





## Elimination of gross outliers

- Values < ref.-value/8 and > ref.-value*8 have been excluded before applying statistical procedures

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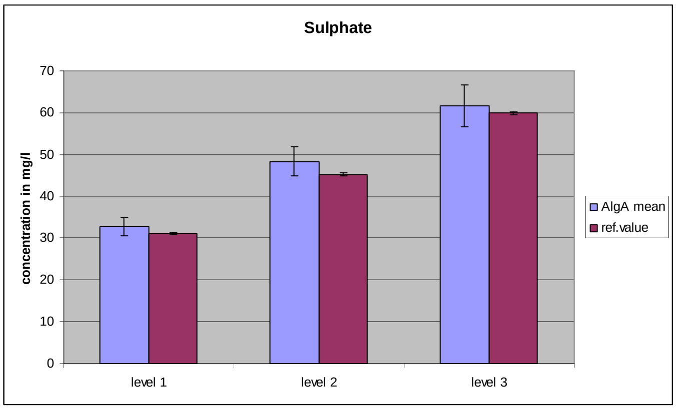
# Sulphate
## Alg.A mean and ref.-value from weighings




Same situation as last year: consensus mean slightly higher than reference value

**Exp. uncertainty of the Alg.A mean is calculated according to ISO 13528:** $U_{c_{mean}} = 2 \cdot u_{c_{mean}} = 2 \cdot 1{,}25 \cdot \frac{s_R}{\sqrt{n}}$

**Exp. uncertainty of the ref.-value from an uncertainty budget**



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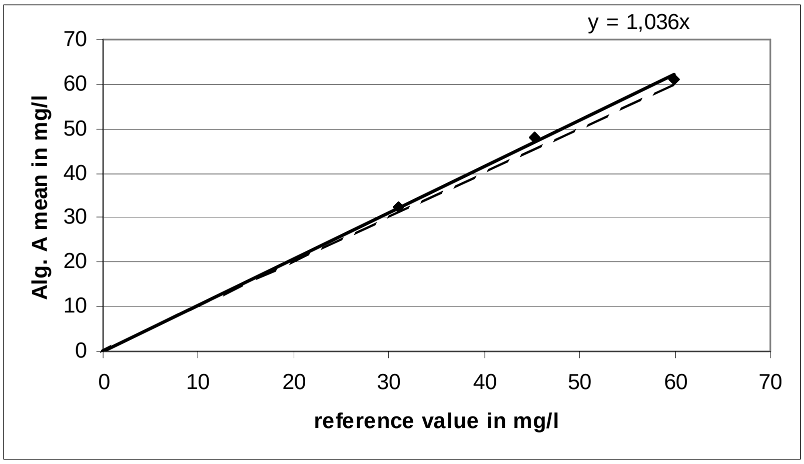
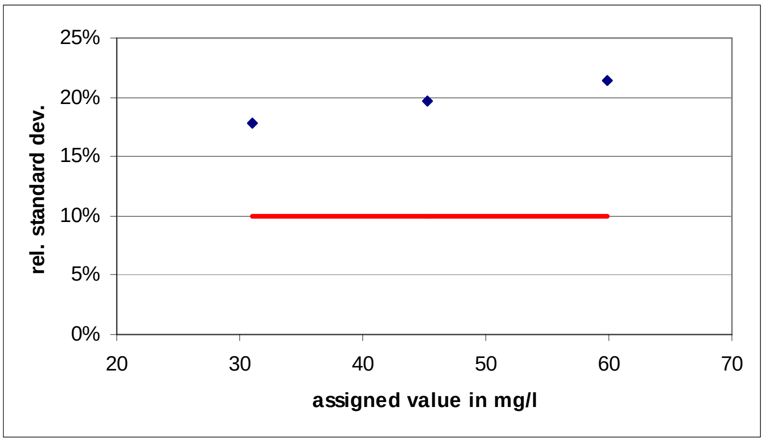
# Sulphate
## mean vs. ref.-value




Average recovery: 103.6%; in 2006: 106.5%

# Sulphate
# calculated standard deviation and limit

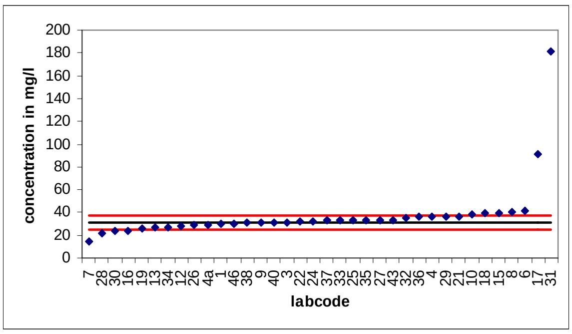



Similar to 2006 data



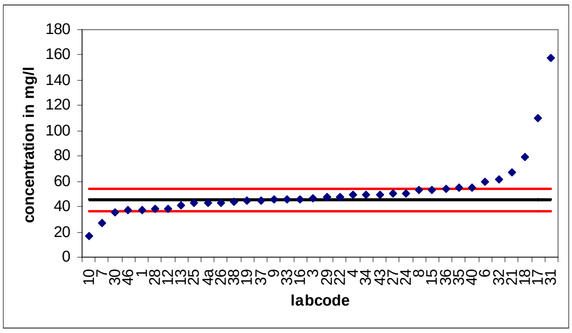


# Sulphate 1




- values: 37
- removed: 1
- Mean: 32.57 mg/l
- Weighing: 31.02 mg/l
- Standard deviation: 5.52 mg/l; 17.8 %
- limit for St.-dev.: 10%
- Upper limit: 37.2 mg/l
- Lower limit: 24.8 mg/l
- too high: 8 values
- too low: 4 values
- outside tolerance limits: 32.4 %

# Sulphate 2




- values: 37
- removed: 0
- Mean: 48.0 mg/l
- Weighing: 45.3 mg/l
- Standard deviation: 8.93 mg/l; 19.7 %
- limit for St.-dev.: 10%
- Upper limit: 54.3 mg/l
- Lower limit: 36.2 mg/l
- too high: 9 values
- too low: 3 values
- outside tolerance limits: 32.4 %



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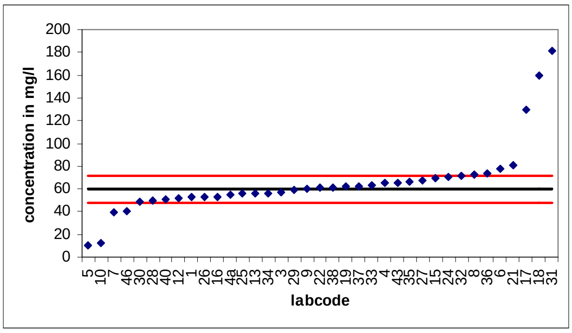
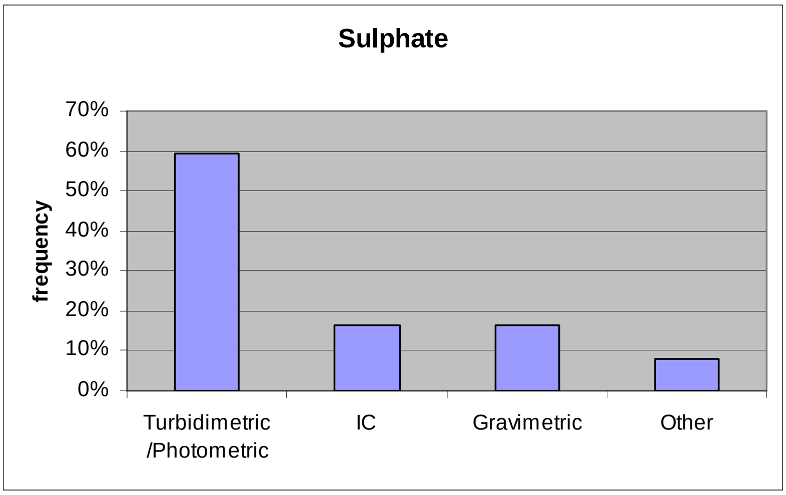
# Sulphate 3




- values: 37
- removed: 0
- Mean: 61.0 mg/l
- Weighing: 59.9 mg/l
- Standard deviation: 12.85 mg/l; 21.5 %
- limit for St.-dev.: 10%
- Upper limit: 71.9 mg/l
- Lower limit: 47.9 mg/l
- too high: 7 values
- too low: 4 values
- outside tolerance limits: 29.7 %

# Used methods



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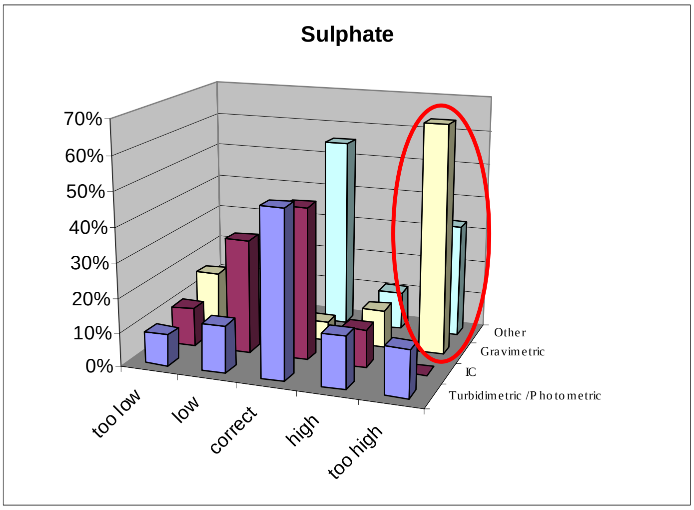
# Comparison of methods



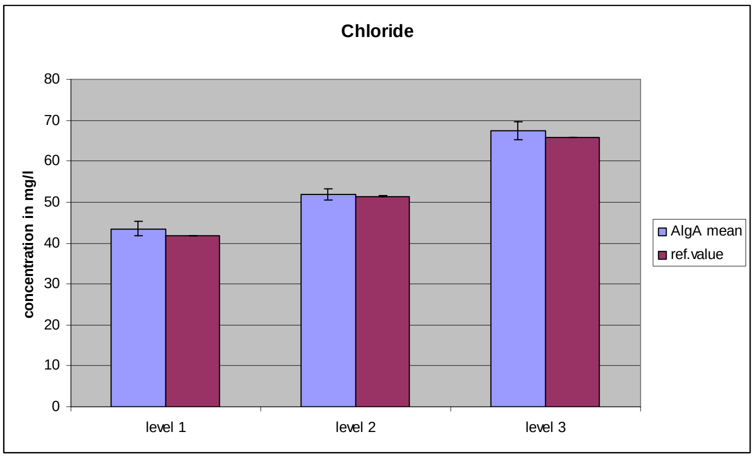
## Summary Sulphate

- mean of analysis higher than reference value
- standard deviation higher than limits
- High portion of  too high values for the gravimetrical method





## Choride
## Alg.A mean and ref.-value from weighings




Similar to 2006 data

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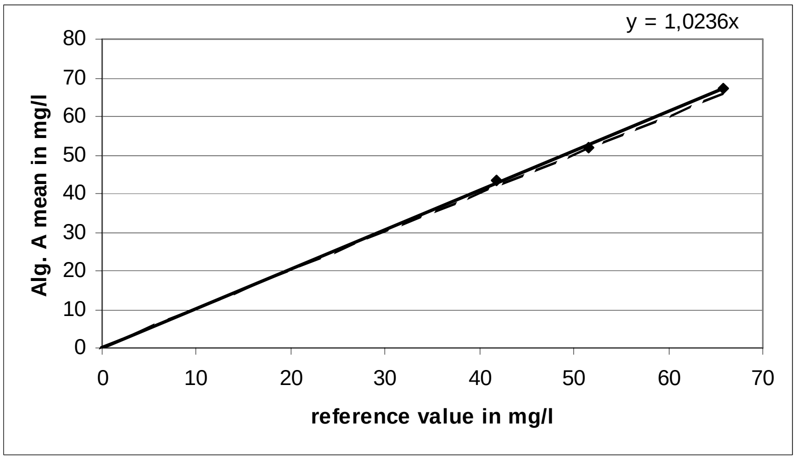
# Chloride
# mean vs. ref.-value




Average recovery: 102.4%; in 2006: 101.6%



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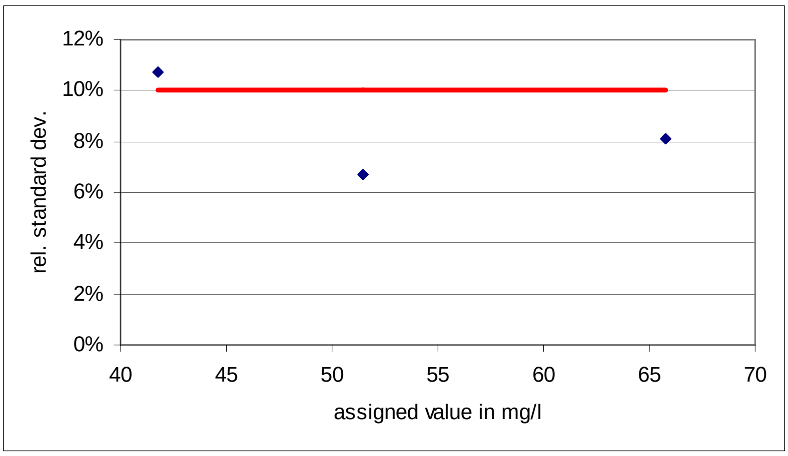
# Chloride
# calculated standard deviation and limit




Slightly better than 2006

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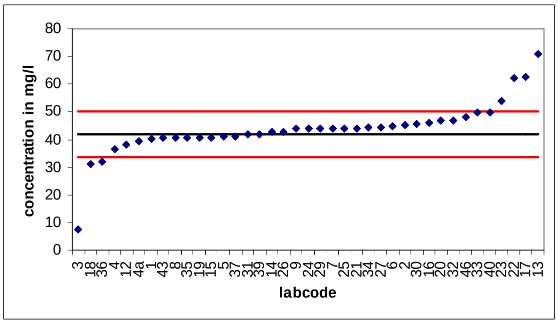
# Chloride 1




- values: 39
- removed: 0
- Mean: 43.52 mg/l
- Weighing: 41.76 mg/l
- Standard deviation: 4.49 mg/l; 10.8 %
- limit for St.-dev.: 10%
- Upper limit: 50.1 mg/l
- Lower limit: 33.4 mg/l
- too high: 4 values
- too low: 3 values
- outside tolerance limits: 17.9 %



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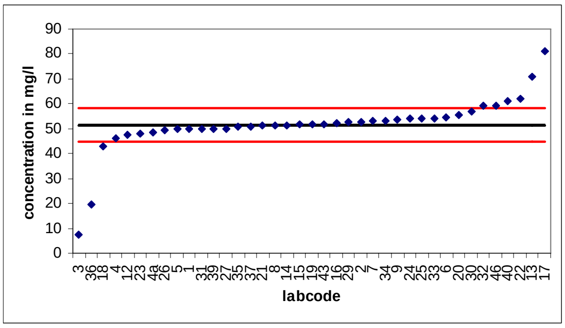
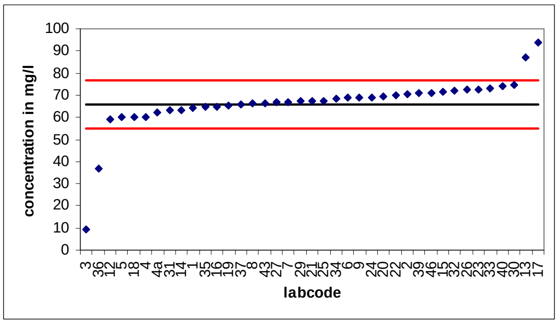
# Chloride 2




- values: 39
- removed: 0
- Mean: 52.0 mg/l
- Weighing: 51.5 mg/l
- Standard deviation: 3.44 mg/l; 6.7 %
- limit for St.-dev.: 10%
- Upper limit: 58.3 mg/l
- Lower limit: 44.6 mg/l
- too high: 6 values
- too low: 3 values
- outside tolerance limits: 23.1%

# Chloride 3

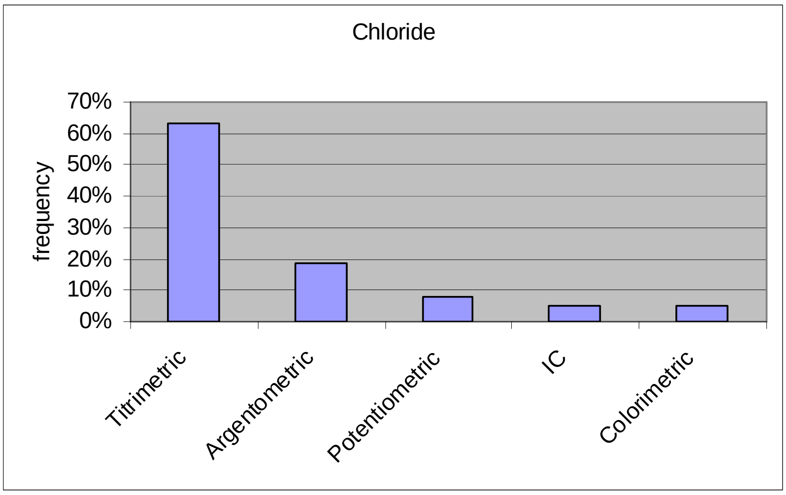



- values: 39
- removed: 0
- Mean: 67.4 mg/l
- Weighing: 65.8 mg/l
- Standard deviation: 5.34 mg/l; 8,1 %
- limit for St.-dev.: 10%
- Upper limit: 76.5 mg/l
- Lower limit: 55.1 mg/l
- too high: 2 values
- too low: 2 values
- outside tolerance limits: 10.3 %

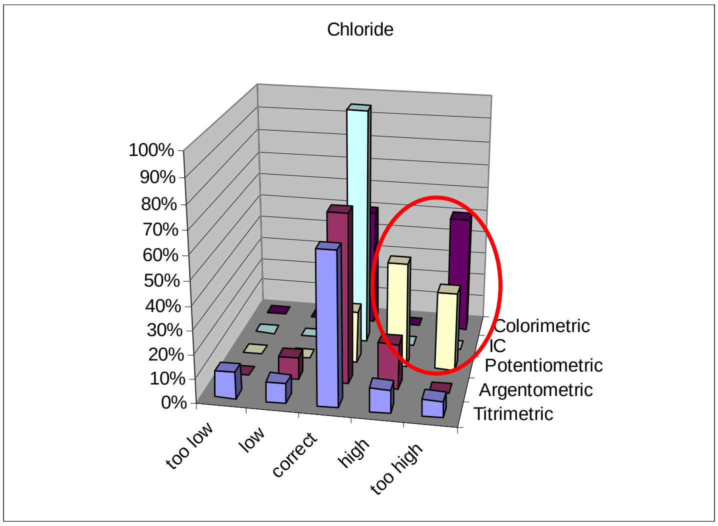




# Used methods



# Comparison of methods



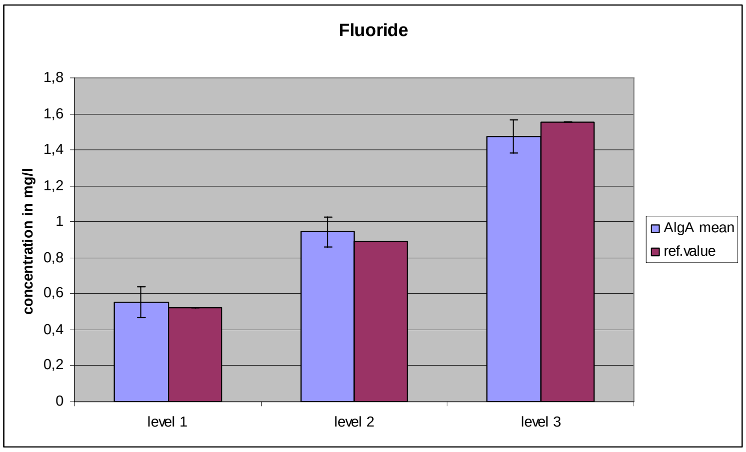





# Summary Chloride

- quite good agreement between mean and reference value
- standard deviation around limit
- what is titrimetric?
- Outliers for colorimetric and potentiometric method

# Fluoride
## Alg.A mean and ref.-value from weighings

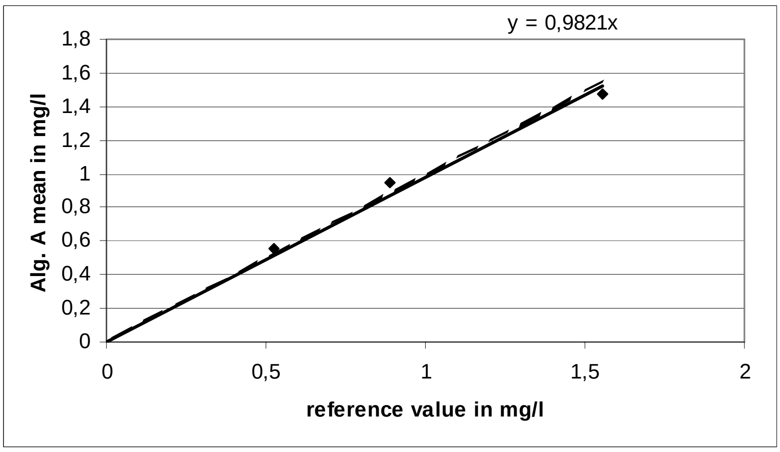



Consensus mean comparable to ref. value



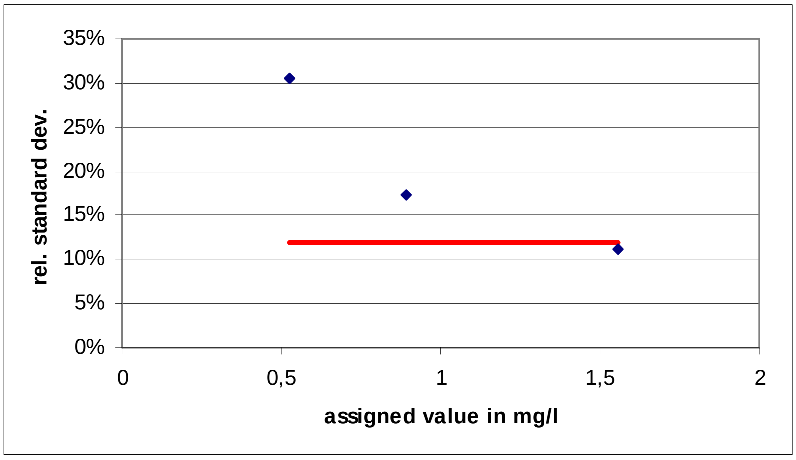


# Fluoride
## mean vs. ref.-value




Average recovery: 98.2%; in 2006: 107.7%

# Fluoride
## calculated standard deviation and limit

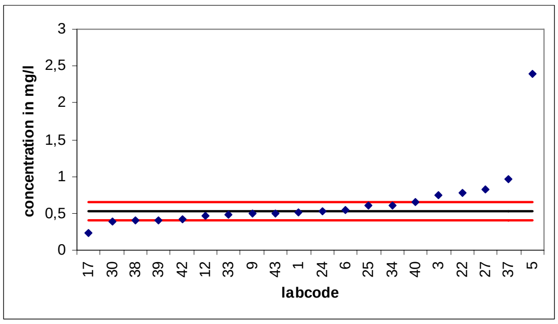



For level 1 worse than 2006



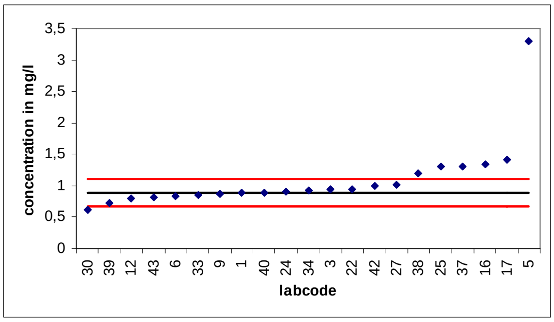


# Fluoride 1




- values: 22
- removed: 2
- Mean: 0.55 mg/l
- Weighing: 0.52 mg/l
- Standard deviation: 0,16 mg/l; 30.6 %
- limit for St.-dev.: 12%
- Upper limit: 0.650 mg/l
- Lower limit: 0.398 mg/l
- too high: 7 values
- too low: 3 values
- outside tolerance limits: 45.5 %

# Fluoride 2




- values: 23
- removed: 2
- Mean: 0.94 mg/l
- Weighing: 0.89 mg/l
- Standard deviation: 0.15 mg/l; 17.3 %
- limit for St.-dev.: 12%
- Upper limit: 1.11 mg/l
- Lower limit: 0.68 mg/l
- too high: 6 values
- too low: 3 values
- outside tolerance limits: 39.1 %



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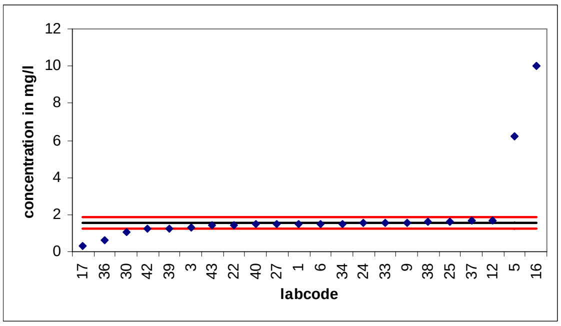
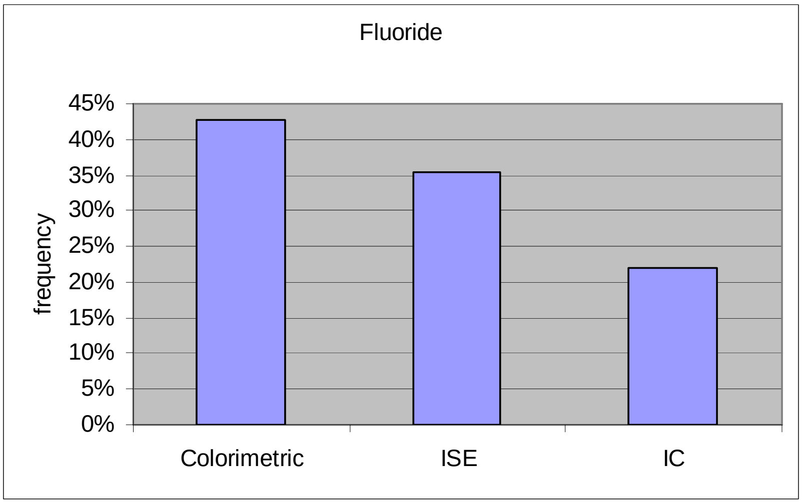
# Fluoride 3




- values: 23
- removed: 0
- Mean: 1.47 mg/l
- Weighing: 1.55 mg/l
- Standard deviation: 0.17 mg/l; 11.3 %
- limit for St.-dev.: 12%
- Upper limit: 1.90 mg/l
- Lower limit: 1.20 mg/l
- too high: 2 values
- too low: 4 values
- outside tolerance limits: 26.1 %

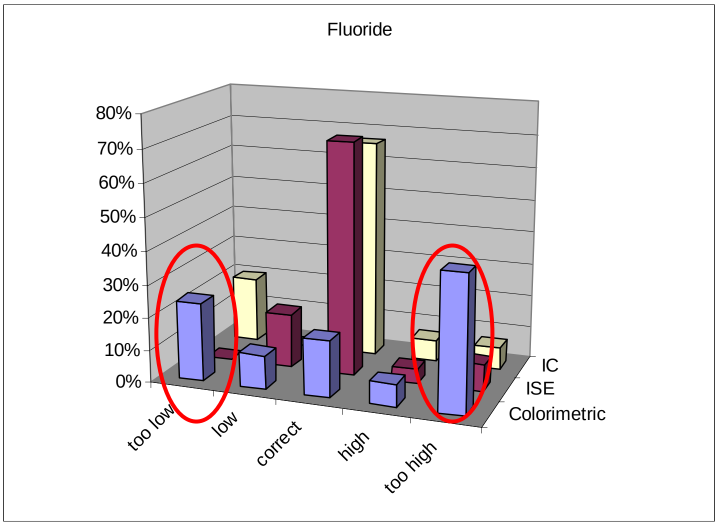
# Used methods








# Comparison of methods



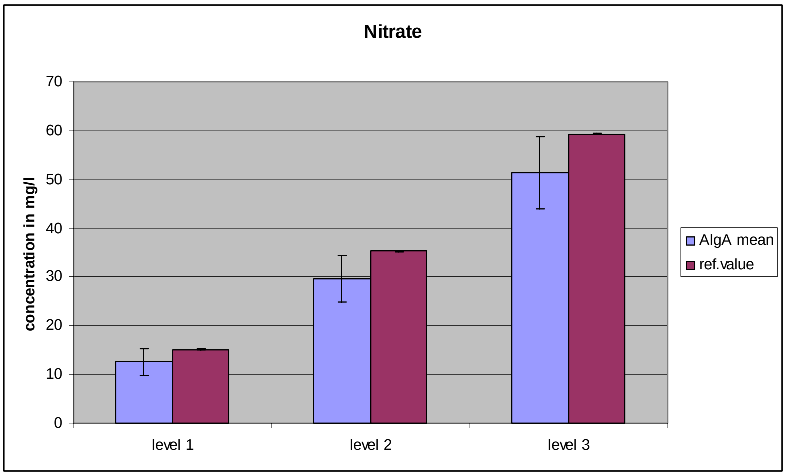
## Summary Fluoride

- mean values around reference values
- standard deviations higher than limit for low concentrations
- colorimetric values not reliable



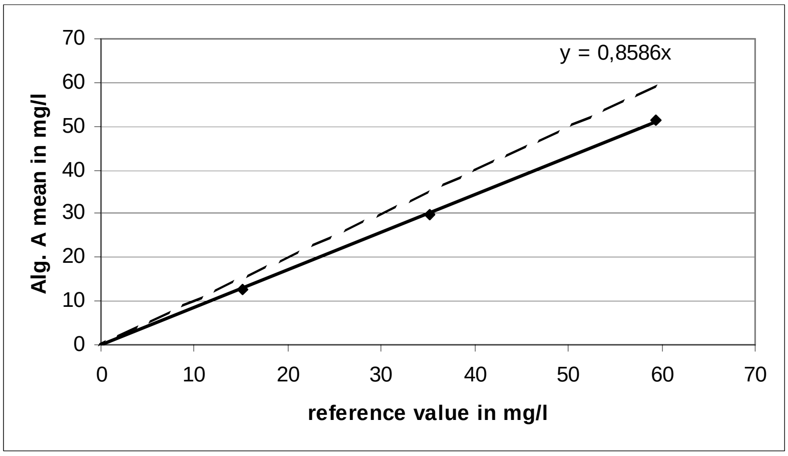


## Nitrate
## Alg.A mean and ref.-value from weighings




More differences between mean and ref. value than 2006

# Nitrate
## mean vs. ref.-value

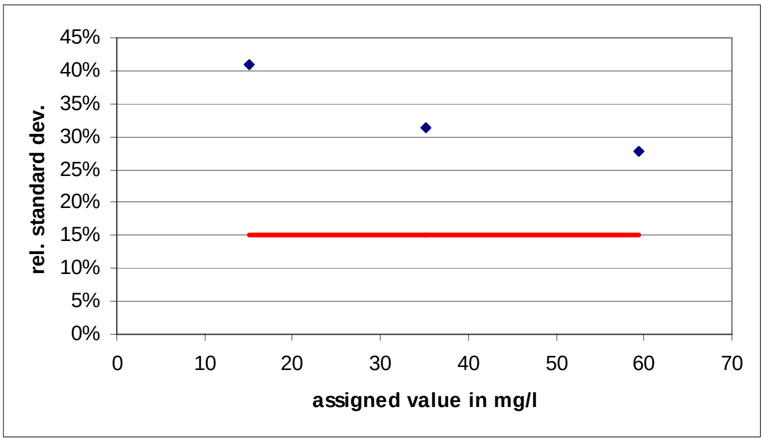



Average recovery: 85.9%; in 2006: 90.6%



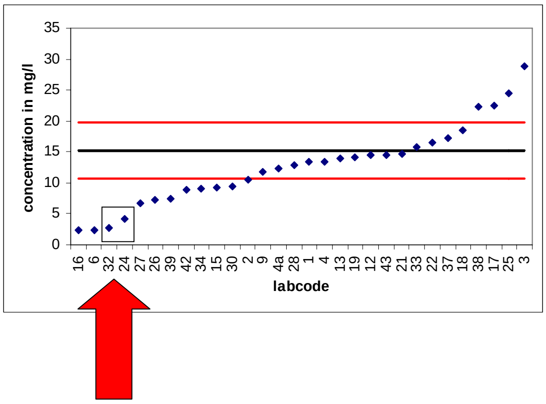


# Nitrate
## calculated standard deviation and limit




Similar to 2006

# Nitrate 1




most probably reported in $NO_3^-$-N instead of $NO_3^-$

marked values would be within the limits

- values: 35
- removed: 5(!)
- Mean: 12.5 mg/l
- Weighing: 15.2 mg/l
- Standard deviation: 6.21 mg/l; 41.0 %
- limit for St.-dev.: 15%
- Upper limit: 19.7 mg/l
- Lower limit: 10.6 mg/l
- too high: 6 values
- too low: 14 values
- outside tolerance limits: 58.8%(!)



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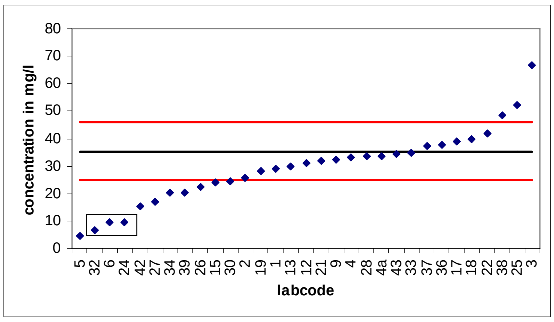
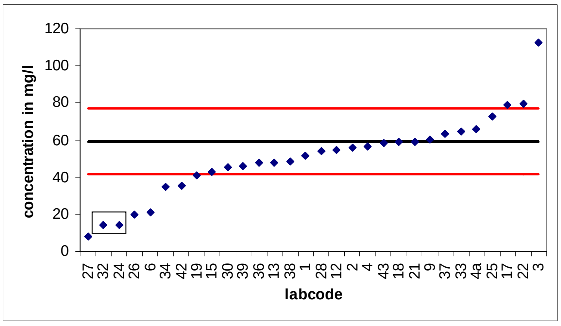
# Nitrate 2




- values: 35
- removed: 4
- Mean: 29.6 mg/l
- Weighing: 35.3 mg/l
- Standard deviation: 11.1 mg/l; 31.4 %
- limit for St.-dev.: 15%
- Upper limit: 45.8 mg/l
- Lower limit: 24.7 mg/l
- too high: 4 values
- too low: 13 values
- outside tolerance limits: 50,0 %(!)

# Nitrate 3

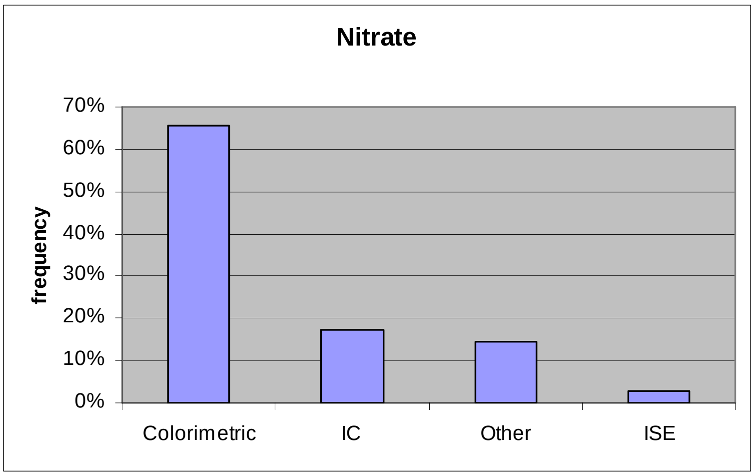



- values: 35
- removed: 5
- Mean: 51.5 mg/l
- Weighing: 59.3 mg/l
- Standard deviation: 16.5 mg/l; 27.8 %
- limit for St.-dev.: 15%
- Upper limit: 77.1 mg/l
- Lower limit: 41.5 mg/l
- too high: 4 values
- too low: 11 values
- outside tolerance limits: 44.1 %





# Used methods



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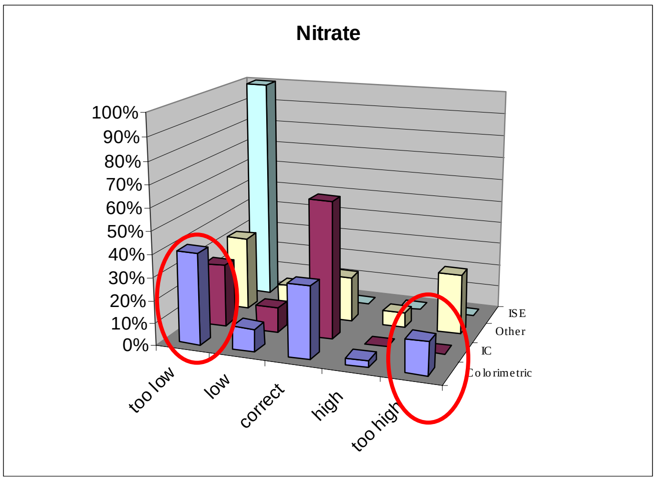
# Comparison of methods



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# Summary Nitrate

- some values obviously reported in wrong units
- high number of outliers
- average quality is very bad!
- parameter needs more emphasis
- harmonization of methods?

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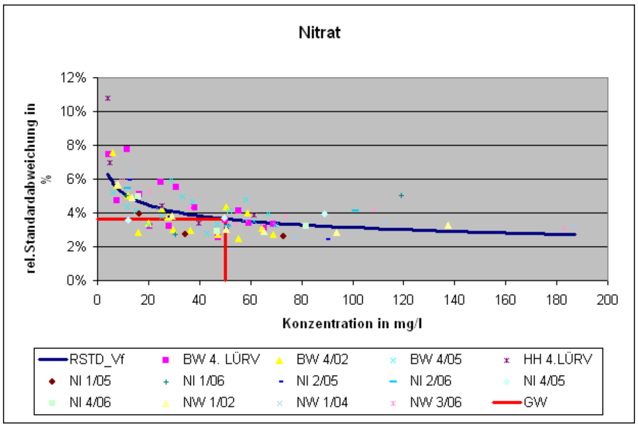
# Nitrate in drinking water PTs in Germany




It is possible!



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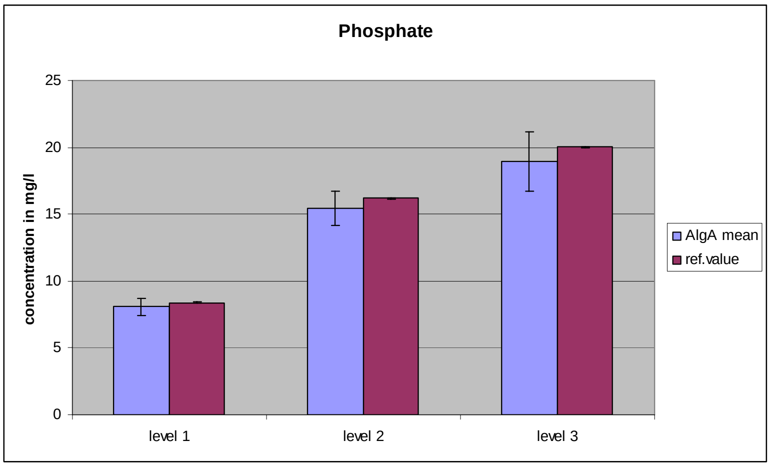
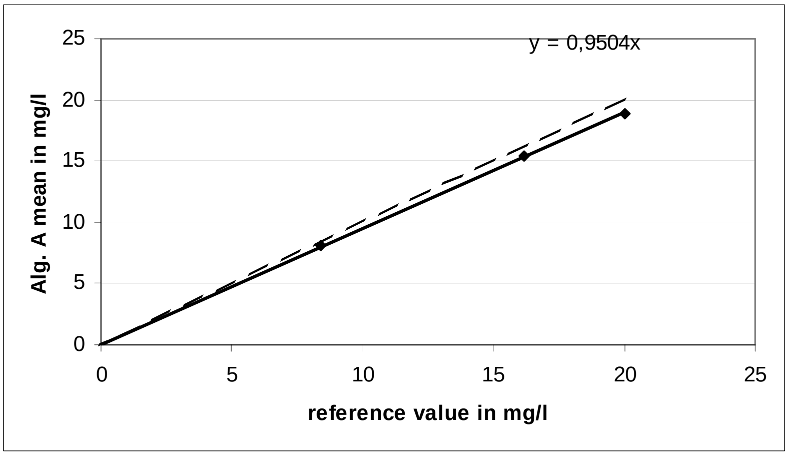
# Phosphate
# Alg.A mean and ref.-value from weighings




similar to 2006

# Phosphate
## mean vs. ref.-value




Average recovery: 95.0%; in 2006: 96.1%



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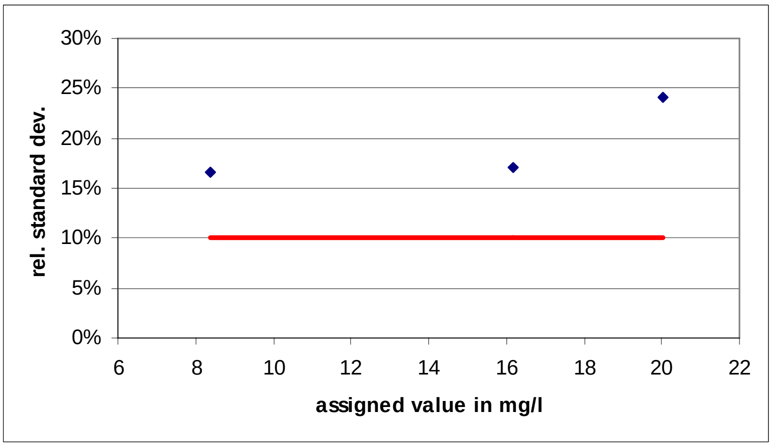
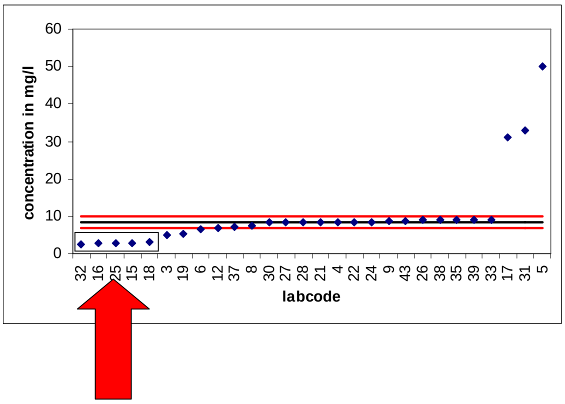
# Phosphate
## calculated standard deviation and limit




highest level worse than 2006

# Phosphate 1




most probably reported in $PO_4^{3-}$-P instead of $PO_4^{3-}$

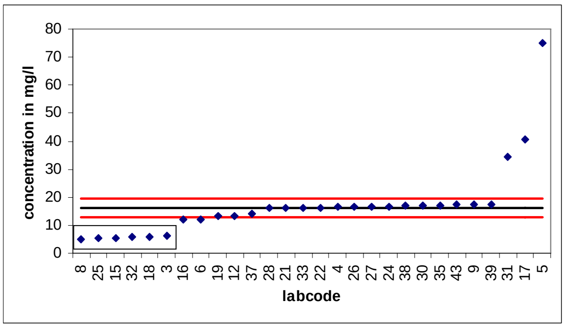
marked values would be within the limits

- values: 30
- removed: 2
- Mean: 8.07 mg/l
- Weighing: 8.40 mg/l
- Standard deviation: 1.40 mg/l; 16.64 %
- limit for St.-dev.: 10%
- Upper limit: 10.08 mg/l
- Lower limit: 6.72 mg/l
- too high: 4 values
- too low: 9 values
- outside tolerance limits: 43.3 %



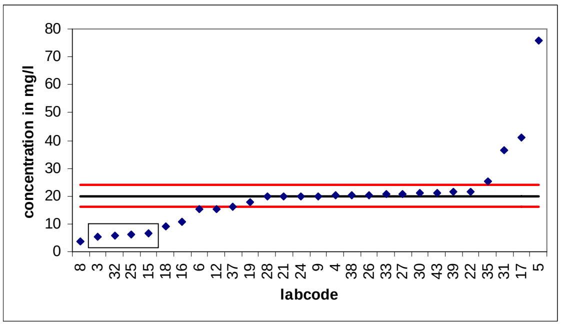


# Phosphate 2




- values: 30
- removed: 2
- Mean: 15.5 mg/l
- Weighing: 16.2 mg/l
- Standard deviation: 2.77 mg/l; 17.1 %
- limit for St.-dev.: 10%
- Upper limit: 19.4 mg/l
- Lower limit: 12.9 mg/l
- too high: 4 values
- too low: 9 values
- outside tolerance limits: 43.3 %

# Phosphate 3

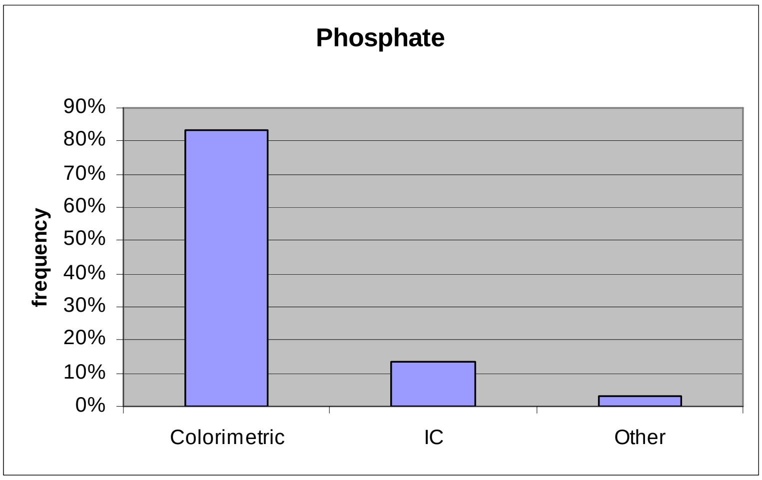



- values: 30
- removed: 2
- Mean: 18.9 mg/l
- Weighing: 20.0 mg/l
- Standard deviation: 4.83 mg/l; 24.1 %
- limit for St.-dev.: 10%
- Upper limit: 24.0 mg/l
- Lower limit: 16.0 mg/l
- too high: 5 values
- too low: 10 values
- outside tolerance limits:  50.0 %





# Used methods



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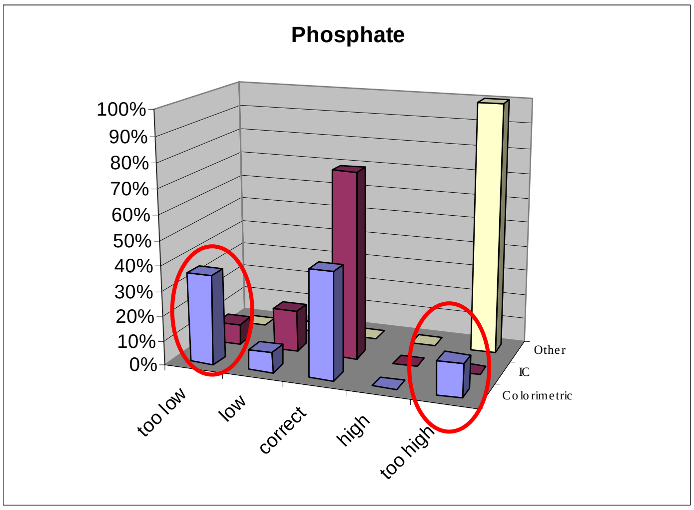
## Comparison of methods



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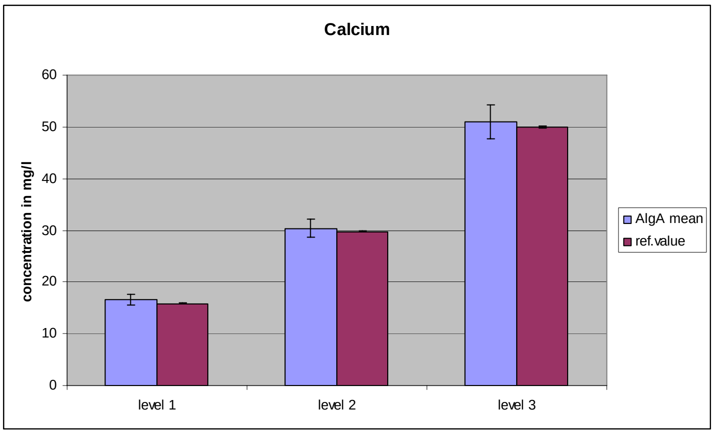
## Summary Phosphate

- values in wrong units
- high standard deviation
- high number of outliers for colorimetry (partially due to wrong units)

# Calcium
## Alg.A mean and ref.-value from weighings

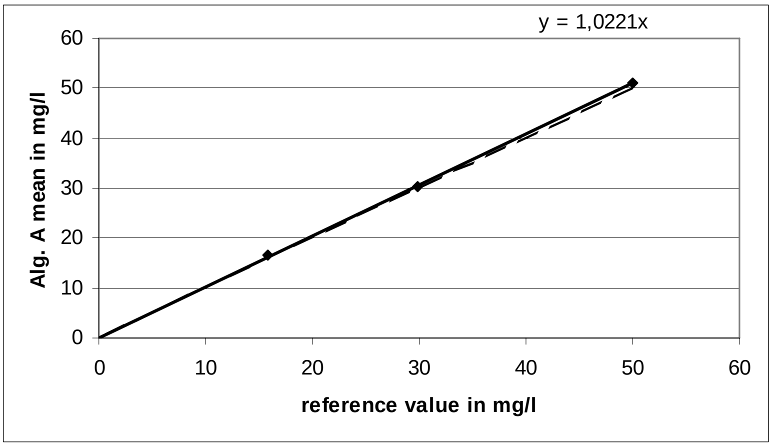



consensus mean close to ref.value



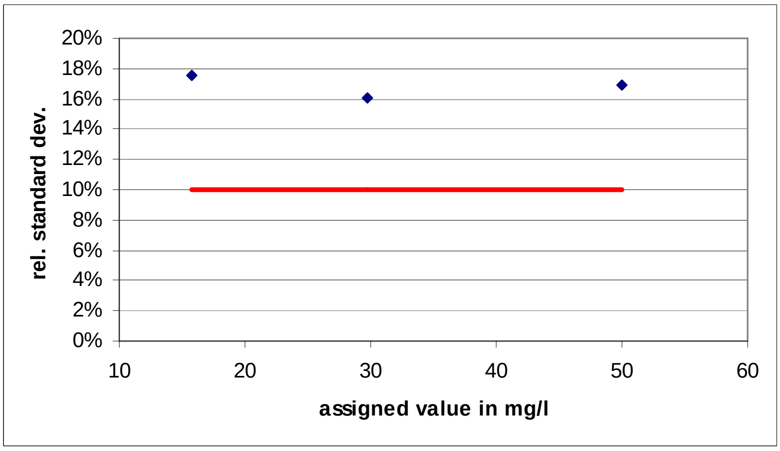


# Calcium
## mean vs. ref.-value




Average recovery: 102.2%; in 2006: 97.2%

# Calcium
# calculated standard deviation and limit

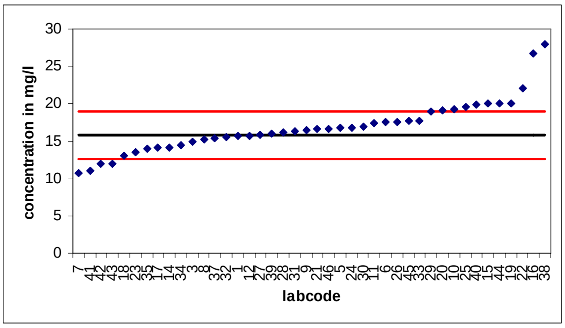



worse than 2006



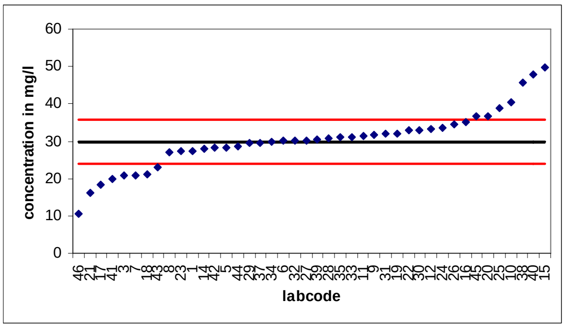


# Calcium 1




- values: 42
- removed: 0
- Mean: 16.6 mg/l
- Weighing: 15.8 mg/l
- Standard deviation: 2.77 mg/l; 17.6 %
- limit for St.-dev.: 10%
- Upper limit: 18.9 mg/l
- Lower limit: 12.6 mg/l
- too high: 10 values
- too low: 4 values
- outside tolerance limits: 33.3 %

# Calcium 2

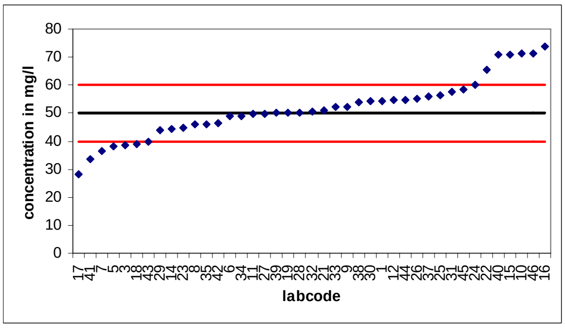



- values: 42
- removed: 0
- Mean: 30.4 mg/l
- Weighing: 29.8 mg/l
- Standard deviation: 4.77 mg/l; 16.0 %
- limit for St.-dev.: 10%
- Upper limit: 35.7 mg/l
- Lower limit: 23.8 mg/l
- too high: 7 values
- too low: 8 values
- outside tolerance limits: 35.7 %



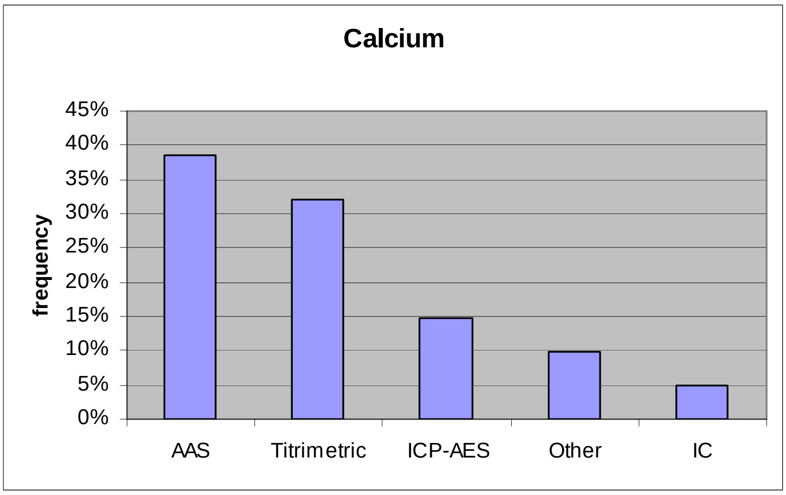


# Calcium 3




- values: 42
- removed: 1
- Mean: 51.0 mg/l
- Weighing: 50.0 mg/l
- Standard deviation: 8.47 mg/l; 17.0 %
- limit for St.-dev.: 10%
- Upper limit: 60.0 mg/l
- Lower limit: 40.0 mg/l
- too high: 7 values
- too low: 7 values
- outside tolerance limits: 33.3 %

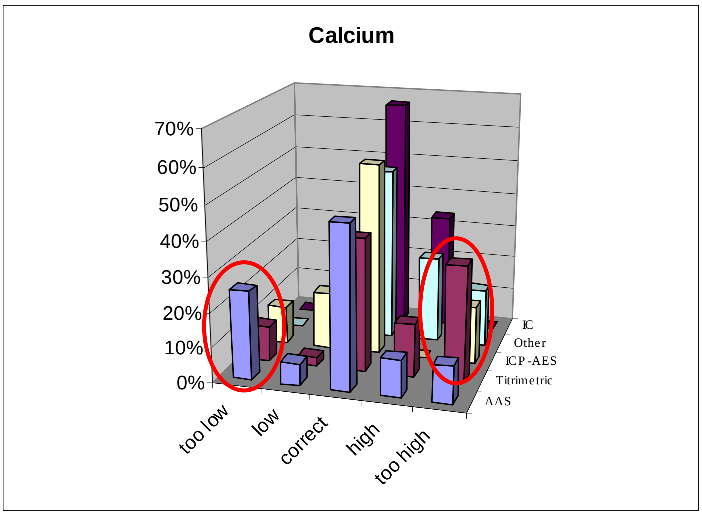
# Used methods








# Comparison of methods



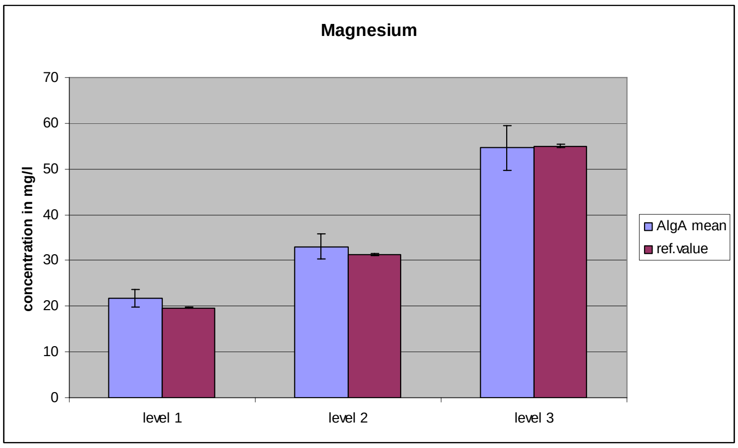
## Summary Calcium

- mean values close to reference values
- standard deviations above limit



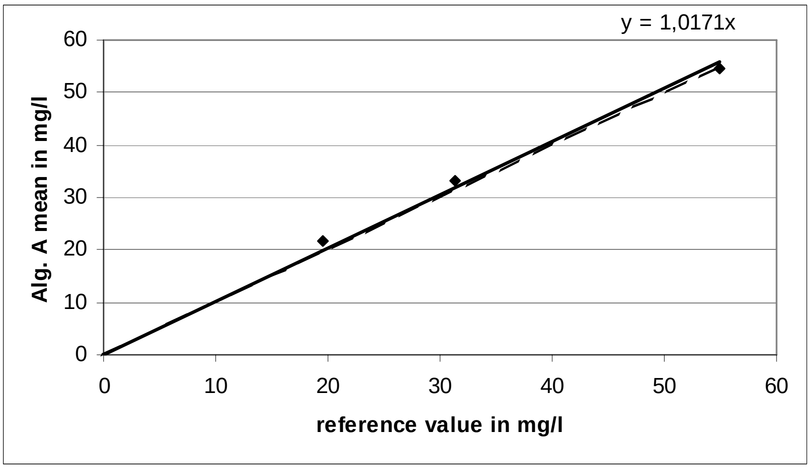


## Magnesium
## Alg.A mean and ref.-value from weighings




consensus mean close to ref.value

# Magnesium
## mean vs. ref.-value

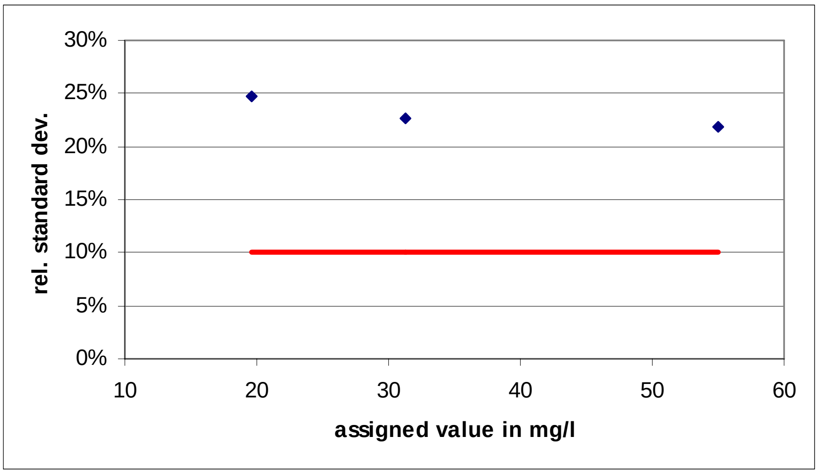



Average recovery: 101.7%; in 2006: 99.6%





# Magnesium
## calculated standard deviation and limit




similar to 2006

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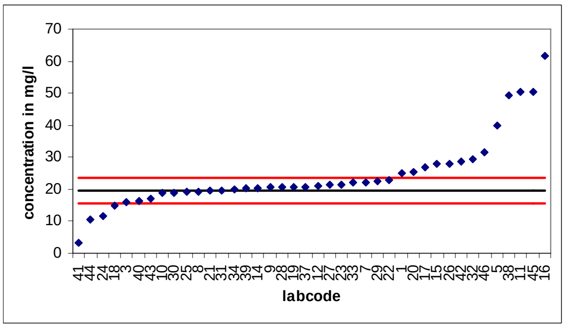
# Magnesium 1




- values: 40
- removed: 0
- Mean: 21.8 mg/l
- Weighing: 19.6 mg/l
- Standard deviation: 4.84 mg/l; 24.7 %
- limit for St.-dev.: 10%
- Upper limit: 23.5 mg/l
- Lower limit: 15.7 mg/l
- too high: 13 values(!)
- too low: 4 values
- outside tolerance limits: 32.5 %



iswa

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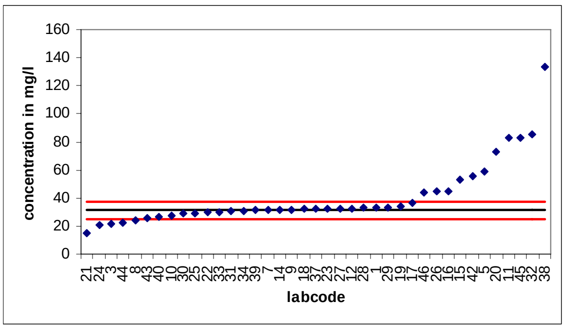
# Magnesium 2

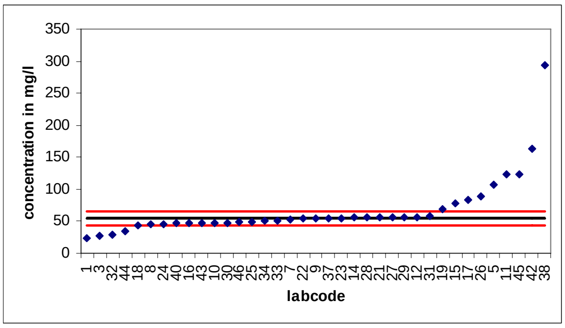



- values: 40
- removed: 1
- Mean: 33.0 mg/l
- Weighing: 31.3 mg/l
- Standard deviation: 7.11 mg/l; 22.7 %
- limit for St.-dev.: 10%
- Upper limit: 37.6 mg/l
- Lower limit: 25.1 mg/l
- too high: 11 values
- too low: 5 values
- outside tolerance limits: 40.0 %



iswa

# Magnesium 3

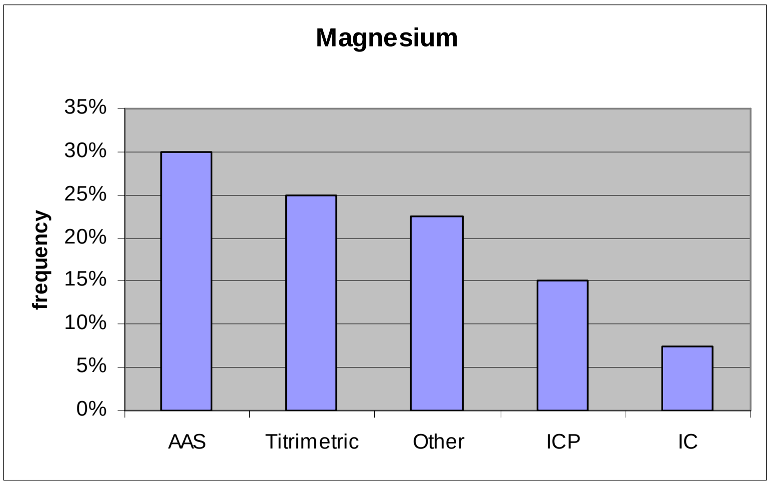



- values: 40
- removed: 3
- Mean: 54.6 mg/l
- Weighing: 55.0 mg/l
- Standard deviation: 12.1 mg/l; 21.9 %
- limit for St.-dev.: 10%
- Upper limit: 66.0 mg/l
- Lower limit: 44.0 mg/l
- too high: 9 values
- too low: 7 values
- outside tolerance limits: 40 %

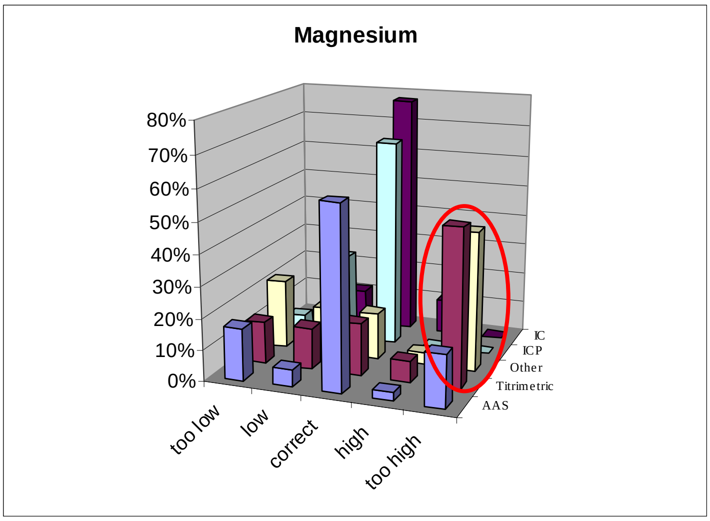




# Used methods



## Comparison of methods



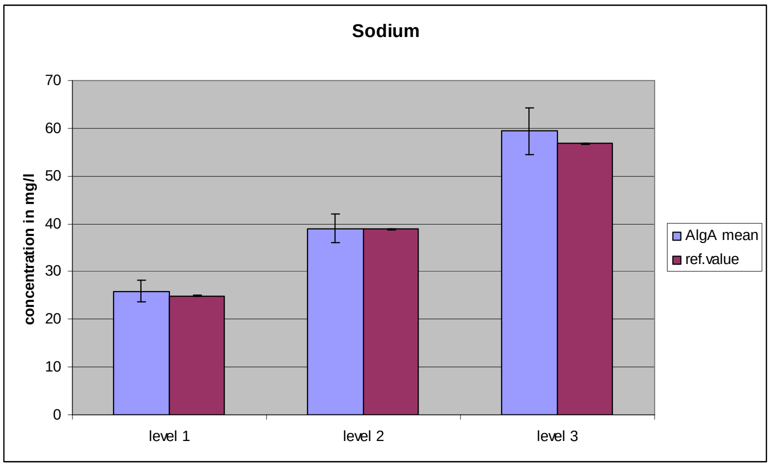





## Summary Magnesium

- mean values around reference values
- standard deviations too high
- titrimetric values not reliable

# Sodium
## Alg.A mean and ref.-value from weighings

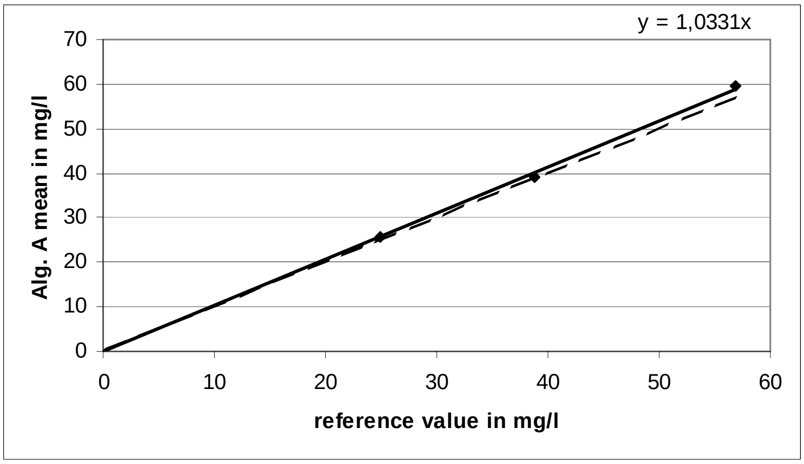



similar to 2006



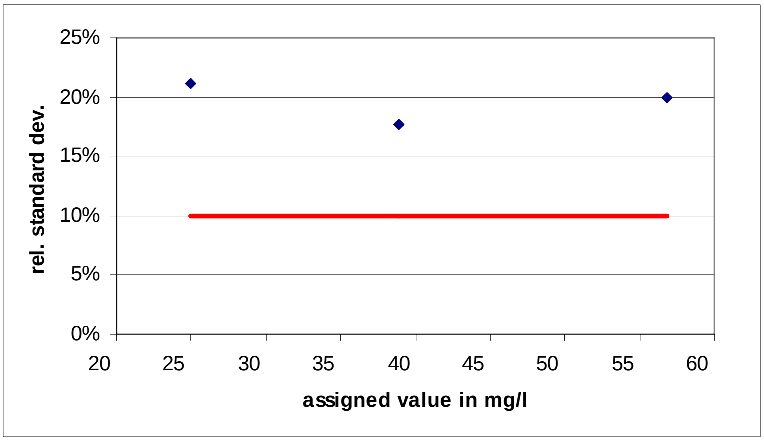


# Sodium
## mean vs. ref.-value




Average recovery: 103.3%; in 2006: 104.4%

# Sodium
# calculated standard deviation and limit

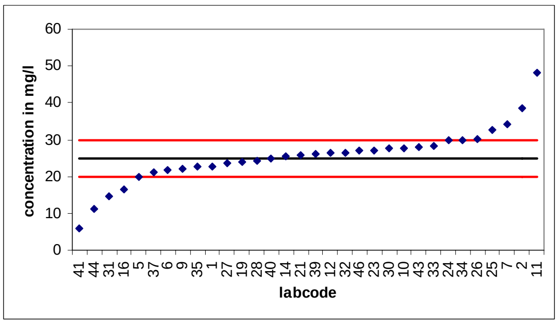



similar to 2006



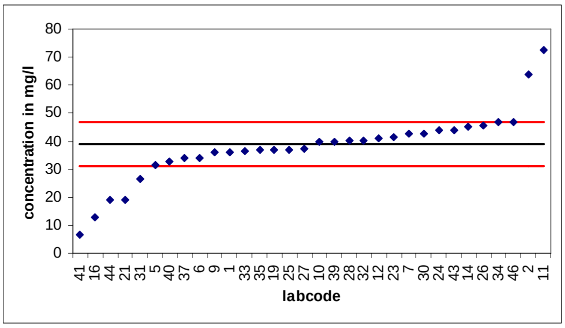


# Sodium 1




- values: 34
- removed: 1
- Mean: 25.9 mg/l
- Weighing: 25.0 mg/l
- Standard deviation: 5.29 mg/l; 21.2 %
- limit for St.-dev.: 10%
- Upper limit: 29.9 mg/l
- Lower limit: 20.0 mg/l
- too high: 8 values
- too low: 6 values
- outside tolerance limits: 41,2 %

# Sodium 2




- values: 34
- removed: 1
- Mean: 39.0 mg/l
- Weighing: 38.9 mg/l
- Standard deviation: 6.89 mg/l; 17.7 %
- limit for St.-dev.: 10%
- Upper limit: 46.6 mg/l
- Lower limit: 31.1 mg/l
- too high: 5 values
- too low: 6 values
- outside tolerance limits:  32.4 %



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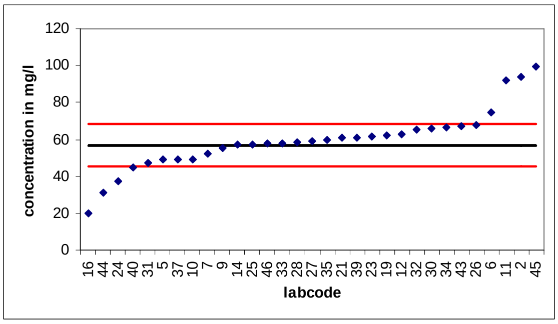
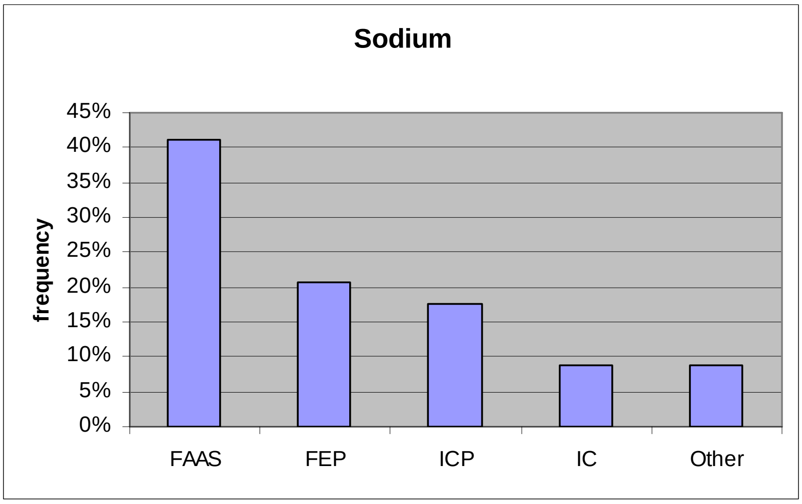
# Sodium 3




- values: 34
- removed: 2
- Mean: 59.4 mg/l
- Weighing: 56.8 mg/l
- Standard deviation: 11.3 mg/l; 19.9 %
- limit for St.-dev.: 10%
- Upper limit: 68.2 mg/l
- Lower limit: 45.5 mg/l
- too high: 5 values
- too low: 6 values
- outside tolerance limits:  32.4 %

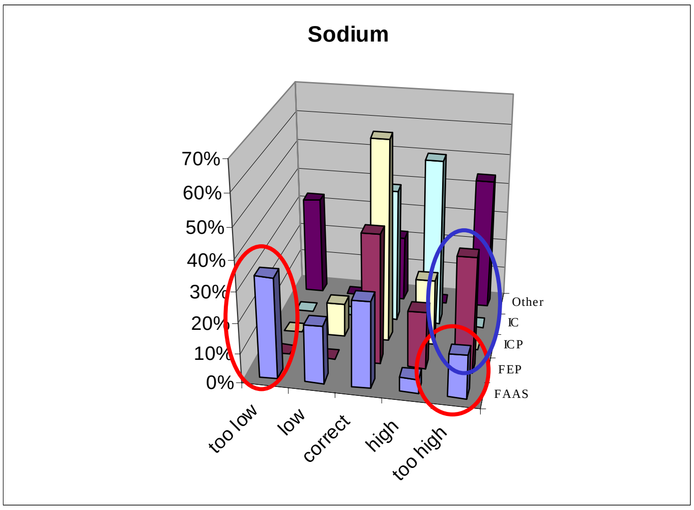
# Used methods








# Comparison of methods



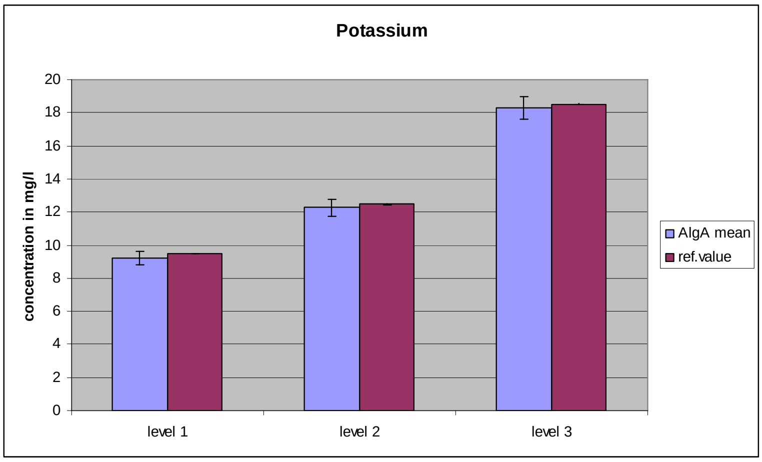
## Summary Sodium

- consensus means close to ref.values
- standard deviations too high
- too high values with FEP
- unreliable data with AAS



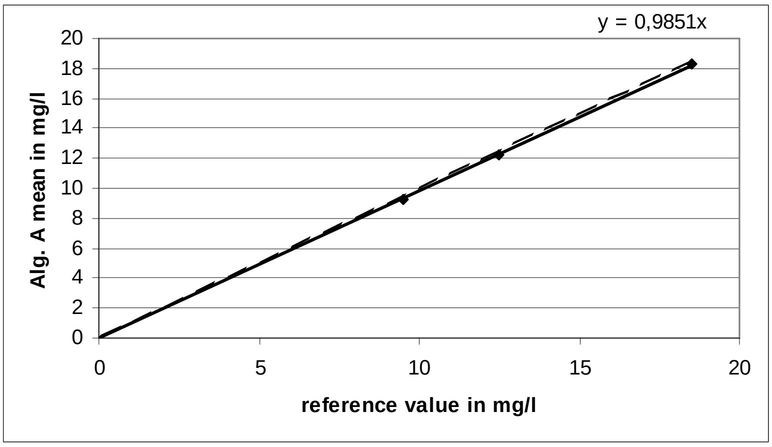


## Potassium
## Alg.A mean and ref.-value from weighings




consensus mean close to ref.value

# Potassium
mean vs. ref.-value

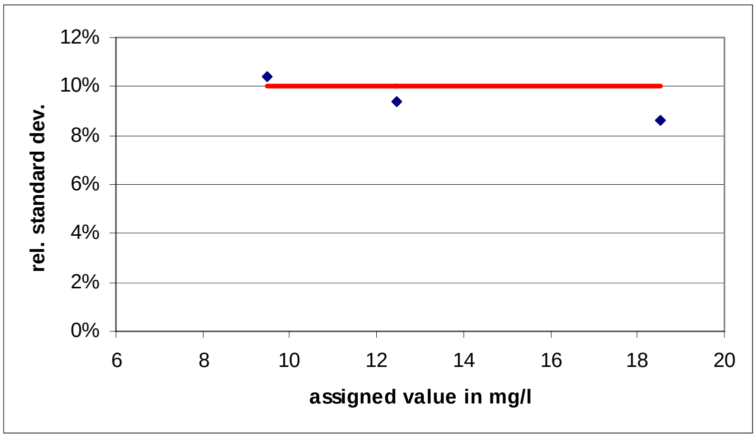



Average recovery: 98.5%; in 2006: 96.9%





# Potassium
calculated standard deviation and limit




Standard deviations better than 2006

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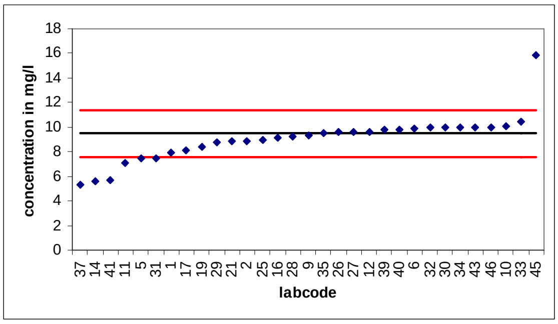
# Potassium 1




- values: 32
- removed: 0
- Mean: 9.23 mg/l
- Weighing: 9.49 mg/l
- Standard deviation: 0.99 mg/l; 10.4 %
- limit for St.-dev.: 10%
- Upper limit: 11.4 mg/l
- Lower limit: 7.59 mg/l
- too high: 2 values
- too low: 6 values
- outside tolerance limits: 25.0 %

81 Koch, M.: PT evaluation – SADCMET PT Workshop 2007 Dar es Salaam

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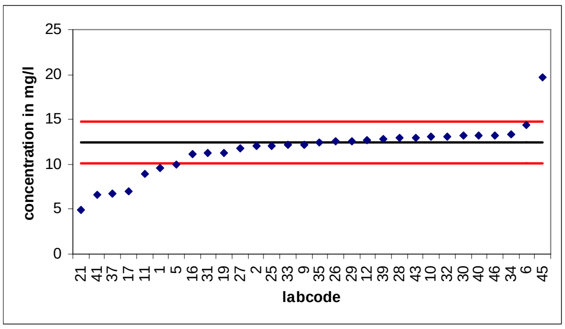
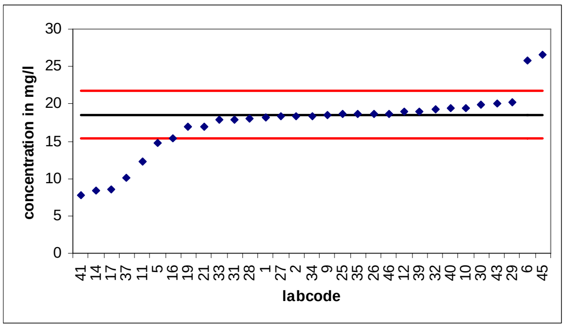
# Potassium 2




- values: 32
- removed: 1
- Mean: 12.3 mg/l
- Weighing: 12.5 mg/l
- Standard deviation: 1.17 mg/l; 9.4 %
- limit for St.-dev.: 10%
- Upper limit: 14.8 mg/l
- Lower limit: 10.1 mg/l
- too high: 2 values
- too low: 8 values
- outside tolerance limits: 31.3 %

82 Koch, M.: PT evaluation – SADCMET PT Workshop 2007 Dar es Salaam

# Potassium 3

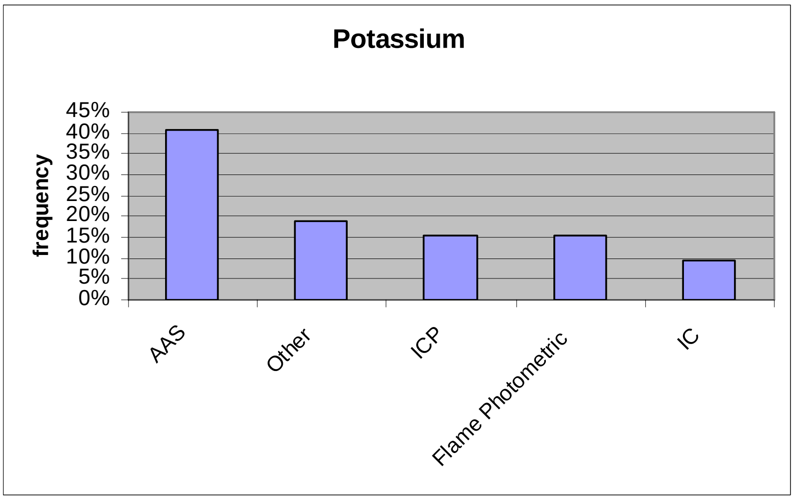



- values: 32
- removed: 0
- Mean: 18.3 mg/l
- Weighing: 18.5 mg/l
- Standard deviation: 1.60 mg/l; 8.64 %
- limit for St.-dev.: 10%
- Upper limit: 21.7 mg/l
- Lower limit: 15.3 mg/l
- too high: 3 values
- too low: 6 values
- outside tolerance limits:  28.1 %

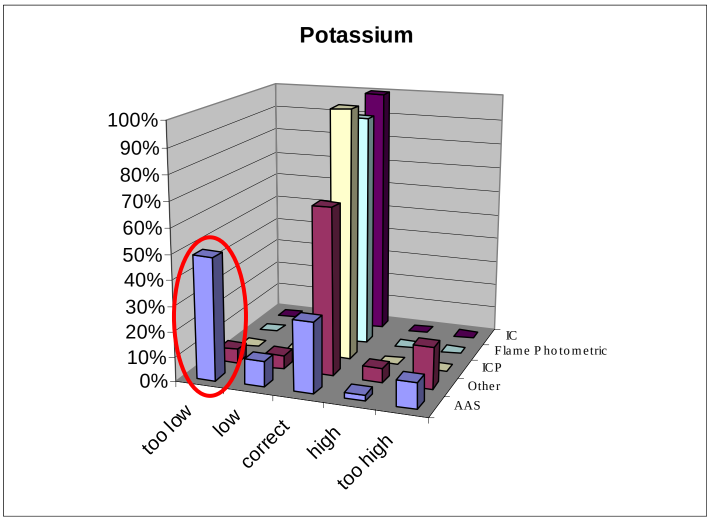




# Used methods



# Comparison of methods








# Summary Potassium

- Mean values close to reference values
- standard deviations a bit higher than limit
- AAS values not reliable

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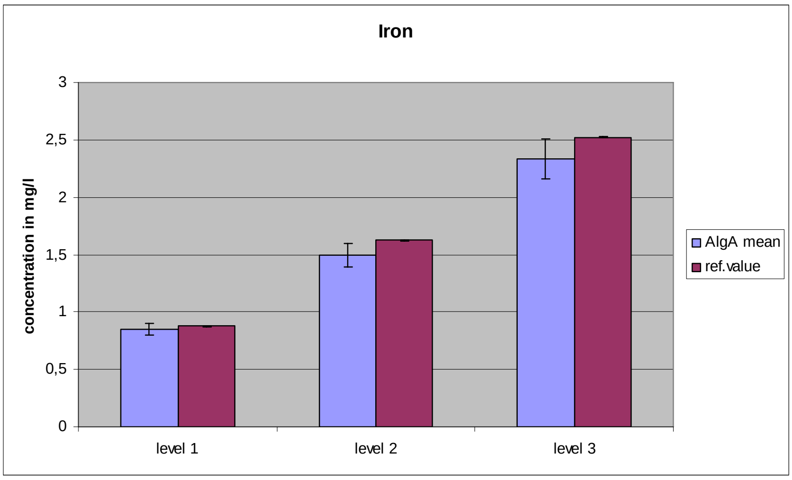
# Iron
## Alg.A mean and ref.-value from weighings



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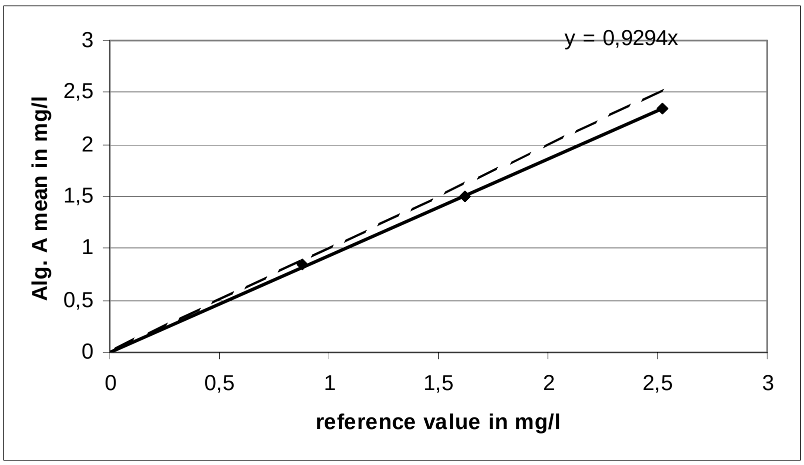
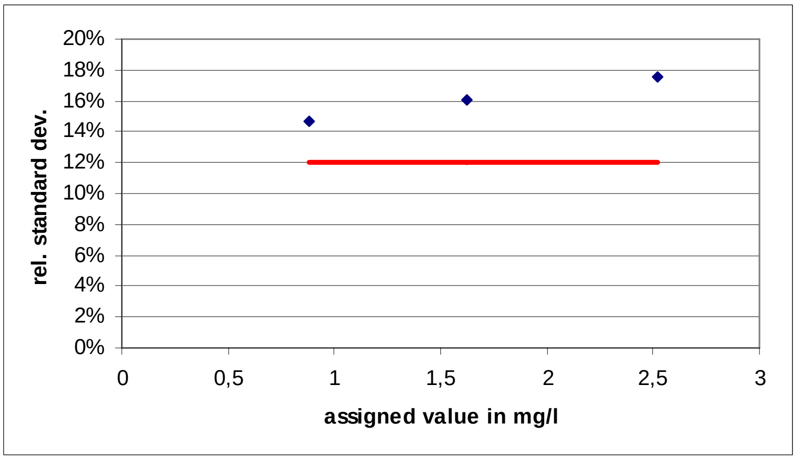
# Iron
## mean vs. ref.-value




Average recovery: 92.9%; in 2006: 88.0%

# Iron
# calculated standard deviation and limit




similar to 2006



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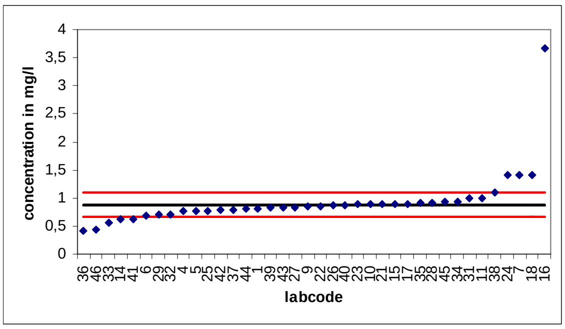
# Iron 1




- values: 39
- removed: 1
- Mean: 0.85 mg/l
- Weighing: 0.89 mg/l
- Standard deviation: 0.129 mg/l; 14.7 %
- limit for St.-dev.: 12%
- Upper limit: 1.09 mg/l
- Lower limit: 0.67 mg/l
- too high: 5 values
- too low: 6 values
- outside tolerance limits: 28.2 %

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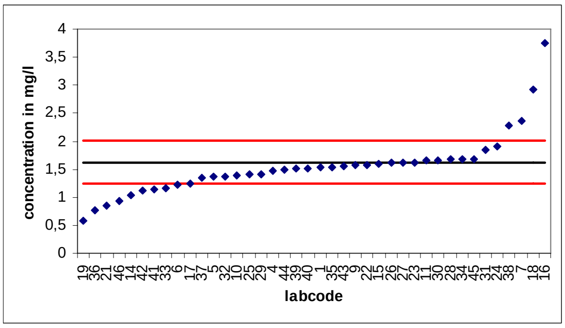
# Iron 2




- values: 40
- removed: 0
- Mean: 1.50 mg/l
- Weighing: 1.62 mg/l
- Standard deviation: 0.261 mg/l; 16.1 %
- limit for St.-dev.: 12%
- Upper limit: 2.01 mg/l
- Lower limit: 1.23 mg/l
- too high: 4 values
- too low: 9 values
- outside tolerance limits: 32.5 %



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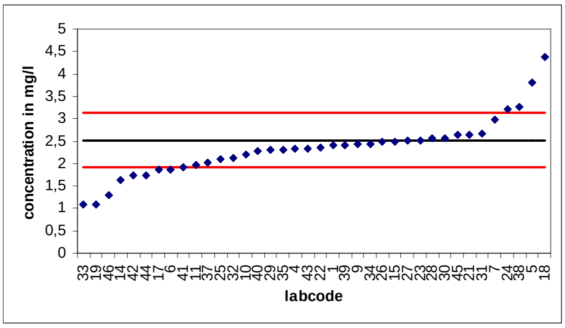
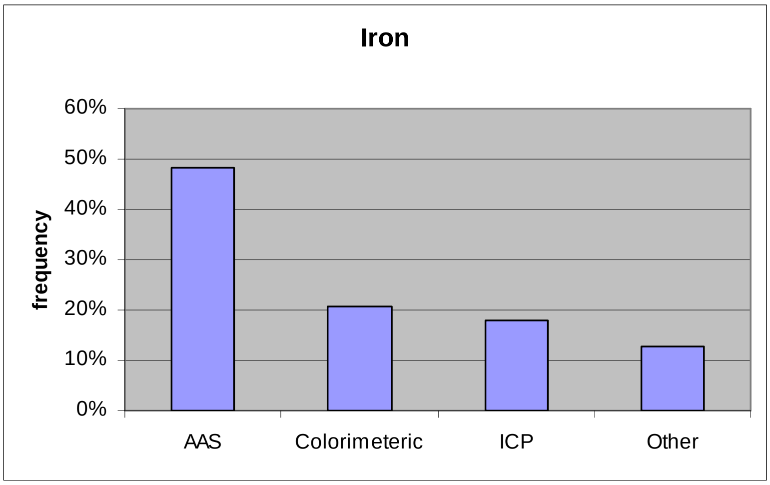
# Iron 3




- values: 40
- removed: 1
- Mean: 2.34 mg/l
- Weighing: 2.52 mg/l
- Standard deviation: 0.441 mg/l; 17.5 %
- limit for St.-dev.: 12%
- Upper limit: 3.12 mg/l
- Lower limit: 1.91 mg/l
- too high: 5 values
- too low: 9 values
- outside tolerance limits: 35.0 %

# Used methods

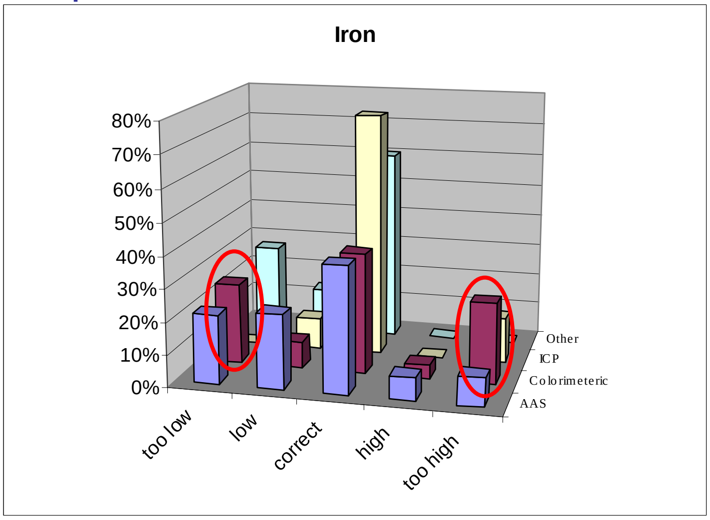



2006: AAS 16.1%, Colorimetric 64.5%





# Comparison of methods



# Summary Iron

- mean lower than reference values
- standard deviations higher than limit
- many outliers with colorimetric method



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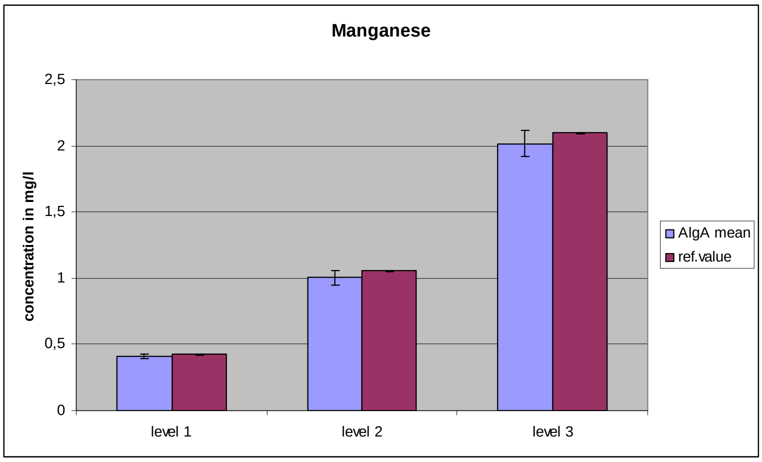
# Manganese
## Alg.A mean and ref.-value from weighings




similar to 2006

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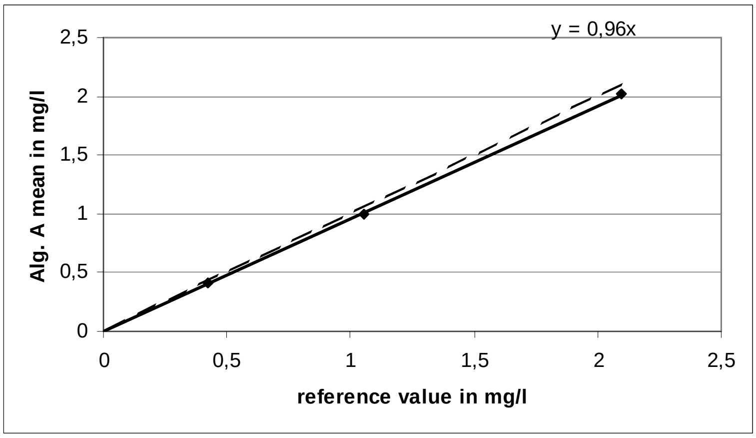
# Manganese
mean vs. ref.-value




Average recovery: 96.0%; in 2006: 95.4%



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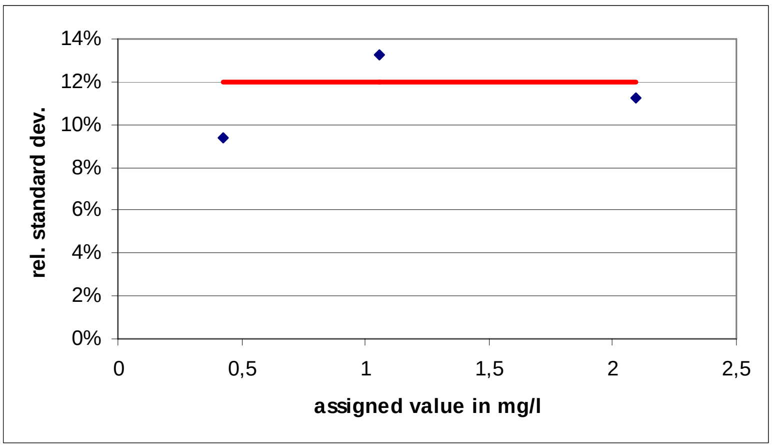
# Manganese
calculated standard deviation and limit




similar to 2006



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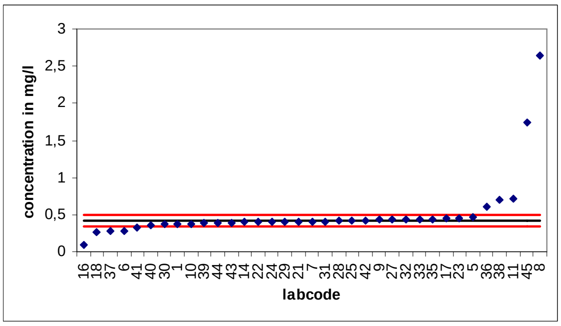
# Manganese 1




- values: 36
- removed: 1
- Mean: 0.41 mg/l
- Weighing: 0.42 mg/l
- Standard deviation: 0.040 mg/l; 9.39 %
- limit for St.-dev.: 12%
- Upper limit: 0.50 mg/l
- Lower limit: 0.34 mg/l
- too high: 5 values
- too low: 6 values
- outside tolerance limits: 30.6 %



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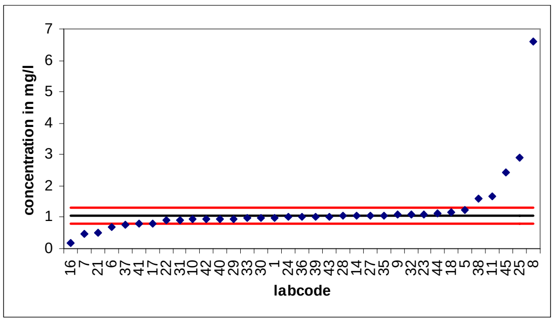
# Manganese 2




- values: 36
- removed: 1
- Mean: 1.00 mg/l
- Weighing: 1.06 mg/l
- Standard deviation: 0.140 mg/l; 13.3 %
- limit for St.-dev.: 12%
- Upper limit: 1.31 mg/l
- Lower limit: 0.80 mg/l
- too high: 5 values
- too low: 7 values
- outside tolerance limits: 33.3 %



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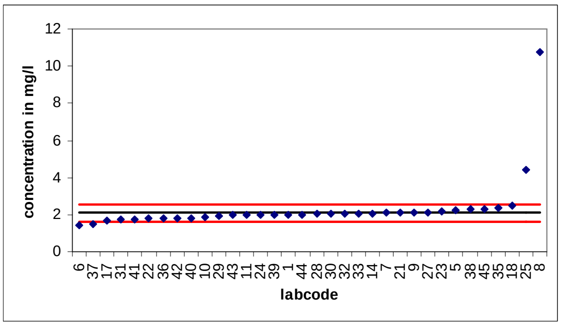
# Manganese 3




- values: 36
- removed: 2
- Mean: 2.02 mg/l
- Weighing: 2,10 mg/l
- Standard deviation: 0.235 mg/l; 11.2 %
- limit for St.-dev.: 12%
- Upper limit: 2.57 mg/l
- Lower limit: 1.63 mg/l
- too high: 2 values
- too low: 4 values
- outside tolerance limits: 16.7 %



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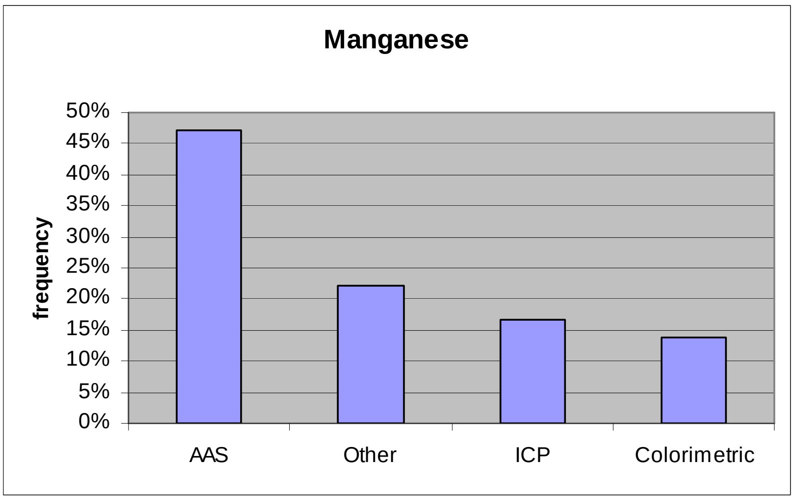
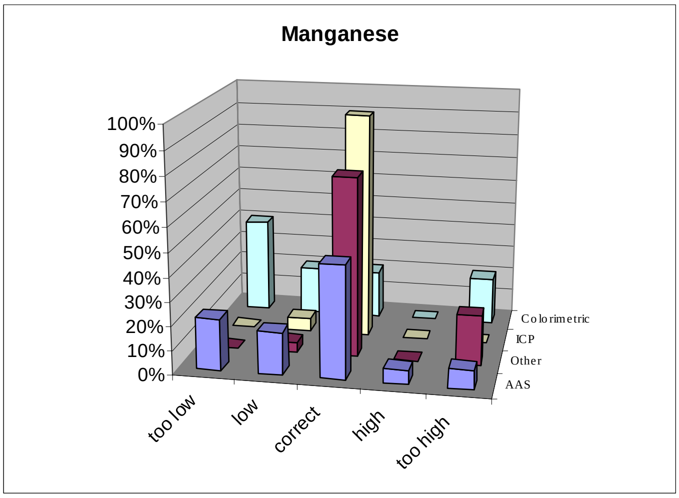
# Used methods



# Comparison of methods



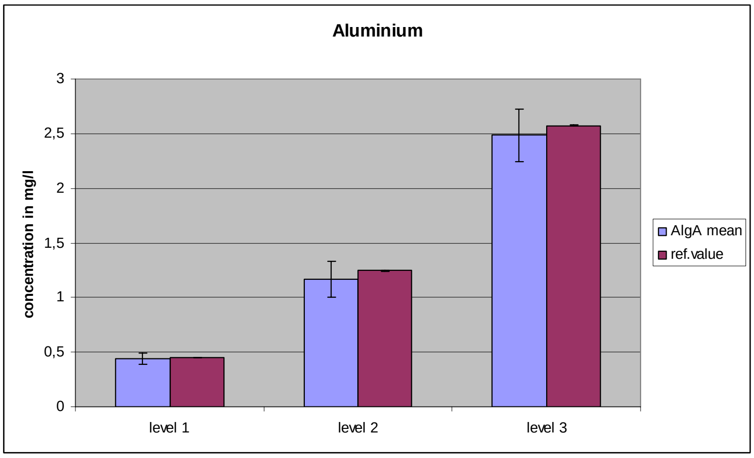





# Summary Manganese

- mean values 4% below reference values
- standard deviation around limit
- broad distribution for AAS values

# Aluminium
## Alg.A mean and ref.-value from weighings

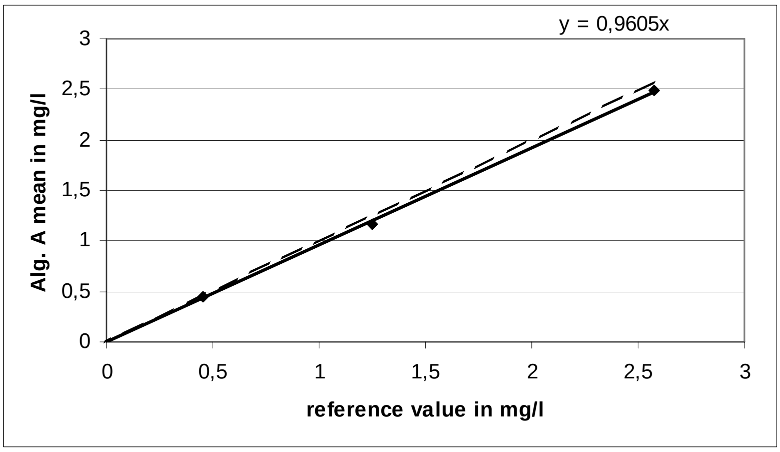



consensus means closer to ref.values then in 2006





# Aluminium
## mean vs. ref.-value




Average recovery: 96.1%; in 2006: 85.7%

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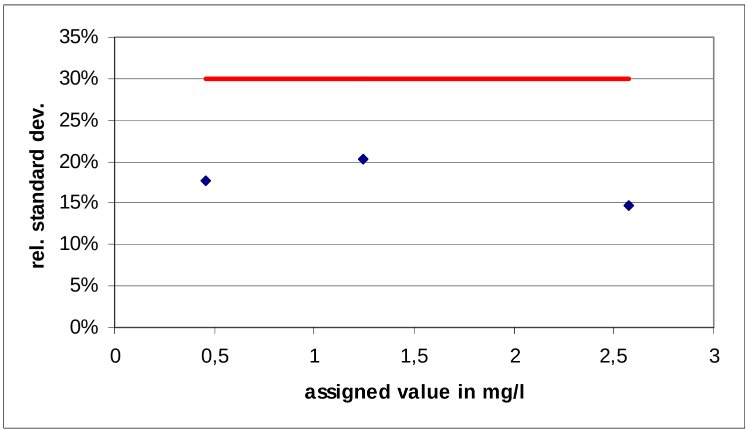
# Aluminium
# calculated standard deviation and limit




107 Koch, M.: PT evaluation – SADCMET PT Workshop 2007 Dar es Salaam

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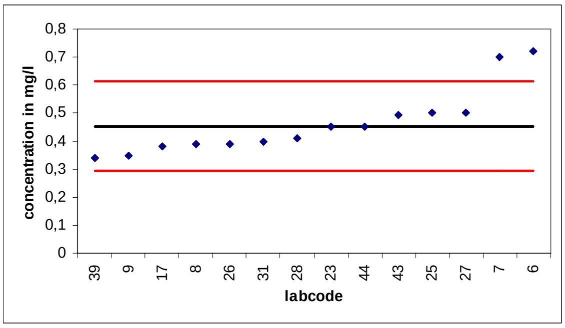
# Aluminium 1




- values: 14
- removed: 0
- Mean: 0.44 mg/l
- Weighing: 0.45 mg/l
- Standard deviation: 0.080 mg/l; 17.7 %
- limit for St.-dev.: 30%
- Upper limit: 0.61 mg/l
- Lower limit: 0.29 mg/l
- too high: 2 values
- too low: 0 values
- outside tolerance limits: 14.3 %

108 Koch, M.: PT evaluation – SADCMET PT Workshop 2007 Dar es Salaam

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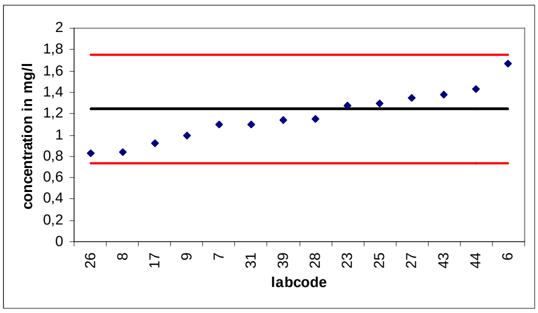
# Aluminium 2




- values: 14
- removed: 0
- Mean: 1.17 mg/l
- Weighing: 1.25 mg/l
- Standard deviation: 0.253 mg/l; 20.3 %
- limit for St.-dev.: 30%
- Upper limit: 1.75 mg/l
- Lower limit: 0.74 mg/l
- too high: 0 values
- too low: 0 values
- outside tolerance limits: 0.0 %

109 Koch, M.: PT evaluation – SADCMET PT Workshop 2007 Dar es Salaam

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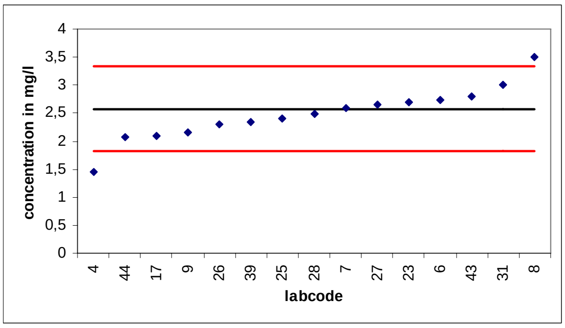
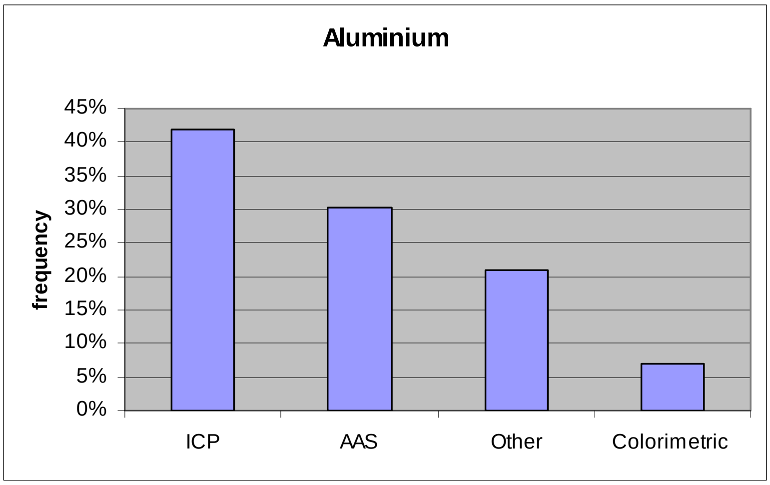
# Aluminium 3




- values: 15
- removed: 0
- Mean: 2.49 mg/l
- Weighing: 2.57 mg/l
- Standard deviation: 0.380 mg/l; 14.8 %
- limit for St.-dev.: 30%
- Upper limit: 3.33 mg/l
- Lower limit: 1.82 mg/l
- too high: 1 values
- too low: 1 values
- outside tolerance limits: 13.3 %

110 Koch, M.: PT evaluation – SADCMET PT Workshop 2007 Dar es Salaam

# Used methods

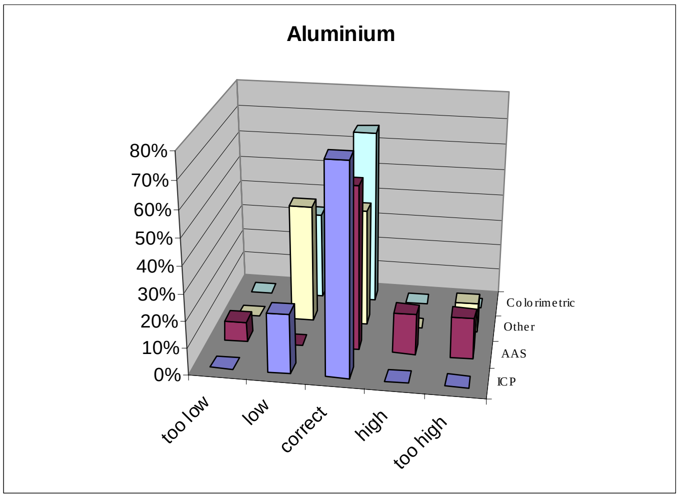



2006: 40% Colorimetric





# Comparison of methods



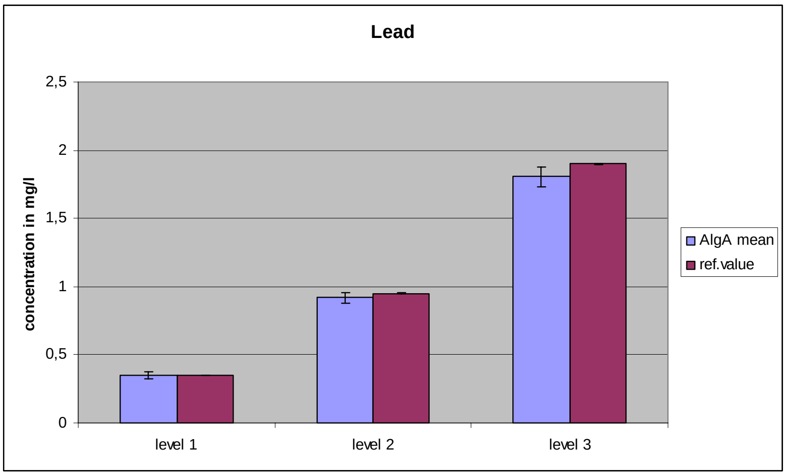
# Summary Aluminium

- small number of values
- mean values a bit below reference values





# Lead
# Alg.A mean and ref.-value from weighings



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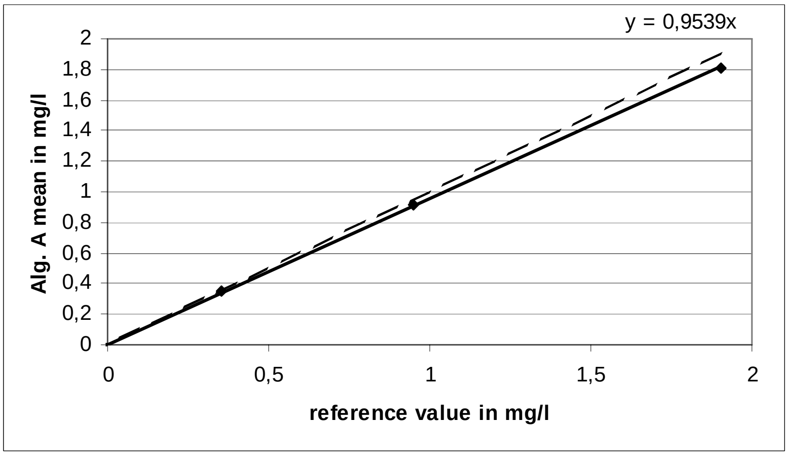
# Lead
## mean vs. ref.-value




Average recovery: 95.4%; in 2006: 95.6%



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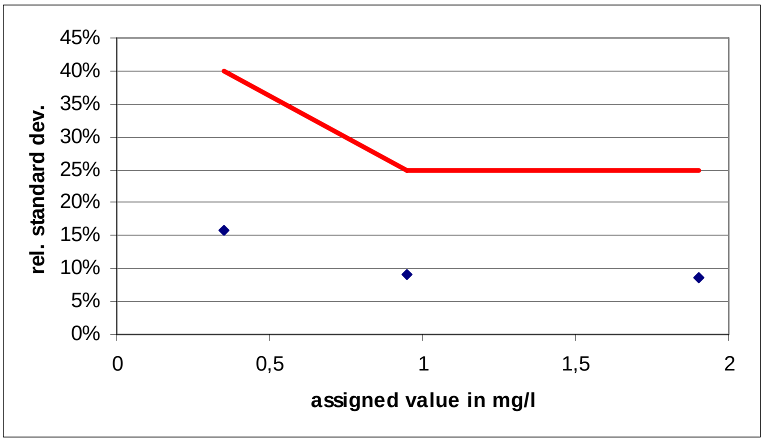
# Lead
## calculated standard deviation and limit




very similar to 2006



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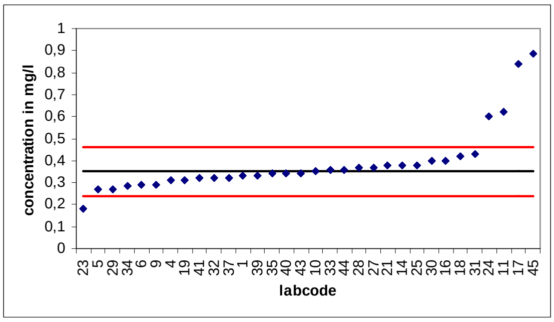
# Lead 1




- values: 32
- removed: 0
- Mean: 0.350 mg/l
- Weighing: 0.352 mg/l
- Standard deviation: 0.056 mg/l; 15.8 %
- limit for St.-dev.: 40%
- Upper limit: 0.463 mg/l
- Lower limit: 0.241 mg/l
- too high: 4 values
- too low: 1 values
- outside tolerance limits: 15.6 %



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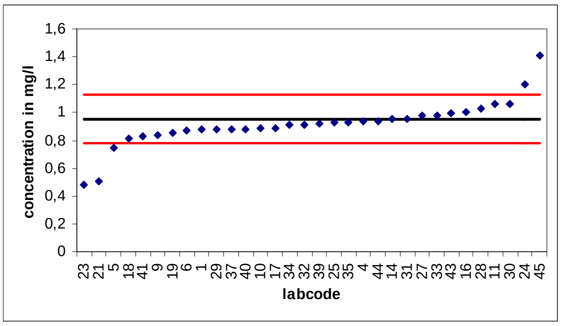
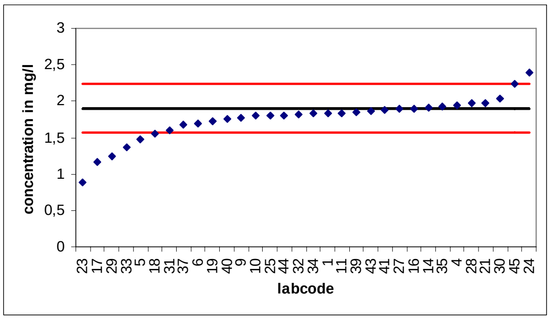
# Lead 2




- values: 32
- removed: 0
- Mean: 0.919 mg/l
- Weighing: 0.951 mg/l
- Standard deviation: 0.087 mg/l; 9.1 %
- limit for St.-dev.: 25%
- Upper limit: 1.12 mg/l
- Lower limit: 0.78 mg/l
- too high: 2 values
- too low: 3 values
- outside tolerance limits: 15.6%

# Lead 3

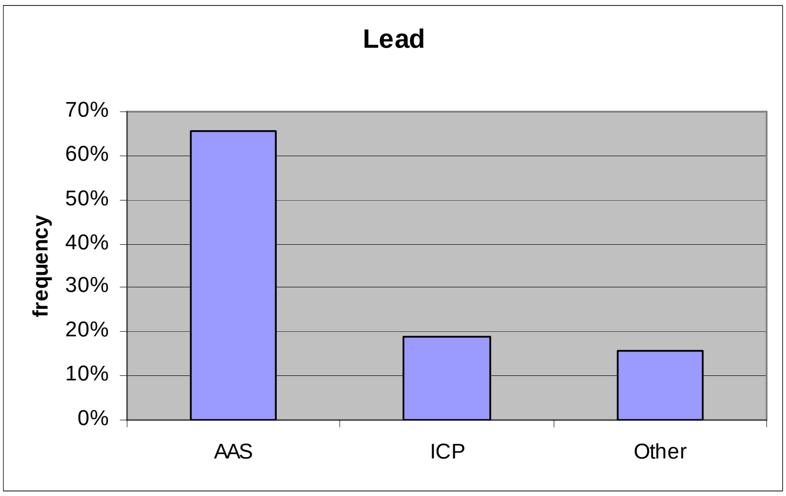



- values: 32
- removed: 0
- Mean: 1.81 mg/l
- Weighing: 1.90 mg/l
- Standard deviation: 0.165 mg/l; 8.7 %
- limit for St.-dev.: 25%
- Upper limit: 2.23 mg/l
- Lower limit: 1.57 mg/l
- too high: 2 values
- too low: 6 values
- outside tolerance limits: 25.0 %

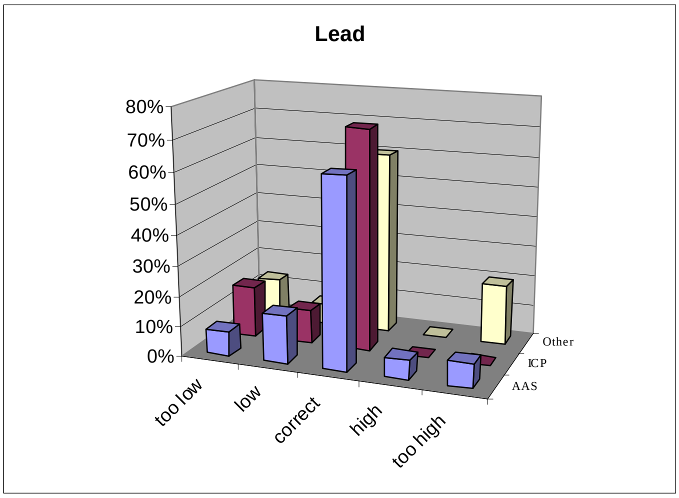




# Used methods



# Comparison of methods



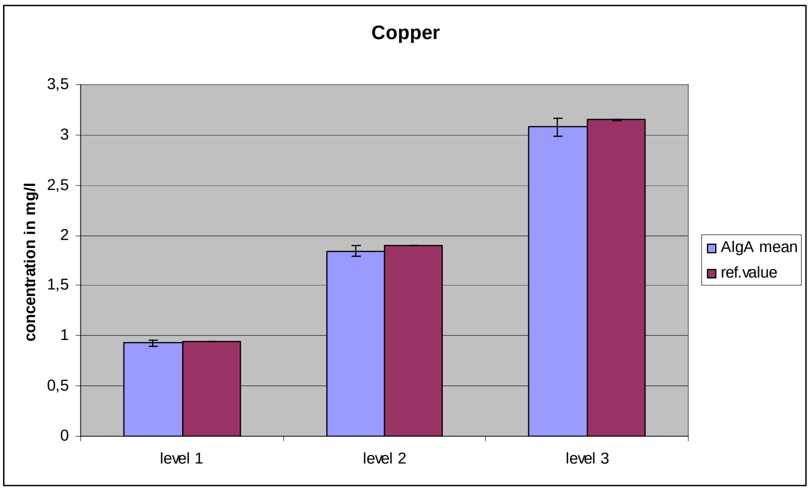





# Summary Lead

- mean values a bit below reference values
- low standard deviation

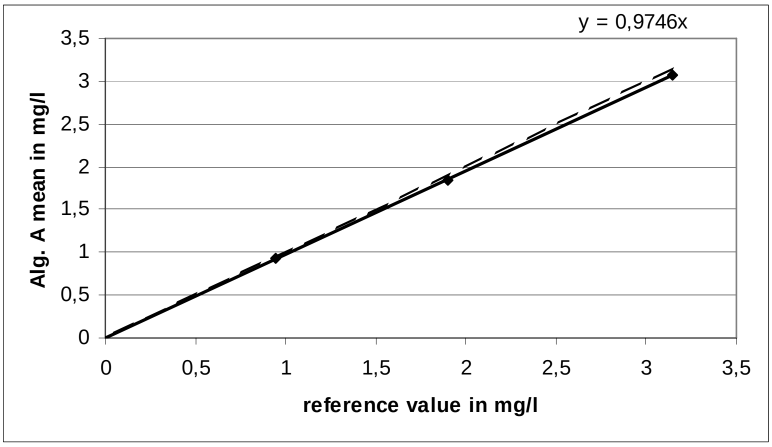
# Copper
## Alg.A mean and ref.-value from weighings





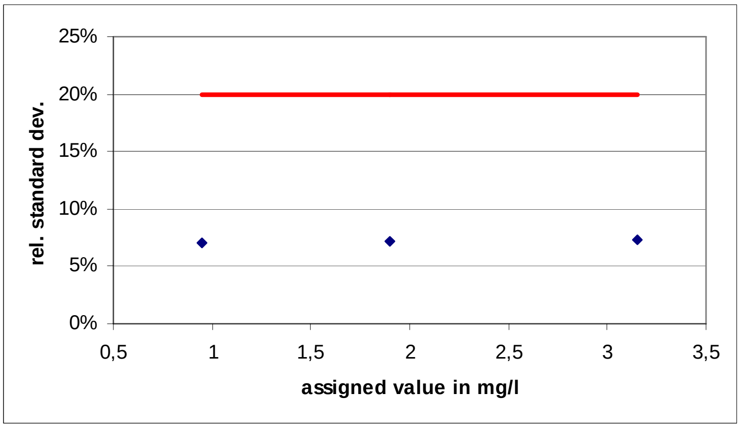



# Copper
## mean vs. ref.-value




Average recovery: 97.5%; in 2006: 98.5%

# Copper
# calculated standard deviation and limit

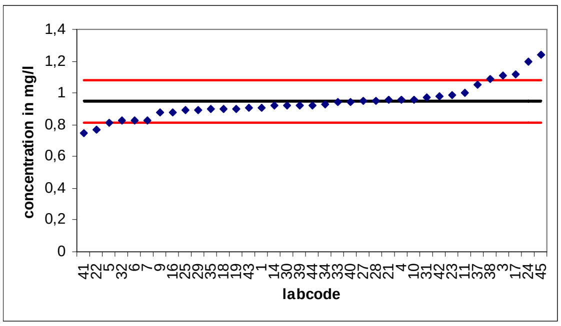



similar to 2006





# Copper 1




- values: 37
- removed: 0
- Mean: 0.93 mg/l
- Weighing: 0.95 mg/l
- Standard deviation: 0.066 mg/l; 7.0 %
- limit for St.-dev.: 20%
- Upper limit: 1.08 mg/l
- Lower limit: 0.82 mg/l
- too high: 5 values
- too low: 3 values
- outside tolerance limits: 21.6 %

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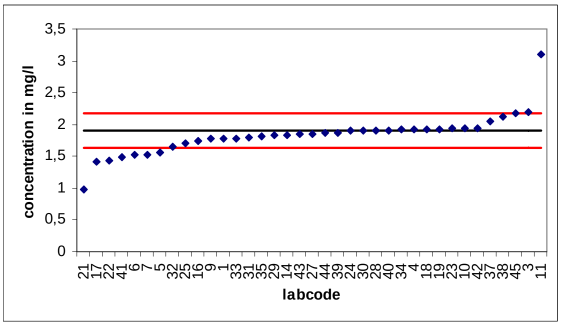
# Copper 2




- values: 37
- removed: 0
- Mean: 1.84 mg/l
- Weighing: 1.90 mg/l
- Standard deviation: 0.136 mg/l; 7.2 %
- limit for St.-dev.: 20%
- Upper limit: 2.17 mg/l
- Lower limit: 1.63 mg/l
- too high: 2 values
- too low: 7 values
- outside tolerance limits: 24.3 %



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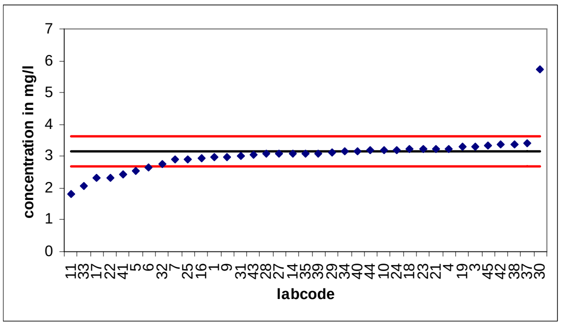
# Copper 3




- values: 37
- removed: 0
- Mean: 3.08 mg/l
- Weighing: 3.15 mg/l
- Standard deviation: 0.231 mg/l; 7.3 %
- limit for St.-dev.: 20%
- Upper limit: 3.61 mg/l
- Lower limit: 2.69 mg/l
- too high: 1 value
- too low: 7 values
- outside tolerance limits: 21.6 %

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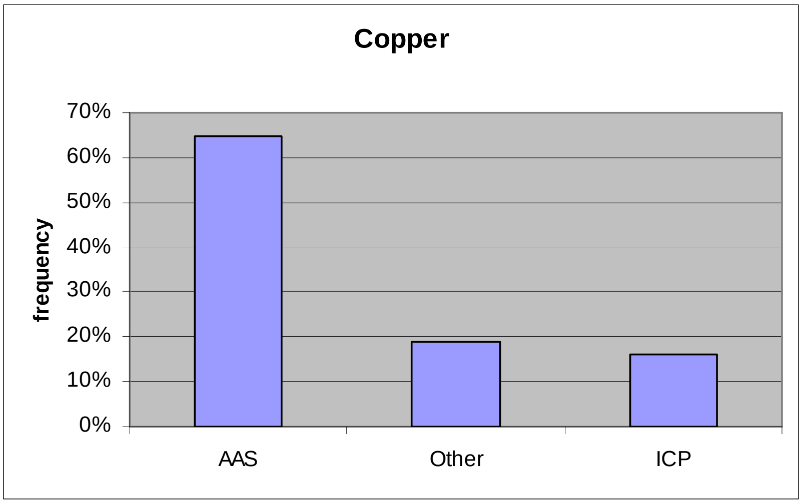
# Used methods



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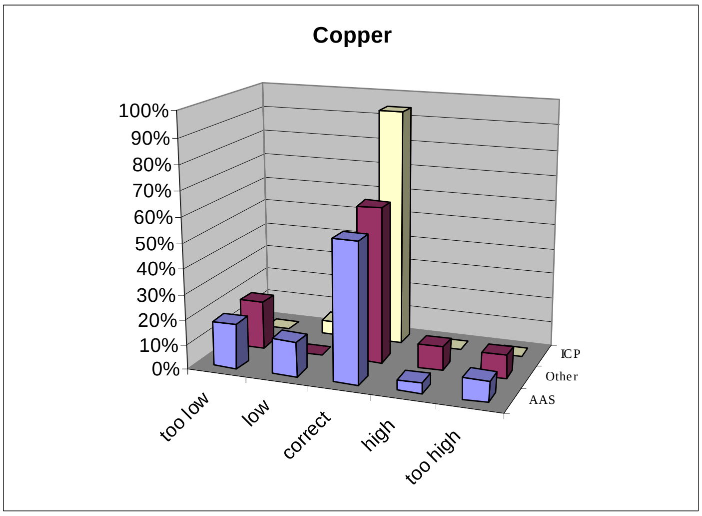
# Comparison of methods



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## Summary Copper

- mean values in good agreement with reference values
- low standard deviation



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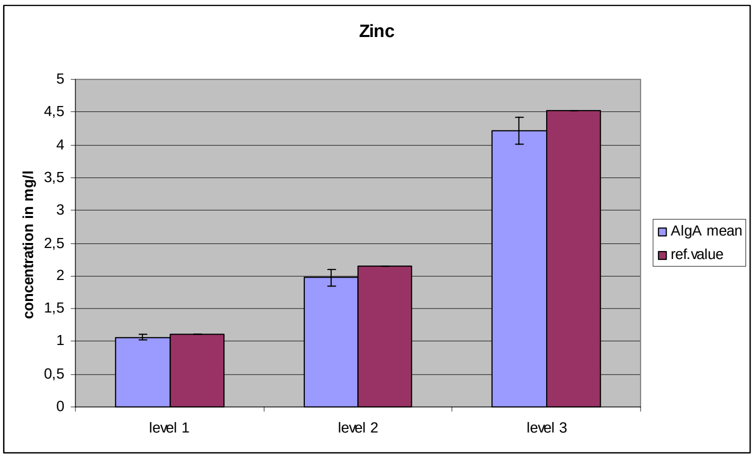
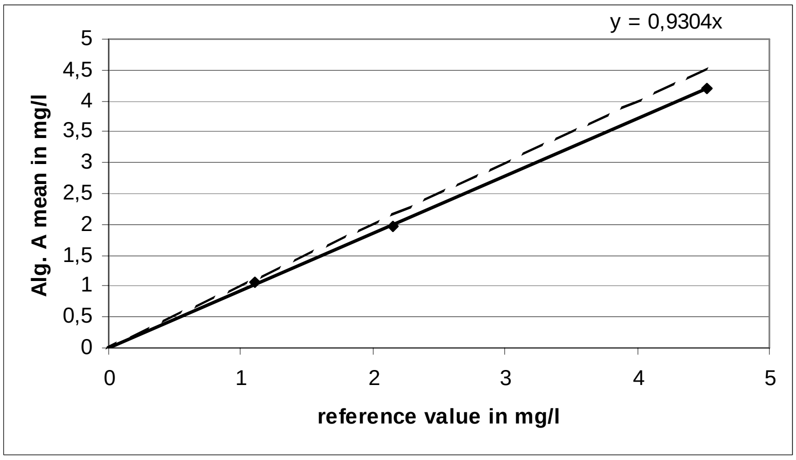
## Zinc
## Alg.A mean and ref.-value from weighings




consensus means slightly lower

# Zinc
## mean vs. ref.-value




Average recovery: 93.0%; in 2006: 96.8%



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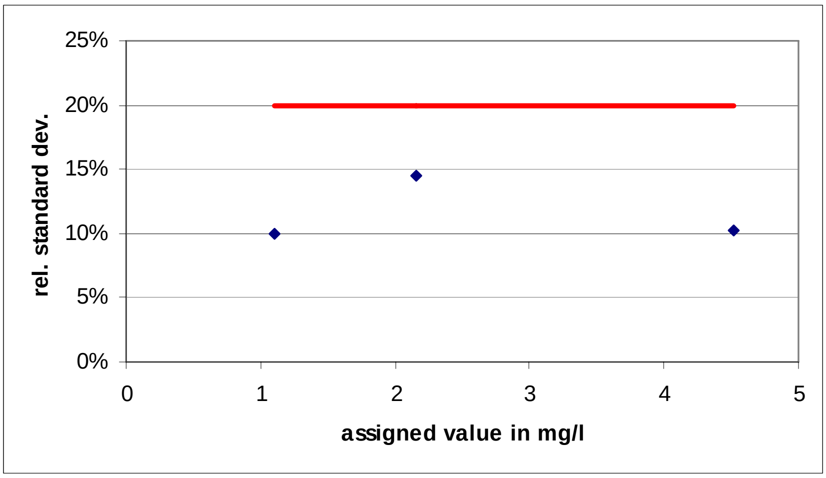
# Zinc
## calculated standard deviation and limit



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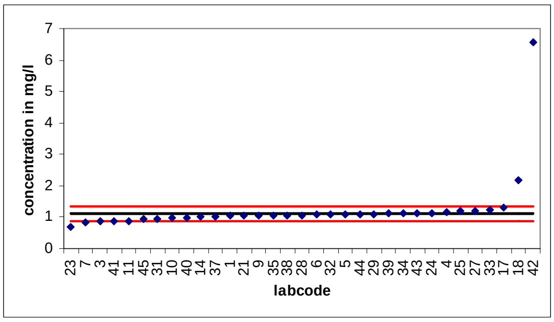
# Zinc 1




- values: 34
- removed: 1
- Mean: 1.07 mg/l
- Weighing: 1.11 mg/l
- Standard deviation: 0.110 mg/l; 9.9 %
- limit for St.-dev.: 20%
- Upper limit: 1.33 mg/l
- Lower limit: 0.89 mg/l
- too high: 2 values
- too low: 6 values
- outside tolerance limits: 23.5 %



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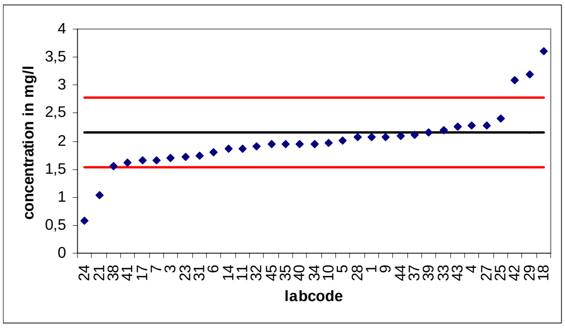
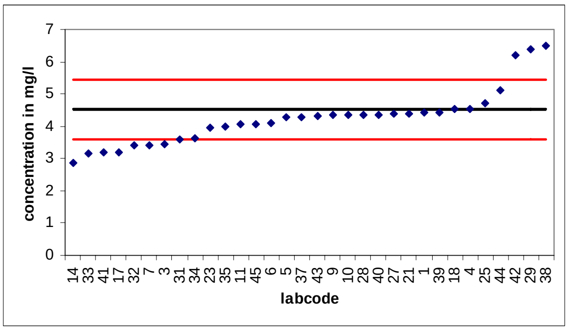
# Zinc 2




- values: 34
- removed: 1
- Mean: 1.97 mg/l
- Weighing: 2.15 mg/l
- Standard deviation: 0.311 mg/l; 14.5 %
- limit for St.-dev.: 20%
- Upper limit: 2.78 mg/l
- Lower limit: 1.53 mg/l
- too high: 3 values
- too low: 3 values
- outside tolerance limits: 17.6 %

# Zinc 3

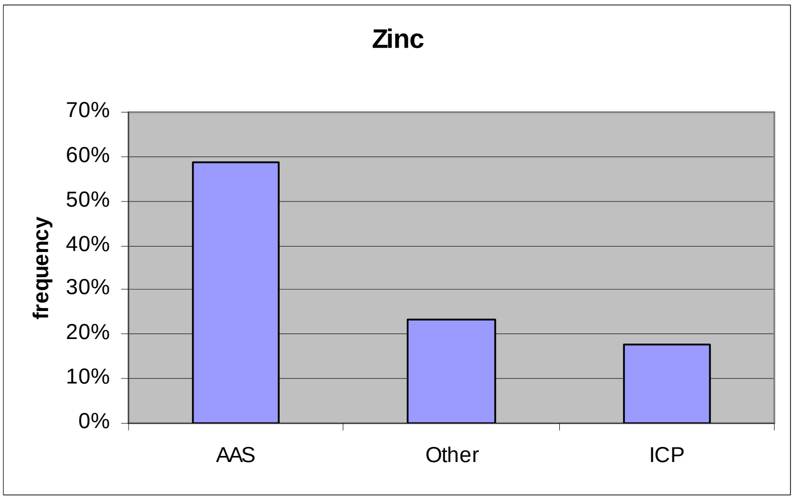



- values: 34
- removed: 2
- Mean: 4.21 mg/l
- Weighing: 4.52 mg/l
- Standard deviation: 0.463 mg/l; 10.3 %
- limit for St.-dev.: 20%
- Upper limit: 5.44 mg/l
- Lower limit: 3.60 mg/l
- too high: 3 values
- too low: 9 values
- outside tolerance limits: 29.4 %

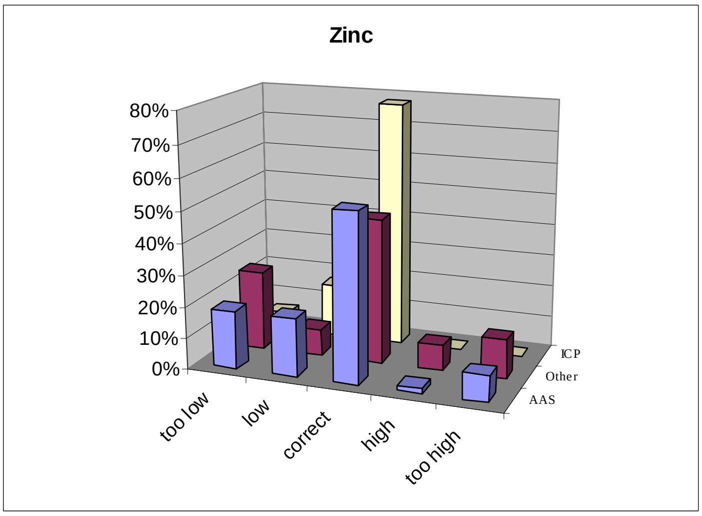




# Used methods



## Comparison of methods



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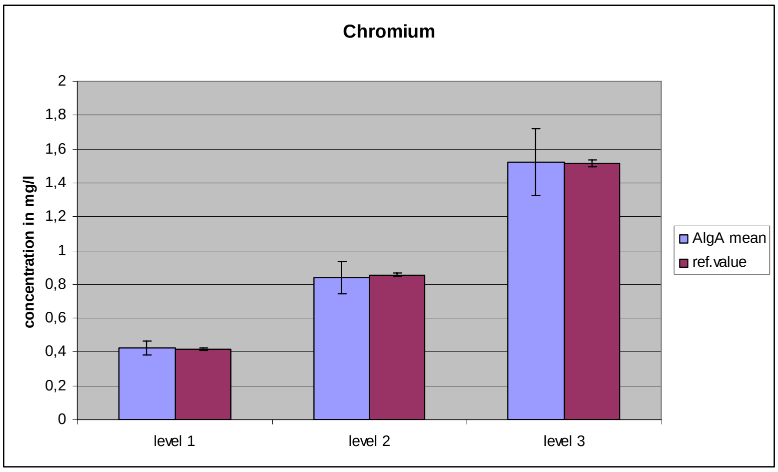
## Summary Zinc

- mean values slightly lower than reference values
- standard deviation below limit

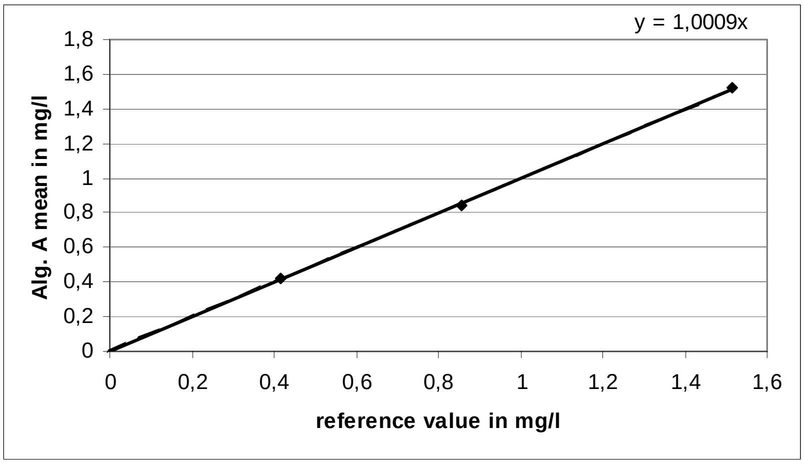
# Chromium
## Alg.A mean and ref.-value from weighings








# Chromium
## mean vs. ref.-value




Average recovery: 100.1%; in 2006: 97.4%

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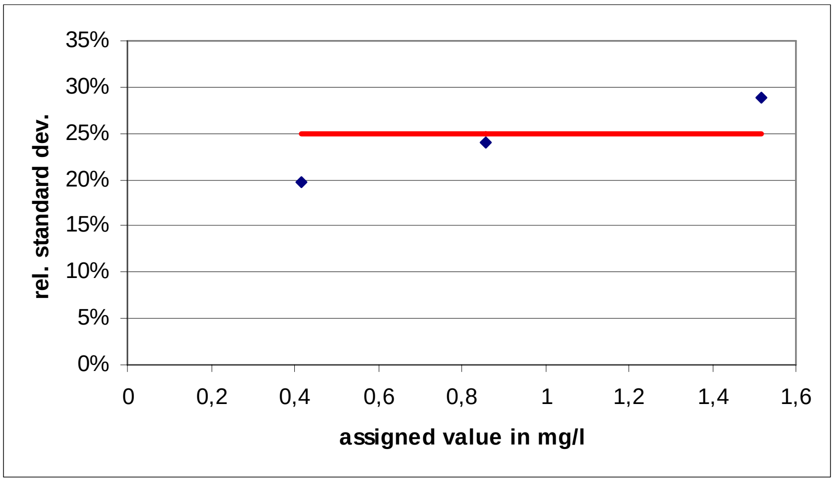
# Chromium
# calculated standard deviation and limit



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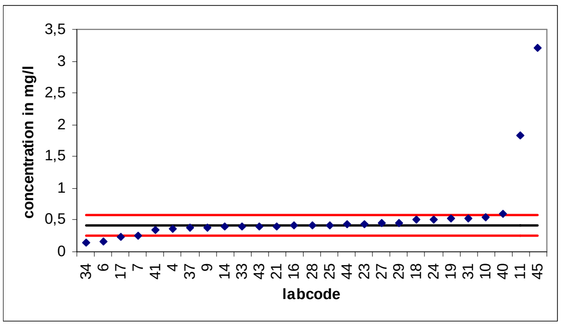
# Chromium 1




- values: 31
- removed: 4
- Mean: 0.42 mg/l
- Weighing: 0.42 mg/l
- Standard deviation: 0.082 mg/l; 19.8 %
- limit for St.-dev.: 25%
- Upper limit: 0.580 mg/l
- Lower limit: 0.252 mg/l
- too high: 5 values
- too low: 5 values
- outside tolerance limits: 32.3 %

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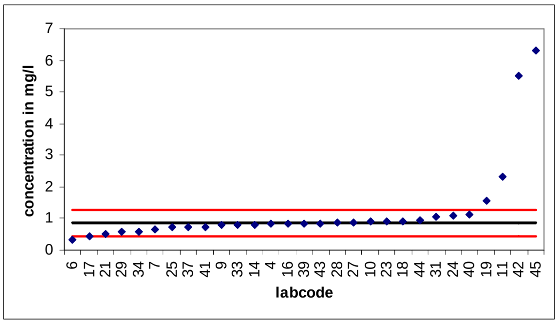
# Chromium 2




- values: 31
- removed: 2
- Mean: 0.84 mg/l
- Weighing: 0.86 mg/l
- Standard deviation: 0.205 mg/l; 24.0 %
- limit for St.-dev.: 25%
- Upper limit: 1.27 mg/l
- Lower limit: 0.44 mg/l
- too high: 4 values
- too low: 3 values
- outside tolerance limits: 22.6 %

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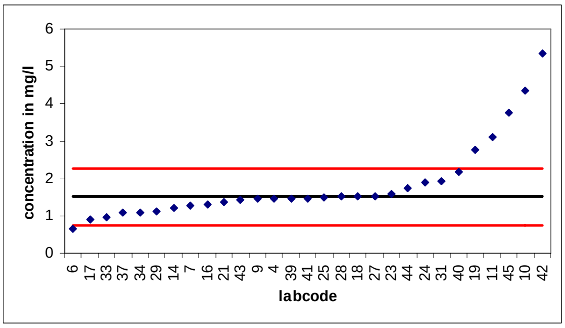
# Chromium 3




- values: 31
- removed: 2
- Mean: 1.52 mg/l
- Weighing: 1.52 mg/l
- Standard deviation: 0.437 mg/l; 28.8 %
- limit for St.-dev.: 25%
- Upper limit: 2.27 mg/l
- Lower limit: 0.76 mg/l
- too high: 5 values
- too low: 3 values
- outside tolerance limits: 25.8 %

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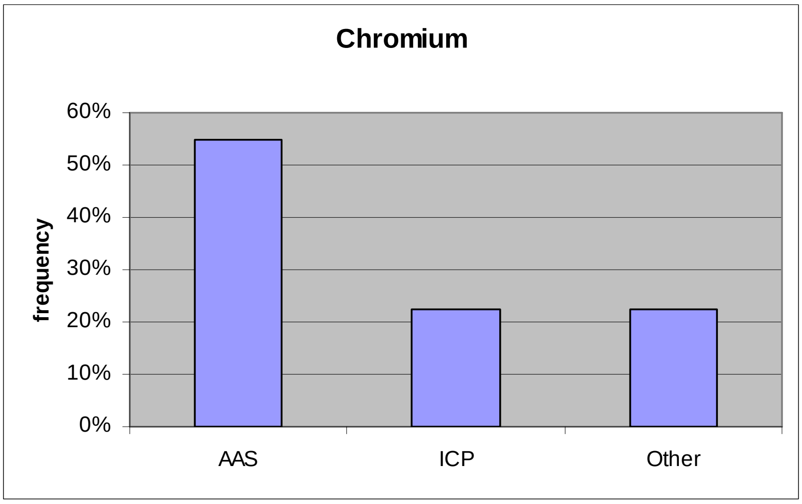
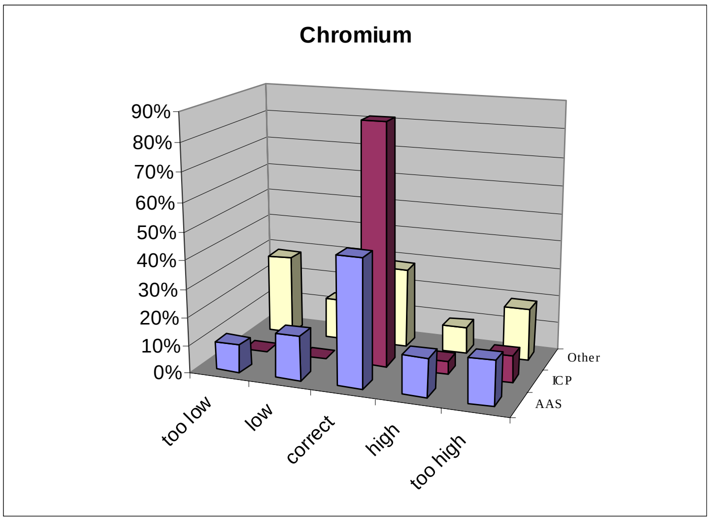
# Used methods








# Comparison of methods



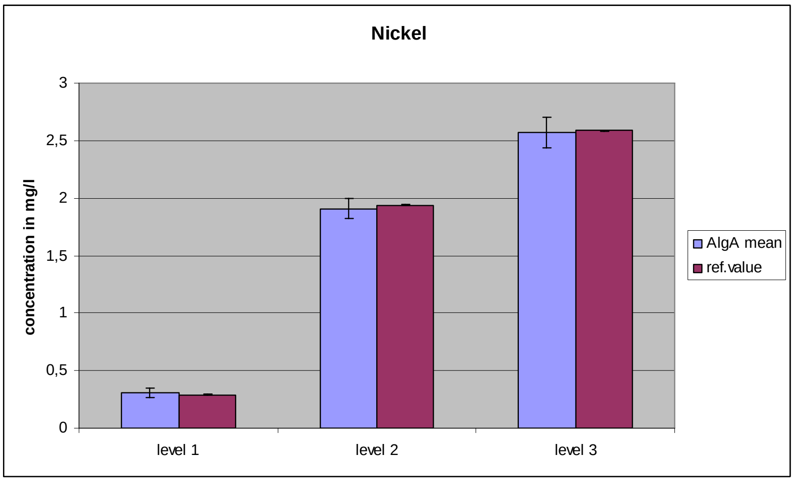
# Summary Chromium

- mean values in quite good agreement with reference values
- standard deviation around limit





# Nickel
# Alg.A mean and ref.-value from weighings



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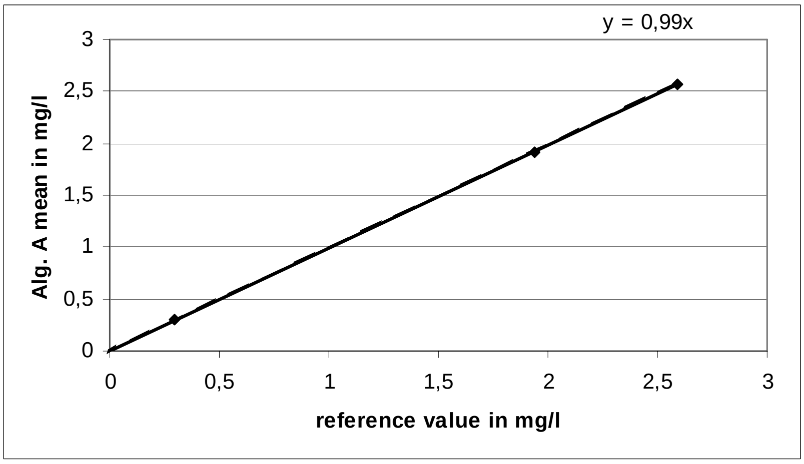
# Nickel
## mean vs. ref.-value




Average recovery: 99.0%; in 2006: 94.6%



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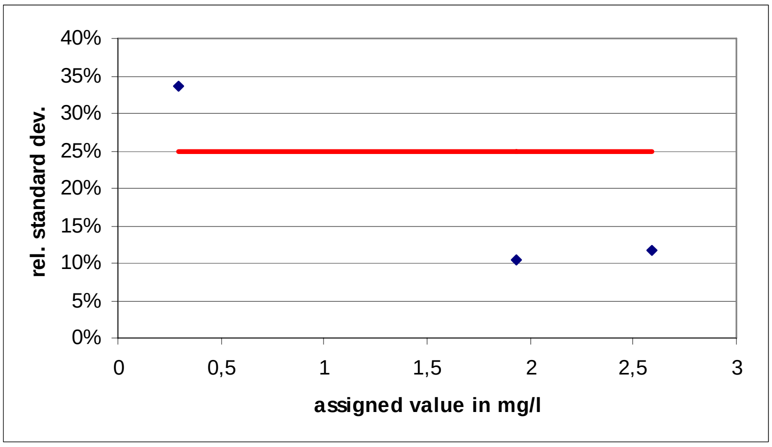
# Nickel
## calculated standard deviation and limit




high std for low level



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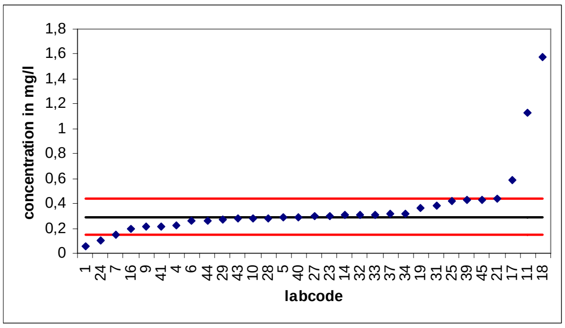
# Nickel 1




- values: 31
- removed: 0
- Mean: 0.31 mg/l
- Weighing: 0.29 mg/l
- Standard deviation: 0.098 mg/l; 33.6 %
- limit for St.-dev.: 25%
- Upper limit: 0.438 mg/l
- Lower limit: 0.146 mg/l
- too high: 4 values
- too low: 2 values
- outside tolerance limits: 19.4 %



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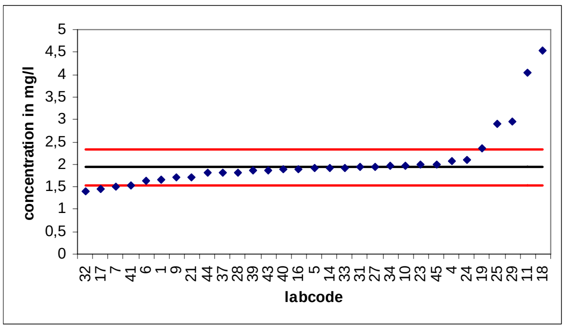
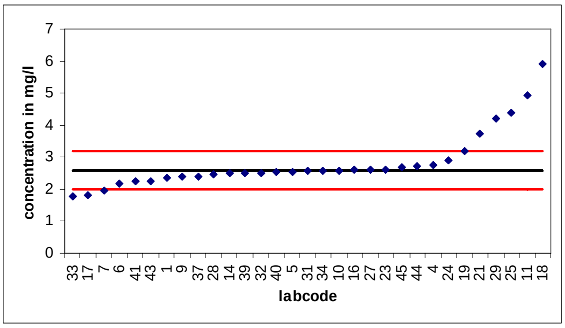
# Nickel 2




- values: 31
- removed: 0
- Mean: 1.91 mg/l
- Weighing: 1.94 mg/l
- Standard deviation: 0.204 mg/l; 10.5 %
- limit for St.-dev.: 25%
- Upper limit: 2.34 mg/l
- Lower limit: 1.53 mg/l
- too high: 5 values
- too low: 3 values
- outside tolerance limits: 25.8 %

# Nickel 3

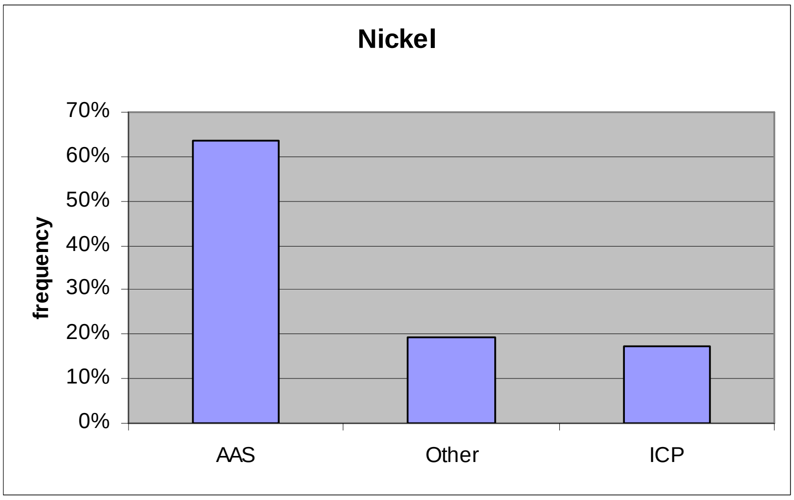



- values: 31
- removed: 0
- Mean: 2.57 mg/l
- Weighing: 2.59 mg/l
- Standard deviation: 0.302 mg/l; 11.7 %
- limit for St.-dev.: 25%
- Upper limit: 3.19 mg/l
- Lower limit: 1.98 mg/l
- too high: 6 values
- too low: 3 values
- outside tolerance limits: 29.0 %

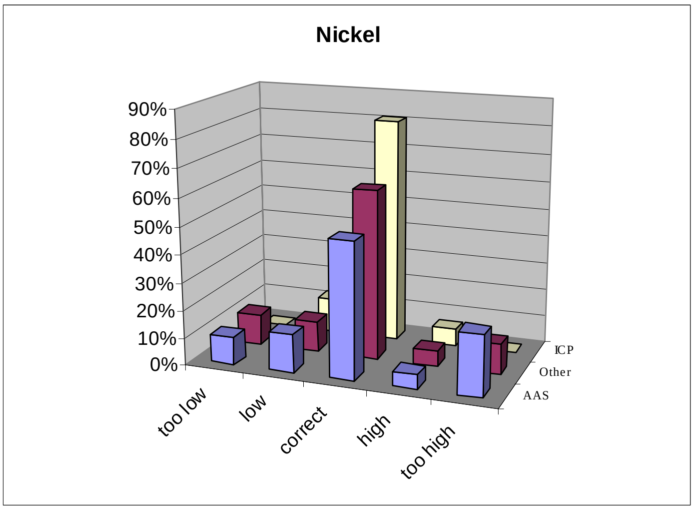




# Used methods



## Comparison of methods



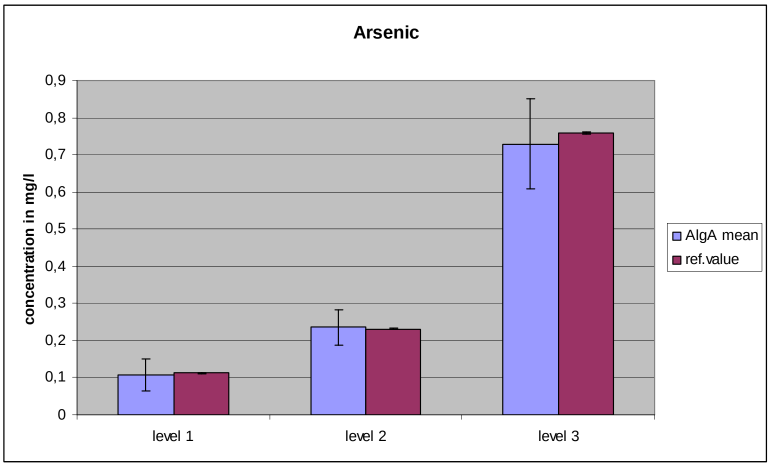





## Summary Nickel

- mean values in quite good agreement with reference values
- low standard deviation for the higher concentrations

# Arsenic
## Alg.A mean and ref.-value from weighings




quite good agreement



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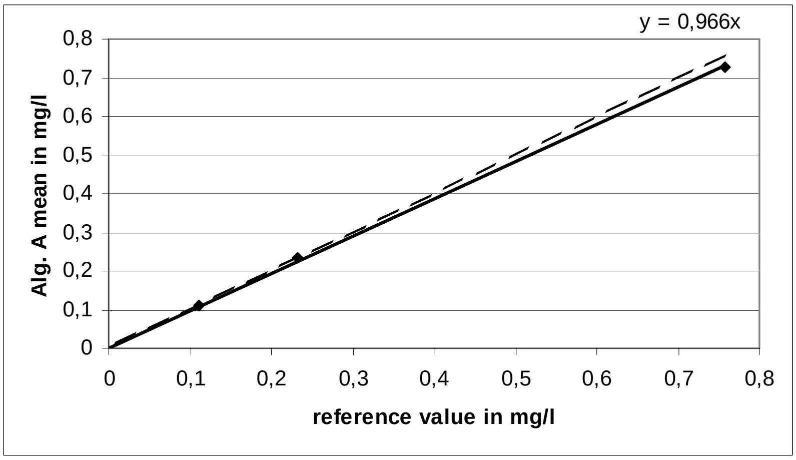
# Arsenic
## mean vs. ref.-value




Average recovery: 96.6%; in 2006: 111.2%

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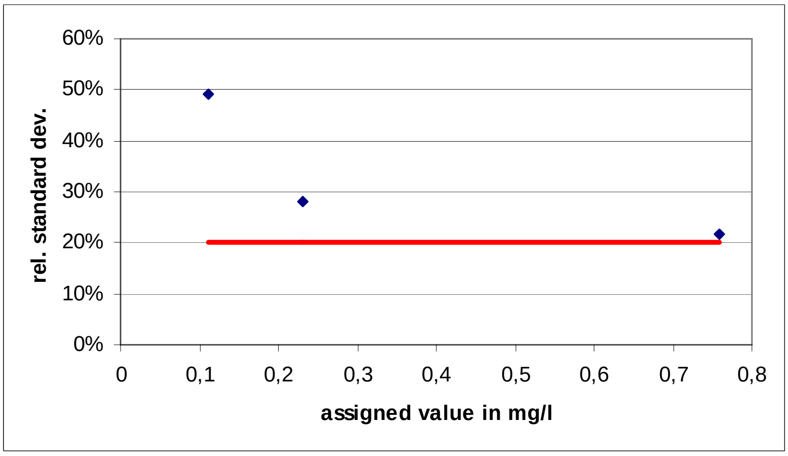
# Arsenic
# calculated standard deviation and limit




lower than 2006



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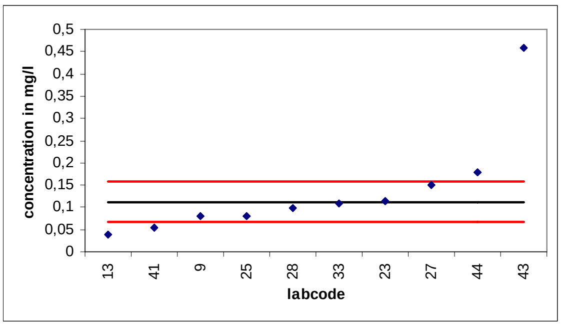
# Arsenic 1




- values: 14
- removed: 4
- Mean: 0.109 mg/l
- Weighing: 0112 mg/l
- Standard deviation: 0.055 mg/l; 49.3 %
- limit for St.-dev.: 20%
- Upper limit: 0.157 mg/l
- Lower limit: 0.067 mg/l
- too high: 4 values
- too low: 3 values
- outside tolerance limits: 50.0 %



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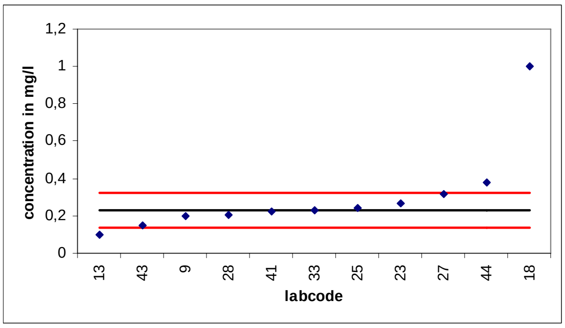
# Arsenic 2




- values: 14
- removed: 3
- Mean: 0.236 mg/l
- Weighing: 0.232 mg/l
- Standard deviation: 0.065 mg/l; 28.1 %
- limit for St.-dev.: 20%
- Upper limit: 0.324 mg/l
- Lower limit: 0.139 mg/l
- too high: 3 values
- too low: 3 values
- outside tolerance limits: 42.9 %



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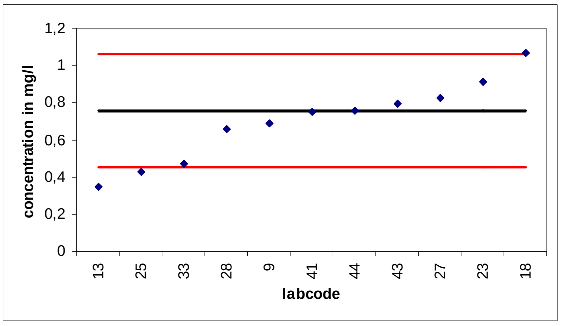
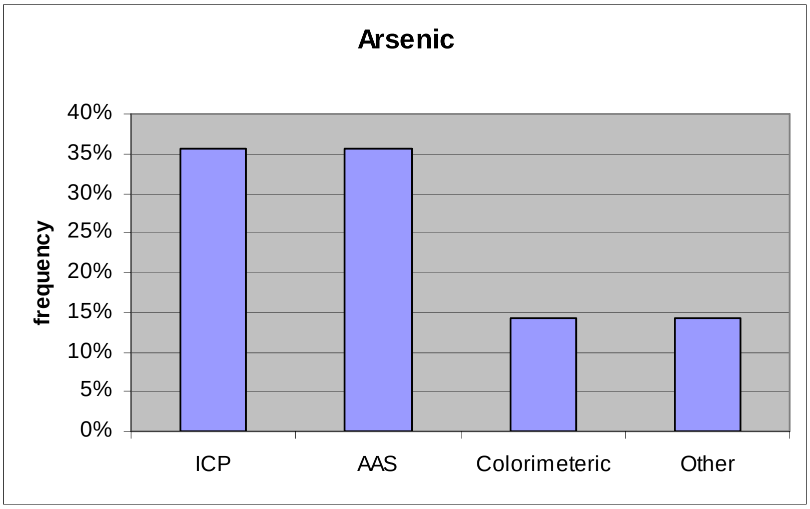
# Arsenic 3




- values: 14
- removed: 3
- Mean: 0.728 mg/l
- Weighing: 0.758 mg/l
- Standard deviation: 0.164 mg/l; 21.7 %
- limit for St.-dev.: 20%
- Upper limit: 1.06 mg/l
- Lower limit: 0.45 mg/l
- too high: 2 values
- too low: 4 values
- outside tolerance limits: 42.9 %

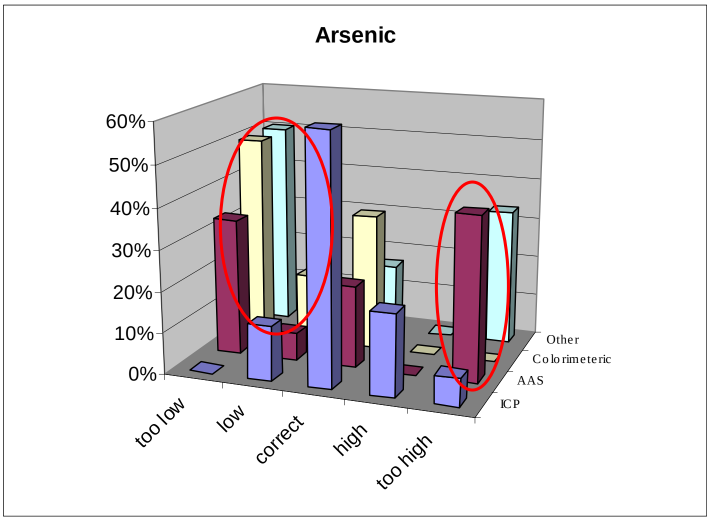
# Used methods








# Comparison of methods



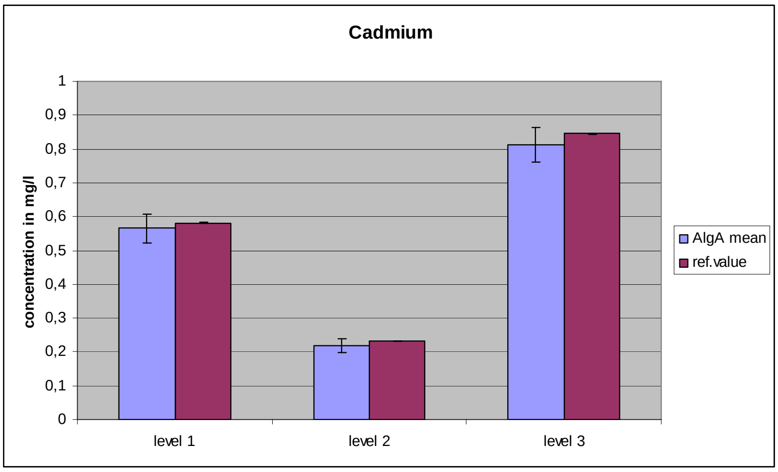
# Summary Arsenic

- low number of values
- mean values close to reference values
- standard deviation around limit



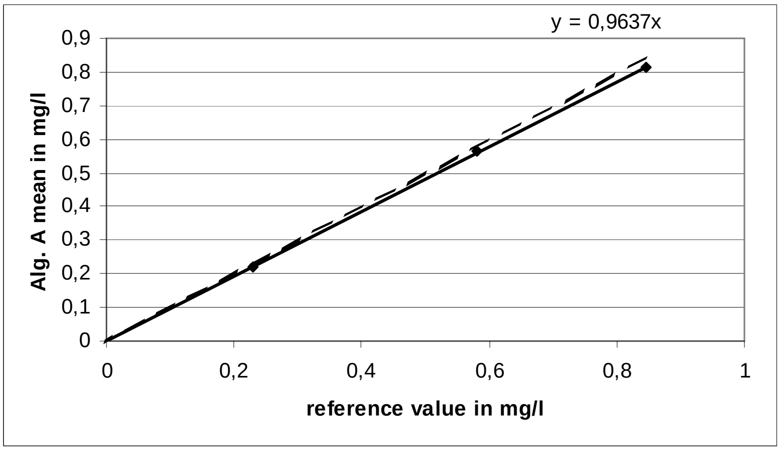


# Cadmium
# Alg.A mean and ref.-value from weighings




consensus means slightly lower, but not significantly different

# Cadmium
## mean vs. ref.-value




Average recovery: 96.4%; in 2006: 96.6%



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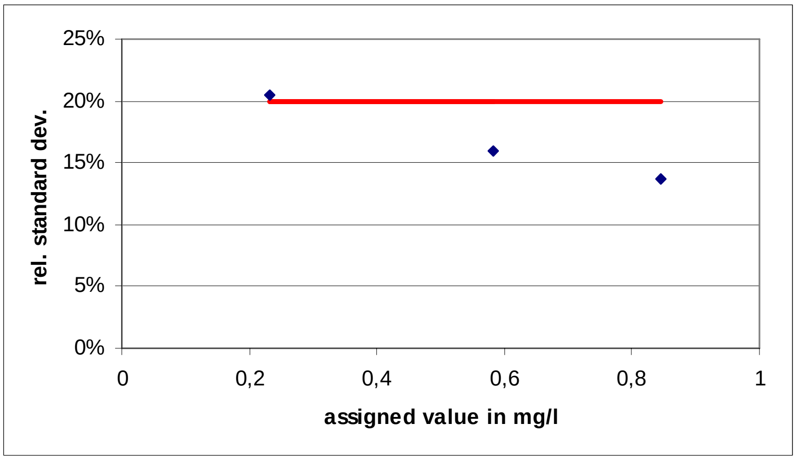
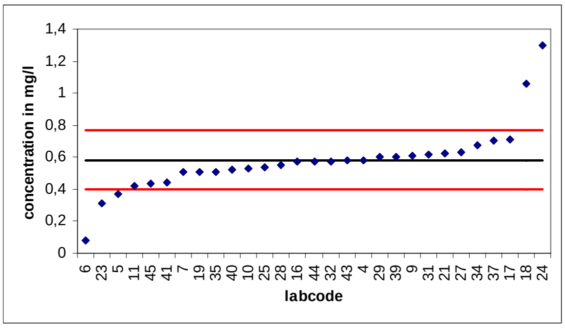
# Cadmium
## calculated standard deviation and limit



# Cadmium 1

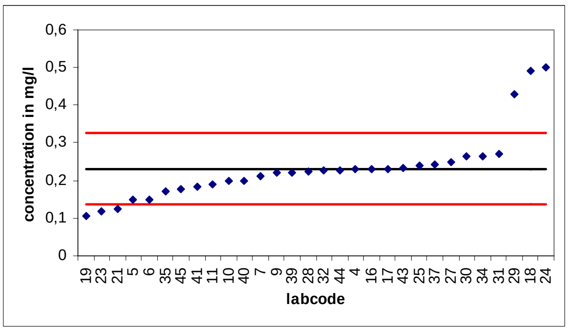



- values: 29
- removed: 0
- Mean: 0.566 mg/l
- Weighing: 0.582 mg/l
- Standard deviation: 0.0927 mg/l; 15.9 %
- limit for St.-dev.: 20%
- Upper limit: 0.767 mg/l
- Lower limit: 0.396 mg/l
- too high: 2 values
- too low: 3 values
- outside tolerance limits: 17.2 %



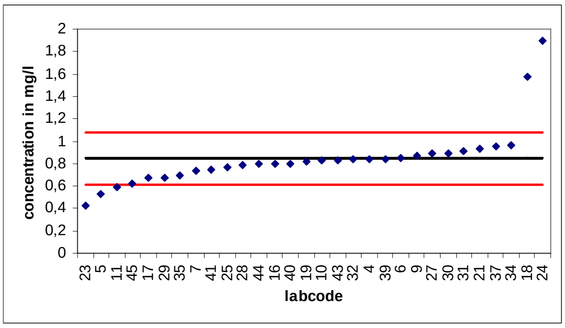


# Cadmium 2




- values: 30
- removed: 0
- Mean: 0.219 mg/l
- Weighing: 0.231 mg/l
- Standard deviation: 0,0473 mg/l; 20.5 %
- limit for St.-dev.: 20%
- Upper limit: 0.323 mg/l
- Lower limit: 0.139 mg/l
- too high: 3 values
- too low: 3 values
- outside tolerance limits: 20.0 %

# Cadmium 3




- values: 30
- removed: 0
- Mean: 0.812 mg/l
- Weighing: 0.845 mg/l
- Standard deviation: 0.115 mg/l; 13.7 %
- limit for St.-dev.: 20%
- Upper limit: 1.08 mg/l
- Lower limit: 0.61 mg/l
- too high: 2 values
- too low: 3 values
- outside tolerance limits:  16.7 %



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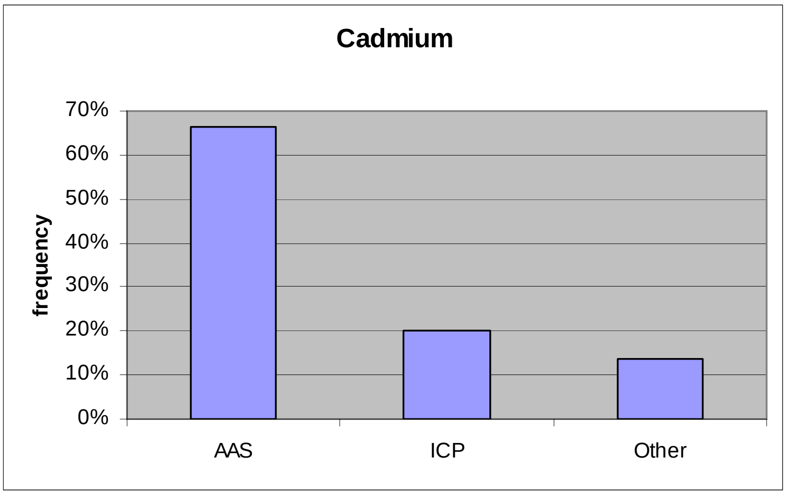
# Used methods



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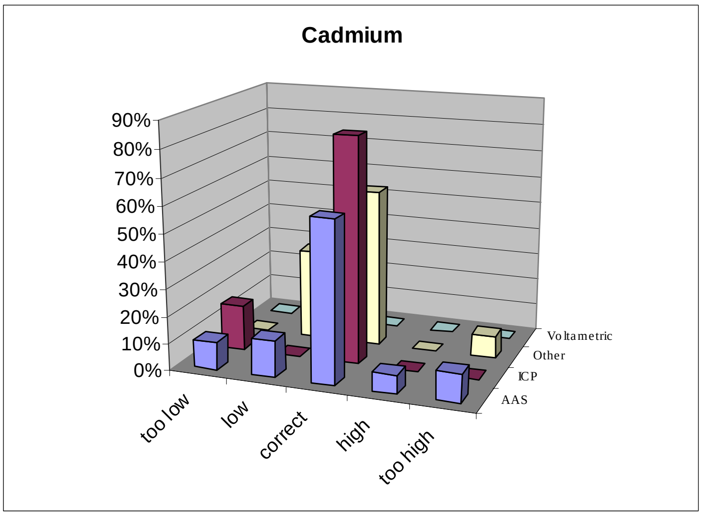
# Comparison of methods



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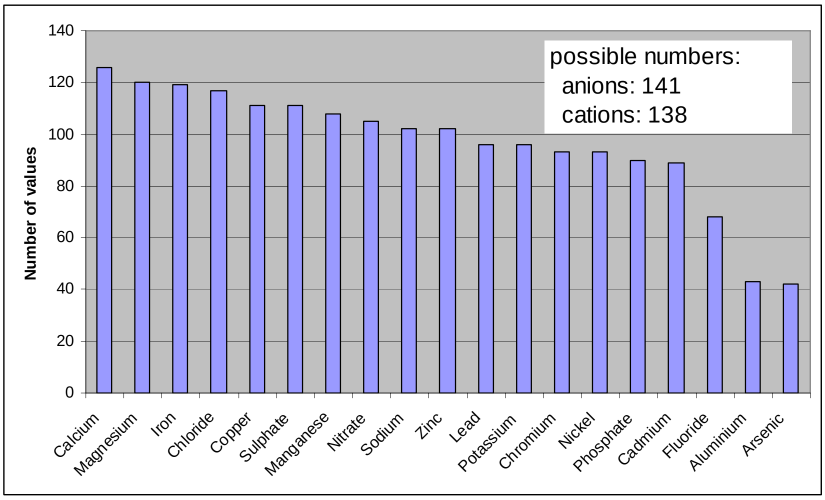
# Summary Cadmium

- mean values a bit below reference values

# Number of values per parameter



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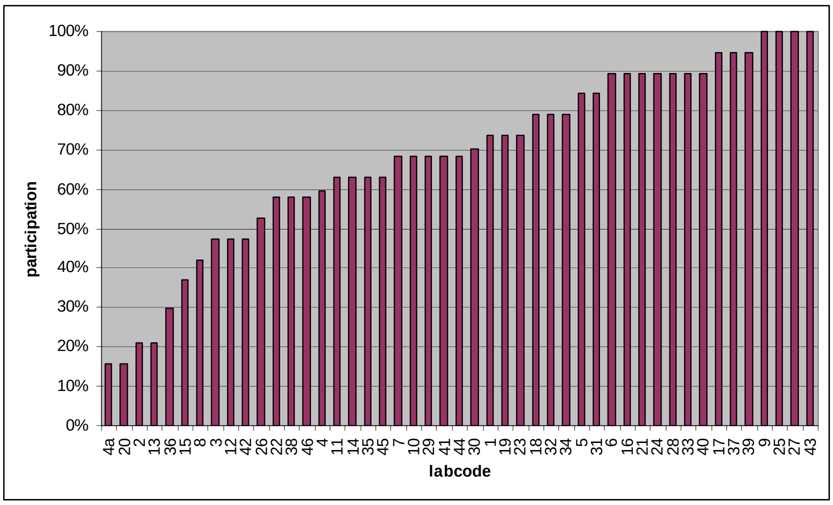
# Overview on participation



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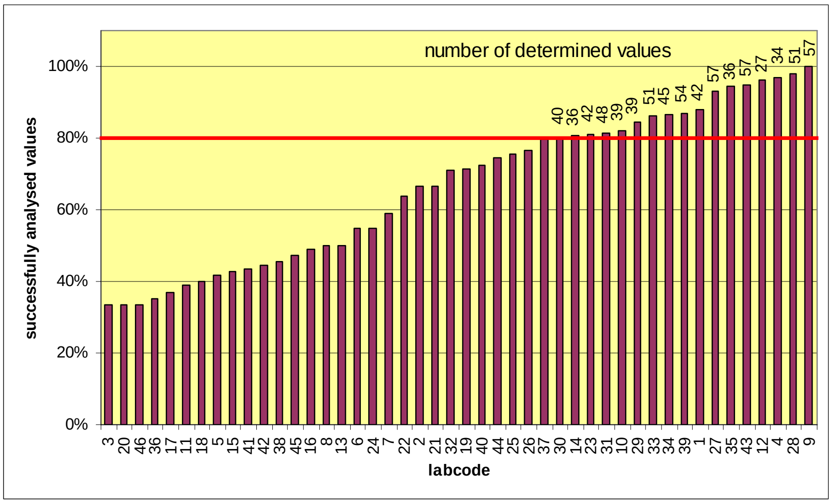
# Overview on participants success



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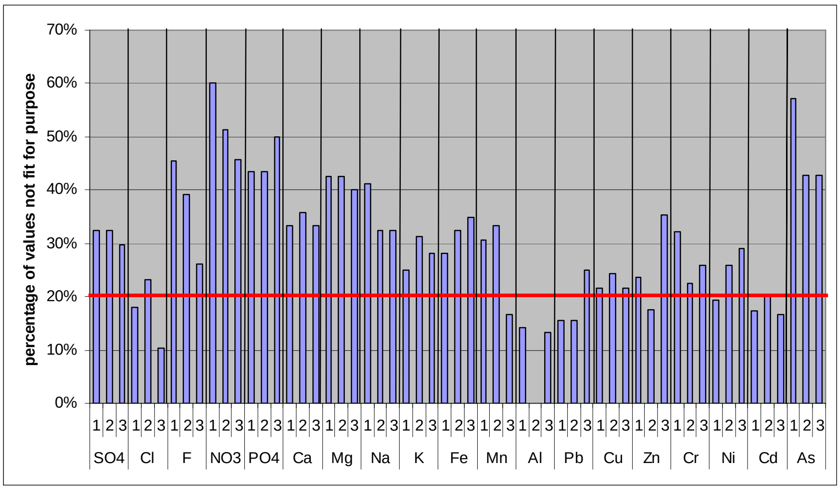
# Values not fit for purpose



# Conclusion

- The PT Provider did a very good job
- The evaluation and assessment procedure is fit for the purpose
- The SADCMET Water PT is a good possibility for the participants to compare with peers and with stated fitness-for-purpose criteria
- The results of many laboratories are still not satisfactory and need improvement
- Special emphasis should be put on corrective actions after unsatisfactory participation

# Development of Standard Deviations over the 4 PT rounds

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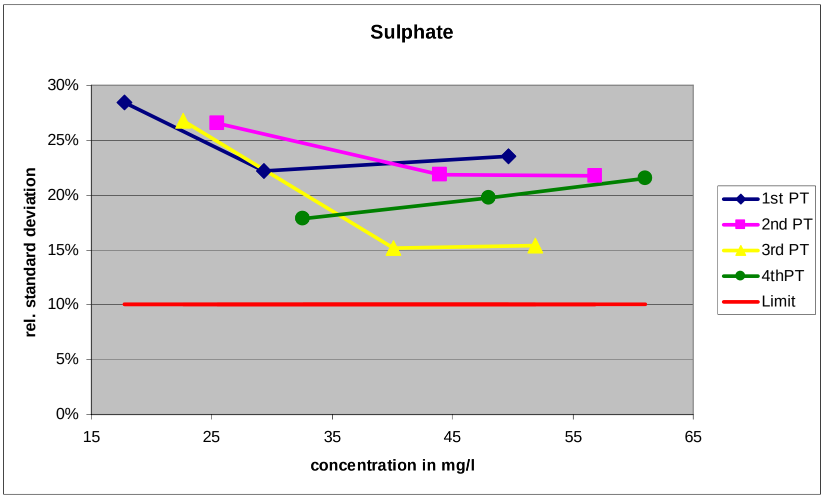

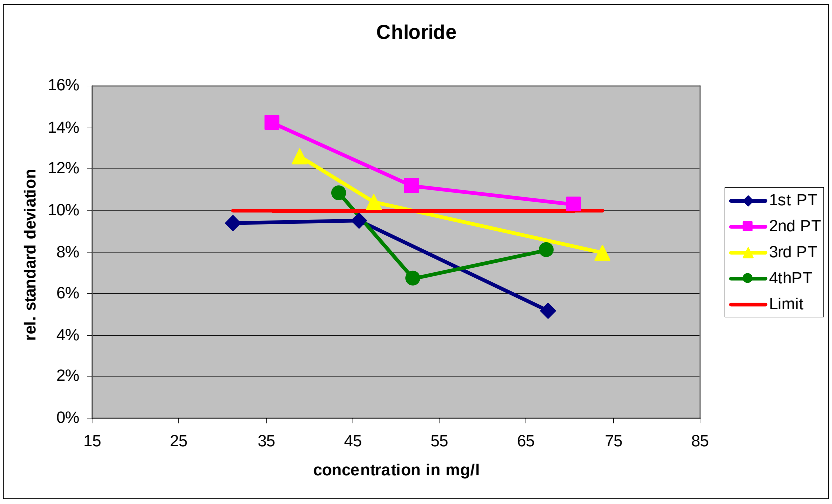




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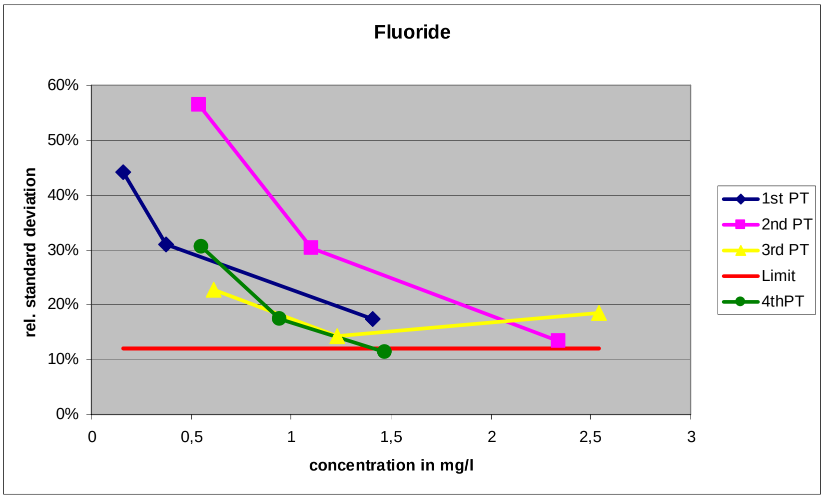


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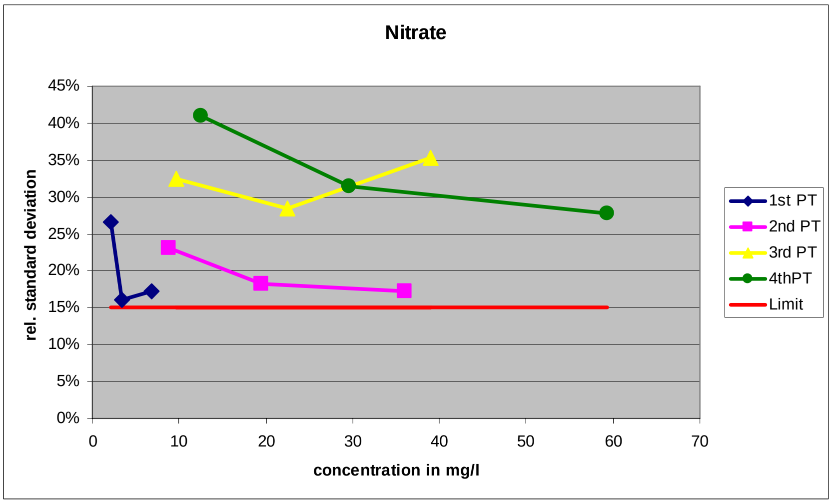


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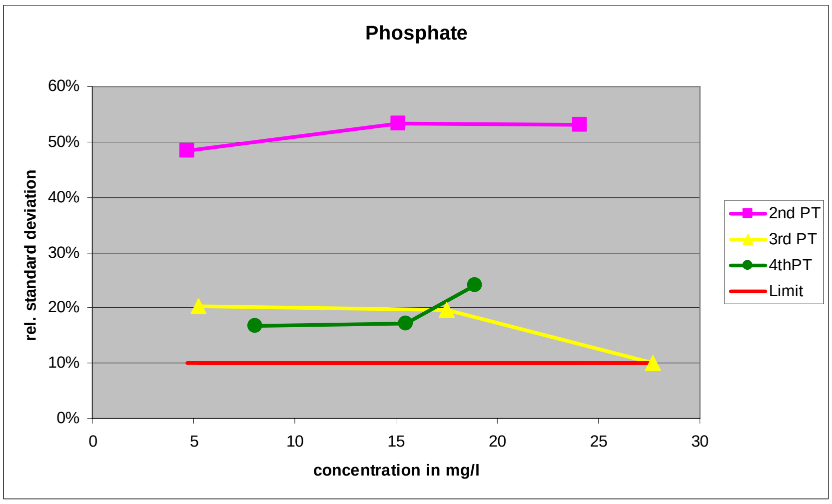


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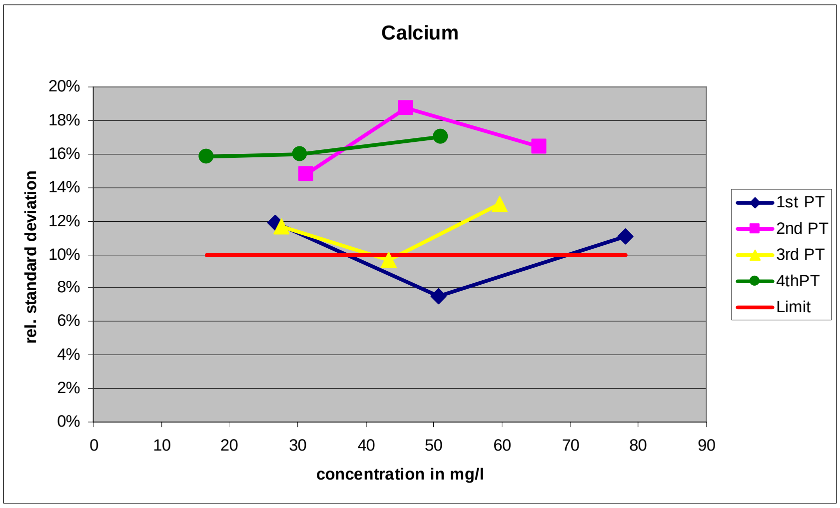


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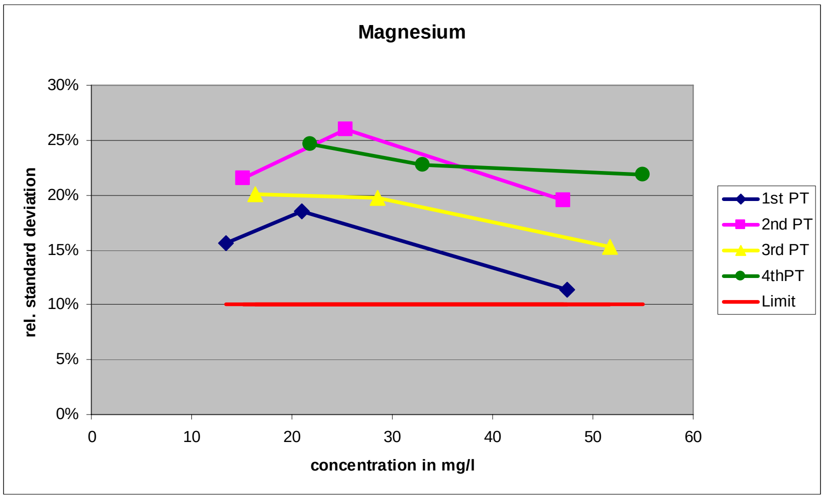


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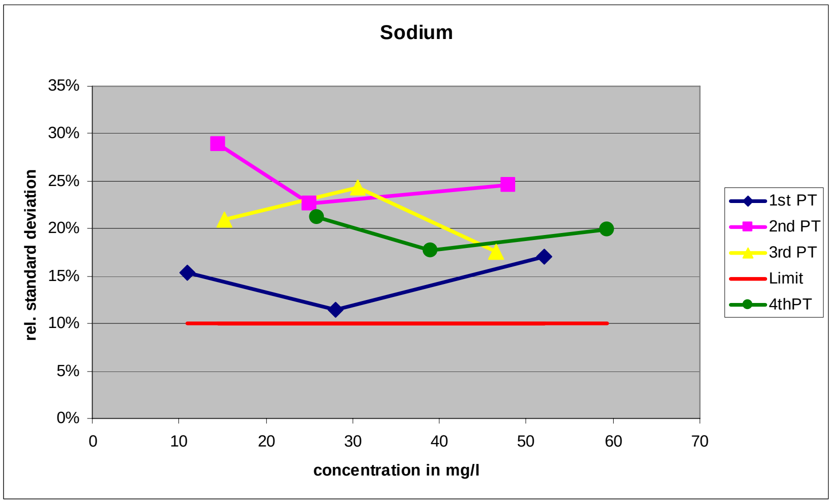
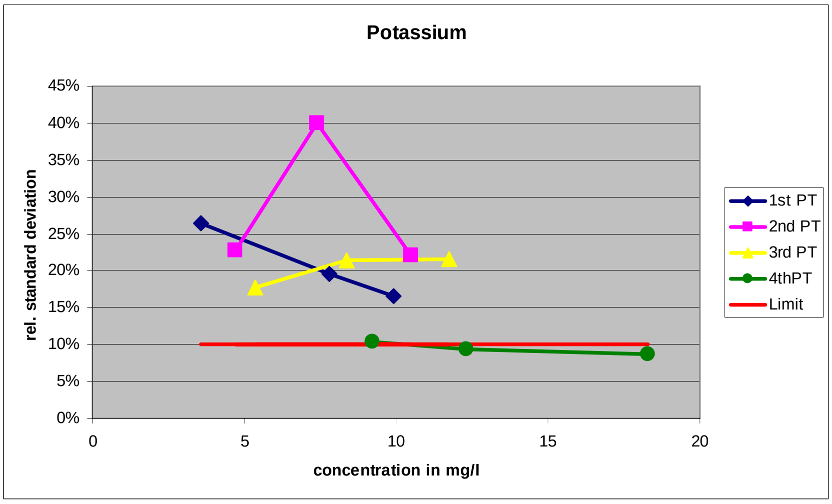
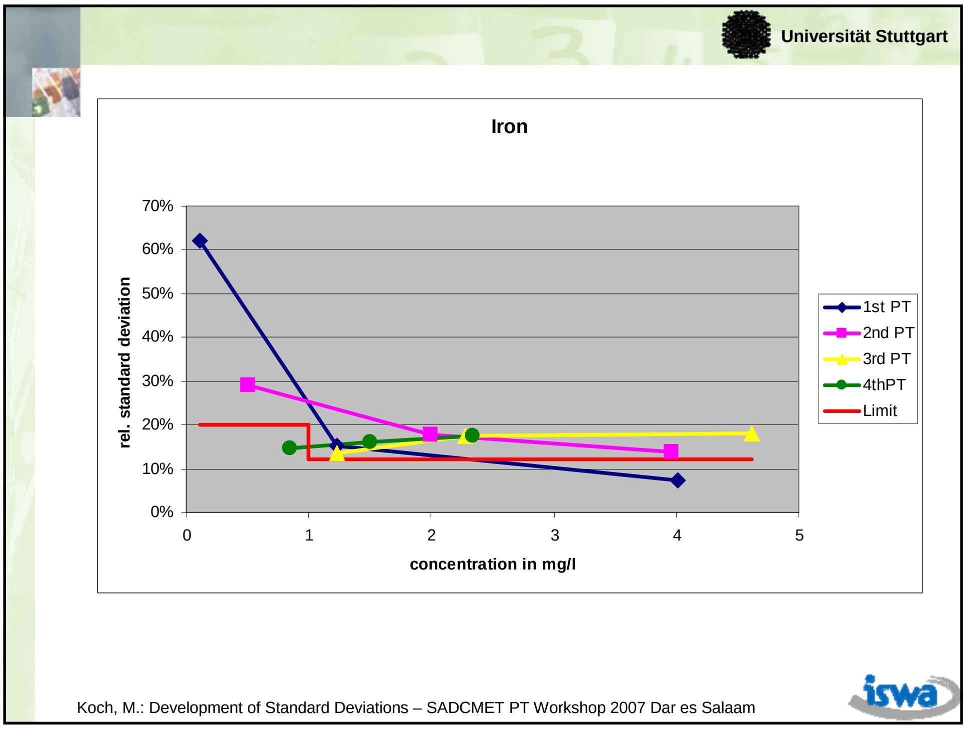

Sodium
rel. standard deviation
35%
30%
25%
20%
15%
10%
5%
0%
0
10
20
30
40
50
60
70
concentration in mg/l
1st PT
2nd PT
3rd PT
Limit
4thPT






Potassium
rel. standard deviation
45%
40%
35%
30%
25%
20%
15%
10%
5%
0%
0
5
10
15
20
concentration in mg/l
1st PT
2nd PT
3rd PT
4thPT
Limit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Iron
rel. standard deviation
70%
60%
50%
40%
30%
20%
10%
0%
0
1
2
3
4
5
concentration in mg/l
1st PT
2nd PT
3rd PT
4thPT
Limit
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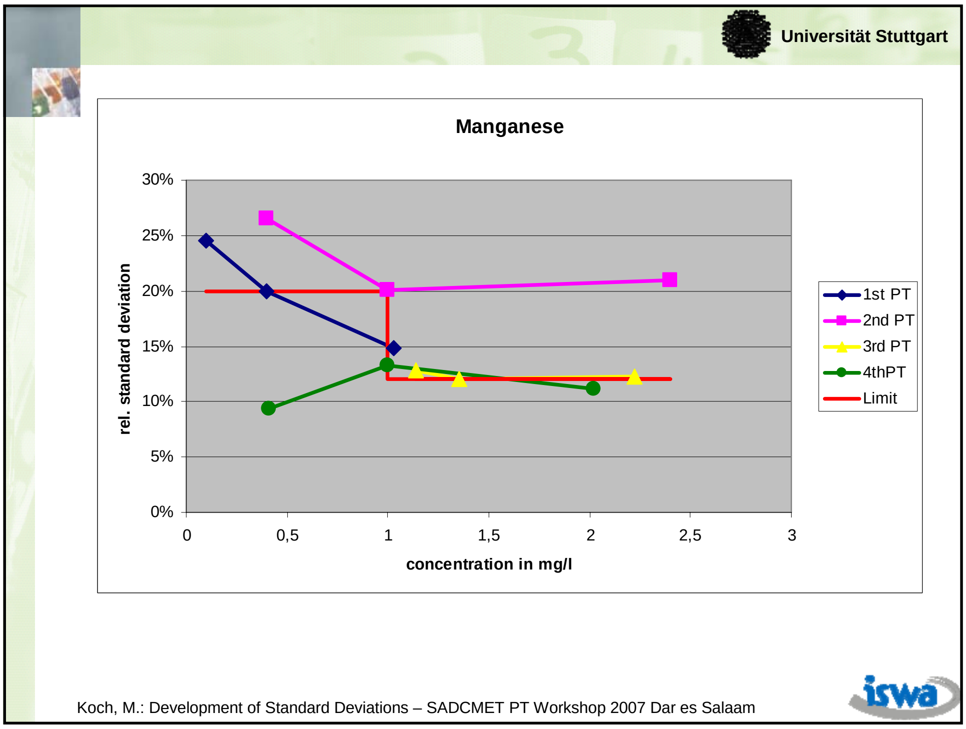
Universität Stuttgart
Manganese
rel. standard deviation
30%
25%
20%
15%
10%
5%
0%
0
0,5
1
1,5
2
2,5
3
concentration in mg/l
1st PT
2nd PT
3rd PT
4thPT
Limit
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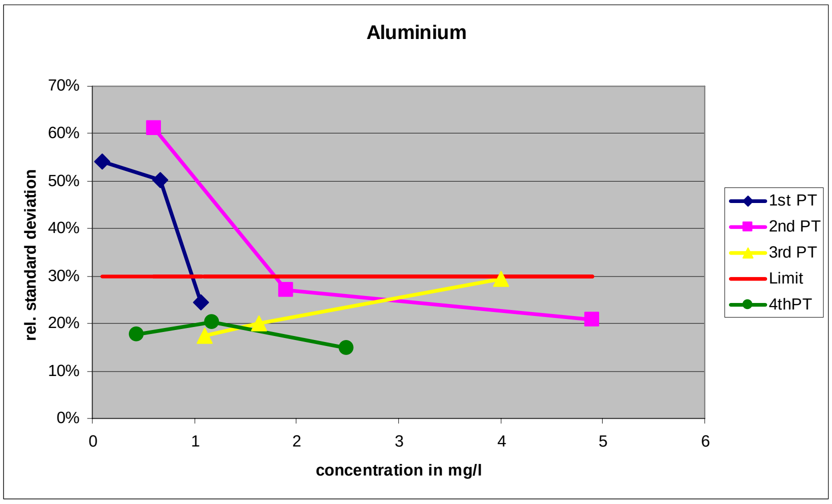




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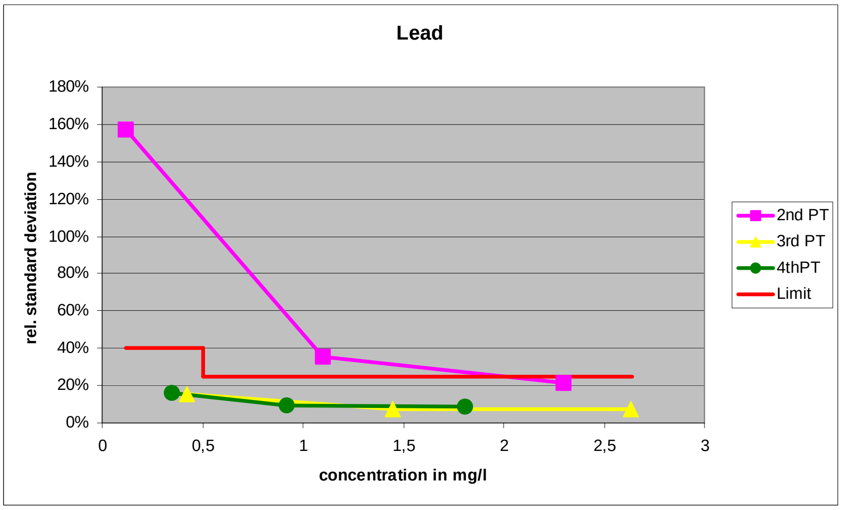


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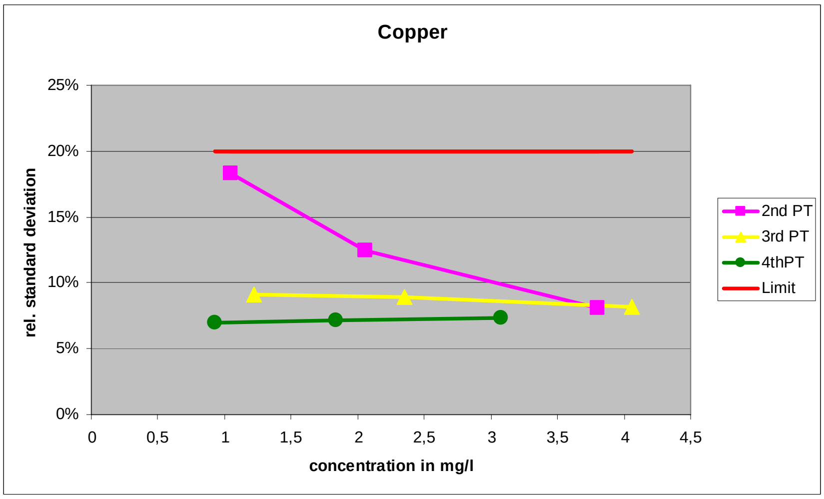
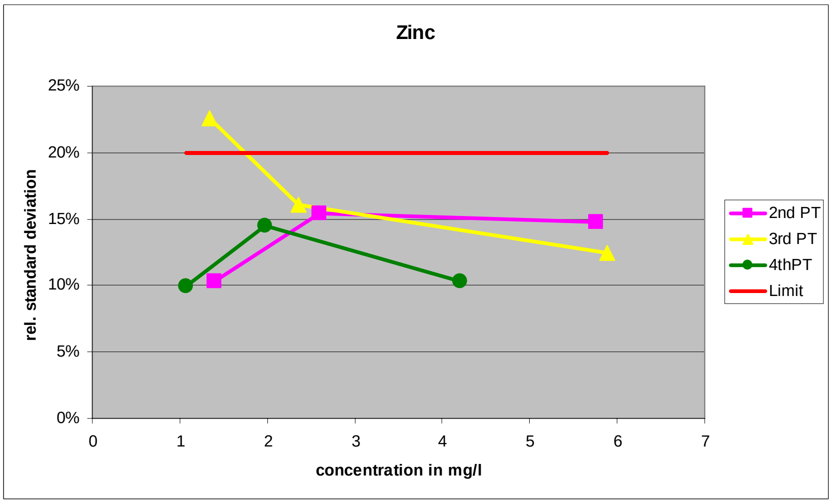

Copper
rel. standard deviation
25%
20%
15%
10%
5%
0%
0
0,5
1
1,5
2
2,5
3
3,5
4
4,5
concentration in mg/l
2nd PT
3rd PT
4thPT
Limit






Zinc
rel. standard deviation
25%
20%
15%
10%
5%
0%
0
1
2
3
4
5
6
7
concentration in mg/l
2nd PT
3rd PT
4thPT
Limit

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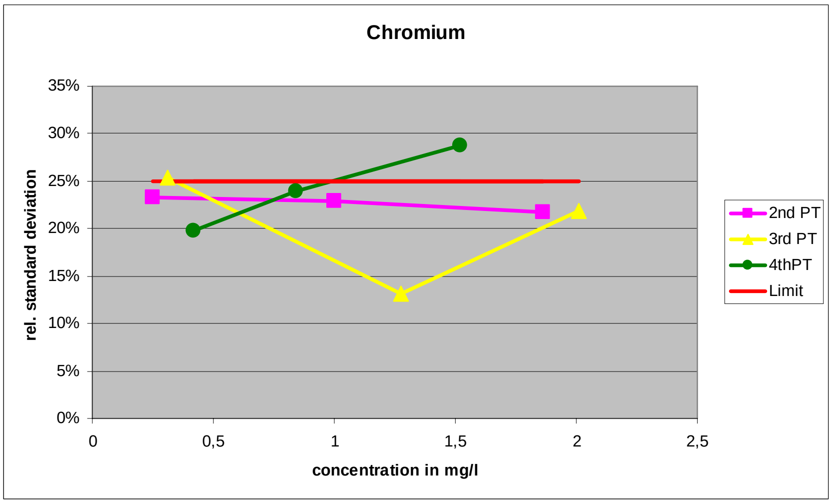


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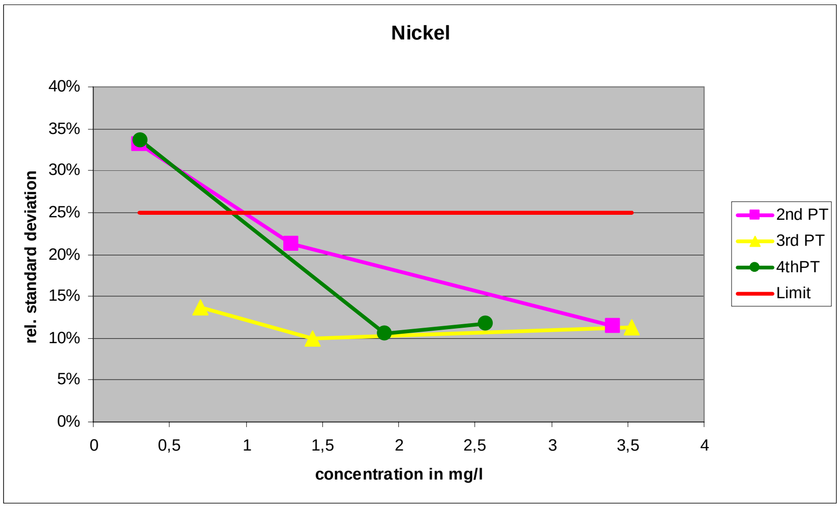


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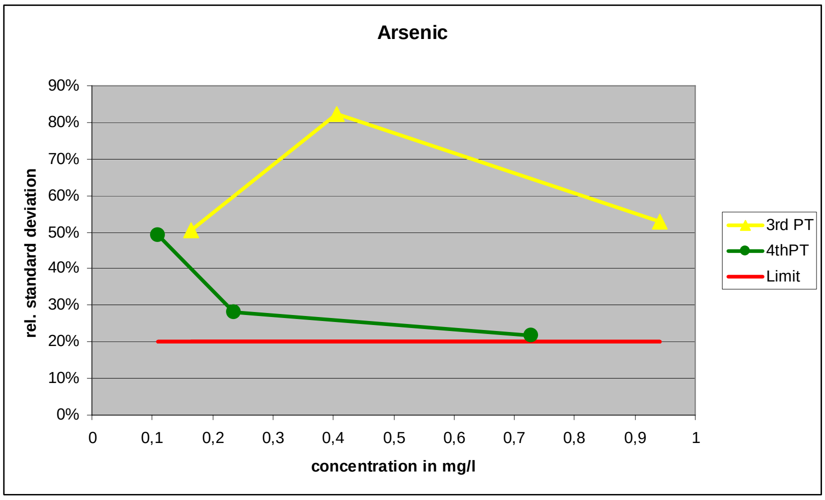


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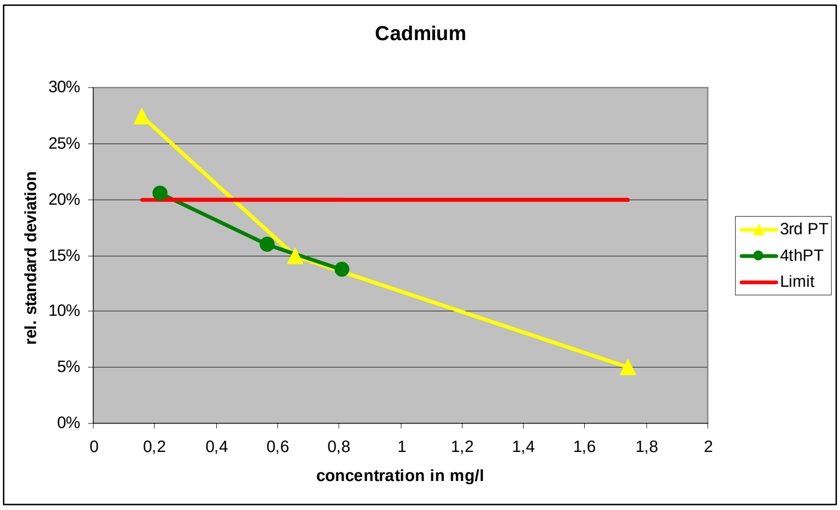


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## Compared to previous PT rounds

- better:
  - potassium, arsenic
- no change:
  - sulphate, chloride, fluoride, phosphate, sodium, iron, manganese, aluminium, lead, copper, zinc, chromium, nickel, cadmium
- worse:
  - nitrate, calcium, magnesium,



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## Compared to our own quality standards

- good
  - aluminium, lead, copper, zinc
- still acceptable
  - chloride, potassium, iron, manganese, chromium, nickel, cadmium
- not acceptable
  - fluoride, arsenic
- bad
  - sulphate, nitrate, phosphate, calcium, magnesium, sodium
- Are we satisfied with our quality standards?

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# Our own quality standards - are they still fit for the purpose?

| parameter | limit |
|---|---|
| Sulphate | 10% |
| Chloride | 10% |
| Fluoride | 12% |
| Nitrate | 15% |
| Phosphate | 10% |
| Calcium | 10% |
| Magnesium | 10% |
| Sodium | 10% |
| Potassium | 10% |
| Iron | <1 mg/l: 20%, >1mg/l: 12% |

| parameter | limit in % |
|---|---|
| Manganese | <1 mg/l: 20%, >1mg/l: 12% |
| Aluminium | 30% |
| Lead | <0,5 mg/l: 40%, >0,5 mg/l: 25% |
| Copper | 20% |
| Zinc | 20% |
| Chromium | 25% |
| Nickel | 25% |
| Arsenic | 20% |
| Cadmium | 20% |



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# The main question

- Why can‘t we see a clear improvement after 4 PT rounds?

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## TITLE: SABS PROFICIENCY TESTING SCHEME, RSA


PRESENTED BY: Ms C. MODIKA

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E-mail : Modikac@sabs.co.za


TANZANIA, 3 – 8 December 2007

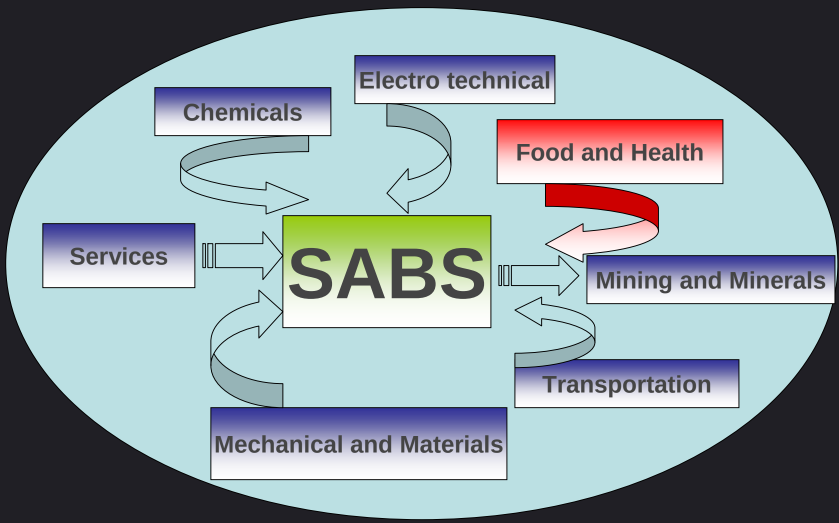
## Mission

### Mission Statement of SABS:

- To offer value-added standardization services on an ethical and principled basis that uplift the African standard and empower South African industry to compete vigorously towards increased market access. In so doing SABS contributes to the economic growth of South Africa and Africa as a whole within a framework that protects consumers and the environment by promoting uncompromised quality of products and services.

## SABS BUSINESS UNITS

SABS






## Purpose of PTS

SABS

- The SABS Commercial (Pty) Ltd (Food Chemistry), is a provider of a proficiency testing scheme (PTS) and recognized by a accreditation body SANAS (South African National Accreditation System) according to ILAC G 13 (Guidelines for the requirements for the competence of providers of proficiency testing schemes).
- It is recognised that schemes conducted may have primary aims such as establishing the effectiveness and precision of test methods, equipment and evaluating the individual performance of laboratory staff.

## Purpose of PTS

- Proficiency testing schemes are used by laboratory accreditation bodies as part of an assessment process to verify competence of a laboratory.
- A high level of confidence is given to an accredited proficiency testing scheme (PTS) based on international acceptable requirements.
- Running a PTS Programme improves the quality system of the laboratory.



## SABS WATER CHECK (PTS)

- SABS Water-Check (PTS) is a high frequency inter-laboratory Inorganic Chemistry Water proficiency-testing programme with the objective of providing a rapid report-back service to participants for self-evaluation
- SABS Water-Check allows flexibility in participation and no specific methods or instrumentation are prescribed.
- The programme is divided into three categories, each category being scheduled on a quarterly basis.

## PTS Provider, SABS is supply the following:

- Preparation of samples for the following groups

***Group 1***

**Heavy metals in water: aluminium, barium, beryllium, boron, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, silicon, strontium, vanadium, zinc, mercury, arsenic and selenium.**

**Scheduled : January, April, July, and October.**



## Provides the following

***Group 2***

**Nutrients and oxygen demand: kjeldahl nitrogen, nitrate, ammonia, total phosphate, orthophosphate, oxygen absorbed , chemical oxygen demand, dissolved organic carbon and total organic carbon.**

**Scheduled : February, May, August, November.**

## Provides the following

***Group 3***

**Major constituents in water: pH, conductivity, dissolved solids, calcium, magnesium, sodium, potassium, chloride, fluoride, sulfate, alkalinity, nitrate and turbidity.**

**Scheduled: March, June, September, and December**



## REPORT

- **REPORT DISCUSSION**

## Conclusion

- List of participating laboratories/Client base locally and Internationally for all the groups (101)

PARTICIPATION ON THE SCHEME MEANS GROWTH, IMPROVEMENT AND TAKING THE LABORATORY TO AN IMPROVED QUALITY SYSTEM.

## SOUTH AFRICAN BUREAU OF STANDARDS - WATER-CHECK PROGRAMME

**TABLE A**

**ANALYTICAL RESULTS** **Okt 07**

**GROUP 1** **Gr 1 (cont)**



| Determinand | | B1 | B3 | B5 | B7 | B8 | B9A | B9B | B10 | B11A | B11B | B14 | B16 | B16a | B19 | B21A | B21B | B22 | B23 | B25 | B30 | B31 | B33 | B34 | B36 | Spike ug/l | Median | Robust SD | n |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium as Al in µg/l | 1 | | | 723,0 | | 792,0 | 803,0 | | 807,0 | 857,0 | | 810,0 | | | 590,0 | 995,0 | 959,0 | 752,0 | 870,0 | 872,0 | 573,0 | 782,0 | | | 804,0 | 750,0 | 802,0 | 105 | 48 |
| | 2 | | | 1523 | | 1582 | 1450 | | 1523 | 1692 | | 1400 | | | 1380 | 2002 | 1861 | 1500 | 1520 | 1600 | 1346 | 1516 | | | 1575 | 1500 | 1552 | 151 | 48 |
| | 3 | | | 211,0 | | 203,0 | 341,0 | | 254,0 | 273,0 | | 30,00 | | | 10,00 | 361,0 | 379,0 | 38,00 | 195,0 | 236,0 | | 356,0 | | | 216,0 | 375,0 | 257,0 | 85 | 47 |
| Barium as Ba in µg/l | 1 | 176,5 | | 200,0 | | 167,0 | 434,0 | | 220,0 | 217,0 | | 185,0 | | | 170,0 | 286,0 | | 146,0 | | 191,0 | | 192,0 | | | 185,0 | 150,0 | 190,0 | 15 | 34 |
| | 2 | 512,5 | | 513,0 | | 468,0 | 470,0 | | 549,0 | 559,0 | | 490,0 | | | 470,0 | 774,0 | | 434,0 | | 489,0 | | 483,0 | | | 491,0 | 450,0 | 488,0 | 27 | 34 |
| | 3 | 326,5 | | 344,0 | | 314,0 | 291,0 | | 307,0 | 388,0 | | 335,0 | | | 320,0 | 525,0 | | 303,0 | | 327,0 | | 336,0 | | | 327,0 | 300,0 | 327,0 | 18 | 34 |
| Beryllium as Be in µg/l | 1 | 36,00 | | 49,00 | | 50,00 | 110,0 | | 51,00 | 52,00 | | 52,00 | | | 50,00 | 53,00 | 47,00 | 34,00 | 50,00 | 51,00 | | | | | | 50,00 | 50,00 | 3 | 25 |
| | 2 | 139,5 | | 149,0 | | 153,0 | 114,0 | | 149,0 | 156,0 | | 155,0 | | | 150,0 | 190,0 | 182,0 | 120,0 | 150,0 | 154,0 | | | | | | 150,0 | 150,0 | 7 | 25 |
| | 3 | 91,00 | | 62,00 | | 91,00 | 77,50 | | 59,00 | 93,00 | | 80,00 | | | 70,00 | 112,0 | 96,00 | 46,00 | 90,00 | 74,00 | | | | | | 100,0 | 81,79 | 14 | 25 |
| Boron as B µg/l | 1 | 425,5 | | 560,0 | | 591,0 | 1480 | | 568,0 | 576,0 | | 550,0 | | | 330,0 | 776,0 | 763,0 | 505,0 | | 572,0 | | 566,0 | | | | 500,0 | 541,0 | 53 | 29 |
| | 2 | 2075 | | 2091 | | 2012 | 1502 | | 2025 | 2135 | | 2000 | | | 1340 | 2761 | 2521 | 1370 | | 2010 | | 2011 | | | | 2000 | 2005 | 162 | 30 |
| | 3 | 1055 | | 1087 | | 1048 | 908,0 | | 1059 | 1108 | | 1000 | | | 750,0 | 1412 | 1370 | 927,0 | | 1070 | | 1033 | | | | 1000 | 1038 | 83 | 30 |
| Cadmium as Cd in µg/l | 1 | 137,5 | | 117,0 | | 115,0 | 478,0 | | 145,0 | 133,0 | | 140,0 | | | 110,0 | 154,0 | 155,0 | 123,0 | 125,0 | 125,0 | 117,0 | 126,0 | 120,0 | | 120,0 | 125,0 | 126,0 | 13 | 51 |
| | 2 | 553,0 | | 517,0 | | 489,0 | 214,0 | | 577,0 | 532,0 | | 540,0 | | | 500,0 | 650,0 | 626,0 | 476,0 | 500,0 | 504,0 | 502,0 | 502,0 | 470,0 | | 489,0 | 500,0 | 502,0 | 33 | 51 |
| | 3 | 263,5 | | 230,0 | | 234,0 | 101,0 | | 231,0 | 265,0 | | 280,0 | | | 240,0 | 320,0 | 313,0 | 228,0 | 240,0 | 233,0 | 242,4 | 252,0 | 230,0 | | 246,0 | 250,0 | 241,0 | 19 | 51 |
| Chromium as Cr in µg/l | 1 | 1060 | | 1248 | 1268 | 1156 | 2910 | | 1208 | 1155 | | 1200 | | | 1100 | 1591 | 1581 | 1103 | 1190 | 1210 | 1189 | 1203 | 1120 | | 1174 | 1200 | 1191 | 52 | 51 |
| | 2 | 2110 | | 2495 | 2674 | 2357 | 366,0 | | 2497 | 2349 | | 2500 | | | 2400 | 3301 | 3177 | 2328 | 2405 | 2450 | 2418 | 2413 | 2320 | | 2385 | 2400 | 2413 | 99 | 51 |
| | 3 | 452,0 | | 413,0 | 515,0 | 314,0 | 1280 | | 424,0 | 397,0 | | 60,00 | | | 340,0 | 512,0 | 611,0 | 30,00 | 385,0 | 342,0 | 327,3 | 550,0 | 370,0 | | 287,0 | 600,0 | 397,0 | 103 | 51 |
| Cobalt as Co in µg/l | 1 | 402,0 | | 377,0 | | 380,0 | 369,0 | | 405,0 | 385,0 | | 450,0 | | | 380,0 | 544,0 | 534,0 | 386,0 | 410,0 | 392,0 | 437,4 | 395,0 | 370,0 | | 398,0 | 400,0 | 397,0 | 18 | 48 |
| | 2 | 798,5 | | 797,0 | | 771,0 | 762,0 | | 801,0 | 769,0 | | 850,0 | | | 780,0 | 1082 | 1060 | 769,0 | 760,0 | 796,0 | 855,0 | 800,0 | 740,0 | | 797,0 | 800,0 | 797,0 | 39 | 48 |
| | 3 | 195,5 | | 168,0 | | 184,0 | 126,0 | | 200,0 | 192,0 | | 220,0 | | | 190,0 | 240,0 | 245,0 | 196,0 | 195,0 | 188,0 | 210,5 | 194,0 | 190,0 | | 200,0 | 200,0 | 195,0 | 10 | 48 |
| Copper as Cu in µg/l | 1 | 379,0 | 311,0 | 317,0 | | 306,0 | 884,0 | | 336,0 | 328,0 | | 350,0 | | | 290,0 | 427,0 | 410,0 | 324,0 | 320,0 | 359,0 | 352,3 | 306,0 | 290,0 | | 324,0 | 300,0 | 322,0 | 24 | 54 |
| | 2 | 1185 | | 1288 | | 1206 | 731,0 | | 1203 | 1247 | | 1200 | | | 1200 | 1643 | 1573 | 1143 | 1170 | 1290 | 1382,0 | 1196 | 1090 | | 1205,0 | 1200 | 1205 | 62 | 53 |
| | 3 | 531,0 | | 388,0 | | 551,0 | 517,0 | | 363,0 | 523,0 | | 520,0 | | | 510,0 | 795,0 | 773,0 | 305,0 | 515,0 | 425,0 | 601,0 | 589,0 | 380,0 | | 464,0 | 600,0 | 490,0 | 117 | 53 |
| Iron as Fe in µg/l | 1 | | 1010 | 1154 | | 1086 | 2150 | | 1171 | 1128 | | 1300 | | | 660,0 | 1491 | | 941,0 | 1120 | 1070 | 1099 | 1285 | 1030 | | 1111 | 1250 | 1099 | 147 | 53 |
| | 2 | | 2546 | 2774 | | 2472 | 1360 | | 2628 | 2614 | | 2600 | | | 1730 | 3393 | | 2293 | 2410 | 2660 | 2725 | 2520 | 2340 | | 2540 | 2500 | 2471 | 120 | 54 |
| | 3 | | 422,0 | 439,0 | | 338,0 | 987,0 | | 454,0 | 481,0 | | 30,00 | | | 150,0 | 505,0 | | 37,00 | 465,0 | 440,0 | 375,7 | 660,0 | 375,0 | | 416,0 | 625,0 | 438,5 | 94 | 54 |
| Lead as Pb in µg/l | 1 | 414,5 | | 124,0 | | 169,0 | 675,0 | | 109,0 | 161,0 | | 150,0 | | | 120,0 | 192,0 | | 123,0 | 175,0 | 150,0 | | 169,0 | 170,0 | | 156,0 | 150,0 | 154,0 | 30 | 50 |
| | 2 | 848,0 | | 604,0 | | 624,0 | 255,0 | | 555,0 | 615,0 | | 616,0 | | | 490,0 | 766,0 | | 526,0 | 520,0 | 582,0 | | 603,0 | 500,0 | | 577,0 | 600,0 | 586,0 | 45 | 50 |
| | 3 | 499,0 | | 185,0 | | 207,0 | 193,0 | | 196,0 | 199,0 | | 16,00 | | | 190,0 | 315,0 | | 24,0 | 230,0 | 167,0 | | 292,0 | 140,0 | | 162,0 | 300,0 | 192,5 | 65 | 50 |
| Manganese as Mn in µg/l | 1 | 248,0 | 281,0 | 246,0 | 224,0 | 247,0 | 854,0 | | 282,0 | 280,0 | | 290,0 | | | 240,0 | 346,0 | 332,0 | 271,0 | 260,0 | 286,0 | 279,7 | 271,0 | | | 278,0 | 250,0 | 270,5 | 17 | 56 |
| | 2 | 1010 | 1072 | 1038 | 1104 | 983,0 | 408,0 | | 1040 | 1049 | | 1000 | | | 990,0 | 1308 | 1304 | 940,0 | 980,0 | 1060 | 1026 | 1015 | | | 1024,0 | 1000 | 1003 | 54 | 56 |
| | 3 | 483,5 | 523,0 | 489,0 | 507,0 | 481,0 | 213,0 | | 551,0 | 530,0 | | 560,0 | | | 500,0 | 651,0 | 655,0 | 470,0 | 495,0 | 531,0 | 519,0 | 511,0 | | | 519,0 | 500,0 | 493,5 | 36 | 56 |
| Mercury as Hg in µg/l | 1 | | 1,900 | | | | 6,000 | | 1,400 | | | 0,770 | | | 0,000 | | | 2,400 | | 10,00 | | | 0,270 | | | 3,000 | 2,400 | 3 | 15 |
| | 2 | 13,50 | 7,800 | | | | 6,000 | | 7,600 | | | 1,540 | | | 0,000 | | | 9,800 | | 15,00 | | | 10,72 | | | 9,000 | 8,800 | 4 | 16 |
| | 3 | | 8,800 | | | | 6,000 | | 2,500 | | | 0,950 | | | 0,000 | | | 1,900 | | 7,000 | | | 0,350 | | | 6,000 | 2,500 | 3 | 15 |
| Molybdenum as Mo in µg/l | 1 | 148,5 | | 74,00 | | 83,00 | 189,0 | | | 98,00 | | 80,00 | | | 80,00 | 106,0 | | 75,00 | | 69,00 | 52,80 | 99,00 | | | | 100,0 | 89,7 | 14 | 29 |
| | 2 | 303,0 | | 267,0 | | 275,0 | 425,0 | | | 306,0 | | 290,0 | | | 250,0 | 377,0 | | 250,0 | | 263,0 | 247,6 | 287,0 | | | | 300,0 | 275,0 | 24 | 30 |
| | 3 | 250,0 | | 187,0 | | 163,0 | 302,0 | | | 199,0 | | 150,0 | | | 180,0 | 194,0 | | 45,00 | | 194,0 | 171,5 | 199,0 | | | | 200,0 | 188,5 | 26 | 30 |
| Nickel as Ni in µg/l | 1 | 1055 | | 1064 | | 1068 | 1180 | | 1094 | 1153 | | 1700 | | | 1070 | 1461 | 1475 | 1068 | 1155 | 1060 | 1156 | 1094 | 1060 | | 1113 | 1100 | 1108 | 62 | 50 |
| | 2 | 2025 | | 2337 | | 2150 | 2300 | | 2202 | 2294 | | 3500 | | | 2190 | 2964 | 2947 | 2147 | 2215 | 2200 | 2289 | 2189 | 2150 | | 2231 | 2200 | 2201 | 111 | 50 |
| | 3 | 504,0 | | 531,0 | | 529,0 | 567,0 | | 577,0 | 577,0 | | 900,0 | | | 550,0 | 734,0 | 728,0 | 540,0 | 630,0 | 556,0 | 573,0 | 549,0 | 570,0 | | 553,0 | 550,0 | 554,8 | 33 | 50 |
| Silicon as Si in µg/l | 1 | | 1890 | 1954 | | 1883 | 1661 | | 1782 | | | 1900 | | | 1150 | 2227 | | 2080 | 1755 | 1950 | | 1721 | | | | - | 1746 | 208 | 30 |
| | 2 | | 1903 | 1745 | | 1790 | 1503 | | 1745 | | | 1800 | | | 1130 | 2211 | | 2003 | 1700 | 1810 | | 1697 | | | | - | 1744 | 178 | 30 |
| | 3 | | 1854 | 3131 | | 1798 | 1540 | | 1692 | | | 1800 | | | 1130 | 2201 | | 2000 | 1690 | 1830 | | 1699 | | | | - | 1691 | 184 | 30 |
| Strontium as Sr in µg/l | 1 | 185,0 | | 178,0 | | 174,0 | 322,0 | | 151,0 | 202,0 | | 150,0 | | | 160,0 | 229,0 | 236,0 | 175,0 | | 184,0 | | 178,0 | | | 177,0 | 80,00 | 176,5 | 13 | 34 |
| | 2 | 353,0 | | 347,0 | | 327,0 | 338,0 | | 325,0 | 380,0 | | 280,0 | | | 330,0 | 443,0 | 451,0 | 371,0 | | 339,0 | | 330,0 | | | 330,0 | 240,0 | 330,0 | 16 | 33 |
| | 3 | 265,0 | | 264,0 | | 251,0 | 244,0 | | 258,0 | 292,0 | | 225,0 | | | 250,0 | 334,0 | 319,0 | 293,0 | | 261,0 | | 255,0 | | | 252,0 | 160,0 | 255,0 | 18 | 33 |
| Vanadium as V in µg/l | 1 | 104,0 | | 90,00 | | 76,00 | 329,0 | | 63,00 | 91,00 | | 90,00 | | | 70,00 | 114,0 | 115,0 | 82,0 | | 70,00 | | 95,00 | | | | 100,0 | 86,0 | 18 | 28 |
| | 2 | 395,0 | | 390,0 | | 404,0 | 287,0 | | 392,0 | 431,0 | | 430,0 | | | 390,0 | 553,0 | | 394,0 | | 415,0 | | 398,0 | | | | 400,0 | 399,5 | 39 | 28 |
| | 3 | 177,0 | | 152,0 | | 108,0 | 109,0 | | 143,0 | 155,0 | | 27,0 | | | 120,0 | 171,0 | | 32,0 | | 128,0 | | 191,0 | | | | 200,0 | 143,5 | 40 | 28 |
| Zinc as Zn in µg/l | 1 | 540,5 | 474,0 | 424,0 | | 452,0 | 481,0 | | 454,0 | 463,0 | | 540,0 | | | 440,0 | 627,0 | | 500,0 | 425,0 | 572,0 | 417,0 | 469,0 | 410,0 | | 457,0 | 40,00 | 460,0 | 52 | 53 |
| | 2 | 504,5 | 448,0 | 386,0 | | 423,0 | 418,0 | | 402,0 | 410,0 | | 480,0 | | | 410,0 | 554,0 | 546,0 | 484,0 | 395,0 | 478,0 | 383,2 | 432,0 | 375,0 | | 429,0 | 120,0 | 425,5 | 43 | 54 |
| | 3 | 309,0 | | 277,0 | | 327,0 | 323,0 | | 326,0 | 352,0 | | 390,0 | | | 340,0 | 448,0 | 426,0 | 320,0 | 315,0 | 362,0 | 308,2 | 353,0 | 300,0 | | 340,0 | 80,00 | 326,0 | 40 | 53 |
| Arsenic as As in µg/l | 4 | | 2,100 | | | | 5,000 | | | | | 5,900 | | | | | | 1,000 | | 11,00 | | | | | | 3,000 | 4,415 | 3 | 12 |
| | 5 | | 15,00 | | | | 18,00 | | | | | 14,00 | | | 20,00 | | | 12,00 | | 25,00 | | | | | | 15,00 | 14,50 | 2 | 14 |
| | 6 | | 8,200 | | | | 11,00 | | | | | 9,100 | | | 10,00 | | | 5,000 | | 16,00 | | | | | | 9,000 | 8,835 | 1 | 12 |
| Selenium as Se in µg/l | 4 | 121,0 | 7,900 | | | | 10,00 | | 8,200 | | | 8,900 | | | | | | 6,500 | | 18,00 | | | | | | 7,500 | 8,900 | 3 | 15 |
| | 5 | 103,5 | 13,00 | | | | 16,00 | | 16,60 | | | 13,00 | | | 20,00 | | | 10,90 | | 20,00 | | | | | | 12,50 | 15,10 | 6 | 17 |
| | 6 | 93,00 | 5,500 | | | | 7,000 | | 16,10 | | | 7,900 | | | 30,00 | | | 3,300 | | 11,00 | | | | | | 5,000 | 7,000 | 5 | 15 |

## SOUTH AFRICAN BUREAU OF STANDARDS - WATER-CHECK PROGRAMME

**TABLE A**

**ANALYTICAL RESULTS** **Okt 07**

**GROUP 1** **Gr 1 (cont)**



| Determinand | | B38 | B39 | B41 | B42 | B45 | B49A | B49B | B63 | B68 | B69A | B69B | B69C | B70 | B71 | B73 | B74 | B76 | B78 | B79 | B81 | B86 | B88 | B91 | Spike ug/l | Median | Robust SD | n |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium as Al in µg/l | 1 | 650,0 | 871,0 | | 754,0 | | 940,0 | 903,0 | 780,0 | 797,0 | 858,0 | | | | 752,7 | 863,0 | 353,0 | 890,0 | | | | 724,0 | | | 750,0 | 802,0 | 105 | 48 |
| | 2 | 1330 | 1829 | | 2518 | | 1450 | 1759 | 1535 | 1515 | 1635 | | | | 1497 | 1812 | 1490 | 1800 | | | | 1458 | | | 1500 | 1552 | 151 | 48 |
| | 3 | 300,0 | 149,0 | | 30,00 | | 470,0 | 260,0 | 224,0 | 312,0 | 273,0 | | | | 173,4 | 117,0 | 317,0 | 270,0 | | | | 199,0 | | | 375,0 | 257,0 | 85 | 47 |
| Barium as Ba in µg/l | 1 | | 176,0 | | 190,0 | | | 155,0 | | 200,0 | 191,0 | | | | 186,4 | 207,0 | 190,0 | 200,0 | | | | | | | 150,0 | 190,0 | 15 | 34 |
| | 2 | | 483,0 | | 487,0 | | | 469,0 | | 480,0 | 472,0 | | | | 474,6 | 519,0 | 490,0 | 510,0 | | | | | | | 450,0 | 488,0 | 27 | 34 |
| | 3 | | 305,0 | | 339,0 | | | 305,0 | | 337,0 | 322,0 | | | | 328,5 | 345,0 | 331,0 | 350,0 | | | | | | | 300,0 | 327,0 | 18 | 34 |
| Beryllium as Be in µg/l | 1 | | | | 48,00 | | | 43,00 | 50,00 | 43,00 | | | | | 49,97 | | | | | | | | | | 50,00 | 50,00 | 3 | 25 |
| | 2 | | | | 146,0 | | | 168,0 | 150,0 | 133,0 | | | | | 151,1 | | | | | | | | | | 150,0 | 150,0 | 7 | 25 |
| | 3 | | | | 50,0 | | | 51,00 | 63,00 | 80,00 | | | | | 81,79 | | | | | | | | | | 100,0 | 81,79 | 14 | 25 |
| Boron as B µg/l | 1 | | | | 518,0 | | | 599,0 | | | | | | | 536,0 | | 261,0 | 620,0 | | | | | | | 500,0 | 541,0 | 53 | 29 |
| | 2 | | | | 1868 | | | 1977 | | | | | | | 1831 | | 1810 | 2230 | | | | | | | 2000 | 2005 | 162 | 30 |
| | 3 | | | | 993,0 | | | 1059 | | | | | | | 943,0 | | 933,0 | 1160 | | | | | | | 1000 | 1038 | 83 | 30 |
| Cadmium as Cd in µg/l | 1 | | 140,0 | | 128,0 | | 120,0 | 113,0 | 125,0 | 110,0 | 128,0 | | | | 112,0 | 135,0 | 109,0 | 140,0 | | | | 122,0 | | | 125,0 | 126,0 | 13 | 51 |
| | 2 | | 601,0 | | 496,0 | | 500,0 | 509,0 | 500,0 | 453,0 | 502,0 | | | | 469,0 | 510,0 | 439,0 | 540,0 | | | | 195,0 | | | 500,0 | 502,0 | 33 | 51 |
| | 3 | | 252,0 | | 253,0 | | 240,0 | 200,0 | 171,0 | 221,0 | 245,0 | | | | 217,0 | 265,0 | 206,0 | 260,0 | | | | 241,0 | | | 250,0 | 241,0 | 19 | 51 |
| Chromium as Cr in µg/l | 1 | | 1237 | | 1187 | | 1410 | 1218 | 1160 | 1187 | 1162 | | | | 1191 | 1216 | 1080 | 1190 | | | | 1131 | | | 1200 | 1191 | 52 | 51 |
| | 2 | | 2583 | | 2388 | | 2990 | 2489 | 2402 | 2464 | 2385 | | | | 2444 | 2496 | 2190 | 2480 | | | | 2348 | | | 2400 | 2413 | 99 | 51 |
| | 3 | | 275,0 | | 27,00 | | 480,0 | 384,0 | 371,0 | 433,0 | 378,0 | | | | 330,0 | 239,0 | 433,0 | 350,0 | | | | 320,0 | | | 600,0 | 397,0 | 103 | 51 |
| Cobalt as Co in µg/l | 1 | | 465,0 | | 397,0 | | 350,0 | 401,0 | 395,0 | 397,0 | 404,0 | | | | 407,7 | 414,0 | 370,0 | 420,0 | | | | 386,0 | | | 400,0 | 397,0 | 18 | 48 |
| | 2 | | 983,0 | | 790,0 | | 720,0 | 800,0 | 779,0 | 777,0 | 804,0 | | | | 804,7 | 829,0 | 716,0 | 850,0 | | | | 768,0 | | | 800,0 | 797,0 | 39 | 48 |
| | 3 | | 238,0 | | 198,0 | | 140,0 | 193,0 | 188,0 | 216,0 | 198,0 | | | | 200,0 | 217,0 | 169,0 | 210,0 | | | | 195,0 | | | 200,0 | 195,0 | 10 | 48 |
| Copper as Cu in µg/l | 1 | | 304,0 | | 321,0 | | 330,0 | 323,0 | 309,0 | 341,0 | 324,0 | | | | 351,8 | 346,0 | 289,0 | 330,0 | | | | 332,0 | | | 300,0 | 322,0 | 24 | 54 |
| | 2 | | 1285 | | 1188 | | 1180 | 1249 | 1210 | 1179 | 1217 | | | | 1335 | 1275 | 1120 | 1270,0 | | | | 1276 | | | 1200 | 1205 | 62 | 53 |
| | 3 | | 255,0 | | 328,0 | | 400,0 | 339,0 | 340,0 | 581,0 | 449,0 | | | | 463,6 | 552,0 | 436,0 | 570,0 | | | | 441,0 | | | 600,0 | 490,0 | 117 | 53 |
| Iron as Fe in µg/l | 1 | 1250 | 871,0 | | 1279 | | 1100 | 1109 | 861,0 | 1223 | 1004 | | | | 943,7 | 1003 | 930,0 | 960,0 | | | | 1006 | | | 1250 | 1099 | 147 | 53 |
| | 2 | 2540 | 2601 | | 2281 | | 2450 | 2473 | 2384 | 2563 | 2543 | | | | 2455 | 2216 | 2230 | 2570 | | | | 2499 | | | 2500 | 2471 | 120 | 54 |
| | 3 | 670,0 | 199,0 | | 24,00 | | 500,0 | 425,0 | 425,0 | 659,0 | 391,0 | | | | 409,8 | 313,0 | 438,0 | 250,0 | | | | 368,0 | | | 625,0 | 438,5 | 94 | 54 |
| Lead as Pb in µg/l | 1 | | 123,0 | | 109,0 | | 190,0 | 162,0 | 98,00 | 179,0 | 154,0 | | | | 161,0 | 91,00 | 104,0 | 150,0 | | | | 137,0 | | | 150,0 | 154,0 | 30 | 50 |
| | 2 | | 625,0 | | 688,0 | | 590,0 | 612,0 | 577,0 | 608,0 | 593,0 | | | | 594,0 | 525,0 | 442,0 | 580,0 | | | | 565,0 | | | 600,0 | 586,0 | 45 | 50 |
| | 3 | | 123,0 | | 20,00 | | 230,0 | 170,0 | 188,0 | 258,0 | 192,0 | | | | 23,00 | 116,0 | 107,0 | 200,0 | | | | 166,0 | | | 300,0 | 192,5 | 65 | 50 |
| Manganese as Mn in µg/l | 1 | 250,0 | 287,0 | | 269,0 | | 260,0 | 289,0 | 272,0 | 90,0 | 267,0 | | | | 270,9 | 288,0 | 246,0 | 280,0 | | | | 259,0 | | | 250,0 | 270,5 | 17 | 56 |
| | 2 | 930,0 | 1111 | | 999,0 | | 1010 | 1064 | 974,0 | 849,0 | 1010 | | | | 1005 | 1051 | 918,0 | 1070 | | | | 971,0 | | | 1000 | 1003 | 54 | 56 |
| | 3 | 480,0 | 539,0 | | 505,0 | | 490,0 | 523,0 | 484,0 | 303,0 | 495,0 | | | | 508,9 | 539,0 | 456,0 | 530,0 | | | | 484,0 | | | 500,0 | 493,5 | 36 | 56 |
| Mercury as Hg in µg/l | 1 | | 8,000 | | | | | <100.0 | | | | | | | | | | | | | | 4,500 | | | 3,000 | 2,400 | 3 | 15 |
| | 2 | | 10,00 | | | | | <100.0 | | | | | | | | | | | | | | 7,500 | | | 9,000 | 8,800 | 4 | 16 |
| | 3 | | 6,000 | | | | | <100.0 | | | | | | | | | | | | | | 1,500 | | | 6,000 | 2,500 | 3 | 15 |
| Molybdenum as Mo in µg/l | 1 | | 7,000 | | | | | 57,00 | 103,0 | 133,0 | | | | | 92,03 | | 77,00 | | | | | 82,00 | | | 100,0 | 89,7 | 14 | 29 |
| | 2 | | 24,00 | | | | | 259,0 | 275,0 | 305,0 | | | | | 267,4 | | 270,0 | | | | | 273,0 | | | 300,0 | 275,0 | 24 | 30 |
| | 3 | | 19,00 | | | | | 160,0 | 219,0 | 228,0 | | | | | 161,8 | | 178,0 | | | | | 192,0 | | | 200,0 | 188,5 | 26 | 30 |
| Nickel as Ni in µg/l | 1 | | 1197 | | 1102 | | 1060 | 1148 | 1086 | 1070 | 1121 | | | | 1120 | 1158 | 1010 | 1160 | | | | 1136 | | | 1100 | 1108 | 62 | 50 |
| | 2 | | 2450 | | 2182 | | 2100 | 2287 | 2196 | 2174 | 2232 | | | | 2250 | 2312 | 2020 | 2340 | | | | 2221 | | | 2200 | 2201 | 111 | 50 |
| | 3 | | 590,0 | | 546,0 | | 530,0 | 563,0 | 503,0 | 526,0 | 549,0 | | | | 563,3 | 594,0 | 496,0 | 560,0 | | | | 572,0 | | | 550,0 | 554,8 | 33 | 50 |
| Silicon as Si in µg/l | 1 | | 1657 | | 1650 | | | 1897 | | 1662 | | | | | 1667 | | 873,0 | | | | | | | | - | 1746 | 208 | 30 |
| | 2 | | 1659 | | 1617 | | | 1843 | | 1596 | | | | | 1649 | | 1630 | | | | | | | | - | 1744 | 178 | 30 |
| | 3 | | 1606 | | 1603 | | | 1856 | | 1649 | | | | | 1627 | | 1640 | | | | | | | | - | 1691 | 184 | 30 |
| Strontium as Sr in µg/l | 1 | | 165,0 | | 181,0 | | | 149,0 | 181,0 | 213,0 | 179,0 | | | | 175,5 | | | | | | | | | | 80,00 | 176,5 | 13 | 34 |
| | 2 | | 349,0 | | 327,0 | | | 316,0 | 335,0 | 378,0 | 326,0 | | | | 331,0 | | | | | | | | | | 240,0 | 330,0 | 16 | 33 |
| | 3 | | 275,0 | | 257,0 | | | 276,0 | 255,0 | 298,0 | 250,0 | | | | 257,0 | | | | | | | | | | 160,0 | 255,0 | 18 | 33 |
| Vanadium as V in µg/l | 1 | | 68,00 | | 82,00 | | | 25,00 | 72,00 | | | | | | 78,70 | | 63,00 | | | | | 78,00 | | | 100,0 | 86,0 | 18 | 28 |
| | 2 | | 426,0 | | 373,0 | | | 415,0 | 421,0 | | | | | | 401,0 | | 368,0 | | | | | 392,0 | | | 400,0 | 399,5 | 39 | 28 |
| | 3 | | 107,0 | | 23,00 | | | 108,0 | 145,0 | | | | | | 131,7 | | 144,0 | | | | | 127,0 | | | 200,0 | 143,5 | 40 | 28 |
| Zinc as Zn in µg/l | 1 | | 557,0 | | 472,0 | | 460,0 | 483,0 | 450,0 | | 461,0 | | | | 446,0 | 491,0 | 410,0 | 500,0 | | | | 427,0 | | | 40,00 | 460,0 | 52 | 53 |
| | 2 | | 529,0 | | 427,0 | | 450,0 | 439,0 | 425,0 | | 426,0 | | | | 419,5 | 455,0 | 380,0 | 450,0 | | | | 383,0 | | | 120,0 | 425,5 | 43 | 54 |
| | 3 | | 363,0 | | 343,0 | | 300,0 | 305,0 | 264,0 | | 333,0 | | | | 333,1 | 339,0 | 285,0 | 370,0 | | | | 316,0 | | | 80,00 | 326,0 | 40 | 53 |
| Arsenic as As in µg/l | 4 | | | | | | | 6,000 | | | | | | | | | 1,260 | | | | | | | | 3,000 | 4,415 | 3 | 12 |
| | 5 | | 14,00 | | | | | 14,00 | | | | | | | | | 11,00 | | | | | | | | 15,00 | 14,50 | 2 | 14 |
| | 6 | | | | | | | 9,000 | | | | | | | | | 8,670 | | | | | | | | 9,000 | 8,835 | 1 | 12 |
| Selenium as Se in µg/l | 4 | | | | | | | <10.00 | | | | | | | | | 9,230 | | | | | 1,800 | | | 7,500 | 8,900 | 3 | 15 |
| | 5 | | 1,000 | | | | | 31,00 | | | | | | | | | 15,60 | | | | | 3,500 | | | 12,50 | 15,10 | 6 | 17 |
| | 6 | | | | | | | <10.00 | | | | | | | | | 4,630 | | | | | 1,500 | | | 5,000 | 7,000 | 5 | 15 |

**TABLE A**

**ANALYTICAL RESULTS** **Okt 07**

**GROUP 1**



| Determinand | | B93 | B94 | B99 | B100 | B101 | B103 | B104 | B105 | B107 | B108 | B109 | B112 | B113 | B115 | B116 | B117 | B121a | B121c | B123 | B124 | B125 | B126 | B127 | B128 | Spike ug/l | Median | Robust SD | n |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium as Al in µg/l | 1 | | | 700,0 | 790,0 | | 98,40 | 873,0 | | | 809,0 | 730,0 | 890,0 | 801,0 | | 1100 | | | | | 786,0 | | | | 776,0 | 750,0 | 802,0 | 105 | 48 |
| | 2 | | | 1600 | 1468 | | 1776 | 1643 | | | 1566 | 1450 | 1538 | 1608 | | 2207 | | | | | 1505 | | | | 1567 | 1500 | 1552 | 151 | 48 |
| | 3 | | | 100,0 | 257,0 | | 445,9 | 261,0 | | | 220,0 | 200,0 | 280,0 | 234,3 | | 269,0 | | | | | 326,0 | | | | 242,0 | 375,0 | 257,0 | 85 | 47 |
| Barium as Ba in µg/l | 1 | | | | 184,0 | | | | | | 203,0 | | | 182,3 | | 181,0 | | | | | | | | | 185,0 | 150,0 | 190,0 | 15 | 34 |
| | 2 | | | | 487,0 | | | | | | 526,0 | | | 473,5 | | 469,0 | | | | | | | | | 471,0 | 450,0 | 488,0 | 27 | 34 |
| | 3 | | | | 324,0 | | | | | | 357,0 | | | 325,0 | | 314,0 | | | | | | | | | 326,0 | 300,0 | 327,0 | 18 | 34 |
| Beryllium as Be in µg/l | 1 | | | | 50,00 | | | | | | 53,00 | | | 50,89 | | | | | | | | | | | 57,00 | 50,00 | 50,00 | 3 | 25 |
| | 2 | | | | 146,0 | | | | | | 163,0 | | | 152,8 | | | | | | | | | | | 169,0 | 150,0 | 150,0 | 7 | 25 |
| | 3 | | | | 83,00 | | | | | | 83,00 | | | 74,10 | | | | | | | | | | | 92,00 | 100,0 | 81,79 | 14 | 25 |
| Boron as B µg/l | 1 | | | | 549,0 | | 529,0 | | | | 511,0 | | | 512,5 | | 487,0 | | | | | | | | | 541,0 | 500,0 | 541,0 | 53 | 29 |
| | 2 | | | | 1863 | | 2030 | | | | 1882 | | | 1909 | | 1930 | | | | | | | | | 1998 | 2000 | 2005 | 162 | 30 |
| | 3 | | | | 960,0 | | 1024 | | | | 975,0 | | | 968,9 | | 971,0 | | | | | | | | | 1043 | 1000 | 1038 | 83 | 30 |
| Cadmium as Cd in µg/l | 1 | | | | 120,0 | 130,0 | 114,6 | 128,0 | 146,0 | | 135,0 | 134,0 | 122,0 | 126,9 | | 108,0 | | 118,0 | | 150,7 | 142,0 | | | | 127,0 | 125,0 | 126,0 | 13 | 51 |
| | 2 | | | | 513,0 | 540,0 | 505,1 | 524,0 | 582,0 | | 538,0 | 512,0 | 501,0 | 501,2 | | 417,0 | | 452,0 | | 541,5 | 503,0 | | | | 527,0 | 500,0 | 502,0 | 33 | 51 |
| | 3 | | | | 243,0 | 260,0 | 243,6 | 254,0 | 280,0 | | 266,0 | 251,0 | 230,0 | 200,9 | | 205,0 | | 189,0 | | 276,2 | 253,0 | | | | 213,0 | 250,0 | 241,0 | 19 | 51 |
| Chromium as Cr in µg/l | 1 | | | 1250 | 1194 | 1230 | 1192 | 1193 | 1172 | | 1302 | 1351 | 1199 | 1190 | | | | 2189 | | 1162 | | | | | 1171 | 1200 | 1191 | 52 | 51 |
| | 2 | | | 2700 | 2500 | 2370 | 2465 | 2400 | 2348 | | 2594 | 2400 | 2399 | 2473 | | | | 4272 | | 2385 | | | | | 2402 | 2400 | 2413 | 99 | 51 |
| | 3 | | | 620,0 | 412,0 | 560,0 | 403,1 | 425,0 | 440,0 | | 411,0 | 343,0 | 305,0 | 391,0 | | | | 926,0 | | 295,8 | | | | | 123,0 | 600,0 | 397,0 | 103 | 51 |
| Cobalt as Co in µg/l | 1 | | | | 386,0 | 400,0 | 406,3 | 399,0 | 422,0 | | 397,0 | 403,0 | 385,0 | 393,6 | | | | 380,0 | | 403,6 | 432,0 | | | | 406,0 | 400,0 | 397,0 | 18 | 48 |
| | 2 | | | | 803,0 | 790,0 | 796,3 | 797,0 | 823,0 | | 829,0 | 799,0 | 913,0 | 791,3 | | | | 738,0 | | 802,6 | 817,0 | | | | 821,0 | 800,0 | 797,0 | 39 | 48 |
| | 3 | | | | 184,0 | 200,0 | 189,3 | 195,0 | 208,0 | | 194,0 | 207,0 | 189,0 | 191,2 | | | | 179,0 | | 202,8 | 218,0 | | | | 203,0 | 200,0 | 195,0 | 10 | 48 |
| Copper as Cu in µg/l | 1 | | | 310,0 | 333,0 | 330,0 | 263,2 | 316,0 | 292,0 | | 329,0 | 316,0 | 348,0 | 305,6 | | 320,0 | | 290,0 | | 303,3 | 327,0 | | | | 335,0 | 300,0 | 322,0 | 24 | 54 |
| | 2 | | | 1180 | 1257 | 1190 | 1177 | 1168 | 1178 | | 1271 | 1242 | 1210 | 1193 | | 1214 | | 1154 | | 1239 | 1217 | | | | 1305 | 1200 | 1205 | 62 | 53 |
| | 3 | | | 570,0 | 544,0 | 610,0 | 342,7 | 439,0 | 636,0 | | 529,0 | 458,0 | 490,0 | 324,9 | | 304,0 | | 452,0 | | 504,3 | 592,0 | | | | 351,0 | 600,0 | 490,0 | 117 | 53 |
| Iron as Fe in µg/l | 1 | | | 1550 | 1046 | 1260 | 1149 | 1043 | 1144 | | 874,0 | 1198 | 913,0 | 855,9 | | 962,0 | | 1041 | | 1137 | 1267 | | | | 1150 | 1250 | 1099 | 147 | 53 |
| | 2 | | | 2600 | 2469 | 2470 | 2502 | 2500 | 2324 | | 2410 | 2602 | 2024 | 2497 | | 2406 | | 2466 | | 2444 | 2450 | | | | 2486 | 2500 | 2471 | 120 | 54 |
| | 3 | | | 750,0 | 490,0 | 620,0 | 470,7 | 476,0 | 438,0 | | 220,0 | 454,0 | 378,0 | 429,1 | | 361,0 | | 598,0 | | 447,0 | 562,0 | | | | 458,0 | 625,0 | 438,5 | 94 | 54 |
| Lead as Pb in µg/l | 1 | | | 200,0 | 150,0 | 126,0 | 350,8 | 166,0 | 178,0 | | 160,0 | 154,0 | 117,0 | 172,1 | | 134,0 | | 854,0 | | 50,14 | 172,0 | | | | 147,0 | 150,0 | 154,0 | 30 | 50 |
| | 2 | | | 570,0 | 595,0 | 600,0 | 774,4 | 546,0 | 604,0 | | 627,0 | 599,0 | 511,0 | 603,6 | | 498,0 | | 1019 | | 520,8 | 553,0 | | | | 571,0 | 600,0 | 586,0 | 45 | 50 |
| | 3 | | | 310,0 | 200,0 | 253,0 | 538,5 | 173,0 | 274,0 | | 181,0 | 212,0 | 185,0 | 213,9 | | 120,0 | | 438,0 | | 141,3 | 249,0 | | | | 67,00 | 300,0 | 192,5 | 65 | 50 |
| Manganese as Mn in µg/l | 1 | | | 280,0 | 241,0 | 270,0 | 245,4 | 267,0 | 290,0 | | 225,0 | 267,0 | 260,0 | 260,3 | | 250,0 | | 254,0 | | 275,6 | 267,0 | | | | 271,0 | 250,0 | 270,5 | 17 | 56 |
| | 2 | | | 940,0 | 997,0 | 1030 | 972,8 | 1013 | 1058 | | 1062 | 964,0 | 919,0 | 1005 | | 925,0 | | 971,0 | | 1030 | 970,0 | | | | 1000 | 1000 | 1003 | 54 | 56 |
| | 3 | | | 470,0 | 440,0 | 480,0 | 464,9 | 510,0 | 516,0 | | 475,0 | 492,0 | 476,0 | 495,3 | | 456,0 | | 461,0 | | 524,4 | 487,0 | | | | 520,0 | 500,0 | 493,5 | 36 | 56 |
| Mercury as Hg in µg/l | 1 | | | | | | 146,5 | | 1,700 | | | | | | | | | | | | | | | | | 3,000 | 2,400 | 3 | 15 |
| | 2 | | | | | | 133,4 | | 7,350 | | | | | | | | | | | | | | | | | 9,000 | 8,800 | 4 | 16 |
| | 3 | | | | | | 183,0 | | 2,150 | | | | | | | | | | | | | | | | | 6,000 | 2,500 | 3 | 15 |
| Molybdenum as Mo in µg/l | 1 | | | | 92,00 | | 80,80 | | | | 90,00 | | | 89,74 | | | | | | | | | | | 88,00 | 100,0 | 89,7 | 14 | 29 |
| | 2 | | | | 288,0 | | 304,2 | | | | 307,0 | | | 277,9 | | | | | | | | | | | 262,0 | 300,0 | 275,0 | 24 | 30 |
| | 3 | | | | 181,0 | | 223,5 | | | | 177,0 | | | 201,0 | | | | | | | | | | | 156,0 | 200,0 | 188,5 | 26 | 30 |
| Nickel as Ni in µg/l | 1 | | | 1160 | 1101 | 1140 | 1129 | 1148 | 1294 | | 1157 | 1100 | 1022 | 1144 | | | | 1013 | | 1098 | 1056 | | | | 1078 | 1100 | 1108 | 62 | 50 |
| | 2 | | | 2040 | 2194 | 2240 | 2298 | 2280 | 2452 | | 2327 | 2190 | 2259 | 2260 | | | | 1995 | | 2179 | 2055 | | | | 2173 | 2200 | 2201 | 111 | 50 |
| | 3 | | | 600,0 | 493,0 | 560,0 | 582,6 | 567,0 | 662,0 | | 576,0 | 505,0 | 550,0 | 565,9 | | | | 519,0 | | 553,5 | 504,0 | | | | 549,0 | 550,0 | 554,8 | 33 | 50 |
| Silicon as Si in µg/l | 1 | | | | 1651 | | 1688 | | 1737 | | 1685 | | 1839 | 738,5 | | | | | | | 1534 | | | | | - | 1746 | 208 | 30 |
| | 2 | | | | 1609 | | 1742 | | 1825 | | 1679 | | 1944 | 731,6 | | | | | | | 1468 | | | | | - | 1744 | 178 | 30 |
| | 3 | | | | 1646 | | 1710 | | 1792 | | 1611 | | 1999 | 730,9 | | | | | | | 1458 | | | | | - | 1691 | 184 | 30 |
| Strontium as Sr in µg/l | 1 | | | | 154,0 | | 21,50 | 169,0 | | | | | | 185,5 | | 173,0 | | | | | | | | | 147,0 | 80,00 | 176,5 | 13 | 34 |
| | 2 | | | | | | 21,70 | 322,0 | | | | | | 347,3 | | 327,0 | | | | | | | | | 276,0 | 240,0 | 330,0 | 16 | 33 |
| | 3 | | | | | | 18,90 | 243,0 | | | | | | 264,8 | | 248,0 | | | | | | | | | 186,0 | 160,0 | 255,0 | 18 | 33 |
| Vanadium as V in µg/l | 1 | | | | 77,00 | | | | | | 91,00 | | | 96,4 | | | | | | | | | | | 91,00 | 100,0 | 86,0 | 18 | 28 |
| | 2 | | | | 410,0 | | | | | | 435,0 | | | 426,9 | | | | | | | | | | | 398,0 | 400,0 | 399,5 | 39 | 28 |
| | 3 | | | | 150,0 | | | | | | 160,0 | | | 171,8 | | | | | | | | | | | 54,00 | 200,0 | 143,5 | 40 | 28 |
| Zinc as Zn in µg/l | 1 | | | 480,0 | 462,0 | 430,0 | 422,9 | 470,0 | 508,0 | | 486,0 | 500,0 | 543,0 | 407,7 | | 342,0 | | 380,0 | | 0,410 | 618,0 | | | | 447,0 | 40,00 | 460,0 | 52 | 53 |
| | 2 | | | 430,0 | 421,0 | 380,0 | 440,7 | 440,0 | 466,0 | | 442,0 | 453,0 | 467,0 | 377,7 | | 311,0 | | 360,0 | | 0,350 | 308,0 | | | | 412,0 | 120,0 | 425,5 | 43 | 54 |
| | 3 | | | 370,0 | 300,0 | 320,0 | 315,7 | 358,0 | 370,0 | | 354,0 | 372,0 | 367,0 | 272,7 | | 241,0 | | 267,0 | | 0,260 | 148,0 | | | | 325,0 | 80,00 | 326,0 | 40 | 53 |
| Arsenic as As in µg/l | 4 | | | | <0.008 | | 115,2 | | | | | | | | | | | | | | | | | | 5,000 | 3,000 | 4,415 | 3 | 12 |
| | 5 | | | | 14,90 | | 138,8 | | | | | | | | | | | | | | | | | | 16,00 | 15,00 | 14,50 | 2 | 14 |
| | 6 | | | | 7,500 | | 158,7 | | | | | | | | | | | | | | | | | | 8,000 | 9,000 | 8,835 | 1 | 12 |
| Selenium as Se in µg/l | 4 | | | | 10,50 | | 55,70 | | | | | | | | | | | | | | | | | | | 7,500 | 8,900 | 3 | 15 |
| | 5 | | | | 15,10 | | 57,50 | | | | | | | | | | | | | | | | | | | 12,50 | 15,10 | 6 | 17 |
| | 6 | | | | 7,450 | | 60,20 | | | | | | | | | | | | | | | | | | | 5,000 | 7,000 | 5 | 15 |

**TABLE A**

**ANALYTICAL RESULTS** **Okt 07**

**GROUP 1** 

| Determinand | | B129 | B130 | B131 | B132 A | B132B | B135 | B138 | B139 | B141 | B142 | B143 | B144 | B147 | B148 | B149 | B152 | B153 | Spike ug/l | Median | Robust SD | n |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium as Al in µg/l | 1 | 574,0 | | | 1082 | 1082 | 831,0 | 863,0 | | 937,0 | | 700,0 | | | 685,2 | 503,0 | | | 750,0 | 802,0 | 105 | 48 |
| | 2 | 1349 | | | 1659 | 1659 | 1695 | 1689 | | 1728 | | 1300 | | | 1423 | 1168 | | | 1500 | 1552 | 151 | 48 |
| | 3 | 150,0 | | | 392,0 | 392,0 | 226,0 | 373,0 | | 275,0 | | 300,0 | | | 262,3 | 101,0 | | | 375,0 | 257,0 | 85 | 47 |
| Barium as Ba in µg/l | 1 | 180,0 | | | 196,0 | 196,0 | 180,0 | 168,0 | | 212,0 | | | | | | 199,0 | | | 150,0 | 190,0 | 15 | 34 |
| | 2 | 489,0 | | | 506,0 | 506,0 | 432,0 | 453,0 | | 526,0 | | | | | | 497,0 | | | 450,0 | 488,0 | 27 | 34 |
| | 3 | 244,0 | | | 334,0 | 334,0 | 299,0 | 317,0 | | 368,0 | | | | | | 339,0 | | | 300,0 | 327,0 | 18 | 34 |
| Beryllium as Be in µg/l | 1 | | | | | | 45,70 | 40,60 | | | | | | | | 44,00 | | | 50,00 | 50,00 | 3 | 25 |
| | 2 | | | | | | 137,0 | 127,0 | | | | | | | | 151,0 | | | 150,0 | 150,0 | 7 | 25 |
| | 3 | | | | | | 83,90 | 83,70 | | | | | | | | 89,00 | | | 100,0 | 81,79 | 14 | 25 |
| Boron as B µg/l | 1 | 382,0 | | | 140,0 | 140,0 | | 405,0 | | | | | | | | 559,0 | | | 500,0 | 541,0 | 53 | 29 |
| | 2 | 1699 | | | 2061 | 2061 | 2176 | 1590 | | | | | | | | 2075 | | | 2000 | 2005 | 162 | 30 |
| | 3 | 781,0 | | | 1063 | 1063 | 1065 | 813,0 | | | | | | | | 1048 | | | 1000 | 1038 | 83 | 30 |
| Cadmium as Cd in µg/l | 1 | 84,00 | | 160,0 | 140,0 | 130,0 | 127,0 | 104,0 | | | | | | | 113,6 | 126,0 | | | 125,0 | 126,0 | 13 | 51 |
| | 2 | 374,0 | | 480,0 | 523,0 | 498,0 | 472,0 | 415,0 | | | | | | | 492,8 | 505,0 | | | 500,0 | 502,0 | 33 | 51 |
| | 3 | 126,0 | | 250,0 | 217,0 | 243,0 | 236,0 | 214,0 | | | | | | | 237,9 | 250,0 | | | 250,0 | 241,0 | 19 | 51 |
| Chromium as Cr in µg/l | 1 | 804,0 | | | 1184 | 1244 | 1110 | 1131 | | 1277 | | | | | 1169 | 1363 | | | 1200 | 1191 | 52 | 51 |
| | 2 | 1861 | | | 2469 | 2632 | 2190 | 2330 | | 2589 | | | | | 2370 | 2606 | | | 2400 | 2413 | 99 | 51 |
| | 3 | 60,00 | | | 394,0 | 537,0 | 481,0 | 501,0 | | 416,0 | | | | | 448,0 | 630,0 | | | 600,0 | 397,0 | 103 | 51 |
| Cobalt as Co in µg/l | 1 | | | | 412,0 | 380,0 | 373,0 | 354,0 | | | | | | | 384,7 | 370,0 | | | 400,0 | 397,0 | 18 | 48 |
| | 2 | | | | 825,0 | 755,0 | 694,0 | 826,0 | | | | | | | 776,1 | 758,0 | | | 800,0 | 797,0 | 39 | 48 |
| | 3 | | | | 200,0 | 181,0 | 180,0 | 164,0 | | | | | | | 193,3 | 192,0 | | | 200,0 | 195,0 | 10 | 48 |
| Copper as Cu in µg/l | 1 | 225,0 | | 260,0 | 331,0 | 312,0 | 302,0 | 270,0 | | 353,0 | | | | | 302,2 | 319,0 | | | 300,0 | 322,0 | 24 | 54 |
| | 2 | 952,0 | | 1230 | 1265 | 1142 | 1070 | 981,0 | | 1369 | | | | | 1152 | 1205 | | | 1200 | 1205 | 62 | 53 |
| | 3 | 119,0 | | 500,0 | 368,0 | 533,0 | 517,0 | 420,0 | | 411,0 | | | | | 564,7 | 581,0 | | | 600,0 | 490,0 | 117 | 53 |
| Iron as Fe in µg/l | 1 | 642,0 | | 850,0 | 1180 | 1180 | 936,0 | 1201 | | 1160 | | 900,0 | | | 1088 | | | | 1250 | 1099 | 147 | 53 |
| | 2 | 1752 | | 1960 | 2460 | 2460 | 2400 | 2471 | | 2725 | | 2000 | | | 2443 | 2617 | | | 2500 | 2471 | 120 | 54 |
| | 3 | 33,00 | | 420,0 | 540,0 | 540,0 | 434,0 | 620,0 | | 482,0 | | 380,0 | | | 510,4 | 701,0 | | | 625,0 | 438,5 | 94 | 54 |
| Lead as Pb in µg/l | 1 | 86,00 | | | 163,0 | 189,0 | 153,0 | 155,0 | | 130,0 | | | | | 147,3 | 148,0 | | | 150,0 | 154,0 | 30 | 50 |
| | 2 | 457,0 | | | 605,0 | 661,0 | 527,0 | 567,0 | | 611,0 | | | | | 564,0 | 522,0 | | | 600,0 | 586,0 | 45 | 50 |
| | 3 | 10,00 | | | 202,0 | 267,0 | 244,0 | 143,0 | | 183,0 | | | | | 226,4 | 230,0 | | | 300,0 | 192,5 | 65 | 50 |
| Manganese as Mn in µg/l | 1 | 201,0 | | 210,0 | 280,0 | 280,0 | 271,0 | 281,0 | | 291,0 | | 270,0 | | | 241,6 | 301,0 | | | 250,0 | 270,5 | 17 | 56 |
| | 2 | 798,0 | | 850,0 | 990,0 | 990,0 | 959,0 | 1022 | | 1071,0 | | 890,0 | | | 909,9 | 1021 | | | 1000 | 1003 | 54 | 56 |
| | 3 | 319,0 | | 420,0 | 470,0 | 470,0 | 452,0 | 525,0 | | 536,0 | | 470,0 | | | 457,0 | 514,0 | | | 500,0 | 493,5 | 36 | 56 |
| Mercury as Hg in µg/l | 1 | | | | | | 2,610 | 1,500 | | | | | | | | | | | 3,000 | 2,400 | 3 | 15 |
| | 2 | | | | | | 11,40 | 6,500 | | | | | | | | | | | 9,000 | 8,800 | 4 | 16 |
| | 3 | | | | | | 3,220 | 0,870 | | | | | | | | | | | 6,000 | 2,500 | 3 | 15 |
| Molybdenum as Mo in µg/l | 1 | | | | 101,0 | 101,0 | 93,70 | 81,00 | | 90,30 | | | | | | | | | 100,0 | 89,7 | 14 | 29 |
| | 2 | | | | 302,0 | 302,0 | 265,0 | 259,0 | | 300,0 | | | | | | 272,0 | | | 300,0 | 275,0 | 24 | 30 |
| | 3 | | | | 227,0 | 227,0 | 171,0 | 190,0 | | 201,0 | | | | | | 178,0 | | | 200,0 | 188,5 | 26 | 30 |
| Nickel as Ni in µg/l | 1 | 829,0 | | | 1123 | 1124 | 1060 | 912,0 | | | | | | | 1084 | 1116 | | | 1100 | 1108 | 62 | 50 |
| | 2 | 1731 | | | 2272 | 2053 | 1950 | 1904 | | | | | | | 2152 | 2142 | | | 2200 | 2201 | 111 | 50 |
| | 3 | 327,0 | | | 571,0 | 563,0 | 503,0 | 467,0 | | | | | | | 545,7 | 530,0 | | | 550,0 | 554,8 | 33 | 50 |
| Silicon as Si in µg/l | 1 | 1087 | | | 1900 | 1900 | 2104 | | | 1835 | | | | | | | | | - | 1746 | 208 | 30 |
| | 2 | 1052 | | | 2400 | 2400 | 2102 | | | 1759 | | | | | | | | | - | 1744 | 178 | 30 |
| | 3 | 1034 | | | 1500 | 1500 | 2076 | | | 1756 | | | | | | | | | - | 1691 | 184 | 30 |
| Strontium as Sr in µg/l | 1 | 151,0 | | | 177,0 | 177,0 | 176,0 | 158,0 | | 188,0 | | | | | | 172,0 | | | 80,00 | 176,5 | 13 | 34 |
| | 2 | 299,0 | | | 322,0 | 322,0 | 308,0 | 319,0 | | 350,0 | | | | | | 329,0 | | | 240,0 | 330,0 | 16 | 33 |
| | 3 | 188,0 | | | 240,0 | 240,0 | 234,0 | 244,0 | | 269,0 | | | | | | 241,0 | | | 160,0 | 255,0 | 18 | 33 |
| Vanadium as V in µg/l | 1 | | | | 155,0 | 155,0 | 94,80 | 76,00 | | | | | | | | | | | 100,0 | 86,0 | 18 | 28 |
| | 2 | | | | 480,0 | 480,0 | 364,0 | 488,0 | | | | | | | | 301,0 | | | 400,0 | 399,5 | 39 | 28 |
| | 3 | | | | 227,0 | 227,0 | 169,0 | 170,0 | | | | | | | | 120,0 | | | 200,0 | 143,5 | 40 | 28 |
| Zinc as Zn in µg/l | 1 | 406,0 | | 360,0 | 498,0 | 460,0 | 353,0 | 444,0 | | 493,0 | | 380,0 | | | 441,7 | 502,0 | | | 40,00 | 460,0 | 52 | 53 |
| | 2 | 344,0 | | 370,0 | 420,0 | 428,0 | 311,0 | 405,0 | | 451,0 | | 360,0 | | | 399,1 | 454,0 | | | 120,0 | 425,5 | 43 | 54 |
| | 3 | 274,0 | | 280,0 | 321,0 | 336,0 | 254,0 | 329,0 | | 356,0 | | 280,0 | | | 334,4 | 375,0 | | | 80,00 | 326,0 | 40 | 53 |
| Arsenic as As in µg/l | 4 | | | | | | 3,830 | 3,100 | | | | | | | | | | | 3,000 | 4,415 | 3 | 12 |
| | 5 | | | | | | 14,10 | 13,00 | | | | | | | | | | | 15,00 | 14,50 | 2 | 14 |
| | 6 | | | | | | | 8,000 | | | | | | | | | | | 9,000 | 8,835 | 1 | 12 |
| Selenium as Se in µg/l | 4 | | | | | | 9,310 | 3,200 | | | | | | | | 7,000 | | | 7,500 | 8,900 | 3 | 15 |
| | 5 | | | | | | 14,30 | 9,300 | | | | | | | | 12,00 | | | 12,50 | 15,10 | 6 | 17 |
| | 6 | | | | | | | 2,200 | | | | | | | | 5,000 | | | 5,000 | 7,000 | 5 | 15 |

**SOUTH AFRICAN BUREAU OF STANDARDS - WATER-CHECK PROGRAMME**
**TABLE B**

**Z-SCORE VALUES** **Okt 07**
**GROUP 1**

**Gr 1 (cont)** 

| Determinand | | B1 | B3 | B5 | B7 | B8 | B9A | B9B | B10 | B11A | B11B | B14 | B16 | B16a | B19 | B21A | B21B | B22 | B23 | B25 | B30 | B31 | B33 | B34 | B36 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium as Al in µg/l | 1 | - | - | -0,76 | - | -0,10 | 0,01 | - | 0,05 | 0,53 | - | 0,08 | - | - | -2,03 | 1,85 | 1,50 | -0,48 | 0,65 | 0,67 | -2,19 | -0,19 | - | - | 0,02 |
| | 2 | - | - | -0,19 | - | 0,20 | -0,67 | - | -0,19 | 0,93 | - | -1,00 | - | - | -1,14 | 2,97 | 2,04 | -0,34 | -0,21 | 0,32 | -1,36 | -0,24 | - | - | 0,15 |
| | 3 | - | - | -0,54 | - | -0,64 | 0,99 | - | -0,04 | 0,19 | - | -2,69 | - | - | -2,92 | 1,23 | 1,44 | -2,59 | -0,73 | -0,25 | - | 1,17 | - | - | -0,49 |
| Barium as Ba in µg/l | 1 | -0,91 | - | 0,67 | - | -1,55 | 16,45 | - | 2,02 | 1,82 | - | -0,34 | - | - | -1,35 | 6,47 | - | -2,97 | - | 0,07 | - | 0,13 | - | - | -0,34 |
| | 2 | 0,92 | - | 0,94 | - | -0,75 | -0,67 | - | 2,29 | 2,66 | - | 0,07 | - | - | -0,67 | 10,71 | - | -2,02 | - | 0,04 | - | -0,19 | - | - | 0,11 |
| | 3 | -0,03 | - | 0,96 | - | -0,73 | -2,02 | - | -1,12 | 3,43 | - | 0,45 | - | - | -0,39 | 11,13 | - | -1,35 | - | 0,00 | - | 0,51 | - | - | 0,00 |
| Beryllium as Be in µg/l | 1 | -4,72 | - | -0,34 | - | 0,00 | 20,23 | - | 0,34 | 0,67 | - | 0,67 | - | - | 0,00 | 1,01 | -1,01 | -5,39 | 0,00 | 0,34 | - | - | - | - | - |
| | 2 | -1,42 | - | -0,13 | - | 0,40 | -4,86 | - | -0,13 | 0,81 | - | 0,67 | - | - | 0,00 | 5,39 | 4,32 | -4,05 | 0,00 | 0,54 | - | - | - | - | - |
| | 3 | 0,67 | - | -1,45 | - | 0,67 | -0,31 | - | -1,67 | 0,82 | - | -0,13 | - | - | -0,86 | 2,21 | 1,04 | -2,62 | 0,60 | -0,57 | - | - | - | - | - |
| Boron as B µg/l | 1 | -2,16 | - | 0,36 | - | 0,94 | 17,59 | - | 0,51 | 0,66 | - | 0,17 | - | - | -3,95 | 4,40 | 4,16 | -0,67 | - | 0,58 | - | 0,47 | - | - | - |
| | 2 | 0,43 | - | 0,53 | - | 0,04 | -3,10 | - | 0,12 | 0,80 | - | -0,03 | - | - | -4,10 | 4,66 | 3,18 | -3,91 | - | 0,03 | - | 0,04 | - | - | - |
| | 3 | 0,20 | - | 0,59 | - | 0,12 | -1,57 | - | 0,25 | 0,84 | - | -0,46 | - | - | -3,47 | 4,50 | 4,00 | -1,34 | - | 0,39 | - | -0,06 | - | - | - |
| Cadmium as Cd in µg/l | 1 | 0,86 | - | -0,67 | - | -0,82 | 26,37 | - | 1,42 | 0,52 | - | 1,05 | - | - | -1,20 | 2,10 | 2,17 | -0,22 | -0,07 | -0,07 | -0,67 | 0,00 | -0,45 | - | -0,45 |
| | 2 | 1,56 | - | 0,46 | - | -0,40 | -8,83 | - | 2,30 | 0,92 | - | 1,16 | - | - | -0,06 | 4,54 | 3,80 | -0,80 | -0,06 | 0,06 | 0,00 | 0,00 | -0,98 | - | -0,40 |
| | 3 | 1,17 | - | -0,57 | - | -0,36 | -7,26 | - | -0,52 | 1,24 | - | 2,02 | - | - | -0,05 | 4,10 | 3,73 | -0,67 | -0,05 | -0,41 | 0,07 | 0,57 | -0,57 | - | 0,26 |
| Chromium as Cr in µg/l | 1 | -2,52 | - | 1,10 | 1,48 | -0,67 | 33,12 | - | 0,33 | -0,69 | - | 0,17 | - | - | -1,75 | 7,71 | 7,51 | -1,70 | -0,02 | 0,37 | -0,04 | 0,23 | -1,37 | - | -0,33 |
| | 2 | -3,05 | - | 0,83 | 2,63 | -0,56 | -20,60 | - | 0,85 | -0,64 | - | 0,88 | - | - | -0,13 | 8,94 | 7,69 | -0,86 | -0,08 | 0,37 | 0,05 | 0,00 | -0,94 | - | -0,28 |
| | 3 | 0,53 | - | 0,15 | 1,14 | -0,80 | 8,54 | - | 0,26 | 0,00 | - | -3,26 | - | - | -0,55 | 1,11 | 2,07 | -3,55 | -0,12 | -0,53 | -0,67 | 1,48 | -0,26 | - | -1,06 |
| Cobalt as Co in µg/l | 1 | 0,28 | - | -1,11 | - | -0,94 | -1,55 | - | 0,44 | -0,67 | - | 2,94 | - | - | -0,94 | 8,16 | 7,60 | -0,61 | 0,72 | -0,28 | 2,24 | -0,11 | -1,50 | - | 0,06 |
| | 2 | 0,04 | - | 0,00 | - | -0,67 | -0,91 | - | 0,10 | -0,73 | - | 1,37 | - | - | -0,44 | 7,39 | 6,82 | -0,73 | -0,96 | -0,03 | 1,50 | 0,08 | -1,48 | - | 0,00 |
| | 3 | 0,05 | - | -2,60 | - | -1,06 | -6,65 | - | 0,48 | -0,29 | - | 2,41 | - | - | -0,48 | 4,33 | 4,82 | 0,10 | 0,00 | -0,67 | 1,49 | -0,10 | -0,48 | - | 0,48 |
| Copper as Cu in µg/l | 1 | 2,40 | -0,46 | -0,21 | - | -0,67 | 23,69 | - | 0,59 | 0,25 | - | 1,18 | - | - | -1,35 | 4,43 | 3,71 | 0,08 | -0,08 | 1,56 | 1,28 | -0,67 | -1,35 | - | 0,08 |
| | 2 | -0,32 | - | 1,33 | - | 0,02 | -7,61 | - | -0,03 | 0,67 | - | -0,08 | - | - | -0,08 | 7,03 | 5,91 | -1,00 | -0,56 | 1,36 | 2,84 | -0,14 | -1,85 | - | 0,00 |
| | 3 | 0,35 | - | -0,87 | - | 0,52 | 0,23 | - | -1,08 | 0,28 | - | 0,26 | - | - | 0,17 | 2,60 | 2,42 | -1,58 | 0,21 | -0,55 | 0,95 | 0,85 | -0,94 | - | -0,22 |
| Iron as Fe in µg/l | 1 | - | -0,61 | 0,37 | - | -0,09 | 7,16 | - | 0,49 | 0,20 | - | 1,37 | - | - | -2,99 | 2,67 | - | -1,08 | 0,14 | -0,20 | 0,00 | 1,27 | -0,47 | - | 0,08 |
| | 2 | - | 0,63 | 2,53 | - | 0,01 | -9,24 | - | 1,31 | 1,19 | - | 1,08 | - | - | -6,16 | 7,68 | - | -1,48 | -0,50 | 1,58 | 2,12 | 0,41 | -1,09 | - | 0,58 |
| | 3 | - | -0,18 | 0,01 | - | -1,07 | 5,86 | - | 0,17 | 0,45 | - | -4,36 | - | - | -3,08 | 0,71 | - | -4,29 | 0,28 | 0,02 | -0,67 | 2,37 | -0,68 | - | -0,24 |
| Lead as Pb in µg/l | 1 | 8,57 | - | -0,99 | - | 0,49 | 17,14 | - | -1,48 | 0,23 | - | -0,13 | - | - | -1,12 | 1,25 | - | -1,02 | 0,69 | -0,13 | - | 0,49 | 0,53 | - | 0,07 |
| | 2 | 5,79 | - | 0,40 | - | 0,84 | -7,32 | - | -0,69 | 0,64 | - | 0,66 | - | - | -2,12 | 3,98 | - | -1,33 | -1,46 | -0,09 | - | 0,38 | -1,90 | - | -0,20 |
| | 3 | 4,75 | - | -0,12 | - | 0,22 | 0,01 | - | 0,05 | 0,10 | - | -2,74 | - | - | -0,04 | 1,90 | - | -2,61 | 0,58 | -0,40 | - | 1,54 | -0,81 | - | -0,47 |
| Manganese as Mn in µg/l | 1 | -1,32 | 0,62 | -1,43 | -2,72 | -1,38 | 34,22 | - | 0,68 | 0,56 | - | 1,15 | - | - | -1,79 | 4,43 | 3,61 | 0,03 | -0,61 | 0,91 | 0,54 | 0,03 | - | - | 0,44 |
| | 2 | 0,14 | 1,28 | 0,66 | 1,88 | -0,36 | -10,98 | - | 0,69 | 0,86 | - | -0,05 | - | - | -0,23 | 5,64 | 5,57 | -1,15 | -0,42 | 1,06 | 0,43 | 0,23 | - | - | 0,40 |
| | 3 | -0,28 | 0,81 | -0,12 | 0,37 | -0,34 | -7,72 | - | 1,58 | 1,00 | - | 1,83 | - | - | 0,18 | 4,33 | 4,44 | -0,65 | 0,04 | 1,03 | 0,70 | 0,48 | - | - | 0,70 |
| Mercury as Hg in µg/l | 1 | - | -0,16 | - | - | - | 1,16 | - | -0,32 | - | - | -0,52 | - | - | -0,77 | - | - | 0,00 | - | 2,44 | - | - | -0,68 | - | - |
| | 2 | 1,29 | -0,28 | - | - | - | -0,77 | - | -0,33 | - | - | -2,00 | - | - | -2,42 | - | - | 0,28 | - | 1,71 | - | - | 0,53 | - | - |
| | 3 | - | 1,98 | - | - | - | 1,10 | - | 0,00 | - | - | -0,49 | - | - | -0,78 | - | - | -0,19 | - | 1,41 | - | - | -0,67 | - | - |
| Molybdenum as Mo in µg/l | 1 | 4,07 | - | -1,09 | - | -0,47 | 6,87 | - | - | 0,57 | - | -0,67 | - | - | -0,67 | 1,13 | - | -1,02 | - | -1,44 | -2,56 | 0,64 | - | - | - |
| | 2 | 1,18 | - | -0,34 | - | 0,00 | 6,32 | - | - | 1,31 | - | 0,63 | - | - | -1,05 | 4,30 | - | -1,05 | - | -0,51 | -1,15 | 0,51 | - | - | - |
| | 3 | 2,40 | - | -0,06 | - | -1,00 | 4,44 | - | - | 0,41 | - | -1,50 | - | - | -0,33 | 0,21 | - | -5,61 | - | 0,21 | -0,66 | 0,41 | - | - | - |
| Nickel as Ni in µg/l | 1 | -0,84 | - | -0,70 | - | -0,63 | 1,16 | - | -0,22 | 0,73 | - | 9,51 | - | - | -0,60 | 5,68 | 5,90 | -0,63 | 0,76 | -0,76 | 0,78 | -0,22 | -0,76 | - | 0,09 |
| | 2 | -1,58 | - | 1,22 | - | -0,46 | 0,89 | - | 0,01 | 0,84 | - | 11,68 | - | - | -0,10 | 6,86 | 6,71 | -0,49 | 0,13 | -0,01 | 0,79 | -0,11 | -0,46 | - | 0,27 |
| | 3 | -1,54 | - | -0,72 | - | -0,78 | 0,37 | - | 0,67 | 0,67 | - | 10,47 | - | - | -0,14 | 5,43 | 5,25 | -0,45 | 2,28 | 0,04 | 0,55 | -0,17 | 0,46 | - | -0,05 |
| Silicon as Si in µg/l | 1 | - | 0,69 | 1,00 | - | 0,66 | -0,41 | - | 0,17 | - | - | 0,74 | - | - | -2,86 | 2,31 | - | 1,60 | 0,04 | 0,98 | - | -0,12 | - | - | - |
| | 2 | - | 0,90 | 0,01 | - | 0,26 | -1,35 | - | 0,01 | - | - | 0,32 | - | - | -3,45 | 2,63 | - | 1,46 | -0,24 | 0,37 | - | -0,26 | - | - | - |
| | 3 | - | 0,89 | 7,83 | - | 0,58 | -0,82 | - | 0,01 | - | - | 0,59 | - | - | -3,05 | 2,77 | - | 1,68 | -0,01 | 0,76 | - | 0,04 | - | - | - |
| Strontium as Sr in µg/l | 1 | 0,66 | - | 0,12 | - | -0,19 | 11,21 | - | -1,97 | 1,97 | - | -2,04 | - | - | -1,27 | 4,05 | 4,59 | -0,12 | - | 0,58 | - | 0,12 | - | - | 0,04 |
| | 2 | 1,41 | - | 1,04 | - | -0,18 | 0,49 | - | -0,31 | 3,07 | - | -3,07 | - | - | 0,00 | 6,93 | 7,42 | 2,51 | - | 0,55 | - | 0,00 | - | - | 0,00 |
| | 3 | 0,56 | - | 0,51 | - | -0,22 | -0,62 | - | 0,17 | 2,08 | - | -1,69 | - | - | -0,28 | 4,44 | 3,60 | 2,14 | - | 0,34 | - | 0,00 | - | - | -0,17 |
| Vanadium as V in µg/l | 1 | 1,19 | - | 0,26 | - | -0,66 | 16,06 | - | -1,52 | 0,33 | - | 0,26 | - | - | -1,06 | 1,85 | 1,92 | -0,26 | - | -1,06 | - | 0,59 | - | - | - |
| | 2 | -0,24 | - | -0,40 | - | 0,05 | -3,71 | - | -0,34 | 0,92 | - | 0,88 | - | - | -0,40 | 4,83 | - | -0,27 | - | 0,40 | - | -0,14 | - | - | - |
| | 3 | 0,84 | - | 0,21 | - | -0,89 | -0,86 | - | -0,01 | 0,29 | - | -2,91 | - | - | -0,59 | 0,69 | - | -2,78 | - | -0,39 | - | 1,19 | - | - | - |
| Zinc as Zn in µg/l | 1 | 1,55 | 0,27 | -0,69 | - | -0,15 | 0,40 | - | -0,12 | 0,06 | - | 1,54 | - | - | -0,39 | 3,22 | - | 0,77 | -0,67 | 2,16 | -0,83 | 0,17 | -0,96 | - | -0,06 |
| | 2 | 1,87 | 0,56 | -0,88 | - | -0,02 | -0,14 | - | -0,51 | -0,33 | - | 1,30 | - | - | -0,33 | 3,02 | 2,84 | 1,40 | -0,67 | 1,26 | -0,95 | 0,19 | -1,14 | - | 0,12 |
| | 3 | -0,42 | - | -1,22 | - | 0,02 | -0,07 | - | 0,00 | 0,65 | - | 1,60 | - | - | 0,35 | 3,05 | 2,50 | -0,15 | -0,27 | 0,90 | -0,44 | 0,67 | -0,65 | - | 0,35 |
| Arsenic as As in µg/l | 4 | - | -0,80 | - | - | - | 0,20 | - | - | - | - | 0,51 | - | - | - | - | - | -1,18 | - | 2,28 | - | - | - | - | - |
| | 5 | - | 0,22 | - | - | - | 1,57 | - | - | - | - | -0,22 | - | - | 2,47 | - | - | -1,12 | - | 4,72 | - | - | - | - | - |
| | 6 | - | -0,43 | - | - | - | 1,46 | - | - | - | - | 0,18 | - | - | 0,79 | - | - | -2,59 | - | 4,83 | - | - | - | - | - |
| Selenium as Se in µg/l | 4 | 39,78 | -0,35 | - | - | - | 0,39 | - | -0,25 | - | - | 0,00 | - | - | - | - | - | -0,85 | - | 3,23 | - | - | - | - | - |
| | 5 | 14,19 | -0,34 | - | - | - | 0,14 | - | 0,24 | - | - | -0,34 | - | - | 0,79 | - | - | -0,67 | - | 0,79 | - | - | - | - | - |
| | 6 | 15,67 | -0,27 | - | - | - | 0,00 | - | 1,66 | - | - | 0,16 | - | - | 4,19 | - | - | -0,67 | - | 0,73 | - | - | - | - | - |

## SOUTH AFRICAN BUREAU OF STANDARDS - WATER-CHECK PROGRAMME
## TABLE B

## Z-SCORE VALUES Okt 07
## GROUP 1



| Determinand | | B38 | B39 | B41 | B42 | B45 | B49 | B49B | B63 | B68 | B69A | B69B | B69C | B70 | B71 | B73 | B74 | B76 | B78 | B79 | B81 | B86 | B88 | B91 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium as Al in µg/l | 1 | -1,45 | 0,66 | - | -0,46 | - | 1,32 | 0,97 | -0,21 | -0,05 | 0,54 | - | - | - | -0,47 | 0,58 | -4,29 | 0,84 | - | - | - | -0,75 | - | - |
| | 2 | -1,47 | 1,83 | - | 6,39 | - | -0,67 | 1,37 | -0,11 | -0,24 | 0,55 | - | - | - | -0,36 | 1,72 | -0,41 | 1,64 | - | - | - | -0,62 | - | - |
| | 3 | 0,51 | -1,28 | - | -2,69 | - | 2,52 | 0,04 | -0,39 | 0,65 | 0,19 | - | - | - | -0,99 | -1,66 | 0,71 | 0,15 | - | - | - | -0,69 | - | - |
| Barium as Ba in µg/l | 1 | - | -0,94 | - | 0,00 | - | - | -2,36 | - | 0,67 | 0,07 | - | - | - | -0,24 | 1,15 | 0,00 | 0,67 | - | - | - | - | - | - |
| | 2 | - | -0,19 | - | -0,04 | - | - | -0,71 | - | -0,30 | -0,60 | - | - | - | -0,50 | 1,16 | 0,07 | 0,82 | - | - | - | - | - | - |
| | 3 | - | -1,24 | - | 0,67 | - | - | -1,24 | - | 0,56 | -0,28 | - | - | - | 0,08 | 1,01 | 0,22 | 1,29 | - | - | - | - | - | - |
| Beryllium as Be in µg/l | 1 | - | - | - | -0,67 | - | - | -2,36 | 0,00 | -2,36 | - | - | - | - | -0,01 | - | - | - | - | - | - | - | - | - |
| | 2 | - | - | - | -0,54 | - | - | 2,43 | 0,00 | -2,29 | - | - | - | - | 0,15 | - | | | - | - | - | - | - | - |
| | 3 | - | - | - | -2,33 | - | - | -2,25 | -1,38 | -0,13 | - | - | - | - | 0,00 | - | - | - | - | - | - | - | - | - |
| Boron as B µg/l | 1 | - | - | - | -0,43 | - | - | 1,09 | - | - | - | - | - | - | -0,09 | - | -5,24 | 1,48 | - | - | - | - | - | - |
| | 2 | - | - | - | -0,84 | - | - | -0,17 | - | - | - | - | - | - | -1,07 | - | -1,20 | 1,39 | - | - | - | - | - | - |
| | 3 | - | - | - | -0,54 | - | - | 0,25 | - | - | - | - | - | - | -1,14 | - | -1,26 | 1,47 | - | - | - | - | - | - |
| Cadmium as Cd in µg/l | 1 | - | 1,05 | - | 0,15 | - | -0,45 | -0,97 | -0,07 | -1,20 | 0,15 | - | - | - | -1,05 | 0,67 | -1,27 | 1,05 | - | - | - | -0,30 | - | - |
| | 2 | - | 3,03 | - | -0,18 | - | -0,06 | 0,21 | -0,06 | -1,50 | 0,00 | - | - | - | -1,01 | 0,25 | -1,93 | 1,16 | - | - | - | -9,41 | - | - |
| | 3 | - | 0,57 | - | 0,62 | - | -0,05 | -2,13 | -3,63 | -1,04 | 0,21 | - | - | - | -1,24 | 1,24 | -1,82 | 0,99 | - | - | - | 0,00 | - | - |
| Chromium as Cr in µg/l | 1 | - | 0,89 | - | -0,08 | - | 4,22 | 0,52 | -0,60 | -0,08 | -0,56 | - | - | - | 0,00 | 0,48 | -2,14 | -0,02 | - | - | - | -1,16 | - | - |
| | 2 | - | 1,71 | - | -0,25 | - | 5,81 | 0,76 | -0,11 | 0,51 | -0,28 | - | - | - | 0,31 | 0,84 | -2,24 | 0,67 | - | - | - | -0,65 | - | - |
| | 3 | - | -1,18 | - | -3,58 | - | 0,80 | -0,13 | -0,25 | 0,35 | -0,18 | - | - | - | -0,65 | -1,53 | 0,35 | -0,45 | - | - | - | -0,74 | - | - |
| Cobalt as Co in µg/l | 1 | - | 3,77 | - | 0,00 | - | -2,61 | 0,22 | -0,11 | 0,00 | 0,39 | - | - | - | 0,59 | 0,94 | -1,50 | 1,28 | - | - | - | -0,61 | - | - |
| | 2 | - | 4,82 | - | -0,18 | - | -2,00 | 0,08 | -0,47 | -0,52 | 0,18 | - | - | - | 0,20 | 0,83 | -2,10 | 1,37 | - | - | - | -0,75 | - | - |
| | 3 | - | 4,14 | - | 0,29 | - | -5,30 | -0,19 | -0,67 | 2,02 | 0,29 | - | - | - | 0,48 | 2,12 | -2,50 | 1,44 | - | - | - | 0,00 | - | - |
| Copper as Cu in µg/l | 1 | - | -0,76 | - | -0,04 | - | 0,34 | 0,04 | -0,55 | 0,80 | 0,08 | - | - | - | 1,26 | 1,01 | -1,39 | 0,34 | - | - | - | 0,42 | - | - |
| | 2 | - | 1,28 | - | -0,27 | - | -0,40 | 0,71 | 0,08 | -0,42 | 0,19 | - | - | - | 2,09 | 1,12 | -1,36 | 1,04 | - | - | - | 1,14 | - | - |
| | 3 | - | -2,01 | - | -1,38 | - | -0,77 | -1,29 | -1,28 | 0,78 | -0,35 | - | - | - | -0,23 | 0,53 | -0,46 | 0,68 | - | - | - | -0,42 | - | - |
| Iron as Fe in µg/l | 1 | 1,03 | -1,55 | - | 1,23 | - | 0,01 | 0,07 | -1,62 | 0,84 | -0,65 | - | - | - | -1,06 | -0,65 | -1,15 | -0,95 | - | - | - | -0,63 | - | - |
| | 2 | 0,58 | 1,09 | - | -1,58 | - | -0,17 | 0,02 | -0,72 | 0,77 | 0,60 | - | - | - | -0,13 | -2,12 | -2,00 | 0,83 | - | - | - | 0,24 | - | - |
| | 3 | 2,47 | -2,56 | - | -4,43 | - | 0,66 | -0,14 | -0,14 | 2,35 | -0,51 | - | - | - | -0,31 | -1,34 | -0,01 | -2,01 | - | - | - | -0,75 | - | - |
| Lead as Pb in µg/l | 1 | - | -1,02 | - | -1,48 | - | 1,18 | 0,26 | -1,84 | 0,82 | 0,00 | - | - | - | 0,23 | -2,07 | -1,64 | -0,13 | - | - | - | -0,56 | - | - |
| | 2 | - | 0,86 | - | 2,26 | - | 0,09 | 0,57 | -0,20 | 0,49 | 0,15 | - | - | - | 0,18 | -1,35 | -3,18 | -0,13 | - | - | - | -0,46 | - | - |
| | 3 | - | -1,08 | - | -2,67 | - | 0,58 | -0,35 | -0,07 | 1,02 | -0,01 | - | - | - | -2,63 | -1,19 | -1,33 | 0,12 | - | - | - | -0,41 | - | - |
| Manganese as Mn in µg/l | 1 | -1,20 | 0,97 | - | -0,09 | - | -0,61 | 1,09 | 0,09 | -10,58 | -0,20 | - | - | - | 0,03 | 1,03 | -1,43 | 0,56 | - | - | - | -0,67 | - | - |
| | 2 | -1,34 | 2,00 | - | -0,06 | - | 0,14 | 1,14 | -0,53 | -2,84 | 0,14 | - | - | - | 0,05 | 0,90 | -1,56 | 1,25 | - | - | - | -0,58 | - | - |
| | 3 | -0,37 | 1,25 | - | 0,32 | - | -0,10 | 0,81 | -0,26 | -5,24 | 0,04 | - | - | - | 0,42 | 1,25 | -1,03 | 1,00 | - | - | - | -0,26 | - | - |
| Mercury as Hg in µg/l | 1 | - | 1,80 | - | - | - | - | 15,28 | - | - | - | - | - | - | - | - | - | - | - | - | - | 0,67 | - | - |
| | 2 | - | 0,33 | - | - | - | - | 11,34 | - | - | - | - | - | - | | - | - | - | - | - | - | -0,36 | - | - |
| | 3 | - | 1,10 | - | - | - | - | 14,90 | - | - | - | - | - | - | - | - | - | - | - | - | - | -0,31 | - | - |
| Molybdenum as Mo in µg/l | 1 | - | -5,73 | - | | - | - | -2,27 | 0,92 | 2,99 | - | - | - | - | 0,16 | - | -0,88 | - | - | - | - | -0,54 | - | - |
| | 2 | - | -10,58 | - | | - | - | -0,67 | 0,00 | 1,26 | - | - | - | - | -0,32 | - | -0,21 | - | - | - | - | -0,08 | - | - |
| | 3 | - | -6,63 | - | - | - | - | -1,11 | 1,19 | 1,54 | - | - | - | - | -1,04 | - | -0,41 | - | - | - | - | 0,14 | - | - |
| Nickel as Ni in µg/l | 1 | - | 1,44 | - | -0,09 | - | -0,76 | 0,65 | -0,35 | -0,60 | 0,22 | - | - | - | 0,20 | 0,81 | -1,57 | 0,84 | - | - | - | 0,46 | - | - |
| | 2 | - | 2,24 | - | -0,17 | - | -0,91 | 0,77 | -0,04 | -0,24 | 0,28 | - | - | - | 0,44 | 1,00 | -1,63 | 1,25 | - | - | - | 0,18 | - | - |
| | 3 | - | 1,07 | - | -0,27 | - | -0,75 | 0,25 | -1,57 | -0,87 | -0,17 | - | - | - | 0,26 | 1,19 | -1,78 | 0,16 | - | - | - | 0,52 | - | - |
| Silicon as Si in µg/l | 1 | - | -0,43 | - | -0,46 | - | - | 0,72 | - | -0,40 | - | - | - | - | -0,38 | - | -4,19 | - | - | - | - | - | - | - |
| | 2 | - | -0,47 | - | -0,71 | - | - | 0,56 | - | -0,83 | - | - | - | - | -0,53 | - | -0,64 | - | - | - | - | - | - | - |
| | 3 | - | -0,46 | - | -0,48 | - | - | 0,90 | - | -0,23 | - | - | - | - | -0,35 | - | -0,28 | - | - | - | - | - | - | - |
| Strontium as Sr in µg/l | 1 | - | -0,89 | - | 0,35 | - | - | -2,12 | 0,35 | 2,81 | 0,19 | - | - | - | -0,08 | - | - | - | - | - | - | - | - | - |
| | 2 | - | 1,16 | - | -0,18 | - | - | -0,86 | 0,31 | 2,94 | -0,25 | - | - | - | 0,06 | - | - | - | - | - | - | - | - | - |
| | 3 | - | 1,12 | - | 0,11 | - | - | 1,18 | 0,00 | 2,42 | -0,28 | - | - | - | 0,11 | - | - | - | - | - | - | - | - | - |
| Vanadium as V in µg/l | 1 | - | -1,19 | - | -0,26 | - | - | -4,03 | -0,93 | - | - | - | - | - | -0,48 | - | -1,52 | - | - | - | - | -0,53 | - | - |
| | 2 | - | 0,75 | - | -0,95 | - | - | 0,40 | 0,59 | - | - | - | - | - | -0,05 | - | -1,11 | - | - | - | - | -0,34 | - | - |
| | 3 | - | -0,91 | - | -3,01 | - | - | -0,89 | 0,04 | - | - | - | - | - | -0,29 | - | 0,01 | - | - | - | - | -0,41 | - | - |
| Zinc as Zn in µg/l | 1 | - | 1,87 | - | 0,23 | - | 0,00 | 0,44 | -0,19 | - | 0,02 | - | - | - | -0,27 | 0,60 | -0,96 | 0,77 | - | - | - | -0,64 | - | - |
| | 2 | - | 2,44 | - | 0,07 | - | 0,60 | 0,35 | 0,02 | - | 0,05 | - | - | - | -0,10 | 0,72 | -1,02 | 0,60 | - | - | - | -0,95 | - | - |
| | 3 | - | 0,92 | - | 0,42 | - | -0,65 | -0,52 | -1,55 | - | 0,17 | - | - | - | 0,18 | 0,32 | -1,02 | 1,10 | - | - | - | -0,25 | - | - |
| Arsenic as As in µg/l | 4 | - | - | - | - | - | - | 0,55 | - | - | - | - | - | - | - | - | -1,09 | - | - | - | - | - | - | - |
| | 5 | - | -0,22 | - | - | - | - | -0,22 | - | - | - | - | - | - | - | - | -1,57 | - | - | - | - | - | - | - |
| | 6 | - | - | - | - | - | - | 0,11 | - | - | - | - | - | - | - | - | -0,11 | - | - | - | - | - | - | - |
| Selenium as Se in µg/l | 4 | - | - | - | - | - | - | -1,38 | - | - | - | - | - | - | - | - | 0,12 | - | - | - | - | -2,52 | - | - |
| | 5 | - | -2,26 | - | - | - | - | 2,55 | - | - | - | - | - | - | - | - | 0,08 | - | - | - | - | -1,86 | - | - |
| | 6 | - | - | - | - | - | - | -0,36 | - | - | - | - | - | - | - | - | -0,43 | - | - | - | - | -1,00 | - | - |

**SOUTH AFRICAN BUREAU OF STANDARDS - WATER-CHECK PROGRAMME**
**TABLE B**

**Z-SCORE VALUES** **Okt 07**
**GROUP 1**

**Gr 1 (cont)** 

| Determinand | | B93 | B94 | B99 | B100 | B101 | B103 | B104 | B105 | B107 | B108 | B109 | B112 | B113 | B115 | B116 | B117 | B121a | B121c | B123 | B124 | B125 | B126 | B127 | B128 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium as Al in µg/l | 1 | - | - | -0,98 | -0,11 | - | -6,73 | 0,68 | - | - | 0,07 | -0,69 | 0,84 | -0,01 | - | 2,85 | - | - | - | - | -0,15 | - | - | - | -0,25 |
| | 2 | - | - | 0,32 | -0,56 | - | 1,48 | 0,60 | - | - | 0,09 | -0,67 | -0,09 | 0,37 | - | 4,33 | - | - | - | - | -0,31 | - | - | - | 0,10 |
| | 3 | - | - | -1,86 | 0,00 | - | 2,23 | 0,05 | - | - | -0,44 | -0,67 | 0,27 | -0,27 | - | 0,14 | - | - | - | - | 0,82 | - | - | - | -0,18 |
| Barium as Ba in µg/l | 1 | - | - | - | -0,40 | - | - | - | - | - | 0,88 | - | - | -0,52 | - | -0,61 | - | - | - | - | - | - | - | - | -0,34 |
| | 2 | - | - | - | -0,04 | - | - | - | - | - | 1,42 | - | - | -0,54 | - | -0,71 | - | - | - | - | - | - | - | - | -0,64 |
| | 3 | - | - | - | -0,17 | - | - | - | - | - | 1,69 | - | - | -0,11 | - | -0,73 | - | - | - | - | - | - | - | - | -0,06 |
| Beryllium as Be in µg/l | 1 | - | - | - | 0,00 | - | - | - | - | - | 1,01 | - | - | 0,30 | - | - | - | - | - | - | - | - | - | - | 2,36 |
| | 2 | - | - | - | -0,54 | - | - | - | - | - | 1,75 | - | - | 0,38 | - | - | - | - | - | - | - | - | - | - | 2,56 |
| | 3 | - | - | - | 0,09 | - | - | - | - | - | 0,09 | - | - | -0,56 | - | - | - | - | - | - | - | - | - | - | 0,75 |
| Boron as B µg/l | 1 | - | - | - | 0,15 | - | -0,22 | - | - | - | -0,56 | - | - | -0,53 | - | -1,01 | - | - | - | - | - | - | - | - | 0,00 |
| | 2 | - | - | - | -0,87 | - | 0,15 | - | - | - | -0,76 | - | - | -0,59 | - | -0,46 | - | - | - | - | - | - | - | - | -0,04 |
| | 3 | - | - | - | -0,94 | - | -0,17 | - | - | - | -0,76 | - | - | -0,83 | - | -0,81 | - | - | - | - | - | - | - | - | 0,06 |
| Cadmium as Cd in µg/l | 1 | - | - | - | -0,45 | 0,30 | -0,85 | 0,15 | 1,50 | - | 0,67 | 0,60 | -0,30 | 0,07 | - | -1,35 | - | -0,60 | - | 1,85 | 1,20 | - | - | - | 0,07 |
| | 2 | - | - | - | 0,34 | 1,16 | 0,10 | 0,67 | 2,45 | - | 1,10 | 0,31 | -0,03 | -0,02 | - | -2,61 | - | -1,53 | - | 1,21 | 0,03 | - | - | - | 0,77 |
| | 3 | - | - | - | 0,10 | 0,99 | 0,13 | 0,67 | 2,02 | - | 1,30 | 0,52 | -0,57 | -2,08 | - | -1,87 | - | -2,70 | - | 1,82 | 0,62 | - | - | - | -1,45 |
| Chromium as Cr in µg/l | 1 | - | - | 1,14 | 0,06 | 0,75 | 0,02 | 0,04 | -0,37 | - | 2,14 | 3,08 | 0,15 | -0,03 | - | - | - | 19,23 | - | -0,55 | - | - | - | - | -0,39 |
| | 2 | - | - | 2,89 | 0,88 | -0,43 | 0,52 | -0,13 | -0,65 | - | 1,82 | -0,13 | -0,14 | 0,60 | - | - | - | 18,71 | - | -0,29 | - | - | - | - | -0,11 |
| | 3 | - | - | 2,16 | 0,15 | 1,58 | 0,06 | 0,27 | 0,42 | - | 0,14 | -0,52 | -0,89 | -0,06 | - | - | - | 5,12 | - | -0,98 | - | - | - | - | -2,65 |
| Cobalt as Co in µg/l | 1 | - | - | - | -0,61 | 0,17 | 0,52 | 0,11 | 1,39 | - | 0,00 | 0,33 | -0,67 | -0,19 | - | - | - | -0,94 | - | 0,37 | 1,94 | - | - | - | 0,50 |
| | 2 | - | - | - | 0,16 | -0,18 | -0,02 | 0,00 | 0,67 | - | 0,83 | 0,05 | 3,01 | -0,15 | - | - | - | -1,53 | - | 0,15 | 0,52 | - | - | - | 0,62 |
| | 3 | - | - | - | -1,06 | 0,48 | -0,55 | 0,00 | 1,25 | - | -0,10 | 1,16 | -0,58 | -0,37 | - | - | - | -1,54 | - | 0,75 | 2,22 | - | - | - | 0,77 |
| Copper as Cu in µg/l | 1 | - | - | -0,51 | 0,46 | 0,34 | -2,48 | -0,25 | -1,26 | - | 0,30 | -0,25 | 1,10 | -0,69 | - | -0,08 | - | -1,35 | - | -0,79 | 0,21 | - | - | - | 0,55 |
| | 2 | - | - | -0,40 | 0,83 | -0,24 | -0,45 | -0,59 | -0,43 | - | 1,06 | 0,59 | 0,08 | -0,19 | - | 0,14 | - | -0,82 | - | 0,55 | 0,19 | - | - | - | 1,61 |
| | 3 | - | - | 0,68 | 0,46 | 1,02 | -1,26 | -0,44 | 1,25 | - | 0,33 | -0,27 | 0,00 | -1,41 | - | -1,59 | - | -0,32 | - | 0,12 | 0,87 | - | - | - | -1,19 |
| Iron as Fe in µg/l | 1 | - | - | 3,07 | -0,36 | 1,10 | 0,34 | -0,38 | 0,31 | - | -1,53 | 0,67 | -1,27 | -1,66 | - | -0,93 | - | -0,40 | - | 0,26 | 1,14 | - | - | - | 0,35 |
| | 2 | - | - | 1,08 | -0,01 | 0,00 | 0,26 | 0,25 | -1,22 | - | -0,50 | 1,09 | -3,72 | 0,22 | - | -0,54 | - | -0,04 | - | -0,22 | -0,17 | - | - | - | 0,13 |
| | 3 | - | - | 3,33 | 0,55 | 1,94 | 0,34 | 0,40 | -0,01 | - | -2,33 | 0,17 | -0,65 | -0,10 | - | -0,83 | - | 1,70 | - | 0,09 | 1,32 | - | - | - | 0,21 |
| Lead as Pb in µg/l | 1 | - | - | 1,51 | -0,13 | -0,92 | 6,47 | 0,39 | 0,79 | - | 0,20 | 0,00 | -1,22 | 0,60 | - | -0,66 | - | 23,03 | - | -3,42 | 0,59 | - | - | - | -0,23 |
| | 2 | - | - | -0,35 | 0,20 | 0,31 | 4,17 | -0,88 | 0,40 | - | 0,91 | 0,29 | -1,66 | 0,39 | - | -1,95 | - | 9,57 | - | -1,44 | -0,73 | - | - | - | -0,33 |
| | 3 | - | - | 1,82 | 0,12 | 0,94 | 5,36 | -0,30 | 1,26 | - | -0,18 | 0,30 | -0,12 | 0,33 | - | -1,12 | - | 3,81 | - | -0,79 | 0,88 | - | - | - | -1,95 |
| Manganese as Mn in µg/l | 1 | - | - | 0,56 | -1,73 | -0,03 | -1,47 | -0,20 | 1,15 | - | -2,66 | -0,20 | -0,61 | -0,60 | - | -1,20 | - | -0,96 | - | 0,30 | -0,20 | - | - | - | 0,03 |
| | 2 | - | - | -1,15 | -0,10 | 0,51 | -0,55 | 0,19 | 1,03 | - | 1,10 | -0,71 | -1,54 | 0,05 | - | -1,43 | - | -0,58 | - | 0,50 | -0,60 | - | - | - | -0,05 |
| | 3 | - | - | -0,65 | -1,47 | -0,37 | -0,79 | 0,45 | 0,62 | - | -0,51 | -0,04 | -0,48 | 0,05 | - | -1,03 | - | -0,89 | - | 0,85 | -0,18 | - | - | - | 0,73 |
| Mercury as Hg in µg/l | 1 | - | - | - | - | - | 46,27 | - | -0,22 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| | 2 | - | - | - | - | - | 34,29 | - | -0,40 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| | 3 | - | - | - | - | - | 56,61 | - | -0,11 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Molybdenum as Mo in µg/l | 1 | - | - | - | 0,16 | - | -0,62 | - | - | - | 0,02 | - | - | 0,00 | - | - | - | - | - | - | - | - | - | - | -0,12 |
| | 2 | - | - | - | 0,55 | - | 1,23 | - | - | - | 1,35 | - | - | 0,12 | - | - | - | - | - | - | - | - | - | - | -0,55 |
| | 3 | - | - | - | -0,29 | - | 1,37 | - | - | - | -0,45 | - | - | 0,49 | - | - | - | - | - | - | - | - | - | - | -1,27 |
| Nickel as Ni in µg/l | 1 | - | - | 0,84 | -0,10 | 0,52 | 0,35 | 0,65 | 2,99 | - | 0,79 | -0,12 | -1,37 | 0,58 | - | - | - | -1,52 | - | -0,15 | -0,83 | - | - | - | -0,47 |
| | 2 | - | - | -1,45 | -0,06 | 0,35 | 0,87 | 0,71 | 2,26 | - | 1,13 | -0,10 | 0,52 | 0,53 | - | - | - | -1,85 | - | -0,20 | -1,31 | - | - | - | -0,25 |
| | 3 | - | - | 1,37 | -1,87 | 0,16 | 0,84 | 0,37 | 3,25 | - | 0,64 | -1,51 | -0,14 | 0,34 | - | - | - | -1,08 | - | -0,04 | -1,54 | - | - | - | -0,17 |
| Silicon as Si in µg/l | 1 | - | - | - | -0,46 | - | -0,28 | - | -0,04 | - | -0,29 | - | 0,45 | -4,84 | - | - | - | - | - | - | -1,02 | - | - | - | - |
| | 2 | - | - | - | -0,76 | - | -0,01 | - | 0,46 | - | -0,36 | - | 1,13 | -5,69 | - | - | - | - | - | - | -1,55 | - | - | - | - |
| | 3 | - | - | - | -0,24 | - | 0,10 | - | 0,55 | - | -0,44 | - | 1,67 | -5,22 | - | - | - | - | - | - | -1,27 | - | - | - | - |
| Strontium as Sr in µg/l | 1 | - | - | - | -1,73 | - | -11,94 | -0,58 | - | - | - | - | - | 0,69 | - | -0,27 | - | - | - | - | - | - | - | - | -2,27 |
| | 2 | - | - | - | - | - | -18,90 | -0,49 | - | - | - | - | - | 1,06 | - | -0,18 | - | - | - | - | - | - | - | - | -3,31 |
| | 3 | - | - | - | - | - | -13,27 | -0,67 | - | - | - | - | - | 0,55 | - | -0,39 | - | - | - | - | - | - | - | - | -3,88 |
| Vanadium as V in µg/l | 1 | - | - | - | -0,59 | - | - | - | - | - | 0,33 | - | - | 0,69 | - | - | - | - | - | - | - | - | - | - | 0,33 |
| | 2 | - | - | - | 0,24 | - | - | - | - | - | 1,04 | - | - | 0,78 | - | - | - | - | - | - | - | - | - | - | -0,14 |
| | 3 | - | - | - | 0,16 | - | - | - | - | - | 0,41 | - | - | 0,71 | - | - | - | - | - | - | - | - | - | - | -2,24 |
| Zinc as Zn in µg/l | 1 | - | - | 0,39 | 0,04 | -0,58 | -0,71 | 0,19 | 0,92 | - | 0,50 | 0,77 | 1,60 | -1,01 | - | -2,27 | - | -1,54 | - | -8,85 | 3,04 | - | - | - | -0,25 |
| | 2 | - | - | 0,14 | -0,07 | -1,02 | 0,39 | 0,37 | 0,98 | - | 0,42 | 0,67 | 1,00 | -1,08 | - | -2,63 | - | -1,49 | - | -9,85 | -2,70 | - | - | - | -0,28 |
| | 3 | - | - | 1,10 | -0,65 | -0,15 | -0,26 | 0,80 | 1,10 | - | 0,70 | 1,15 | 1,02 | -1,33 | - | -2,12 | - | -1,47 | - | -8,14 | -4,45 | - | - | - | -0,02 |
| Arsenic as As in µg/l | 4 | - | - | - | -1,53 | - | 38,31 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 0,20 |
| | 5 | - | - | - | 0,18 | - | 55,88 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 0,67 |
| | 6 | - | - | - | -0,90 | - | 101,06 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | -0,56 |
| Selenium as Se in µg/l | 4 | - | - | - | 0,57 | - | 16,61 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| | 5 | - | - | - | 0,00 | - | 6,81 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| | 6 | - | - | - | 0,08 | - | 9,70 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |

## SOUTH AFRICAN BUREAU OF STANDARDS - WATER-CHECK PROGRAMME
## TABLE B
## Z-SCORE VALUES
## GROUP 1

**Okt 07**



| Determinand | | B129 | B130 | B131 | B132 A | B132B | B135 | B138 | B139 | B141 | B142 | B143 | B144 | B147 | B148 | B149 | B152 | B153 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Aluminium as Al in µg/l | 1 | -2,18 | - | - | 2,68 | 2,68 | 0,28 | 0,58 | - | 1,29 | - | -0,98 | - | - | -1,12 | -2,86 | - | - |
| | 2 | -1,34 | - | - | 0,71 | 0,71 | 0,95 | 0,91 | - | 1,16 | - | -1,67 | - | - | -0,85 | -2,54 | - | - |
| | 3 | -1,27 | - | - | 1,60 | 1,60 | -0,37 | 1,37 | - | 0,21 | - | 0,51 | - | - | 0,06 | -1,85 | - | - |
| Barium as Ba in µg/l | 1 | -0,67 | - | - | 0,40 | 0,40 | -0,67 | -1,48 | - | 1,48 | - | - | - | - | - | 0,61 | - | - |
| | 2 | 0,04 | - | - | 0,67 | 0,67 | -2,10 | -1,31 | - | 1,42 | - | - | - | - | - | 0,34 | - | - |
| | 3 | -4,66 | - | - | 0,39 | 0,39 | -1,57 | -0,56 | - | 2,30 | - | - | - | - | - | 0,67 | - | - |
| Beryllium as Be in µg/l | 1 | - | - | - | - | - | -1,45 | -3,17 | - | - | - | - | - | - | - | -2,02 | - | - |
| | 2 | - | - | - | - | - | -1,75 | -3,10 | - | - | - | - | - | - | - | 0,13 | - | - |
| | 3 | - | - | - | - | - | 0,15 | 0,14 | - | - | - | - | - | - | - | 0,53 | - | - |
| Boron as B µg/l | 1 | -2,98 | - | - | -7,51 | -7,51 | - | -2,55 | - | - | - | - | - | - | - | 0,34 | - | - |
| | 2 | -1,88 | - | - | 0,34 | 0,34 | 1,05 | -2,56 | - | - | - | - | - | - | - | 0,43 | - | - |
| | 3 | -3,09 | - | - | 0,30 | 0,30 | 0,33 | -2,71 | - | - | - | - | - | - | - | 0,12 | - | - |
| Cadmium as Cd in µg/l | 1 | -3,15 | - | 2,55 | 1,05 | 0,30 | 0,07 | -1,65 | - | - | - | - | - | - | -0,93 | 0,00 | - | - |
| | 2 | -3,92 | - | -0,67 | 0,64 | -0,12 | -0,92 | -2,67 | - | - | - | - | - | - | -0,28 | 0,09 | - | - |
| | 3 | -5,97 | - | 0,47 | -1,24 | 0,10 | -0,26 | -1,40 | - | - | - | - | - | - | -0,16 | 0,47 | - | - |
| Chromium as Cr in µg/l | 1 | -7,46 | - | - | -0,13 | 1,02 | -1,56 | -1,16 | - | 1,66 | - | - | - | - | -0,43 | 3,31 | - | - |
| | 2 | -5,56 | - | - | 0,56 | 2,20 | -2,24 | -0,84 | - | 1,77 | - | - | - | - | -0,43 | 1,94 | - | - |
| | 3 | -3,26 | - | - | -0,03 | 1,35 | 0,81 | 1,01 | - | 0,18 | - | - | - | - | 0,49 | 2,25 | - | - |
| Cobalt as Co in µg/l | 1 | - | - | - | 0,83 | -0,94 | -1,33 | -2,39 | - | - | - | - | - | - | -0,68 | -1,50 | - | - |
| | 2 | - | - | - | 0,73 | -1,09 | -2,67 | 0,75 | - | - | - | - | - | - | -0,54 | -1,01 | - | - |
| | 3 | - | - | - | 0,48 | -1,35 | -1,44 | -2,99 | - | - | - | - | - | - | -0,16 | -0,29 | - | - |
| Copper as Cu in µg/l | 1 | -4,09 | - | -2,61 | 0,38 | -0,42 | -0,84 | -2,19 | - | 1,31 | - | - | - | - | -0,83 | -0,13 | - | - |
| | 2 | -4,06 | - | 0,40 | 0,96 | -1,01 | -2,17 | -3,60 | - | 2,63 | - | - | - | - | -0,86 | 0,00 | - | - |
| | 3 | -3,17 | - | 0,09 | -1,04 | 0,37 | 0,23 | -0,60 | - | -0,67 | - | - | - | - | 0,64 | 0,78 | - | - |
| Iron as Fe in µg/l | 1 | -3,11 | - | -1,70 | 0,55 | 0,55 | -1,11 | 0,69 | - | 0,42 | - | -1,36 | - | - | -0,07 | - | - | - |
| | 2 | -5,98 | - | -4,25 | -0,09 | -0,09 | -0,59 | 0,00 | - | 2,12 | - | -3,92 | - | - | -0,23 | 1,22 | - | - |
| | 3 | -4,33 | - | -0,20 | 1,08 | 1,08 | -0,05 | 1,94 | - | 0,46 | - | -0,62 | - | - | 0,77 | 2,80 | - | - |
| Lead as Pb in µg/l | 1 | -2,24 | - | - | 0,30 | 1,15 | -0,03 | 0,03 | - | -0,79 | - | - | - | - | -0,22 | -0,20 | - | - |
| | 2 | -2,85 | - | - | 0,42 | 1,66 | -1,30 | -0,42 | - | 0,55 | - | - | - | - | -0,49 | -1,41 | - | - |
| | 3 | -2,83 | - | - | 0,15 | 1,15 | 0,80 | -0,77 | - | -0,15 | - | - | - | - | 0,53 | 0,58 | - | - |
| Manganese as Mn in µg/l | 1 | -4,07 | - | -3,54 | 0,56 | 0,56 | 0,03 | 0,62 | - | 1,20 | - | -0,03 | - | - | -1,69 | 1,79 | - | - |
| | 2 | -3,78 | - | -2,82 | -0,23 | -0,23 | -0,80 | 0,36 | - | 1,27 | - | -2,08 | - | - | -1,71 | 0,34 | - | - |
| | 3 | -4,80 | - | -2,02 | -0,65 | -0,65 | -1,14 | 0,87 | - | 1,17 | - | -0,65 | - | - | -1,00 | 0,56 | - | - |
| Mercury as Hg in µg/l | 1 | - | - | - | - | - | 0,07 | -0,29 | - | - | - | - | - | - | - | - | - | - |
| | 2 | - | - | - | - | - | 0,72 | -0,63 | - | - | - | - | - | - | - | - | - | - |
| | 3 | - | - | - | - | - | 0,23 | -0,51 | - | - | - | - | - | - | - | - | - | - |
| Molybdenum as Mo in µg/l | 1 | - | - | - | 0,78 | 0,78 | 0,27 | -0,61 | - | 0,04 | - | - | - | - | - | - | - | - |
| | 2 | - | - | - | 1,14 | 1,14 | -0,42 | -0,67 | - | 1,05 | - | - | - | - | - | -0,13 | - | - |
| | 3 | - | - | - | 1,50 | 1,50 | -0,68 | 0,06 | - | 0,49 | - | - | - | - | - | -0,41 | - | - |
| Nickel as Ni in µg/l | 1 | -4,47 | - | - | 0,25 | 0,26 | -0,76 | -3,14 | - | - | - | - | - | - | -0,38 | 0,14 | - | - |
| | 2 | -4,23 | - | - | 0,64 | -1,33 | -2,26 | -2,67 | - | - | - | - | - | - | -0,44 | -0,53 | - | - |
| | 3 | -6,90 | - | - | 0,49 | 0,25 | -1,57 | -2,66 | - | - | - | - | - | - | -0,27 | -0,75 | - | - |
| Silicon as Si in µg/l | 1 | -3,16 | - | - | 0,74 | 0,74 | 1,72 | - | - | 0,43 | - | - | - | - | - | - | - | - |
| | 2 | -3,89 | - | - | 3,69 | 3,69 | 2,01 | - | - | 0,09 | - | - | - | - | - | - | - | - |
| | 3 | -3,57 | - | - | -1,04 | -1,04 | 2,09 | - | - | 0,35 | - | - | - | - | - | - | - | - |
| Strontium as Sr in µg/l | 1 | -1,97 | - | - | 0,04 | 0,04 | -0,04 | -1,43 | - | 0,89 | - | - | - | - | - | -0,35 | - | - |
| | 2 | -1,90 | - | - | -0,49 | -0,49 | -1,35 | -0,67 | - | 1,23 | - | - | - | - | - | -0,06 | - | - |
| | 3 | -3,76 | - | - | -0,84 | -0,84 | -1,18 | -0,62 | - | 0,79 | - | - | - | - | - | -0,79 | - | - |
| Vanadium as V in µg/l | 1 | - | - | - | 4,56 | 4,56 | 0,58 | -0,66 | - | - | - | - | - | - | - | - | - | - |
| | 2 | - | - | - | 2,49 | 2,49 | -1,24 | 2,75 | - | - | - | - | - | - | - | -3,26 | - | - |
| | 3 | - | - | - | 2,09 | 2,09 | 0,64 | 0,66 | - | - | - | - | - | - | - | -0,59 | - | - |
| Zinc as Zn in µg/l | 1 | -1,04 | - | -1,93 | 0,73 | 0,00 | -2,06 | -0,31 | - | 0,64 | - | -1,54 | - | - | -0,35 | 0,81 | - | - |
| | 2 | -1,86 | - | -1,26 | -0,09 | 0,09 | -2,63 | -0,44 | - | 0,63 | - | -1,49 | - | - | -0,58 | 0,70 | - | - |
| | 3 | -1,30 | - | -1,15 | -0,12 | 0,25 | -1,80 | 0,07 | - | 0,75 | - | -1,15 | - | - | 0,21 | 1,22 | - | - |
| Arsenic as As in µg/l | 4 | - | - | - | - | - | -0,20 | -0,45 | - | - | - | - | - | - | - | - | - | - |
| | 5 | - | - | - | - | - | -0,18 | -0,67 | - | - | - | - | - | - | - | - | - | - |
| | 6 | - | - | - | - | - | - | -0,56 | - | - | - | - | - | - | - | - | - | - |
| Selenium as Se in µg/l | 4 | - | - | - | - | - | 0,15 | -2,02 | - | - | - | - | - | - | - | -0,67 | - | - |
| | 5 | - | - | - | - | - | -0,13 | -0,93 | - | - | - | - | - | - | - | -0,50 | - | - |
| | 6 | - | - | - | - | - | - | -0,87 | - | - | - | - | - | - | - | -0,36 | - | - |

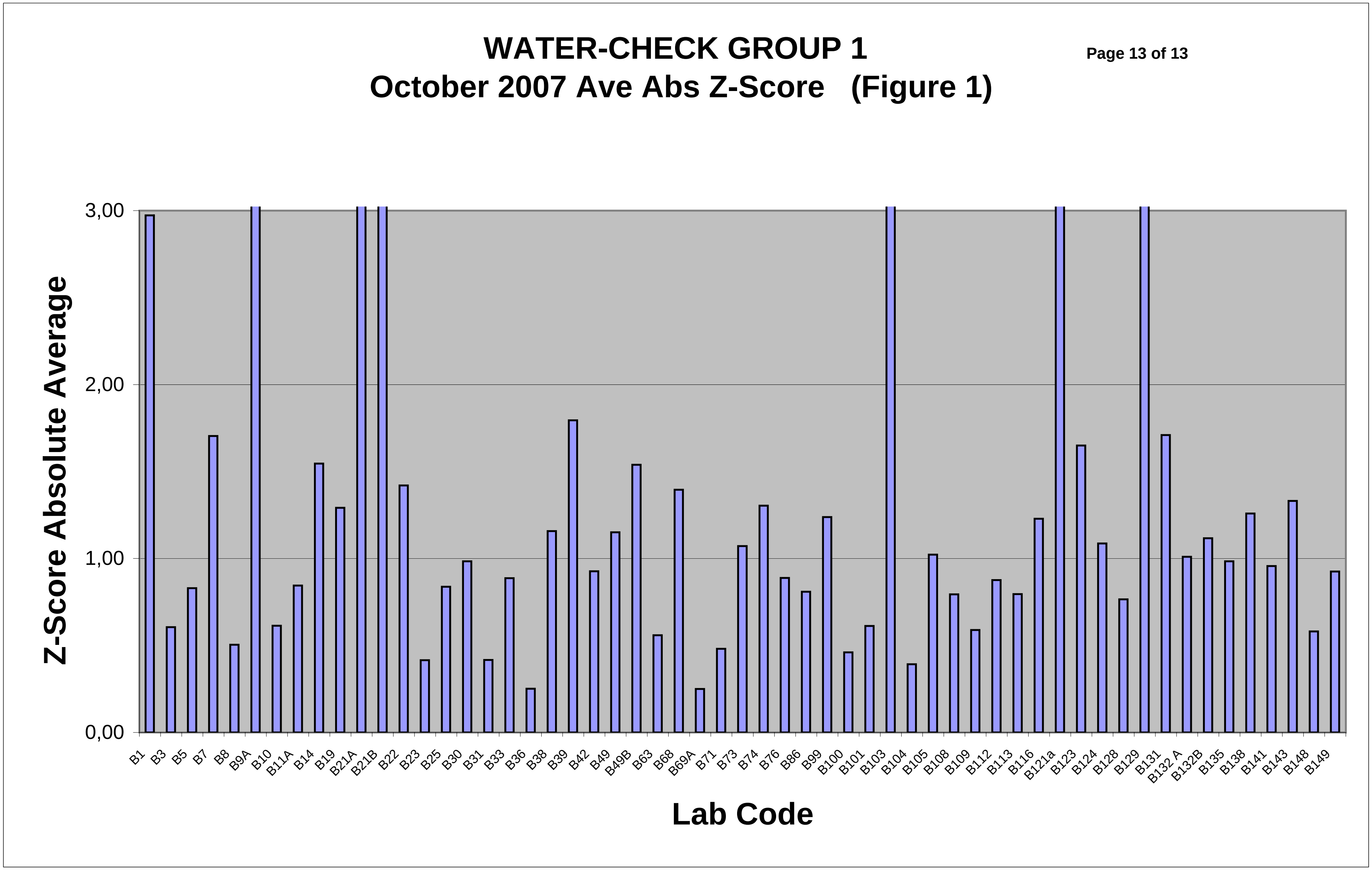
**Table C: Statistical summary**

| Determinand | | Spike µg/l | Median | Robust SD | n |
|---|---|---|---|---|---|
| Aluminium as Al in µg/l | 1 | 750,0 | 802,0 | 105 | 48 |
| | 2 | 1500 | 1552 | 151 | 48 |
| | 3 | 375,0 | 257,0 | 85 | 47 |
| Barium as Ba in µg/l | 1 | 150,0 | 190,0 | 15 | 34 |
| | 2 | 450,0 | 488,0 | 27 | 34 |
| | 3 | 300,0 | 327,0 | 18 | 34 |
| Beryllium as Be in µg/l | 1 | 50,00 | 50,00 | 3 | 25 |
| | 2 | 150,0 | 150,0 | 7 | 25 |
| | 3 | 100,0 | 81,79 | 14 | 25 |
| Boron as B µg/l | 1 | 500,0 | 541,0 | 53 | 29 |
| | 2 | 2000 | 2005 | 162 | 30 |
| | 3 | 1000 | 1038 | 83 | 30 |
| Cadmium as Cd in µg/l | 1 | 125,0 | 126,0 | 13 | 51 |
| | 2 | 500,0 | 502,0 | 33 | 51 |
| | 3 | 250,0 | 241,0 | 19 | 51 |
| Chromium as Cr in µg/l | 1 | 1200 | 1191 | 52 | 51 |
| | 2 | 2400 | 2413 | 99 | 51 |
| | 3 | 600,0 | 397,0 | 103 | 51 |
| Cobalt as Co in µg/l | 1 | 400,0 | 397,0 | 18 | 48 |
| | 2 | 800,0 | 797,0 | 39 | 48 |
| | 3 | 200,0 | 195,0 | 10 | 48 |
| Copper as Cu in µg/l | 1 | 300,0 | 322,0 | 24 | 54 |
| | 2 | 1200 | 1205 | 62 | 53 |
| | 3 | 600,0 | 490,0 | 117 | 53 |
| Iron as Fe in µg/l | 1 | 1250 | 1099 | 147 | 53 |
| | 2 | 2500 | 2471 | 120 | 54 |
| | 3 | 625,0 | 438,5 | 94 | 54 |
| Lead as Pb in µg/l | 1 | 150,0 | 154,0 | 30 | 50 |
| | 2 | 600,0 | 586,0 | 45 | 50 |
| | 3 | 300,0 | 192,5 | 65 | 50 |
| Manganese as Mn in µg/l | 1 | 250,0 | 270,5 | 17 | 56 |
| | 2 | 1000 | 1003 | 54 | 56 |
| | 3 | 500,0 | 493,5 | 36 | 56 |
| Mercury as Hg in µg/l | 1 | 3,000 | 2,400 | 3 | 15 |
| | 2 | 9,000 | 8,800 | 4 | 16 |
| | 3 | 6,000 | 2,500 | 3 | 15 |
| Molybdenum as Mo in µg/l | 1 | 100,0 | 89,7 | 14 | 29 |
| | 2 | 300,0 | 275,0 | 24 | 30 |
| | 3 | 200,0 | 188,5 | 26 | 30 |
| Nickel as Ni in µg/l | 1 | 1100 | 1108 | 62 | 50 |
| | 2 | 2200 | 2201 | 111 | 50 |
| | 3 | 550,0 | 554,8 | 33 | 50 |
| Silicon as Si in µg/l | 1 | - | 1746 | 208 | 30 |
| | 2 | - | 1744 | 178 | 30 |
| | 3 | - | 1691 | 184 | 30 |
| Strontium as Sr in µg/l | 1 | 80,00 | 176,5 | 13 | 34 |
| | 2 | 240,0 | 330,0 | 16 | 33 |
| | 3 | 160,0 | 255,0 | 18 | 33 |
| Vanadium as V in µg/l | 1 | 100,0 | 86,0 | 18 | 28 |
| | 2 | 400,0 | 399,5 | 39 | 28 |
| | 3 | 200,0 | 143,5 | 40 | 28 |
| Zinc as Zn in µg/l | 1 | 40,00 | 460,0 | 52 | 53 |
| | 2 | 120,0 | 425,5 | 43 | 54 |
| | 3 | 80,00 | 326,0 | 40 | 53 |
| Arsenic as As in µg/l | 4 | 3,000 | 4,415 | 3 | 12 |
| | 5 | 15,00 | 14,50 | 2 | 14 |
| | 6 | 9,000 | 8,835 | 1 | 12 |
| Selenium as Se in µg/l | 4 | 7,500 | 8,900 | 3 | 15 |
| | 5 | 12,50 | 15,10 | 6 | 17 |
| | 6 | 5,000 | 7,000 | 5 | 15 |

| Lab code | Average absolute z-score | Number of tests performed |
|---|---|---|
| B1 | 2,97 | 46 |
| B3 | 0,61 | 21 |
| B5 | 0,83 | 51 |
| B7 | 1,70 | 6 |
| B8 | 0,50 | 51 |
| B9A | 6,27 | 60 |
| B10 | 0,61 | 54 |
| B11A | 0,84 | 48 |
| B14 | 1,55 | 60 |
| B19 | 1,29 | 58 |
| B21A | 4,21 | 51 |
| B21B | 4,10 | 33 |
| B22 | 1,42 | 60 |
| B23 | 0,42 | 36 |
| B25 | 0,84 | 60 |
| B30 | 0,98 | 29 |
| B31 | 0,42 | 48 |
| B33 | 0,89 | 27 |
| B36 | 0,25 | 36 |
| B38 | 1,16 | 9 |
| B39 | 1,80 | 50 |
| B42 | 0,93 | 48 |
| B49 | 1,15 | 30 |
| B49B | 1,54 | 60 |
| B63 | 0,56 | 42 |
| B68 | 1,39 | 42 |
| B69A | 0,25 | 36 |
| B71 | 0,48 | 51 |
| B73 | 1,07 | 33 |
| B74 | 1,30 | 51 |
| B76 | 0,89 | 36 |
| B86 | 0,81 | 42 |
| B99 | 1,24 | 24 |
| B100 | 0,46 | 55 |
| B101 | 0,61 | 27 |
| B103 | 8,91 | 51 |
| B104 | 0,39 | 33 |
| B105 | 1,02 | 33 |
| B108 | 0,79 | 48 |
| B109 | 0,59 | 30 |
| B112 | 0,88 | 33 |
| B113 | 0,80 | 51 |
| B116 | 1,23 | 30 |
| B121a | 3,86 | 27 |
| B123 | 1,65 | 27 |
| B124 | 1,09 | 30 |
| B128 | 0,76 | 51 |
| B129 | 3,35 | 39 |
| B131 | 1,71 | 15 |
| B132 A | 1,01 | 48 |
| B132B | 1,12 | 48 |
| B135 | 0,98 | 57 |
| B138 | 1,26 | 57 |
| B141 | 0,96 | 33 |
| B143 | 1,33 | 12 |
| B148 | 0,58 | 30 |
| B149 | 0,92 | 48 |

Z < 2 = SATISFACTORY
2 < Z < 3 = QUESTIONABLE *****
Z > 3 = UNSATISFACTORY

*** Note: A Z-score of an individual result > 2 (questionable) should be investigated by the participating laboratory.**



WATER-CHECK GROUP 1
October 2007 Ave Abs Z-Score (Figure 1)
Page 13 of 13
Z-Score Absolute Average
3,00
2,00
1,00
0,00
B1 B3 B5 B7 B8 B9A B10 B11A B14 B19 B21A B21B B22 B23 B25 B30 B31 B33 B36 B38 B39 B42 B49 B49B B63 B68 B69A B71 B73 B74 B76 B86 B99 B100 B101 B103 B104 B105 B108 B109 B112 B113 B116 B121a B123 B124 B128 B129 B131 B132 A B132B B135 B138 B141 B143 B148 B149
Lab Code

## Sample Results

| Determinand | Sample 2007/ / | Results mg/ l | Range mg/ l | Method Reference |
|---|---|---|---|---|
| Kjeldahl nitrogen as **N** in mg / l | 1 | | 1.0 - 10.0 | |
| | 2 * | | | |
| | 3 * | | | |
| Total phosphate as **P** in mg / l | 1 | | 1.0 - 10.0 | |
| | 2 * | | | |
| | 3 * | | | |
| Ammonia as **N** in mg / l | 1 | | 1.0 - 10.0 | |
| | 4 * | | | |
| | 5 * | | | |
| Nitrate as **N** in mg / l | 1 | | 1.0 - 10.0 | |
| | 4 * | | | |
| | 5 * | | | |
| Ortho-phosphate as **P** in mg / l | 1 | | 0.1 - 10.0 | |
| | 4 * | | | |
| | 5 * | | | |
| Oxygen absorbed as $\mathbf{O_2}$ in mg / l | 1 | | --- | |
| Chemical oxygen demand as $\mathbf{O_2}$ in mg / l | 1 | | 20.0 - 200.0 | |
| | 4 * | | | |
| | 5 * | | | |
| Dissolved organic carbon as C in mg / l | 1 | | --- | |
| | 4 * | | | |
| | 5 * | | | |
| Total organic carbon as C in mg / l | 1 | | --- | |

# SABS

**Water - Check**

## Month:

## Group 2

## Lab code: B

**Due date:**

**Enquiries:**

**Tel:**

**Fax:**

**E-mail:**

**Signed:**

**Comments:**

**NOTES:**

**1. Sample 1:** Purified sewage effluent preserved with 1,5 ml / litre $H_2SO_4$ (conc).

**2. * Dilution:**

**Samples 2, 3, 4 and 5** are synthetic water samples.
Dilute by pipetting **20 ml** of the synthetic concentrate of samples
**2,3,4 and 5** respectively into separate **1000 ml** volumetric flasks and dilute to volume with distilled/deionised water
Use Grade A volumetric glassware.

**NB:** ***Do not correct analytical results for these dilutions.***

**3. Testing:** Please analyse by single test on a routine basis and express results as one decimal.

**4. Ranges:** The range values are only valid for the diluted synthetic samples.

# Classification of errors
# Corrective Actions

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## Different kind of errors

- Constant systematic errors, due to
  - increased blank values
  - incomplete recovery
- Proportional systematic errors, due to
  - wrong calibration
  - dilution errors
  - wrong calculation / wrong unit
- Gross and indefinable errors, due to
  - anything

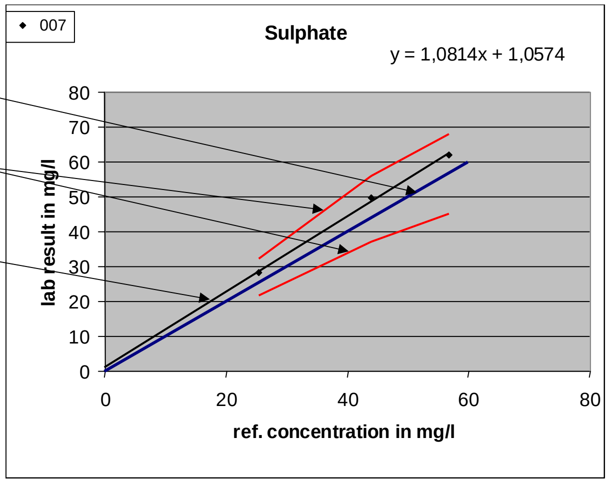
# How to identify the kind of error?

- Graphical display of analytical result vs. assigned value

100 % recovery

tolerance limits

linear regression line

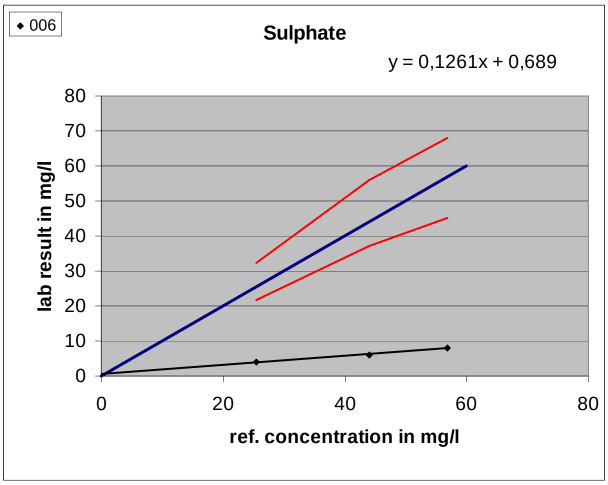



good analysis!
No serious error





proportional systematic error!
Dilution error, calibration error or gross calibration error



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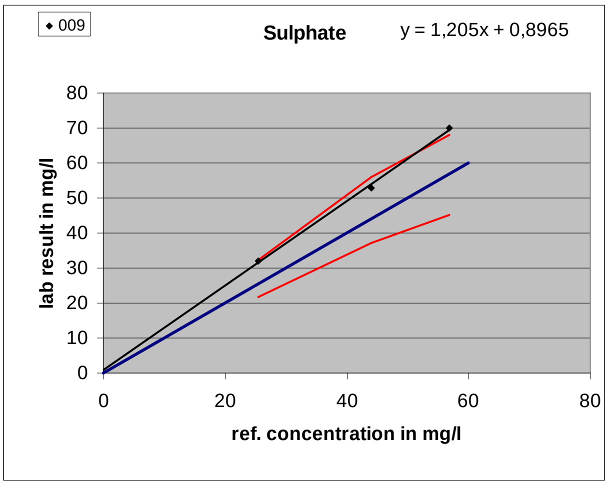
proportional systematic error! calibration error, leading to results just at the limit

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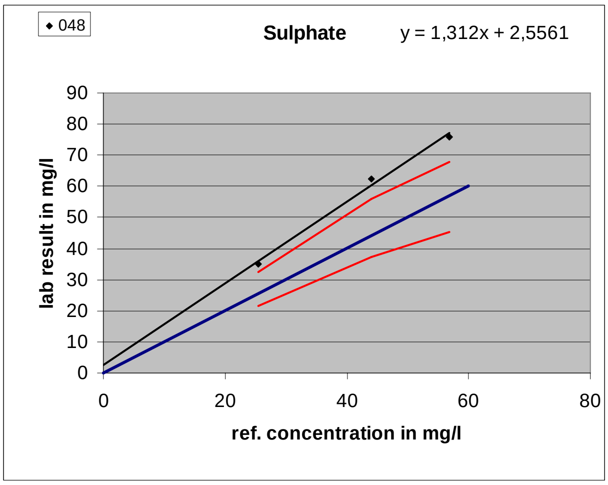
proportional systematic error! calibration error, leading to results beyond the limit

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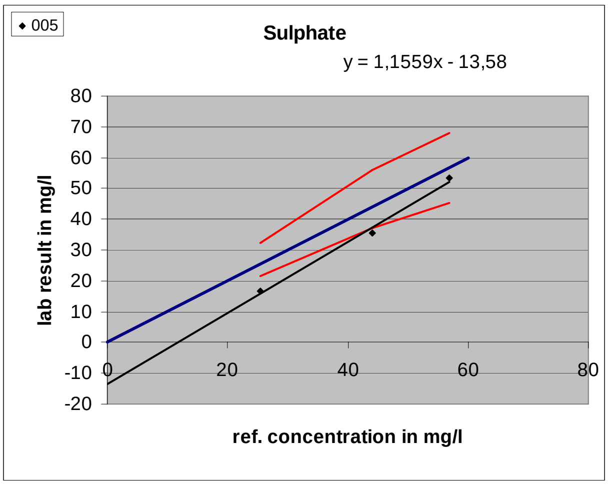
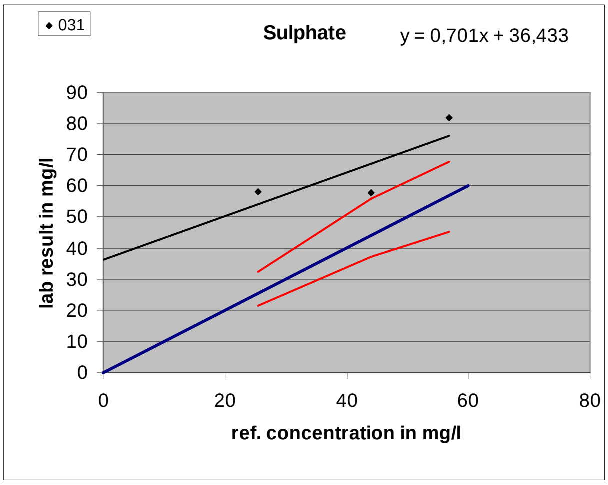
constant systematic error? recovery too low?








indefinable, gross error



## What corrective actions to apply?

- If you found a proportional systematic error:
  - Check calibration
- Check for precision using internal quality control data (Control Charts)
- Check for bias using a certified or in-house reference material
- If you can't find the problem, carry out full method validation

# Method validation

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## Glossary - Validation

- Definition
  - Confirmation, through the provision of objective evidence, that the requirements for a specific intended use or application have been fulfilled (EN ISO 9000)
- Description
  - The validation shows with the help of laboratory experiments, that the corresponding parameters of a method fulfil the requirements of the intended chemical analytical application
  - Relevant chemical analytical parameters:
    - Precision
    - Trueness
    - Limit of detection
    - Limit of determination
    - Selectivity
    - Linearity
    - Robustness

## Why is Method Validation Necessary?

- Very simple

**To prove that the method is fit for purpose**





## The Professional Duty of the Analytical Chemist

- To increase reliability of laboratory results
- To increase trust of laboratory customers
- To prove the truth

## When should Methods be Validated

- New method development
- Revision of established methods
- When established methods are used in different laboratories/different analysts etc.
- QC indicates method changes
- Comparison of methods
- if the lab fails in a PT and the problem could not be found





## Validation of Standard Methods?

- Standard methods can be assumed as validated to a basic degree
- I.e., one can assume that the method is suitable for the scope mentioned in the standard
- The laboratory has to verify that it can reach the precision, trueness and other parameters described in the standard

## Validation of In-house Methods

- In-house methods or the use of standard methods outside the scope of the standard require a complete validation
- I.e., all method characteristics have to be determined and compared with the requirements of the intended purpose



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## Determination of Method Characteristics

- Some of the method characteristics of the basic method (determination of calibration standards) are determined during the basic calibration of the method
  - Working range
  - Homogeneity of variances
  - Linearity
  - Standard deviation of residues $s_y$
  - Slope of the calibration function / sensitivity b
  - Process standard deviation $s_{x0}$
- This is described e.g. in: Funk, Dammann, Donnevert (1995): Quality Assurance in Analytical chemistry. Wiley

## Basic Calibration

- If the analytical procedure needs a calibration the measurement does not lead directly to the result
- The measurement result can be converted into the analytical result using the **analytical function**

$$\hat{x} = f(\hat{y}) \quad \textit{with}: \begin{array}{l} \hat{x} \text{ analytical result} \\ \hat{y} \text{ measured value} \end{array}$$

- Basing upon the **calibration function**:

$$y = f(x) \quad \textit{with}: \begin{array}{l} x \text{ content of substance in the standard solution} \\ y \text{ corresponding measured value} \end{array}$$



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## Basic Calibration

- During the basic calibration the analytical method is calibrated only with standard solutions
- I.e., no sample preparation (extraction digestion etc.), only standard solutions in pure solvent

# Definition the Working Range

- First step: Definition of a preliminary working range on the basis of:
  - The practical need
  - The practically feasible possibilities
    - Measurement result at the lower limit of the working range must be significantly different from the blank values
    - The required analytical precision must be reached over the whole working range
    - If we want to use a simple linear regression the residues must be homogeneous and there must a linear relationship between analyte content and measured value





# Preparation of Standard Samples

- Requirements:
  - Purity, free from matrix resp. defined matrix
  - Homogeneity
  - Representativeness for real samples
    - Chemically similar compounds
    - Same oxidation state
    - etc.
  - Stability, possibilities to preserve
  - No influence by sample containers and environmental conditions

# Preparation of Standard Samples

- Production of Standard Samples
  - Consider precision of balances and volume measuring equipment
  - Weighing is always more precise and should therefore be favoured
  - Avoid successive dilutions
  - Prepare 6...10 standard samples with equidistant concentration over the whole working range

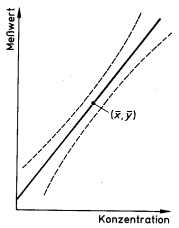




# Linear Calibration Function

- The regression analysis delivers the calibration function y = a + bx
- Slope (Sensitivity)

$$b = \frac{\sum\left[(x_i - \bar{x}) \cdot (y_i - \bar{y})\right]}{\sum (x_i - \bar{x})^2}$$



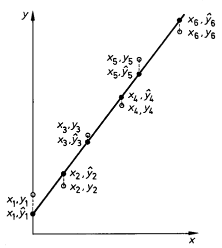

- Intercept

$$a = \bar{y} - b\bar{x}$$

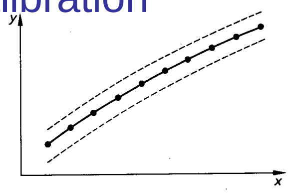
- Standard deviation of residues (dispersion of values around the regression line)

$$s_y = \sqrt{\frac{\sum (y_i - \hat{y}_i)^2}{N-2}} \quad \text{mit } \hat{y}_i = a + bx_i$$

- Process standard deviation $s_{x0} = \frac{s_y}{b}$
- Process variation coefficient $V_{x0} = \frac{s_{x0}}{\bar{x}} \cdot 100\%$



# Non-linear second-order calibration function y=a + bx + cx²




- Calculation is a bit more complex (see ISO 8466-2)
- Function coefficients

$$a = \left(\sum y_i - b \cdot \sum x_i - c \cdot \sum x_i^2\right) / N$$

$$b = \frac{Q_{xy} - c \cdot Q_{x^3}}{Q_{xx}}$$

$$c = \frac{Q_{xy} \cdot Q_{x^3} - Q_{x^2y} \cdot Q_{xx}}{\left(Q_{x^3}\right)^2 - Q_{xx} \cdot Q_{x^4}}$$

$$Q_{xx} = \sum x_i^2 - \frac{\left(\sum x_i\right)^2}{N}$$

$$Q_{xy} = \sum (x_i y_i) - \left(\sum x_i \frac{\left(\sum y_i\right)}{N}\right)$$

$$Q_{x^3} = \sum (x_i^3) - \left(\sum x_i \frac{\left(\sum x_i^2\right)}{N}\right)$$

$$Q_{x^4} = \sum (x_i^4) - \left(\frac{\left(\sum x_i^2\right)^2}{N}\right)$$

$$Q_{x^2y} = \sum (x_i^2 y_i) - \left(\sum y_i \cdot \frac{\sum x_i^2}{N}\right)$$



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# Second-order calibration function

- Standard deviation of residues

$$s_y = \sqrt{\frac{\sum (y_i - \hat{y}_i)^2}{N-3}} \quad \text{with} \quad \hat{y}_i = a + bx_i + cx_i^2$$

- Sensitivity
  - First derivation of the calibration function $E(x) = b + 2c \cdot x$
  - Resp. in the middle of the working range $E(\bar{x}) = b + 2c \cdot \bar{x}$
- Process standard deviation

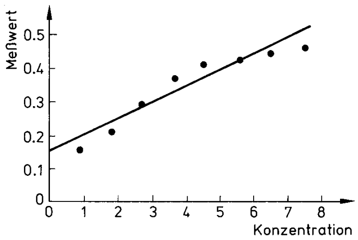
$$s_{x0} = \frac{s_y}{E(\bar{x})}$$

- Process variation coefficient

$$V_{x0} = \frac{s_{x0}}{\bar{x}} \cdot 100\%$$

## Check for Linearity

- If possible always use linear calibration function, polynomial regression only in special cases
- Visual linearity test
  - Graphical display incl. Calibration line
  - If there is an obvious non-linearity refrain from a statistical test



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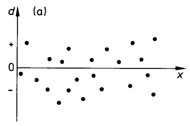
## Check for linearity

- Mandel-test
  - Calculation of the linear calibration function y=a+bx and the second-order calibration function $y=a+bx+cx^2$ including the corresponding standard deviations of residues $s_{y1}$ (linear) and $s_{y2}$ (non-linear)
  - Calculation of the difference of variances $DS^2$:

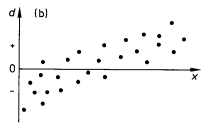
    $DS^2 = (N-2)s_{y_1}^2 - (N-3)s_{y_2}^2$ with a degree of freedom $f = 1$
  - Check with F-test $$F_{observed} = \frac{DS^2}{s_{y_2}^2}$$
  - Compare with tabulated value $F_{critical}$ for $f_1=1$, $f_2=N-3$, P=99%
  - If $F_{observed} < F_{critical}$, then we get **no** better adjustment with the second-order calibration function
  - The calibration function then is linear

# Residual Analysis

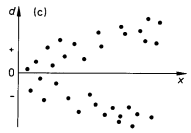
- Residues are the vertical distances of the measure values from the regression line
- Residues should be normally distributed



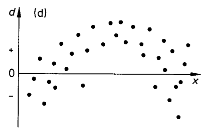

Normally distributed residues
correct model




linear trend
wrong model or calculation error




Increasing variances
inhomogeneity of variances



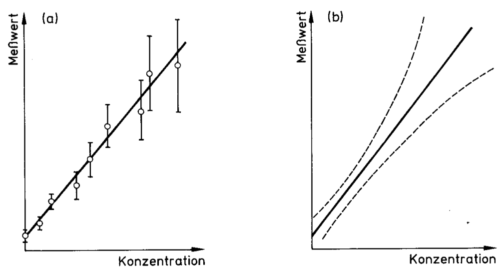

Non-linear
wrong regression function





# Homogeneity of Variances

- Linear regression assumes constant (homogeneous) imprecision (variance of values) over the whole working range
- Inhomogeneous variances:




- Inhomogeneity of variances not only leads to a higher imprecision, but due to a possible change in the slope of the regression line to a higher bias

# Check for Homogeneity of Variances

- Measure highest and lowest standard sample ten times each
- Calculate variances for both data sets

$$s_i^2 = \frac{\sum (y_{ij} - \bar{y}_i)^2}{n_i - 1}$$

- Check with the F-test

$$F_{observed} = \frac{s_N^2}{s_1^2}$$

- If $F_{observed} > F_{critical}$, then the variances are **not** homogeneous
- Possible consequences:
  - Reduce working range
  - Weighted regression
  - Multiple-Curve-Fitting





# Outlier test

- Calibration data have to be free from outliers
- The test for outliers assumes the correctness of the chosen regression approach
- From the residual analysis potential outliers can be identified
- The residual standard deviation is calculated with all values ($s_{y,A1}$) and without the outlier-suspect value ($s_{y,A2}$)
- The check can be made using the F-test or the t-test

# Outlier Test using F-test

- The residual standard deviations are checked for significant differences
- Calculate

$$F_{observed} = \frac{(N_{A1}-2)s^2_{y_{A1}} - (N_{A2}-2)s^2_{y_{A2}}}{s^2_{y_{A2}}}$$

- And compare with the critical value from the table with $f_1$=1, $f_2$=$N_{A2}$-2, P=95%
- If $F_{observed} < F_{critical}$, no outlier





# Outlier T using t-test

- Calculate prediction interval of the regression line without outlier

$$PI(\hat{y}_O) = \hat{y}_O \pm t \cdot s_{y_{A2}} \cdot \sqrt{1 + \frac{1}{N_A} + \frac{(x_O - \bar{x})^2}{\sum x_i^2 - \frac{1}{N_A}\left(\sum x_i\right)^2}}$$

$$= a_2 + b_2 \cdot x_O \pm t \cdot s_{y_{A2}} \cdot \sqrt{1 + \frac{1}{N_A} + \frac{(x_O - \bar{x})^2}{\sum x_i^2 - \frac{1}{N_A}\left(\sum x_i\right)^2}}$$

t = tabulated value of t - distribution ($P = 95\%, f = N_A$-2)
$N_A$ = $N$-1
$x_O$ = concentration of eliminated outlier
$\bar{x}$ = mean of all $x_i$ (without $x_A$)

- If the potential outlier lies within the prediction interval, it has to be included again in the data set
- **If a value is statistically proven to be an outlier, then the cause for the outlying value must be searched and eliminated. Then repeat the complete calibration.**

## Limit of Detection, Limit of Quantitation

- With these values the lower limit of the working range can be characterised
- There are numerous different definitions and calculation methods





## Glossary – Limit of Detection (lod)

- The limit of detection is the lowest amount (of substance) of the analyte in a sample, that can be detected, but not necessarily quantified as an exact value
- Statistically
  - If this value is exceeded, we recognise with an error probability of $\alpha$, that the amount of the analyte is higher than that in a blank sample

## Estimate for the Limit of Detection

- Coarse Estimate:
  LoD = $B+3S_0$ or $0+3S_0$
  (for fortified samples; typically, three times the noise level)
  - B=Blank
  - $S_0$=standard deviation of 10 measurements
- Alternative method (mostly used in chromatography): Signal-Noise-Ratio=3





## Expression of the LoD

- Analyze
  - 10 independent sample blanks and get the mean sample blank value (B) **or**
  - 10 independent sample blanks fortified at lowest acceptable concentration.
- Express LoD as the analyte concentration corresponding to
  - B+3s or
  - 0+3s

  (s being the sample standard deviation).

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# Detection Limits – the IUPAC Approach

- Concepts related to the detection limit are based on two theoretical probabilities:
  - $\alpha$ - the probability of obtaining an analytical response above a certain limit
  - $\beta$ - the probability of obtaining an analytical response below the critical limit when the analyte is present at some higher concentration



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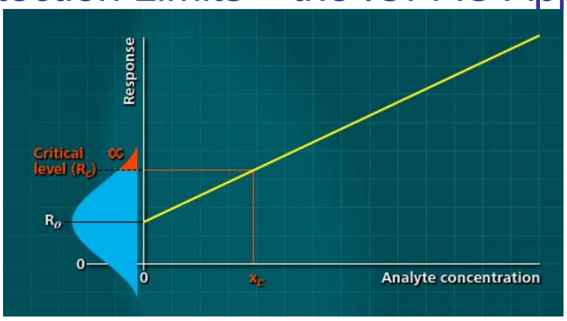
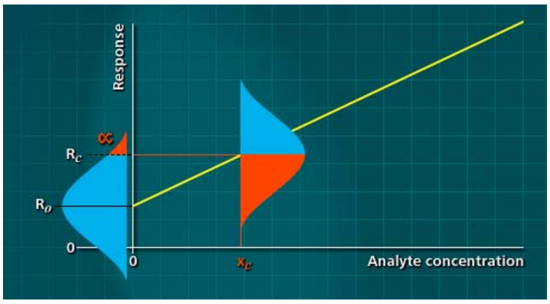
# Detection Limits – the IUPAC Approach




- Distribution of results at a real concentration of zero
- The results are centred around $R_0$ with a standard deviation of $\sigma$
- There is a probability of $\alpha$, that a result would exceed the *critical value* $R_c$ for the signal, or the corresponding value $x_c$, if the analyte were really absent (false positive result)
- This level therefore is a decision limit, at which we can say the analyte is present with a level of confidence ($1-\alpha$)
- For 95% confidence ($\alpha$=0.05): $R_c=R_0+1.65\sigma$)

# Detection Limits – the IUPAC Approach




- If the analyte is really present at concentration $x_c$, half the results would be detected below $R_c$: i.e. they would be not detected (false negative)
- There must be some higher concentration where the possibility of „not detected“ is low



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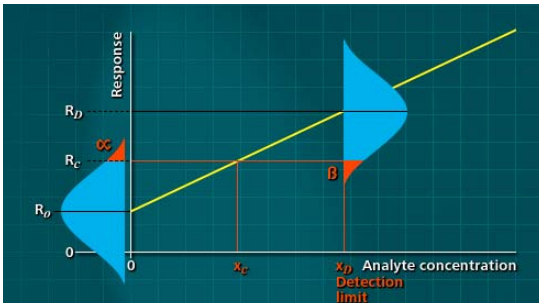
Detection Limits – the IUPAC Approach




- At at true concentration of $x_D$ there is a probability of $\beta$ of seeing a response below $R_c$
- By letting $\beta$ become sufficiently small we reduce the „not detected“ to an acceptable level
- The corresponding concentration is the detection limit
- Usually both $\alpha$ and $\beta$ are set to give 95% confidence, leading to $R_D=R_0+3.3\sigma$
- By using the calibration curve to convert to concentrations, we see that the detection limit is $x_D=3\sigma_x$

## Glossary – Limit of Quantitation (loq)

- The limit of determination is the lowest amount (of substance) of the analyte in a sample, that can be quantified with a sufficient accuracy



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## Estimate for the Limit of Quantitation

- Coarse Estimate:
  $LoQ = B+10S_0$ or $0+10S_0$
  - B=Blank
  - $S_0$=standard deviation of 10 measurements
- Alternative method (mostly used in chromatography):
  Signal-Noise-Ratio=10

## Glossary - Selectivity

- Selectivity is a measure that shows to what extend a method can be used to determine certain analytes in mixtures and matrices without interferences caused by other components which have a similar behaviour
- IUPAC recommends, to use the similar term "specificity" not any more
- During a validation it is necessary to check if the method has a sufficient selectivity for the intended purpose

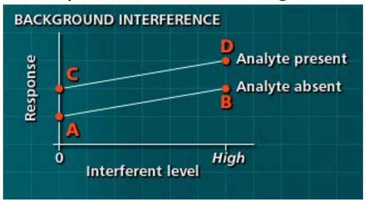


## Lack of Selectivity - Interferences

- Interferences can be detected by adding a potential interfering substance to a „normal" matrix and analysing with and without the interfering substance
- A suitable procedure uses 4 solutions:

| Analyte | Content of interfering substance zero | high |
|---|---|---|
| without | A | B |
| with | C | D |

- One possible interfering influence is the background interference:




A, B, C, D are the measurement results

If A≠B, then there is a background interference (shift of the measurement results).

An interfering substance, different from the analyte, produces a measurement value. This happens also in the absence of the analyte

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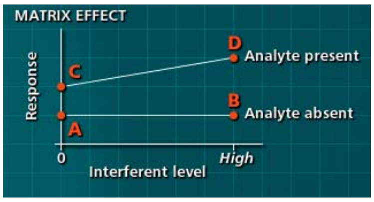
# Lack of Selectivity - Interferences

- Another interference is he matrix effect




A, B, C, D again are measurement results

If (D-C)≠(B-A), then there is a matrix effect.

This type of interference changes the slope of the calibration function (i.e. change of sensitivity)

To check, if the differences are significant, repeat the measurements of A, B, C and D and test with 2-sample-t-test

Matrix effects can also be uncovered with the standard addition procedure



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# Glossary – Robustness/Ruggedness

- Robustness/Ruggedness is the insensitiveness of a method to small deviation in the experimental procedure described in the method
- ‚Soft' methods, sensitive to slight deviations, are unlikely to perform well in interlaboratory comparisons
- Possible
- Potential topics to be checked in a robustness study:
    - Volumes
    - Concentrations of reagents
    - Duration of heating and extraction procedures
    - Temperatures
    - pH
    - ...

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# Ruggedness Test

- There is an economical design (a fractional factorial design) for testing for ruggedness.
- Up to n factors can be tested simultaneously in an experiment requiring $2^k > n > 2^{k-1}$ runs of the experiment (k is an integer)
- Thus, for an experiment involving seven factors, eight runs are required.
- Each run contains a combination of factors at perturbed levels
- The perturbed levels should be either higher (+) or lower (-) than the levels specified in the method procedure.
- The degree of perturbation should represent the maximum excursion from the specified level likely to be encountered in normal practice, e.g. if the method requires heating to 100°C for 1 hour, reasonable perturbed times might be 50 and 70 minutes



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# Layout of a Ruggedness Test - Example

| Factor | Run number | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Sample weigth | + | + | + | + | - | - | - | - |
| Conc. reagent 1 | + | + | - | - | + | + | - | - |
| Conc. reagent 2 | + | - | + | - | + | - | + | - |
| Total volume | - | - | + | + | + | + | - | - |
| Time of heating | - | + | - | + | + | - | + | - |
| Reaction temperature | - | + | + | - | - | + | + | - |
| pH of solution | + | - | - | + | - | + | + | - |
| Analyte found | 68 | 59 | 67 | 64 | 64 | 66 | 60 | 70 |
| + = positive perturbation - = negative perturbation | | | | | | | | |

- The effect of a factor is given by:
  (mean of runs with +-perturbed)-(mean of runs with --perturbed)
- In the example the effect of the time of heating is
  (59+64+64+60)/4 – (68+67+66+70)/4=-6
- The method is easy to interpret so long as only one or two of the factors are sensitive

## Trueness

- Trueness of the analytical method can be examined by several methods
  - Analysis of a reference material
  - Analysis of a certified reference material
  - Analysis of an in-house reference material
  - Interlaboratory comparison
  - Reference methods
  - Recovery experiments





## Precision

- Precision of the method can be examined by repeated measurement
- Repetitions can be made under
  - Repeatability conditions
  - Between-batch-conditions
- Precision check is often done in combination with control charts

## Standard Addition Procedure - What's that?

- Standard addition procedure is a calibration in the real sample by stepwise addition of a defined amount of analyte





## Standard Addition Procedure – in which Cases?

- If differences in the composition of the matrix have a strong influence on the trueness of the result (matrix effects)
- If no matrix-matched calibration standards are available
- If only a few samples have to be analysed

# Standard Addition Procedure - Preconditions

- Blank and background corrected measurement values $y_1$
- Linear correlation between measurand y and content x
- Standard deviation of residues $s_{y,x}$ independent from y (Homogeneity of variances)
- Homogeneous sub-sampling must be possible
- Precise addition of analyte must be possible



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# Standard Addition Procedure - Procedure

- Division in n equal sub-samples
- Addition of known increasing portions $z_i$ of the analyte to n-1 sub-samples in equidistant steps and normalisation of all sub-samples
  $\rightarrow$ pairs o variates $(x_{z_1,j};y_{1,j}),(x_{z_2,j};y_{2,j}),\ldots(x_{z_n,n_a};y_{n,n_a})$
- Linea Regression
  $\rightarrow \; y = a + b \cdot x$

x = content quantity
$y_i$ = blank and background corrected measurement
$n_a$ = number of measurements per sub-sample
j = index for repeated measurements
$x_A$ = content of the analysed sample

- Extrapolation to the intercept point with the abscissa delivers the sought content
  $\rightarrow \; x_A = -x_{(y=0)} = -a/b$

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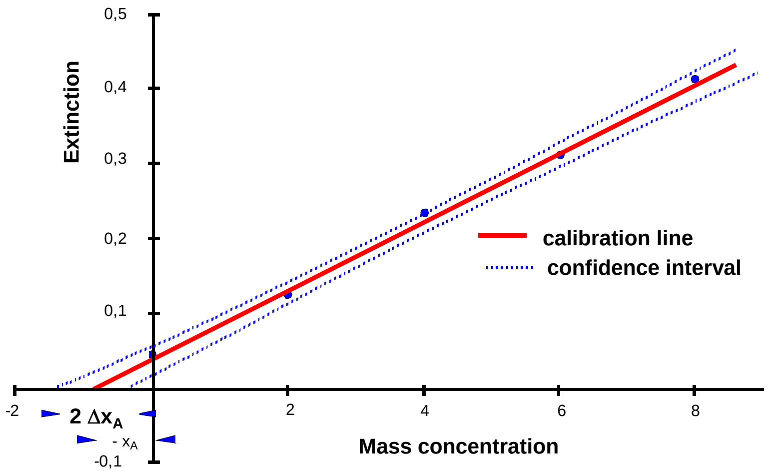
# Standard Addition Procedure - Graphical Display

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# Standard Addition Procedure - Uncertainty

- The uncertainty of the calculated value $x_A$ can be quantified with the half width of the confidence interval of the result

$$\Delta x_A = \frac{t_{f,\alpha} \cdot s_{y,x}}{b} \cdot \sqrt{\frac{1}{n \cdot n_A} + \frac{[\bar{x}_z - (-x_A)]^2}{\sum (x_{z_i} - \bar{x}_z)^2}}$$

$x_A$ = half width of the confidence interval of $x_A$
$t_{f,\alpha}$ = two - sided quantile of the t - distribution with probability $\alpha$
$\bar{x}_z$ = arithmetic mean of $x_{z_i}$
$\sum (x_{z_i} - \bar{x}_z)^2$ = sum of all squares of deviations of all $x_{z_i}$

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# Measurement uncertainty revisited
## Alternative approaches to uncertainty evaluation

based on EUROLAB Technical Report No. 1/2007

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# GUM – Guide to the expression of uncertainty in measurement

- acknowledged as the master document of measurement uncertainty
- Main GUM principles:
  - uncertainty evaluation is comprehensive, accounting for all relevant sources of measurement error
  - uncertainties arising from random and systematic effects are treated alike, i.e. are expressed and combined as variances of associated probability distributions
  - statistical evaluation of measurements (Type A) and alternative techniques, based on other data / information (Type B), are recognised and utilised as equally valid tools
  - uncertainties of final results are expressed as standard deviations (standard uncertainty) or by multiples of standard deviations (expanded uncertainty) with a specified numerical factor (coverage factor).

## Why is the GUM often criticised as inapplicable?

- the GUM almost exclusively treats a single approach for uncertainty evaluation: the "**modelling approach**", based on a comprehensive mathematical model of the measurement procedure, where every uncertainty contribution is associated with a dedicated input quantity, the uncertainty contributions are evaluated individually and combined as variances.
- This is often (mis)conceived as being "the GUM approach" for uncertainty evaluation





## Other approaches

- the GUM principles admit a variety of approaches, but this fact was buried under a plethora of papers and lectures celebrating the "modelling approach" as a new paradigm in measurement quality assurance.
- Alternative "empirical approaches" have only recently received greater attention.
- Data utilised in these approaches are typically precision and bias data obtained from within-laboratory validation studies, quality control, interlaboratory method validation studies, or proficiency tests

## Are those alternative approaches GUM-conform?

- Yes, if the GUM principles are observed
  - a clear definition of the measurand, i.e. the quantity to be measured
  - a comprehensive specification of the measurement procedure and the test items, and
  - a comprehensive analysis of the effects impacting the measurement results.



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## Empirical approaches

- use of reproducibility standard deviation from an interlaboratory method validation study
- use of within-laboratory data (data from method validation studies and quality control carried out in the lab)
- use of laboratory performance data from PT

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# Uncertainty evaluation is a difficult task, prone to mistakes

- Measurement uncertainty is often significantly underestimated
  - In the modelling approach e.g. major uncertainty contributions may be lacking, input uncertainties may be misestimated, and correlations may be overlooked
  - In the empirical approach, significant effects which have not been included in the experimental design for the method performance investigation, e.g. variations of test items or test conditions, will be missing in a (collaborative or within-laboratory) reproducibility standard deviation



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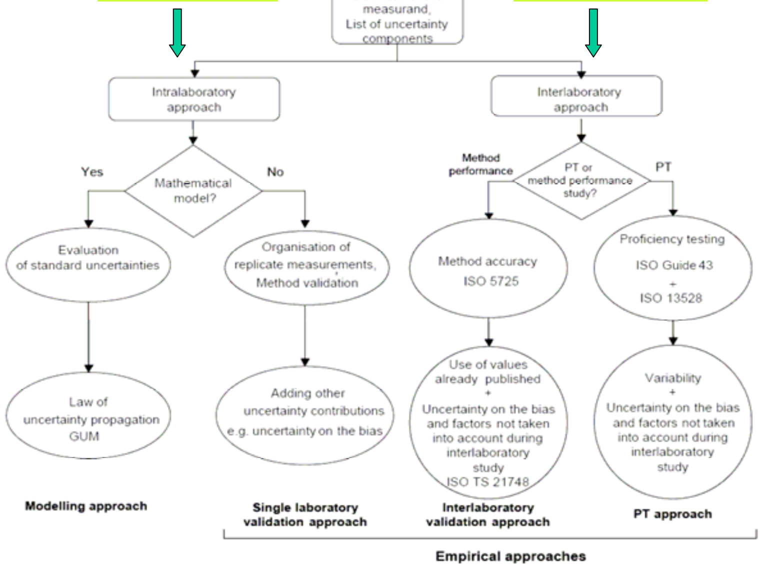
**within the own lab** | **collaborative study**

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# Common points between the different approaches

- always important
  - Define clearly, with no ambiguity the measurand or the characteristic to be measured, analysed or tested
  - Analyse the measuring or testing process carefully in order to identify the major components of uncertainty and to examine if they are taken on board in the application of the law of propagation of uncertainty or if they are active during the repetition of observations organised to evaluate repeatability and reproducibility or if they are included in collaborative studies.
  - It is also important to admit that in some situations, it is not possible to identify the individual components of the uncertainty. The symptom of this can be seen when the uncertainty evaluated by applying the modelling approach leads to a smaller uncertainty than the variation observed in laboratory intercomparisons

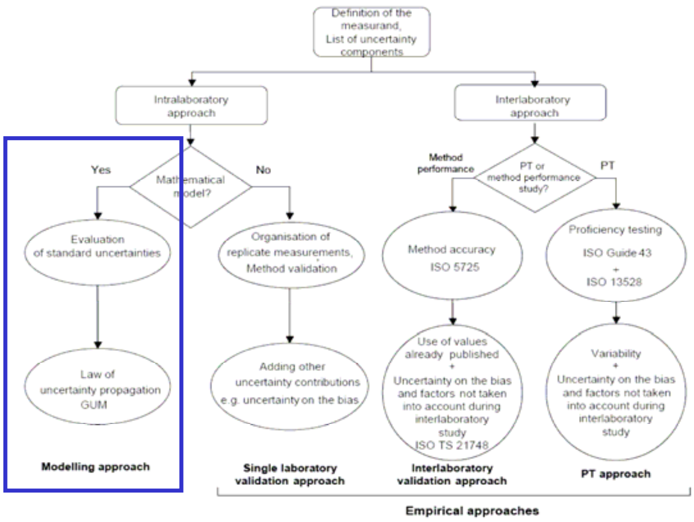




# Sampling

- Where sampling activities are performed, it is also important to define the measurand clearly
  - do we seek information related to the test item transmitted to the laboratory for analysis or
  - do we need information concerning the batch (the sampling target)
- It is obvious that the uncertainty will be different in both cases

# The modelling approach








# The modelling approach

- based on a model formulated to account for the interrelation of all the influence quantities that significantly affect the measurand
- corrections are assumed to be included in the model to account for all recognised, significant systematic effects
- the application of the law of propagation of uncertainty enables evaluation of the combined uncertainty on the result
- the approach depends on partial derivatives for each influence quantity, so depends on an equation for the measured result

## The modelling approach

- typical output of the modelling approach is an "uncertainty budget"
- for each input quantity $x_i$
  - the standard uncertainty $u(x_i)$ is determined
  - and the sensitivity coefficient $c_i = \partial y/\partial x_i$
  - resulting in the uncertainty contribution $u_i(y) = c_i \times u(x_i)$
- Unless correlation among input quantities has to be taken into account, the standard uncertainty u(y) is given by the root sum of squares of the uncertainty contributions $u_i$

$$u(y) = \sqrt{\sum u_i^2(y)}$$



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## The modelling approach

- By default in an uncertainty budget absolute uncertainties are used. Conversion to relative uncertainties is always possible but requires due care (other sensitivity coefficients)
- As an obvious benefit, an uncertainty budget provides information about the relative magnitude of the various uncertainty contributions. This information is particularly useful when planning improvements of the measurement procedure.

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# The modelling approach
# Example: PT reference values for As

- Description of the measurand:
  We want to know the concentration of As in the final PT sample



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# The modelling approach
# Example: PT reference values for As

- Description of the procedure:
  - A stock solution is prepared by dissolving a $As_2O_3$ (with a certain purity; difference weighing on an analytical balance) in a certain amount of analytical grade water (difference weighing on a toploader balance)
  - This stock solution is diluted by weighing a certain amount of the stock solution (difference weighing on a toploader balance) and filling up to a certain amount (also difference weighing on a toploader balance)

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## The modelling approach
## Example: PT reference values for As

- Description of the procedure:
  - A certain amount of this dilute solution is weighed (difference weighing on a toploader balance) and diluted to the final amount (difference weighing on a bigger balance)
  - The density is gravimetrically measured with a pycnometer to calculate the concentration





## The modelling approach
## Example: PT reference values for As

- The input quantities can be derived from the mathematical model
- For all weighings of material with a density significantly different from the calibration mass pieces, a buoyancy correction has to applied (in our case all weighings of aqueous solutions)

# The modelling approach
# Example: PT reference values for As

- The mathematical model

$$c_{lot} = \frac{m_{As_2O_3} \cdot P \cdot F_{As/As_2O_3}}{m_{ss\_t} \cdot K} \cdot \frac{m_{ss} \cdot K}{m_{dil\_t} \cdot K} \cdot \frac{m_{dil} \cdot K}{m_{lot} \cdot K} \cdot \rho_{lot}$$

$$= \frac{m_{As_2O_3} \cdot F_{As/As_2O_3} \cdot P \cdot m_{ss} \cdot \rho_{lot} \cdot m_{dil}}{m_{ss\_t} \cdot m_{lot} \cdot K \cdot m_{dil\_t}}$$

$m_{As2O3}$ = mass of arsenic oxide in stock solution in g
P = purity
$F_{As/As2O3}$ = quotient of molecular masses
$m_{ss\_t}$ = total mass of stock solution in g
K = buoyancy correction factor
$m_{ss}$ = mass of stock solution in the diluted solution in g
$m_{dil\_t}$ = total mass of diluted solution
$m_{dil}$ = mass of diluted solution in the final lot
$m_{lot}$ = total mass of the lot in g
$\rho_{lot}$ = density of the lot in g/l





# The modelling approach
# Example: PT reference values for As

- Identifying the sources of uncertainties
  - for all weighings
    - precision of the weighing
    - trueness of the balance (linearity)
    - uncertainty of the buoyancy correction factor
  - the purity of the chemical
  - the molecular masses of As and O
  - density measurement

## The modelling approach
## Example: PT reference values for As

- All uncertainty contributions have to be quantified as standard uncertainty $u(x_i)$ of the input quantity $x_i$
  - with type A estimation (statistical information)
  - or type B estimation (all other informations)



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## The modelling approach
## Example: PT reference values for As



- quantifying the precision of weighings
  - modelling experiments using approximately the same masses as during sample preparation
  - 20 difference weighings → standard deviation = standard uncertainty

40g + 2g

| tare | total | difference |
|---|---|---|
| 40,0029 | 42,0029 | 2,0000 |
| 40,0027 | 42,0027 | 2,0000 |
| 40,0026 | 42,0028 | 2,0002 |
| 40,0026 | 42,0028 | 2,0002 |
| 40,0027 | 42,0027 | 2,0000 |
| 40,0026 | 42,0027 | 2,0001 |
| 40,0026 | 42,0026 | 2,0000 |
| 40,0025 | 42,0026 | 2,0001 |
| 40,0025 | 42,0026 | 2,0001 |
| 40,0025 | 42,0026 | 2,0001 |
| 40,0024 | 42,0026 | 2,0002 |
| 40,0024 | 42,0026 | 2,0002 |
| 40,0024 | 42,0026 | 2,0002 |
| 40,0024 | 42,0026 | 2,0002 |
| 40,0024 | 42,0026 | 2,0002 |
| 40,0024 | 42,0026 | 2,0002 |
| 40,0024 | 42,0026 | 2,0002 |
| 40,0024 | 42,0025 | 2,0001 |
| 40,0024 | 42,0025 | 2,0001 |
| 40,0024 | 42,0025 | 2,0001 |
| | mean | 2,0001 |
| | std | 7,86398E-05 |
| | rstd | 0,004% |

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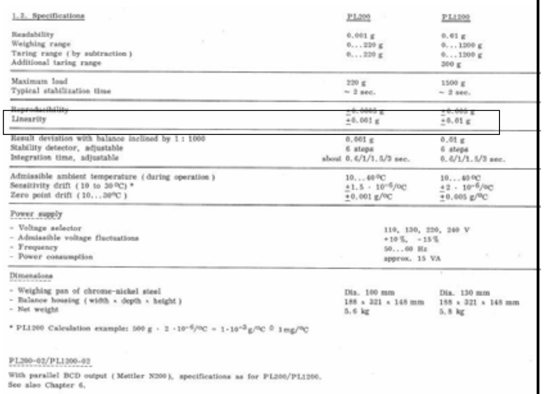
# The modelling approach
# Example: PT reference values for As

- quantifying the trueness of weighings
  - the manufacturer allows for a certain tolerance in the linearity of the balance
  - this tolerance is taken as rectangular distribution
  - → s = a/√3



| 1.3. Specifications | PL200 | PL1200 |
|---|---|---|
| Readability | 0.001 g | 0.01 g |
| Weighing range | 0...220 g | 0...1200 g |
| Taring range (by subtraction) | 0...220 g | 0...1200 g |
| Additional taring range | | 300 g |
| Maximum load | 220 g | 1500 g |
| Typical stabilization time | ~ 2 sec. | ~ 2 sec. |
| Reproducibility | ±0.0005 g | ±0.005 g |
| Linearity | ±0.001 g | ±0.01 g |
| Result deviation with balance inclined by 1 : 1000 | 0.001 g | 0.01 g |
| Stability detector, adjustable | 6 steps | 6 steps |
| Integration time, adjustable | about 0.4/1/1.5/3 sec. | 0.4/1/1.5/3 sec. |
| Admissible ambient temperature (during operation) | 10...40 °C | 10...40 °C |
| Sensitivity drift (10 to 30 °C) * | ±1.5 · 10⁻⁶/°C | ±2 · 10⁻⁶/°C |
| Zero point drift (10...30 °C) | ±0.001 g/°C | ±0.005 g/°C |
| **Power supply** | | |
| - Voltage selector | 110, 130, 220, 240 V | |
| - Admissible voltage fluctuations | +10 %, -15 % | |
| - Frequency | 50...60 Hz | |
| - Power consumption | approx. 15 VA | |
| **Dimensions** | | |
| - Weighing pan of chrome-nickel steel | Dia. 100 mm | Dia. 130 mm |
| - Balance housing (width × depth × height) | 188 × 321 × 148 mm | 188 × 321 × 148 mm |
| - Net weight | 5.6 kg | 5.8 kg |

* PL1200 Calculation example: 500 g · 2 · 10⁻⁶/°C = 1 · 10⁻³ g/°C ≙ 1 mg/°C

PL200-02/PL1200-02

With parallel BCD output (Mettler N200), specifications as for PL200/PL1200. See also Chapter 6.



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# The modelling approach
# Example: PT reference values for As

- uncertainty of the balance
  - since precision and trueness are additive the sensitivity coefficients $c_i = \partial y / \partial x_i = 1$
  - with that $u_{balance} = \sqrt{u^2_{precision} + 2 \cdot u^2_{trueness}}$

| **Uncertainty for** | **200g + 500g** | | | | | |
|---|---|---|---|---|---|---|
| *parameter* | *specification* | *probability distribution* | *divisor* | *standard uncertainty* | *sensitivity coefficient* | *uncertainty contribution* |
| precision | 0,065211881 | normal | 1 | 0,06521188 | 1 | 0,065211881 |
| trueness (lin) | 0,01 | rectangular | √3 | 0,0057735 | 1 | 0,005773503 |
| trueness (lin) | 0,01 | rectangular | √3 | 0,0057735 | 1 | 0,005773503 |
| | | | | | **$u_c$** | **0,065721047** |

# The modelling approach
# Example: PT reference values for As

- buoyancy correction

$$K_i = \frac{1 - \frac{\rho_{air}}{\rho_{cal}}}{1 - \frac{\rho_{air}}{\rho_i}}$$

with $\rho_{air}$ = 1,1788 g/l (average air density) and
$\rho_{cal}$ = 8000 g/l (approximate density of the metallic calibration mass pieces) and
$\rho_i$ = 1001 g/l (approximate density of an aqueous solution
we get K = 1.00103

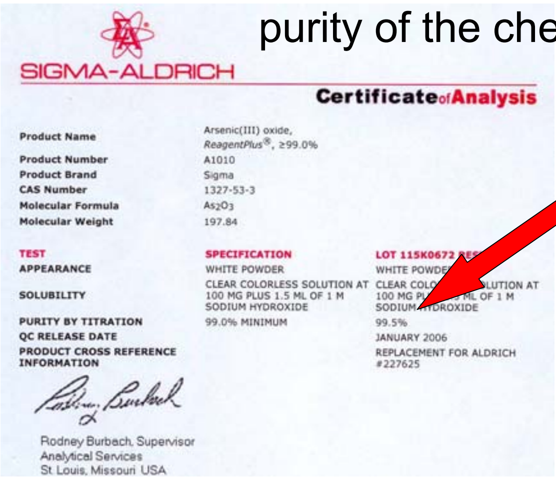
the uncertainty can be estimated from possible variations in the lab environment
from O. Rienitz (PTB) PhD Thesis: $u_K$ = 0.00011





# The modelling approach
# Example: PT reference values for As

## purity of the chemical


SIGMA-ALDRICH

Certificate of Analysis

| | | |
|---|---|---|
| Product Name | Arsenic(III) oxide, *ReagentPlus*®, ≥99.0% | |
| Product Number | A1010 | |
| Product Brand | Sigma | |
| CAS Number | 1327-53-3 | |
| Molecular Formula | $As_2O_3$ | |
| Molecular Weight | 197.84 | |
| TEST | SPECIFICATION | LOT 115K0672 RE[illegible] |
| APPEARANCE | WHITE POWDER | WHITE POWDE[illegible] |
| SOLUBILITY | CLEAR COLORLESS SOLUTION AT 100 MG PLUS 1.5 ML OF 1 M SODIUM HYDROXIDE | CLEAR COLO[illegible]LUTION AT 100 MG PL[illegible] ML OF 1 M SODIUM [illegible]DROXIDE |
| PURITY BY TITRATION | 99.0% MINIMUM | 99.5% |
| QC RELEASE DATE | | JANUARY 2006 |
| PRODUCT CROSS REFERENCE INFORMATION | | REPLACEMENT FOR ALDRICH #227625 |

Rodney Burbach, Supervisor
Analytical Services
St Louis, Missouri USA

99.5%

Uncertainty?
It is assumed that the manufacturer can distinguish between 99.5% and 99.6% if they report 99.5%
Therefore rectangular distribution ±0.1%

$$u_P = \frac{0.001}{\sqrt{3}} = 0.00057$$

# The modelling approach
# Example: PT reference values for As

- Molecular masses of As and O
  - taken from an IUPAC publication
  - uncertainty is neglected





# The modelling approach
# Example: PT reference values for As

- Density measurement – procedure
  - Bring the sample and a bottle of analytical grade water to the same temperature
  - Weigh the empty pycnometer
  - Fill the pycnometer with sample and weigh it
  - Fill the pycnometer with water and weigh it
- Calculation

$$\frac{\rho_{\text{sample}}}{\rho_{\text{water}}} = \frac{m_{\text{pycn+sample}} - m_{\text{pycn}}}{m_{\text{pycn+water}} - m_{\text{pycn}}} \rightarrow \rho_{\text{sample}} = \frac{m_{\text{pycn+sample}} - m_{\text{pycn}}}{m_{\text{pycn+water}} - m_{\text{pycn}}} \cdot \rho_{\text{water}}$$

- and with buoyancy correction

$$\rho_{\text{sample}} = \frac{m_{\text{pycn+sample}} - m_{\text{pycn}}}{m_{\text{pycn+water}} - m_{\text{pycn}}} \cdot \rho_{\text{water}} \cdot \left(1 - \frac{\rho_{\text{air}}}{\rho_{\text{water}}}\right) + \rho_{\text{air}}$$

$\rho_{\text{water}}$ taken from a PTB table for the measured temperature

# The modelling approach
# Example: PT reference values for As

- Density measurement uncertainty
  - own uncertainty budget
  - uncertainty sources:
    - balance – as shown above
    - table – uncertainty neglected
    - temperature measurement – uncertainty of the thermometer taken from the calibration certificate
    - density of the air – from normal variations in the lab



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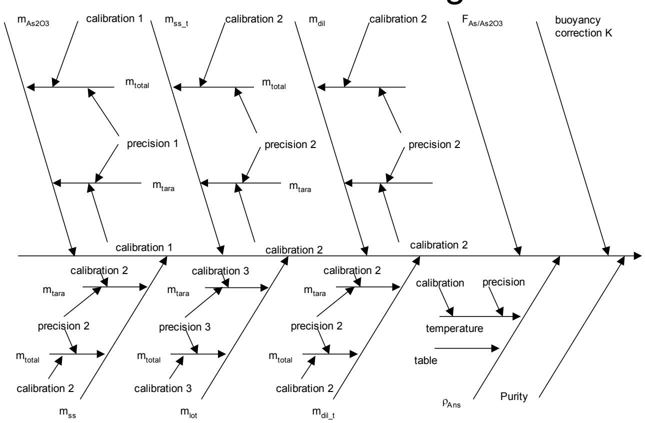
# The modelling approach
# Example: PT reference values for As



- all that uncertainty contributions can be illustrated in a fishbone diagram



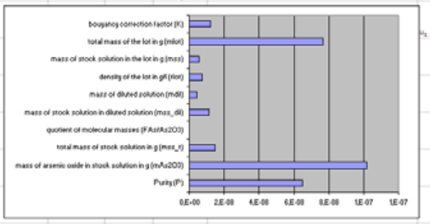
# The modelling approach
# Example: PT reference values for As

- For each input quantity we calculate in a spreadsheet (as shown by Angelique in 2005)
  - its standard uncertainty $u(x_i)$
  - its sensitivity coefficient $c_i = \partial y / \partial x_i$
  - its uncertainty contribution $u_i(y) = c_i \times u(x_i)$



$$c_{lot} = \frac{m_{As_2O_3} \cdot F_{As/As_2O_3} \cdot P \cdot m_{ss} \cdot \rho_{lot} \cdot m_{ss\_dil}}{m_{ss\_t} \cdot m_{lot} \cdot K \cdot m_{dil}}$$

| | parameter | estimated value | specification | probability distribution | divisor | standard uncertainty ($u_i$) | sensitivity coefficient ($c_i$) | sensitivity coefficient ($c_i$) | uncertainty contribution ($c_i u_i$) | abs | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 3 | Purity (P) | 99,50% | 0,10% | Rechteck | $\sqrt{3}$ | 0,00057735 | $\frac{m_{As_2O_3} \cdot F_{As/As_2O_3} \cdot m_{ss} \cdot \rho_{lot} \cdot m_{ss\_dil}}{m_{ss\_t} \cdot m_{lot} \cdot K \cdot m_{dil}}$ | 0,000112682 | 6,5057E-08 | 6,5057E-08 | from MERCK certificate |
| 4 | mass of arsenic oxide in stock solution in g ($m_{As2O3}$) | 0,1853 | 1602MP 40-0,2 | | | 0,000167986 | $\frac{F_{As/As_2O_3} \cdot P \cdot m_{ss} \cdot \rho_{lot} \cdot m_{ss\_dil}}{m_{ss\_t} \cdot m_{lot} \cdot K \cdot m_{dil}}$ | 0,000605065 | 1,01642E-07 | 1,01642E-07 | uncertainty of balance 1 |
| 5 | total mass of stock solution in g ($m_{ss\_t}$) | 499,41 | PL1200 200-500 | | | 0,065721047 | $-\frac{m_{As_2O_3} \cdot F_{As/As_2O_3} \cdot P \cdot m_{ss} \cdot \rho_{lot} \cdot m_{ss\_dil}}{m_{ss\_t}^2 \cdot m_{lot} \cdot K \cdot m_{dil}}$ | -2,24502E-07 | -1,47545E-08 | 1,47545E-08 | uncertainty of balance 2 |
| 6 | quotient of molecular masses ($F_{As/As2O3}$) | 0,75739018 | | | | 0 | $\frac{m_{As_2O_3} \cdot P \cdot m_{ss} \cdot \rho_{lot} \cdot m_{ss\_dil}}{m_{ss\_t} \cdot m_{lot} \cdot K \cdot m_{dil}}$ | 0,000148033 | 0 | 0 | from IUPAC data; uncertainty negligible |
| 7 | mass of stock solution in diluted solution ($m_{ss\_dil}$) | 100,00 | PL1200 200-200 | | | 0,010160985 | $\frac{m_{As_2O_3} \cdot F_{As/As_2O_3} \cdot P \cdot m_{ss} \cdot \rho_{lot}}{m_{ss\_t} \cdot m_{lot} \cdot K \cdot m_{dil}}$ | 1,12119E-06 | 1,13923E-08 | 1,13923E-08 | uncertainty of balance 2 |
| 8 | mass of diluted solution ($m_{dil}$) | 996,45 | PL1200 200-1000 | | | 0,039310953 | $-\frac{m_{As_2O_3} \cdot F_{As/As_2O_3} \cdot P \cdot m_{ss} \cdot \rho_{lot} \cdot m_{ss\_dil}}{m_{ss\_t} \cdot m_{lot} \cdot K \cdot m_{dil}^2}$ | -1,12510E-07 | -4,42319E-09 | 4,42319E-09 | uncertainty of balance 2 |
| 9 | density of the lot in g/l ($\rho_{lot}$) | 997,907535 | | | | 0,06596093 | $\frac{m_{As_2O_3} \cdot F_{As/As_2O_3} \cdot P \cdot m_{ss} \cdot m_{ss\_dil}}{m_{ss\_t} \cdot m_{lot} \cdot K \cdot m_{dil}}$ | 1,12354E-07 | 7,41095E-09 | 7,41095E-09 | see separate calculation |
| 10 | mass of stock solution in the lot in g ($m_{ss}$) | 200 | PL1200 200-200 | | | 0,010160985 | $\frac{m_{As_2O_3} \cdot F_{As/As_2O_3} \cdot P \cdot \rho_{lot} \cdot m_{ss\_dil}}{m_{ss\_t} \cdot m_{lot} \cdot K \cdot m_{dil}}$ | 5,60593E-07 | 5,69617E-09 | 5,69617E-09 | uncertainty of balance 2 |
| 11 | total mass of the lot in g ($m_{lot}$) | 49900 | BFW300 | | | 34,09481105 | $-\frac{m_{As_2O_3} \cdot F_{As/As_2O_3} \cdot P \cdot m_{ss} \cdot \rho_{lot} \cdot m_{ss\_dil}}{m_{ss\_t} \cdot m_{lot}^2 \cdot K \cdot m_{dil}}$ | -2,24686E-09 | -7,66064E-08 | 7,66064E-08 | uncertainty of balance 3 |
| 12 | bouyancy correction factor (K) | 1,00103149 | | | | 0,00011 | $-\frac{m_{As_2O_3} \cdot F_{As/As_2O_3} \cdot P \cdot m_{ss} \cdot \rho_{lot} \cdot m_{ss\_dil}}{m_{ss\_t} \cdot m_{lot} \cdot K^2 \cdot m_{dil}}$ | -0,000112003 | -1,23203E-08 | 1,23203E-08 | from PTB informations |
| 13 | result (g/l) | 0,00011212 | | | | | | $u_c$ | 1,45046E-07 | | |
| 14 | **result in mg/l** | **0,11211854** | | | | | | | | | |
| 15 | **standard uncertainty in mg/l** | **0,00014506** | | | | | | | | | |
| 16 | **rel. uncertainty** | **0,13%** | | | | | | | | | |
| 17 | **exp. uncertainty** | **0,00029009** | | | | | | | | | |
| 18 | **exp. rel. uncertainty** | **0,26%** | | | | | | | | | |

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## The modelling approach
## Example: PT reference values for As

- The big advantage of the modelling approach:
  - the biggest contribution can be identified
  - in this case the weighing of the chemical



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## The modelling approach

- Scope of uncertainty data
  - An uncertainty budget refers to a specified measurement.
  - But the algorithm behind the uncertainty budget applies to all measurements made using the same measurement system and procedure on comparable test items.
  - For any new measurement, the (combined) standard uncertainty u(y) is obtained by plugging the input data $x_i$ and $u(x_i)$ for this measurement into the algorithm, which then will return y and u(y).
  - Of course, if the input data are close to those for a previous measurement, the standard uncertainty u(y) will be about the same as obtained before

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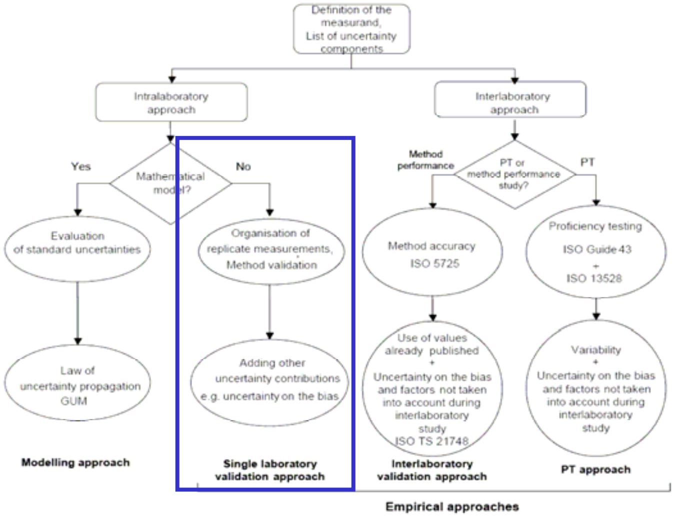
## The single laboratory validation approach



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## The single laboratory validation approach

- Basic principle
  - *Measurement accuracy = precision + trueness*
  - *Measurement uncertainty =*
    *within-lab reproducibility + uncertainty on the bias*
- Measurement uncertainty is estimated as a root sum of squares of a standard deviation s characterising the (im)precision of the measurement and an estimate b accounting for measurement bias, which gives the standard uncertainty u according to the schematic equation

$$u = \sqrt{s^2 + b^2}$$

# The single laboratory validation approach

- Bias correction
  - measurement bias is investigated, and corrective actions are taken to remove/reduce such bias to the greatest possible extent.
  - The bias-related uncertainty estimate accounts for the potential bias left after correction.
  - In practice, however, it happens quite often that significant bias is found, but the data are not sufficient for deriving a sound correction.
  - For example, it may be doubtful whether a single-level correction, based on measurements of a single standard, is applicable to the entire measuring range.
  - Then additional measurements, e.g. including another standard, should be made in order to characterise the bias to an appropriate degree. If this is not possible or not practical, a pragmatic alternative is to increase the uncertainty to account for the observed bias instead of attempting any correction





# The single laboratory validation approach

- Data on precision
  - The precision of a measurement procedure is investigated during method validation, monitored in quality control, and quantified by standard deviations obtained from replicate measurements on appropriate test items.
  - Depending on the conditions two different standard deviations can be obtained
    - $s_{rw}$ the within-laboratory repeatability standard deviation, obtained under repeatability conditions: same operator, same equipment, short-time repetition.
    - $s_{Rw}$ the within-laboratory reproducibility standard deviation, obtained under within-laboratory reproducibility conditions (often called “intermediate conditions”): different operators (if applicable), different equipment (if applicable), long-time repetition.

## The single laboratory validation approach

- Data on precision
  - For the purpose of estimating measurement uncertainty, the **within-laboratory reproducibility standard deviation $s_{Rw}$** will be used.
  - The repeatability standard deviation $s_{rw}$ is **not** normally a suitable uncertainty estimate, since it excludes major uncertainty contributions.



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## The single laboratory validation approach

- Data on bias
  - It is understood that measurement bias is eliminated to the greatest possible extent.
  - Residual bias is investigated during method validation, monitored in quality control, and quantified by deviations of measurement results on appropriate test items from corresponding reference values.
  - Most often reference materials are used for this purpose, but alternatively a reference measurement procedure may be used.

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## The single laboratory validation approach

- The bias contribution to measurement uncertainty is obtained from the mean deviation, the uncertainty of the reference value, and the (im)precision of the mean value of the replicate measurements made in the bias investigation:

$$b = \sqrt{\Delta^2 + u_{ref}^2 + \frac{s^2}{n}}$$





## The single laboratory validation approach

- Often different data on bias, obtained from different measurement series, will be available.
- Then these data should be compared and combined into a joint estimate for the uncertainty on bias, preferably as a function of the measurand level.
- In absence of within-laboratory bias investigations the PT approach (see later) may be used. In this case bias estimates are obtained from PT data (deviation of the laboratory´s result from the assigned value) while the within-laboratory reproducibility standard deviation is used as precision estimate.
- If bias estimates are not available at all, a pragmatic approach would be to expand the within-laboratory standard deviation using a rule-of-thumb factor. For the chemical field, e.g., average proportions between various within-laboratory and interlaboratory precision data were published.
- Considering that a factor of two is quite commonly observed in such studies, $u \approx 2\, s_{Rw}$ could be used as a preliminary estimate of measurement uncertainty in absence of bias data.

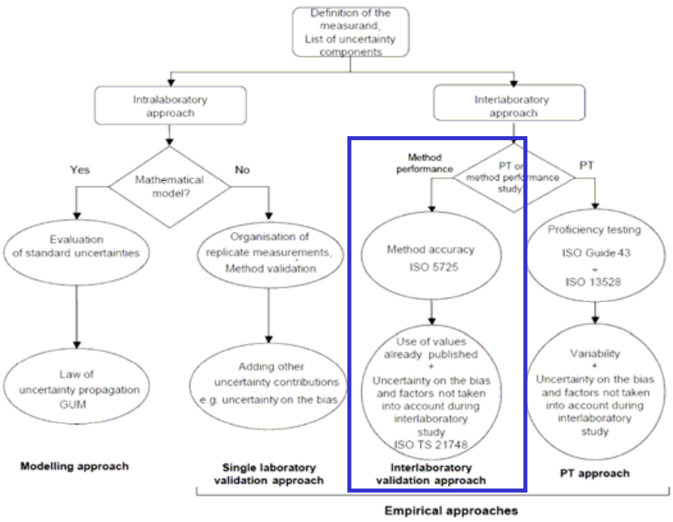
# The single laboratory validation approach

- Scope of uncertainty data
  - provided that the measurements are under statistical control, uncertainty estimates obtained using this approach are applicable for all measurements within the scope of the measurement procedure.
  - The application range of the uncertainty estimates is determined by the range covered in the validation study and the on-going quality control.
  - Therefore these investigations should include appropriate within-scope variations, e.g. different levels of the measurand and different types of test items





# The interlaboratory validation approach



# The interlaboratory validation approach

- For standard test procedures, trueness and precision are usually determined by an interlaboratory comparison (see ISO 5725-2).
- The main performance characteristics obtained in such studies are
  - $s_r$ the repeatability standard deviation
  - $s_R$ the interlaboratory reproducibility standard deviation
- For the purpose of estimating measurement uncertainty, the reproducibility standard deviation $s_R$ will be used.
- The repeatability standard deviation $s_r$ is **not** normally a suitable uncertainty estimate, since it excludes major uncertainty contributions.



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# The interlaboratory validation approach

- Bias
  - When suitable reference test objects are available, the interlaboratory validation study may also include an investigation of bias.
  - However, since the (interlaboratory) reproducibility standard deviation already comprises systematic effects due to different ways of operation in the laboratories involved (laboratory bias), such study will only address method bias.
  - Most often method bias is not significant or not relevant and is not specified as a separate performance characteristic.

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## The interlaboratory validation approach

- Estimation of uncertainty
  - the default uncertainty estimate from an interlaboratory validation study is, as a standard uncertainty u:

$$u = s_R$$



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## The interlaboratory validation approach

- According to *ISO/TS 21748 Guide to the use of repeatability, reproducibility and trueness estimates in measurement uncertainty estimation* this estimation may be applied if the laboratory can prove
  - that the tests are carried out in conformity with the standard, and in particular
  - that the measuring conditions and test items are consistent with those in the interlaboratory comparison, and
  - that for its implementation of the test procedure, trueness and precision are compatible with the inter-laboratory comparison data

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## The interlaboratory validation approach

- Scope of uncertainty data
  - Provided that the measurements are under statistical control, the reproducibility standard deviation $s_R$ is applicable for all measurements within the scope of the standard procedure.
  - For out-of scope applications, i.e. if the test conditions or the test objects substantially deviate from those in the interlaboratory validation study, the effect of these deviations has to be estimated and combined with the reproducibility standard deviation.
  - For this purpose the following schematic equation applies:

$$u = \sqrt{s_R^2 + \sum u_{other}^2}$$





## Approach using PT data

- The use of PT data for estimating measurement uncertainty is still under debate and authoritative references are few
- But if a laboratory has successfully participated in an inter-laboratory proficiency test, it may also utilise the results for estimating the measurement uncertainty for the measurement procedure used

## Approach using PT data

- PT data normally deliver
  - a reproducibility standard deviation $s_R$
  - the laboratory's deviation $\Delta$ from the assigned value
  - an uncertainty estimate $u_{ass}$ for the assigned value should also be available



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## Approach using PT data

- Similar to the single laboratory validation approach the uncertainty could be estimated according to $u^2 = s^2 + b^2$, where
  - precision s could be derived from within-laboratory standard deviation (e.g. control charts)
  - and bias from the deviation $\Delta$ in the PT according to the formula

$$b = \sqrt{\Delta^2 + u_{ass}^2 + \frac{s^2}{n}}$$

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## Approach using PT data

- Correction for bias
  - The bias estimate from PT studies should not normally be used for any correction of the results.
  - If the observed bias is regarded as unacceptable the laboratory has to take action and resolve this issue.



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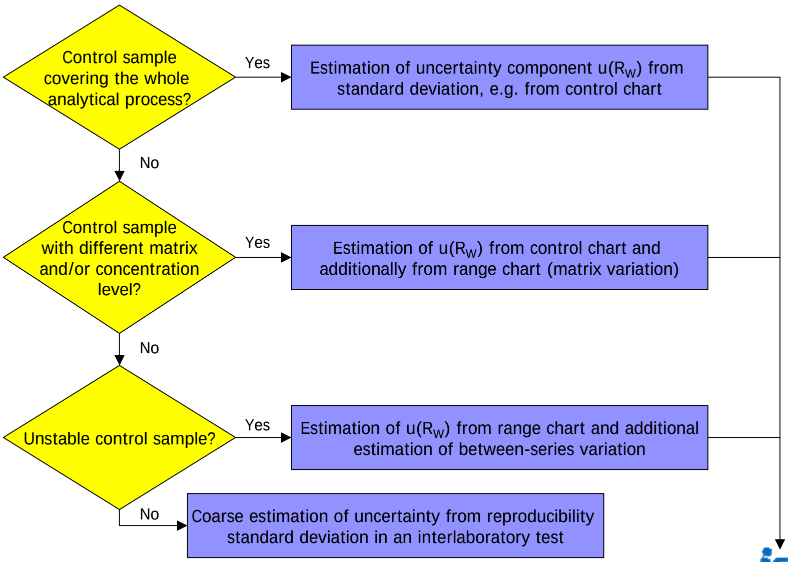
## NORDTEST approach

- An approach using a combination of single laboratory validation, interlaboatory validation and PT data is described in the NORDTEST „Handbook for calculation of measurement uncertainty in environmental laboratories“ and in a German Guideline for estimating measurement uncertainty based on validation data

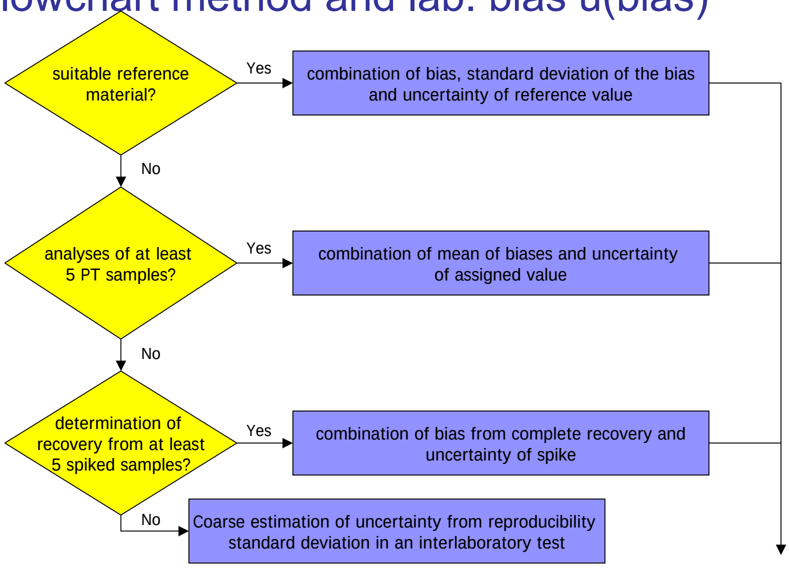
# Flowchart reproducibility $u(R_W)$








# Flowchart method and lab. bias u(bias)



# Reproducibility within-laboratory

- quantification of random variations has to be done under the same conditions as in routine analysis
- i.e.:
  - neither under repeatability conditions
  - nor under reproducibility conditions
  - but under between-series conditions
- this is called here „reproducibility within-laboratory“





# Reproducibility within the laboratory $R_w$ - method 1

## Control sample covering the whole analytical process

- if
  - the control sample covers the whole analytical process and
  - has a matrix similar to the samples,
- the within-laboratory reproducibility at that concentration level can simply be estimated from the analyses of the control sample
- If the analyses performed cover a wide range of concentration levels, also control samples of other concentration levels should be used.

| | | value | rel. Uncertainty | Comments |
|---|---|---|---|---|
| **Reproducibility within the lab $R_w$** | | | | |
| control sample 1<br>$\overline{X}$ = 20.01 µg/l | $s_{Rw}$ | standard deviation<br>0.5 µg/l | 2.5 % | from 75 measure-ments in 2002 |
| control sample 1<br>$\overline{X}$ = 250.3 µg/l | $s_{Rw}$ | standard deviation<br>3.7 µg/l | 1.5 % | from 50 measure-ments in 2002 |
| other components | | --- | | |

# Reproducibility within the laboratory $R_w$ – method 2

## Control samples for different matrices and concentrations

- if
  - a synthetic control solution is used for quality control, and
  - the matrix type of the control sample is **not** similar to the natural samples
- we have to take into consideration uncertainties arising from different matrices
- These can be estimated from the repeatability with different matrices (range control chart)

| | | value | u(x) | Comments |
|---|---|---|---|---|
| **Reproducibility within the lab $R_w$** | | | | |
| low level (2-15 µg/l) | $s_{Rw}$ | 0.5 µg/l from the mean control chart<br>0.37 µg/l from the range control chart | 0.6 µg/l | Absolute: $u(x)=\sqrt{0.5^2+0.37^2}$ |
| high level (>15 µg/l) | $s_{Rw}$ | 1.5 % from the mean control chart<br>3.6 % from the range control chart | 3.9 % | Relative: $u(x)=\sqrt{1.5\%^2+3.6\%^2}$ |

Note: The repeatability component is included two times!!



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# Reproducibility within the laboratory $R_w$ – method 3

## Unstable control samples

- if
  - the laboratory does not have access to stable control samples (e.g. measurement of dissolved oxygen)
- it is possible only to estimate uncertainty components from repeatability via the range control chart
- the „long-term“ uncertainty component (from batch to batch) has to be estimated e.g. by a qualified guess

| | | value | u(x) | Comments |
|---|---|---|---|---|
| **Reproducibility within the laboratory $R_w$** | | | | |
| Duplicate measurements of natural samples | $s_r$ | s = 0.024 mg/l<br>mean: 7.53 mg/l | 0.32 % | from 50 measurements |
| Estimated variation from differences in calibration over time | | s = 0.5 % | 0.5 % | based on experience |
| Combined uncertainty for $R_w$<br>Repeatability + Reproducibility in calibration | | $\sqrt{0.32\%^2+0.5\%^2}=0.59\%$ | | |

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## Method and Laboratory bias

- can be estimated from
  - the analysis of certified reference materials
  - the participation in proficiency tests
  - from recovery experiments
- Sources of bias should always be eliminated if possible
- According to GUM a measurement result should always be corrected if the bias is significant and based on reliable data such as analysis of a CRM.
- In many cases the bias can vary depending on changes in matrix. This can be reflected when analysing several matrix CRMs



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## Method and Laboratory bias u(bias) Components of uncertainty

- the bias (as % difference from the nominal or certified value)
- the uncertainty of the bias determination
- the uncertainty of the nominal/certified value $u(C_{ref})$

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## Method and Laboratory bias u(bias) - method 1a
## Use of one certified reference material

- The reference material should be analysed in at least 5 different analytical series
- Example: Certified value: 11.5 ± 0.5 (95% confidence interval)

| Uncertainty component from the uncertainty of the certified value | |
|---|---|
| Convert the confidence interval | The confidence interval is ± 0.5. Divide this by 1.96 to convert it to standard uncertainty: 0.5/1.96=0.26 |
| Convert to relative uncertainty $u(C_{ref})$ | 100·(0.26/11.5)=2.21% |





## Method and Laboratory bias u(bias) - method 1a
## Use of one certified reference material

- Quantify the bias
  - the CRM was analysed 12 times. The mean is 11.9 with a standard deviation of 2.2%
  - This results in:

$$bias = 100 \cdot (11.9 - 11.5)/11.5 = 3.48\% \quad and$$

$$s_{bias} = 2.2\% \quad with \quad n = 12$$

- Therefore the standard uncertainty is:

$$u(bias) = \sqrt{(bias)^2 + \left(\frac{s_{bias}}{\sqrt{n}}\right)^2 + u(C_{ref})^2} =$$

$$\sqrt{(3.48\%)^2 + \left(\frac{2.2\%}{\sqrt{12}}\right)^2 + 2.21\%^2} = 4.2\%$$

## Method and Laboratory bias u(bias) - method 1b
## Use of several certified reference material

- Quantification of the bias
  - bias CRM1 is 3.48%, s=2.2% (n=12), $u(C_{ref})$=2.21%
  - bias CRM2 is –0.9%, s=2.0% (n=7), $u(C_{ref})$=1.8%
  - bias CRM3 is 2.4%, s=2.8% (n=10), $u(C_{ref})$=1.8%
  - $RMS_{bias}$ then is:

$$RMS_{bias} = \sqrt{\frac{\sum (bias_i)^2}{n}} = \sqrt{\frac{3.48\%^2 + (-0.9\%)^2 + 2.4\%^2}{3}} = 2.5\%$$

  - and the mean uncertainty of the certified value $u(C_{ref})$: 1.9%
- This results in the total standard uncertainty of the bias:

$$u(bias) = \sqrt{RMS_{bias}^2 + u(C_{ref})^2} = \sqrt{2.5\%^2 + 1.9\%^2} = 3.1\%$$



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## Method and Laboratory bias u(bias) – method 2
## Use of PT results

- In order to have a reasonably clear picture of the bias from interlaboratory comparison results, a laboratory should participate at least 6 times within a reasonable time interval

| Uncertainty component from the uncertainty of the nominal value | |
|---|---|
| between laboratory standard deviations $s_R$ | $s_R$ has been on average 9% in the 6 exercises |
| Convert to relative uncertainty $u(C_{ref})$ | Mean number of participants= 12 $u(C_{ref}) = \frac{s_R}{\sqrt{n}} = \frac{9\%}{\sqrt{12}} = 2.6\%$ |

Or: $u(C_{ref}) = 1.25 \cdot \frac{s_R}{\sqrt{n}}$ for a robust mean to be in accordance with ISO 13528

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## Method and Laboratory bias u(bias) – method 2
## Use of PT results

- Quantification of the bias
  - In the 6 participations the biases have been: 2%, 7%, -2%, 3%, 6% and 5%
  - Therefore $RMS_{bias}$ is:

$$RMS_{bias} = \sqrt{\frac{\sum (bias_i)^2}{n}} = \sqrt{\frac{2\%^2 + 7\%^2 + (-2\%)^2 + 3\%^2 + 6\%^2 + 5\%^2}{6}} = 4.6\%$$

- and the total standard uncertainty of the bias:

$$u(bias) = \sqrt{RMS_{bias}^2 + u(C_{ref})^2} = \sqrt{4.6\%^2 + 2.6\%^2} = 5.3\%$$





## Method and Laboratory bias u(bias) – method 3
## From Recovery Tests

- Recovery tests, for example the recovery of a standard addition to a sample in the validation process, can be used to estimate the systematic error. In this way, validation data can provide a valuable input to the estimation of the uncertainty.
- Example: In an experiment the recoveries for an added spike were 95 %, 98 %, 97 %, 96 %, 99 % and 96 % for 6 different sample matrices. The spike of 0.5 mL was added with a micropipette.

| **uncertainty component from spiking** | |
|---|---|
| uncertainty of the concentration of the spike u(conc) | from the certificate:<br>95% confidence intervall = ± 1.2 %<br>u(conc) = 0.6 % |
| uncertainty of the added volume u(vol) | from the manufacturer of the micro pipette:<br>max. bias: 1% (rectangular interval),<br>repeatability: max. 0.5% (standard dev.)<br>$u(vol) = \sqrt{\left(\frac{1\%}{\sqrt{3}}\right)^2 + 0.5\%^2} = 0.76\%$ |
| uncertainty of the spike $u(c_{recovery})$ | $\sqrt{u(conc)^2 + u(vol)^2} = \sqrt{0.6\%^2 + 0.76\%^2} = 1.0\%$ |

## Method and Laboratory bias u(bias) – method 3 From Recovery Tests

- Quantification of the bias:
- $RMS_{bias}$:

$$RMS_{bias} = \sqrt{\frac{5\%^2 + 2\%^2 + 3\%^2 + 4\%^2 + 1\%^2 + 4\%^2}{6}} = 3.44\%$$

- Therefore the total standard uncertainty of the bias is:

$$u(bias) = \sqrt{RMS_{bias}^2 + u(C_{recovery})^2} = \sqrt{3.44\%^2 + 1.0\%^2} = 3.6\%$$



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## Combination of the uncertainties

(Reproducibility within-laboratory and bias)

- Reproducibility $R_w$ (from control samples and other estimations)
- bias u(bias) (from CRM, PT or recovery tests)
- Combination:

$$u_c = \sqrt{u(R_w)^2 + u(bias)^2}$$

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## Calculation of the expanded uncertainty

- for the conversion to an approx. 95% confidence level

$$U = 2 \cdot u_c$$





## Coarse estimation by direct use of reproducibility standard deviations

- If the demand on uncertainty is low: $u_c = s_R$
- The expanded uncertainty becomes: $U = 2 \cdot S_R$
- This may be an overestimate depending on the quality of the laboratory – worst-case scenario
- It may also be an underestimate due to sample inhomogeneity or matrix variations

## Reproducibility standard deviation from a standard

- The laboratory must first prove that it is able to perform in accordance with the standard method
  - „no“ significant bias
  - verification of the repeatability
- The expanded uncertainty then is:

$$U = 2 \cdot s_R$$





## Reproducibility standard deviation from a standard Example – Mercury according to EN 1483

**Tabelle 2: Verfahrenskenndaten** (reproducibility variation coefficient → $VC_R$)

| | Alle Laboratorien | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Probe | $l$ | $n$ | $NAP$ % | Wahrer Wert µg/l | $\bar{\bar{x}}$ µg/l | $\sigma_R$ µg/l | $VC_R$ % | $\sigma_r$ µg/l | $VC_r$ % | Wiederfindungsrate % |
| drinking water | A | 21 | 62 | 9 | 0,819 | 0,831 | 0,2500 | 30,1 | 0,1310 | 15,8 | 101,5 |
| surface water | B | 20 | 59 | 13 | 1,474 | 1,459 | 0,3918 | 26,9 | 0,1855 | 12,7 | 99,0 |
| waste water | C | 21 | 68 | 0 | 5,732 | 5,799 | 1,3745 | 23,7 | 0,5746 | 9,9 | 101,2 |

- Expanded uncertainty for drinking water:
  $U = 2 \cdot VC_R \approx 60\ \%$

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# Reproducibility standard deviation from a PT

- The laboratory must have been successfully participating in the PT
- If the comparison covers all relevant uncertainty components and steps (matrix?)
- The expanded uncertainty then also is:

$$U = 2 \cdot s_R$$



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# Reproducibility standard deviation from a PT Example – Mercury in a Univ. Stuttgart PT

reproducibility variation coefficient

| Niveau | Vorgabe [µg/l] | rob. Standarda... chung [µg/l] | ...Standardab... hung [%] | Ausschlussgre... ben [µg/l] | Ausschlussgre... nten [µg/l] | Ausschlussgre... ben [%] | Ausschlussgrenze unten [%] | Anzahl Werte | außerhalb unten | außerhalb oben | außerhalb [%] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0,584 | 0,1334 | 22,86 | 0,889 | 0,341 | 52,25 | -41,60 | 37 | 3 | 1 | 10,8 |
| 2 | 1,248 | 0,2256 | 18,09 | 1,748 | 0,830 | 40,07 | -33,46 | 39 | 3 | 1 | 10,3 |
| 3 | 1,982 | 0,3502 | 17,67 | 2,756 | 1,333 | 39,06 | -32,75 | 39 | 1 | 0 | 2,6 |
| 4 | 3,238 | 0,4726 | 14,60 | 4,263 | 2,352 | 31,65 | -27,36 | 41 | 2 | 2 | 9,8 |
| 5 | 3,822 | 0,4550 | 11,90 | 4,793 | 2,960 | 25,40 | -22,55 | 38 | 0 | 1 | 2,6 |
| 6 | 4,355 | 0,7704 | 17,69 | 6,057 | 2,927 | 39,10 | -32,78 | 40 | 1 | 0 | 2,5 |
| 7 | 5,421 | 0,7712 | 14,23 | 7,090 | 3,973 | 30,78 | -26,71 | 41 | 1 | 1 | 4,9 |
| 8 | 6,360 | 0,7361 | 11,57 | 7,928 | 4,963 | 24,65 | -21,96 | 38 | 5 | 1 | 15,8 |
| 9 | 6,553 | 0,9177 | 14,00 | 8,536 | 4,829 | 30,25 | -26,31 | 39 | 2 | 0 | 5,1 |
| 10 | 7,361 | 0,9965 | 13,54 | 9,508 | 5,486 | 29,16 | -25,48 | 40 | 1 | 3 | 10,0 |
| 11 | 8,063 | 1,0672 | 13,24 | 10,357 | 6,051 | 28,46 | -24,94 | 38 | 5 | 2 | 18,4 |
| 12 | 9,359 | 0,9854 | 10,53 | 11,444 | 7,481 | 22,29 | -20,06 | 40 | 2 | 2 | 10,0 |
| | | | | | | | Summe | 470 | 26 | 14 | 8,5 |

- $u_c = s_R \approx 20\%$
- $U \approx 40\%$

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## Conclusion

- The method described is an easy way to estimate measurement uncertainty from data that are already available in many cases
- It is a holistic approach, you cannot forget an important uncertainty source
- It does not give you information about the source of the uncertainty

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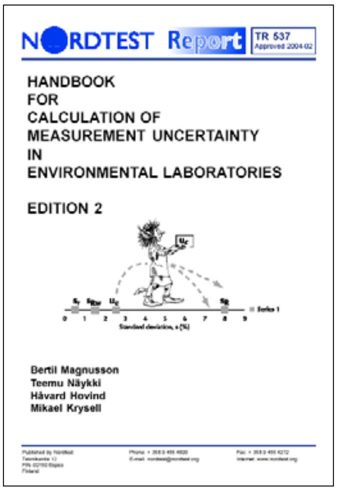
## Where to get the NORDTEST-Handbook?


NORDTEST Report TR 537 Approved 2004-02

HANDBOOK
FOR
CALCULATION OF
MEASUREMENT UNCERTAINTY
IN
ENVIRONMENTAL LABORATORIES

EDITION 2

Bertil Magnusson
Teemu Näykki
Håvard Hovind
Mikael Krysell

- The Handbook is available from http://www.nordicinnovation.net/nordtest.cfm as technical report No. 537 and on the workshop CD

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## Verification of measurement uncertainty estimates

- From where do we know that our estimate is realistic?
- We have to check that
- But how?





## Verification of measurement uncertainty estimates

- Checks using within-laboratory precision
  - Compare the estimated standard uncertainty with the standard deviation of a series of results on an appropriate test item over a period of time
  - The standard uncertainty for a routine test method should never be smaller than the long-term precision for the same method and test material;
  - if the standard uncertainty is significantly smaller than the observed within-laboratory standard deviation, the uncertainty estimate should be reviewed immediately.

## Verification of measurement uncertainty estimates

- Checks based on certified reference materials (CRM) or suitable test materials
  - Measure a suitable test material or CRM of known assigned value $x_{ref}$ with small uncertainty.
  - Check the difference d between observed value x and reference value $x_{ref}$ against the expanded uncertainty U(x).
  - If the difference d is equal to or greater than the expanded uncertainty U(d), it should be concluded that the uncertainty fails to account for the observed bias on the material.
  - The uncertainty estimate should be reviewed and appropriate steps taken to identify the source of the bias.



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## Verification of measurement uncertainty estimates

- Checks based on reference methods
  - Reference methods provide independent reference values.
  - A single such value can be used to check an uncertainty estimate in the same way as using a single CRM value

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## Verification of measurement uncertainty estimates

- Checking an uncertainty estimate against proficiency test results
  - The assessment of the uncertainty estimates is performed using the zeta score

$$\zeta = \frac{x - x_a}{\sqrt{u(x)^2 + u(x_a)^2}}$$

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## Verification of measurement uncertainty estimates

- Interpretation of ζ-scores
  - Uncertainty overestimated
    |ζ| always significantly < 2
    - The estimated uncertainty is clearly higher than the laboratory performance suggests.
    - This could be acceptable, especially if the reported uncertainty is lower than or equal to the target value of uncertainty (that is, within the customer's requirements).
    - However if there is a need for lower uncertainty, a new estimate has to be made.

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## Verification of measurement uncertainty estimates

- Interpretation of ζ-scores
  - Correct
    most values of |ζ| in the range 0 to 2
    - Here one could think that all is clear-cut, but we have to bear in mind that there are many sources that are not always tested in a PT scheme, including sampling, analyte stability, sample inhomogeneity in real samples, and other concentration levels



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## Verification of measurement uncertainty estimates

- Interpretation of ζ-scores
  - Uncertainty underestimated
    |ζ| frequently over 2
    - The estimated uncertainty is clearly lower than the laboratory is performing.
    - The uncertainty estimate should be revised to obtain a more realistic estimate

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## Verification of measurement uncertainty estimates

- Checks based on comparison of results with other laboratories
  - The same principles used for checks based on proficiency testing can be used for comparison with other laboratories after collaborative measurement of several test items.



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## Verification of measurement uncertainty estimates

- Comparison with other uncertainty estimates
  - When checking whether two uncertainty estimates agree or disagree, one should keep in mind that the precision of uncertainty estimates is often very limited.
  - For example, for an empirical standard deviation determined from 10 repeated measurements, the coefficient of variation is 24 %, and F-tests on two such standard deviations would not be considered significant with standard deviations differing by less than a factor of about 1.8.
  - It would therefore be unreasonable to expect different uncertainty estimates to agree very closely.

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## Examples and literature

- The EUROLAB technical report contains 10 detailed examples
- The report also contains a list of 27 relevant standards, guidelines, books and internet websites

## REPORT ON STATUS OF MICROBIOLOGY WATER PT SCHEME

### 1. ITEMS RECEIVED FROM PTB

| | Description of item | Quantity | Date received |
|---|---|---|---|
| 1. | Lactose TTC agar | 2x500g | 22-03-2007 |
| 2. | Magnesium sulphate heptahydrate | 500g | 22-03-2007 |
| 3. | Calcium chloride dihydrate | 1kg | 22-03-2007 |
| 4. | Di-potasium hydrogenphosphate | 1kg | 22-03-2007 |
| 5. | Supplement solution | 100ml | 22-03-2007 |
| 6. | 2,3,5,-TTC | 10g | 22-03-2007 |
| 7. | Heraeus Labofuge 400R (centrifuge)<br>Accessories<br>▪ Swing out rotor<br>▪ Round buckets<br>▪ Aerosol tight caps<br>▪ Centri-lap adapter<br>▪ Centrifuge tubes | 1<br><br>1<br>4<br>4<br>4<br>20 | 13-07-2007 |

### 2. TRAINING (Microbiology Staff)

| Topics | Number of staff | Date of training |
|---|---|---|
| ▪ Quality control of strains from culture; transport medium and trial samples<br>▪ Stability and purity of trial samples and strains during handling<br>▪ Harvesting strains (important stages of growth phase)<br>▪ Bacterial counts of stock solution (solution E)<br>▪ Calculations for spiking<br>▪ Logistics (packaging, labelling, temperature control etc) | 4 | 18-07-2007 |
| ▪ Practical preparation of stock solution<br>▪ Serial dilutions and spiking of samples<br>▪ Analysis of intra lab samples | 3 | 01-11-2007 |

### 3. TRIAL RUN

A trial run was performed to see if the laboratory was able to prepare the stock culture sample (Solution E), which is the base culture for the preparation of the PT samples. The culture used was *Escherichia coli* (*E. coli*). The following issues were noted:

- On checking the purity of the base culture (solution E) there was some contamination observed (contamination was not identified). However this did not affect the stability of the solution.
- Counts were made as follows:

- 01-11-2007 $1.4x10^5$ cfu/ml
- 03-11-2007 $1.6x10^6$ cfu/ml
- 06-11-2007 $1.7x10^6$ cfu/ml
- 13-11-2007 $1.3x10^6$ cfu/ml

- It was concluded from the results that the culture was harvested while still in the growth phase. The step for harvesting the cultures will have to be assessed further to ensure that the cultures are stable.
- Intra lab samples were prepared and analysed. The counts were found to be lower than expected. The serial dilutions were prepared using buffered peptone water (standard diluent used in the lab), which may have affected the growth of the E. coli. The transport medium will be used as the diluent in the next trial.

## 4. PACKAGING

Items available in Kampala:

- Cardboard box
- Foam (for inner lining of box)
- Ice packs

*Note: A budget for these items will be forwarded later.*

Items not available in Kampala:

- Sterile plastic bottles (100ml)
- Sterile plastic bottles (10ml)

## 5. WORK PLAN

| | Activity | Scheduled date | Remarks |
|---|---|---|---|
| 1. | Checking the stability of the serial dilutions for spiking | 10-11-2007 | ▪ Transport medium will be used instead of Buffered Peptone Water (BPW) |
| 2. | Trial run 2: Preparation of a pure stock solution | Jan 2008 | ▪ Purity checks done at all stages |
| 3. | Effect of different storage temperature on PT sample | Feb 2008 | |
| 4. | Effect of packaging on stability of sample | Feb 2008 | |
| 5. | Trial run 3: Preparation of pure stock solution and PT sample | March 2008 | |
| 6. | Preparation of PT sample for distribution | May 2008 | ▪ Results of all Trial runs are favourable.<br>▪ All packaging material is received |

**Prepared by**: Patricia Ejalu

# Evaluation Questionnaire

For the evaluation of the success of this workshop, please answer the following questions:

| **How do you judge:** | Very good | good | fair | poor | very poor |
| --- | --- | --- | --- | --- | --- |
| The venue of the workshop (accommodation, food, conference room) | | | | | |
| The content of the presentations | | | | | |
| The material distributed | | | | | |
| The working group discussions | | | | | |

| **How do you judge the different parts of this workshop** | Very useful 1 | 2 | 3 | 4 | not useful 5 |
| --- | --- | --- | --- | --- | --- |
| Evaluation of the chemistry PT | | | | | |
| Training | | | | | |
| Lab Visit | | | | | |
| SADCWaterLab meeting | | | | | |

**The five most important topics for me have been:**

1) ..........................................................................................................

2) ..........................................................................................................

3) ..........................................................................................................

4) ..........................................................................................................

5) ..........................................................................................................

Did the workshop fulfill your expectations? Yes No

If No, why not?

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What benefits did you draw from the workshop?

..........................................................................................................

Please use back side for any other comments