6th Evaluation Workshop within the SADCMET Proficiency Testing Scheme for Water Testing Laboratories

Mahé, Seychelles

16 – 18 November 2009

Report on the 6th Evaluation Workshop within the SADCMET Proficiency Testing Scheme for Water Testing Laboratories

Mahé, Seychelles, 16 – 18 November 2009

Prepared by Dr.-Ing. Michael Koch

Summary

The workshop covered the evaluation of the 6th SADCMET Water PT round and all aspects that could be derived from the results. As in the previous year the results showed that there is - generally seen - no improvement over the 5 PT rounds. Most probably this is still due to the absence of adequate corrective actions after failures in the PT and improper use of analytical methods and use of improper methods.

Therefore the focus of the discussions during the workshop was on one hand, how to motivate the participating labs that failed in one or more parameters to perform the necessary corrective actions and on the other hand to find a suitable procedure to develop a list of recommended methods. The role of SADCWaterLab is crucial for both aspects. Up to now networking within SADCWaterLab not really worked. So during the workshop two working groups within SADCWaterLab were formed.

Most of the participants are still very enthusiastic. So despite of the stagnating quality of the PT results it is recommended to continue the PT system. The structure of local coordinators is very useful, but still has to be improved. The commitment of local coordinators differs very much. But to minimize logistical problems and to increase the number of participants the local coordinators play a crucial role. One of the main obstacles for further expansion of the system and for improvement of the quality of the labs the lack of awareness on the importance of PT or – even more basic – the importance on quality assurance in the chemical lab was identified. To overcome this the results of this workshop have to be better communicated to all participating laboratories via a short report. To raise awareness amongst the policy makers in the laboratories a leaflet will be prepared explaining the importance of quality management in the laboratory and participation in PT schemes. In addition workshops on national level are indispensable. Since most of the local organizations are not able to do that a training for trainers will be organized mid of 2010. In this training course material for a basic course on quality assurance in the analytical laboratory will be provided and the participants trained to present this in a workshop.

To support the participants in performing the corrective actions, a short guideline on how to do that was sent out again to the participants.

The assessment procedure of the PT using limited standard deviations has again proven to be very effective, the statistical methods are in accordance with the internationally recommended procedures.

The chemistry evaluation workshop took place on 16th to 18th of November and was followed by the SADWATERLAB General Assembly where also the participants from microbiology workshop were present. For the microbiology workshop see separate report.

Introduction

The workshop reported here followed previous workshops held in Windhoek, Namibia (Feb 2004), Pretoria, South Africa (Nov 2004), Dar es Salaam, Tanzania (Nov 2005), Gaborone, Botswana (Nov 2006), Dar es Salaam (Dec 2007) and Kampala, Uganda (Dec 2008). The reports are available from http://www.sadcmet.org. As a result of these workshops 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). The main aim of this workshop on the Seychelles was the discussion of the evaluation of the sixth PT round on chemical parameters.
The improvement of cooperation between laboratories within the SADCWaterLab Association was also discussed during the workshop.

Participants

The chemistry workshop was attended by 26 participants from the following countries:

- Botswana 1
- Kenya 2
- Lesotho 1
- Malawi 1
- Mauritius 1
- Namibia 3
- Seychelles 9
- South Africa 1
- Swaziland 2
- Tanzania 1
- Uganda 1
- Zambia 2
- Zimbabwe 1

A complete list of participants with e-mail addresses is given in annex 1.

PT Workshop Programme

Monday, 16 November 2009:

Welcome, Opening, Experience of the PT provider, Reports of the local coordinators,

Tuesday, 17 November 2009:

Evaluation results, working group and plenary discussion on PT results, presentation on value assignment, working group and plenary discussion on how to improve and what is needed for that.

Wednesday, 18 November 2009:

Constitution of two working group: Methods and Survey on needs
SADCWaterLab general assembly

Monday, 16 November 2009

Opening

The Workshop was officially opened by

Mrs. Amy Quatre, chief executive officer of SBS
Ms. Kathrin Wunderlich, PTB
Mr. Donald Masuku, SADCMET Regional Coordinator
Mrs. Marise Berlouis, Principal Secretary for Industry, Republic of Seychelles.

M. Koch: Introduction

All participants shortly introduced themselves and Dr. Koch gave an overview on the workshop programme.

M. Conradie: Experiences of the PT provider

Merylinda Conradie reported about her experiences with this 6th PT round (annex 2).

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	2008	2009
Angola	1	1	1	0	1	0
Botswana	2	2	2	4	2	3
Ethiopia	1	1	1	0	0	0
Kenya	2	2	4	3	3	7
Lesotho	1	1	0	1	1	1
Madagascar	0	0	2	2	3	3
Malawi	2	2	2	3	1	1
Mauritius	1	3	4	3	5	6
Mozambique	2	3	2	0	0	0
Namibia	2	2	3	3	3	3
Seychelles	1	2	2	1	1	1
Swaziland	1	1	0	1	2	3
South Africa	0	0	0	1	1	1
Tanzania	2	8	5	12	11	12
Uganda	1	3	6	5	5	5
Zambia	1	4	2	3	1	3
Zimbabwe	2	3	3	5	5	5
total number	22	44	39	46	45	54

She listed the parameters to be analysed in this PT round (table 2). No change was made compared to the 5th round.

Table 2: List of parameters in the 6th PT round

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

She described the planning including the chemicals used for spiking, the necessary materials for sample preparation and packaging, choice of courier and necessary balances. Some problems were encountered with the courier Fedex, where some packages were mixed up and delivered to wrong countries

In detail she explained the preparation of the samples including

- Cleaning of bottles
- Weighing of chemicals
- Documentation of the weighings with printer attached to the balances
- Digestion of metals
- Preparation of stock solutions
- Documentation of weighings
- Labelling of bottles
- Preparation of final batches
- pH adjustment
- Ensuring homogeneity
- Sample dispensing
- Storage
- Preparation of documentation
- Packaging
- Information to courier
- Shipment

Customs problems were reported only from Zambia.
Results were received by fax or e-mail.
Evaluation was done using the programme developed especially for the SADCMET PT scheme.
Local coordinators were again very helpful.
She reported some details of the evaluation:

- Number of parameter analyzed by each lab
- The percentage success for all labs
- The number of acceptable and non-acceptable results

Some measurements were also done by the National Metrology Institute of South Africa (NMISA). For some values there are discrepancies between the measurements and the reference values calculated from the weighings.
The provider faced some general problems:

- The provision of the PT with its heavy work load sometimes is difficult to realize besides the normal routine work

- Late request for participation and late confirmations caused additional problems
- Registration forms sometimes were not sent to the provider, so it was difficult to contact the participant
- Communication problems: unclear faxes – E-mail communication failed
- Late deliveries of results

M. Conradie expressed her thanks to PTB for the financial support, to SADCMET regional coordinator and 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

To facilitate the organisation of the PT rounds and to reduce shipment costs local coordinators (LC) for each country have been installed. During the workshop the local coordinators were requested to give a short report on their activities.
The local coordinators were asked to report about their activities, based on the following guiding questions:

1. How did you promote the PT scheme?
2. What feedback did you get from laboratories?
3. How many labs did participate in your country?
4. Do you know about reasons for non-participation?
5. Any activities for a common payment? If yes, did it work?
6. Any customs problems?
7. Did you pro-actively inform customs authorities in your country?
8. Do you need additional support or guidance for your task as local coordinator?
9. Any additional comments?

- **Botsuana**
  - Promotion of the PT scheme was done in an ISO 17025 forum in Botsuana and in national PT schem evaluation workshops
  - The feedback was satisfactory, many labs showed interest, but finally only 3 labs participated. The communication between the PT provider and the LCs needs to be improved
  - Potential reason for non-participation might be:
    - The PT is not in the lab's budget
    - Water analyses are not the core business of the lab
    - Lack of interest in PT in general
    - Existence of a national scheme
  - No need for common payments was identified
  - No problems with courier and customs

- **Kenya**
  - No report available

- **Lesotho**
  - There is only one lab functioning in Lesotho. So there is no need for coordination activities

- **Malawi**
  - Promotion of the scheme through sending out flyers
  - Lots of positive responses, but many labs seem to be not well enough equipped and capacities in the labs are missing
  - A local workshop will be organized
  - No common payment seemed to be necessary and no customs problems were encountered
  - Presentation material for a local workshop is needed

- **Mauritius**
  - The flyer and personal contacts were used for advertising the scheme
  - Many labs easily could be convinced since many of the labs want to be accredited
  - So the feedback generally was very good
  - Six labs participated in the PT round. There is only one more lab in Mauritius.
  - No common payment was made and no customs problems were encountered
  - It was discussed whether an accreditation of the scheme is necessary? Since it is not necessary for accreditation to participate in an accredited scheme, there is no need at the moment
- **Namibia**
  - E-mails contacts and the brochure were used for advertising the PT scheme
  - Merylinda Conradie gave a presentation about the PT Scheme at the Test and Measurement Conference in Johannesburg
  - The 3 main labs existing in Namibia took part
  - There was no need for a common payment and no customs
  - Improvement of communication was seen necessary
- **Swaziland**
  - The PT scheme was promoted in laboratory meetings for preparation of accreditation with the brochures
  - Three labs participated in the PT round
  - One major problem is that the management staff does not understand the need participation in PT
  - Some labs do not want to pay the fee
  - There was no need for common payments and no customs problems
- **Seychelles**
  - The PT round was advertised by sending out the flyers
  - The response was not very good
  - Only 1 lab finally participated
  - One reason could be that the PT participation was not budgeted in time
  - No common payment, no customs problems
- **Tanzania**
  - The local coordinator used e-mails, letters, visits, phoning forums and meetings to advertise the PT scheme
  - The response was very positive, but this was not always reflected by participation; 12 labs participated
  - The awareness is quite low, decision makers do not appreciate such a scheme. They need to be educated in this respect
  - No common payment, no customs problems

    - The training of trainers is needed very much
- **Uganda**
    - No report available
- **Zambia**
    - The LC sent out 8 letters and used phonecalls, visits and the brochure for promotion.
    - There were only 3 responses.
    - One reason is participation in other schemes
    - No common payment
    - There were customs problems: The samples stayed 14 days at the customs and the LC had to pay for clearance
    - A leaflet on importance of PT would be highly welcome
    - More networking within SADCWaterLab is necessary
- **Zimbabwe**
    - The lab association database, the brochures, for a, lab suppliers, seminars and conferences were used to advertise the scheme
    - There will be a seminar on 4th of December on PT and accreditation awareness
    - The response was quite positive
    - % lab participated, but due to courier problems 2 labs didn't get the samples
    - No common payment, no customs problems
    - Awareness is the key to a growing PT scheme
    - The IT equipment and software in the labs is usually quite old
    - The PT is very useful. It helps to get the accreditation
    - A PT for DDT in tobacco would be needed

Tuesday, 17 November 2009

M. Koch: Evaluation of the 6th 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 %	Parameter	limit in %
Sulphate	10	Manganese	<1 mg/l: 20, >1 mg/l: 12
Chloride	10	Aluminium	30
Fluoride	12	Lead	< 0,5 mg/l: 40, > 0,5 mg/l: 25
Nitrate	15	Copper	20
Phosphate	10	Zinc	20
Calcium	10	Chrome	25
Magnesium	10	Nickel	25
Sodium	10	Cadmium	20
Potassium	10	Arsenic	20
Iron	<1 mg/l: 20, >1 mg/l: 12	Cobalt	20

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 3.
Special emphasis was put on the comparison of the results with those from last years' rounds. Comparison of the standard deviations calculated from the data set showed for almost all parameters showed no improvement over time. On the contrary for most parameters these values are higher than in the last years. Since this only shows the performance of the labs on average he took a closer look to the individual laboratories. For all laboratories the average of the absolute values of all values was calculated for each year and shown in a diagram. Since the limit for acceptability of a value in the PT is a score in the range of ± 2, the value of 2 was taken to distinguish between well performing and bad performing labs.
Laboratories were grouped into 4 classes:

- Performing well in the previous round and well in the current round (constantly good)
- Performing bad in the previous round and bad in the current round (constantly bad)
- Performing bad in the previous round and well in the current round (improving)
- Performing well in the previous round and bad in the current round (getting worse)

In the presentation this is shown with horizontal arrows (above or below the 2.0-line) and with arrows going up (getting worse) or down (improving). The number indicates the number of the respective labs.

The example shown here for Sulphate shows 15 labs performing constantly well and 16 constantly bad, 3 were improving and 6 got worse.

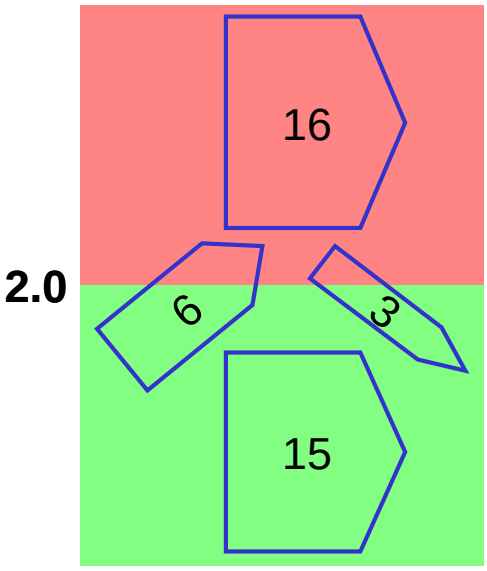


Fig.1

For the individual parameters the following conclusions could be derived from the data:

- Sulphate: There is a good agreement between the means of the data and the reference value. The standard deviations were higher than ever before. More than 50 % of the labs have unsatisfactory results. The turbidimetrically and gravimetrically determined values showed a high portion of too high or too low values
- Chloride: There was a quite good agreement between the data means and the reference values. The standard deviations were too high – no improvement could be seen. Only 2/3 of the labs have good results. There seems to be

problems with the endpoint detection in argentometric determination. Obviously there are also some problems with the spectrometric method

- Fluoride: The mean values were higher than the reference values. The standard deviations were very high, no improvement over time. The colorimetrically determined values had a very high portion of non-reliable values, as in the last years.
- 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, no improvement over time. The parameter still 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 very high.
- Calcium: The mean of the values were close to the reference values. The standard deviations were very high. The percentage of unsatisfactory results was quite high. Obviously there were many errors in the application of analytical methods that generally would be suitable
- Magnesium: The mean values were around the reference values, but the standard deviations were much too high. Titrimetrically determined values in general were not reliable (as in the last years).
- Sodium: The means were close to the reference values. The standard deviations were around the average of the last rounds, but still too high. There was a slight improvement in the number of satisfactory results.
- Potassium: The means of the values were close to the reference values, the standard deviations were higher than in the last years with a higher percentage of non-satisfactory results. AAS values contained many non-reliable data.
- Iron: The means were close to the reference values and the standard deviations were too high, no improvement. 1/3 of the results was not satisfactory. The AAS method delivered many outlying values.
- Manganese: The means were close to the reference values, the standard deviation higher than ever before. 1/3 of the results was not satisfactory.
- Aluminium: Only few participants analysed this parameter. Therefore the number of values was small. The standard deviation nwas better than last year, but not really good.
- Lead: The means of the datasets were around the reference values. The standard deviations of the datasets was similar than last year. So it was still too high.
- Copper: For this parameter the data means also were in good agreement with the reference values. The standard deviation was better than in the previous year.
- Zinc: The mean values were close to the reference values (except the lowest level). The standard deviation was higher than ever before. No improvement could be seen.
- Chromium: The mean values were significantly lower than the reference values, the standard deviation for the lowest level was very high. The percentage of non-satisfactory results is steadily increasing over the years. Obviously there were some problems with the AAS method.
- Nickel: The data means also showed no bias, the standard deviations were high compared to the last years. No improvement could be seen.

- Arsenic: Only a few laboratories analysed for arsenic. So the number of values was very low. The standard deviations were like the years before.
- Cadmium: The mean values of the data sets were slightly lower than the reference values. The standard deviations were higher than ever before. The percentage of non-satisfactory results is increasing.
- Cobalt: The consensus means were close to the reference values, the standard deviations were higher than last year.

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

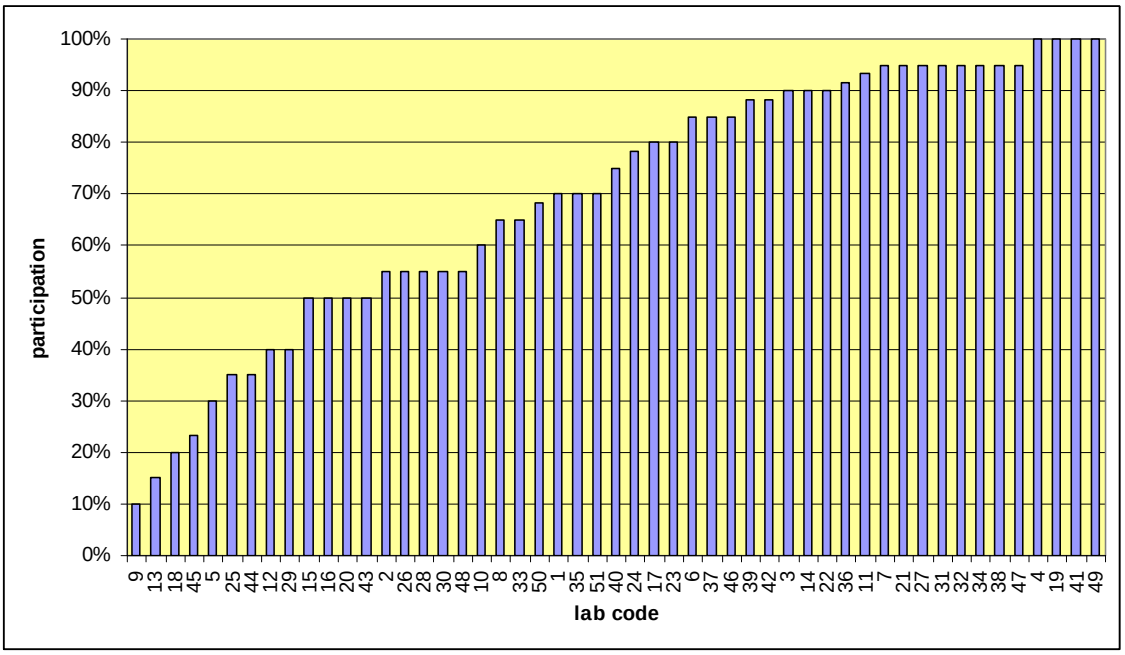


Figure 2: Percentage of participation for each participant

12 participants managed to analyse more than 80% of their values within the tolerance limits (compared to 16 labs in 2008 and 17 labs in 2007). 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.

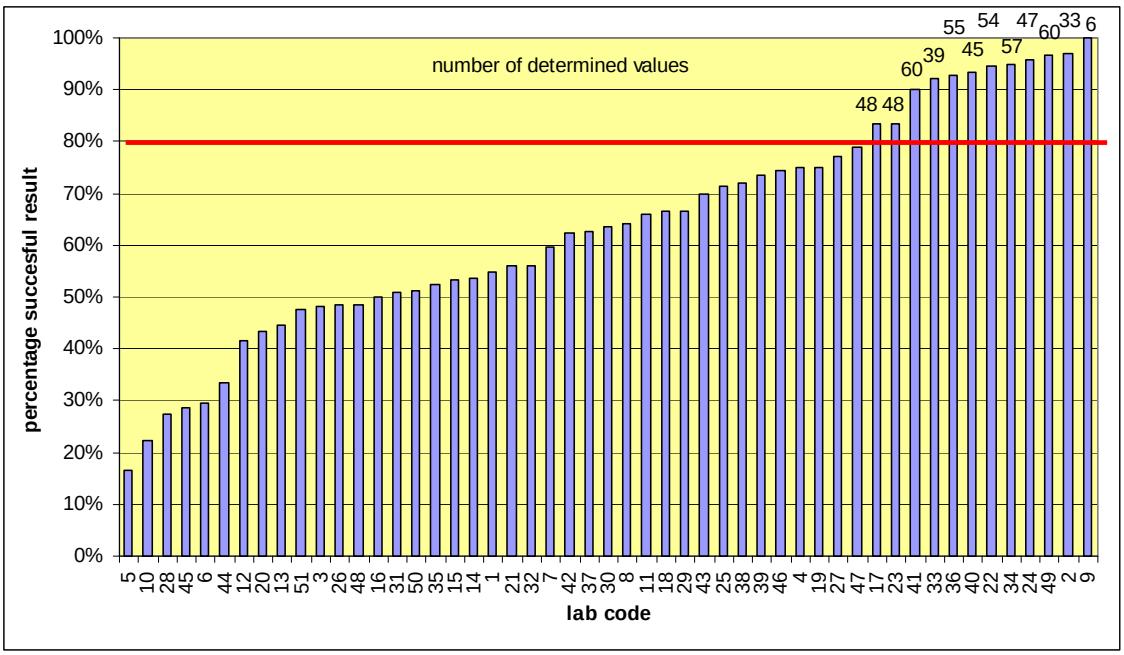


Figure 3: Percentage of successfully analysed values for each participant

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.

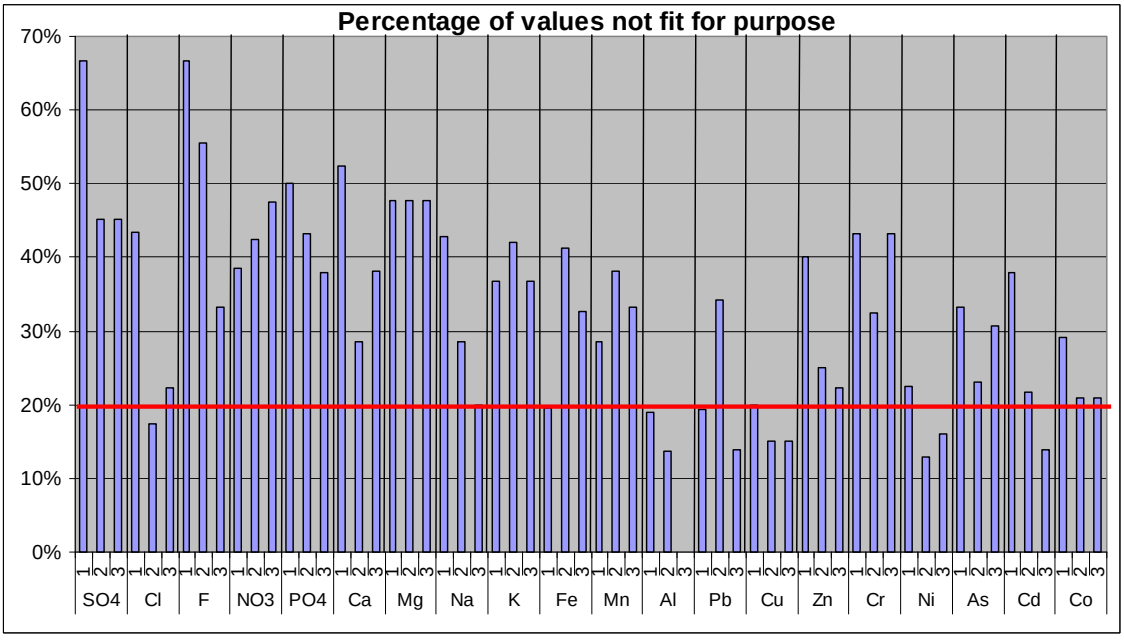


Figure 4: Percentage of values outside the tolerance limits for all samples

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 or getting worse
- More emphasis should be put on corrective actions after unsatisfactory participation
- There should be a discussion
    - How to select suitable methods? (recommendations by SADCWaterLab?)
    - How to help laboratories to proper apply the methods?
- The gaps that prevent labs from proper application should be identified

All: Discussion

In the discussion the following points were highlighted:

- Obviously suitable methods often were wrongly applied
- Laboratories don't care about corrective actions
- Again values were reported in wrong units
- Some methods are not reliable. So there is need to recommend methods
- It is necessary to disseminate the information from the evaluation workshop to all participants in the form of an additional short report

All: Working group discussion

In three working groups the following questions were discussed:

1. How do you judge the outcome of the PT round?
2. What are the reasons for not improving?
3. What could be done by SADCWaterLab to assist laboratories to improve?
4. What are the reasons that networking didn't work within SADCWaterLab?

The working groups came to the following conclusions:

1. How do you judge the outcome of the PT round?
    - Increase of the number of participating labs
    - No improvement (except some anions)
    - The least satisfactory PT round
    - There is a considerable effort needed to improve the anion analysis
    - Some labs are not analysing many parameters
    - The PT still delivers valuable information to the participants
2. What are the reasons for not improving?
    - Labs not doing corrective actions
    - No or no proper quality management systems
    - No quality control
    - Lack of proper training
    - Different people analysing
    - High staff turnover
    - No proper maintenance for equipment
    - No training for servicing equipment
    - Methods not validated
3. What could be done by SADCWaterLab to assist laboratories to improve?
    - Training of trainers could improve quality on national levels
    - Recommendation na d therwith harmonization of methods, but no prescription
    - Corrective action guidelines send out again
    - Summary of findings from evaluation workshop to be sent to all participants

- Training of staff in accredited labs
- Provide training for maintenance of equipment
- Evaluation workshop feedback from LC to labs in their country (workshop)
- Improved networking

4. What are the reasons that networking didn't work within SADCWaterLab?
    - Local coordinators not communicating back to participants
    - Feedback is needed from the participants directly (evaluation questionnaire to be sent out with the findings from the workshop)
    - Some participants seem to have only restricted access to e-mails
    - Report might be too long – short summary is necessary
    - Lack of awareness of the possible benefits
    - The possibility of networking within SADCWaterLab was not marketed properly

M. Linsky: Analytical approaches frequently used in value assignment in Analytical Chemistry

Mare Linsky (NMISA) gave a presentation on value assignment in analytical chemistry. The complete presentation is included in annex 4.

All: Working group discussion

In three working groups the following questions were discussed:

What kind of activities are needed and how can we implement these activities?

The working groups came to the following conclusions:

- Need for biannual newsletter, content from members by mid of January
- More networking to identify problems
- Working group looking at the methods, focusing on the most problematic methods (e.g. phosphate) based on PT results and develop recommendations
- Training on basic information on laboratory QM system
- Survey on analytical gaps the labs have, what are they lacking, what do they know about PT etc.
- Working groups on method validation, corrective actions, root cause analysis
- Affiliate with other lab associations

Based on this results it was decided

- to publish a biannual newsletter, edited by the regional coordinator with help from the PMC. All members to write articles. Deadline for the 1st newsletter is mid of January 2010.
- To immediately create two SADCWaterLab Working Groups
    - WG "methods"
    - WG "survey"

Wednesday, 18 November 2009

SADCWaterLab Working group sessions

The two SADCWaterLab working groups “methods” and “survey on needs” had their constitutional meeting on Wednesday morning.
Merylinda Conradie was elected as chair for the method WG and Teddy Ditsabatho as chair for the survey WG.
Reports on the outcome of this first meeting will be published as separate reports on the SADCMET website and in the first SADCWaterLab newsletter.

Evaluation questionnaire

M. Koch distributed an evaluation questionnaire (see annex 5) for the chemistry part of the workshop to be filled out by all participants.
The results of this questionnaire were as follows:

The judgement of the participants regarding

- **The hotel (accommodation, food):**
  Very good: 2
  Good: 8
  Fair: 6
  Poor: 1
  Mean: 2.4 (1 for very good, 2 for good, 3 for fair, 4 for poor)
- **The venue of the workshop:**
  Very good: 5
  Good: 16
  Fair: 1
  Mean: 1.8 (1 for very good, 2 for good, 3 for fair)

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

- **Report of the PT provider**
  1: 17
  2: 4
  3: 2
  4: 0
  5: 0
  Mean: 1.3
- **Local coordinators’ reports**
  1: 4
  2: 13
  3: 6
  4: 1
  5: 1
  Mean: 2,3
- **Evaluation of the chemistry PT**
  1: 16
  2: 5
  3: 4

4: 0
5: 0
Mean: 1.5

- **NMISA-presentation on reference values**
  1: 6
  2: 13
  3: 5
  4: 0
  5: 0
  Mean: 2.0

- **WG discussion “future activities”**
  1: 13
  2: 10
  3: 1
  4: 0
  5: 0
  Mean: 1.5
- **Working groups “methods” and “survey”**
  1: 13
  2: 10
  3: 2
  4: 0
  5: 0
  Mean: 1.6
- **SADCWaterLab General Assembly**
  1: 15
  2: 9
  3: 0
  4: 1
  5: 0
  Mean: 1.5

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

- Evaluation and presentation of the PT results (19)
- Methods (9)
- Working group for preparation of survey (8)
- Working group on methods (8)
- Presentation of NMISA about assigned values (6)
- SADCWaterLab General Assembly (5)
- Discussion of progress in PT over years (3)
- Marketing of and improvement needed for SADCWaterLab (3)
- Local coordinators’ reports (3)
- Group discussions (3)
- Training of trainers (2)
- Development of newsletter (2)
- Group discussions especially on how to improve (2)
- Discussion on future activities (2)

- Recommendations from the results (1)
- Assistance for networking (1)
- Mistakes made from misreporting of results (1)
- Comparison of reference and assigned values (1)
- Importance of PT (1)
- Different equipment (1)
- Need for continual improvement (1)
- The use of PT results to implement corrective actions (1)
- Appreciation of statistical analysis of PT results (1)
- Report given by the PT provider on process under which it was carried out (1)
- Work programme for 2010 (1)
- PMC meetings (1)

Did the workshop fulfil your expectations?

Yes: all

What benefits did you draw from the workshop?

- Apply corrective actions and help other labs with their methods
- I have a better idea about the PT programme. This is my first time participating as observer in the workshop
- More awareness on water PT (SADC), and related activities
- Knowledge of the benefits of participating in such a scheme
- Have an idea on how the PT programme works, because it's my first time that I participate
- Anomalies that occurred to our lab in the last PT round
- Commitment – Quality Management System is a must for an analytical lab
- Very important to participate in PT as a form of validation for national test results
- It will help me to improve and maintain good QC during my lab activities
- To improve my instrumentation
- I have equipped myself with knowledge and skills through group discussions which can be passed on to PT participants and possibly market it to many other labs
- General understanding of benefits attached with participation in a PT
- There is hope for improvement! There are expectations for improvement: Plans, commitment and assistance for the laboratories who do not perform will be available
- The outcome will boost the initiative to improve the lab results through identification of weaknesses
- How important the PT is and what it is
- Importance of carefully following testing procedures when carrying out analyses
- Identified challenges that are limiting performance as a lab and the necessary corrective and preventive actions will be implemented as it will be reflected in the next PT
- Insight into the results of the PT, appreciating the strengths/weaknesses of the different test methods and possible causes for incorrect results.
- The ability to discuss the methods of analysis and sharing the experiences on the application of these methods

- The importance of corrective actions on PT results
- Lay emphasis on taking corrective actions so as to improve quality of test results

Any other comments:

- I think more technical presentations on analytical methods used by participants would be useful

SADCWaterLab General Assembly

After the SADCWaterLab working group sessions the day was finalised with the SADCWaterLab General Assembly. Minutes of this General Assembly will be prepared by the secretary and published in the newsletter.

Closure of the meeting

Kezia Mbwambo, Donald Masuku, Kathrin Wunderlich, Katrin Luden and Michael Koch closed the workshop and thanked all participants for their cooperation.

Report prepared by Dr.-Ing Michael Koch
Stuttgart, 25.1.2010

Summary on conclusions and decisions

- The organization of the PT round worked quite well.
- The PT provider did an excellent job
- There were problems with one courier and customs problems in Zambia
- Most of the local coordinators tried hard to promote the scheme and to assist the provider. Nevertheless continuous effort is necessary. No report was available form Kenya and Uganda.
- New local coordinators have to be identified for Mocambique, Ethiopia and Angola (**secretariat**)
- A PT leaflet will be developed to convince decision makers on the necessity to participate in PT schemes **(M Koch)**
- To support **national workshops** and therewith to create increased awareness on the importance of quality assurance and proficiency testing a **training for trainers** is will be organized **(M Koch, D Masuku)**. Candidates to be nominated by the **local coordinators**. Decision through **PMC**
- The evaluation of the PT round showed disappointing results. Generally there was no improvement over the various rounds in the last years. The following measures are recommended for help in this respect:
    - The guideline on how to perform a root cause analysis and corrective action will be re-distributed **(M Conradie)**
    - Communication channels to be improved within SADCWaterLab **(D Masuku)**.
    - WG “method” to prepare recommendations for methods
    - WG “survey to prepare a survey on needs in the laboratories
- SADCMET website to be updated **(D Masuku)** with
    - Reports
    - List of LCs
    - Membership list
    - Application form
    - New announcement
    - Announcement of ToT
    - Newsletter
    - WG structure
- A biannual newsletter to be prepared. **D Masuku** to edit the newsletter with the help of all **PMC members**. **All SADCWaterLab members** to write contributions and send them to the secretariat. Deadline for the 1st newsletter mid of January 2010
- New PTs on meat and fish analysis to be discussed

Annex 1

List of participants - Chemistry Workshop

MrMs	Name	First Name	Country	Affiliation	e-mail 1	e-mail 2	e-mail 3
Mr.	Koch	Michael	Germany	Universität Stuttgart	Michael.Koch@iswa.uni-stuttgart.de		
Mrs.	Conradie	Merylinda	Namibia	Namwater	conradiem@namwater.com.na	conradie@inay.na	
Mr.	Ditsabatho	Teddy	Botswana	Water Utilities Corporation	TDitsabatho@wuc.bw	teddyboykieditsabatho@yahoo.com	
Mr.	Kiarie	Timothy	Kenya	Nairobi Water Co.	jmumbi@nairobiwater.co.ke	tkiarie@nairobiwater.co.ke	
Ms.	Makhaba	'Mapaseka	Lesotho	Water and Sewerage Authority	mmakhaba@wasa.co.ls	mpasimakhaba@yahoo.com	
Mr.	Chirwa	Isaac	Malawi	MBS	isaacchirwa@mbsmw.org	chirwai2000@yahoo.uk.co	
Mr.	Ghoorun	Shabbir Hammad	Mauritius	MSB	shghoorun@msb.intnet.mu	orient@intnet.mu	
Mr.	de Klerk	Venus Ferdinand	Namibia	City of Windhoek	vdk@windhoekcc.org.na	ijv@windhoekcc.org.na	
Ms.	Kriess	Silke	Namibia	Namwater	KriessS@namwater.com.na		
Mr.	Dlamini	Meshack	Swaziland		meshbdlamini@yahoo.com		
Ms.	Sgwane	Zanele	Swaziland	Rural Water Supply	zanelesgwane@webmail.co.za	Khanyac@gov.sw	
Mrs.	Mbwambo	Kezia	Tanzania	TBS	kmbwambo@yahoo.co.uk	info@tbstz.org	kezia.mbwambo@tbstz.org
Mr.	Iberet	Joseph	Uganda	UNBS	joseph.iberet@unbs.go.ug	iberet38@yahoo.com	
Mrs.	Mazhamo	Margaret Sakala	Zambia	Food and Drugs Control Labora	mazhamoms@yahoo.com		
Mr.	Kamekela	Mfuta Ray	Zambia	Zambia Bureau of Standards	rkamekela@yahoo.com	ray@zabs.org.zm	
Mr.	Gabi	Benson	Zimbabwe	Standards Association of Zimba	sazlabs@mweb.co.zw	gabibenson@yahoo.com	
Mr.	Radegonde	Vivian	Seychelles	SBS	vivianradegonde@hotmail.com	radegondev@yahoo.com	
Mrs.	Tirant	Dora	Seychelles		tirantdora@yahoo.com		
Mr.	Barra	Cliff	Seychelles	SBS	c.ixoye@yahoo.com		
Mrs.	Antat	Veronica	Seychelles		veronicaantat@yahoo.com		
Mrs.	Kante	Mariam	Seychelles	SBS	mkante@seychelles.sc	sbsorg@seychelles.net	
Mr.	Anacoura	Don	Seychelles	SPHL	d.anacoura@hotmail.com		
Ms.	Malbrook	Monica	Seychelles	PUC	mmalbrook@puc.sc		
Ms.	Rose	Kathleen	Seychelles	IOT	kathleen.rose@mwbrands.com		
Ms.	Mémé	Nathalie	Seychelles	Agro Industries	nthl_mm@yahoo.com	nthl_mm@hotmail.com	
Ms.	Achieng	Celestine	Kenya	KEBS	achiengc@kebs.org		
Ms.	Maré	Linsky	South Africa	NMISA	mlinsky@nmisa.org		

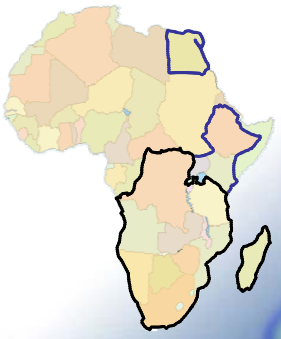
6th SADCMET WATER PT
Experiences of the provider

Merylinda Conradie Pr. Sci.Nat
Namibia Water Corporation (NamWater)
Water Quality and Environmental Services
Windhoek, Namibia

Dr.-Ing. Dipl.-Chem. Michael Koch
Water Quality and Solid Waste Management
Department Hydrochemistry
University of Stuttgart, Germany

Stefan Wallerath / Kathrin Wunderlich
Project Coordinator
Physikalisch-Technische Bundesanstalt (PTB)
Braunschweig, Germany

Donald Masuku
SADCMET Regional Coordinator
NMISA
Pretoria, South Africa



NAMWATER

Namibia Water Corporation (NamWater)

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Overview

- Background of SADCMET PT
- Project activities
- Changes and progress of participation
- Growth of the SACMET PT scheme
- Changes and Progress of parameters
- Planning
- Steps of a PT round
- Details of the processes
- Evaluation & assessment
- Closure

Background of SADCMET PT

- Established by SADCMET in cooperation with the SADC-secretariat and the SADC organisation to strengthen the competence of laboratories in Africa
- The National Metrology Institute of Germany (PTB) assists the project on behalf of the German Ministry of Economic Cooperation and Development
- Established to support SQAM-program (SQAM = Standardization, Quality, Accreditation, Metrology)
- Directed by the SADCWaterLab, a union of laboratories with common interests
- Participants are SADC countries and associated members of SADCMET
- NamWater is the provider since 2006

Project Activities

February 2004	Kick-off workshop in Windhoek, Namibia, with participants from 16 countries with training on basic issues of quality in analytical laboratories
2005	2nd PT round; Evaluation workshop with training on measurement uncertainty (Dar es Salaam)
2007	4th PT round; Evaluation workshop (Dar es Salaam) with training on validation and measurement uncertainty
2009	Test & Measurement conference 2009 : Presentation of Chemical analyses of water in Africa 6th PT round; Evaluation workshop (Seychelles)

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Participation per country

Country	2004	2005	2006	2007	2008	2009
Angola	1	1	1	0	1	0
Botswana	2	2	2	4	2	3
Ethiopia	1	1	1	0	0	0
Kenya	2	2	4	3	3	7
Lesotho	1	1	0	0	1	1
Madagascar	0	0	2	2	3	3
Malawi	2	2	2	3	1	1
Mauritius	1	3	4	3	5	6
Mozambique	2	3	2	0	0	0
Namibia	2	2	3	3	3	3
Republic of Seychelles	1	2	2	1	1	1
Swaziland	1	1	0	1	2	3
South Africa	0	0	0	1	1	1
Tanzania	2	8	5	12	11	12
Uganda	1	3	6	5	5	5
Zambia	1	4	2	3	1	3
Zimbabwe	2	3	3	5	5	5

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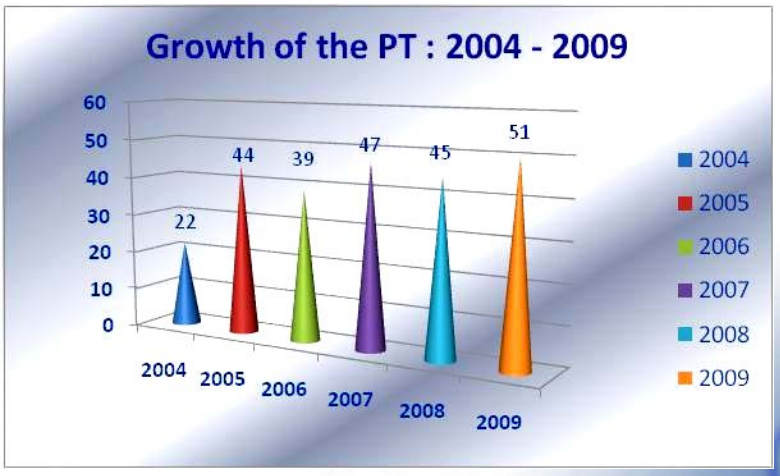
Growth of PT SADCMET Scheme



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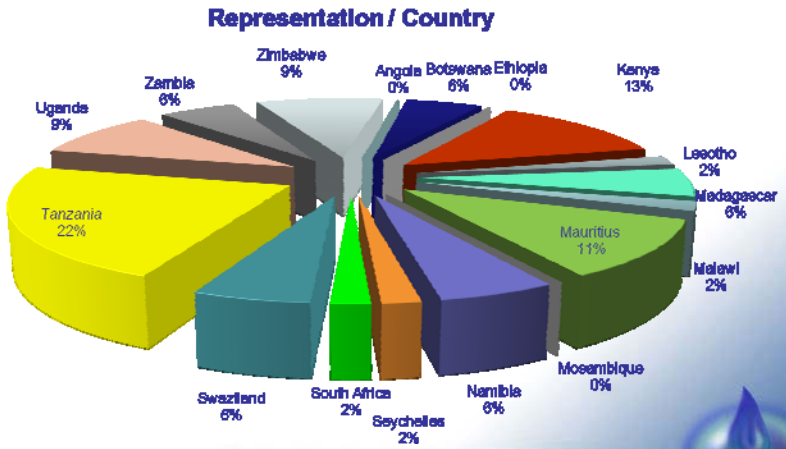
% Representation / Country



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Changes and Progress of parameters

Parameter	Concentration in mg/l
PT round 1	
Calcium	25 – 80
Magnesium	13 – 50
Sodium	11 – 55
Potassium	3.5 – 12
Iron	0.1 – 4.6
Manganese	0.1 – 2.5
Aluminium	0.1 – 4
Sulphate	18 – 60
Chloride	30 – 75
Fluoride	0.15 – 2.5
Nitrate	2-40

3 different level for each parameter

Parameter	Concentration in mg/l
Additionally in PT round 2	
Lead	0.1 – 2.6
Copper	1 – 4
Zinc	1.4 – 5.8
Chromium	0.25 – 2
Nickel	0.3 – 3.5
Phosphate	4.5 – 28
Additionally in PT round 3	
Arsenic	0.15 – 0.9
Cadmium	0.15 – 1.8
Additionally in PT round 5 - 6	
Cobalt	

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Planning

- Calculation of the target values
- Order chemicals, consumables e.g crates, beakers and volumetric flasks and sample bottles.
- Order packaging material (boxes, shredded paper, packaging tape, labels, envelopes, paper)
- Prepare labels for distribution
- Download COA from internet
- 100 liter containers with tap
- Quotations and choice of courier

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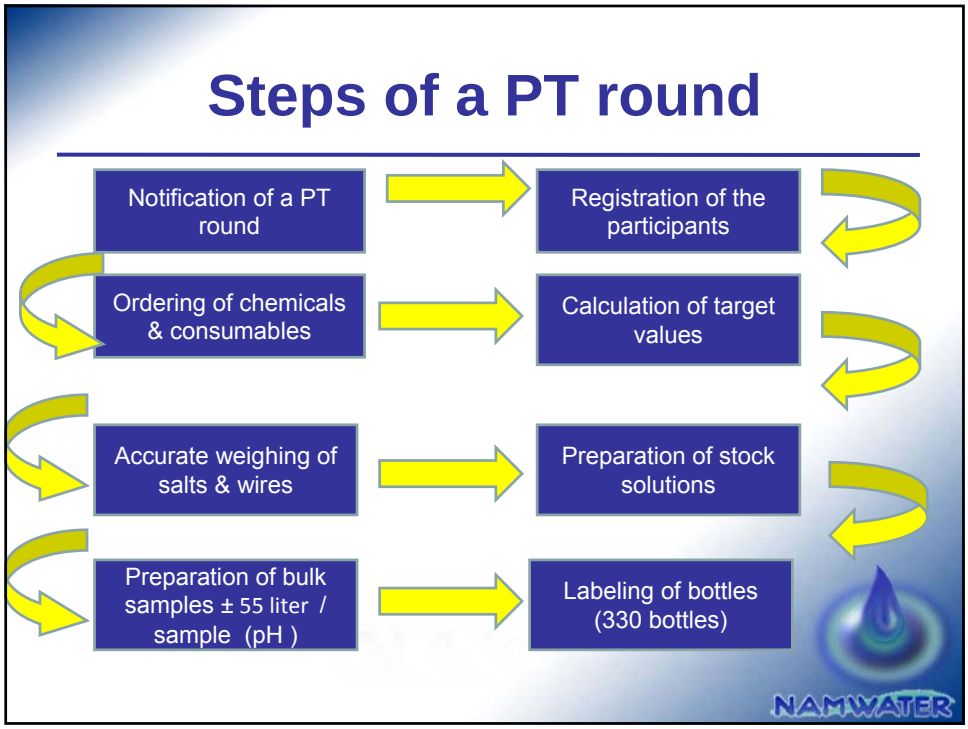
Planning (cont.)

- 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

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


Steps of a PT round
Notification of a PT round
Registration of the participants
Ordering of chemicals & consumables
Calculation of target values
Accurate weighing of salts & wires
Preparation of stock solutions
Preparation of bulk samples ± 55 liter / sample (pH)
Labeling of bottles (330 bottles)
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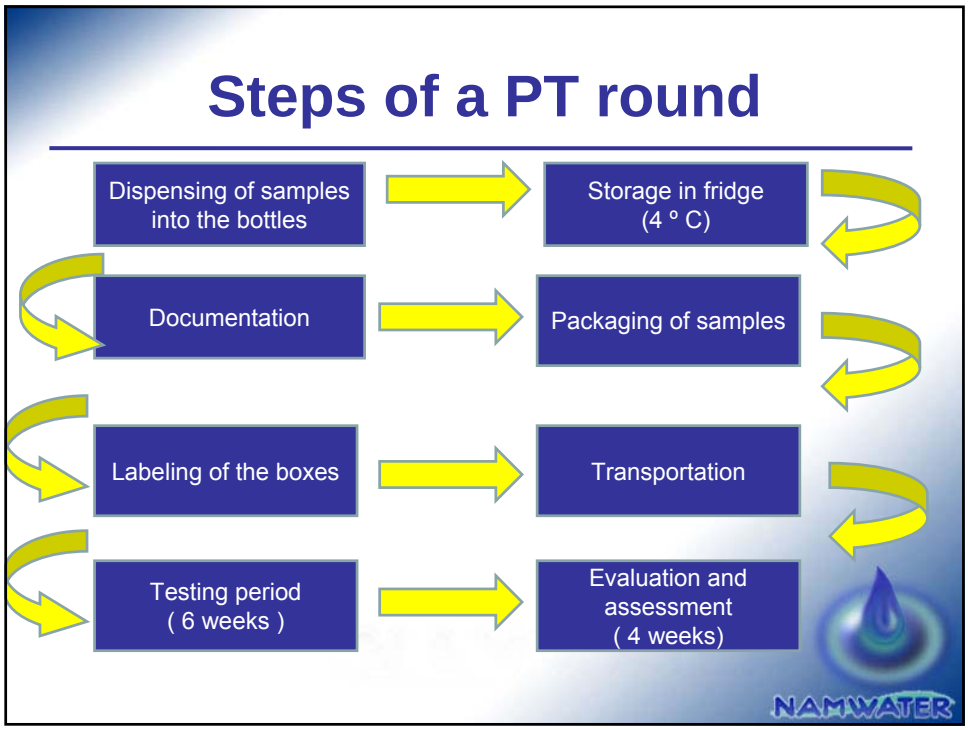
Steps of a PT round
Dispensing of samples into the bottles
Storage in fridge (4 ° C)
Documentation
Packaging of samples
Labeling of the boxes
Transportation
Testing period (6 weeks)
Evaluation and assessment (4 weeks)
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Sample bottle preparation

- Wash all 350 bottles
- Bottles were rinsed twice with deionised water
- Bottles & caps were put in the oven @ 60 °C overnight
- Check dryness
- Cap bottles to prevent them from dust
- Store them in the crates until needed

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Weighing of salts /wires

Weigh target weight of salt / wires

↓

Weigh the 20 substances for three levels

↓

Continue to prepare the stock solution

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Digestion of the wires

Preparation of stock solutions

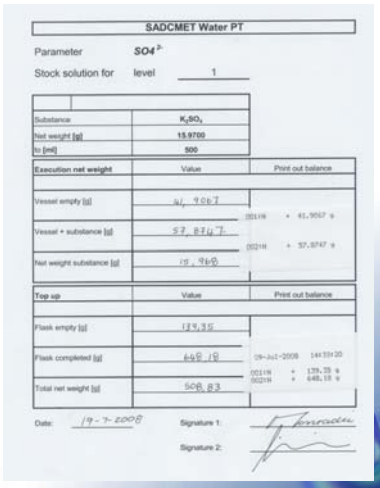
Fill the 500 ml volumetric flask by weight

Wash accurately into a 500ml volumetric flask

Repeat for all 20 parameters – 3 levels

Documentation of weighing

- Proof of printings were pasted against all weighings
- Cut and pasted next to the written weighing for proof of the traceability
- Calculation were checked signed
- Confirmed by 2nd person



SADCMET Water PT

Parameter $SO4^{2-}$

Stock solution for level 1

Substance	K_2SO_4
Net weight [g]	15,9700
to [ml]	500

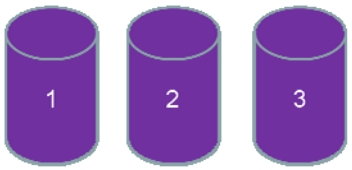
Execution net weight	Value	Print out balance
Vessel empty [g]	41,9067	
Vessel + substance [g]	57,8747	
Net weight substance [g]	15,9680	

Top up	Value	Print out balance
Flask empty [g]	139,35	
Flask completed [g]	648,18	
Total net weight [g]	508,83	

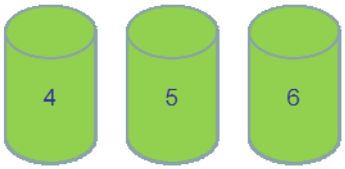
Date: 19-7-2008 Signature 1: Signature 2:

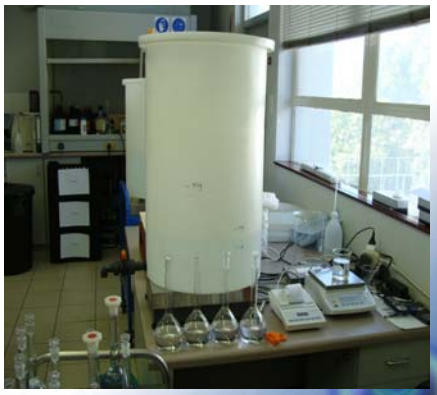
Preparation of bulk samples

Anions : SO_4^{2-}, Cl^-, NO_3^-, F^-, PO_4^{3-}



Cations : Na, K, Ca, Mg, Fe, Mn, Cd, Cu, Pb, Zn, Al, As, Cr, Co





pH adjustment

- Continuously stirring while preparing samples and during the process
- Filled container by weight
- Final stirring for 15 minutes
- Document the final pH

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Sample dispensing

- Samples bottles (50) were filled after each batch
- Put in crates in fridge at 4 ° C
- Tank washed properly (3 x) 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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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

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Labeling & sorting

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Sample pick-up and dispatch

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Transportation

DHL, TNT, Fedex

Courier costs

Courier	Amount in NAD
TNT	
Zambia	2401.56
Malawi	1082.96
Seychelles	2237.3
Kenya	4994.01
Total 1 for TNT	10715.83
DHL	
Tanzania	10768.23
Uganda	5098.32
Botswana	1293.47
Lesotho	595.41
Swaziland	1269.65
Madagascar	4215.48
Total 1 for DHL	23240.56
Fedex	
Zimbabwe	2900.53
Mauritus	3712.16
South Africa	388.65
Total 1 for Fedex	7001.34
Total distribution costs	**40 957.73**
	3691.95 EUR

Evaluation and Assessment

- Calculate the reference values from synthetic, gravimetrical sample with an uncertainty budget
- The assessment of performance is based on z-scores
- Calculation of standard deviation using Algorithm A method from ISO 13528 provided it is lower than the fitness-for-purpose value agreed on between participants.
- Limitation of the standard deviation as a “fitness for purpose” requirement

Evaluation and Assessment (cont.)

- Where the calculated value is higher, the fitness-for-purpose value is used.
- Values < ref.-value/8 and > ref.-value*8 have been excluded before applying statistical procedures
- Graphical display of lab. results vs. assigned value to assist in corrective actions
- A method specific evaluation is made and help is provided for laboratories that need corrective actions.

Evaluation and Assessment (cont.)

- Participants agreed on assigned value
  - Partially high standard deviations in the data sets
  - Consensus mean was not reliable
  - Some of the data sets were are very low
- During annual evaluation workshop –
  - Detailed presentation on all problems
  - Number of improvements

Interpretation of the Z –score

- Make use of the 'z-score'
- This score reflects :
  - Actual accuracy achieved - the difference between the participant's result and the reference value
  - A score of zero implies a perfect result
  - Laboratories produce scores falling between - 2 and 2.
  - The sign (i.e., + or -) of the score indicates a negative or positive error respectively.
    - $|z\text{-score}| \leq 2$ – satisfactory
    - $2 < |z\text{-score}| \leq 3$ – questionable
    - $|z\text{-score}| > 3$ – unsatisfactory

Limits for standard deviation

Parameter	Std limit	Parameter	Std limit
Sulphate	10 %	Manganese	20 % / 12 %
Chloride	10 %	Aluminium	30 %
Fluoride	12 %	Lead	40 % / 25 %
Nitrate	15 %	Copper	20 %
Phosphate	10 %	Zinc	20 %
Calcium	10 %	Chromium	25 %
Magnesium	10 %	Nickel	25 %
Sodium	10 %	Cadmium	20 %
Potassium	10 %	Arsenic	20 %
Iron	20 % / 12 %	Cobalt	20 %

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Measurement uncertainty of reference values

- Uncertainty components of all the weighings - for each balance and weighing range separately
- Purity of the reagents /component - certificate from the manufacturer
- Density test for each sample
- Buoyancy correction
- Determine combined uncertainty for each parameter – 3 levels

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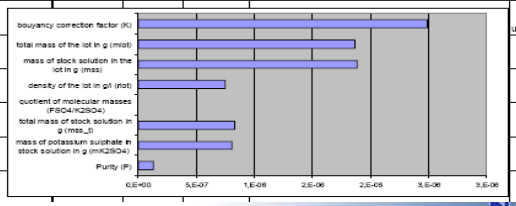
Calculation of measurement uncertainty

$$c_{lot} = \frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot m_{zz} \cdot \rho_{lot}}{m_{zz\_t} \cdot m_{lot} \cdot K}$$

parameter	estimated value	specification	probability distribution	divisor	standard uncertainty (u_i)	sensitivity coefficient (c_i)	senaitivity coefficient (c_i)
Purity (P)	0,99999	0,00001	Rechteck	$\sqrt{3}$	5,7735E-06	$\frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot m_{zz} \cdot \rho_{lot}}{m_{zz\_t} \cdot m_{lot} \cdot K}$	0,022641974
mass of potassium sulphate in stock solution in g (m_{K2SO4})	5,1308				0,000183291	$\frac{F_{SO_4/K_2SO_4} \cdot P \cdot m_{zz} \cdot \rho_{lot}}{m_{zz\_t} \cdot m_{lot} \cdot K}$	0,004412908
total mass of stock solution in g (m_{zz_t})	501,44				0,018412909	$-\frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot m_{zz} \cdot \rho_{lot}}{m_{zz\_t}^2 \cdot m_{lot} \cdot K}$	-4,51535E-05
quotient of molecular masses ($F_{SO4/K2SO4}$)	0,55126425				0	$\frac{m_{K_2SO_4} \cdot P \cdot m_{zz} \cdot \rho_{lot}}{m_{zz\_t} \cdot m_{lot} \cdot K}$	0,041072403
density of the lot in g/l (ρ_{lot})	997,5835337				0,032977358	$\frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot m_{zz}}{m_{zz\_t} \cdot m_{lot} \cdot K}$	2,26966E-05
mass of stock solution in the lot in g (m_{zz})	201				0,016735821	$\frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot \rho_{lot}}{m_{zz\_t} \cdot m_{lot} \cdot K}$	0,000112646
total mass of the lot in g (m_{lot})	49901				4,111707712	$-\frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot m_{zz} \cdot \rho_{lot}}{m_{zz\_t} \cdot m_{lot}^2 \cdot K}$	-4,53733E-07
bouyancy correction factor (K)	1,001031487				0,00011	$-\frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot m_{zz} \cdot \rho_{lot}}{m_{zz\_t} \cdot m_{lot} \cdot K^2}$	-0,022618417
result (g/l)	0,022641747						u_c
result in mg/l	22,64174733						
standard uncertainty in mg/l	0,063831994						
rel Unsicherheit	0,02%						
erw. Unsicherheit	0,007783987						
erw. rel. Unsicherheit	0,03%						



Uncertainty components

	Standard uncertainty					Standard uncertainty		
	u_c in mg/l					u_c in mg/l		
Parameter	Min	Max	Biggest uncertainty component	Parameter	Sample	Min	Max	Biggest uncertainty component,
SO_4	0.0333	0.1766	Purity of K_2SO_4		Mn	0.001	0.002	Mass of stock solution; Purity of Mn powder
Cl	0.0315	0.0542	Purity of KCl		Al	0.001	0.001	Mass of stock solution
F	0.0005	0.0009	Density of lot		Pb	0.000	0.001	Mass of stock solution, Purity of Pb(NO3)2
NO_3	0.0070	0.0104	Purity of KNO_3		Cu	0.001	0.002	Mass of stock solution
PO_4	0.0049	0.0156	Purity of KH_2PO_4		Zn	0.001	0.002	Mass of stock solution
Ca	0.0400	0.1374	Purity of CaCl		Cr	0.001	0.005	Purity of Cr
Mg	0.0311	0.1398	Purity of $Mg(NO3)_2.6H_2O$		Ni	0.000	0.002	Mass of stock solution
Na	0.0121	0.0536	Purity of NaCl		As	0.000	0.001	Mass of stock solution
K	0.0065	0.0171	Purity of KCl		Cd	0.001	0.008	Mass of stock solution
Fe	0.0008	0.0016	Mass of stock solution		Co	0.001	0.005	Purity of Co

Documentation

- Certificates are documented:
  - Certificate of analyses (COA) for reagents used
  - Calibration certificate for thermometer
  - Calibration certificate for pycnometer
  - Calibration certificates for balances
- Weighings are printed and readings were pasted to the calculated mass for proof and for verification purposes - confirmed by a second person

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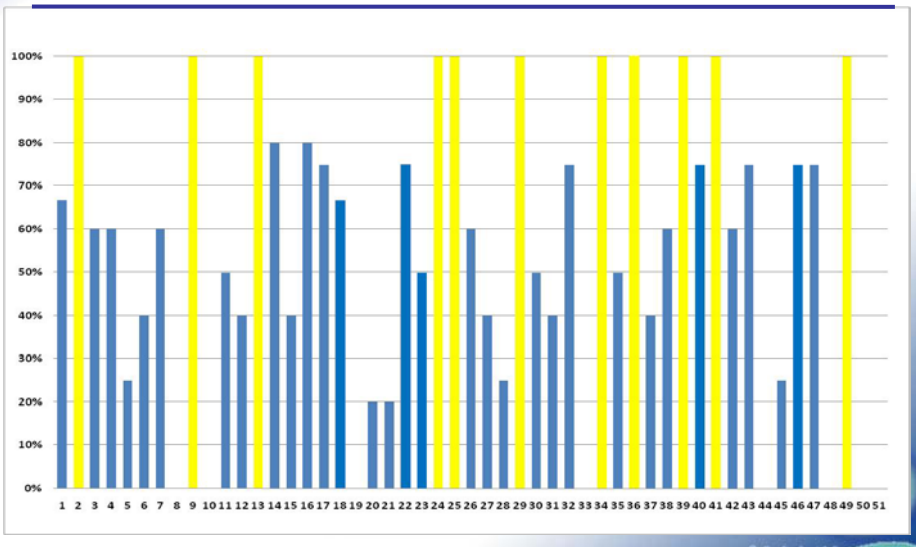
% Success: Anions

11

Number of acceptable values / Total number of anions done



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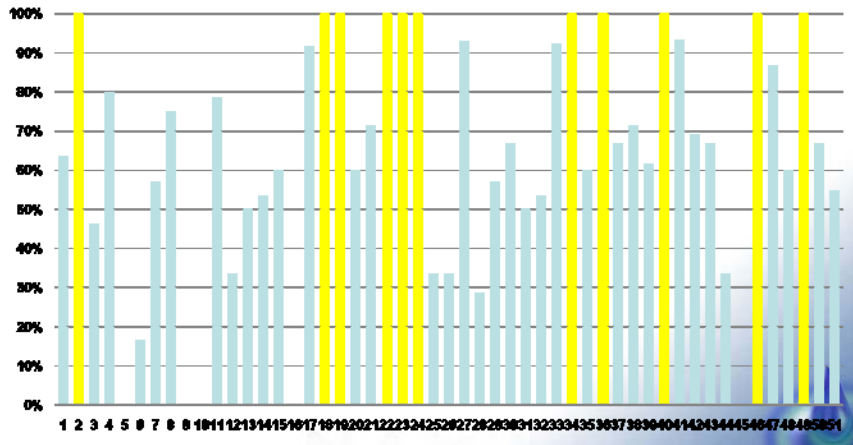
% Success: Cations

11

Number of acceptable values / Total number of anions done



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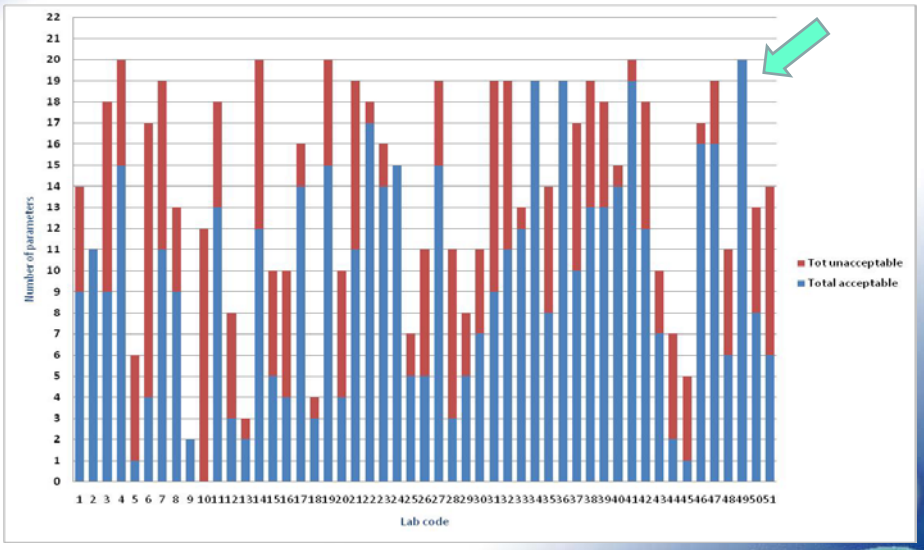
Total # Acceptable vs. Total # Unacceptable values



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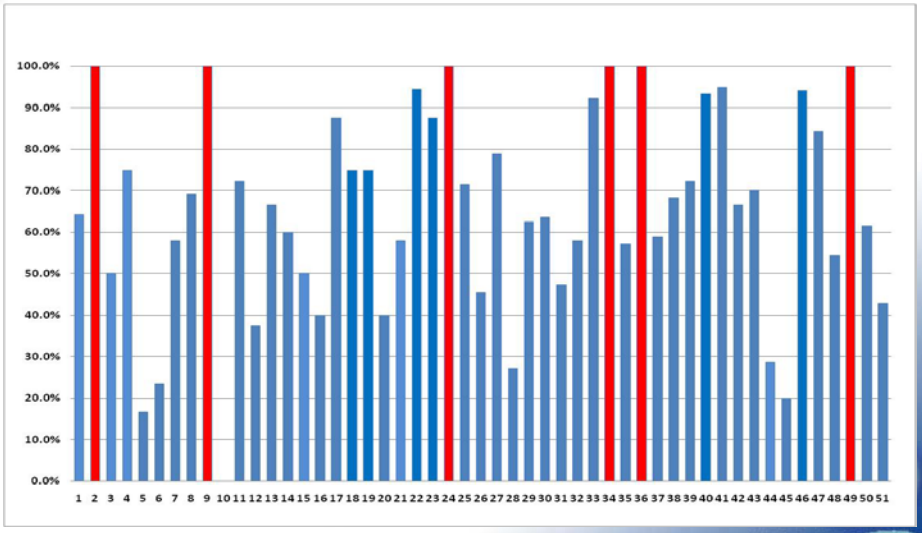
% Success

Number of acceptable values / Total number of elements analysed



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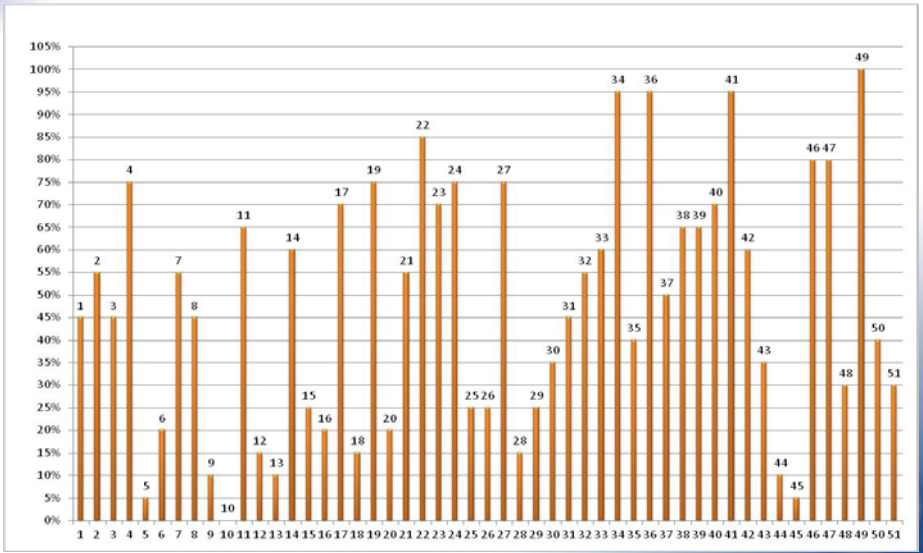
Overall Performance

% Success x % Done



NAMWATER

Reference values vs. Nmisa

Parameter	Sample 4		Sample 5		Sample 6	
	Concentration (µg/ml)	Expanded Uncertainty (µg/ml)	Concentration (µg/ml)	Expanded Uncertainty (µg/ml)	Concentration (µg/ml)	Expanded Uncertainty (µg/ml)
Al	0.488	0.027	0.809	0.046	1.231	0.065
	0.523	0.001	0.834	0.003	1.316	0.003
As	0.423	0.043	0.294	0.034	0.05	0.014
	0.596	0.002	0.370	0.001	0.071	0.000
Ca	47.6	2.1	14.02	0.62	38.9	1.7
	46.931	0.275	13.656	0.080	38.771	0.227
Cd	0.789	0.015	0.074	0.002	0.434	0.01
	0.834	0.002	0.078	0.000	0.459	0.002
Co	1.355	0.045	2.326	0.077	0.713	0.024
	1.377	0.007	2.332	0.011	0.709	0.004
Cr	1.331	0.051	1.883	0.051	0.253	0.011
	1.533	0.008	2.172	0.011	0.275	0.001
Cu	0.681	0.02	1.908	0.072	3.314	0.1
	0.701	0.001	1.874	0.003	3.371	0.004
Fe	0.995	0.036	1.764	0.066	0.816	0.03
	0.993	0.003	1.714	0.003	0.721	0.002
K	14.4	0.56	8.56	0.31	22.68	0.78
	15.411	0.022	9.257	0.013	24.405	0.034
Mg	11.04	0.57	36.3	1.8	49.7	2.4
	10.609	0.062	34.987	0.205	47.767	0.280
Mn	2.292	0.091	0.576	0.024	1.182	0.053
	2.431	0.004	0.586	0.002	1.206	0.003
Na	74.7	3	32.9	1.2	16.78	0.62
	76.572	0.107	32.727	0.046	17.237	0.024
Ni	0.227	0.013	3.44	0.15	1.918	0.085
	0.207	0.000	3.180	0.004	1.743	0.003
Pb	1.442	0.05	0.276	0.013	0.927	0.033
	1.529	0.003	0.285	0.001	0.964	0.002
Zn	3.128	0.097	1.154	0.027	3.52	0.11
	2.973	0.004	0.843	0.003	3.345	0.004
Calculated refernce value						
NMISA						

General problems

- Dedicated time for the preparation and evaluation period without interruptions
- Late confirmations and requests of participation caused problems
- Registration forms are not sent to the provider - difficult to contact participants
- Receipt of results by fax unclear
- E-mail problems
- Return date for the results : 28th of August 2009 with an extension of two weeks for some of the laboratories due to late deliveries.
- Three labs did not take part due to courier problems

Reporting Problems

- Again high standard deviations > higher than limits
- High portion of outliers - gravimetrical methods
- Non-standard methods are still used
- Significant figure problems e.g. 0.69585
- Reporting of results in wrong units (N and not NO_3^- and as P and not PO_4^{3-}
- Improvement was not good enough
- Corrective actions not implemented

Conclusions

- The SADCMET Water PT is a good possibility for the participants to improve there daily analyses – corrective actions are however not implemented
- SADCMET lab association is a good platform for networking and mutual help to improve the quality – it is not utilized
- The results achieved over the past 6 years die not improve enough
- Effort and emphasis were spent on corrective actions – but still no significant improvement
- Trade is important for Africa - how can results be trusted from different laboratories if that is the outcome ?

Acknowledgments

- **PTB assistance**
  - Stefan Wallerath / Kathrin Wunderlich
  - Rebecca Alt
- **SADCMET**
  - Donald Masuku
  - Margaret Ngobeni
- **University of Stuttgart**
  - Dr Michael Koch
- **NamWater**
- **Local coordinators**
- **Participants**
- **Seychelles Bureau of Standards**
  - Charles Celestine

Quality

"Quality is never an accident; it is always the result of high intention, sincere effort, intelligent direction and skilful execution; it represents the wise choice of many alternatives"

William A. Foster

Universität Stuttgart

Evaluation of the 6th SADCMET Water PT

Evaluation Workshop
Seychelles 2009

Dr.-Ing. Michael Koch
Institute for Sanitary Engineering, Water Quality and Solid Waste Management
Universität Stuttgart
Dep. Hydrochemie
Bandtäle 2
D-70569 Stuttgart
Tel.: +49 711 685 65444 / Fax: +49 711 685 67809
E-Mail: Michael.Koch@iswa.uni-stuttgart.de

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Evaluation and Assessment

- according to same procedure as in the last rounds
  - assigned value from the formulation of the samples (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)

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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 %
iron	20 % / 12 %

parameter	std limit
manganese	20 % / 12 %
aluminium	30 %
lead	40 % / 25 %
copper	20 %
zinc	20 %
chromium	25 %
nickel	25 %
cadmium	**20 %**
arsenic	**20 %**
cobalt	20 %

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Elimination of gross outliers

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

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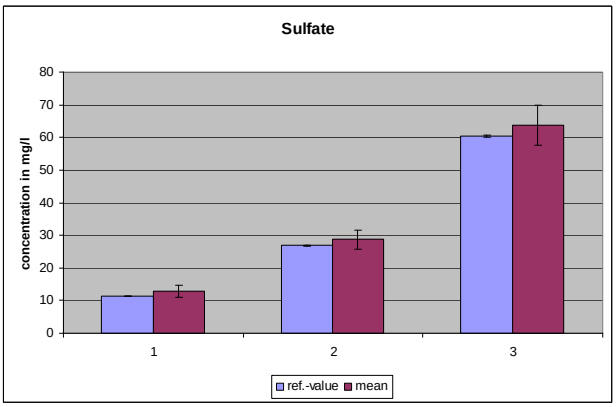
Sulphate
Alg.A mean and ref.-value from weighings



Quite good agreement, a bit higher

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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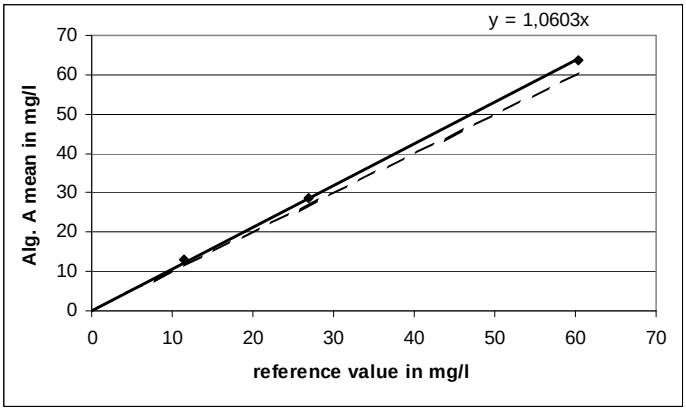
Sulphate
mean vs. ref.-value



Average recovery	
2009	106.0
2008	99.6
2007	103.6
2006	106.5

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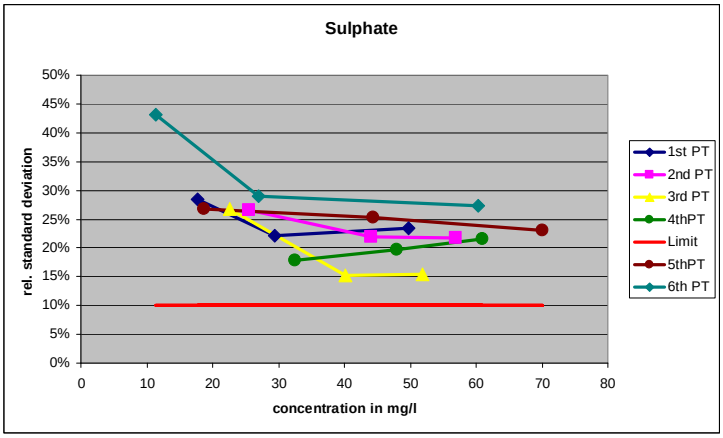
Sulphate
calculated standard deviation and limit



2009 worst standard deviations of all PTs

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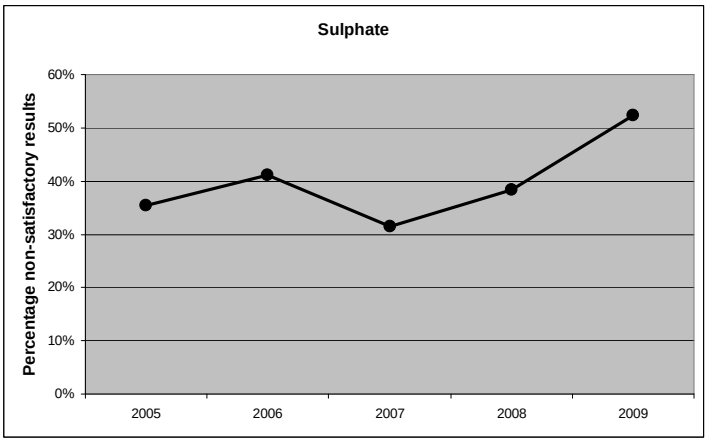
Sulphate
Percentage non-satisfactory results



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Individual performance development

- For all labs participating in 2008 and in 2007 (or 2006)
- Calculation of the mean of the absolute values of z-scores of the 3 values
- Graphical display
  - all values
  - How man labs are
    - Consistently lower than 2.0 (good)
    - Consistently higher than 2.0 (bad)
    - Improving from > 2.0 to < 2.0
    - Getting worse from < 2.0 to > 2.0

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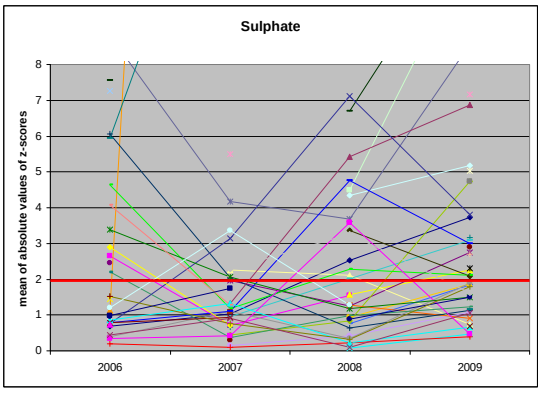
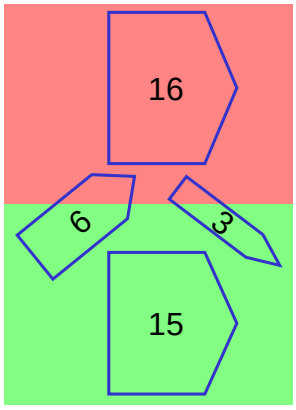
Sulphate
Individual performance development





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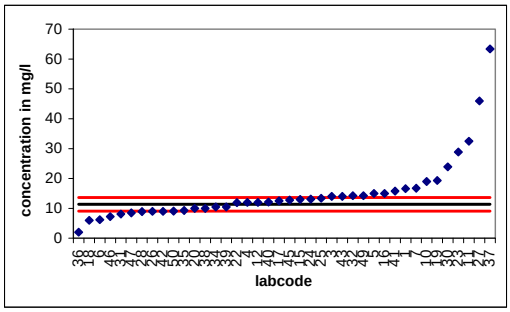
Sulphate 1



values:	42
removed:	2
mean:	12,90
ref.-value:	11,37
recovery:	113,4%
std:	4,894
rstd:	43,0%
std limit:	10%
upper limit:	13,65
lower limit:	9,10
too high:	17
too low:	11
outside limits:	28

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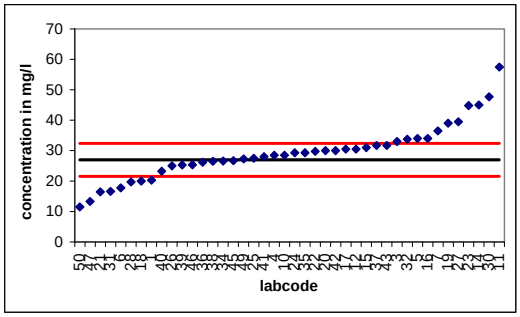
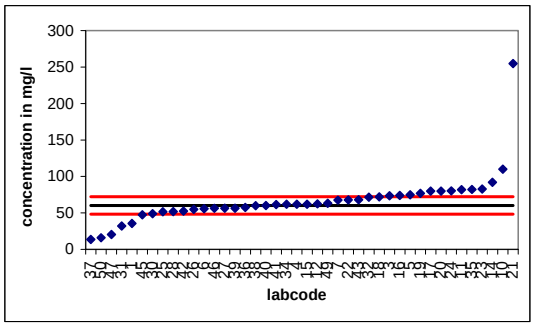
Sulphate 2



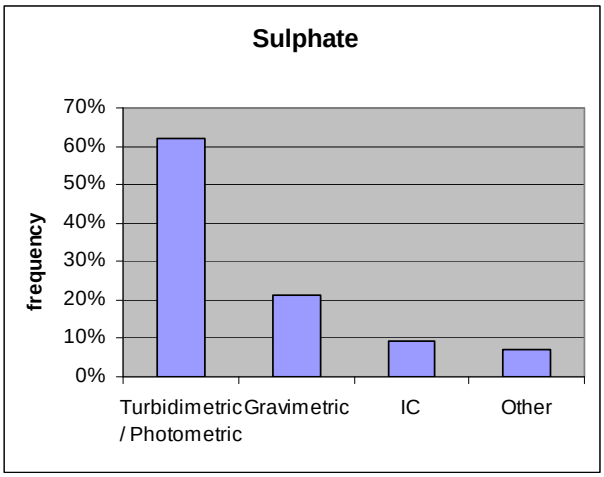
values:	42
removed:	0
mean:	28,70
ref.-value:	26,96
recovery:	106,4%
std:	7,811
rstd:	29,0%
std limit:	10%
upper limit:	32,35
lower limit:	21,57
too high:	11
too low:	8
outside limits:	19

Sulphate 3



values:	**42**
removed:	**0**
mean:	**63,74**
ref.-value:	**60,31**
recovery:	**105,7%**
std:	**16,504**
rstd:	**27,4%**
std limit:	**10%**
upper limit:	**72,37**
lower limit:	**48,25**
too high:	**13**
too low:	**6**
outside limits:	**19**

Used methods



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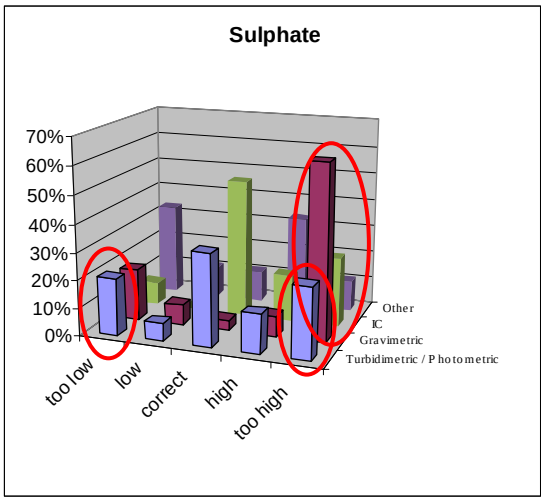
Comparison of methods



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Summary Sulphate

- Quite good agreement between means and ref.-values; means a bit too high
- Standard deviation higher than ever before
- More than 50% of the labs have unsatisfactory results
- High portion of outliers for the turbidimetric and especially for the gravimetrical method

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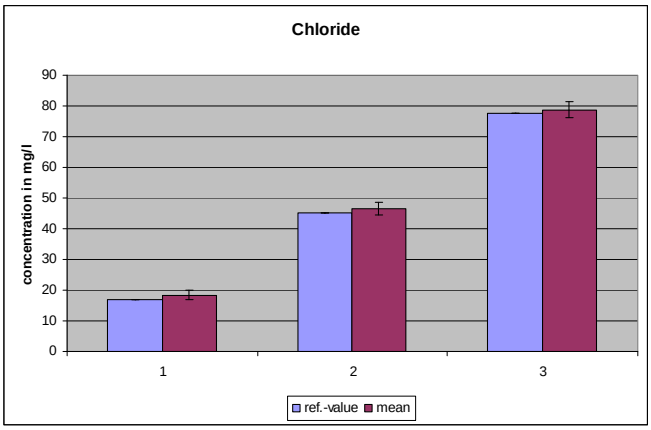
Choride
Alg.A mean and ref.-value from weighings



Similar to last years: means a little bit higher then ref.-values

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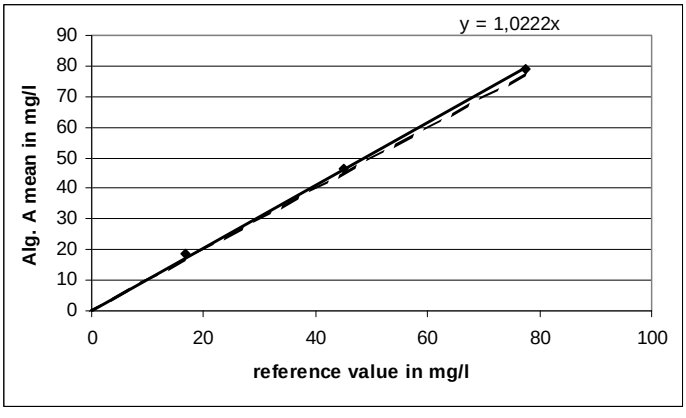
Chloride
mean vs. ref.-value



Average recovery	
2009	102.2
2008	101.0
2007	102.4
2006	101.6

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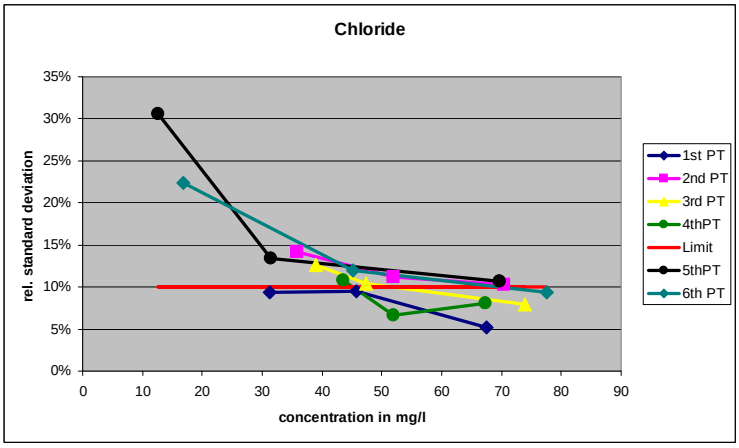
Chloride
calculated standard deviation and limit



No improvement over time; standard deviation as high as in 2008

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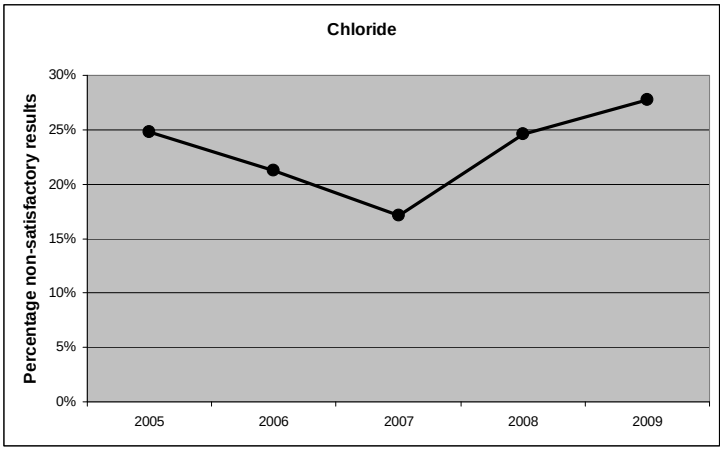
Chloride
Percentage non-satisfactory results



No improvement over time; more unsatisfactory results than ever before

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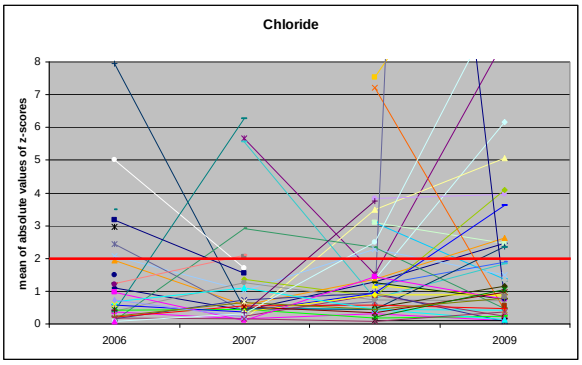
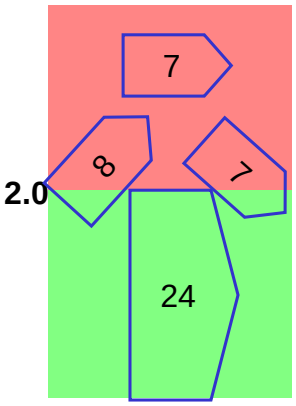
Chloride
Individual performance development





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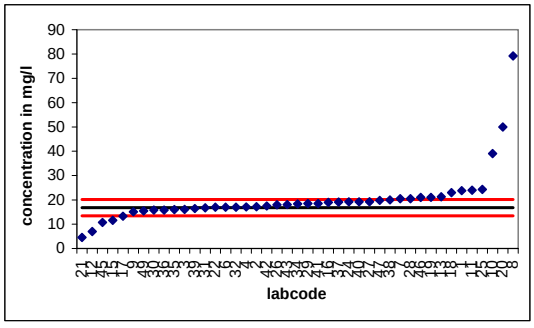
Chloride 1



values:	**46**
removed:	**3**
mean:	**18,45**
ref.-value:	**16,79**
recovery:	**109,9%**
std:	**3,750**
rstd:	**22,3%**
std limit:	**10%**
upper limit:	**20,15**
lower limit:	**13,43**
too high:	**13**
too low:	**7**
outside limits:	**20**

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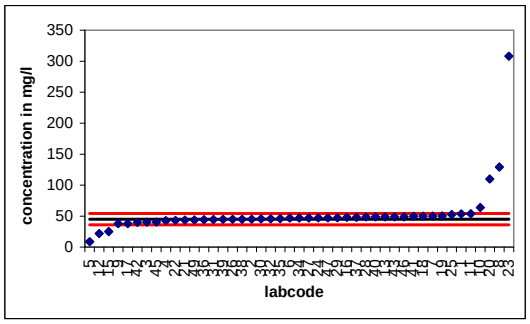
Chloride 2



values:	46
removed:	1
mean:	46,57
ref.-value:	45,15
recovery:	103,1%
std:	5,400
rstd:	12,0%
std limit:	10%
upper limit:	54,18
lower limit:	36,12
too high:	4
too low:	4
outside limits:	8

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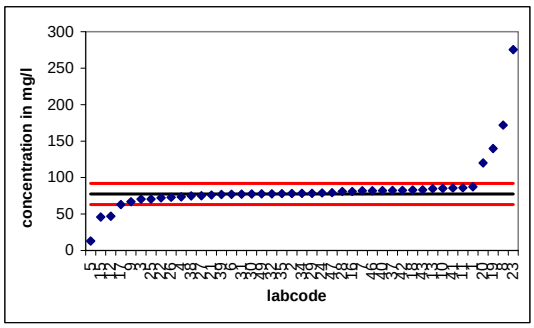
Chloride 3



values:	45
removed:	2
mean:	78,77
ref.-value:	77,57
recovery:	101,5%
std:	7,233
rstd:	9,3%
std limit:	10%
upper limit:	92,04
lower limit:	63,10
too high:	4
too low:	6
outside limits:	10

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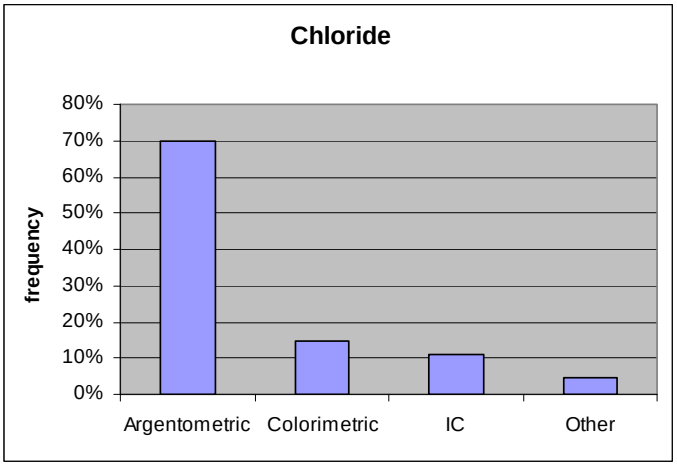
Used methods



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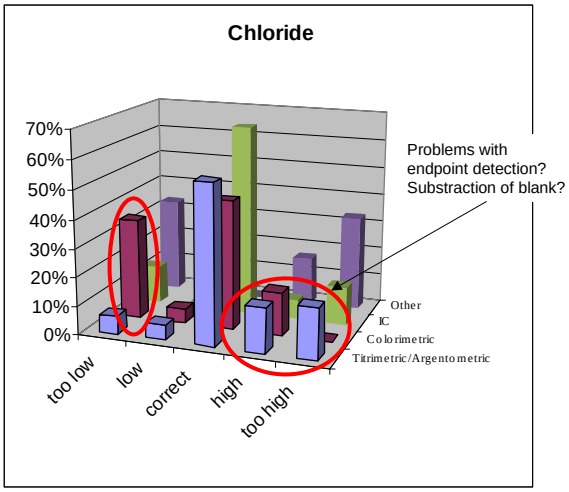
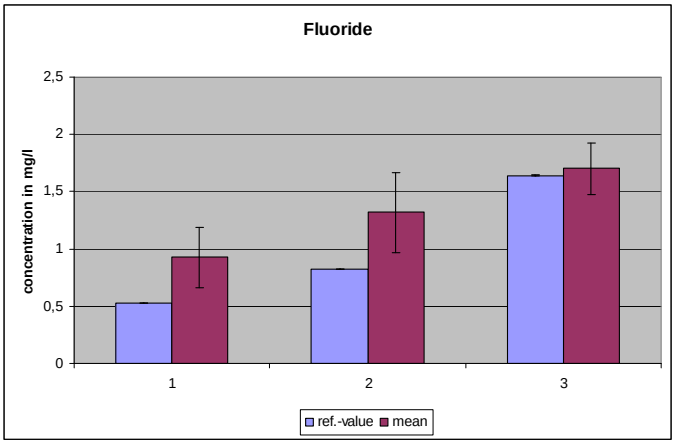
Comparison of methods



Summary Chloride

- Quite good agreement between mean and reference value
- Standard deviation too high – no improvement
- More unsatisfactory results than ever before
- Only 2/3 of the labs have good results
- Problems with the endpoint detection in argentometric determination
- Obviously some problems with the spectrometric method

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



As in 2008: means significantly higher than ref. value, especially for low concentration

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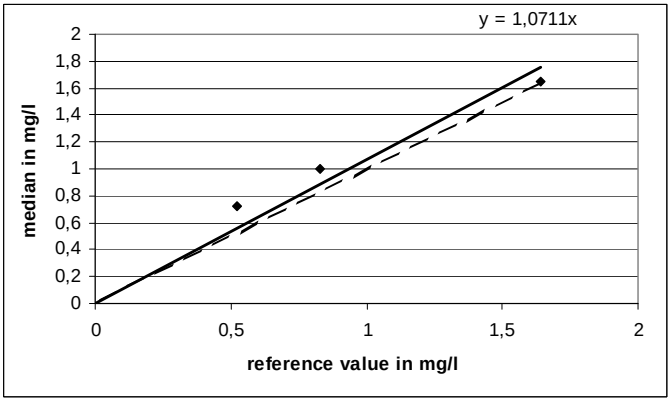
Fluoride
mean vs. ref.-value



Average recovery	
2009	107.1
2008	112.0
2007	98.2
2006	107.7

Recovery ok only for the highest concentration

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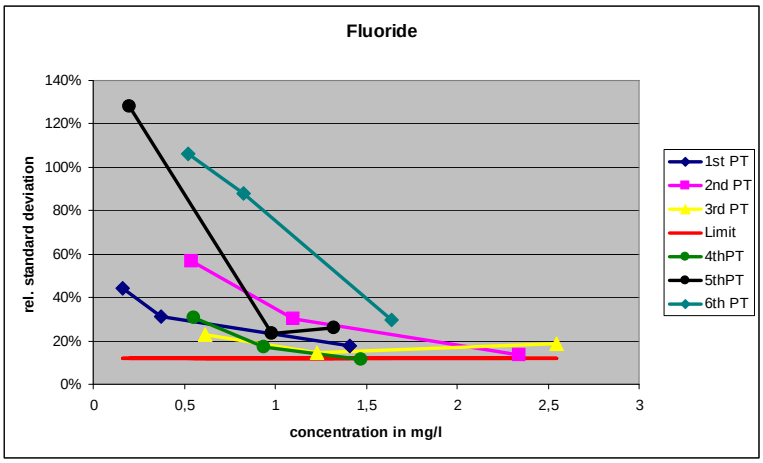
Fluoride
calculated standard deviation and limit



Very high standard deviations – no improvement

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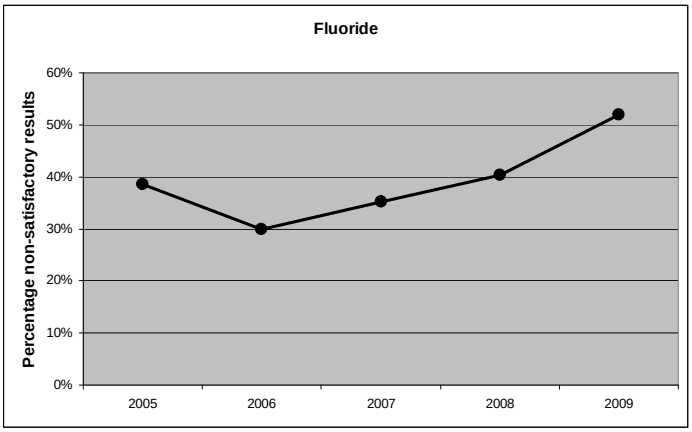
Fluoride
Percentage non-satisfactory results



Highest value – more than 50%!!

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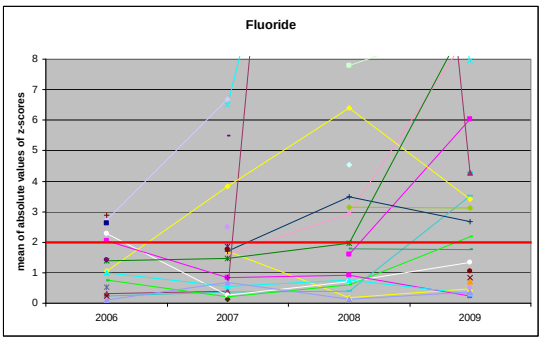
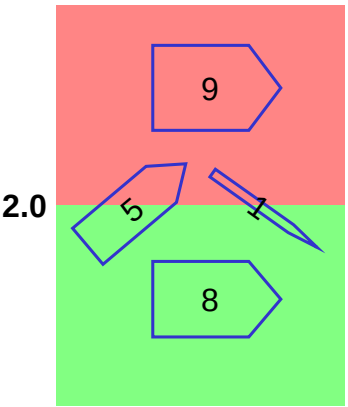
Fluoride
Individual performance development





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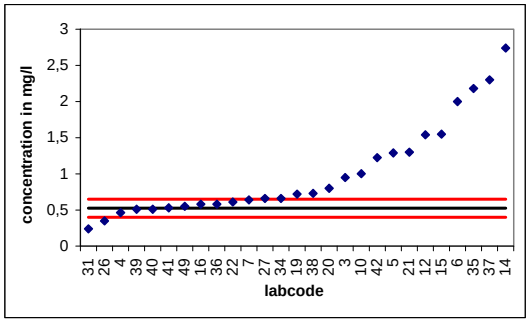
Fluoride 1



values:	27
removed:	0
mean:	0,93
ref.-value:	0,52
recovery:	176,8%
std:	0,556
rstd:	106,0%
std limit:	12%
upper limit:	0,65
lower limit:	0,40
too high:	16
too low:	2
outside limits:	18

No real consensus between the participants

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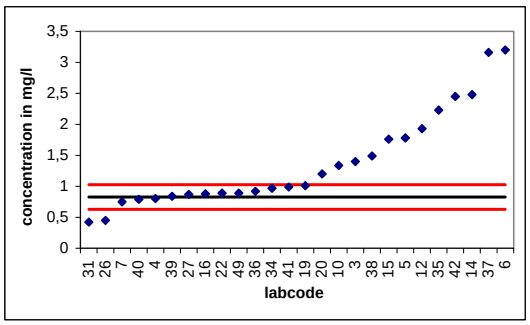
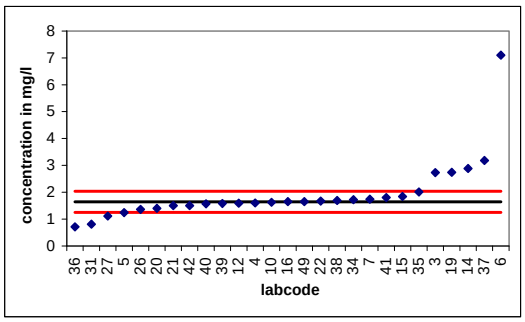
Fluoride 2



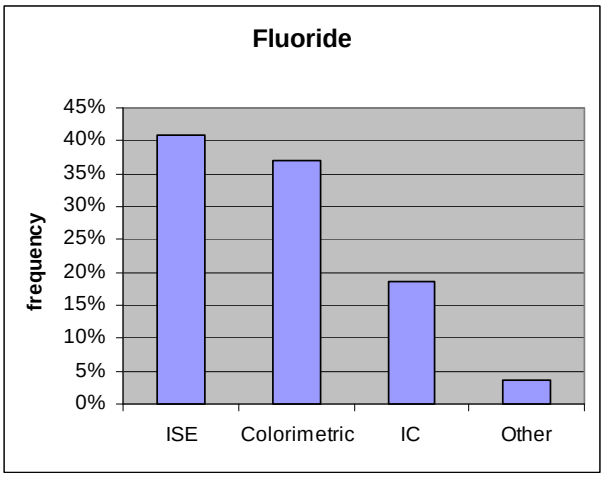
values:	27
removed:	1
mean:	1,32
ref.-value:	0,83
recovery:	159,3%
std:	0,729
rstd:	88,2%
std limit:	12%
upper limit:	1,03
lower limit:	0,63
too high:	13
too low:	2
outside limits:	15

Fluoride 3

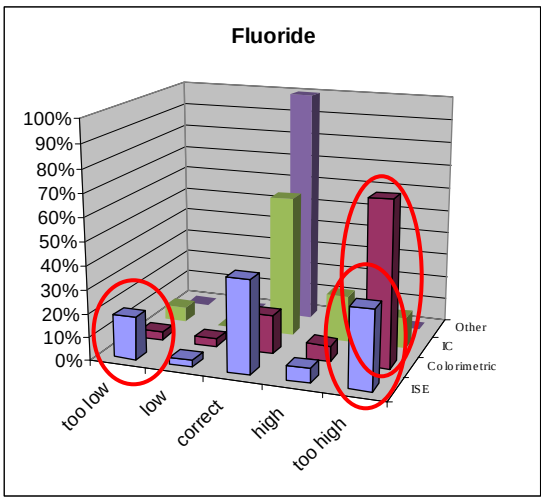


values:	27
removed:	0
mean:	1,70
ref.-value:	1,64
recovery:	103,6%
std:	0,483
rstd:	29,4%
std limit:	12%
upper limit:	2,04
lower limit:	1,25
too high:	5
too low:	4
outside limits:	9

Used methods



Comparison of methods



Colorimetric method fails completely for the low concentrations

Obviously some problems with ISE

Summary Fluoride

- Mean values higher than reference values
- Standard deviations very high – no improvement
- More than 50% of the values not satisfactory
- Colorimetric values not reliable (as in the last years!)
- Obviously some problems with ISE

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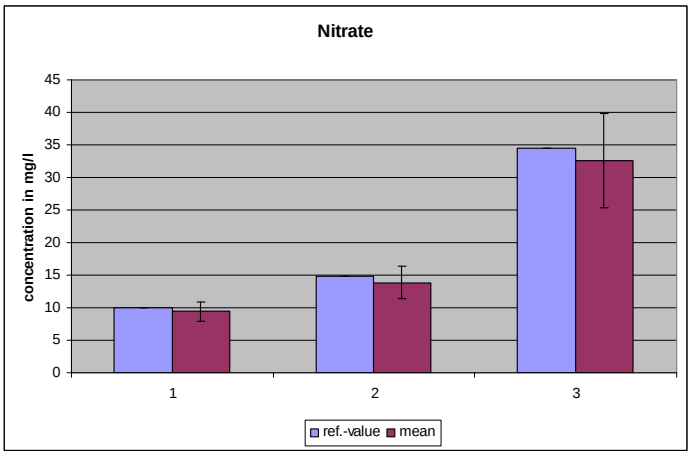
Nitrate
Alg.A mean and ref.-value from weighings



Means slightly lower than reference values

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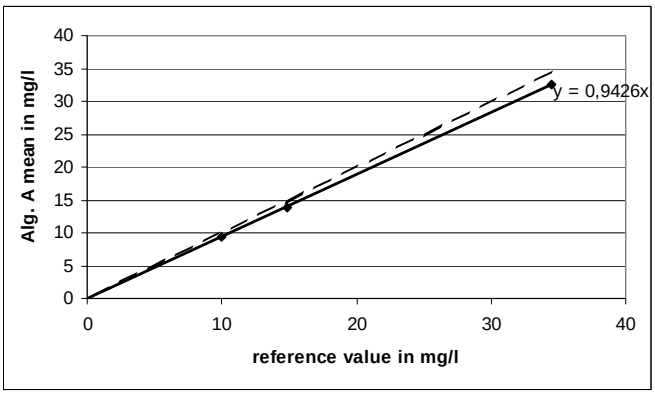
Nitrate
mean vs. ref.-value



Average recovery	
2009	94.3
2008	92.0
2007	85.9
2006	90.6

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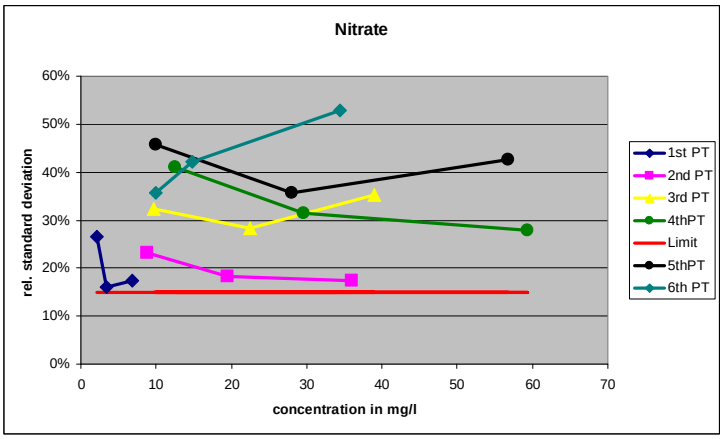
Nitrate
calculated standard deviation and limit



Highest standard deviation ever!!

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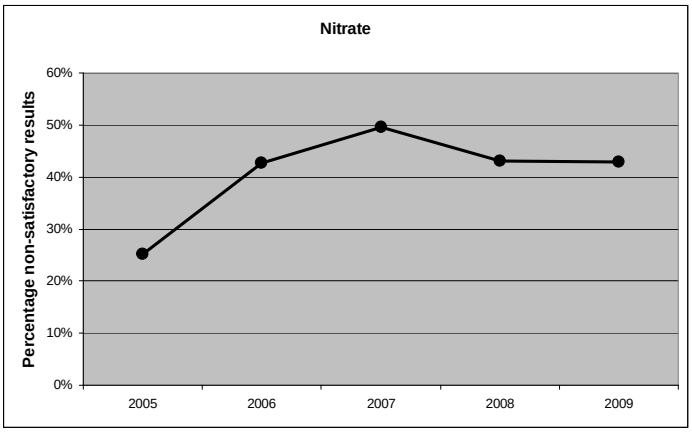
Nitrate
Percentage non-satisfactory results



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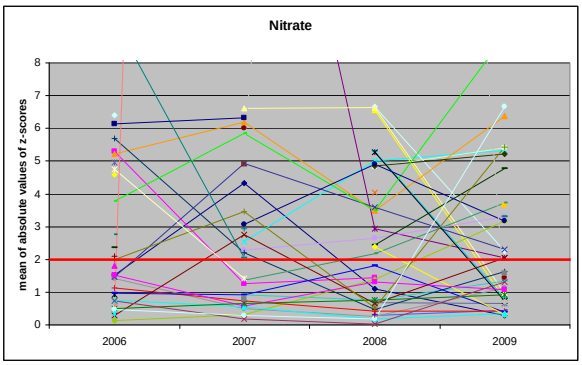
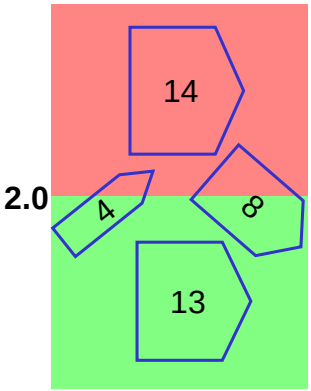
Nitrate
Individual performance development





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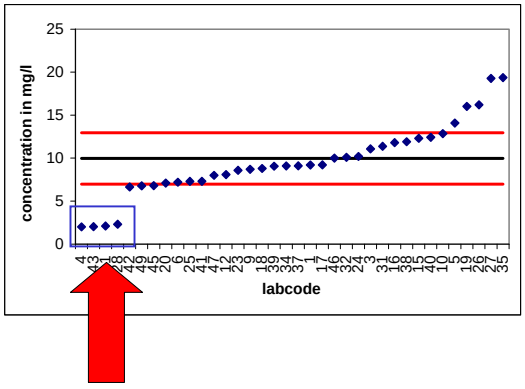
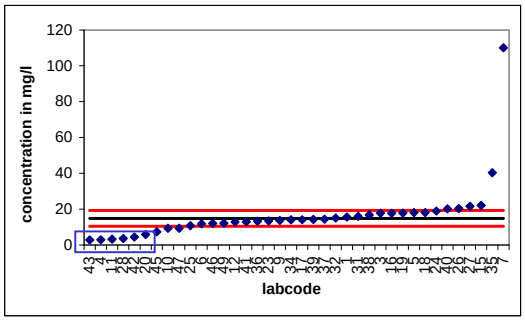
Nitrate 1



values:	**39**
removed:	**3**
mean:	**9,47**
ref.-value:	**9,96**
recovery:	**95,0%**
std:	**3,552**
rstd:	**35,7%**
std limit:	**15%**
upper limit:	**12,95**
lower limit:	**6,97**
too high:	**6**
too low:	**9**
outside limits:	**15**

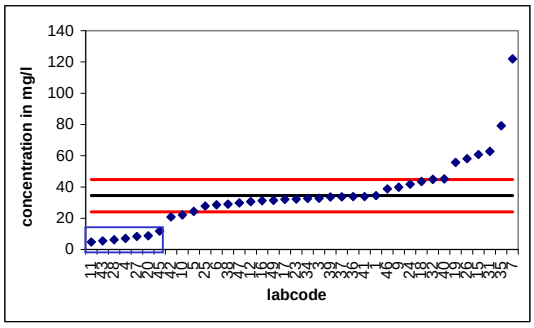
most probably reported as NO_3^--N instead of NO_3^-

Nitrate 2



values:	40
removed:	2
mean:	13,84
ref.-value:	14,82
recovery:	93,4%
std:	6,234
rstd:	42,1%
std limit:	15%
upper limit:	19,27
lower limit:	10,37
too high:	6
too low:	11
outside limits:	17

Nitrate 3



values:	40
removed:	2
mean:	32,51
ref.-value:	34,46
recovery:	94,4%
std:	18,241
rstd:	52,9%
std limit:	15%
upper limit:	44,80
lower limit:	24,12
too high:	8
too low:	11
outside limits:	19

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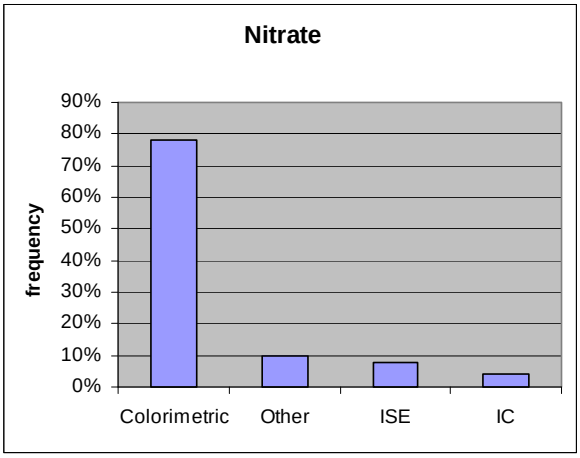
Used methods



Many different methods hidden behind “colorimetric”

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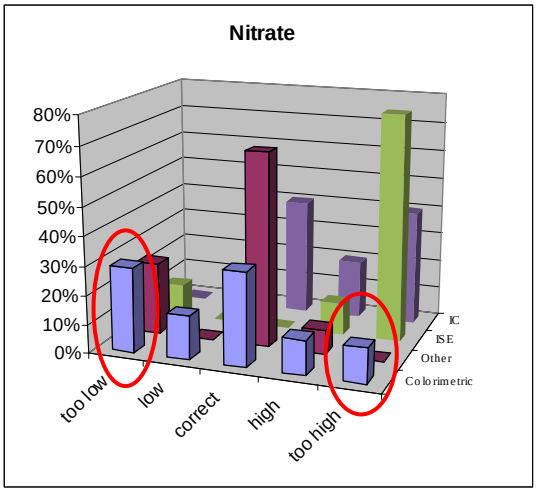
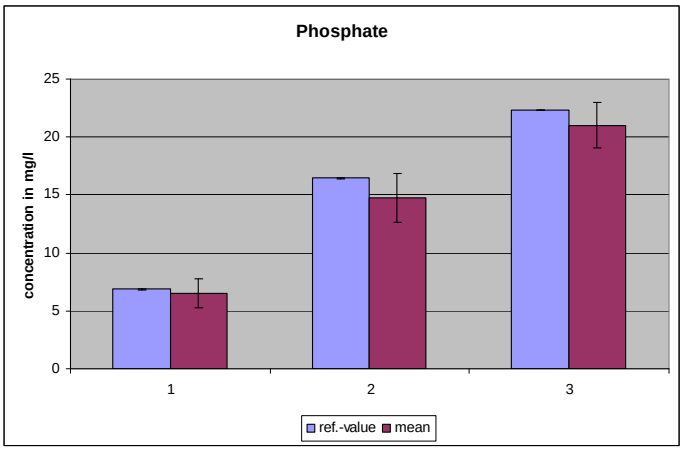
Comparison of methods



Summary Nitrate

- some values obviously again reported in wrong units (most probably 4 labs, 2 of them identical with 2008)
- high number of outliers
- Standard deviation very high! – no improvement!
- harmonization of methods?

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



Means slightly lower than reference values

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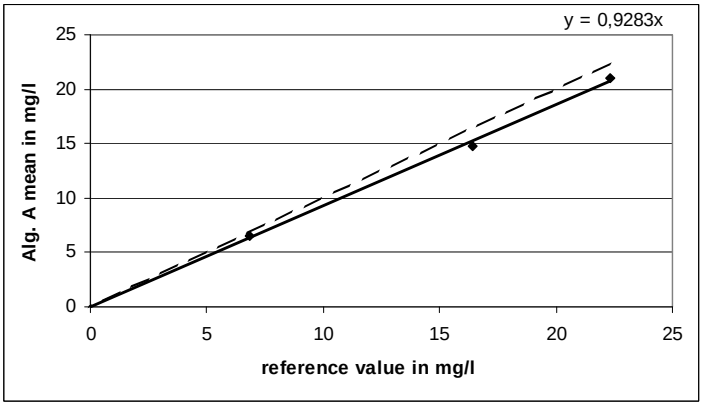
Phosphate
mean vs. ref.-value



Average recovery	
2009	92.8
2008	83.6
2007	95.0
2006	96.1

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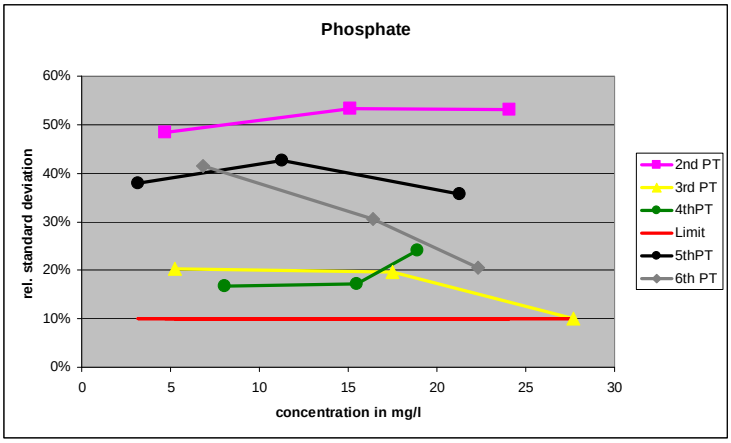
Phosphate
calculated standard deviation and limit



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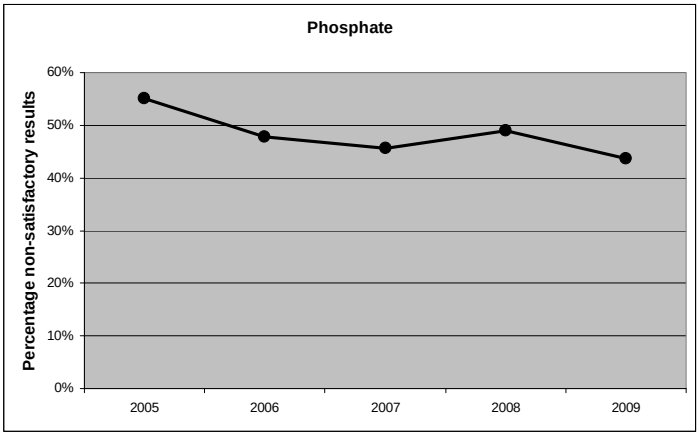
Phosphate
Percentage non-satisfactory results



Slight improvement, but still very high

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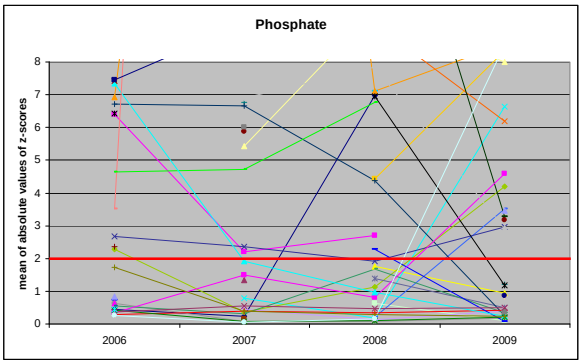
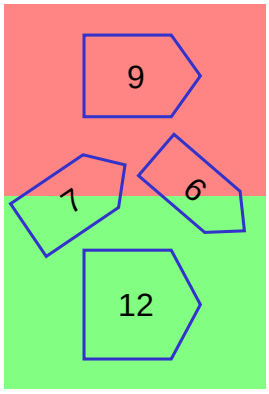
Phosphate
Individual performance development





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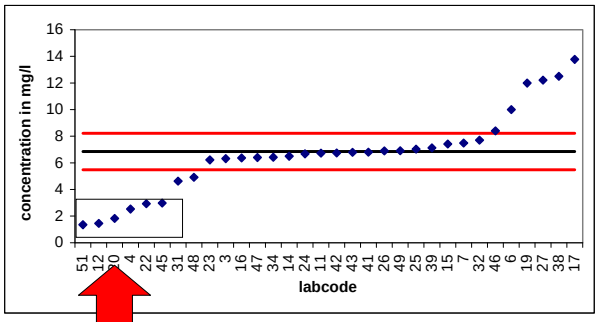
Phosphate 1



values:	36
removed:	4
mean:	6,53
ref.-value:	6,85
recovery:	95,3%
std:	2,847
rstd:	41,6%
std limit:	10%
upper limit:	8,22
lower limit:	5,48
too high:	7
too low:	11
outside limits:	18

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

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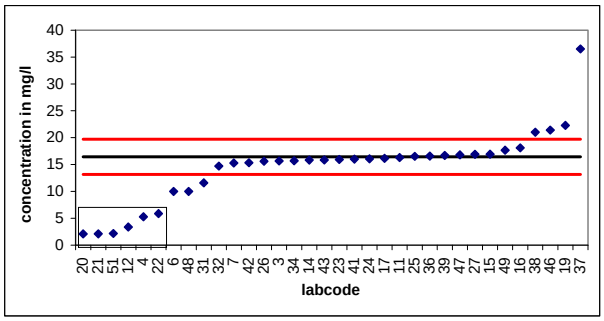
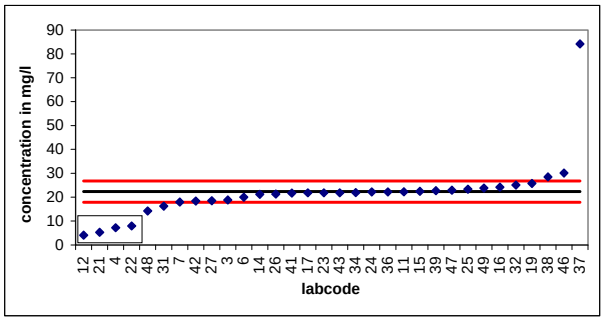
Phosphate 2



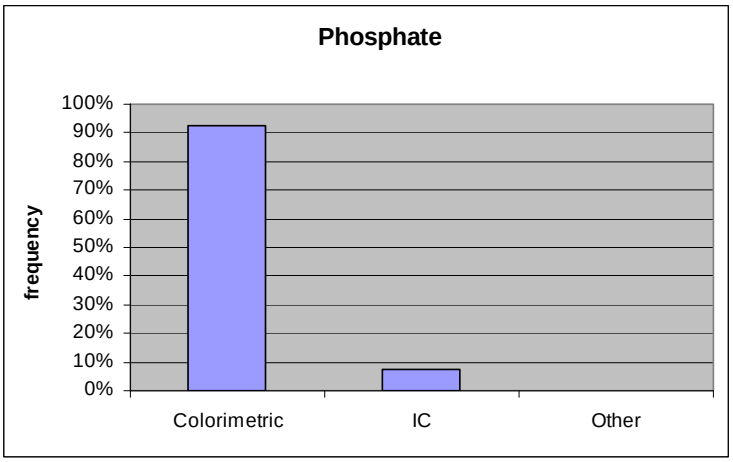
values:	37
removed:	3
mean:	14,78
ref.-value:	16,43
recovery:	90,0%
std:	5,026
rstd:	30,6%
std limit:	10%
upper limit:	19,71
lower limit:	13,14
too high:	4
too low:	12
outside limits:	16

Phosphate 3

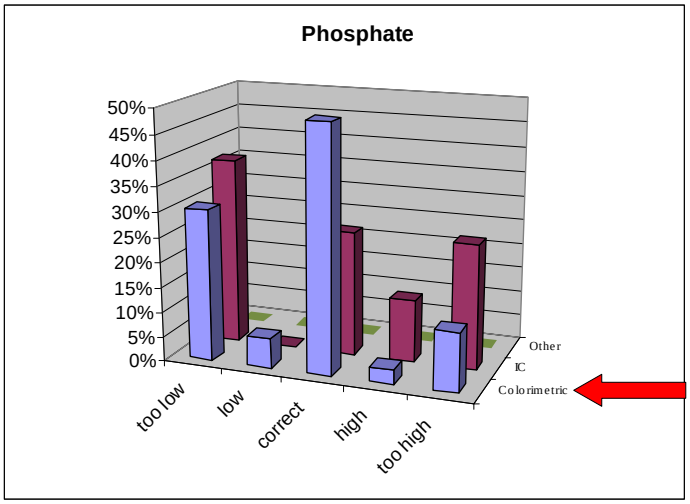


values:	**37**
removed:	**5**
mean:	**21,02**
ref.-value:	**22,33**
recovery:	**94,2%**
std:	**4,585**
rstd:	**20,5%**
std limit:	**10%**
upper limit:	**26,79**
lower limit:	**17,86**
too high:	**3**
too low:	**11**
outside limits:	**14**

Used methods



Comparison of methods



Strange distribution

Summary Phosphate

- Values in wrong units
- Still very high standard deviation
- More than 40% of the values not satisfactory

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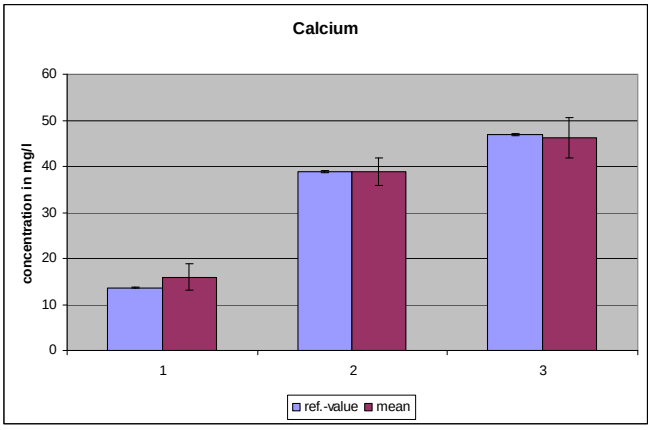
Calcium
Alg.A mean and ref.-value from weighings



mean close to ref.value

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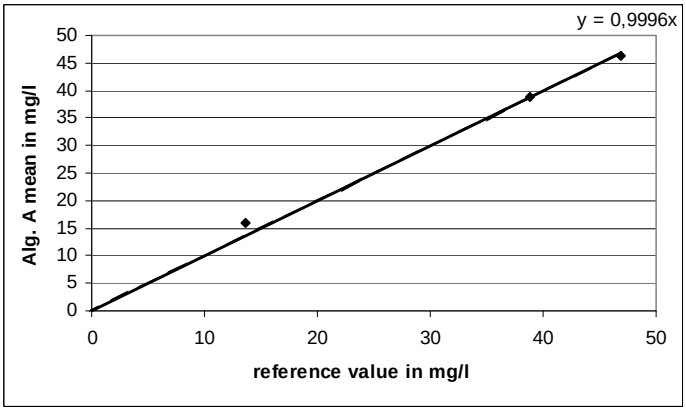
Calcium
mean vs. ref.-value



Average recovery	
2009	100.0
2008	101.6
2007	102.2
2006	97.2

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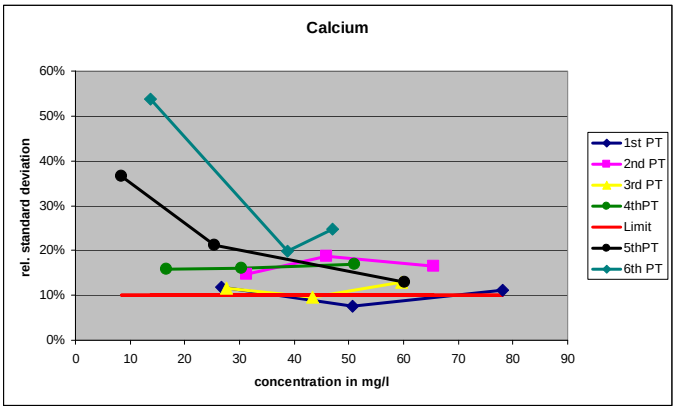
Calcium
calculated standard deviation and limit



worse than in the last years

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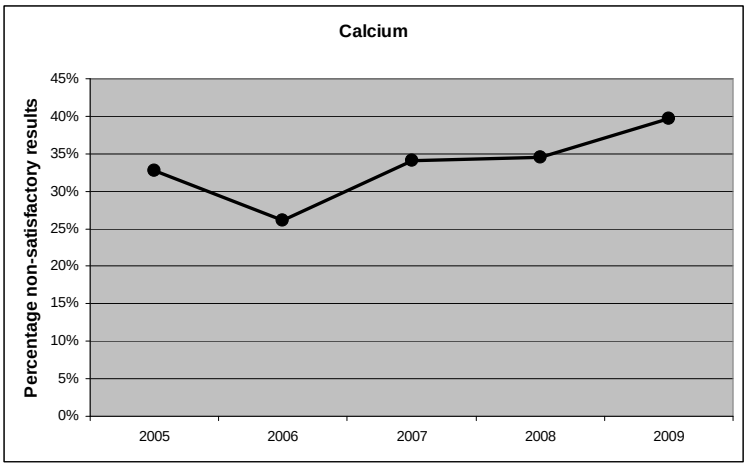
Calcium
Percentage non-satisfactory results



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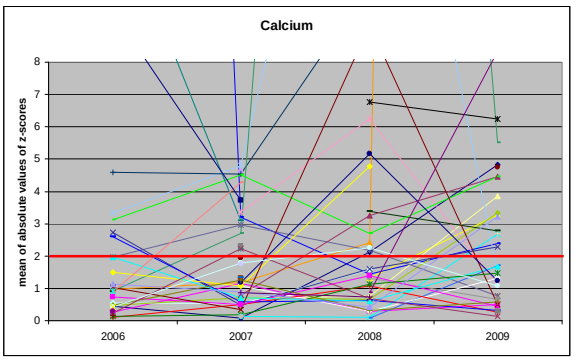
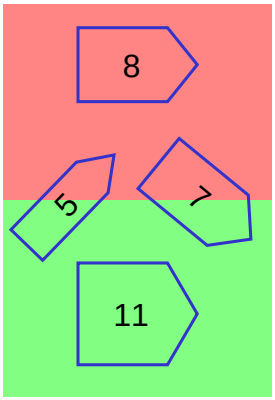
Calcium
Individual performance development



2.0



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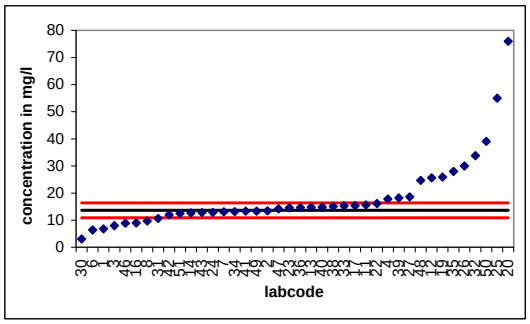
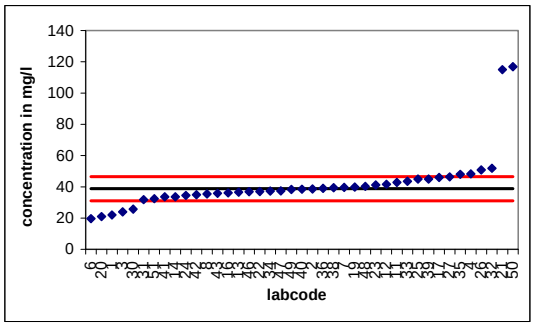
Calcium 1



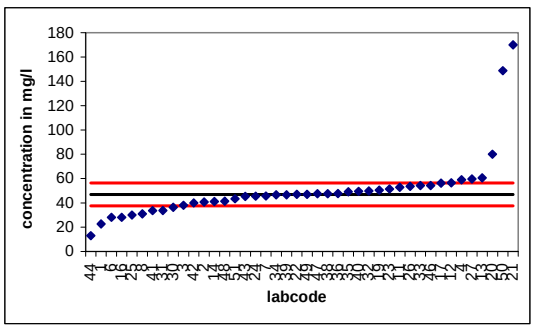
values:	**42**
removed:	**2**
mean:	**15,92**
ref.-value:	**13,66**
recovery:	**116,6%**
std:	**7,354**
rstd:	**53,8%**
std limit:	**10%**
upper limit:	**16,39**
lower limit:	**10,93**
too high:	**13**
too low:	**9**
outside limits:	**22**

Calcium 2



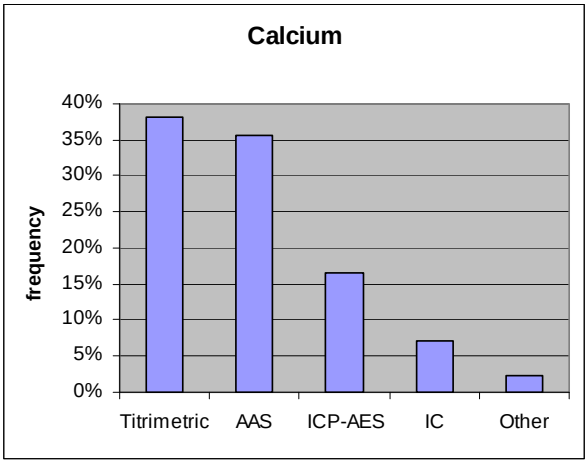
values:	42
removed:	1
mean:	38,86
ref.-value:	38,77
recovery:	100,2%
std:	7,654
rstd:	19,7%
std limit:	10%
upper limit:	46,53
lower limit:	31,02
too high:	6
too low:	6
outside limits:	12

Calcium 3

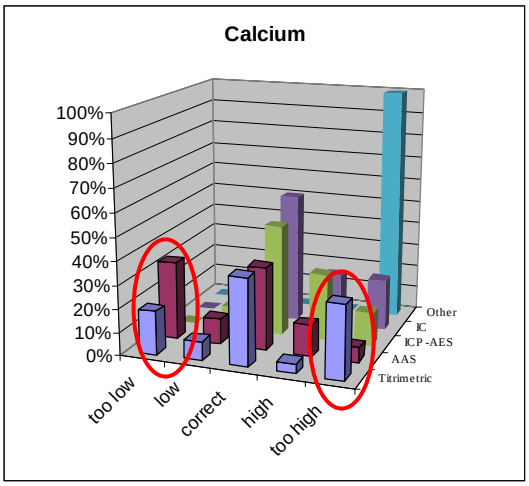


values:	42
removed:	0
mean:	46,16
ref.-value:	46,93
recovery:	98,4%
std:	11,609
rstd:	24,7%
std limit:	10%
upper limit:	56,32
lower limit:	37,55
too high:	7
too low:	9
outside limits:	16

Used methods



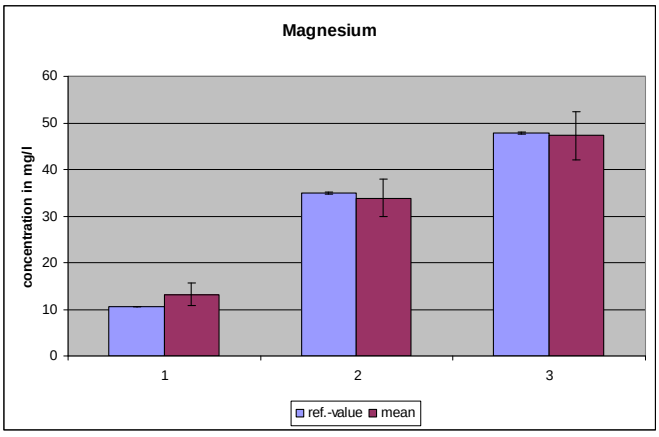
Comparison of methods



Summary Calcium

- Mean values close to reference values
- Standard deviations very high
- High percentage of non-satisfactory results
- Errors in the application of analytical methods

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



mean close to ref.value

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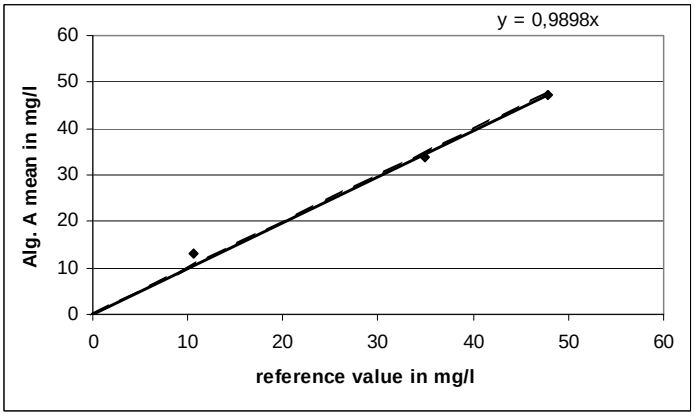
Magnesium
mean vs. ref.-value



Average recovery	
2009	99.0
2008	100.2
2007	101.7
2006	99.6

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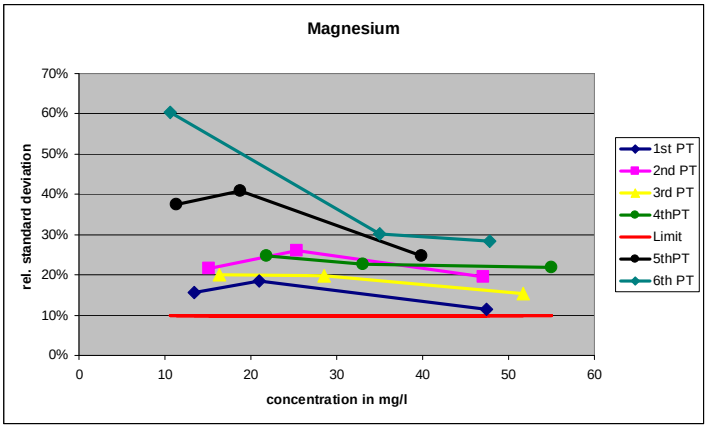
Magnesium
calculated standard deviation and limit



Much worse than in the last years

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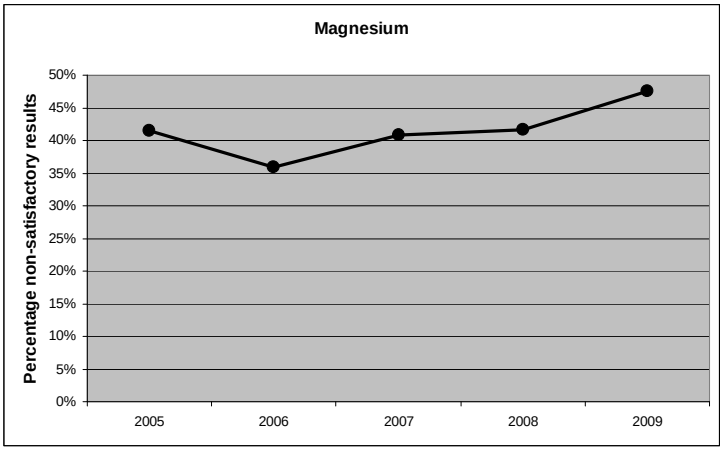
Magnesium
Percentage non-satisfactory results



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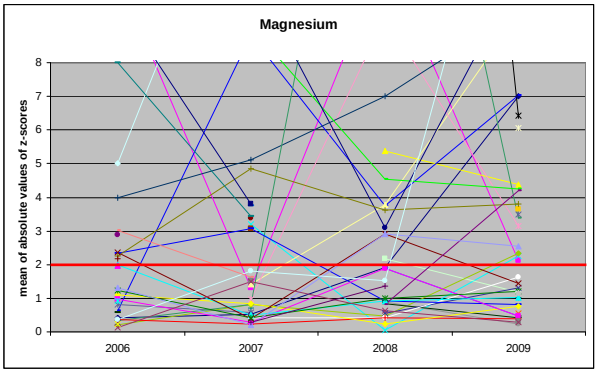
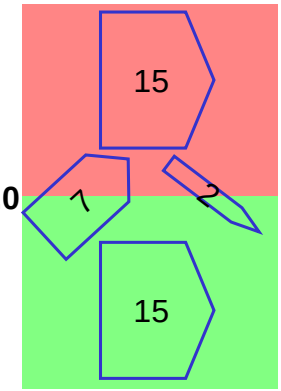
Magnesium
Individual performance development





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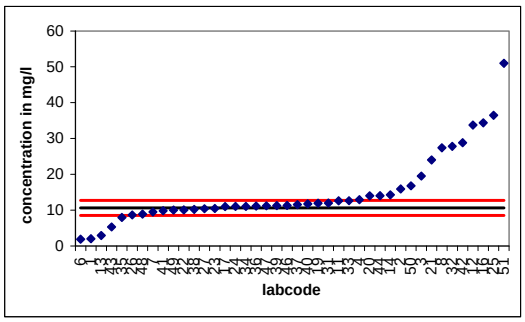
Magnesium 1



values:	42
removed:	0
mean:	13,13
ref.-value:	10,61
recovery:	123,7%
std:	6,409
rstd:	60,4%
std limit:	10%
upper limit:	12,73
lower limit:	8,49
too high:	15
too low:	5
outside limits:	20

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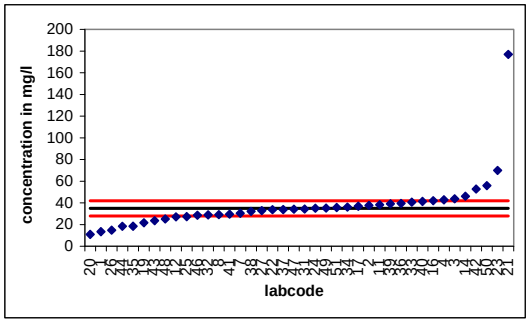
Magnesium 2



values:	42
removed:	2
mean:	33,86
ref.-value:	34,99
recovery:	96,8%
std:	10,519
rstd:	30,1%
std limit:	10%
upper limit:	41,98
lower limit:	27,99
too high:	9
too low:	11
outside limits:	20

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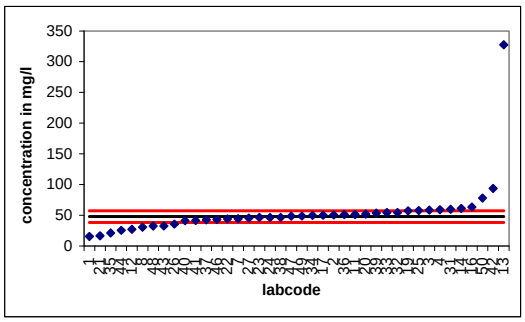
Magnesium 3



values:	42
removed:	2
mean:	47,26
ref.-value:	47,77
recovery:	98,9%
std:	13,565
rstd:	28,4%
std limit:	10%
upper limit:	57,32
lower limit:	38,21
too high:	9
too low:	11
outside limits:	20

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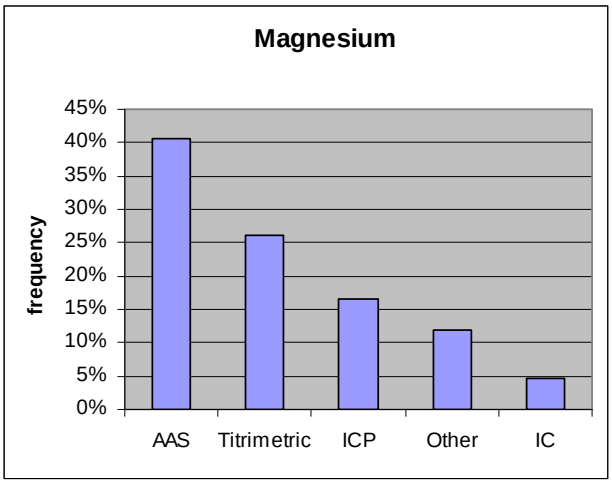
Used methods



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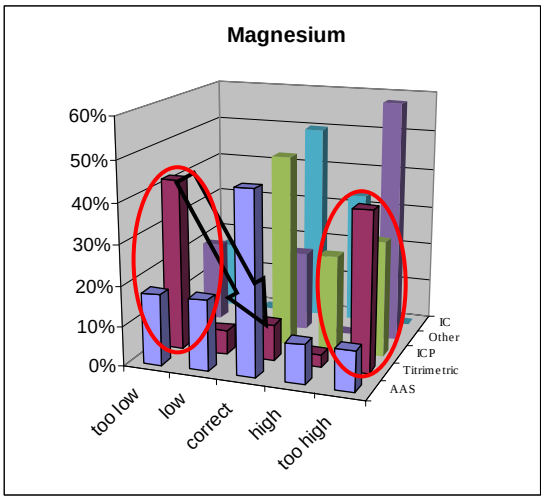
Comparison of methods



Bad results with titration
(as in the last years)

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Summary Magnesium

- Mean values around reference values
- Standard deviations much too high
- Almost 50% of the values not satisfactory
- Titrimetric values not reliable

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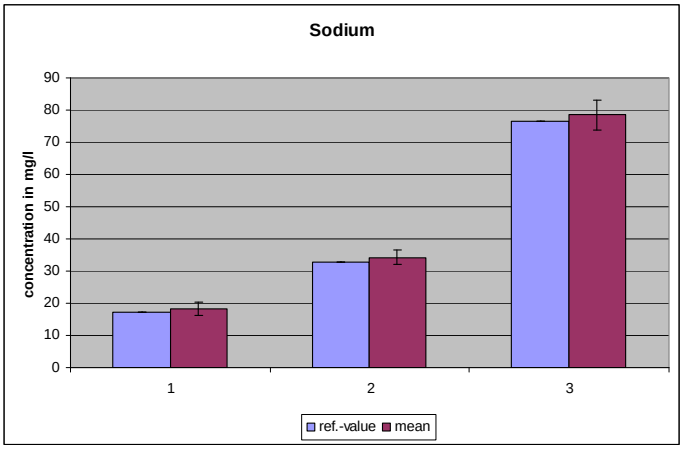
Sodium
Alg.A mean and ref.-value from weighings



Means close to ref.-values

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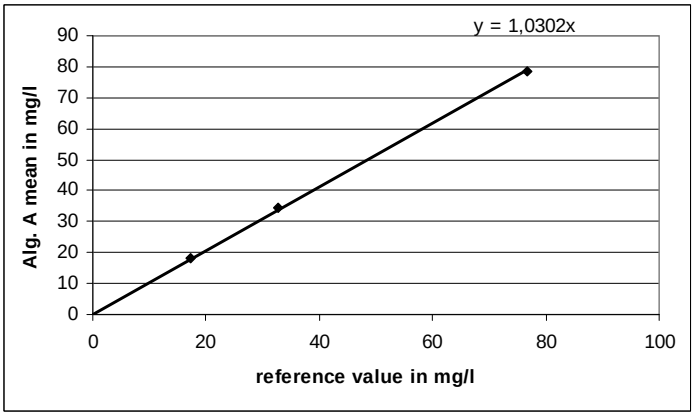
Sodium
mean vs. ref.-value



Average recovery	
2009	103.0
2008	100.4
2007	103.3
2006	104.4

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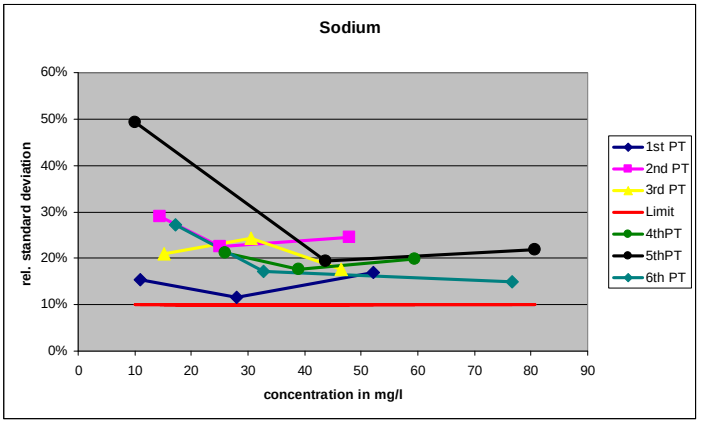
Sodium
calculated standard deviation and limit



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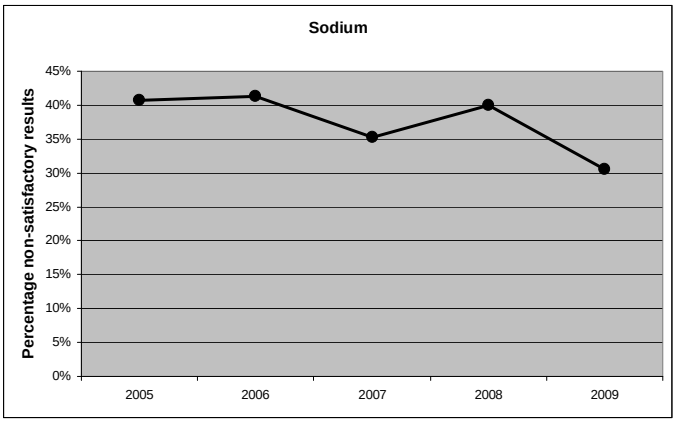
Sodium
Percentage non-satisfactory results



Slight improvement

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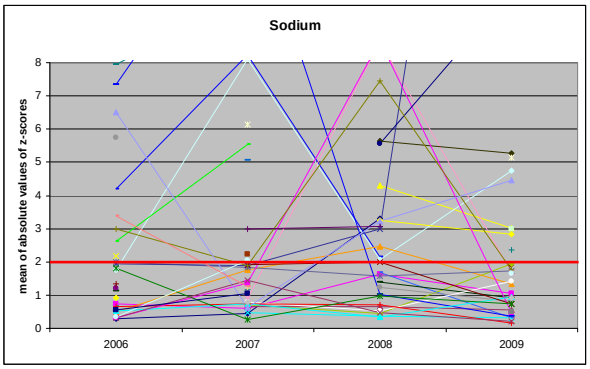
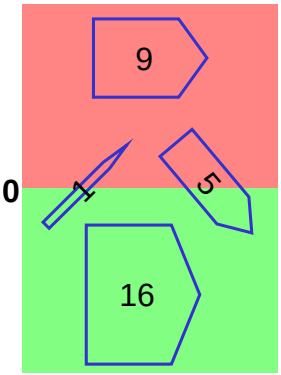
Sodium
Individual performance development





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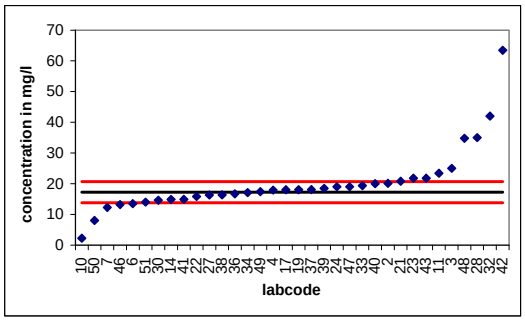
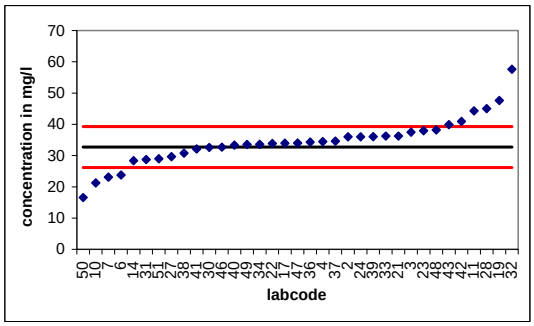
Sodium 1



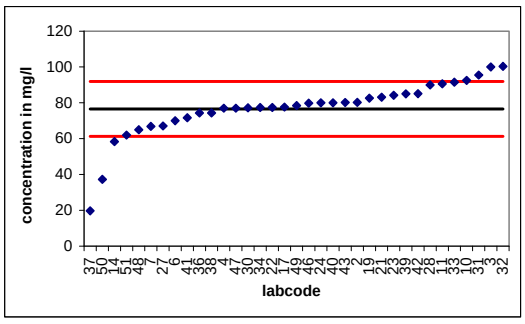
values:	**35**
removed:	**1**
mean:	**18,28**
ref.-value:	**17,24**
recovery:	**106,1%**
std:	**4,702**
rstd:	**27,3%**
std limit:	**10%**
upper limit:	**20,68**
lower limit:	**13,79**
too high:	**10**
too low:	**5**
outside limits:	**15**

Sodium 2



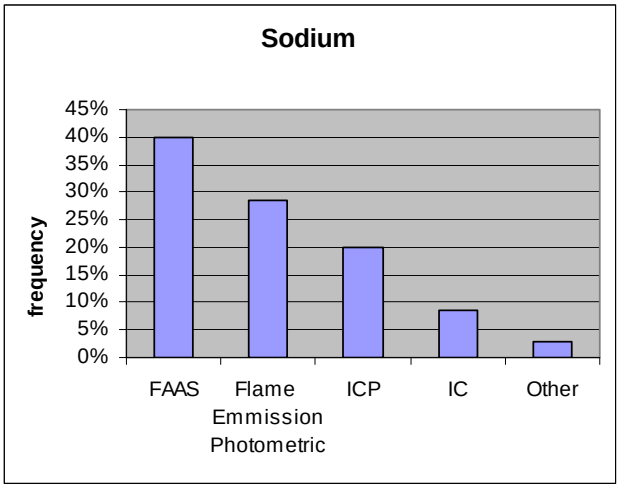
values:	35
removed:	0
mean:	34,25
ref.-value:	32,73
recovery:	104,7%
std:	5,606
rstd:	17,1%
std limit:	10%
upper limit:	39,27
lower limit:	26,18
too high:	6
too low:	4
outside limits:	10

Sodium 3

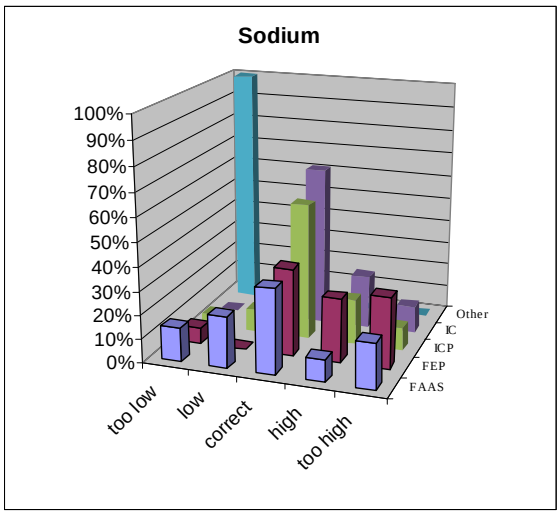


values:	35
removed:	0
mean:	78,54
ref.-value:	76,57
recovery:	102,6%
std:	11,431
rstd:	14,9%
std limit:	10%
upper limit:	91,89
lower limit:	61,26
too high:	4
too low:	3
outside limits:	7

Used methods



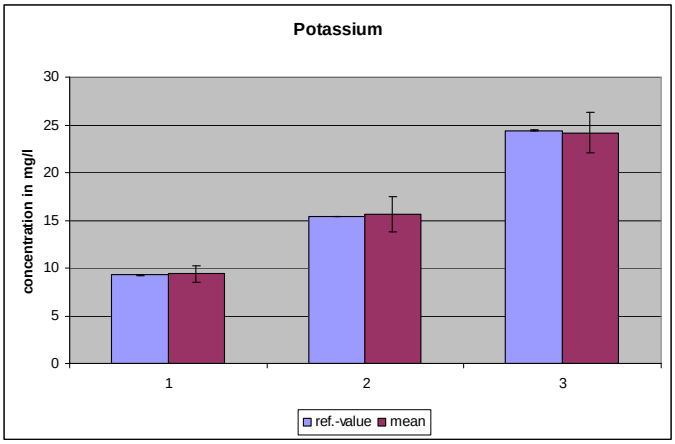
Comparison of methods



Summary Sodium

- Consensus means close to ref.values
- Average standard deviations, but still too high
- Slight improvement in the number of satisfactory results

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



consensus mean close to ref.value

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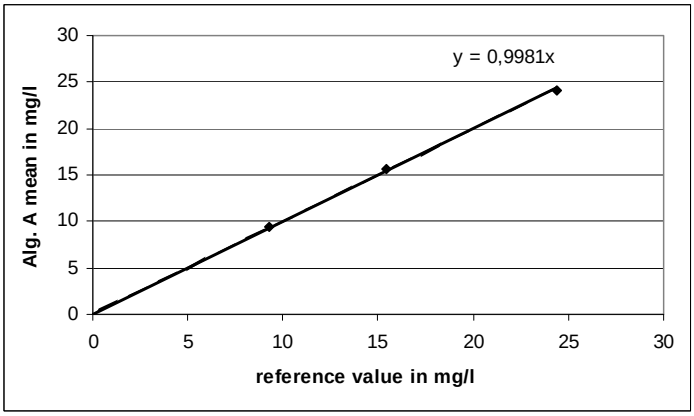
Potassium
mean vs. ref.-value



Average recovery	
2009	99.8
2008	99.0
2007	98.5
2006	96.9

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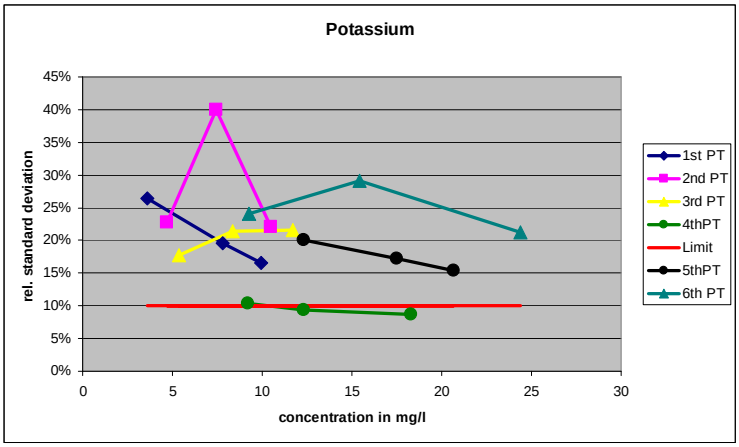
Potassium
calculated standard deviation and limit



Standard deviations worse than in the last two years

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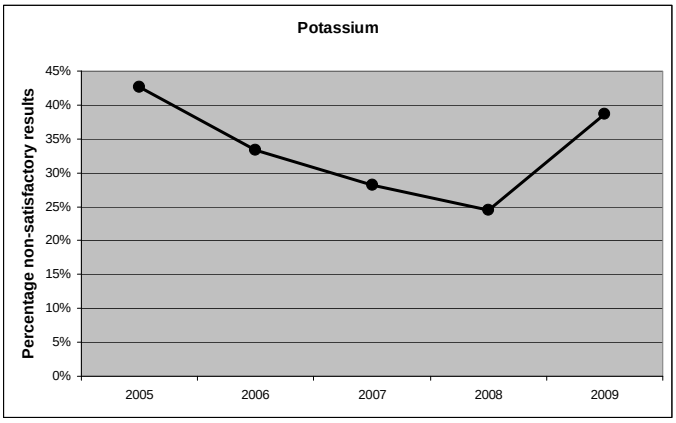
Potassium
Percentage non-satisfactory results



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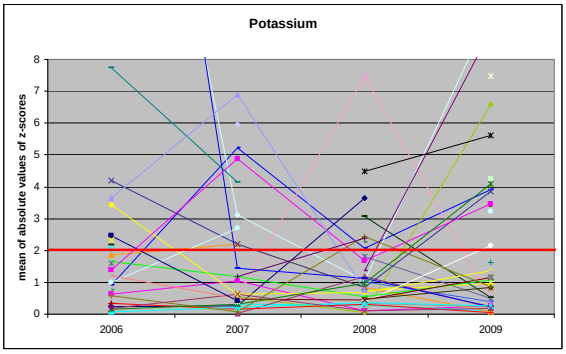
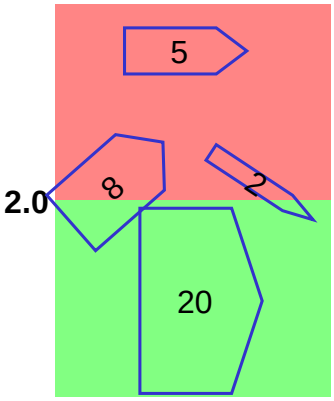
Potassium
Individual performance development





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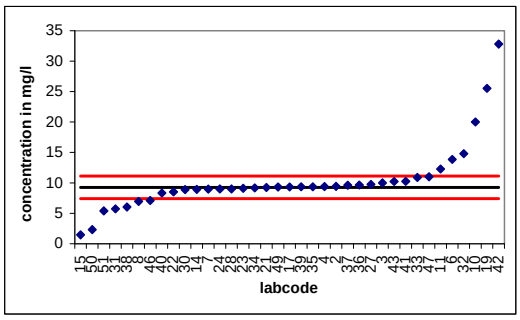
Potassium 1



values:	38
removed:	1
mean:	9,37
ref.-value:	9,26
recovery:	101,3%
std:	2,228
rstd:	24,1%
std limit:	10%
upper limit:	11,11
lower limit:	7,41
too high:	6
too low:	8
outside limits:	14

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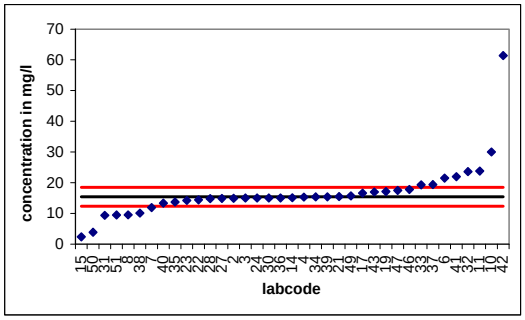
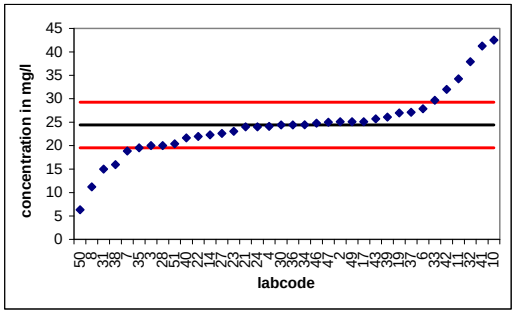
Potassium 2



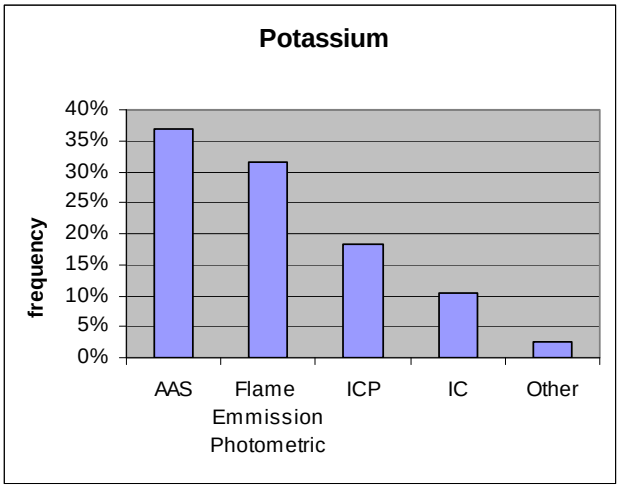
values:	38
removed:	1
mean:	15,63
ref.-value:	15,41
recovery:	101,4%
std:	4,479
rstd:	29,1%
std limit:	10%
upper limit:	18,49
lower limit:	12,33
too high:	8
too low:	8
outside limits:	16

Potassium 3

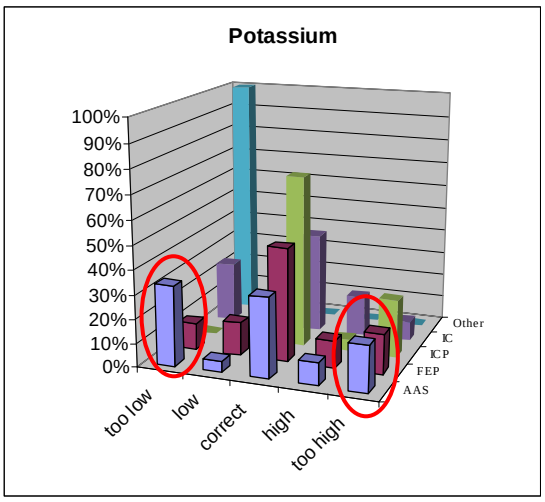


values:	**38**
removed:	**2**
mean:	**24,15**
ref.-value:	**24,41**
recovery:	**99,0%**
std:	**5,191**
rstd:	**21,3%**
std limit:	**10%**
upper limit:	**29,29**
lower limit:	**19,52**
too high:	**6**
too low:	**8**
outside limits:	**14**

Used methods



Comparison of methods



Summary Potassium

- Mean values close to reference values
- standard deviations higher than last years
- Higher percentage of non-satisfactory results
- Problems with AAS

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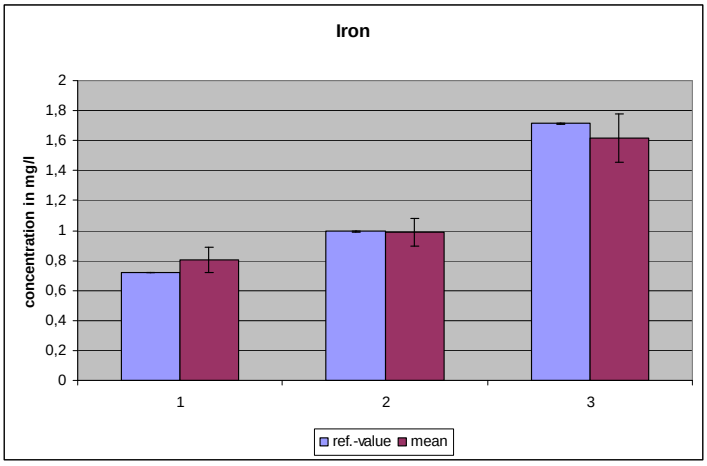
Iron
Alg.A mean and ref.-value from weighings



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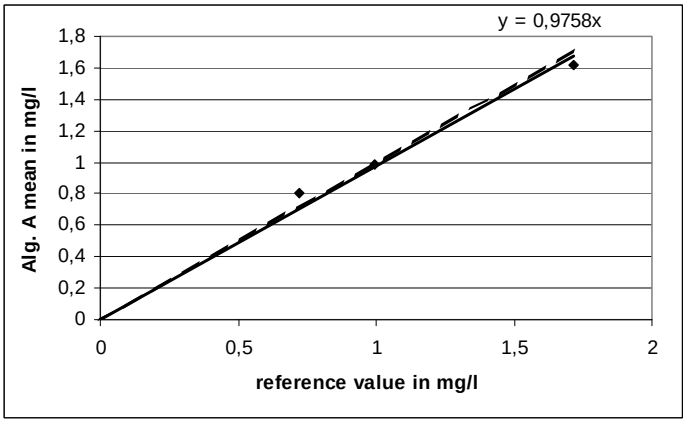
Iron
mean vs. ref.-value



Average recovery	
2009	97.6
2008	99.9
2007	92.9
2006	88.0

For lowest level mean a bit too high

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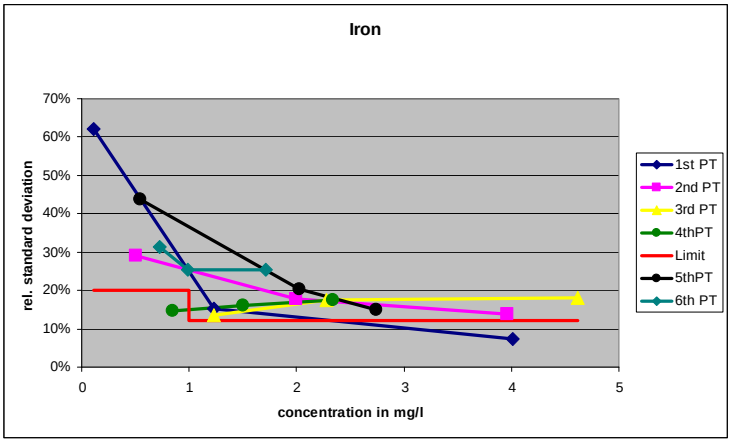
Iron
calculated standard deviation and limit



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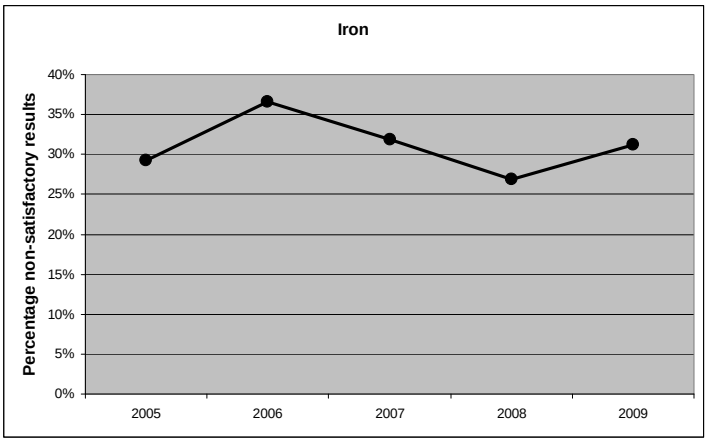
Iron
Percentage non-satisfactory results



No improvement

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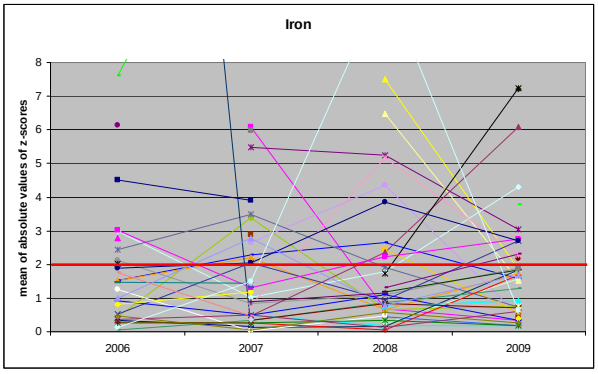
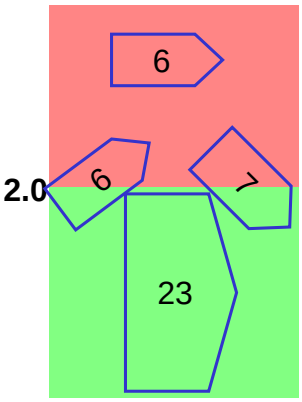
Iron
Individual performance development





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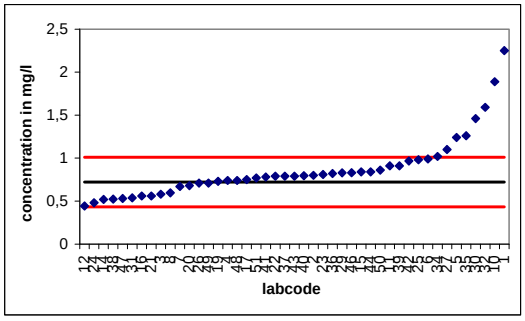
Iron 1



values:	**46**
removed:	**1**
mean:	**0,80**
ref.-value:	**0,72**
recovery:	**111,5%**
std:	**0,227**
rstd:	**31,4%**
std limit:	**20%**
upper limit:	**1,01**
lower limit:	**0,43**
too high:	**8**
too low:	**1**
outside limits:	**9**

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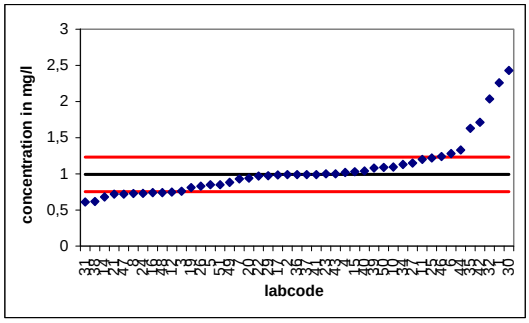
Iron 2



values:	46
removed:	1
mean:	0,99
ref.-value:	0,99
recovery:	99,6%
std:	0,251
rstd:	25,3%
std limit:	12%
upper limit:	1,23
lower limit:	0,75
too high:	8
too low:	11
outside limits:	19

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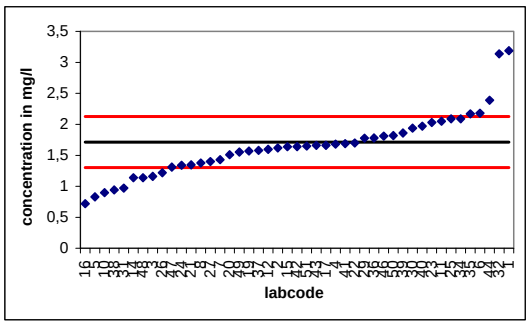
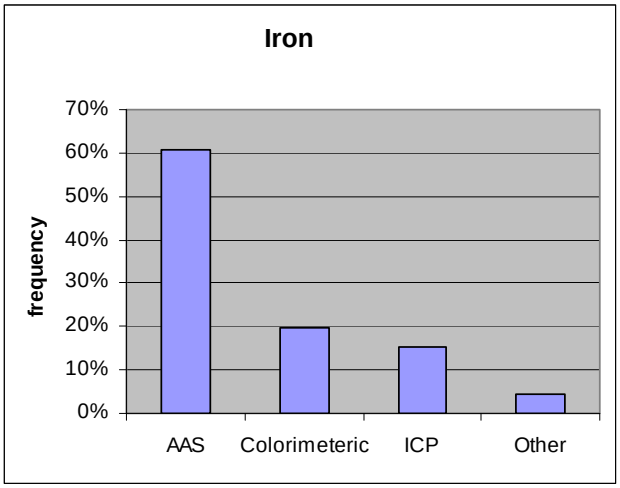
Iron 3

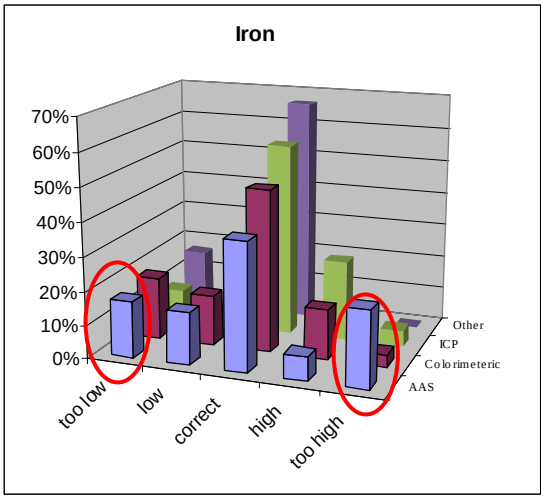


values:	46
removed:	1
mean:	1,62
ref.-value:	1,71
recovery:	94,4%
std:	0,436
rstd:	25,4%
std limit:	12%
upper limit:	2,13
lower limit:	1,30
too high:	5
too low:	10
outside limits:	15

Used methods



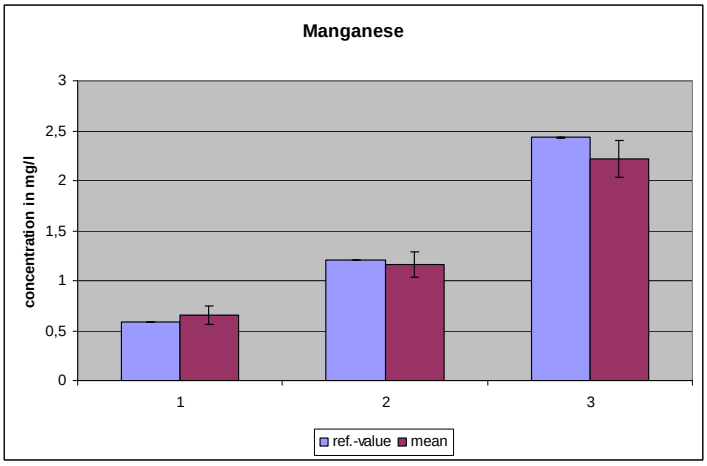
Comparison of methods



Summary Iron

- Means close to reference values
- Standard deviations too high
- 1/3 of the values not satisfactory
- Problems with AAS

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



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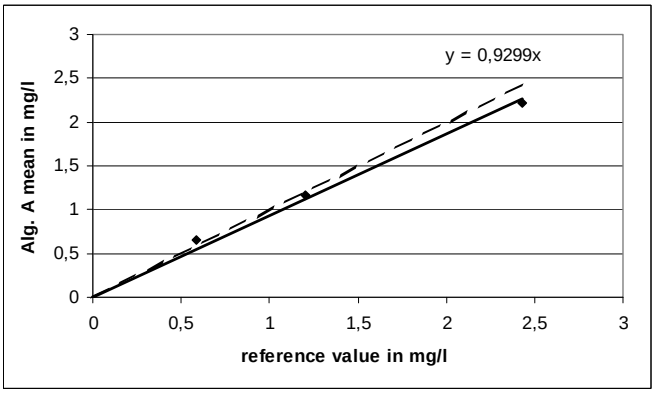
Manganese
mean vs. ref.-value



Average recovery	
2009	93.0
2008	96.7
2007	96.0
2006	95.4

Low recovery mostly caused by the highest level

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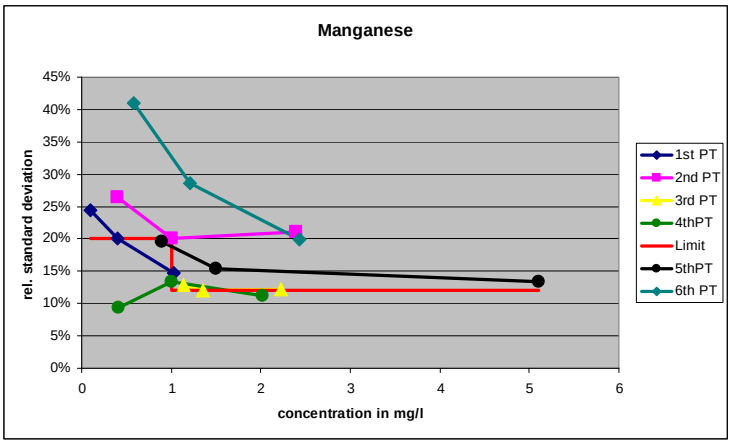
Manganese
calculated standard deviation and limit



Highest standard deviation of all PT rounds

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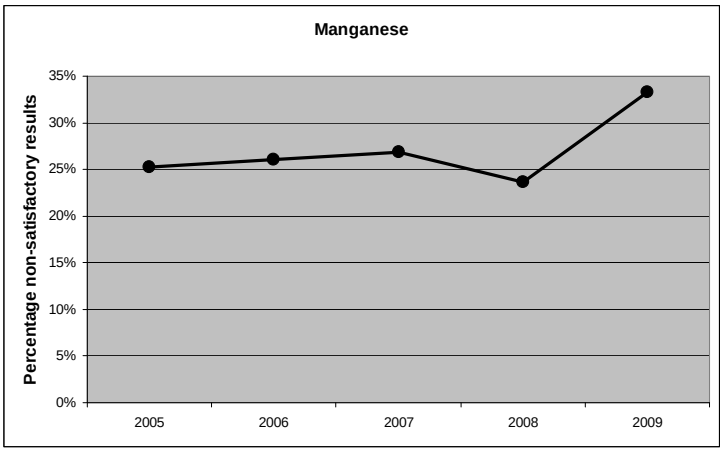
Manganese
Percentage non-satisfactory results



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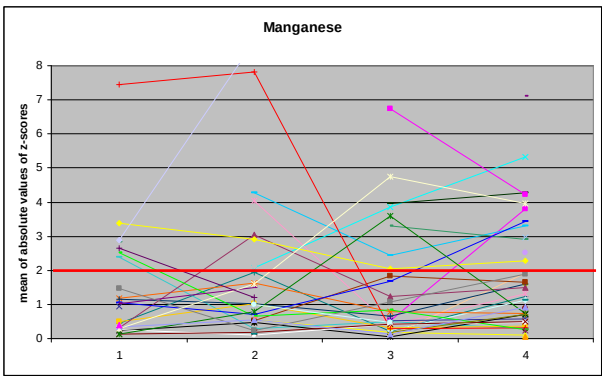
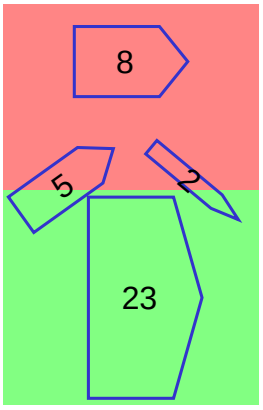
Manganese
Individual performance development



2.0



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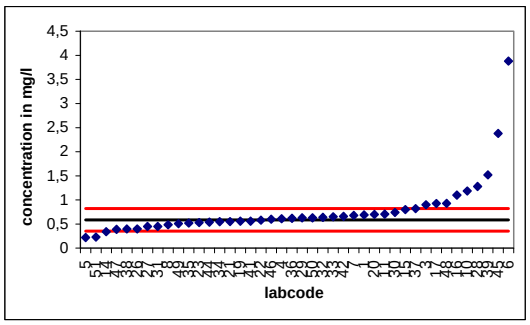
Manganese 1



values:	42
removed:	0
mean:	0,65
ref.-value:	0,59
recovery:	111,3%
std:	0,240
rstd:	40,9%
std limit:	20%
upper limit:	0,82
lower limit:	0,35
too high:	9
too low:	3
outside limits:	12

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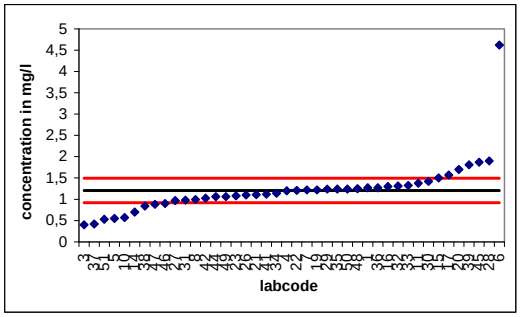
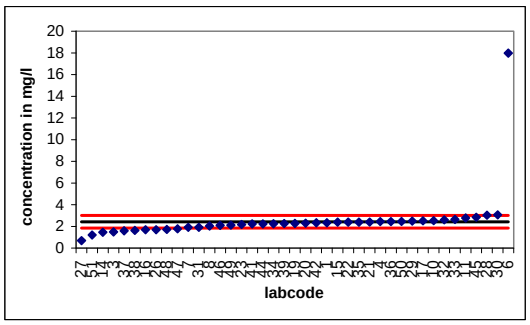
Manganese 2



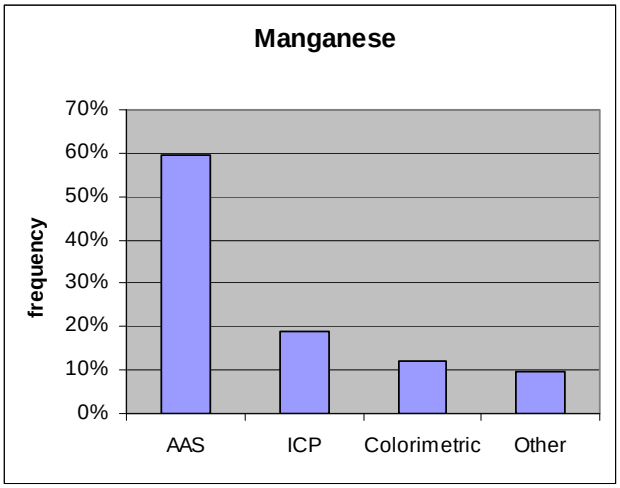
values:	42
removed:	0
mean:	1,16
ref.-value:	1,21
recovery:	96,2%
std:	0,345
rstd:	28,6%
std limit:	12%
upper limit:	1,50
lower limit:	0,92
too high:	7
too low:	9
outside limits:	16

Manganese 3

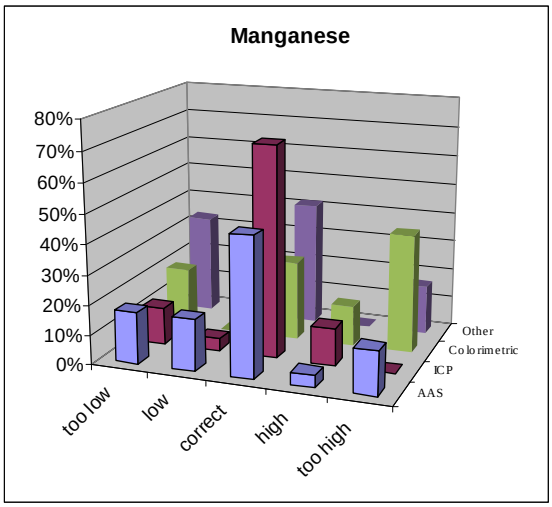


values:	42
removed:	1
mean:	2,22
ref.-value:	2,43
recovery:	91,1%
std:	0,483
rstd:	19,9%
std limit:	12%
upper limit:	3,01
lower limit:	1,85
too high:	3
too low:	11
outside limits:	14

Used methods



Comparison of methods



Summary Manganese

- mean values close to reference values (except highest level)
- standard deviation higher than ever before
- 1/3 of the values not satisfactory

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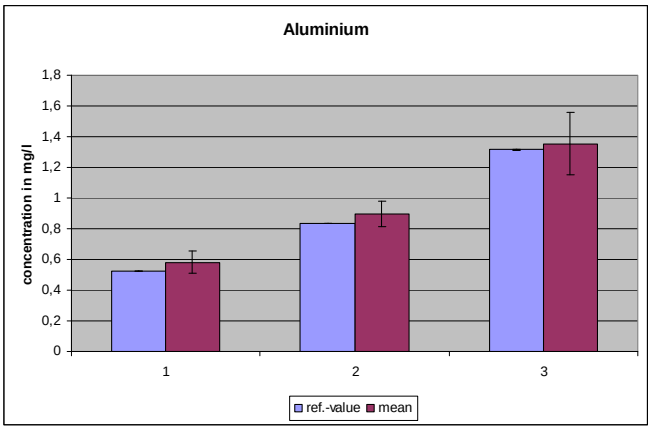
Aluminium
Alg.A mean and ref.-value from weighings



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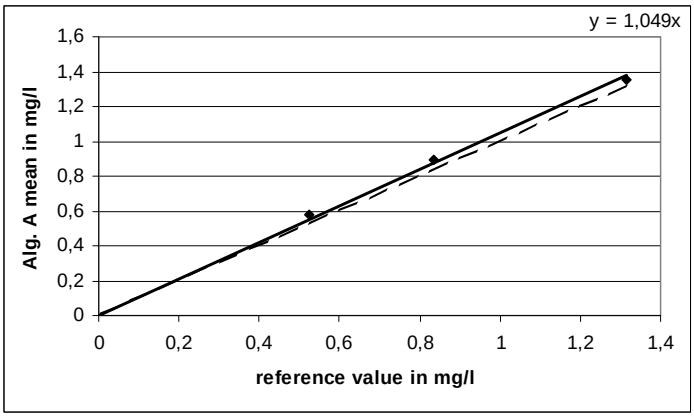
Aluminium
mean vs. ref.-value



Average recovery	
2009	104.9
2008	93.9
2007	96.1
2006	85.7

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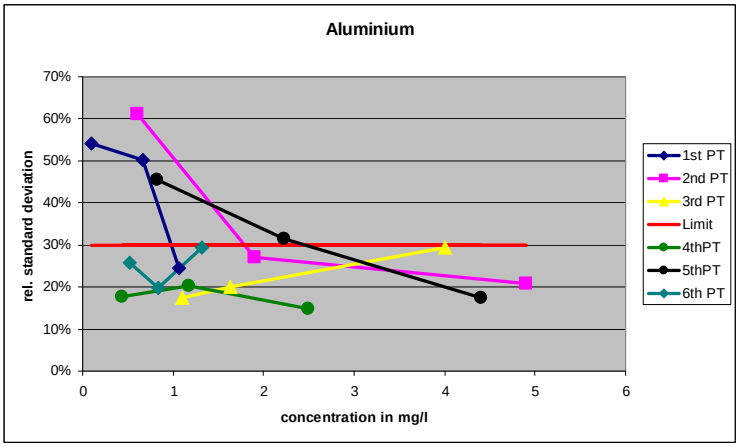
Aluminium
calculated standard deviation and limit



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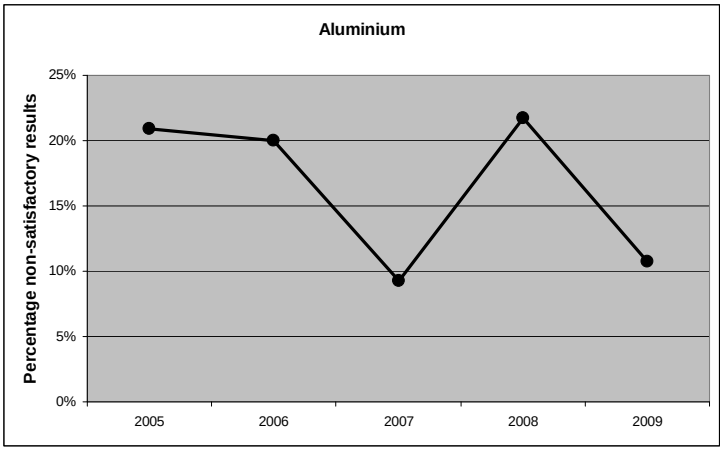
Aluminium
Percentage non-satisfactory results



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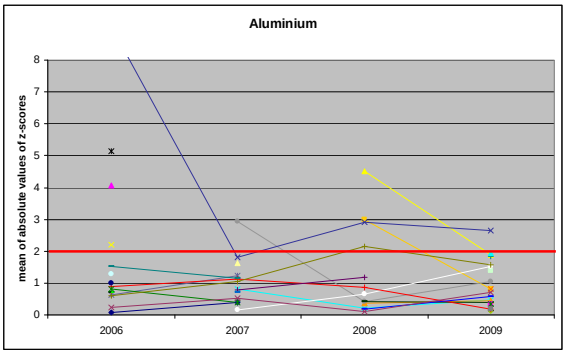
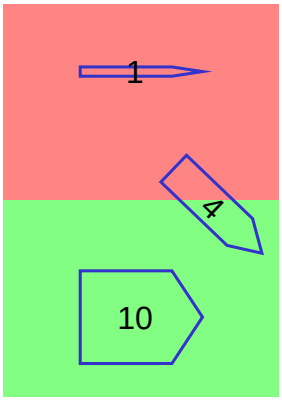
Aluminium
Individual performance development



2.0



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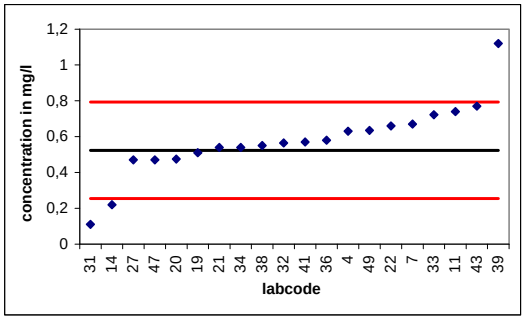
Aluminium 1



values:	**21**
removed:	**1**
mean:	**0,58**
ref.-value:	**0,52**
recovery:	**111,2%**
std:	**0,135**
rstd:	**25,7%**
std limit:	**30%**
upper limit:	**0,79**
lower limit:	**0,25**
too high:	**1**
too low:	**3**
outside limits:	**4**

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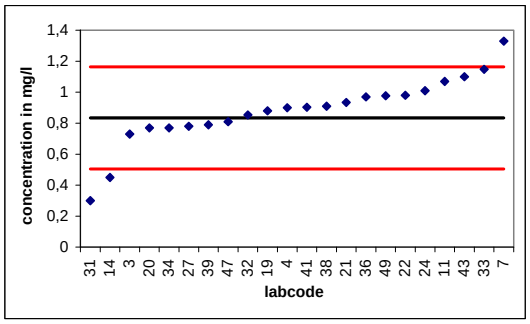
Aluminium 2



values:	22
removed:	0
mean:	0,90
ref.-value:	0,83
recovery:	107,5%
std:	0,165
rstd:	19,8%
std limit:	30%
upper limit:	1,16
lower limit:	0,50
too high:	1
too low:	2
outside limits:	3

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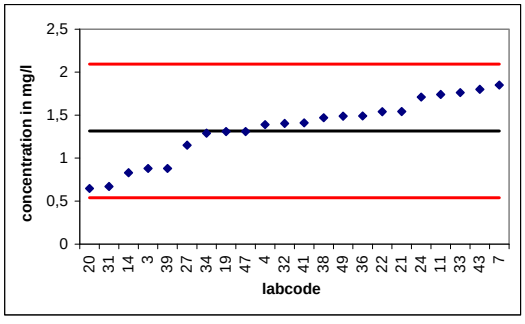
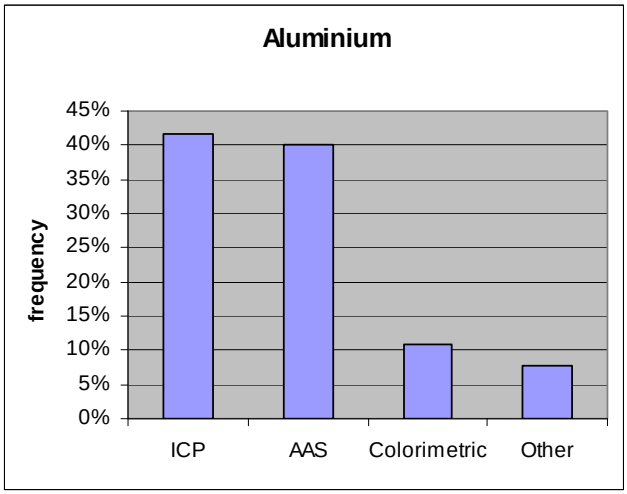
Aluminium 3

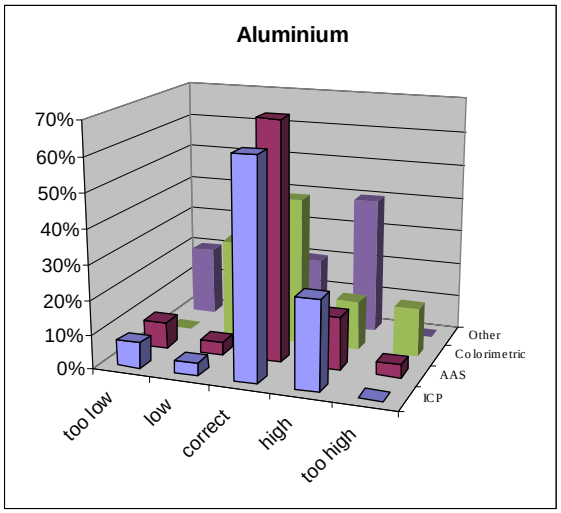


values:	22
removed:	0
mean:	1,35
ref.-value:	1,32
recovery:	102,9%
std:	0,389
rstd:	29,5%
std limit:	30%
upper limit:	2,09
lower limit:	0,54
too high:	0
too low:	0
outside limits:	0

Used methods



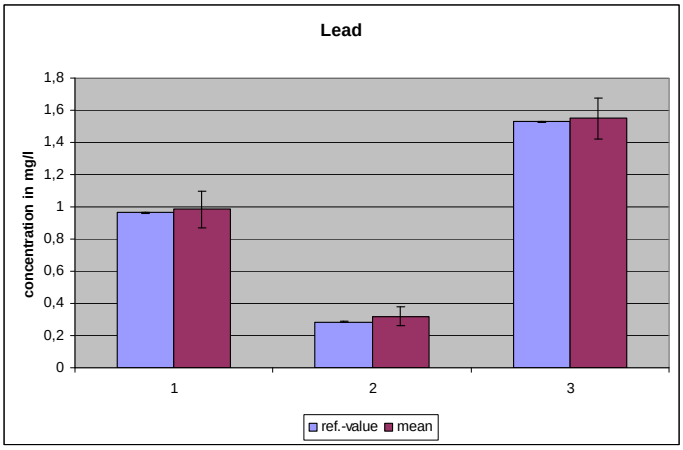
Comparison of methods



Summary Aluminium

- small number of values
- mean values close to reference values
- Standard deviation better than last year, but not really good
- Slight improvement of the percentage of satisfactory values

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



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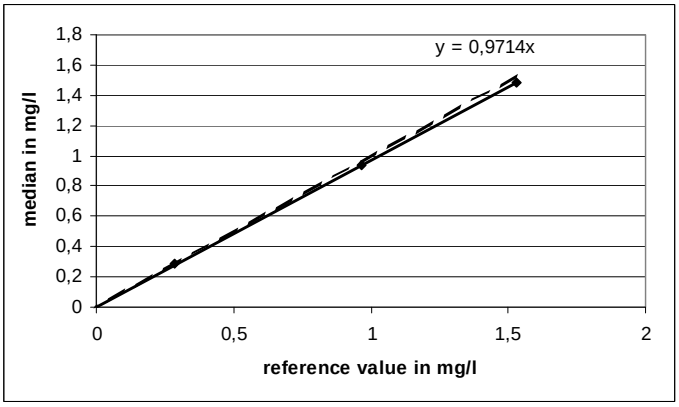
Lead
mean vs. ref.-value



Average recovery	
2009	97.1
2008	103.7
2007	95.4
2006	95.6

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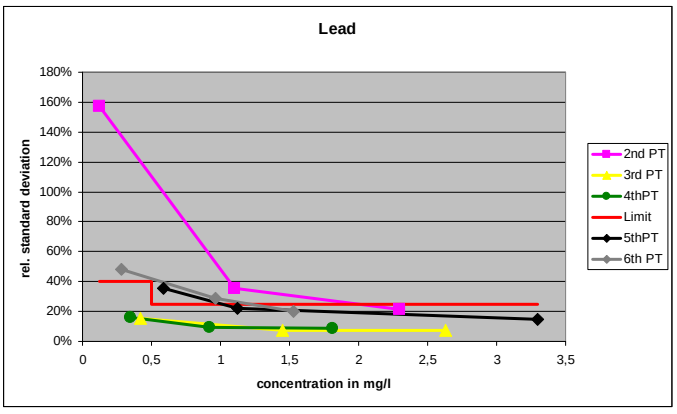
Lead
calculated standard deviation and limit



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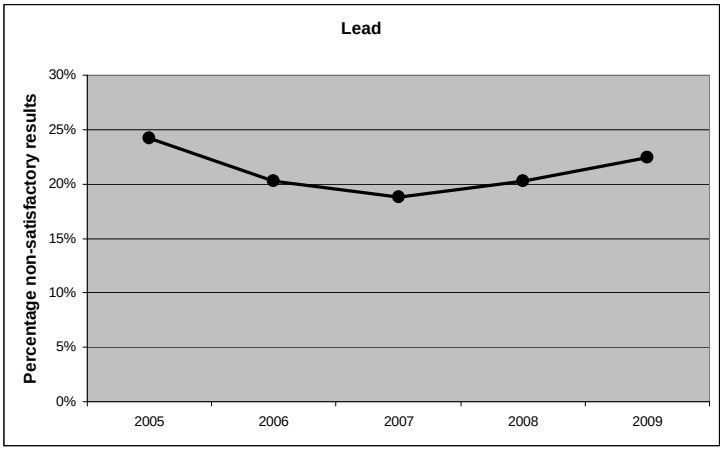
Lead
Percentage non-satisfactory results



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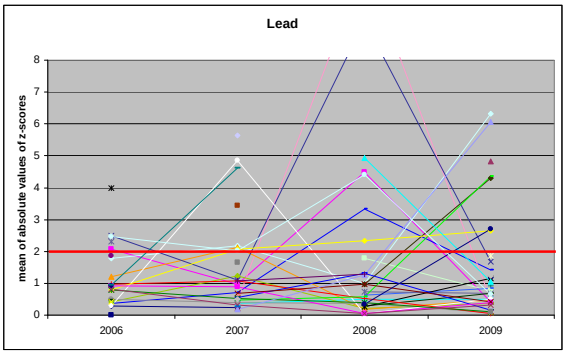
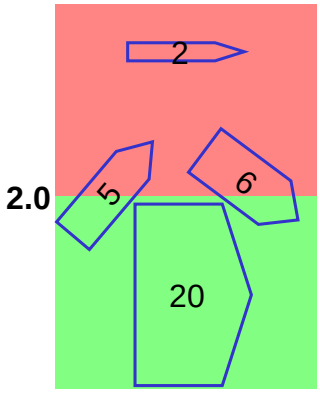
Lead
Individual performance development





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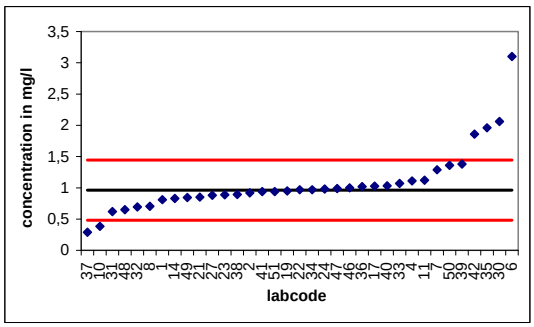
Lead 1



values:	36
removed:	1
mean:	0,98
ref.-value:	0,96
recovery:	102,2%
std:	0,275
rstd:	28,5%
std limit:	25%
upper limit:	1,45
lower limit:	0,48
too high:	4
too low:	3
outside limits:	7

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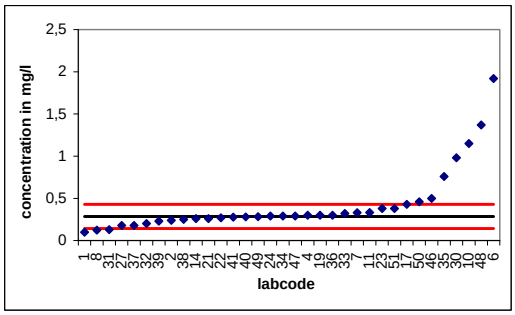
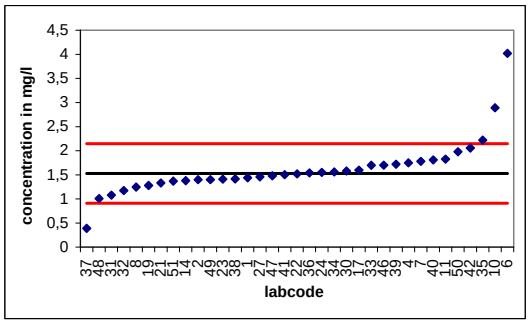
Lead 2



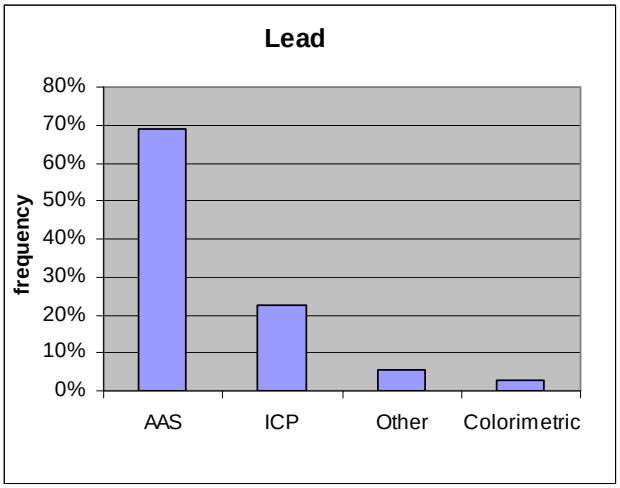
values:	35
removed:	1
mean:	0,32
ref.-value:	0,29
recovery:	111,4%
std:	0,138
rstd:	48,5%
std limit:	25%
upper limit:	0,43
lower limit:	0,14
too high:	8
too low:	4
outside limits:	12

Lead 3

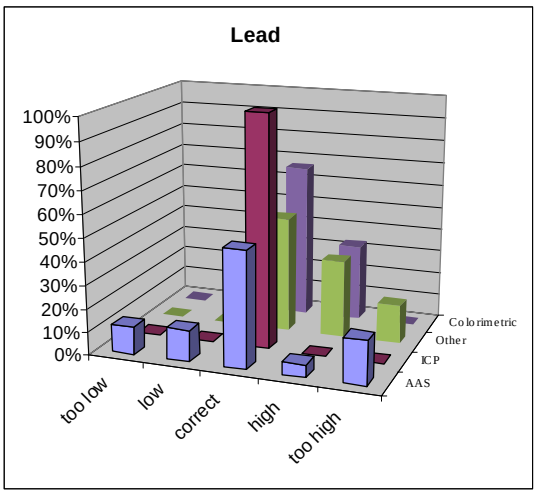


values:	**36**
removed:	**1**
mean:	**1,55**
ref.-value:	**1,53**
recovery:	**101,3%**
std:	**0,309**
rstd:	**20,2%**
std limit:	**25%**
upper limit:	**2,15**
lower limit:	**0,91**
too high:	**3**
too low:	**2**
outside limits:	**5**

Used methods



Comparison of methods



Summary Lead

- Mean values around reference values
- Standard deviation similar to last year – too high
- No improvement
- Problems with AAS?

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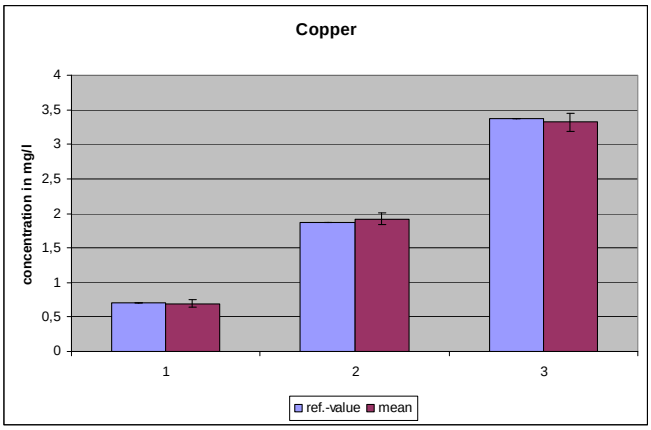
Copper
Alg.A mean and ref.-value from weighings



Good agreement

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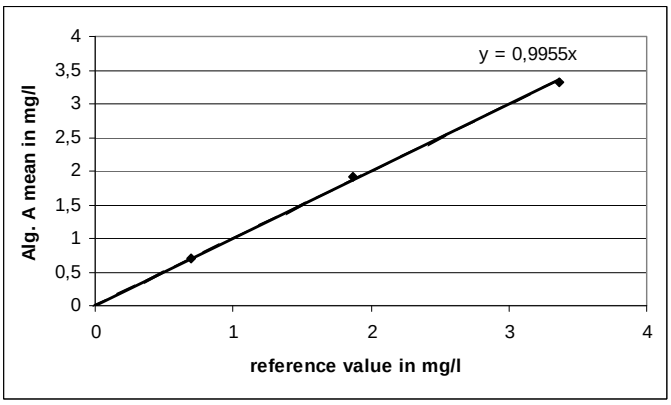
Copper
mean vs. ref.-value



Average recovery	
2009	99.6
2008	95.1
2007	97.5
2006	98.5

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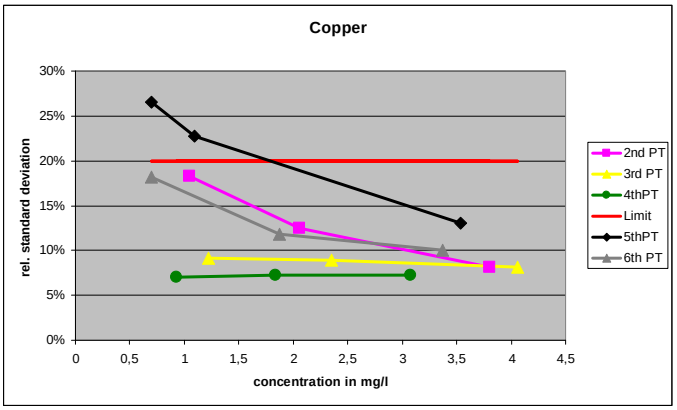
Copper
calculated standard deviation and limit



Better than in previous PT

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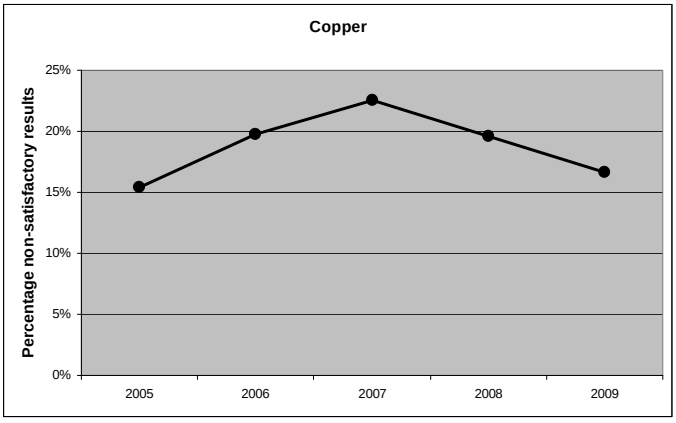
Copper
Percentage non-satisfactory results



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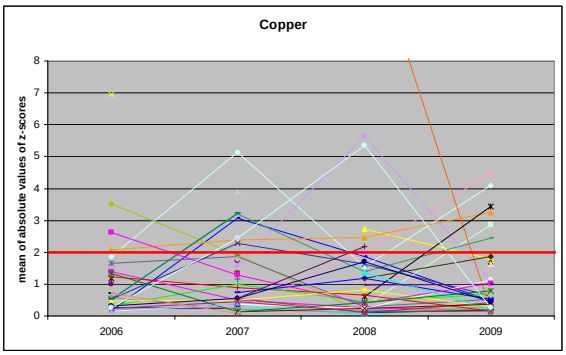
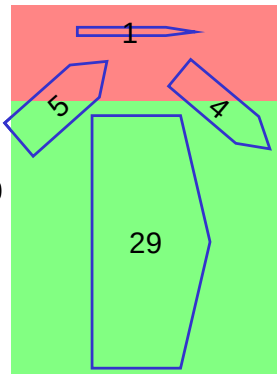
Copper
Individual performance development



2.0



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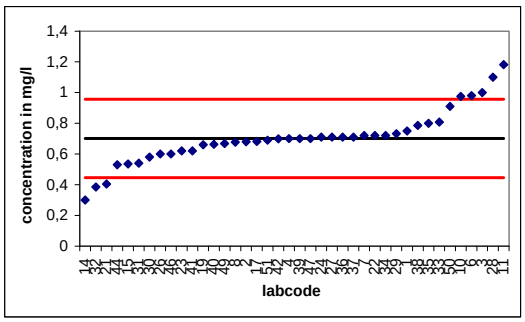
Copper 1



values:	**40**
removed:	**0**
mean:	**0,70**
ref.-value:	**0,70**
recovery:	**99,4%**
std:	**0,128**
rstd:	**18,2%**
std limit:	**20%**
upper limit:	**0,96**
lower limit:	**0,45**
too high:	**5**
too low:	**3**
outside limits:	**8**

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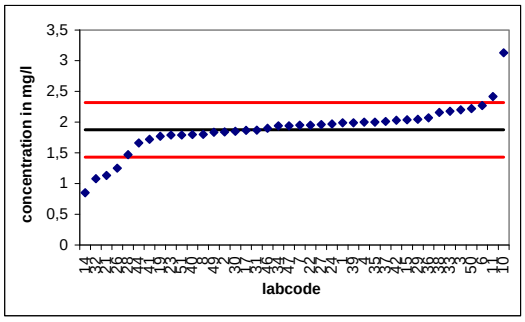
Copper 2



values:	40
removed:	0
mean:	1,92
ref.-value:	1,87
recovery:	102,5%
std:	0,222
rstd:	11,9%
std limit:	20%
upper limit:	2,32
lower limit:	1,43
too high:	2
too low:	4
outside limits:	6

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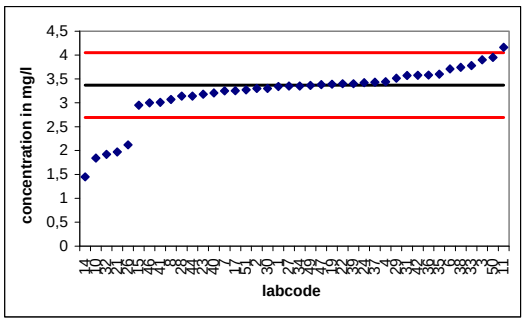
Copper 3



values:	40
removed:	0
mean:	3,32
ref.-value:	3,37
recovery:	98,6%
std:	0,339
rstd:	10,0%
std limit:	20%
upper limit:	4,05
lower limit:	2,69
too high:	1
too low:	5
outside limits:	6

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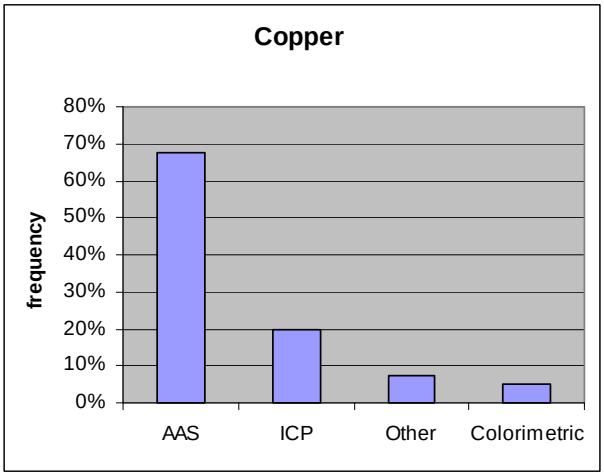
Used methods



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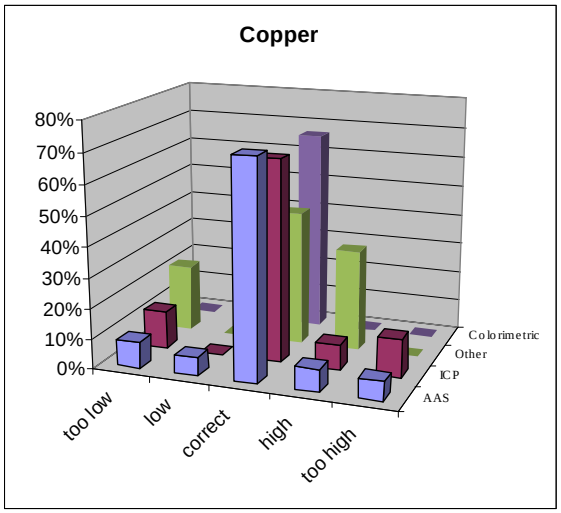
Comparison of methods



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Summary Copper

- mean values in quite good agreement with reference values
- standard deviation better than in previous year

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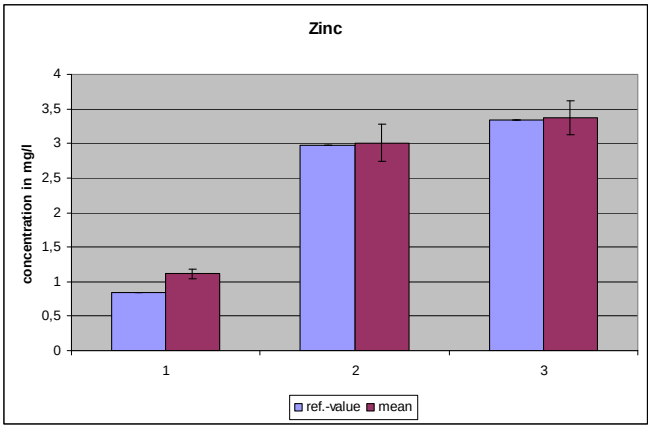
Zinc
Alg.A mean and ref.-value from weighings



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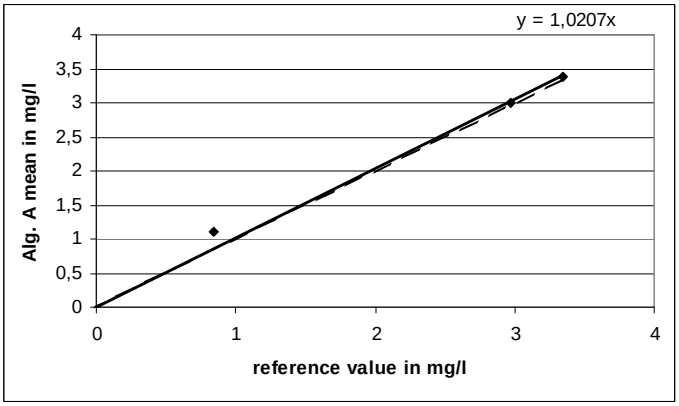
Zinc
mean vs. ref.-value



Average recovery	
2009	102.1
2008	95.5
2007	93.0
2006	96.8

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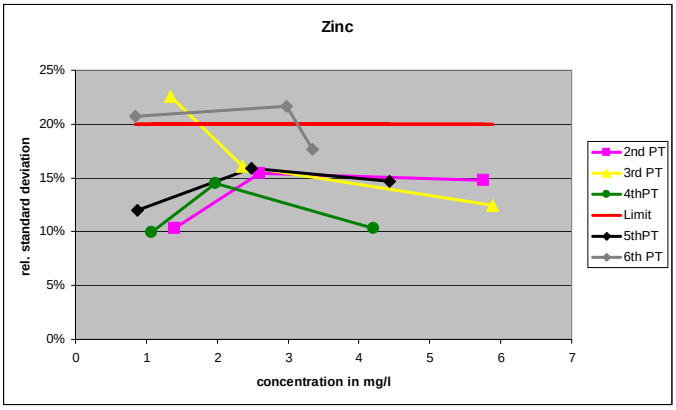
Zinc
calculated standard deviation and limit



Higher than in previous years

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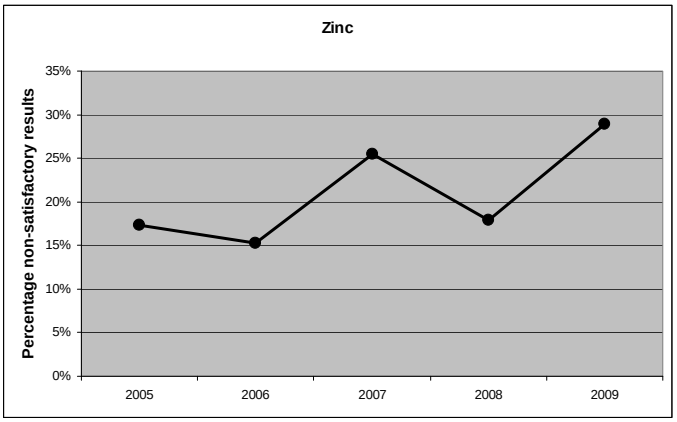
Zinc
Percentage non-satisfactory results



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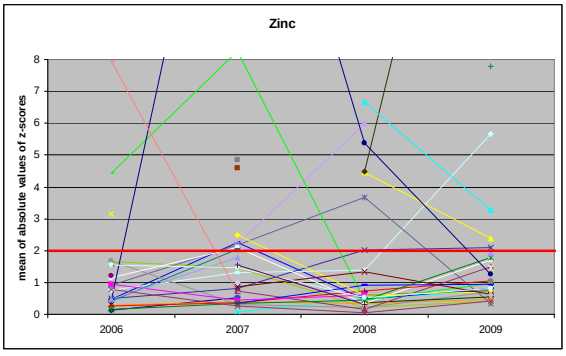
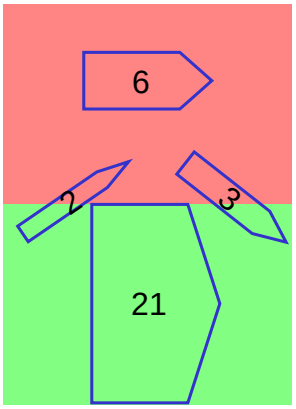
Zinc
Individual performance development



2.0



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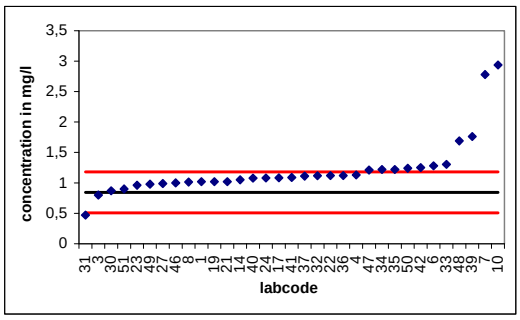
Zinc 1



values:	35
removed:	2
mean:	1,11
ref.-value:	0,84
recovery:	131,8%
std:	0,175
rstd:	20,7%
std limit:	20%
upper limit:	1,18
lower limit:	0,51
too high:	13
too low:	1
outside limits:	14

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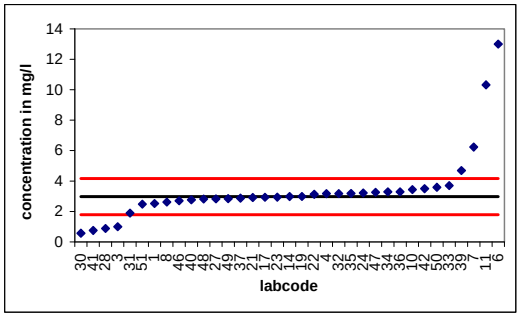
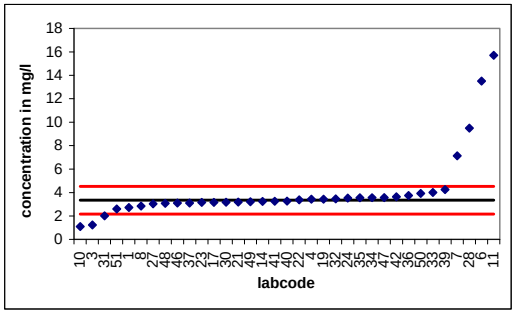
Zinc 2



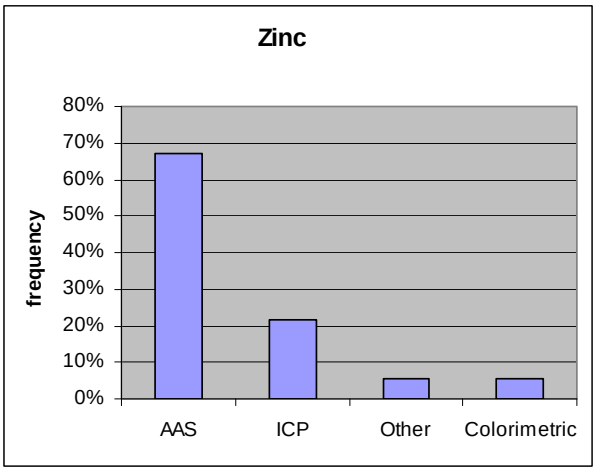
values:	36
removed:	1
mean:	3,01
ref.-value:	2,97
recovery:	101,2%
std:	0,645
rstd:	21,7%
std limit:	20%
upper limit:	4,16
lower limit:	1,78
too high:	5
too low:	4
outside limits:	9

Zinc 3

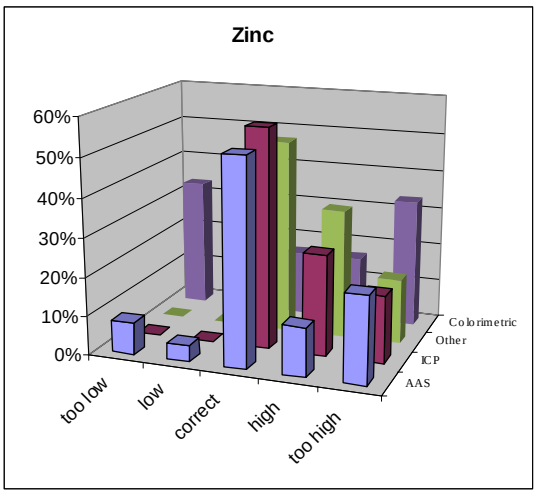


values:	**36**
removed:	**1**
mean:	**3,37**
ref.-value:	**3,34**
recovery:	**100,9%**
std:	**0,590**
rstd:	**17,6%**
std limit:	**20%**
upper limit:	**4,52**
lower limit:	**2,17**
too high:	**5**
too low:	**3**
outside limits:	**8**

Used methods



Comparison of methods



Summary Zinc

- mean values close to reference values (except lowest value)
- standard deviation higher than ever before
- No improvement

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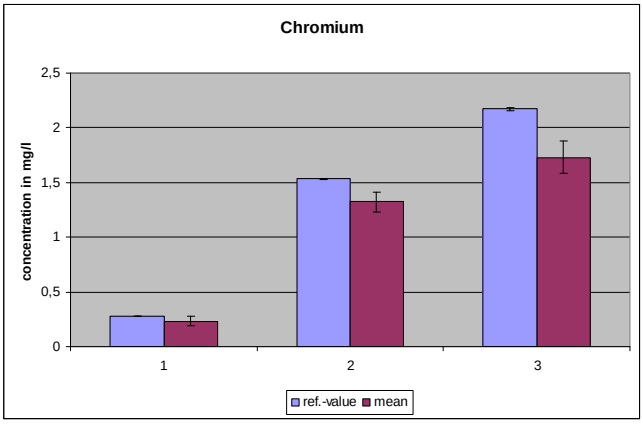
Chromium
Alg.A mean and ref.-value from weighings



Means significantly lower than reference values

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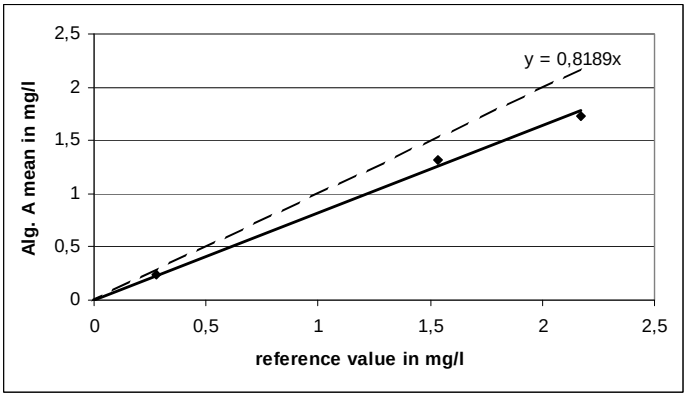
Chromium
mean vs. ref.-value



Average recovery	
2009	81.9
2008	94.2
2007	100.1
2006	97.4

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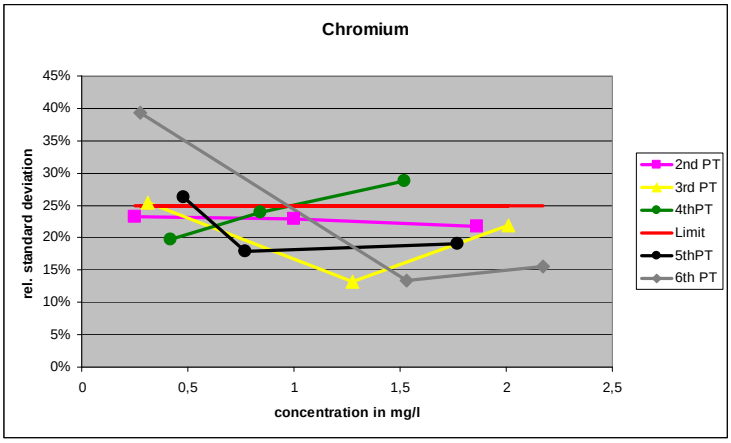
Chromium
calculated standard deviation and limit



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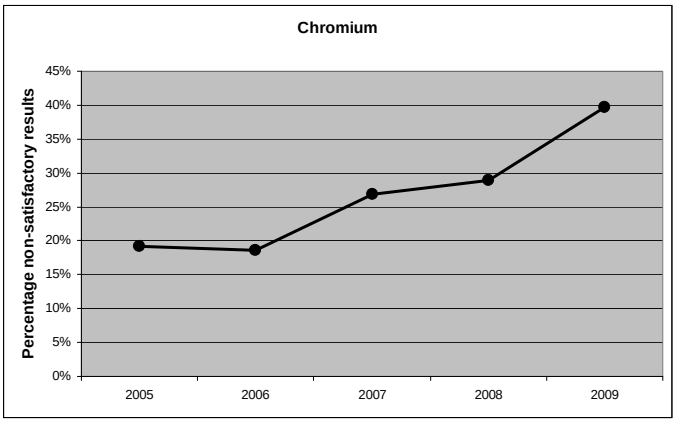
Chromium
Percentage non-satisfactory results



Percentage of non-satisfactory results steadily increasing

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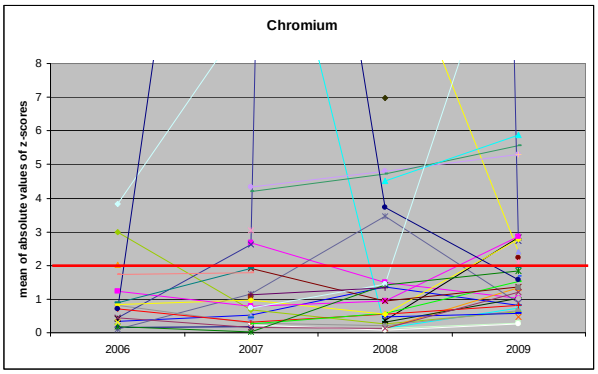
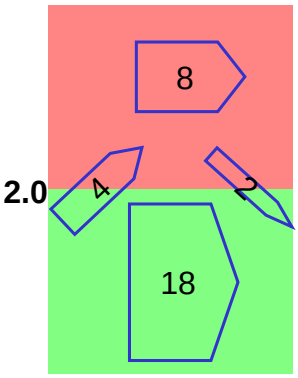
Chromium
Individual performance development





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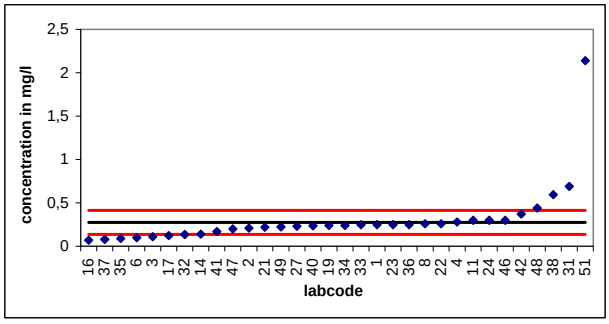
Chromium 1



values:	**37**
removed:	**5**
mean:	**0,23**
ref.-value:	**0,28**
recovery:	**84,8%**
std:	**0,108**
rstd:	**39,4%**
std limit:	**25%**
upper limit:	**0,41**
lower limit:	**0,14**
too high:	**5**
too low:	**11**
outside limits:	**16**

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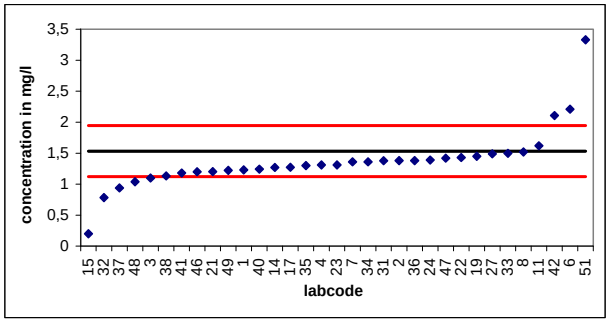
Chromium 2



values:	37
removed:	4
mean:	1,32
ref.-value:	1,53
recovery:	86,2%
std:	0,206
rstd:	13,4%
std limit:	25%
upper limit:	1,95
lower limit:	1,12
too high:	4
too low:	8
outside limits:	12

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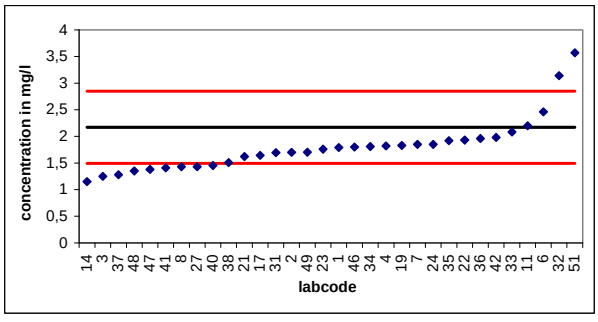
Chromium 3



values:	37
removed:	5
mean:	1,73
ref.-value:	2,17
recovery:	79,7%
std:	0,339
rstd:	15,6%
std limit:	25%
upper limit:	2,85
lower limit:	1,49
too high:	3
too low:	13
outside limits:	16

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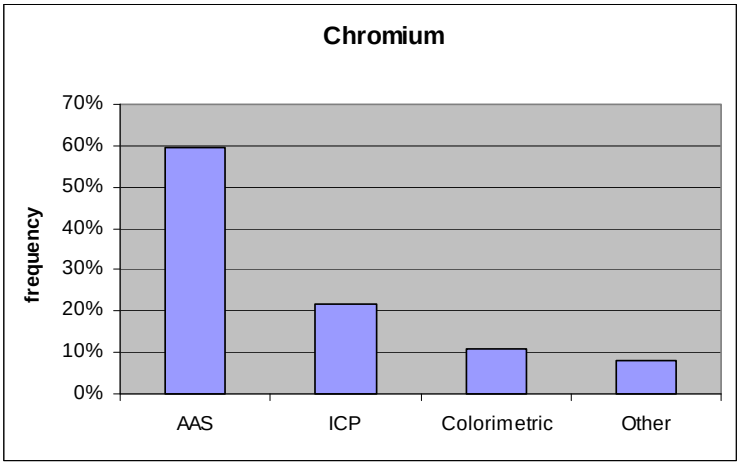
Used methods



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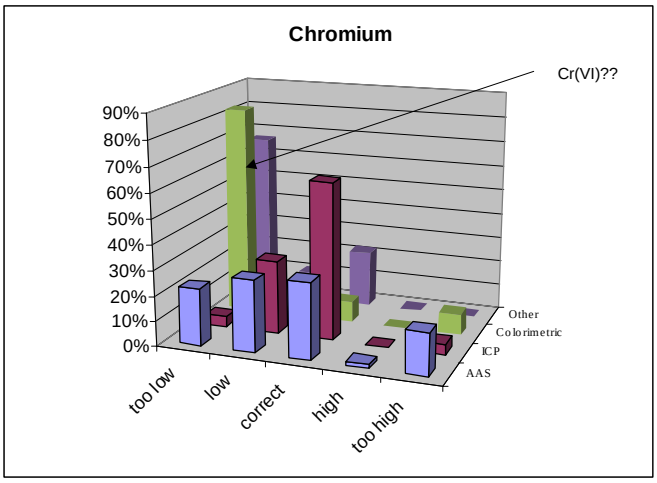
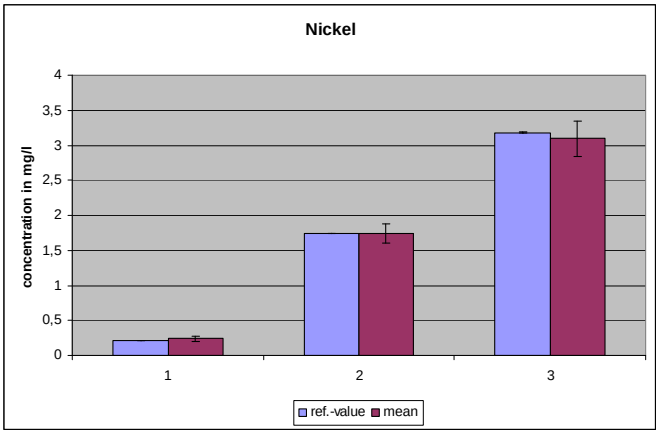
Comparison of methods



Summary Chromium

- Mean values significantly lower than reference values
- Standard deviation very high for lowest level
- Percentage of non-satisfactory results steadily increasing
- No improvement
- Problems with AAS
- Colorimetric method??

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



Good agreement

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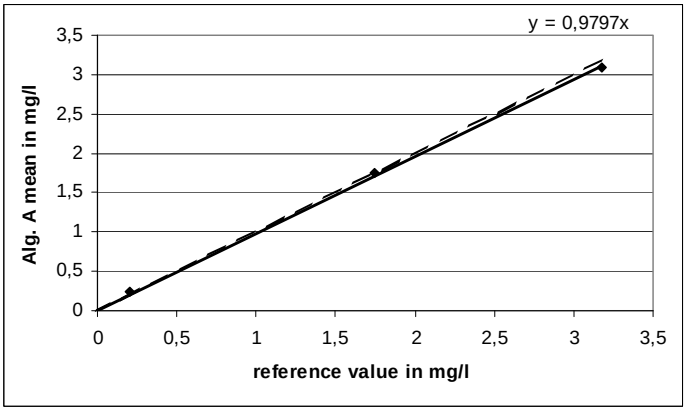
Nickel
mean vs. ref.-value



Average recovery	
2009	98.0
2008	98.7
2007	99.0
2006	94.6

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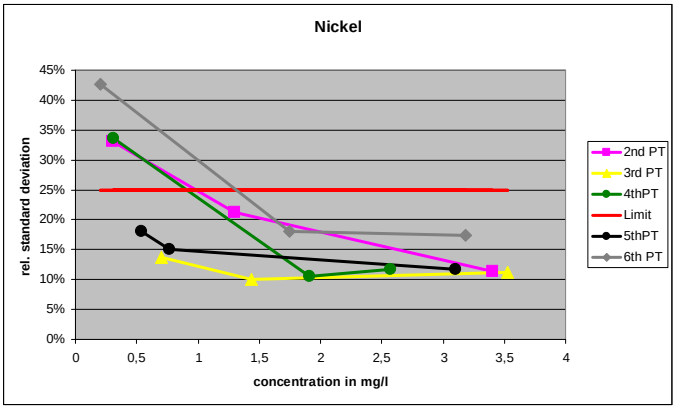
Nickel
calculated standard deviation and limit



Higehts standard deviations of all rounds

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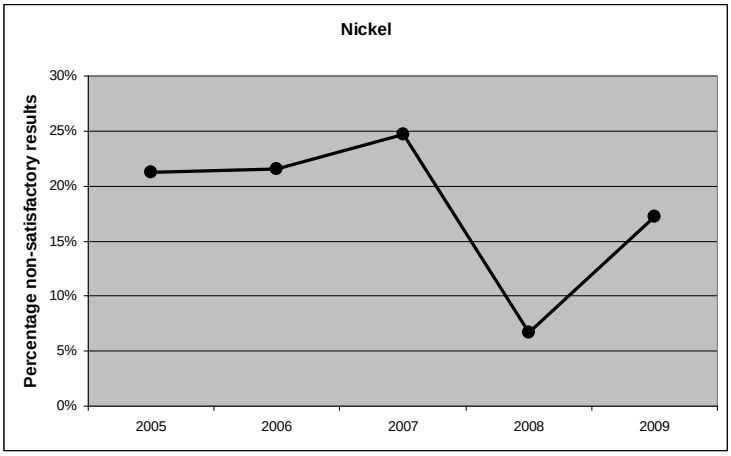
Nickel
Percentage non-satisfactory results



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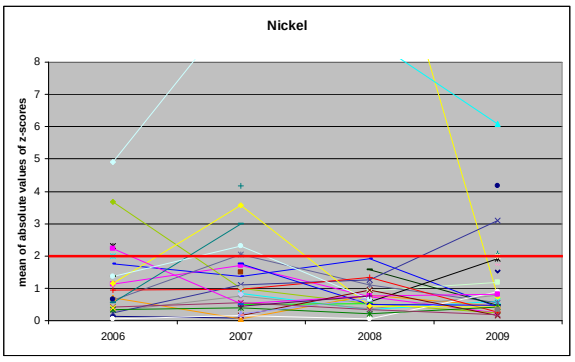
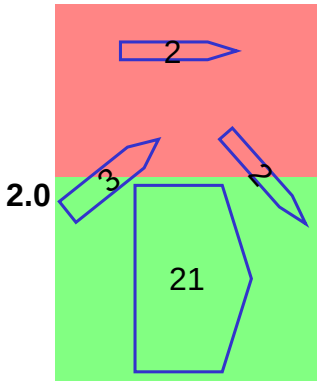
Nickel
Individual performance development





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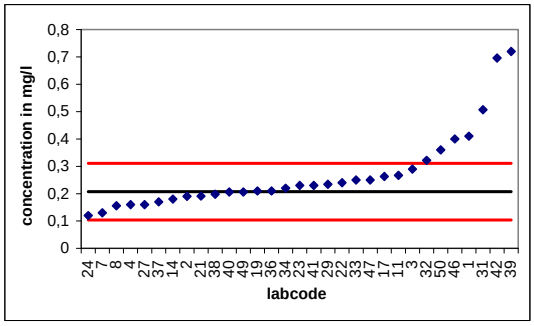
Nickel 1



values:	31
removed:	0
mean:	0,24
ref.-value:	0,21
recovery:	117,0%
std:	0,088
rstd:	42,7%
std limit:	25%
upper limit:	0,31
lower limit:	0,10
too high:	7
too low:	0
outside limits:	7

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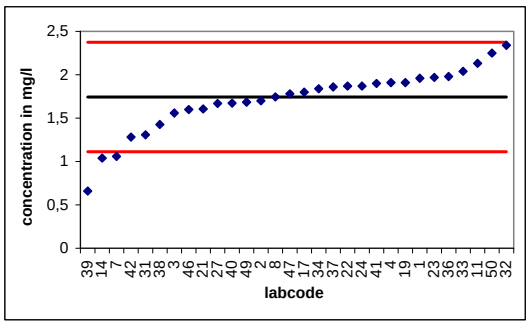
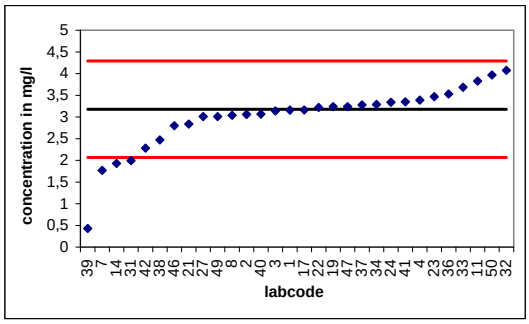
Nickel 2



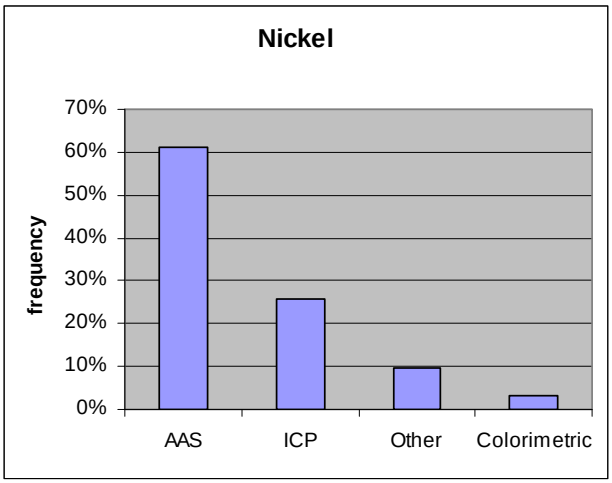
values:	31
removed:	1
mean:	1,74
ref.-value:	1,74
recovery:	100,0%
std:	0,315
rstd:	18,1%
std limit:	25%
upper limit:	2,37
lower limit:	1,11
too high:	1
too low:	3
outside limits:	4

Nickel 3

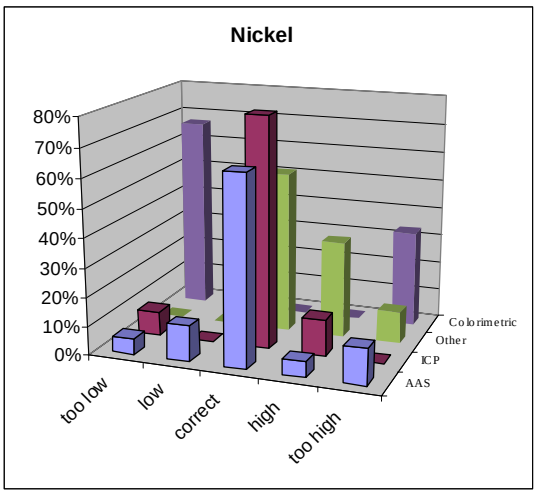


values:	**31**
removed:	**1**
mean:	**3,09**
ref.-value:	**3,18**
recovery:	**97,3%**
std:	**0,556**
rstd:	**17,5%**
std limit:	**25%**
upper limit:	**4,29**
lower limit:	**2,07**
too high:	**1**
too low:	**4**
outside limits:	**5**

Used methods



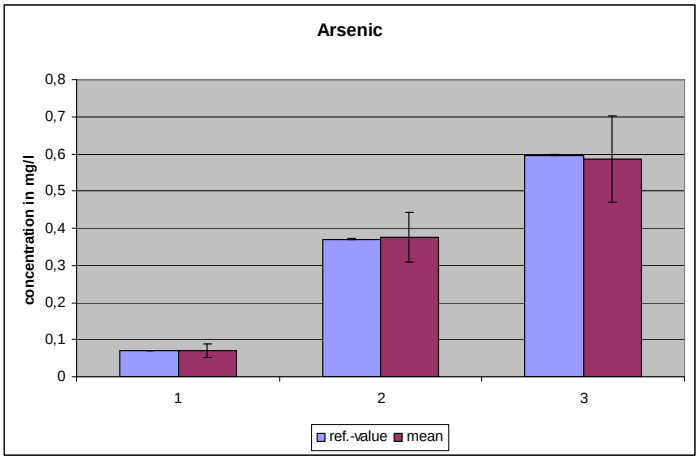
Comparison of methods



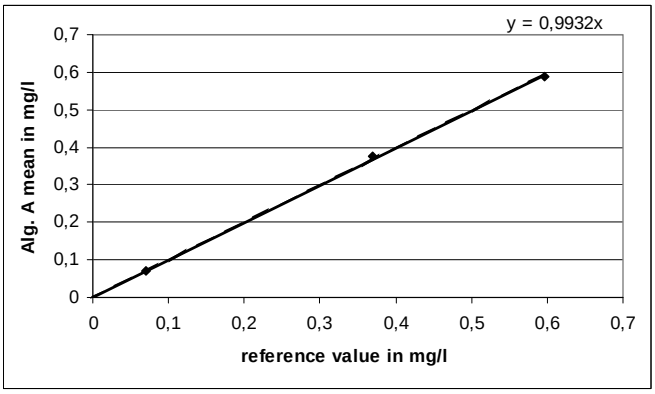
Summary Nickel

- mean values in quite good agreement with reference values
- standard deviation high compared to last rounds
- No improvement

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

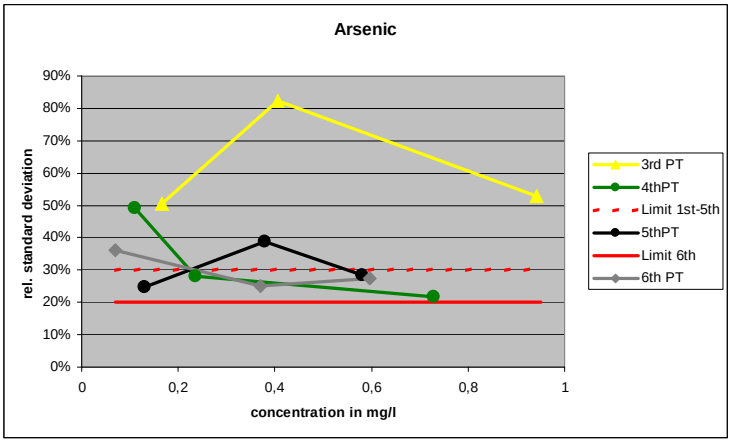


Arsenic
mean vs. ref.-value



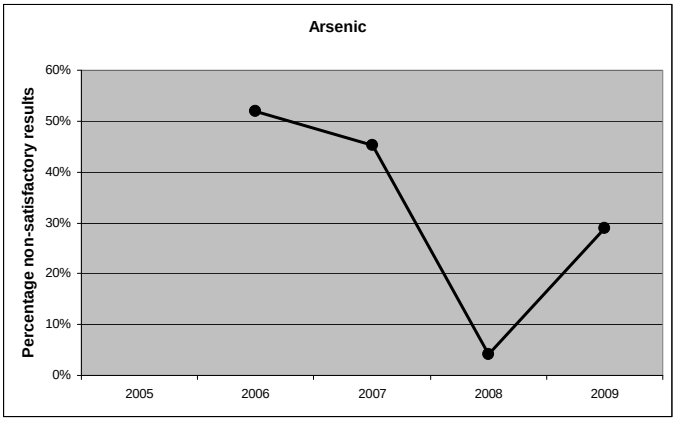
Average recovery	
2009	99.3
2008	92.4
2007	96.6
2006	111.2

Arsenic
calculated standard deviation and limit



Similar to last years

Arsenic
Percentage non-satisfactory results



Only partially due to lower limit (4/11)

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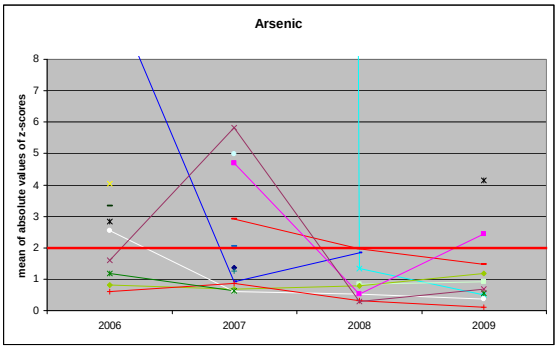
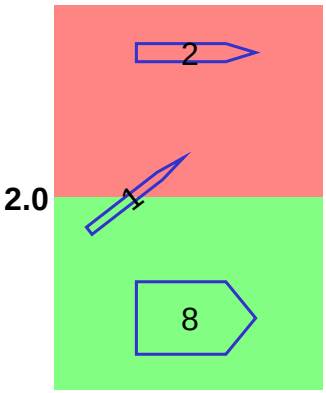
Arsenic
Individual performance development





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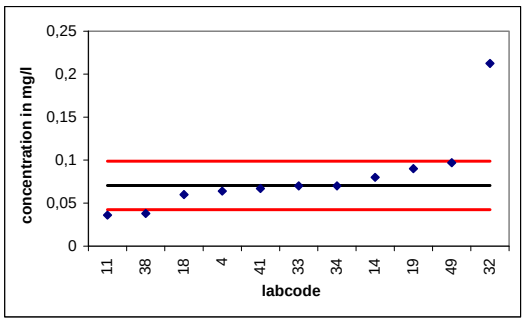
Arsenic 1



values:	**12**
removed:	**1**
mean:	**0,07**
ref.-value:	**0,07**
recovery:	**100,6%**
std:	**0,026**
rstd:	**36,3%**
std limit:	**20%**
upper limit:	**0,10**
lower limit:	**0,04**
too high:	**2**
too low:	**2**
outside limits:	**4**

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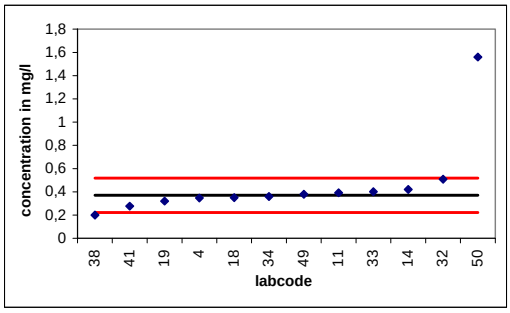
Arsenic 2



values:	13
removed:	1
mean:	0,38
ref.-value:	0,37
recovery:	101,4%
std:	0,093
rstd:	25,1%
std limit:	20%
upper limit:	0,52
lower limit:	0,22
too high:	2
too low:	1
outside limits:	3

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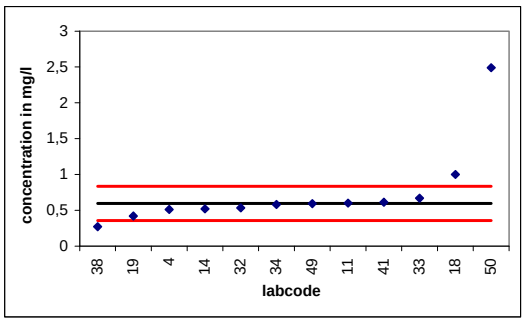
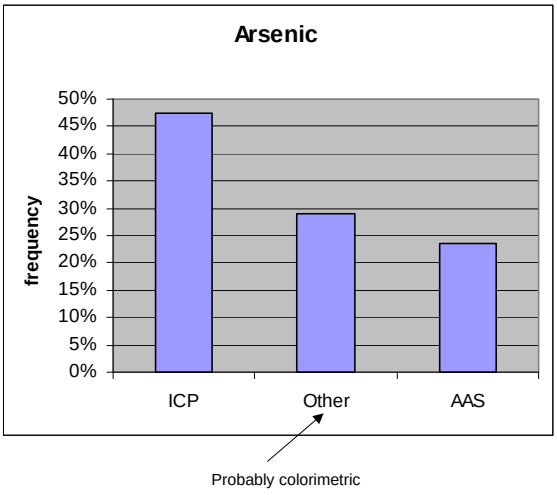
Arsenic 3

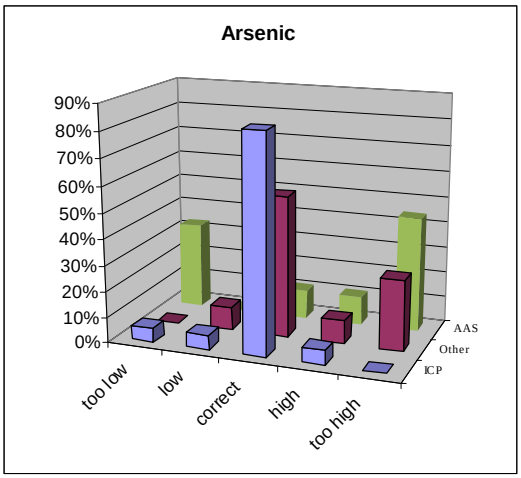


values:	13
removed:	1
mean:	0,59
ref.-value:	0,60
recovery:	98,5%
std:	0,164
rstd:	27,5%
std limit:	20%
upper limit:	0,83
lower limit:	0,36
too high:	3
too low:	1
outside limits:	4

Used methods



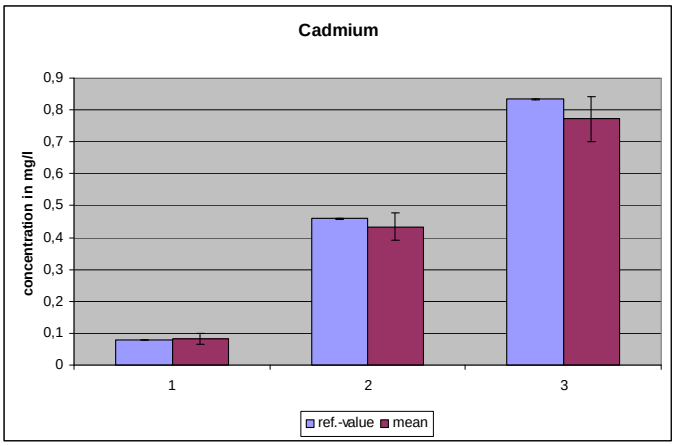
Comparison of methods



Summary Arsenic

- Low number of values
- Good agreement between reference values and means
- Standard deviation like the years before
- Methods?

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



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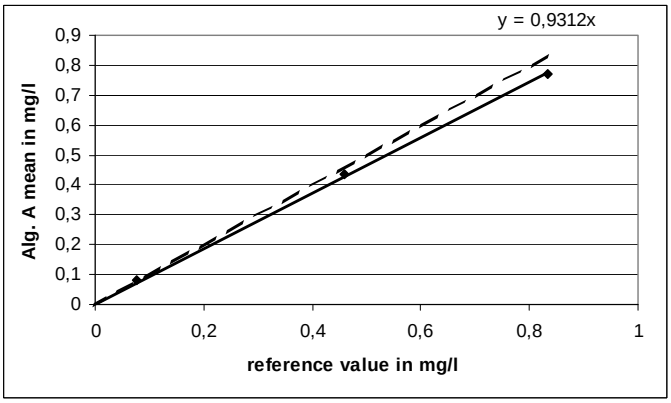
Cadmium
mean vs. ref.-value



Average recovery	
2009	93.1
2008	99.1
2007	96.4
2006	96.6

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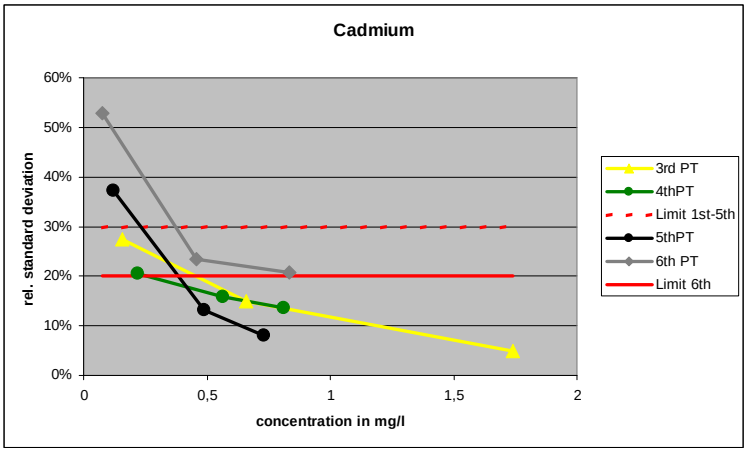
Cadmium
calculated standard deviation and limit



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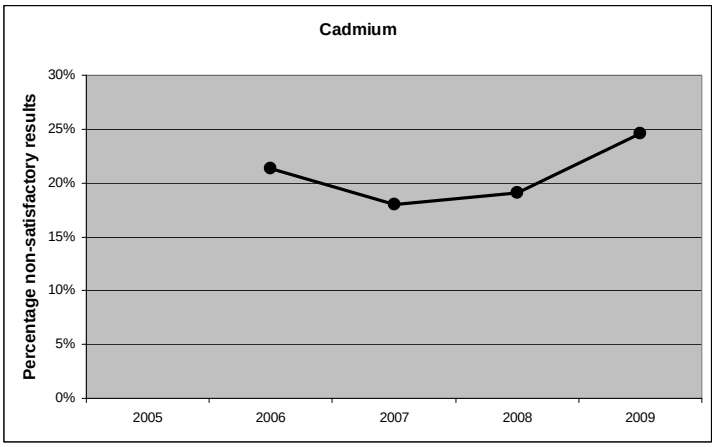
Cadmium
Percentage non-satisfactory results



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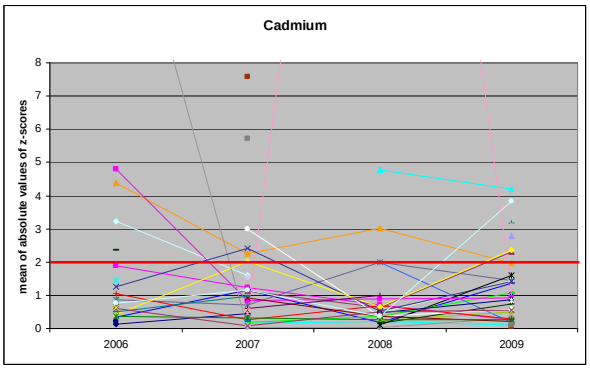
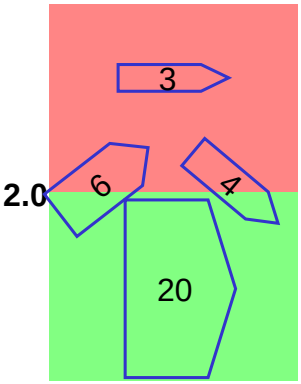
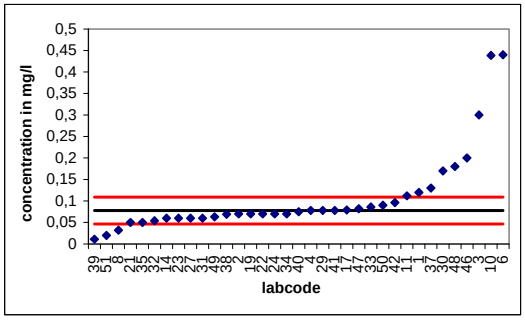
Cadmium
Individual performance development



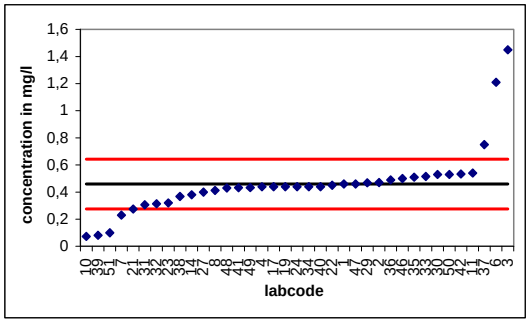


Cadmium 1



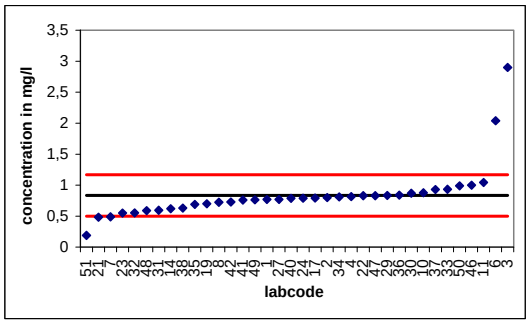
values:	37
removed:	2
mean:	0,08
ref.-value:	0,08
recovery:	107,7%
std:	0,041
rstd:	53,0%
std limit:	20%
upper limit:	0,11
lower limit:	0,05
too high:	10
too low:	4
outside limits:	14

Cadmium 2



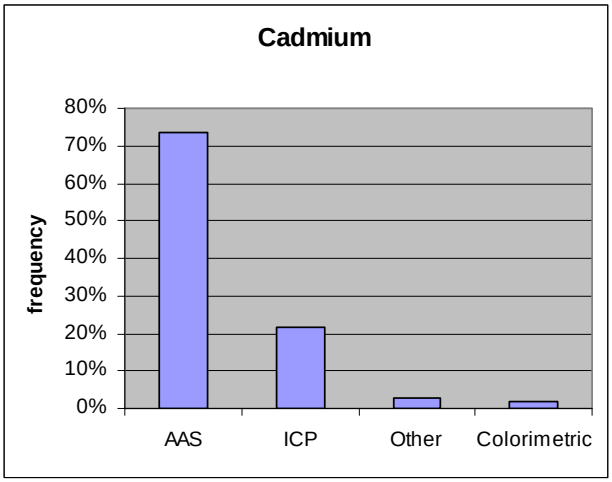
values:	37
removed:	0
mean:	0,43
ref.-value:	0,46
recovery:	94,4%
std:	0,108
rstd:	23,4%
std limit:	20%
upper limit:	0,64
lower limit:	0,28
too high:	3
too low:	5
outside limits:	8

Cadmium 3

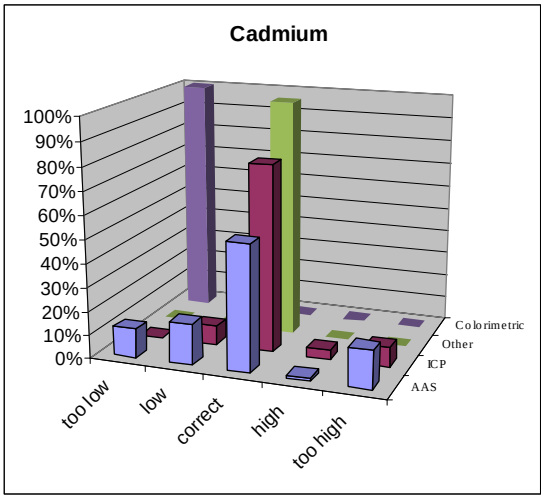


values:	**36**
removed:	**0**
mean:	**0,77**
ref.-value:	**0,83**
recovery:	**92,6%**
std:	**0,173**
rstd:	**20,8%**
std limit:	**20%**
upper limit:	**1,17**
lower limit:	**0,50**
too high:	**2**
too low:	**3**
outside limits:	**5**

Used methods



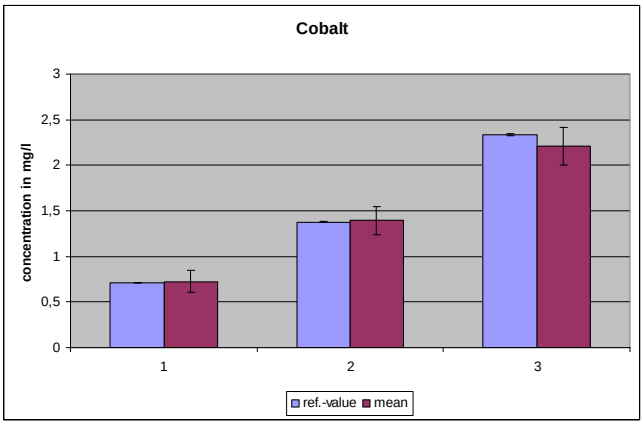
Comparison of methods



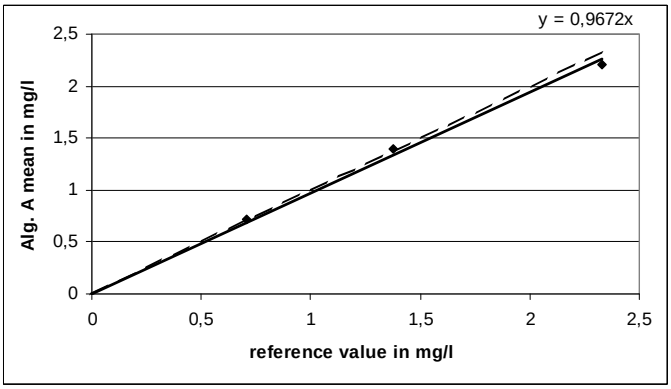
Summary Cadmium

- Mean values slightly lower than reference values
- Highest standard deviation of all PT rounds
- Percentage of non-satisfactory results increasing

Cobalt
Alg.A mean and ref.-value from weighings



Cobalt
mean vs. ref.-value



Average recovery	
2009	96,7
2008	99.8
2007	-
2006	-

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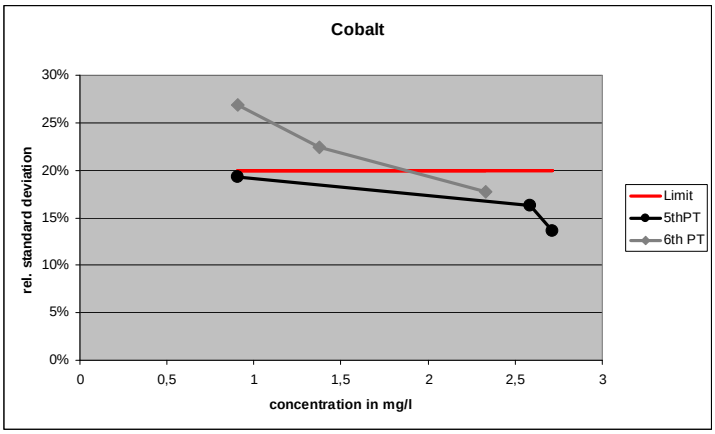
Cobalt
calculated standard deviation and limit



Higher than last year

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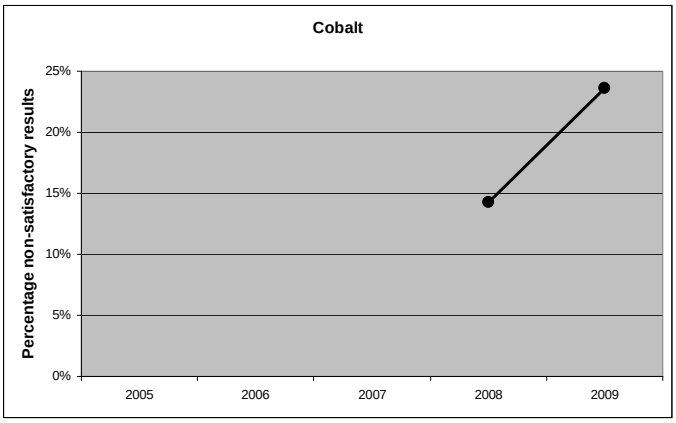
Cobalt
Percentage non-satisfactory results



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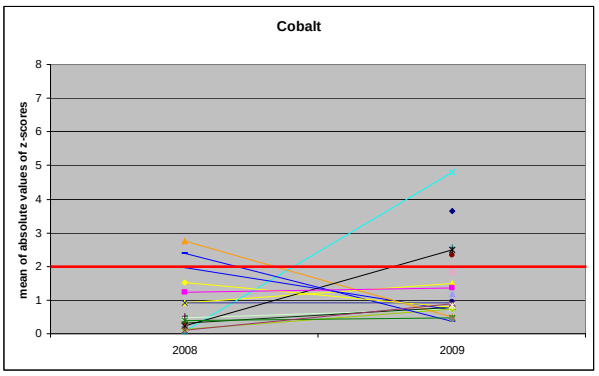
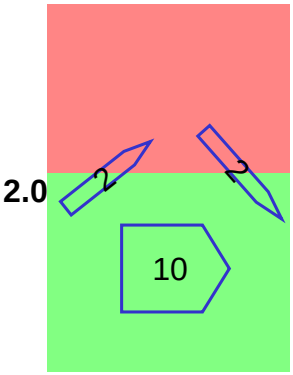
Cobalt
Individual performance development





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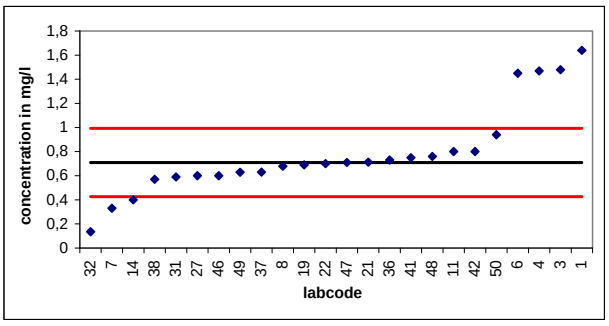
Cobalt 1



values:	**24**
removed:	**0**
mean:	**0,72**
ref.-value:	**0,71**
recovery:	**102,0%**
std:	**0,243**
rstd:	**34,3%**
std limit:	**20%**
upper limit:	**0,99**
lower limit:	**0,43**
too high:	**4**
too low:	**3**
outside limits:	**7**

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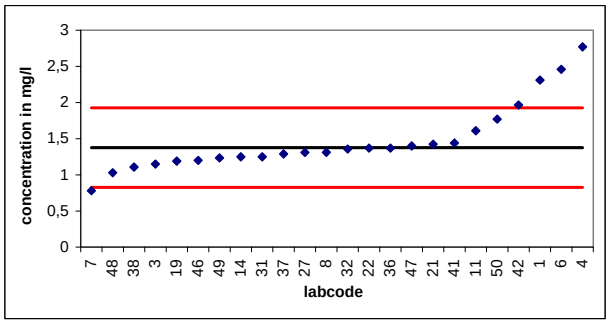
Cobalt 2



values:	24
removed:	0
mean:	1,39
ref.-value:	1,38
recovery:	101,2%
std:	0,309
rstd:	22,4%
std limit:	20%
upper limit:	1,93
lower limit:	0,83
too high:	4
too low:	1
outside limits:	5

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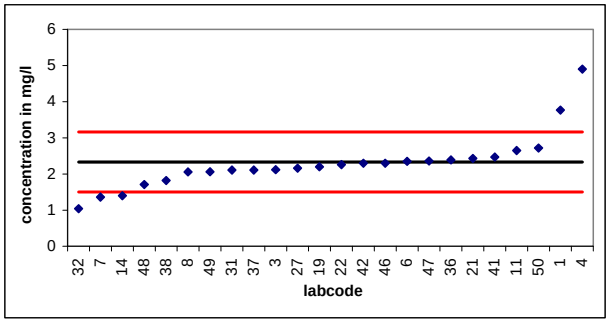
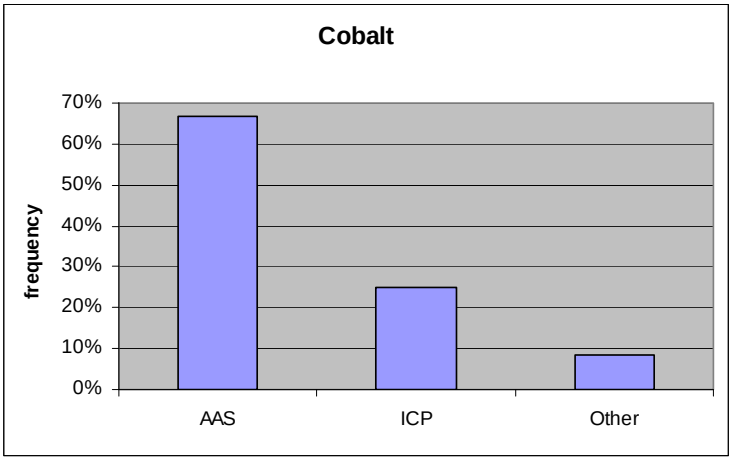
Cobalt 3

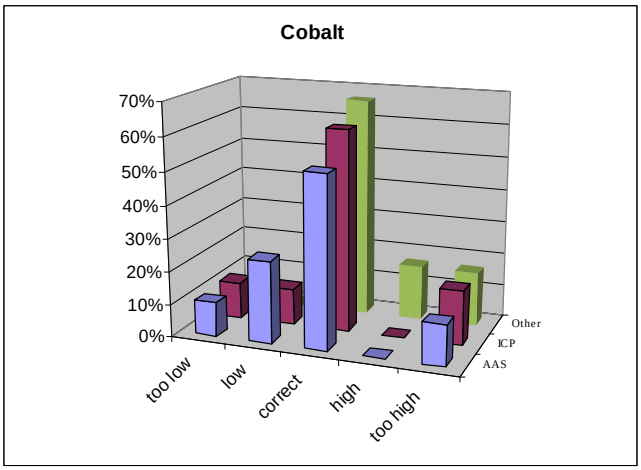


values:	24
removed:	0
mean:	2,21
ref.-value:	2,33
recovery:	94,7%
std:	0,415
rstd:	17,8%
std limit:	20%
upper limit:	3,16
lower limit:	1,50
too high:	2
too low:	3
outside limits:	5

Used methods



Comparison of methods



Summary Cobalt

- Means close to reference values
- Standard deviation higher than last year

Reference values vs. Nmisa

Parameter	Sample 4		Sample 5		Sample 6	
	Concentration (µg/ml)	Expanded Uncertainty (µg/ml)	Concentration (µg/ml)	Expanded Uncertainty (µg/ml)	Concentration (µg/ml)	Expanded Uncertainty (µg/ml)
Al	0.488	0.027	0.809	0.046	1.231	0.065
	0.523	0.001	0.834	0.003	1.316	0.003
As	0.423	0.043	0.294	0.034	0.05	0.014
	0.596	0.002	0.370	0.001	0.071	0.000
Ca	47.6	2.1	14.02	0.62	38.9	1.7
	46.931	0.275	13.656	0.080	38.771	0.227
Cd	0.789	0.015	0.074	0.002	0.434	0.01
	0.834	0.002	0.078	0.000	0.459	0.002
Co	1.355	0.045	2.326	0.077	0.713	0.024
	1.377	0.007	2.332	0.011	0.709	0.004
Cr	1.331	0.051	1.883	0.051	0.253	0.011
	1.533	0.008	2.172	0.011	0.275	0.001
Cu	0.681	0.02	1.908	0.072	3.314	0.1
	0.701	0.001	1.874	0.003	3.371	0.004
Fe	0.995	0.036	1.764	0.066	0.816	0.03
	0.993	0.003	1.714	0.003	0.721	0.002
K	14.4	0.56	8.56	0.31	22.68	0.78
	15.411	0.022	9.257	0.013	24.405	0.034
Mg	11.04	0.57	36.3	1.8	49.7	2.4
	10.609	0.062	34.987	0.205	47.767	0.280
Mn	2.292	0.091	0.576	0.024	1.182	0.053
	2.431	0.004	0.598	0.002	1.206	0.003
Na	74.7	3	32.9	1.2	16.78	0.62
	76.572	0.107	32.727	0.046	17.237	0.024
Ni	0.227	0.013	3.44	0.15	1.918	0.085
	0.207	0.000	3.180	0.004	1.743	0.003
Pb	1.442	0.05	0.276	0.013	0.927	0.033
	1.529	0.003	0.285	0.001	0.964	0.002
Zn	3.128	0.097	1.154	0.027	3.52	0.11
	2.973	0.004	0.843	0.003	3.345	0.004
Calculated reference value						
NMISA						

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Possible causes for disagreement

- The PT reference values is biased
  - Because of unrecognized effect on the concentration of the parameter
  - Which is not reflected in the uncertainty budget
- The NMISAs measurement uncertainty is underestimated

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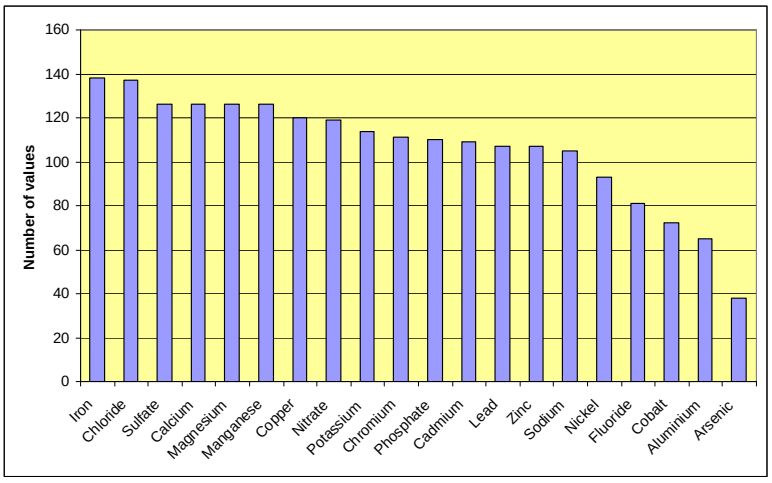
Number of values per parameter



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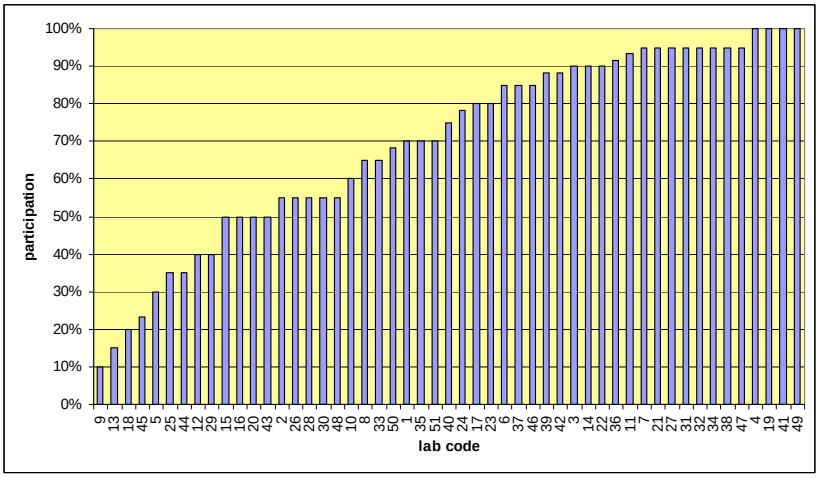
Overview on participation



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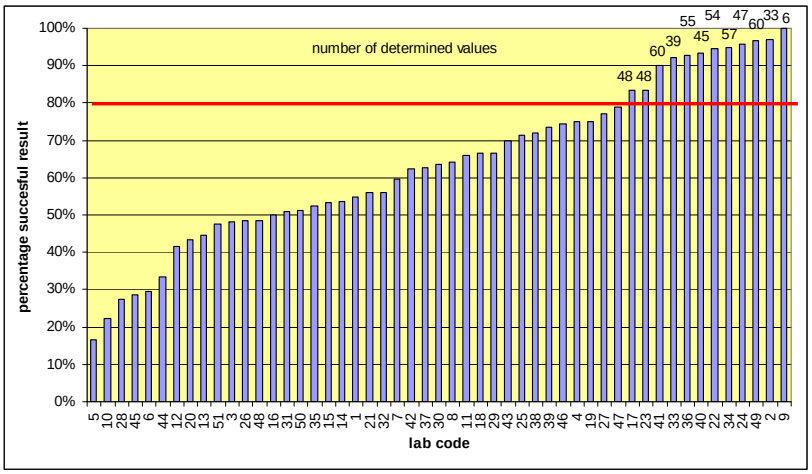
Overview on participants' success



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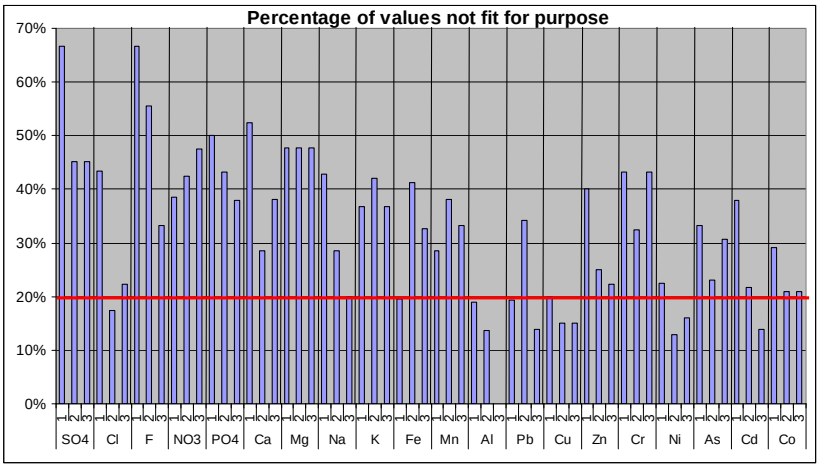
Values not fit for purpose



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Conclusion I

- 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 or getting worse
- More emphasis should be put on corrective actions after unsatisfactory participation

Conclusion II

- There should be a discussion
  - How to select suitable methods? (recommendations by SADCWaterLab?)
  - How to help laboratories to proper apply the methods?
- The gaps that prevent labs from proper application should be identified

nmisa
National Metrology Institute of South Africa

Analytical approaches frequently used in value assignment in Analytical Chemistry

Your measure of excellence

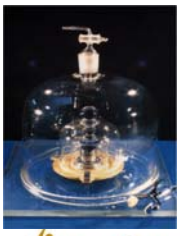
Introduction

- Background
  - CCQM
  - Chemistry at NMISA
- Value assignment in Chemistry
  - Overview of measurement techniques often used
- Examples from CCQM Intercomparison Studies

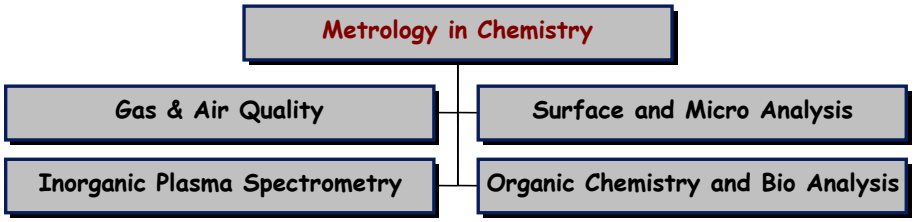
nmisa

Background: CCQM

- Metrology in Chemistry: Science of Measurement in Chemistry
- Responsibility to promote the concepts of:
  - International traceability to SI
    - Amount of substance (mole)
    - Mass fraction (kilogram)
  - Reduce Technical Barriers to Trade
- Mutual Recognition Arrangement (MRA)
  - Calibration and Measurement Capabilities (CMCs)
- Peer reviewed Quality system
- Proven technical capability (successful participation in relevant interlaboratory comparison studies)
  - Analytical Techniques employed:
    - Primary Analysis Methods
    - Best Measurement Practice approach



nmisa
National Metrology Institute of South Africa

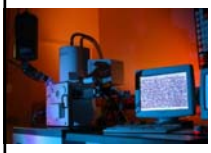


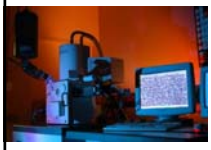
nmisa
National Metrology Institute of South Africa

Gas Metrology

- Established 1998
- Calibration of breathalysers
- Preparation of primary gas reference mixtures (PRMs) in nitrogen (N_2) and air matrices by gravimetry
  - CO_2; CO; NO; NO_2; SO_2; H_2S; C_3H_8; Stack gas mixtures
- Purity analysis
  - GC-FID; GC-PDHID; FTIR; NDIR; GC-MSD; CRDS
- Certification of gas mixtures
- Calibration of air pollution analysers
- Accreditation: Gravimetric preparation of gas mixtures
  - ISO 17025
  - ISO Guide 34

Surface and Micro-analysis





- Established in 1998
- Instrumentation
  - XPS; SEM-EDS / EBSD; TOF-SIMS; XRD; GD-OES
- Focus Areas
  - Industrial support
    - Imaging (nano-scale and elemental mapping)
    - Elemental composition and binding energies
    - Crystal structure
    - Surface layers and coatings (thickness and composition)
    - Surface chemistry (catalysis, functional groups)
  - Polymer research and analysis
    - FTIR-TGA
  - Proficiency Testing
    - Electron microscopy magnification calibration
    - Elemental analysis by EDS

Organic Chemistry and Bio-Analysis

- Established 2001/2002
- Instrumentation:
  - GCxGC-FID; GC-MS; GCxGC-TOFMS; LC-MS; HPLC; DSC, UPLC/MS/MS
- Focus Areas:
  - POPs
  - Aqueous ethanol and sodium fluoride standards
    - Certified Reference Materials
    - Proficiency Testing Scheme: Department of Health
  - Mycotoxin analysis
  - Purity analysis on chemical compounds
  - Adulteration in foodstuffs and wine
  - Investigations into a bio-analysis capability
  - Method development for biodiesel analysis
- Accreditation: Preparation of aqueous ethanol and sodium fluoride calibration standards
  - ISO 17025
  - ISO Guide 34

IPS Laboratory

- Established in 2000
- Instrumentation:
  - HR-ICPMS, Laser Ablation ICPMS, Axial ICP-OES
  - Focus Areas: Trace and ultra-trace analysis in Food & Environmental samples
  - CCQM Intercomparisons:
    - Food, environmental, metal and metal alloys and advanced materials
  - Collaboration on Certification of Reference Materials:
    - Minerals, food, environmental samples
  - Participation / value assignment in selected PT Schemes:
    - IAEA – AFRA: Nuclear Research Reactors and Analytical laboratories in Africa
      - Geological material / minerals
      - Food & environmental material
    - NMISA : Stainless steel – Elemental analysis by EDS
  - Support to Industry:
    - Maize, Animal supplements, Plastic, Nano-materials
  - Feasibility study: Primary inorganic standard solutions
- Accreditation: ISO 17025

Reference Value assignment in Chemistry

- Applications
  - Production of Certified Reference Materials (CRMs)
  - Production of Reference Materials (RMs)
  - Proficiency Testing schemes / Inter-laboratory comparisons
- Analysis approaches:
  - Single method (e.g. primary) in a single laboratory, with confirmation method of higher order,
  - Analysis by multiple methods in a number of expert laboratories
  - Analysis by multiple methods in a large number of routine laboratories
  - Analysis by a single, specified method (e.g. standard method) in a large number of routine laboratories
- Other considerations:
  - Stability
  - Homogeneity
  - Appropriate combination of all data (statistical considerations)
  - Uncertainty of Measurement

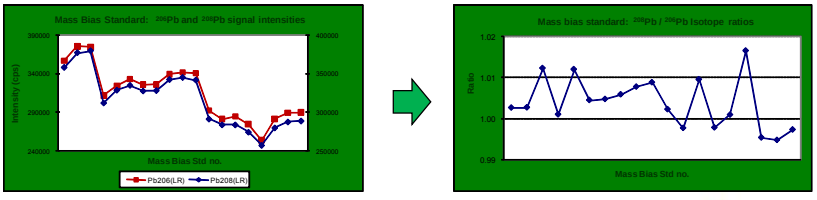
Analytical methods used in Reference Value assignment

- Primary methods: Highest metrological order

  Highest metrological qualities … operation can be completely described and understood … complete uncertainty statement can be written down in terms of SI units … traceability to the mole

  –Primary Direct Method: No reference to standard of the same quantity
  - Gravimetry
  - Electrogravimetry
  - Titrimetry
  - Coulometry

  –Primary Ratio Method: Measures ratio of unknown to a standard of the same quantity, complete measurement equation required.
  - Isotope Dilution – Mass Spectrometry
  - *Neutron Activation Analysis (NAA)*



Analytical methods used in Reference Value assignment

- Secondary methods: Shortest possible chain of traceability to the SI
  - Gravimetric preparation of samples and standards
  - High precision experimental designs
  - Internal standardisation
  - Matrix matching
  - Standard Addition
  - Applicable to most analytical techniques / instruments

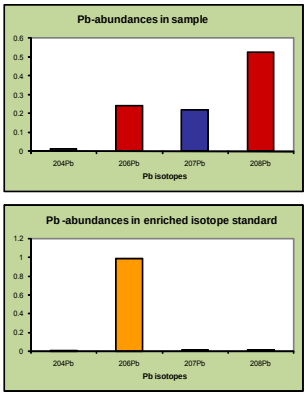


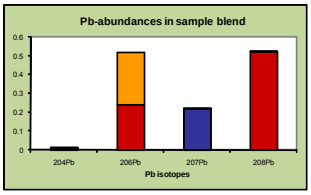


Primary Ratio: Isotope Dilution Mass Spectrometry

Principle: Isotope ratio in a known amount of sample is altered through the addition of a known amount of an enriched isotope standard.

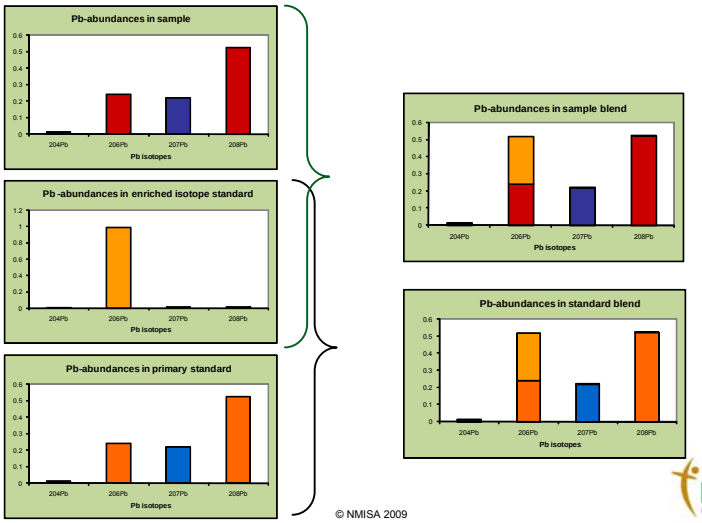
Potential Techniques applicable to:
- ICP-MS, GC-ICP-MS, HPLC-ICP-MS
- GC-MS, GC-MS/MS
- LC-MS, HPLC-MS
- LC-TOFMS
- TIMS





Primary Ratio: Double Isotope Dilution -MS

$$C_{x(n)} = C_z \cdot \frac{G \cdot B \cdot M_y \cdot M_z \cdot (K_y \cdot R_y - K_b \cdot R_b) \cdot (K_{b'} \cdot R_{b'} - K_z \cdot R_z)}{w \cdot M_x \cdot M_{y'} \cdot (K_b \cdot R_b - K_x \cdot R_x) \cdot (K_y \cdot R_y - K_{b'} \cdot R_{b'})} \cdot \frac{\sum (K_{ix} \cdot R_{ix})}{\sum (K_{iz} \cdot R_{iz})}$$



Primary Ratio: Isotope Dilution Mass Spectrometry

- Advantages
  - Excellent accuracy and precision
  - Once isotopic equilibration between sample and enriched isotope spike has been achieved, accuracy will not be affected by any subsequent loss, e.g. incomplete recovery, extraction, precipitation, etc.
  - Variation in instrument sensitivity (e.g. drift) will not effect the measurement of the isotope ratio.
- Limitations
  - Determination of mono-isotopic elements such as As, Mn, Co & Rh is not possible.
  - High cost:
    - Isotopically enriched standards
    - MS-instruments
    - Experienced staff
    - Time
  - Availibility of isotopically enriched standards
  - Isotopic equilibration could be problematic for methods where complete digestion of sample cannot be achieved, e.g. extraction.

Neutron Activation Analysis (NAA)

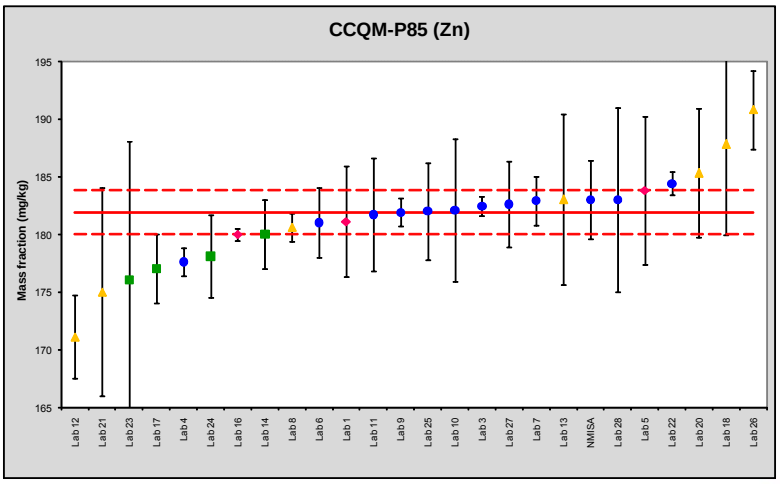
- Procedure:
  - Irradiate sample with flux of neutrons
  - Stable isotopes converted to radioactive isotopes
  - Measure γ-irradiation produced by decay of radioactive isotope at characteristic half-life.
- Advantages
  - Can analyse most forms of sample, e.g. liquids, solids, slurries, etc.
  - Typically non-destructive (excluding RNAA) and minimal to no sample preparation required
  - Small sample sizes needed (100-200mg)
  - Negligible matrix effects
  - Can analyse 70% of elements on Periodic table
- Limitations
  - Need a neutron reactor
    - IAEA – AFRA: Nuclear Research Reactors and Analytical laboratories in Africa (5-9 participants)
  - Skilled analysts

Other Calibration Strategies for Value Assignment / Secondary methods

- All based on Gravimetric Sample preparation
- External calibration
  - Internal standardisation
    - High Precision measurements:
      - Repeated analysis of samples and standards to measure and correct for drift
      - Close matching of standards' and samples' intensities (R ~ 1)
  - Matrix matched standards
  - Standard Addition
- Potential applicable analytical methods
  - ICP-OES, ICP-MS, FAAS, GFAAS, GC, LC, HPLC, UPLC, XRF
- Advantages:
  - High precision and small uncertainties (approaching that of primary methods)
  - Wide range of potential appications
- Disadvantages:
  - Time-consuming
  - Extensive post-analysis calculations required

CCQM-Examples: Different techniques' performance

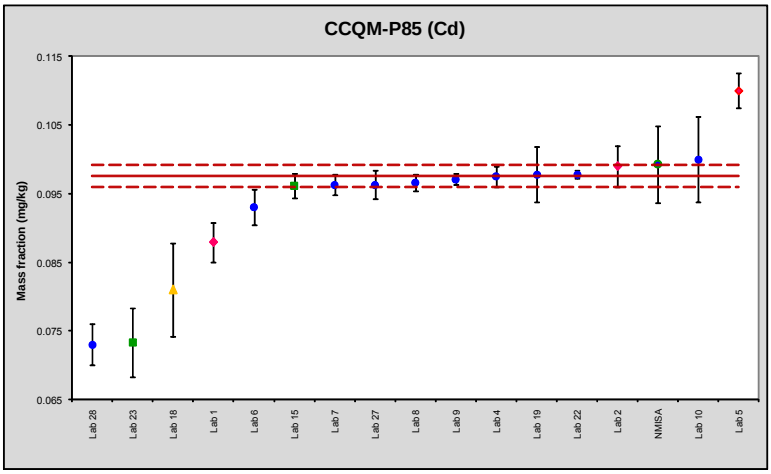
- CCQM-P85: Trace elements in Bovine Liver



Blue: ID-ICPMS
Red: ICPMS
Yellow: AAS
Green: NAA

CCQM-Examples: Different techniques' performance

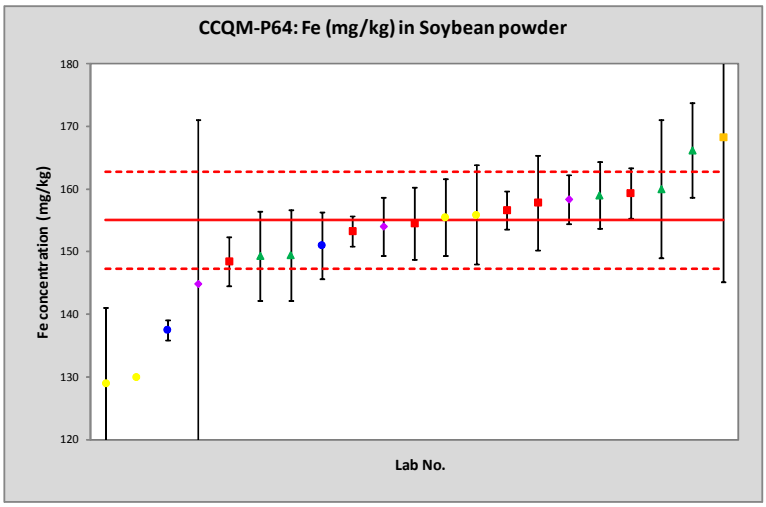
- CCQM-P85: Trace elements in Bovine Liver



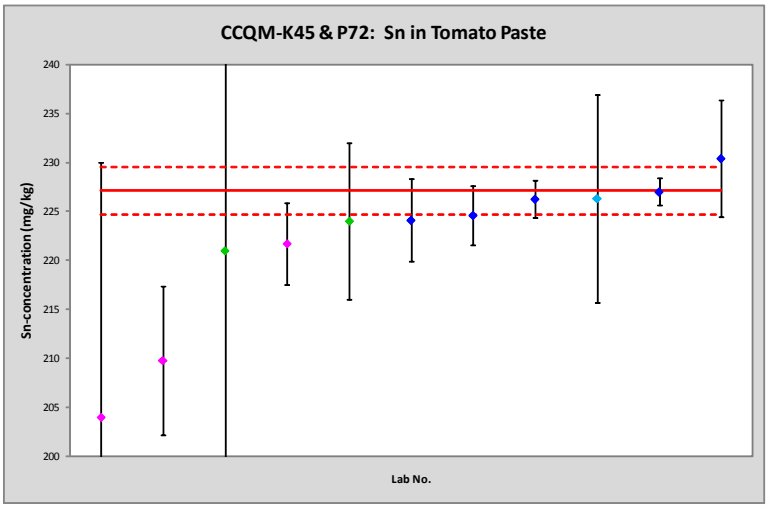
Blue: ID-ICPMS
Red: ICPMS
Yellow: AAS
Green: NAA

CCQM-Examples: Different techniques' performance

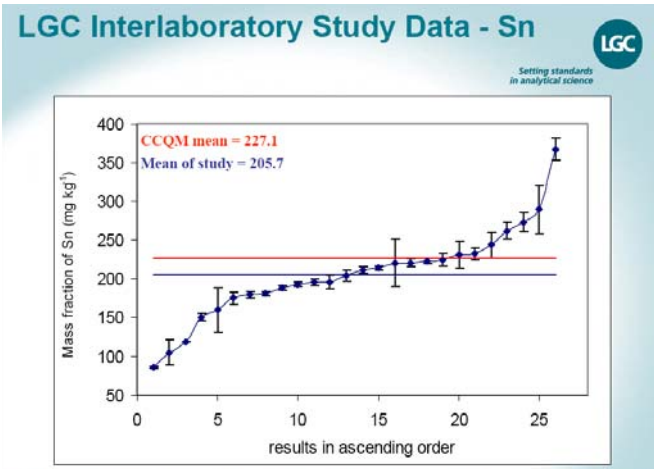
- CCQM-P64: Nutritional elements in a low fat soybean powder



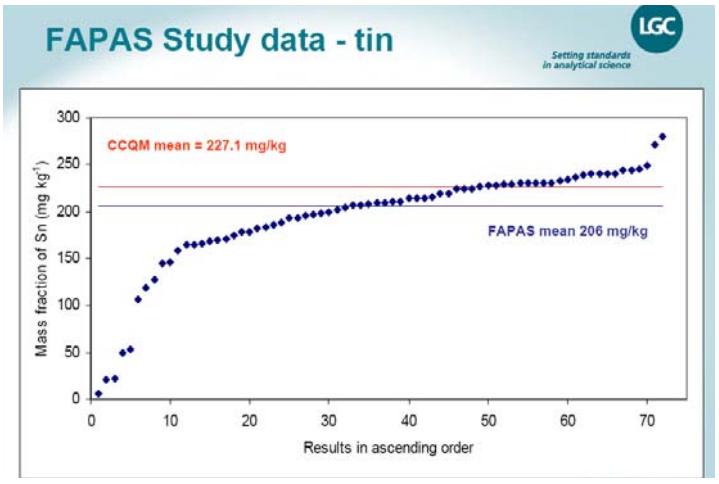
FAPAS Example: Sn in Tomato Paste



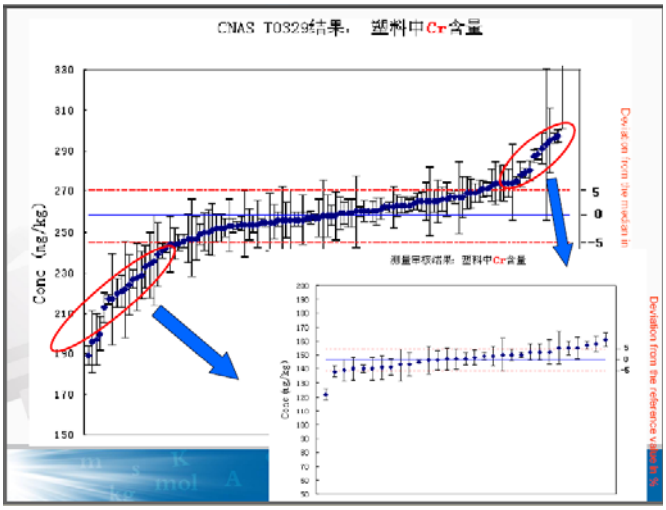
FAPAS Example: Sn in Tomato Paste



FAPAS Example: Sn in Tomato Paste



China example: Implementation of Corrective Action



Conclusions

- Various approaches available for reference value assignment
  - Primary methods
  - Secondary methods
- Select approach that is fit for purpose
  - Time
  - Cost
  - Uncertainty required

Acknowledgements

- CCQM Intercomparison participants
- DTI, South Africa

Thank you

Maré Linsky
mlinsky@nmisa.org

NMISA: Typical Food analysis performed

Element	Matrix	Technique
Pb, Cd, Cu, Fe	Red Wine	Double-ID-ICPMS
Cu, Zn, Fe, Ca	Soybean powder	Double-ID-ICPMS
Pb	Maize powder	Double-ID-ICPMS
Cd	Rice flour	Double-ID-ICPMS
Sn, Pb	Tomato Paste	Double-ID-ICPMS
Se	Pharmaceutical supplement	Double-ID-CV-ICPMS
Fe, Zn, Pb, Cd	Bovine Liver	Double-ID-ICPMS
Analyte	**Matrix**	**Technique**
Veterinary drug residues - antibiotics e.g. chloramphenicol	Bovine Milk, Pork muscle	IDMS HPLC/MS/MS
Pesticides, polychlorinated biphenyls	Mussel tissue	GC-MSD, GCxGC-TOFMS
Selenomethionine	Wheat flour	IDMS UPLC/MS/MS
Mycotoxins Aflatoxins Fumonisins Ochratoxin	Maize, grains, nuts, wine, milk	IDMS UPLC/MS/MS
Nutrients Fat soluble vitamins Water soluble vitamins	Infant formula, infant cereals	IDMS UPLC/MS/MS

nmisa
National Metrology Institute of South Africa

Evaluation Questionnaire – Chemistry workshop

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 hotel (accommodation, food)	☐	☐	☐	☐	☐
The venue of the workshop (conference room)	☐	☐	☐	☐	☐

How do you judge the different parts of this workshop	Very useful 1	2	3	4	not useful 5
Report of the PT provider	☐	☐	☐	☐	☐
Local coordinators' reports	☐	☐	☐	☐	☐
Evaluation of the chemistry PT	☐	☐	☐	☐	☐
NMISA-presentation on reference values	☐	☐	☐	☐	☐
WG discussion "future activities"	☐	☐	☐	☐	☐
Working groups "methods" and "survey"	☐	☐	☐	☐	☐
SADCWATERLAB General Assembly	☐	☐	☐	☐	☐

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?

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

.....

Please use back side for any other comments