9th Evaluation Workshop within the SADCMET Proficiency Testing Scheme for Water Testing Laboratories Chemistry part

Addis Ababa, Ethiopia

19 – 22 November 2012

Report on the 9th Evaluation Workshop within the SADCMET Proficiency Testing Scheme for Water Testing Laboratories

Addis Ababa, Ethiopia, 19 – 22 November 2012

Prepared by Dr.-Ing. Michael Koch

Summary

The workshop covered the evaluation of the 9th SADCMET Water PT round and all aspects that could be derived from the results. The results showed more or less the same picture as in the previous year. Still there are some laboratories that continue to fail in the PT, most probably due to the absence of adequate corrective actions, improper use of suitable analytical methods and also use of non-suitable methods.

Two SADCWaterLab working groups were established during the 2009 meeting in the Seychelles. One is dealing with recommendations for suitable analytical methods, the other one with the follow-up the Training of Trainers held in 2010 in Livingstone, Zambia.

Most of the participants are still very enthusiastic. So despite of the only slow improvement of the quality of the PT results it is recommended to continue the PT system. Nevertheless the system should move more to sustainability. As a first step to sustainability, travel costs to the workshop reported here had to be covered by the participants themselves. 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 is the lack of awareness on the importance of PT or – even more basic – the importance on quality assurance in the chemical lab. To overcome this problem the results of this workshop were communicated to all participating laboratories via a short report. To raise awareness amongst the policy makers in the laboratories the leaflet prepared by SADCWaterLab explaining the importance of quality management in the laboratory and participation in PT schemes should be used. In addition workshops on national level are indispensable. This is mainly the task of the persons trained at the training for trainers in Livingstone, Zambia, in August 2010. In this training course material for a basic course on quality assurance in the analytical laboratory was provided and the participants were trained to present this in a workshop.

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 evaluation workshop also contained training sessions on “Calibration”, “Certified Reference Materials” and “Metrology in Chemistry” as well as the SADWATERLAB General Assembly.

Introduction

The workshop reported here followed previous workshops held in

- Windhoek, Namibia (Feb 2004),
- Pretoria, South Africa (Dec 2004),
- Dar es Salaam, Tanzania (Nov 2005),
- Gaborone, Botswana (Nov 2006),
- Dar es Salaam (Dec 2007),
- Kampala, Uganda (Dec 2008),
- Mahé, Seychelles (Nov. 2009),
- Windhuk, Namibia (Nov. 2010) and
- Port Louis, Mauritius (Nov. 2011).

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 in Addis Ababa was the discussion of the evaluation of the ninth PT round on chemical parameters and to find a way to sustainability of the PT scheme.
The improvement of cooperation between laboratories within the SADCWaterLab Association was also discussed during the workshop.

Participants

The chemistry workshop was attended by 36 participants from the following countries:

- Botswana 2
- DRC 2
- Ethiopia 9
- Kenya 3
- Lesotho 1
- Malawi 1
- Namibia 2
- Seychelles 1
- Swaziland 1
- Tanzania 7
- Uganda 3
- Zambia 1
- Zimbabwe 3

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

PT Workshop Programme

Monday, 19 November 2012:

Welcome, Opening, reports of local coordinators, reports from SADCWaterLab working groups, report of the PT provider

Tuesday, 20 November 2012:

Evaluation workshop, PMC meeting

Wednesday, 21 November 2012:

SADCWaterLab working group meetings, training, PMC meeting

Thursday, 22 November 2012:

SADCWaterLab General Assembly, lab visit at Ethiopian Conformity Assessment Enterprise (ECAE)

Monday, 19 November 2012

Welcome and Opening

The participants of the workshop were welcomed and the workshop was officially opened by

- Mr. Donald Masuku, SADCMET Regional coordinator, National metrology institute of South Africa
- Mr. Vivian Radegonde SADCWaterLab vice chair, Seychelles Bureau of Standards
- Ms. Kathrin Wunderlich, PTB
- Mr. Gashaw Tesfaye, Director of the Ethiopian Conformity Assessment Enterprise

Donald Masuku explained the programme of the workshop.

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 for participants of both workshops on their activities.

Angola
No representative

Botswana
Currently there are five Laboratories in Botswana that are potential participants. Three of them participated, one had problems to pay the fee. There are four additional laboratories in the mining industry, but they do not intend to participate.
The Water Utilities Center will be accredited soon.
The LC wants to organize a local training workshop in March or April 2013.

Democratic Republic of Congo
From the 20 labs in DRC (8 in the water sector) five laboratories participated in the PT. So there is hope that next year it will be eight participants. In 2012 a control charts training was conducted. More training is planned for 2013.

Lesotho
A national laboratory association was registered, but not all of the members are doing water testing. Visits to the labs were done to provide advice. Currently there is only one active lab in the water sector (Water Sewage Company). No training was organized by the trained trainers.

Ethiopia
Three labs have been contacted, but no budget was available to participate. A five-day training in ECAE was performed for measurement uncertainty estimation and validation of methods. Ethiopia has a national laboratory association which also is marketing the PT scheme.

Malawi
Changes in persons were the major challenges in Malawi. A national lab association was formed. This structure will be used to market the PT scheme. No training was organized.

Kenya
Marketing the PT scheme is an ongoing process. In 2012 15 laboratories participated and the LC is still trying to recruit more participants for the next years. Customs problems were encountered in 2012. Two trainings were organized: One on ISO 17025 at the National Quality Institute and one for the sugar sector at KENAS. Training was also offered in conjunction with the food PT evaluation workshop. In December 2012 a regional metrology conference will be organized.

Mauritius (written report)
10 laboratories were invited for participation, but finally only three of them participated. Different reasons for not participating were reported. MSB will continue to market the scheme.

Madagascar
No report available. Two labs participated

Namibia
There are three water laboratories in Namibia and all of them participated. Maybe one of the mining laboratories will participate in future. The questionnaire for the fish PT was forwarded to a laboratory in Walfishbay. A SADCAS training with a Swedish expert took place and a training on statistical method validation with Prof. Paul de Bievre. The National Standards Institute is trying to find our possibilities for a national laboratory association.

Seychelles
Only SBS participated in the PT although marketing was done to other labs. Currently there is no training planned.

Swaziland
The local coordinator passed away in 2012.
There are 7 laboratories for water analysis in Swaziland (two only occasionally). No one participated in the 2012 round. The low participation is mainly due to the currently very low economy. One laboratory was recently accredited for microbiology and soon also for chemistry. A national laboratory accreditation was just formed. One of the trainers trained in Livingstone is still present, but up to now there have been not enough participants to organize a training. This hopefully will change in 2013. Two laboratories are interested in a microbiology PT.

Tanzania
12 laboratories participated in the PT round.
Together with other trainers many training workshops have been organized (on ISO 17025, method validation, control charts, reference materials and other challenges). Continuity of staff and lack of awareness are the major problems. At the moment there is no national laboratory association in place, but a new structure for water quality labs will be installed with 16 labs for 25 regions within Tanzania.

Uganda
Five laboratories initially registered for the PT, but only four delivered results. The number of participants was limited, because parameters and matrix of the PT do not exactly match the needs of the labs. In future the LC will target those labs that exactly analyze the offered matrix. Training on QA issues was conducted in 2011. UNBS benefitted very much from the SACMET PT scheme in the accreditation process. Major challenges are the low awareness and difficult e-mail communication. Often there is no response, so phone calls are preferable.

Zambia
The local coordinator was not present. There should be more than seven laboratories for water testing, but only two participated. No information was available on activities of the local coordinator. Information was passed to five laboratories by Zambia Bureau of Standards (ZABS), but in those labs no budget for participation was available. No training from the trained trainers has taken place. A national laboratory association was registered early 2012 carrying out 3 trainings (GLP, validation, uncertainty). The rained trainers are members of the executive committee of the lab association. It is expected that the lab association increases awareness in QA topics.

Zimbabwe
Seven laboratories participated in the PT. The national laboratory association performed a 5-day-training in March 2012 with support from PTB on statistics, control charts, metrology, ISO 17025, validation, principle of PTs, SADCMET PT.

T. Ditsabatho: Report from the ToT working group

Teddy Ditsabatho explained the objectives of the ToT programme. Trained persons were obliged to perform training activities in their countries. A database of trainers was compiled. The following challenges were identified:

- Not all workshops were done as promised
- For workshops being done not in all cases this was reported to the secretariat
- Corrective actions were not done in all participating countries
- Staff turnover leads to unavailability of trained persons

Although there is the possibility of sponsorship for workshops from PTB, this opportunity was not used in all countries.
There were intensive discussions on the future of the ToT programme and how to ensure that training activities are done in all countries. Standard associations and national lab associations could help.
There was also a long discussion on how to do corrective actions. M Koch stated that all tools for corrective actions are given in the trainings. K Mbwambo summarized that mutual help between laboratories is crucial.

M. Conradie: Report from the methods working group

Methods for analyzing anions were collected and sent back to all participants. Only comments from Mauritius and the Seychelles were received. The chair of the working group was changed to Vivian Radegonde (Seychelles).

M. Conradie: Report of the PT provider

Merylinda Conradie gave a report on the 8th PT round. For the people participating for the first time she shortly introduced Namwater and gave a short overview on the project activities since 2004. With 57 participants in the PT round the overall number is quite stable, but the distribution between countries is changing. In 2012 there were a lot participants from Kenya and Tanzania (12 each), but for other countries it is still low or decreasing. An increasing number of participants would be beneficial in the interest of sustainability.
She also explained all the steps of the PT provision.
In detail she explained the gravimetric preparation of the PT samples and the calculation of the reference values including its uncertainties. Procedures for documentation storage of samples and dispatch including packaging and labelling were shown.
Evaluation and assessment was made as in the previous years using a reference value derived from gravimetric formulation as assigned value and the standard deviation of the data with fitness-for-purpose limits for the proficiency assessment. Scoring was made using z-scores.

- Angola: One laboratory paid the fee, but did not submit results
- In Kenya there was a serious delay due to customs problems. One lab from Kenya requested 2 parcels and an additional parcel was sent separately. In this case there was no customs problem. So it seems to be completely unpredictable.
- Again there were problems with files > 5MB. Such big files are blocked by NamWater IT and cannot be received
- Shortage of staff in and scheduling of a PT round between normal laboratory activities is an ongoing challenge.
- Registration forms in some cases were not received in time or sometimes not at all. So laboratory information and contacts are not available
- Registration forms often were not clear
- Return date for the results was 10th of August 2012, but last results were received in October only. This caused a delay with the evaluation report. Therefore the evaluation report was not distributed according to schedule

The complete presentation is enclosed in annex 2.

Tuesday, 20 November 2012

M. Conradie: PT evaluation results

Merylinda Conradie explained in detail the results of the evaluation, including the evaluation and assessment process, the performance scoring, and the limits for the standard deviation for proficiency assessment. She also showed the progress of parameters over the previous rounds and the concentration ranges used.
Then she went through all the parameters in detail with the following steps:

- Reference values and mean of participants as well as the results of the expert laboratories. Uncertainties were shown where available
- Graphical display of the means vs. the reference values
- Standard deviation of the data sets vs. the concentration including the limit used for the proficiency assessment
- Development of the standard deviation over the various PT rounds
- Development of the percentage of non-satisfactory results
- The performance development in the individual laboratories
- Graphical display and statistics of all data sets
- Percentage of methods used
- Comparison of methods
- A summary for the respective parameter.

The complete presentation is included in annex 3.

The summaries for all the parameters were as follows:

Sulphate:

- Average recovery (93,4%) was lower than in the last rounds
- STD are still quite high, especially for low conc.
- Still many data outside the limits, especially for the low level
- Gravimetric methods often delivers too low values
- Not a big change compared to 2011

Chloride:

- STD not much different from last rounds, maybe a bit better
- 24% of the data outside – no change
- Argentometric titration has many high values (exactly as in last rounds!)– incorrect recognition of endpoint?
- As in 2011 problems with spectrometric method

Fluoride:

- A lot of too high results for lowest level (21 out of 31 data) (all of the colorimetric results!)
- STD very similar to last year (very high, > 100%, for the low level)
- Increased percentage of non-satisfactory results (54%)
- Method specific evaluation exactly as in 2011
- All in all exactly the same problems as in 2011

Nitrate:

- More labs reporting in wrong units; labs either do not read / do not understand / are not able to calculate or convert to the correct unit
- STDs very high – mostly because of wrong units
- Percentage of non-satisfactory results again very high (units!) – 48%
- What means colorimetric? Many different methods behind that!

Phosphate:

- Again some labs reported in wrong units; therefore average recovery low
- STD a bit better 17 -30%
- Percentage of non-satisfactory results slightly better (31%)

TDS:

- Although it was clearly specified that a gravimetric determination is required – method information was not reported - “other”
- Methods were reported as “an electrode method”? These are obviously different measurands!!
- Average recovery of 95% is not too bad
- STD better than last year, but still too high
- Percentage of non-satisfactory results slightly better (30%), but it was made clear now, that the determination should be gravimetric

Conductivity:

- Obviously serious problems with units
- STD of the values with correct units are not bad
- Percentage of non-satisfactory results is very high (50%)

Calcium:

- Perfect average recovery
- STD – no change compared to 2011
- Percentage of non-satisfactory results 31% - no improvement
- Method specific evaluation very similar to 2011

Magnesium:

- More titrimetric results than in 2011 - with the problems of a high portion of too results for this method
- STD higher than last year
- Results worse than last year

Sodium:

- Problems with high results for lowest level – high blank?
- No improvement in the STDs
- Percentage of non-satisfactory results higher (41%) mainly due to problems with lowest level

Potassium:

- Average recovery is ok
- STDs higher than in previous rounds
- Percentage of non-satisfactory results with 34% a bit worse than in 2011

Iron:

- Problems with the lowest level – high blank?, high STD (68%!)
- Same picture as in 2011

Manganese:

- STDs much better than last year, comparable to previous rounds
- Improved percentage of non-satisfactory results (17%)

Aluminium:

- Higher concentrations than last year
- STDs similar to previous rounds
- Problems with the low level (52% of the results outside the limits)
- Problems with the colorimetric method

Lead:

- Obviously problems with the lowest level – high blank? high STD (83%!)
- STDs for the other levels is fine
- Similar picture for the methods

Copper:

- Similar performance to last year
- Good standard deviations - around 10 %

Zinc:

- Similar to last year
- But the STD for lowest level is significantly higher, maybe due to a lower conc.
- For the two higher levels everything is fine

Chromium:

- Blank problems with the lowest level?
- The mean of the labs is quite low in comparison with ISWA and IWW as well
- The calculation of the reference values were checked for transcription errors and confirmed to be correct
- The colorimetric methods again has a high number of too low values – is that a method to determine Cr(VI)?

Nickel:

- High STD for the lowest level just as in the previous rounds

Arsenic:

- Low number of values
- STDs higher
- Obviously problems with AAS

Cadmium:

- STDs better than last year, but in the same range as in the previous rounds

Cobalt:

- Slight improvement in the STDs

Overall picture

The number of parameters analyzed by the participants varies very much. Only 5 laboratories analyzed all parameters. Three of them were successful in all parameters.

Merylinda Conradie drew the following conclusions:

- There is no real improvement, the standard deviations are still high
- The same mistakes are being done as in previous rounds; e.g.

    - Reporting of results in wrong units (N and not NO_3^- and as P and not PO_4^{3-}
    - Use of non-standard methods
- Stating the concentration ranges obviously did not help to improve the results
- Corrective actions (investigate problems / determine the root cause) are still not implemented
- Recommended methods must be finalized and implemented

She identified the following challenges for 2013:

- Use old PT samples to implement corrective action immediately
- Use the ranges to avoid complete outliers
- Apply internal quality control
- Equipment, method comparison, assistance and continuous education amongst the SADCMET lab association is very important and a good platform for networking

Group discussions on the evaluation results

The participants divided into 4 groups to discuss issues around the PT round and the way to proceed. Several questions were given as a basis for discussion and the results of the discussions were then presented to all participants.

Is the selection of parameters still fit for purpose?

- Yes, but there is a need to consider other parameters – pesticides? (not in this scheme)
- Yes, but additional parameters should be considered (pH, Hg, Se)
- Yes, but consider to include alkalinity, total hardness and Hg

Decision: The PT provider will check the possibility to use anion sample to include pH

Are the concentrations ok?

- Yes, but WHO limits should be considered especially for cations (one level below the limit!)

Decision: PT provider will check the WHO guidelines

Are the standard deviation limits still ok?

- Yes, but in future they could be made uniform
- For now they should be maintained
- For anions to keep at 10%, cations to keep at 20%, for difficult analytes consider increasing to 25% (for low levels)

Decision: PT provider (together with consultant) will decide whether to increase limits for low concentrations

What could the PT provider do to resolve the problem with wrong units?

- It‘s not the task of the PT provider
- LCs should communicate to participants the issue of units and any other guidelines
- PT provider clearly states what unit to use
- In the reports to individual labs these problems should be highlighted
- Use national forums to discuss this issue

- The PT provider can do nothing; everything necessary is already done
- Results in wrong units should not be considered

Decision: PT provider will include a leaflet especially dealing with the unit problem

How can bad performing labs be convinced to do corrective actions?

- Forms to be provided by the PT provider for corrective action and root cause analysis
- Because of confidentiality issues the information should not go to 3rd party
- LCs to organise follow-up meetings
- Corrective paper to be recirculated with report every year
- Networking to be encouraged
- Lab association to take action (LC)
- LC to organise meetings with participants to highlight this
- Training on how to handle PT results
- PT provider to link labs

Decision: It was decided that no action is required.

Any suggestions for changing reporting of results in the workshop and in the written report?

- Information given is ok
- More information on methods would be beneficial
- Written report should be accompanied with a certificate and comment on the need for corrective action
- Summary instead of detailed report in the workshop
- Format for the report is ok; method information is valuable
- Written report: adding annex with a table of lab code, z-score and method information (no countries)

Decision: PT provider and consultant to decide how to shorten the report at the workshop

How to achieve sustainability?

- Cost analysis by the PT provider to get an idea what is needed
- LCs to market the scheme to potential participants
- Awareness creation on the benefits of the PT, target decision makers and lab community through different forums at national level (lab association)
- Labs should include PT participation in their budget
- Consider increasing fee from 200 $ to 250 $ (transportation costs around 250$ per parcel)
- Membership fees for lab association
- Encourage organisations to support their labs and the PT scheme
- Workshop to be reduced; training on national level
- Training with fees (partly supporting the PT scheme)
- Future hosts consider to use their own facilities to reduce costs

Decision: More discussions needed. Further decisions to be taken by SADCWaterLab Association.

What participation fee would be adequate and affordable?

- 200 $ is ok, depending on cost analysis
- PT provider to provide real costs to see what is realistic

Decision: To be decided after discussion of cost analysis

Do we need a workshop every year?

- At least every two years
- Yes, it‘s still needed for capacity building in the labs
- Yes, still necessary, but consider to have them on a 2 years basis

Decision: Workshop could be reduced to 2 days (one for evaluation, one for SADCWaterLab issues), use e.g. hosts‘ facilities, enable accommodation in cheaper hotels, on the longer term maybe workshop every two years

Wednesday, 21 November 2012

SADCWaterLab Working GroupS

Both working groups (Methods and ToT) had a meeting. The results of these discussions will be published in the SADCWaterLab Newsletter.

Training session on “Calibration”

Kezia Mbwambo (Tanzania) gave a training on “Calibration”. The complete presentation is included in annex 4.

Training session on “Metrology in Chemistry and Traceability of Measurement Results”

David Koech (Kenya) presented the principles of “Metrology in Chemistry and Traceability of Measurement Results”. His slides are included in annex 5.

Training session on “Reference Materials in Analytical Chemistry”

Vivian Radegonde (Seychelles) finalized the training with a presentation on “Reference Materials in Analytical Chemistry”. The slides are available in annex 6.

Thursday, 22 November 2012

SADCWaterLab General Assembly

SADCWaterLab had its General Assembly in the morning. There will be minutes prepared by the secretary.

As a summary the decision taken in the General Assembly are noted here:

- Fish-PT: Vivian Radegonde will contact IAEA in Monaco to find out if there possibilities to participate in their Fish-PT
- Next evaluation workshop: 3-day workshop (for evaluation, training and SADCWaterLab one day each); training will be given by external experts as a refresher for trained trainers; PTB will sponsor accommodation for 25 participants and food during the workshop.
- PT participation fee: will stay at 200 US-$ (total actual costs are currently around 400 US-$ per participant)
- SADCWaterLab Newsletter: contributions to be sent to secretariat by 15th January

- Local Coordinators reports: a quarterly review is required about what is going on in their respective country. This will be coordinated by the SADCMET secretariat.
- Microbiology PT: Many thanks to UNBS for their efforts. It turned out that it is not possible to transfer the German PT system to the African region (mainly due to climate and transportation issues). Other possibilities will be checked.
- Next PT round: announcement will go out end of February

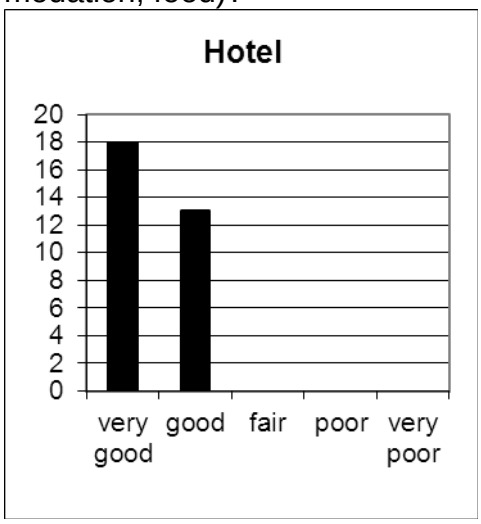
Evaluation questionnaire

M. Koch distributed an evaluation questionnaire (see annex 7) for the chemistry part of the workshop to be filled out by all participants.

The results of this questionnaire are given on the following pages:

Hotel and conference facilities

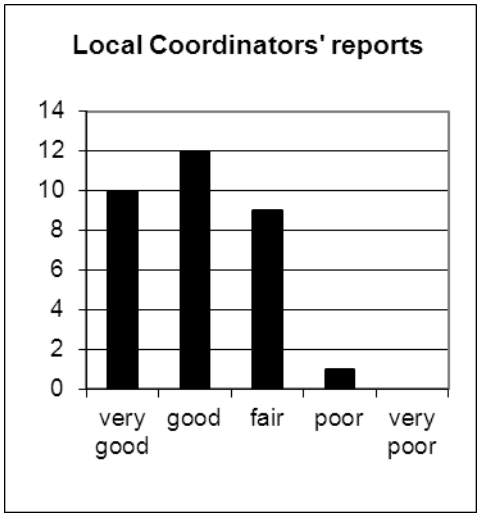
How do you judge the hotel (accommodation, food)?



How do judge the venue of the workshop (conference room)?

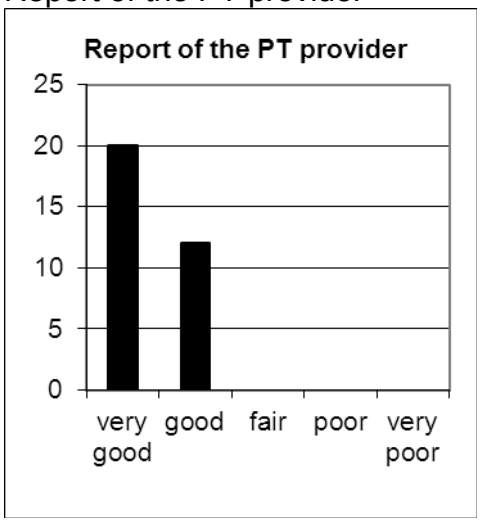
How do you judge the different parts of this workshop?

Local Coordinators' reports

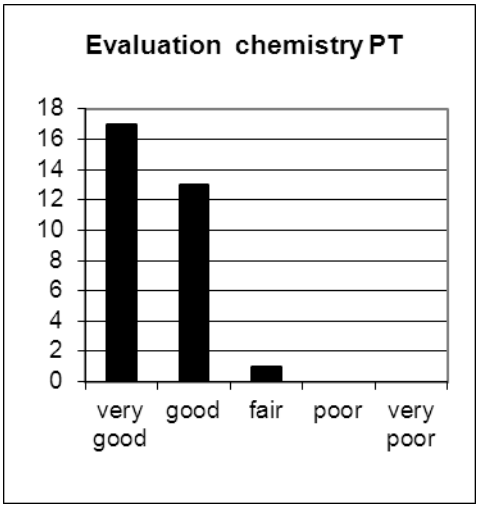


Reports from the SADCWaterLab working groups

Report of the PT provider

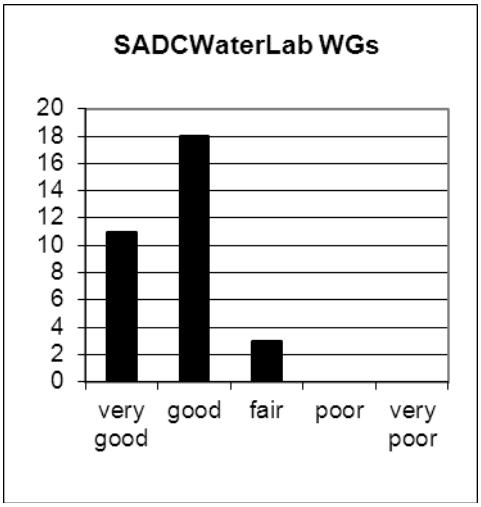


Evaluation of the PT

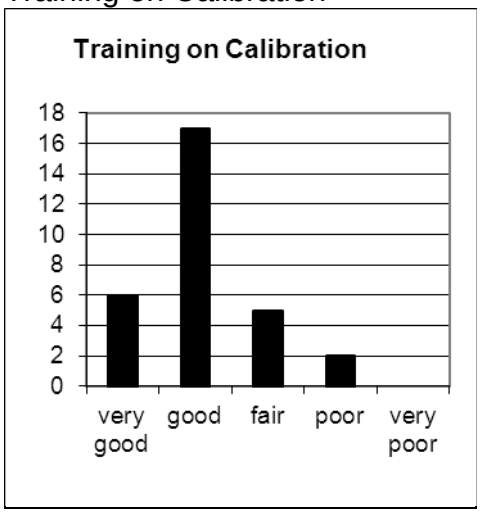


Discussion about necessary changes in the PT scheme and the way to sustainability

SADCWaterLab WGs “methods” and “training”

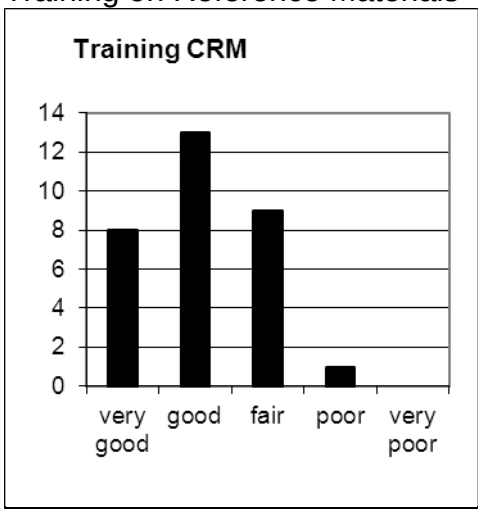


Training on Calibration

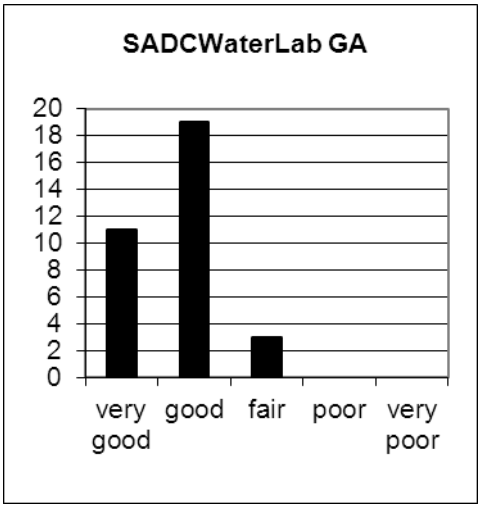


Training on Metrology in Chemistry

Training on Reference Materials



SADCWaterLab General Assembly



The five most important topics

- Training on calibration (22)
- PT evaluation (21)
- Training on Metrology in Chemistry (19)
- PT provider report (18)
- Training on CRM (18)
- Methods WG (9)
- Sustainability of PT without PTB (7)
- SADCWaterLab General Assembly (7)
- ToT WG (7)
- Local coordinators' reports (5)
- Discussion about necessary changes (3)
- Report from WG (3)
- Methods validation and measurement uncertainty (2)
- Local trainings (2)
- Group discussions (1)
- Importance of regional integration of labs (1)
- Control chart software (1)
- PT programme in the world (1)
- Root cause analysis and corrective action (1)

Expectations fulfilled?

29 participants answered „Yes“, one was partially satisfied (without giving any reasons), two participants were not satisfied because of the following reasons:

- I was expecting detailed discussion on each analysis and the way forward
- Reports from local coordinators are lacking in content

Benefits

- Performance of my laboratory over time and efficiency of corrective actions implemented.
- From this workshop I am benefited on recommendations about the methods and in what way the PT samples were prepared to adopt for interlaboratory comparison of analysts' performance.
- Networking and clarification of issues.
- Networking
- Networking with different technical personnel
- An urge to improve on Quality Control in testing labs
- (1) Importance of Quality Control and Quality Assurance. (2) Comparison of the different methods used in the PT process in terms of accuracy and efficiency
- Networking with participants
- Interaction with participants
- I have been able to discuss analytical problems facing several labs in our region and how these issues or problems can possibly be solved
- Learning and networking
- The ultimate benefit was the interactive nature of the workshop and the feedback on the PT results. Training was also equally impressively given.
- I realized the need for discussions
- Networking and understanding of the SADCMET programs and objectives
- Training
- As the first time in this workshop, I find the PT provider arrangement very useful
- Motivation
- On how best we can use best method for analysis of some parameters
- Networking and sharing of experience with other labs/participants
- Methods performing well and the opportunity to network
- Training
- Sharing and exchange of knowledge from lab community
- Importance of corrective actions and training
- Networking and information sharing
- It is good for experience sharing
- Shared experience with other colleagues
- I benefited a lot on calibration and using statistical date

Other comments

- I feel that PTB should have provided dinner on arrival night and on 22/11/12 seeing as they were paying for my night and breakfast on 22/11/12. I would like to express my sincere appreciation for the support that PTB has given us regarding this PT scheme. I would also like to appreciate the PT provider for the work she puts into preparing samples for us. I would also like to thank ECAE for the hospitality.
- Training: The "training" that was offered during the workshop were more of presentations rather than training. Consider referring to them as such or, if training is a necessary component of the workshop, then there should be an

evaluation of the effectiveness of training, i.e. test. There is also need to engage participants through exercises after each presentation.

- (1) Please ensure proper and organized local coordinator reports at the workshop. (2) Ensure all laboratories' personnel participating in the scheme are given opportunity to attend the workshop. (3) Provide more time in the workshop for exercise of the training topic to ensure understanding of the topics.
- I would like to see more practices on training than theories, e.g. on calibration topics you show people how to calibrate
- On the presentations it should be included which method would be best
- Enlighten on the need for accelerating process for accreditation of water testing labs
- Organizing such workshops and standardizing our labs at regional and national level is very important. In the coming year I will organize at least 4 PT training programs with or without external assistance

Report prepared by

Dr.-Ing Michael Koch
Stuttgart, 31.1.2013

Annex 01

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9th Proficiency testing scheme for chemical analysis of Water in Africa

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AQS Baden-Württemberg iswa

PTB

NAMWATER

NamWater

- Officially registered as a company on 9 December 1997
- The bulk water supplier for industries, municipalities and ministries
- Strive to supply a reliable source of quality water at the lowest possible rates
- Operates on a cost recovery basis
- Namibian Government is the sole shareholder

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Overview

- Participation per country
- Project activities
- Growth of the SACMET PT scheme
- % Presentation per country
- Steps of a PT round
- Details of the PT processes
- Evaluation & assessment
- Measurement uncertainty
- Closure

Project Activities

2004	The first workshop was held in February in Windhoek, Namibia, with participants from 16 countries where the need for a PT scheme was identified. Training on basic issues of quality in analytical laboratories was also addressed at this workshop.
2004	1st PT round; Evaluation workshop (Pretoria)
2005	2nd PT round; Evaluation workshop with training on measurement uncertainty (Dar es Salaam)
2006	3rd PT Round; Evaluation workshop with training on validation and control charts (Gaborone)
2007	4th PT round; Evaluation workshop (Dar es Salaam) with training on validation and measurement uncertainty
2008	5th PT round; Evaluation workshop (Kampala) with training on management requirements. October: Poster presentation at the Eurachem Workshop in Proficiency testing in analytical chemistry, microbiology and laboratory medicine in Rome

Project Activities II

2009	Test & Measurement conference : Presentation of Chemical analyses of water in Africa, South Africa 6th round; Evaluation workshop (Seychelles)
2010	7th round:Evaluation workshop (Windhoek) with training on estimation of measurement uncertainty using validation and quality control.
2011	8th round:Evaluation workshop (Mauritius) with training on Ensuring the Quality of Analytical Results – Trueness and Precision October: Poster presentation at the Eurachem Workshop in Proficiency testing in analytical chemistry, microbiology and laboratory medicine in Istanbul

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Participation per country

	2006	2007	2008	2009	2010	2011	2012
Angola	0	0	1	0	0	0	0
Botswana	2	4	2	3	3	3	3
Burundi					1	1	1
Congo					4	5	3
Ethiopia	1	0	0	0	0	1	1
Ghana						1	0
Kenya	5	3	3	7	9	7	12
Lesotho	1	1	1	1	1	1	1
Madagascar	2	2	3	3	2	2	2
Malawi	2	3	1	1	2	2	1
Mauritius	4	3	5	6	6	5	4
Mosambique	2	0	0	0	0	0	0
Namibia	3	3	3	3	3	3	3
Rwanda					1	1	1
Seychelles	2	1	1	1	1	1	1
South Africa	0	1	1	1	1	1	1
Swaziland	0	1	2	3	0	0	0
Tanzania	6	12	11	12	13	10	12
Uganda	5	5	5	5	4	5	4
Zambia	2	3	1	3	3	1	1
Zimbabwe	2	5	5	5	4	4	6
TOTAL	39	47	45	54	58	54	57

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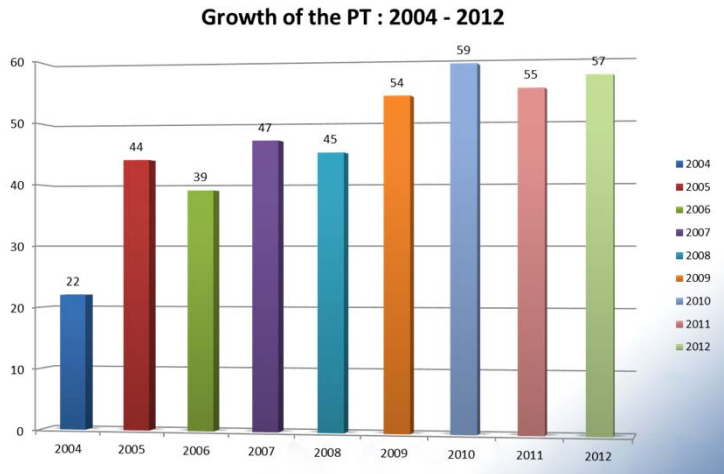
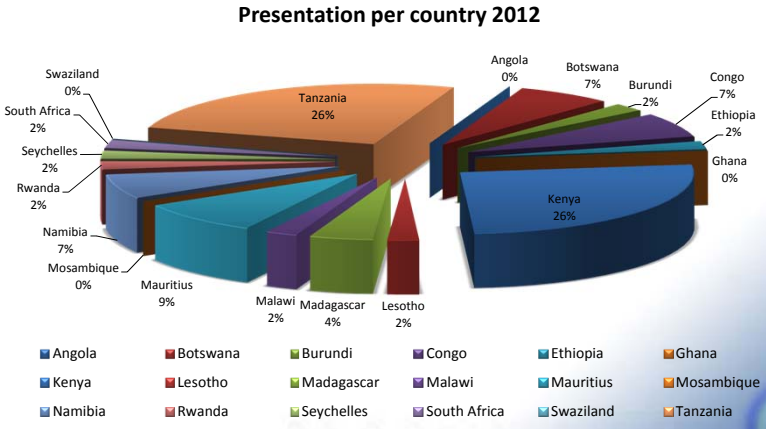
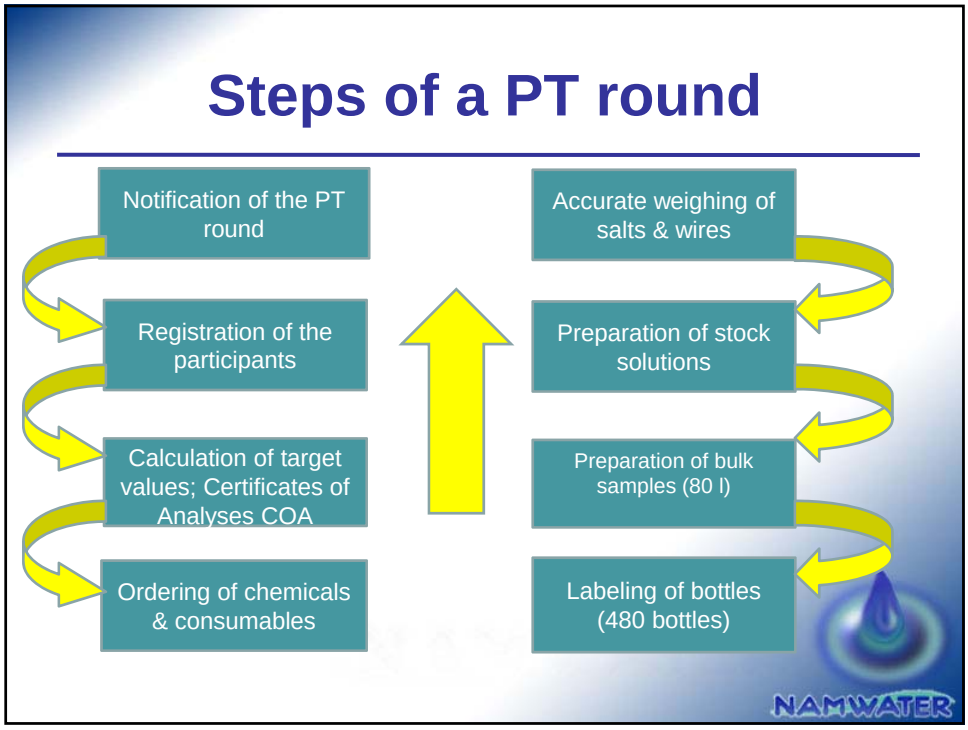
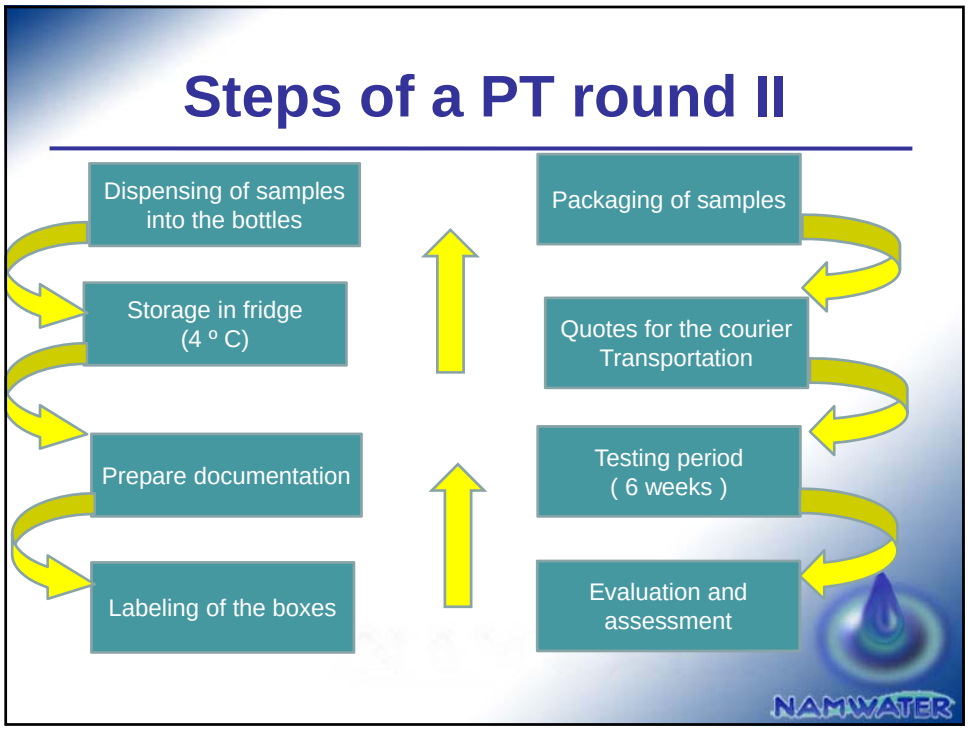
Growth of PT SADCMET Scheme



% Representation / Country




Steps of a PT round
Notification of the PT round
Registration of the participants
Calculation of target values; Certificates of Analyses COA
Ordering of chemicals & consumables
Accurate weighing of salts & wires
Preparation of stock solutions
Preparation of bulk samples (80 l)
Labeling of bottles (480 bottles)
NAMWATER


Steps of a PT round II
Dispensing of samples into the bottles
Storage in fridge (4 ° C)
Prepare documentation
Labeling of the boxes
Packaging of samples
Quotes for the courier Transportation
Testing period (6 weeks)
Evaluation and assessment
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Sample bottle preparation

- Wash all 480 bottles twice with deionised water
- Bottles & caps were put in the oven @ 60 °C overnight
- Check dryness
- Cap bottles to prevent them from dust
- Label and store them until needed

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Labeling of bottles

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Weighing of substances

Start of by weighing the different target masses for the 3 levels of each parameter in a beaker, difference, balance 1

Start of with the wires , digest wires until completely dissolved, continue with salts

Continue to prepare the stock solution

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Digestion of the wires

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Preparation of stock solutions

Weigh empty flask, transfer of substance into flask, fill, weigh full flask, balance 2

Dilution (where necessary) – Weigh 100g of diluted stock solution in beaker, difference weighing, balance 2

Repeat for all 20 parameters – 3 levels

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Preparation of bulk samples

Weigh empty 100 l container and stirrer, balance 3
Weigh empty 25 l container , balance 3

Partly filled container with water
Fill with deionised water only

Rinse solution solutions in 100 l container to nearly complete

Calculate target weight from density 0,998 g/ml

Fill to target weight I, balance 3
Fill to target weight I, balance 3

Stir for combined solution for 20 minutes

Fill samples bottles

Determine the density of samples

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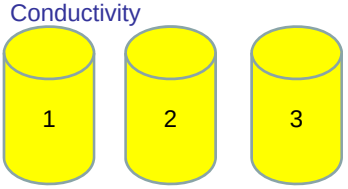
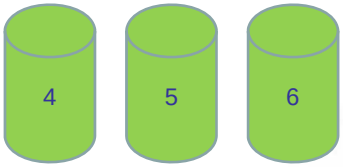
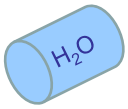
Preparation of bulk samples

Anions : SO_4, Cl, NO_3, F, PO_4, TDS, Conductivity



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





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Sample dispensing

Samples bottles (80) were filled after each batch

↓

Put in crates in fridge at 4 º C

↓

Tank washed properly (3 x) in between the batches

↓

Start to prepare for the next batch

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Storing of the samples

Fridge

- Space limited in the fridge
- Stack the samples in crates
- Samples were stored at 4 ° C until all six batches were prepared

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

Packaging of the samples

Packaging of the samples

Labeling & sorting

Sample pick-up and dispatch

Transport of parcels DHL , 29 June 2012

Calculation of reference values

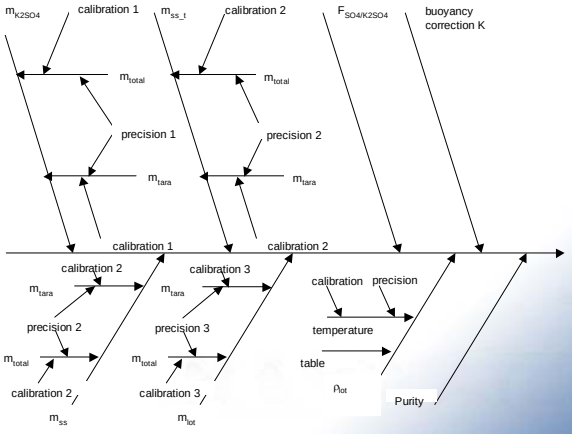
- Identify all sources of uncertainty in the analytical measurements and list them with the use of a fishbone diagram.
- The identified sources were:
  - Purities the chemicals
  - Uncertainty of the three balances used:
    - Sartorius Balance ED124S
    - Sartorius Balance ED42025-CW
    - Sartorius Balance FBG64EDE-H
  - Uncertainties of molecular mass were neglected
  - Densities of final samples
  - Buoyancy

Measurement uncertainty of reference values

- The combined standard uncertainties (mg/l), the combined relative standard uncertainty (%) , the combined expanded uncertainties (mg/l) and the combined relative standard uncertainty (%) were calculated and reported.
- The size of the different contributions was compared using a histogram showing all the standard uncertainties.
- The reference values were calculated with the combined expanded standard uncertainty taken into consideration for all the parameters for the different levels.

Identification of uncertainties using fishbone diagram

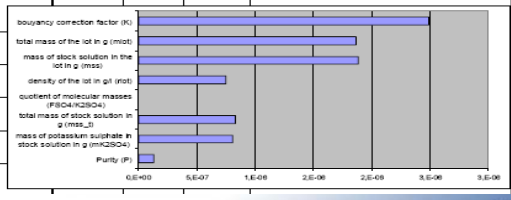
$$c_{lot} = \frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot m_{ss} \cdot \rho_{lot}}{m_{ss\_t} \cdot m_{lot} \cdot K}$$



Calculation of measurement uncertainty

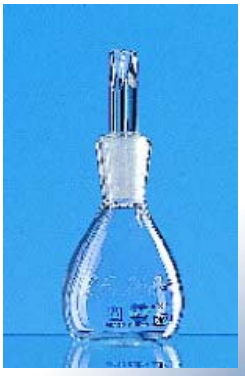
$$c_{lot} = \frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot m_{ss} \cdot \rho_{lot}}{m_{ss\_t} \cdot m_{lot} \cdot K}$$

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	$\frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot m_{ss} \cdot \rho_{lot}}{m_{ss\_t} \cdot m_{lot} \cdot K}$	0,022641974
mass of potassium sulphate in stock solution in g (m_{K2SO4})	5,1308				0,000163291	$\frac{F_{SO_4/K_2SO_4} \cdot P \cdot m_{ss} \cdot \rho_{lot}}{m_{ss\_t} \cdot m_{lot} \cdot K}$	0,004412908
total mass of stock solution in g (m_{ss_t})	501,44				0,016412909	$-\frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot m_{ss} \cdot \rho_{lot}}{m_{ss\_t}^2 \cdot m_{lot} \cdot K}$	-4,51535E-05
quotient of molecular masses ($F_{SO4/K2SO4}$)	0,55126425				0	$\frac{m_{K_2SO_4} \cdot P \cdot m_{ss} \cdot \rho_{lot}}{m_{ss\_t} \cdot m_{lot} \cdot K}$	0,041072403
density of the lot in g/l (ρ_{lot})	997,5835337				0,032977359	$\frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot m_{ss}}{m_{ss\_t} \cdot m_{lot} \cdot K}$	2,26966E-05
mass of stock solution in the lot in g (m_{ss})	201				0,016735821	$\frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot \rho_{lot}}{m_{ss\_t} \cdot m_{lot} \cdot K}$	0,000112646
total mass of the lot in g (m_{lot})	49901				4,111707712	$-\frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot m_{ss} \cdot \rho_{lot}}{m_{ss\_t} \cdot m_{lot}^2 \cdot K}$	-4,53733E-07
bouyancy correction factor (K)	1,001031487				0,00011	$-\frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot m_{ss} \cdot \rho_{lot}}{m_{ss\_t} \cdot m_{lot} \cdot K^2}$	-0,022618417
result (g/l)	0,022641747						u_c
result in mg/l	**22,64174733**						
standard uncertainty in mg/l	**0,063891594**						
rel Unsicherheit	**0,02%**						
erw. Unsicherheit	**0,007783987**						
erw. rel. Unsicherheit	**0,03%**						



Density

- Samples and a bottle with pure water were put in the weighing room.
- Temperature of the water and the samples were measured using a calibrated thermometer.
- A 100 ml empty pycnometer was weighed 10 times.
- Pycnometer was filled with water and weighed again 10 times.
- Between each measurement the pycnometer was opened and filled again - uncertainty of the filling process.
- The pycnometer was filled and weighed with the samples (3 x)
- The densities and uncertainty of the measurements were calculated.



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Biggest uncertainty components from histograms

Mass of the stock solution

- F, Fe, Mn, Al,
- Pb, Cu, Zn, Cr,
- Ni, As, Cd,Co

Purity

- K_2SO_4,KCl,KNO_3,
- KH_2PO_4,CaCl,
- $Mg(NO_3)_2.6H_2O$,NaCl,
- Cr

NAMWATER

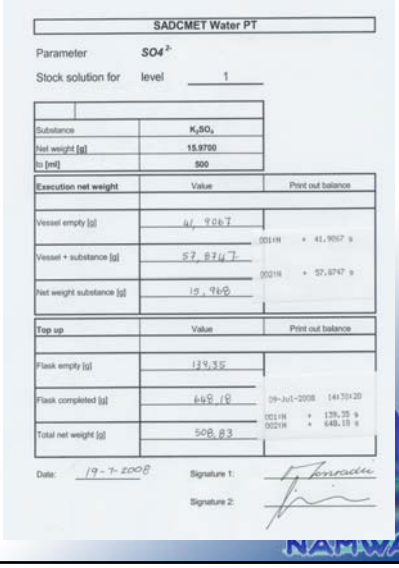
Documentation

Certificates are documented:

- Certificate of analyses (COA) for reagents used
- Calibration certificate for thermometer
- Calibration certificate for pycnometer
- Calibration certificates for balances

Documentation of weighing

- Proof of printings were pasted against all weighings
- Cut and pasted next to the written weighing for proof of the traceability
- Calculations are 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	0011N + 41.9067 g
Vessel + substance [g]	57.8747	0021N + 57.8747 g
Net weight substance [g]	15.968	

Top up	Value	Print out balance
Flask empty [g]	139.35	
Flask completed [g]	648.18	09-Jul-2008 14:30:20 0011N + 139.35 g 0021N + 648.18 g
Total net weight [g]	508.83	

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

Problems during 2012

- Angola: Paid but did not submit results
- Kenya: Delay with customs
- Kenya: One lab requested 2 parcels and an additional parcel was sent without any delays.
- Again problems with files > 5MB is blocked by NamWater IS and cannot be received
- Shortage of staff in and scheduling of a PT round between normal laboratory activities is a challenge.

Problems

- Registration forms not received in time or some not at all
- Laboratory information and contacts are not available
- Registration forms often not all clear
- Return date for the results : 10th of August 2012
- Last results were received in October only
  - caused a delay with evaluation report
- The evaluation report not distributed according to schedule

Closure

Evaluation of the 9th SADCMET Water PT

Evaluation Workshop
Ethiopia 2012

Merylinda Conradie *Pr. Sci.Nat*
NamWater
Water Quality and Environmental Sciences

Dr.-Ing Michael Koch
Institute for Sanitary Engineering, Water Quality and Solid Waste Management
University of Stuttgart

Evaluation and assessment

- Reference values are calculated the from synthetic, gravimetrical samples with an uncertainty budget
- Calculation of standard deviation is done by using the Algorithm A method from ISO 13528 provided it is lower than the calculated value
- Where the calculated value is higher, the fitness-for-purpose value is used.
- The fitness-for-purpose [limit] value was agreed on between participants.
- Elimination of gross outliers - 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
- Assistance is provided for laboratories that need corrective actions

Performance scoring

- The assessment of performance is based on Z-scores
- Z-scores are a common practise in the assessment of laboratory results
- Z-scores reflects the 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 between - 2 and 2.
- The sign (i.e., + or -) of the score indicates a negative or positive error respectively.
  - $|z\text{-score}| \leq 2.0$ - satisfactory
  - $2.0 < |z\text{-score}| < 3.0$ - questionable
  - $|z\text{-score}| \geq 3.0$ - unsatisfactory

Limits for standard deviation 2012

	std limit	parameter	std limit
Sulphate	10 %	Iron	20 %
Chloride	10 %	Manganese	20 %
Fluoride	10 %	Aluminium	20 %
Nitrate	10 %	Lead	20 %
Phosphate	10 %	Copper	20 %
TDS	10 %	Zinc	20 %
Conductivity	10 %	Chromium	20 %
Calcium	10 %	Nickel	20 %
Magnesium	10 %	Cadmium	20 %
Sodium	10 %	Arsenic	20 %
Potassium	10 %	Cobalt	20 %

Changes and Progress of parameters

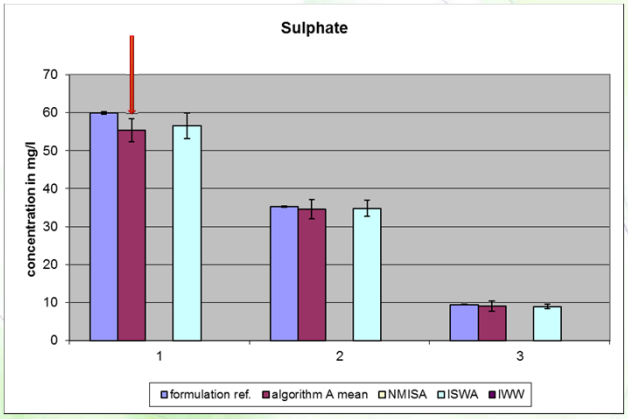
Parameter	Concentration in mg/l
PT round 1-8	
Calcium	8.4 – 60.50
Magnesium	7.45 – 55.30
Sodium	8.5 – 80.50
Potassium	5 – 22.40
Iron	0.09 – 4.61
Manganese	0.05 – 5.1
Aluminum	0.05 – 4.41
Sulphate	9.5 – 70.5
Chloride	12.6 – 73.4
Fluoride	0.21 – 2.54
Nitrate	9.1 – 88.0

Parameter	Concentration in mg/l
Additionally in PT round 2 - 8	
Lead	0.1 – 3.33
Copper	0.35 – 4.05
Zinc	0.45 – 5.89
Chromium	0.05 – 2.90
Nickel	0.15 – 3.55
Phosphate	3.2 – 30
Additionally in PT round 3 - 8	
Arsenic	0.05 – 0.75
Cadmium	0.05 – 1.20
Additionally in PT round 5 - 8	
Cobalt	0.15 – 2.68
Additionally in PT round 8	
TDS	120.6 – 382.8
Additionally in PT round 9	
Conductivity	38.8 - 41.1

Ranges for parameters

Parameter	Ranges	Parameter	Ranges
Sulphate	0-100 mg/l	Iron	0- 5.0 mg/l
Chloride	0-100 mg/l	Manganese	0- 5.0 mg/l
Fluoride	0-10 mg/l	Aluminum	0- 5.0 mg/l
Nitrate	0-50 mg/l	Lead	0- 5.0 mg/l
Phosphate	0-50 mg/l	Copper	0- 5.0 mg/l
TDS	0-1000 mg/l	Zinc	0- 5.0 mg/l
Conductivity	0-50 mS/m	Chromium	0- 5.0 mg/l
Calcium	0-100 mg/l	Nickel	0- 5.0 mg/l
Magnesium	0-50 mg/l	Cadmium	0- 5.0 mg/l
Sodium	0-100 mg/l	Arsenic	0- 5.0 mg/l
Potassium	0-50 mg/l	Cobalt	0- 5.0 mg/l

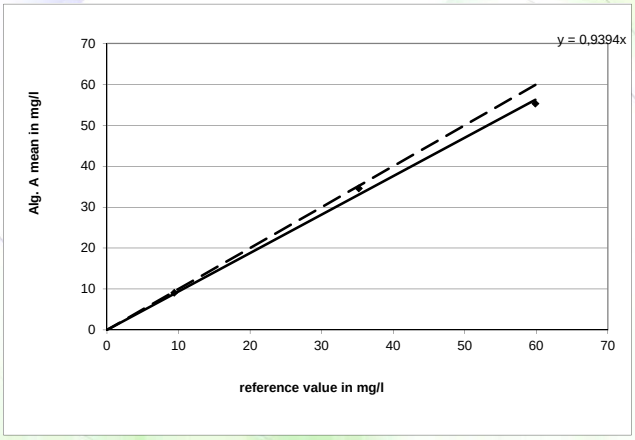
Sulphate
mean vs. ref.-value



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

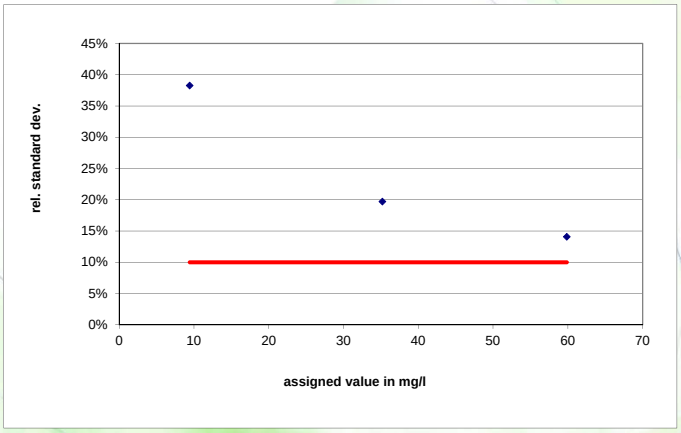
Exp. uncertainty of the ref.-value from an uncertainty budget

Sulphate
Alg. A mean vs. Reference value

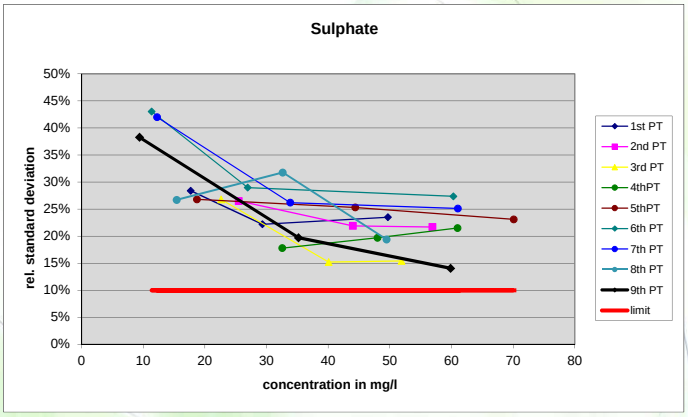


Average recovery	
2012	93.4
2011	100,7
2010	98,8
2009	106.0
2008	99.6
2007	103.6
2006	106.5

Sulphate
Calculated standard deviation and limit

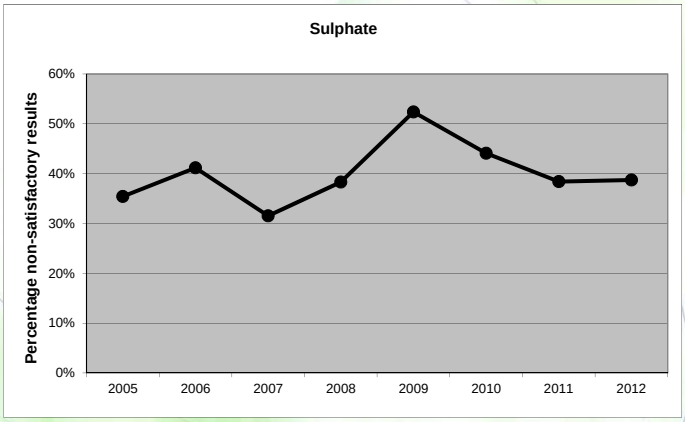


Sulphate
calculated standard deviation and limit



Std deviation still above the limit

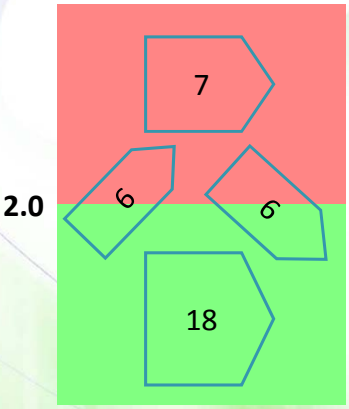
Sulphate
Percentage non-satisfactory results



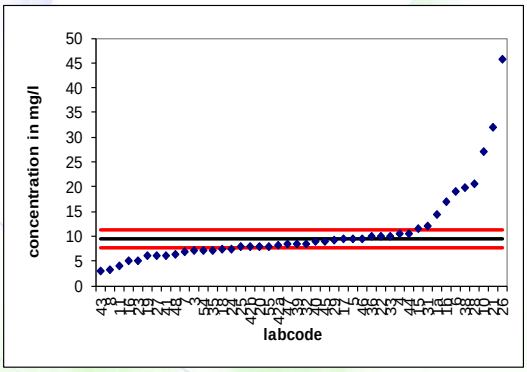
Individual performance development

- For all labs also participating in the previous years
- Calculation of the mean of the absolute values of z-scores of the 3 values
- Graphical display
  - 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

Sulphate
Individual performance development

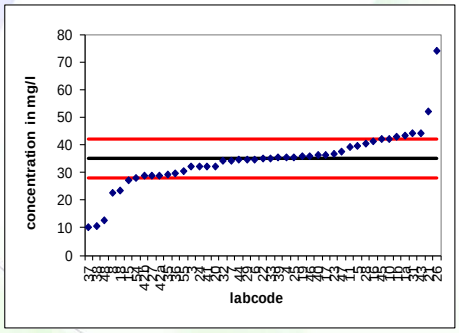


Sulphate 1



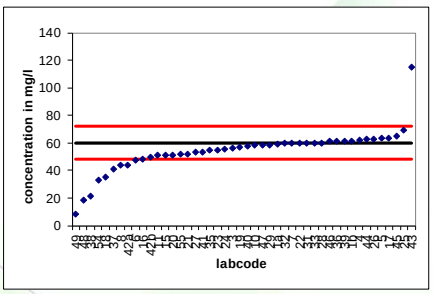
values:	46
removed:	2
mean:	9,06
ref.-value:	9,42
recovery:	96,2%
std:	3,605
rstd:	38,3%
std limit:	10%
upper limit:	11,31
lower limit:	7,54
too high:	10
too low:	17
outside limits:	27

Sulphate 2



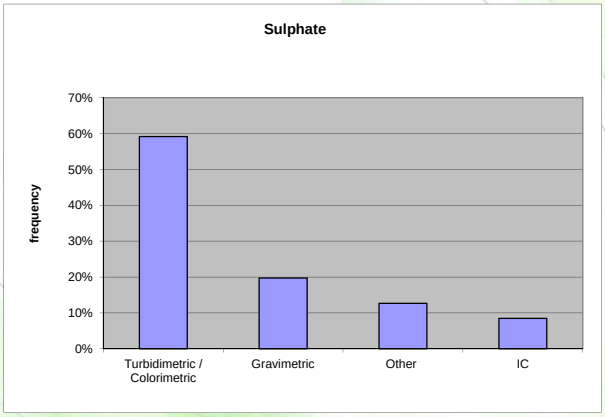
values:	48
removed:	3
mean:	34.58
ref.-value:	35.21
recovery:	98.2%
std:	6.936
rstd:	19.7%
std limit:	10%
upper limit:	42.25
lower limit:	28.17
too high:	6
too low:	10
outside limits:	16

Sulphate 3

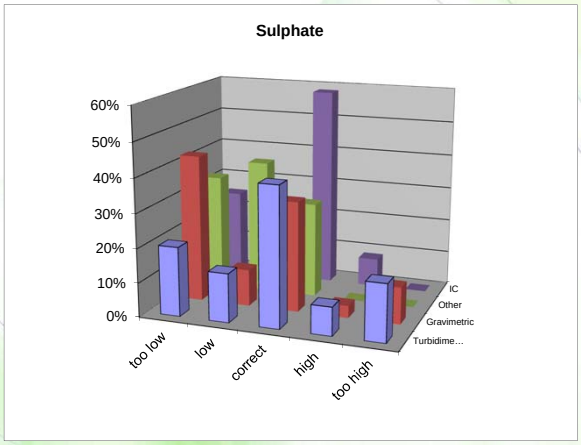


values:	48
removed:	2
mean:	55.33
ref.-value:	59.88
recovery:	92.4%
std:	8.415
rstd:	14.1%
std limit:	10%
upper limit:	71.85
lower limit:	47.90
too high:	1
too low:	11
outside limits:	12

Methods used



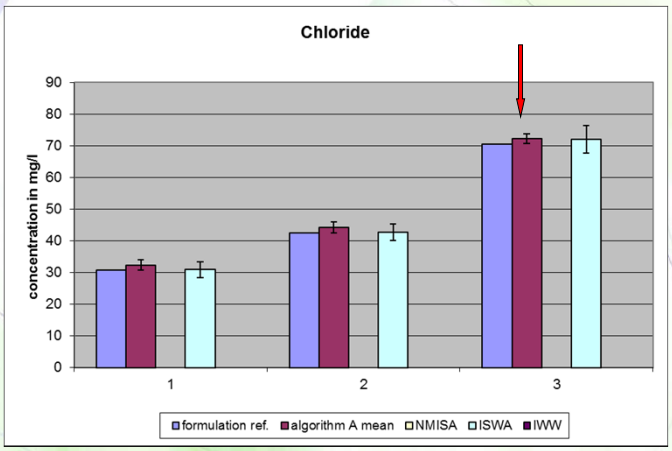
Comparison of methods



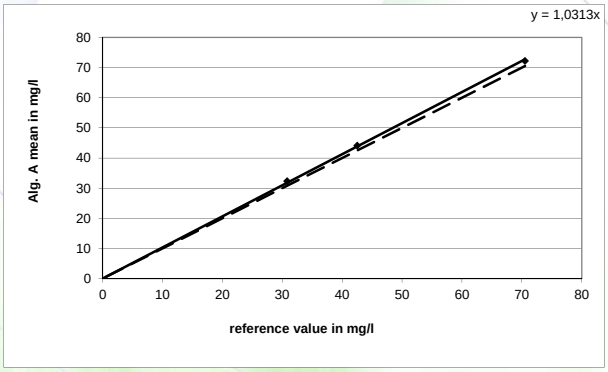
Summary Sulphate

- Average recovery (93,4%) was lower than in the last rounds
- STD are still quite high, especially for low conc.
- Still many data outside the limits, especially for the low level
- Gravimetric methods often delivers too low values
- Not a big change compared to 2011

Chloride
mean vs. ref.-value

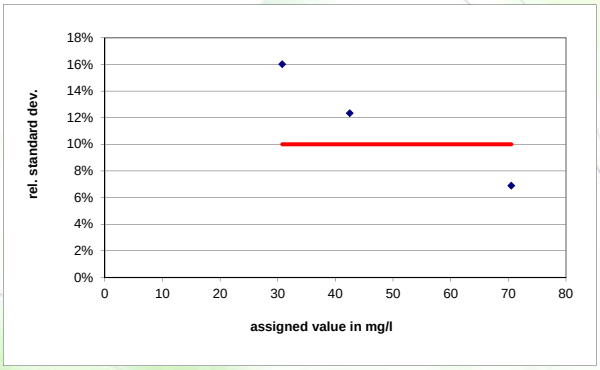


Chloride
Alg. A mean vs. Reference value

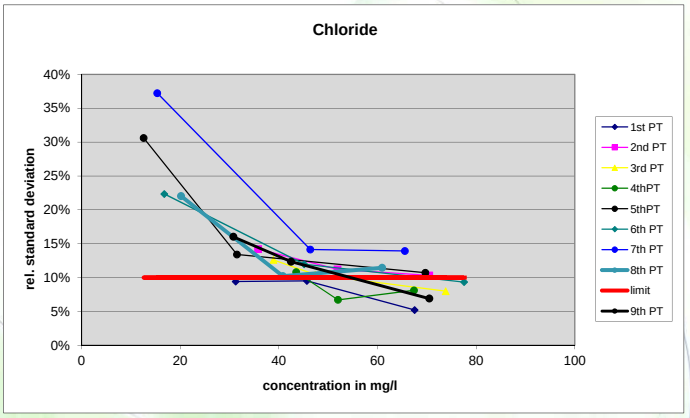


Average recovery	
2012	103.1
2011	102,1
2010	105,2
2009	102.2
2008	101.0
2007	102.4
2006	101.6

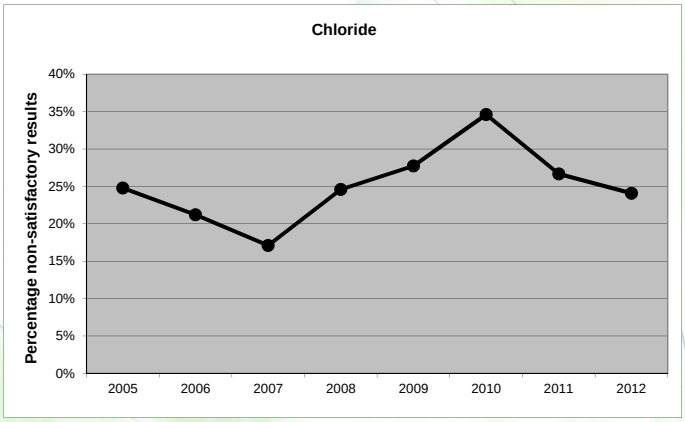
Chloride
Calculated standard deviation and limit



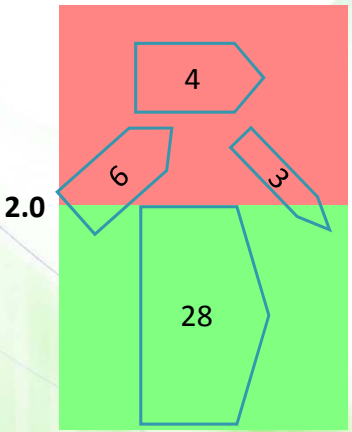
Chloride
calculated standard deviation and limit



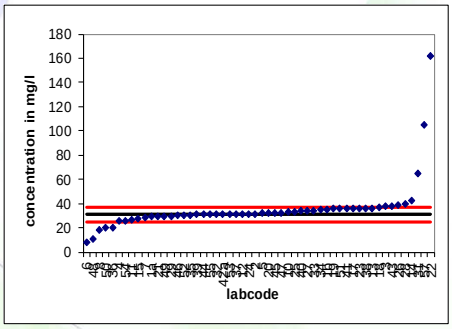
Chloride
Percentage non-satisfactory results



Chloride
Individual performance development

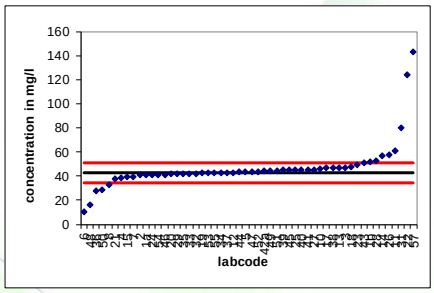


Chloride 1



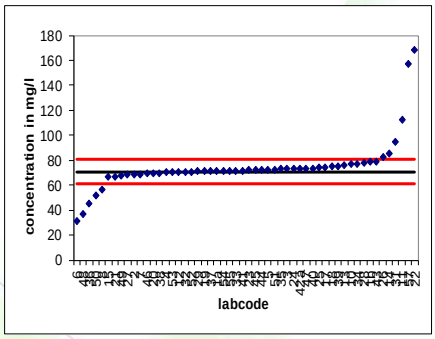
values:	54
removed:	0
mean:	32.38
ref.-value:	30.79
recovery:	105.2%
std:	4.929
rstd:	16.0%
std limit:	10%
upper limit:	36.95
lower limit:	24.63
too high:	9
too low:	5
outside limits:	14

Chloride 2



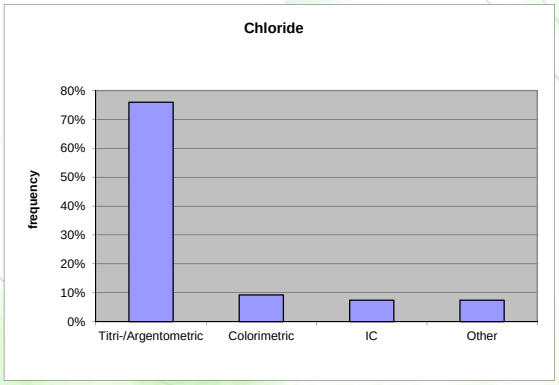
values:	54
removed:	0
mean:	44.14
ref.-value:	42.50
recovery:	103.9%
std:	5.242
rstd:	12.3%
std limit:	10%
upper limit:	50.99
lower limit:	34.00
too high:	9
too low:	5
outside limits:	14

Chloride 3

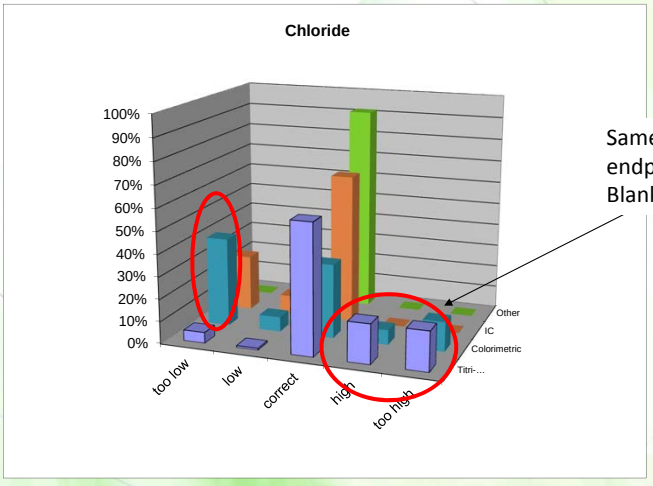


values:	54
removed:	0
mean:	72.27
ref.-value:	70.52
recovery:	102.5%
std:	4.858
rstd:	6.9%
std limit:	10%
upper limit:	80.24
lower limit:	60.81
too high:	6
too low:	5
outside limits:	11

Methods used



Comparison of the methods



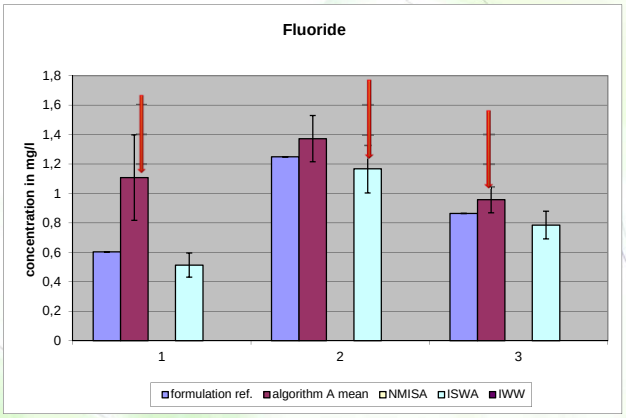
Same problems with endpoint detection & Blank subtraction?

Exactly as in 2009; 2010 and 2011

Summary Chloride

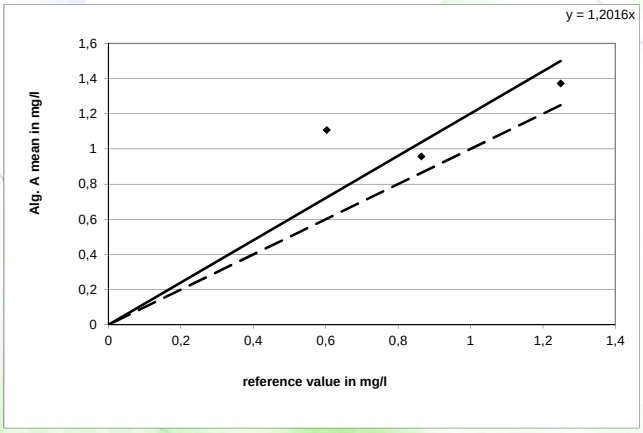
- STD not much different from last rounds, maybe a bit better
- 24% of the data outside – no change
- Argentometric titration has many high values (exactly as in last rounds!)– incorrect recognition of endpoint?
- As in 2011 problems with spectrometric method

Fluoride
mean vs. ref.-value



Fluoride

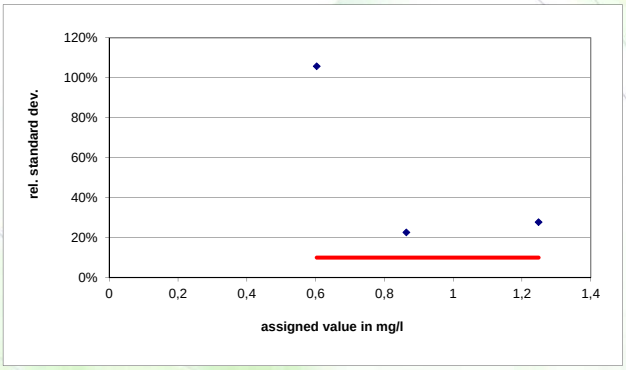
Alg. A mean vs. Reference value



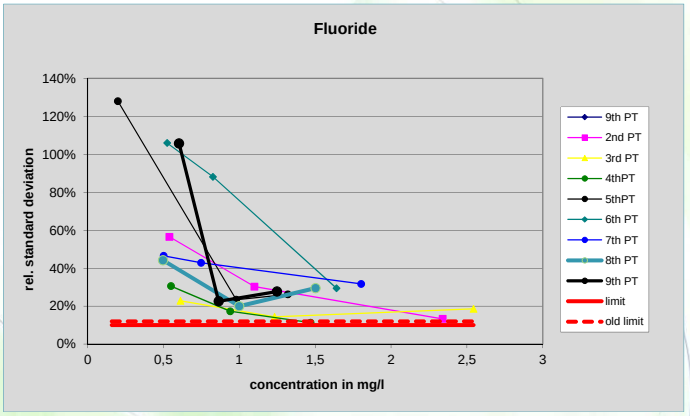
Average recovery	
2012	120.2
2011	96
2010	98,7
2009	107.1
2008	112.0
2007	98.2
2006	107.7

Fluoride

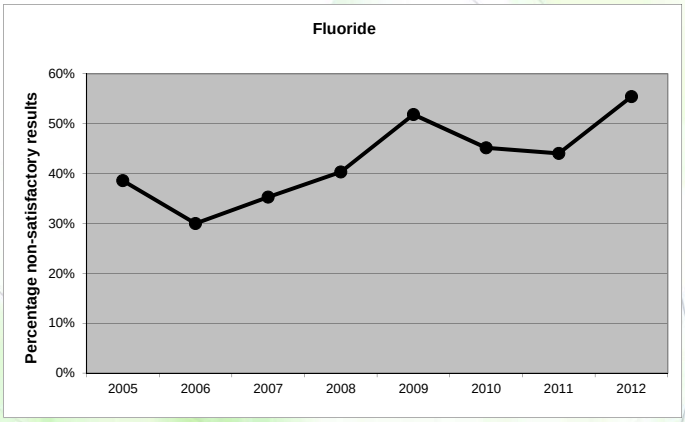
Calculated standard deviation and limit



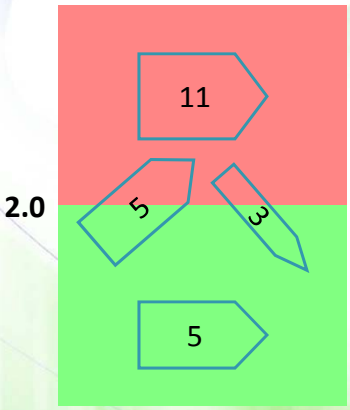
Fluoride
calculated standard deviation and limit



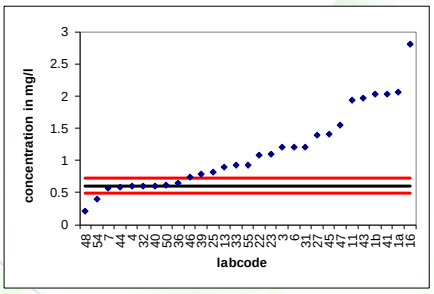
Fluoride
Percentage non-satisfactory results



Fluoride
Individual performance development

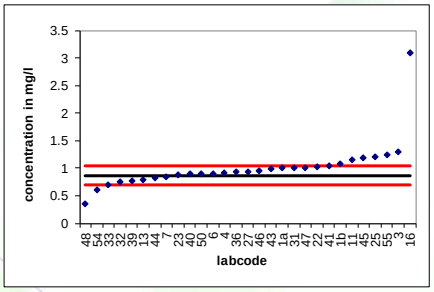


Fluoride 1



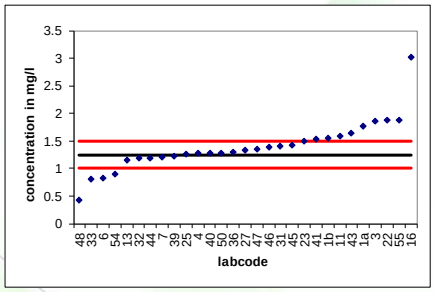
values:	31
removed:	2
mean:	1.11
ref.-value:	0.60
recovery:	183.6%
std:	0.638
rstd:	105.7%
std limit:	10%
upper limit:	0.72
lower limit:	0.48
too high:	21
too low:	3
outside limits:	24

Fluoride 2



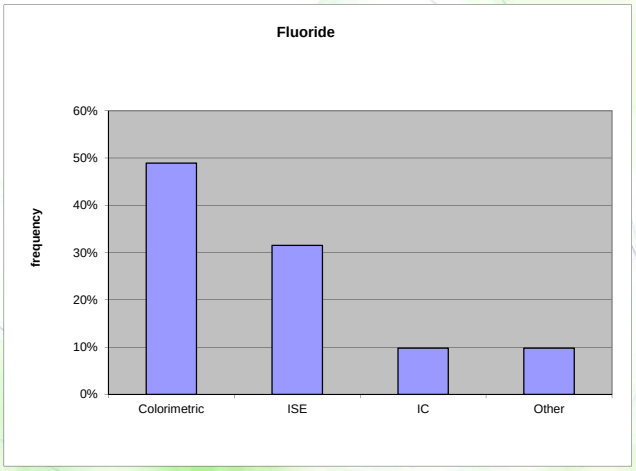
values:	30
removed:	1
mean:	0.96
ref.-value:	0.86
recovery:	110.8%
std:	0.195
rstd:	22.6%
std limit:	10%
upper limit:	1.04
lower limit:	0.69
too high:	9
too low:	2
outside limits:	11

Fluoride 3

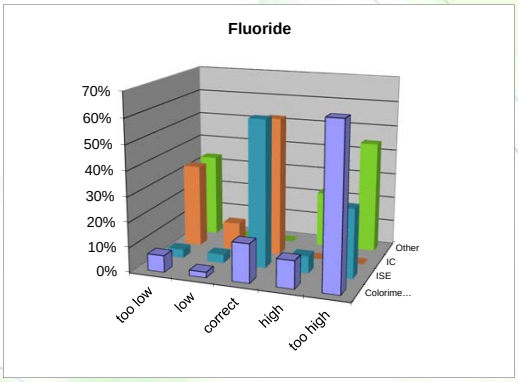


values:	31
removed:	2
mean:	1.37
ref.-value:	1.25
recovery:	109.9%
std:	0.346
rstd:	27.7%
std limit:	10%
upper limit:	1.50
lower limit:	1.00
too high:	11
too low:	5
outside limits:	16

Methods used



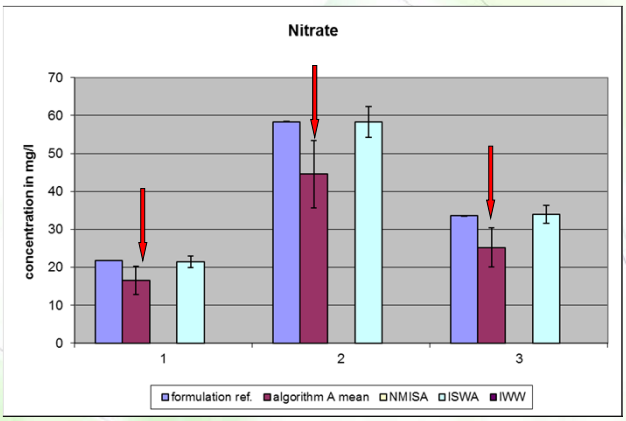
Comparison of the methods



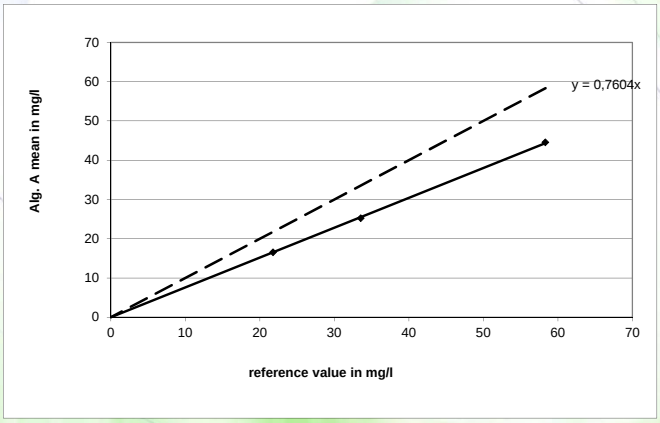
Summary Fluoride

- A lot of too high results for lowest level (21 out of 31 data) (all of the colorimetric results!)
- STD very similar to last year (very high, > 100%, for the low level)
- Increased percentage of non-satisfactory results (54%)
- Method specific evaluation exactly as in 2011
- All in all exactly the same problems as in 2011

Nitrate
mean vs. ref.-value

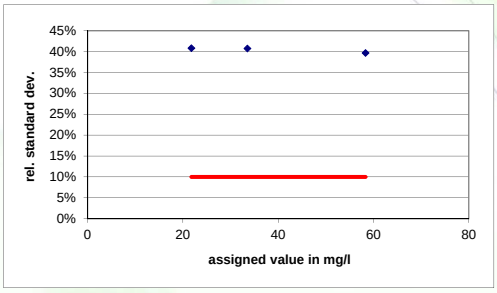


Nitrate
Alg. A mean vs. Reference value

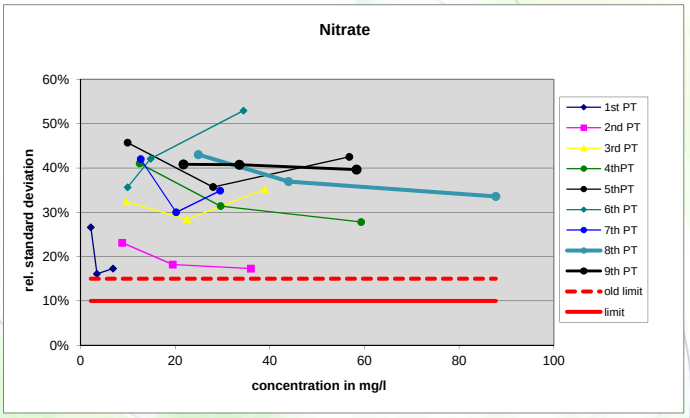


Average recovery	
2012	70.0
2011	81,3
2010	88,7
2009	94.3
2008	92.0
2007	85.9
2006	90.6

Nitrate
Calculated standard deviation and limit

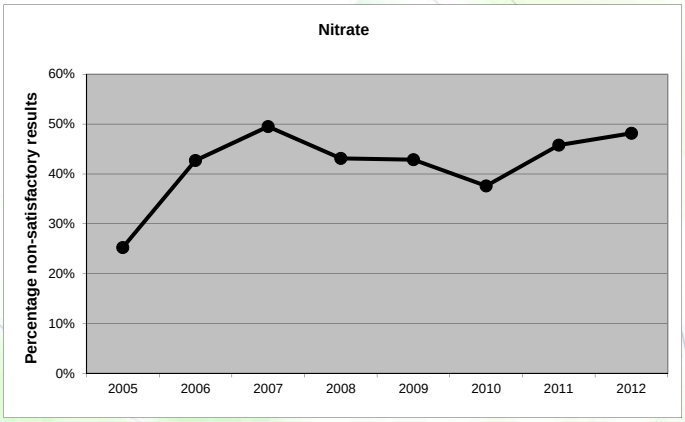


Nitrate
calculated standard deviation and limit

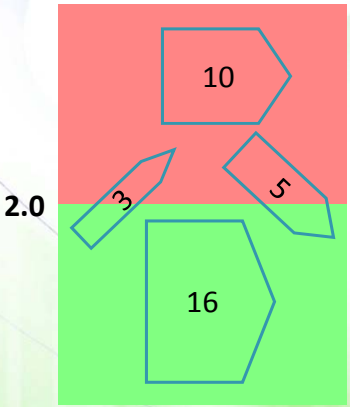


Standard deviations still very high – worse than 2011

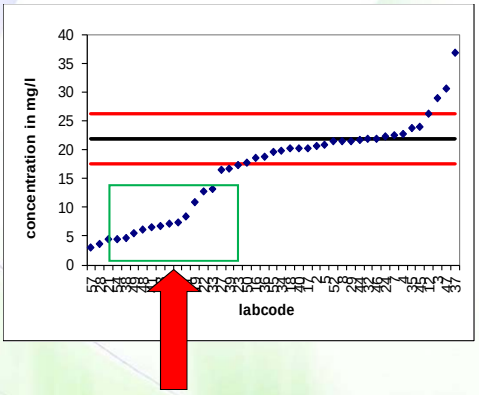
Nitrate
Percentage non-satisfactory results



Nitrate
Individual performance development



Nitrate 1

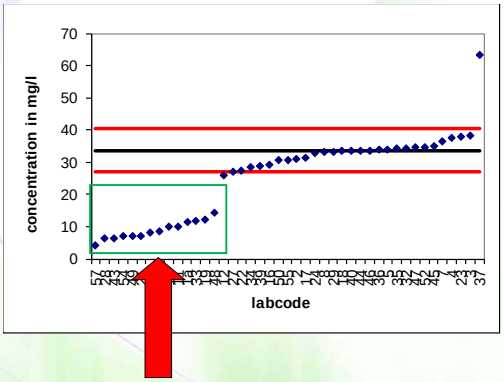


values:	45
removed:	2
mean:	16,54
ref.-value:	21,77
recovery:	75,9%
std:	8,884
rstd:	40,8%
std limit:	10%
upper limit:	26,13
lower limit:	17,42
too high:	4
too low:	20
outside limits:	24

Wrong units again as NO_3^--N instead of NO_3^-

last year 6 labs – this year even more!

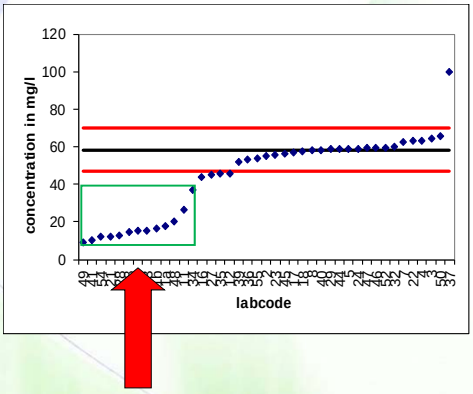
Nitrate 2



values:	46
removed:	3
mean:	25,23
ref.-value:	33,55
recovery:	75,2%
std:	13,666
rstd:	40,7%
std limit:	10%
upper limit:	40,26
lower limit:	26,84
too high:	1
too low:	18
outside limits:	19

Wrong units again as NO_3^--N instead of NO_3^-

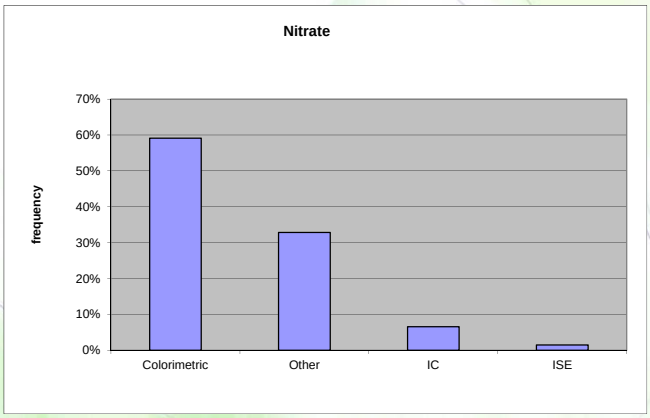
Nitrate 3



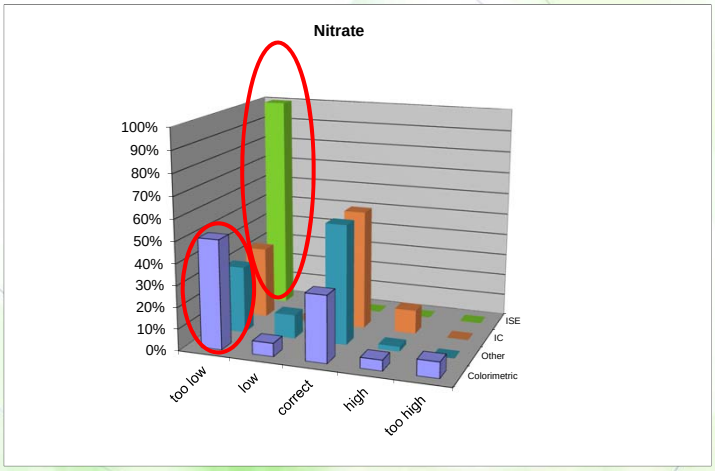
values:	46
removed:	5
mean:	44,53
ref.-value:	58,33
recovery:	76,3%
std:	23,119
rstd:	39,6%
std limit:	10%
upper limit:	70,00
lower limit:	46,67
too high:	1
too low:	22
outside limits:	23

Wrong units again as NO_3^--N instead of NO_3^-

Methods used



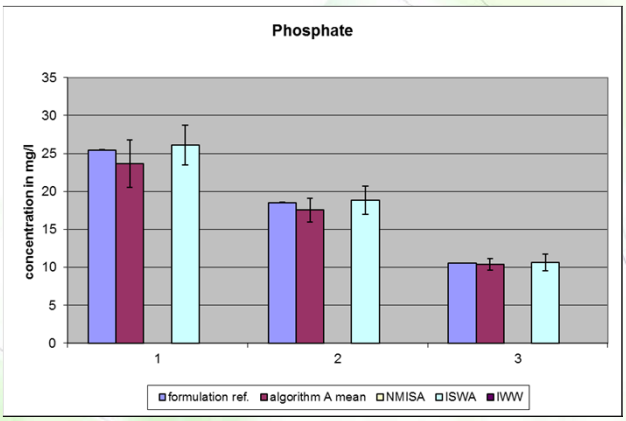
Comparison of methods



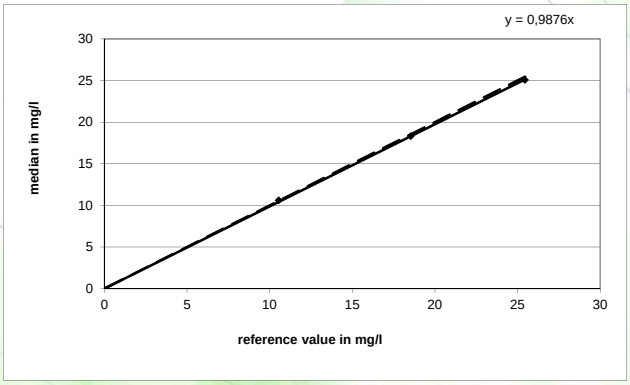
Summary Nitrate

- More labs reporting in wrong units
- Labs either do not read / do not understand / are not able to calculate or convert to the correct unit
- STDs very high – mostly because of wrong units
- percentage of non-satisfactory results again very high (units!) – 48%
- what means colorimetric? Many different methods behind that!

Phosphate
mean vs. ref.-value

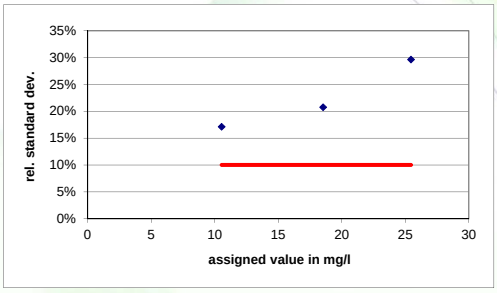


Phosphate
Alg. A mean vs. Reference value

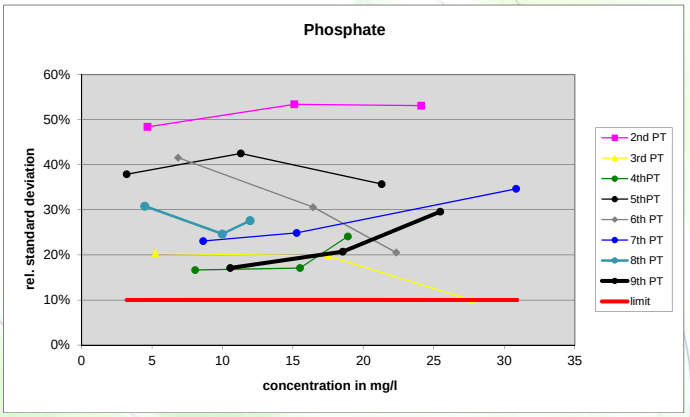


Average recovery	
2012	98.8
2011	101,2
2010	84,0
2009	92.8
2008	83.6
2007	95.0
2006	96.1

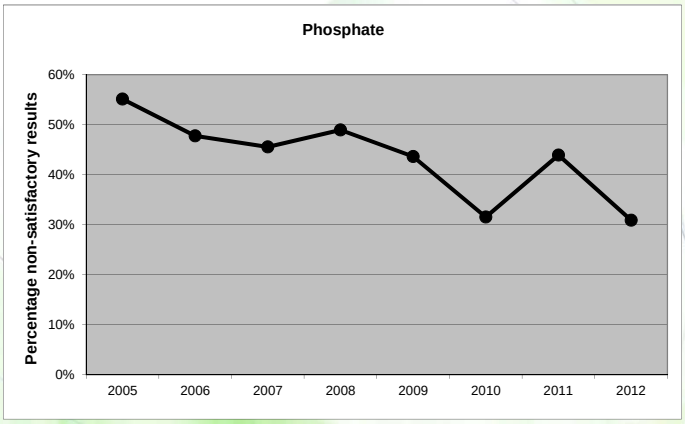
Phosphate
Calculated standard deviation and limit



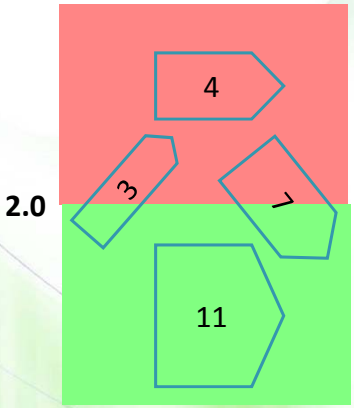
Phosphate
calculated standard deviation and limit



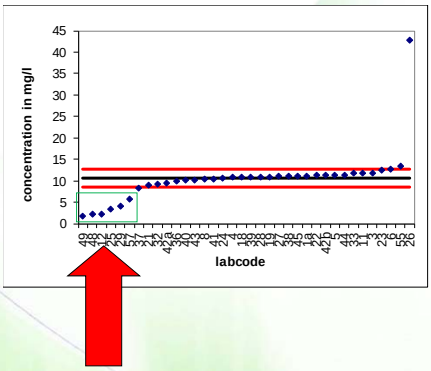
Phosphate
Percentage non-satisfactory results



Phosphate
Individual performance development



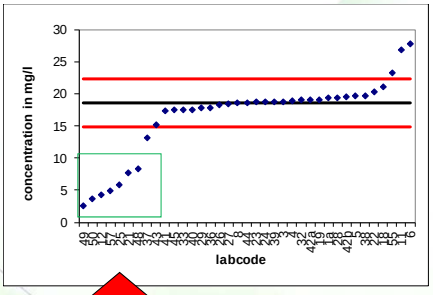
Phosphate 1



values:	37
removed:	1
mean:	10,38
ref.-value:	10,55
recovery:	98,3%
std:	1,806
rstd:	17,1%
std limit:	10%
upper limit:	12,66
lower limit:	8,44
too high:	2
too low:	8
outside limits:	10

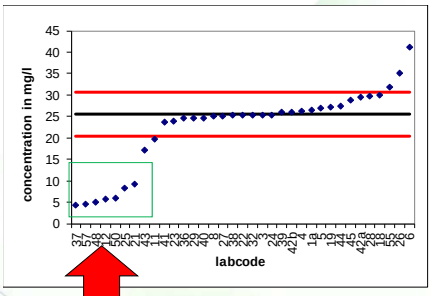
most probably reported in PO_4^{3-}-P instead of PO_4^{3-}

Phosphate 2



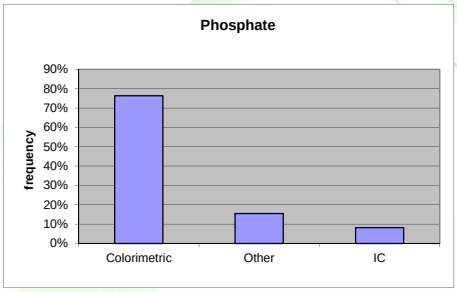
values:	37
removed:	0
mean:	17,56
ref.-value:	18,54
recovery:	94,7%
std:	3,845
rstd:	20,7%
std limit:	10%
upper limit:	22,25
lower limit:	14,83
too high:	3
too low:	8
outside limits:	11

Phosphate 3

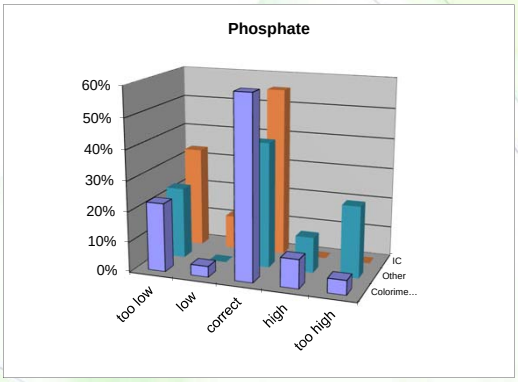


values:	36
removed:	1
mean:	23,63
ref.-value:	25,46
recovery:	92,8%
std:	7,537
rstd:	29,6%
std limit:	10%
upper limit:	30,55
lower limit:	20,37
too high:	3
too low:	10
outside limits:	13

Methods used



Comparison of methods

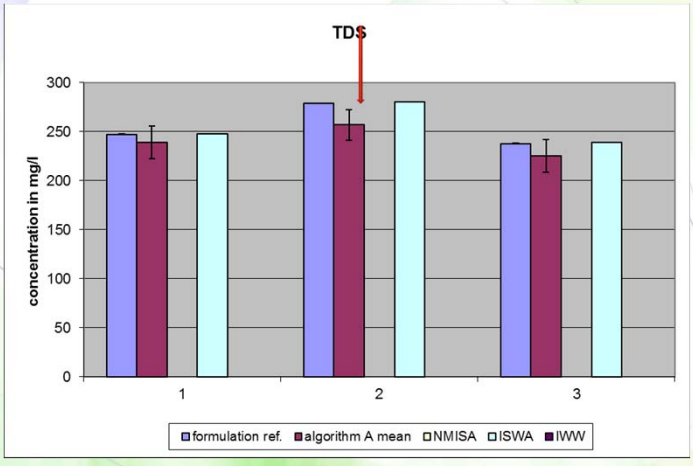


Summary Phosphate

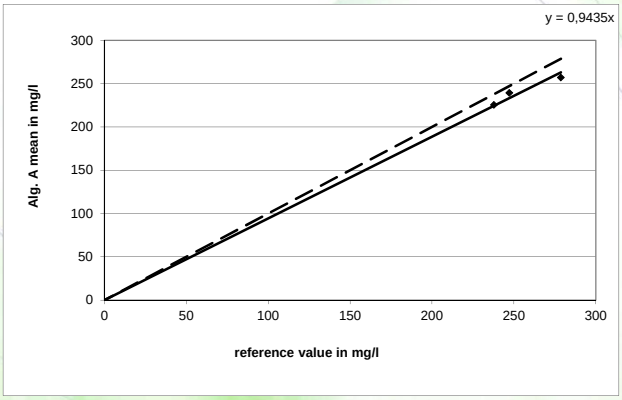
- Again some labs reported in wrong units
- Therefore average recovery low
- STD a bit better 17 -30%
- percentage of non-satisfactory results slightly better (31%)

TDS

mean vs. ref.-value

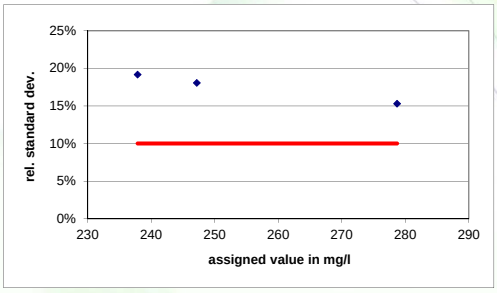


TDS
Alg. A mean vs. Reference value

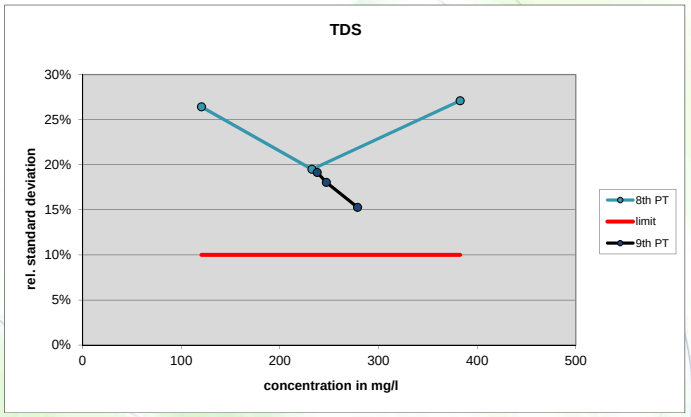


Average recovery	
2012	94.3
2011	101,2
2010	-
2009	-
2008	-
2007	-
2006	-

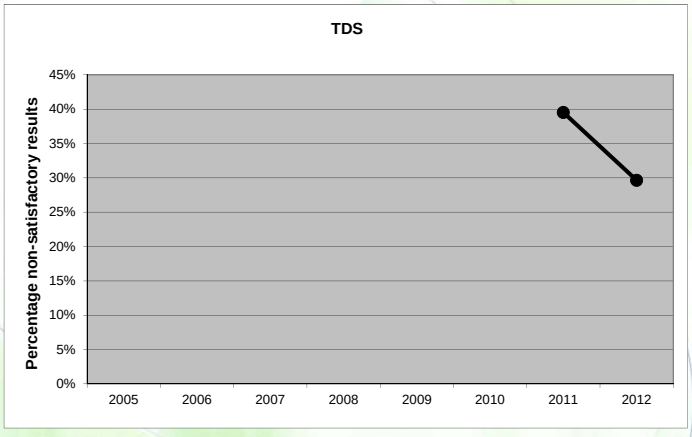
TDS
Calculated standard deviation and limit



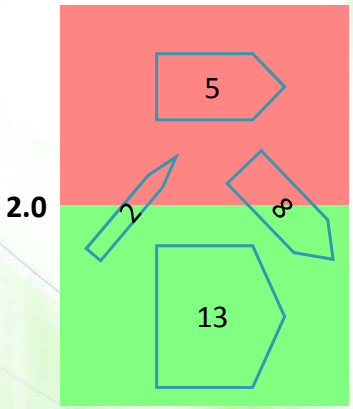
TDS
calculated standard deviation and limit



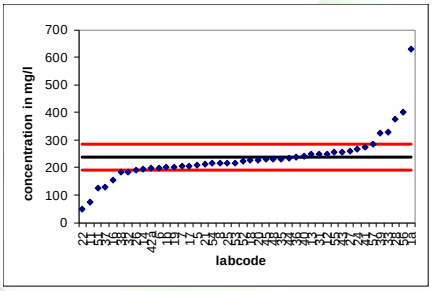
TDS
Percentage non-satisfactory results



TDS
Individual performance development

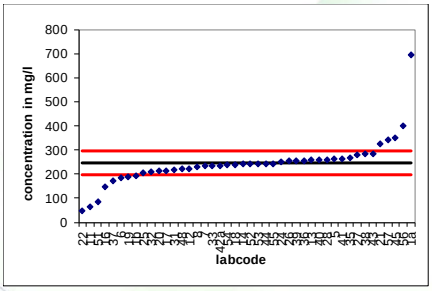


TDS 1



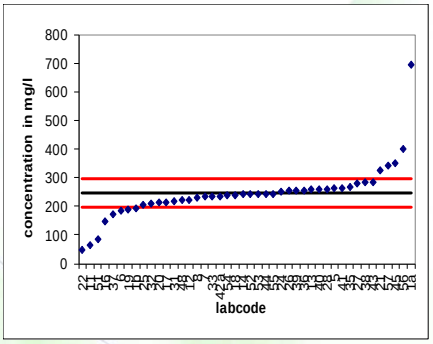
values:	45
removed:	1
mean:	225,37
ref.-value:	237,86
recovery:	94,7%
std:	45,559
rstd:	19,2%
std limit:	10%
upper limit:	285,43
lower limit:	190,29
too high:	5
too low:	9
outside limits:	14

TDS 2



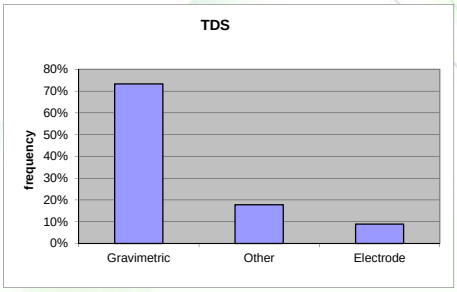
values:	45
removed:	1
mean:	239,15
ref.-value:	247,20
recovery:	96,7%
std:	44,606
rstd:	18,0%
std limit:	10%
upper limit:	296,63
lower limit:	197,76
too high:	5
too low:	9
outside limits:	14

TDS 2

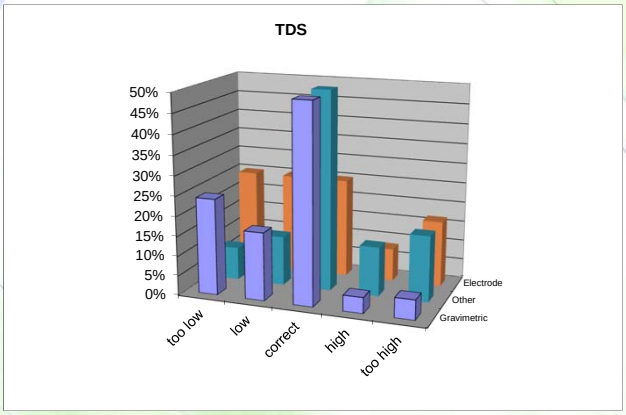


values:	45
removed:	1
mean:	239.15
ref.-value:	247.20
recovery:	96.7%
std:	44.606
rstd:	18.0%
std limit:	10%
upper limit:	296.63
lower limit:	197.76
too high:	5
too low:	9
outside limits:	14

Methods used



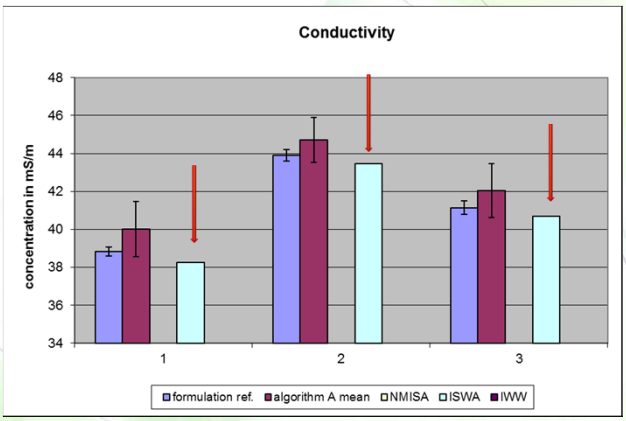
Comparison of methods



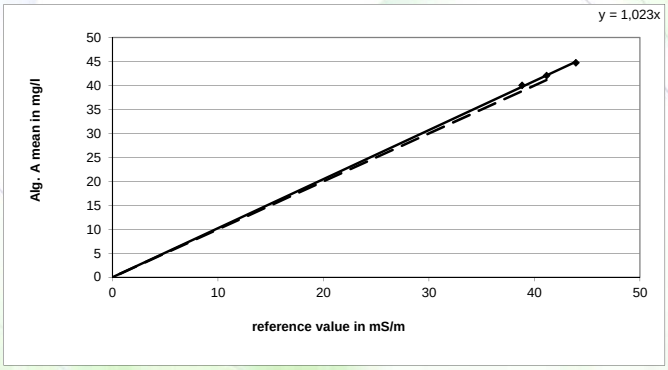
Summary TDS

- Although is was clearly specified that a gravimetric determination is required – method information was not reported - “other”
- Methods was reported as “an electrode method”? These are obviously different measurands!!
- Average recovery of 95% is not too bad
- STD better than last year, but still too high
- percentage of non-satisfactory results slightly better (30%), but it was made clear now, that the determination should be gravimetric

Conductivity
mean vs. ref.-value

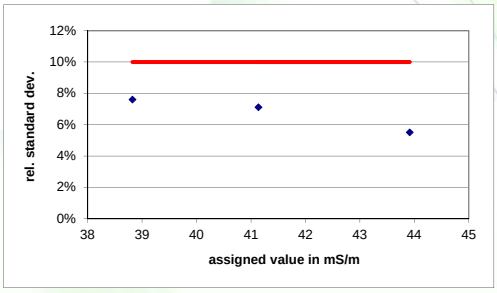


Conductivity
Alg. A mean vs. Reference value

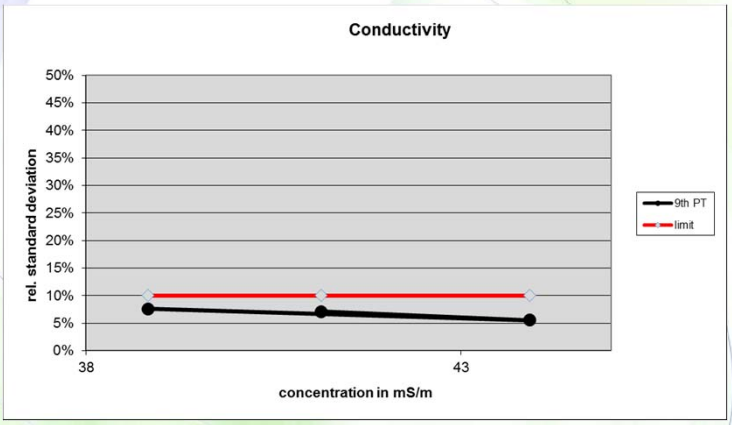


Average recovery	
2012	102.3
2011	-
2010	-
2009	-
2008	-
2007	-
2006	-

Conductivity
Calculated standard deviation and limit

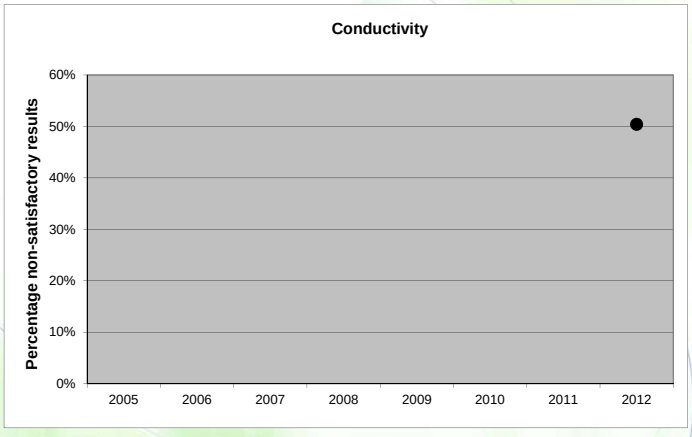


Conductivity
calculated standard deviation and limit

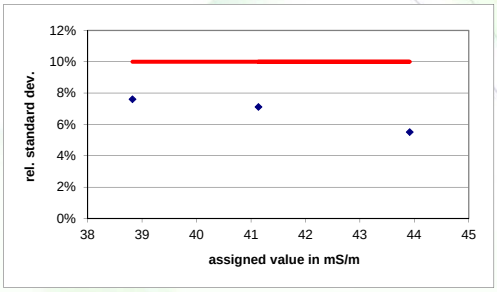


After the all the outliers were removed !
Percentage outliers was 50%

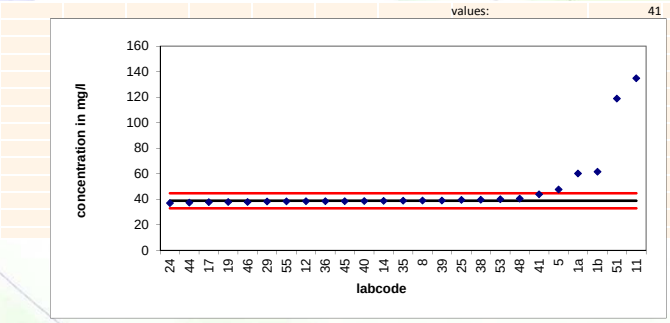
Conductivity
Percentage non-satisfactory results



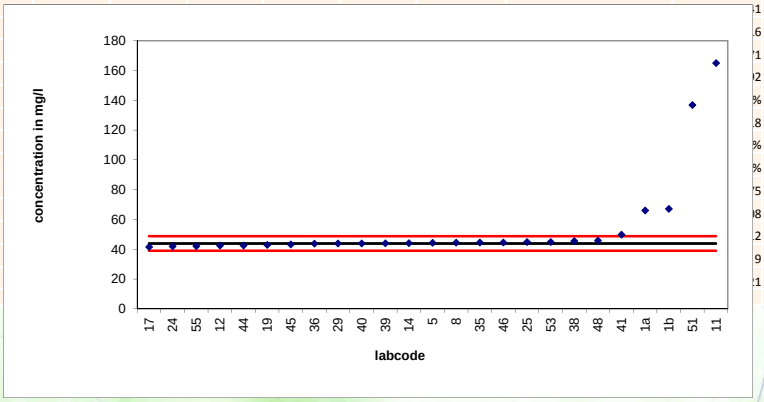
Conductivity
Calculated standard deviation and limit



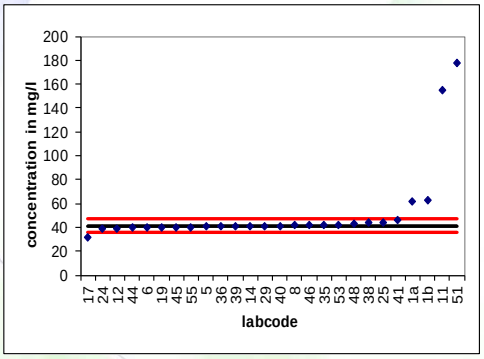
Conductivity 1



Conductivity 2

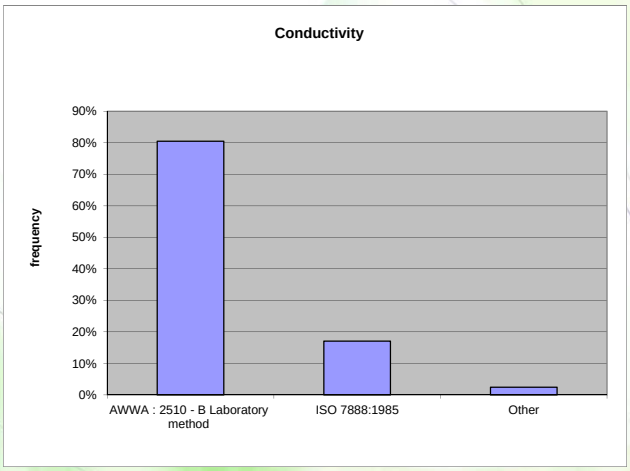


Conductivity 3

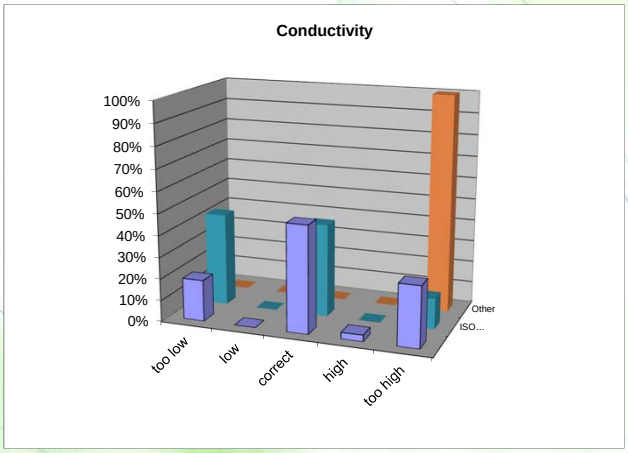


values:	41
removed:	15
mean:	42.04
ref.-value:	41.14
recovery:	102.2%
std:	2.923
rstd:	7.1%
std limit:	10%
upper limit:	46.98
lower limit:	35.29
too high:	10
too low:	10
outside limits:	20

Methods used



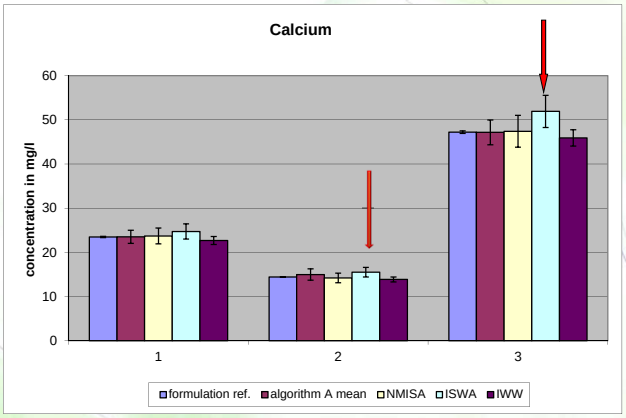
Comparison of the methods



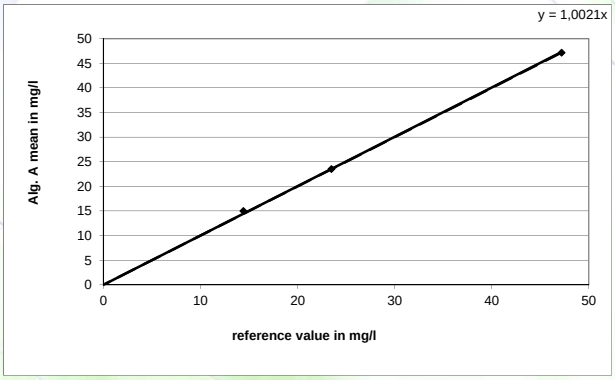
Summary Conductivity

- Obviously serious problems with units
- STD of the values with correct units are not bad
- percentage of non-satisfactory results is very high (50%)

Calcium
mean vs. ref.-value

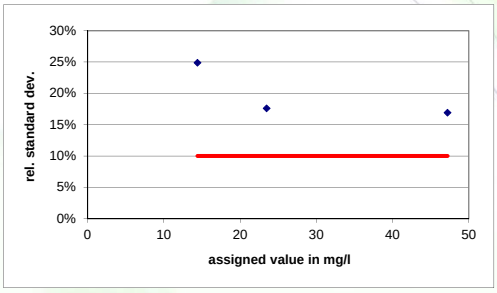


Calcium
Alg. A mean vs. Reference value

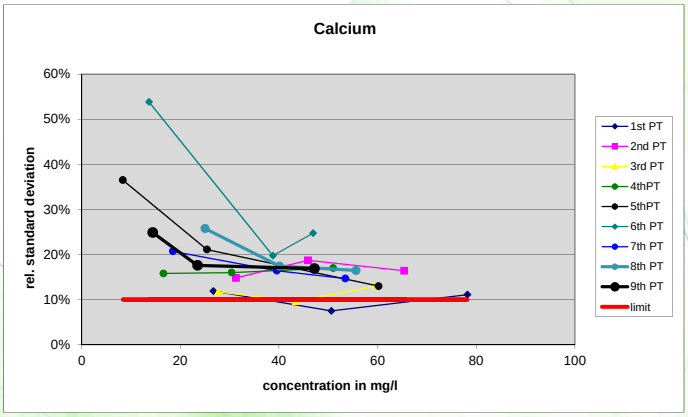


Average recovery	
2012	1022.2
2011	102,1
2010	98,8
2009	100.0
2008	101.6
2007	102.2
2006	97.2

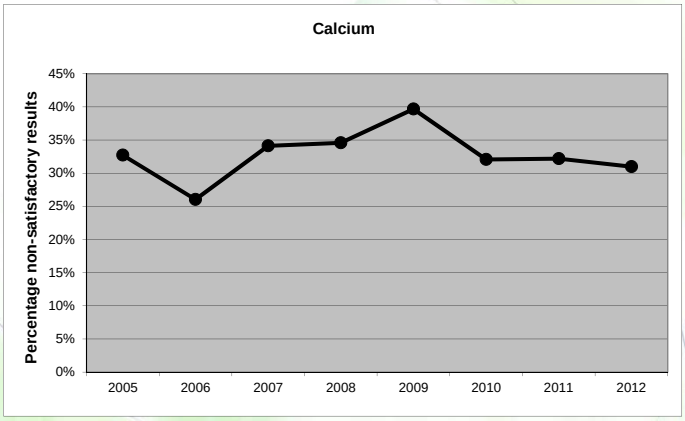
Calcium
Calculated standard deviation and limit



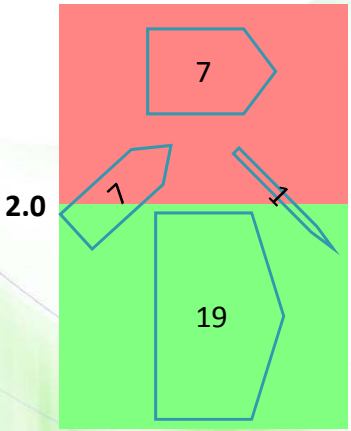
Calcium
calculated standard deviation and limit



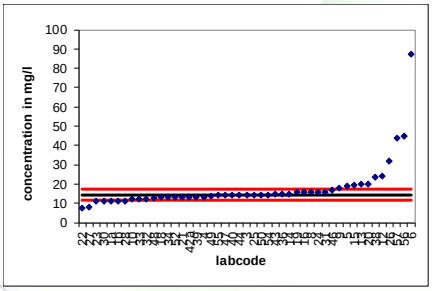
Calcium
Percentage non-satisfactory results



Calcium
Individual performance development

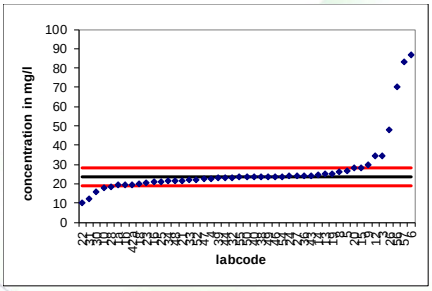


Calcium 1



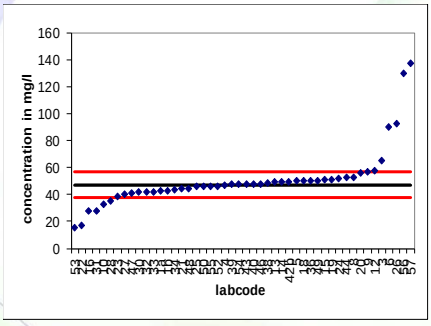
values:	47
removed:	0
mean:	14,98
ref.-value:	14,42
recovery:	103,9%
std:	3,586
rstd:	24,9%
std limit:	10%
upper limit:	17,30
lower limit:	11,54
too high:	11
too low:	7
outside limits:	18

Calcium 2



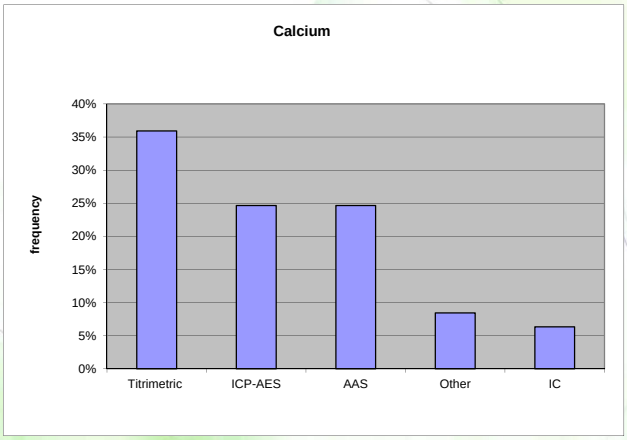
values:	47
removed:	0
mean:	23,51
ref.-value:	23,48
recovery:	100,1%
std:	4,130
rstd:	17,6%
std limit:	10%
upper limit:	28,18
lower limit:	18,79
too high:	8
too low:	5
outside limits:	13

Calcium 3

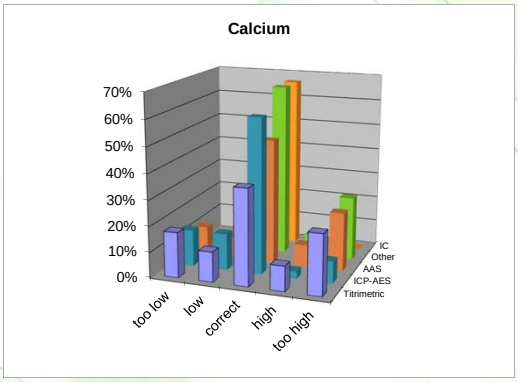


values:	48
removed:	0
mean:	47.15
ref.-value:	47.20
recovery:	99.9%
std:	7.980
rstd:	16.9%
std limit:	10%
upper limit:	56.64
lower limit:	37.76
too high:	7
too low:	6
outside limits:	13

Methods used



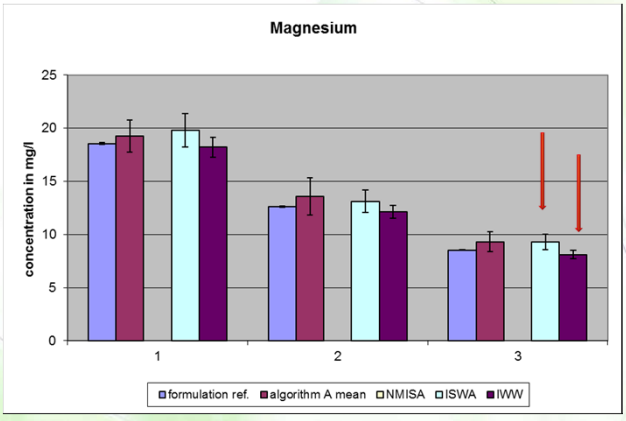
Comparison of the methods



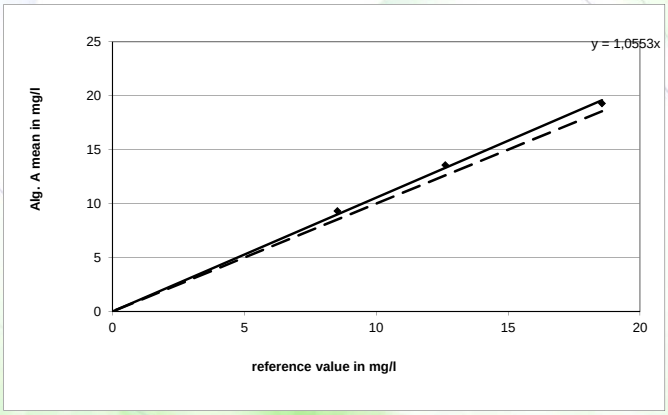
Summary Calcium

- Perfect average recovery
- STD – no change compared to 2011
- percentage of non-satisfactory results 31% - no improvement
- method specific evaluation very similar to 2011

Magnesium
mean vs. ref.-value

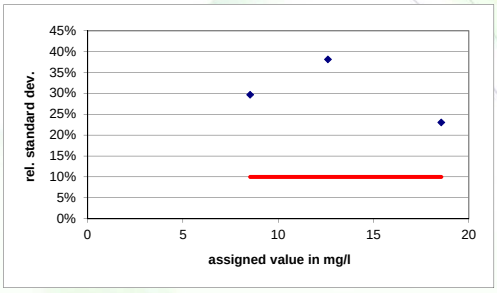


Magnesium
Alg. A mean vs. Reference value

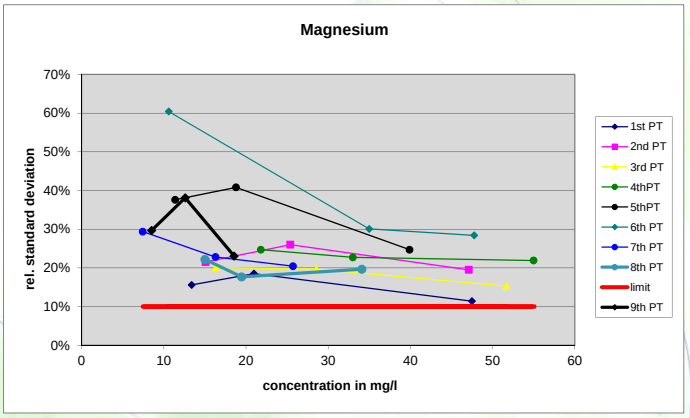


Average recovery	
2012	105.53
2011	99,2
2010	98,9
2009	99.0
2008	100.2
2007	101.7
2006	99.6

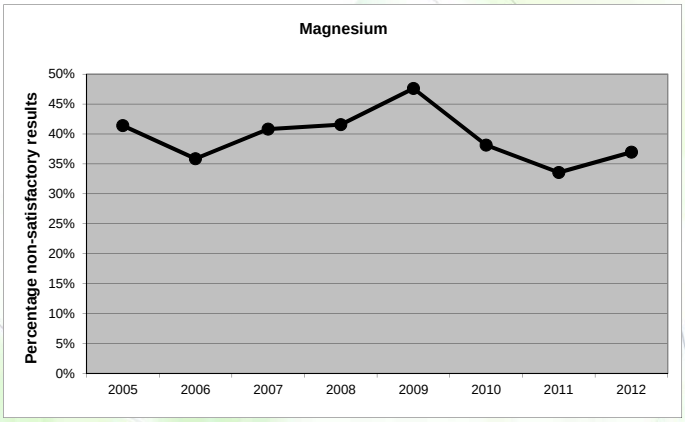
Magnesium
Calculated standard deviation and limit



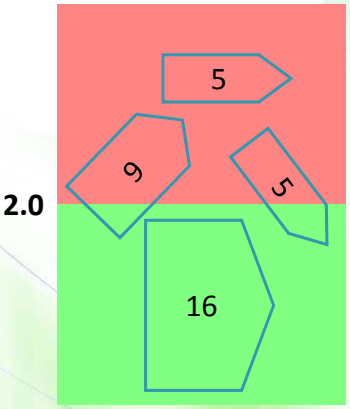
Magnesium
calculated standard deviation and limit



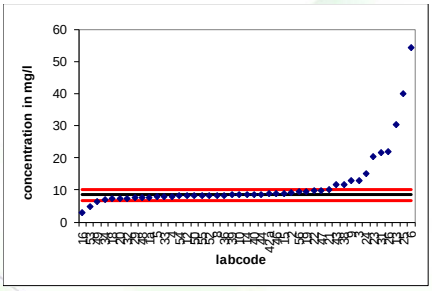
Magnesium
Percentage non-satisfactory results



Magnesium
Individual performance development

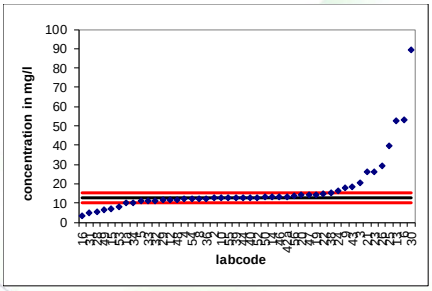


Magnesium 1



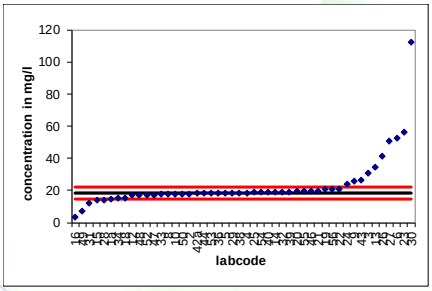
values:	48
removed:	3
mean:	9,31
ref.-value:	8,53
recovery:	109,2%
std:	2,529
rstd:	29,7%
std limit:	10%
upper limit:	10,23
lower limit:	6,82
too high:	14
too low:	3
outside limits:	17

Magnesium 2



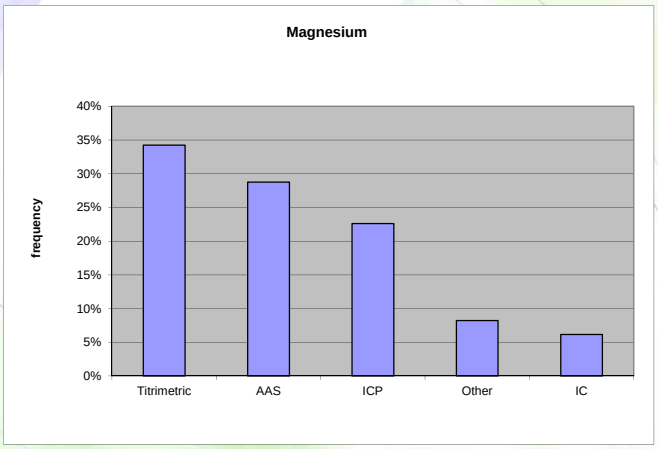
values:	49
removed:	3
mean:	13,56
ref.-value:	12,61
recovery:	107,5%
std:	4,807
rstd:	38,1%
std limit:	10%
upper limit:	15,14
lower limit:	10,09
too high:	14
too low:	7
outside limits:	21

Magnesium 3

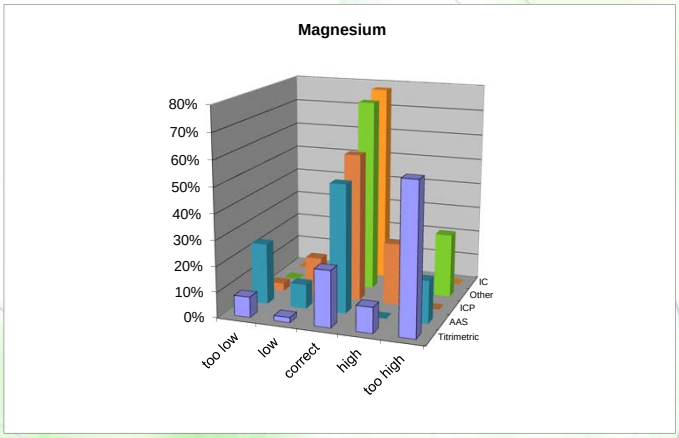


values:	49
removed:	1
mean:	19,27
ref.-value:	18,56
recovery:	103,8%
std:	4,274
rstd:	23,0%
std limit:	10%
upper limit:	22,27
lower limit:	14,85
too high:	11
too low:	5
outside limits:	16

Methods used



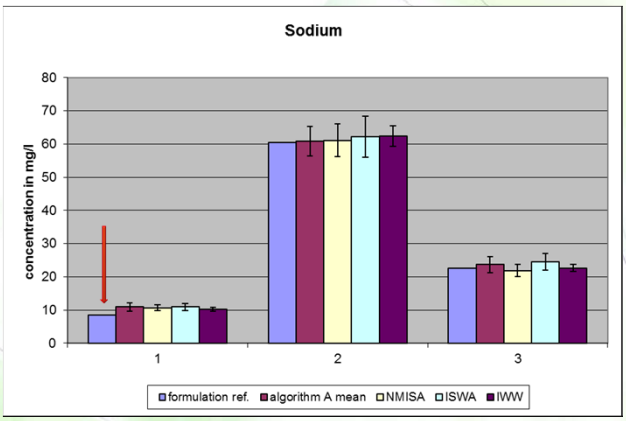
Comparison of methods



Summary Magnesium

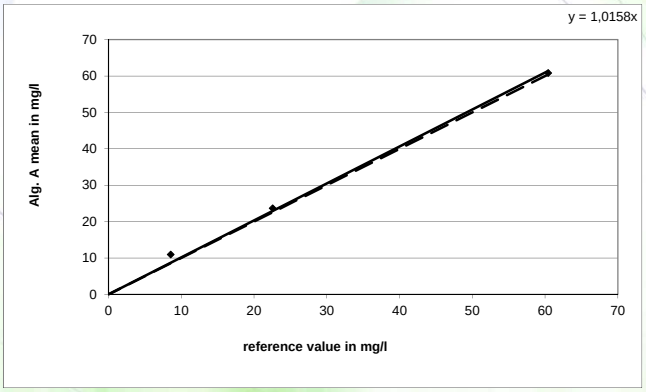
- More titrimetric results than in 2011 - with the problems of a high portion of too results for this method
- STD higher than last year
- Results worse than last year

Sodium
mean vs. ref.-value



Sodium

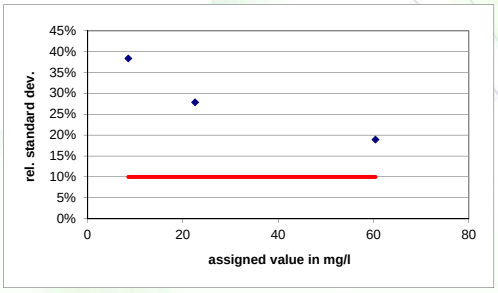
Alg. A mean vs. Reference value



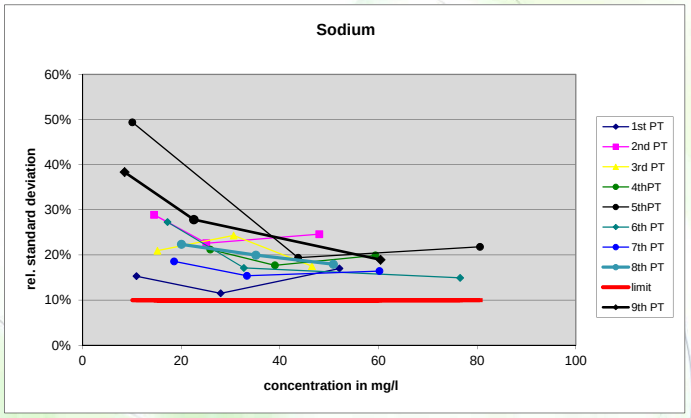
Average recov101.58ery	
2012	
2011	102,3
2010	102,2
2009	103.0
2008	100.4
2007	103.3
2006	104.4

Sodium

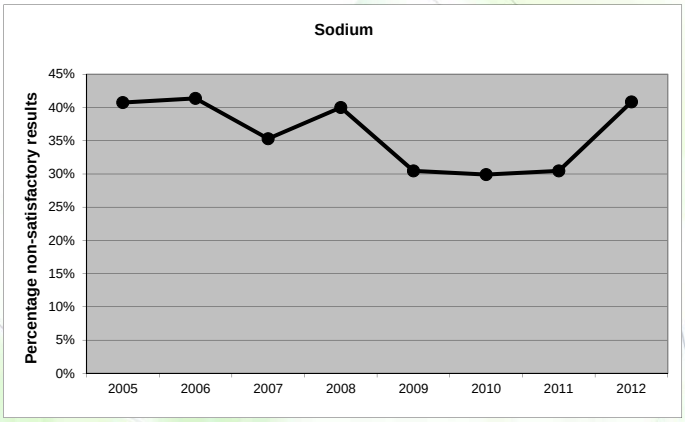
Calculated standard deviation and limit



Sodium
calculated standard deviation and limit

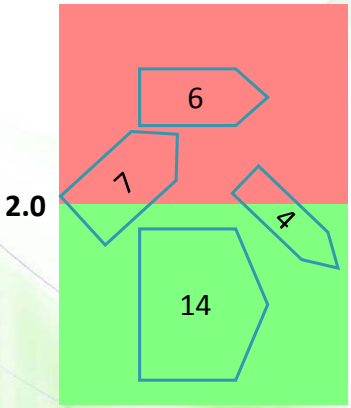


Sodium
Percentage non-satisfactory results

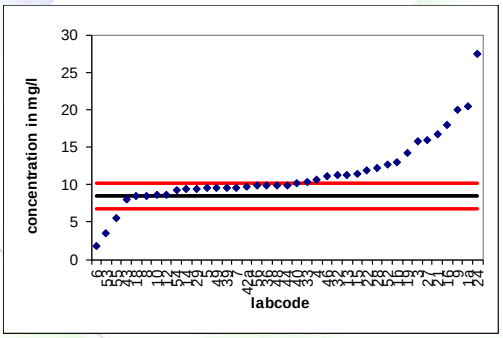


No improvement compared last year, still very high

Sodium
Individual performance development

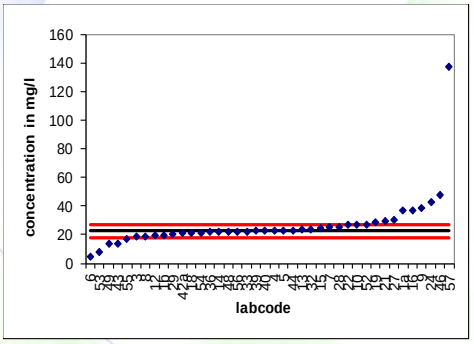


Sodium 1



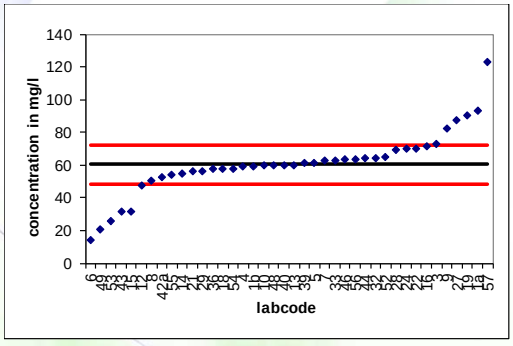
values:	40
removed:	1
mean:	10,95
ref.-value:	8,55
recovery:	128,0%
std:	3,279
rstd:	38,4%
std limit:	10%
upper limit:	10,26
lower limit:	6,84
too high:	19
too low:	3
outside limits:	22

Sodium 2



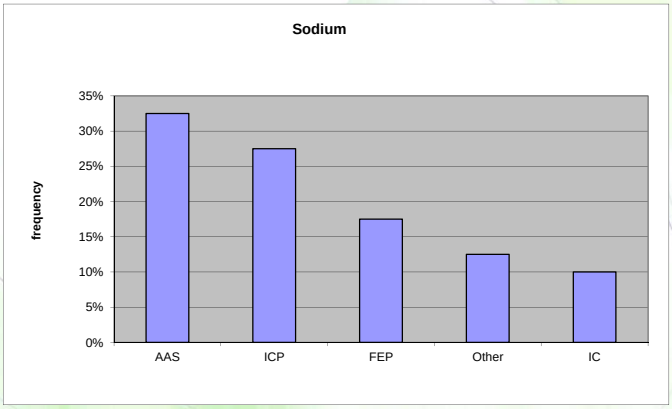
values:	40
removed:	0
mean:	23.66
ref.-value:	22.58
recovery:	104.8%
std:	6.282
rstd:	27.8%
std limit:	10%
upper limit:	27.09
lower limit:	18.06
too high:	10
too low:	5
outside limits:	15

Sodium 3

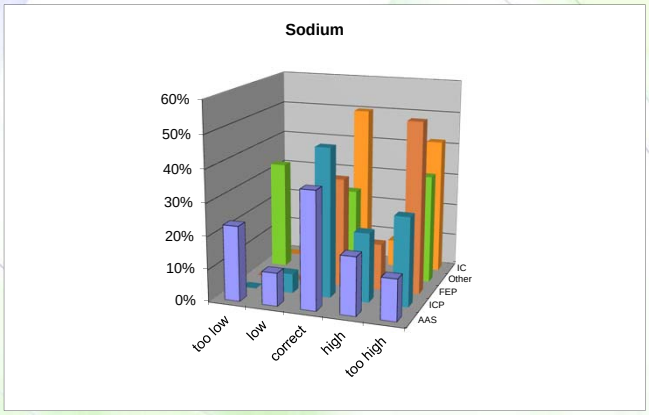


values:	40
removed:	0
mean:	60,79
ref.-value:	60,43
recovery:	100,6%
std:	11,436
rstd:	18,9%
std limit:	10%
upper limit:	72,52
lower limit:	48,34
too high:	6
too low:	6
outside limits:	12

Methods used



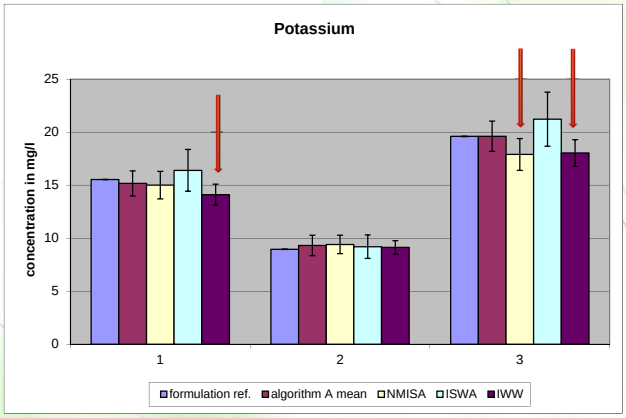
Comparison of methods



Summary Sodium

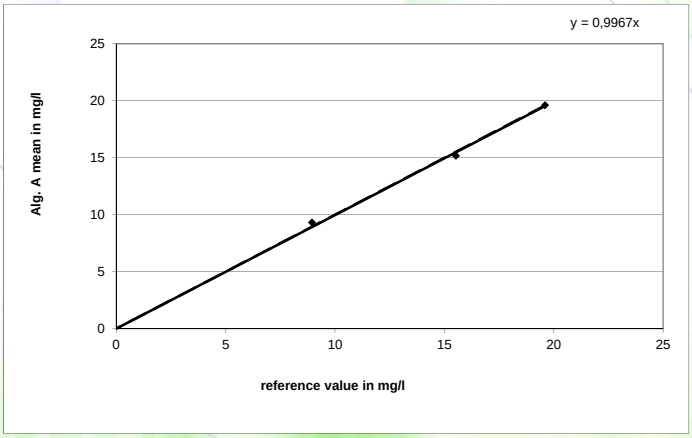
- Problems with high results for lowest level – high blank?
- No improvement in the STDs
- percentage of non-satisfactory results higher (41%) mainly due to problems with lowest level

Potassium
mean vs. ref.-value



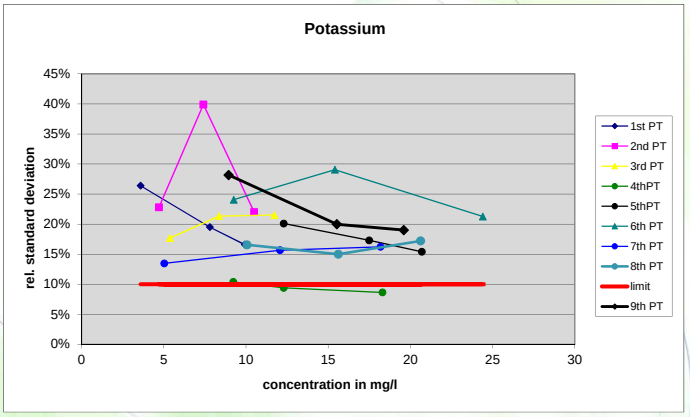
ISWA results too high

Potassium
Alg. A mean vs. Reference value

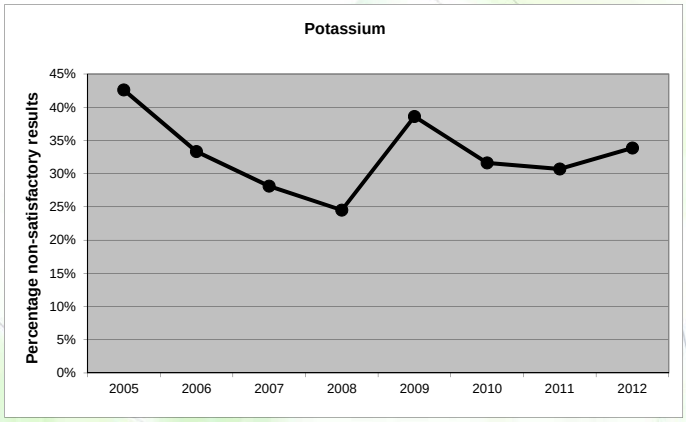


Average recovery	
2012	99.7
2011	102,0
2010	98,7
2009	99.8
2008	99.0
2007	98.5
2006	96.9

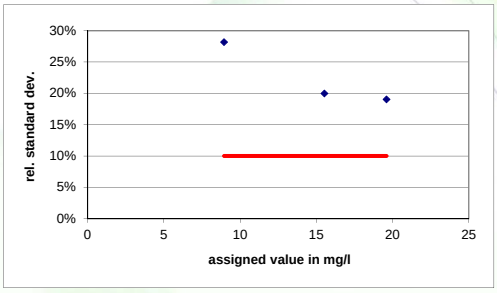
Potassium
calculated standard deviation and limit



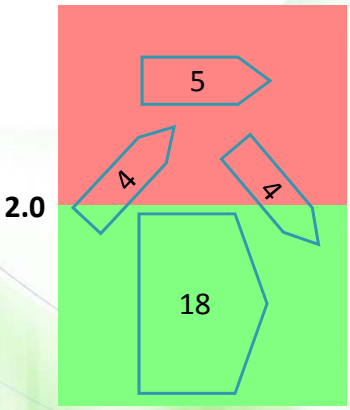
Potassium
Percentage non-satisfactory results



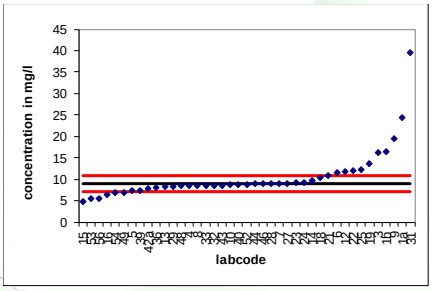
Potassium
Calculated standard deviation and limit



Potassium
Individual performance development

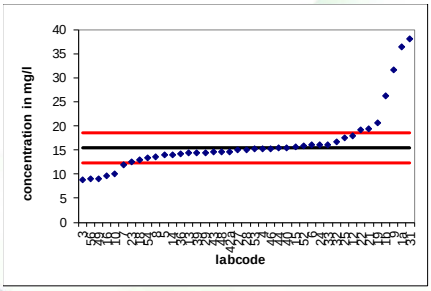


Potassium 1



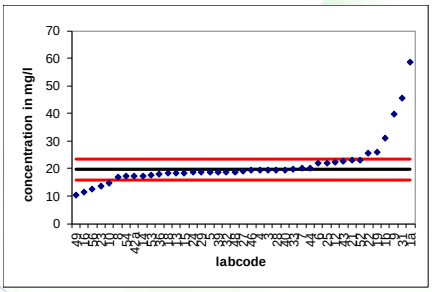
values:	42
removed:	1
mean:	9,31
ref.-value:	8,95
recovery:	104,0%
std:	2,521
rstd:	28,2%
std limit:	10%
upper limit:	10,74
lower limit:	7,16
too high:	12
too low:	6
outside limits:	18

Potassium 2



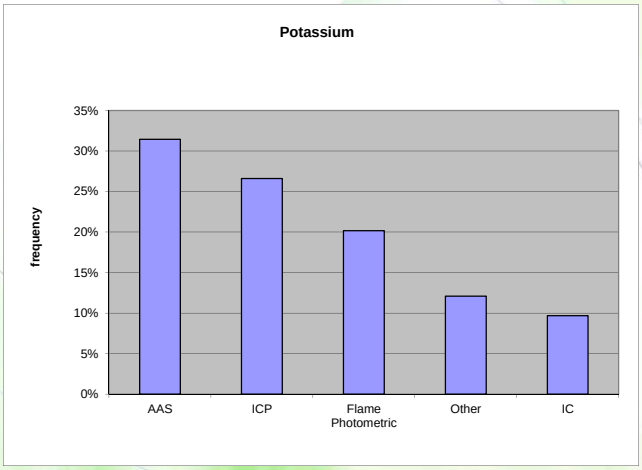
values:	41
removed:	0
mean:	15,17
ref.-value:	15,53
recovery:	97,7%
std:	3,102
rstd:	20,0%
std limit:	10%
upper limit:	18,64
lower limit:	12,42
too high:	7
too low:	6
outside limits:	13

Potassium 3

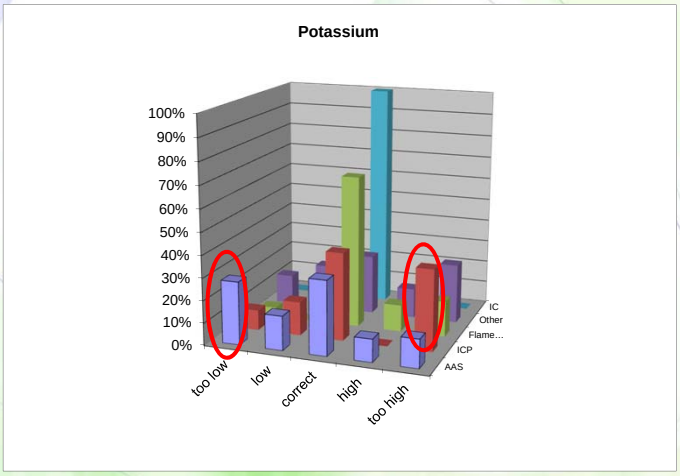


values:	41
removed:	0
mean:	19,61
ref.-value:	19,60
recovery:	100,0%
std:	3,726
rstd:	19,0%
std limit:	10%
upper limit:	23,52
lower limit:	15,68
too high:	6
too low:	5
outside limits:	11

Methods used



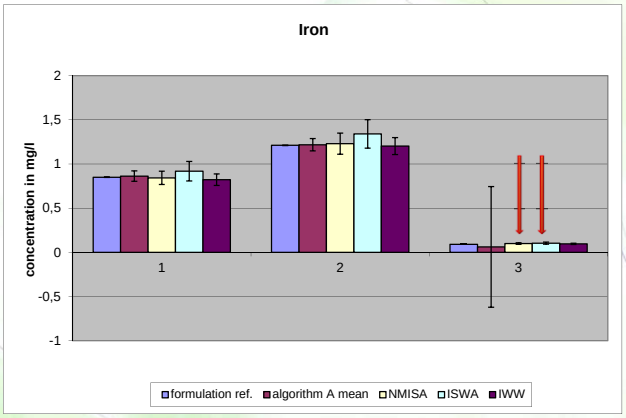
Comparison of methods



Summary Potassium

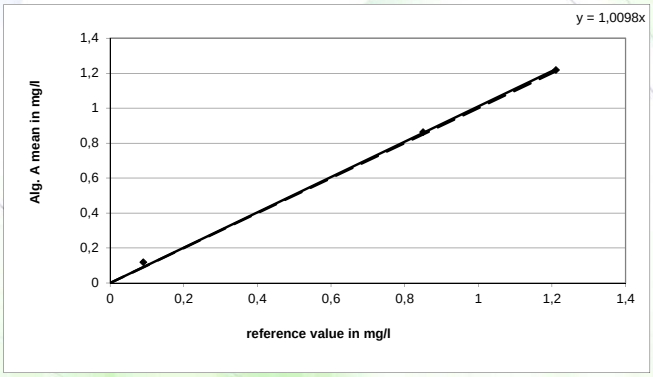
- Average recovery is ok
- STDs higher than in previous rounds
- percentage of non-satisfactory results with 34% a bit worse than in 2011

Iron
mean vs. ref.-value



Iron

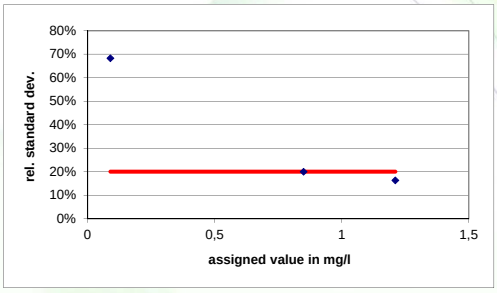
Alg. A mean vs. Reference value



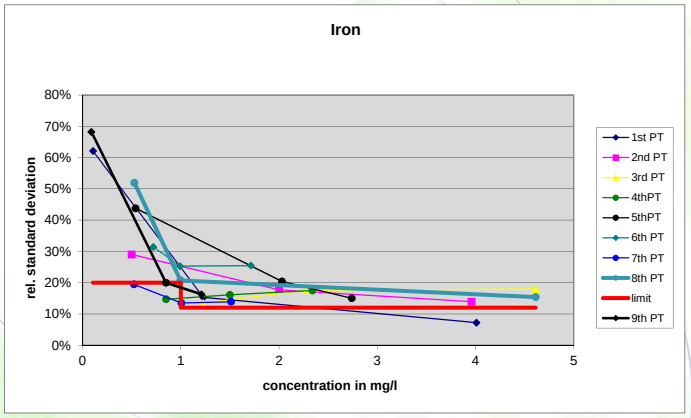
Average recovery	
2012	100.98
2011	99,9
2010	100,3
2009	97.6
2008	99.9
2007	92.9
2006	88.0

Iron

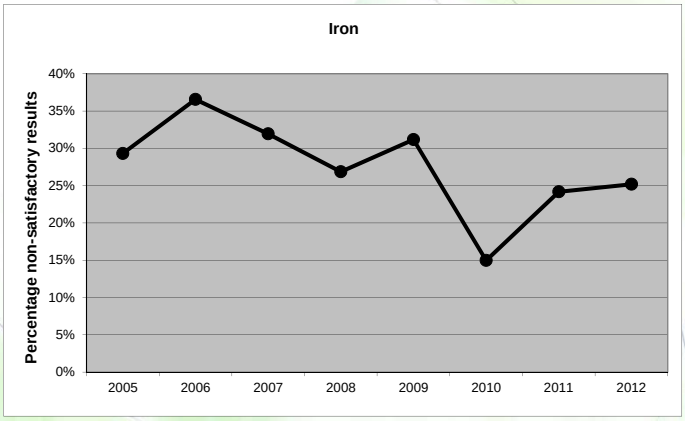
Calculated standard deviation and limit



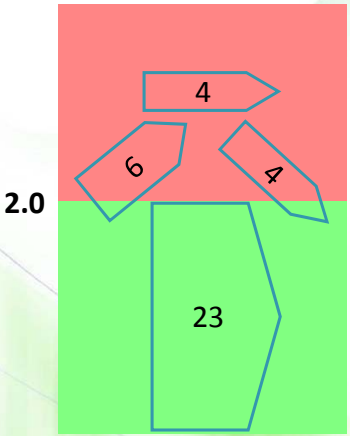
Iron
calculated standard deviation and limit



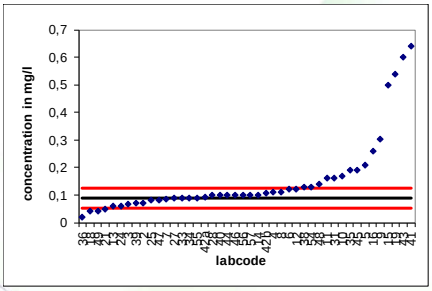
Iron
Percentage non-satisfactory results



Iron
Individual performance development

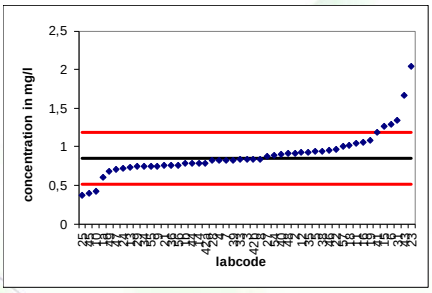


Iron 1



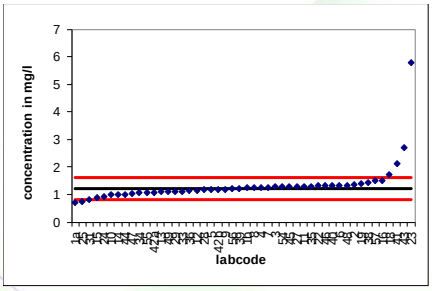
values:	45
removed:	1
mean:	0,12
ref.-value:	0,09
recovery:	130,9%
std:	0,061
rstd:	68,2%
std limit:	20%
upper limit:	0,13
lower limit:	0,05
too high:	16
too low:	4
outside limits:	20

Iron 2



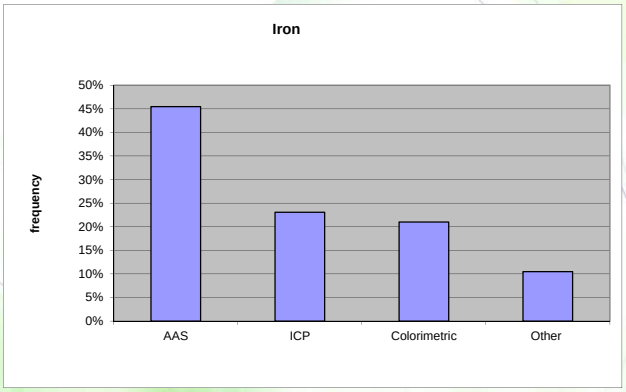
values:	49
removed:	0
mean:	0,86
ref.-value:	0,85
recovery:	101,5%
std:	0,170
rstd:	20,0%
std limit:	20%
upper limit:	1,19
lower limit:	0,51
too high:	5
too low:	3
outside limits:	8

Iron 3

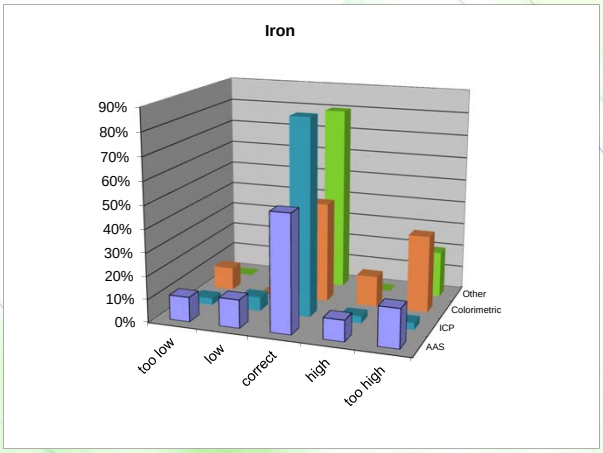


values:	49
removed:	1
mean:	1,22
ref.-value:	1,21
recovery:	100,6%
std:	0,197
rstd:	16,3%
std limit:	20%
upper limit:	1,60
lower limit:	0,82
too high:	4
too low:	4
outside limits:	8

Methods used



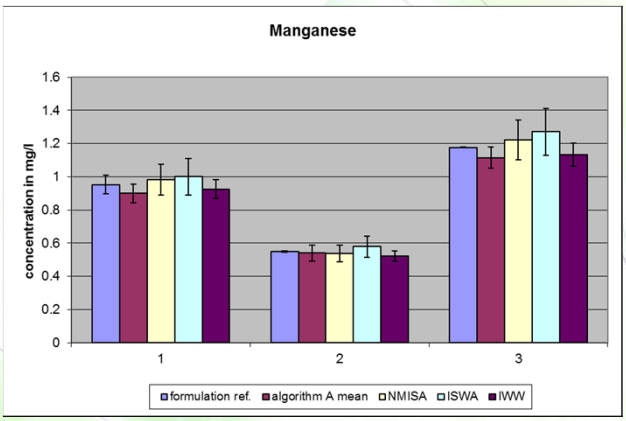
Comparison of methods



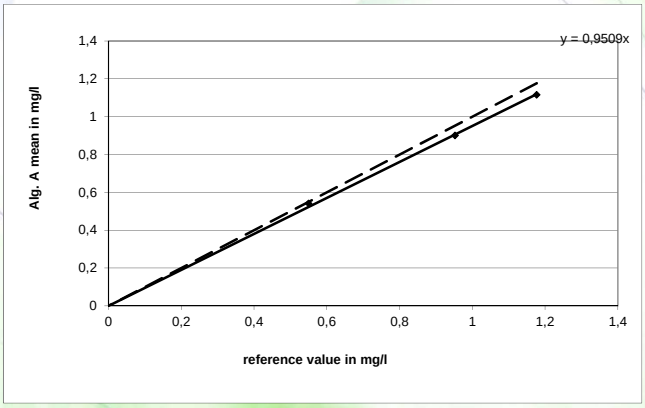
Summary Iron

- Problems with the lowest level – high blank?, high STD (68%!)
- Same picture as in 2011

Manganese
mean vs. ref.-value

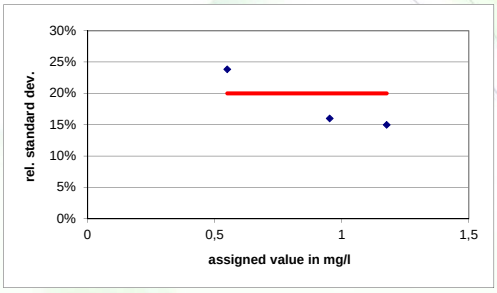


Manganese
Alg. A mean vs. Reference value

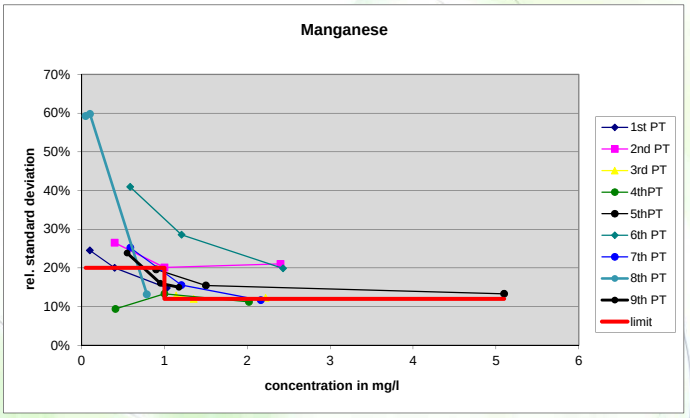


Average recovery	
2012	95.1
2011	95,2
2010	98,9
2009	93.0
2008	96.7
2007	96.0
2006	95.4

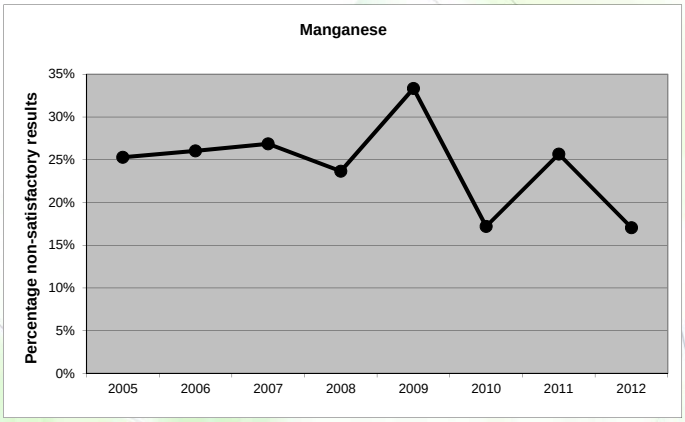
Manganese
Calculated standard deviation and limit



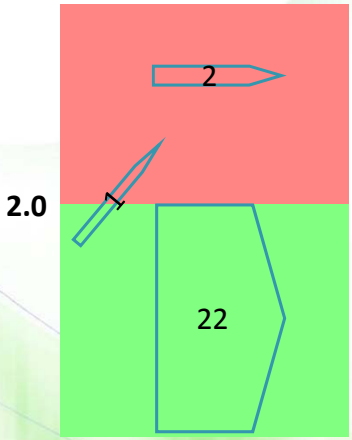
Manganese
calculated standard deviation and limit



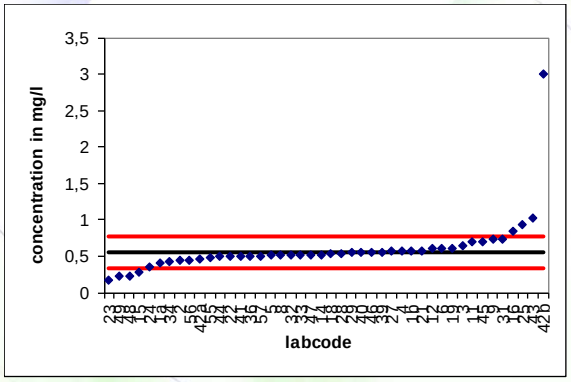
Manganese
Percentage non-satisfactory results



Manganese
Individual performance development

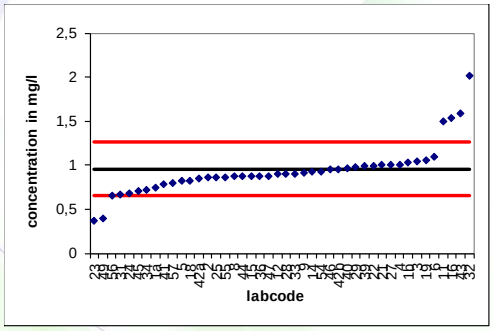


Manganese 1



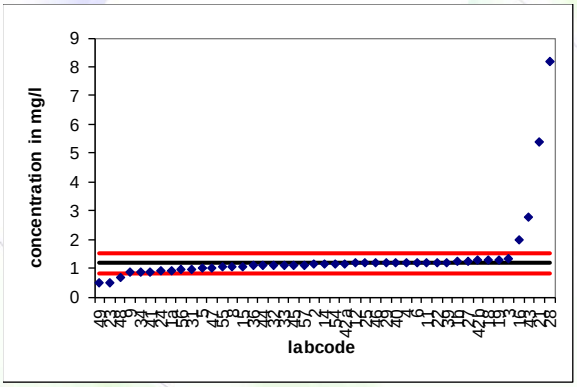
values:	45
removed:	1
mean:	0,54
ref.-value:	0,55
recovery:	98,3%
std:	0,131
rstd:	23,8%
std limit:	20%
upper limit:	0,77
lower limit:	0,33
too high:	4
too low:	5
outside limits:	9

Manganese 2



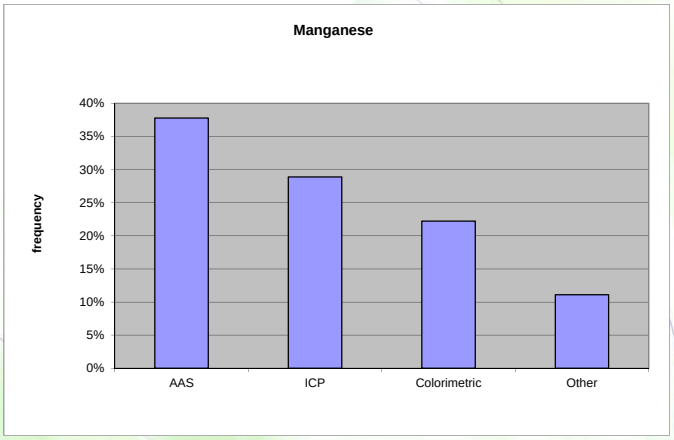
values:	45
removed:	1
mean:	0,90
ref.-value:	0,95
recovery:	94,5%
std:	0,152
rstd:	16,0%
std limit:	20%
upper limit:	1,26
lower limit:	0,65
too high:	4
too low:	3
outside limits:	7

Manganese 3

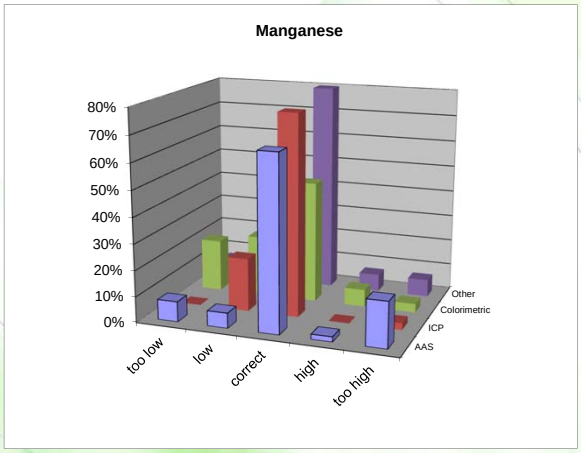


values:	45
removed:	0
mean:	1,12
ref.-value:	1,18
recovery:	94,8%
std:	0,176
rstd:	15,0%
std limit:	20%
upper limit:	1,53
lower limit:	0,82
too high:	4
too low:	3
outside limits:	7

Methods used



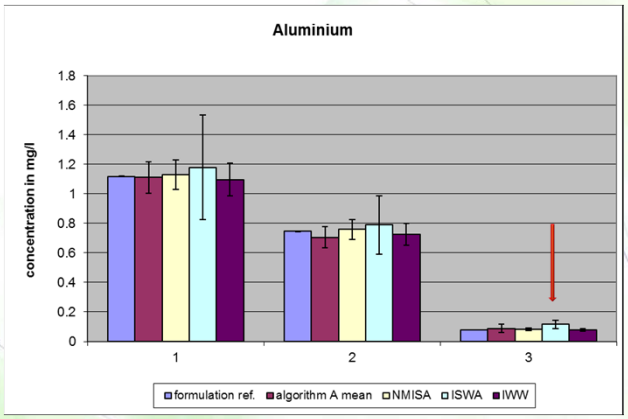
Comparison of methods



Summary Manganese

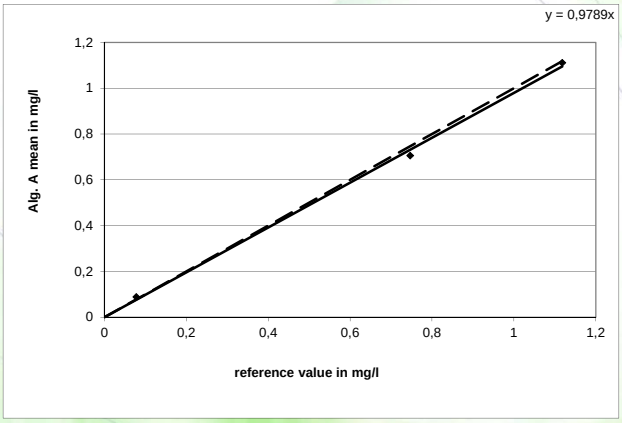
- STDs much better than last year, comparable to previous rounds
- Improved percentage of non-satisfactory results (17%)

Aluminium
mean vs. ref.-value



Aluminium

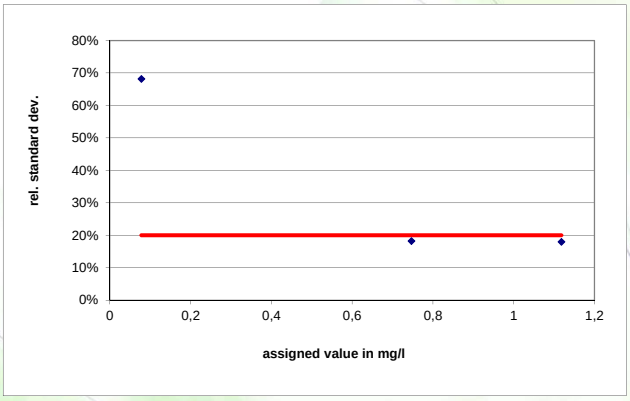
Alg. A mean vs. Reference value



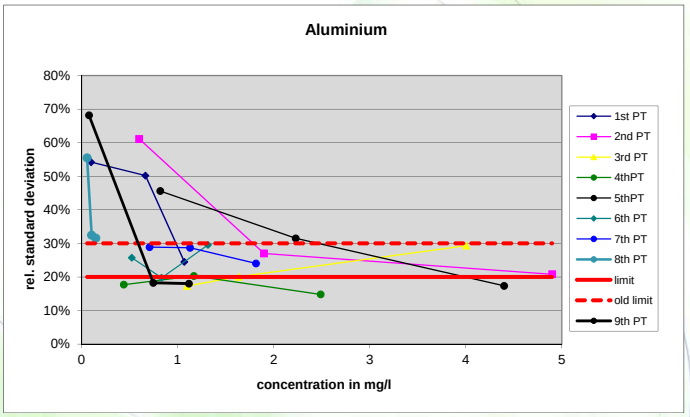
Average recovery	
2012	97.9
2011	103.2
2010	99.4
2009	104.9
2008	93.9
2007	96.1
2006	85.7

Aluminium

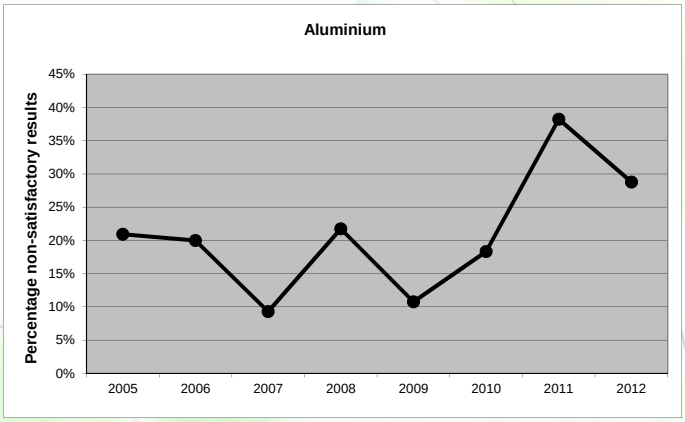
Calculated standard deviation and limit



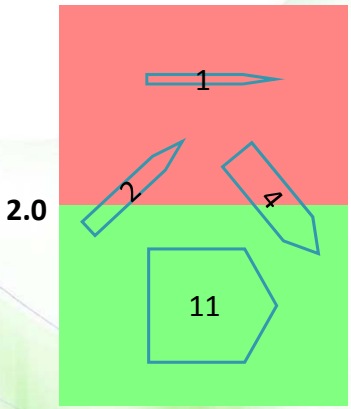
Aluminium
calculated standard deviation and limit



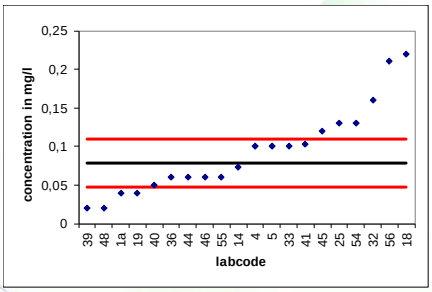
Aluminium
Percentage non-satisfactory results



Aluminium
Individual performance development

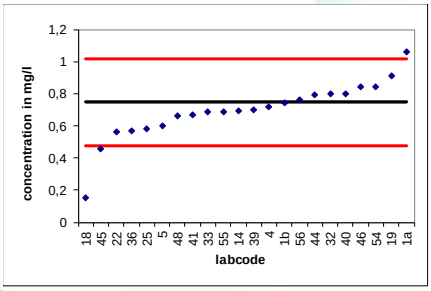


Aluminium 1



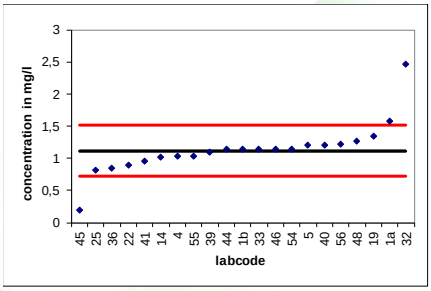
values:	21
removed:	1
mean:	0,09
ref.-value:	0,08
recovery:	112,8%
std:	0,053
rstd:	68,2%
std limit:	20%
upper limit:	0,11
lower limit:	0,05
too high:	6
too low:	5
outside limits:	11

Aluminium 2



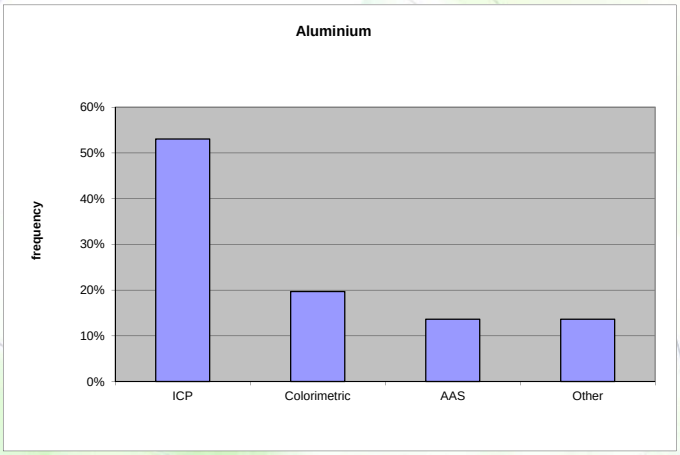
values:	22
removed:	0
mean:	0,71
ref.-value:	0,75
recovery:	94,5%
std:	0,136
rstd:	18,3%
std limit:	20%
upper limit:	1,02
lower limit:	0,47
too high:	1
too low:	2
outside limits:	3

Aluminium 3

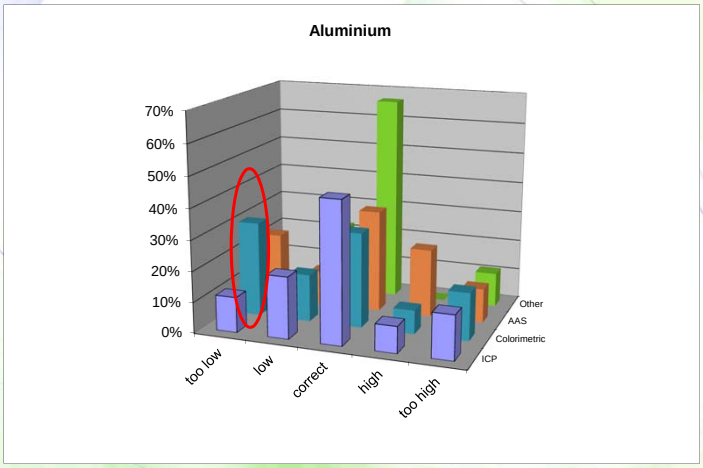


values:	23
removed:	2
mean:	1,11
ref.-value:	1,12
recovery:	99,3%
std:	0,201
rstd:	18,0%
std limit:	20%
upper limit:	1,52
lower limit:	0,72
too high:	2
too low:	3
outside limits:	5

Methods used



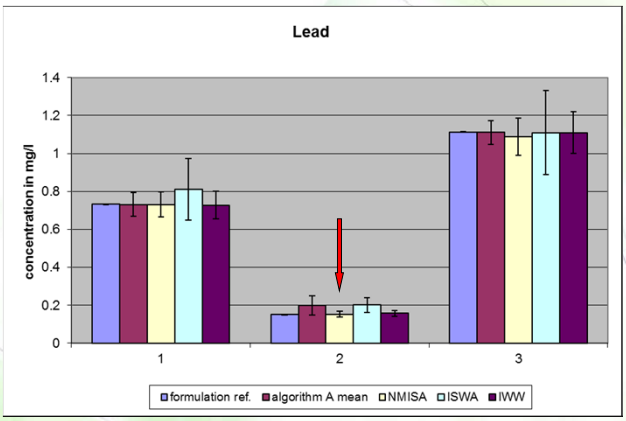
Comparison of methods



Summary Aluminium

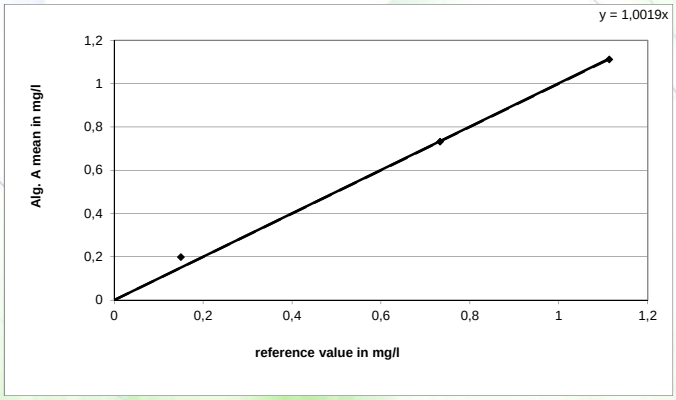
- Higher concentrations than last year
- STDs similar to previous rounds
- Problems with the low level (52% of the results outside the limits)
- Problems with the colorimetric method

Lead
mean vs. ref.-value



Lead

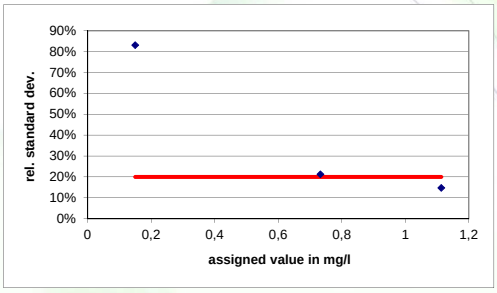
Alg. A mean vs. Reference value



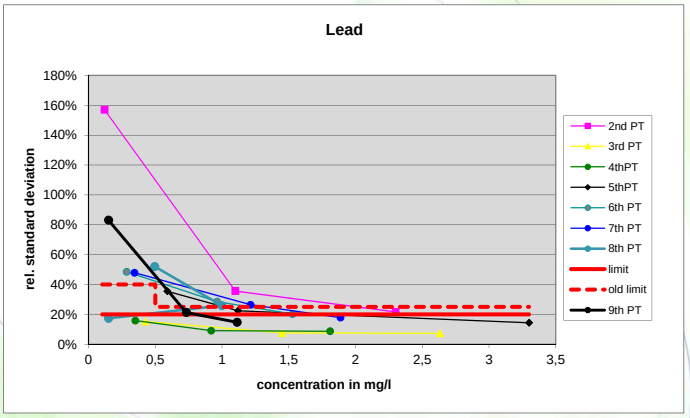
Average recovery	
2012	100.19
2011	106.4
2010	102.1
2009	97.1
2008	103.7
2007	95.4
2006	95.6

Lead

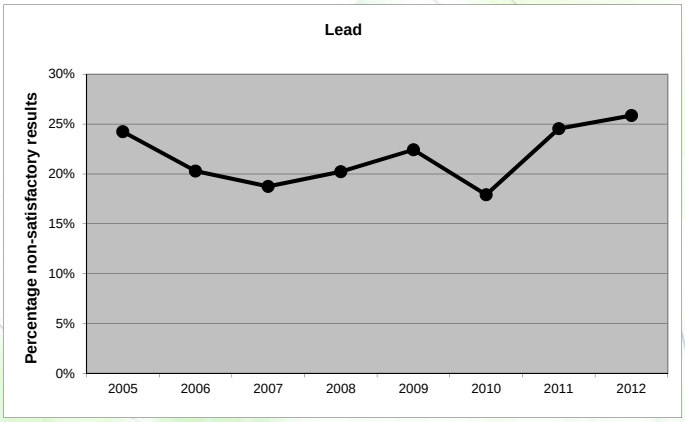
Calculated standard deviation and limit



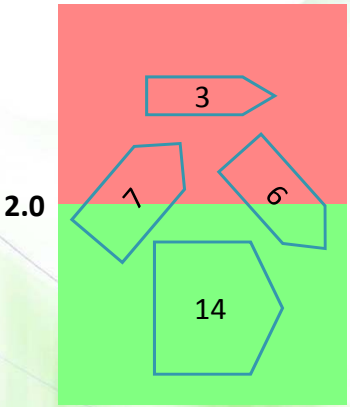
Lead
calculated standard deviation and limit



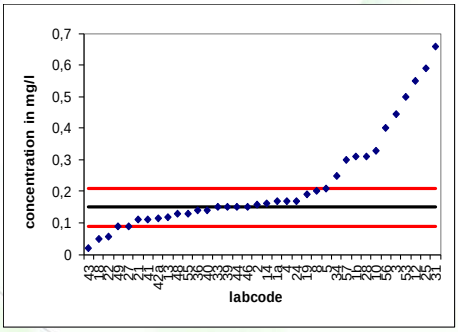
Lead
Percentage non-satisfactory results



Lead
Individual performance development

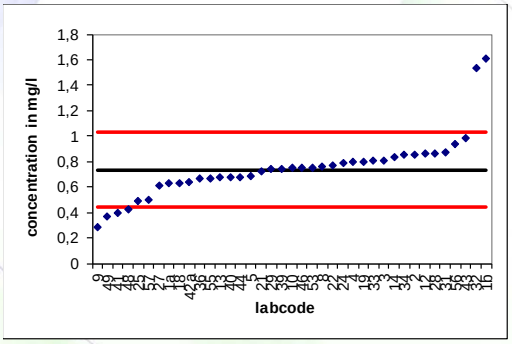


Lead 1



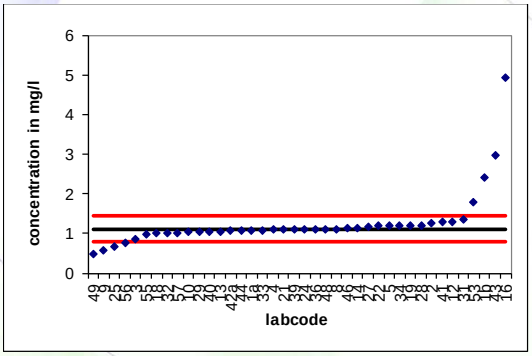
values:	37
removed:	1
mean:	0,20
ref.-value:	0,15
recovery:	132,1%
std:	0,125
rstd:	83,1%
std limit:	20%
upper limit:	0,21
lower limit:	0,09
too high:	12
too low:	4
outside limits:	16

Lead 2



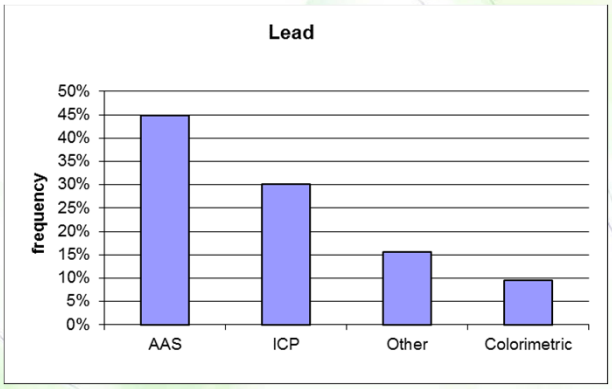
values:	39
removed:	0
mean:	0,73
ref.-value:	0,73
recovery:	99,8%
std:	0,156
rstd:	21,2%
std limit:	20%
upper limit:	1,03
lower limit:	0,44
too high:	2
too low:	4
outside limits:	6

Lead 3

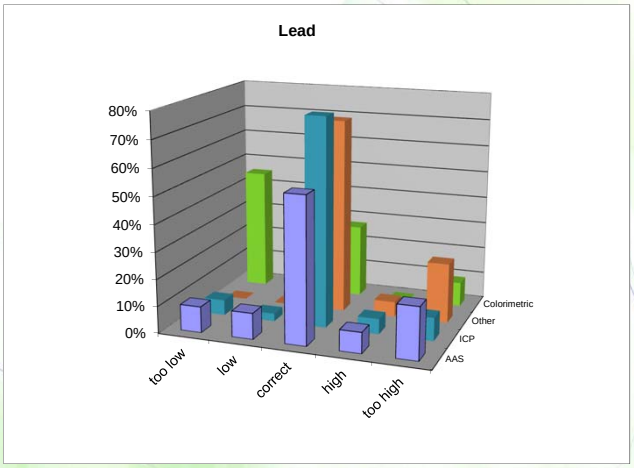


values:	40
removed:	0
mean:	1,11
ref.-value:	1,11
recovery:	99,8%
std:	0,164
rstd:	14,7%
std limit:	20%
upper limit:	1,44
lower limit:	0,79
too high:	4
too low:	4
outside limits:	8

Methods used



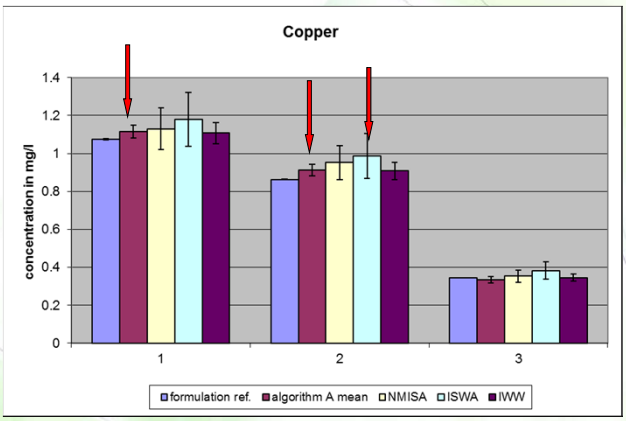
Comparison of methods



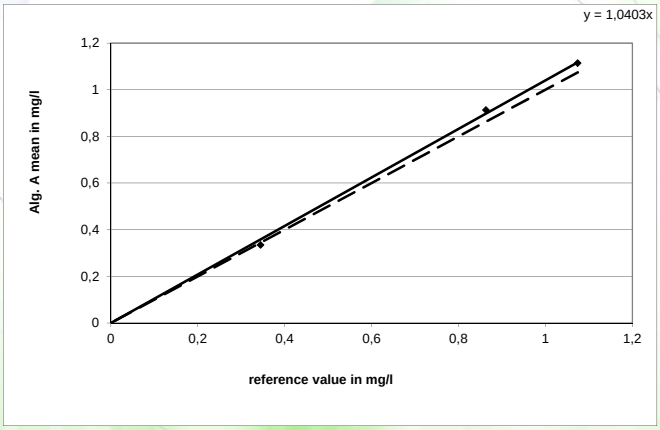
Summary Lead

- Obviously problems with the lowest level – high blank?, high STD (83%!)
- STDs for the other levels is fine
- Similar picture for the methods

Copper
mean vs. ref.-value

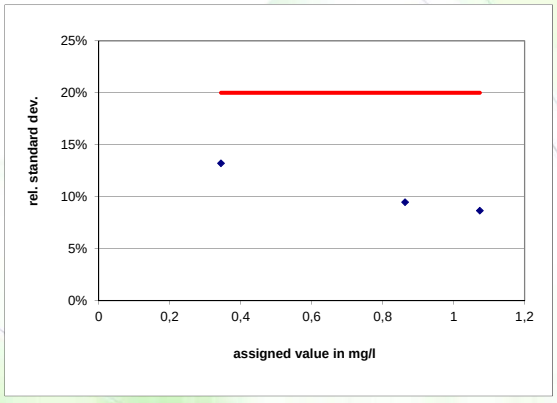


Copper
Alg. A mean vs. Reference value

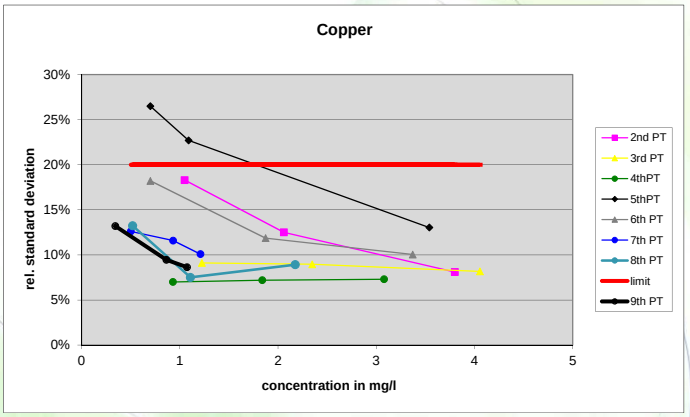


Average recovery	
2012	104.0
2011	98.8
2010	103.7
2009	99.6
2008	95.1
2007	97.5
2006	98.5

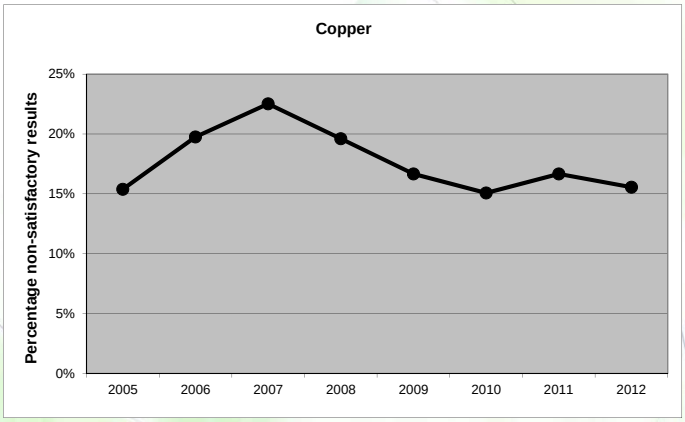
Copper
Calculated standard deviation and limit



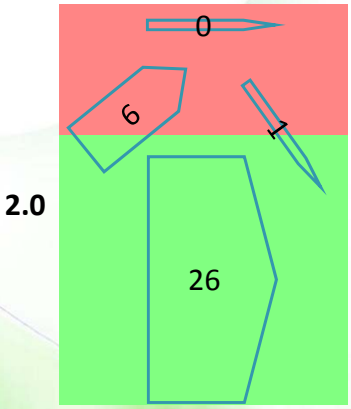
Copper
calculated standard deviation and limit



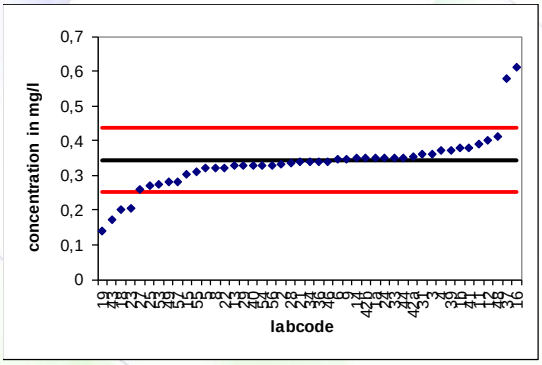
Copper
Percentage non-satisfactory results



Copper
Individual performance development

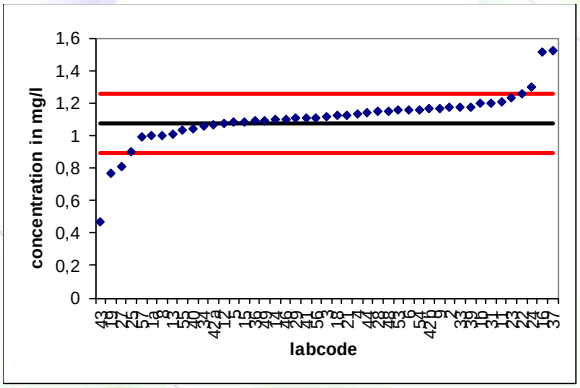


Copper 1



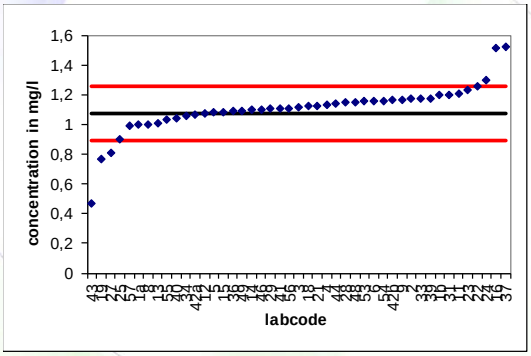
values:	45
removed:	0
mean:	0,33
ref.-value:	0,34
recovery:	97,0%
std:	0,045
rstd:	13,2%
std limit:	20%
upper limit:	0,44
lower limit:	0,25
too high:	2
too low:	4
outside limits:	6

Copper 2



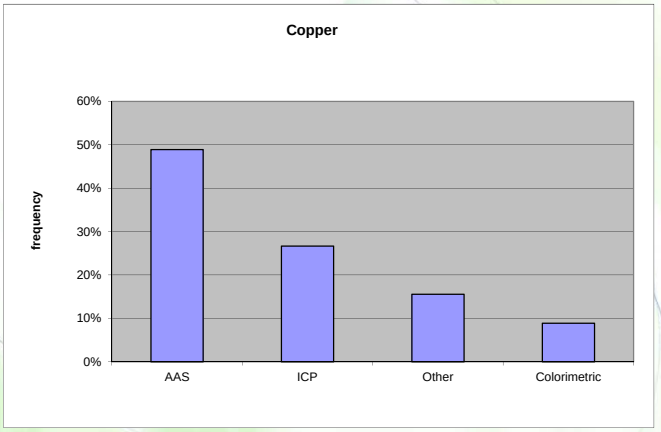
values:	45
removed:	0
mean:	1,11
ref.-value:	1,07
recovery:	103,7%
std:	0,093
rstd:	8,6%
std limit:	20%
upper limit:	1,26
lower limit:	0,89
too high:	3
too low:	3
outside limits:	6

Copper 3

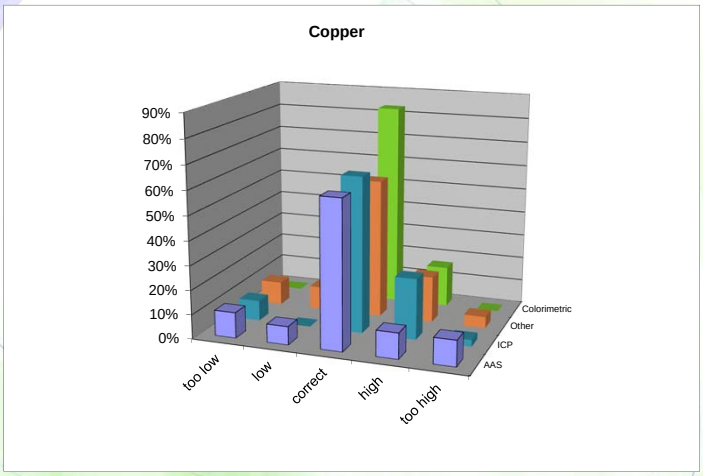


values:	45
removed:	0
mean:	1,11
ref.-value:	1,07
recovery:	103,7%
std:	0,093
rstd:	8,6%
std limit:	20%
upper limit:	1,26
lower limit:	0,89
too high:	3
too low:	3
outside limits:	6

Methods used



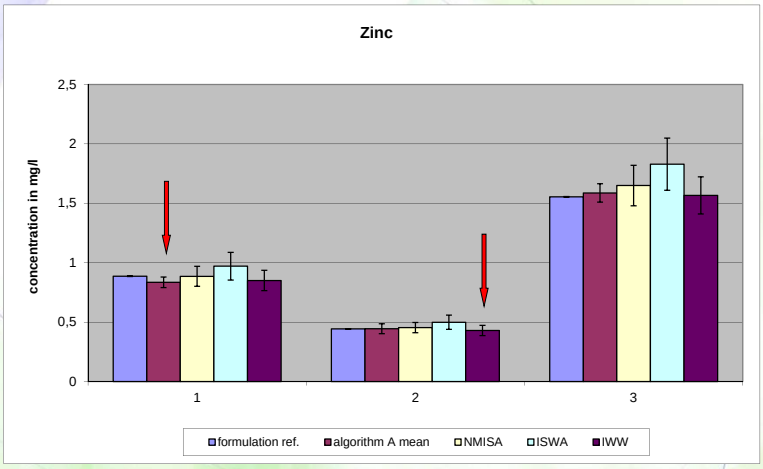
Comparison of methods



Summary Copper

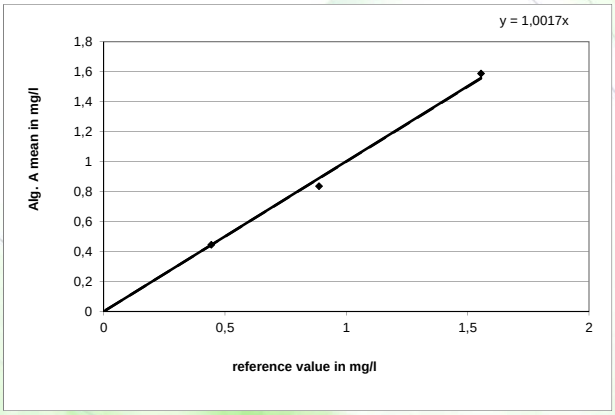
- Similar performance to last year
- Good standard deviations - around 10 %

Zinc
mean vs. ref.-value



Zinc

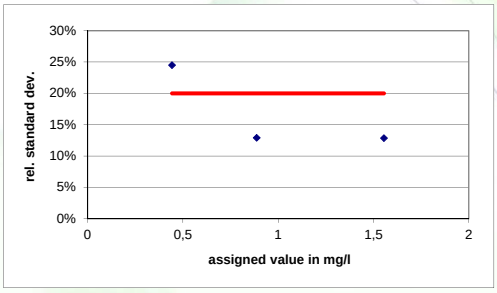
Alg. A mean vs. Reference value



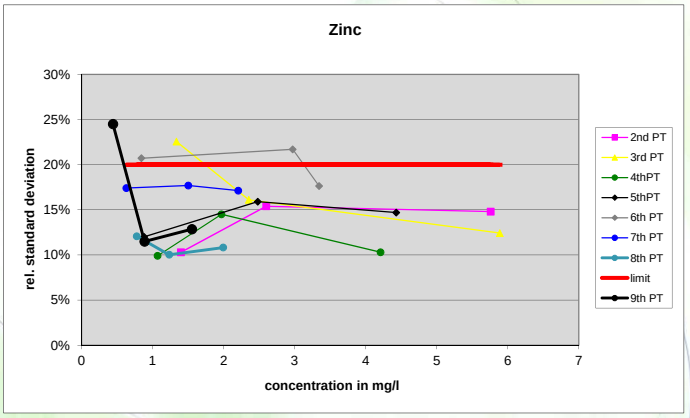
Average recovery	
2012	100.17
2011	102.9
2010	100.1
2009	102.1
2008	95.5
2007	93.0
2006	96.8

Zinc

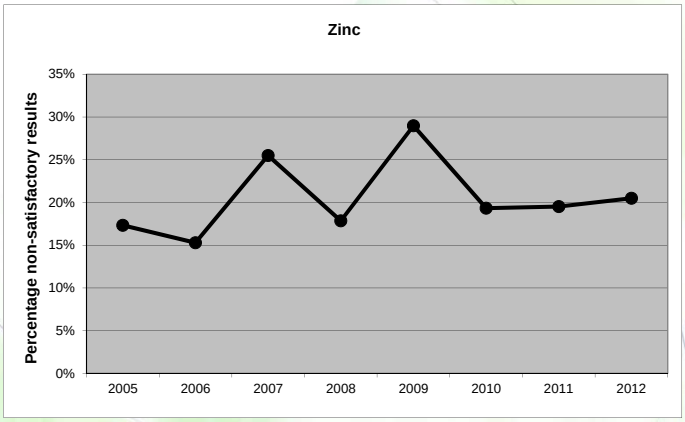
Calculated standard deviation and limit



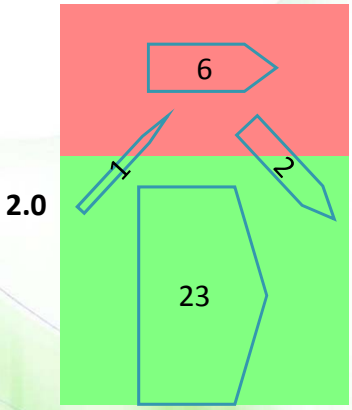
Zinc
calculated standard deviation and limit



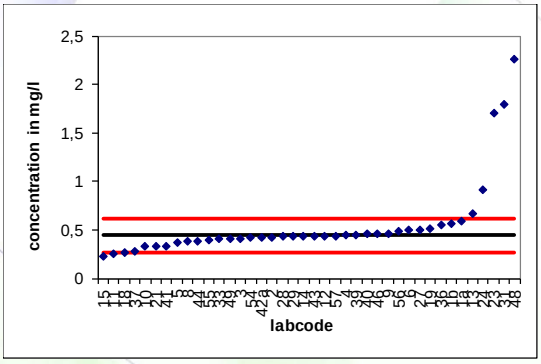
Zinc
Percentage non-satisfactory results



Zinc
Individual performance development

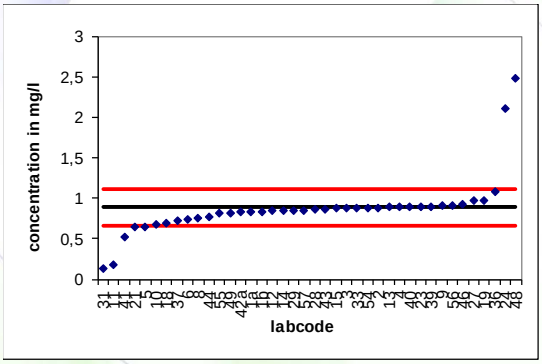


Zinc 1



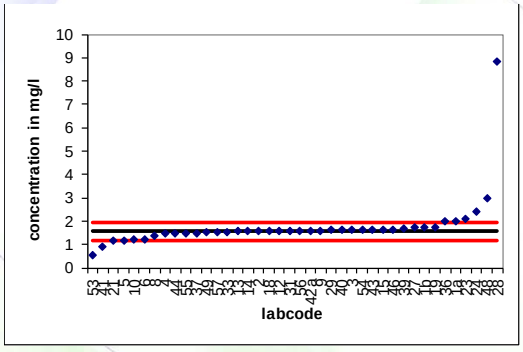
values:	40
removed:	0
mean:	0,44
ref.-value:	0,44
recovery:	100,3%
std:	0,109
rstd:	24,5%
std limit:	20%
upper limit:	0,62
lower limit:	0,27
too high:	5
too low:	3
outside limits:	8

Zinc 2



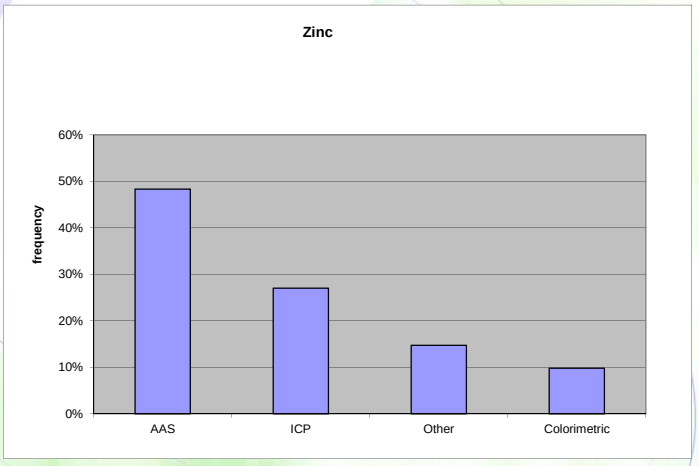
values:	41
removed:	1
mean:	0,84
ref.-value:	0,89
recovery:	94,2%
std:	0,115
rstd:	12,9%
std limit:	20%
upper limit:	1,12
lower limit:	0,66
too high:	2
too low:	6
outside limits:	8

Zinc 3

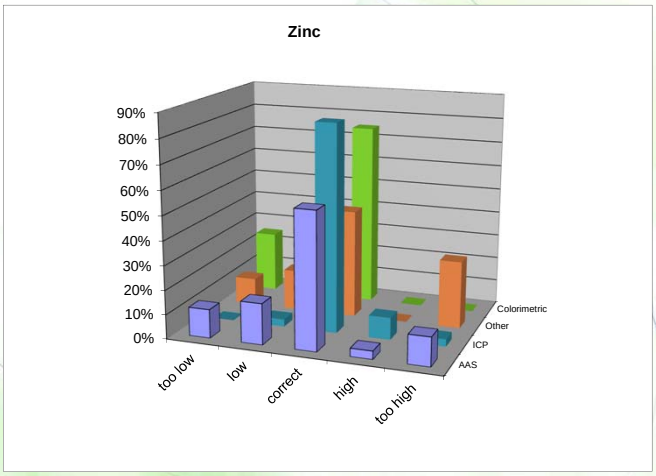


values:	41
removed:	1
mean:	1,59
ref.-value:	1,55
recovery:	102,1%
std:	0,200
rstd:	12,8%
std limit:	20%
upper limit:	1,95
lower limit:	1,16
too high:	6
too low:	3
outside limits:	9

Methods used



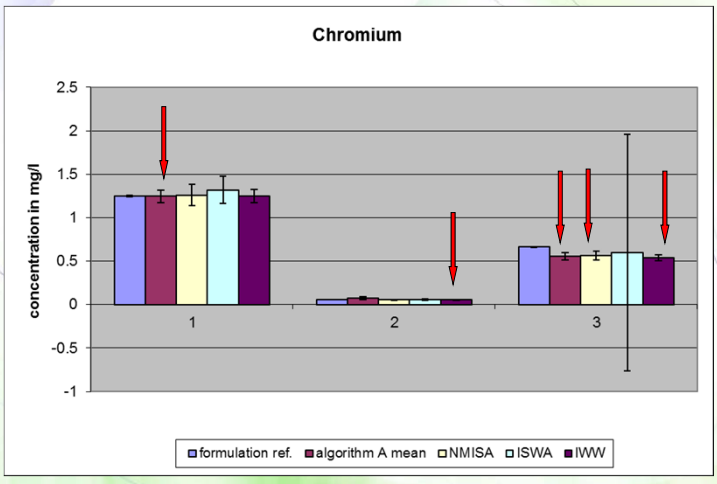
Comparison of methods



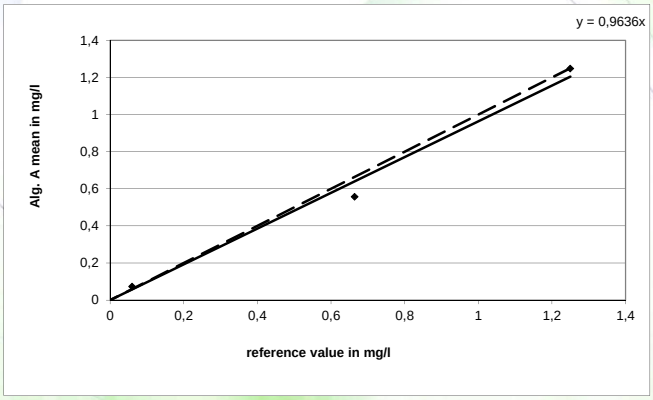
Summary Zinc

- Similar to last year
- But the STD for lowest level is significantly higher, maybe due to a lower conc.
- For the two higher levels everything is fine

Chromium
mean vs. ref.-value

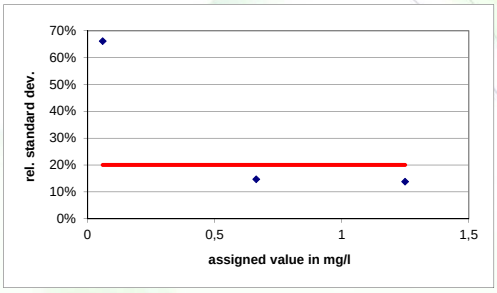


Chromium
Alg. A mean vs. Reference value

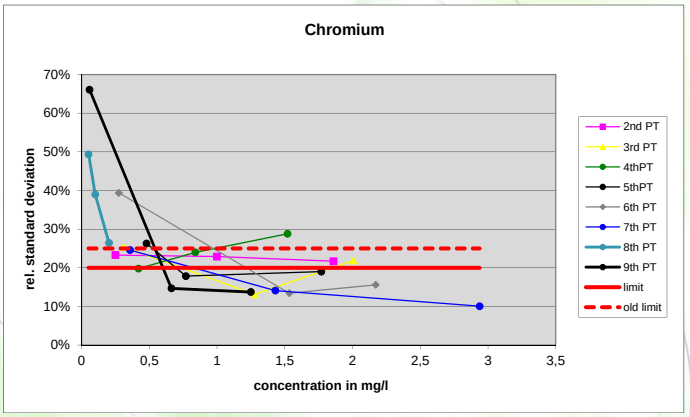


Average recovery	
2012	96.4
2011	90.9
2010	100.4
2009	81.9
2008	94.2
2007	100.1
2006	97.4

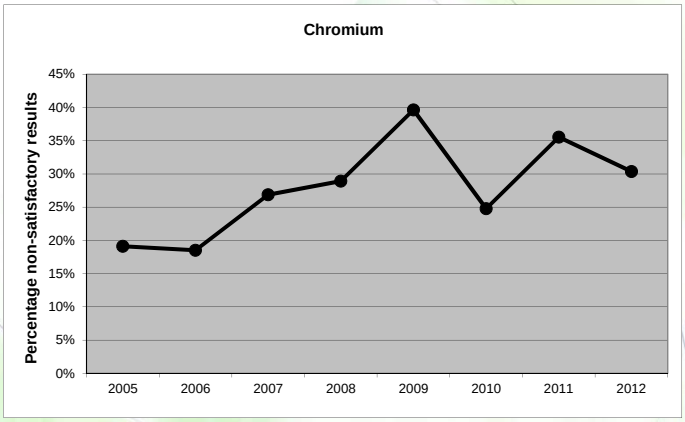
Chromium
Calculated standard deviation and limit



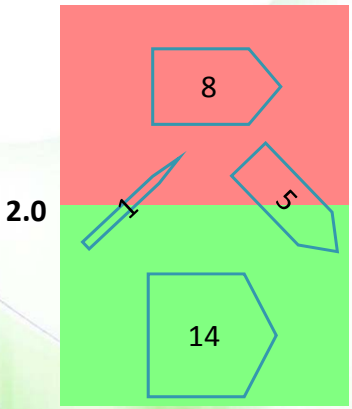
Chromium
calculated standard deviation and limit



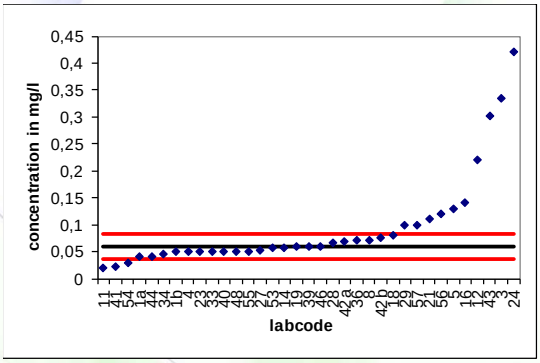
Chromium
Percentage non-satisfactory results



Chromium
Individual performance development

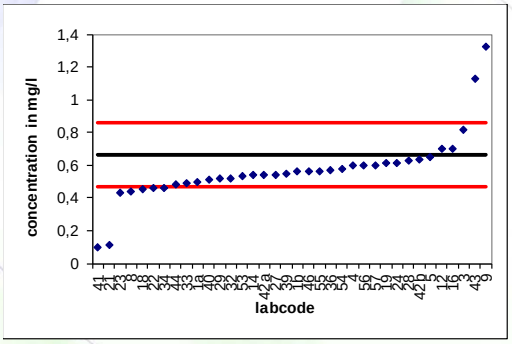


Chromium 1



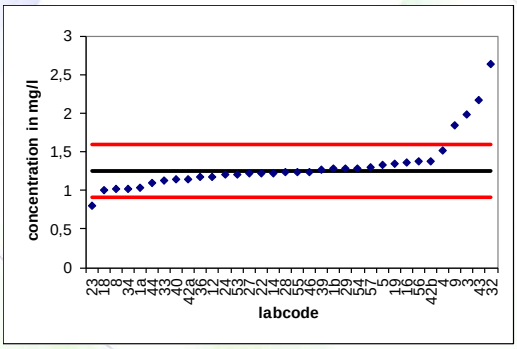
values:	36
removed:	1
mean:	0,07
ref.-value:	0,06
recovery:	122,1%
std:	0,039
rstd:	66,1%
std limit:	20%
upper limit:	0,08
lower limit:	0,04
too high:	11
too low:	3
outside limits:	14

Chromium 2



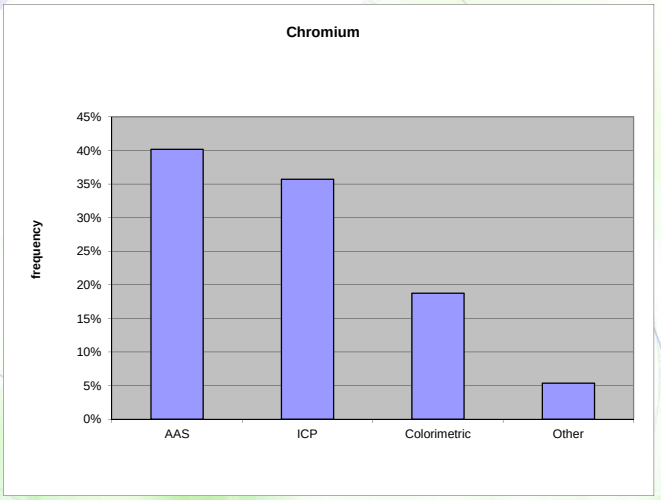
values:	38
removed:	2
mean:	0,56
ref.-value:	0,66
recovery:	83,9%
std:	0,097
rstd:	14,7%
std limit:	20%
upper limit:	0,86
lower limit:	0,47
too high:	2
too low:	9
outside limits:	11

Chromium 3

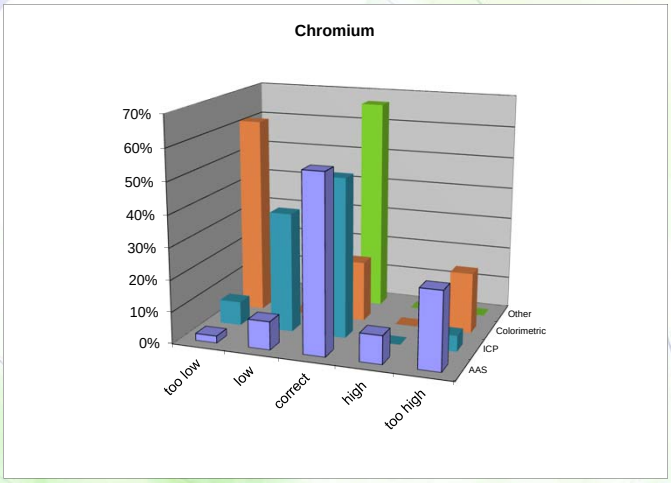


values:	38
removed:	4
mean:	1,25
ref.-value:	1,25
recovery:	99,8%
std:	0,172
rstd:	13,7%
std limit:	20%
upper limit:	1,59
lower limit:	0,91
too high:	4
too low:	5
outside limits:	9

Methods used



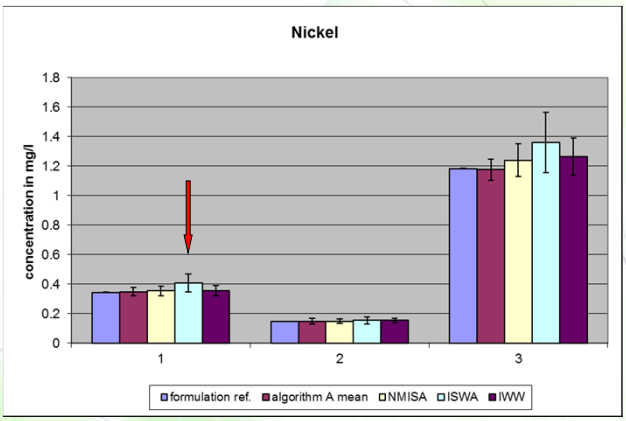
Comparison of methods



Summary Chromium

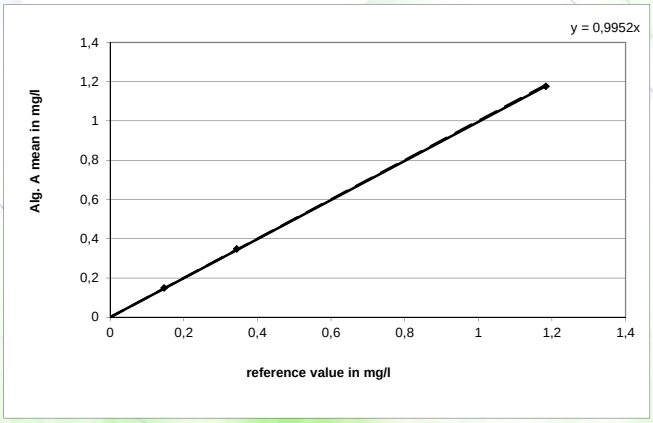
- Blank problems with the lowest level?
- The mean of the labs is quite low in comparison with ISWA and IWW as well
- The calculation of the reference values were checked for transcription errors and confirmed to be correct
- The colorimetric methods again has a high number of too low values – is that a method to determine Cr(VI)?

Nickel
mean vs. ref.-value



Nickel

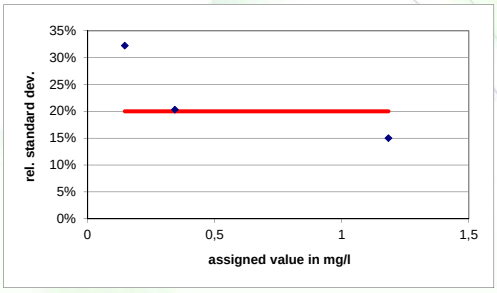
Alg. A mean vs. Reference value



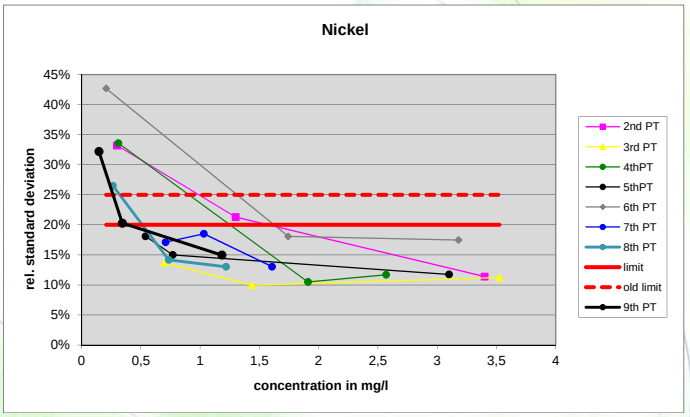
Average recovery	
2012	99.52
2011	98.3
2010	100.5
2009	98.0
2008	98.7
2007	99.0
2006	94.6

Nickel

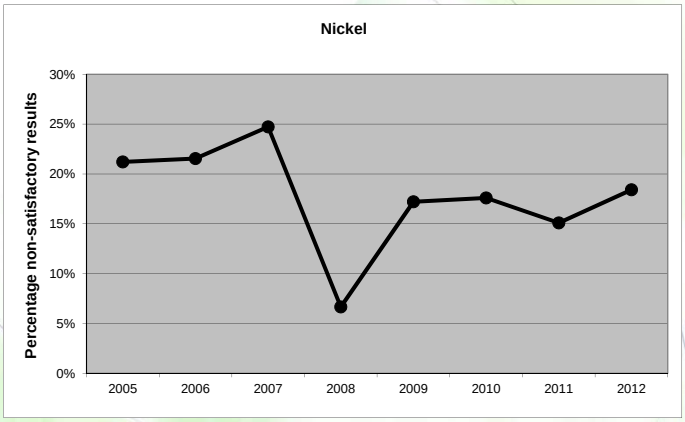
Calculated standard deviation and limit



Nickel
calculated standard deviation and limit

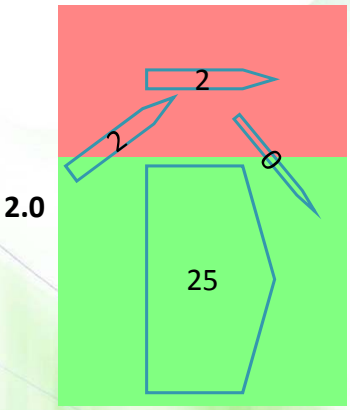


Nickel
Percentage non-satisfactory results



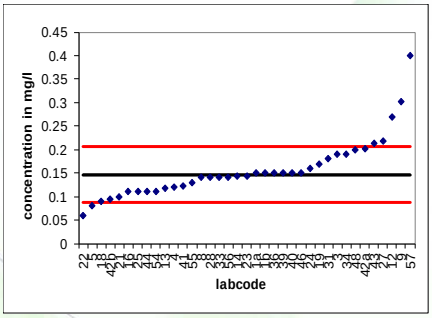
Nickel

Individual performance development



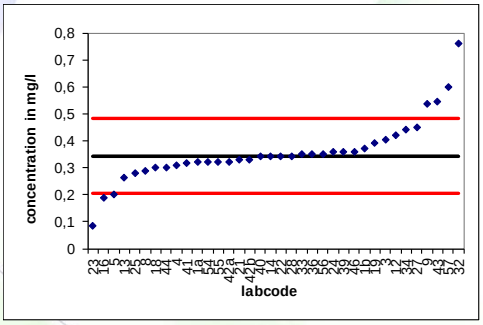
2.0

Nickel 1



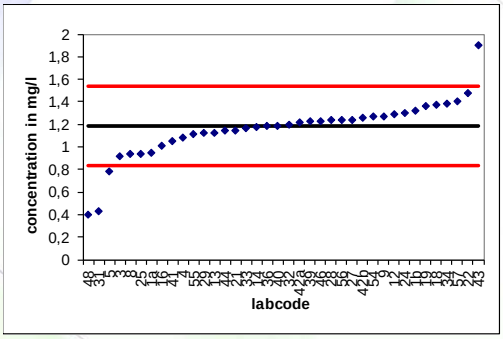
values:	37
removed:	0
mean:	0.15
ref.-value:	0.15
recovery:	101.4%
std:	0.047
rstd:	32.2%
std limit:	20%
upper limit:	0.21
lower limit:	0.09
too high:	5
too low:	2
outside limits:	7

Nickel 2



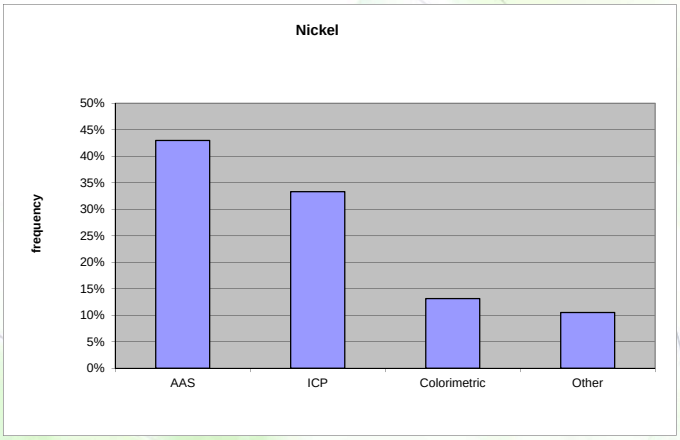
values:	38
removed:	2
mean:	0,35
ref.-value:	0,34
recovery:	101,1%
std:	0,070
rstd:	20,3%
std limit:	20%
upper limit:	0,48
lower limit:	0,21
too high:	4
too low:	5
outside limits:	9

Nickel 3

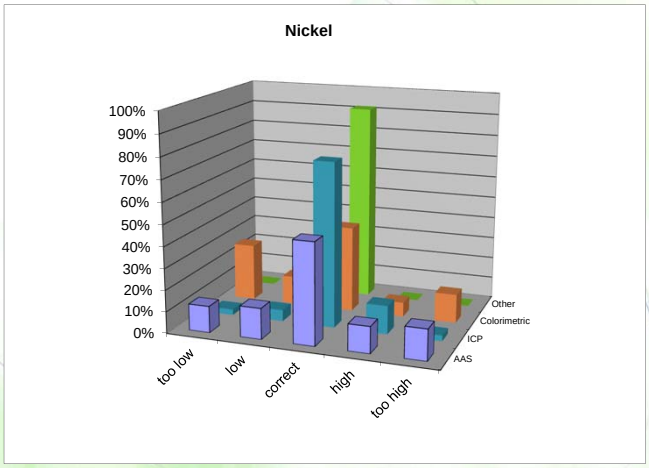


values:	39
removed:	1
mean:	1,18
ref.-value:	1,18
recovery:	99,4%
std:	0,177
rstd:	15,0%
std limit:	20%
upper limit:	1,54
lower limit:	0,83
too high:	1
too low:	4
outside limits:	5

Methods used



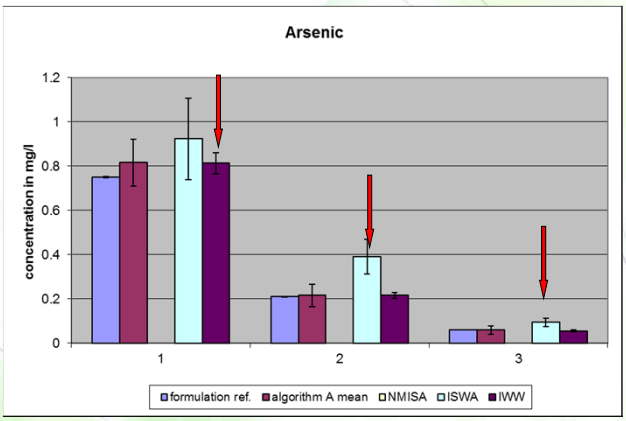
Comparison of methods



Summary Nickel

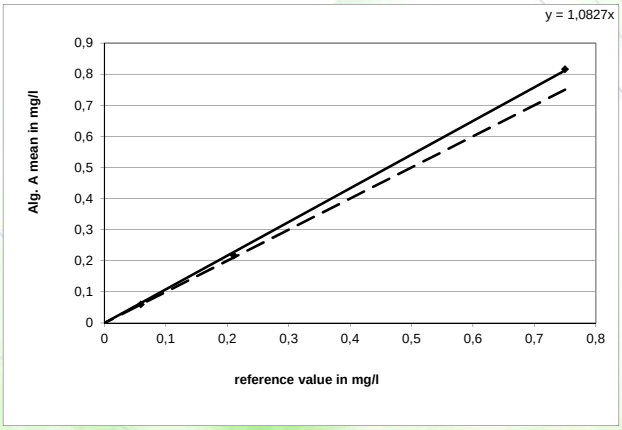
- High STD for the lowest level just as in the previous rounds

Arsenic
mean vs. ref.-value



Arsenic

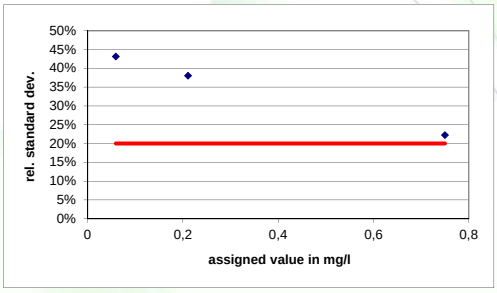
Alg. A mean vs. Reference value



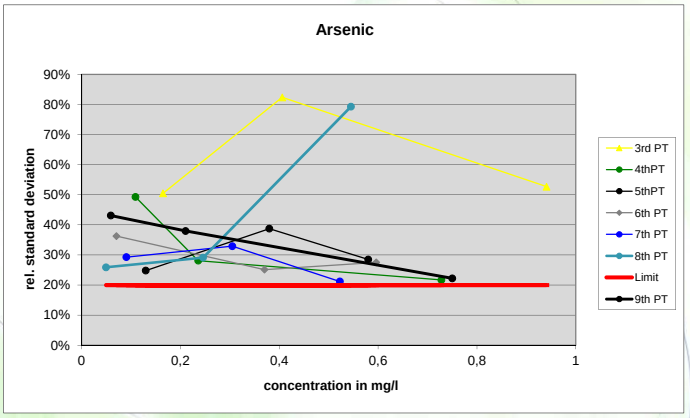
Average recovery	
2012	108.27
2011	120.9
2010	97.0
2009	99.3
2008	92.4
2007	96.6
2006	111.2

Arsenic

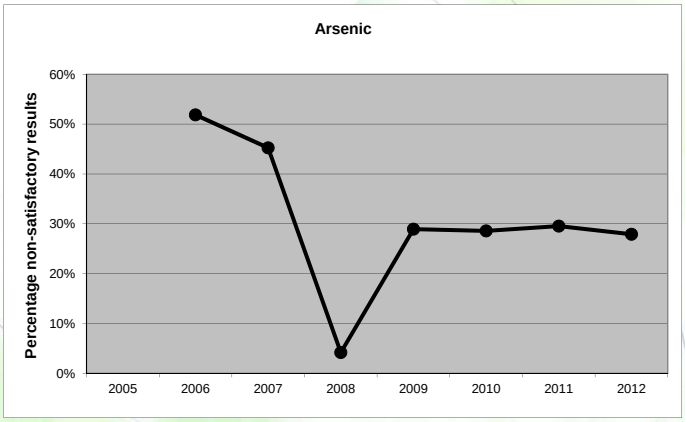
Calculated standard deviation and limit



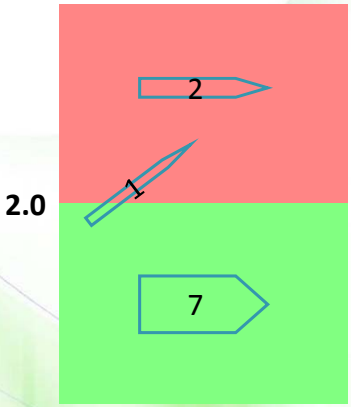
Arsenic
calculated standard deviation and limit



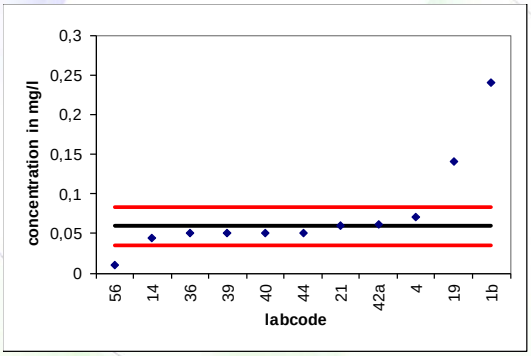
Arsenic
Percentage non-satisfactory results



Arsenic
Individual performance development

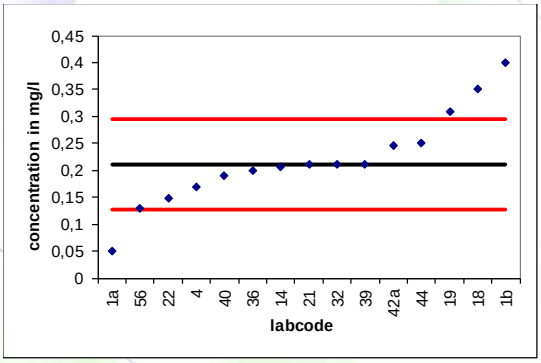


Arsenic 1



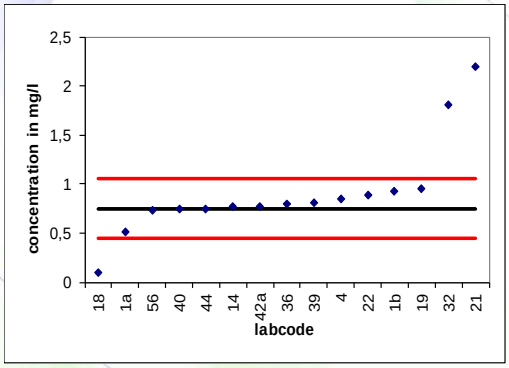
values:	13
removed:	2
mean:	0,06
ref.-value:	0,06
recovery:	100,1%
std:	0,026
rstd:	43,1%
std limit:	20%
upper limit:	0,08
lower limit:	0,04
too high:	4
too low:	1
outside limits:	5

Arsenic 2



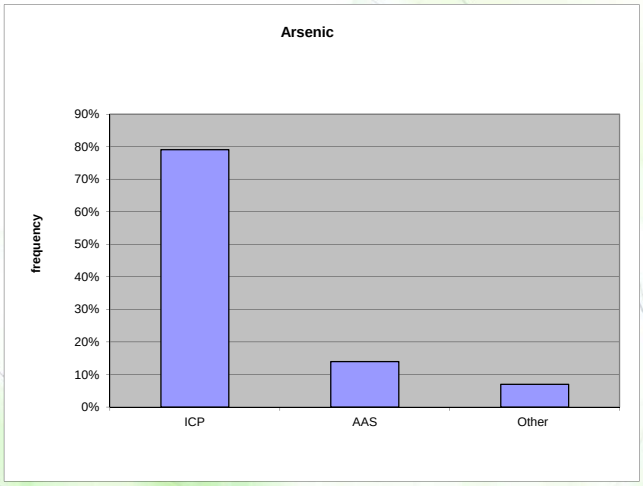
values:	15
removed:	0
mean:	0,22
ref.-value:	0,21
recovery:	102,9%
std:	0,080
rstd:	38,0%
std limit:	20%
upper limit:	0,29
lower limit:	0,13
too high:	3
too low:	1
outside limits:	4

Arsenic 3

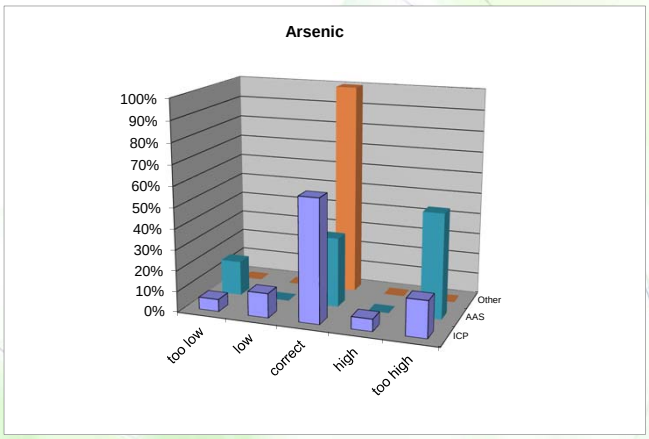


values:	15
removed:	0
mean:	0,82
ref.-value:	0,75
recovery:	108,7%
std:	0,167
rstd:	22,2%
std limit:	20%
upper limit:	1,05
lower limit:	0,45
too high:	2
too low:	1
outside limits:	3

Methods used



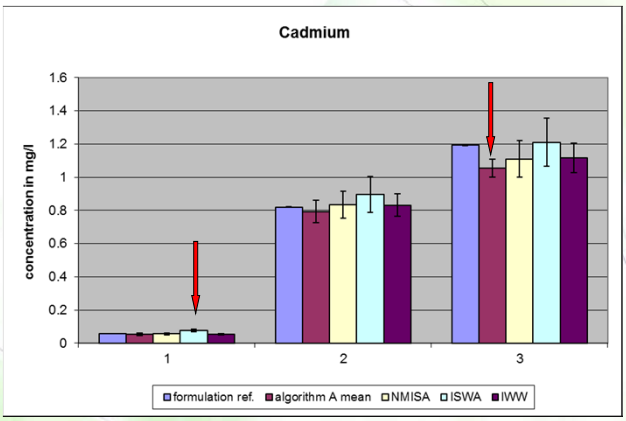
Comparison of methods



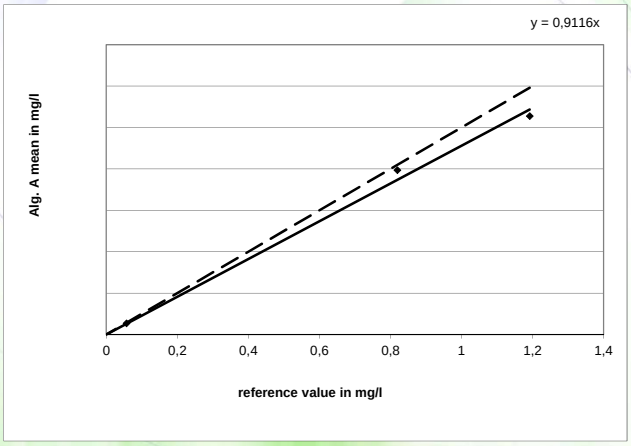
Summary Arsenic

- Low number of values
- STDs higher
- Obviously problems with AAS

Cadmium
mean vs. ref.-value

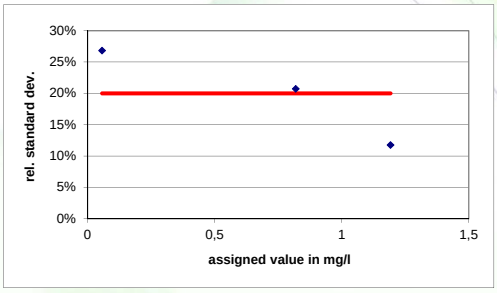


Cadmium
Alg. A mean vs. Reference value

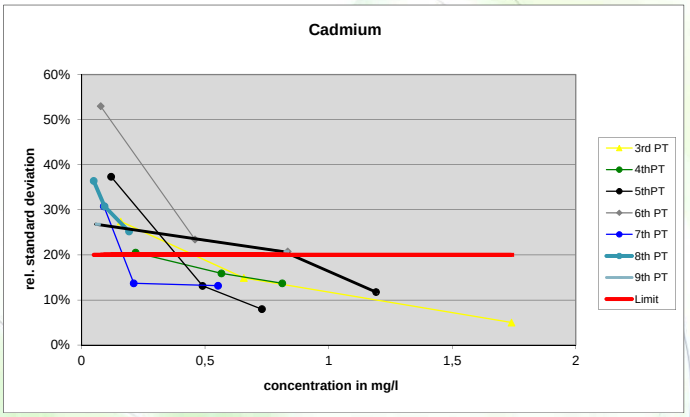


Average recovery	
2012	91.16
2011	96.8
2010	91.1
2009	93.1
2008	99.1
2007	96.4
2006	96.6

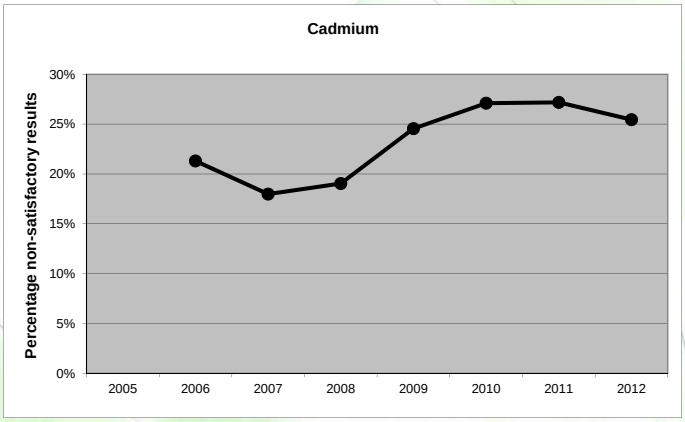
Cadmium
Calculated standard deviation and limit



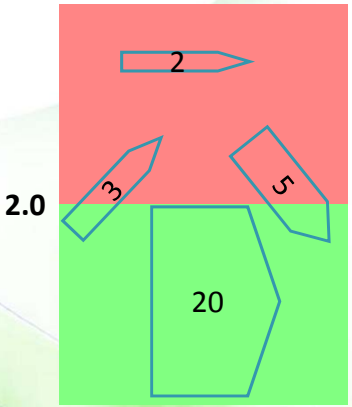
Cadmium
calculated standard deviation and limit



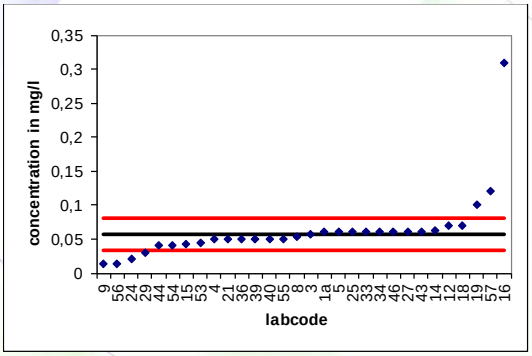
Cadmium
Percentage non-satisfactory results



Cadmium
Individual performance development

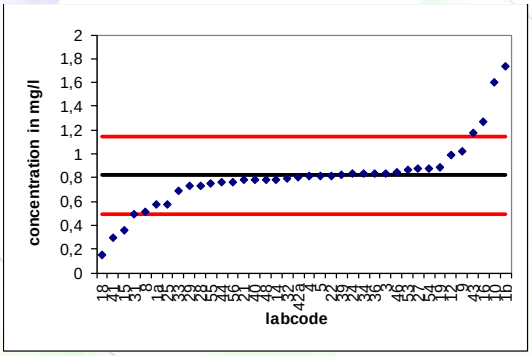


Cadmium 1



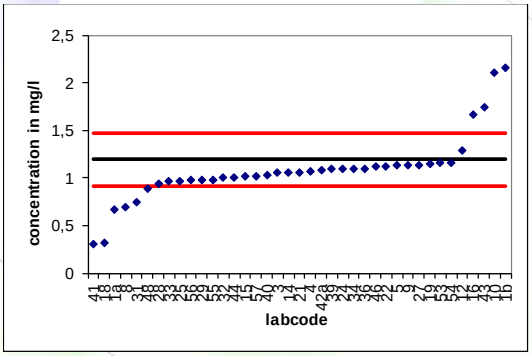
values:	33
removed:	3
mean:	0,05
ref.-value:	0,06
recovery:	94,3%
std:	0,015
rstd:	26,8%
std limit:	20%
upper limit:	0,08
lower limit:	0,03
too high:	6
too low:	4
outside limits:	10

Cadmium 2



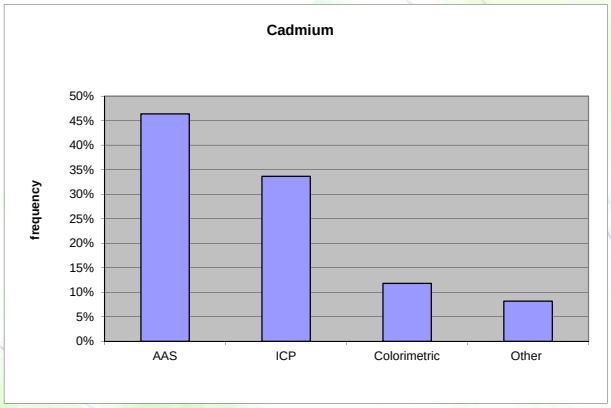
values:	38
removed:	0
mean:	0,79
ref.-value:	0,82
recovery:	96,8%
std:	0,170
rstd:	20,7%
std limit:	20%
upper limit:	1,15
lower limit:	0,49
too high:	4
too low:	4
outside limits:	8

Cadmium 3

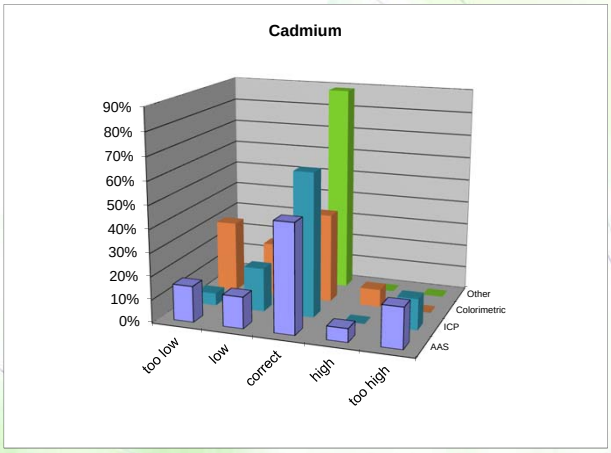


values:	39
removed:	0
mean:	1,05
ref.-value:	1,19
recovery:	88,5%
std:	0,140
rstd:	11,8%
std limit:	20%
upper limit:	1,47
lower limit:	0,91
too high:	4
too low:	6
outside limits:	10

Methods used



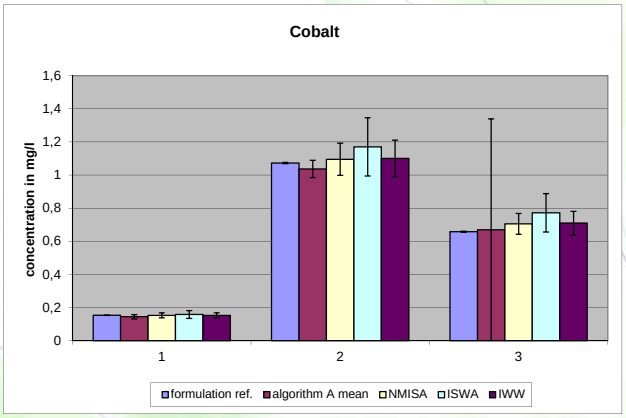
Comparison of methods



Summary Cadmium

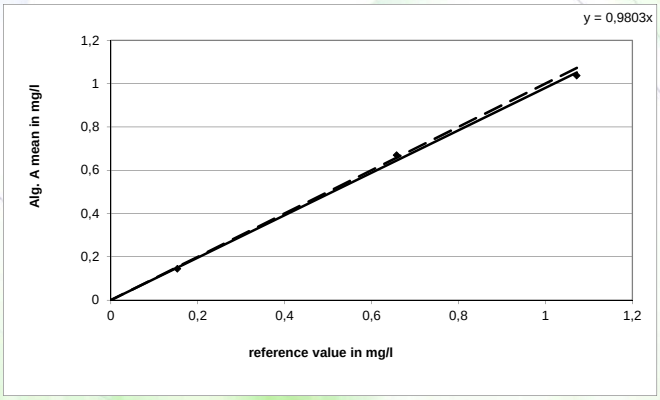
- STDs better than last year, but in the same range as in the previous rounds

Cobalt
mean vs. ref.-value



Cobalt

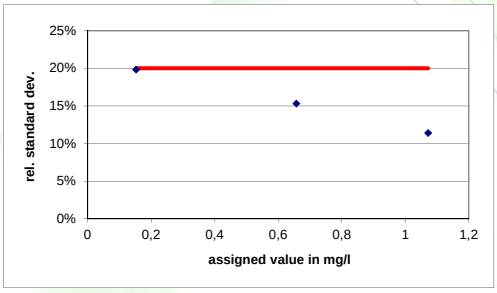
Alg. A mean vs. Reference value



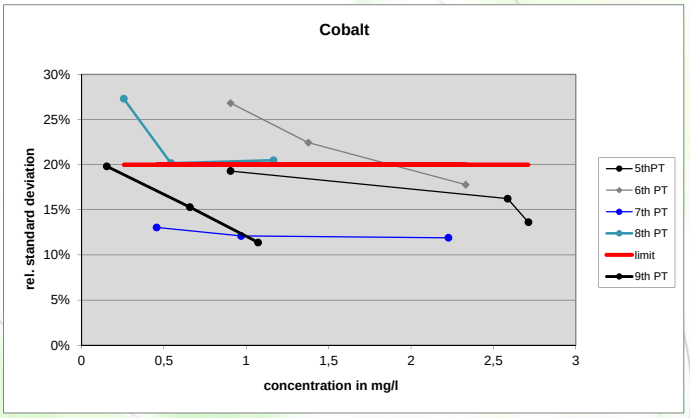
Average recovery	
2012	98.03
2011	103.6
2010	97.0
2009	96.7
2008	99.8
2007	-
2006	-

Cobalt

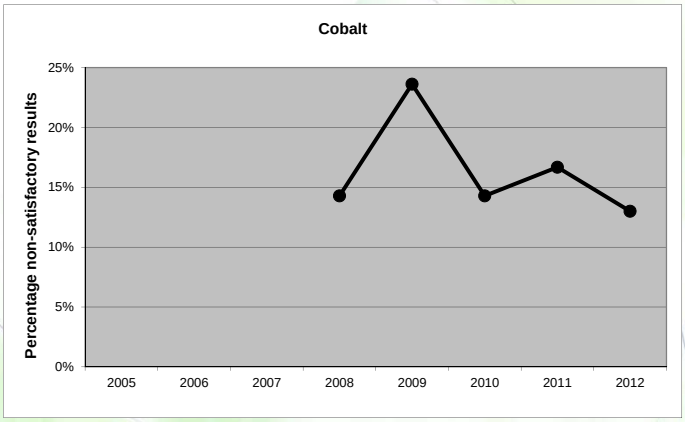
Calculated standard deviation and limit



Cobalt
calculated standard deviation and limit

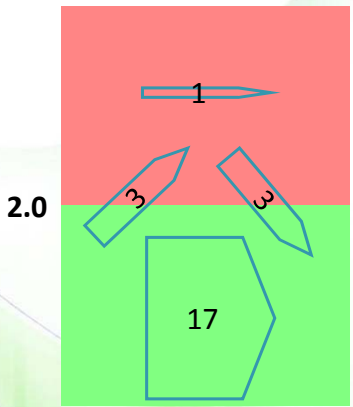


Cobalt
Percentage non-satisfactory results

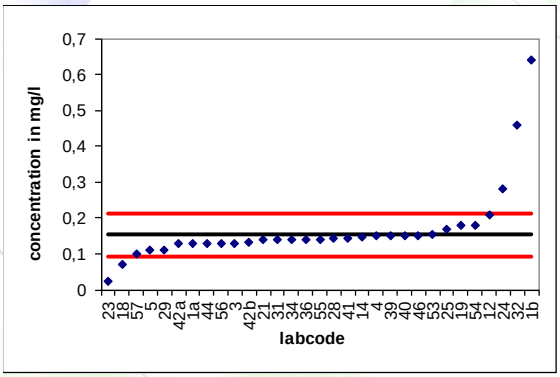


Cobalt

Individual performance development

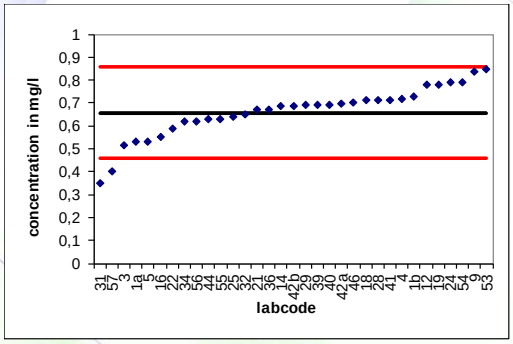


Cobalt 1



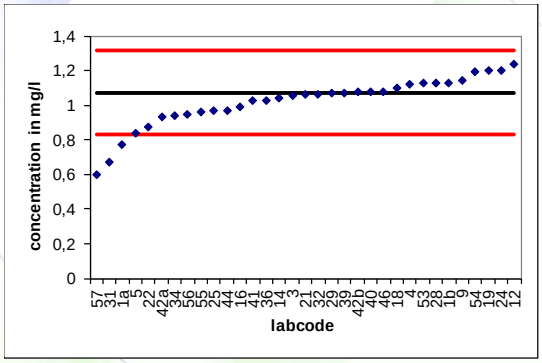
values:	32
removed:	1
mean:	0,14
ref.-value:	0,15
recovery:	94,4%
std:	0,030
rstd:	19,8%
std limit:	20%
upper limit:	0,21
lower limit:	0,09
too high:	3
too low:	3
outside limits:	6

Cobalt 2



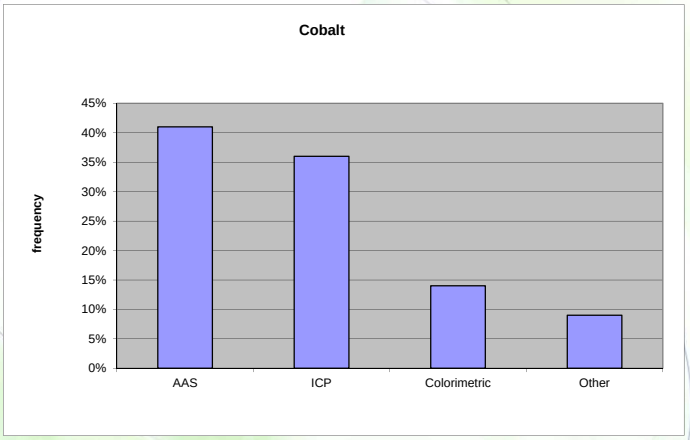
values:	34
removed:	1
mean:	0,67
ref.-value:	0,66
recovery:	101,8%
std:	0,101
rstd:	15,3%
std limit:	20%
upper limit:	0,86
lower limit:	0,46
too high:	0
too low:	3
outside limits:	3

Cobalt 3

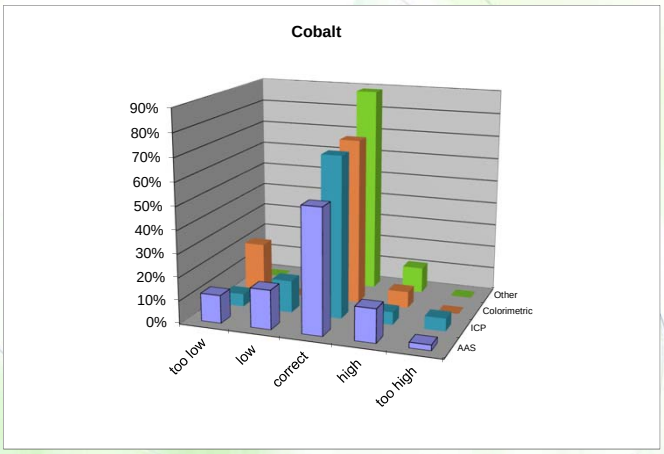


values:	34
removed:	1
mean:	1,04
ref.-value:	1,07
recovery:	96,7%
std:	0,122
rstd:	11,4%
std limit:	20%
upper limit:	1,32
lower limit:	0,83
too high:	0
too low:	4
outside limits:	4

Methods used



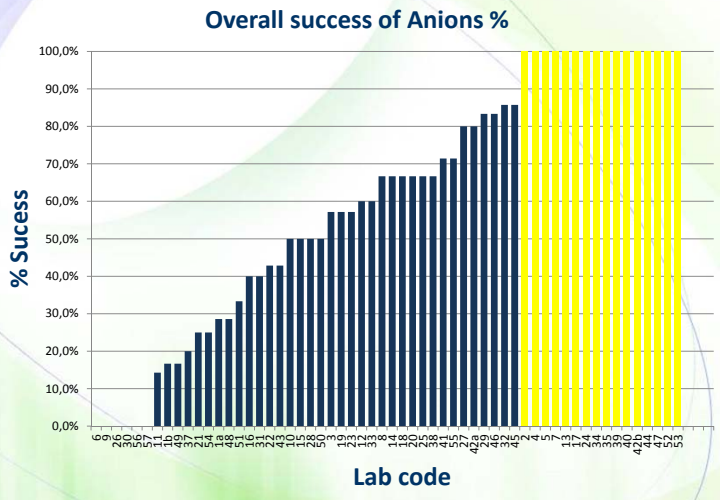
Comparison of methods



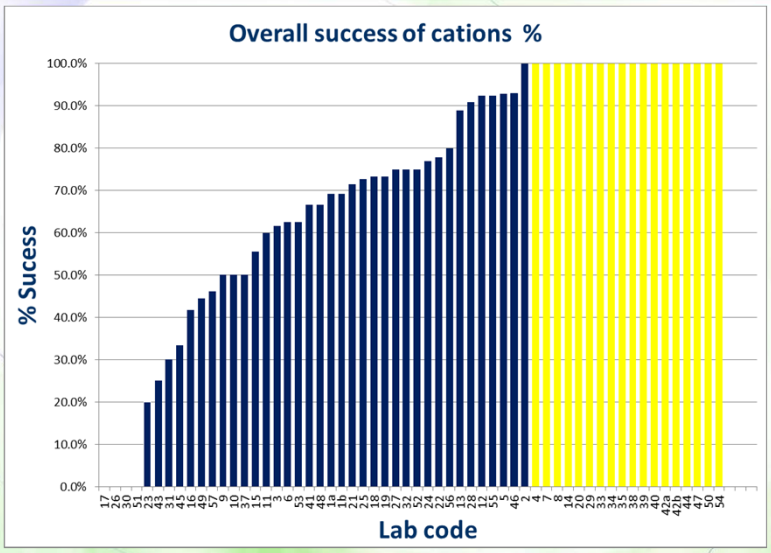
Summary Cobalt

- Slight improvement in the STDs

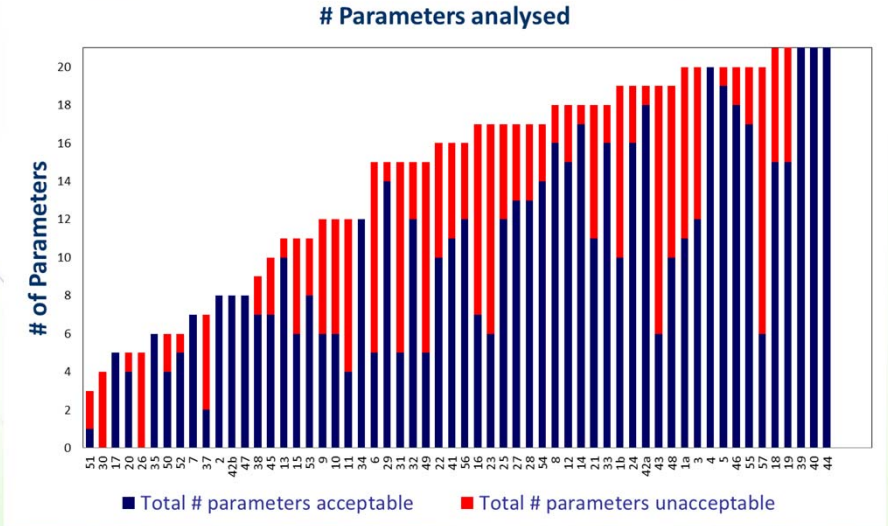
Success of the anions = 16



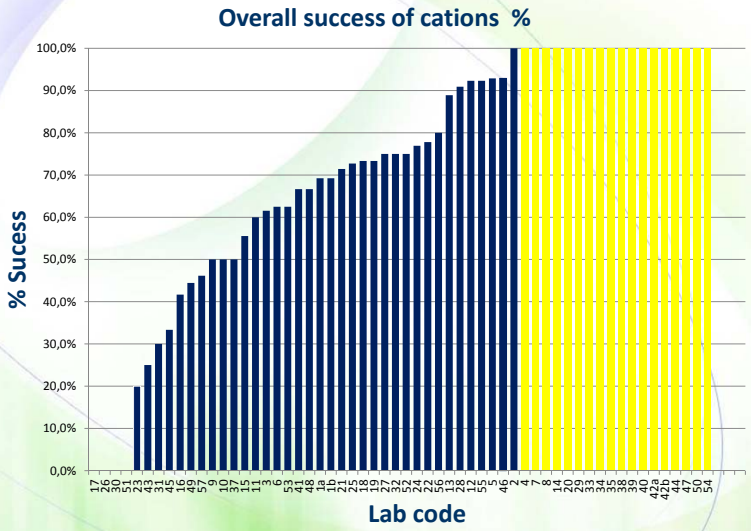
Success of the Cations = 19



Overview on participation



Overall success



Overall

- No real improvement – still high standard deviations
- The same mistakes are being done - Reporting of results in wrong units (N and not NO_3 and as P and not PO_4;Use of non-standard methods
- The ranges do not help to improve the results
- Corrective actions are still not implemented - Investigate problems / determine the root cause
- Recommended methods must be finalised and implemented

Challenges for 2013

- Use old PT samples to implement corrective action immediately
- Use the ranges to avoid complete outliers
- Application of internal quality control
- Equipment, method comparison, assistance and continuous education amongst the SADCMET lab association important and a good platform for networking.

Acknowledgments

- **PTB assistance**
  - Kathrin Wunderlich
  - Karin Vondeberg
- **SADCMET**
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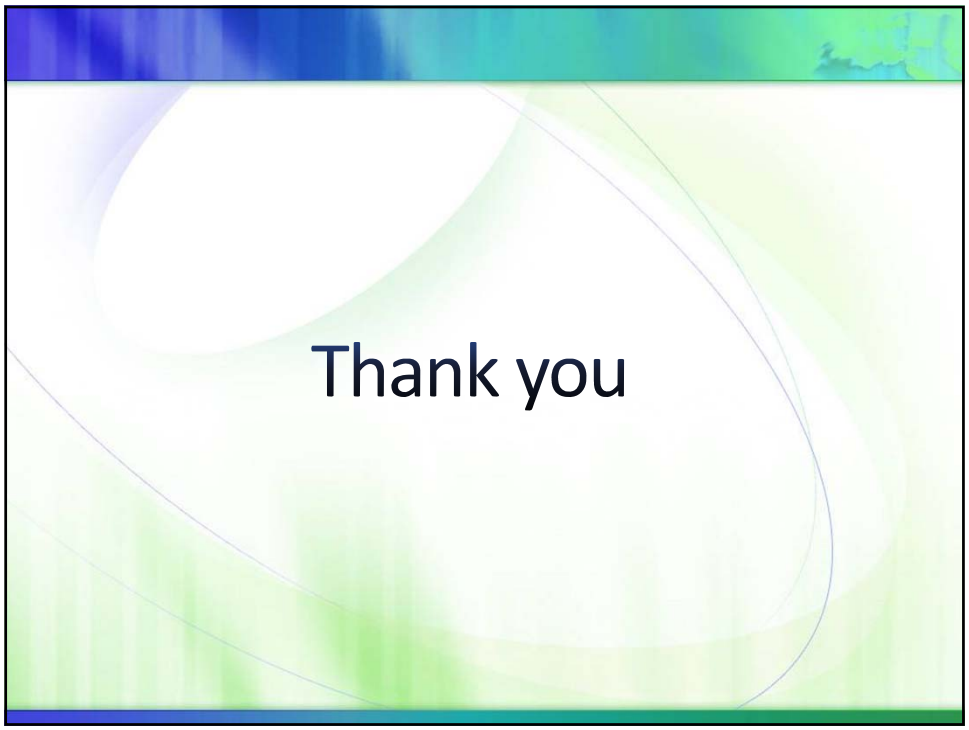
- **University of Stuttgart**
  - Dr Michael Koch
- **NamWater personnel**
- **Expert labs – NMISA; ISWA; IWW**
- **Local coordinators**
- **Participants**


Thank you

Calibration

Presented by Kezia Mbwambo
Addis Ababa Ethiopia

Contents

- Introduction
- Basics of Calibration
- Limits of detection, quantification
- Standard Addition Method

1

What is Calibration?

- Calibration is the process of establishing how the response of a measurement process varies with respect to the parameter being measured
- The usual way to perform calibration is to subject known amounts of the parameter (e.g. using a measurement standard or reference material) to the measurement process and monitor the measurement response

2

What is Calibration?..

- Calibration is an important process in
  - Establishing the link between a signal of the measuring instrument and the associated quantity (e.g. concentration) of the measurand
  - Establishing traceability
  - Method validation to get the performance characteristics

3

Two Major Aims

- Establishing a mathematical function which describes the dependency of the system's parameter (e.g. concentration) on the measured value
- Gaining statistical information and characteristics of the analytical system, e.g. sensitivity, precision

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Calibration Concepts

- External standard

  Measurement of separate samples containing known amount of analyte compared to the signal from both the calibration sample and unknown sample.

- Internal standard

  Addition of known amount of substance which has properties similar to the analyte.

- Standard addition

  Known amount of analyte is added to the sample and from the increase in signal the original content is extrapolated.

5

Goals of Calibration

- "Ability to calculate a (measurement) result in a secure (safe) working range"

(Funk, W., Dammann, V., and Donnevert, G.: "Quality Assurance in Analytical Chemistry")

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First Steps to the Goal

- Establishing the calibration function
  - Choosing the preliminary working range
  - Measuring several calibration standards
  - Linear regression
  - Test of non linear regression
  - Test of variance homogeneity
  - Calculate performance characteristics
  - Fix the working range

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In Routine

- Calculating the (measurement) results
  - Conversion of the calibration function into an analytical function
  - Reporting the measurement results

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Basics of Calibration

- Mathematical Functions
  - Simple linear function without intercept
    $y = m\,x$
  - Linear function
    (intercept a, slope b)
    $y = a + bx$
  - Quadratic function
    (intercept a, slope 2cx+b)
    $y = a + bx + cx^2$

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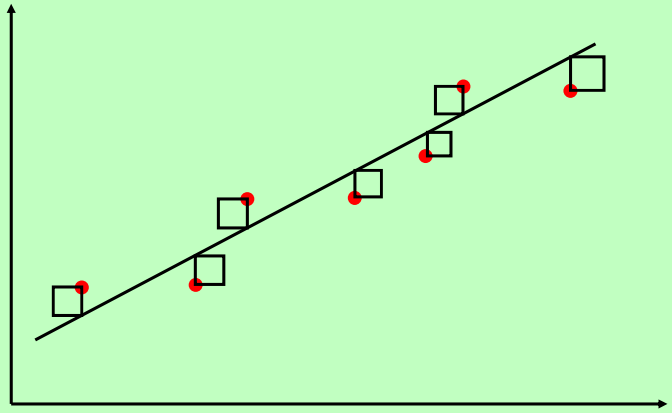
Principle of Linear Regression



- Minimizing the sum of the squares of the residuals

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International Standards

- ISO 8466 Water quality– Calibration and evaluation of analytical methods and estimation of performance characteristics
  - Part 1: Statistical evaluation of the linear calibration function
  - Part 2: Calibration strategy for non-linear second order calibration functions

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Analytical Function / Calibration Function

- With calibration standards we get a measurement result y for each content x of the analyte in the standard
  With that we get (by regression analysis) the **calibration function**

$$y = f(x)$$

- If we invert the function we can calculate the content of analyte in the unknown sample from the result of the measurement.
  This function is the **analytical function**

$$\hat{x} = f(\hat{y})$$

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Basic Calibration

- With the Basic Calibration only the measurement step itself is calibrated
- I.e. no sample preparation like extraction, digestion etc. is done
- We simply analyse standards in pure solvent

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Choosing the Preliminary Working Range

- Take into consideration
  - The practical application of the analysis (the purpose)
  - The possibilities that are technically feasible
    - Measurement results at the lower application limit must be significantly different from blanks
    - The requested analytical precision (or measurement uncertainty) has to be achieved over the whole working range
    - If a linear regression procedure has to be applied the variances have to be homogeneous over the whole range and linearity has to be assured

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Preparation of the Standard Samples

- Requirements:
  - Purity, matrix free or defined matrix
  - Homogeneity
  - Representative for real samples
    - Species similar in chemistry
    - Same oxidation state
    - etc.
  - Stability, preserveability
  - No influence on the sample from the container and external conditions

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Preparation of the Standard Samples

- Production of standard samples
  - Consider precision of balance and volumetric equipment
  - Weighings are always more precise and therefore to be preferred
  - Avoid successive dilutions
  - Prepare 6...10 standard samples, equidistant over the whole working range

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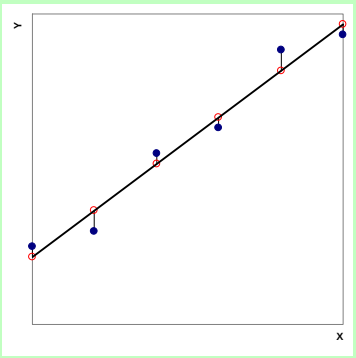
Linear Calibration



- Regression analysis delivers the calibration function
  y = a + bx
- slope (sensitivity)

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

- Intercept

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

- Residual standard deviation (vertical scattering of the results around the regression line)

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

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

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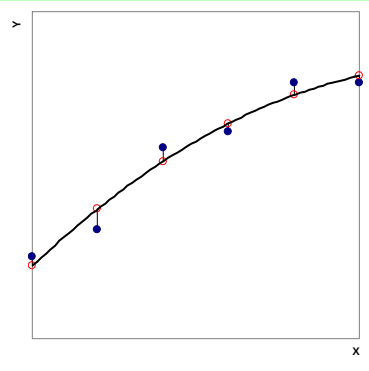
Second Order Calibration Function $y = a + bx + cx^2$

- Calculations are somewhat more difficult here
- For details see ISO 8466-2



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Second Order Calibration Function

- Residual standard deviation

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

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

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

- Process variation coefficient

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

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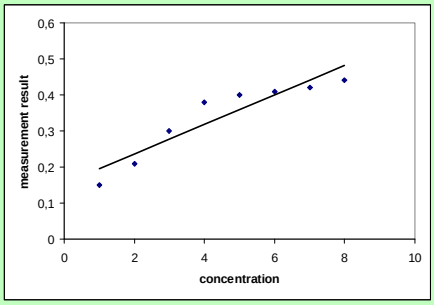
Linearity Check

- If possible, the linear calibration function should be used, only in special circumstances second order calibration should be used
- Visual linearity check
  - Graphical display incl. calibration line
  - If non-linearity is obvious you may abstain from a statistical linearity check



Linearity Check

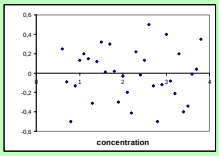
- Mandel test
  - Calculation of linear calibration function y=a+bx and the 2nd order calibration function $y=a+bx+cx^2$ including the respective residual standard deviations s_{y1} (linear) and s_{y2} (quadratic)
  - Calculation of the differences of variances DS^2:

    $DS^2 = (N-2)s_{y_1}^2 - (N-3)s_{y_2}^2$ with degree of freedom $f = 1$

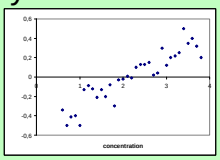
  - Check with F-test $F_{observed} = \frac{DS^2}{s_{y_2}^2}$
  - Comparison with the critical value from the table $F_{critical}$ for $f_1=1$, $f_2=N-3$, P=99%
  - If $F_{observed} < F_{critical}$, the 2nd order function does **not** give a significant better result
  - Linear calibration function should then be used

Residual Analysis

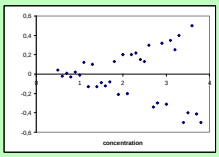
- Residuals are the vertical distances of the results from the regression line
- Residuals should be normally distributed



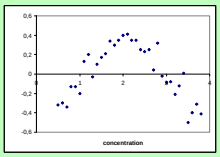
Normally distributed residuals
correct modelling approach



linear trend
wrong approach or calculation error



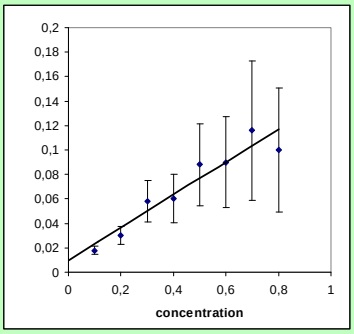
Increasing variances
inhomogeneity of variances



Non linear
wrong regression function

Homogeneity of Variances

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



- Inhomogeneity of variances not only leads to increased imprecision, but also may affect bias due to a changed slope of the regression line

Homogeneity Check for Variances

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

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

- Check with F-test

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

- If $F_{observed} > F_{critical}$, variances are not homogeneous
- Possible consequences:
  - Reduced working range
  - Weighted regression

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Outlier Test

- Calibration data always have to be free from outliers
- The outlier test assumes that the chosen regression approach is correct
- Potential outliers can be identified from the residual analysis
- First calculate the residual standard deviation $s_{y,A1}$ using all results; than eliminate the potential outlier and calculate again $s_{y,A2}$
- Check with F-test or t-test

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Outlier Test using the F-Test

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

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

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

Outlier Test using the t-Test

- Calculate the prognostic interval of the regression line <u>without</u> the potential outlier

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

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

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

- If the potential outlier is located within the prognostic interval, it‘s no outlier
- **If an outlier is identified statistically, the error source <u>has</u> to be found and eliminated. Than the <u>complete</u> calibration has to be repeated.**

Calibration Strategies in Routine Analysis

- The basic calibration as described up to here is part of the (re-)validation of an analytical method
- For routine use calibration strategies with less effort are used
- The effort made depends on the demands of the customer and the stability of the method

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Calibration Strategies in Routine Analysis

- Number of calibration points in routine
  - Where the calibration of the method is very stable a one-point calibration to verify a previous multi-point calibration may be sufficient
  - In other, less stable circumstances a 3- or 5-point calibration may be needed
- Frequency of calibration
  - Also depends on the stability of calibration
  - Some analytical methods need a daily calibration whereas other calibrations may last for months. At least check of the calibration is adviceable in any case

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Internal Standard

- Advisable for methods including a complex sample preparation procedure like extraction and clean-up
- Addition of a known amount of a substance different from the analyte and not present in the sample, but chemically behaving in the same way as the analyte
- Correction of the measurement result for the analyte with the recovery rate of the internal standard
- In mass spectrometry isotope marked analytes are often used for this purpose

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Limits of detection, quantification

Limit of Detection (LoD)
Limit of Quantification (LoQ)

- Are used to quantify detection and quantification capabilities (the lower end of the working range)
- Limit of detection (LoD)
  - The lowest concentration that can be detected with a certain level of confidence
- Limit of quantification (LoQ)
  - the minimum content that can be quantified with a certain confidence

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Specification of Measurement Process

- LoD and LoQ cannot be specified in the absence of a fully defined measurement process including interferences and type of sample matrix
- "Interference free detection limits" and "Instrument detection limits", for example, do not specify the measurement capabilities of a complex measurement process including sample preparation

(IUPAC Orange Book)

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Calculation of LoD

- There is no uniform way to calculate LoD values in the scientific community
- Two possibilities are described in the following slides (both taken from IUPAC Orange Book)

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LoD – Simple Approach

- The value of the LOD is given by

$$LoD = \bar{x}_{bl} + k \cdot s_{bl}$$

with

$\bar{x}_{bl}$ = mean of blanks

s_{bl} = standard deviation of blanks

k = numerical factor defining the confidence level

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LoD – Simple Approach

- The mean of measurements of blanks and their standard deviation must be found experimentally by making a sufficiently large number of measurements
- A value of 3 for k is strongly recommended
  - At low concentrations non-Gaussian distributions are more likely
  - The mean and standard deviations are only estimates of the population characteristics
  - So the 3 s_{bl} value usually corresponds to a confidence level of about 90%

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Limit of Quantification (LoQ)

- Quantification limits are performance characteristics that mark the ability of a analytical method to adequately "quantify" an analyte (IUPAC Orange book)

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LoQ

- The ability to quantify is generally expressed in terms of the signal or analyte (true) value that will produce estimates having a specified relative standard deviation (RSD), commonly 10 %

$$LoQ = k \cdot s_{LoQ}$$

with

s_{LoQ} = standard deviation at the LoQ concentration

k = multiplier (reciprocal = selected quantifying RSD)

- The IUPAC default value for k is 10
- If the variances are homogeneous $s_{LoQ} = s_{blank}$

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Standard Addition Method

- Standard addition is calibration in the real sample by stepwise addition of known amounts of the analyte

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When should the Standard Addition Method be Used?

- If the composition of the sample matrix has high influence on the accuracy of analysis
- If no matrix-adjusted calibration standards are available
- If only few samples have to be analysed

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Requirements

- Analytical results that are corrected for blank and background
- Linear relation between concentration x and signal y
- Homogeneity of variances
- Possibility to homogeneously divide samples into sub-samples
- Analyte can precisely be added to the sample

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Procedure

- Take n sample aliquots
- Add linear increasing amounts of the analyte to (n-1) sample aliquots in equidistant steps
- Apply linear least square regression to the pairs of values

  $\rightarrow\ y = a + b \cdot x$

- Extrapolite to the intersection with the x-axis
- This value delivers the sought content

  $\rightarrow\ x_A = -x_{(y=0)} = -a/b$

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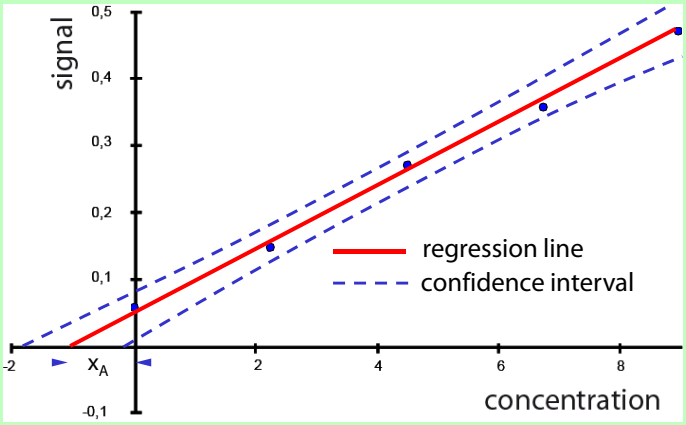
Graphical Presentation



42

Uncertainty

- The uncertainty of the calculated value x_A may be quantified from the half-width of the confidence interval

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

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

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THANK YOU

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Metrology in Chemistry and Traceability of Measurement Results

David Koech: BSc, MSc
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Index

- *Metrology*
  - need for measurement quality
- International Measurement System
- Traceability of measurement results

1

What is a Measurement ?

Process of experimentally obtaining one or more **quantity values**

Quantity is a property which has a magnitude that can be expressed as a number and a unit e.g.

- Quantity: ***Cadmium (mass)concentration***
- Quantity value: ***12 mg/l Cd***
- Measurement result: ***12 ± 2 mg/l Cd***

(VIM, 3rd edition)

2

What is Measurement Quality ?

- Results should be fit for purpose – regarding several parameters e.g uncertainty, price and comparability

Comparability - measurements need to be comparable over:

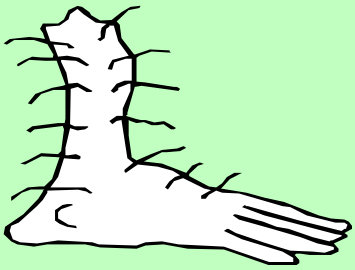
- Time 1900 2000 2100 year
- Between different laboratories
- Between different countries

measured once – accepted everywhere

3

… Lack of Standard …

King's foot



4

… Lack of Standard …
Variations of One Unit of Length (Ell)

- The "ell", a unit originating from the custom of measuring cloth using one's forearms, existed in many countries.
- In order to make trade possible at all in these days, conversion tables were used.
  (Buskes and van Gerven)

5

… Lack of Standard …

country	ell(m)	city	ell(m)
England	1.14	Vienna(A)	0.78
Scotland	0.94	Bruges (B)	0.70
Germany	0.6	Amsterdam (NL)	0.69
Russia	0.5		

(Buskes and van Gerven)

6

Meter Convention

- The lack of standards was resolved in the second half of 19th century with the signing of meter convention on 20th may 1875 in Paris by representatives of 17 nations
- This treaty established the international system of units (SI) for the signatory countries
- Currently there are 54 signatory countries and 37 associate members (as at 22/10/2012)

7

Aims of the meter convention

- Achieve international uniformity in measurement
- Establish common system of units
- Harmonise laws and regulations
- Achieve mutual recognition of measurements

8

Meter Convention

- The Convention of the Metre (*Convention du Mètre*) is a treaty that created :
  - International Bureau of Weights and Measures (BIPM)
  - Intergovernmental organization under the authority of the General Conference on Weights and Measures (CGPM) and
  - the supervision of the International Committee for Weights and Measures (CIPM).
- The BIPM acts in matters of world metrology

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SI

International System of Units

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SI Base Quantities

quantity	unit	symbol
Length	metre	m
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Thermodynamic temperature	kelvin	K
Amount of substance	mole	mol
Luminous intensity	candela	cd

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SI Derived Quantities Examples

quantity	unit	symbol
▪ Speed, velocity	metre per second	m/s
▪ Density	kilogram per cubic metre	kg/m^3
▪ Concentration (of amount of substance)	mole per cubic metre	mol/m^3

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Chemical measurements

Remember your dinner

- Raw meat
- Smoked salmon
- Chicken tandoori
- Rice curry
- New York Steak
- Cheese platter
- Fruit cocktail
- Great Wall red wine
- Non-alcoholic drinks
- Tea or coffee

Bon Appetit !

Are you sure ? Did you measure the quality values?

13

Remember recent Food scandals

- Growth hormones in beef
- BSE in beef
- Dioxine and melamine in milk
- Salmonella in eggs
- Heavy metals in rice and wine
- Glycol in wine, diesel oil in olive oil
- Toxic residues in fish, oyster, shrimp (from all waste water)
- Pesticides in fruits and honey

We have to analyse/measure ! And results should be accurate and comparable

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Trade, Health and Food Safety

Recent examples of temporary closure of markets due to the presence of residues

- Antibiotics in pork, Japan
- Antibiotics in meat, Korea
- Antibiotics in salmon, Japan
- Crystal violet in salmon, EU
- Leucomalachite green in salmon, Chinese Taipei
- Amphenicol in salmon, Canada
- Dioxin in pig meat, South Korea
- Melamine in milk
- Carbaryl in wine
- Cd in mussels
-

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Chemical measurements used:

- Monitoring conformity assessment & product spec
- Protect consumers against fraud & counterfeit products
- Assist hospital physicians
- Support justice system
- Forensic evidence
- Revenue for govt
- Free movement of trade

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Lack of Measurement Quality can Lead to:

- Duplication of measurements
- Use of extra resources
- Lack of trust
- Negative economic impact
- Disasters/accidents
- Loss of business & trade

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Effect on Trade

❖Lake Victoria fish (EU ban caused damage of 100 million US$ p.a. and 150 000 people jobless).

❖Sri Lanka tea export (90 billion Rs p.a. (800 million US$) hindered due to inability to measure pesticides and lack of international recognition).

❖Chilean export of marine, fish, meat, milk and agricultural products (10.5 billion USD p.a.) vulnerable due to lack of sufficient credible traceable testing

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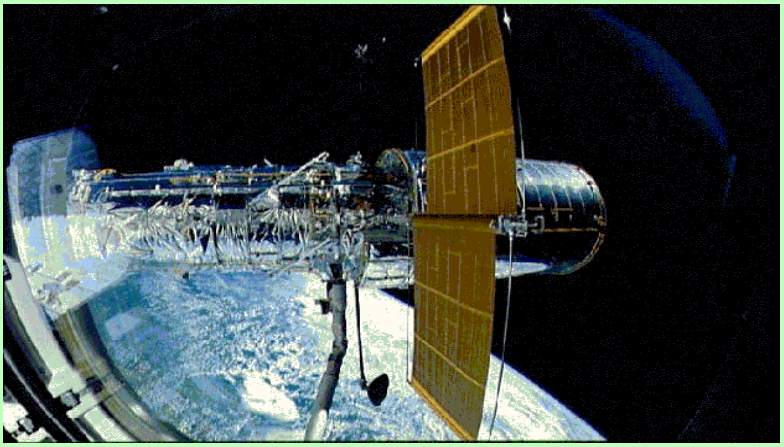
Disasters



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Mars Climate Orbiter

...confusion about units leads to crash...

- On 23 September 1999 the Mars Climate Orbiter,one of the missions in a long-term program of Mars exploration, burned out completely.
- The accident was not due to a technical problem, but the result of the different measurement units used by the NASA teams.
- Flight system software used the metric unit newton while the ground software uses imperial measure pound force (ibf)other used the English units. The spacecraft encountered Mars at an improperly low altitude and led to the loss of the orbiter.

The fate of the Mars Climate Orbiter clearly shows the need for standardization of units

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Loss of Revenue

- A subsidiary of an oil company in the Far East analysed a batch of petrol. Their local lab established that the gum content (components in the gasoline that polymerize during combustion) was much too high.
- On the basis of this analysis the company sold the batch to a trader for a much lower price.
- The trader asked a second lab to perform an analysis in order to find out what he could do with the off-spec petrol.
- He was very pleasantly surprised to find that the gasoline was actually on-spec and he was able to make a healthy profit selling the batch for the normal price.

The oil company only found out much later that the problem was not the petrol, but an error at their own lab. By then this error had already cost them $ 10 million.

(Buskes and van Gerven)

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Wastage

- The 800-mile trans-Alaska pipeline pumps oil from the northern coast to the southern border of Alaska.
- Construction started in 1973 and was completed 4 years later.
- The pipeline was originally budgeted $ 900 million, but the cost escalated to exceed $ 1 billion.
- A steel manufacturer was awarded the multimillion dollar contract to supply steel for the pipeline with S content of less than 0.005%.
- When several of the joint welds in the pipeline began to fail, it became clear that the S content was much higher than specified.

The poor quality of the steel, in part due to inadequate or lack of measurements, set the project back several millions of dollars, once again emphasizing the need for accurate measurements.

(Buskes and van Gerven)

22

Save on cost

- A high measurements uncertainty for cholesterol can lead to an unnecessary costly treatment or a higher health risk.
- Reducing the measurement uncertainty from 23.7% in 1949 to 5% in 1995, saves to the Unites States alone $ 100 million every year in health care costs.

Standard reference materials played an important role in lowering the measurement uncertainty.

(W. May)

Note: Today other compounds (lipoproteins) are used for risk markers of myocardial diseases

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Decisions on chemical measurements

- Means
  - Food can be eaten
  - Goods can be sold
  - Patients should be treated
  - Support health care, trade, production social problems

  But results from PT shows quality of results not satisfactory. Why???– Metrological aspects probably not considered

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Are we really doing the right job ?

• Do we know what we really like/intend to measure
• Did we clearly define the measurand
• Are we really measuring what we intend to measure
• Are our measurement results comparable, traceable
• Do we use validated methods and procedures
• Do we use the right reference measurement standards; Certified Reference Materials
• Do we know the accuracy/measurement uncertainty
• Does a reliable (accredited) measurement and testing infrastructure exist.

If not, we have a problem !

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Metrology – Science of Measurement

- Metrology includes all theoretical and practical aspects of measurement, whatever the **measurement uncertainty** and field of application.

(VIM, 3rd edition)

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Before

Quality of chemical measurements based on:

- A quality management system
- Accreditation

Now:

• In addition, principle of measurement science (metrology)

• First applied in Physics but also applicable to chemistry as well

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Metrological traceability

✓Property of a **measurement result** whereby the result can be related to a reference **through an unbroken chain of** calibrations, each contributing to the **measurement uncertainty .** *JCGM 200:2008 (VIM 3).*

✓Traceability to the SI, or if not (yet) possible to another internationally agreed reference (hardness, pH, WHO International Units)

"Once measured, accepted everywhere " requires Comparability through Traceability

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Metrological Principles

- Uncertainty of measurements
- Traceability
- Validation of measurements procedures
- Statistical tools used for uncertainty evaluation.
- CRM
- Interlaboratory

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Key players

- Measurement service providers
  - NMI
  - National labs
  - Reference labs
  - Quality control labs
- National accreditation bodies
- Organization for education & training

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Metrology in chemistry

Comparison btw chemistry & phyiscs		
	Physics	**Chemistry**
Measurement	Quantity e.g tempt	Quantity of analyte, eg DDT in milk
Units	m, s, K	Mol/l, mg/Kg
Influenced by	Direct measurements	Various factors
Major Impact	Equipment calibrations	Chemical measurements
Depended on	Sample independent	Sample dependant
Example	Length of table	Conc. Pb (eg blood)

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Chemistry in SI
It is quite new!

- Amount of substance (AoS)
- Agreed on 1971
- Mole (mol)

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Progress in development of metrology in chemistry

- BIPM- CCQM (consultative committee on quality of materials)
- EURACHEM &CITAC- GUM
- ISO/IEC 17025:199

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Consultative Committee for Amount of Substance CCQM - Metrology in Chemistry

- Established by the CIPM in 1993
- About 40 member and observer organizations (NMIs, Designated Institutes and others)

Functions:

- Primary methods for measuring amount of substances
- International comparisons
- Establishment of international equivalence between national laboratories
- Advice to CIPM on matters concerned with metrology in chemistry

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CCQM – Metrology in Chemistry

CCQM Working Groups

• Key Comparisons and CMC Quality	NMIA	L. Mackay
• Organic Analysis	NIST	W. May
• Inorganic Analysis	LGC	M. Sargent
• Gas Analysis	NPL	M. Milton
• Electro-chemical Analysis	SMU	M. Mariassy
• Surface Analysis	BAM	W. Unger
• Bio-Analysis	LGC	H. Parkes

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Traceability

Key: Reliability of result to be traceable to stated reference through unbroken chain of comparisons all having stated uncertainties. *(VIM, 3rd edition)*

To establish & demonstrate traceability

- Specify measurand & model equation
- Choose measurement procedure
- Validate methods
- Choose reference standard
- Estimate uncertainty

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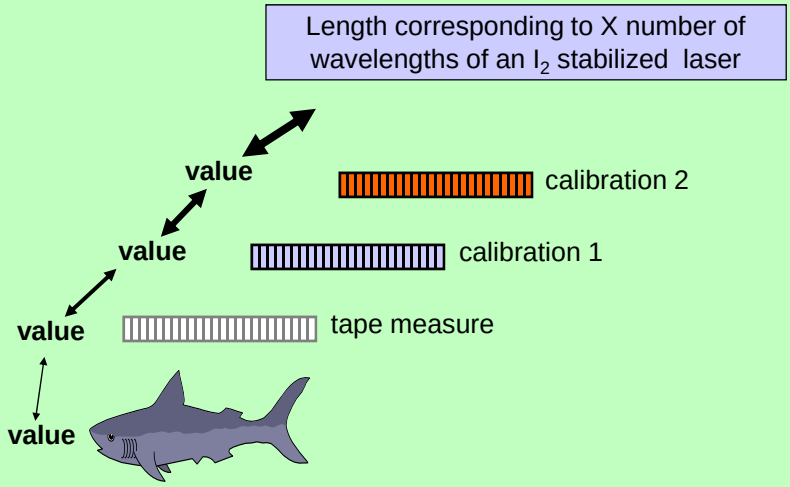
Traceability of Length Measurements



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analytical measurements
need to be comparable
in time and space

traceability is the best
way to achieve this

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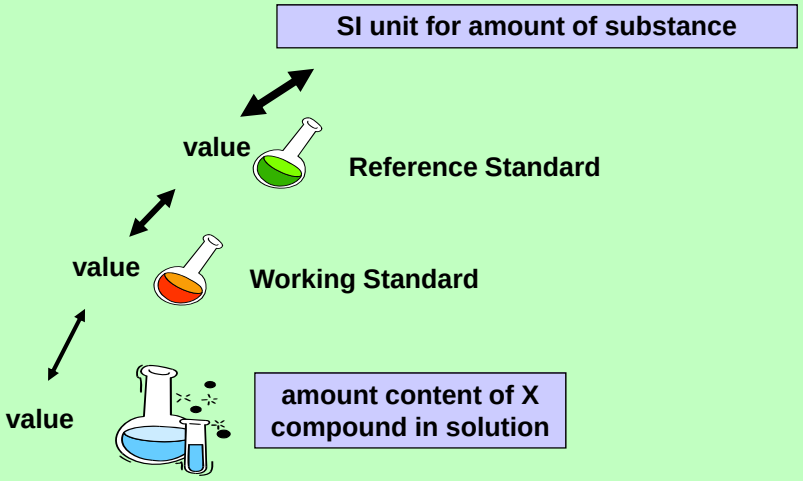
Traceability of Chemical Measurements



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Problems...

- Absence of reference standards
- Absence of links to common basis
- Appropriate use of standards by laboratories
- Appropriate use of uncertainty

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stated references

stated uncertainty

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Stated References – 3 different

- In VIM 3 examples of different stated references are given
  - A measurement unit (VIM 1.9), e.g. mol/l, °C
  - A measurement standard (VIM 5.1), e.g. the certified reference material SRM 2193, a $CaCO_3$ pH standard.
  - A measurement procedure (VIM 2.6), e.g. ISO 1736:2008 Dried milk … - Determination of fat content.
  - Determination of amount of substance requires in most cases measurements of different properties
    - Sample mass — mass reference – measurement unit
    - Analyte identity — pure material – measurement standard
    - Molar or Atomic weight — published data or measured

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Several References for one measurand

*For **measurements** with more than one **input quantity in the measurement model,** each of the input **quantity values** should itself be metrologically traceable...*

NOTE 4 in VIM on Traceability

Example: Mercury in tuna fish (with a AAS after microwave digestion)

Measurement result: 4.03 ± 0.11 mg/kg, reported as total Hg on dry weight basis (105 ºC, 12 h)

Traceability has to be demonstrated for:

- Mass concentration of the Hg solution **1.00 g/l Hg** - a CRM certificate
- mass of sample **0.5 g** - calibration certificate of the balance
- volume of volumetric flask **100 ml** - calibration certificate
- drying temperature **105°C** - calibration of oven
- drying time **12 h** - ordinary clock or stopwatch
- Microwave digestion conditions **0.5 h at 180 ºC** - check according to specifications

(from Eurachem Traceability leaflet – www.eurachem.org)

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Stated references

Quality	Analyte	Measurand	Unit	Stated reference
Conc	DDT	Conc. of DDT	ng/l	SI
Content	Pb	Conc	Mg/L	SI
pH	H^+	Conc. of H^+	pH unit	pH scale

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Stated Uncertainty

- An interval around the measurement result
- The uncertainty budget including:
  - Uncertainties carried by the references
  - Uncertainties introduced by the measurement process

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Stated Uncertainty

Usually the contribution of the uncertainties carried by the references to the total uncertainty is small relative to the contributions that originate from the measurement process

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Reference Materials

- Values carried by reference materials should be traceable to other references
- The same features which are valid for the analytical laboratories are also valid for the reference materials producers

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More Information

- www.bipm.org
- www.euramet.org
- www.citac.ws
- www.eurachem.org
- www.eurolab.org
- www.irmm.jrc.be
- www.nist.gov
- www.labnetwork.org

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Things to Remember

- Metrology in chemistry is still "young"
- There is a lot to learn
- *Traceability is not an aim by itself but it helps achieving reliable results*
- *Traceability can only be claimed if uncertainty statement includes all the uncertainties from references and the measurement procedure*

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What will you take for lunch?

- What will be the measurement quality of food?
  - -Color
  - - Raw meat
  - - bouquet, smell
  - - rare, medium, well cooked
  - - plain on your tongue, taste
  - - after-taste
- Need for “soft” metrology!!
  - - color
  - - taste
  - - smell
  - - glance

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THANK YOU

ACKNOWLEDGMENT:
Dr. Michael Koch
Katrin Wunderlich
PTB
Donald Masuku
All participants

51

SADCWaterLab PT Evaluation Workshop
19-22 November 2012
Addis Ababa, Ethiopia

Reference Materials in Analytical Chemistry

Vivian Radegonde

Seychelles Bureau of Standards

Overview

- Definition
- Statement of purpose
- Role of reference materials in the field of chemical metrology
- Requirements for CRM
- General challenges in the preparation and certification of CRM
- Preparation of CRM
- Selection criteria of CRM
- Use of CRM
- Traceability of measurement through use of CRM
- Sources of information

Definition of CRM

- A Reference Material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes its traceability to an accurate realisation of the unit in which the property values are expressed and for which each certified value is accompanied by an uncertainty at a stated level of confidence.

Statement of purpose

Anyanalytical measurement should be reliable and invariant

-in time
-in space
-method independent
-analyst independent

Realized by standardisation, harmonisation and assuring the quality of measurements

Statement of purpose

- The goal of any analytical measurement is to get accurate, reliable and consistent data
- Prerequisites for achieving accurate results:
  - -Correct sampling
  - -Correct weighing of the samples and standards
  - -Use of well maintained and calibrated equipment
  - -Qualify operators
  - -Validated methods and procedures
  - -Use of accurate standards or certified reference materials

- Reference materials provide the benefit of comparability between results obtained at different times, in different places, by different analysts, and using different methods.

When is an analytical result acceptable ?

The result is acceptable when

it has been obtained by an established method

- All the uncertainties (systematic and random) have been taken into consideration in the uncertainty value being quoted

- the method used has been validated by analysing a known secondary (working) reference material
- The method used has been calibrated with a known certified reference material whose value is traceable to international metrological unit

The role of certified reference material

- Certified reference materials (CRM) (i.e., with a statement of uncertainty and traceability), when available and of suitable composition, are ideal control materials.
- Regarded for traceability purposes as ultimate standards of trueness
- In the past CRMs were regarded as being for reference purposes only and not for routine use.
- A more modem approach is to treat CRMs as consumable and therefore suitable for IQC.
- The use of CRMs in this way is, however, subject to a number of constraints

The role of certified reference material

- (i) Despite the constantly increasing range of CRMs available, for the majority of analyses there is no closely matching CRM available.
- (ii) Although the cost of CRMs is not prohibitive in relation to the total costs of analysis, it may not be possible for a laboratory with a wide range of activities to stock every relevant kind of reference material.

The role of certified reference material

- (iii) The concept of the reference material is not applicable to materials where either the matrix or the analyte is unstable.
- (iv) CRMs are not necessarily available in sufficient amounts to provide for IQC use over extended
- periods.
- (v) It must be remembered that not all apparently certified reference materials are of equal quality.
- Caution is suggested when the information on the certificate is inadequate.

- **Primary standard:** Material designated or widely acknowledged as having the highest metrological qualities and whose value is accepted without reference to other standards of the same quantity.
- e.g uranium metal or plutonium metal.

- **Secondary standard:** Material whose values is assigned by comparison with a primary standard of the same quantity.

- eg.uranium dioxide pellets or plutonium oxide. Their reference value is assigned by comparison with the respective metal standard.

- **Working standard**: Used routinely to calibrate or check materials measured, measuring instruments or reference materials.

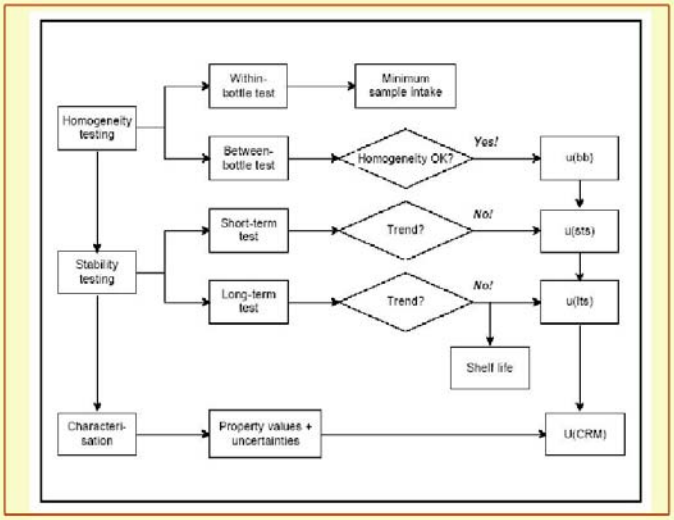
  e.g . Mercury standards prepared in-house.
- **Certified Reference Material (CRM)** : A reference material accompanied by a certificate one or more of whose properties are certified by a procedure which establishes traceability to an international unit of metrology.
- The certified value is accompanied by an uncertainty a stated level of confidence.

Requirements for certified reference material

- The compounds and concentration should be similar as possible to the unknown sample.
- The material should be 'matrix matched'. Unfortunately full matrix matching frequently is an unrealistic requirement.
- The reference material should be homogeneous (homogeneity test)
- If there is a risk for segregation during transport or storage the material must be re-homogenized homogenized before use.

- The certified properties of the reference material and the matrix should be stable.
- The material should be checked for stability as part of the verification process
- The uncertainty of the value should be estimated for certified reference materials.

Certification CRM



General Challenges in the Preparation and Certification

- Reference materials (RMs) serve as the basis for millions of measurements performed each year.
- The “reliability "of these materials, the associated reference value and the stated uncertainty are of key importance.
- A high degree of confidence needs to be put in the measurements and in the reference materials.
- Preparation and certification of reference materials is a very demanding task. It requires a thorough understanding of the demanding task. It requires a thorough understanding of the processes involved.

Preparation of Reference Materials

- 1. Definitive method

  The method must be based on first, principles have very high precision and essentially zero systematic error.
- An example is the use of isotope dilution mass spectrometry for the characteristics of trace level elements in natural matrix elements. The certification is done in a single laboratory

Methods identified as having the potential to be primary

- Isotope dilution with mass spectrometry (IDMS)
- Coulometry
- Gravimetry (a) gas mixtures and b) gravimetric analysis
- Titrimetry
- Determination of freezing-point depression
- Measurements of amount of substance to be considered primary must be made using method which is specific for a defined substance and for which the values of all parameters or corrections which depend on other species or the matrix are known or can be calculated with appropriate uncertainty.

Preparation of Reference Materials

2. Independent measurement method

Two or more reliable independent methods are used. The method must be proven to give accurate results. The certification is done in a single laboratory.

3. Interlaboratory consensus method

A number of laboratories analyze in replicate one or more units of the material being characterized. The participating laboratories may choose their own method or all laboratories may use the same method. The consensus value is usually taken as the mean

Selection Criteria for CRMs

- A reference material is selected by comparing the uncertainty contribution of the reference material(Ir) to the total analytical uncertainty(IT) and by evaluating this as satisfactory, acceptable or incompatible.

IT/Ir>10: Satisfactory

10>IT/Ir>4: Acceptable

4>IT/Ir>2: Acceptable if no other solution exists ; upwardup revision of IT undoubtedly necessary

IT/Ir<2: Unsatisfactory situation; implies reviewing the total uncertainty, the method , applied and the choice of reference material

Use of Reference Materials

(a) Method Validation and Measurement Uncertainty

- Bias estimation, one of the most difficult elements

-Appropriate RMs provide information within the limits of the uncertainty in certified value(s) and the uncertainty of the method

(b) Verification of the Correct Use of a Method

-RM can be used for training purpose

-For checking infrequently used methods

-For trouble shooting when unexpected results are obtained.

Use of Reference Materials

- (c) Calibration

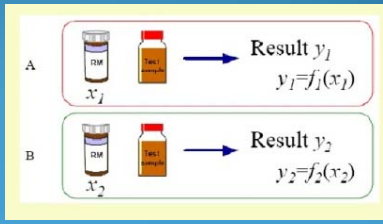
-Normally a pure substance RM is used for calibration

-Other components such as sample digestion, separation and derivatisation are not covered.

–The uncertainty associated with RM purity will contribute to the total uncertainty of the measurement.

Traceability of the measurements

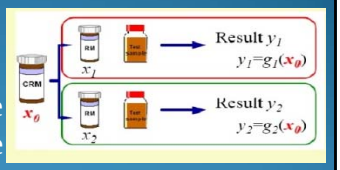
Consider two laboratories A and B carrying out measurements on samples of broadly the same type. Each calibrates their equipment using a reference standard with a known nominal concentration (x1 and x2 respectively). They calculate their respective results y1 and y2 from a equation calibration including the respective values of values of x



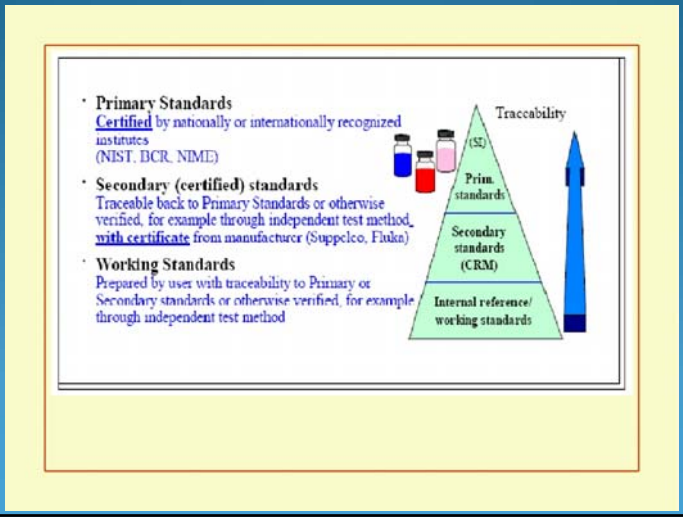
Traceability of the measurements

If, however the two reference standards are both calibrated against some common reference, a comparison becomes meaningful. Now, both results are derived from the same value(xo). Both will now have the same units of units of measurements (same scale and units as xo), and a direct comparison of the values y1 and y2 is now not only possible but also meaningful.

By analogy of course, xo could also be derived from a yet higher reference to allow global comparisons.



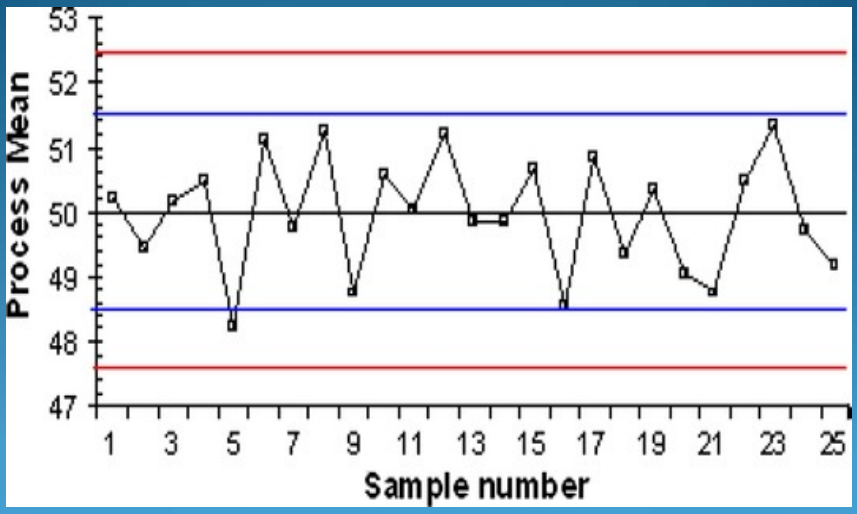
Traceability of the measurements



Used of certified reference materials

- Control charts and reference materials:
  -Demonstration of measurement procedure performing within given limits.
  (Warning limits and Control limits)
- If the control value is outside the limits, no analytical results are reported and remedial actions have to be taken to identify the sources of error and to remove such errors.

Example of control chart



Examples of CRMs

Sources

(1) K.L. Ramakumar
Bhabha Atomic Research CentreMumbai 400 085
Klram@barc.gov.in

(2) Papadakis, I.: (Certified Reference Materials)
In: Wenclawiak, Koch, Hadjicostas (eds.)

THANK YOU

Annex 7

Evaluation Questionnaire – PT evaluation workshop Addis Ababa

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
Local coordinators' reports	☐	☐	☐	☐	☐
Reports from the SADCWaterLab working groups	☐	☐	☐	☐	☐
Report of the PT provider	☐	☐	☐	☐	☐
Evaluation of the PT	☐	☐	☐	☐	☐
Discussion about necessary changes in the PT scheme and the way to sustainability	☐	☐	☐	☐	☐
SADCWaterLab WGs "methods" and "training"	☐	☐	☐	☐	☐
Training on Calibration	☐	☐	☐	☐	☐
Training on Metrology in Chemistry	☐	☐	☐	☐	☐
Training on Certified Reference Materials	☐	☐	☐	☐	☐
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?

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What benefits did you draw from the workshop?

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Please use back side for any other comments