8^{th} Evaluation Workshop within the SADCMET Proficiency Testing Scheme for Water Testing Laboratories Chemistry part

Port Louis, Mauritius

14 – 17 November 2011

Report on the 8th Evaluation Workshop within the SADCMET Proficiency Testing Scheme for Water Testing Laboratories

Port Louis, Mauritius, 14 – 17 November 2011

Prepared by Dr.-Ing. Michael Koch

Summary

The workshop covered the evaluation of the 8th 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.

One important point is to proceed with recommendations for suitable methods. This will be the task of SADCWaterLab working group established during the 2009 meeting in the Seychelles

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. The structure of local coordinators is very useful, but still has to be improved. The commitment of local coordinators differs very much. But to minimize logistical problems and to increase the number of participants the local coordinators play a crucial role. One of the main obstacles for further expansion of the system and for improvement of the quality of the labs the lack of awareness on the importance of PT or – even more basic – the importance on quality assurance in the chemical lab was identified. To overcome this the results of this workshop 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 limits were lowered in 2011 according to decisions taken in the 2010 workshop in Namibia. The concentrations, especially for heavy metals were also lowered in the 2011 PT round. Of course this lead to an increased difficulty for the analyses. Therefore some of the results seem to be worse this year compared to 2010. The statistical methods are in accordance with the internationally recommended procedures.

The evaluation workshop also contained a 1-day training on "Ensuring the Quality of Analytical Results – Trueness and Precision" and the SADWATERLAB General Assembly where also the participants from microbiology workshop were present. For the microbiology workshop see separate report.

Introduction

The workshop reported here followed previous workshops held in

- Windhoek, Namibia (Feb 2004),
- Pretoria, South Africa (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) and
- Windhuk, Namibia (Nov. 2010).

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 Mauritius was the discussion of the evaluation of the seventh 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 32 participants from the following countries:

- Angola 1
- Botswana 3
- Burundi 1
- DRC 1
- Ethiopia 1
- Kenya 2
- Lesotho 1
- Madagascar 1
- Malawi 2
- Mauritius 10
- Namibia 1
- Seychelles 1
- South Africa 1
- Tanzania 3
- Uganda 1
- Zambia 1
- Zimbabwe 1

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

PT Workshop Programme

Monday, 14 November 2011:

Welcome, Opening, Training

Tuesday, 15 November 2011:

Reports of local coordinators, reports on the follow-up of the training of trainers, SADCWaterLab working group meetings, Training, report of the PT provider

Wednesday, 16 November 2011:

PT evaluation, group discussions, PMC meeting

Thursday, 17 November 2011:

SADCWaterLab General Assembly, visit to drinking water treatment plant, lab visit

Monday, 14 November 2011

Welcome and Opening

The participants of both workshops were welcomed and the Workshop was officially opened by

- Mr. K Ramful, Director Mauritius Standards Bureau
- Ms. Kezia Mbwambo, SADCWaterLab chair
- Ms. Kathrin Wunderlich, PTB
- Mr. Cader Sayed Hossen, Minister of Industry, Commerce and Consumer Protection, Republic of Mauritius

M. Koch: Introduction

After splitting into the two groups for the different workshops, Mr. Koch announced some changes in the programme due to the fact that two participants from Uganda couldn't arrive in time. So training was scheduled for the first and part of the second day. All participants shortly introduced themselves and Dr. Koch gave an overview on the workshop programme.

Training – part 1

"Ensuring the quality of analytical results" was the topic of the training of the workshop in Mauritius. In a first part M. Koch concentrated on the possibilities to check the trueness of analytical result. Trueness is strongly related to traceability. After explaining the principles of traceability the problems of traceability in analytical chemistry were discussed. The traceability of balances, volumetric equipment and thermometers used in the lab can be ensured using different methods which were explained in detail. Nevertheless this is not sufficient since biases in the analysis can also result from other steps like sample preparation. Trueness of the final result therefore has to be checked using (certified) reference materials, interlaboratory test samples or spiking experiments. This also explained in detail. The full presentation is attached in annex 2.

After the presentation the participants had the opportunity to share their experiences about trueness checks performed in their laboratories in small working groups.

Training – part 2

In a second part M. Koch focused on precision and the possibilities to quantify it. After explaining the basic precision terms and a short excursion into the basics of statistics he explained the basics of how to use quality control charts including the following topics:

- Principle of control charts
- Relevant literature
- What are warning and action limits
- How to fix those limits
- Comparison with quality requirements
- What are out-of-control situations and how to handle them
- Different types of control charts
- Control samples
- Selection of suitable control charts
- Control charts in accreditation

The complete presentation is enclosed as annex 3.

Demonstration of EXCELKONTROL

The EXCELKONTROL software for control charts was explained by Mr. Koch. This software is available free of charge from his website www.aqsbw.de.

Tuesday, 15 November 2011

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. Reports were given from the following countries

- Angola (Lopes Ferreira Baptista)
- Botswana (Teddy Ditsabatho)
- Burundi (Leandre Budigiye)
- DRC (Jean-Paul Munongo)
- Ethiopia
- Ghana
- Kenya (Jacqueline Kang'iri, Timothy Kiarie)
- Lesotho (Mapaseka Makhaba)
- Madagascar (Yves Mong)
- Malawi (Steve Afuleni)
- Mauritius (Shabbir Ghoorun)
- Namibia (Merylinda Conradie)
- Seychelles (Vivian Radegonde)
- Tanzania (Kezia Mbwambo)
- Uganda (Aziz Mukota)
- Zambia (Margaret Mazhamo)
- Simbabwe (Penia Mubika)

Details of the Local coordinators' reports will be included in the report on the Microbiology workshop

Reports on the follow-up of the training of trainers

A training of trainers for Quality Assurance in Analytical Chemistry was conducted in August 2010 in Zambia, organised by SADCWaterLab and sponsored by PTB. 28 participants from 14 countries were trained on the topics. The trained people were obliged to organize national workshops on that topic.
The following reports on the follow-up so far were given in Mauritius:

- Mauritius (Baichoo Chundunsing): The course has to be approved by MQA. A course was advertised, but not enough participants registered because of competition from other companies
- Namibia (Merylinda Conradie): No course took place because of the limited number of laboratories. She will try to liaise with the national bureau of standards. The University in Windhuk gives lectures on quality assurance Friday afternoons. M. Conradie is in contact with them
- Seychelles (Vivian Radegonde): A workshop was organized from 1-3 August 2011 with sponsorship from PTB and help from David Koech (Kenya) as trainer. In total there were 4 trainers
- Tanzania (Kezia Mbwambo): Workshops have been organized using also trainers from other activities and form universities. A report on these workshops will be delivered for the SADCWaterLab newsletter
- Uganda (Aziz Mukota): A workshop was organized with assistance from PTB and David Koech. A report was prepared for the SADCWaterLab newsletter. Two other workshops were carried out without PTB assistance in 2011.
- Zimbabwe (Naume Mandizha): A workshop will be organised in the 1st quarter of 2012 expecting around 40 participants. The two trained people and additional trainers will be used.
- Zambia (Margaret Mazhamo): No workshop was conducted up to now, but there are other trainings planned by UNIDO for 2012. A national lab association is planned. One of its objectives will be training.
- DRC (Jean-Paul Munongo): A workshop is planned for January 2012.
- Botswana (Teddy Ditsabatho): Due to major restructuring in the company no workshop could be organised up to now, but 2 workshops are planned in 2012 (in March and in October)
- Kenya: Workshops were organized whereby one was sponsored by PTB. A report was included in the SADCWaterLab newsletter.
- Lesotho: A lab association will be installed, Invitations were sent out in November 2011
- Malawi: The trained trainers are not available due to changed responsibilities, no workshop carried out so far.
- Swaziland: no report
- Rwanda: no report

SADCWaterLab working groups

Within SADCWaterLab working groups were installed to deal with special topics.

Working group 1 is dealing with recommendations for analytical methods in chemical analysis to help participants of the PT scheme. Some method descriptions were sent by participants. Secretary and chair will distribute it to all members. At first the focus was on anion analysis.
Further progress will be reported in the SADCWaterLab newsletter.

Working group 2 will take care on the follow-up of the training of trainers. The most important task is the preparation of a database of trainers and to make this database available. Reports from national workshops will be collected and published in the newsletter.

Report from International PT workshop

Kezia Mbwambo gave a short report from the 7th EURACHEM Workshop "Proficiency Testing in Analytical Chemistry, Microbiology and Laboratory Medicine – Current Practice and Future Directions" taking place 3-6 October 2011 in Istanbul, Turkey. Kezia Mbwambo gave a keynote lecture on "Establishing PT/EQA Schemes in Developing Countries – Examples from Africa" and chaired a working group (together with M. Koch) on the same topic. A paper will be published in "Accreditation and Quality Assurance". Posters have been presented by the PT providers of both SADCWaterLab schemes and the EAC schemes.

Training – part 3

The third training session concentrated on practical demonstration of control charts. Using an EXCEL-spreadsheet designed for this purpose M. Koch showed the principles, problems and advantages of control charts.

M. Conradie: Report of the PT provider

Merylinda Conradie gave a report on the 7th PT round. She started with an overview on the project activities since its beginning in 2004. Participation with 56 participants was more or less stable since 2009. Nevertheless an increasing number of participants would be beneficial in the interest of sustainability. The changes in parameters over the years and the current concentration ranges were shown. She also explained 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. For all parameters concentration ranges were given in this PT round. Nevertheless some participants reported results outside this ranges.
The following problems arose during this round:

- Angola: Paid, but did not submit results
- Kenya: One parcel was delivered to another laboratory
- Files over 5 MB are blocked by NamWater IS and cannot be received
- Organising a PT round between normal laboratory activities and obligations remains a challenge.
- Late registrations from participants are still a problem.
- Still some registration forms were not received – laboratory information and contacts are not available
- Sometime the written registration forms are not all clear
- Return date for the results : 19th of August 2011 with an delay from two laboratories due to problems with equipment – caused a delay with evaluation report
- Again high standard deviations > higher than limits
- Some laboratories do not see the ranges supplied
- High number of outliers for the gravimetrical methods

- Non-standard methods are still used
- Significant figure problems e.g. 0.69585
- Reporting of results in wrong units (as N and not as NO_3 and as P and not as PO_4 respectively
- Corrective actions are still not implemented

The following challenges remain for 2012 for the provider and the participants:

- Maximum participation in SADCWATER Lab PT in terms of parameters
- Recommended methods must be finalized and implemented
- Investigate problems or determine the root cause
- Corrective actions are an on-going process – laboratories should keep on applying it to get the desired results
- Choose appropriate methodology
- 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 SADCWaterLab association are important and a good platform for networking

The complete presentation is enclosed in annex 4.

Wednesday, 16 November 2011

M. Koch: Evaluation results

Michael Koch explained in detail the results of the evaluation.
The standard deviations for the assessment were calculated using Algorithm A from ISO 13528. These standard deviations were used for the calculation of z-scores, if they were below the limits for the standard deviations agreed upon during the previous workshops (table 1).

Table 1: Limits for standard deviations

Parameter	limit in %	Parameter	limit in %
Sulphate	10	Manganese	<1 mg/l: 20, >1 mg/l: 12
Chloride	10	Aluminium	20
Fluoride	10	Lead	20
Nitrate	10	Copper	20
Phosphate	10	Zinc	20
TDS	10	Chrome	20
Calcium	10	Nickel	20
Magnesium	10	Cadmium	20
Sodium	10	Arsenic	20
Potassium	10	Cobalt	20
Iron	<1 mg/l: 20, >1 mg/l: 12		

In order not to affect the statistical calculations by gross outliers all values outside the range ref.-value/8 to ref.-value*8 were excluded prior to these calculations.
The detailed presentation is included in annex 5.
As in 2010 special emphasis was put on the comparison of the results with those from last years' rounds.

No improvement could be seen compared to last year's round. Looking to individual results of the laboratories it became clear – as in the previous year - that quite a few participants are continuously performing well, some are improving, some getting worse, but a substantial part of the participants are performing bad and do not change anything.

For all laboratories the average of the absolute values of all values was calculated for each year and shown in a diagram. Since the limit for acceptability of a value in the PT is a score in the range of $\pm$ 2, the value of 2 was taken to distinguish between well performing and bad performing labs.

Laboratories were grouped into 4 classes:

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

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

The example shown here for Sulphate shows 14 labs performing constantly well and 10 constantly bad, 9 were improving and 3 got worse.

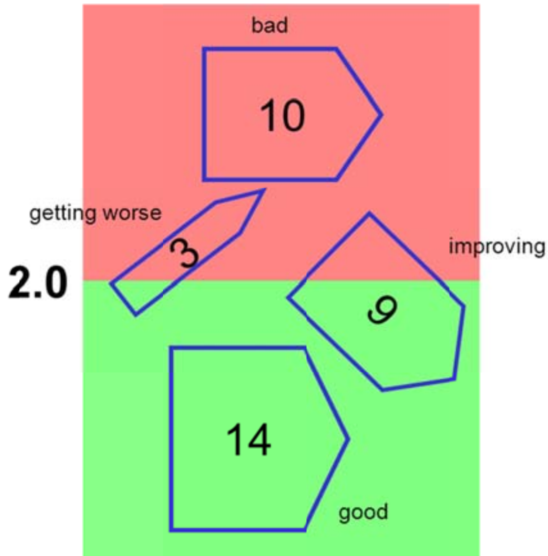


Fig.1

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

Sulphate

- Quite good agreement between means and ref.-values
- Standard deviation still too high
- Too many labs with unsatisfactory results, but some are quite good
- High portion of outliers for the turbidimetric and the gravimetrical method – mistakes in executing the methods
- exactly as in 2010

Chloride

- Average standard deviation – no real improvement
- Many labs have good results, but some are continuously deviating
- Problems with the endpoint detection in argentometric determination
- Obviously some problems with the spectrometric method

Fluoride

- Standard deviations still very high

- Again about 45% of the values are not satisfactory
- Colorimetric values not reliable (as in the last years!)
- Obviously some problems with IC

Nitrate

- Some values obviously again reported in wrong units (most probably 6 labs, at least 1 of them identical with 2010, 2009 and 2008)
- High number of outliers, almost half of the values are wrong
- Standard deviation still too high
- Harmonization of methods needed!!

Phosphate

- Results from 2 labs in wrong units and some very high results
- Average standard deviation
- 44 % of the values are outside the limits

Total dissolved solids

- Standard deviations are quite high
- number of out-of-range values quite high
- Is TDS from conductivity really comparable with gravimetric TDS??

Calcium

- Standard deviations still too high
- 2/3 of the labs are ok, 1/3 consistently out-of-range

Magnesium

- Average standard deviations, no significant improvement
- 1/3 of the results out-of-range
- Titrimetric values still not really reliable

Sodium

- Average standard deviation – still too high
- Still 30% of the results ot-of-range

Potassium

- Standard deviations as last year
- 1/3 of non-satisfactory results
- Problems with AAS

Iron

- Standard deviations higher again
- Problems especially with low concentrations
- Problems with colorimetric method

Manganese

- Standard deviation much worse
- Serious problems with low concentrations
- At low concentrations many values much too high – why? – contamination?

Aluminium

- Low concentrations only
- Lowered standard deviation for proficiency assessment
- Therefore increased number of values out-of-range
- Problems with AAS

Lead

- Lowered standard deviation for proficiency assessment
- Experimental standard deviation still too high
- Especially at low concentrations many too high values

Copper
- Good standard deviation
- Percentage of non-satisfactory results at a constant low stage

Zinc
- Standard deviations ok
- Percentage of outliers ok
- Only a few bad performing labs

Chromium
- Low concentrations
- Standard deviation limit lowered
- Experimental standard deviations are still quite high

Nickel
- Despite of the low concentrations and the lowered standard deviation limit an improvement could be seen

Arsenic
- Low number of values
- High standard deviation estimate
- 30% of the values out-of-range

Cadmium
- Low concentrations
- Average standard deviation
- More or less constant performance

Cobalt
- Standard deviation high
- But most labs are consistently well performing

Only 5 participants (one of those being the University of Stuttgart) analysed all parameters. The percentage of participation per laboratory is shown in fig. 2.

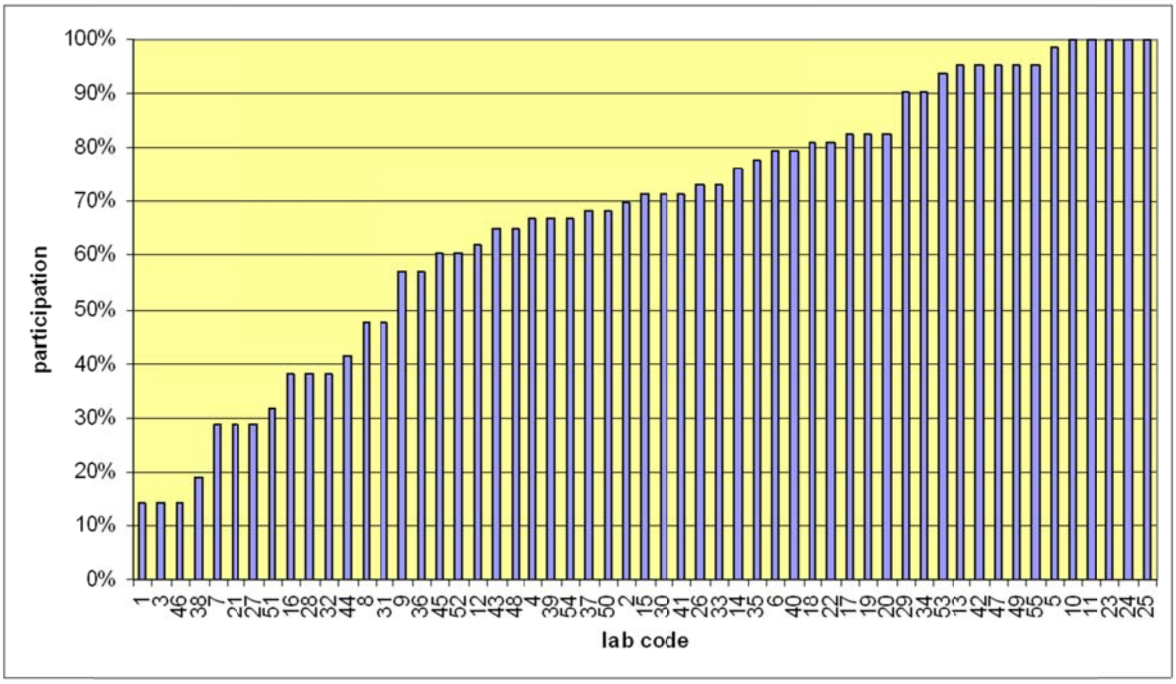


Figure 2: Percentage of participation for each participant

Only 16 participants (including two from Germany) managed to analyse more than 80% of their values within the tolerance. Fig. 3 shows the proportion of successfully analysed parameters for each participant.

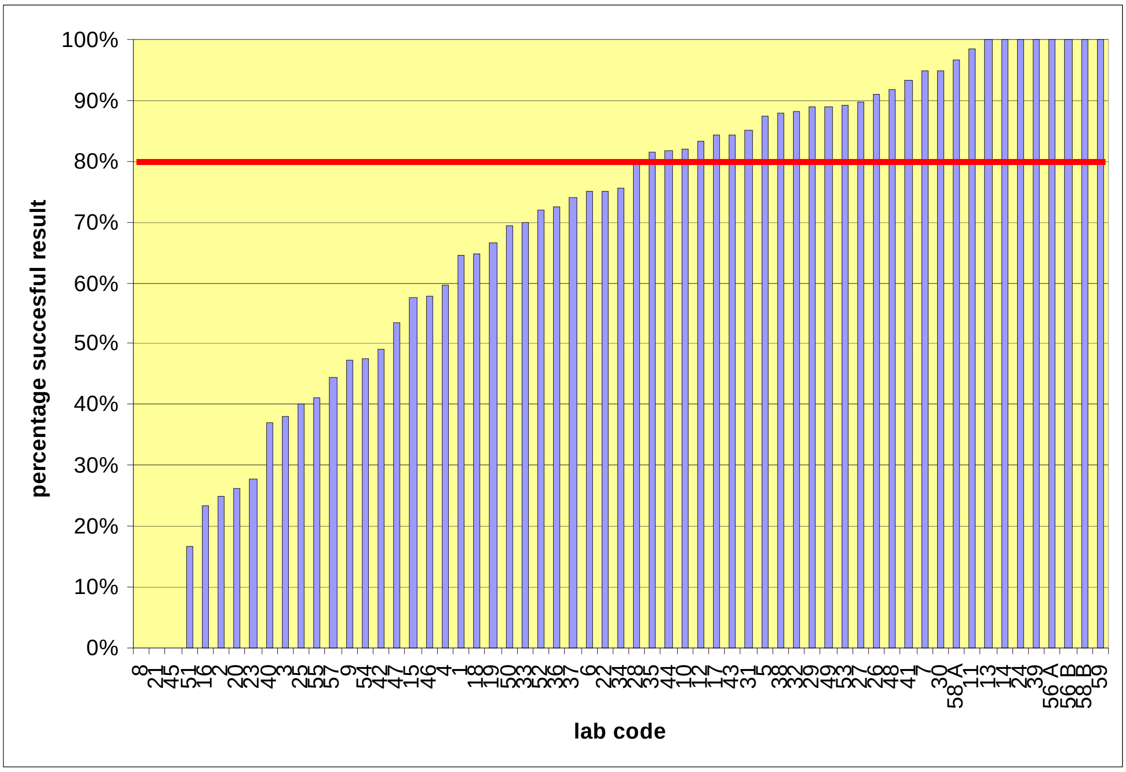


Figure 3: Percentage of successfully analysed values for each participant

Table 2 shows the percentage of labs that succeeded to have more than 80% of the values within tolerance limits over the last years.

Table 2: Percentage of labs that succeeded to have more than 80% of the values within tolerance limits

Year	percentage of labs
2005	23,9 %
2006	25,6 %
2007	37,0 %
2008	35,6 %
2009	23,5 %
2010	45,8 %
2011	29,1 %

It clearly can be seen that the percentage in 2011 is significantly lower than in 2010, which was the best of all. This drop is mainly due to lowered limits for the standard deviation, compared to previous years, as decided at the 2010 workshop in Windhuk. For some parameters also the concentration ranges have been lowered, which also made the analyses more difficult.

The definition of fitness-for-purpose criteria (in the form of limits for the standard deviation) resulted in a higher proportion of values outside the tolerance limits. The stronger the requirements are, the more values will be outside.
Experience from Germany shows that normally up to 20% of non-successfully analysed values can be expected for each parameter.

Fig. 4 shows for each parameter the percentage of values outside the tolerance limits. The figure shows that – on the basis of the current fitness-for-purpose-criteria - improvement is still necessary for most of the parameters. It can be seen here that especially for the lowest level of each parameter the percentage of values otside the tolerance limits is higher than for the others.

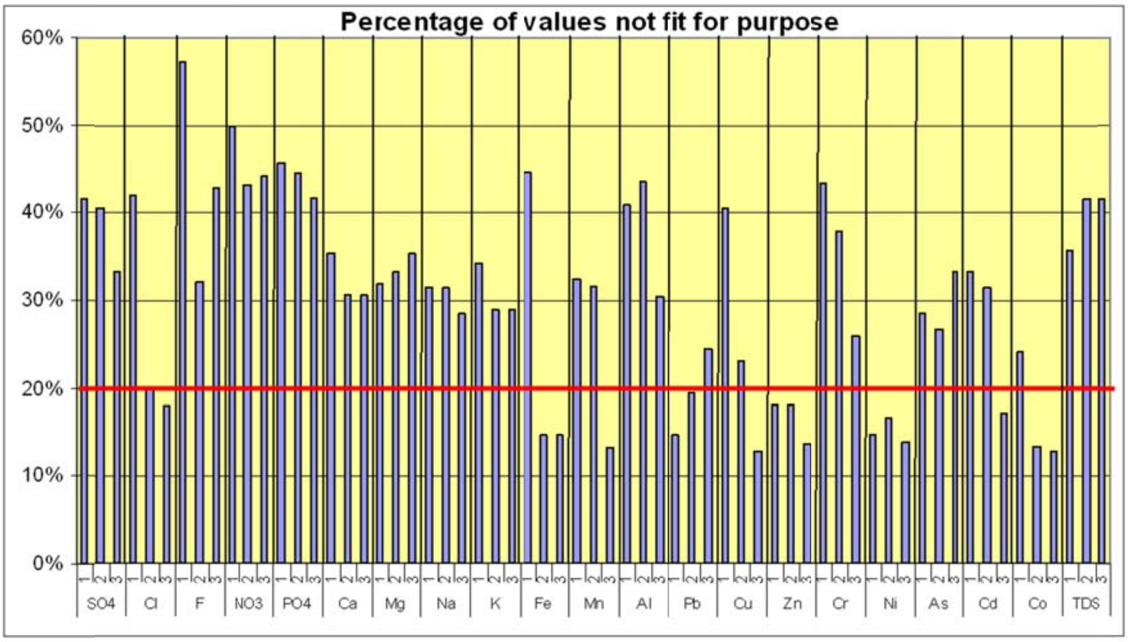


Figure 4: Percentage of values outside the tolerance limits for all samples

Michael Koch came to the following conclusions:

- Again the PT Provider did a very good job
- The evaluation and assessment procedure is fit for the purpose
- The SADCMET Water PT is a good possibility for the participants to compare with peers and with stated fitness-for-purpose criteria
- Overall the results of this PT round show a good performance for many labs, but the results of some laboratories continuously are not satisfactory or getting worse
- More emphasis should be put on corrective actions after unsatisfactory participation
- Some participating labs seem to be resistant against advice; in an accreditation procedure they will wake up
- There should be a discussion
  - How to proceed with recommendation of suitable methods?
  - How to help laboratories to proper apply these methods?
  - How to convince the “resistant” labs that participating in PTs without corrective actions is waste of money and resources
- The gaps that prevent labs from proper application of the methods should be identified

The complete presentation is enclosed in annex 5.

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.

Are the concentration levels and standard deviation limits ok?

- There was a general agreement between all groups that both should stay as they are

Should we change the parameters?

- One group mentioned pesticides. But it is not possible to add those to the same PT round. Another PT round would have to be provided for that. The current PT provider does not have the capacities to do that. In addition another PT scheme (for fish) is in preparation
- There was some discussion about adding As, Sb or Hg and to take out some other parameters. Hg would be difficult since the samples would need a special conservation. No consensus could be reached, so nothing will be changed with regard to that
- It was decided to add the parameter electrical conductivity to the anion samples and to clearly state that total dissolved solids requires a gravimetric determination

Anything else to be changed?

- It was suggested to have 2 rounds per year. The decision on that will depend on the cost analysis to be done by the PT provider
- There was some discussion about issuing certificates. At the end it was decided in future to issue certificates with all parameters and its assessment

How can well performing labs help the others?

- Well performing labs should be ready and willing to help when contacted by other labs or the PT provider
- Sharing experiences on mistakes that have previously been made and resolved would be helpful
- It was suggested to establish a group e-mail to discuss various topics (maybe facebook could be used); a discussion forum on the website (troubleshooting page) was suggested
- Finally it was decided to encourage participants to report about successful corrective actions and publish them on a troubleshooting web page. There wil be further discussions in SADCWaterLab working group 1 on this topic.

How can bad performing labs seek for assistance?

- They should be encouraged to contact the PT provider to get into contact with good labs, but first(!) a root cause analysis should be done
- There was decision to refer those labs also to the troubleshooting webpage

How to improve advertisement for the PT scheme, to attract more participants?

- It was decided to translate the brochures into French and Portuguese
- Local coordinators should to be more “aggressive” and use national meetings and national lab associations, use institutions websites and organize seminars
- Local coordinators that are too busy with other obligations should be substituted
- A cooperation between regional organisations (e.g. SADCAS) could be helpful
- Local coordinators should to raise the awareness: “PT is the way forward to accreditation”

What costs can be covered by the participants?

- There was an agreement that participants should be able to pay for the transport (air ticket) to the workshop, if a convenient venue is selected
- One group also stated that participants also could pay for the sample transport

Is the fee adequate?

- The majority of the group said that the fee is too low.
- The new fee should be dependent on the cost analysis of the PT provider
- It was decided to recommend to the General Assembly to increase the fee for the 2012 round to 200 US-$

Is it absolutely necessary to have an evaluation workshop after each PT round?

- No agreement could be reached in this regard
- It was decided to postpone this question to the 2012 workshop

Other ideas to ensure the sustainability of the scheme?

- Seek for support from the CEOs of the laboratory institutions
- More training in the workshops, advertised at the beginning could attract more participants
- Find another sponsor
- Review participation fee continuously
- Encourage labs to include the scheme and its fees in their budget
- Lobbying within SADC
- SADC/PTB to approach CEOs
- Create awareness among clients

Thursday, 17 November 2010

SADCWaterLab General Assembly

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

Evaluation questionnaire

M. Koch distributed an evaluation questionnaire (see annex 6) 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 (accomo-dation, food)?

How do judge the venue of the work-shop (conference room)?

How do you judge the different parts of this workshop?

Training on trueness checks

Training on Control Charts

Local coordinators’ reports

Reports on the follow-up of the ToT

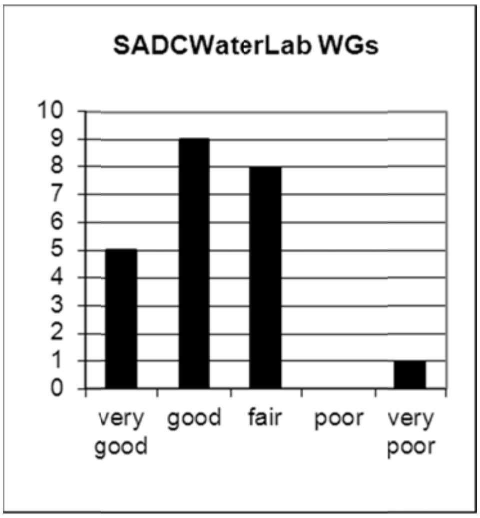
Reports from the SADCWaterLab working groups

Report of the PT provider

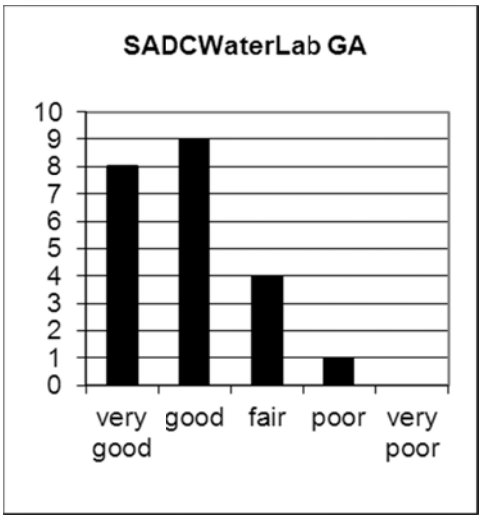
Discussion about necessary changes in the PT scheme

Discussion about the way to sustainability

SADCWaterLab WGs “methods” and “training”



SADCWaterLab General Assembly



The five most important topics

- control charts training (21)
- trueness training (19)
- PT evaluation (17)
- PT provider report (10)
- Methods WG (7)
- Sustainability of PT without PTB (4)
- SADCWaterLab General Assembly (3)
- Group discussions (3)
- ToT WG (2)
- Corrective action / root cause analysis (2)
- Discussion about necessary changes (2)
- trueness vs. precision (1)
- Methods validation and measurement uncertainty (1)
- PT statistical evaluation (1)
- ISO 17025 technical requirements (1)
- Cost sharing (1)
- Networking (1)
- Report from WG (1)
- Accuracy and lab evaluation (1)
- Method assessment (1)
- Improvement suggestions in analytical work (1)
- Potential to extend scope (1)
- Control chart software (1)
- Necessity of CRM (1)
- Parameters to include in PT scheme (1)
- Report of the follow-up from ToT (1)
- Local coordinators' reports (1)

Expectations fulfilled

- Yes 22
- Partly: 1 („Training component was very brief“)

Benefits

- Networking
- Interactions with participants from other countries and sharing of their experiences
- Evaluation presentation (Chemistry)
- Training on use of x-charts and check for trueness
- Training; contact with labs
- More skills on trueness checks and control charts
- New techniques in the analytical skills approach
- Exchange of experiences; training
- Training
- More awareness of the PT scheme and PTB contribution; more awareness on the microbiology PT scheme
- Experience sharing with other professionals; to be able to visit Mauritius and know about Mauritius culture (THANKS)
- The training was good and the methods recommendation will be good for the labs
- I am benefited on PT participation, way towards accreditation
- Evaluation of PT 2011; training on control charts and trueness; requirements to local coordinators; interaction with others
- Areas of improvement have been identified, noted and shall be implemented
- Networking and knowledge acquired from training
- Training; commitment
- The use of control charts as a tool of quality control
- Opportunity to meet all local coordinators
- I was able to benefit through technical discussions and also provider input

Report prepared by

Dr.-Ing Michael Koch
Stuttgart, 13.1.2012

Annex 1

List of participants - Chemistry Workshop

MrMs	Name	First Name	Country	Affiliation	e-mail 1	e-mail 2	e-mail 3
Mr.	Baptista	Lopes Ferreira	Angola	Agostinho Neto University	Antonio.goncalves@geologia-uan.com	Lopes.baptista@geologia-uan.com	LFmaioral@yahoo.es
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Ensuring the Quality of Analytical Results
Part I - Trueness

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Quality of analytical results

- In order to get accurate results we need to ensure

trueness **precision**

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Trueness

- Closeness of agreement between the average of an infinite number of replicate **measured quantity values** and a **reference quantity value** [VIM]
  - A reference quantity value is a value with little (or ideally no) systematical error
  - Perfect trueness cannot be achieved, so trueness in its analytical meaning is always trueness within certain limits
    - These limits may be narrow at a high concentration level and wide at the trace level
  - The lack of trueness is called bias

True value

- Quantity value consistent with the definition of a quantity [VIM]
  - The true value is a theoretical concept and, in general, cannot be known exactly
  - It is a value that would be obtained by a perfect measurement
  - True values are by nature indeterminate

Conventional True Value

- Value attributed to a particular quantity and accepted, sometimes by convention, as having an uncertainty appropriate for a given purpose [IUPAC Orange Book]
  - A result obtained by using several independent methods in several expert laboratories on one measurand is regarded as conventional true value of a quantity
    - even if it is not the "true" value
  - A conventional true value is in general, regarded as sufficiently close to the true value

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Metrological traceability

- is closely related to trueness
- property of a **measurement result** whereby the result can be related to a reference through a documented unbroken chain of **calibrations**, each contributing to the **measurement uncertainty**

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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)

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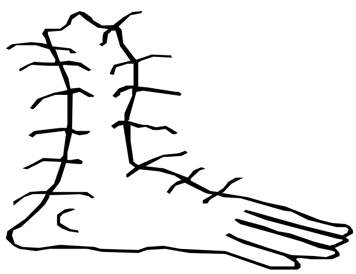
… Lack of Standard …

King's foot



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… 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.

… 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		

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Meter Convention

- Diplomatic treaty
- 20th May 1875, in Paris
- SI system
- 52 signatory countries
- 36 associate members

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Meter Convention
Aims

- International uniformity in measurement
- Common system of units
- Equivalent measurement standards
- Harmonised laws and regulations
- Mutual recognition of measurements

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SI International System of Units
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

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

Chemistry in SI
It is quite new!

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

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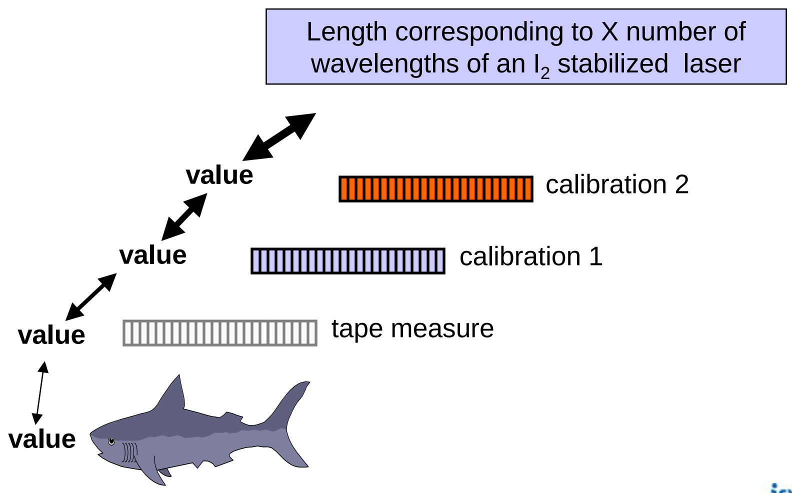
Traceability of Length Measurements



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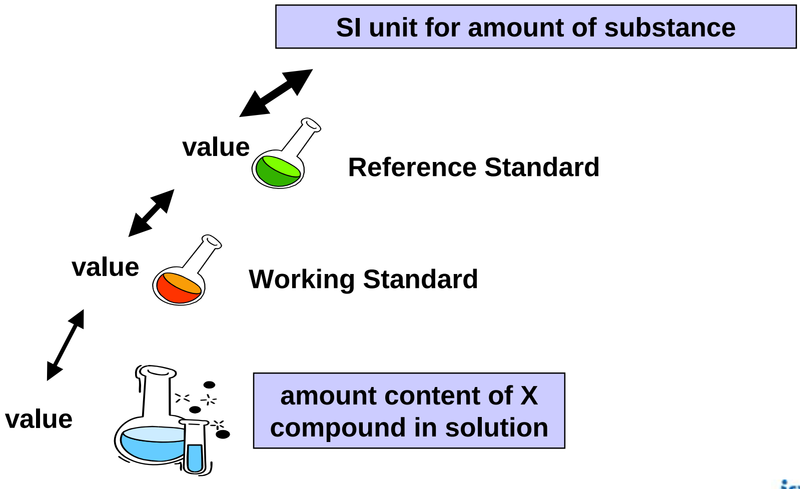
Traceability of Chemical Measurements



Traceability needs

- stated references
- stated uncertainty

Stated References – 3 different

- Examples of different stated references
  - A measurement unit, e.g. mol/l, °C
  - A measurement standard, e.g. the certified reference material SRM 2193, a $CaCO_3$ pH standard.
  - A measurement procedure, 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

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)

Traceability in the analytical lab

- What needs to be traceable?
  - balance
  - thermometer
  - volumetric equipment
- How can I do that?
  - commission a calibration laboratory
  - do it yourself

How to check a balance

- We need a reference – a calibrated mass piece
- with a sufficiently small measurement uncertainty
- the OIML has defined classes for weights
  - e.g. 1 g
    class E1: ± 0.000 01 g
    class E2: ± 0.000 03 g
    class F1: ± 0.000 1 g
    class F2: ± 0.000 3 g
    class M1: ± 0.001 g
    class M2: ± 0.003 g
    class M3: ± 0.01 g
- the higher the uncertainty of the mass piece the higher will be your uncertainty
- check the age of the certificate

Check of the trueness of the balance

- The measurement procedure should be as close as possible to the routine procedure
- The deviation of the reading from the target value should be smaller than the standard deviation of the weighing (precision of the balance)
- If this is not the case, you have to correct for the deviation or include it in your measurement uncertainty budget

Check of the precision of the balance

- Use routine weighing procedure
- Weigh the mass piece at least 10 times
- Calculate the standard deviation of the weighings

Don‘t forget

- to document all calibrations
- in order to be able to prove the traceability to auditors

How to check a thermometer

- Compare with a calibrated thermometer
- Again check for the measurement uncertainty of the calibrated thermometer (certificate!)
- check the age of the certificate

How to check and ensure traceability of volumetric equipment?

- Traceability to SI unit for length is not feasible
- Instead traceability to
  - mass reference
  - density reference for pure water
  - density reference for air
  - temperature

How can we realise the references?

- mass → calibrated balance
- density reference for pure water → ISO 4787
- density reference for air → ISO 4787
- temperature → calibrated thermometer

Selection of suitable balance

- The necessary accuracy of the balance depends on the volume to be checked
- recommended balance:

Selected volume under test V	Resolution mg	Standard deviation (repeatability) mg	Linearity mg
100 µl < V ≤ 10 ml	0.1	0.2	0.2
10 ml < V < 1000 ml	1	1	2
1000 ml ≤ V ≤ 2000 ml	10	10	20
V > 2000 ml	100	100	200

Thermometer and Calibration liquid

- Maximum deviation of the thermometer
  - for V < 1000 ml: max. 0.2 K
  - for V ≥ 1000 ml: max. 0.1 K
- calibration liquid is distilled or deionised water

Principle of testing

- The calibration is based on the determination of the water volume contained in or released from the volumetric equipment.
- The water volume is calculated from the mass, taking into account a buoyancy correction and density taken from a table
- Cleanliness of the equipment is crucial for good results!!

Testing equipment and accessories

- Storage vessel
  - Filled with testing liquid (distilled or deionised water). Allow to adjust to room temperature
- Weighing vessel
  - Erlenmeyer flask with a suitable volume
- Funnel
  - to fill volumetric instrument
- Thermometer
  - Accuracy 0.2 °C
- Balance with required accuracy
- For the testing of pipettes and burettes calibrated "EX" (to deliver), a support for mounting the instrument vertically is required.
- Stopwatch
  - to keep track of the waiting time, accuracy ± 1 s.
- Lint-free tissue for wiping
- Pipetting aid
- Barometer
  - For testing the atmospheric pressure, accuracy ± 5 hPa

Procedure for instruments calibrated „IN“

(Volumetric flasks, graduated cylinders and mixing cylinders)

- Determine testing temperature (testing liquid).
- Determine empty weight of the dry volumetric instrument. (W1)
- Fill the instrument with testing liquid to approx. 5 mm above the ring mark.
- The glass wall must not be wetted above the meniscus. If this happens, wipe it dry with tissue.
- Adjust the meniscus precisely to the ring mark by removing liquid with a pipette.
- The lowest point of the meniscus must be aligned with the upper edge of the mark.
- Read without parallax; i.e. your eye must be at the same level. (The meniscus is easier to see if the flask is placed against a white sheet of paper.)
- Determine the weight of filled instrument. (W2)

Procedure for instruments calibrated „EX“

I - Bulb pipettes and graduated pipettes

- Determine testing temperature (testing liquid)
- Determine weight of weighing vessel. (W1)
- Clamp the pipette vertically to the support.
- Using a pipetting aid, fill the pipette to approx. 5 mm above the top mark.
- Dry the outside of the pipette tip with tissue.
- Adjust the meniscus precisely by releasing liquid.
  - The lowest point of the meniscus must be aligned with the upper edge of the mark.
  - Read without parallax; i.e. your eye must be at the same level. If a drop still adheres to the tip, wipe it off against the inner wall of the weighing vessel.
- Allow the liquid to run off into the weighing vessel, while the pipette tip touches the inclined wall of the vessel. At the moment that the meniscus comes to a standstill inside the pipette tip, start to measure the waiting time.
- After 15 seconds waiting time (use stopwatch), wipe off the tip against the inside of the vessel. If a drop still adheres to the tip, wipe it off against the inner wall of the weighing vessel.
- Determine weight of the weighing vessel again. (W2)
- Note: In the case of pipettes graduated for partial delivery, let the water run out until approx. 10 mm above the lower mark, while the pipette tip touches the inclined wall of the weighing vessel. After 15 seconds waiting time, adjust the meniscus precisely to the mark.

Procedure for instruments calibrated „EX“

II - Burettes and automatic burettes

- Determine testing temperature (testing liquid).
- Determine weight of weighing vessel. (W1)
- Clamp the burette vertically to the support.
- Fill the burette to approx. 5 mm above the zero mark. To bleed the burette stopcock, let liquid run off not further than to the nominal capacity mark. After the first filling, a small air bubble may remain in the burette stopcock. To remove this bubble, hold the burette at an angle and tap a finger against the bubble.
- Fill the burette to approx. 5 mm above the zero mark. The glass wall must not be wetted above the zero mark. (If this happens, wipe it dry with tissue.)
- Set to zero precisely by releasing liquid. The lowest point of the meniscus and the upper edge of the mark must be at the same level. Read without parallax. Burettes with Schellbach stripe: the point where the two arrows touch must be aligned with the zero mark. Read without parallax; i.e. your eye must be at the same level.
- Let the liquid run off into the weighing vessel until approx. 5 mm above the nominal capacity mark. The burette tip must not touch the wall of the vessel!
- After 30 seconds waiting time (use stopwatch), adjust the meniscus precisely to the nominal capacity mark, and wipe off the tip against the inside of the vessel. If a drop adheres to the tip, wipe it off against the inner wall of the weighing vessel.
- Determine the weight of the weighing vessel again. (W2)

Repetitions

- The necessary number of tests depends primarily upon the skill of the tester.
- Generally, one test should suffice in the case of all volumetric instruments calibrated "IN" (to contain).
- In case of instruments calibrated "EX" (to deliver), to be on the safe side, it is advisable to use the mean value resulting from 3 measurements.
- The scatter of the individual results should not be greater than 1/4 of the admissible error limit (tolerance) of the measuring instrument.
  - Example: error limit of a 10 ml bulb pipette is ±0.020 ml. The scatter of measuring results must be below ±0.005 ml. If the scatter is greater, the testing procedure should be revised, and the test should be repeated.

Evaluation

- General equation (ISO 4787)

$$V_{20} = (I_L - I_E) \times (\rho_W - \rho_A)^{-1} \times \left(1 - \frac{\rho_A}{\rho_B}\right) \times [1 - \gamma(t - 20)]$$

- with
  - I_L weight of the filled instrument
  - I_E weight of the empty instrument
  - ρ_W density of water at temperature t
  - ρ_A density of air at temp. t and the present air pressure
  - ρ_B density of the mass pieces for the calibration of the balance
  - γ cubic heat expansion coefficient for the material of the volumetric equipment
  - t temperature of the water in °C

Simplified evaluation

- Introducing a factor Z

$$V_{20} = (I_L - I_E) \times Z$$

- Z is mainly dependent on
  - Material of the volumetric equipment
  - Temperature of the water
  - air pressure
- Z can be found in published tables (e.g. in ISO 4787 or from manufacturers)

Detailed description of the cailbration procedure

- might be found
  - in ISO 4787
  - from manufacturers websites
    e.g.
    http://www.brand.de/fileadmin/user/pdf/SOPs/SOP_BLAUBRAND_EN.pdf

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Calibration of piston-operated volumetric apparatus

- Similar procedure described in ISO 8655-6
- Due to the usual low volumes evaporation losses during the procedure have to be taken into account
- Detailed description on the use and calibration of such pipettes:
  http://www.pipette.com/Support/OnlineLecture/UKAS%20MGP%20Guide%2069_Calibration%20and%20Use%20of%20Piston%20Pipettes.pdf

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Now we have checked and calibrated all our equipment

- Can we be sure that we measure results with good trueness?
- No, because there might be some hidden biases in the analytical procedure, e.g. incomplete extraction or overtitrations etc.
- So, how to check that?

Trueness check

- To check the trueness of the whole analytical procedure we have to analyse samples with a known of analyte
  - certified reference materials (CRM)
  - reference materials (RM)
  - interlaboratory test samples
  - spiked samples

Reference Material Definition

Material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials

Certified Reference Material Definition

Reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes 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

Certified Reference Material (CRM)

- All CRMs lie within the definition of "measurement standards" and therefore can be used as reference for traceability
- CRMs are generally prepared in batches for which the property values are determined within stated uncertainty limits by measurements on samples representative of the whole batch

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Different types of CRM

- **Pure substances**
  - characterised for chemical purity and/or trace impurities
- **Standard solutions and gas mixtures**
  - often prepared gravimetrically from pure substances and used for calibration purposes
- **Matrix reference materials**
  - characterised for the composition of specified major, minor or trace chemical constituents. Such materials may be prepared from matrices containing the components of interest, or by preparing synthetic mixtures
- **Physico-chemical reference materials**
  - characterised for properties such as melting point, viscosity, and optical density
- **Reference objects or artefacts**
  - characterised for functional properties such as taste, odour, octane number, flash point and hardness. This type also includes microscopy specimens characterised for properties ranging from fibre type to microbiological specimens

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In General High Quality CRMs Should…

- State traceability of certified value
  (e.g. traceability to SI, or to values obtained with method XYZ)
- State an ISO-GUM uncertainty of certified value
- Demonstrate traceability & uncertainty of certified value
  (e.g. in a certification report; experimental evidence of demonstrated capability from participation to international comparisons)
- Preferably be produced according to the guidelines of ISO-35

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Use of CRMs

- (Ideally) supplier should give advice
- Storage temperature
- Influence of moisture on long term stability (e.g. biological activity)
- Influence of contamination
- Possibility to divide in different portions after opening

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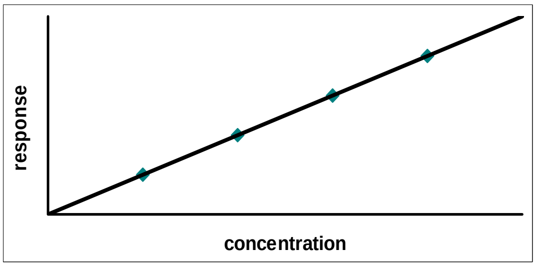
Use of CRMs

How can CRMs help my measurements?

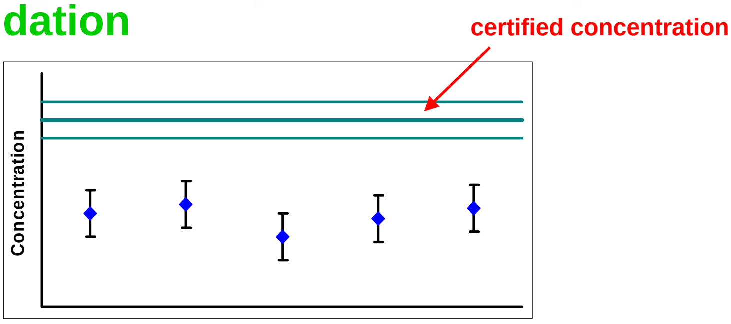
- Calibration (?)
- Validation (?)
- Measurement control (?)

Calibration



Use as a matrix matched calibrant
(direct or via working standards)
to ensure traceability of results
to an external reference (the CRM)

Validation

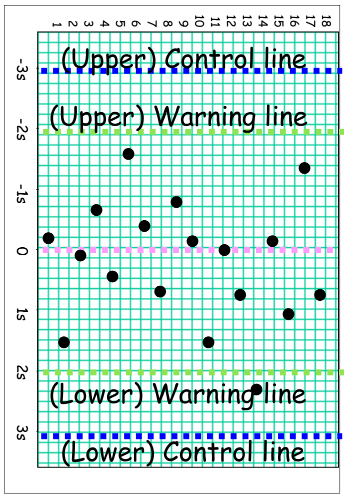


Check the measurement results in terms of validity:

- Is there any method specific bias ?
- Is there any systematic error ?

Measurement Control

- Abuse of CRM
- Instead: use in-house materials or quality control materials
  (i.e. of proven homogeneity and stability; sometimes named in-house RMs or laboratory RMs)

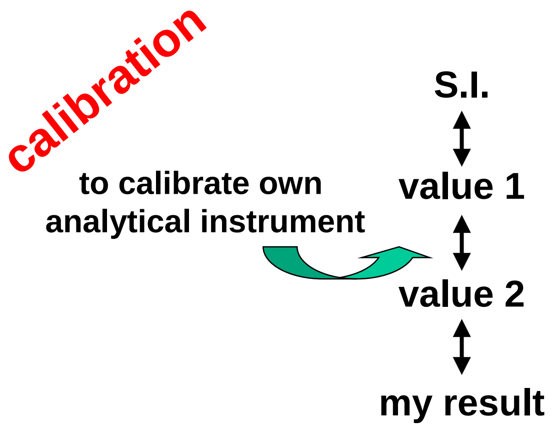


Use of CRMs

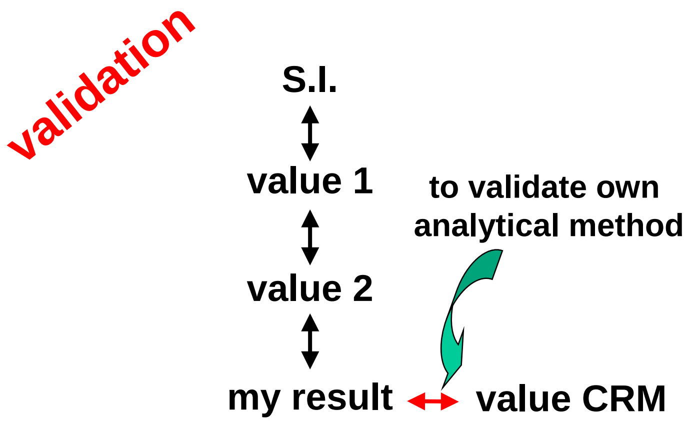
how can CRMs help my measurements?

- calibration X(?) YES
- validation X(?) YES
- measurement control X(?) NO

How CRMs are Used in Terms of Traceability?



How CRMs are Used in Terms of Traceability?



Selection of CRMs

- Availability (problem with matrix CRMs)
- Concentration range of certified property
- Uncertainty of certified property
- Traceability of certified property
- What is your uncertainty requirement
- Contribution of CRM uncertainty on your measurement uncertainty
- Demonstrated competence of CRM producer
- CRM matrix
- Cost

CRM Producers

- General
  - COMAR database: http://www.comar.bam.de
- Individual suppliers
  - IRMM: http://www.irmm.jrc.be
  - BAM: http://www.bam.de
  - LGC: http://www.lgc.co.uk
  - NIST: http://www.nist.gov
  - others...

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Preparation of in-house reference materials

- A guide for the production of in-house reference materials is available from http://www.nmschembio.org.uk: Brookman, B., and Walker, R.: Guidelines for the in-house production of Reference Materials, July 1998
- Select a proper material
- Ensure homogeneity and stability
- Measure reference value

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Measurement of reference value

- if the RM is to be used for assessing the performance of an analytical system, it should be referenced against a CRM
  - measure RM and CRM under repeatability conditions
- if a CRM does not exist the reference value needs to be obtained by
  - a definitive (primary) method
  - two or more methods and preferably include some independent check
  - an interlaboratory exercise involving a reasonable number of participants

Interlaboratory test samples

- Assigned values from interlaboratory tests might be used, if we can assume that the assigned value is sufficiently close to the "true" value
- SADCWaterLab chemistry PT → traceable reference values from formulation

Other PTs

- Consensus mean values are often used instead of reference values
- there often remains some doubt concerning the reliability of assigned values used in proficiency testing schemes
- 'the majority' is not necessarily correct and as a consequence the values carry some undisclosed element of uncertainty
- the interpretation of proficiency testing data thus needs to be carried out with caution

Spiked samples for recovery experiments

- are an alternative where neither RMs or ILCs are available
- Spike a real sample with a known amount of analyte
- Measure spiked and non-spiked sample
- Calculate recovery rate: Difference of measurement results divided by spiked amount

Problems with recovery studies

- Spiking must be very accurate
- Analyte must be the same chemical species as in real samples
- Type of bond to the matrix should be similar

Otherwise we do not get a reliable answer

Ensuring the Quality of Analytical Results
Part II – Precision/Control Charts

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Quality of analytical results

- In order to get accurate results we need to ensure

trueness **precision**

Precision

- Closeness of agreement between **indications** or **measured quantity values** obtained by replicate **measurements** on the same or similar objects under specified conditions
  [VIM]

- The precision of a set of results of measurements can be quantified e.g. as a standard deviation

Repeatability condition of measurement

- condition of measurement, out of a set of conditions that includes
  - the same measurement procedure,
  - same operators,
  - same measuring system,
  - same operating conditions and
  - same location,
- and replicate measurements
  - on the same or similar objects
  - over a **short period of time**

[VIM]

Intermediate precision condition of measurement

- condition of measurement, out of a set of conditions that includes
  - the same measurement procedure,
  - same location,
- and replicate measurements
  - on the same or similar objects
  - over an extended period of time,
- but may include other conditions involving changes

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Reproducibility condition of measurement

- condition of measurement, out of a set of conditions that includes
  - different locations,
  - different operators,
  - different measuring systems,
- and replicate measurements on the same or similar objects

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What kind of precision am I interested in?

- It depends on the question
  - how close are the values measured one directly after the other?
    → repeatability precision
    → range control chart
  - what is the day-to-day variation in the lab?
    → intermediate precision
    → X control chart

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Normal Distribution

- First studied in the 18th century by Carl Friedrich Gauss
- He found that the distribution of errors could be closely approximated by a curve called the „normal curve of errors“

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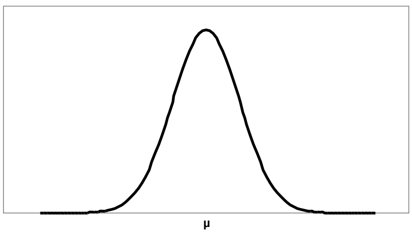
Normal Distribution

- We often use this „normal distribution“ as a model for measurement variation.
- The normal distribution is an algebraic function, developed theoretically to describe variations in the results of measurements.
- In fact it usually (but not always) corresponds well with what we find in practice and plays a key role in statistics.

Normal Distribution

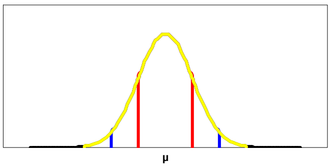
- bell shaped
- completely determined by μ and σ



$$y = \frac{1}{\sigma\sqrt{2\pi}} e^{\frac{(x-\mu)^2}{2\sigma^2}}$$

Normal Distribution – Important Properties

- the curve is symmetrical about μ
- the greater the value of σ the greater the spread of the curve
- approximately 68% (68,27%) of the data lie within μ±1σ
- approximately 95 % (95,45%) of the data lie within μ±2σ
- approximately 99,7 % (99,73%) of the data lie within μ±3σ



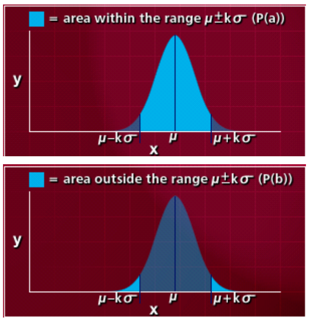
$$y = \frac{1}{\sigma\sqrt{2\pi}} e^{\frac{(x-\mu)^2}{2\sigma^2}}$$

Normal Distribution – a Useful Model

- With the mean and the standard deviation areas under the curve can be defined
- These areas can be interpreted as proportions of observations falling within these ranges defined by μ and σ

Areas under the Normal Curve

- For a normally distributed population with mean μ and standard deviation σ, the following table gives the probability that an observation x will fall:
  a) within the range μ±kσ (μ-kσ < x < μ+kσ)
  b) outside the range μ±kσ
- These are called **two-tailed** probabilities



k	P(a)	P(b)
1	0.683	0.317
1.64	0.900	0.100
1.96	0.950	0.050
2	0.954	0.046
3	0.997	0.003

≈2/3

≈19/20

≈3/1000

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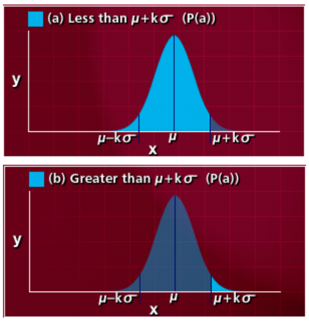
Areas under the Normal Curve

- For a normally distributed population with mean μ and standard deviation σ, the table gives the probability that an observation x will fall:
  a) less than the mean plus k standard deviations (x < μ+kσ)
  b) greater than the mean plus k standard deviations (x > μ±kσ)
- These are called **one-tailed** probabilities



k	P(a)	P(b)
1	0.841	0.159
1.64	0.950	0.050
1.96	0.975	0.025
2	0.977	0.023
3	0.998	0.002

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What are quality control charts?

- Graphical tool (e.g. according to Shewhart) on statistical basis, to continuously monitor and control a process, in order to intervene immediately if deviations occur. This also is called statistical process control
- Quality control charts contain warning and action limits

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History

- developed by Shewhart 1930 for the industrial product control
- I.e. for a product that has a constant property within certain limits (e.g. the length of a screw)
- Shewhart took N samples during one production period and measured the property n times
- From the means of all samples he calculated the grand mean over all samples and put this value in the control chart

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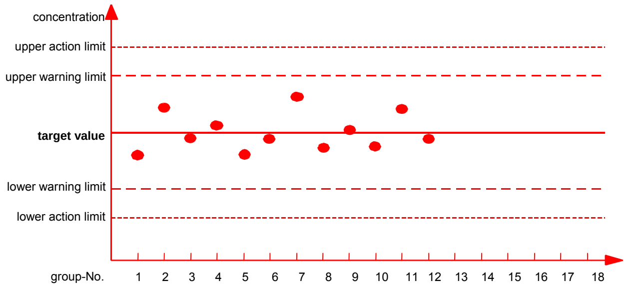
Quality control charts

- Take samples during the process
- Measure a quality indicator
- Mark the measurement in a chart with warning and action limits



Purpose of Shewhart quality control charts

- Suddenly occurring serious changes in the production as well as slow, but steady worsening of the quality could be read directly from the graph
- Immediate correcting measure on the production reduce the risk of producing waste and of customer complaints

Principle of control charts

- Graphical display of quality based on
  - A target value and
  - Quality limits
- With the following different control limits:
  - Warning limits: exceeding once is tolerated
  - Action limits: exceeding requires immediate action

Problems in the use for chemical analysis

- Monitoring of means would block the laboratory completely
- The „control product“ has to be produced for this purpose, since the routine samples don‘t have a uniform quality indicator

Guidelines and literature

- ISO 8258 – Control Charts
- Funk, Dammann and Donnevert: Quality Assurance in Analytical Chemistry. Wiley
- NORDTEST: Internal Quality Control – Handbook for Chemical Laboratories, TR 569, www.nordicinnovation.net/nordtest.cfm
- ISO TR 13530: Guide to analytical quality control for water analysis

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Statistics and quality control charts

- Statistical procedures are used to calculate the warning and action limits of control charts from a pre-period (mean and standard deviation)
- With the help of statistical tests (t- test and F- test) it can be checked whether data from the control period are significantly different from those of the pre-period

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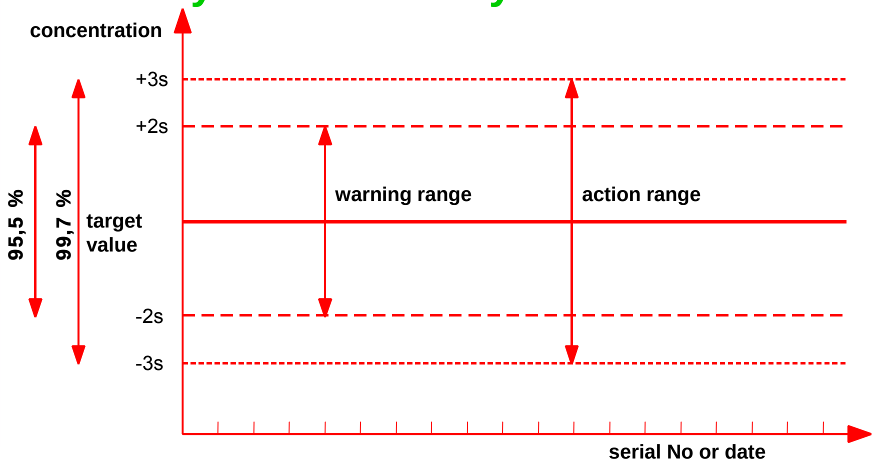
Normal distribution and quality control charts

- The usual calculations for control charts in principal require normal distribution of data
- Strictly seen this calculation procedure can be applied only if the population of all data is normally distributed and this can be proved
- Usually we refrain from doing that
- This does not affect the “alarm function” of quality control charts

Quality control charts in analytical chemistry



Warning limits

- 4.5% of the (correct) values are outside the warning limits.
- This is not very unlikely
- Therefore this is only for warning, no immediate action required

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Action limits

- There is probability of only 0.3 % that a (correct) measurement is outside the action limits (3 out of 1000 measurements)
- Therefore the process should be stopped immediately and searched for errors

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Target value and quality limits for X-charts

- These data have to be determined uder conditions similar to routine analysis, i.e.
  - not under repeatability conditions,
  - nor under reproducibility conditions,
  - but under day-to-day intermediate conditions (1 value per working day)
- Determination from a pre-period of 20 working days

Quality and quality objectives

- Quality is the property of a product or service to fulfil stipulated requirements
- Quality objectives for the analysis (how accurate is the analysis needed) depends on the requirements of the customer!!

Quality limits of the control chart and quality objectives for the analysis

- Usually the quality limits are determined from the standard deviation in a pre-period
- **In order for a quality control chart to make sense, a comparison with the quality objectives for the analysis is indispensable**
- **no blind use!**

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Warning and action limits

- Usually from the standard deviation in the pre-period
- Alternative: from fitness-for-purpose criteria $\rightarrow$ target control chart

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Requirements for the pre-period

- Conditions as similar as possible to the control period
  - not more care
  - if necessary with change of operator
  - intermediate conditions like in routine
    - repeatability ➔ too narrow limits
    - reproducibility (PT) ➔ too wide limits

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What are Out-of-control-situations?

- The control chart shows, that the current situation is very unlikely to occur for normal distributed data

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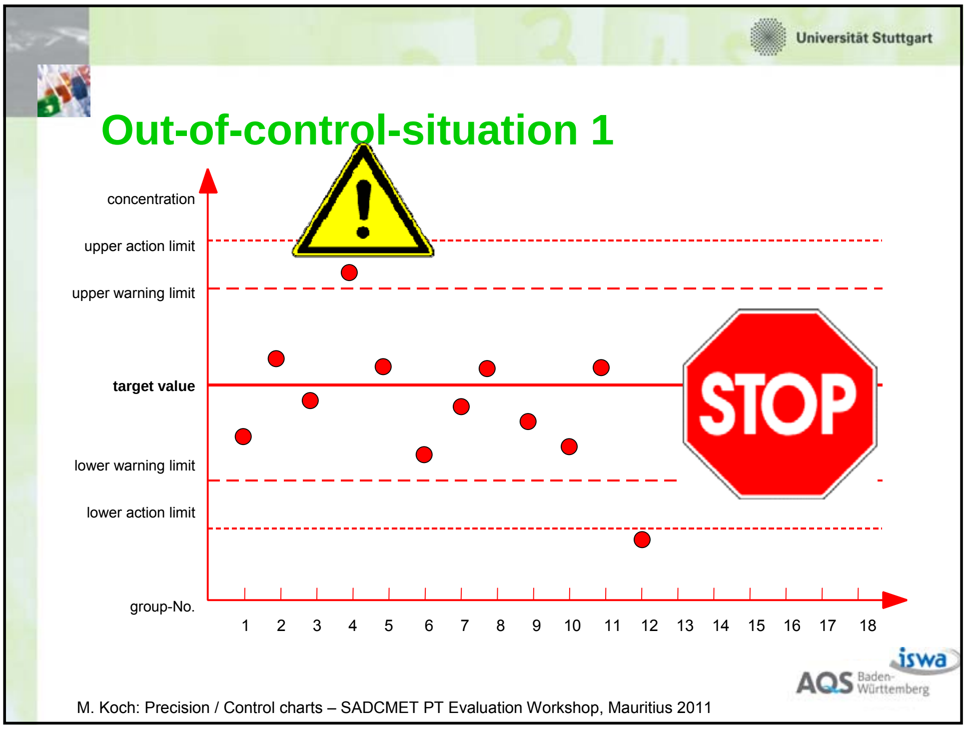
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Out-of-control-situation 1
concentration
upper action limit
upper warning limit
target value
lower warning limit
lower action limit
group-No.
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
STOP
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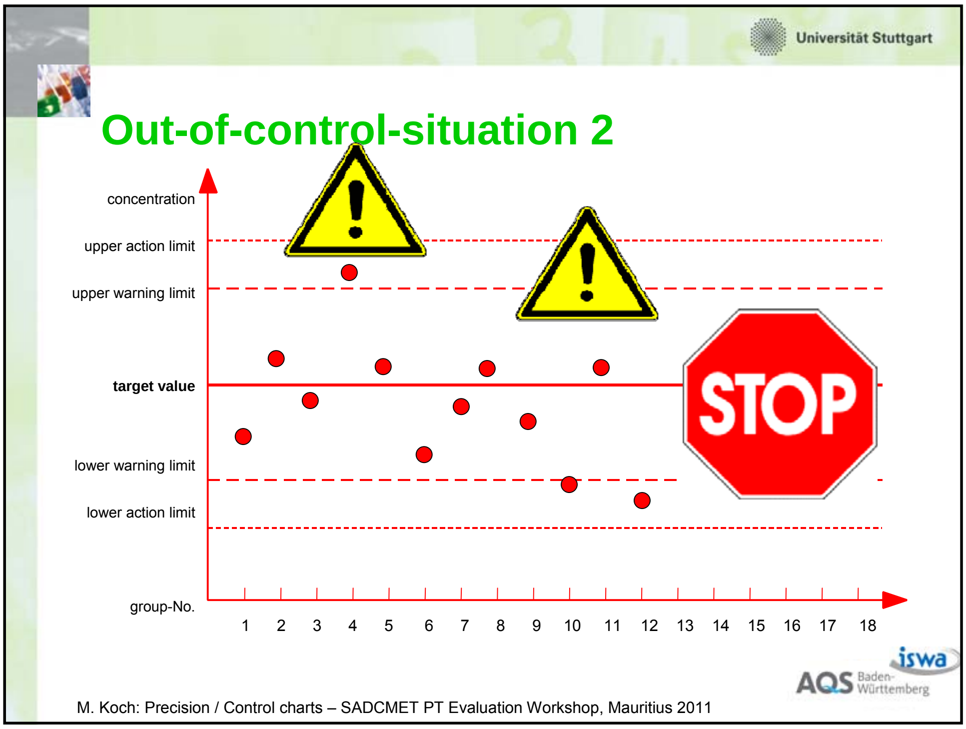
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Out-of-control-situation 2
concentration
upper action limit
upper warning limit
target value
lower warning limit
lower action limit
group-No.
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
STOP
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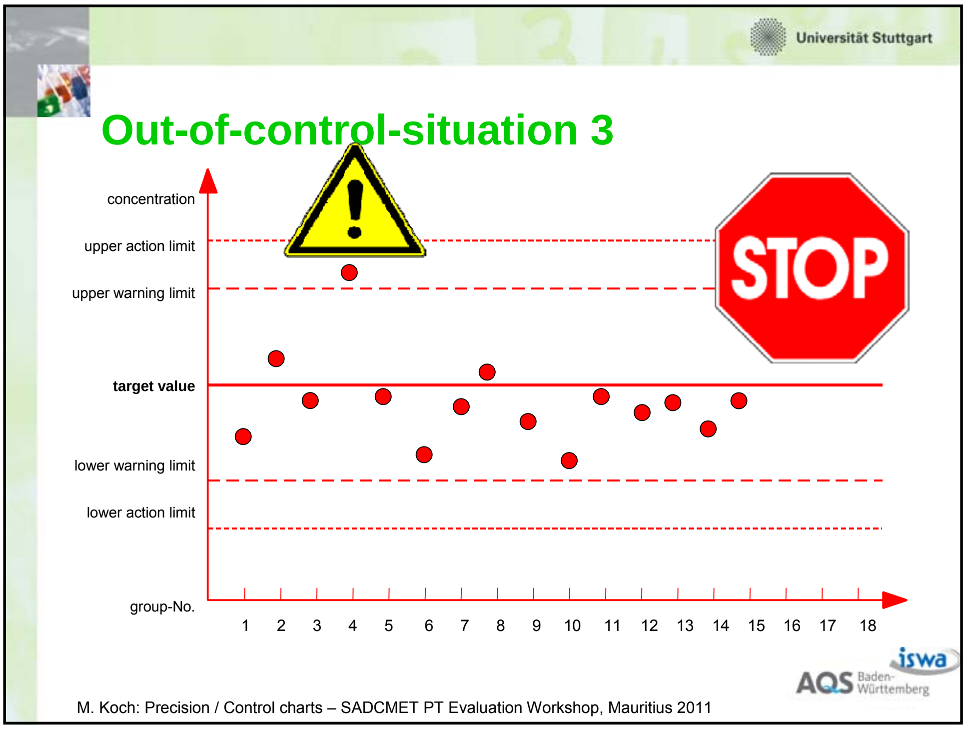
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Out-of-control-situation 3
concentration
upper action limit
upper warning limit
target value
lower warning limit
lower action limit
group-No.
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
STOP
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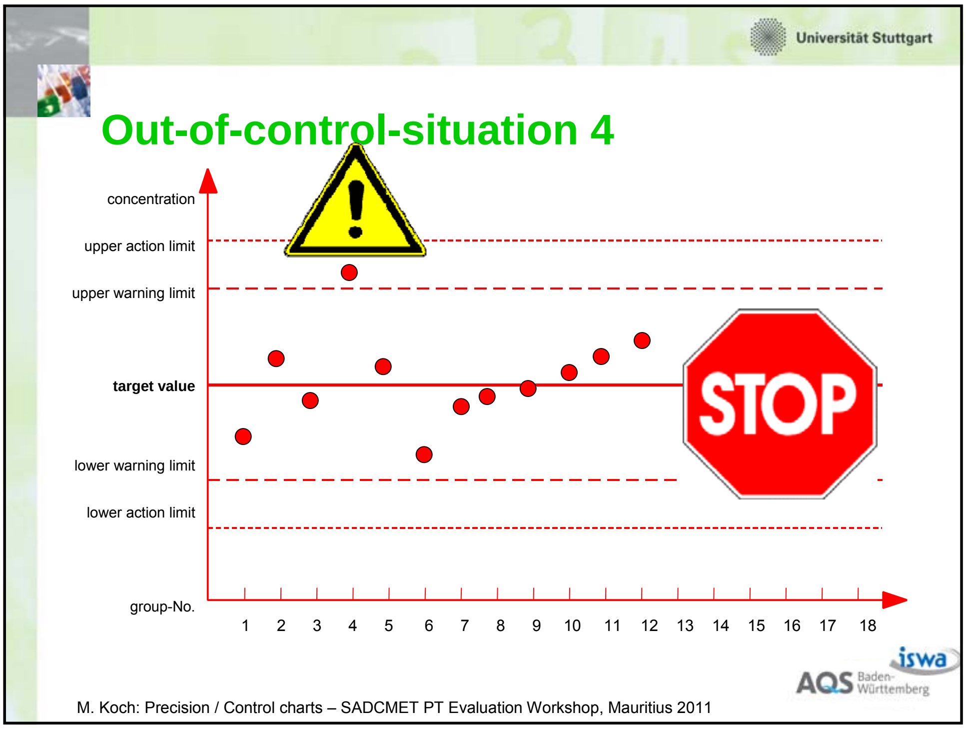
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Out-of-control-situation 4
concentration
upper action limit
upper warning limit
target value
lower warning limit
lower action limit
group-No.
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
STOP
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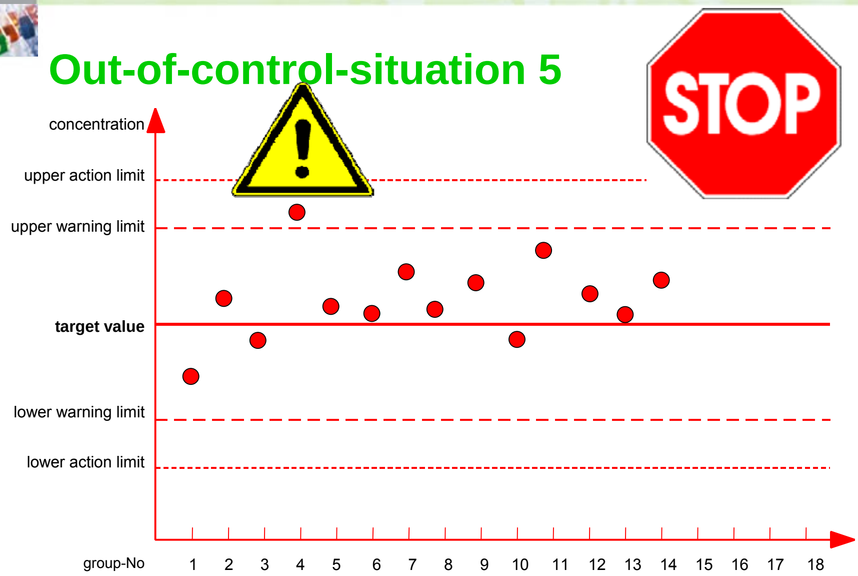
Out-of-control-situation 5



Out-of-control-situations in different publications - Funk, Dammann, Donnevert

1. One point beyond action limits
2. Two out of three points in a row beyond warning limits
3. Seven points in a row on the same side of the central line
4. Seven points in a row steadily increasing or decreasing
5. 10 out of 11 points in a row on the same side of the central line

Out-of-control-situations in different publications - ISO 8258

1. One point beyond action limits
2. Nine points in a row on the same side of the central line
3. Six points in a row steadily increasing or decreasing
4. Fourteen points in a row alternating up and down
5. Two out of three points in a row beyond warning limits
6. Four out of five points in a row beyond 1s limits on the same side
7. Fifteen points in a row within 1s limits
8. Eight points in a row beyond 1s limits on both sides of the central line

Out-of-control-situations in different publications - NORDTEST TR569

1. out of control
   a. One point beyond action limits
   b. Two out of three points in a row beyond warning limits
2. in control, but out of statistical control
   a. Seven points in a row steadily increasing or decreasing
   b. 10 out of 11 points in a row on the same side of the central line

Out-of-control-situations in different publications - ISO TR 13530

1. One point beyond action limits
2. Two consecutive values beyond warning limits
3. 7 points in a row steadily increasing or decreasing
4. 10 out of 11 points in a row on the same side of the central line (for X-charts only)
5. 7 consecutive control values lie above the mean range (for range-charts only)

Which one to choose?

- It is up to you to decide
- There is no prescription, no bible
- Control charts are just a tool
- Select the one that fits best for your needs

What do Out-of-control Situations Mean? How do I have to React?

- Out-of-control situations do **not** mean:
  - throw away everything!
  - start again!
- they rather mean:
  - Attention! An improbable situation has happened in the process!
  - Stop the process!
  - Look what has happened!

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What do I have to do?

- Do not report any results to the client! Recall already reported results!
- Do not continue to measure!
- Look for the mistakes!
- The type of out-of-control situation can give valuable hints!

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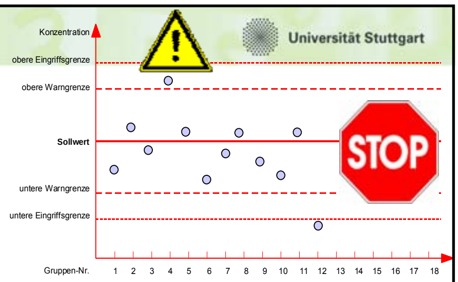

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Reaction to Situation 1

- Possibly a singular mistake happened during the analyses of the control sample. Analyse it again.
- If the value is confirmed, the analytical process must be inspected for a suddenly occurring change.
- When the mistake is found, continue with measurements!

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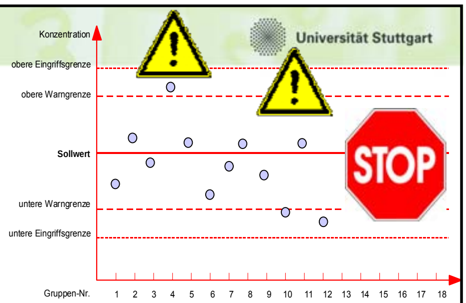

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Reaction to Situation 2

- A mistake has occurred which either decreased the precision of the analyses or which led to a shift of the values in one direction (only if the deviation is in the same direction)
- Possible causes: change of operator, change in the procedure, in the environmental conditions, in the status of the analytical devices etc.
- Look for the mistake! When the mistake is found, continue with measurements!

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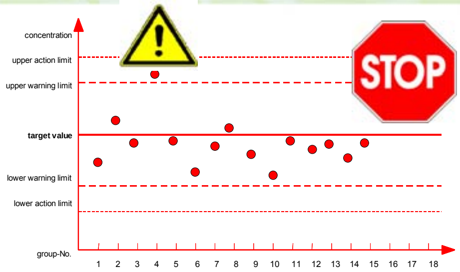
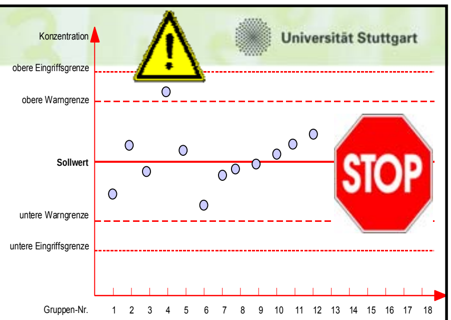
Reaction to Situation 3/5



- The mean has shifted
- Possible causes:
  change of the lot of chemical, solvent etc., new adjustment or calibration of an instrument, change of operator, change in the procedure, in the environmental conditions, in the status of the analytical devices etc.
- Look for the cause! When the cause is found, continue with measurements!
- Attention! The new mean could eventually be less biased!

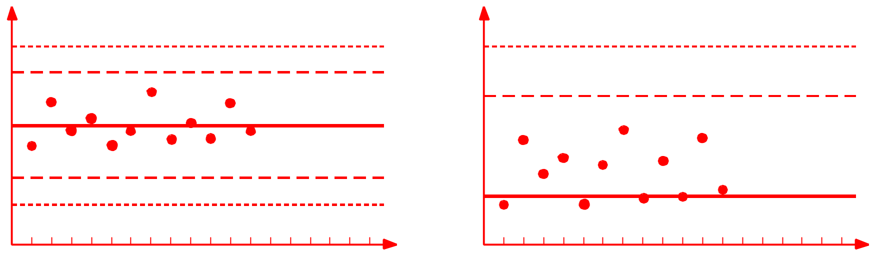
Reaction to Situation 4



- The mean shows a trend
- Possible causes:
  Chemicals used are changing, a part of the instrument is changing, the environmental conditions are changing continuously
- Look for the cause! When the cause is found, continue with measurements!

Control chart types

- Mean- / X - Control chart
- Recovery rate - control chart
- Differences - control chart
- Blank value - control chart
- Range - control chart



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Different control charts
x-chart

- original Shewhart-chart
- with single values from analytics
- mainly to validate precision
- trueness with reference materials
- also possible for calibration parameters (slope, intercept)

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Different control charts
blank value chart

- analysis of a sample, which can be assumed to not contain the analyte
- special form of the Shewhart chart
- information about
  - the reagents
  - the state of the analytical system
  - contamination from environment
- enter direct measurements, not calculated values

Different control charts
recovery rate chart - I

- reflects influence of the sample matrix
- Principle:
  - analyse actual sample
  - spike this sample with a known amount of analyte
  - analyse again
- Recovery rate:

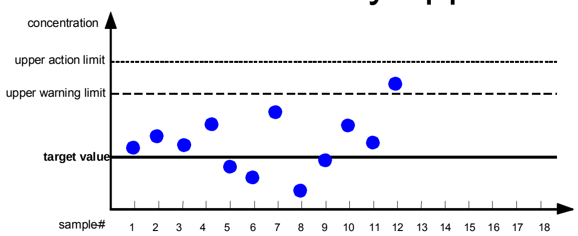
$$\mathrm{RR} = \left(\frac{x_{\mathrm{spiked}} - x_{\mathrm{unspiked}}}{\Delta x_{\mathrm{expected}}} \right) \cdot 100\%$$

Different control charts
recovery rate chart - II

- detects only proportional systematic errors
- constant systematic errors remain undetected
- spiked analyte might be bound differently to the sample matrix ➔ better recovery rate for the spike
- Target value: 100%

Different control charts
range chart

- absolute difference between the highest and lowest value of multiple analyses
- precision check
- control chart has only upper limits



Parameters of range charts

- The central line is the mean of the ranges over a long time period
- The standard deviation of the data (repeatability) can be calculated from the ranges according to the following formula (ISO 8258)
  - s = mean range / 1,128 for duplicate measurements
  - s = mean range / 1,693 for triplicate measurements
  - s = mean range / 2,059 for 4 measurements
  - s = mean range / 2,326 for 5 measurements
- Warning limit: + 2,83 · s
- Action limit: + 3,69 · s

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Different control charts
difference chart - I

- uses difference with its sign
  - analyse actual sample at the beginning of a series
  - analyse same sample at the end of the series
- calculate difference (2^{nd} value – 1^{st} value)
- mark in control chart with the sign

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Different control charts difference chart - II

- target value: 0
  - otherwise: drift in the analyses during the series
- appropriate for precision and drift check

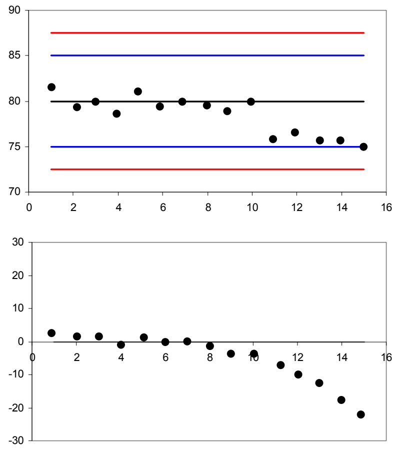
Different Control Charts Cusum Chart - I

- highly sophisticated control chart
- cusum = cumulative sum = sum of all errors from one target value
- target value is subtracted from every control analyses and difference added to the sum of all previous differences

Different Control Charts - Cusum Chart - II

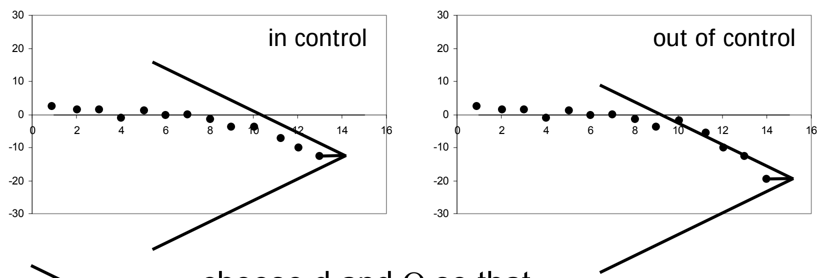
T = 80   s = 2.5

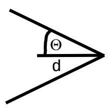
Nr.	x	x-T	Cusum
1	82	+2	+2
2	79	-1	+1
3	80	0	+1
4	78	-2	-1
5	82	+2	+1
6	79	-1	0
7	80	0	0
8	79	-1	-1
9	78	-2	-3
10	80	0	-3
11	76	-4	-7
12	77	-3	-10
13	76	-4	-14
14	76	-4	-18
15	75	-5	-23



Different Control Charts - Cusum Chart - III

- V-mask as indicator for out-of-control situation





- choose d and Θ so that
  - very few false alarms occur when the process is under control but
  - an important change in the process mean is quickly detected

Different Control Charts
Cusum Chart - IV

- Advantages
  - it indicates at what point the process went out of control
  - the **average run length** is shorter
    - number of points that have to be plotted before a change in the process mean is detected
  - the size of a change in the process mean can be estimated from the average slope

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Control samples

- are useful for the control of the quality of the measurements over longer time period
- Requirements:
  - representative for matrix and concentration
  - choose concentration so that the important range is covered (limits!)
  - sufficient amount for longer time period
  - stability for several months (if possible)
  - no influence of the container
  - no changes due to subsampling

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Control samples
Standard solutions

- to verify the calibration
- control sample must be completely independent from calibration solutions
- influence of sample matrix can not be detected
- limited control for precision
- very limited control for trueness

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Control samples
Blank samples

- samples which probably do not contain the analyte
- to detect errors due to
  - changes in reagents
  - new batches of reagents
  - carryover errors
  - drift of apparatus parameters
- blank value at the start and at the end allow identification of some systematic trends

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Control samples
Real samples

- multiple analyses for range and differences charts
- if necessary separate charts for different matrices
- rapid precision control
- no trueness check

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Control samples
Real samples spiked with analyte

- for recovery rate control chart
- detection of matrix influence
- if necessary separate charts for different matrices
- substance for spiking must be representative for the analyte in the sample (binding form!)
- limited check for trueness

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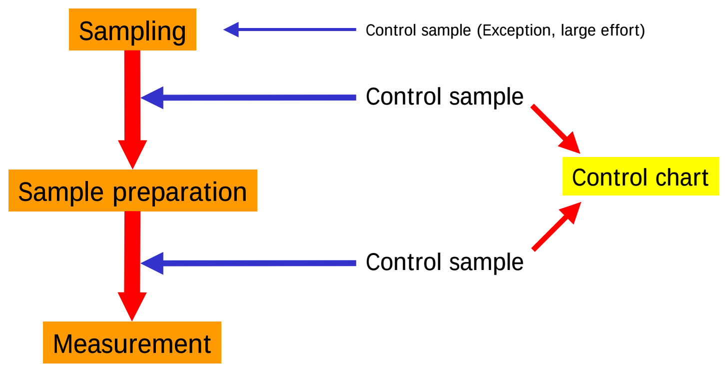
Control samples
Reference materials

- CRM are ideal control samples, but are
  - often too expensive or
  - not available
- In-house reference materials are a good alternative
  - can be checked regularly against a CRM
  - if the value is well known ➔ good possibility for trueness check
- sample material from interlaboratory tests

Control Samples and the Analytical Process



Which One?

- There are a lot of possibilities
- Which one is appropriate?
- How many are necessary?
- There is no general rule!

- The laboratory manager has to decide!
- But there can be assistance

Choice of Control Charts - I

- the more frequent a specific analysis is done the more sense a control chart makes.
- if the analyses are always done with the same sample matrix, the sample preparation should be included. If the sample matrix varies, the control chart can be limited to the measurement only.

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Choice of Control Charts - II

- Some standards or decrees include obligatory measurement of control samples or multiple measurements. Then it is only a minimal additional effort to document these measurements in control charts.
- In some cases the daily calibration gives values (slope and/or intercept) that can be integrated into a control chart with little effort

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Which control chart?

- Sometimes the calibration delivers values for a control chart (e.g. slope and intercept of the calibration line)
- Makes sense only, if the calibration is known to be the weak point

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Which control chart?

- For parameters known to be sensible for blank values, a blank value chart is highly recommended

Which control chart?

The choice of control charts is up to the laboratory manager or the person responsible for the analysis

Assuring the Quality of Test and Calibration Results - ISO/IEC 17025 – 5.9

- *The laboratory shall have quality control procedures for monitoring the validity of tests and calibrations undertaken.*
- *The resulting data shall be recorded in such a way that trends are detectable and, where practicable, statistical techniques shall be applied to the reviewing of the results.*

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Assuring the Quality of Test and Calibration Results - ISO/IEC 17025 – 5.9

- *This monitoring shall be planned and reviewed and may include, but not be limited to, the following:*
  - *regular use of certified reference materials and/or internal quality control using secondary reference materials;*
  - *participation in interlaboratory comparison or proficiency-testing programmes;*
  - *replicate tests or calibrations using the same or different methods;*
  - *retesting or recalibration of retained items;*
  - *correlation of results for different characteristics of an item.*

Advantages of graphical display

- much faster
- more illustrative
- clearer

Rarely used analytical procedures

- Quality control is also needed for analytical procedures that are executed occasionally only or only within short time periods. Under these circumstances quality control causes disproportionate effort compared to routine analysis.
- In the introduction phase of these analytical procedures extensive investigations on the performance and performance characteristics should be made.

...

- Because a statistical control is not possible due to the low frequency, the following control procedures are recommended in this case:
  - recovery check of spikes in the respective matrix (sample),
  - repeated measurements,
  - determination of the blank value of the procedure,
  - check of calibration function using standard material of different origin,
  - analysis of reference materials (certified, if possible)

Special questions
Should the pre-period be renewed from time to time?

- only if the target value changes
- or if it is necessary to adapt the quality targets because of
  - worsening of the analytical precision
  - or because the present limits are not fit for the purpose any more

Special questions
How to convert the control period to a new pre-period?

- If this is required
  - check the mean for a significant change
    $\rightarrow$ t-test
  - check the variance for a significant change
    $\rightarrow$ F-test

Estimation of measurement uncertainty from control charts

- Question: Is it possible to use control charts for the estimation of measurement uncertainty?
- Answer: clearly Yes!
  The measurement uncertainty of a procedure consists of a precision part and a trueness part
  - the precision part can determined e.g. from control charts
  - for the determination of the trueness part, analysis of CRM, analysis of PT samples or recovery experiments are necessary
- Please find more details in NORDTEST TR 537 or ISO/DIS 11352

Special questions
Rounding of measurement results

- Should results be rounded as usual prior to entering in the control chart?
- **not rounded** – rounded values falsify all statistical calculations

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Benefits of using control charts

- a very powerful tool for internal quality control
- changes in the quality of analyses can be detected very rapidly
- good possibility to demonstrate ones quality and proficiency to clients and auditors

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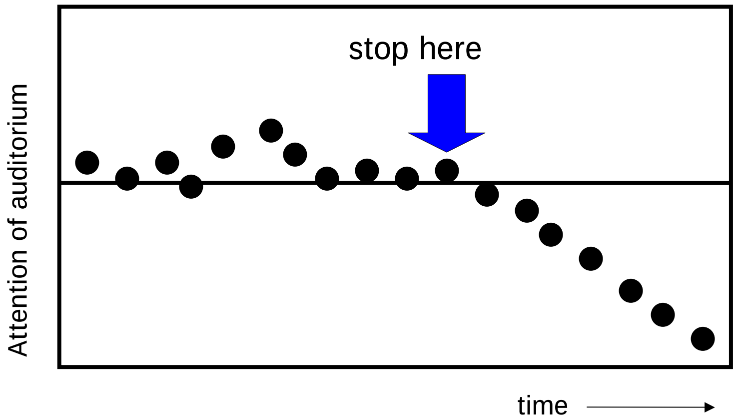
M. Koch: Precision / Control charts – SADCMET PT Evaluation Workshop, Mauritius 2011

Quality control charts for presentations



8^{th} 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

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

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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 October: Poster presentation at the Eurachem Workshop in Proficiency testing in analytical chemistry, microbiology and laboratory medicine in Rome

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Project Activities II

2008	5th PT round; Evaluation workshop (Kampala) with training on management requirements.
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	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
Angola	0	0	1	0	0	0
Botswana	2	4	2	3	3	3
Burundi					1	1
Congo					4	5
Ethiopia	1	0	0	0	0	1
Germany					1	2
Ghana						1
Kenya	5	3	3	7	9	7
Lesotho	1	1	1	1	1	1
Madagascar	2	2	3	3	2	2
Malawi	2	3	1	1	2	2
Mauritius	4	3	5	6	6	5
Mosambique	2	0	0	0	0	0
Namibia	3	3	3	3	3	3
Rwanda					1	1
Seychelles	2	1	1	1	1	1
South Africa	0	1	1	1	1	1
Swaziland	0	1	2	3	0	0
Tanzania	6	12	11	12	13	10
Uganda	5	5	5	5	4	5
Zambia	2	3	1	3	3	1
Zimbabwe	2	5	5	5	4	4
Total	**39**	**47**	**45**	**54**	**59**	**56**

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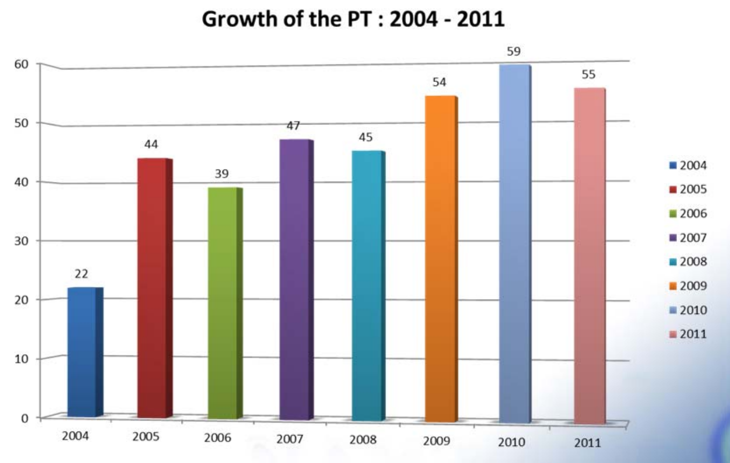
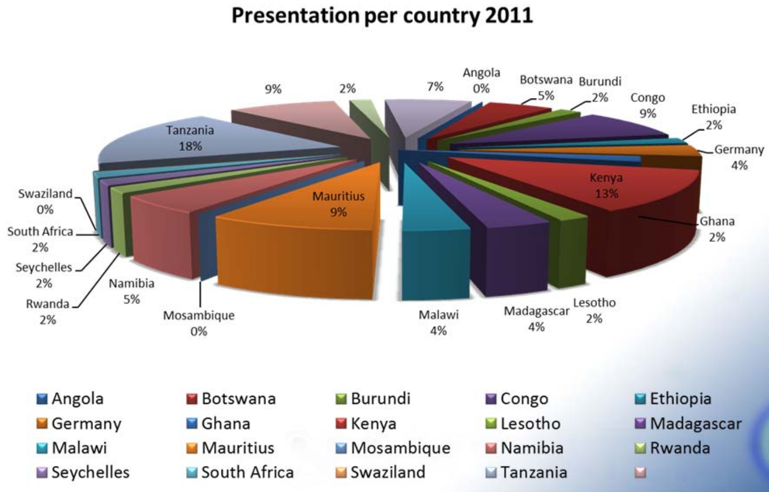
Growth of PT SADCMET Scheme



% Representation / Country



Changes and Progress of parameters

Parameter	Concentration in mg/l
PT round 1-8	
Calcium	8.4 – 60.5
Magnesium	7.5 – 55.3
Sodium	10.1 – 80.5
Potassium	5 – 22.4
Iron	0.1 – 4.61
Manganese	0.05 – 5.1
Aluminum	0.05 – 4.41
Sulphate	10.5 – 70.5
Chloride	12.6 – 73.4
Fluoride	0.21 – 2.54
Nitrate	9.1 - 88

Parameter	Concentration in mg/l
Additionally in PT round 2 - 8	
Lead	0.1 – 3.33
Copper	0.5 – 4.05
Zinc	0.6 – 5.89
Chromium	0.05 – 2.9
Nickel	0.19 – 3.55
Phosphate	3.2 – 30
Additionally in PT round 3 - 8	
Arsenic	0.05 – 0.75
Cadmium	0.05 – 0.9
Additionally in PT round 5 - 8	
Cobalt	0.25 – 2.68
Additionally in PT round 8	
TDS	120 – 400

3 different levels for each parameter

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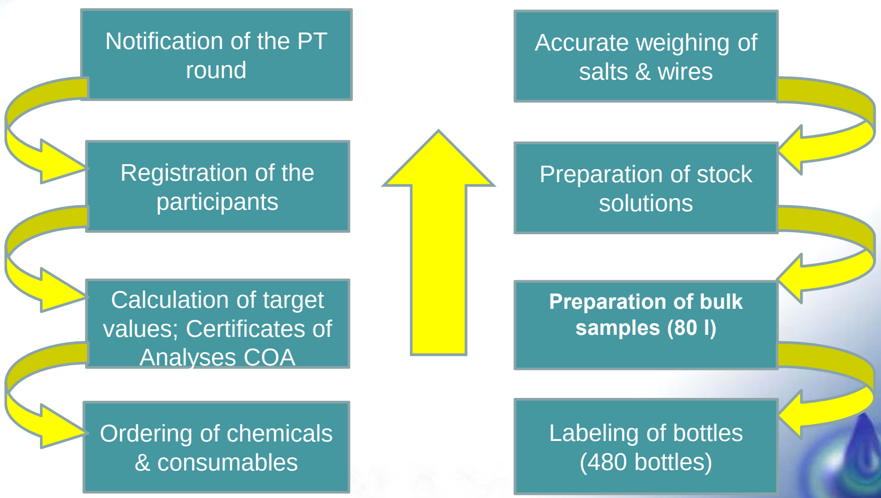
Steps of a PT round



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Steps of a PT round

- Dispensing of samples into the bottles
- Storage in fridge (4 ° C)
- Prepare documentation
- Labeling of the boxes
- Evaluation and assessment
- Testing period (6 weeks)
- Quotes for the courier Transportation
- Packaging of samples

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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 l, balance 3
Fill to target weight l, balance 3

↓

Stir for combined solution for 20 minutes

↓

Fill samples bottles

↓

Determine the density of samples

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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 water experiment.
- The densities and uncertainty of the measurements were calculated. .

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Preparation of bulk samples

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

H_2O

1 2 3

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

4 5 6

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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

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Packaging of the samples

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Packaging of the samples


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Labeling & sorting

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Sample pick-up and dispatch

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Transport of parcels DHL , 24 June 2011

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Evaluation and Assessment

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

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Evaluation and Assessment (cont.)

- Where the calculated value is higher, the fitness-for-purpose value is used.
- 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 and
- Assistance is provided for laboratories that need corrective actions.

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Performance scoring

- Z-scores are a common practise in the assessment of laboratory results

  This score 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 falling between - 2 and 2.
- The sign (i.e., + or -) of the score indicates a negative or positive error respectively.
  - **|z-score| ≤ 2.0 - satisfactory**
  - **2.0 < |z-score| < 3.0 - questionable**
  - **|z-score| ≥ 3.0 - unsatisfactory**

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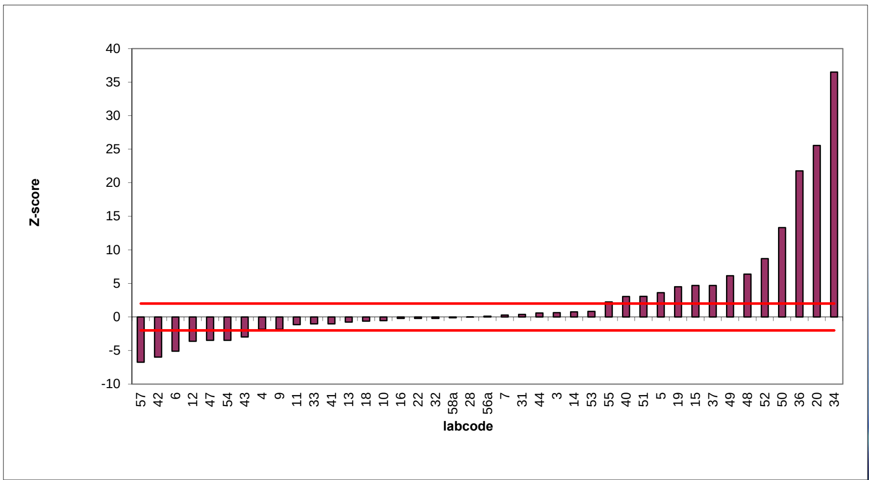
Z-score diagram



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Limits for standard deviation 2011

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

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Ranges for parameters

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

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Measurement uncertainty of reference values

- All sources of uncertainty in the analytical measurements were identified and listed by using the 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

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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 expanded 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.

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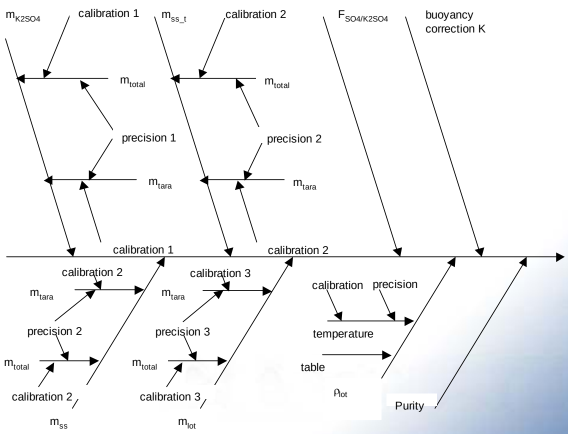
Identification of uncertainties using fishbone diagram

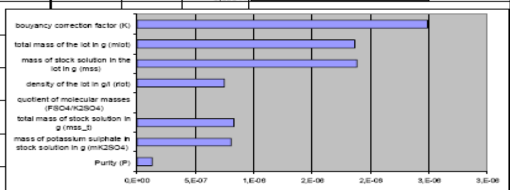
$$c_{lot} = \frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot m_{ss} \cdot \rho_{lot}}{m_{ss\_t} \cdot m_{lot} \cdot K}$$



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)	sensitivity 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				0,000183291	$\frac{F_{SO_4/K_2SO_4} \cdot P \cdot m_{ss} \cdot \rho_{lot}}{m_{ss\_t} \cdot m_{lot} \cdot K}$	0,004412908
total mass of stock solution in g (m_{ss_t})	501,44				0,018412909	$-\frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot m_{ss} \cdot \rho_{lot}}{m_{ss\_t}^2 \cdot m_{lot} \cdot K}$	-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				0,032977358	$\frac{m_{K_2SO_4} \cdot F_{SO_4/K_2SO_4} \cdot P \cdot m_{ss}}{m_{ss\_t} \cdot m_{lot} \cdot K}$	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	**0,003891994**						
rel Unsicherheit	**0,02%**						
erw. Unsicherheit	**0,007783987**						
erw. rel. Unsicherheit	**0,03%**						



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

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Documentation

Certificates are documented:

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

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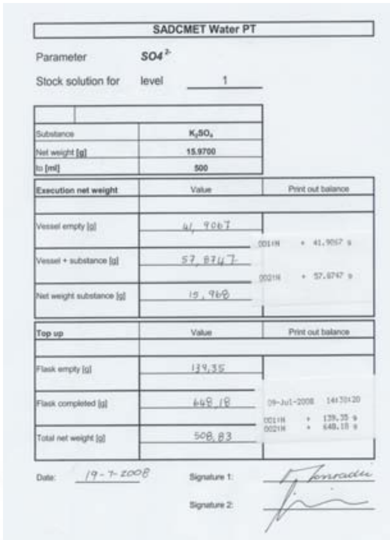
Documentation of weighing

- 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 SO_4^{2-}

Stock solution for level 1

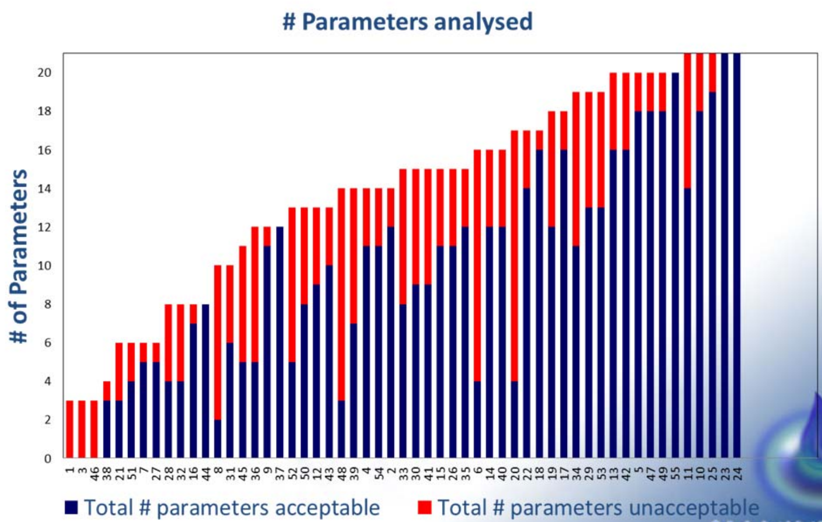
Substance	K_2SO_4
Net weight [g]	15.9700
to [ml]	500

Execution net weight	Value	Print out balance
Vessel empty [g]	41,9067	001IN + 41.9067 g
Vessel + substance [g]	57,8747	002IN + 57.8747 g
Net weight substance [g]	15,968	

Top up	Value	Print out balance
Flask empty [g]	139,35	09-Jul-2008 14:30:20
Flask completed [g]	648,18	001IN + 139.35 g
Total net weight [g]	508,83	002IN + 648.18 g

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

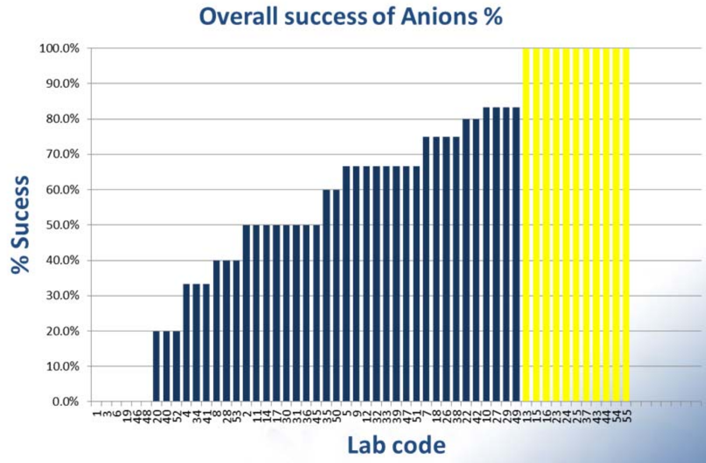
Number of parameters analysed



% Success: Anions

11

Number of acceptable values / Total number of anions done



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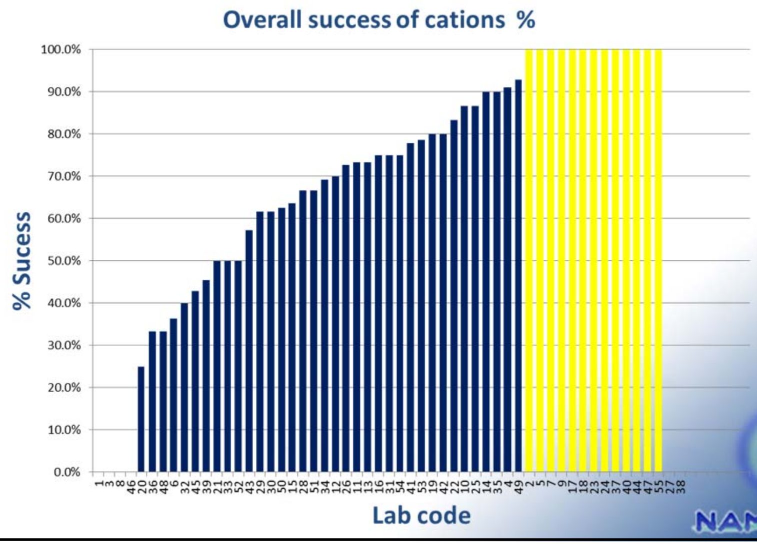
% Success: Cations

13

Number of acceptable values / Total number of anions done



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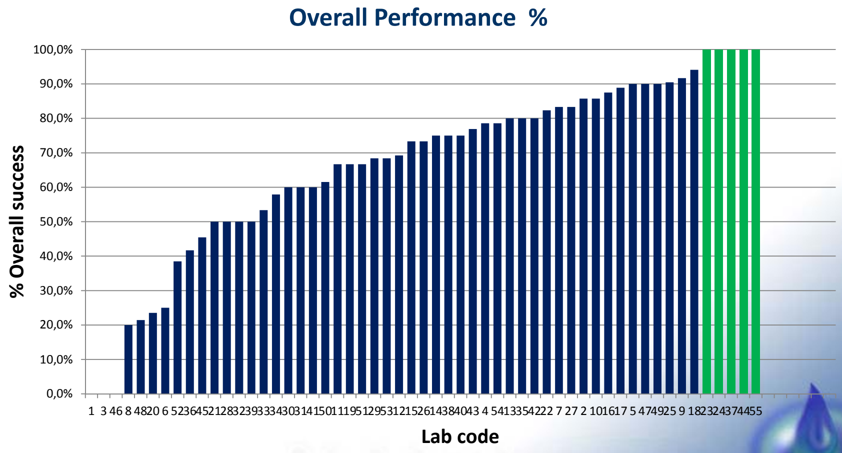
4

Overall Performance

% Success x % Done



Problems

- Angola: Paid but did not submit results
- Kenya: Crop Nutrition parcel was delivered to another laboratory
- Files over 5MB is blocked by NamWater IS and cannot be received Organising a PT round between normal laboratory activities and obligations remains a challenge.
- Late registration from participants still a problem.

Problems

- Still some registration forms not received – laboratory information and contacts are not available
- Sometime the written registration forms are not all clear
- Return date for the results : 19th of August 2011 with an delay from two laboratories due to problems with equipment – caused a delay with evaluation report

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Reporting Problems

- Again high standard deviations > higher than limits
- Some laboratories do not see the ranges supplied
- High number of outliers - gravimetrical methods
- Non –standard methods are still used
- Significant figure problems e.g. 0.69585
- Reporting of results in wrong units (N and not NO_3 and as P and not PO_4
- Corrective actions still not implemented

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Challenges for 2012

- Maximum participation in SADCWATER Lab PT in terms of parameters
- Recommended methods must be finalised and implemented
- Investigate problems or determine the root cause
- Corrective actions are an on-going process –laboratories should keep on applying it to get the desired results
- Choose appropriate methodology

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Challenges for 2012

- 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.

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Acknowledgments

- **PTB assistance**
  - Kathrin Wunderlich
  - Rebecca Bahrmann
- **SADCMET**
  - Donald Masuku
  - Margaret Ngobeni
- **University of Stuttgart**
  - Dr Michael Koch
- **NamWater personnel**
- **Expert labs**
- **Local coordinators**
- **Participants**

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Thank you

?

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Evaluation of the 8th SADCMET Water PT

Evaluation Workshop
Mauritius 2011

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Evaluation and Assessment

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

Limits for standard deviation

parameter	std limit	parameter	std limit
sulphate	10 %	manganese	20 % / 12 %
chloride	10 %	aluminium	20 % (30 %)
fluoride	10 % (12%)	lead	20 % (40 % / 25 %)
nitrate	10 % (15 %)	copper	20 %
phosphate	10 %	zinc	20 %
calcium	10 %	chromium	20 % (25 %)
magnesium	10 %	nickel	20 % (25 %)
sodium	10 %	cadmium	20 %
potassium	10 %	arsenic	20 %
iron	20 % / 12 %	cobalt	20 %
		TDS	10 %

Elimination of gross outliers

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

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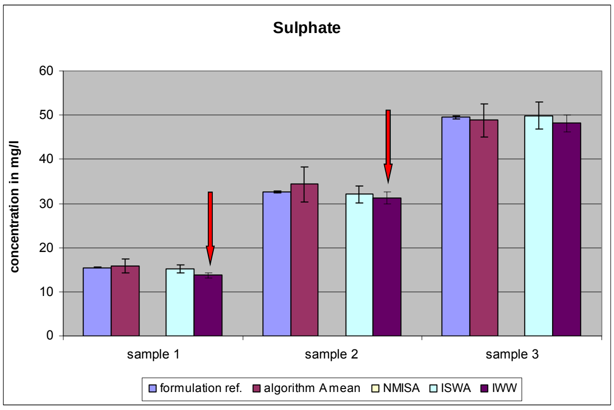
Sulphate
Reference value and measurements



IWW:
slightly underestimated uncertainty for sample 1 and 2

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

iswa AQS Baden-Württemberg

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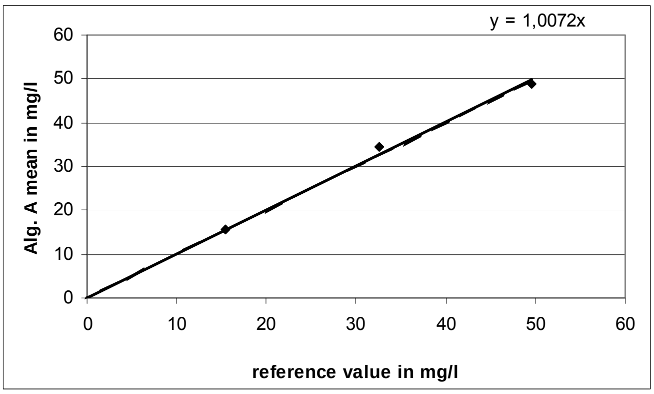
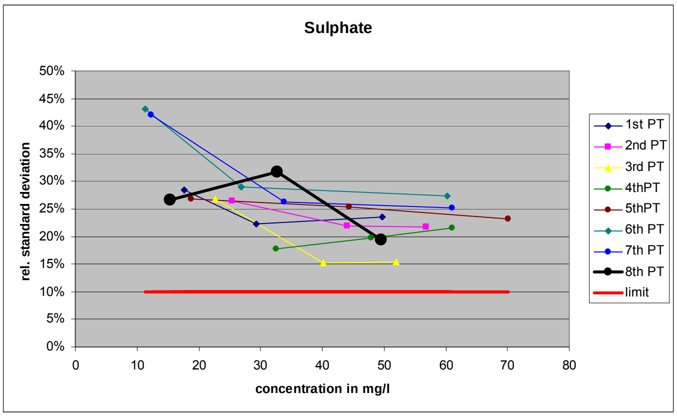
Sulphate
mean vs. ref.-value



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

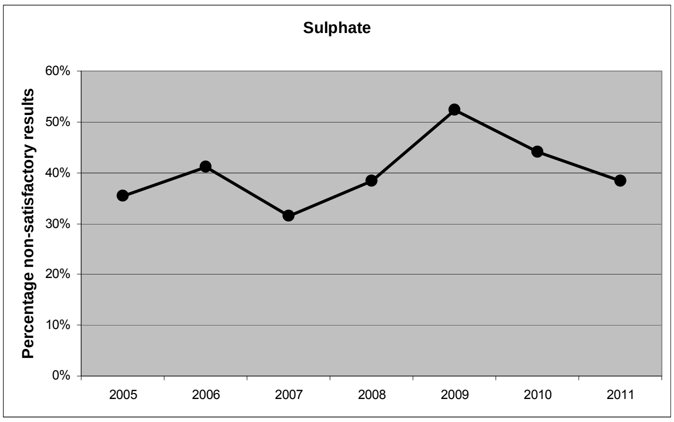
iswa AQS Baden-Württemberg

Sulphate
calculated standard deviation and limit



no difference – still very high

Sulphate
Percentage non-satisfactory results

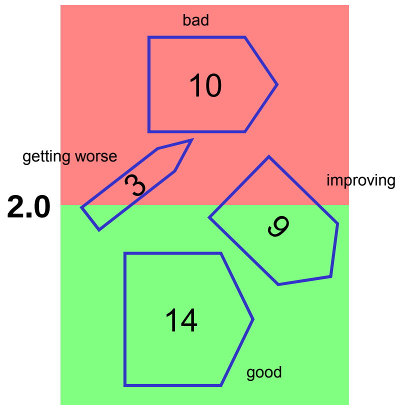


a bit better, but still very high

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



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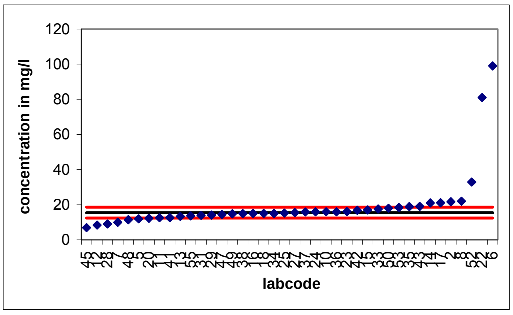
Sulphate 1



values:	**41**
removed:	**1**
mean:	**15,80**
ref.-value:	**15,46**
recovery:	**102,2%**
std:	**4,129**
rstd:	**26,7%**
std limit:	**10%**
upper limit:	**18,55**
lower limit:	**12,37**
too high:	**9**
too low:	**8**
outside limits:	**17**

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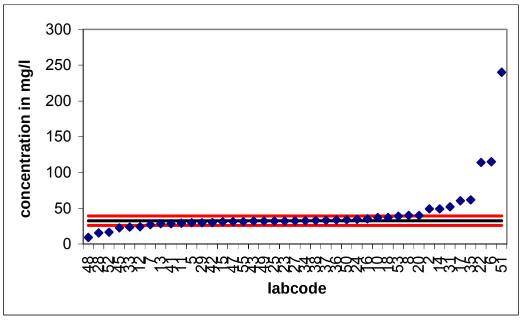
Sulphate 2



values:	**42**
removed:	**1**
mean:	**34,37**
ref.-value:	**32,65**
recovery:	**105,3%**
std:	**10,370**
rstd:	**31,8%**
std limit:	**10%**
upper limit:	**39,18**
lower limit:	**26,12**
too high:	**10**
too low:	**7**
outside limits:	**17**

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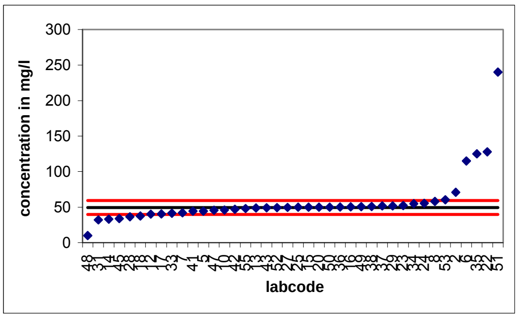
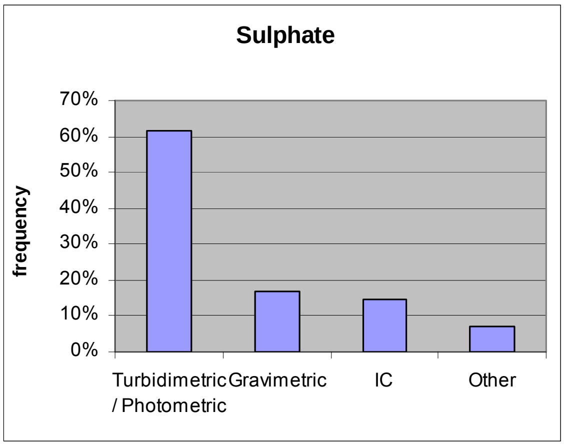
Sulphate 3



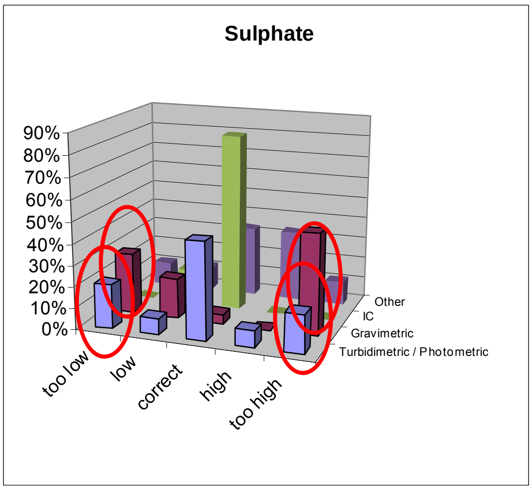
values:	**42**
removed:	**2**
mean:	**48,80**
ref.-value:	**49,49**
recovery:	**98,6%**
std:	**9,597**
rstd:	**19,4%**
std limit:	**10%**
upper limit:	**59,39**
lower limit:	**39,59**
too high:	**6**
too low:	**8**
outside limits:	**14**

Used methods



compared to 2010 increased use of turbidimetry instead of gravimetry

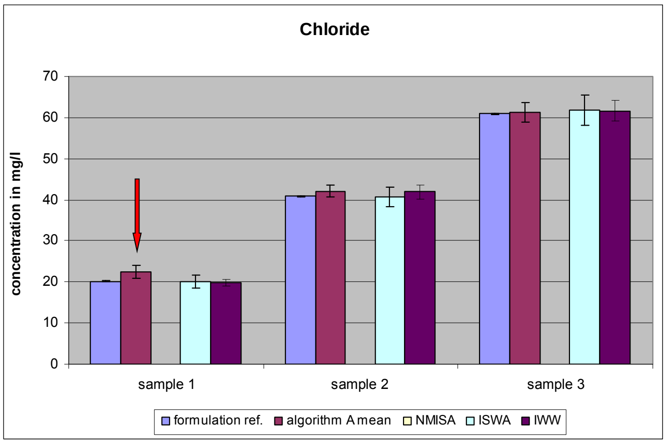
Comparison of methods



Summary Sulphate

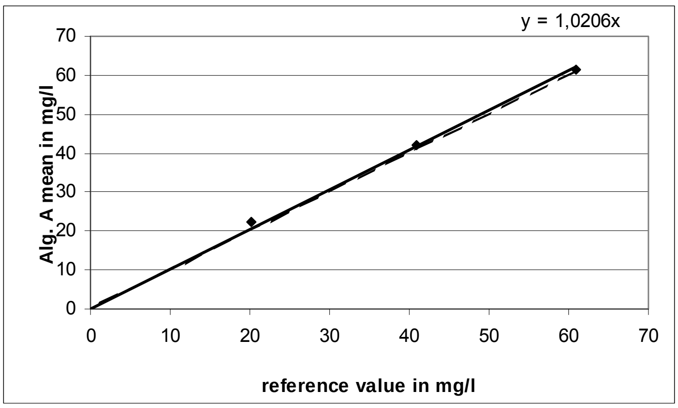
- Quite good agreement between means and ref.-values
- Standard deviation still too high
- Too many labs with unsatisfactory results, but some are quite good
- High portion of outliers for the turbidimetric and the gravimetrical method – mistakes in executing the methods
- exactly as in 2010

Choride
Reference value and measurements



AQS Baden-Württemberg iswa

Chloride
mean vs. ref.-value



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

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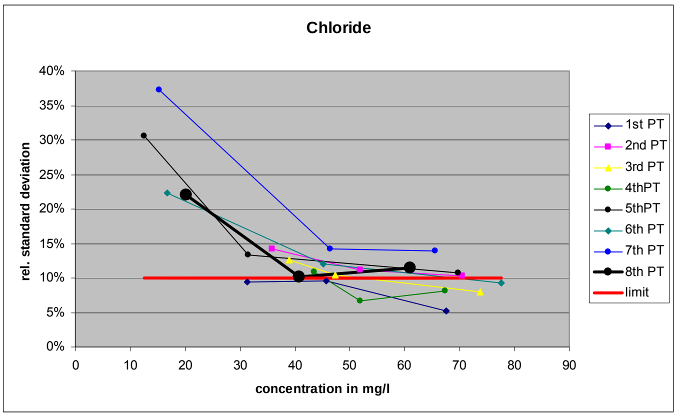
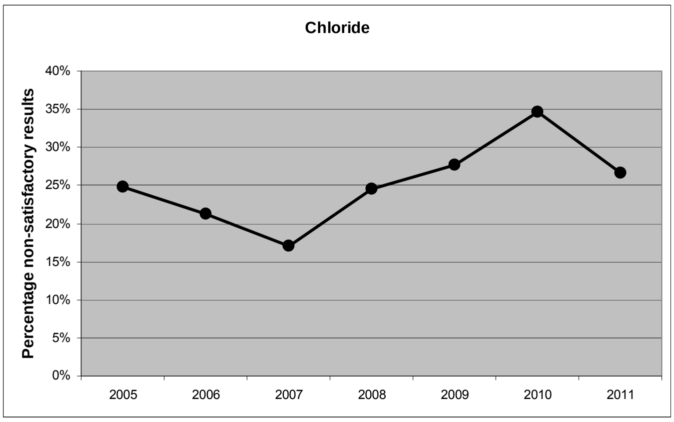
Chloride
calculated standard deviation and limit



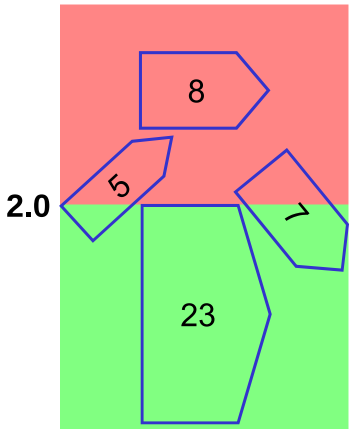
average result

Chloride
Percentage non-satisfactory results

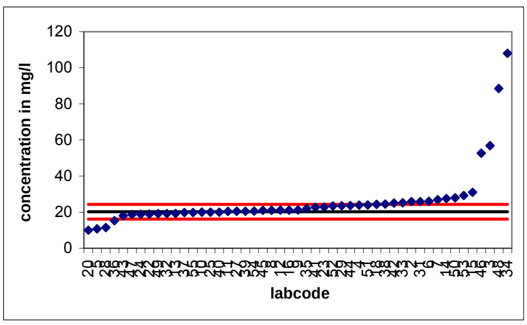


A bit lower than last year

Chloride
Individual performance development

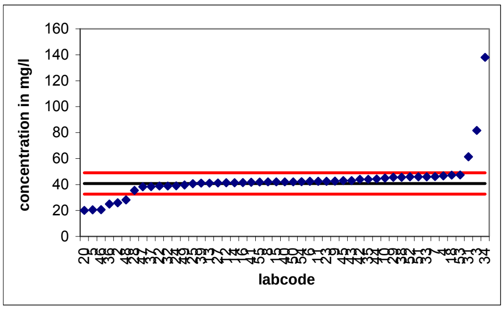


Chloride 1



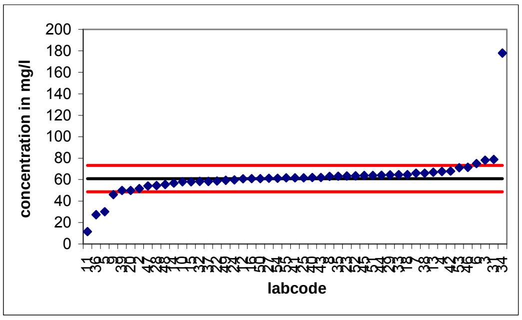
values:	50
removed:	1
mean:	22,49
ref.-value:	20,20
recovery:	111,4%
std:	4,448
rstd:	22,0%
std limit:	10%
upper limit:	24,24
lower limit:	16,16
too high:	16
too low:	5
outside limits:	21

Chloride 2



values:	50
removed:	1
mean:	42,04
ref.-value:	40,83
recovery:	103,0%
std:	4,170
rstd:	10,2%
std limit:	10%
upper limit:	49,00
lower limit:	32,67
too high:	3
too low:	7
outside limits:	10

Chloride 3



values:	50
removed:	1
mean:	61,35
ref.-value:	60,96
recovery:	100,6%
std:	6,972
rstd:	11,4%
std limit:	10%
upper limit:	73,15
lower limit:	48,77
too high:	4
too low:	5
outside limits:	9

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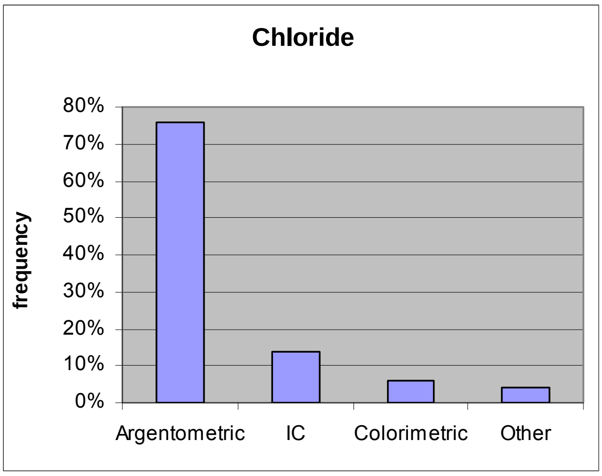
Used methods



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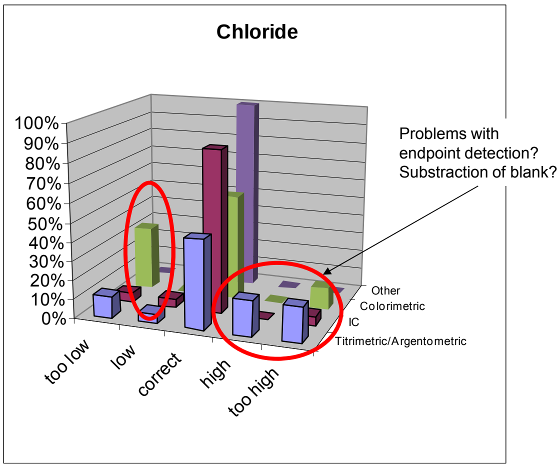
Comparison of methods



Exactly as in 2009 and in 2010

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Summary Chloride

- Average standard deviation – no real improvement
- Many labs have good results, but some are continuously deviating
- Problems with the endpoint detection in argentometric determination
- Obviously some problems with the spectrometric method

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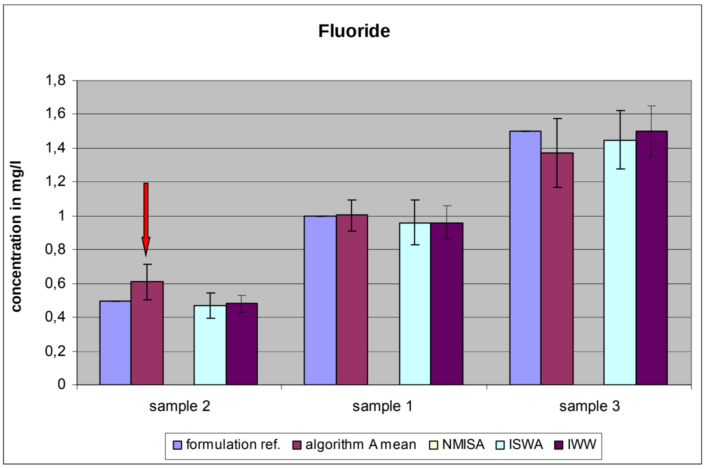
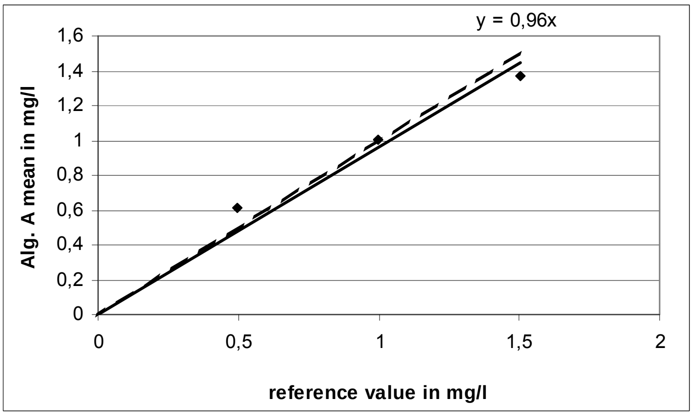
Fluoride
Reference value and measurements



AQS Baden-Württemberg iswa

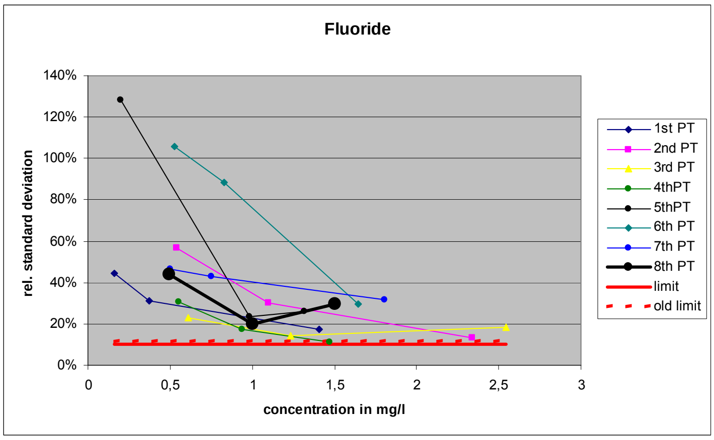
Fluoride
mean vs. ref.-value



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

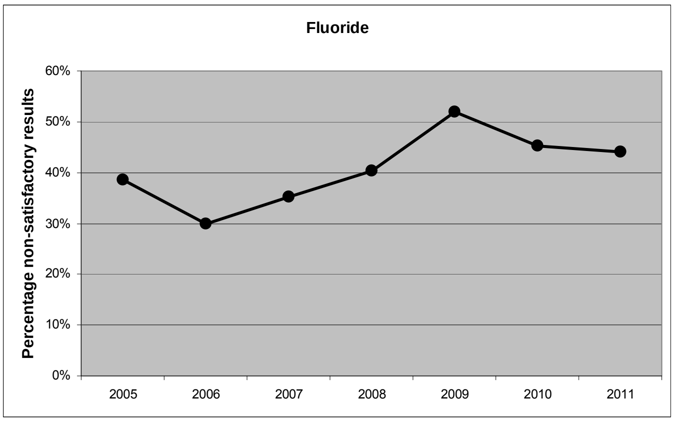
As in 2010: Recovery low for the highest concentration, too high for the low concentrations

Fluoride
calculated standard deviation and limit



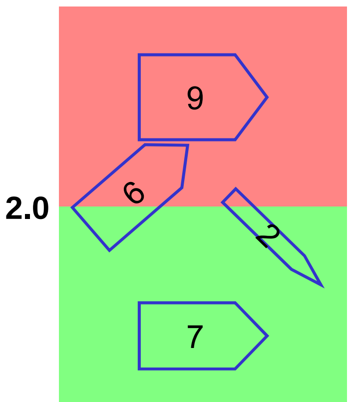
Average standard deviations

Fluoride
Percentage non-satisfactory results



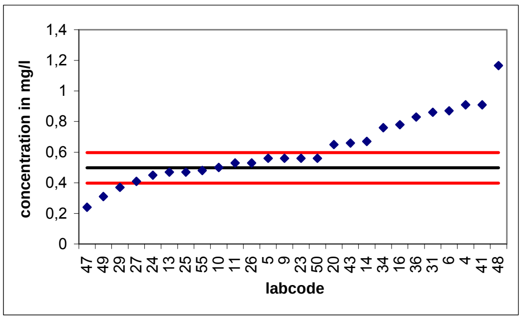
Still very high

Fluoride
Individual performance development



More labs getting worse than improving

Fluoride 1



values:	**28**
removed:	**2**
mean:	**0,61**
ref.-value:	**0,50**
recovery:	**122,8%**
std:	**0,220**
rstd:	**44,2%**
std limit:	**10%**
upper limit:	**0,60**
lower limit:	**0,40**
too high:	**13**
too low:	**3**
outside limits:	**16**

Concentration obviously too low for many labs

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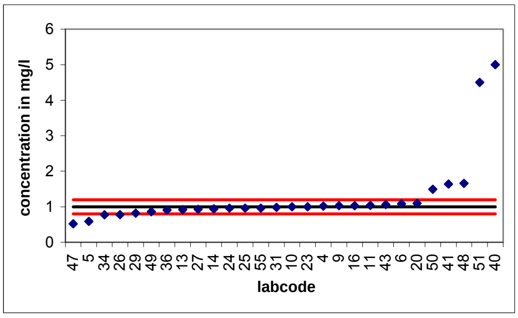
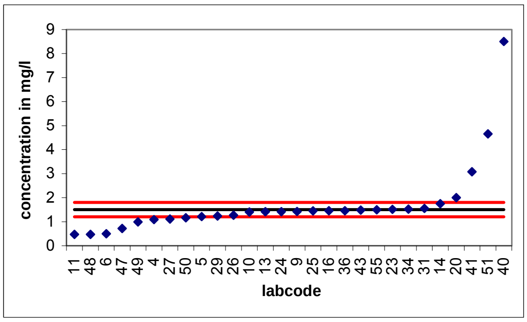
Fluoride 2



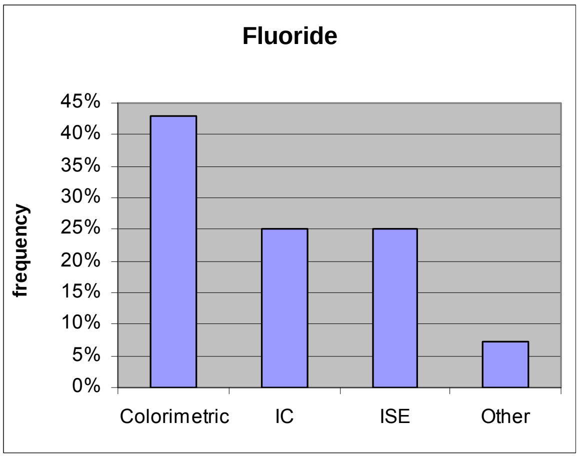
values:	**28**
removed:	**0**
mean:	**1,00**
ref.-value:	**1,00**
recovery:	**100,2%**
std:	**0,200**
rstd:	**20,0%**
std limit:	**10%**
upper limit:	**1,20**
lower limit:	**0,80**
too high:	**5**
too low:	**4**
outside limits:	**9**

Fluoride 3



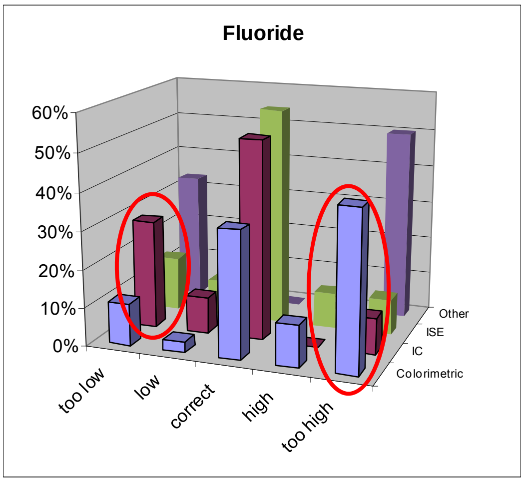
values:	28
removed:	0
mean:	1,37
ref.-value:	1,50
recovery:	91,2%
std:	0,444
rstd:	29,5%
std limit:	10%
upper limit:	1,80
lower limit:	1,20
too high:	4
too low:	8
outside limits:	12

Used methods



More IC, less ISE

Comparison of methods



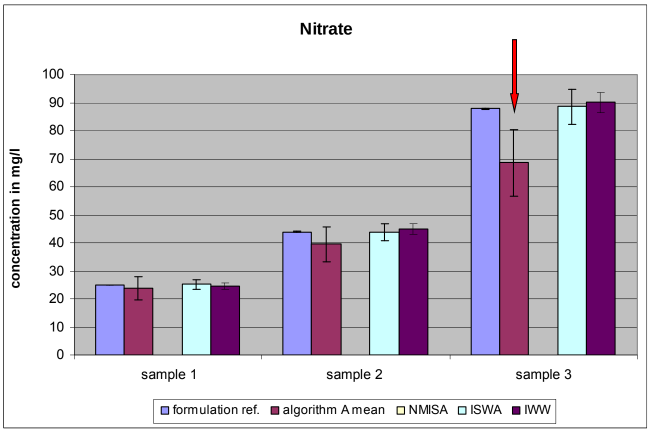
Colorimetric method: many values too high, especially for the lowest level

Obviously some problems with IC

Summary Fluoride

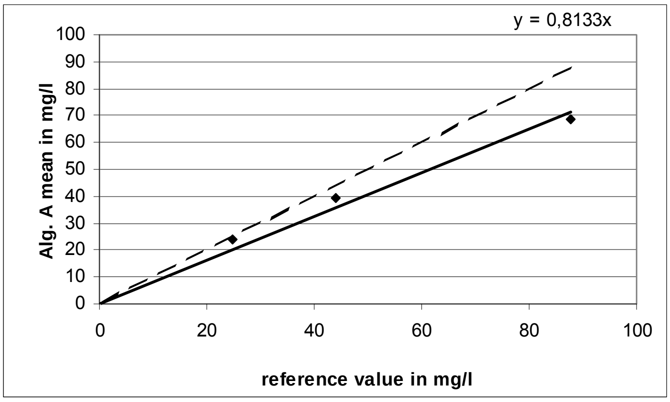
- Standard deviations still very high
- Again about 45% of the values are not satisfactory
- Colorimetric values not reliable (as in the last years!)
- Obviously some problems with IC

Nitrate
Reference value and measurements



Means lower than reference values

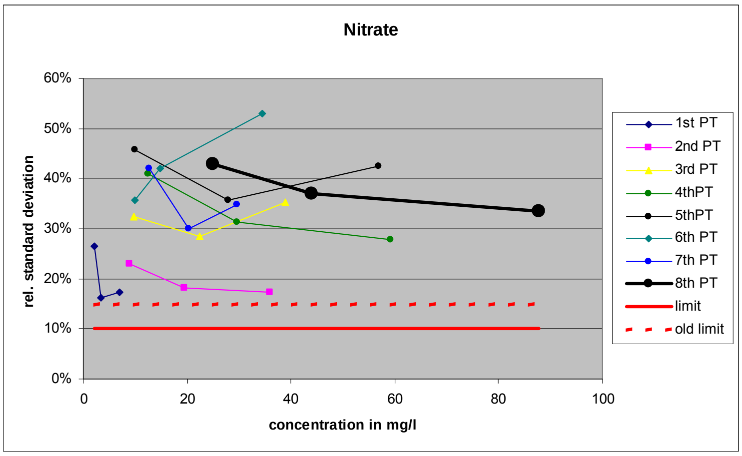
Nitrate
mean vs. ref.-value



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

Average recovery very low, especially because of the highest level

Nitrate
calculated standard deviation and limit



Standard deviations <u>very</u> high

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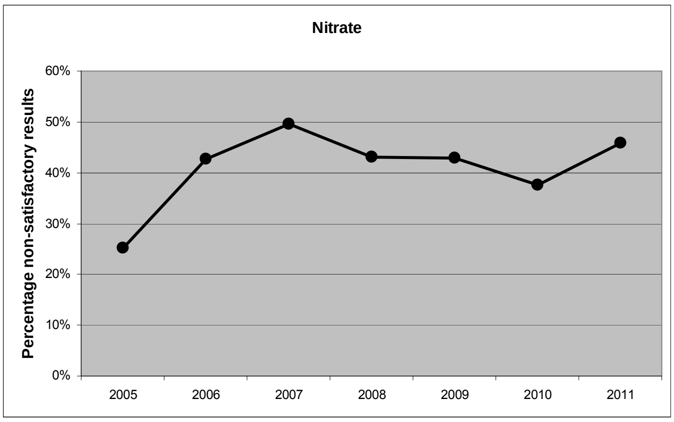
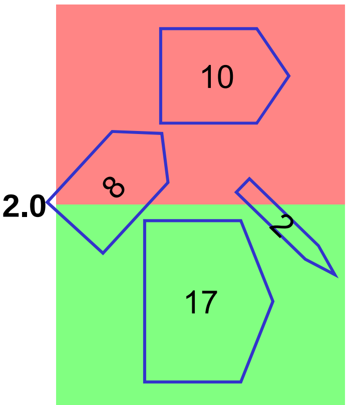
Nitrate
Percentage non-satisfactory results



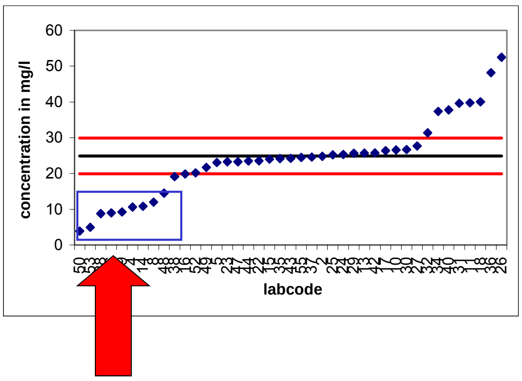
increasing again

Nitrate
Individual performance development



More labs getting worse than improving

Nitrate 1



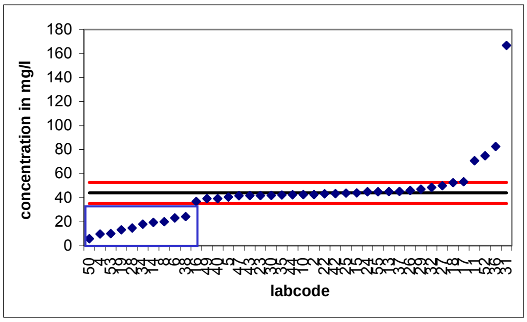
values:	**44**
removed:	**3**
mean:	**23,77**
ref.-value:	**24,91**
recovery:	**95,4%**
std:	**10,710**
rstd:	**43,0%**
std limit:	**10%**
upper limit:	**29,90**
lower limit:	**19,93**
too high:	**8**
too low:	**14**
outside limits:	**22**

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

last year 6 labs – this year again at least 6 labs!

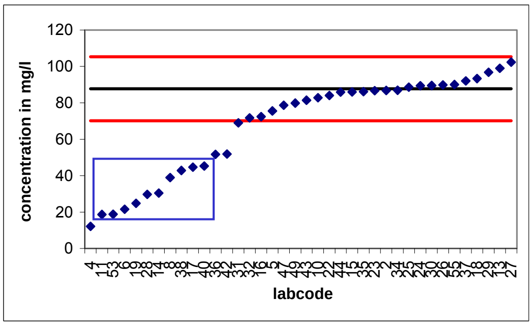
at least one lab is the same

Nitrate 2



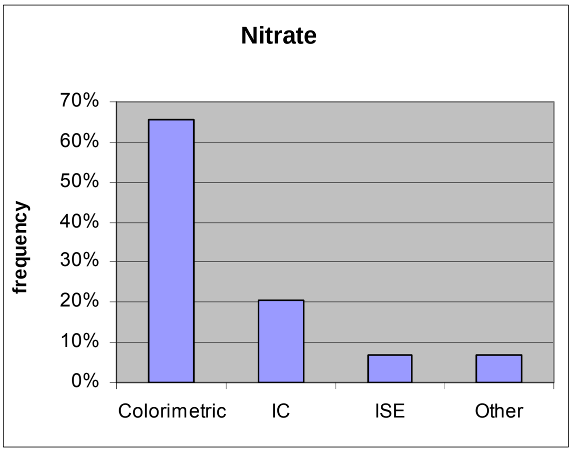
values:	**44**
removed:	**4**
mean:	**39,51**
ref.-value:	**43,93**
recovery:	**89,9%**
std:	**16,232**
rstd:	**36,9%**
std limit:	**10%**
upper limit:	**52,72**
lower limit:	**35,15**
too high:	**5**
too low:	**14**
outside limits:	**19**

Nitrate 3



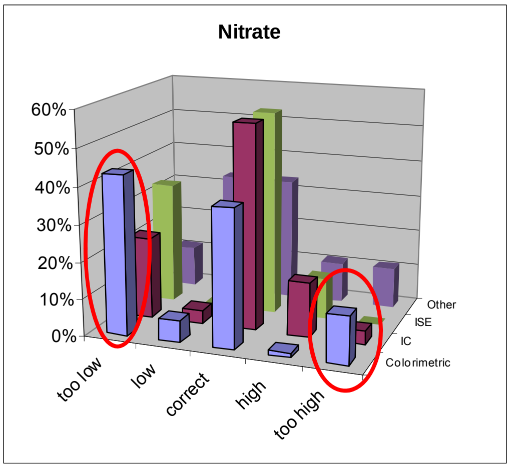
values:	**43**
removed:	**5**
mean:	**68,49**
ref.-value:	**87,77**
recovery:	**78,0%**
std:	**29,453**
rstd:	**33,6%**
std limit:	**10%**
upper limit:	**105,32**
lower limit:	**70,21**
too high:	**0**
too low:	**19**
outside limits:	**19**

Used methods



Still a lot of confusion which photometric method to use
Many different methods hidden behind “colorimetric”

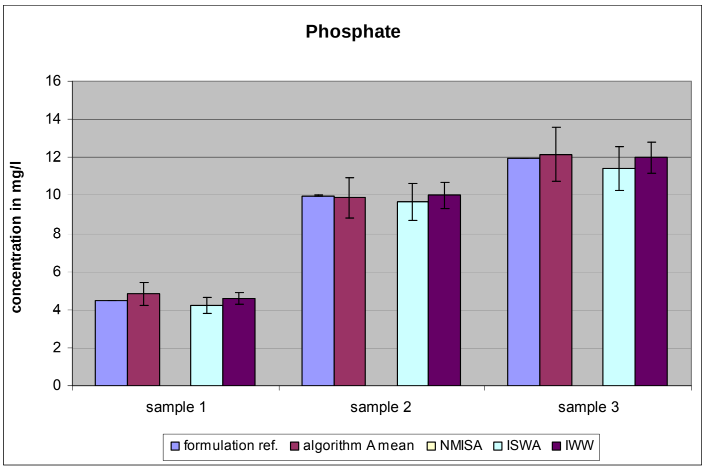
Comparison of methods



Summary Nitrate

- Some values obviously again reported in wrong units (most probably 6 labs, at least 1 of them identical with 2010, 2009 and 2008)
- High number of outliers, almost half of the values are wrong
- Standard deviation still too high
- Harmonization of methods needed!!

Phosphate
Reference value and measurements



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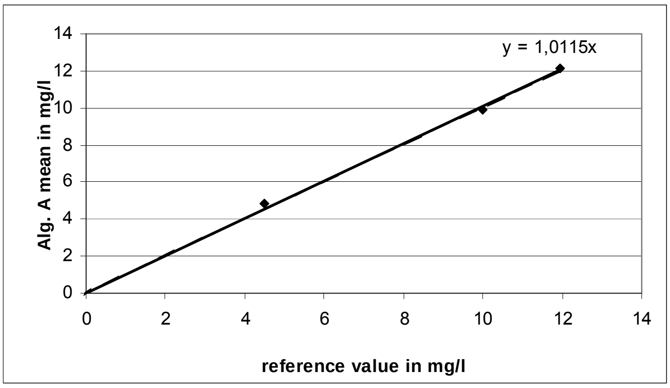
Phosphate
mean vs. ref.-value



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

Average recovery much better than in previous years

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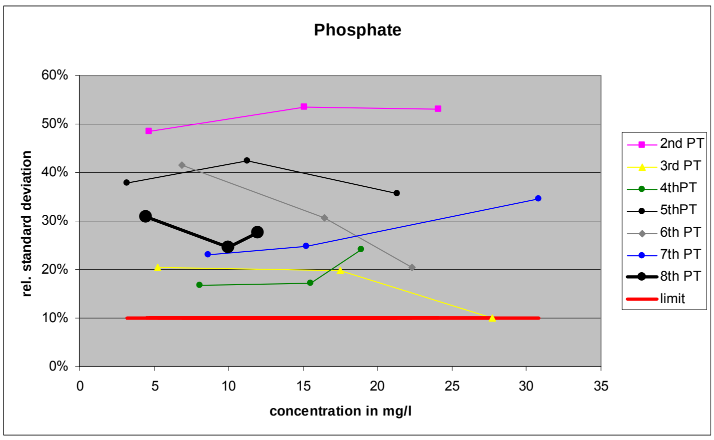
Phosphate
calculated standard deviation and limit



Average standard deviation – no improvements

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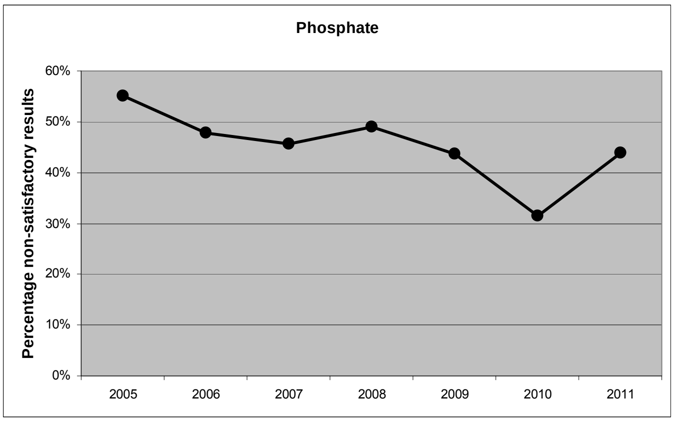
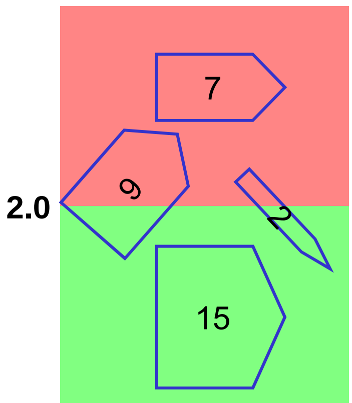
Phosphate
Percentage non-satisfactory results



Increasing again

Phosphate
Individual performance development



More labs getting worse than improving

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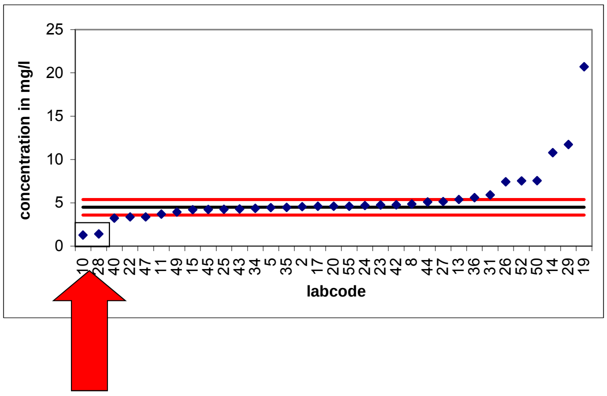
Phosphate 1



values:	**35**
removed:	**2**
mean:	**4,83**
ref.-value:	**4,49**
recovery:	**107,6%**
std:	**1,383**
rstd:	**30,8%**
std limit:	**10%**
upper limit:	**5,39**
lower limit:	**3,59**
too high:	**10**
too low:	**6**
outside limits:	**16**

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

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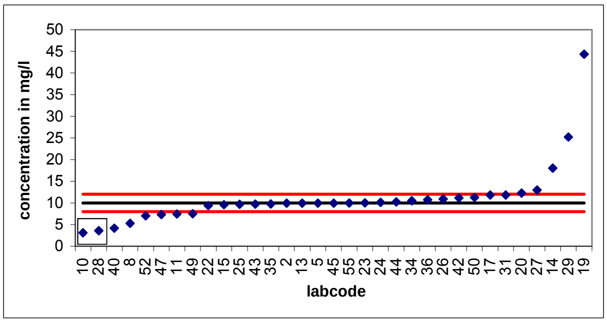
Phosphate 2



values:	**36**
removed:	**3**
mean:	**9,89**
ref.-value:	**9,99**
recovery:	**99,1%**
std:	**2,461**
rstd:	**24,6%**
std limit:	**10%**
upper limit:	**11,98**
lower limit:	**7,99**
too high:	**6**
too low:	**10**
outside limits:	**16**

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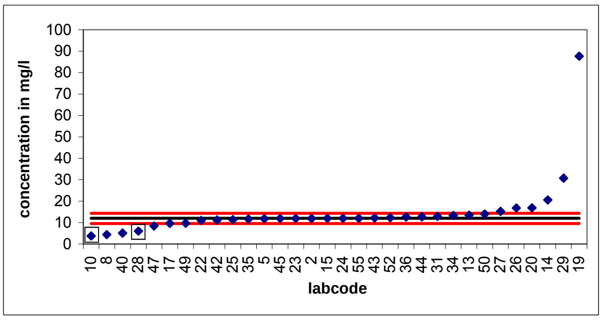
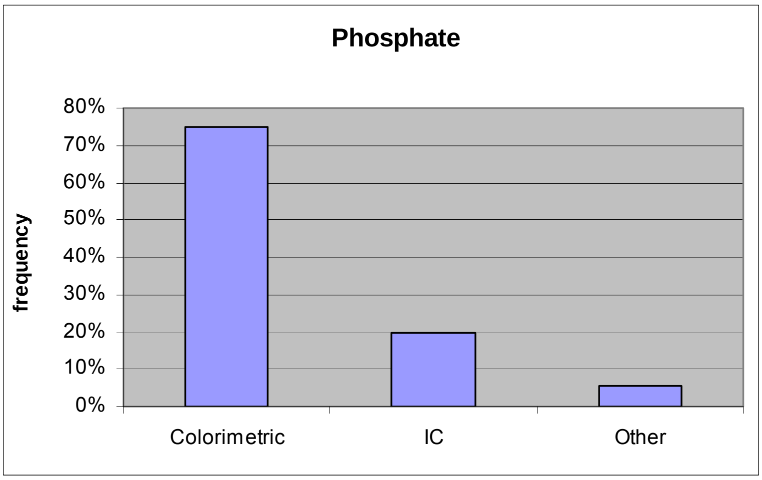
Phosphate 3



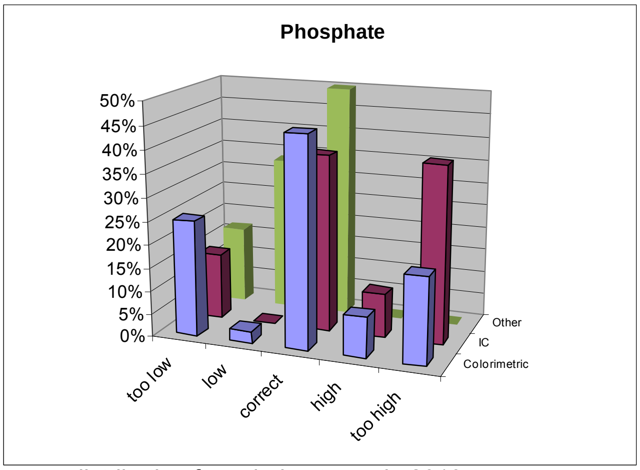
values:	**36**
removed:	**4**
mean:	**12,16**
ref.-value:	**11,96**
recovery:	**101,7%**
std:	**3,300**
rstd:	**27,6%**
std limit:	**10%**
upper limit:	**14,35**
lower limit:	**9,57**
too high:	**7**
too low:	**8**
outside limits:	**15**

Used methods



some more IC results

Comparison of methods



same distribution for colorimetry as in 2010
bad results for IC are new

Summary Phosphate

- Results from 2 labs in wrong units and some very high results
- Average standard deviation
- 44 % of the values are outside the limits

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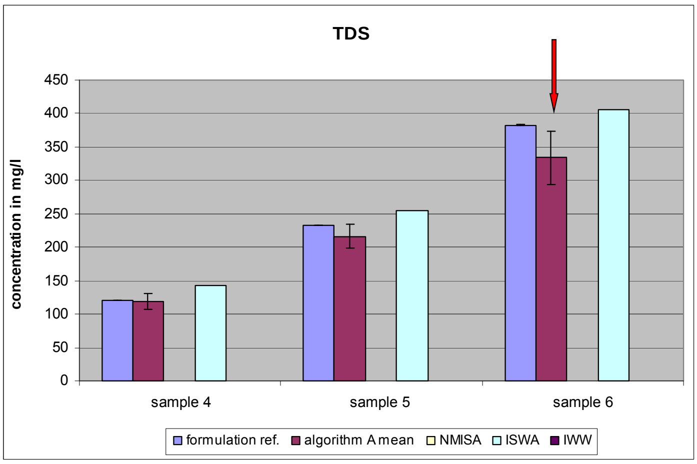
TDS
Reference value and measurements



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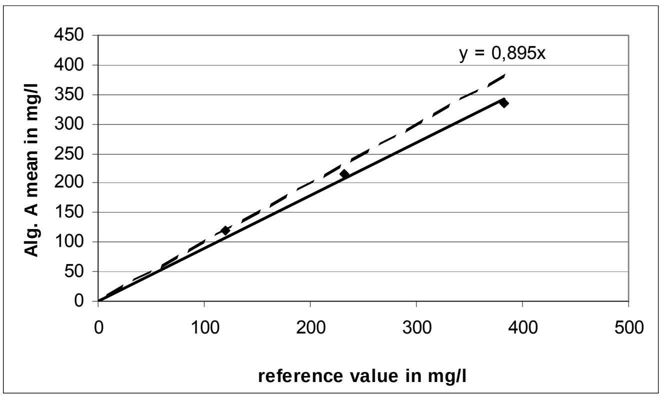
TDS
mean vs. ref.-value



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

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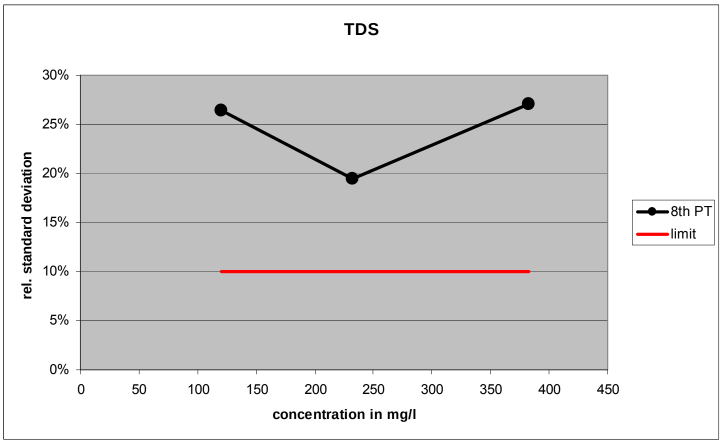
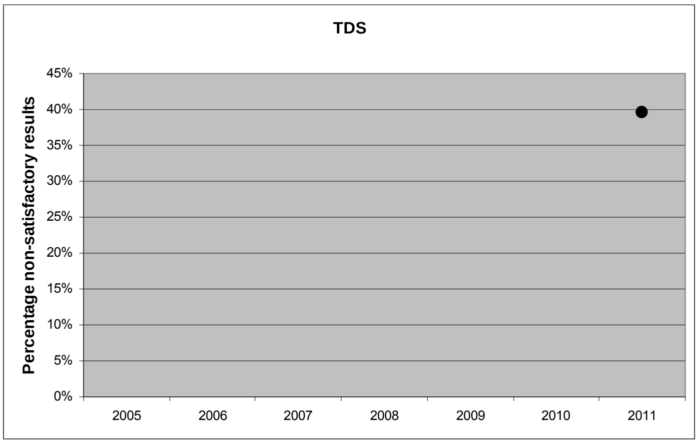
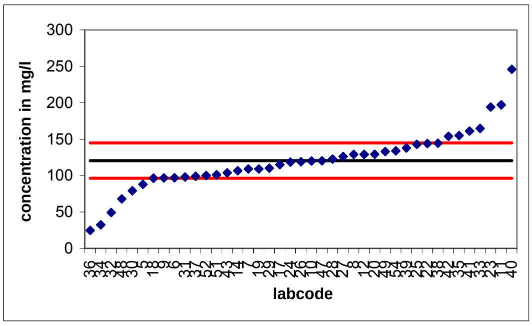
TDS
calculated standard deviation and limit



TDS
Percentage non-satisfactory results

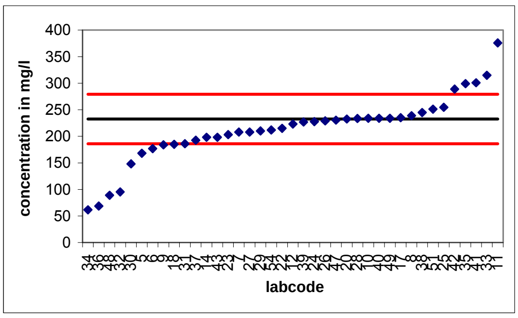


TDS 1



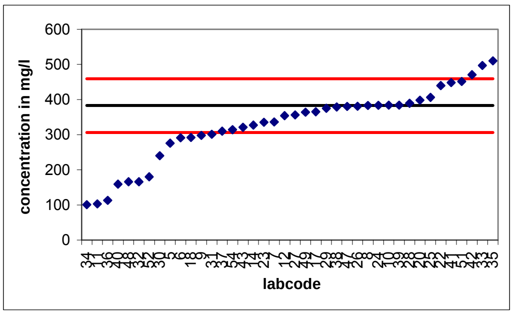
values:	42
removed:	1
mean:	118,97
ref.-value:	120,64
recovery:	98,6%
std:	31,872
rstd:	26,4%
std limit:	10%
upper limit:	144,76
lower limit:	96,51
too high:	7
too low:	8
outside limits:	15

TDS 2



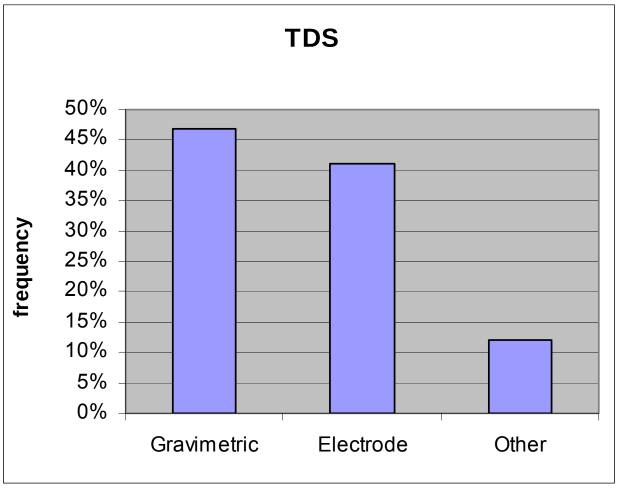
values:	41
removed:	2
mean:	216,39
ref.-value:	232,55
recovery:	93,1%
std:	45,346
rstd:	19,5%
std limit:	10%
upper limit:	279,06
lower limit:	186,04
too high:	5
too low:	12
outside limits:	17

TDS 3

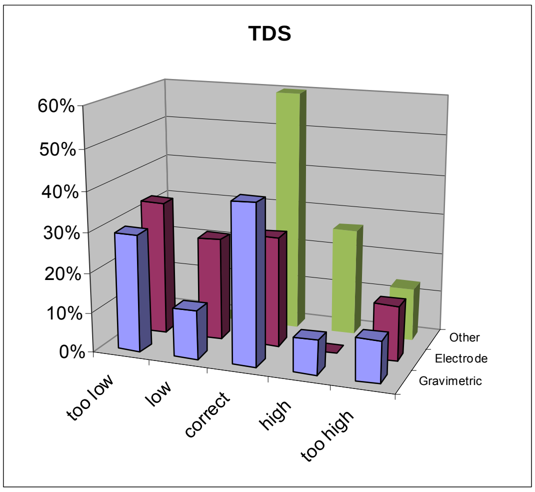


values:	**41**
removed:	**1**
mean:	**334,10**
ref.-value:	**382,81**
recovery:	**87,3%**
std:	**103,754**
rstd:	**27,1%**
std limit:	**10%**
upper limit:	**459,37**
lower limit:	**306,25**
too high:	**3**
too low:	**14**
outside limits:	**17**

Used methods



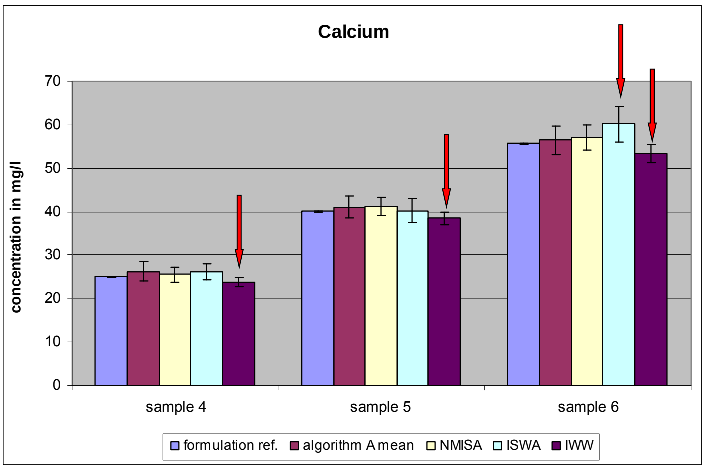
Comparison of methods



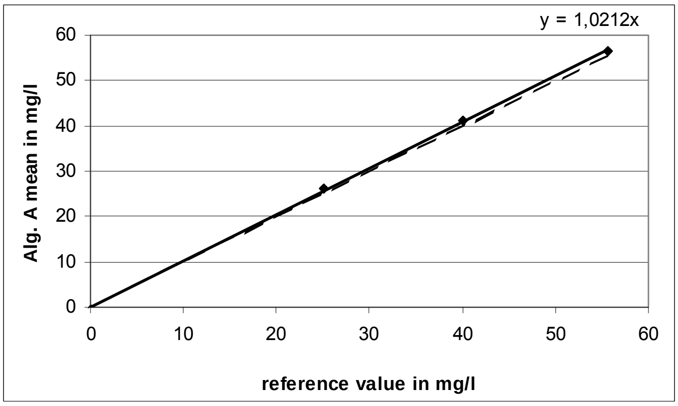
Summary TDS

- Standard deviations are quite high
- number of out-of-range values quite high
- Is TDS from conductivity really comparable with gravimetric TDS??

Calcium
Reference value and measurements



Calcium
mean vs. ref.-value



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

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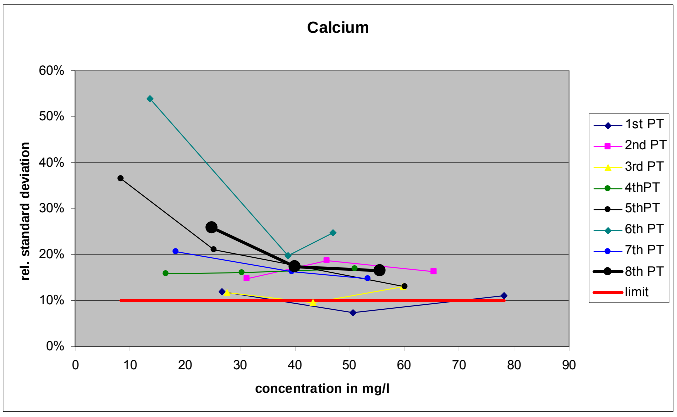
Calcium
calculated standard deviation and limit



no improvement

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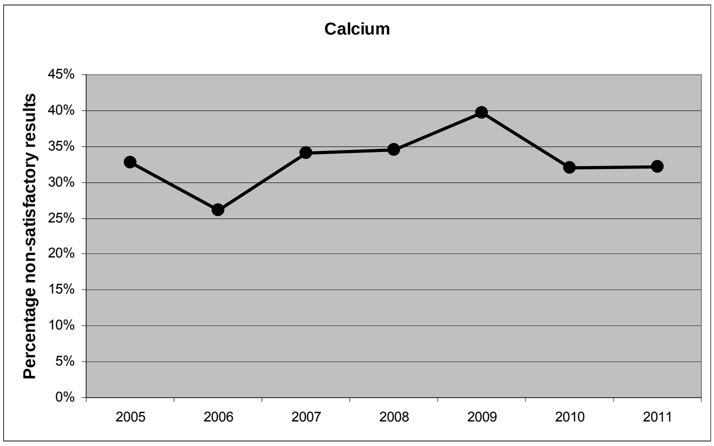
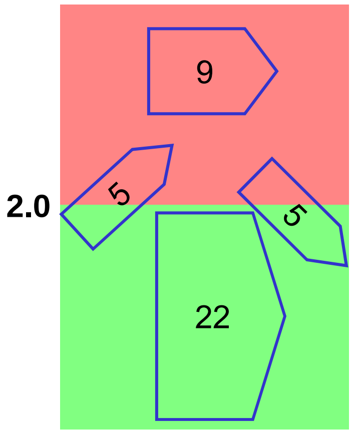
Calcium
Percentage non-satisfactory results



no improvement

AQS Baden-Württemberg iswa

Calcium
Individual performance development



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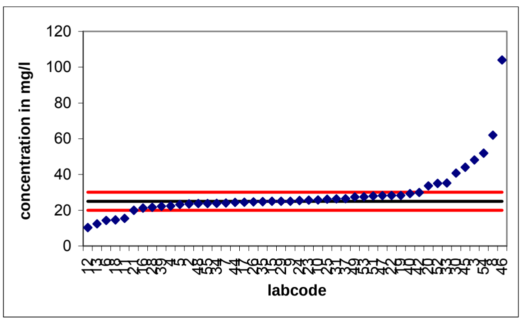
Calcium 1



values:	**48**
removed:	**2**
mean:	**26,26**
ref.-value:	**25,02**
recovery:	**105,0%**
std:	**6,447**
rstd:	**25,8%**
std limit:	**10%**
upper limit:	**30,02**
lower limit:	**20,01**
too high:	**9**
too low:	**8**
outside limits:	**17**

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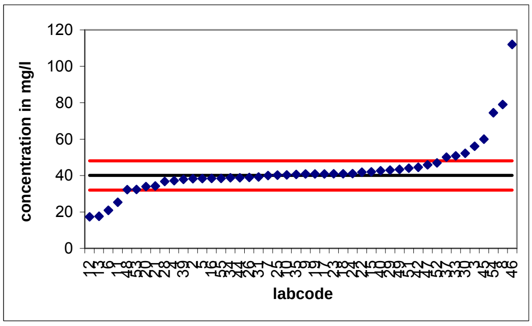
Calcium 2



values:	**49**
removed:	**3**
mean:	**41,03**
ref.-value:	**40,13**
recovery:	**102,3%**
std:	**6,996**
rstd:	**17,4%**
std limit:	**10%**
upper limit:	**48,15**
lower limit:	**32,10**
too high:	**8**
too low:	**7**
outside limits:	**15**

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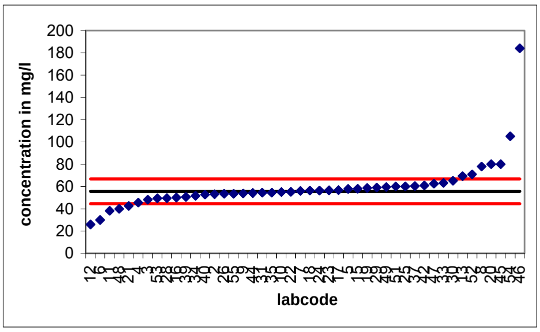
Calcium 3



values:	**49**
removed:	**3**
mean:	**56,43**
ref.-value:	**55,61**
recovery:	**101,5%**
std:	**9,157**
rstd:	**16,5%**
std limit:	**10%**
upper limit:	**66,74**
lower limit:	**44,49**
too high:	**7**
too low:	**8**
outside limits:	**15**

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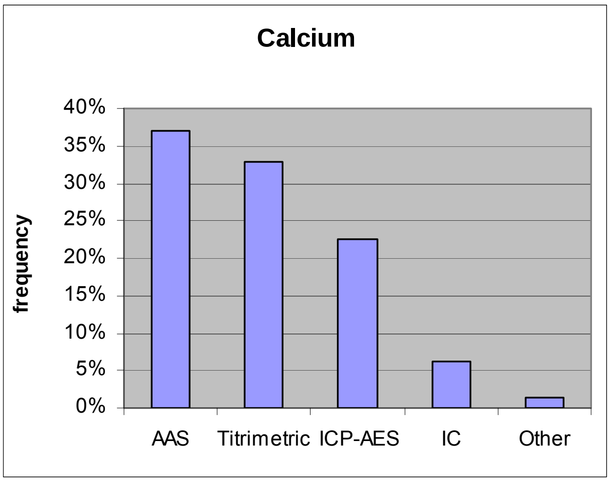
Used methods



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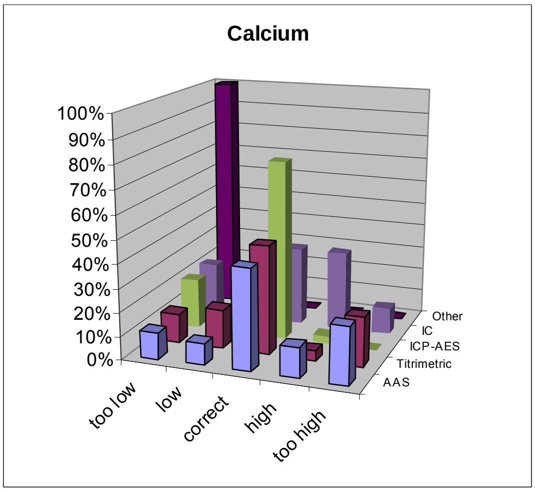
Comparison of methods



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Summary Calcium

- Standard deviations still too high
- 2/3 of the labs are ok, 1/3 consistently out-of-range

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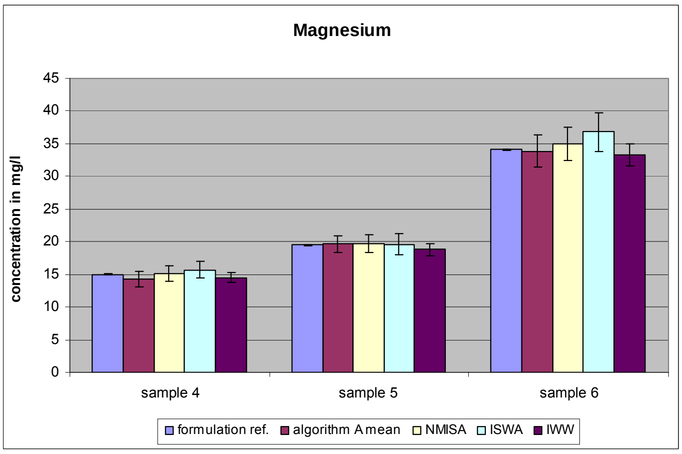
Magnesium
Reference value and measurements



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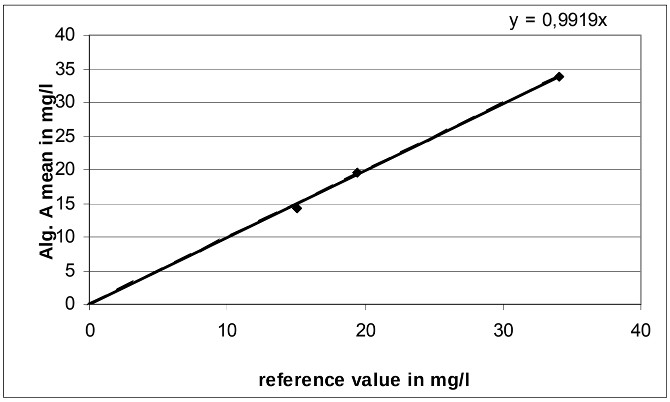
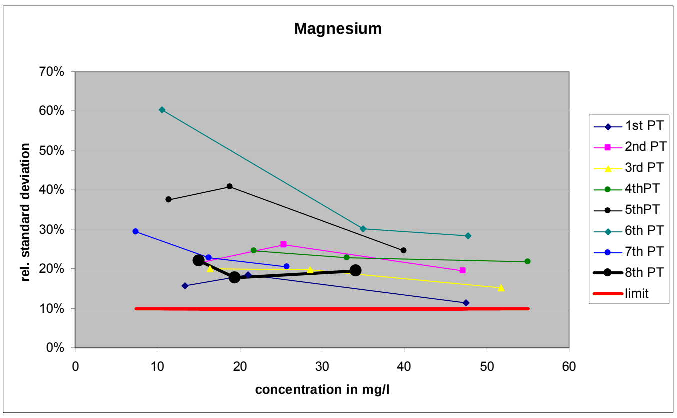
Magnesium
mean vs. ref.-value

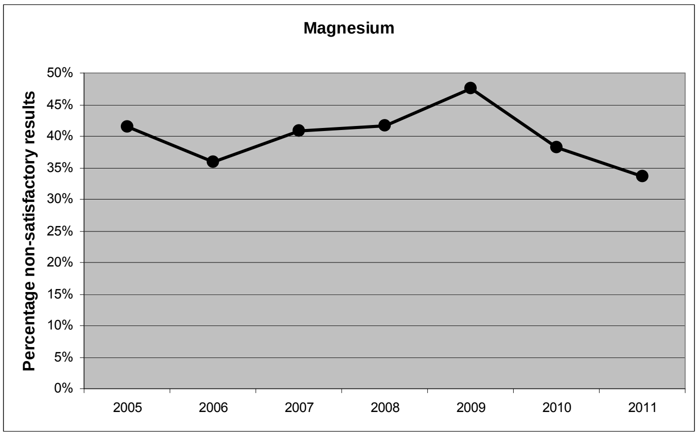


Average recovery	
2011	99,2
2010	98,9
2009	99.0
2008	100.2
2007	101.7
2006	99.6

Magnesium
calculated standard deviation and limit

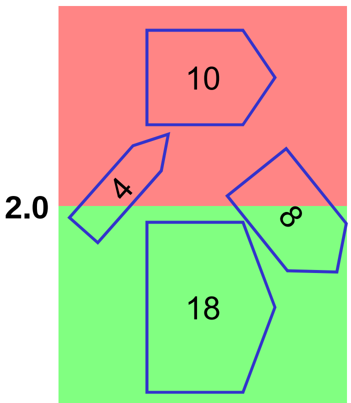


Magnesium
Percentage non-satisfactory results



slight improvement

Magnesium
Individual performance development



some improvement

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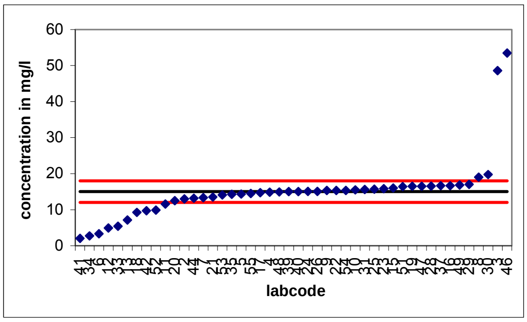
Magnesium 1



values:	47
removed:	1
mean:	14,32
ref.-value:	15,01
recovery:	95,4%
std:	3,328
rstd:	22,2%
std limit:	10%
upper limit:	18,02
lower limit:	12,01
too high:	4
too low:	11
outside limits:	15

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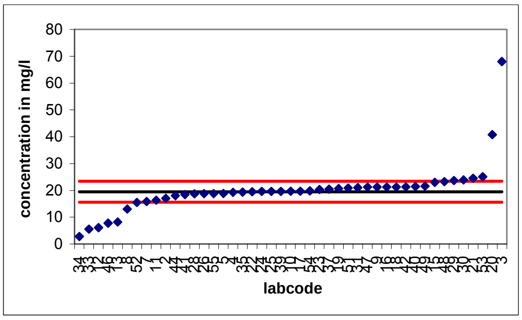
Magnesium 2



values:	48
removed:	3
mean:	19,66
ref.-value:	19,47
recovery:	101,0%
std:	3,438
rstd:	17,7%
std limit:	10%
upper limit:	23,37
lower limit:	15,58
too high:	6
too low:	10
outside limits:	16

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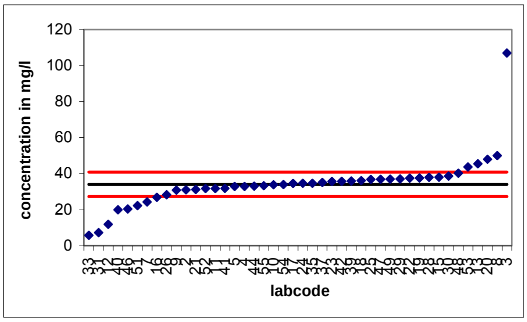
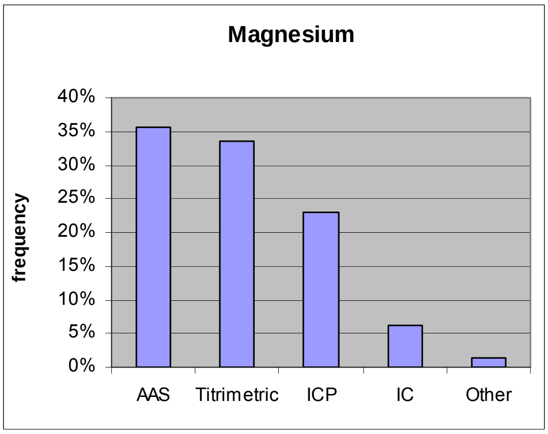
Magnesium 3



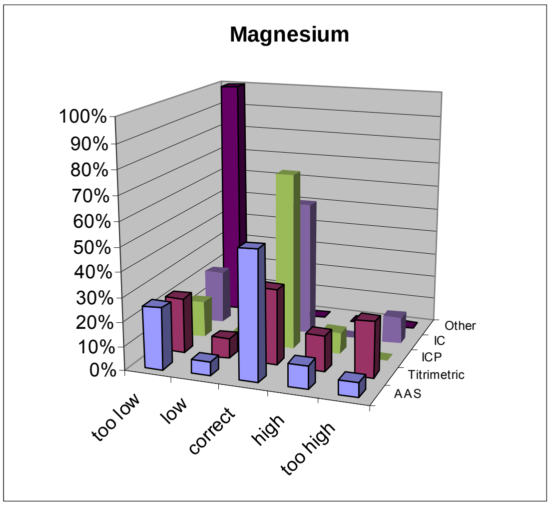
values:	**48**
removed:	**4**
mean:	**33,88**
ref.-value:	**34,10**
recovery:	**99,4%**
std:	**6,695**
rstd:	**19,6%**
std limit:	**10%**
upper limit:	**40,91**
lower limit:	**27,28**
too high:	**5**
too low:	**12**
outside limits:	**17**

Used methods



more ICP results

Comparison of methods



some improvement for titration results, but still not really ok

Summary Magnesium

- Average standard deviations, no significant improvement
- 1/3 of the results out-of-range
- Titrimetric values still not really reliable

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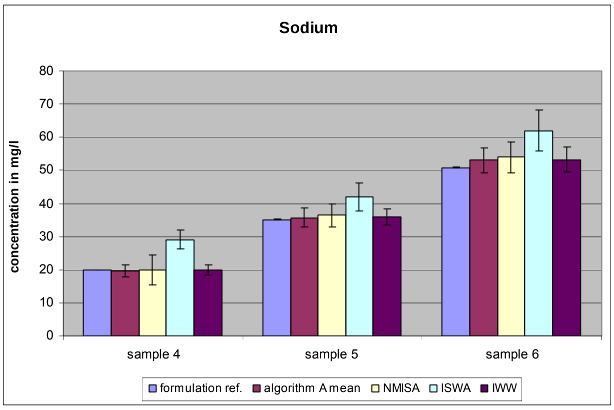
Sodium
Reference value and measurements



ISWA results too high

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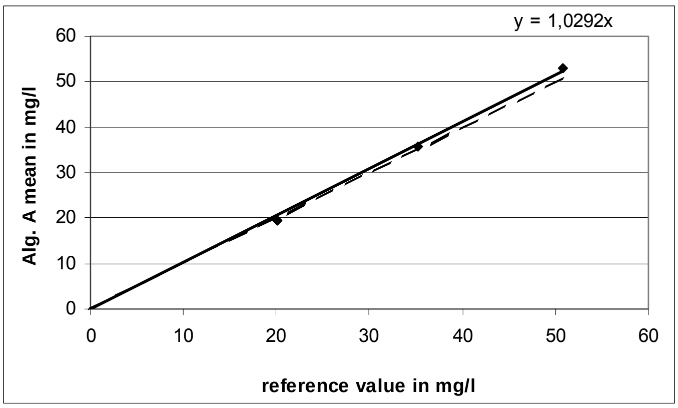
Sodium
mean vs. ref.-value



Average recovery	
2011	102,3
2010	102,2
2009	103.0
2008	100.4
2007	103.3
2006	104.4

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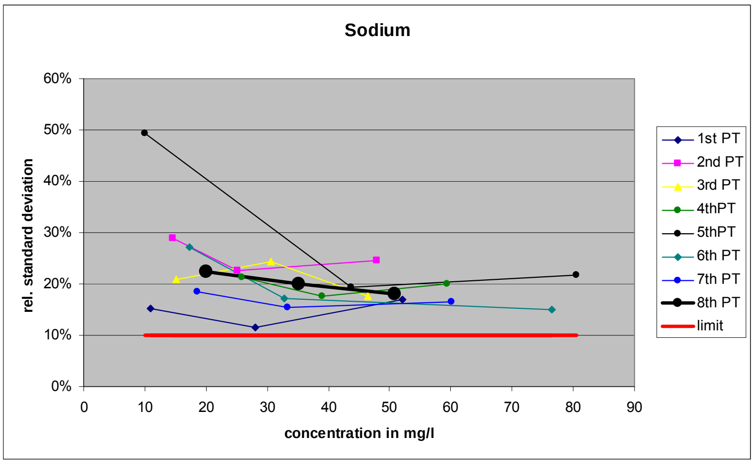
Sodium
calculated standard deviation and limit



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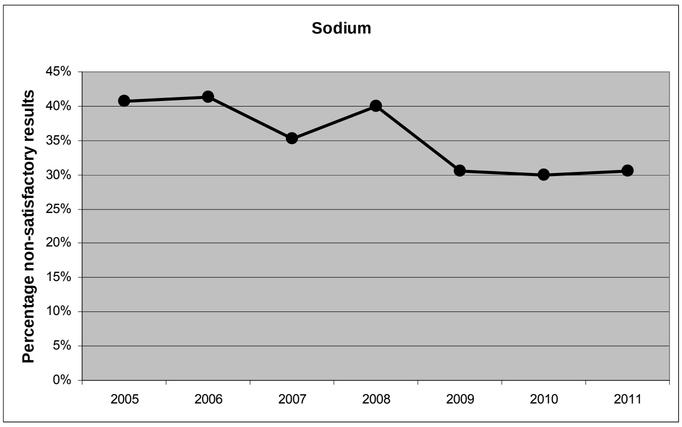
Sodium
Percentage non-satisfactory results



No improvement compared to last years, still very high

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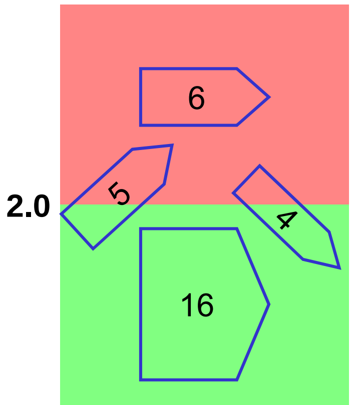
Sodium
Individual performance development



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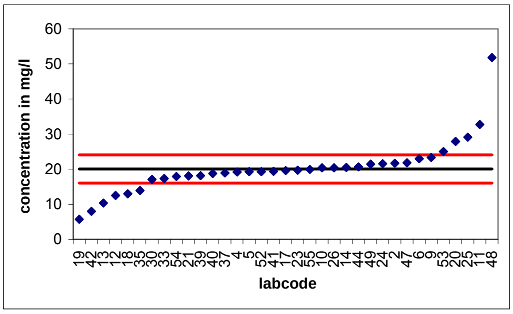
Sodium 1



values:	**35**
removed:	**0**
mean:	**19,60**
ref.-value:	**20,05**
recovery:	**97,7%**
std:	**4,482**
rstd:	**22,4%**
std limit:	**10%**
upper limit:	**24,07**
lower limit:	**16,04**
too high:	**5**
too low:	**6**
outside limits:	**11**

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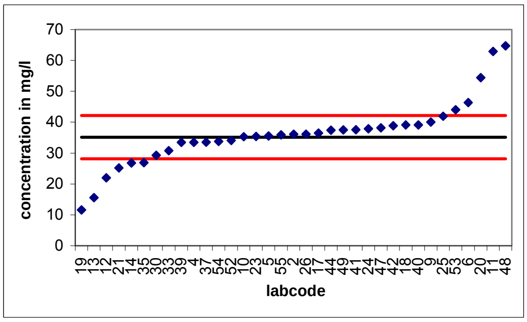
Sodium 2



values:	**35**
removed:	**0**
mean:	**35,71**
ref.-value:	**35,15**
recovery:	**101,6%**
std:	**7,014**
rstd:	**20,0%**
std limit:	**10%**
upper limit:	**42,18**
lower limit:	**28,12**
too high:	**5**
too low:	**6**
outside limits:	**11**

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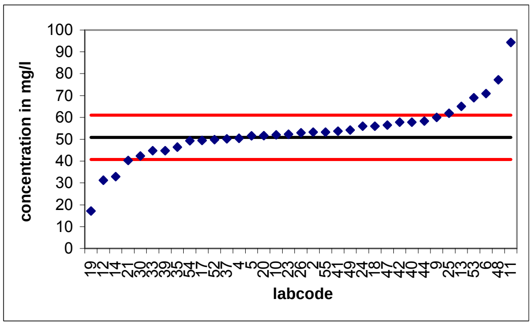
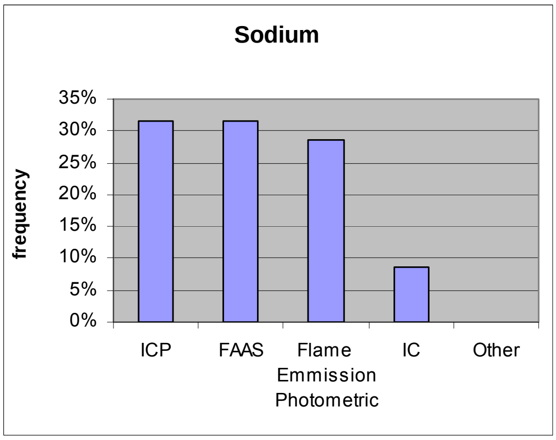
Sodium 3



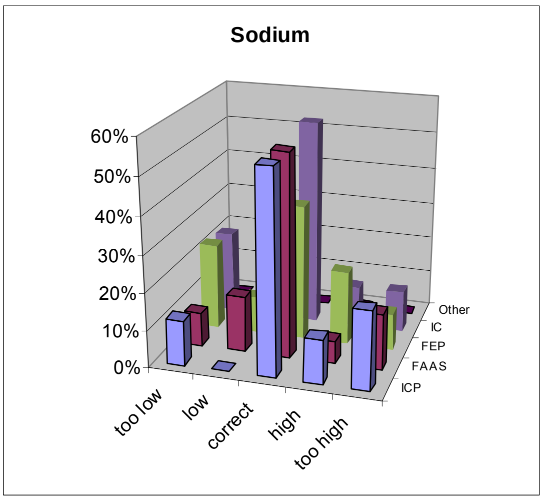
values:	**35**
removed:	**0**
mean:	**53,06**
ref.-value:	**50,85**
recovery:	**104,3%**
std:	**9,124**
rstd:	**17,9%**
std limit:	**10%**
upper limit:	**61,02**
lower limit:	**40,68**
too high:	**6**
too low:	**4**
outside limits:	**10**

Used methods



more ICP results

Comparison of methods



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Summary Sodium

- Average standard deviation – still too high
- Still 30% of the results ot-of-range

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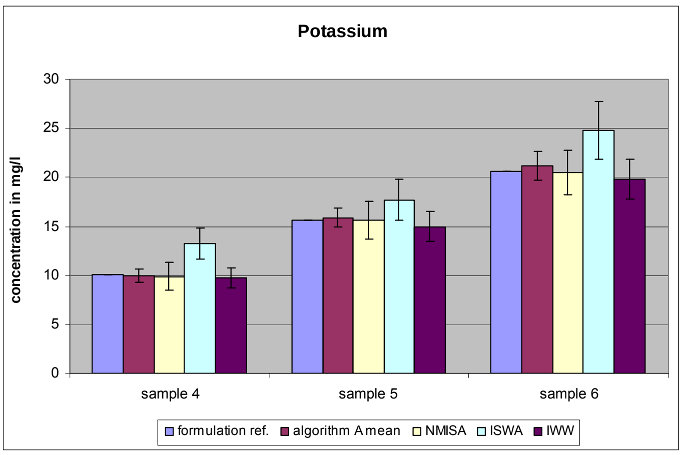
Potassium
Reference value and measurements



ISWA results too high

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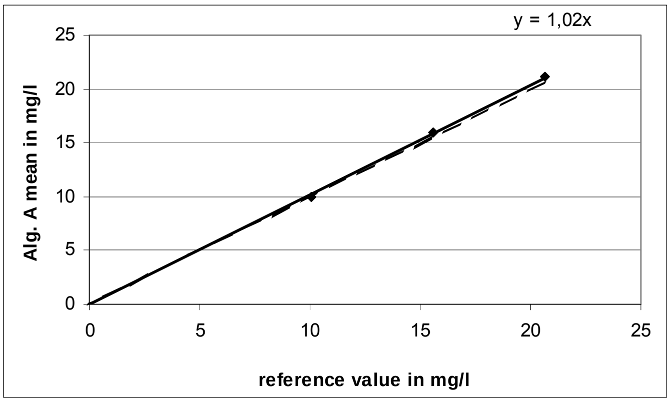
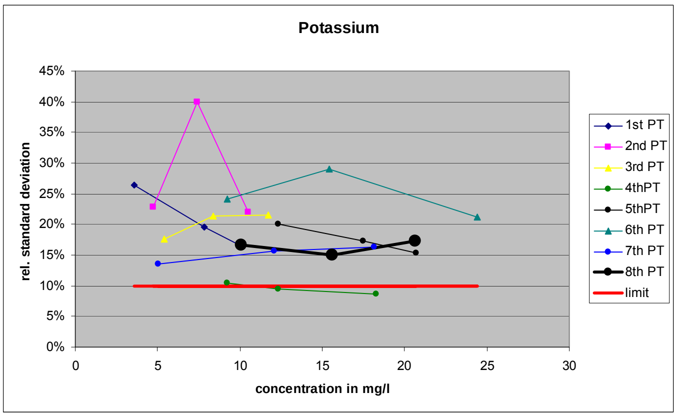
Potassium
mean vs. ref.-value



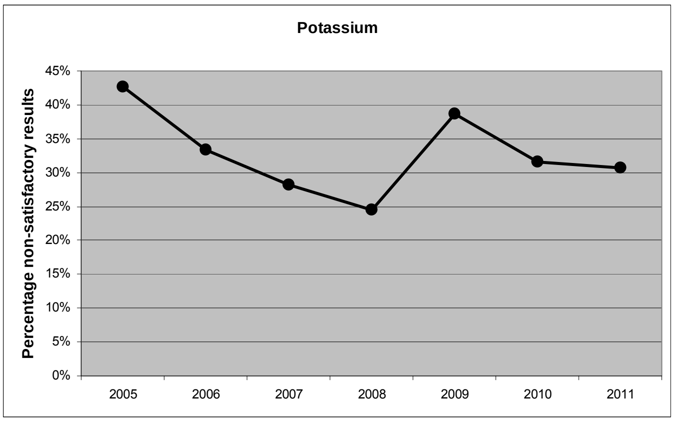
Average recovery	
2011	102,0
2010	98,7
2009	99.8
2008	99.0
2007	98.5
2006	96.9

Potassium
calculated standard deviation and limit



Standard deviations as last year

Potassium
Percentage non-satisfactory results



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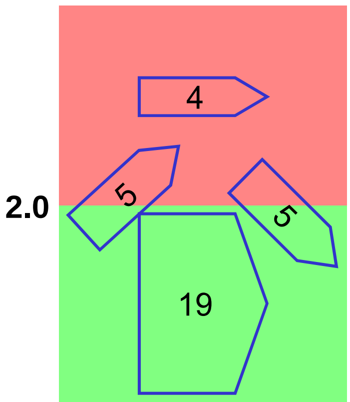
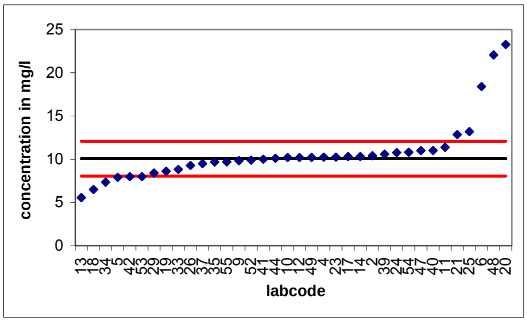
Potassium
Individual performance development



Potassium 1



values:	**38**
removed:	**2**
mean:	**10,02**
ref.-value:	**10,07**
recovery:	**99,5%**
std:	**1,667**
rstd:	**16,6%**
std limit:	**10%**
upper limit:	**12,08**
lower limit:	**8,05**
too high:	**6**
too low:	**7**
outside limits:	**13**

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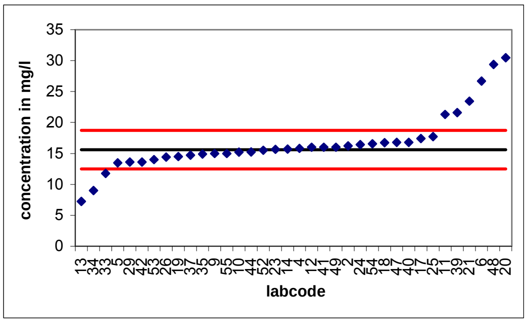
Potassium 2



values:	**38**
removed:	**2**
mean:	**15,91**
ref.-value:	**15,61**
recovery:	**101,9%**
std:	**2,342**
rstd:	**15,0%**
std limit:	**10%**
upper limit:	**18,74**
lower limit:	**12,49**
too high:	**7**
too low:	**4**
outside limits:	**11**

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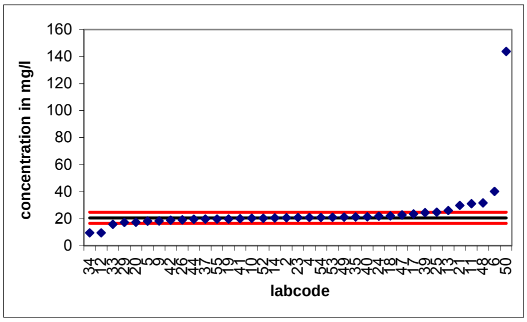
Potassium 3



values:	**38**
removed:	**1**
mean:	**21,18**
ref.-value:	**20,62**
recovery:	**102,7%**
std:	**3,551**
rstd:	**17,2%**
std limit:	**10%**
upper limit:	**24,75**
lower limit:	**16,50**
too high:	**7**
too low:	**4**
outside limits:	**11**

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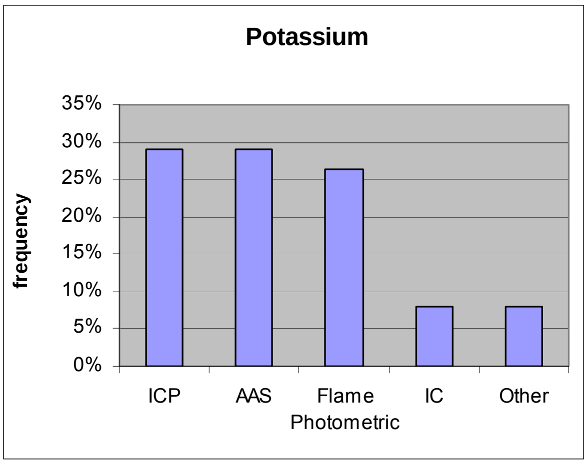
Used methods



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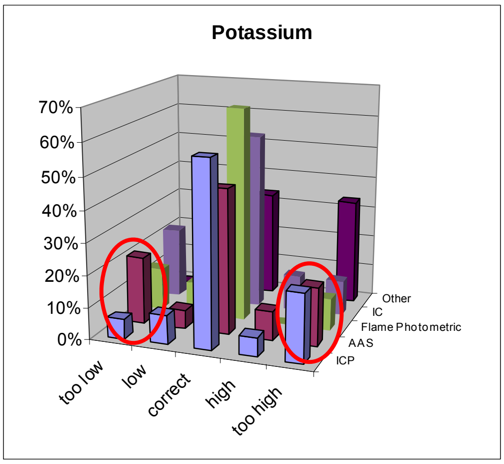
Comparison of methods



still problems with AAS

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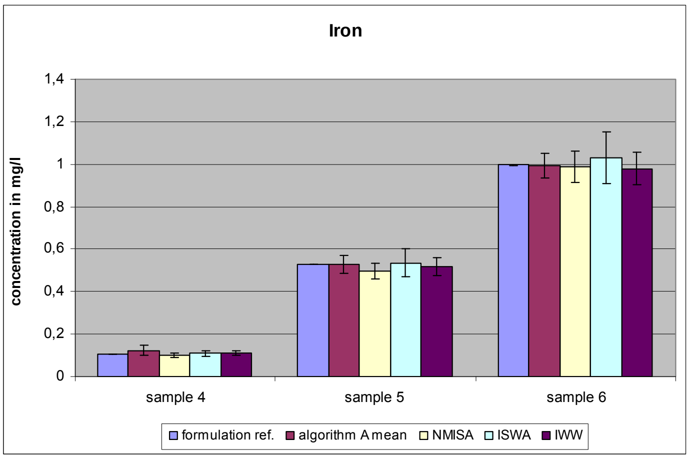
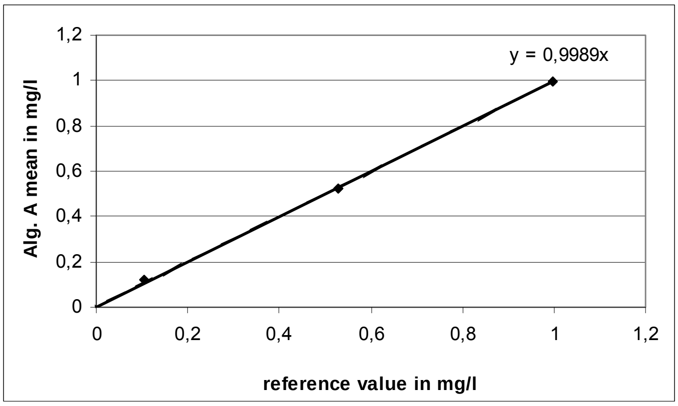
Summary Potassium

- Standard deviations as last year
- 1/3 of non-satisfactory results
- Problems with AAS

Iron
Reference value and measurements

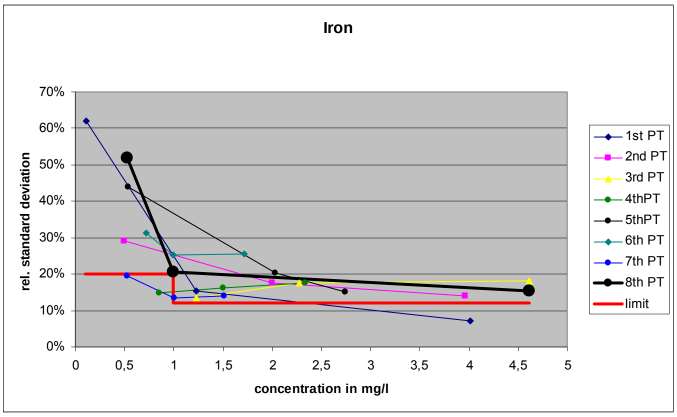


Iron
mean vs. ref.-value



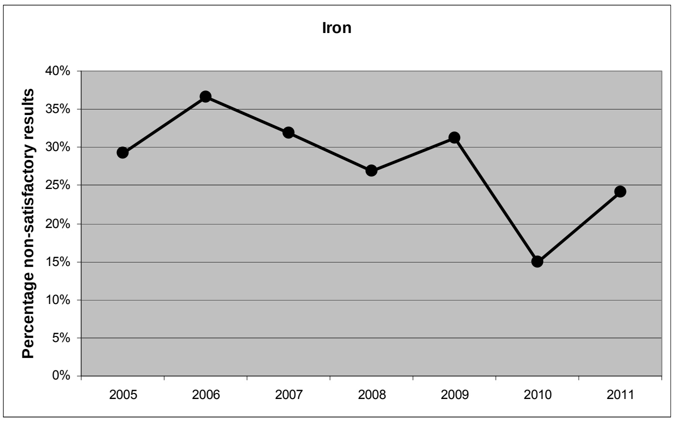
Average recovery	
2011	99,9
2010	100,3
2009	97.6
2008	99.9
2007	92.9
2006	88.0

Iron
calculated standard deviation and limit



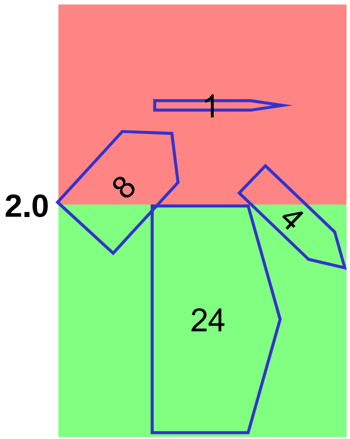
average standard deviations, very high for lowest level

Iron
Percentage non-satisfactory results



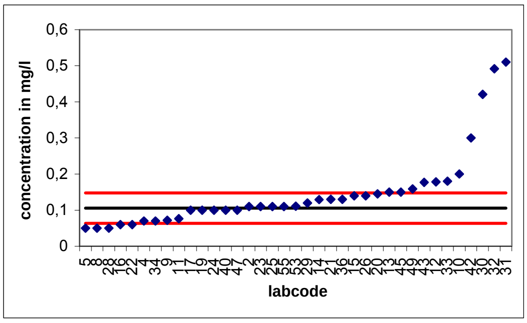
worse again

Iron
Individual performance development



More labs getting worse than improving

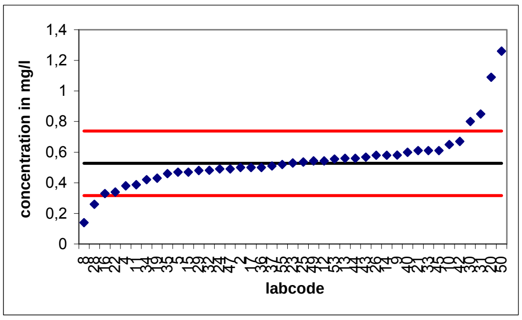
Iron 1



values:	**38**
removed:	**1**
mean:	**0,12**
ref.-value:	**0,11**
recovery:	**116,7%**
std:	**0,055**
rstd:	**51,9%**
std limit:	**20%**
upper limit:	**0,15**
lower limit:	**0,06**
too high:	**12**
too low:	**5**
outside limits:	**17**

no consensus

Iron 2



values:	41
removed:	0
mean:	0,53
ref.-value:	0,53
recovery:	99,8%
std:	0,109
rstd:	20,7%
std limit:	20%
upper limit:	0,74
lower limit:	0,32
too high:	4
too low:	2
outside limits:	6

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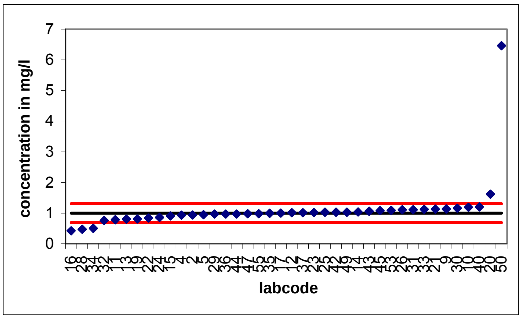
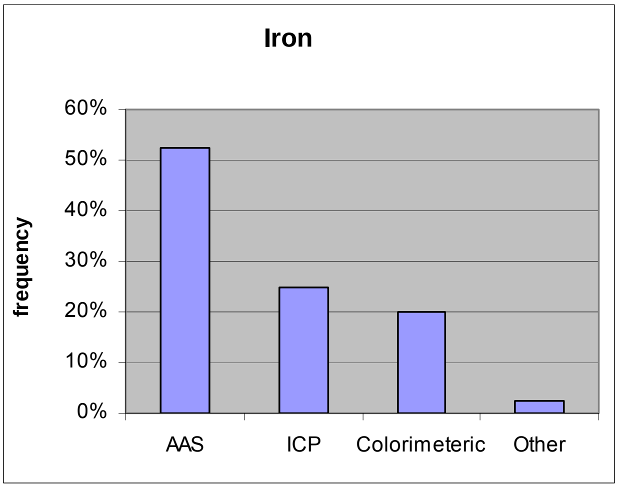
Iron 3

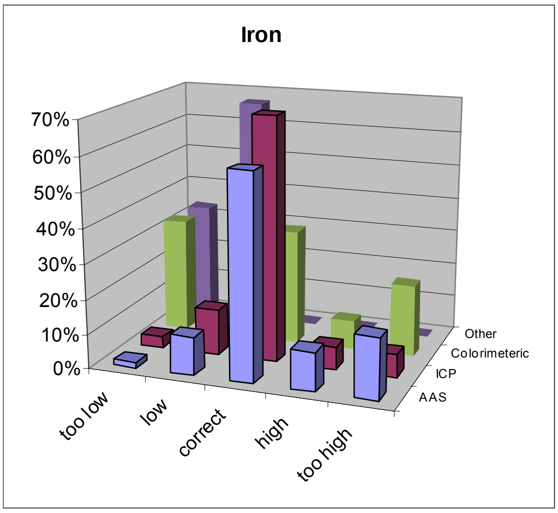


values:	41
removed:	1
mean:	0,99
ref.-value:	1,00
recovery:	99,7%
std:	0,153
rstd:	15,4%
std limit:	20%
upper limit:	1,30
lower limit:	0,69
too high:	2
too low:	4
outside limits:	6

Used methods



Comparison of methods



problems with colorimetric method

Summary Iron

- Standard deviations higher again
- Problems especially with low concentrations
- Problems with colorimetric method

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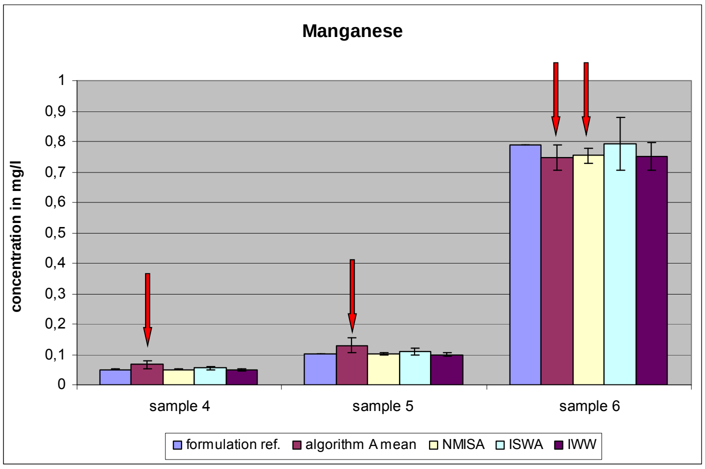
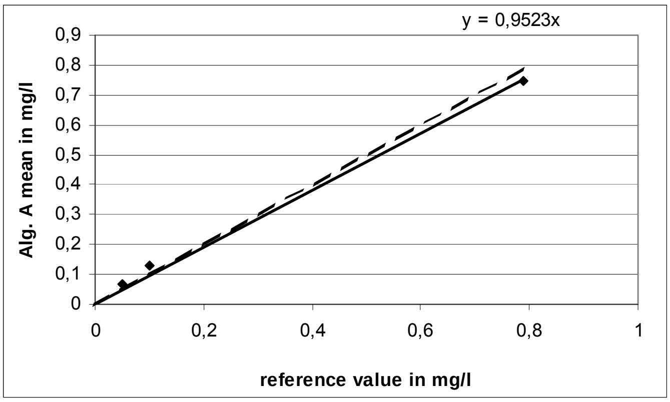
Manganese
Reference value and measurements

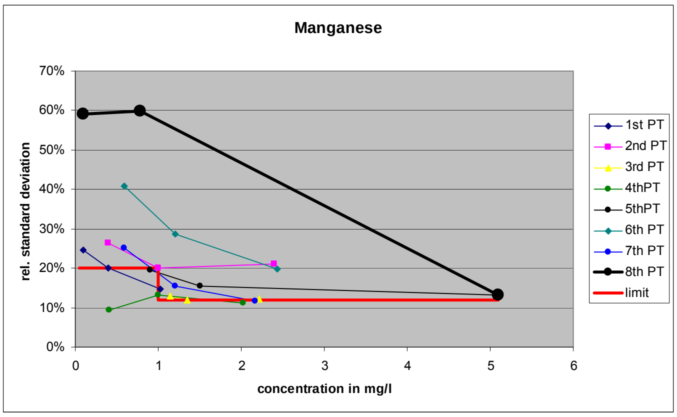


Manganese
mean vs. ref.-value



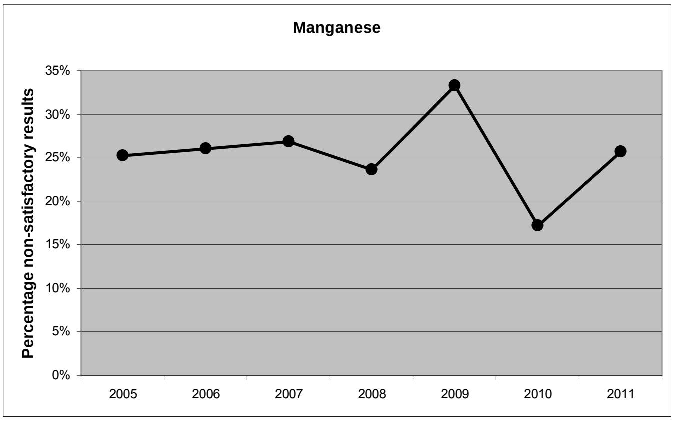
Average recovery	
2011	95,2
2010	98,9
2009	93.0
2008	96.7
2007	96.0
2006	95.4

Manganese
calculated standard deviation and limit



Highest standard deviation

Manganese
Percentage non-satisfactory results



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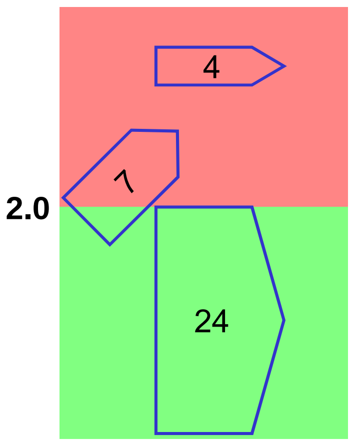
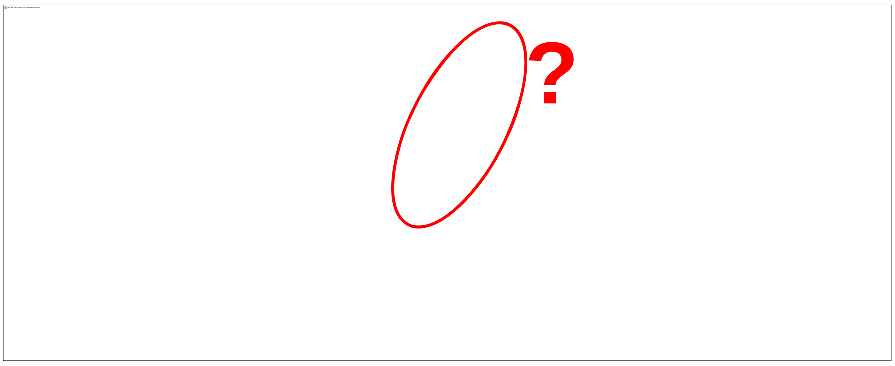
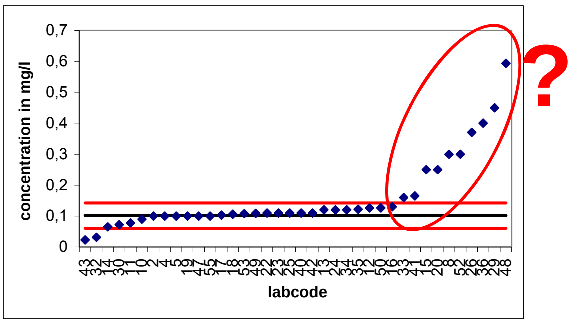
Manganese
Individual performance development



Manganese 1

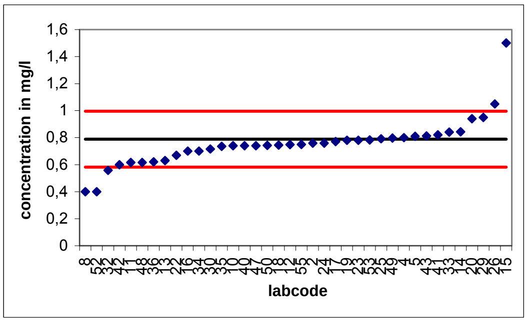


Manganese 2



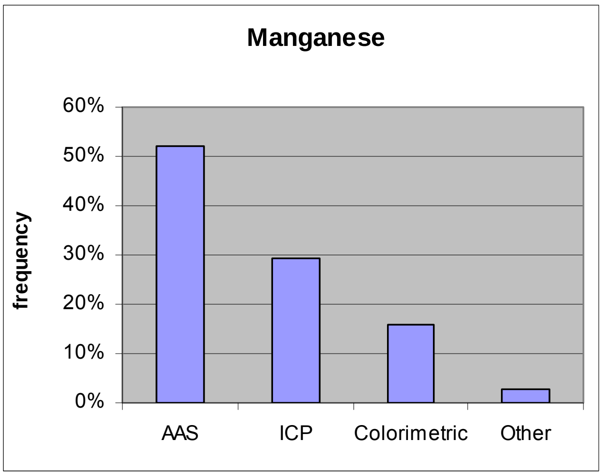
values:	**38**
removed:	**0**
mean:	**0,13**
ref.-value:	**0,10**
recovery:	**127,3%**
std:	**0,061**
rstd:	**59,8%**
std limit:	**20%**
upper limit:	**0,14**
lower limit:	**0,06**
too high:	**10**
too low:	**2**
outside limits:	**12**

Manganese 3

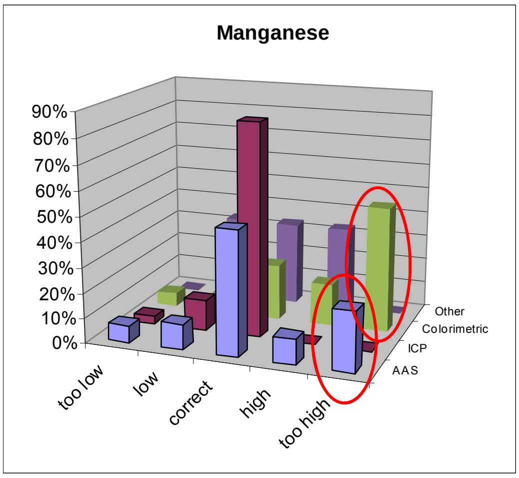


values:	**38**
removed:	**0**
mean:	**0,75**
ref.-value:	**0,79**
recovery:	**94,6%**
std:	**0,104**
rstd:	**13,1%**
std limit:	**20%**
upper limit:	**1,00**
lower limit:	**0,58**
too high:	**2**
too low:	**3**
outside limits:	**5**

Used methods



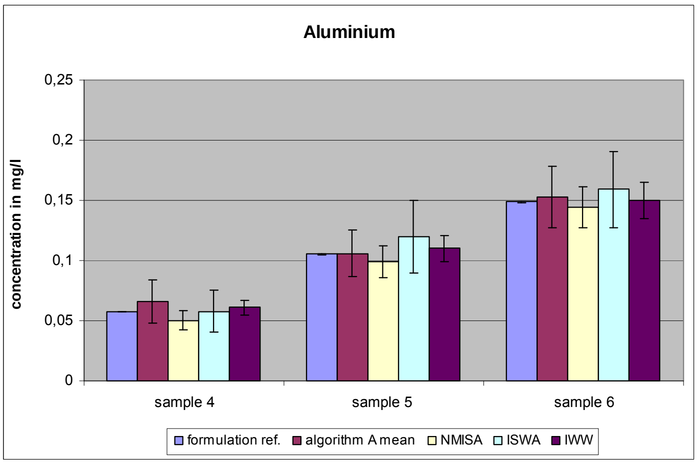
Comparison of methods



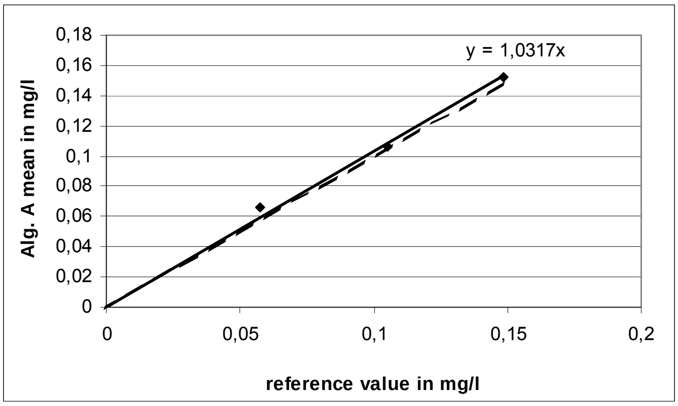
Summary Manganese

- Standard deviation much worse
- Serious problems with low concentrations
- At low concentrations many values much too high – why? – contamination?

Aluminium
Reference value and measurements

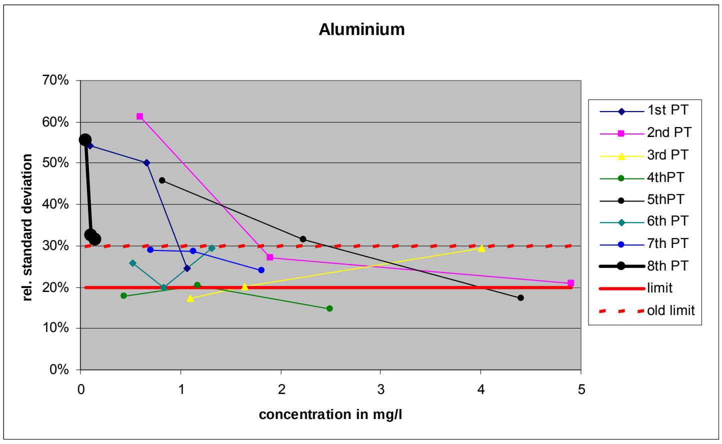


Aluminium
mean vs. ref.-value



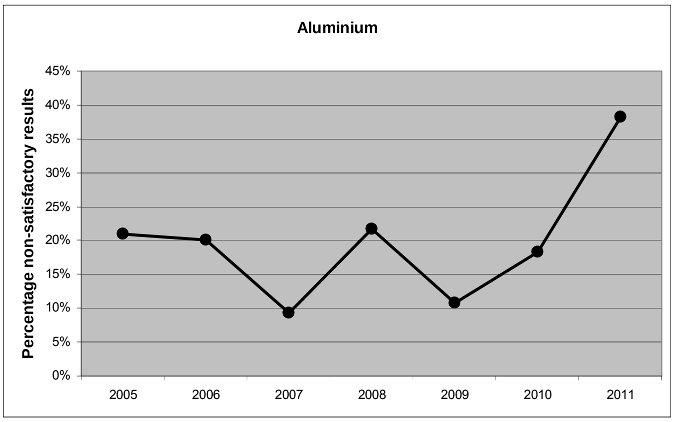
Average recovery	
2011	103.2
2010	99.4
2009	104.9
2008	93.9
2007	96.1
2006	85.7

Aluminium
calculated standard deviation and limit



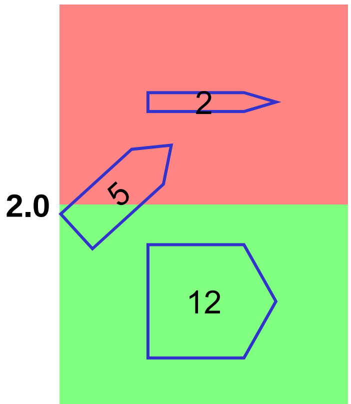
lowered standard deviation for proficiency assessment (from 30% to 20%)

Aluminium
Percentage non-satisfactory results

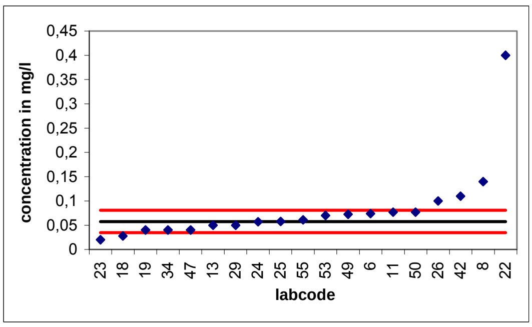


increasing due to low concentrations and lowered standard deviation for proficiency assessment

Aluminium
Individual performance development

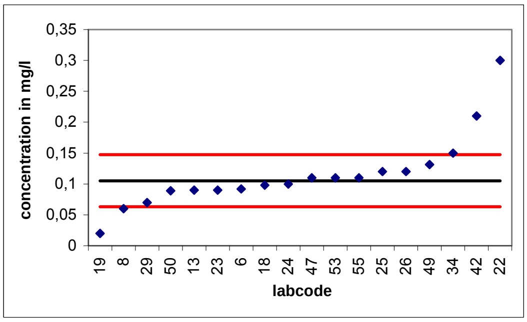


Aluminium 1



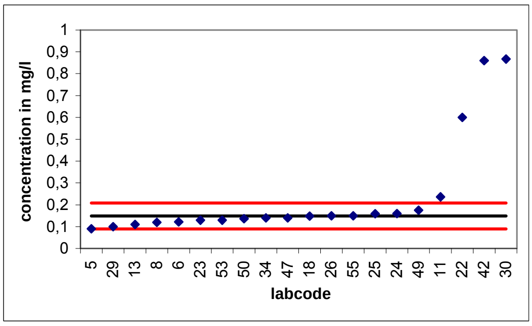
values:	**22**
removed:	**3**
mean:	**0,07**
ref.-value:	**0,06**
recovery:	**114,3%**
std:	**0,032**
rstd:	**55,5%**
std limit:	**20%**
upper limit:	**0,08**
lower limit:	**0,03**
too high:	**7**
too low:	**2**
outside limits:	**9**

Aluminium 2



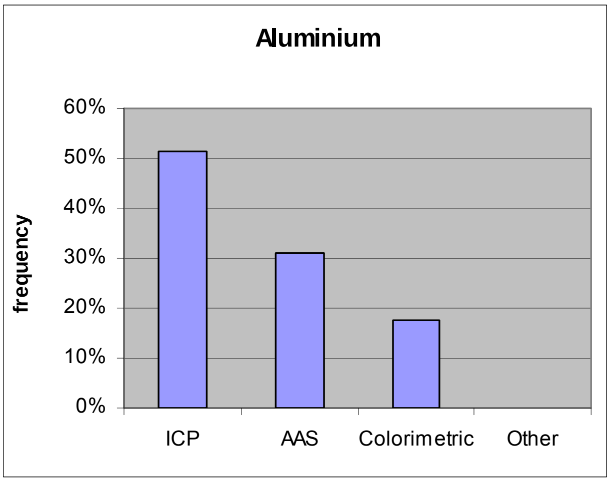
values:	**23**
removed:	**5**
mean:	**0,11**
ref.-value:	**0,11**
recovery:	**100,8%**
std:	**0,034**
rstd:	**32,4%**
std limit:	**20%**
upper limit:	**0,15**
lower limit:	**0,06**
too high:	**7**
too low:	**3**
outside limits:	**10**

Aluminium 3

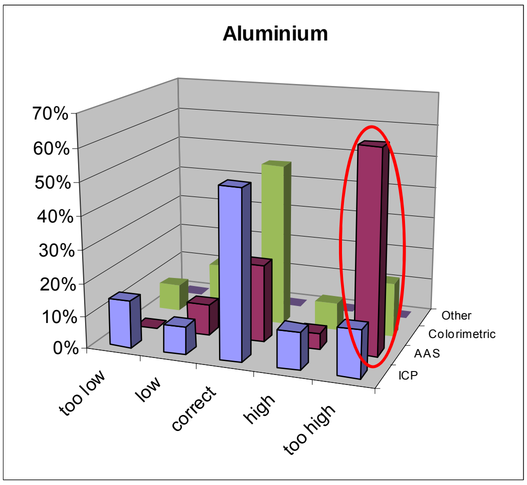


values:	**23**
removed:	**3**
mean:	**0,15**
ref.-value:	**0,15**
recovery:	**102,7%**
std:	**0,047**
rstd:	**31,6%**
std limit:	**20%**
upper limit:	**0,21**
lower limit:	**0,09**
too high:	**6**
too low:	**1**
outside limits:	**7**

Used methods



Comparison of methods



obviously some serious problems with AAS

Summary Aluminium

- low concentrations only
- lowered standard deviation for proficiency assessment
- therefore increased number of values out-of-range
- problems with AAS

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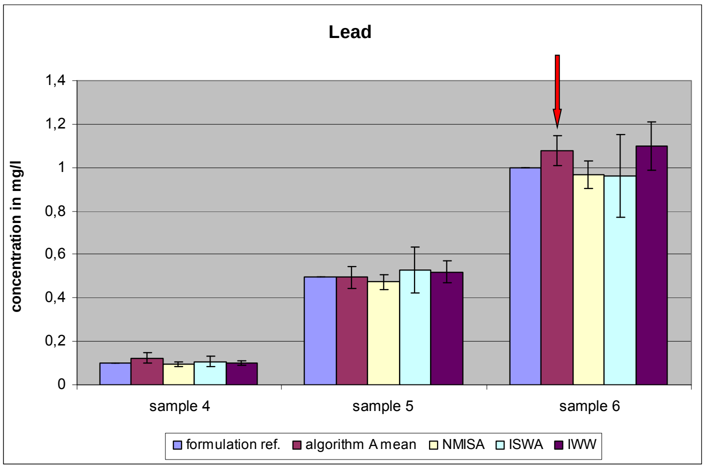
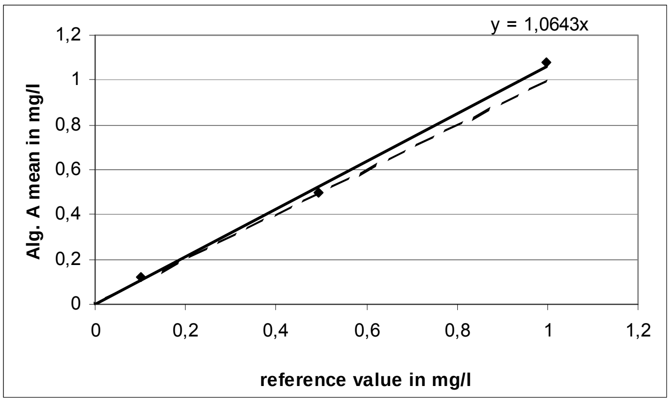
Lead
Reference value and measurements



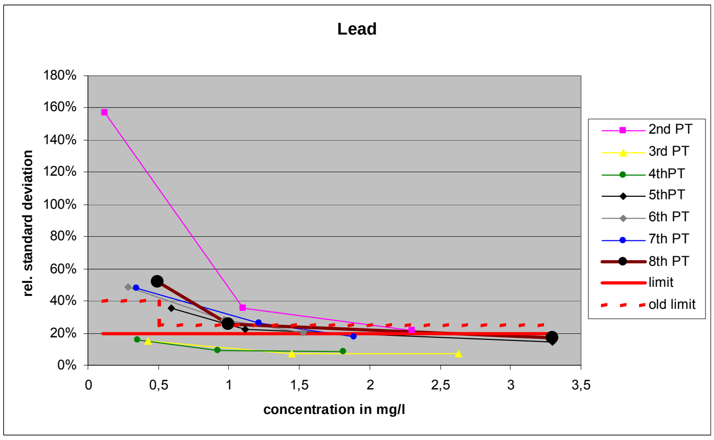
Lead
mean vs. ref.-value



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

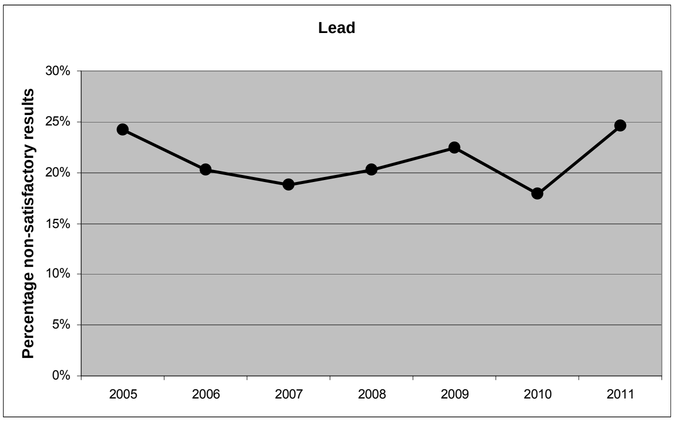
participants' mean for the highest level is too high

Lead
calculated standard deviation and limit



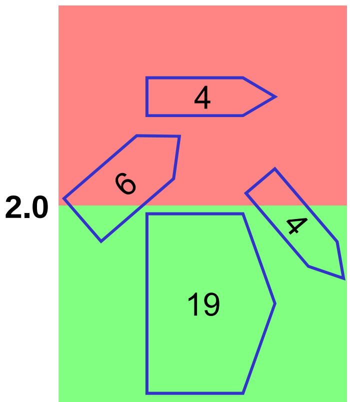
average standard deviations – limit lowered

Lead
Percentage non-satisfactory results



increase probably due to lowered limit for standard deviation

Lead
Individual performance development



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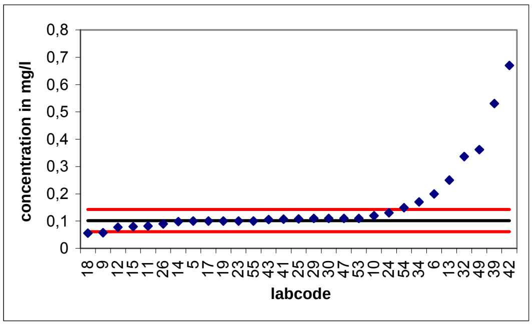
Lead 1



values:	32
removed:	3
mean:	0,12
ref.-value:	0,10
recovery:	121,4%
std:	0,053
rstd:	52,1%
std limit:	20%
upper limit:	0,14
lower limit:	0,06
too high:	10
too low:	3
outside limits:	13

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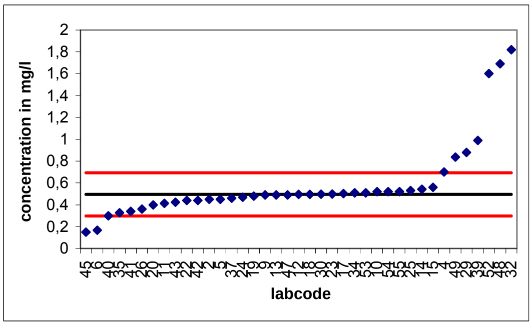
Lead 2



values:	39
removed:	0
mean:	0,50
ref.-value:	0,50
recovery:	100,3%
std:	0,128
rstd:	25,9%
std limit:	20%
upper limit:	0,69
lower limit:	0,30
too high:	7
too low:	2
outside limits:	9

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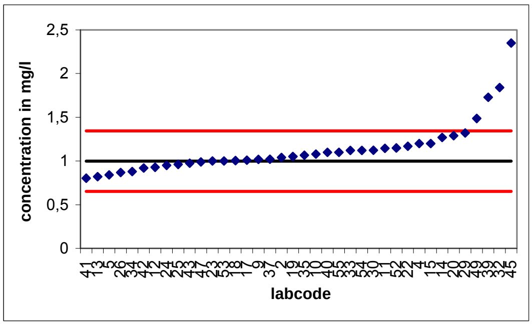
Lead 3



values:	**39**
removed:	**1**
mean:	**1,08**
ref.-value:	**1,00**
recovery:	**107,8%**
std:	**0,173**
rstd:	**17,3%**
std limit:	**20%**
upper limit:	**1,34**
lower limit:	**0,65**
too high:	**4**
too low:	**1**
outside limits:	**5**

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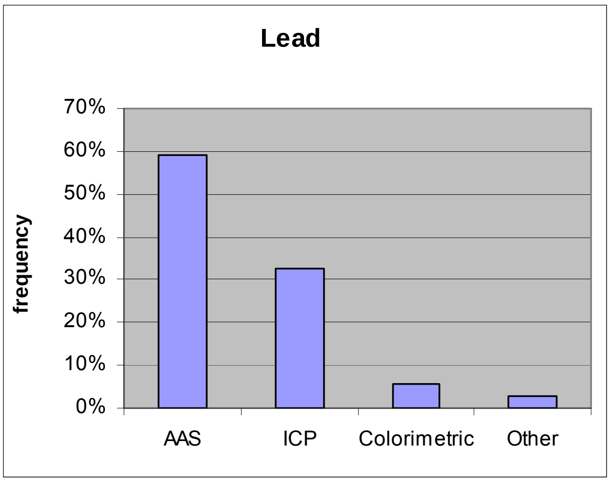
Used methods



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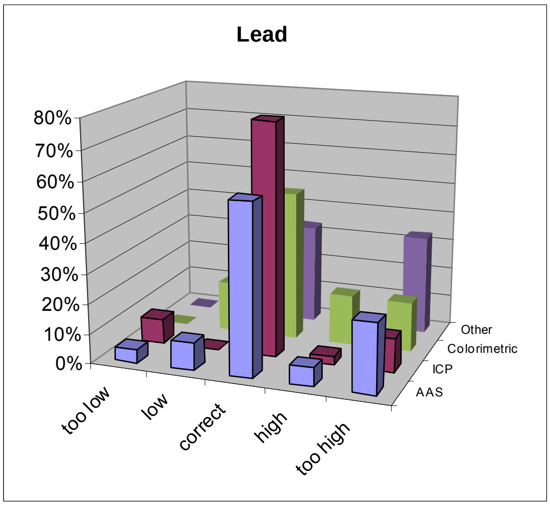
Comparison of methods



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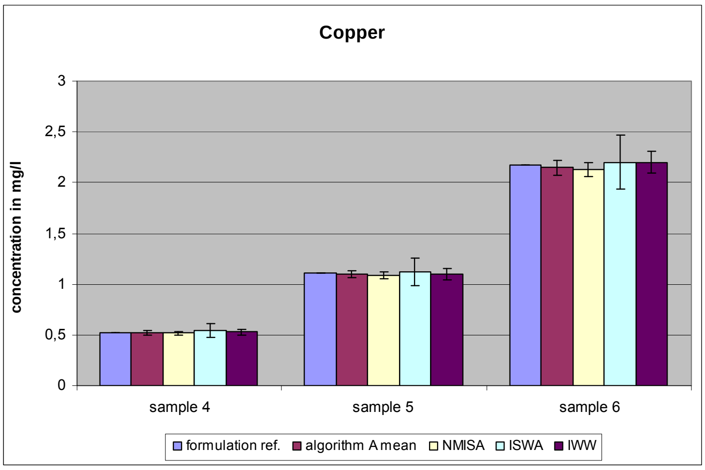
Summary Lead

- Lowered standard deviation for proficiency assessment
- Experimental standard deviation still too high
- Especially at low concentrations many too high values

Copper
Reference value and measurements



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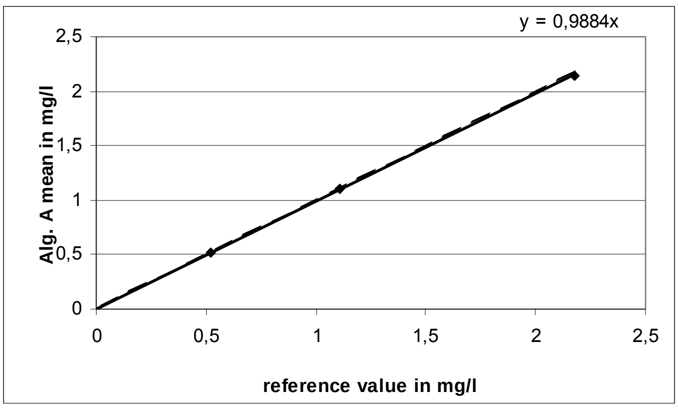
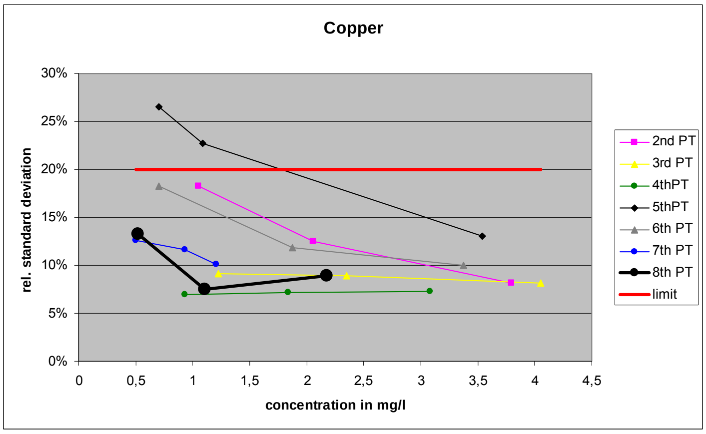
Copper
mean vs. ref.-value



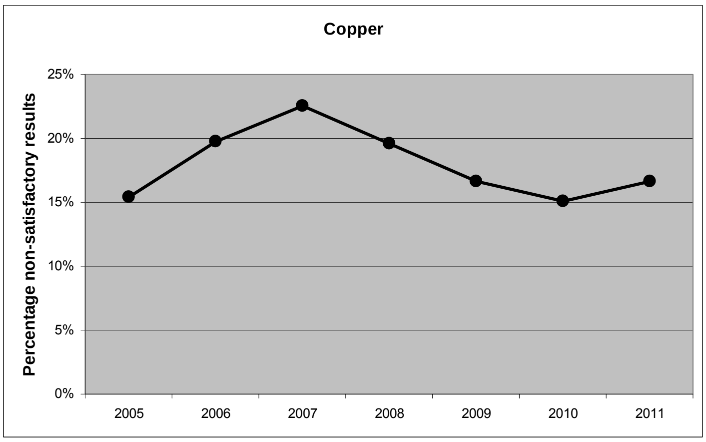
Average recovery	
2011	98.8
2010	103.7
2009	99.6
2008	95.1
2007	97.5
2006	98.5

Copper
calculated standard deviation and limit

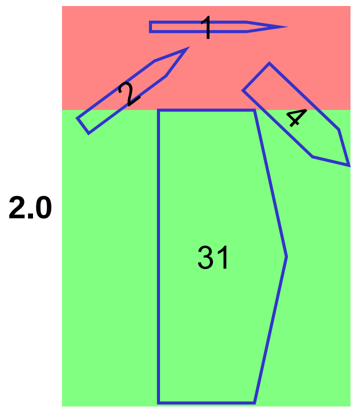


one of the best PT rounds

Copper
Percentage non-satisfactory results

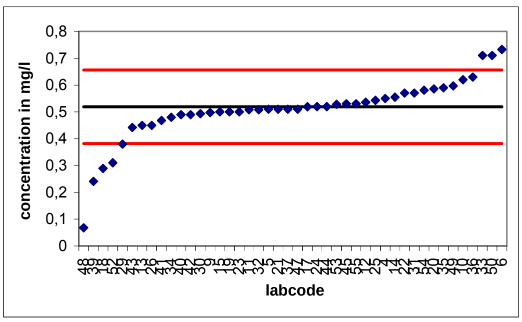


Copper
Individual performance development



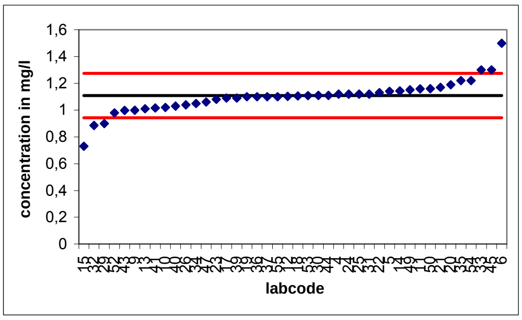
many good labs

Copper 1



values:	**44**
removed:	**0**
mean:	**0,52**
ref.-value:	**0,52**
recovery:	**99,9%**
std:	**0,069**
rstd:	**13,2%**
std limit:	**20%**
upper limit:	**0,66**
lower limit:	**0,38**
too high:	**3**
too low:	**5**
outside limits:	**8**

Copper 2



values:	44
removed:	2
mean:	1,10
ref.-value:	1,11
recovery:	99,1%
std:	0,083
rstd:	7,5%
std limit:	20%
upper limit:	1,28
lower limit:	0,94
too high:	3
too low:	5
outside limits:	8

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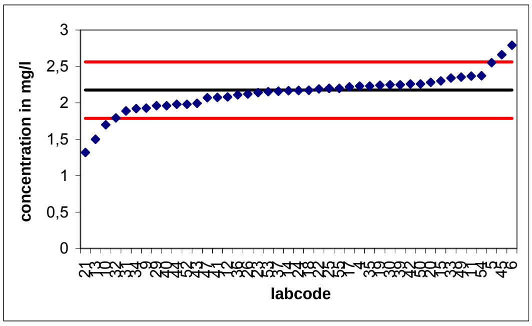
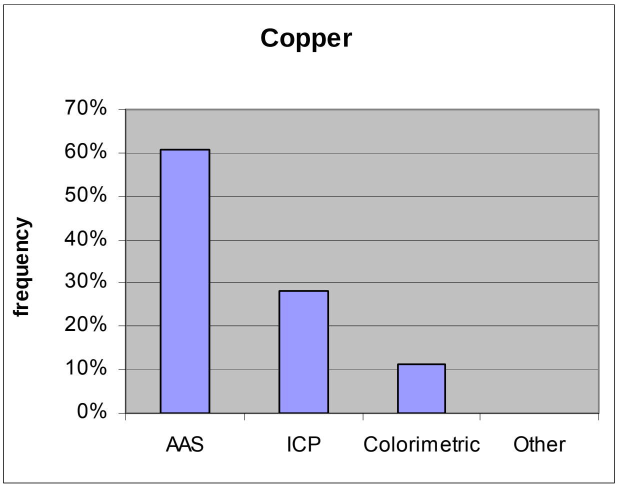
Copper 3

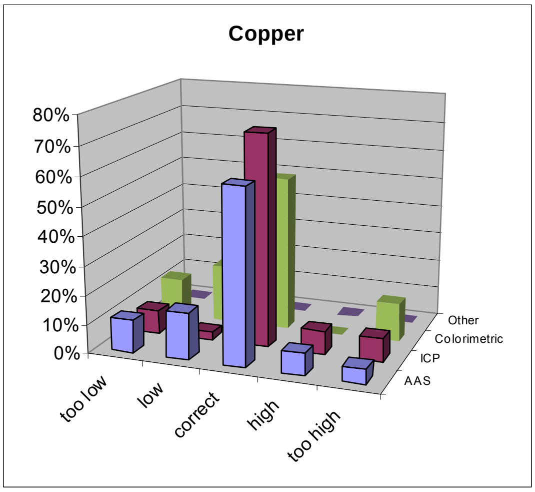


values:	44
removed:	1
mean:	2,15
ref.-value:	2,17
recovery:	98,7%
std:	0,194
rstd:	8,9%
std limit:	20%
upper limit:	2,56
lower limit:	1,79
too high:	2
too low:	4
outside limits:	6

Used methods



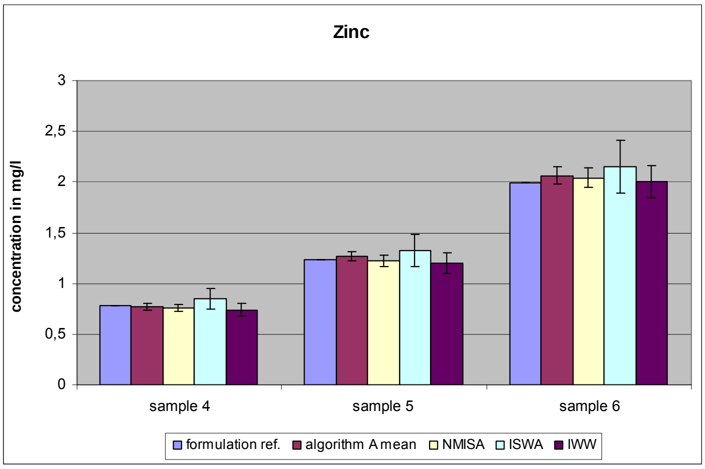
Comparison of methods



Summary Copper

- Good standard deviation
- Percentage of non-satisfactory results at a constant low stage

Zinc
Reference value and measurements

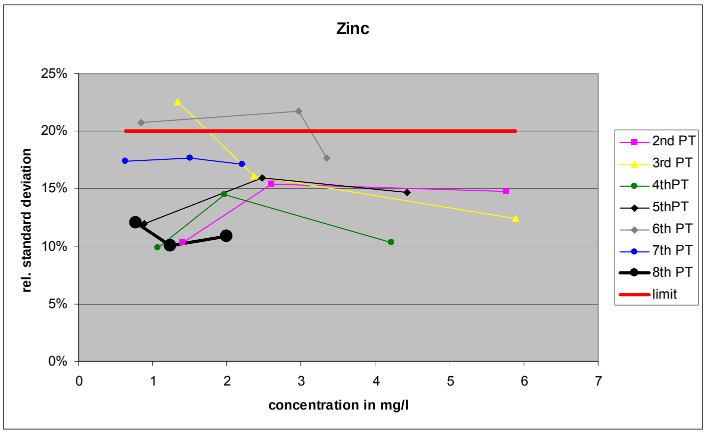


Zinc
mean vs. ref.-value

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

AQS Baden-Württemberg iswa

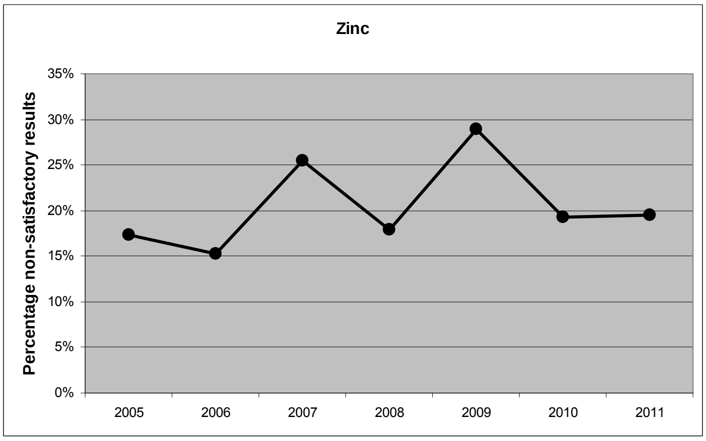
Zinc
calculated standard deviation and limit



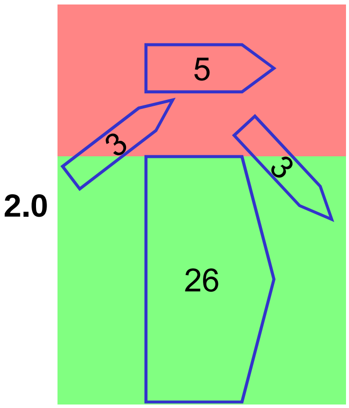
good standard deviations

AQS Baden-Württemberg iswa

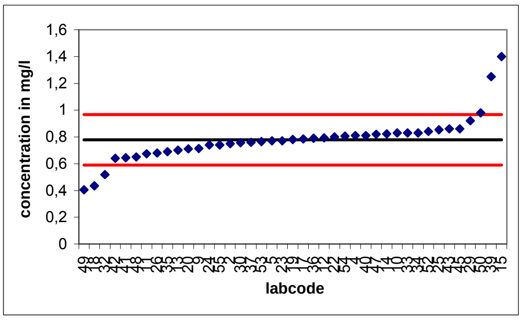
Zinc
Percentage non-satisfactory results



Zinc
Individual performance development



Zinc 1



values:	41
removed:	0
mean:	0,77
ref.-value:	0,78
recovery:	99,1%
std:	0,094
rstd:	12,1%
std limit:	20%
upper limit:	0,97
lower limit:	0,59
too high:	3
too low:	3
outside limits:	6

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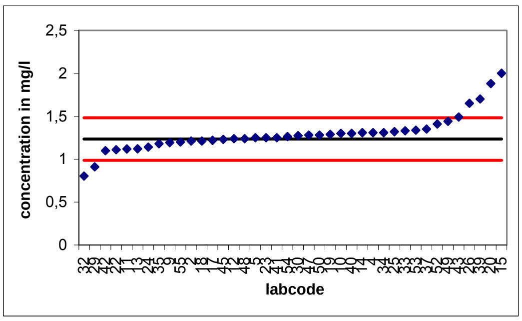
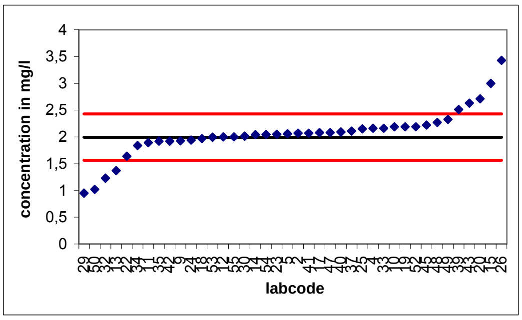
Zinc 2



values:	41
removed:	1
mean:	1,27
ref.-value:	1,23
recovery:	102,9%
std:	0,124
rstd:	10,0%
std limit:	20%
upper limit:	1,48
lower limit:	0,99
too high:	5
too low:	3
outside limits:	8

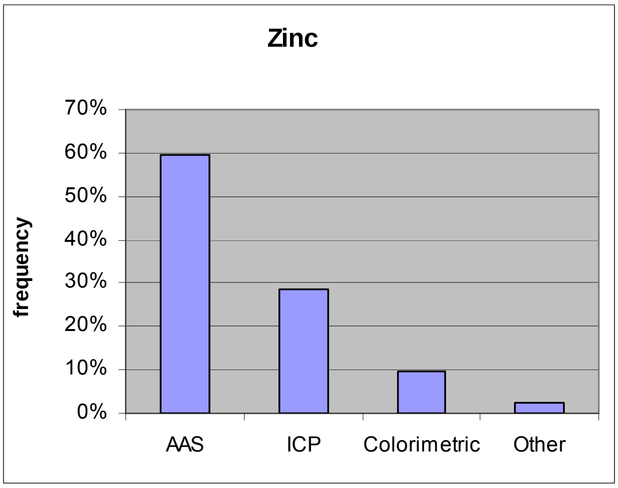
AQS Baden-Württemberg iswa

Zinc 3



values:	**41**
removed:	**1**
mean:	**2,07**
ref.-value:	**1,99**
recovery:	**103,6%**
std:	**0,216**
rstd:	**10,8%**
std limit:	**20%**
upper limit:	**2,43**
lower limit:	**1,56**
too high:	**5**
too low:	**5**
outside limits:	**10**

Used methods



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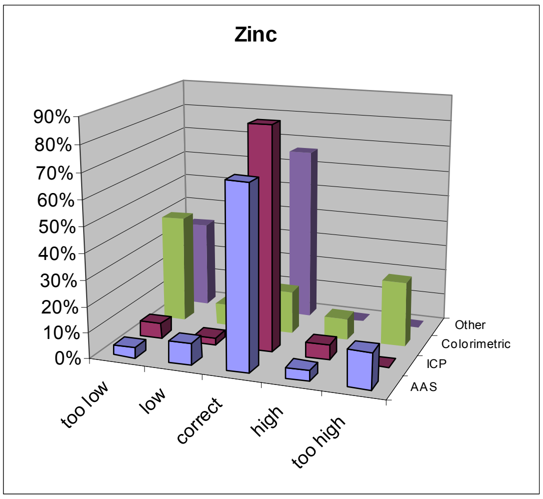
Comparison of methods



AQS Baden-Württemberg iswa

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Summary Zinc

- standard deviations ok
- percentage of outliers ok
- only a few bad performing lab

AQS Baden-Württemberg iswa

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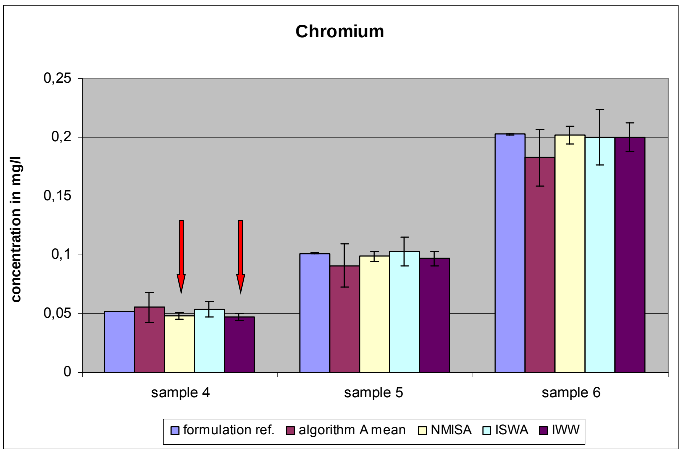
Chromium
Reference value and measurements



AQS Baden-Württemberg iswa

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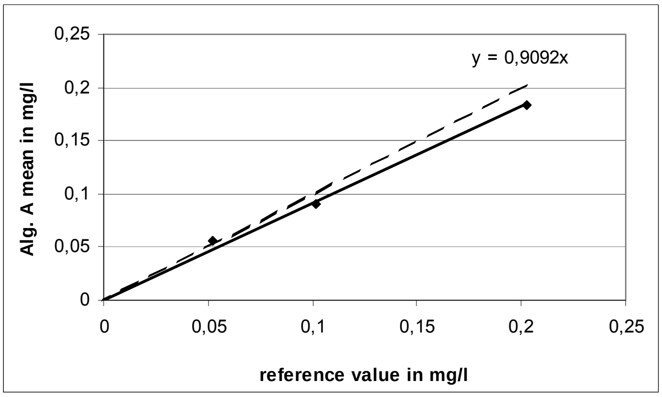
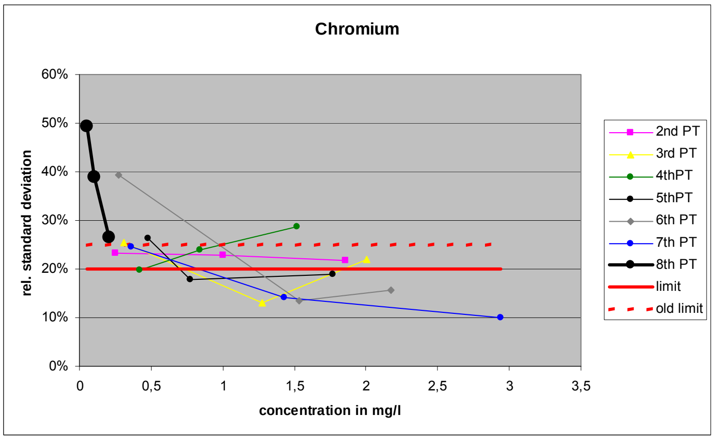
Chromium
mean vs. ref.-value



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

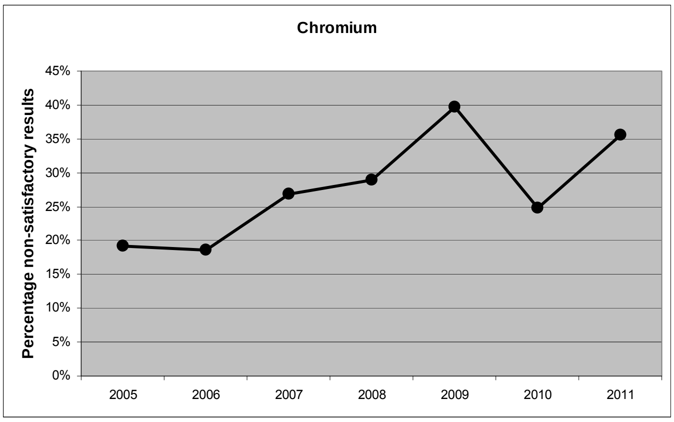
AQS Baden-Württemberg iswa

Chromium
calculated standard deviation and limit



low concentrations and lowered standard deviation limit
standard deviations are quite high

Chromium
Percentage non-satisfactory results



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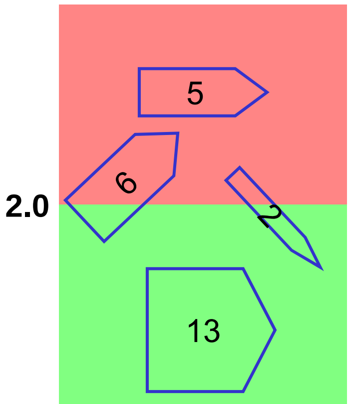
Chromium
Individual performance development



AQS Baden-Württemberg iswa

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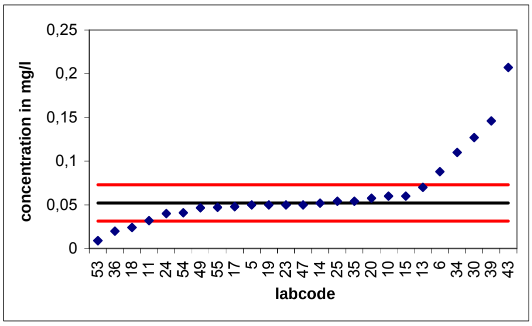
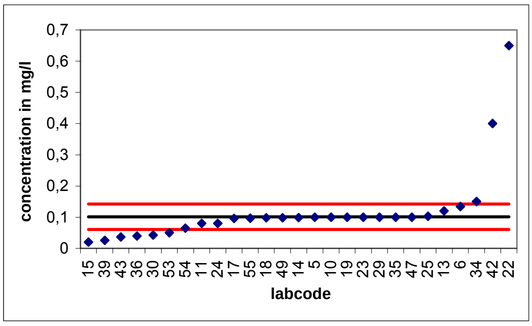
Chromium 1



values:	30
removed:	5
mean:	0,06
ref.-value:	0,05
recovery:	106,5%
std:	0,026
rstd:	49,4%
std limit:	20%
upper limit:	0,07
lower limit:	0,03
too high:	10
too low:	3
outside limits:	13

AQS Baden-Württemberg iswa

Chromium 2



values:	29
removed:	2
mean:	0,09
ref.-value:	0,10
recovery:	89,6%
std:	0,040
rstd:	39,0%
std limit:	20%
upper limit:	0,14
lower limit:	0,06
too high:	4
too low:	7
outside limits:	11

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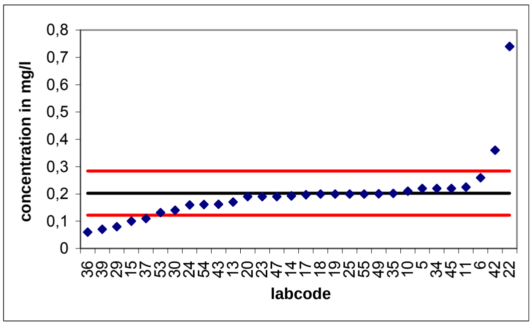
Chromium 3



values:	31
removed:	1
mean:	0,18
ref.-value:	0,20
recovery:	90,2%
std:	0,054
rstd:	26,5%
std limit:	20%
upper limit:	0,28
lower limit:	0,12
too high:	3
too low:	5
outside limits:	8

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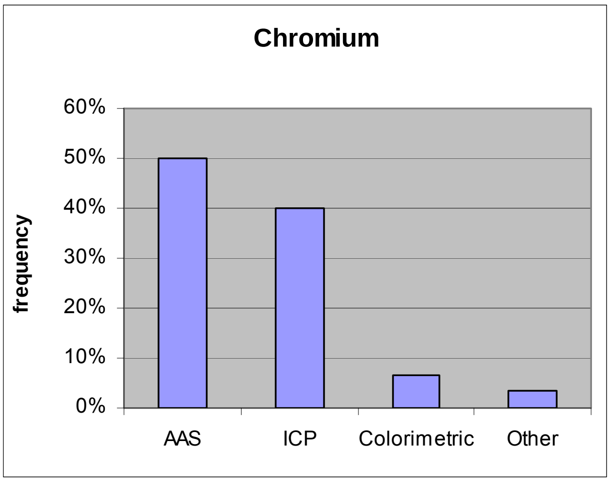
Used methods



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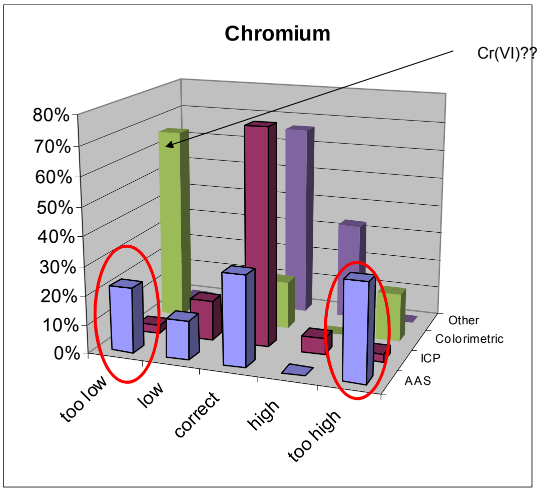
Comparison of methods



Cr(VI)?? exactly as in 2009 and 2010

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Summary Chromium

- low concentrations
- standard deviation limit lowered
- experimental standard deviations are still quite high

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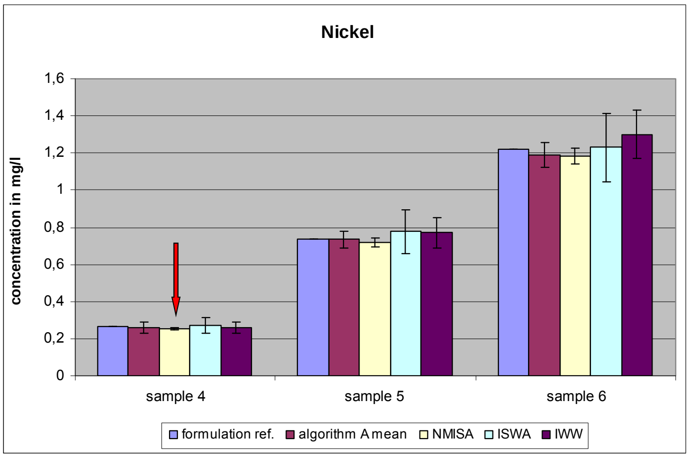
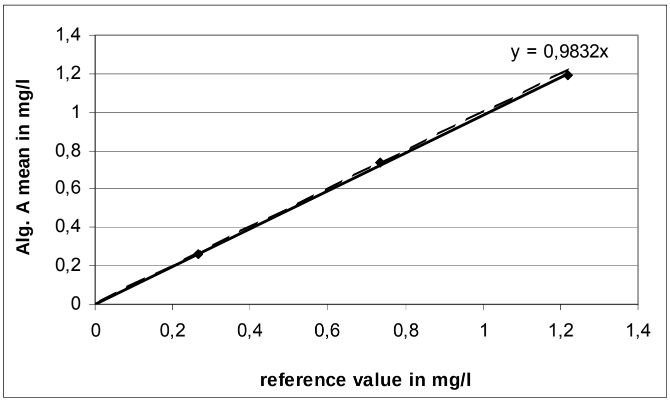
Nickel
Reference value and measurements

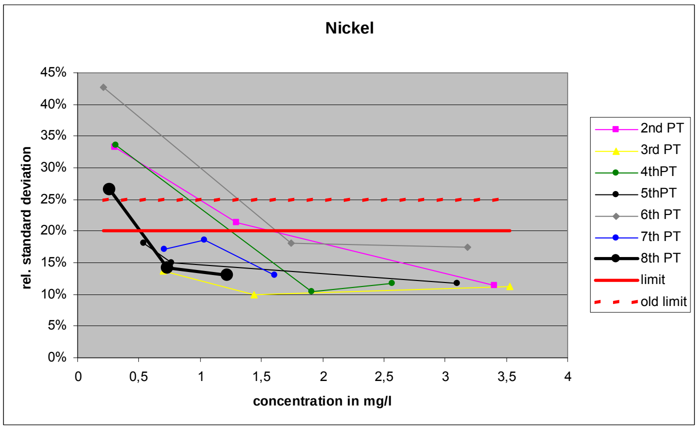


Nickel
mean vs. ref.-value



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

Nickel
calculated standard deviation and limit



low concentrations and lowered standard deviation limit

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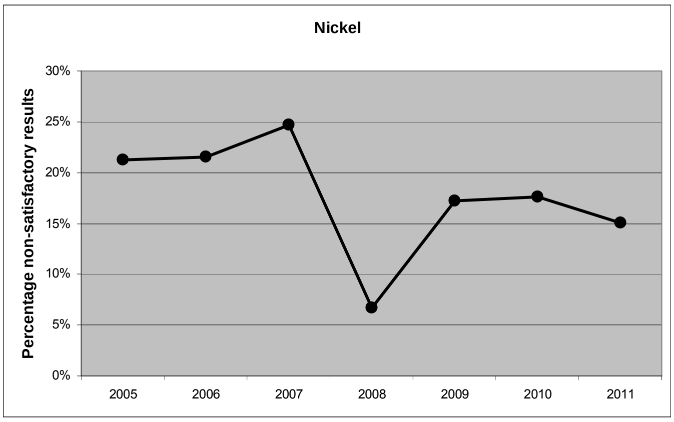
Nickel
Percentage non-satisfactory results



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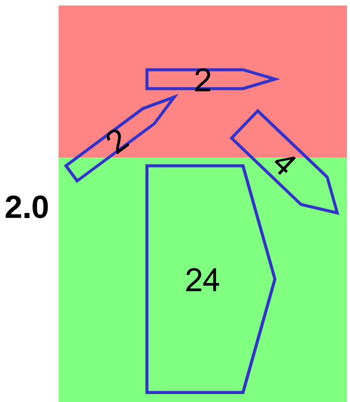
Nickel
Individual performance development



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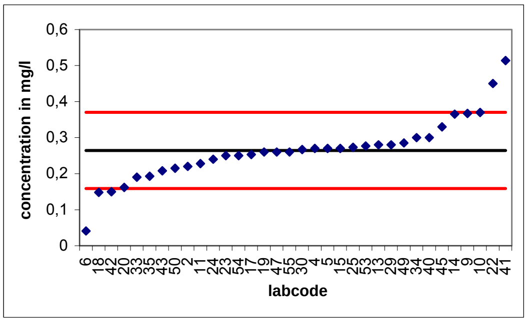
Nickel 1



values:	34
removed:	0
mean:	0,26
ref.-value:	0,26
recovery:	98,9%
std:	0,070
rstd:	26,5%
std limit:	20%
upper limit:	0,37
lower limit:	0,16
too high:	2
too low:	3
outside limits:	5

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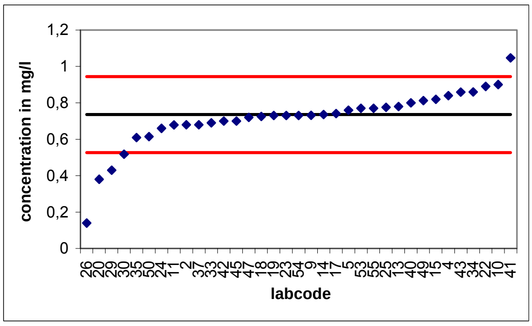
Nickel 2



values:	36
removed:	1
mean:	0,73
ref.-value:	0,74
recovery:	99,8%
std:	0,104
rstd:	14,2%
std limit:	20%
upper limit:	0,94
lower limit:	0,53
too high:	1
too low:	5
outside limits:	6

AQS Baden-Württemberg iswa

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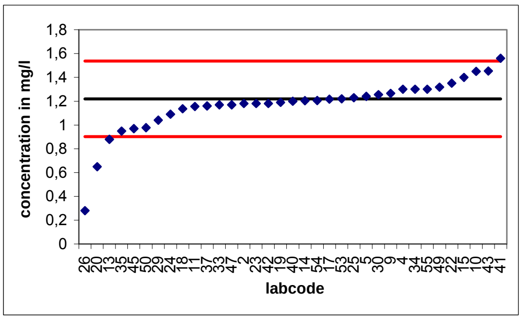
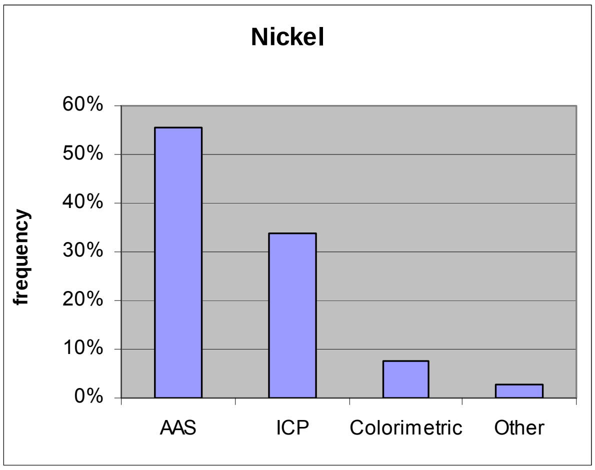
Nickel 3

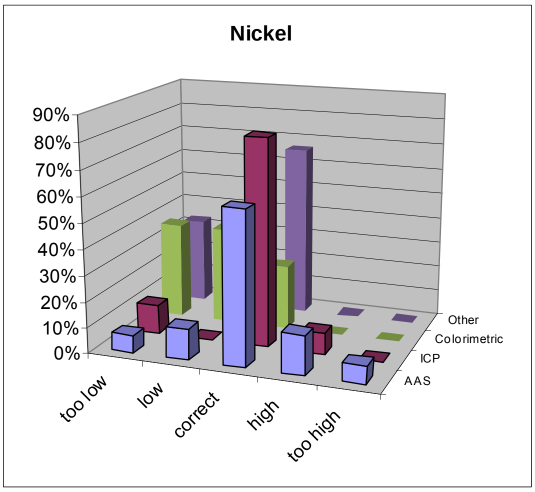


values:	**36**
removed:	**1**
mean:	**1,19**
ref.-value:	**1,22**
recovery:	**97,8%**
std:	**0,159**
rstd:	**13,0%**
std limit:	**20%**
upper limit:	**1,54**
lower limit:	**0,90**
too high:	**1**
too low:	**4**
outside limits:	**5**

Used methods



Comparison of methods



Summary Nickel

- despite of the low concentrations and the lowered standard deviation limit an improvement could be seen

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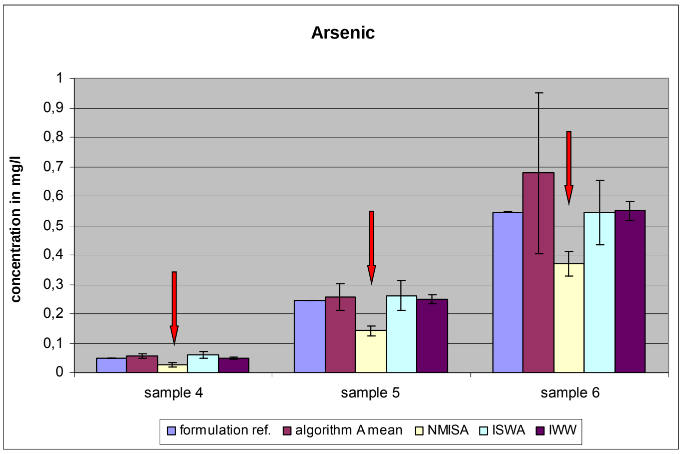
Arsenic
Reference value and measurements



NMISA results too low

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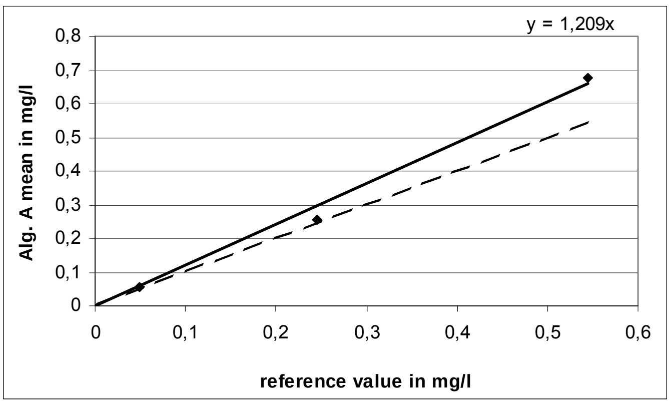
Arsenic
mean vs. ref.-value



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

regression line mainly determined by the highest value

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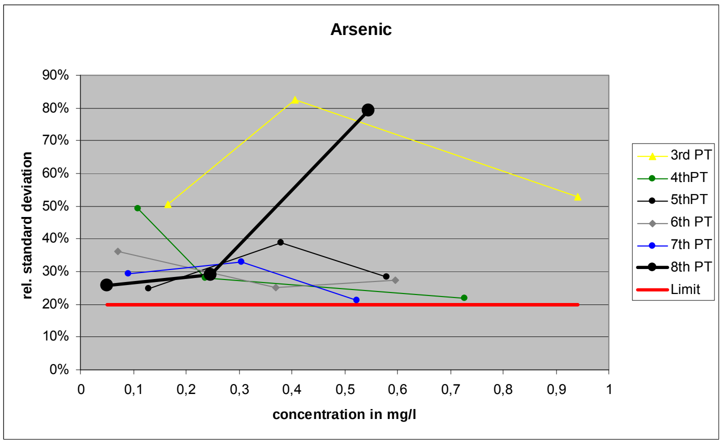
Arsenic
calculated standard deviation and limit



Standard deviation for the highest value level much too high

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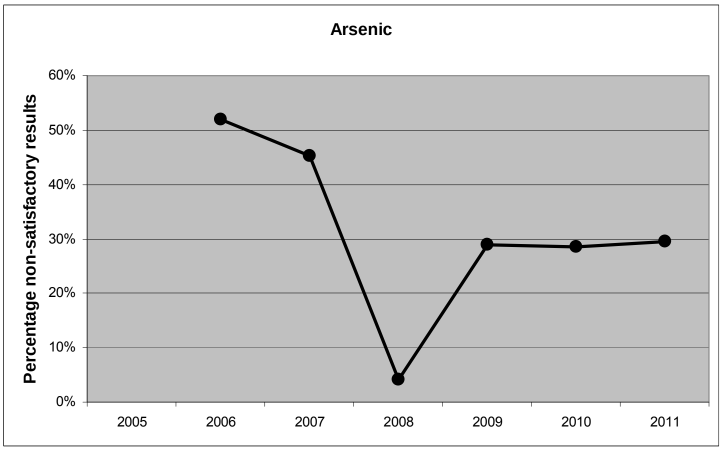
Arsenic
Percentage non-satisfactory results



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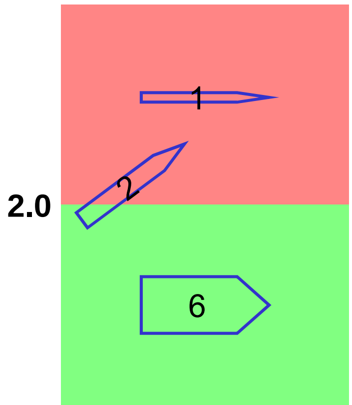
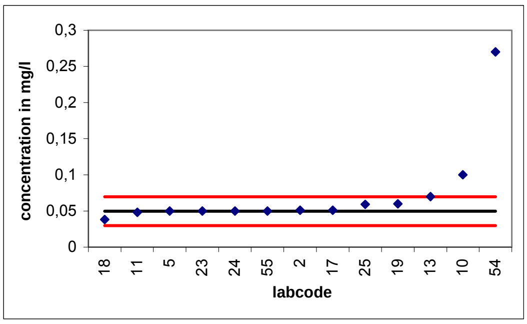
Arsenic
Individual performance development

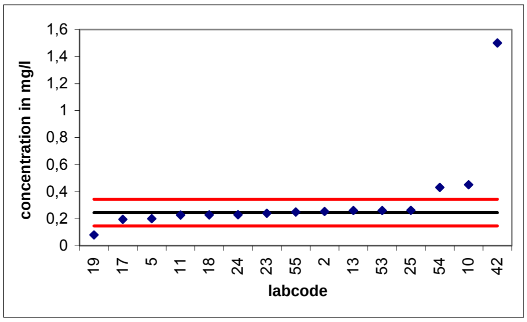


Arsenic 1



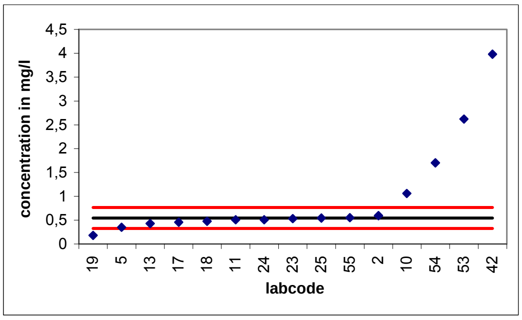
values:	**14**
removed:	**1**
mean:	**0,06**
ref.-value:	**0,05**
recovery:	**112,6%**
std:	**0,013**
rstd:	**25,9%**
std limit:	**20%**
upper limit:	**0,07**
lower limit:	**0,03**
too high:	**4**
too low:	**0**
outside limits:	**4**

Arsenic 2



values:	15
removed:	0
mean:	0,26
ref.-value:	0,25
recovery:	104,3%
std:	0,072
rstd:	29,1%
std limit:	20%
upper limit:	0,34
lower limit:	0,15
too high:	3
too low:	1
outside limits:	4

Arsenic 3



values:	15
removed:	0
mean:	0,68
ref.-value:	0,55
recovery:	124,3%
std:	0,432
rstd:	79,3%
std limit:	20%
upper limit:	0,76
lower limit:	0,33
too high:	4
too low:	1
outside limits:	5

high standard deviation caused by the four high results

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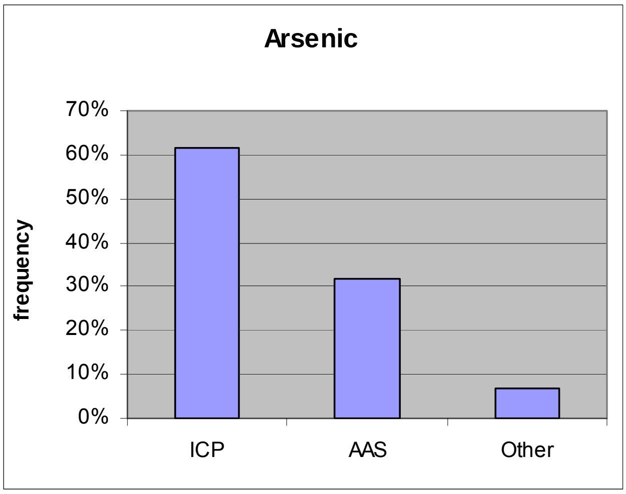
Used methods



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AQS Baden-Württemberg iswa

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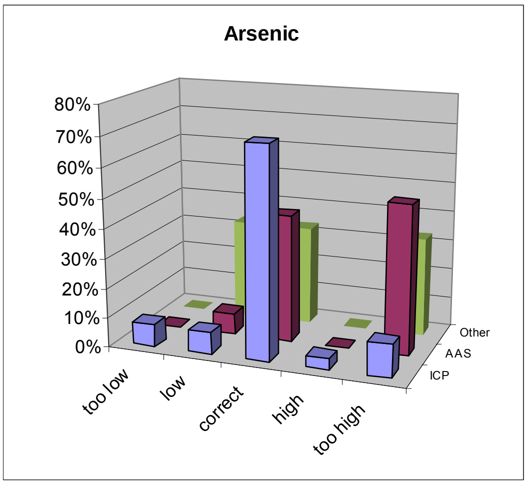
Comparison of methods



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Summary Arsenic

- low number of values
- high standard deviation estimate
- 30% of the values out-of-range

AQS Baden-Württemberg iswa

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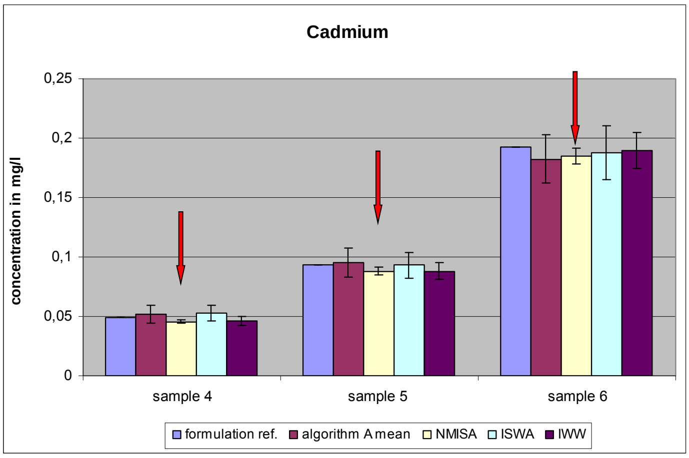
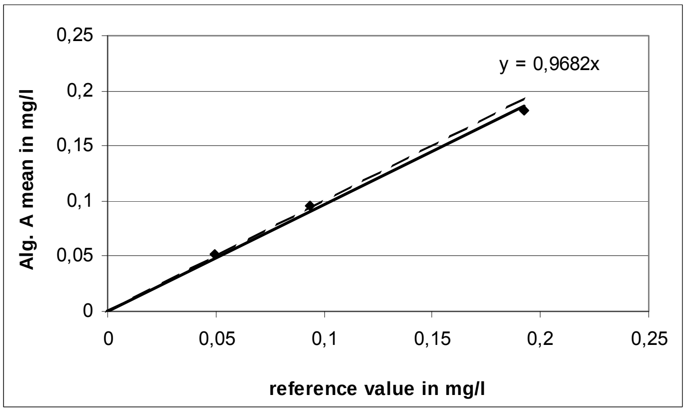
Cadmium
Reference value and measurements



AQS Baden-Württemberg iswa

Cadmium
mean vs. ref.-value



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

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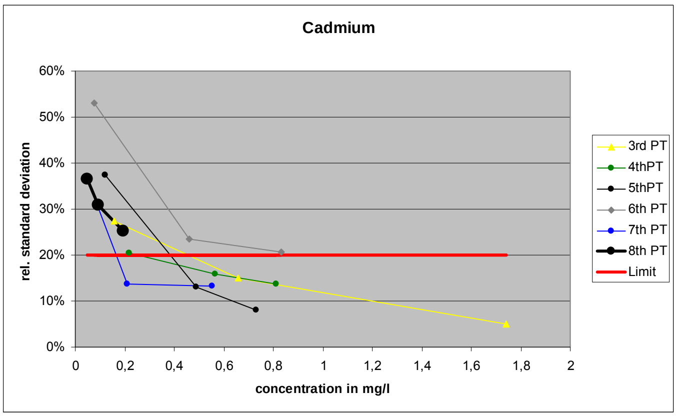
Cadmium
calculated standard deviation and limit



low concentrations

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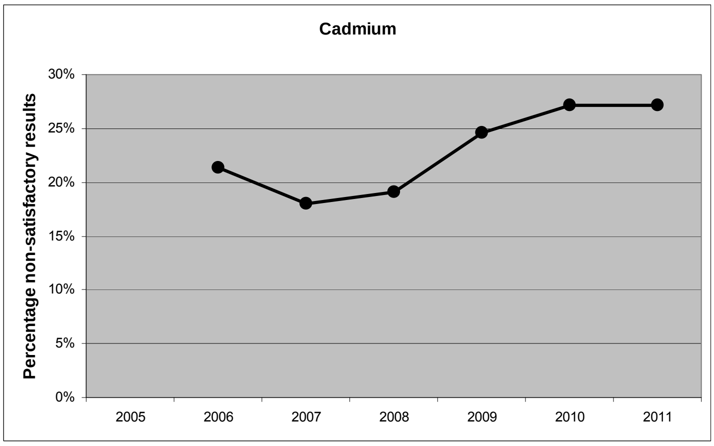
Cadmium
Percentage non-satisfactory results



AQS Baden-Württemberg iswa

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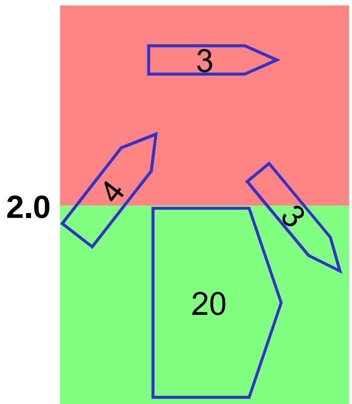
Cadmium
Individual performance development



AQS Baden-Württemberg iswa

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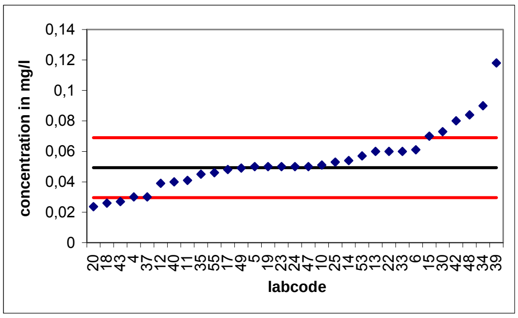
Cadmium 1



values:	**33**
removed:	**2**
mean:	**0,05**
ref.-value:	**0,05**
recovery:	**105,4%**
std:	**0,018**
rstd:	**36,4%**
std limit:	**20%**
upper limit:	**0,07**
lower limit:	**0,03**
too high:	**7**
too low:	**4**
outside limits:	**11**

AQS Baden-Württemberg iswa

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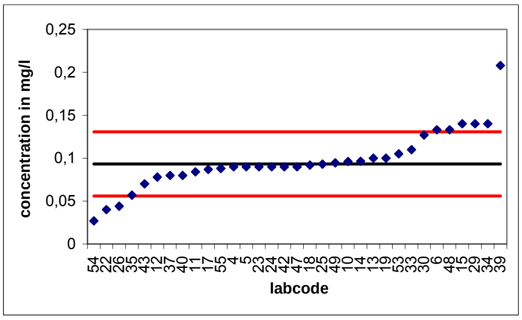
Cadmium 2



values:	**35**
removed:	**2**
mean:	**0,10**
ref.-value:	**0,09**
recovery:	**102,5%**
std:	**0,029**
rstd:	**30,8%**
std limit:	**20%**
upper limit:	**0,13**
lower limit:	**0,06**
too high:	**6**
too low:	**5**
outside limits:	**11**

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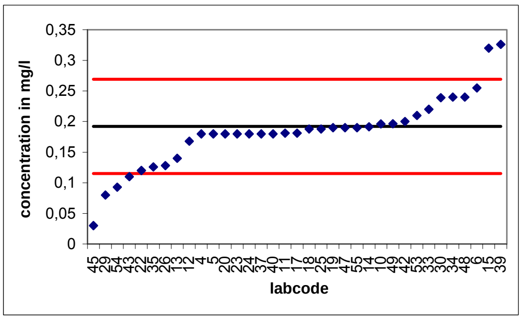
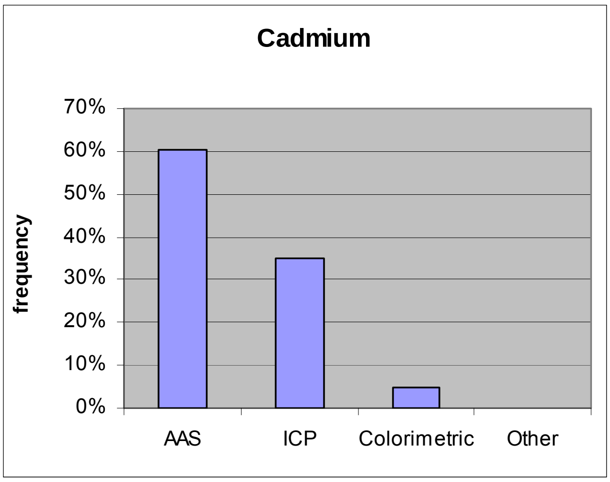
Cadmium 3



values:	35
removed:	0
mean:	0,18
ref.-value:	0,19
recovery:	94,9%
std:	0,048
rstd:	25,2%
std limit:	20%
upper limit:	0,27
lower limit:	0,12
too high:	2
too low:	4
outside limits:	6

Used methods



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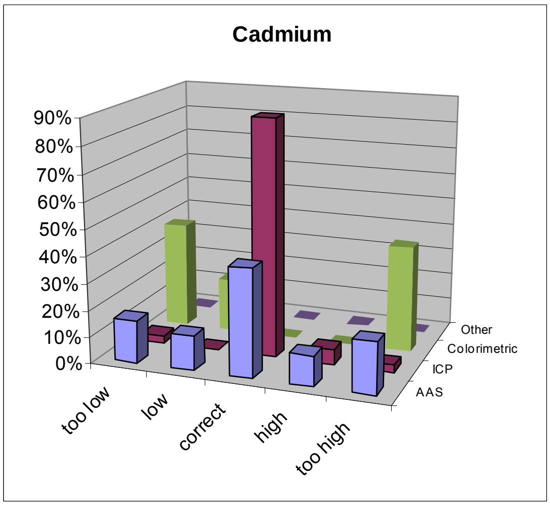
Comparison of methods



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Summary Cadmium

- low concentrations
- average standard deviation
- more or less constant performance

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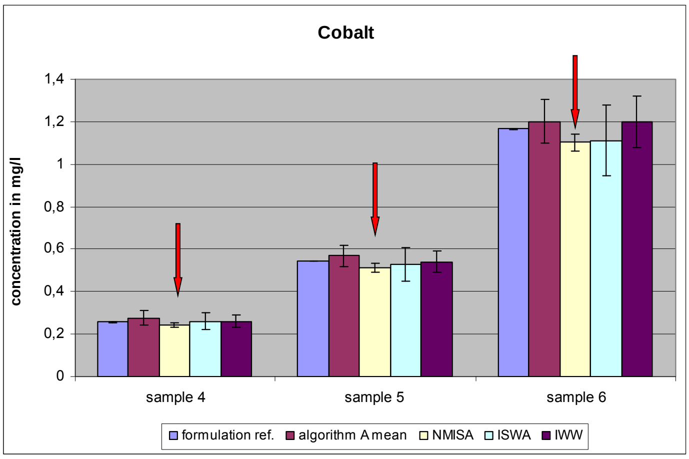
Cobalt
Reference value and measurements



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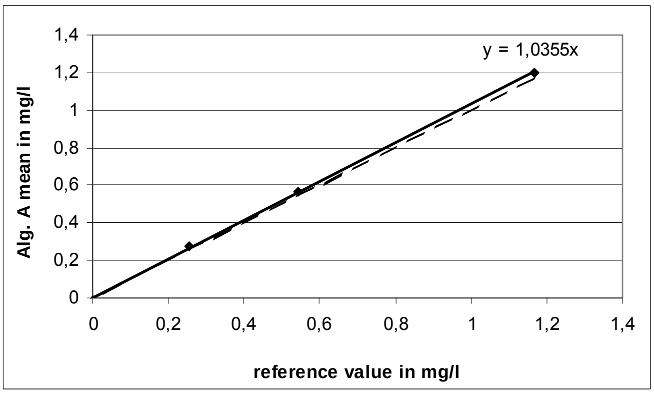
Cobalt
mean vs. ref.-value



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

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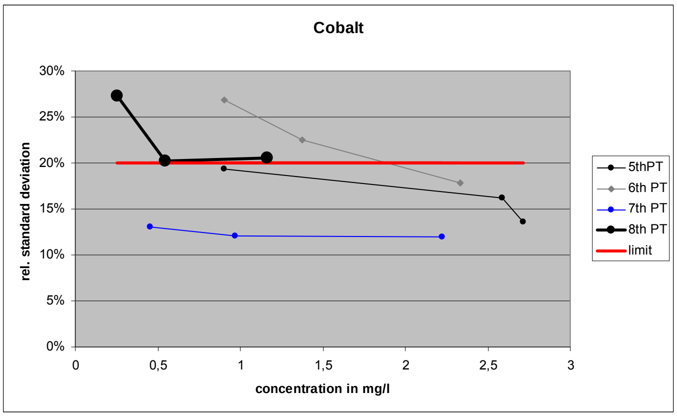
Cobalt
calculated standard deviation and limit



low concentrations – high standard deviation

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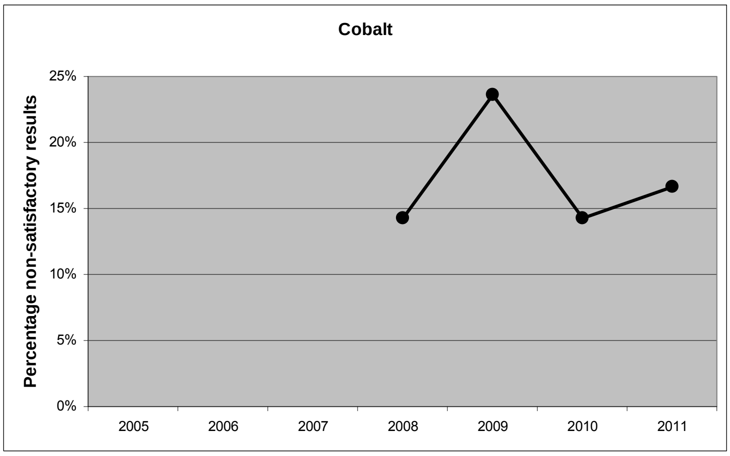
Cobalt
Percentage non-satisfactory results



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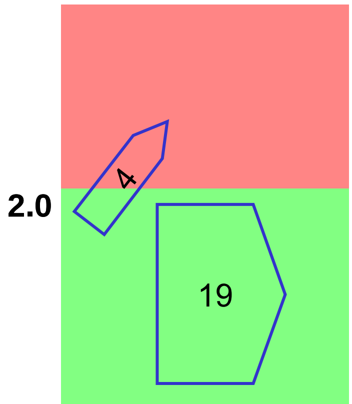
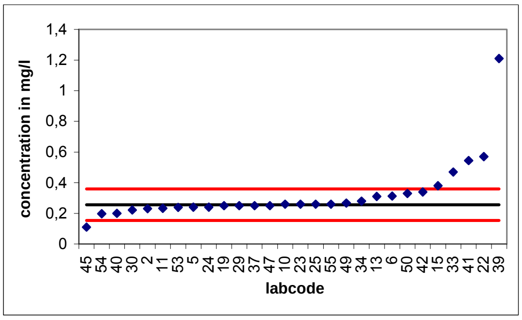
Cobalt
Individual performance development

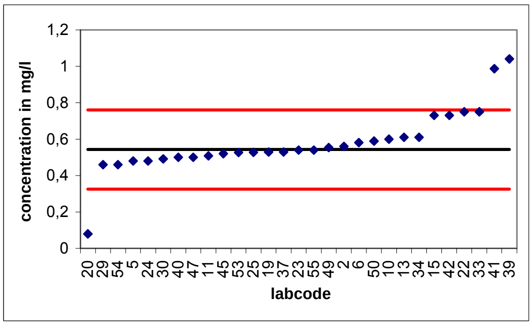


Cobalt 1



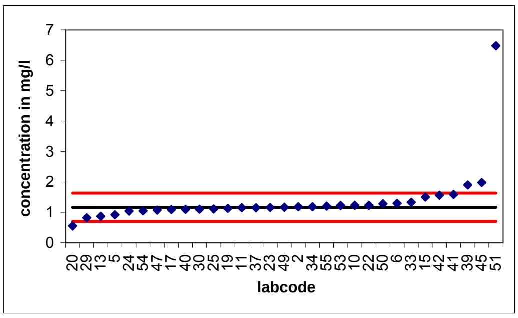
values:	**29**
removed:	**1**
mean:	**0,28**
ref.-value:	**0,26**
recovery:	**108,2%**
std:	**0,070**
rstd:	**27,3%**
std limit:	**20%**
upper limit:	**0,36**
lower limit:	**0,15**
too high:	**6**
too low:	**1**
outside limits:	**7**

Cobalt 2



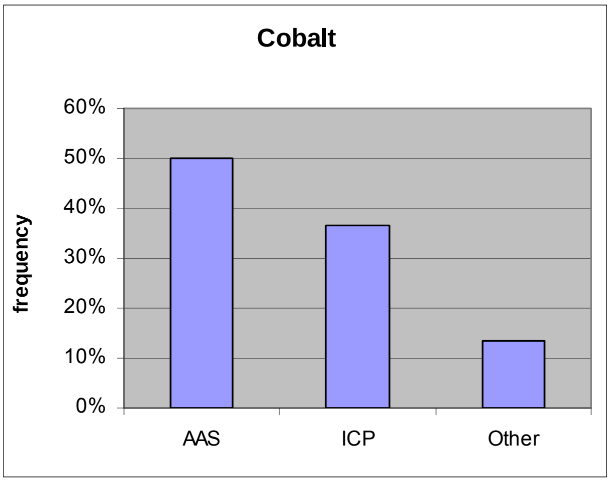
values:	**30**
removed:	**1**
mean:	**0,57**
ref.-value:	**0,54**
recovery:	**104,7%**
std:	**0,110**
rstd:	**20,2%**
std limit:	**20%**
upper limit:	**0,76**
lower limit:	**0,33**
too high:	**3**
too low:	**1**
outside limits:	**4**

Cobalt 3

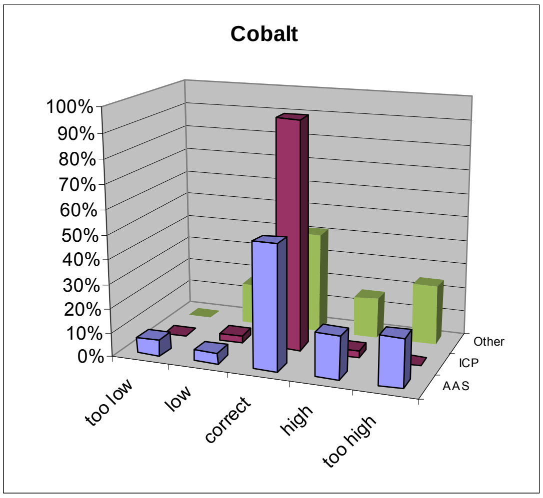


values:	**31**
removed:	**0**
mean:	**1,20**
ref.-value:	**1,17**
recovery:	**103,1%**
std:	**0,239**
rstd:	**20,5%**
std limit:	**20%**
upper limit:	**1,63**
lower limit:	**0,70**
too high:	**3**
too low:	**1**
outside limits:	**4**

Used methods



Comparison of methods



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Summary Cobalt

- standard deviation high
- but most labs are consistently well performing

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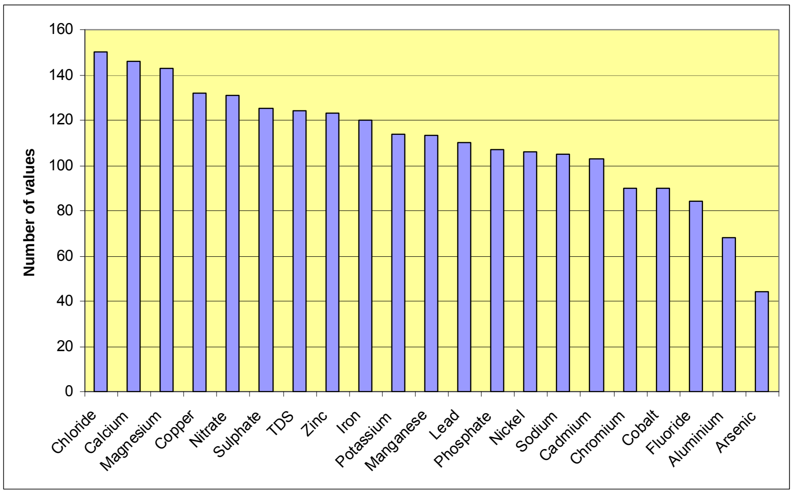
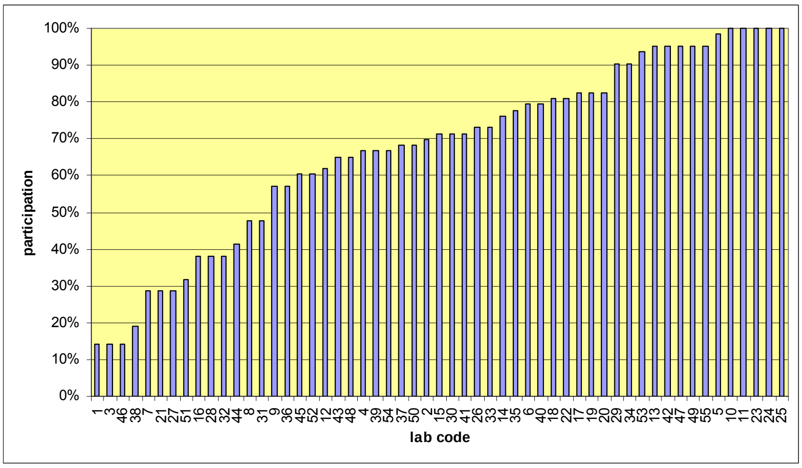
Number of values per parameter



Overview on participation



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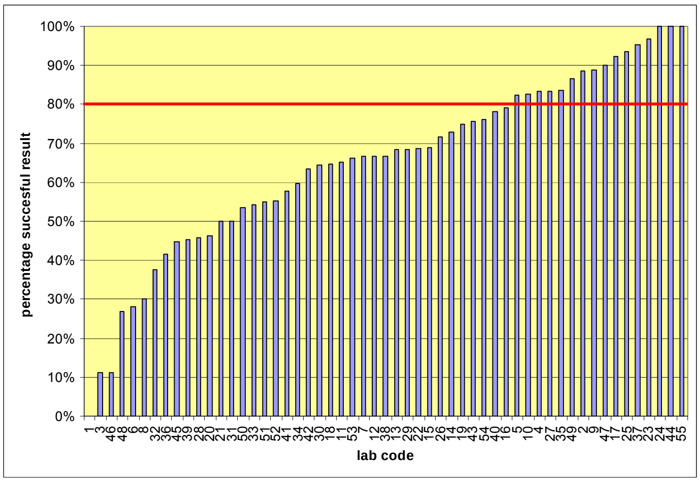
Overview on participants’ success



>80%:
in 2005 23,9 % of the labs
in 2006 25,6 % of the labs
in 2007 37,0 % of the labs
in 2008 35,6 % of the labs
in 2009 23,5 % of the labs
in 2010 45,8 % of the labs
in 2011 29,1 % of the labs

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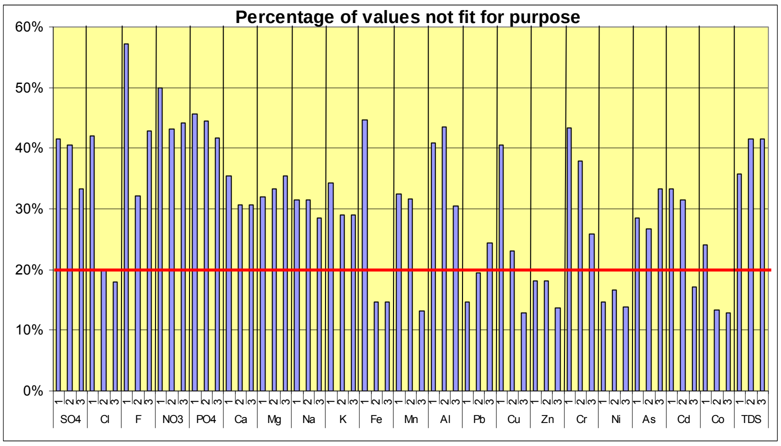
Values not fit for purpose

≤ 20%: in 2009 – 14
in 2010 – 20
in 2011 – 15



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Conclusion I

- Again the PT Provider did a very good job
- The evaluation and assessment procedure is fit for the purpose
- The SADCMET Water PT is a good possibility for the participants to compare with peers and with stated fitness-for-purpose criteria
- Overall the results of this PT round show a good performance for many labs, but the results of some laboratories continuously are not satisfactory or getting worse
- More emphasis should be put on corrective actions after unsatisfactory participation

Conclusion II

- Some participating labs seem to be resistant against advice; in an accreditation procedure they will wake up
- There should be a discussion
  - How to proceed with recommendation of suitable methods?
  - How to help laboratories to proper apply these methods?
  - How to convince the “resistant” labs that participating in PTs without corrective actions is waste of money and resources
- The gaps that prevent labs from proper application of the methods should be identified

Evaluation Questionnaire – Chemistry workshop

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

How do you judge:	Very good	good	fair	poor	very poor
The hotel (accommodation, food)	☐	☐	☐	☐	☐
The venue of the workshop (conference room)	☐	☐	☐	☐	☐

How do you judge the different parts of this workshop	Very useful 1	2	3	4	not useful 5
Training on trueness checks	☐	☐	☐	☐	☐
Training on Control Charts	☐	☐	☐	☐	☐
Local coordinators' reports	☐	☐	☐	☐	☐
Report on the follow-up of the ToT	☐	☐	☐	☐	☐
Reports from the SADCWaterLab working groups	☐	☐	☐	☐	☐
Report of the PT provider	☐	☐	☐	☐	☐
Evaluation of the chemistry PT	☐	☐	☐	☐	☐
Discussion about necessary changes in the PT scheme	☐	☐	☐	☐	☐
Discussion about the way to sustainability	☐	☐	☐	☐	☐
SADCWaterLab WGs "methods" and "training"	☐	☐	☐	☐	☐
SADCWaterLab General Assembly	☐	☐	☐	☐	☐

The five most important topics for me have been:

1) ....

2) ....

3) ....

4) ....

5) ....

Did the workshop fulfill your expectations? ☐ Yes ☐ No
If No, why not?

....

What benefits did you draw from the workshop?

....

Please use back side for any other comments