Workshop

Evaluation of the Pilot PT for Water Testing

Pretoria
1 – 2 November 2004

Report on the Workshop
Proficiency Testing for Water Testing Laboratories

Pretoria, South Africa, 1 – 2 November 2004

Prepared by Dr.-Ing. Michael Koch

Summary

Access to proper potable water is a human right. This is why the heads of governments agreed in 2002 in Johannesburg during the world summit for sustainable development on the goal to halve by 2015 the proportion of people without sustainable access to safe drinking water and basic sanitation. In the same direction targets the resolution of Evian where the 8 heads of states of the G8 countries adopted an action plan to improve proper water management in Africa. The improvement of water supply systems is crucial in the combat against worldwide poverty, to reduce the potential for conflicts and to strengthen the international security.

Concretely this means that sustainable concepts for the construction of satisfactory water supply systems for spread classes of society have to be developed in the concerned regions. In this process it is pivotal to investigate the pertinency of potential water resources in a very early stage of planning. For that purpose the execution of hydro geological investigations are of vital importance. Hydro geologists have to rely on water analysis, which are carried out in specialized water testing laboratories.

It is of advantage if these analysis can be carried out in local water testing laboratories. However, the experience gained during the implementation of projects in the water sector showed that the results of local water testing laboratories are sometimes unreliable with the consequence that in these cases unsuitable water resources are used within water supply systems. In these cases a negative impact on the health of the concerned population and high investments for a necessary after treatment of potable water can be the consequence.

Existing drinking water supply systems are also kept under surveillance by local laboratories. The special interest is here on the microbiological quality, where the water is analysed for pathogenic and potentially pathogenic germs. It is in the nature of these analyses, that they have to be especially reliable because peoples health depends on them.

But water analysis is a testing field, which has not only high influence on peoples health but on the total welfare of all people, because it also concerns the international trade, which suffers from incorrect analyses and the non-acceptance of results due to the absence of an accreditation of the laboratories.

The SADCMET pilot proficiency test has been carried out within the project "Support to SADC in implementing the SQAM-program", (**S**tandardisation, **Q**uality, **A**ccreditation, **M**etrology), which is implemented by the German Metrology Institute PTB on behalf the German Federal Ministry for Economic Cooperation and Development in cooperation with the SADC-secretariat and the SADC SQAM organisations SADCMET, SADCMEL, SADCA and SADCSTAN. It was an important component for the improvement of these analyses and a help for the laboratories on their way to accreditation. The PT showed weaknesses at the laboratories with regard to precision (too high standard deviations between laboratories) and trueness (bias of the

mean for some parameters). A big part of the participants was not able to reach the necessary limit of determination for the analysis of iron at the lowest level. This shows that there is a necessity to further support the laboratories with ongoing proficiency testing but also with training. As can be seen from the evaluation questionnaire for this workshop, this was also recognised by the participants themselves.

The PT activity therefore should be flanked by supportive activities for water testing laboratories to implement quality management systems, to increase their technical competence and to integrate them in a accreditation system. It would be of advantage if for these supportive activities the knowledge of analytical chemists, familiar with quality management systems, and hydro geologists could be made available.

The workshop in Pretoria reported here was an important component on the way to improve the analytical quality in the water testing laboratories.

It was possible to show the participants where the weaknesses of the analyses are and what could be possible causes. The participants showed to be highly motivated to tackle these problems. The workshop not only allowed the advice and training of the participants, but formed also the basis for a network between the laboratories in the different countries. This network will enable a mutual support between the labs.

The participants are also highly motivated to go further on this way. They are willing, as far as possible, to bear the costs for these proficiency tests. The next PT is planned to be organised in march 2005. Financial support is necessary only to pay for the transportation costs to the national coordinator, which are very high because of the unfavourable geographical conditions.

The general conditions for this PT, which is extended compared with the pilot PT, were arranged during this workshop.

To optimize the mutual support it was decided to establish an “Association of Water Testing Labs in the SADC Countries”. The participants of the pilot PT are supposed to be the preliminary steering committee and the SADCMET secretary is willing to hold also the secretariat of this new association.

The assurance of the quality of microbiological analyses is also very important for the laboratories. The results of these analyses have a direct influence on peoples health (drinking water is an important infection path for diseases). It is therefore considered to be very urgent to assure this analyses via proficiency testing, to uncover weaknesses und to offer assistance to the laboratories. For practical implementation it is recommended to train a potential PT provider in southern Africa in Germany first. After a preparation phase for the PT in Africa it would be helpful during the organisation and preparation of the samples to have support from an experienced German expert on site.

In summary it can be said that the implementation of a PT system for water testing laboratories in the SADC countries up to now was a big success. The laboratories are highly motivated, to do their best to push the process of quality enhancement.

The opportunity should be taken to support the laboratories on this way.

Zusammenfassung

Der Zugang zu geeignetem Trinkwasser ist ein Menschenrecht. Deshalb haben sich die Regierungschef auf dem Weltgipfel für nachhaltige Entwicklung 2002 in Johannesburg auf das Ziel geeinigt, den Anteil der Bevölkerung ohne nachhaltigen Zugang zu sicherem Grundwasser und grundlegenden sanitären Einrichtungen bis zum Jahre 2015 zu halbieren. In dieselbe Richtung zielt die Resolution von Evian, in der die 8 Staatsoberhäupter der G8 Staaten einen Aktionsplan zur Verbesserung des Wassermanagements in Afrika verabschiedeten. Die Verbesserung der Wasserversorgungssysteme ist entscheidend im Kampf gegen die weltweite Armut. Sie reduziert das Konfliktpotential und stärkt damit die internationale Sicherheit.

Konkret bedeutet das, dass nachhaltige Konzepte für den Aufbau geeigneter Wasserversorgungssysteme für alle Gesellschaftsschichten in den betroffenen Regionen aufgebaut werden müssen. In diesem Prozess ist es unverzichtbar, die Eignung der Wasservorkommen in einem sehr frühen Stadium der Planung zu untersuchen. Dafür ist die Durchführung hydrogeologischer Untersuchungen von vitalem Interesse. Die Hydrogeologen müssen sich jedoch auf die Wasseranalysen verlassen können, die von den darauf spezialisierten Laboratorien durchgeführt werden.

Es ist von Vorteil, wenn diese Analysen in einem lokalen Wasserlabor durchgeführt werden können. Die Erfahrungen, die während der Durchführung dieser Projekte im Wassersektor gesammelt wurden, zeigen jedoch, dass die Ergebnisse der lokalen Wasserlaboratorien manchmal unzuverlässig sind. In solchen Fällen kann eine negative Auswirkung auf die Gesundheit der betroffenen Bevölkerung und hohe Investitionen für eine notwendige Nachbehandlung des Trinkwassers die Folge sein.

Auch bestehende Trinkwasserversorgungssysteme werden von den lokalen Laboratorien untersucht. Von besonderem Interesse ist dabei auch die mikrobiologische Qualität des Wassers, bei der das Wasser auf das Vorhandensein potentieller oder tatsächlicher Krankheitserreger geprüft wird. Es liegt in der Natur der Sache, dass auf die Ergebnisse dieser Untersuchungen aus Gründen des Gesundheitsschutzes für die Bevölkerung Verlass sein muss.

Die Wasseranalytik ist ein Prüfgebiet, dessen Ergebnisse großen Einfluss auf das Wohl der Bevölkerung haben. Dies beginnt bei den direkten Einwirkungen auf die Gesundheit (Trinkwasseruntersuchungen), erstreckt sich aber auch auf den Handel, der unter fehlerhaften Analysen und der Nichtakzeptanz von Analysenergebnissen aufgrund fehlender Akkreditierung der Laboratorien leidet.

Der SADCMET Pilotringversuch wurde durchgeführt im Rahmen des Projekts „Unterstützung der SADC bei der Einführung eines SQAM-Programms“ (**S**tandardisation, **Q**uality, **A**ccreditation, **M**etrology), das von der Physikalisch-technischen Bundesanstalt im Auftrag des Bundesministerium für wirtschaftliche Zusammenarbeit und Entwicklung in Zusammenarbeit mit dem SADC-Sekretariat und den SADC SQAM-Organisationen SADCMET, SADCMEL, SADCA und SADCSTAN ausgeführt wird. Er war ein wichtiger Baustein zur Verbesserung dieser Analytik und eine Hilfe für die Laboratorien auf ihrem Weg zu einer Akkreditierung. Der Ringversuch zeigte Schwächen bei den Laboratorien sowohl hinsichtlich der Präzision (zu große Vergleichsstandardabweichungen) als auch hinsichtlich der Richtigkeit (systematische Abweichungen des Mittelwerts für einige Parameter). Im Falle der Eisenbestimmung konnte eine große Anzahl der Teilnehmer auch die erwartete Bestimmungsgrenze nicht erreichen. Dies zeigt, dass ein Bedarf besteht für eine weitere Unterstützung dieser

Laboratorien, durch die Fortsetzung des Ringversuchsprogramms, aber auch durch Fortbildung des Personals. Wie man aus den Ergebnissen des Fragebogens zu diesem Workshop ablesen kann, haben die Laboratorien dies auch selbst erkannt.

Die Ringversuchsaktivitäten sollten daher durch flankierende Maßnahmen unterstützt werden, die den Laboratorien helfen Qualitätsmanagementsysteme aufzubauen, ihre technische Kompetenz zu verbessern und sie in ein Akkreditierungssystem zu integrieren. Es wäre vorteilhaft, wenn für diese unterstützenden Maßnahmen die Fachkenntnisse von analytischen Chemikern, die mit Qualitätsmanagementsystemen vertraut sind, und von Hydrogeologen verfügbar gemacht werden könnten.

Der Workshop in Pretoria, über den hier berichtet wird, war ein wichtiger Baustein zur Verbesserung der Qualität der Wasserlaboratorien. Den Teilnehmern des Workshops konnte gezeigt werden, wo die Schwachstellen der Analytik liegen und welches die möglichen Ursachen sind. Die Teilnehmer zeigten sich hoch motiviert, diese Probleme anzugehen. Der Workshop ermöglichte nicht nur die Beratung und Schulung der Teilnehmer, sondern bildete vor allem die Basis für die Bildung eines Netzwerks zwischen den Laboratorien der unterschiedlichen Ländern, das es ihnen ermöglichen kann, sich gegenseitig zu unterstützen.

Die Teilnehmer sind hoch motiviert, auf dem eingeschlagenen Weg weiter zu gehen. Sie sind auch bereit, im Rahmen ihrer Möglichkeiten, die Kosten für diese Ringversuche selbst zu tragen. Ein nächster Ringversuch zur chemischen Analytik ist für März 2005 geplant. Eine finanzielle Unterstützung ist lediglich für die Begleichung der aus geographischen Gründen sehr hohen Transportkosten vom Ringversuchsveranstalter zum jeweiligen nationalen Koordinator notwendig. Die Rahmenbedingungen für diesen gegenüber dem Pilot-Ringversuch erweiterten Ringversuch wurden während des Workshops abgesprochen.

Um die gegenseitige Unterstützung zu optimieren, wurde beschlossen eine „Vereinigung der Wasserprüflaboratorien in den SADC-Ländern“ zu gründen. Die Teilnehmer des Pilot-Ringversuchs sollen dabei die vorläufige Lenkungsgruppe bilden und das SADCMET-Sekretariat ist bereit, auch für diese Vereinigung das Sekretariat zu übernehmen.

Ganz besonders wichtig für die Laboratorien ist die Sicherung der Qualität der mikrobiologischen Analysen. Die Ergebnisse dieser Untersuchungen haben einen noch direkteren Effekt auf die Gesundheit der Bevölkerung (Trinkwasser ist ein Übertragungsweg für Krankheiten). Es wird daher als sehr dringend angesehen, auch diese Analytik über Ringversuche abzusichern, Schwachstellen aufzuzeigen und Hilfen bei der Durchführung der Analysen anzubieten. Für die praktische Umsetzung wird empfohlen, den potentiellen Ringversuchsveranstalter im südlichen Afrika zunächst in Deutschland diesbezüglich zu schulen. Nach einer Vorbereitungsphase für den Ringversuch in Afrika wäre es hilfreich, bei der eigentlichen Durchführung des Ringversuchs Unterstützung durch eine deutsche Fachkraft vor Ort zu haben.

Zusammenfassend kann gesagt werden, dass die Implementierung eines Ringversuchssystems für Wasserlaboratorien in den SADC-Ländern bislang ein großer Erfolg war. Die Laboratorien sind hoch motiviert, alles Ihnen Mögliche dazu beizutragen, den Prozess der Qualitätsverbesserung voranzutreiben. Diese Chance sollte ergriffen werden, indem die Laboratorien hier unterstützt werden.

Introduction

The workshop reported here was a follow-up of a previous workshop held in Windhuk, Namibia in February 2004 (see annex 1 and the report on the windhuk workshop, available from http://www.sadcmet.org). As a result of this first workshop a pilot proficiency test for water testing laboratories was organised. The workshop in Pretoria was to evaluate and assess this first PT and to find ways forward to a regular PT system and other supportive measures.

Participants and Organisation

The workshop was attended by 23 participants from the following countries:

- Angola 1
- Botswana 2
- Ethiopia 1
- Kenya 2
- Lesotho 1
- Malawi 2
- Mauritius 1
- Mozambique 2
- Namibia 2
- Seychelles 1
- South Africa 1
- Swaziland 1
- Tanzania 2
- Uganda 1
- Zambia 1
- Zimbabwe 2

The Workshop was organised by

Dr. Mukayi Musarurwa, CSIR, South Africa
Dr. Michael Koch, Universität Stuttgart, Germany

and leaded by

Dr. Michael Koch, Universität Stuttgart, Germany

Additional presentations were given by

Merle Smuts, Umgeni Waters, Pietermaritzburg, South Africa

A complete list of participants is given in Annex 2.

Workshop Programme

Day 1 – The Pilot-PT

Morning-Session – 08:30 to 13:00 (with break from 10:00 to 10:30):

- ***M. Musarurwa***: Opening
- ***M. Smuts***: Experiences of the PT provider – planning, sample preparation, sample distribution, problems
- ***All Participants***: Experiences of participants – logistic problems, analytical problems
- ***M. Smuts***: Preliminary evaluation and assessment

Afternoon-Session – 14:00 to 17:30 (with break from 15:00 to 15:30):

- ***M. Koch***: Comparison of different evaluation and assessment methods
- ***M. Koch***: Fitness for purpose – discussion about quality goals and consequences of bad results in routine analysis
- ***M. Smuts and M. Koch***: Method comparison, possible error sources

All: Decision about the most appropriate evaluation and assessment method

Day 2 – The way forward

Morning-Session – 08:30 to 13:00 (with break from 10:00 to 10:30):

- Discussion in working groups:
  Evaluation of the Pilot PT: benefits - weak points, what should be kept for future PTs? What should be changed? Is the PT a help on the way to accreditation? Are the costs appropriate?
- Summary for the Pilot PT
- Are there laboratories that didn't participate? Why not?
- Discussion in working groups:
  How can the participants help each other? Is a SADC Laboratory Association possible? First steps? What other measures can be taken to improve quality of measurements? Parameters for the next chemistry PT?
- Microbiological PT – possibilities and challenges? Which parameters are desirable – which are possible? Possibilities of know-how transfer from Germany to the SADC region.

Lab tours to NML and SABS – 14:30 to 16:30

Evening braai (sponsored by NML) – 18:00 – 21:00

Monday, 01 November 2004

Opening

The Workshop was opened at 8:30 by Dr. Michael Koch.

M. Smuts: Experiences of the PT provider – planning, sample preparation, sample distribution, problems

Merle Smuts reported about her experiences in the Pilot PT (Annex 3). The planning for the PT mainly was made during the workshop in Namibia. The realization was financially made possible with support from PTB, Germany. The selection of bottles was controlled by the availability in South Africa. After consultation with experts in Germany it was decided to distribute the original samples and not concentrates, although this raised the transportation costs.
Mrs. Smuts calculated the amounts for the spiking of the samples and the total volume required to supply all participants with samples. She prepared a result template to distribute together with the samples. DHL was chosen as courier to ensure the fastest possible delivery of the samples although this carrier was very expensive.
For the preparation of samples laboratory grade water was spiked with chemicals as shown in the following table:

		Cation samples (constituted to 25L)		
Determinand	**Chemical**	**2004/06/1**	**2004/06/2**	**2004/06/3**
Calcium	$CaCl_2 \cdot 2H_20$	2.3489 g	4.4224 g	7.0465 g
Magnesium	$MgCl_2 \cdot 6H_20$	2.7041 g	4.3243 g	9.8145 g
Sodium	NaCl	0.6726 g	1.6555 g	3.2398 g
Potassium	KCl	0.1638 g	0.3658 g	0.4620 g
Iron	Fe Spectroscopic Grade Stock Solution (1000 mg/L)	2.50 mL	30.0 mL	100 mL
Manganese	Mn Spectroscopic Grade Stock Solution (1000 mg/L)	2.50 mL	10.0 mL	25.0 mL
Aluminium	Al Spectroscopic Grade Stock Solution (1000 mg/L)	2.50 mL	15.0 mL	25.0 mL
Preservative	HNO_3 (conc)	37.5 mL	37.5 mL	37.5 mL

		Anion samples (constituted to 25L)		
Determinand	**Chemical**	**2004/06/4**	**2004/06/5**	**2004/06/6**
Sulphate	K_2SO_4	0.7521 g	1.2808 g	2.2274 g
Chloride	KCl	1.5316 g	2.2499 g	3.4558 g
Fluoride	NaF	0.6517g in 500mL water (Stock) 5.00mL Stock used	2.0127g in 500mL water (Stock) 5.00mL Stock used	2.0127g in 500mL water (Stock) 20.0mL Stock used
Nitrate	KNO_3	0.3831 g	0.6401 g	1.265 g

With this procedure a good estimate for the “true” value can be obtained from the weighing.
25 litre for each sample were prepared, thoroughly mixed, dispensed in bottles and labelled. Cations samples were stabilized using nitric acid, no preservation was made for anions.
For homogeneity check the first and the last dispensed sample was analysed at least 6 times each. For stability check these samples were analysed after 5 weeks again. No significant difference could be found using the F-Test.
Prior to shipping the customs documentation has to be completed.
Unexpectedly customs were no problem for this PT. All samples arrived at the laboratories within five days.

24 out of 27 participating laboratories reported results. One lab didn't report results because these chemical analyses were not routinely carried out, one lab had an instrumental breakdown and one lab didn't answer at all.
The result were sent back mainly by e-mail, some by fax.
A preliminary evaluation was done using simple robust methods. The median was used as assigned value and the normalized interquartile range (difference between 1st and 3rd quartile, normalised using a factor 0.7413) was used as standard deviation to calculate Z-scores.
The PT provider encountered no problems that hindered the progress, no problems occurred with the courier and fortunately no problems with customs. In some cases technical communication problems between PT provider and participants had to be overcome.

All Participants: Experiences of participants – logistic problems, analytical problems

All participants in general were very happy with the PT. The samples arrived at the labs in almost all cases in good condition. Only one bottle was leaking and one package was opened.
The participants expressed their gratitude to have to possibility to participate in such a PT. Participation was seen as a good opportunity and motivation for the improvement of the analytical quality.

M. Smuts: Preliminary evaluation and assessment

Merle Smuts explained (annex 4), how she made the preliminary evaluation using the median as assigned value and the normalized interquartile range to calculate Z-scores. She presented lists of all Z-scores for each parameter and each laboratory and the parameter assessment for each laboratory. For an assessment as "successful" two of the three Z-scores had to be in the range between –2 and 2.
She showed a graphical display of the percentage of successfully analysed parameters per laboratory. 58% of the laboratories (14 out of 24) analysed 80% or more of the parameters, in which they took part, successfully.
Mrs. Smuts distributed a preliminary evaluation report to each participant. An example can be found in annex 5

M. Koch: Comparison of different evaluation and assessment procedures

Dr. Koch used 5 different methods for evaluation and assessment to prepare a comparison between these procedures (see annex 6):

- Method 1: Hampel-estimator/q-method for calculation of the statistical parameters mean and standard deviation and use of Z_U-scores, i.e. modified Z-scores, for the assessment. This method is described in DIN 38402-A45 and used for water PTs in Germany.
- Method 2: Median / normalized interquartile range and Z-scores. These robust methods were used by the provider of the pilot PT for preliminary assessment.
- Method 3: Algorithm A. This method, described and recommended in ISO/FDIS 13528, is also recommended in the draft for the new "International harmonized protocol for the proficiency testing of (chemical) analytical laboratories". It is uses the Huber estimator for the calculation of the mean and a robust method derived from that for the estimation of standard deviation.

- Method 4: Conventional statistics (arithmetic mean and standard deviation) after outlier elimination via Grubbs test. Assessment with Z-score.
- Method 5: identical with method 1, but with limitation of the standard deviation based on experience from previous PTs in Germany and fitness for purpose criteria. The standard deviation first was calculated as in method 1, but if this value exceeds the limit, this limit is chosen for calculation of Z_U-scores instead of the standard deviation. The following limits were used
    - Sulphate: 8%
    - Chloride: 9%
    - Ca, Mg, Na, nitrate: 10%
    - K, Fe, fluoride: 12%
    - Mn: 15%
    - Al: 30%

In some cases it can be seen that the distribution of data is not normal but skewed. The 4 different statistical procedures showed that in most cases the **mean values lay close together**, but sometimes there were **big differences in the estimated standard deviation**, although all methods are widely accepted by the scientific community.
The standard deviations in many cases are too high, not fit for the purpose. So, if the calculated standard deviations are used for the assessment, this gives a **falsely good impression of the quality of the analyses**. In addition the comparison between spiked amounts and the mean of the participants results **for some parameters** showed a **strong bias of the analytical results**. In this case a reference value should be preferred as assigned value.
It could be seen from the calculated standard deviations that for the parameters iron the lowest level was below the limit of determination for most of the laboratories.

M. Koch: Fitness for purpose – discussion about quality goals and consequences of bad results in routine analysis

Quality of analytical measurements is sufficient, if the accuracy of the results is fit for the purpose. In a strong sense these fit-for-purpose-criteria have to be set by the customer. For water analyses this is often very difficult, because either the customer is not able to define such criteria or there is no concrete customer, that could do this job. Dr. Koch gave hints from previous interlaboratory tests for proficiency testing as well as for method validation and from other sources like the European drinking water regulations (see annex 7). For each parameter of the pilot PT it was discussed with the participants, what the appropriate quality goal for the standard deviation could be, in order to define limits for the value which is used for the calculation of z-scores. In future proficiency testing rounds these limit will be applied. The participants agreed on the following limits:

- Calcium: 10%
- Magnesium: 10%
- Sodium: 10%
- Potassium: 10%
- Iron: > 1 mg/l: 12%
< 1 mg/l: 20%
- Manganese: > 0.5 mg/l: 12%
< 0.5 mg/l: 20%
- Aluminium: 30%
- Sulphate: 10%
- Chloride: 10%
- Fluoride: > 0.5 mg/l: 12%
< 0.5 mg/l: 20%
- Nitrate: 15%

M. Koch: Method comparison, possible error sources

Dr. Koch presented a comparison between the different methods applied by the participants (annex 8). Sometimes it was difficult to identify from the specifications of the participants which method really was applied. In future PTs it is recommended to include a list of the mainly used methods. The participants can then mark the applied method with a cross.

Calcium:
The data measured with AAS included a remarkable amount of values with values which are too low. The data measured by titration had a very broad statistical distribution.

Magnesium:
The titrimetric data also showed a very large variability for this parameter, which is comprehensible, because the Mg concentration is calculated from the difference of the measured sum of Ca/Mg and the concentration of Ca.

Sodium/Potassium:
For both parameters the values measured with ICP-OES showed a better interlaboratory precision.

Iron/Manganese:
The spectrophotometric measurement gave a higher interlaboratory standard deviation for both elements.

Aluminium:
The data set measured with AAS included a noticeable larger number of outliers. The mean of the values measured with spectrophotometric methods is biased to lower values.

Sulphate:
The gravimetric data set showed more outliers than the other methods. The concentrations of sulphate might be too low for this method. The means for the turbidimetric and for the spectrophotometric methods are biased to higher values. This caused also the bias of the overall mean which was used as assigned value.

Chloride:
Most of the data were measured with the argentometric method (Mohr). The mean of these data is biased to higher values which is also the cause for the bias of the overall mean. As a consequence some of the values measured with the ion chromatographic method are lower than the (biased) assigned value.

Fluoride:
It is remarkable that the data set measured with the spectrophotometric method had more outliers with too high values.

Nitrate:
The information about the spectrophotometric methods used by the participants were not very clear. So it is difficult to recognize trend for the different methods. It is highly recommended to limit the number of methods used in the future. The best way to do this is to develop a list of recommended methods in a working group of water testing laboratories in the SADC countries.

All: Decision about the most appropriate evaluation and assessment method

The information presented were discussed in detail among all participants. It was then decided to have an assessment for this pilot PT in the way Umgeni Water made the preliminary evaluation, i.e. using the median as assigned value and calculating the standard deviation from the normalised interquartile range. Z-scores are calculated with these parameters, and |Z-score|=2 is used as tolerance limit. In addition

Umgeni Water is asked to prepare an additional assessment just for information using the limits for the standard deviation decided earlier this day.
For future PTs the latter method should be applied for the official assessment. Dr. Koch recommended to keep the decision open to use other statistical methods, especially the so-called algorithm A, which is recommended in the ISO draft 13528 as well as in the new draft for the “International harmonized protocol for the proficiency testing of (chemical) analytical laboratories” published by ISO, IUPAC and AOAC.
There was also an extensive discussion on the need to have further PTs as help to ensure good quality of analyses. The following consequences resulting from possibly bad results were discussed:

- Health hazards (drinking water analyses)
- Unnecessary treatment costs
- Pollution charges
- Environmental pollution penalties
- Legal requirements that might be failed
- Problems with accreditation, which could cause barriers to trade
- Export as well as import problems
- Loss of customers confidence
- Costs for repeated analyses
- Delay because of unnecessary repetition of analyses
- Wrong decision by the customer (e.g. during exploration)

Summary of the decisions concerning the pilot PT

- The preliminary evaluation of the pilot PT is accepted to be the final evaluation and assessment
- Umgeni Water is asked to prepare an additional evaluation and assessment for information purposes only using the following limits of the standard deviation decided by the participants:
  - Ca: 10%
  - Mg: 10%
  - Na: 10%
  - K: 10%
  - Fe: > 1 mg/l: 12%
< 1 mg/l: 20%
  - Mn: > 0.5 mg/l: 12%
< 0.5 mg/l: 20%
  - Al: 30%
  - SO_4^{2-}: 10%
  - Cl^-: 10%
  - F^-: > 0.5 mg/l: 12%
< 0.5 mg/l: 20%
  - NO_3^-: 15%
- All participants expressed their sincere gratitude to Umgeni Water for providing the pilot PT and to PTB and SADCMET for enabling this highly valuable PT

Tuesday, 02 November 2004

The main subject of the second was the discussion on the way forward with proficiency tests for water analyses in the SADC countries.

Working group discussion: Evaluation of the pilot PT

Three working groups were formed to discuss the following questions on the evaluation of the pilot PT:

- Benefits - weak points ?
- What should be kept for future PTs - what should be changed ?
- Is the PT a help on the way to accreditation?
- Which costs are affordable and appropriate?

The working groups came to the following conclusion:

Benefits - weak points ?

Group I

- Benefits:
  - helped in identification of weak and strong points in our laboratories
  - opportunity for comparison with other laboratories
  - opportunity of networking with other labs/countries
- Weaknesses:
  - some labs were not specific on methods (e.g. spectrophotometric)
  - the costs and if we will be able to pay them

Group II

- Benefits:
  - analyst/customer confidence
  - accreditation possibilities
  - learning experience from labs (e.g. methodology)
  - weak points in the lab highlighted
  - self assessment tool
  - QC tool
- Weaknesses:
  - Differing capacity of labs
  - Type of sample: should be health significant, concentration levels of PT should match reality of potable water

Group III

- Benefits:
  - positive improvement towards accreditation; PT participation is a major requirement for accreditation ti ISO/IEC 17025
  - increases staff confidence and morale
  - QA tool for credible and reliable results
  - Pilot PT was free and easy for the labs to participate
  - Helped to evaluate different test methods and to evaluate reliability of different instrumental techniques
  - Better than other PTS which do not give participants information on methods/techniques used
  - Fully participatory PTS where all participants were involved in the planning from the onset. Hence ownership of scheme by participants. We are SADCMET PTS!
  - Managed to identify weak areas in the labs and also got hints on troubleshooting

- Weaknesses:
    - Communication problems with e-mail. Some participants did nmot re-ceive detailed results prior to the workshop.
    - PTS provider not accredited as such to ISO Guide 43
    - Too much time allowed for tests. 1 month would be ok. Hence less rounds per annum (4 rounds would be ideal)

What should be kept for future PTs - what should be changed ?

Group I:

- In terms of parameters: all parameters to be included and concentration of SO_4^{2-} and Fe to be increased. Add COD, phosphate, pH/alkalinity
- Courier: alternative skynet (point-to-point delivery), TNT, Fedex
- The costs are not affordable. Suggestion: PTB continues sponsoring until we stabilize
- The statistical assessment method 2 should be maintained
- PT rounds twice a year

Group II:

- Retain current parameters
- Make sure that Nitrate is reported and not N

Group III:

- parameters should be the same and PT provider should remain the same
- more information on support rates should be provided to participants when making travel arrangements
- microbiology should be included
- increase number of participants per country

Is the PT a help on the way to accreditation?

All groups: definitely yes

Which costs are affordable and appropriate?

Group II: if you pay for something, you appreciate it more

Group III:

- uniform costs for all countries
- request PTB to support 2nd round of PTS for sustainability
- US-$ 50 per annum for all participants should be levied. Shortfalls could be subsidised by PTB for the subsequent rounds

A summary was made on the statements by Dr. Koch (annex 9) and agreed by all participants.

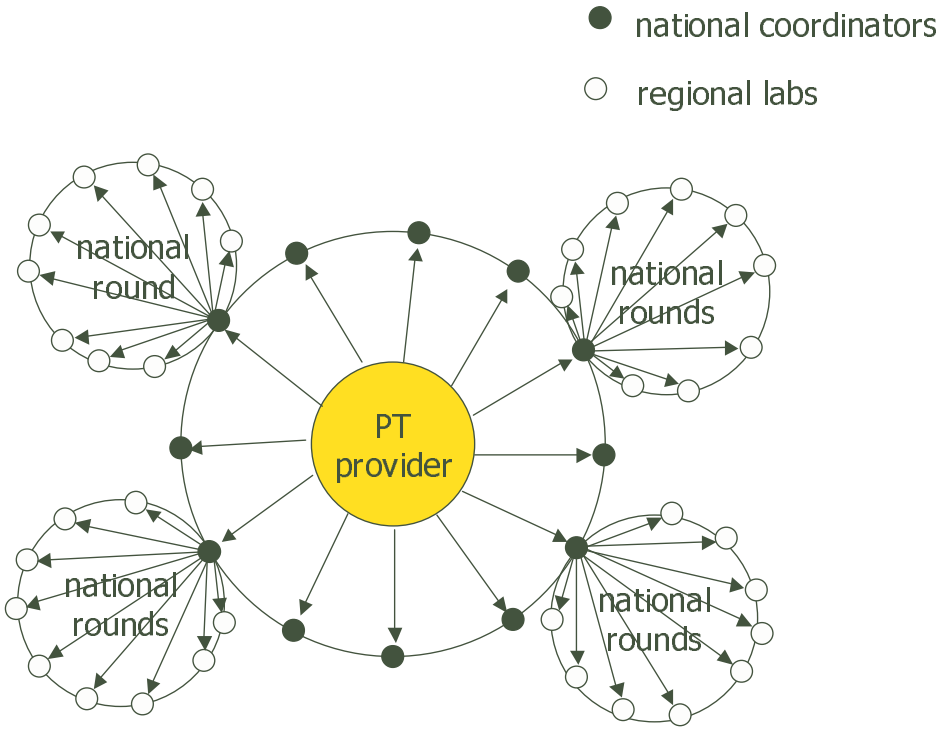
Discussion about future structure of PTs

After an intense discussion the group agreed on the following statements regarding the next PT rounds:

- It would be beneficial, if more labs would participate
- It is reasonable that the participants pay for the PT samples itself, i.e. the costs for preparation etc., as well as the evaluation costs
- The biggest part of the costs were transportation costs, due to the difficult situations in southern Africa.
- To keep the transportation costs as low as possible the following structure is proposed:

- o A national coordinator for each country will be nominated; it's obvious to ask one of the participants in the first round to do this job
- o The national coordinator looks for as many potential participants as possible in his country
- o Samples are prepared for each participants, but are sent to the national coordinator only. He is responsible for the transport to the participants.
- o PTB is asked to sponsor the transportation from PT provider to the national coordinator. All other costs are on the participants.
- o Results and the assessment will be communicated between all participants and the PT provider directly.

The following diagram shows this structure:



Working group discussions: The way forward

The three working groups discussed the following questions:

- How can the participants help each other?
- Is a SADC Laboratory Association possible? - First steps?
- What other measures can be taken to improve quality of measurements?
- Parameters for the next chemistry PT?

The working groups came to the following conclusion:

How can the participants help each other?

Group I:

- Information exchange on test methods and sharing experiences in operational issues
- Participants can act as hubs in regional networking to facilitate contact with suppliers in their respective countries on behalf of other labs.
- SADCMET PTS could be included on SADCMET webpage

- Participants could form clusters / small groups to check on communication and ensure cluster group members are up to date in respect of communication with the PTS provider

Group II:

- PT provider to have a website / database for informations
- Each lab to point out their strength through the capability of SADCMET
- Information sharing
- Capacity building and cost sharing

Group III:

- Laboratory networking through exchange of information e.g. methods of analysis, laboratory consumables and equipment
- Training – capacity building, attachment to laboratories with existing equipment

Is a SADC Laboratory Association possible? - First steps?

Group I:

- It is possible
- SADCMET could spearhead the formation of the association
    - Initial meeting with country representatives
    - This (SADCMET PTS) group could be the steering committee as it is highly motivated and enthusiastic
    - Drafting constitution
    - Inaugural meeting

Group II:

- Yes – to address the above – but not now
- First steps:
    - To draw up a constitution
    - Write a proposal for funding
    - PT group should the members

Group III:

- Yes, it is possible
- This (PT group) to be an interim group for the association
- SADCMET to be the interim chairman and secretariat

What other measures can be taken to improve quality of measurements?

Group I:

- PTB could provide CRMs to PTS members
- Training on
    - Implementation of ISO/IEC 17025
    - Validation of test methods
    - Uncertainty of measurement
    - Specific analytical areas such as toxicology
- Centre of excellence for calibration of laboratory glassware and other chemistry laboratory specific traceability requirements

Group II:

- Training of laboratory personnel
    - Quality management system
    - Route to accreditation
    - QC tools
    - Method validation

    - Uncertainty of measurement
- Practical attachments of participants to other labs – like it is done in metrology labs

Group III:

- More training by SADCMET
    - Calibration of equipment
    - Quality control in analysis
    - Statistics
    - Uncertainty of measurement
- Procurement – supplier evaluation, where members help each other with information about suppliers
- Small cluster groups for exchange of information

Parameters for the next chemistry PT?

Group I:

- Same as per pilot scheme until results are satisfactory for all participants in all parameters

Group II:

- Include the previous and add the following: Cu, Zn, Pb, Cr, Conductivity, pH, TOC, Ni, As
- All the elements to be together in one sample

Group III:

- All parameter from this PT including COD, Alkalinity, pH, phosphate. Add some more cations (Pb, As, Zn) in another PT

All: Discussion on the way forward

Laboratory Association

All participants are very interested to have a laboratory association for mutual help between the laboratories in the different countries. The SADCMET secretary was asked to act as a secretary also for this association and he agreed. It was decided to start first only with water testing laboratories and to include other testing fields later. The SADC Water Testing Laboratory Association will have the possibility to use the SADCMET webpage as a platform for its work. The aim is to have in future national laboratory associations which are linked together in the SADC Lab Association. Each member of the new association is requested to check the possibility to install a national laboratory association in his/her country.

Chemistry PT

After some discussion there was a decision to propose to have the next PT in march 2005 in the structure shown above, provided that there is funding for the transportation, with the following parameters (new parameters in bold characters):

- Ca
- Mg
- Na
- K
- Fe
- Mn
- Al
- **Pb**
- **Cu**
- **Cr**
- **Zn**
- **Ni**
- **As (if possible)**
- SO_4^{2-}
- Cl^-
- F^-
- NO_3^-
- **PO_4^{3-}**

Umgeni Water is requested to organise the future PTs. The statistical evaluation method used in the pilot PT will be applied also for the next PT, but with limitations for the standard deviation for calculation of Z-Scores, as shown above.
Dr. Koch pointed out that it could be wise to change the statistical evaluation method to the algorithm A, if in future this method is generally recommended by ISO.

M. Koch: Microbiological PT – possibilities and challenges? Which parameters are desirable – which are possible? Possibilities of know-how transfer from Germany to the SADC region

Dr. Koch presented in formation about microbiological PTs for drinking water in Germany (annex 10).

The discussion after the presentation showed, that all laboratories are interested to have also a PT for microbiological parameters.
The following parameters were mentioned:

- coliformic bacteria
- E. coli
- salmonella
- total counts
- vibrio
- clostridium

The organization of a microbiological PT requires special skills for the provider. Umgeni Water is willing to act as a provider also for these PTs. In order to achieve this, it is proposed to accept the offer of the Public Health Authority of Lower Saxony (NLGA) to help to train the future PT provider in this sector. The best way would be to have a visit of the potential provider in Germany (if possible during a PT preparation). The second step could be to make all necessary preparation for a PT in the SADC countries (with advice form NLGA). In the third step an experienced person from NLGA could help during the preparation of the first microbiological PT.
For this first trial to install a PT system for microbiology funding is indispensable.

Summary for the proposed way forward

Next chemistry PT

- Parameters: Ca, Mg, Na, K, Fe, Mn, Al, Pb, Cu, Cr, Zn, Ni, As (if possible), SO_4^{2-}, Cl^-, F^-, NO_3^-, PO_4^{3-}
- Same PT provider
- Same evalution method but with the following limitations for the standard deviation for calculation of Z-scores:
  - Ca: 10%
  - Mg: 10%
  - Na: 10%
  - K: 10%
  - Fe: > 1 mg/l: 12%
< 1 mg/l: 20%
  - Mn: > 0.5 mg/l: 12%
< 0.5 mg/l: 20%
  - Al: 30%
  - SO_4^{2-}: 10%
  - Cl^-: 10%
  - F^-: > 0.5 mg/l: 12%
< 0.5 mg/l: 20%
  - NO_3^-: 15%
  - Limits for the other parameters are still to be decided
- Distribution of samples in march 2005
- Distribution from PT provider only to national coordinators; PTB will be asked to cover the costs for this transport
- All other costs for the PT provider should be covered by participation fees
- National coordinators are asked to look for as other participants in their respective country
- Communication of results and evaluation should be directly between each participant and the PT provider

Microbiological PT

All laboratories are highly interested to have also a microbiological PT.
PTB is asked for funding for:

- Training of the potential PT provider in Germany
- Preparation of a microbiological PT in the SADC countries
- Assistance during the first PT round by an experienced person from Germany
- Costs for the transport and evaluation of the first round

SADC Laboratory Association for Water Testing Labs

It was decided to establish this association. The group of PT participants in the pilot PT will act as a preliminary steering committee for this association. The SADCMET secretariat agreed to preliminary hold also the secretariat of this association. All members try to install also national associations or act a contact point for their national colleagues.

Evaluation questionnaire

All participants were requested to fill out an evaluation questionnaire (annex 11). Evaluation see below.

Closure of lecture part

Dr. Musarurwa and Dr. Koch closed the workshop and thanked Mrs Merle Smuts for her excellent job in the preparation of the pilot PT and all participants for their enthusiastic cooperation.

Lab visit and evening braai

The participants had the opportunity to visit three different laboratories in the CSIR in the afternoon.
In the evening all participants were invited by the national metrology lab of South Africa. At this opportunity certificates of attendance signed by Dr. Koch and Dr. Musarurwa were distributed to all participants by the head of the national metrology laboratory.

Evaluation of the questionnaire

The judgement of the participants regarding

- **The venue of the workshop:**
  Very good 3
  Good 13
  Fair 6
  No answer 1
  Mean: 2.14 (1 for very good, 2 for good and 3 for fair)
- **The content of the presentations:**
  Very good 11
  Good 12
  Mean: 1.52 (1 for very good, 2 for good and 3 for fair)
- **The handout and documents:**
  Very good 5
  Good 13
  Fair 5
  Mean: 2.00 (1 for very good, 2 for good and 3 for fair)
- **The working group discussions:**
  Very good 12
  Good 11
  Mean: 1.48 (1 for very good, 2 for good and 3 for fair)

Were all aspects of the pilot PT covered?

Yes: 22
No: 0
No answer: 1

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

Comparison of evaluation and assessment methods: (20)
Method comparison: (14)
Setting limits for the standard deviations for assessment / quality goals: (13)
Experiences of the PT provider: (9)

Working group discussions: (8)
Microbiology PT: (8)
Preliminary evaluation of the PT: (7)
Error sources / troubleshooting: (6)
Experiences of the participants: (5)
Benefits of PT / what does PT mean: (5)
SADC Lab Association: (5)
Next chemistry PT: (5)
Consequences of bad results: (5)
Measures for improvement of quality: (1)
Strength and weaknesses of statistical methods: (1)
Recovery and bias information: (1)
Summary for the Pilot PT: (1)
Confidence in results after evaluation procedure: (1)
PT costs: (1)
Analytical problems: (1)
Toxic analyses: (1)

Did the workshop fulfil your expectations?

Yes: 22
No: 1

Why not: “It hasn’t point out how an outlier lab can take some corrective action / it hasn’t forward anything”

What benefits did you draw from the workshop?

- Exchange of information and probable corrective action for next PT round
- Sharing of experiences with participants. Learned about the five different assessment methods.
- Greater appreciation of statistical techniques. Had insight into possible causes for deviations from expected results.
- Continued networking, future progress of PTS, commitment and motivation of all participants
- Problems faced by various laboratories and how similar they were. Networking and experience sharing among the participants
- As I was attending for the 1st time, I was able to meet all the other PTS members and share my experiences with them and learn more on the methods of evaluation and assessment of the results
- I have learned new methods of analysis and the ways of improving the previous ones.
- Sharing experiences with peer groups
- Information on different methods and outline of my weakness / lab weakness
- The interaction between peers which has set a base for future communication
- I can improve some methodology that I use, for example calculate the bias
- Quality control by the assessment methods
- I learned how to improve my laboratory organization in terms of procedure and analytical method choice, because this influences a lot my results.
- Opportunity for quality improvement in the laboratory and exchange of information and networking. Better enlightened on statistical evaluation of results.
- The experiencing mistakes while analysis

- Coordinated networking
- Learning from others experience, networking
- Sharing information and improve laboratory analyses
- Information ?? is always invaluable, PTS is a requirement for accreditation, peers from other countries for networking
- Evaluation of PT results
- I had the possibility to understand the various methods that may be used for PT assessment and understand the measures that nee to be taken for improvement
- The importance of PT
- To take corrective actions on my lab's defects on water analyses

Any other comments:

- Keep it up. We hope our labs will greatly improve
- Would like training on setting up of quality management system to ensure output of results with min 99 % confidence limit
- This was an all embracing evaluation workshop, where current as well as future needs were identified and addressed. The initiative to start a regional laboratory association is most welcome. Well done to the organisers and facilitators!
- It is very important that this programme continues by continual improvement in operations of our laboratories and at the same time validation of methods and checking of efficiency of our equipment. Workshop and participation in the PT was an eye opener of the condition of our laboratory and the corrective measures to be taken
- Training of the laboratory personnel on improvement of quality measurements and assistance in getting accredited are crucial for the PTS members
- Water PTS is a true development for accreditation and lab quality improvement therefore should be encouraged
- The program should be a bit relaxed to allow time for site seeing
- Accommodation was very good; food and the conference room ok; but the service is not very good.
  Some of us are not statisticians, do not practise. The little we knew about statistics and this means that we are not implementing full data analysis and do not even have quality checks in place
- I have problems in my lab with SO_4 and Al. I can see that this not my problem only and I can learn some methods to improve my work
- A second PT round and review workshop is suggested
- Capacity building / strengthening in QMS, AQA/OC, traceability and method verification
- Interesting information
- I hope that we shall be able to participate in future PT schemes and that a training programme will be organized for uncertainty of measurements, method validation, repeatability, reproducibility etc.
- I think that the PT samples should reflect the real samples with regard to their physico-chemical properties (intereferences) and concentrations
- I think there is a lot to be learned by most SADC labs. They are ignorant as far as QC, CRMs and method validation is concerned. That's why the PT results are so poor.

- Water shouldn’t be the only agenda. Other areas of testing should be included.

Summary of the evaluation
From the questionnaires the conclusion can be drawn, that almost all of the participants were very happy with the workshop. The expectations of the particpnats have been fulfilled and most of them were quite enthusiastic. Almost all topics were mentioned in the list of most important topics, showing that there was constant interest throughout the whole workshop.

Stuttgart, 25 November 2004

Dr.-Ing Michael Koch

Annex 1 – from SADCMET Newsletter 2004

Namibia's water 'amongst best in Africa'

NAMIBIA'S and South Africa's potable water supplies are among the safest in the region but the quality of water elsewhere in southern Africa and the continent is cause for grave concern. Access to clean potable water is considered a basic human right, and analysis of water samples by laboratories cannot be overlooked, says the German Embassy in Namibia.

According to Dr Mukayi Musarurwa of the CSIR-NML, Regional Co-ordinator for SADC Metrology, unreliable results obtained from water laboratories across Africa has left many communities exposed to potential health threats. Representatives from all SADC countries, as well as from Kenya, Ethiopia, and Uganda, met in Windhoek during February 2004 to discuss the establishment of a regional proficiency testing scheme for water testing laboratories throughout the region - with the aid of specialists from Europe.

Musarurwa said people throughout Africa had lost faith in the claims of city and town councils that their water was not only safe for consumption but of good quality.

“In many rural areas, he said, the quality of water was not even known.”

Musarurwa said with limited water resources available in many of the region's countries, the issue of quality and reliability of measurements were of prime importance.

"Namibia is far better off than other countries. And there are lessons to be learned here for putting in place a system that is reliable and credible," said Musarurwa.

During their stay, conference delegates visited the water testing laboratories of NamWater and the City of Windhoek.

With limited water resources, the City relies on the Gammams Reclamation Plant for 30 per cent of its potable water. The German government also pledged its continued commitment to the good management of cross-boundary natural resources, and set aside N$60 million for this purpose last year.

German Ambassador to Namibia, Wolfgang Massing, reminded delegates of water's role as a basic service and human need and that safeguarding its quality was of the utmost importance.

Annex 2: List of participants

SACDMET PROFICIENCY WORKSHOP -1 & 2 November 2004.

COUNTRY	NAME	Organisation	Contact
Angola **1**	POLICARPOSANTOS/ VANDA MR	The Environment and Chemistry Unit Sonangol Laboratory	Telephone 09244 2 325681 Fax 09244 2 634119 vanda.policarpo@sonangol.co,ao
Botswana **2**	DITSABATHO/TEDDY MR LAETSANG MS	Water Utilities Corporation Dept of Geological Survey	Tel: +267 3975 179/3932 136 Fax: +267 3975 187 Email: TDitsabatho@wuc.bw Tel: + 267 533 6790/533 0327 Fax: + 267 533 2013 Mlaetsang@gov.bw
Ethiopia **1**	ABEBE/JOSEPH MR	QSAE	Tel+251 1 185991 Fax: +251 1 613177/8 wayoseph@yahoo.com testing@qsae.org
Kenya **2**	OLOLO/TOBIAS MR MIRARA/MUMBI/JANE MS	KEBS Nairobi City COUNCIL Water Testing Laboratory	09254 2 60 5387 09254 2 503 293 ololot@kebs.org Tel: 0722 320 607 kahonge@yahoo.com
Lesotho **1**	MAKHABA/MAPASEKA MS	Maseru Water Supply	Tel: +266 22 313 943 Cell + 266 58855783 Fax: +266 22 325 815 mpasimakhaba@yahoo.com
Malawi **2**	BANDA/LEWIS MR NAYEJA/PATRICIA MS	Northern Region water Board Malawi Bureau Of Standards	09265 1 334 617/254 92273 09265 1 332 082/4921 lewisbanda@yahoo.com Office: 09 265 670-488 Fax:09 265 670-756 Mobile: 09511134 patnayeja@yahoo.com davlin@mbs.malawi.net
Mauritius **1**	GHOORUN/SHABBIR MR	MBS	Tel:09 230 433-3648 Fax: 09 230 433-5051 shghoorun@msb.intnet.mu
Mozambique **2**	RHODA NUVUNGA LUIS MABUI/MOISES DR	MINISTRY OF HEALTH LNHAA LEM	Cell: +258 1 82 862661 weihnachte@yahoo.co.uk 258 1 475 268/70/71 mabui1971@yahoo.com.mz
Namibia **2**	CONRADIE/M MRS HINDA/CECILIA MS	Namwater CITY OF WINDHOEK	Tel + 264 61 710000 Fax: + 264 61 713257 conradiem@namwater.com.na Tel.+ 264 61 240997 Fax + 264 61 262679. cvi@windhoekcc.org.na
Seychelles **1**	RADEGONDE/VIVIAN MR	SBS	Tel: +248 380 400 Fax: +248 375 151 sbsorg@seychelles.net vivianradegonde@hotmail.com

Swaziland **1**	SGWANE/ZANELE MS	Rural Water Supply	Tel: +248 380 400 Fax: +248 375 151 sbsorg@seychelles.net vivianradegonde@hotmail.com
South Africa **1**	SMUTS/MERLE MRS	UMGENI Water	27 33 341 1308 27 33 341 1501 merle.smuts@umgeni.co.za
Tanzania **2**	KIBAKAYA/ISAAC MR MBWAMBO/KEZIA MS	Water Laboratories Unit TBS	Tel No:+ 255 22 2450047 Fax No:+ 255 22 451447 dwl-sec@maji.go.tz dwl@maji.go.tz kmbwambo@yahoo.co.uk
Uganda **1**	KAMUSIIME/HOPE MS	UNBS	Tel:+ 256 41 222-367 Mobile: + 256 77 430361 Fax: + 256 41 286123 Hope.kamusiime@unbs.org
Zambia **1**	MAZHAMO/MARGARET MS	Food and Drugs Control Laboratory	Tel-260-1-252855/252873/252875 Telefax +260 1 252875 Email mazhamoms@yahoo.com Email Fdcl@zamnet.zm
Zimbabwe **2**	MANDIZHA/NAUME MS GABI/BENSON MR	ZIMLAB Standards Association of Zimbabwe	Tel:263 4 4814 90/4814 97 Fax: 263 4 481 445 zimlab@africaonline.co.zw Fax: 263 4 7491 81 sazcft@mweb.co.zw

Annex 3: Merle Smuts: Experiences of the PTS Provider

Experiences of the PTS Provider

Merle Smuts
Umgeni Water Laboratory Services
310 Burger Street
Pietermaritzburg
Tel.: +27 33 341 1308 Fax: +27 33 341 1501
E-mail: merle.smuts@umgeni.co.za
http://www.umgeni.co.za

The PTS Project

- Planning
- Sample Preparation
- Sample Distribution
- Evaluation

Planning

- Original project plan developed Workshop (Windhoek)
- Project well defined in signed contract with PTB
  - Number of samples, parameters and concentration ranges
  - Deadlines for sample delivery, result receipt and report submission

Planning

- Volume of sample provided
- Bottle type
- Calculation of masses and total volume required
- Logistics and resources
- Results template
- Choice of courier

Sample Preparation

- Laboratory water spiked with parameter of interest
- True value calculated from mass of spike
- Constituted to 25 liter and thoroughly mixed
- Dispensed
- Labelled

Homogeneity and Stability Check

- First and last sample dispensed
- Samples analysed at least six times each at time of dispensing
- Samples re-analysed after 5 weeks
- Statistics indicated results were equivalent (F-test)

Sample Distribution

- Samples packaged to protect integrity
- Customs documentation completed
- Samples dispatched
- Samples tracked

Evaluation

- Robust statistics
- Assigned value = Median (central value)
- Std. Dev. = Normalized IQR
  - difference between 1st and 3rd quartile, normalised to a standard deviation using a factor (0.7413)
- Evaluation of performance using Z-scores

Problems encountered

- No problems that hindered progress
- Receipt of results by fax
- Only 3 (out of 27) Laboratories did not participate
  - Chemical analyses not routinely carried out
  - Instrumental breakdown
  - No response at all

Annex 4: Merle Smuts: Preliminary evaluation and assessment

Preliminary Evaluation and Assessment

Merle Smuts
Umgeni Water Laboratory Services
310 Burger Street
Pietermaritzburg
Tel.: +27 33 341 1308 Fax +27 33 341 1501
E-mail: merle.smuts@umgeni.co.za
http://www.umgeni.co.za

Evaluation

- Robust statistics
- Assigned value = Median (central value)
- Std. Dev. = Normalized IQR
  - difference between 1st and 3rd quartile, normalised to a standard deviation using a factor (0.7413)
- Evaluation of performance using z-scores

Evaluation

- Laboratory considered successful analysing a parameter if two or more z-scores for a parameter are satisfactory

- Performance Assessment

$|z\text{-Score}| \leq 2$: Satisfactory

$2 < |z\text{-Score}| \leq 3$: Questionable

$|z\text{-Score}| > 3$: Unsatisfactory

Calcium				74%
Lab Code	1	2	3	Successful
003	-0.71	3.48	4.54	N
004	-0.04	-0.88	-0.04	Y
005	-0.09	-0.28	-0.19	Y
006	1.79	0.45	0.79	Y
007	0.81	-0.64	-0.67	Y
008	4.88	0.20	0.43	Y
009	8.34	6.80	0.76	N
010	-9.73	-13.7	-8.03	N
011	-10.6	-14.8	-8.70	N
012	-1.05	-2.15	-0.94	Y
013	-2.99	-4.00	-2.14	N
014	-1.70	0.00	-1.15	Y
016				
017	-0.91	-1.24	-1.05	Y
018	4.21	1.02	0.36	Y
019	-0.56	-1.01	-0.41	Y
020	-0.28	0.73	-1.38	Y
021	0.28	0.00	0.04	Y
022	0.04	0.38	0.53	Y
023	0.00	-0.06	0.13	Y
024	0.12	0.11	0.31	Y
025	131	183	110	N
026	0.00	-0.21	0.49	Y
027	0.24	0.55	-0.24	Y
Number of Labs participating				23

Magnesium				71%
Lab Code	1	2	3	Successful
003	1.61	2.90	1.52	Y
004	-0.12	0.94	0.22	Y
005	0.34	0.33	0.40	Y
006	-4.65	-1.32	-0.39	Y
007	-0.69	-0.07	0.04	Y
008	-4.22	9.67	-7.64	N
009	-4.33	-2.92	-4.41	N
010	-7.21	-6.3	-7.74	N
011				
012	0.16	0.00	-1.05	Y
013	-0.36	-0.66	-0.95	Y
014	-0.48	-0.38	-1.32	Y
016				
017	0.00	-0.80	-0.48	Y
018	4.21	3.03	1.94	N
019				
020	12.5	11.7	14.8	N
021	0.86	-0.15	0.02	Y
022	1.38	0.97	0.54	Y
023	-0.29	-0.12	-0.18	Y
024	0.06	0.01	0.00	Y
025	91.4	80.5	109	N
026	-0.35	-0.09	0.00	Y
027	0.00	0.30	-0.52	Y
Number of Labs participating				21

Sodium				86%
Lab Code	1	2	3	Successful
003	-0.16	0.78	-3.60	Y
004	1.69	0.65	1.65	Y
005	-1.07	0.54	1.01	Y
006	-1.23	-2.25	-1.31	Y
007	4.33	3.88	2.04	N
008				
009	4.69	0.22	-1.06	Y
010	-0.94	0.3	0.42	Y
011	-5.4	-4.9	-4.82	N
012	0.55	0.02	-0.72	Y
013	-1.21	-2.16	-1.01	Y
014	-0.45	-1.12	-0.34	Y
016				
017	1.12	2.17	1.33	Y
018	-0.16	-0.40	0.15	Y
019	-0.05	-0.60	-0.53	Y
020	0.48	0.12	0.76	Y
021	-3.30	-2.08	-0.42	N
022	0.05	-0.93	-0.45	Y
023	-0.30	-0.65	-0.15	Y
024	0.05	0.00	0.44	Y
025	1.48	0.62	1.01	Y
026	0.05	-0.19	0.24	Y
027	0.12	0.00	0.20	Y
Number of Labs participating				22

Potassium				77%
Lab Code	1	2	3	Successful
003	1.61	9.57	8.69	N
004	-0.47	0.94	-1.78	Y
005	-0.33	-0.05	-0.39	Y
006	0.87	-0.31	-0.05	Y
007	-2.57	-3.26	-3.55	N
008				
009	7.90	0.17	-4.81	N
010	0.75	-2.1	1.39	Y
011	-2.8	-1.4	-3.28	N
012	-0.96	-1.64	-0.11	Y
013	-0.71	-0.26	0.16	Y
014	2.17	1.18	1.26	Y
016				
017	1.74	2.90	2.02	N
018	0.14	1.19	1.94	Y
019	0.85	-0.06	-0.64	Y
020	-0.54	-0.52	-0.57	Y
021	-1.81	-2.33	-1.59	Y
022	0.42	0.72	0.84	Y
023	-0.23	-0.09	-0.18	Y
024	0.51	0.17	0.05	Y
025	-0.23	1.02	0.05	Y
026	0.04	0.05	0.37	Y
027	-0.04	0.08	0.21	Y
Number of Labs participating				22

Iron				81%
Lab Code	1	2	3	Successful
003	2.15	2.76	-8.34	N
004	7.05	-0.06	0.09	Y
005	-0.04	0.03	-0.13	Y
006	0.13	0.77	0.15	Y
007	2.64	1.09	0.36	Y
008	0.76	-0.84	-2.00	Y
009	-0.80	-7.84	-1.37	Y
010	-0.88	4.30	13.47	N
011	0.35	0.77	0.07	Y
012	-0.80	-0.39	0.02	Y
013	-0.02	0.08	0.81	Y
014	0.02	-2.18	-2.61	N
016	1.25	2.51	-1.60	Y
017	1.17	12.65	2.00	N
018	-0.22	0.39	-0.20	Y
019				
020				
021	-0.47	-0.96	0.00	Y
022	1.39	-0.90	-1.10	Y
023	-0.06	-0.26	-0.29	Y
024	-0.06	-0.51	0.36	Y
025				
026	-0.14	-0.58	-0.61	Y
027	-0.22	0.00	0.25	Y
Number of Labs participating				21

Manganese				80%
Lab Code	1	2	3	Successful
003	1.56	-0.29	-1.18	Y
004	0.29	0.58	0.29	Y
005	-0.38	-0.45	-0.70	Y
006	-0.73	-1.03	-1.36	Y
007	0.29	0.73	23.1	Y
008	12.7	2.91	1.25	N
009				
010	-0.03	-2.91	0.52	Y
011	1.30	0.22	-0.07	Y
012				
013	-0.50	-0.63	-0.79	Y
014	-0.67	-2.04	-2.88	N
016	6.32	-1.46	0.52	Y
017	-0.03	0.00	-0.96	Y
018	-0.03	0.98	0.52	Y
019				
020	0.03	9.91	19.4	N
021	-2.57	-2.91	0.22	N
022	2.89	1.95	0.59	Y
023				
024	-0.03	-0.29	-0.74	Y
025	1.21	0.15	-1.43	Y
026	-0.03	0.00	-0.52	Y
027	0.60	0.44	0.07	Y
Number of Labs participating				20

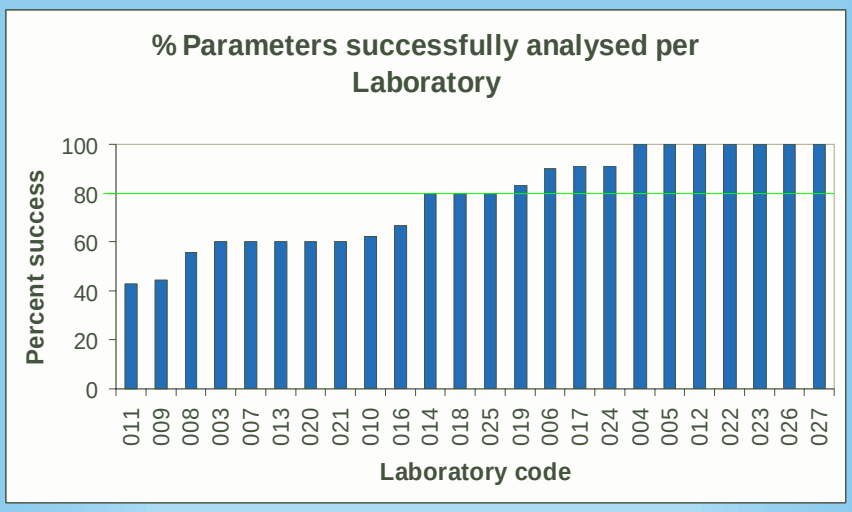
Aluminium				85%
Lab Code	1	2	3	Successful
003				
004	0.00	-0.07	0.02	Y
005	5.03	0.64	0.36	Y
006	-1.45	-1.77	-1.23	Y
007				
008	-0.48	-1.20	-0.46	Y
009				
010				
011				
012				
013	7.36	4.16	2.96	N
014				
016				
017	-1.20	-1.29	-1.11	Y
018				
019				
020	0.82	0.07	0.00	Y
021	-1.69	-2.46	-2.19	N
022	11.8	1.41	0.24	Y
023				
024	0.00	0.06	0.22	Y
025	-0.53	-0.97	-1.18	Y
026	0.48	0.15	0.24	Y
027	0.17	0.00	-0.02	Y
Number of Labs participating				13

Sulphate				71%
Lab Code	4	5	6	Successful
003	-0.48	0.00	-0.41	Y
004	-0.34	0.17	0.76	Y
005	-0.50	-0.78	-0.45	Y
006	-0.26	0.29	0.03	Y
007	-2.19	-2.88	-2.16	N
008	2.85	5.34	2.40	N
009	-0.48	-0.44	-0.43	Y
010	0.95	0.3	-1.14	Y
011	-2.8	-6.2	-5.34	N
012	0.93	3.17	1.39	Y
013	4.88	6.76	2.71	N
014	1.31	2.82	1.43	Y
016	0.08	0.08	-0.08	Y
017	0.31	1.03	0.98	Y
018	-1.52	-2.75	0.10	Y
019	-2.05	-3.84	-3.13	N
020	0.42	-4.49	-2.69	N
021	0.95	0.06	-0.76	Y
022	0.00	-0.59	-0.03	Y
023	-0.25	-0.11	0.11	Y
024	1.31	3.45	2.40	N
025	0.28	-1.56	-0.12	Y
026	-0.34	-0.32	0.04	Y
027	-0.31	-0.32	0.05	Y
Number of Labs participating				24

Chloride				96%
Lab Code	4	5	6	Successful
003	1.71	0.43	2.29	Y
004	-0.71	-0.02	-0.15	Y
005	-0.69	-0.68	-0.57	Y
006	-0.01	0.59	-0.22	Y
007	0.03	1.36	1.28	Y
008	1.40	0.02	0.04	Y
009	3.74	4.16	4.99	N
010	-0.63	-1.25	-1.88	Y
011	-1.06	-0.45	-0.45	Y
012	0.01	-0.23	-0.57	Y
013	0.27	-0.22	0.53	Y
014	-0.48	0.30	0.66	Y
016	3.96	0.85	1.09	Y
017	0.40	0.18	0.55	Y
018	-0.44	-0.73	-0.04	Y
019	-1.23	-1.35	-1.80	Y
020	2.17	1.39	1.37	Y
021	2.97	1.20	0.93	Y
022	0.17	0.41	0.28	Y
023	-1.21	-0.75	-0.18	Y
024	-1.25	-1.18	-1.64	Y
025	0.13	0.80	0.74	Y
026	-0.56	-0.77	-0.55	Y
027	-0.94	-0.70	-0.58	Y
Number of Labs participating				24

Fluoride				79%
Lab Code	4	5	6	Successful
003	-0.85	-0.57	-0.08	Y
004	0.36	1.58	0.12	Y
005	1.04	-0.50	-2.38	Y
006	3.15	2.70	9.08	N
007	0.00	0.22	-0.08	Y
008	0.48	0.22	0.33	Y
009	1.69	-2.17	-1.33	Y
010				
011				
012	0.24	1.18	0.17	Y
013	4.11	0.62	-3.79	N
014	-1.81	-0.34	0.29	Y
016	271	177	88.2	N
017	-0.12	-0.89	-2.75	Y
018	-0.73	-1.05	-1.92	Y
019				
020	0.60	9.00	2.41	N
021				
022				
023	-0.12	-0.26	-0.37	Y
024	-0.45	-0.39	-0.62	Y
025	-0.65	-0.22	0.00	Y
026	-0.60	0.14	0.58	Y
027	-0.44	0.00	0.41	Y
Number of Labs participating				19

Nitrate				65%
Lab Code	4	5	6	Successful
003	14.2	24.7	16.0	N
004	-0.49	-0.08	0.22	Y
005	0.71	0.70	0.18	Y
006				
007	-2.00	-3.40	-2.27	N
008	-0.97	-3.02	-2.94	N
009	-4.33	-7.65	-4.60	N
010				
011				
012	-0.03	0.48	0.17	Y
013				
014	-0.57	-0.59	0.42	Y
016	28.9	101	15.1	N
017	0.03	-0.59	-0.86	Y
018	-2.68	-4.44	-2.55	N
019	0.43	0.30	0.08	Y
020	1.12	3.62	-1.26	Y
021	2.84	4.84	0.38	N
022	7.36	-0.37	-0.15	Y
023	-0.53	-0.70	-0.32	Y
024	0.67	0.63	0.48	Y
025	0.05	0.83	0.74	Y
026	-0.37	-0.25	-0.42	Y
027	-0.05	0.08	-0.08	Y
Number of Labs participating				20



58% of participating laboratories analysed 80%, or more, of the 11 parameters successfully

Managing Water for Life

SADCMET PTS July 2004

PTS Provider: Umgeni Water Laboratory Services

Enquiries: M Smuts

Tel: +27 33 341 1308

email:merle.smuts@umgeni.co.za

Date: 22 October 2004

Name removed

Laboratory Code: 003

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UMGENI WATER
HEAD OFFICE • PO Box 9 • Pietermaritzburg 3200
310 Burger Street • Pietermaritzburg 3201 • Republic of South Africa
341-1084
E-mail: http://www.umgeni.co.za

Chief Executive: G Moloi
General Managers: • M Msiwa • M Hildebrand • N Gevers • P Maphoshe • P Jonas

INTRODUCTION

The July 2004 SADCMET PTS consisted of the analysis of 6 synthetic water samples, 3 of which contained the cations calcium, magnesium, sodium, potassium, iron, manganese and aluminium, and 3 contained the anions sulphate, chloride, fluoride and nitrate.

1. STUDY DESIGN

1.1 SAMPLE PREPARATION

Samples 2004/06/1, 2 and 3 were constituted as follows and preserved with 1.5 mL HNO_3 (conc) per litre of sample:

		Cation samples (constituted to 25L)		
Determinand	**Chemical**	**2004/06/1**	**2004/06/2**	**2004/06/3**
Calcium	$CaCl_2.2H20$	2.3489 g	4.4224 g	7.0465 g
Magnesium	$MgCl_2.6H20$	2.7041 g	4.3243 g	9.8145 g
Sodium	NaCl	0.6726 g	1.6555 g	3.2398 g
Potassium	KCl	0.1638 g	0.3658 g	0.4620 g
Iron	Fe Spectroscopic Grade Stock Solution (1000mg/L)	2.50 mL	30.0 mL	100 mL
Manganese	Mn Spectroscopic Grade Stock Solution (1000mg/L)	2.50 mL	10.0 mL	25.0 mL
Aluminium	Al Spectroscopic Grade Stock Solution (1000mg/L)	2.50 mL	15.0 mL	25.0 mL
Preservative	HNO_3 (conc)	37.5 mL	37.5 mL	37.5 mL

Samples 2004/06/4, 5 and 6 were constituted as follows:

		Anion samples (constituted to 25L)		
Determinand	**Chemical**	**2004/06/4**	**2004/06/5**	**2004/06/6**
Sulphate	$K2SO_4$	0.7521 g	1.2808 g	2.2274 g
Chloride	KCl	1.5316 g	2.2499 g	3.4558 g
Fluoride	NaF	0.6517g in 500mL water (Stock) 5.00mL Stock used	2.0127g in 500mL water (Stock) 5.00mL Stock used	2.0127g in 500mL water (Stock) 20.0mL Stock used
Nitrate	KNO_3	0.3831 g	0.6401 g	1.265 g

NOTES:

1. Grade A volumetric glassware and calibrated autopipettes, verified as complying to the relevant standard specification, were used in the preparation of stocks and samples.

2. AR grade chemicals, supplied by Merck, Riedel-de Haën and BDH, were used.
3. Grade I quality laboratory water (ISO 3696: 1987, Water for analytical laboratory use - Specification and test methods) was used for the preparation of the stocks and samples.

1.2 **SAMPLE DISPATCH**

Samples were dispatched to the participating laboratories on 22 July 2004. Single test analysis of the samples, as supplied, was requested. A Result Template was included. The return date for results was set as 31 August 2004.

2. STATISTICAL EVALUATION

2.1 The participants' results were statistically evaluated using z-scores based on robust summary statistics (the median and normalized interquartile ratios). Robust statistics minimize the effect of extreme results without excluding such data from the evaluation. The assigned value was calculated using the median of all results obtained.

3. RESULTS

The results are detailed in the following Appendices:

Appendix A: Individual Participant's results and evaluation assessment

Appendix B: All results received, and summary statistics

Appendix C: Z-scores for all Participants

Appendix D: Graphical display of all results per parameter

Appendix E: Graphical display of frequency and performance of methodologies used

4. COMMENTS

Please use the email system as the preferred medium of communication. All queries, comments and feedback may forwarded to the PTS Provider.

M Smuts

PTS Provider : SADCMET PTS July 2004

APPENDIX A: Individual Participant's results and evaluation assessment

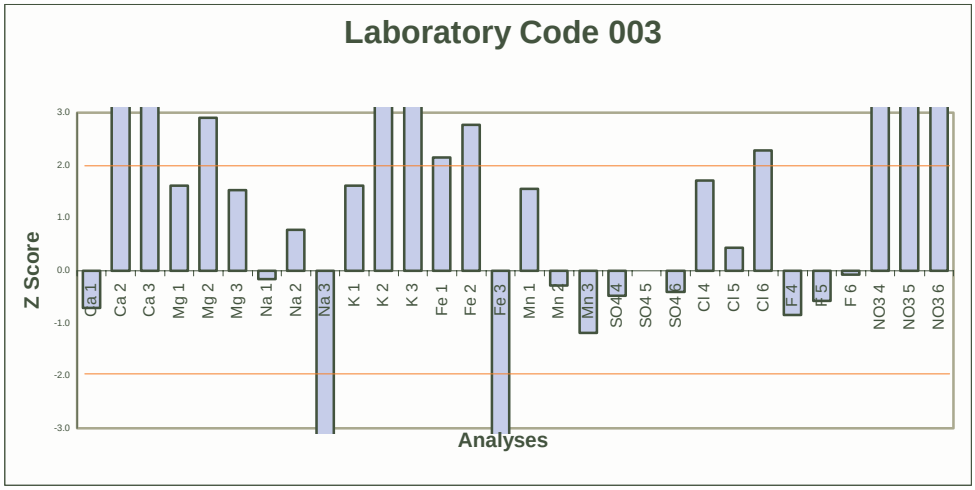
LABORATORY CODE 003

Parameter	Sample No.	Laboratory Results	Assigned value	z-score	% Satisfactory Results per parameter
Calcium as Ca in mgl/L	1	24.9	26.7	-0.71	33
	2	62.5	50.6	3.48	
	3	119	78.2	4.54	
Magnesium as Mg in mgl/L	1	16.2	13.4	1.61	67
	2	30.0	21.0	2.90	
	3	56.0	47.5	1.52	
Sodium as Na in mgl/L	1	10.7	10.9	-0.16	67
	2	30.5	28.0	0.78	
	3	24.0	52.1	-3.60	
Potassium as K in mgl/L	1	4.90	3.59	1.61	33
	2	19.0	7.80	9.57	
	3	21.0	9.93	8.69	
Iron as Fe in mgl/L	1	0.37	0.11	2.15	0
	2	1.66	1.23	2.76	
	3	0.30	4.01	-8.34	
Manganese as Mn in mgl/L	1	0.15	0.10	1.56	100
	2	0.38	0.40	-0.29	
	3	0.87	1.03	-1.18	
Aluminium as Al in mgl/L	1	--		-	-
	2	--		-	
	3	--		-	

Parameter	Sample No.	Laboratory Results	Assigned value	z-score	% Satisfactory Results per parameter
Sulphate as SO4 in mgl/L	4	15.4	18.5	-0.48	100
	5	29.6	29.6	0.00	
	6	45.9	49.7	-0.41	
Chloride as Cl in mgl/L	4	35.7	31.3	1.71	67
	5	47.6	45.7	0.43	
	6	76.0	67.6	2.29	
Fluoride as F in mgl/L	4	0.09	0.16	-0.85	100
	5	0.30	0.37	-0.57	
	6	1.40	1.42	-0.08	
Nitrate as N in mgl/L	4	9.34	2.19	14.25	0
	5	14.6	3.47	24.7	
	6	30.7	6.88	15.97	

% Satisfactory Results Overall	57%

Z-score Graph for individual parameters



Performance Assessment

|z-Score| ≤ 2: Satisfactory

2 < |z-Score| ≤ 3: Questionable

|z-Score| > 3: Unsatisfactory

APPENDIX B: All results received and summary statistics

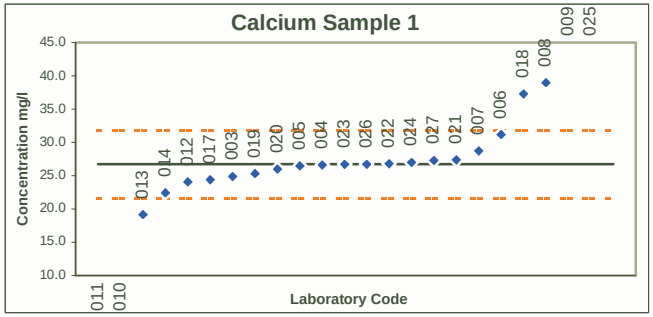
Lab Code		003	004	005	006	007	008	009	010	011	012	013	014	016	017	018	019	020	021	022	023	024	025	026	027	Assigned value (mgl/L)	Robust Std Dev (mgl/L)	Upper limit (mgl/L)	Lower limit (mgl/L)	Rel.STD (%)	Number of values	Outside limits (high)	Outside limits (low)	Outside limits (%)	Results acceptable (%)
Calcium	1	24.9	26.6	26.5	31.2	28.7	39.0	47.7	2.20	0.0	24.1	19.2	22.4	-	24.4	37.3	25.3	26.0	27.4	26.8	26.7	27.0	356	26.7	27.3	26.7	2.52	31.7	21.7	9.4	22	4	3	32	68
as Ca in	2	62.5	47.6	49.7	52.1	48.4	51.3	73.8	3.80	0.0	43.3	37.0	50.6	-	46.4	54.1	47.2	53.1	50.6	51.9	50.4	51.0	675	49.9	52.5	50.6	3.41	57.4	43.8	6.7	22	3	4	32	68
mgl/L	3	119	77.8	76.5	85.3	72.2	82.1	85.0	6.00	0.0	69.7	59.0	67.9	-	68.8	81.4	74.5	65.8	78.6	83.0	79.4	81.0	1070	82.6	76.0	78.2	8.99	96.2	60.2	11.5	22	2	3	23	77
Magnesium	1	16.2	13.2	14.0	5.34	12.2	6.08	5.89	0.90	-	13.7	12.8	12.6	-	13.4	20.7	-	35.0	14.9	15.8	12.9	13.5	172	12.8	13.4	13.4	1.73	16.9	9.93	12.9	21	3	4	33	67
as Mg in	2	30.0	23.9	22.0	16.9	20.8	51.0	11.9	1.50	-	21.0	18.9	19.8	-	18.5	30.4	-	57.4	20.5	24.0	20.6	21.0	271	20.7	21.9	21.0	3.11	27.2	14.8	14.8	21	5	2	33	67
mgl/L	3	56.0	48.7	49.7	45.3	47.7	4.86	22.9	4.30	-	41.6	42.2	40.1	-	44.8	58.3	-	130	47.6	50.5	46.5	47.5	656	47.5	44.6	47.5	5.58	58.7	36.3	11.7	21	2	3	24	76
Sodium	1	10.7	13.3	9.43	9.20	17.0	-	17.5	9.60	3.38	11.7	9.23	10.3	-	12.5	10.7	10.9	11.6	6.30	11.0	10.5	11.0	13.0	11.0	11.1	10.9	1.40	13.7	8.12	12.8	22	2	2	18	82
as Na in	2	30.5	30.1	29.7	20.8	40.5	-	28.7	29.1	12.3	28.1	21.0	24.4	-	35.0	26.7	26.1	28.4	21.3	25.0	25.9	28.0	30.0	27.4	28.0	28.0	3.22	34.4	21.6	11.5	22	2	4	27	73
mgl/L	3	24.0	65.0	60.0	41.9	68.0	-	43.8	55.4	14.5	46.5	44.2	49.5	-	62.5	53.3	47.9	58.0	48.8	48.6	50.9	55.5	60.0	54.0	53.7	52.1	7.81	67.7	36.5	15.0	22	1	2	14	86
Potassium	1	4.90	3.21	3.33	4.30	1.50	-	10.0	4.20	1.30	2.81	3.01	5.35	-	5.00	3.70	4.28	3.15	2.12	3.93	3.40	4.00	3.40	3.62	3.56	3.59	0.81	5.21	1.97	22.6	22	2	2	18	82
as K in	2	19.0	8.90	7.75	7.44	3.99	-	8.00	5.40	6.20	5.89	7.50	9.18	-	11.2	9.20	7.73	7.20	5.08	8.65	7.70	8.00	9.00	7.86	7.90	7.80	1.17	10.1	5.47	15.0	22	2	3	23	77
mgl/L	3	21.0	7.66	9.44	9.86	5.41	-	3.80	11.7	5.75	9.79	10.1	11.5	-	12.5	12.4	9.11	9.20	7.90	11.0	9.70	10.0	10.0	10.4	10.2	9.93	1.27	12.5	7.38	12.8	22	2	3	23	77
Iron	1	0.37	0.97	0.10	0.12	0.43	0.20	0.01	0.00	0.15	0.01	0.11	0.11	0.26	0.25	0.08	-	-	0.05	0.28	0.10	0.10	-	0.09	0.08	0.11	0.12	0.35	-0.14	114	20	3	0	15	85
as Fe in	2	1.66	1.22	1.23	1.35	1.40	1.10	0.01	1.90	1.35	1.17	1.24	0.89	1.62	3.20	1.29	-	-	1.08	1.09	1.19	1.15	-	1.14	1.23	1.23	0.16	1.54	0.92	12.7	21	4	2	29	71
mgl/L	3	0.30	4.05	3.95	4.08	4.17	3.12	3.40	10.00	4.04	4.02	4.37	2.85	3.30	4.90	3.92	-	-	4.01	3.52	3.88	4.17	-	3.74	4.12	4.01	0.44	4.90	3.12	11.1	21	2	3	24	76
Manganese	1	0.15	0.11	0.09	0.08	0.11	0.50	-	0.10	0.14	-	0.09	0.08	0.30	0.10	0.10	-	0.10	0.02	0.19	-	0.10	0.14	0.10	0.12	0.10	0.03	0.16	0.04	31.2	20	3	1	20	80
as Mn in	2	0.38	0.44	0.37	0.33	0.45	0.60	-	0.20	0.42	-	0.36	0.26	0.30	0.40	0.47	-	1.08	0.20	0.53	-	0.38	0.41	0.40	0.43	0.40	0.07	0.54	0.26	17.2	20	2	3	25	75
mgl/L	3	0.87	1.07	0.94	0.85	4.17	1.20	-	1.10	1.02	-	0.92	0.64	1.10	0.90	1.10	-	3.66	1.06	1.11	-	0.93	0.84	0.96	1.04	1.03	0.14	1.30	0.76	13.2	20	2	1	15	85
Aluminium	1	-	0.10	0.31	0.04	-	0.08	-	-	-	-	0.41	-	-	0.05	-	-	0.13	0.03	0.59	-	0.10	0.08	0.12	0.11	0.10	0.04	0.18	0.02	41.5	13	3	0	23	77
as Al in	2	-	0.65	0.81	0.26	-	0.39	-	-	-	-	1.62	-	-	0.37	-	-	0.68	0.10	0.99	-	0.68	0.44	0.70	0.67	0.67	0.23	1.13	0.21	34.5	13	1	1	15	85
mgl/L	3	-	1.08	1.22	0.56	-	0.88	-	-	-	-	2.30	-	-	0.61	-	-	1.07	0.16	1.17	-	1.16	0.58	1.17	1.06	1.07	0.42	1.90	0.24	38.8	13	1	1	15	85
Sulphate	4	15.4	16.3	15.2	16.8	4.3	37.0	15.4	24.7	0.00	24.5	50.2	27.0	19.0	20.5	8.64	5.15	21.2	24.7	18.5	16.9	27.0	20.3	16.3	16.5	18.5	6.50	31.5	5.51	35.1	23	2	3	22	78
as SO4 in	5	29.6	30.4	25.9	31.0	15.9	55.0	27.5	30.8	0.00	44.7	61.7	43.0	30.0	34.5	16.5	11.3	8.23	29.9	26.8	29.1	46.0	22.2	28.1	28.1	29.6	4.76	39.1	20.1	16.1	23	5	5	43	57
mgl/L	6	45.9	56.8	45.5	50.0	29.6	72.0	45.7	39.1	0.01	62.6	74.9	63.0	49.0	58.8	50.6	20.6	24.7	42.6	49.4	50.7	72.0	48.6	50.1	50.2	49.7	9.3	68.3	31.1	18.7	24	3	4	29	71
Chloride	4	35.7	29.4	29.4	31.2	31.3	34.9	41.0	29.6	28.5	31.3	32.0	30.0	41.6	32.3	30.1	28.1	36.9	39.0	31.7	28.1	28.0	31.6	29.8	28.8	31.3	2.61	36.5	26.0	8.34	24	4	0	17	83
as Cl in	5	47.6	45.6	42.7	48.3	51.7	45.8	64.0	40.2	43.7	44.7	44.7	47.0	49.5	46.5	42.5	39.7	51.8	51.0	47.5	42.4	40.5	49.2	42.3	42.6	45.7	4.40	54.5	36.9	9.63	24	1	0	4	96
mgl/L	6	76.0	67.0	65.5	66.7	72.3	67.7	86.0	60.6	65.9	65.4	69.5	70.0	71.6	69.6	67.4	60.9	72.6	71.0	68.6	66.9	61.5	70.3	65.5	65.4	67.6	3.70	74.9	60.2	5.47	24	2	0	8	92
Fluoride	4	0.09	0.19	0.25	0.42	0.16	0.20	0.30	-	-	0.18	0.50	<0.01	22.6	0.15	0.10	-	0.21	-	-	0.15	0.12	0.11	0.11	0.124	0.16	0.08	0.33	-0.01	51.7	19	3	0	16	84
as F in	5	0.30	0.57	0.31	0.71	0.40	0.40	0.10	-	-	0.52	0.45	0.33	22.6	0.26	0.24	-	1.50	-	-	0.34	0.32	0.34	0.39	0.372	0.37	0.13	0.62	0.12	33.7	19	3	1	21	79
mgl/L	6	1.40	1.45	0.85	3.60	1.40	1.50	1.10	-	-	1.46	0.51	1.49	22.6	0.76	0.96	-	2.00	-	-	1.33	1.27	1.42	1.56	1.52	1.42	0.24	1.90	0.94	16.9	19	3	3	32	68
Nitrate	4	9.34	1.94	2.54	-	1.18	1.70	0.01	-	-	2.17	-	1.90	16.7	2.20	0.84	2.40	2.75	3.61	5.88	1.92	2.52	2.21	2.00	2.16	2.19	0.50	3.19	1.18	23.0	20	4	3	35	65
as N in	5	14.6	3.43	3.78	-	1.93	2.10	0.01	-	-	3.68	-	3.20	49.3	3.20	1.46	3.60	5.10	5.65	3.30	3.15	3.75	3.84	3.35	3.50	3.47	0.45	4.37	2.56	13.0	20	4	4	40	60
mgl/L	6	30.7	7.21	7.15	-	3.50	2.50	0.01	-	-	7.14	-	7.50	29.5	5.60	3.08	7.00	5.00	7.45	6.65	6.41	7.59	7.99	6.25	6.76	6.88	1.49	9.86	3.90	21.7	20	2	4	30	70
																														SUM	681	87	74	24	76

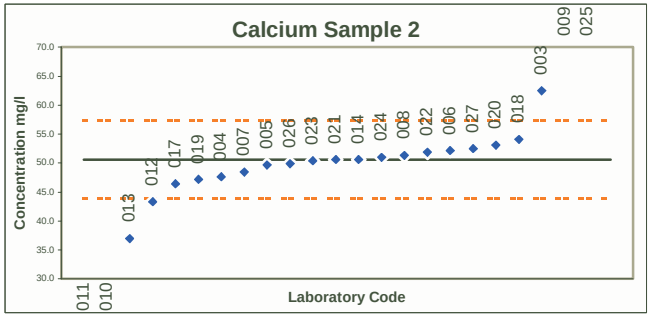
APPENDIX C: Z-scores for all participants

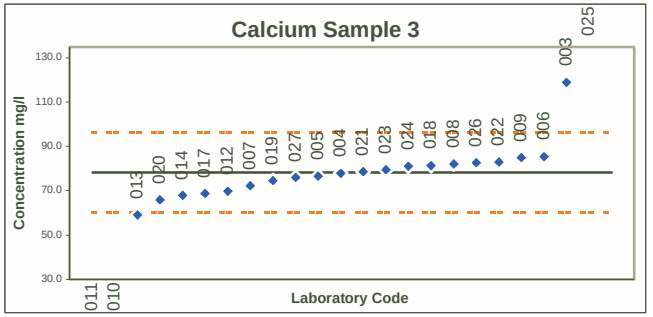
Lab Code		003	004	005	006	007	008	009	010	011	012	013	014	016	017	018	019	020	021	022	023	024	025	026	027
Calcium as Ca in mgl/L	1	-0.71	-0.04	-0.09	1.79	0.81	4.88	8.34	-9.73	-10.6	-1.05	-2.99	-1.70	-	-0.91	4.21	-0.56	-0.28	0.28	0.04	0.00	0.12	131	0.00	0.24
	2	3.48	-0.88	-0.28	0.45	-0.64	0.20	6.80	-13.7	-14.8	-2.15	-4.00	0.00	-	-1.24	1.02	-1.01	0.73	0.00	0.38	-0.06	0.11	183	-0.21	0.55
	3	4.54	-0.04	-0.19	0.79	-0.67	0.43	0.76	-8.03	-8.70	-0.94	-2.14	-1.15	-	-1.05	0.36	-0.41	-1.38	0.04	0.53	0.13	0.31	110	0.49	-0.24
Magnesium as Mg in mgl/L	1	1.61	-0.12	0.34	-4.65	-0.69	-4.22	-4.33	-7.21	-	0.16	-0.36	-0.48	-	0.00	4.21	-	12.45	0.86	1.38	-0.29	0.06	91	-0.35	0.00
	2	2.90	0.94	0.33	-1.32	-0.07	9.67	-2.92	-6.27	-	0.00	-0.66	-0.38	-	-0.80	3.03	-	11.73	-0.15	0.97	-0.12	0.01	80	-0.09	0.30
	3	1.52	0.22	0.40	-0.39	0.04	-7.64	-4.41	-7.74	-	-1.05	-0.95	-1.32	-	-0.48	1.94	-	14.77	0.02	0.54	-0.18	0.00	109	0.00	-0.52
Sodium as Na in mgl/L	1	-0.16	1.69	-1.07	-1.23	4.33	-	4.69	-0.94	-5.38	0.55	-1.21	-0.45	-	1.12	-0.16	-0.05	0.48	-3.30	0.05	-0.30	0.05	1.48	0.05	0.12
	2	0.78	0.65	0.54	-2.25	3.88	-	0.22	0.34	-4.89	0.02	-2.16	-1.12	-	2.17	-0.40	-0.60	0.12	-2.08	-0.93	-0.65	0.00	0.62	-0.19	0.00
	3	-3.60	1.65	1.01	-1.31	2.04	-	-1.06	0.42	-4.82	-0.72	-1.01	-0.34	-	1.33	0.15	-0.53	0.76	-0.42	-0.45	-0.15	0.44	1.01	0.24	0.20
Potassium as K in mgl/L	1	1.61	-0.47	-0.33	0.87	-2.57	-	7.90	0.75	-2.82	-0.96	-0.71	2.17	-	1.74	0.14	0.85	-0.54	-1.81	0.42	-0.23	0.51	-0.23	0.04	-0.04
	2	9.57	0.94	-0.05	-0.31	-3.26	-	0.17	-2.06	-1.37	-1.64	-0.26	1.18	-	2.90	1.19	-0.06	-0.52	-2.33	0.72	-0.09	0.17	1.02	0.05	0.08
	3	8.69	-1.78	-0.39	-0.05	-3.55	-	-4.81	1.39	-3.28	-0.11	0.16	1.26	-	2.02	1.94	-0.64	-0.57	-1.59	0.84	-0.18	0.05	0.05	0.37	0.21
Iron as Fe in mgl/L	1	2.15	7.05	-0.04	0.13	2.64	0.76	-0.80	-0.88	0.35	-0.80	-0.02	0.02	1.25	1.17	-0.22	-	-	-0.47	1.39	-0.06	-0.06	-	-0.14	-0.22
	2	2.76	-0.06	0.03	0.77	1.09	-0.84	-7.84	4.30	0.77	-0.39	0.08	-2.18	2.51	12.65	0.39	-	-	-0.96	-0.90	-0.26	-0.51	-	-0.58	0.00
	3	-8.34	0.09	-0.13	0.15	0.36	-2.00	-1.37	13.5	0.07	0.02	0.81	-2.61	-1.60	2.00	-0.20	-	-	0.00	-1.10	-0.29	0.36	-	-0.61	0.25
Manganese as Mn in mgl/L	1	1.56	0.29	-0.38	-0.73	0.29	12.66	-	-0.03	1.30	-	-0.50	-0.67	6.32	-0.03	-0.03	-	0.03	-2.57	2.89	-	-0.03	1.21	-0.03	0.60
	2	-0.29	0.58	-0.45	-1.03	0.73	2.91	-	-2.91	0.22	-	-0.63	-2.04	-1.46	0.00	0.98	-	9.91	-2.91	1.95	-	-0.29	0.15	0.00	0.44
	3	-1.18	0.29	-0.70	-1.36	23.15	1.25	-	0.52	-0.07	-	-0.79	-2.88	0.52	-0.96	0.52	-	19.39	0.22	0.59	-	-0.74	-1.43	-0.52	0.07
Aluminium as Al in mgl/L	1	-	0.00	5.03	-1.45	-	-0.48	-	-	-	-	7.36	-	-	-1.20	-	-	0.82	-1.69	11.83	-	0.00	-0.53	0.48	0.17
	2	-	-0.07	0.64	-1.77	-	-1.20	-	-	-	-	4.16	-	-	-1.29	-	-	0.07	-2.46	1.41	-	0.06	-0.97	0.15	0.00
	3	-	0.02	0.36	-1.23	-	-0.46	-	-	-	-	2.96	-	-	-1.11	-	-	0.00	-2.19	0.24	-	0.22	-1.18	0.24	-0.02
Sulphate as SO4 in mgl/L	4	-0.48	-0.34	-0.50	-0.26	-2.19	2.85	-0.48	0.95	-2.85	0.93	4.88	1.31	0.08	0.31	-1.52	-2.05	0.42	0.95	0.00	-0.25	1.31	0.28	-0.34	-0.31
	5	0.00	0.17	-0.78	0.29	-2.88	5.34	-0.44	0.25	-6.22	3.17	6.76	2.82	0.08	1.03	-2.75	-3.84	-4.49	0.06	-0.59	-0.11	3.45	-1.56	-0.32	-0.32
	6	-0.41	0.76	-0.45	0.03	-2.16	2.40	-0.43	-1.14	-5.34	1.39	2.71	1.43	-0.08	0.98	0.10	-3.13	-2.69	-0.76	-0.03	0.11	2.40	-0.12	0.04	0.05
Chloride as Cl in mgl/L	4	1.71	-0.71	-0.69	-0.01	0.03	1.40	3.74	-0.63	-1.06	0.01	0.27	-0.48	3.96	0.40	-0.44	-1.23	2.17	2.97	0.17	-1.21	-1.25	0.13	-0.56	-0.94
	5	0.43	-0.02	-0.68	0.59	1.36	0.02	4.16	-1.25	-0.45	-0.23	-0.22	0.30	0.85	0.18	-0.73	-1.35	1.39	1.20	0.41	-0.75	-1.18	0.80	-0.77	-0.70
	6	2.29	-0.15	-0.57	-0.22	1.28	0.04	4.99	-1.88	-0.45	-0.57	0.53	0.66	1.09	0.55	-0.04	-1.80	1.37	0.93	0.28	-0.18	-1.64	0.74	-0.55	-0.58
Fluoride as F in mgl/L	4	-0.85	0.36	1.04	3.15	0.00	0.48	1.69	-	-	0.24	4.11	-1.81	271	-0.12	-0.73	-	0.60	-	-	-0.12	-0.45	-0.65	-0.60	-0.44
	5	-0.57	1.58	-0.50	2.70	0.22	0.22	-2.17	-	-	1.18	0.62	-0.34	177	-0.89	-1.05	-	9.00	-	-	-0.26	-0.39	-0.22	0.14	0.00
	6	-0.08	0.12	-2.38	9.08	-0.08	0.33	-1.33	-	-	0.17	-3.79	0.29	88.2	-2.75	-1.92	-	2.41	-	-	-0.37	-0.62	0.00	0.58	0.41
Nitrate as N in mgl/L	4	14.25	-0.49	0.71	-	-2.00	-0.97	-4.33	-	-	-0.03	-	-0.57	28.9	0.03	-2.68	0.43	1.12	2.84	7.36	-0.53	0.67	0.05	-0.37	-0.05
	5	24.7	-0.08	0.70	-	-3.40	-3.02	-7.65	-	-	0.48	-	-0.59	101	-0.59	-4.44	0.30	3.62	4.84	-0.37	-0.70	0.63	0.83	-0.25	0.08
	6	15.97	0.22	0.18	-	-2.27	-2.94	-4.60	-	-	0.17	-	0.42	15.15	-0.86	-2.55	0.08	-1.26	0.38	-0.15	-0.32	0.48	0.74	-0.42	-0.08

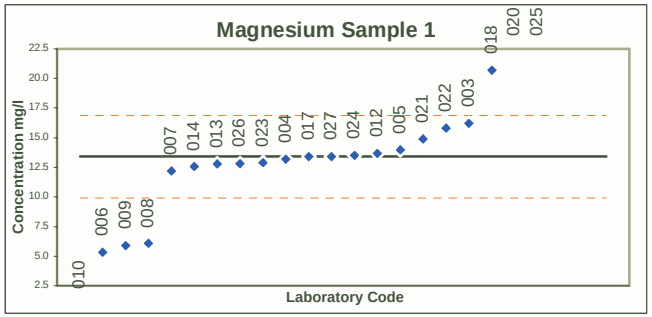
APPENDIX D: Graphical display of all results per parameter

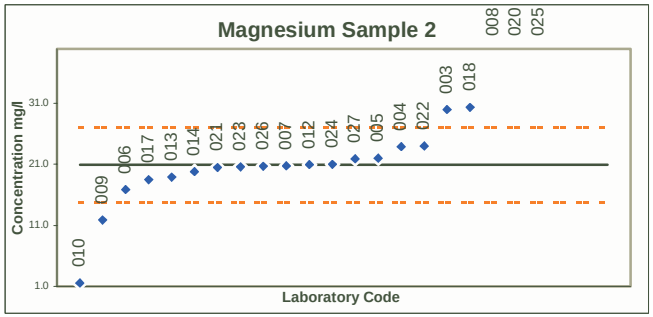
LEGEND: _____ Assigned value - - - - - - Limits

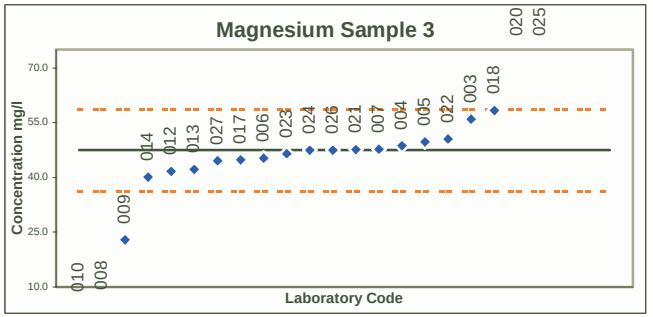


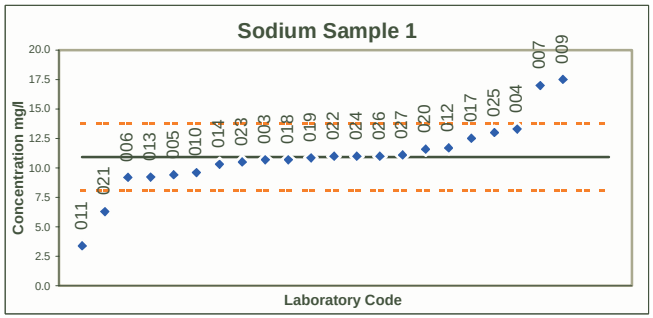


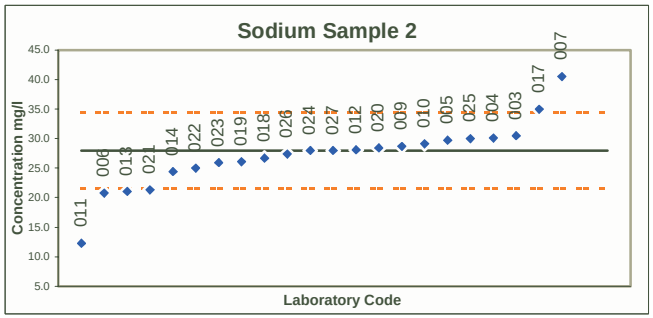


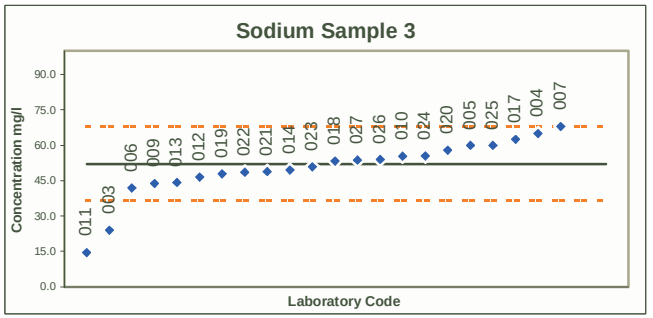




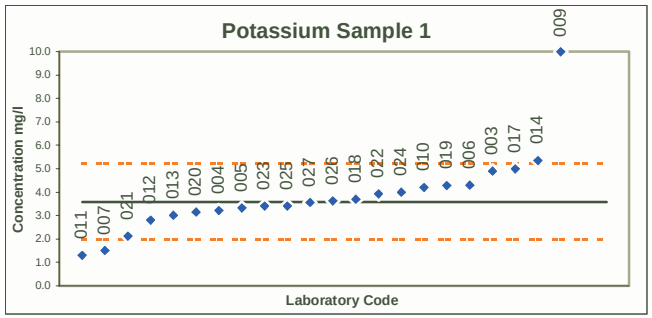


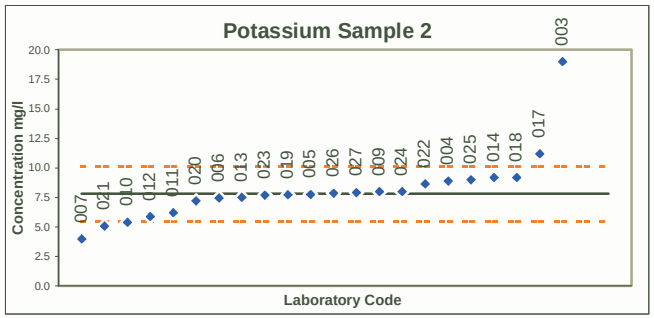


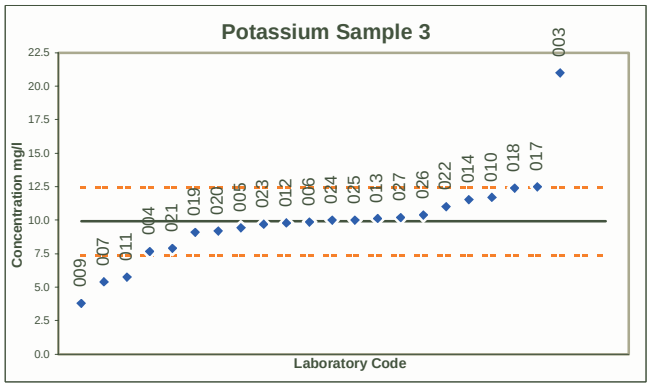


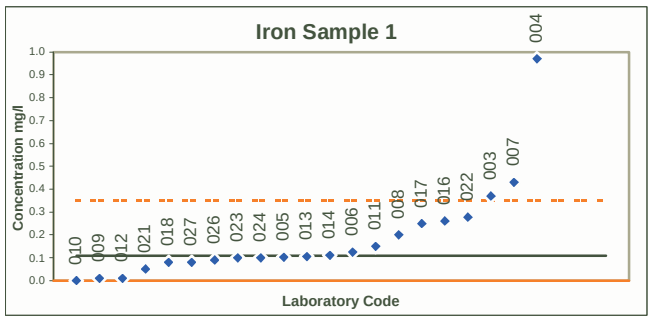


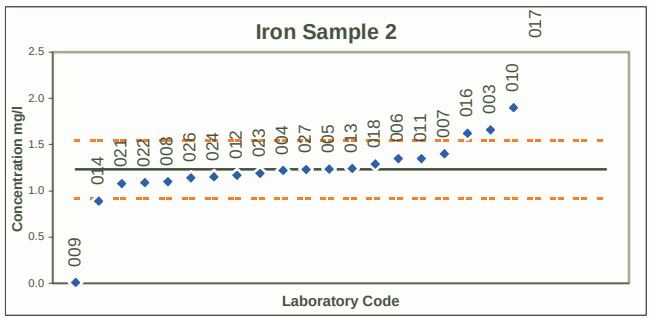
APPENDIX D: Graphical display of all results per parameter

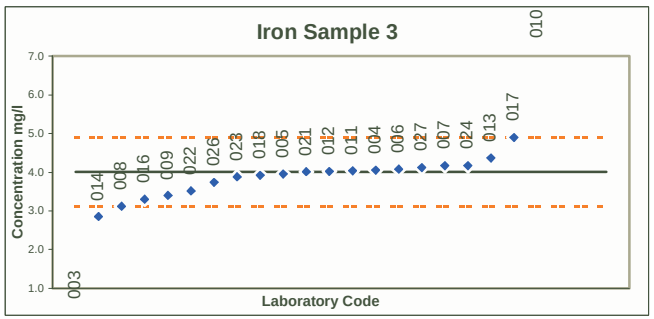


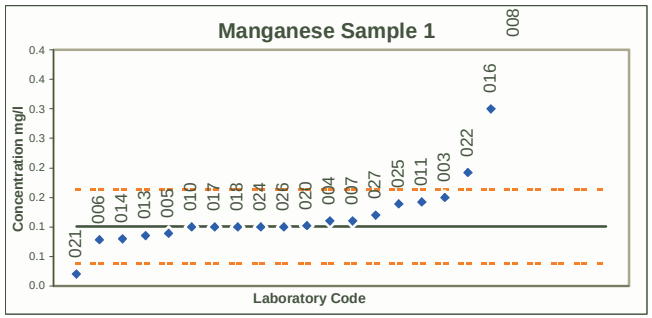


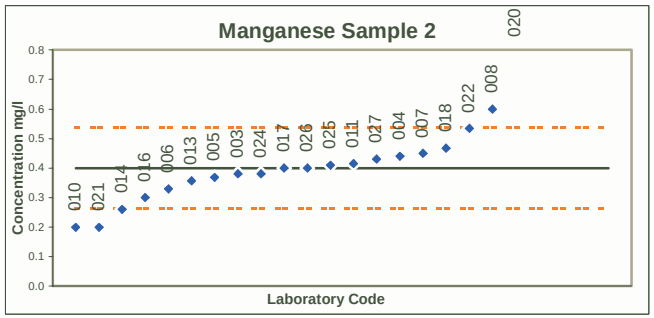


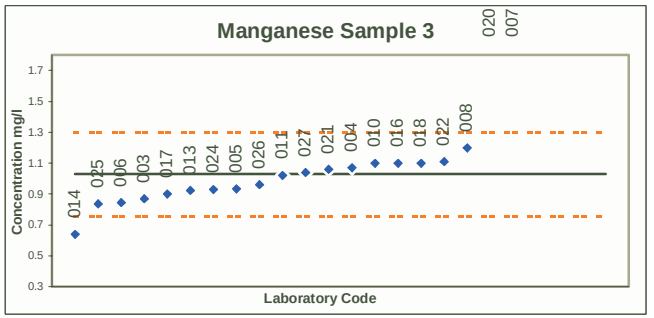




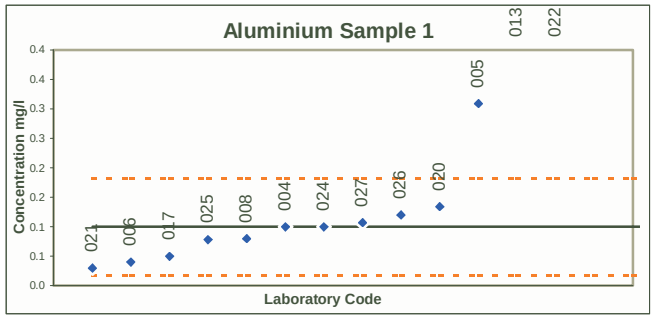


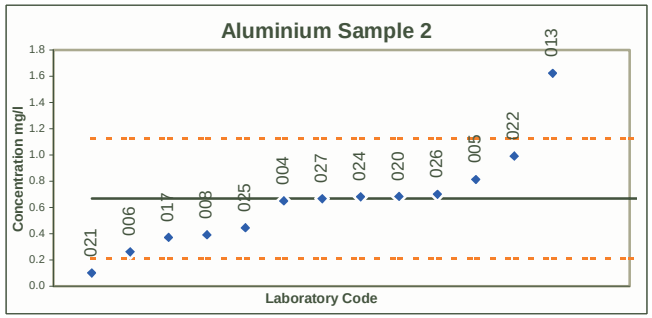


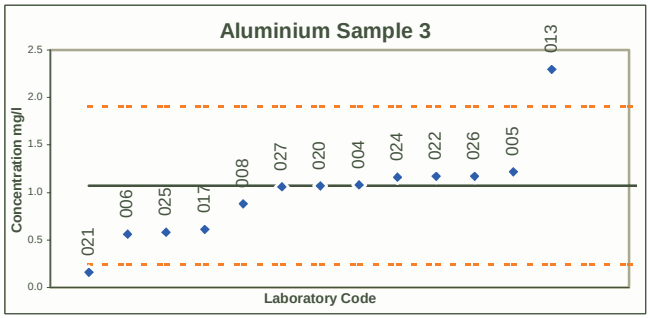


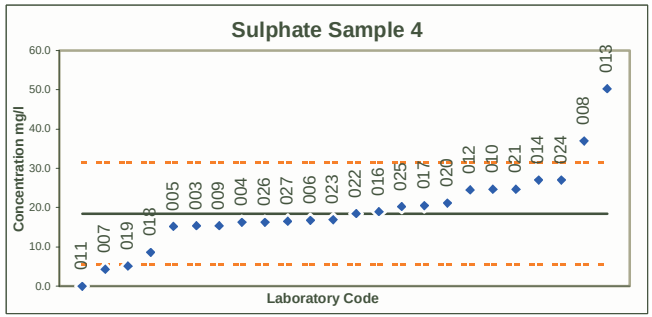


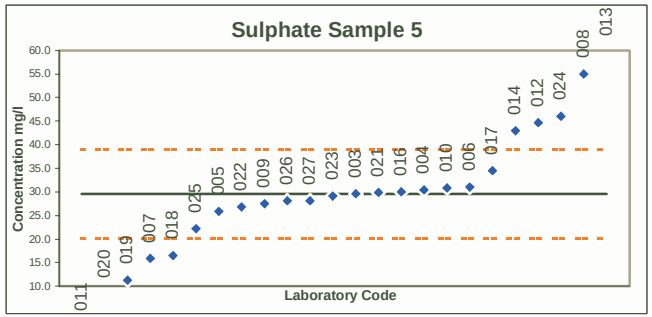
APPENDIX D: Graphical display of all results per parameter

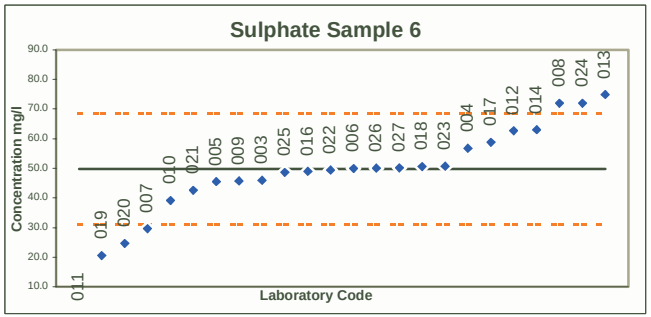


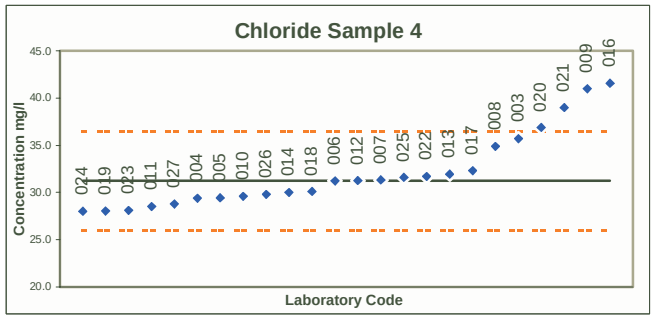


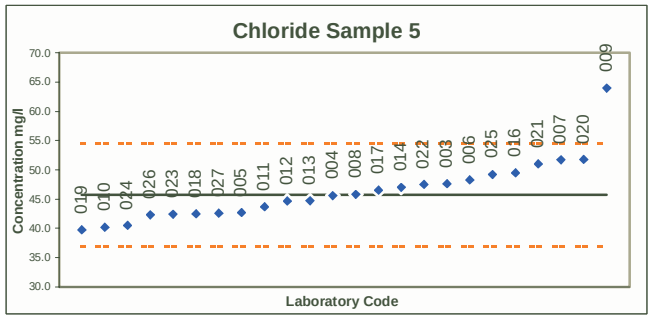


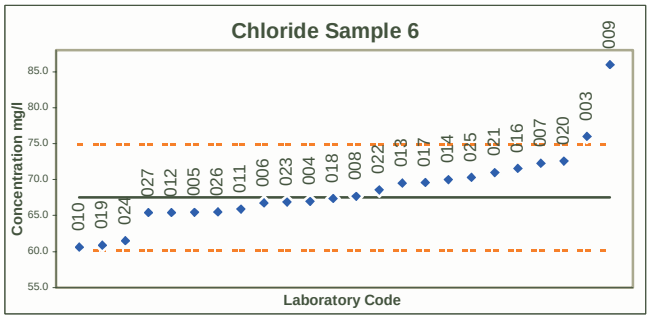




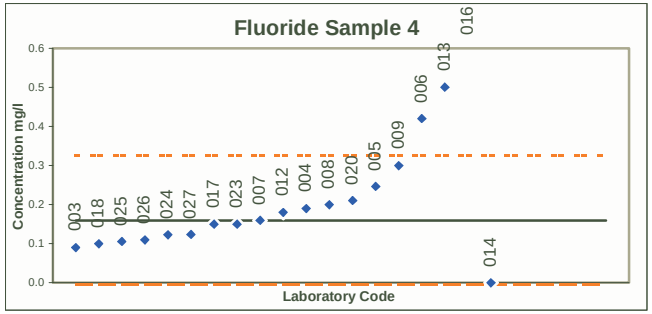


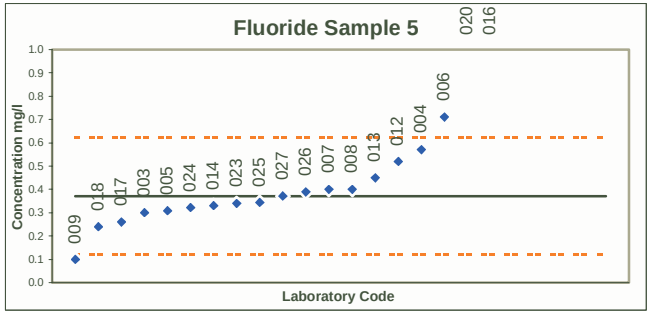


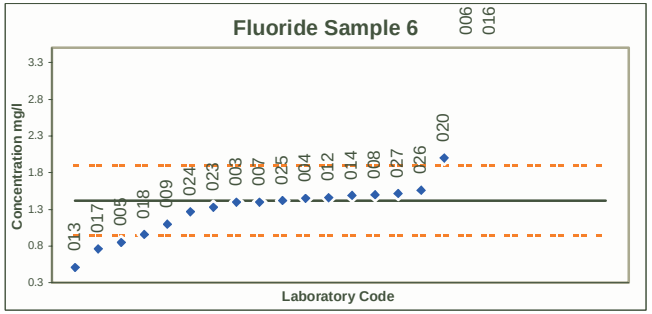


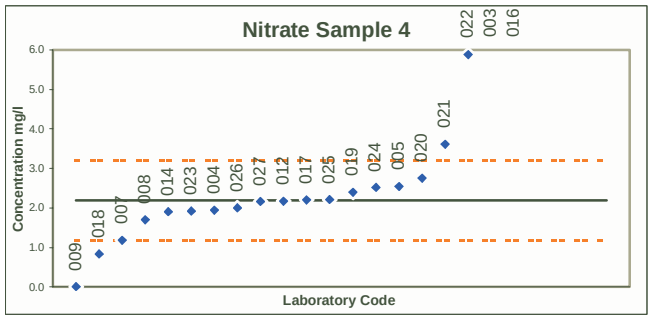


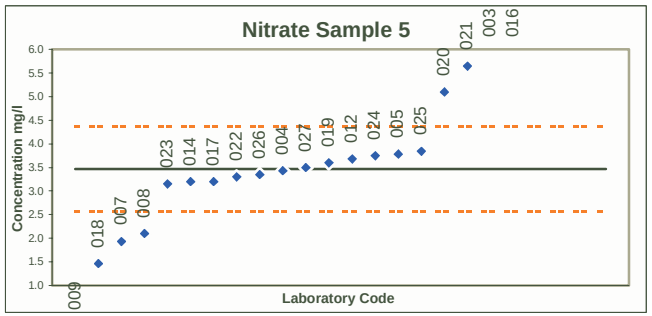
APPENDIX D: Graphical display of all results per parameter

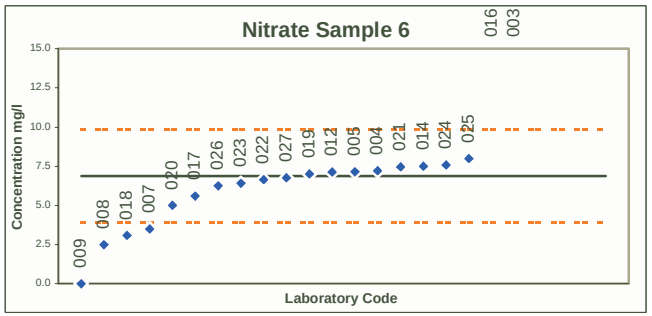






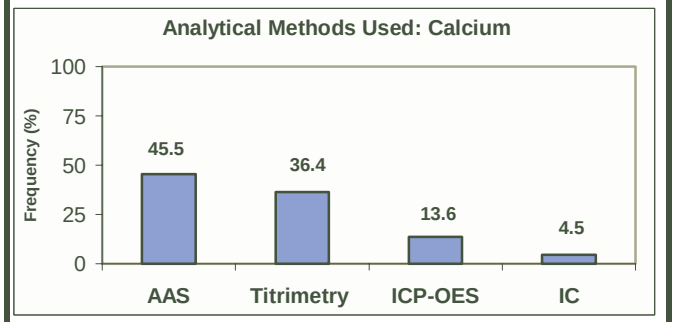


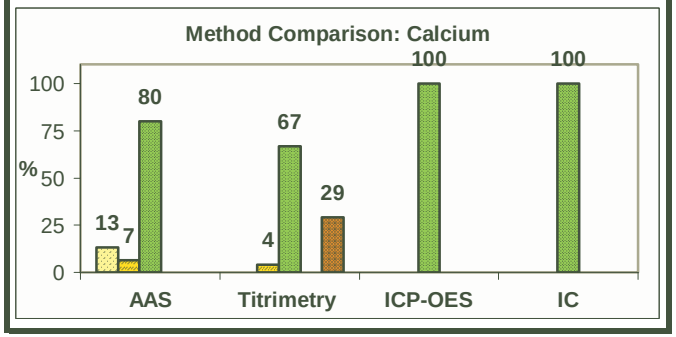


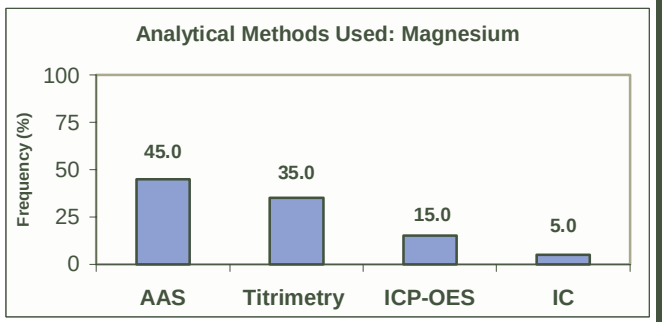


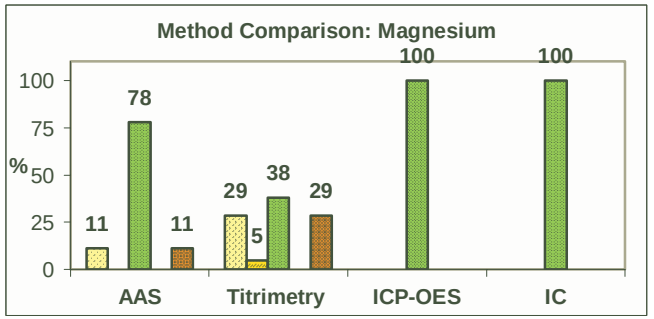
APPENDIX E: Graphical display of frequency and performance of methodologies used

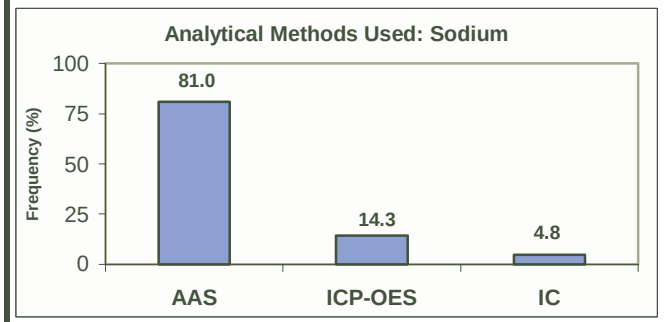
Method Comparison LEGEND: %Too Low | %Low | %Correct | %High | %Too high

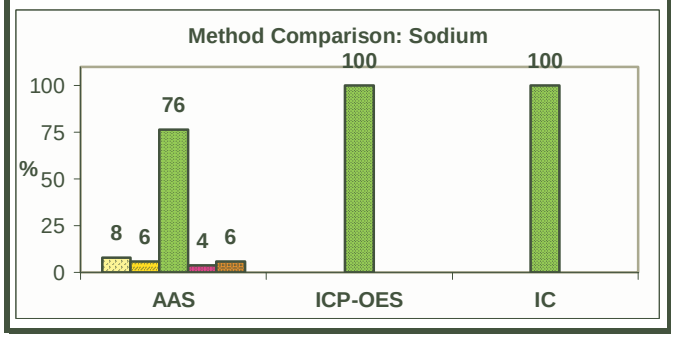


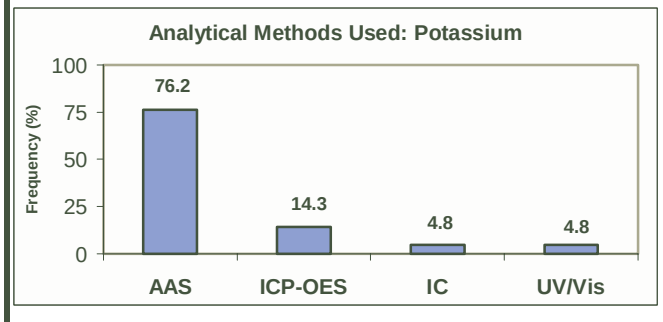


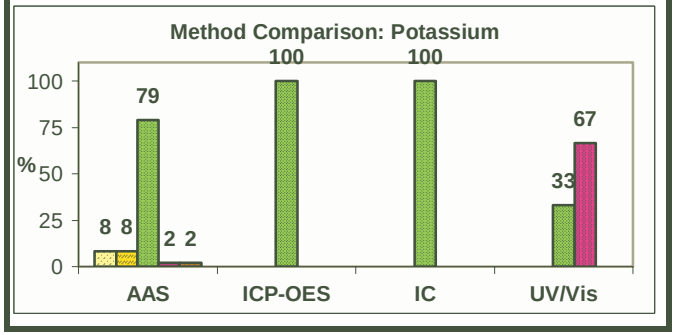


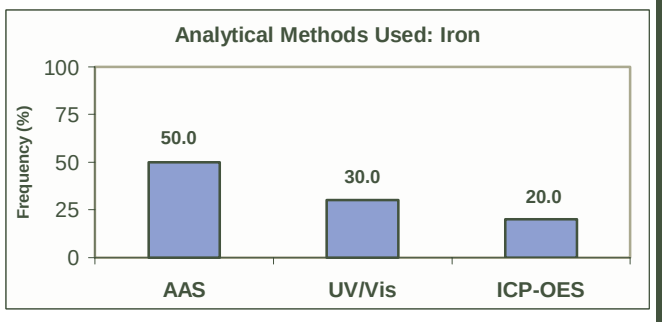


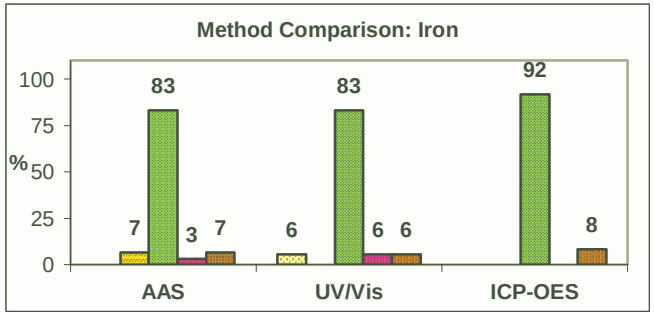


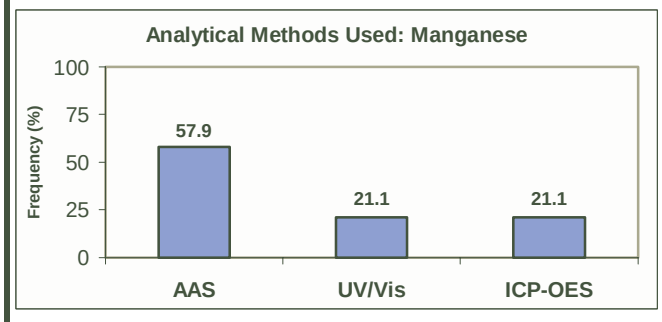


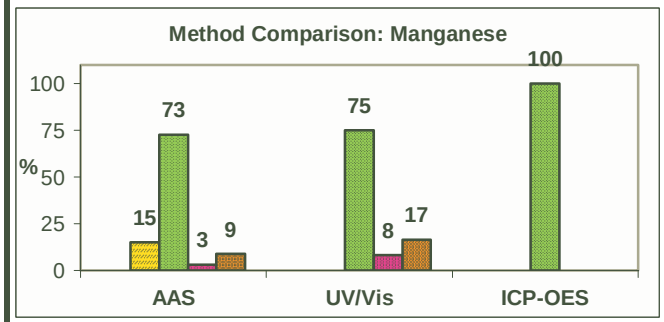




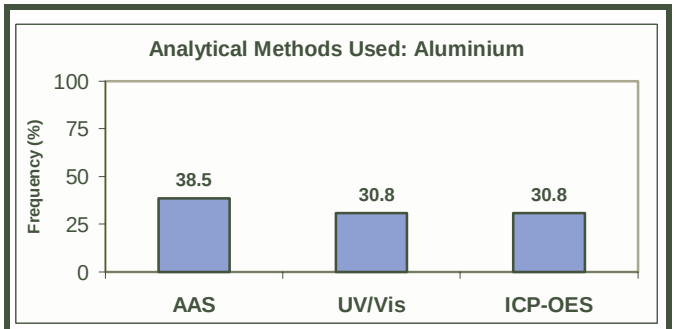


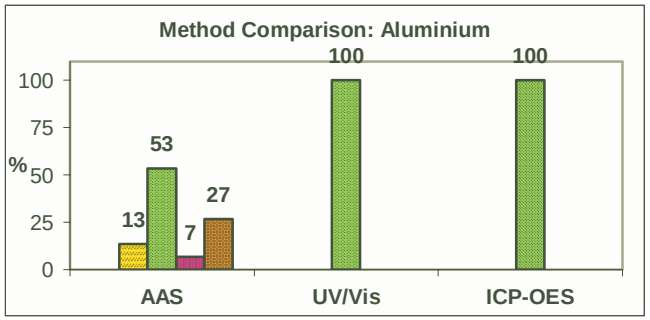


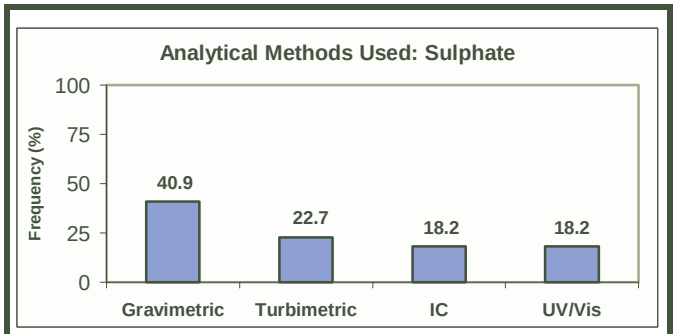


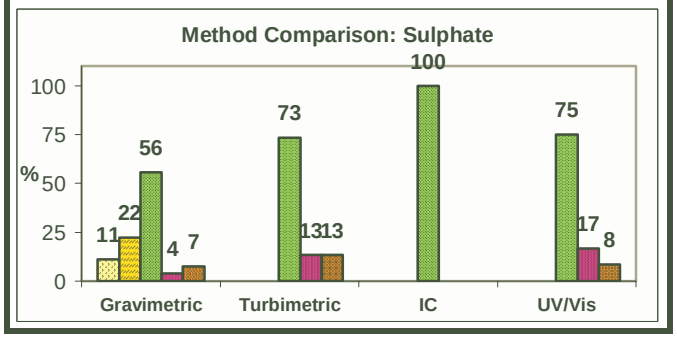


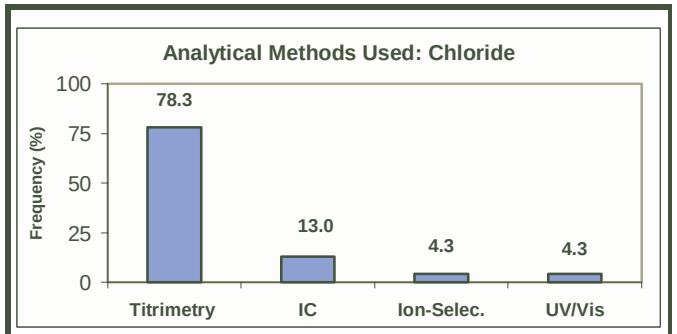
APPENDIX E: Graphical display of frequency and performance of methodologies used

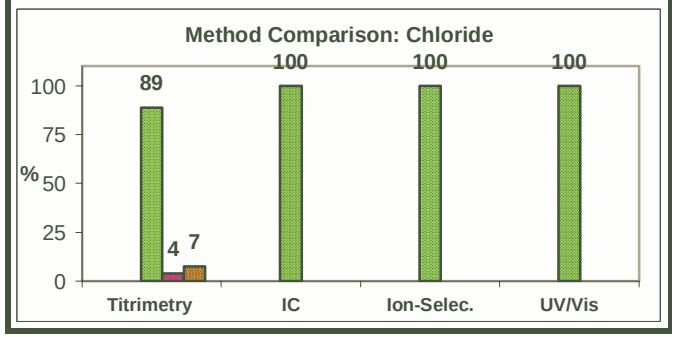


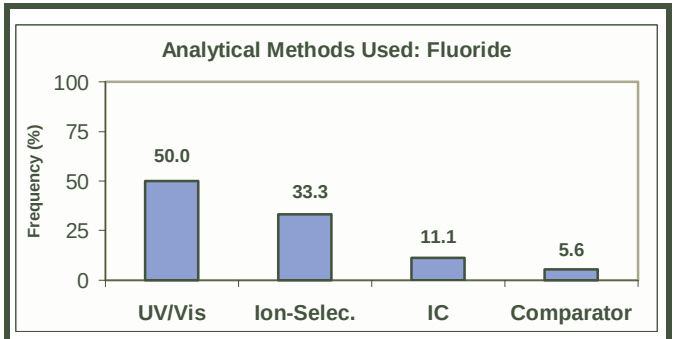


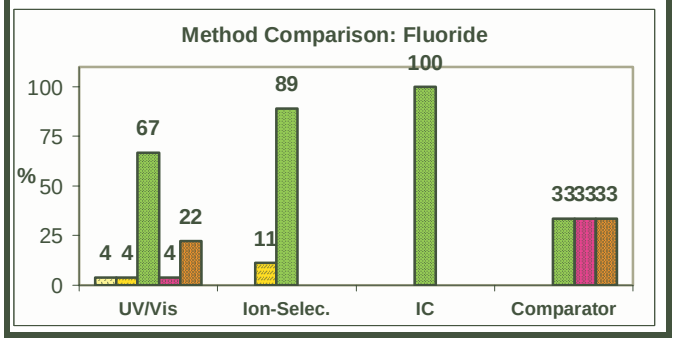


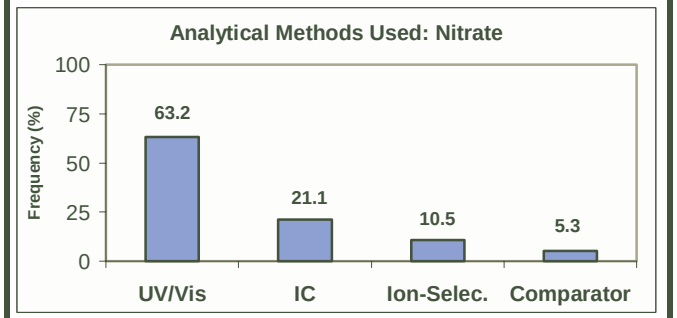


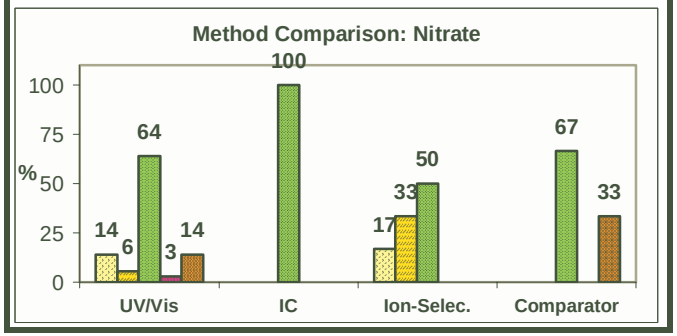












Universität Stuttgart

Comparison of different evaluation and assessment procedures

Dr.-Ing. Michael Koch

Institute for Sanitary Engineering, Water Quality and Solid Waste Management, Universität Stuttgart
Dep. Hydrochemistry
Bandtäle 2, 70569 Stuttgart
Tel.: +49 711/685-5444 Fax: +49 711/685-7809
E-mail: Michael.Koch@iswa.uni-stuttgart.de
http://www.iswa.uni-stuttgart.de/ch

1

Method 1 – Hampel estimator / q-method Z_U-scores

- from DIN 38402 –A45
- robust method used in Germany
- mean: hampel estimator

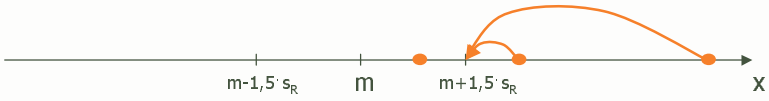
- std: q-method
  - from 1st quartile of the absolute differences
- modified, unsymmetrical Z-scores

Method 2 – Median / normalized IQR

- method used by Umgeni for the evaluation
- mean: median (central value)
- std: normalized IQR
  - difference between 1st and 3rd quartile, normalized to a standard deviation with a factor 0.7413
- Z-scores

Method 3 – Algorithm A

- recommended by ISO/DIS 13528
- mean: Huber estimator



- std:

$$s = 1.134\sqrt{\frac{\left(x_i^* - m^*\right)^2}{n-1}}$$

x_i^*: transformed values

- Z-scores

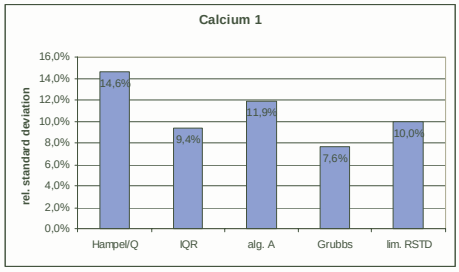
Method 4 – mean/std with Grubbs-test

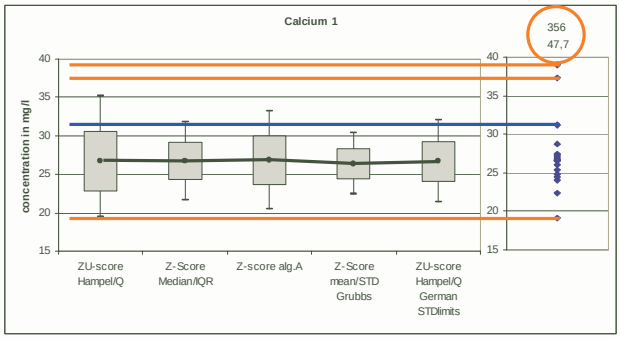
- Conventional statistics after elimination of outliers with the Grubbs-test
- Z-scores

Method 5 – limited std

- identical with method 1, but with limitation of the standard deviation based on experience from previous PTs
  - sulphate: 8%
  - chloride: 9%
  - Ca, Mg, Na, nitrate: 10%
  - K, Fe, fluoride: 12%
  - Mn: 15%
  - Al: 30%

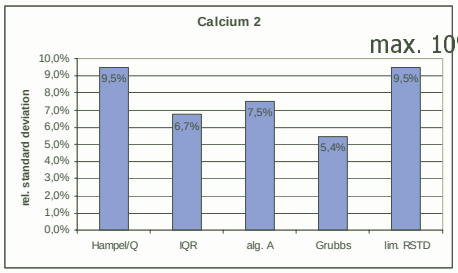
Calcium - 1

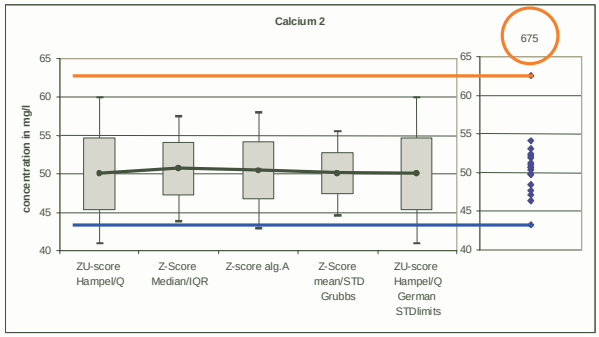




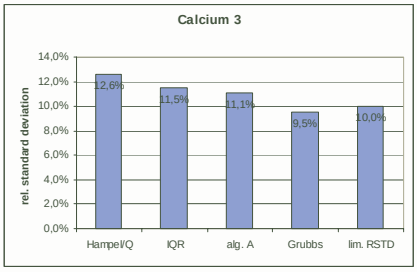
Calcium - 2

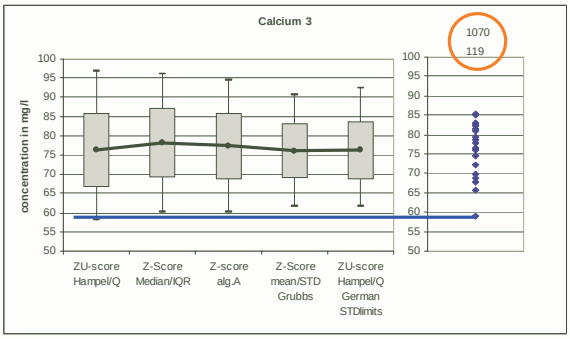
max. 10%





Calcium - 3



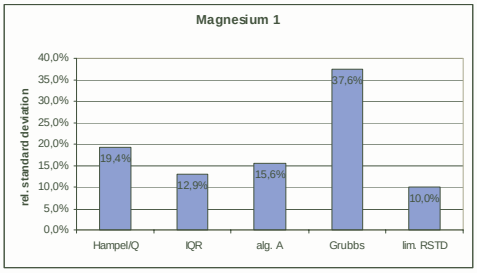


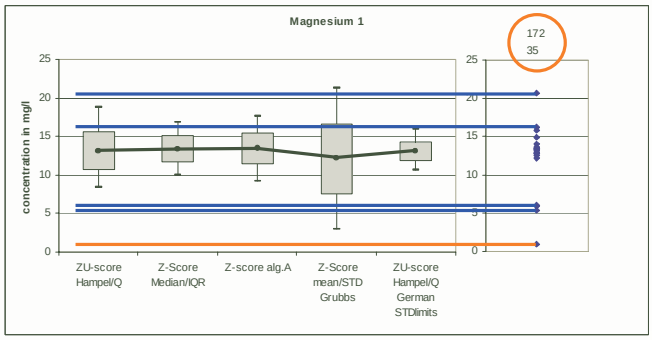
Calcium

- convention: 2 wrong values → not successful
- 5 labs completely out of range
- no difference in the assessment of labs between the 5 methods

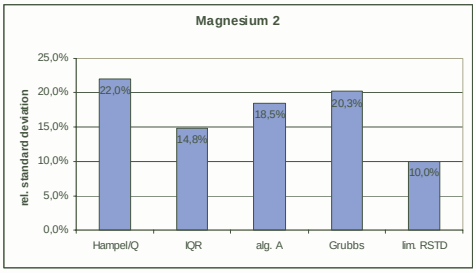
	calcium success				
	ZU-score Hampel/Q	Z-Score Median/IQR	Z-score alg.A	Z-Score mean/STD Grubbs	ZU-score Hampel/Q German STDlimits
1					
2					
3	Y N N	Y N N	Y N N	Y N N	Y N N
4	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
5	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
6	Y Y Y	Y Y Y	Y Y Y	N Y Y	Y Y Y
7	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
8	N Y Y	N Y Y	N Y Y	N Y Y	N Y Y
9	N N Y	N N Y	N N Y	N N Y	N N Y
10	N N N	N N N	N N N	N N N	N N N
11					
12	Y Y Y	Y N Y	Y Y Y	Y N Y	Y Y Y
13	N N Y	N N N	N N N	N N N	N N N
14	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
15					
16					
17	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
18	N Y Y	N Y Y	N Y Y	N Y Y	N Y Y
19	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
20	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
21	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
22	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
23	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
24	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
25	N N N	N N N	N N N	N N N	N N N
26	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
27	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y

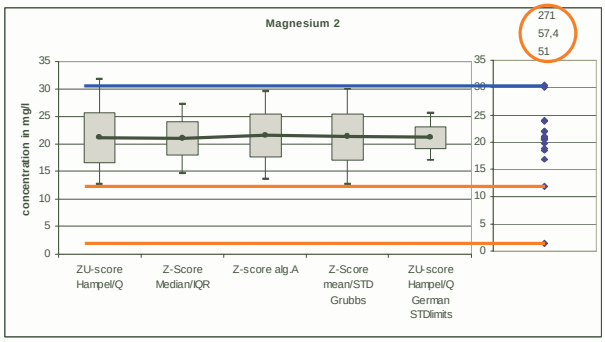
Magnesium - 1



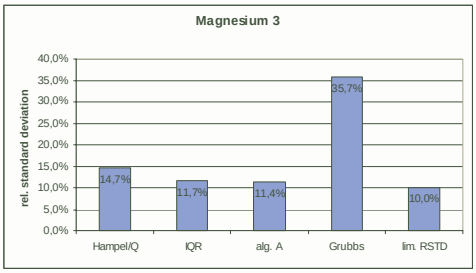


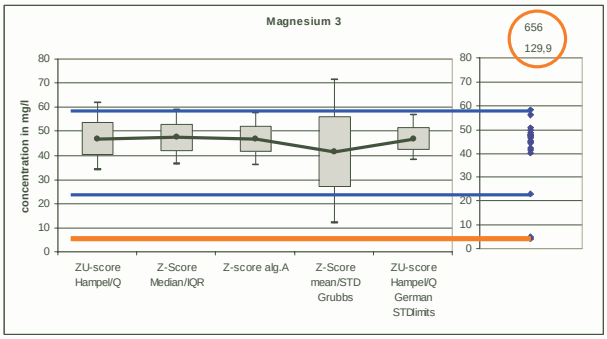
Magnesium - 2





Magnesium - 3



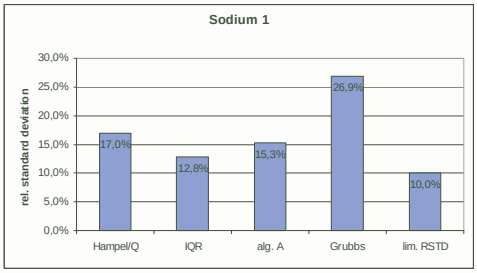


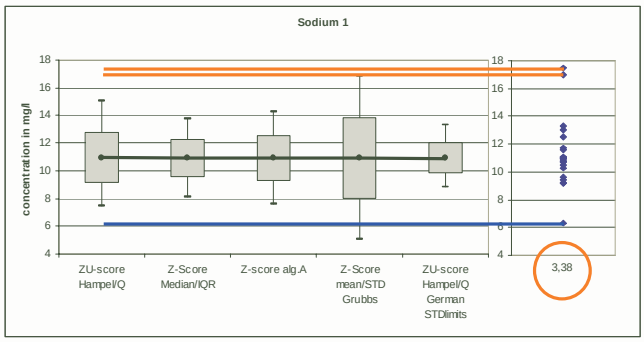
Magnesium

- 5(4) labs completely out of range
- 1 additional lab failed when using median/IQR, algorithm A or limited std (10%)
- 2 additional labs failed when using limited std (10%)

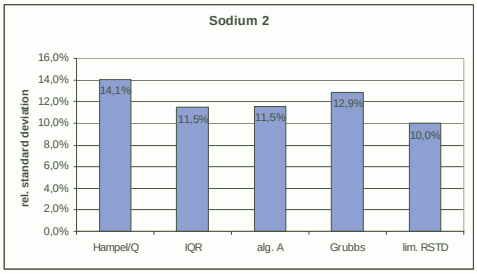
	magnesium success				
	ZU-score Hampel/Q	Z-Score Median/IQR	Z-score alg.A	Z-Score mean/STD Grubbs	ZU-score Hampel/Q German STDlimits
1					
2					
3	Y Y Y	Y N Y	Y N Y	Y N Y	N N Y
4	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
5	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
6	N Y Y	N Y Y	N Y Y	Y Y Y	N N Y
7	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
8	N N N	N N N	N N N	Y N N	N N N
9	N N N	N N N	N N N	Y N Y	N N N
10	N N N	N N N	N N N	N N N	N N N
11					
12	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
13	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
14	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
15					
16					
17	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
18	N Y Y	N N Y	N N N	Y N Y	N N N
19					
20	N N N	N N N	N N N	N N N	N N N
21	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
22	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
23	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
24	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
25	N N N	N N N	N N N	N N N	N N N
26	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
27	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y

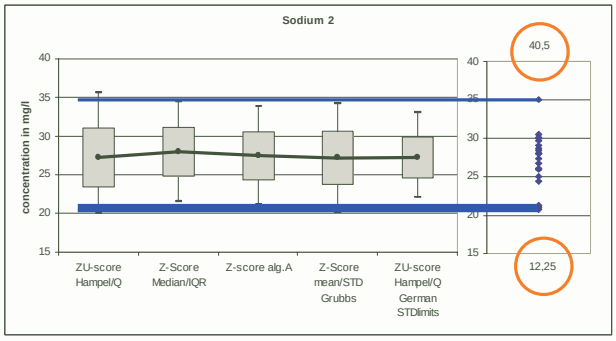
Sodium - 1



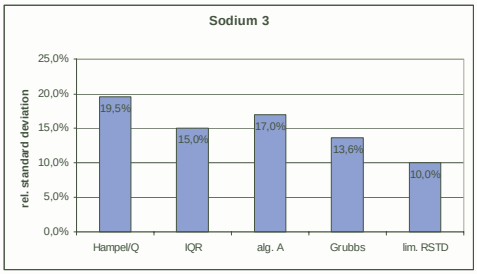


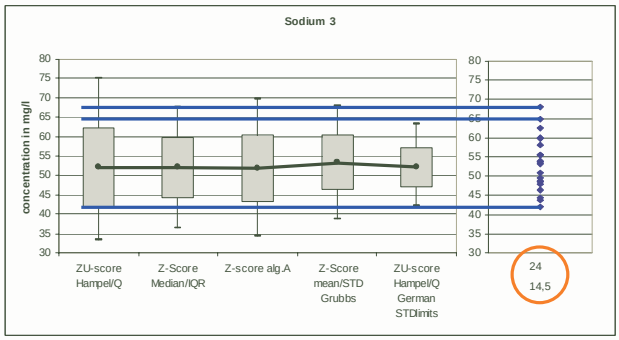
Sodium - 2





Sodium - 3



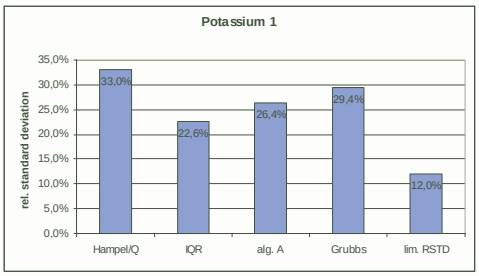


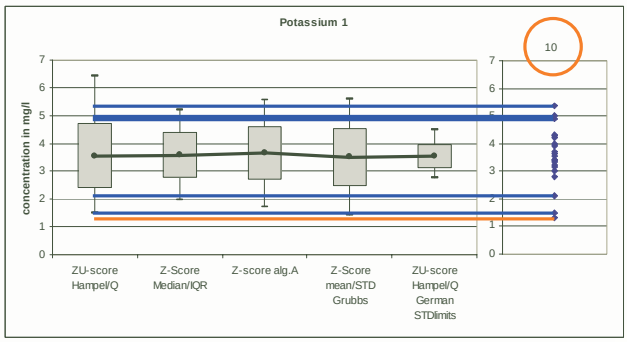
Sodium

- 2 labs completely out of range
- 1 additional lab failed when using median/IQR or limited std (10%)
- 2 additional labs failed when using limited std (10%)

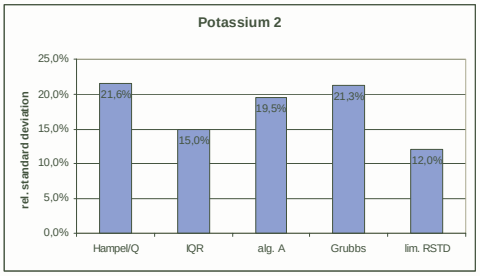
	sodium success				
	ZU-score Hampel/Q	Z-Score Median/IQR	Z-score alg.A	Z-Score mean/STD Grubbs	ZU-score Hampel/Q German STDlimits
1					
2					
3	Y Y N	Y Y N	Y Y N	Y Y N	Y Y N
4	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y N
5	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
6	Y Y Y	Y N Y	Y N Y	Y Y Y	Y N N
7	N N Y	N N N	N N Y	N N N	N N N
8					
9	N Y Y	N Y Y	N Y Y	N Y Y	N Y Y
10	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
11	N N N	N N N	N N N	N N N	N N N
12	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
13	Y Y Y	Y N Y	Y N Y	Y Y Y	Y N Y
14	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
15					
16					
17	Y Y Y	Y N Y	Y N Y	Y N Y	Y N Y
18	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
19	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
20	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
21	N Y Y	N N Y	N Y Y	Y Y N	N N Y
22	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
23	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
24	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
25	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
26	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
27	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y

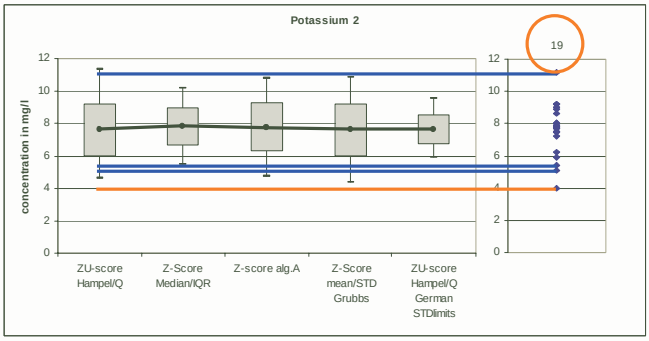
Potassium - 1



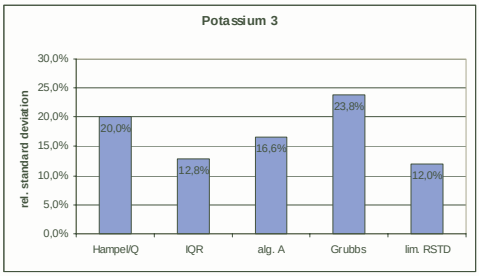


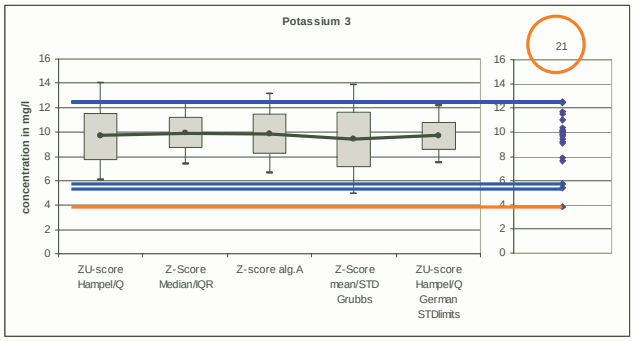
Potassium - 2





Potassium - 3



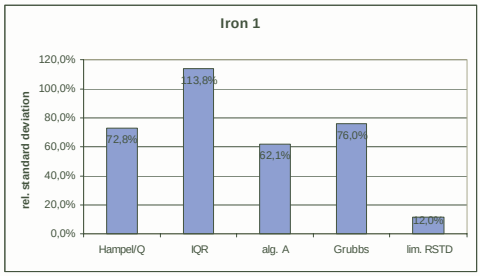


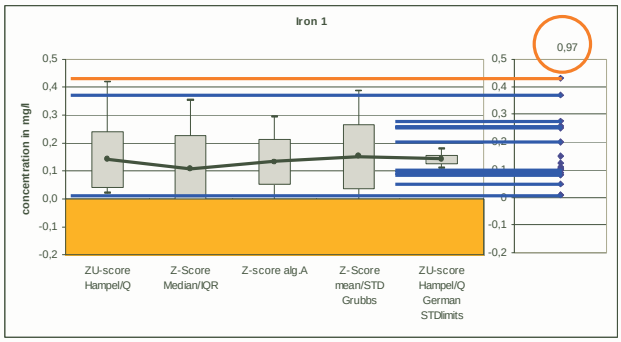
Potassium

- 2 labs completely out of range
- 2 additional labs out of range except for mean/std with Grubbs-test
- 1 additional lab failed when using median/IQR or limited std (12%)
- 1 additional lab failed when using limited std (12%)

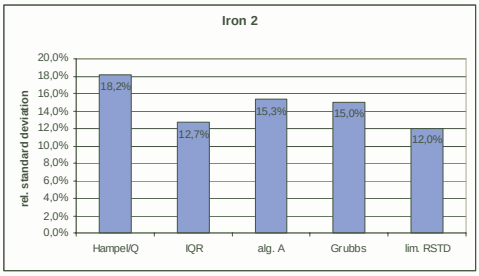
	potassium success				
	ZU-score Hampel/Q	Z-Score Median/IQR	Z-score alg.A	Z-Score mean/STD Grubbs	ZU-score Hampel/Q German STDlimits
1					
2					
3	Y N N	Y N N	Y N N	Y N N	N N N
4	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
5	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
6	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
7	N N N	N N N	N N N	Y N Y	N N N
8					
9	N N N	N Y N	N N N	N Y N	N Y N
10	Y Y Y	Y N Y	Y Y Y	Y Y Y	Y N Y
11	N N N	N Y N	N N N	N Y Y	N Y N
12	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
13	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
14	Y Y Y	N Y Y	Y Y Y	Y Y Y	N Y Y
15					
16					
17	Y Y Y	Y N N	Y N Y	Y N Y	N N N
18	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y N
19	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
20	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
21	Y Y Y	Y N Y	Y Y Y	Y Y Y	N N Y
22	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
23	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
24	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
25	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
26	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
27	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y

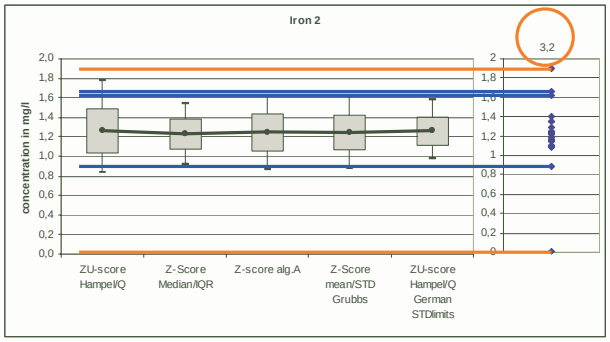
Iron - 1


Iron 1
rel. standard deviation
120,0%
100,0%
80,0%
60,0%
40,0%
20,0%
0,0%
72,8%
113,8%
62,1%
76,0%
12,0%
Hampel/Q
IQR
alg. A
Grubbs
lim. RSTD

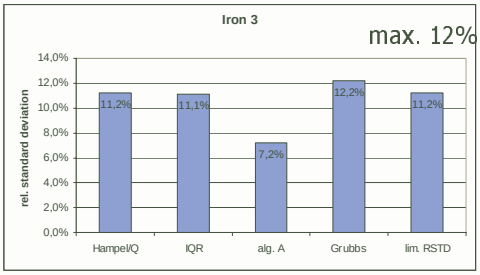

Iron 1
concentration in mg/l
0,97
ZU-score Hampel/Q
Z-Score Median/IQR
Z-score alg.A
Z-Score mean/STD Grubbs
ZU-score Hampel/Q German STDlimits

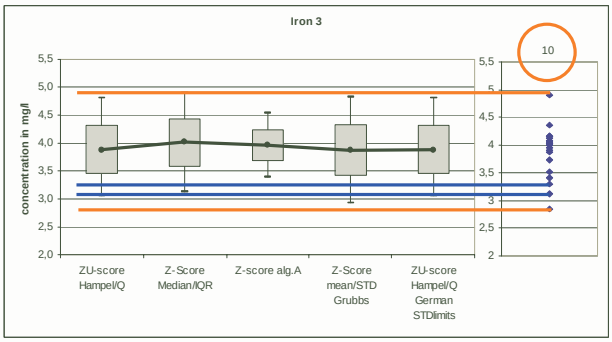
Iron - 2


Iron 2
rel. standard deviation
20,0%
18,0%
16,0%
14,0%
12,0%
10,0%
8,0%
6,0%
4,0%
2,0%
0,0%
18,2%
12,7%
15,3%
15,0%
12,0%
Hampel/Q
IQR
alg. A
Grubbs
lim. RSTD


Iron 2
concentration in mg/l
3,2
ZU-score Hampel/Q
Z-Score Median/IQR
Z-score alg.A
Z-Score mean/STD Grubbs
ZU-score Hampel/Q German STDlimits

Iron - 3



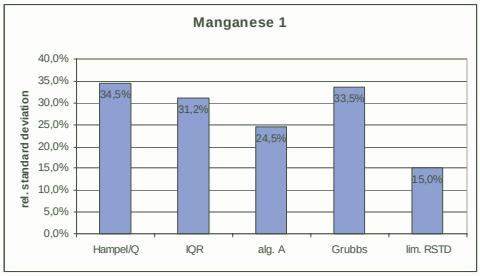


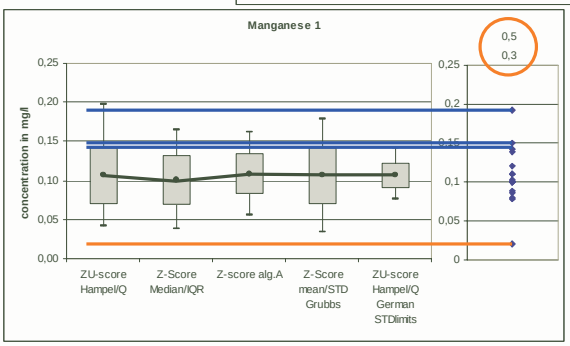
Iron

- 2 labs completely out of range
- 1 additional lab out of range except for Hampel/Z_U
- 1 additional lab failed when using Hampel/Z_U or limited std (12%)
- 2 additional labs failed when using limited std (12%)

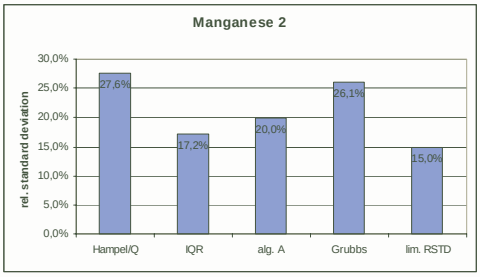
	iron success				
	ZU-score Hampel/Q	Z-Score Median/IQR	Z-score alg.A	Z-Score mean/STD Grubbs	ZU-score Hampel/Q German STDlimits
1					
2					
3	Y Y N	N N N	N N N	Y N N	N N N
4	N Y Y	N Y Y	N Y Y	N Y Y	N Y Y
5	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y
6	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
7	N Y Y	N Y Y	N Y Y	N Y Y	N Y Y
8	Y Y Y	Y Y N	Y Y N	Y Y Y	N Y Y
9	N N Y	Y N Y	Y N Y	Y N Y	N N Y
10	N N N	N N N	N N N	N N N	N N N
11	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
12	N Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y
13	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y
14	Y Y N	Y N N	Y Y N	Y Y N	Y N N
15					
16	Y Y Y	Y N Y	Y Y N	Y N Y	N N Y
17	Y N N	Y N N	Y N N	Y N N	N N N
18	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y
19					
20					
21	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y
22	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y
23	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y
24	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y
25					
26	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y
27	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y

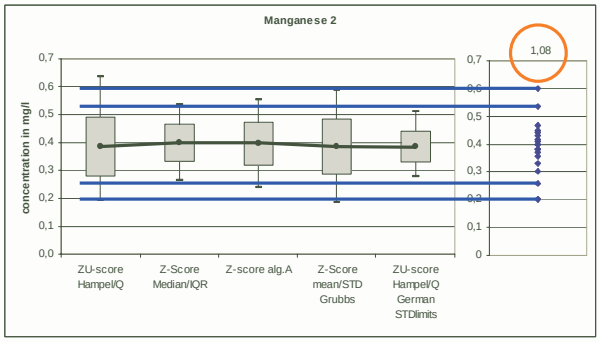
Manganese - 1



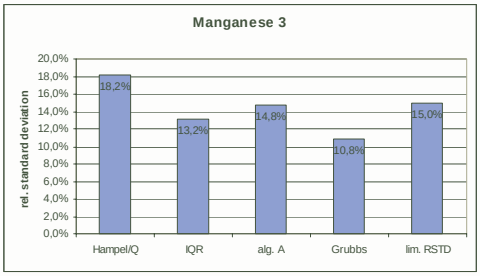


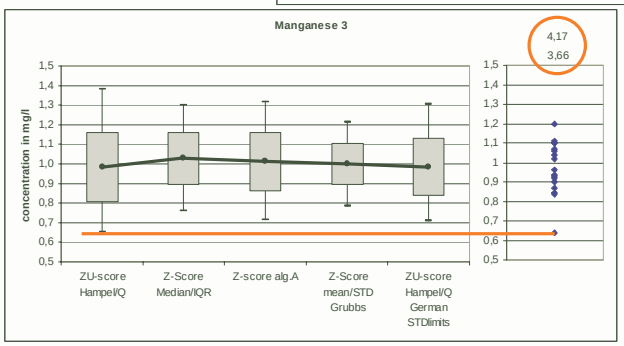
Manganese - 2





Manganese - 3





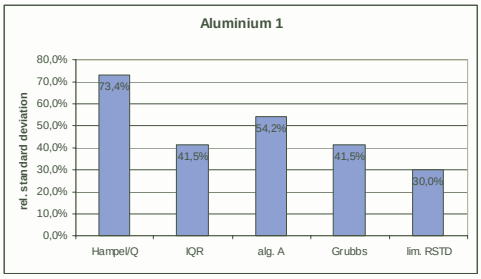
Manganese

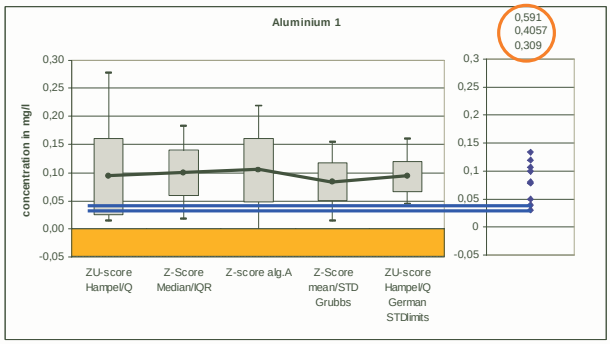
- 1 lab completely out of range
- 1 additional labs out of range except for Hampel/Z_U
- 1 additional lab out of range except for Hampel/Z_U and mean/std with Grubbs-test
- 1 additional lab failed when using median/IQR or limited std (15%)

manganese success

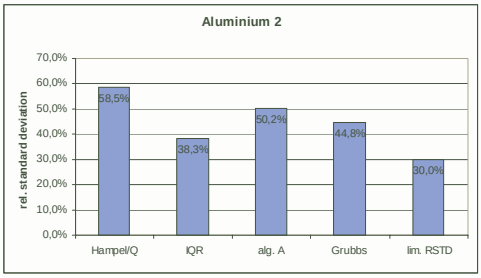
	ZU-score Hampel/Q	Z-Score Median/IQR	Z-score alg.A	Z-Score mean/STD Grubbs	ZU-score Hampel/Q German STDlimits
1					
2					
3	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y
4	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
5	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
6	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
7	Y Y N	Y Y N	Y Y N	Y Y N	Y Y N
8	N Y Y	N N Y	N N Y	N N Y	N N Y
9					
10	Y Y Y	Y N Y	Y N Y	Y Y Y	Y N Y
11	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y
12					
13	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
14	Y Y N	Y N N	Y Y N	Y Y N	Y N N
15					
16	N Y Y	N Y Y	N Y Y	N Y Y	N Y Y
17	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
18	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
19					
20	Y N N	Y N N	Y N N	Y N N	Y N N
21	N Y Y	N N Y	N N Y	N Y Y	N N Y
22	Y Y Y	N Y Y	N Y Y	N Y Y	N N Y
23					
24	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
25	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
26	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
27	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y

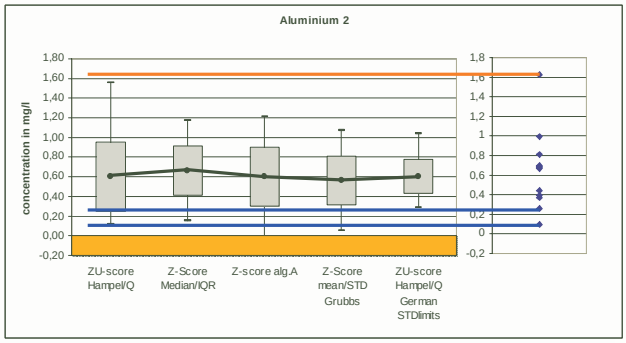
Aluminium - 1



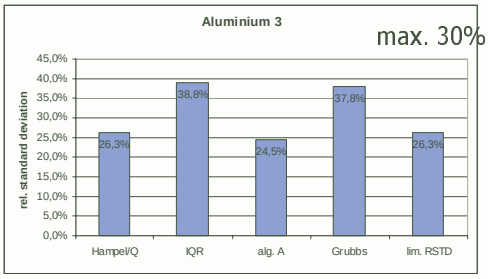


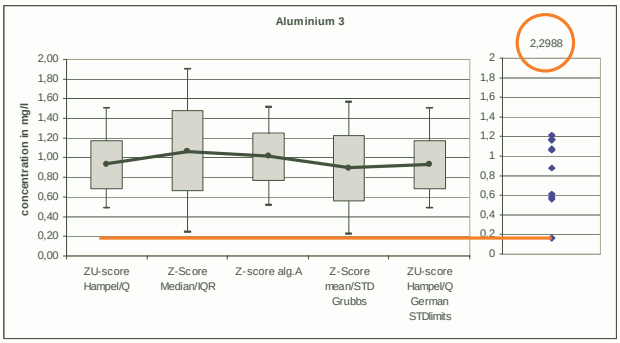
Aluminium - 2





Aluminium - 3



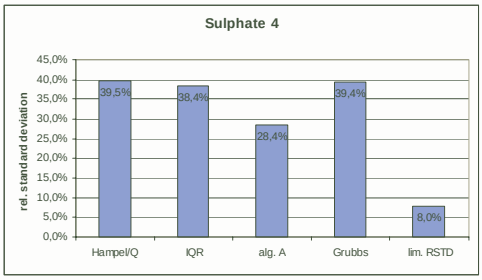


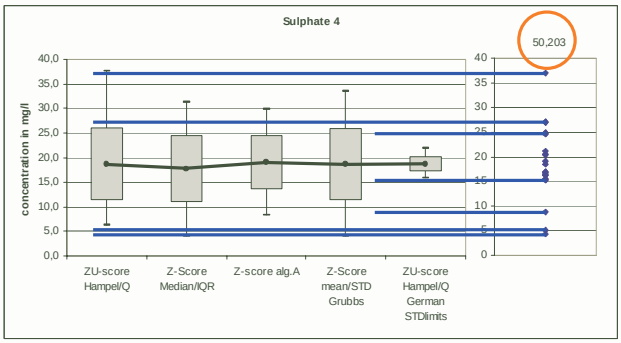
Aluminium

- 1 lab completely out of range
- 1 additional lab out of range except for algorithm A and mean/std with Grubbs-test
- 1 additional lab failed when using limited std (30%)

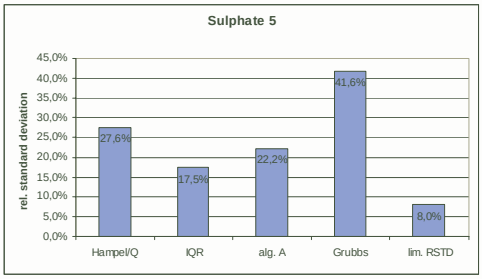
	success				
	ZU-score Hampel/Q	Z-Score Median/IQR	Z-score alg.A	Z-Score mean/STD Grubbs	ZU-score Hampel/Q German STDlimits
1					
2					
3					
4	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
5	N Y Y	N Y Y	N Y Y	N Y Y	N Y Y
6	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N N Y
7					
8	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
9					
10					
11					
12					
13	N N N	N N N	N N N	N N N	N N N
14					
15					
16					
17	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
18					
19					
20	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
21	Y N N	Y N N	Y Y N	Y Y N	N N N
22	N Y Y	N Y Y	N Y Y	N Y Y	N Y Y
23					
24	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
25	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
26	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
27	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y

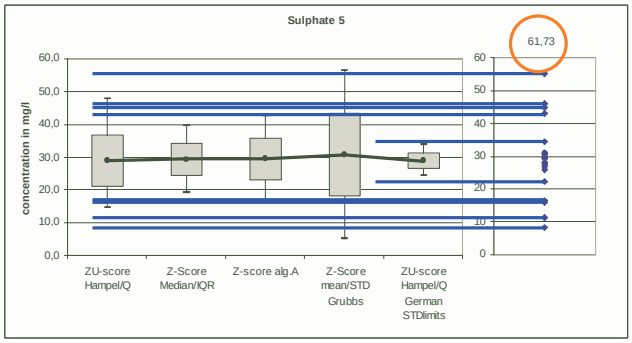
Sulphate - 4



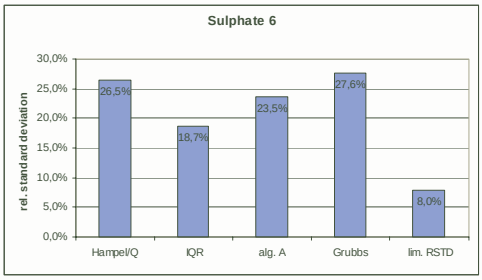


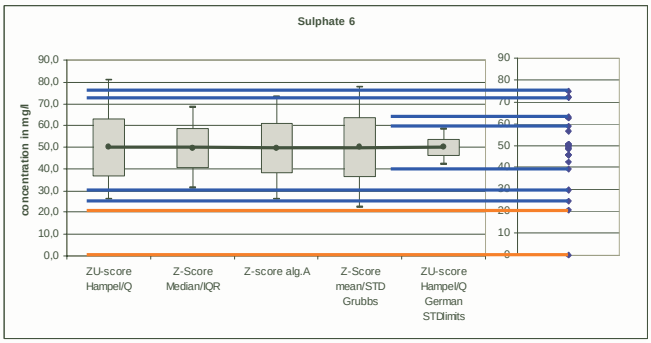
Sulphate - 5





Sulphate - 6





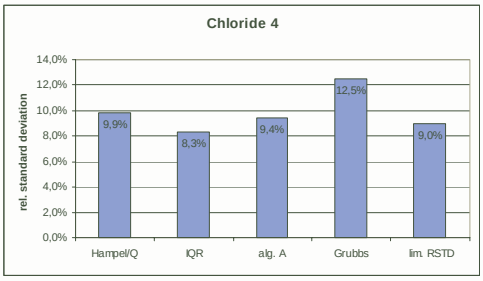
Sulphate

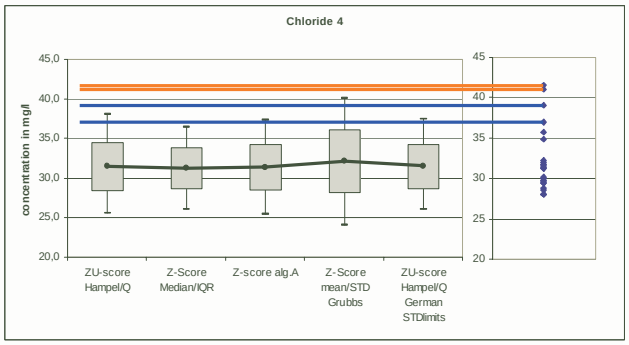
- 2 labs completely out of range
- 2 additional labs out of range except for mean/std with Grubbs-test
- 2 additional labs out of range except for Hampel/Z_U and mean/std with Grubbs-test
- 1 additional lab failed when using median/IQR or limited std (8%)
- 5 additional labs failed when using limited std (8%)

sulphate success

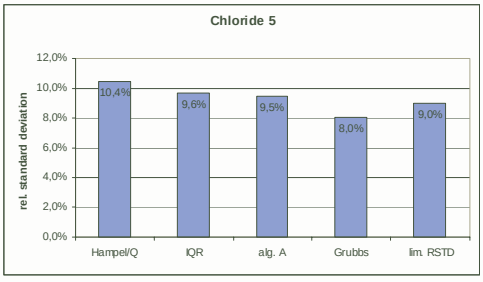
	ZU-score Hampel/Q	Z-Score Median/IQR	Z-score alg.A	Z-Score mean/STD Grubbs	ZU-score Hampel/Q German STDlimits
1					
2					
3	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y
4	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
5	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y
6	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
7	N Y Y	Y N N	N N Y	Y Y Y	N N N
8	Y N Y	N N N	N N Y	N Y Y	N N N
9	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y
10	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y N
11	N N N	N N N	N N N	N N N	N N N
12	Y Y Y	Y N Y	Y N Y	Y Y Y	N N N
13	N N Y	N N N	N N N	N N Y	N N N
14	Y Y Y	Y N Y	Y N Y	Y Y Y	N N N
15					
16	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
17	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y N N
18	Y Y Y	Y N Y	Y Y Y	Y Y Y	N N Y
19	N N N	Y N N	N N N	Y Y N	N N N
20	Y N N	Y N N	Y N N	Y Y Y	Y N N
21	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y
22	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
23	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
24	Y Y Y	Y N N	Y N Y	Y Y Y	N N N
25	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y N Y
26	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
27	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y

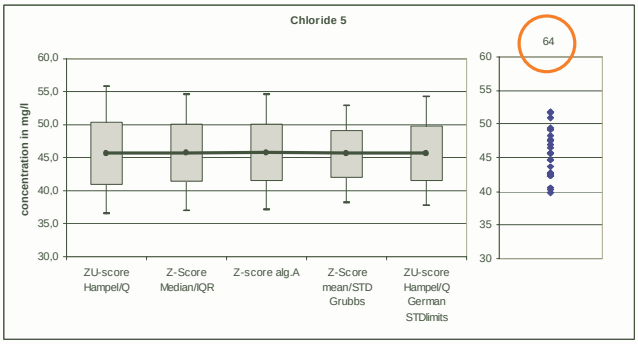
Chloride - 4



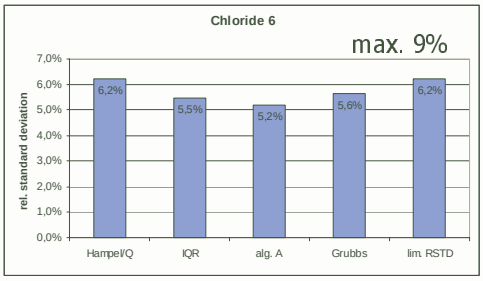


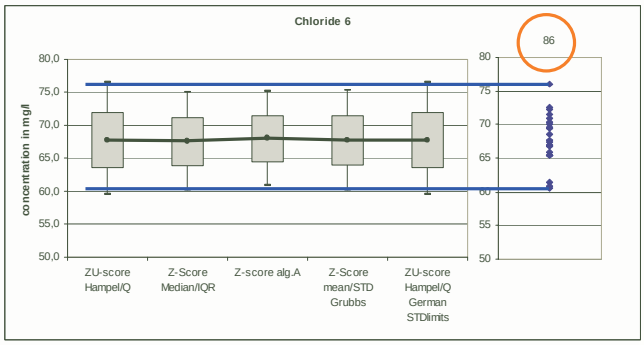
Chloride - 5





Chloride - 6



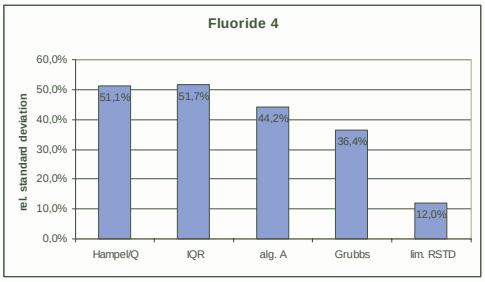


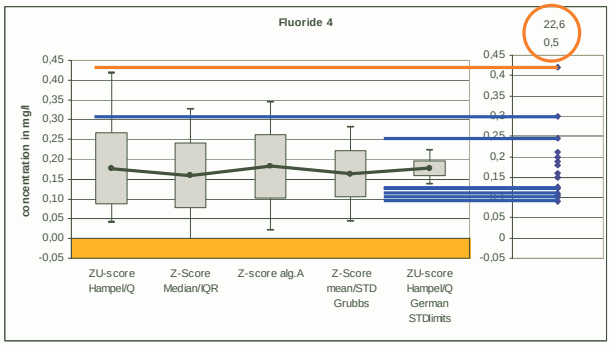
Chloride

- 1 lab completely out of range

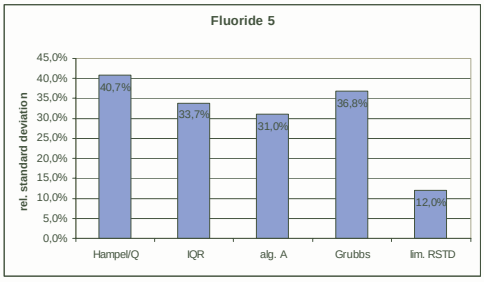
	chloride success				
	ZU-score Hampel/Q	Z-Score Median/IQR	Z-score alg.A	Z-Score mean/STD Grubbs	ZU-score Hampel/Q German STDlimits
1					
2					
3	Y Y Y	Y Y N	Y Y N	Y Y N	Y Y Y
4	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
5	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
6	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
7	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
8	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
9	N N N	N N N	N N N	N N N	N N N
10	Y Y Y	Y Y Y	Y Y N	Y Y Y	Y Y Y
11	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
12	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
13	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
14	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
15					
16	N Y Y	N Y Y	N Y Y	N Y Y	N Y Y
17	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
18	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
19	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
20	Y Y Y	N Y Y	Y Y Y	Y Y Y	Y Y Y
21	N Y Y	N Y Y	N Y Y	Y Y Y	N Y Y
22	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
23	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
24	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
25	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
26	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
27	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y

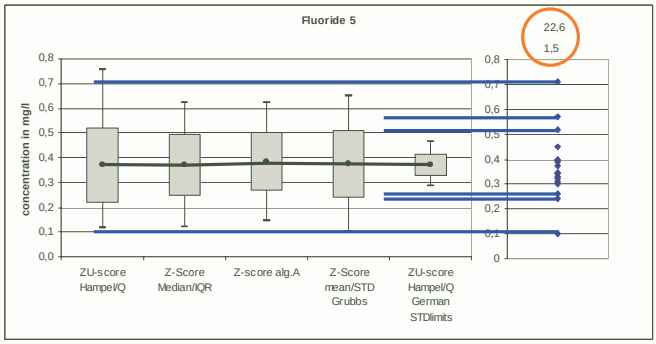
Fluoride - 4



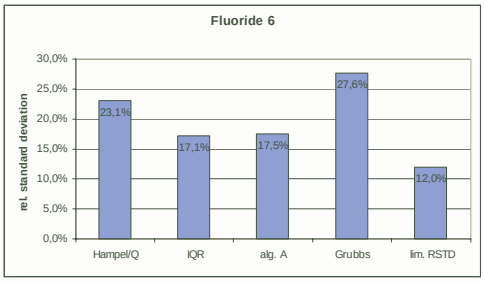


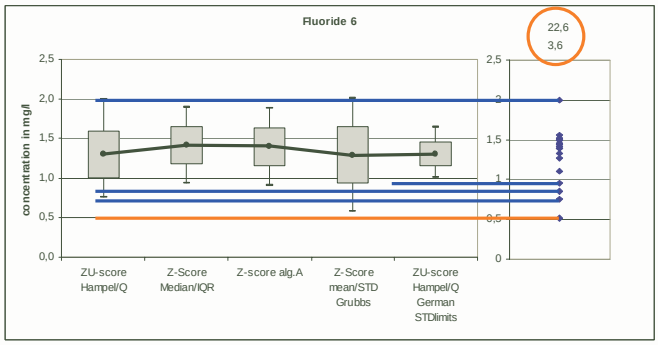
Fluoride - 5





Fluoride - 6



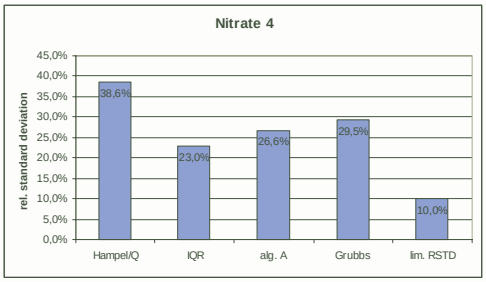


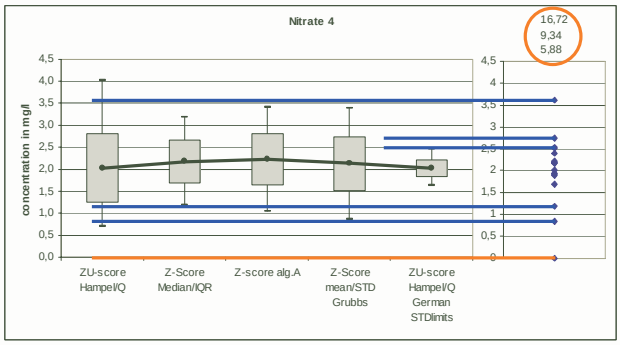
Fluoride

- 3 labs completely out of range
- 1 additional lab out of range except for mean/std with Grubbs-test
- 3 additional labs failed when using limited std (12%)

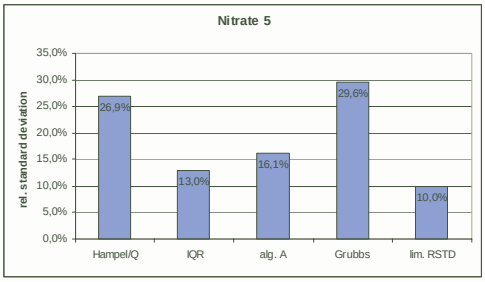
	fluoride success				
	ZU-score Hampel/Q	Z-Score Median/IQR	Z-score alg.A	Z-Score mean/STD Grubbs	ZU-score Hampel/Q German STDlimits
1					
2					
3	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y
4	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y N Y
5	Y Y Y	Y Y N	Y Y N	Y Y Y	N N N
6	N N N	N N N	N N N	N N N	N N N
7	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
8	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
9	Y N Y	Y N Y	Y N Y	N Y Y	N N Y
10					
11					
12	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y N Y
13	N N N	N N N	N N N	N N N	N N N
14	N Y Y	N Y Y	N Y Y	N Y Y	N Y Y
15					
16	N N N	N N N	N N N	N N N	N N N
17	Y Y Y	Y Y N	Y Y N	Y Y Y	Y N N
18	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N N N
19					
20	Y N N	Y N N	Y N N	Y N Y	Y N N
21					
22					
23	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
24	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y
25	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y
26	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y
27	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y

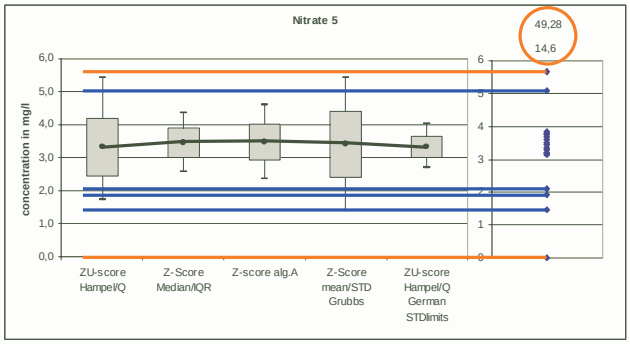
Nitrate - 4



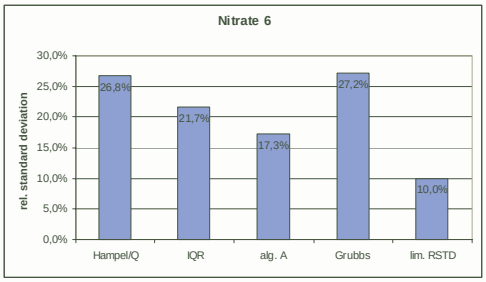


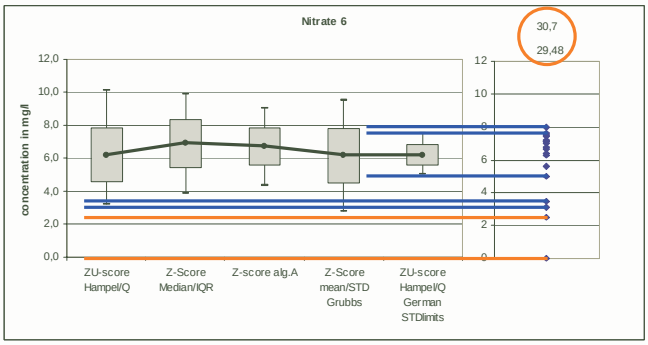
Nitrate - 5





Nitrate - 6



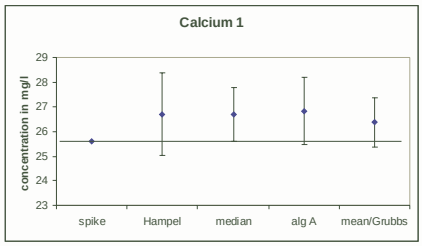


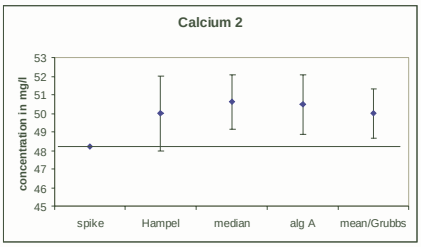
Nitrate

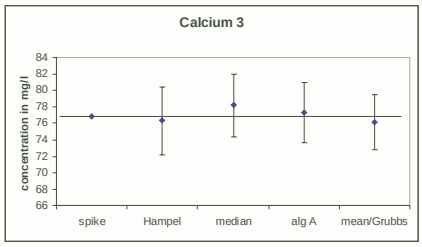
- 3 labs completely out of range
- 1 additional lab out of range except for mean/std with Grubbs-test
- 1 additional lab out of range except for Hampel/Z_U
- 2 additional labs out of range except for Hampel/Z_U and mean/std with Grubbs-test
- 2 additional labs failed when using limited std (10%)

	nitrate success				
	ZU-score Hampel/Q	Z-Score Median/IQR	Z-score alg.A	Z-Score mean/STD Grubbs	ZU-score Hampel/Q German STDlimits
1					
2					
3	N N N	N N N	N N N	N N N	N N N
4	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
5	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N Y Y
6					
7	Y Y Y	N N N	Y N N	Y Y Y	N N N
8	Y Y N	Y N N	Y N N	Y Y N	Y N N
9	N N N	N N N	N N N	N N N	N N N
10					
11					
12	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
13					
14	N Y Y	N Y Y	N Y Y	N Y Y	N Y Y
15					
16	N N N	N N N	N N N	N N N	N N N
17	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
18	Y N N	N N N	N N N	N Y Y	N N N
19	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
20	Y Y Y	Y N Y	Y N Y	Y Y Y	N N N
21	Y N Y	N N Y	N N Y	N N Y	N N Y
22	N Y Y	N Y Y	N Y Y	N Y Y	N Y Y
23	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
24	Y Y Y	Y Y Y	Y Y Y	Y Y Y	N N N
25	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y N
26	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y
27	Y Y Y	Y Y Y	Y Y Y	Y Y Y	Y Y Y

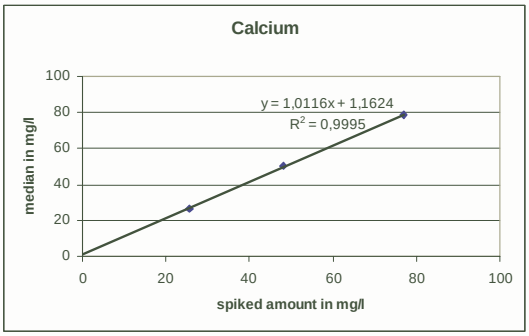
Calcium





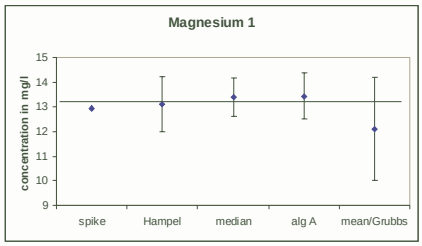


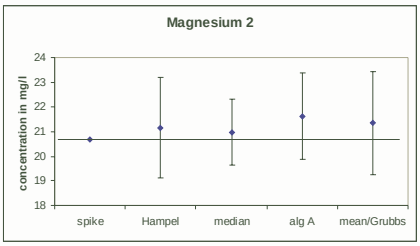
Calcium
Median vs. spiked amount

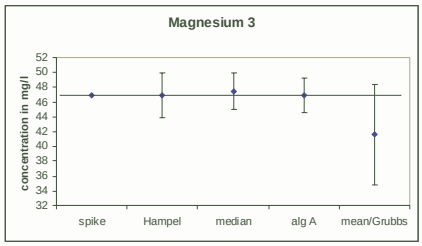


- recovery rate: 101.2 %
- constant bias: 1.2 mg/l (4.54% of the lowest value)

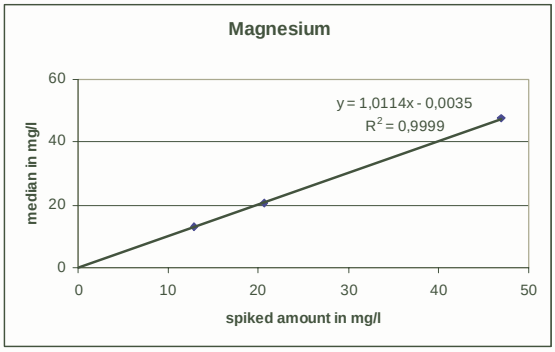
Magnesium





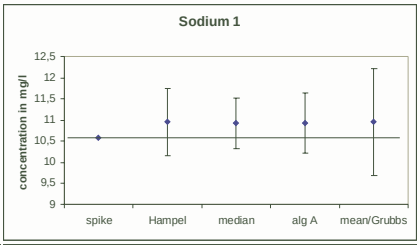


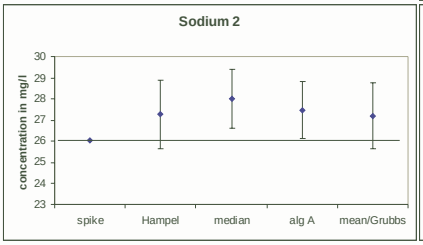
Magnesium
Median vs. spiked amount

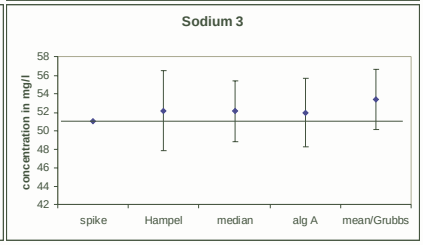


- recovery rate: 101.1 %
- constant bias: -0.004 mg/l (-0.03% of the lowest value)

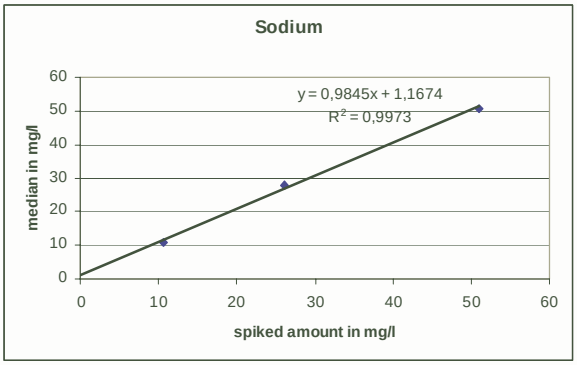
Sodium





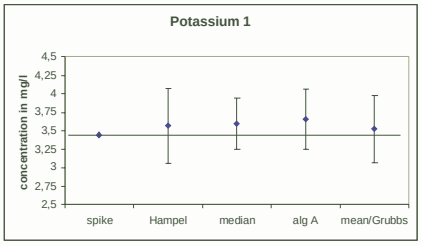


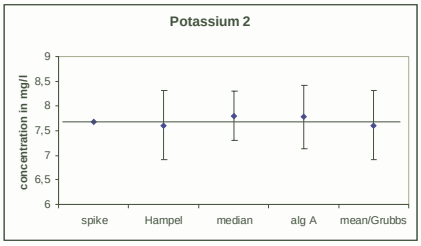
Sodium
Median vs. spiked amount

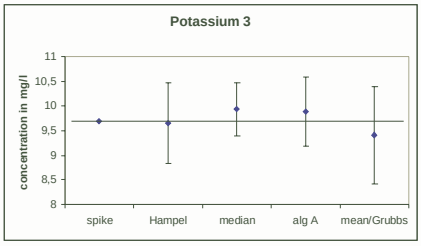


- recovery rate: 98.5%
- constant bias: 1.2mg/l (11.03% of the lowest value)

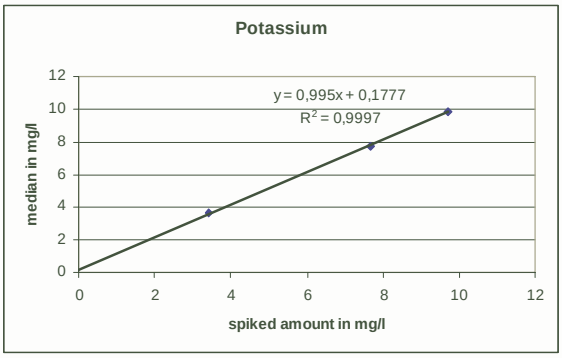
Potassium





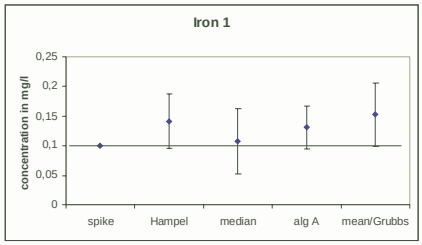


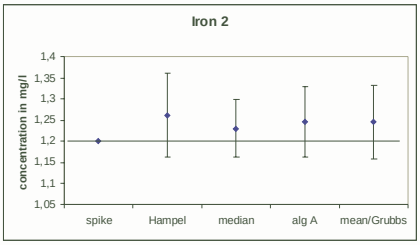
Potassium
Median vs. spiked amount

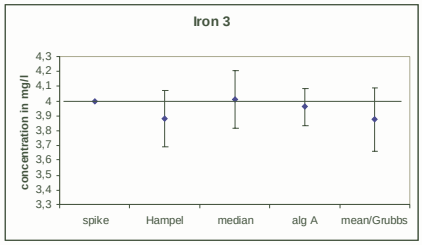


- recovery rate: 99.5%
- constant bias: 0.18mg/l (5.17% of the lowest value)

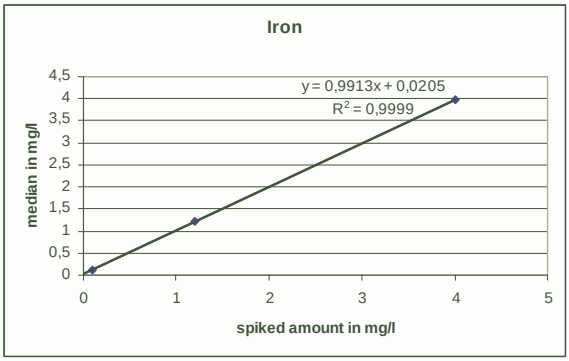
Iron





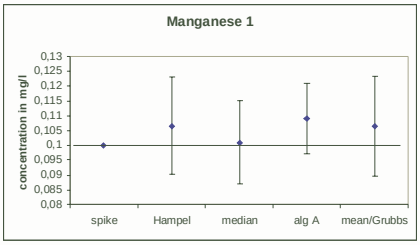


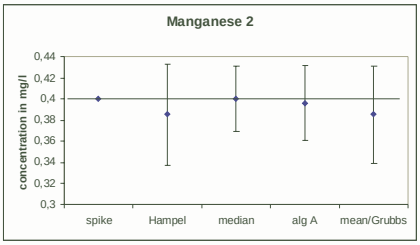
Iron
Median vs. spiked amount

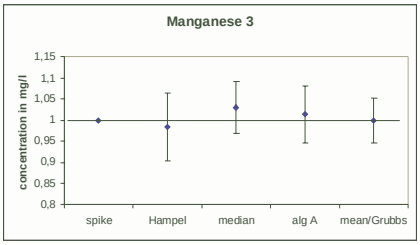


- recovery rate: 99.1%
- constant bias: 0.02mg/l (20% of the lowest value, 1.67% of the second value)

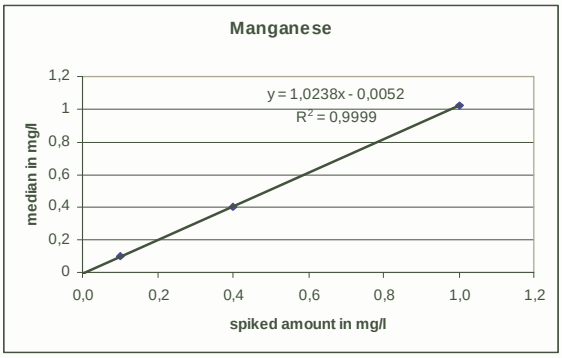
Manganese





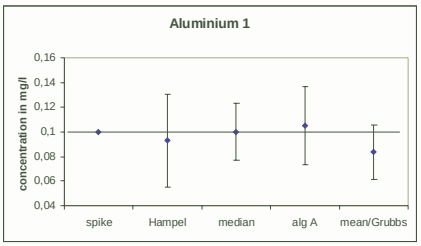


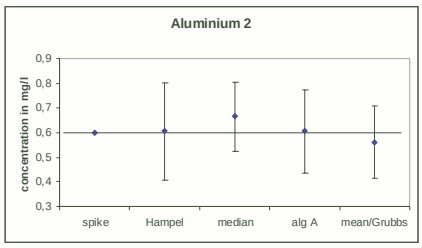
Manganese
Median vs. spiked amount

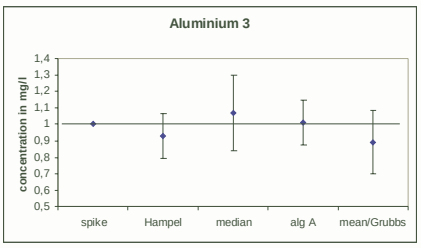


- recovery rate: 102.4%
- constant bias: -0.005mg/l (-5.2% of the lowest value, -1,3% of the second value)

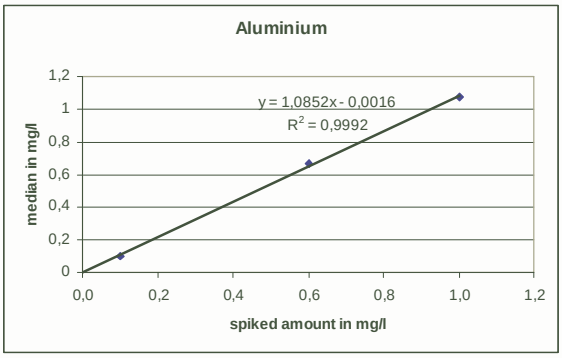
Aluminium





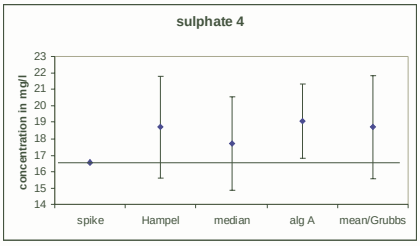


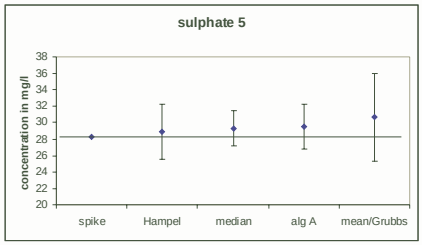
Aluminium
Median vs. spiked amount

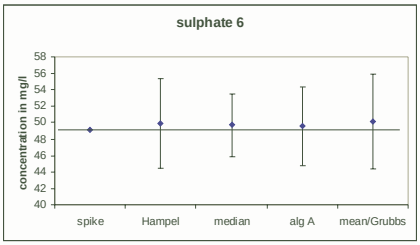


- recovery rate: 108.5%
- constant bias: -0.002mg/l (-1.6% of the lowest value)

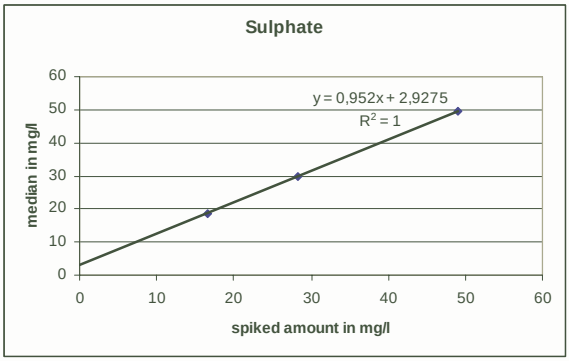
Sulphate





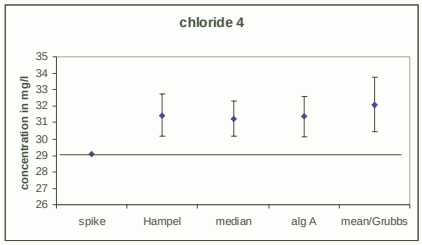


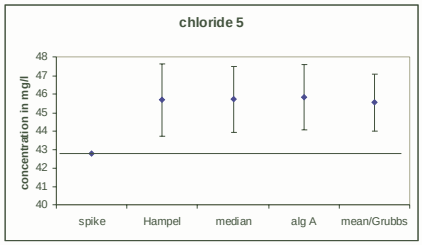
Sulphate
Median vs. spiked amount

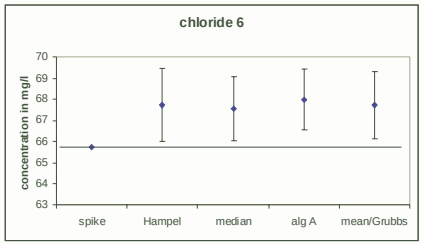


- recovery rate: 95.2%
- constant bias: 2.9mg/l (17.66% of the lowest value)

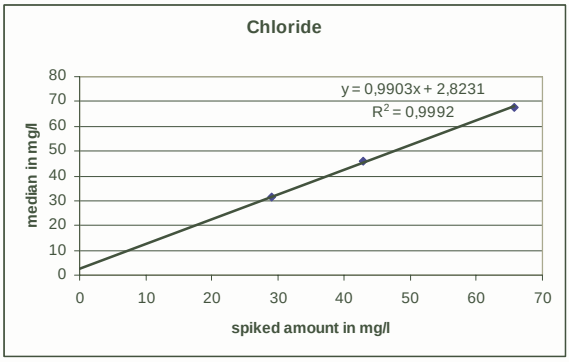
Chloride





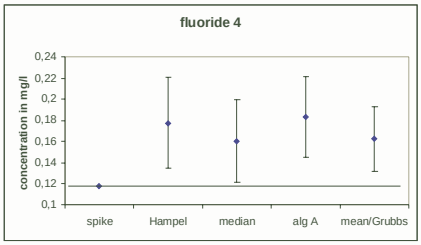


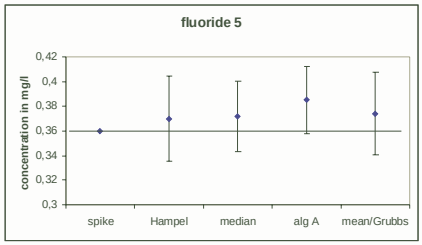
Chloride
Median vs. spiked amount

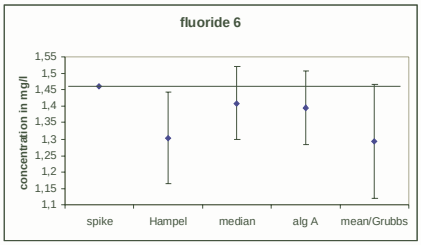


- recovery rate: 99.0%
- constant bias: 2.8mg/l (9.7% of the lowest value)

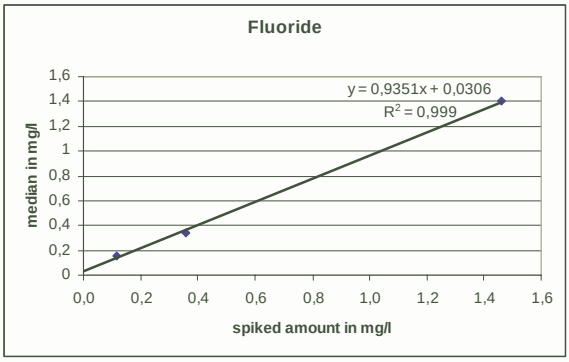
Fluoride





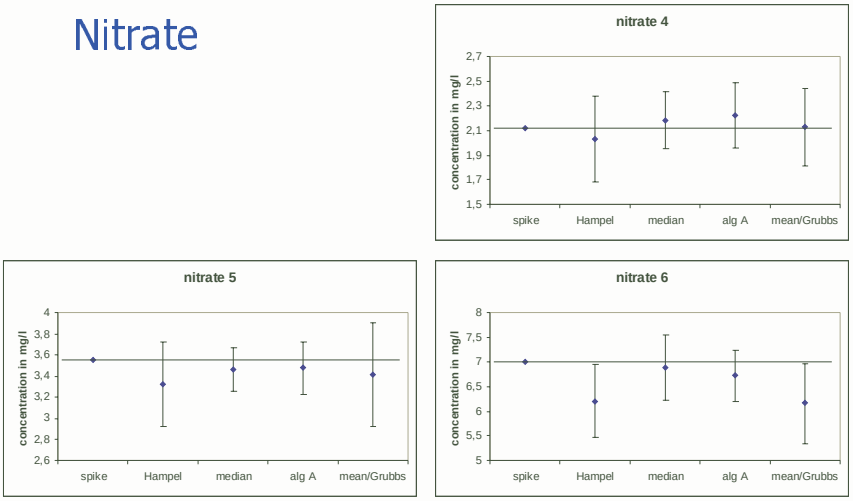


Fluoride
Median vs. spiked amount

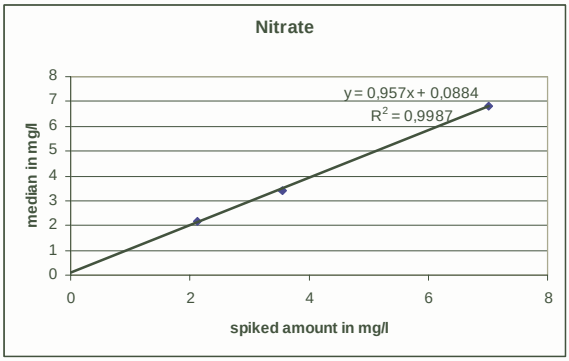


- recovery rate: 93.5%
- constant bias: 0.03mg/l (25.9% of the lowest value)
  (might be an artefact due to the low value for sample 6)

Nitrate



Nitrate
Median vs. spiked amount



- recovery rate: 95.7%
- constant bias: 0.09mg/l (4,17% of the lowest value)
  (might be an artefact due to the high value for sample 4)

Method 1
Hampel estimator / q-method
Z_U-scores

Hampel / Q-method

Lab-No.	Ca	Mg	Na	K	Fe	Mn	Al	SO4	Cl	F	NO3				
1															
2															
3	-	+	+	-	+	+		+	+	+	-	7	of	10	70%
4	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
5	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
6	+	+	+	+	+	+	+	+	+	-		9	of	10	90%
7	+	+	-	-	+	+		+	+	+	+	8	of	10	80%
8	+	-			+	+	+	+	+	+	+	8	of	9	89%
9	-	-	+	-	-			+	-	+	-	3	of	9	33%
10	-	-	+	+	-	+		+	+			5	of	8	63%
11			-	-	+	+		-	+			3	of	6	50%
12	+	+	+	+	+			+	+	+	+	9	of	9	100%
13	-	+	+	+	+	+	-	-	+	-		6	of	10	60%
14	+	+	+	+	+	+		+	+	+	+	10	of	10	100%
15															
16					+	+		+	+	-	-	4	of	6	67%
17	+	+	+	+	-	+	+	+	+	+	+	10	of	11	91%
18	+	+	+	+	+	+		+	+	+	-	9	of	10	90%
19	+		+	+				-	+		+	5	of	6	83%
20	+	-	+	+		-	+	-	+	-	+	6	of	10	60%
21	+	+	+	+	+	+	-	+	+		+	9	of	10	90%
22	+	+	+	+	+	+	+	+	+		+	10	of	10	100%
23	+	+	+	+	+			+	+	+	+	9	of	9	100%
24	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
25	-	-	+	+		+	+	+	+	+	+	8	of	10	80%
26	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
27	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
												7	below		80%
												9	with		100%

Method 2
Median / norm. IQR Z-scores

Median / IQR

Lab-No.	Ca	Mg	Na	K	Fe	Mn	Al	SO4	Cl	F	NO3				
1															
2															
3	-	+	+	-	-	+		+	+	+	-	6	of	10	60%
4	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
5	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
6	+	+	+	+	+	+	+	+	+	-		9	of	10	90%
7	+	+	-	-	+	+		-	+	+	-	6	of	10	60%
8	+	-			+	-	+	-	+	+	-	5	of	9	56%
9	-	-	+	-	+			+	-	+	-	4	of	9	44%
10	-	-	+	+	-	+		+	+			5	of	8	63%
11			-	-	+	+		-	+			3	of	6	50%
12	+	+	+	+	+			+	+	+	+	9	of	9	100%
13	-	+	+	+	+	+	-	-	+	-		6	of	10	60%
14	+	+	+	+	-	-		+	+	+	+	8	of	10	80%
15															
16					+	+		+	+	-	-	4	of	6	67%
17	+	+	+	-	-	+	+	+	+	+	+	9	of	11	82%
18	+	-	+	+	+	+		+	+	+	-	8	of	10	80%
19	+		+	+				-	+		+	5	of	6	83%
20	+	-	+	+		-	+	-	+	-	+	6	of	10	60%
21	+	+	-	+	+	-	-	+	+		-	6	of	10	60%
22	+	+	+	+	+	+	+	+	+		+	10	of	10	100%
23	+	+	+	+	+			+	+	+	+	9	of	9	100%
24	+	+	+	+	+	+	+	-	+	+	+	10	of	11	91%
25	-	-	+	+		+	+	+	+	+	+	8	of	10	80%
26	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
27	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
												10	below		80%
												7	with		100%

Method 3
Algorithm A
Z-scores

Algorithm A

Lab-No.	Ca	Mg	Na	K	Fe	Mn	Al	SO4	Cl	F	NO3				
1															
2															
3	-	+	+	-	-	+		+	+	+	-	6	of	10	60%
4	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
5	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
6	+	+	+	+	+	+	+	+	+	-		9	of	10	90%
7	+	+	-	-	+	+		-	+	+	-	6	of	10	60%
8	+	-			+	-	+	-	+	+	-	5	of	9	56%
9	-	-	+	-	+			+	-	+	-	4	of	9	44%
10	-	-	+	+	-	+		+	+			5	of	8	63%
11			-	-	+	+		-	+			3	of	6	50%
12	+	+	+	+	+			+	+	+	+	9	of	9	100%
13	-	+	+	+	+	+	-	-	+	-		6	of	10	60%
14	+	+	+	+	+	+		+	+	+	+	10	of	10	100%
15															
16					+	+		+	+	-	-	4	of	6	67%
17	+	+	+	+	-	+	+	+	+	+	+	10	of	11	91%
18	+	-	+	+	+	+		+	+	+	-	8	of	10	80%
19	+		+	+				-	+		+	5	of	6	83%
20	+	-	+	+		-	+	-	+	-	+	6	of	10	60%
21	+	+	+	+	+	-	+	+	+		-	8	of	10	80%
22	+	+	+	+	+	+	+	+	+		+	10	of	10	100%
23	+	+	+	+	+			+	+	+	+	9	of	9	100%
24	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
25	-	-	+	+		+	+	+	+	+	+	8	of	10	80%
26	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
27	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
												9	below		80%
												9	with		100%

Method 4
Arithm. Mean / Std. after Grubbs outlier test
Z-scores

Arithm. mean / Std after Grubbs test

Lab-No.	Ca	Mg	Na	K	Fe	Mn	Al	SO4	Cl	F	NO3				
1															
2															
3	-	+	+	-	-	+		+	+	+	-	6	of	10	60%
4	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
5	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
6	+	+	+	+	+	+	+	+	+	-		9	of	10	90%
7	+	+	-	+	+	+		+	+	+	+	9	of	10	90%
8	+	-			+	-	+	+	+	+	+	7	of	9	78%
9	-	+	+	-	+			+	-	+	-	5	of	9	56%
10	-	-	+	+	-	+		+	+			5	of	8	63%
11			-	+	+	+		-	+			4	of	6	67%
12	+	+	+	+	+			+	+	+	+	9	of	9	100%
13	-	+	+	+	+	+	-	-	+	-		6	of	10	60%
14	+	+	+	+	+	+		+	+	+	+	10	of	10	100%
15															
16					+	+		+	+	-	-	4	of	6	67%
17	+	+	+	+	-	+	+	+	+	+	+	10	of	11	91%
18	+	+	+	+	+	+		+	+	+	+	10	of	10	100%
19	+		+	+				+	+		+	6	of	6	100%
20	+	-	+	+		-	+	+	+	+	+	8	of	10	80%
21	+	+	+	+	+	+	+	+	+		-	9	of	10	90%
22	+	+	+	+	+	+	+	+	+		+	10	of	10	100%
23	+	+	+	+	+			+	+	+	+	9	of	9	100%
24	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
25	-	-	+	+		+	+	+	+	+	+	8	of	10	80%
26	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
27	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
												7	below		80%
												11	with		100%

Method 1 Hampel estimator / q-method with lim. std Z_U-scores

Hampel / Q-methode with limitations

Lab-No.	Ca	Mg	Na	K	Fe	Mn	Al	SO4	Cl	F	NO3				
1															
2															
3	-	-	+	-	-	+		+	+	+	-	5	of	10	50%
4	+	+	-	+	+	+	+	+	+	+	+	10	of	11	91%
5	+	+	+	+	+	+	+	+	+	-	+	10	of	11	91%
6	+	-	-	+	+	+	-	+	+	-		6	of	10	60%
7	+	+	-	-	+	+		-	+	+	-	6	of	10	60%
8	+	-			+	-	+	-	+	+	-	5	of	9	56%
9	-	-	+	-	-			+	-	-	-	2	of	9	22%
10	-	-	+	+	-	+		-	+			4	of	8	50%
11			-	-	+	+		-	+			3	of	6	50%
12	+	+	+	+	+			-	+	+	+	8	of	9	89%
13	-	+	+	+	+	+	-	-	+	-		6	of	10	60%
14	+	+	+	+	-	-		-	+	+	+	7	of	10	70%
15															
16					-	+		+	+	-	-	3	of	6	50%
17	+	+	+	-	-	+	+	-	+	-	+	7	of	11	64%
18	+	-	+	+	+	+		-	+	-	-	6	of	10	60%
19	+		+	+				-	+		+	5	of	6	83%
20	+	-	+	+		-	+	-	+	-	-	5	of	10	50%
21	+	+	-	-	+	-	-	+	+		-	5	of	10	50%
22	+	+	+	+	+	-	+	+	+		+	9	of	10	90%
23	+	+	+	+	+			+	+	+	+	9	of	9	100%
24	+	+	+	+	+	+	+	-	+	+	-	9	of	11	82%
25	-	-	+	+		+	+	+	+	+	+	8	of	10	80%
26	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
27	+	+	+	+	+	+	+	+	+	+	+	11	of	11	100%
												14	below		80%
												3	with		100%

Conclusions

- 4 different statistical procedures showed:
  - mean values laying close together
  - sometimes big differences in the standard deviation
- but all methods are widely accepted by the scientific community
- statistics always are to some extend arbitrary
- the standard deviations in many cases are too high, not fit for the purpose
- if the calculated standard deviations are used for the assessment, this gives a falsely good impression about the quality of the analyses
- for some parameters the means of the participants are strongly biased
- a reference values should be preferred in these cases

Universität Stuttgart

Quality goals
Fitness for purpose

Dr.-Ing. Michael Koch

Institute for Sanitary Engineering, Water Quality and Solid Waste Management, Universität Stuttgart
Dep. Hydrochemistry
Bandtäle 2, 70569 Stuttgart
Tel.: +49 711/685-5444 Fax: +49 711/685-7809
E-mail: Michael.Koch@iswa.uni-stuttgart.de
http://www.iswa.uni-stuttgart.de/ch

1

Calcium

- Limitation of std in German drinking water PT: 4% – 10%
- Working Group of the German Federal States on water issues - quality goal for repeatability std: 2% (VC_R→about 4%)
- Reproducibility std in interlaboratory tests:
  - ISO 7980 – AAS: 3,5% - 4,6%
  - ISO 11885 - ICP-OES: 6,1%
  - E34 - ISO 14911 - IC: 3,8 - 8,5%
  - SM 3111 - Flame AAS: 4,2%
  - SM 3120 - ICP-OES: 12,3%
  - SM 3500 Ca-Titrimetry: 9,2%
  - AQS-BW 4/02: 2,8% - 4,6%

Magnesium

- Limitation of std in German drinking water PT: 4% – 10%
- Working Group of the German Federal States on water issues - quality goal for repeatability std: 2% (VC_R→about 4%)
- Reproducibility std in interlaboratory tests:
  - ISO 7980 - AAS: 2,9% - 6,9%
  - ISO 11885 - ICP-OES: 3,1%
  - ISO 14911 - IC: 5,4 - 8,0%
  - SM 3111 - Flame AAS: 10,5%
  - SM 3120 - ICP-OES: 6,1%
  - AQS-BW 4/02: 2,8% - 7,0%

Sodium

- EU drinking water directive:
  - accepted bias 10% at 200 mg/l (VC_R→about 5%)
- Limitation of std in German drinking water PT: 5% – 10%
- Working Group of the German Federal States on water issues - quality goal for repeatability std: 3% (VC_R→about 6%)
- Reproducibility std in interlaboratory tests:
  - DIN 38406-14 - AAS: 3,5 - 3,8 %
  - ISO 11885 - ICP-OES: 5,7%
  - ISO 14911 - IC: 4,8 - 13,4%
  - SM 3111 - Flame AAS: 4,5%
  - SM 3120 - ICP-OES: 21,0%
  - SM 3500-Na Flame Emission: 17,3%
  - AQS-BW 4/02: 3,5% - 7,4%

Potassium

- Limitation of std in German drinking water PT: 5% – 12%
- Working Group of the German Federal States on water issues - quality goal for repeatability std: 4% (VC_R→about 8%)
- Reproducibility std in interlaboratory tests:
  - DIN 38406-13 - AAS: 3,6 - 5,9%
  - ISO 14911 - IC: 4,3 - 17,0%
  - SM 3120 - ICP-OES: 9,3%
  - SM 3500-K Flame photom.: 15,5%
  - AQS-BW 4/02: 4,9 - 11,8%

Iron

- EU drinking water directive:
  - accepted bias 10% at 200 µg/l (VC_R→about 5%)
- Limitation of std in German drinking water PT: 5% – 12%
- Working Group of the German Federal States on water issues - quality goal for repeatability std: 3% (VC_R→about 6%)
- Reproducibility std in interlaboratory tests:
  - DIN38406-1 - Photom.: 2,5%(1 mg/l), 6,3%(0,5mg/l), 13,4%(0,1mg/l), 24,4%(0,05 mg/l)
  - ISO 11885 - ICP-OES: 6,8%
  - DIN 38406-32 - AAS: 8,8% - 18,1%
  - SM 3111 - Flame AAS: 5,8% - 16,5%
  - SM 3120 - ICP-OES: 6,8%
  - SM 3500-Fe Photom.: 25,5% (0,3mg/l)
  - AQS-BW 4/02: 5,7% - 12,8%

Manganese

- EU drinking water directive:
  - accepted bias 10% at 50 µg/l (VC_R→about 5%)
- Limitation of std in German drinking water PT: 5% – 15%
- Working Group of the German Federal States on water issues - quality goal for repeatability std: 4% (VC_R→about 8%)
- Reproducibility std in interlaboratory tests:
  - DIN 38406-2 - Photom.: 4,8%(2 mg/l), 5,9%(1mg/l), 23,5%(0,5mg/l), 28,2%(0,1 mg/l)
  - ISO 11885 - ICP-OES: 2,7%
  - DIN 38406-33 - AAS: 7,1% - 15,2%
  - SM 3111 - Flame AAS: 7,8% - 13,5%
  - SM 3120 - ICP-OES: 3,2%
  - AQS-BW 4/02: 4,9% - 12,2%

Aluminium

- EU drinking water directive:
  - accepted bias 10% at 200 µg/l (VC_R→about 5%)
- Limitation of std in German drinking water PT: 10% – 30%
- Working Group of the German Federal States on water issues - quality goal for repeatability std: 6% (VC_R→about 4%)
- Reproducibility std in interlaboratory tests:
  - ISO 12020 - AAS: 1,0(47µg/l) - 1,6 %(10µg/l)
  - ISO 10566 - Photom. (Brenzcatechinviolett): 19,5%(8µg/l), 8,6%(30µg/l), 6,9%(140µg/l), 2,9%(1mg/l)
  - SM 3111 - Flame AAS: 4,2%
  - SM 3120 - ICP-OES: 5,6%
  - SM 3500-Al Eriochrome Cyanin: 28,8% - 34,4%
  - AQS-BW 4/02: 11,1% - 28,1%

Sulphate

- EU drinking water directive:
  - accepted bias 10% at 250 mg/l ($VC_R \rightarrow$about 5%)
- Working Group of the German Federal States on water issues - quality goal for repeatability std: 2% ($VC_R \rightarrow$about 4%)
- Reproducibility std in interlaboratory tests:
  - ISO 10304-1 - IC: 4,2% - 7,6%
  - SM 4110C IC: 15%
  - SM 4500-SO_4^{2-} - Gravimetrye: 4,7% (260mg/l)
  - SM 4500-SO_4^{2-} - Turbidimetry: 1,7%(7,5mg/l)
  - AQS-BW 4/02: 2,3% - 4,7%

Chloride

- EU drinking water directive:
  - accepted bias 10% 250 mg/l ($VC_R \rightarrow$about 5%)
- Limitation of std in German drinking water PT: 3% – 9%
- Working Group of the German Federal States on water issues - quality goal for repeatability std: 3% ($VC_R \rightarrow$about 6%)
- Reproducibility std in interlaboratory tests:
  - DIN 38405-1 - Mohr: 1,2% - 4,5%
  - ISO 10304-1 - IC: 4,8% - 7,5%
  - SM 4110C IC: 11,9%
  - SM 4500-Cl^- - Mohr: 4,2%
  - AQS-BW 4/02: 1,9% - 5,0%

Fluoride

- EU drinking water directive:
  - accepted bias 10% at 1,5 mg/l ($VC_R \rightarrow$about 5%)
- Limitation of std in German drinking water PT: 5% – 12%
- Working Group of the German Federal States on water issues - quality goal for repeatability std: 5% ($VC_R \rightarrow$about 10%)
- Reproducibility std in interlaboratory tests:
  - ISO 10304-1 - IC: 6,7% - 9,1%
  - DIN 38405-4 - ISE: 2,5% - 7,4%
  - SM 4500-F^- - SPE: 2,9%
  - SM 4500-F^- - SPADNS: 2,8% - 17,2%
  - AQS-BW 4/02: 4,9 - 10,7%

Nitrate

- EU drinking water directive:
  - accepted bias 10% at 50 mg/l ($VC_R \rightarrow$about 5%)
- Limitation of std in German drinking water PT: 4% – 10%
- Working Group of the German Federal States on water issues - quality goal for repeatability std: 4% ($VC_R \rightarrow$about 8%)
- Reproducibility std in interlaboratory tests:
  - ISO 10304-1 - IC: 5,1% - 19,0%
  - ISO 7890 - Photom. (Sulfosalicylic acid): 1,6% - 10,9%
  - SM 4110C IC: 23,7%
  - AQS-BW 4/02: 2,5% - 7,6%

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Method comparison

Dr.-Ing. Michael Koch

Institute for Sanitary Engineering, Water Quality and Solid Waste Management, Universität Stuttgart
Dep. Hydrochemistry
Bandtäle 2, 70569 Stuttgart
Tel.: +49 711/685-5444 Fax: +49 711/685-7809
E-mail: Michael.Koch@iswa.uni-stuttgart.de
http://www.iswa.uni-stuttgart.de/ch

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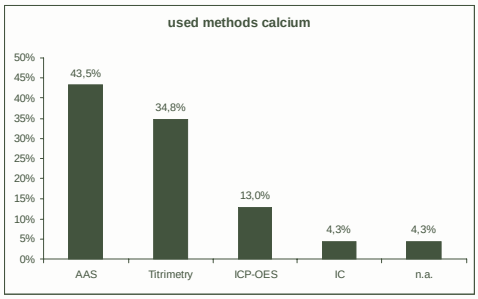
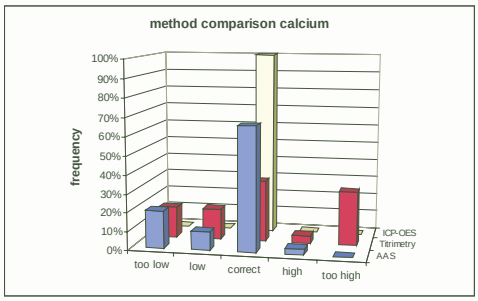
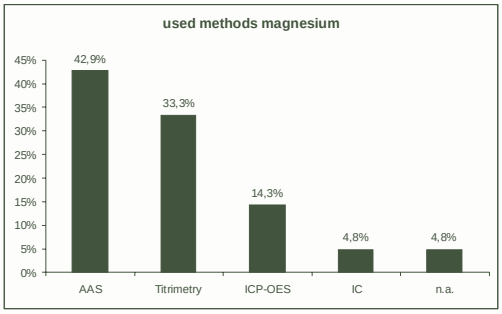
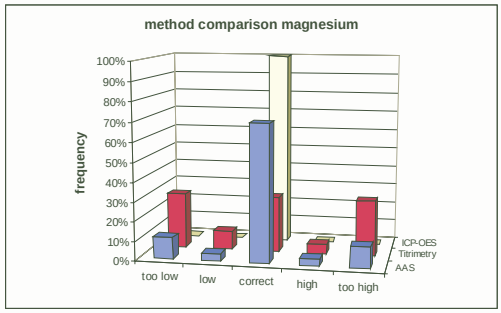
Calcium



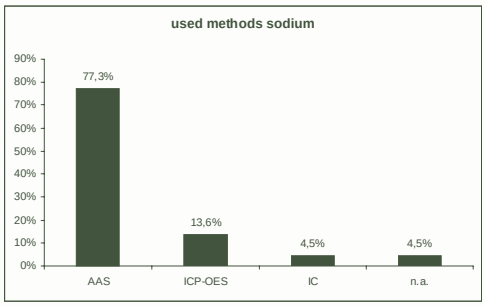


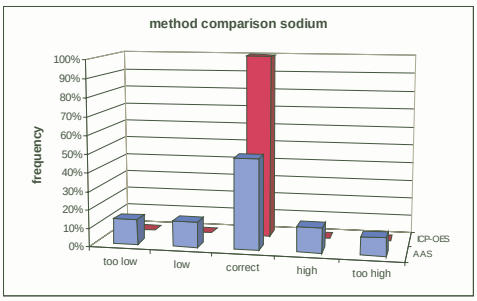
Magnesium



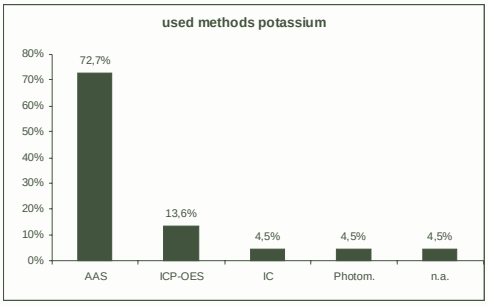


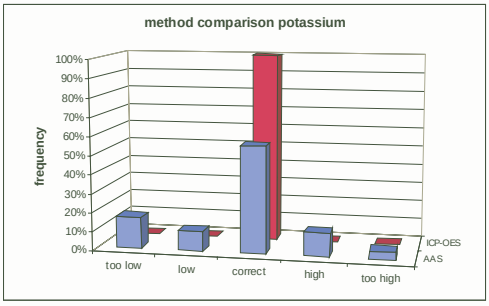
Sodium





Potassium





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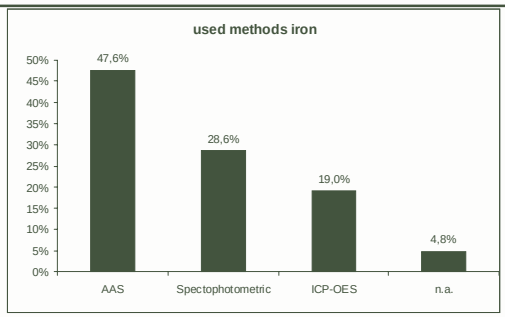
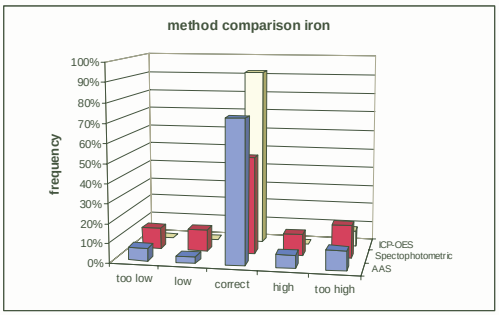
Iron





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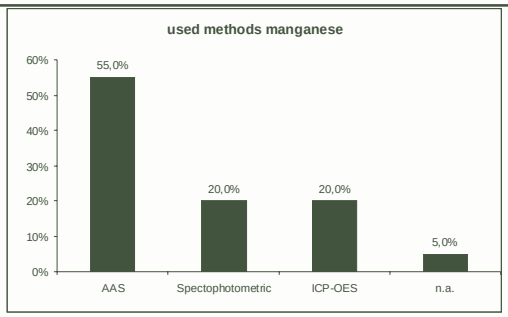
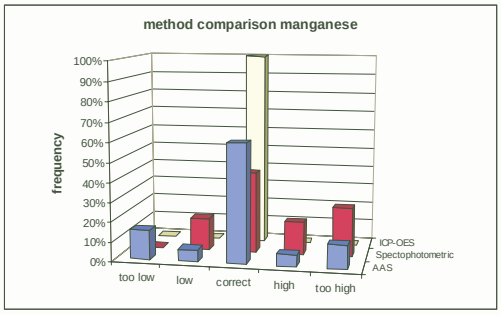
Manganese





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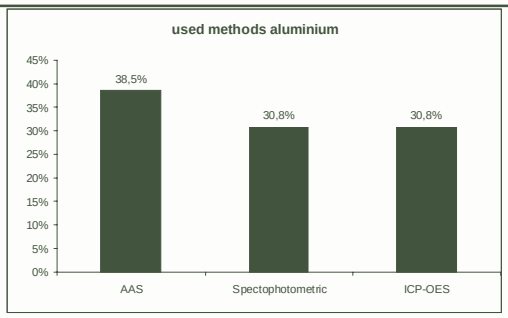
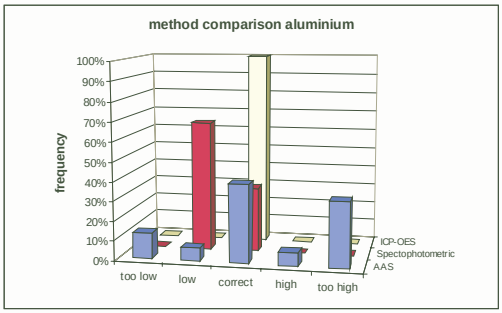
Aluminium





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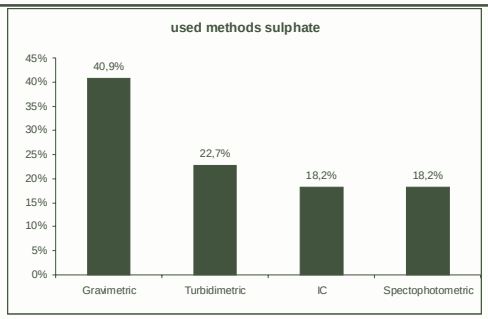
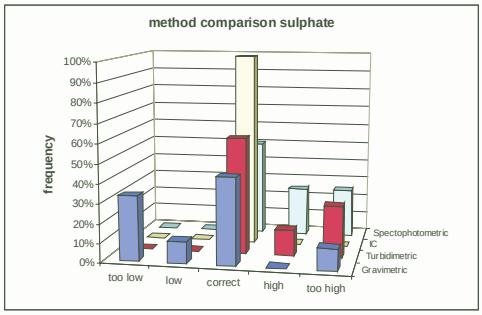
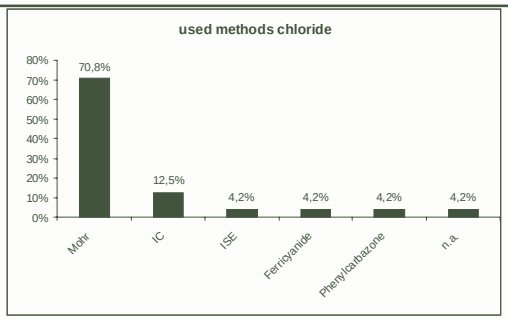
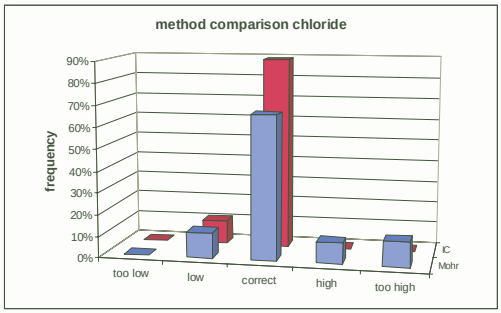
Sulphate



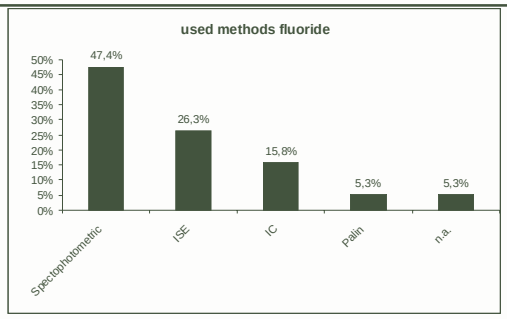


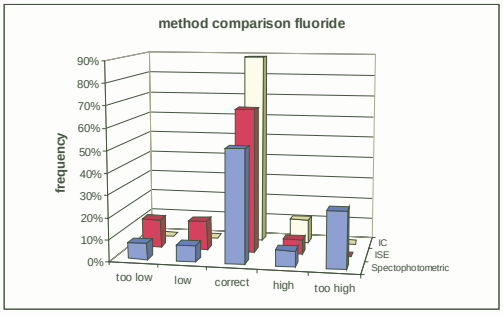
Chloride



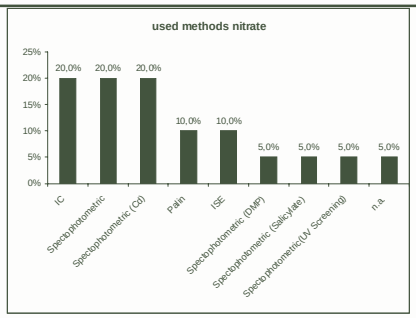


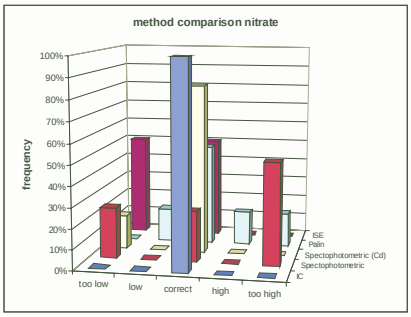
Fluoride





Nitrate





Benefits

- Identification of strong and weak points in the lab
- Opportunity to compare with other labs
- Opportunity for networking with other labs (used methods, error sources)
- Increased customer and staff confidence
- Opportunity for learning from others
- Self assessment tool
- QC tool
- Improvement towards accreditation
- Pilot PT was free and easy for the labs to participate
- Made evaluation of different test methods possible
- Good information on methods/techniques
- It's the participants "own" PT

Weak points

- Some labs were not specific on methods used
- future costs could be too high
- type of sample:
  - should be health significant
  - concentration closer to reality
- technical communication problems
- PT provider should go for accreditation

What should be kept

- Parameters (+ more others)
- The statistical procedure should be kept
- PT provider should be the same

What should be changed?

- Microbiology should be included
- Increase number of participants per country
- Nitrate definitely as NO_3^-
- Cheaper solutions for transportation

Is the PT a help to accreditation?

- Yes

Costs

- PTB is asked for further sponsorship for the transportation costs to national coordinators until the systems stabilizes
- The actual costs of the PT (without transportation) should be paid by the participants
- „If you pay for something, you appreciate it more"

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PT for microbiological parameters

in the Public Health Authority
of Lower Saxony

Dr.-Ing. Michael Koch

Institute for Sanitary Engineering, Water Quality and Solid
Waste Management, Universität Stuttgart
Dep. Hydrochemistry
Bandtäle 2, 70569 Stuttgart
Tel.: +49 711/685-5444 Fax: +49 711/685-7809
E-mail: Michael.Koch@iswa.uni-stuttgart.de
http://www.uni-stuttgart.de/siwa/ch

Microbiological PT

- The Public Health Authority of Lower Saxony is PT provider for microbiological measurements in drinking water in Germany
- Each year:
  - 4 PT rounds for E. coli, coliformic bacteria, enterococci, colony forming units
  - 2 PT rounds for pseudomonas aeruginosa, clostridium perfringens, legionella

2 Possibilities

- NLGA-method
  - preparation of fresh samples in a mineral salt solution
  - the laboratory must be able to cultivate the microorganisms
  - cold room must be available
  - with permanent cooling stable for 2-4 days
  - relatively cheap
- UK-method
  - freeze-dried samples
  - longer stability
  - equipment must be available
  - expensive

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20-Liter-bottles for preparing the lots

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Homogenisation – 3 days!!

Public Health Authority of Lower Saxony

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Bottling under special care

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Prepared and labeled bottles

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View into a shipping container

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Packaging

Shipping

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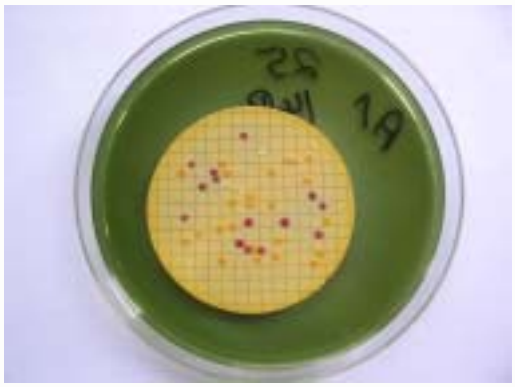
Quality control



Coliformic and other bacteria on a lactose-TTC agar

Public Health Authority of Lower Saxony

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Possibilities for know-how-transfer

- The NLGA people are willing to come to Africa to teach a possible PT provider here
- or to host people from Africa in their lab in Northern Germany
- provided that there is funding

Public Health Authority of Lower Saxony

Institute for Sanitary Engineering, Water Quality and Solid Waste Management, Universität Stuttgart

Annex 11

Evaluation Questionnaire

In order to evaluate the success of this workshop, we want to ask you to answer the following questions:

How do you judge:	Very good	good	fair	poor	very poor
The venue of the workshop (accommodation, food, conference room)	☐	☐	☐	☐	☐
The content of the presentations	☐	☐	☐	☐	☐
The handouts and documents	☐	☐	☐	☐	☐
The working group discussions	☐	☐	☐	☐	☐

Were all aspects of the pilot PT covered? ☐ Yes ☐ No

If No, which aspects were missing:.....

.....

The five most important topics for me have been:

1).....

2).....

3).....

4).....

5).....

Did the workshop fulfil your expectations? ☐ Yes ☐ No

If No, why not?.....

.....

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

.....

Any other comments:.....

.....

.....

.....