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Key comparison CCQM-K59

Determination of nitrite and nitrate in calibration solutions

Final report

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Contents

Abstract

In this key comparison anion calibration solutions of nitrate and nitrite were investigated. The mass fractions of the anions in both solutions were about 1 g/kg. For the nitrate comparison 8 participants provided results; 3 analytical techniques were used: ion chromatography, capillary electrophoresis and coulometry after ion exchange. The nitrite amount content was determined by 7 participants using one of the following 3 techniques: ion chromatography, titrimetry, and capillary electrophoresis.
The following institutes participated in this key comparison:
INTI (Argentina), KRISS (Korea), LNE (France), NIM (P.R.China), NIST (USA), NMIJ (Japan), SMU (Slovakia), and VNIIM (Russia).

The variability (RSD) of the results is about 0.75% for both the nitrite and the nitrate solutions. Compared to the key comparison CCQM-K29 the results of CCQM-K59 were significantly worse. This is in part due to the measurement methods used, possibly also due to the standards used by the institutes.
A pilot study (P89) was performed in parallel on the same calibration solutions used in this K59 comparisons study by laboratories preferring to participate in the pilot study and on a seawater sample containing about 0.1 mg/kg nitrite and 1 mg/kg nitrate. The results of the pilot study are reported separately.

1. Introduction

Aqueous solutions of anions are widely used for the calibration in analytical chemistry. Therefore they are a decisive factor for the reliability of measurement results. This is especially true in the field of environmental and medical investigation. The mass concentration of the analyte in commercial standards is often declared as 1.000 g/L with an uncertainty of 0.002 – 0.005 g/L. In practice, deviations up to several percent of the declared value can be found. Therefore, the CCQM inorganic working group proposed the analysis of some anionic calibration solutions. Previous study and key comparison (CCQM-P32 and CCQM-K29) focused on chloride and phosphate calibration solutions, where mainly titration and spectral methods were used. Nitrate and nitrite are analytes of major importance for the food and environment sectors. This key comparison CCQM-K59 was agreed by the Inorganic Analysis Working Group of CCQM in April 2006 and it was carried out in a manner similar to CCQM-K29 with SMU and NRC as the coordinating laboratories.

2. Participants

The following 8 institutes participated in CCQM-K59 (NIST registered for analysis of nitrate solution only):

Table 1 Participating institutes, contacts, and dates of sample receipt

Institute / Organisation		Country	Contact	Sample delivery date
INTI	Instituto Nacional de Tecnologia Industrial	Argentina	Ana Hernández	21.2.2007
KRISS	Korean Research Institute of Standards and Science	Korea	Joung Hae Lee	29.1.2007
LNE	Laboratoire National d'Essais	France	Chantal Royer	29.1.2007
NIM	National Research Center for Certified Reference Materials	China	Jingbo Chao	29.1.2007
NMIJ	National Metrology Institute of Japan	Japan	Akiharu Hioki	1.2.2007
NIST	National Institute of Standards and Technology	USA	Gregory Turk	29.1.2007
SMU	Slovak Institute of Metrology	Slovakia	Michal Máriássy	--
VNIIM	All-Russia D.I.Mendeleev Scientific and Research Institute for Metrology	Russia	Leonid A. Konopelko	31.1.2007

3. Samples

For each analyte, a solution of a mass fraction of about 1 g/kg (relative to the anion) was prepared by mass using a high purity salt and ultrapure water (in the case of nitrite also a small amount of sodium hydroxide as a stabilizer). Potassium nitrate was dried at 130 °C for 4 hours. The nitrite solution was prepared by using sodium nitrite purified according to [1]. The solutions were bottled into high-density polyethylene bottles, sealed and welded into Mylar type bags. A homogeneity study carried out on 3 of the 21 prepared bottles using high-accuracy coulometry (for the nitrate solution) or titration (for the nitrite solution) did not reveal any significant inhomogeneity. Stability was checked based on any change in mass of the bottles from the filling

to the end of the measurement period, as well as by coulometry and titration (as in the homogeneity study) and the changes were less than 0.015%.

Uncertainty due to transpiration and inhomogeneity was included into the uncertainty budget of the reference value for nitrate solution; for nitrite solution this contribution is covered in the spread of participants' values. Detailed information and handling instructions are given in Appendix A (technical protocol) of this report. About 220 mL of each solution were provided to the participants.

The samples were sent to the participants on January 26, 2007 by FedEx (except VNIIM, where UPS was used based on request of VNIIM). All samples arrived at their destination without damage.

The deadline for reporting results was set as 31 March, 2007 in order to allow preparation of draft A report for discussion at the CCQM WG meeting in April 2007. Several participants reported instrumental problems; therefore, it was decided to extend the deadline by one month to April 30. All participants observed this extended deadline reported their results in time.

4. Methods of measurement

The participants applied the following measurement techniques:

Table 2 Measurement techniques used

Participant	Nitrate solution	Nitrite solution
INTI	ion chromatography	ion chromatography
KRISS	ion chromatography	ion chromatography
LNE	ion chromatography	ion chromatography
NIM	ion chromatography	ion chromatography
NMIJ	ion chromatography	ion chromatography
NIST	ion chromatography	-
SMU	ion exchange + coulometry	Titrimetry
VNIIM	capillary electrophoresis	capillary electrophoresis
Total results	8	7

More details (extracted from the participants' reports) can be found in Appendix C of this report.

5. Results

The following table gives the results reported including the expanded uncertainties (k=2):

Table 3 Results

| Participant	Date results reported	Nitrate solution		Nitrite solution	
		$w(NO_3)$ /g kg^{-1}	U (k=2) /g kg^{-1}	$w(NO_2)$ /g kg^{-1}	U (k=2) /g kg^{-1}
INTI	30 April 2007	1,022	0,005	1,016	0,004
KRISS	30 April 2007	1,0194	0,0010	1,0156	0,0018
LNE	6 April 2007	1,0122	0,0047	0,9961	0,0066
NIM	30 March 2007	1,0171	0,0011	1,0139	0,0013
NMIJ	30 March 2007	1,0154	0,0016	1,0118	0,0020
NIST	12 April 2007	1,0209	0,0024	-	-
SMU	30 March 2007	1,0167	0,00087	1,0120	0,0016
VNIIM	3 April 2007	0,9984	0,0145	1,0038	0,0105
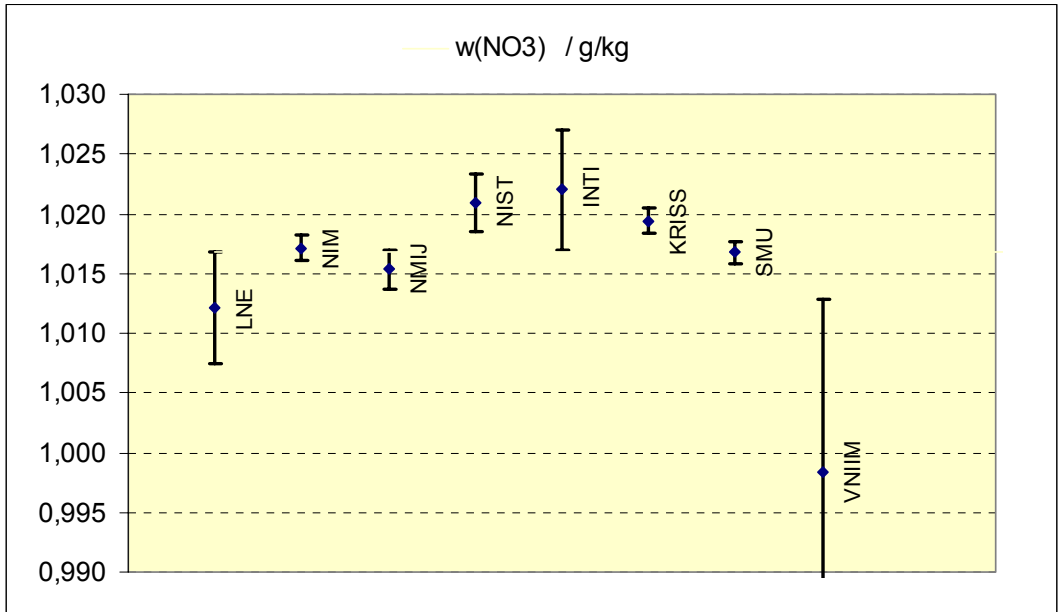
Figure 1 Results (with expanded uncertainty shown) for nitrate calibration solution
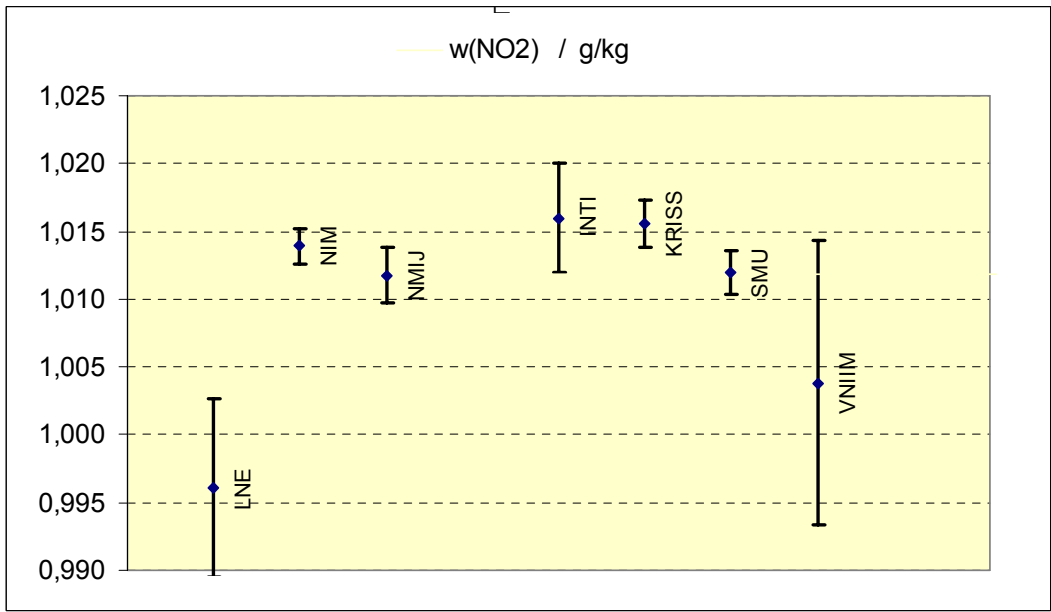

Figure 2 Results (with expanded uncertainty shown) for nitrite calibration solution

6. Key Comparison Reference Value (KCRV)

The possible estimators for reference value are presented in Table 4. The uncertainty of the mean was calculated as the standard deviation of the mean. For the inverse variance weighted mean the "reduced chi-square" (Birge ratio) has a value of 2.72 which is significantly larger than

one, implying the dataset is not consistent. Therefore the uncertainty of the inverse variance weighted mean was calculated using the so called external consistency method [2] according to the formula

$$u_{WM}{}^2 = \frac{\sum_{i=1}^{N}\left(\frac{1}{u_i{}^2}\cdot(x_i-x_R)^2\right)}{(N-1)\cdot\sum_{i=1}^{N}\frac{1}{u_i{}^2}\cdot}$$

using the stated uncertainties. The uncertainty of the median is estimated based on median absolute deviation (MAD) according to the formula [3]:

$$u_{KCRV} = \frac{1.858\cdot MEDIAN\big(ABS(x_i-KCRV)\big)}{\sqrt{n-1}}$$

The MM-median [4] and its uncertainty were calculated using spreadsheet PDFMakerTotal from D. Duewer. Details of the calculation of the values from preparation and the corresponding uncertainty statements are described in Appendix B of this report.

Table 4 Alternatives considered as possible reference values

	Nitrate solution		Nitrite solution	
	$w(NO_3)$ /g.kg^{-1}	U (k=2) /g.kg^{-1}	$w(NO_2)$ /g.kg^{-1}	U (k=2) /g.kg^{-1}
Preparation	1,0168	0,0007	1,0119	0,0018
Mean	1,0153	0,0053	1,0099	0,0055
Weighted mean	1,0175	0,0013	1,0132	0,0021
Median	1,0169	0,0045	1,0120	0,0054
MM-median	1,0169	0,0034	1,0125	0,0052

In the previous comparisons values from preparation were used as reference values. Due to incomplete characterisation of the source sodium nitrite it was proposed to use the value from preparation as the reference value for the nitrate sample only. For the nitrite sample, the weighted mean of all results was proposed as the KCRV. At the working group meeting in October 2007 it was suggested to use either the preparation value or median as the KCRV for nitrite solution. Due to large uncertainties of most estimators the differences between the alternative reference values are insignificant for both solutions, however a large uncertainty would certainly make the judgement of institutes' performance difficult.

Value from preparation gives directly only the maximum possible concentration of nitrite (assuming 100% purity and normal isotopic composition) in the solution. The reliability of the preparation value is not too high, as is was not intended originally to use it as a reference. The value calculated using the a posteriori determined weight loss on drying agrees excellently with the median (this is the case for nitrate solution, too), and is not in contradiction with other estimators. This can be regarded as supporting evidence for use of the preparation value as a reference for nitrite solution in this special case. It should be cautioned, however, that a use of not completely characterised materials is generally not recommendable (see also below).

Agreed reference values:
Nitrate: $w(NO_3) = 1{,}0168$ g.kg^{-1} ; $U(k=2) = 0{,}0007$ g.kg^{-1}
Nitrite: $w(NO_2) = 1{,}0119$ g.kg^{-1} ; $U(k=2) = 0{,}0018$ g.kg^{-1}

7. Equivalence statements

Equivalence statements were calculated for each of the participating laboratories according to the following expressions:

$$D_i = (x_i - x_R); \quad U_i^2 = 2^2 (u_i^2 + u_R^2)$$

where D_i is the difference between the laboratory mean value, x_i, and the KCRV, x_R. The degree of equivalence uncertainty, U_i, for each laboratory is the combined uncertainty of the KCRV with that for each laboratory.

The degrees of equivalence are given in Table 5 and graphically displayed in Figures 3 and 4.

Table 5 Degrees of equivalence

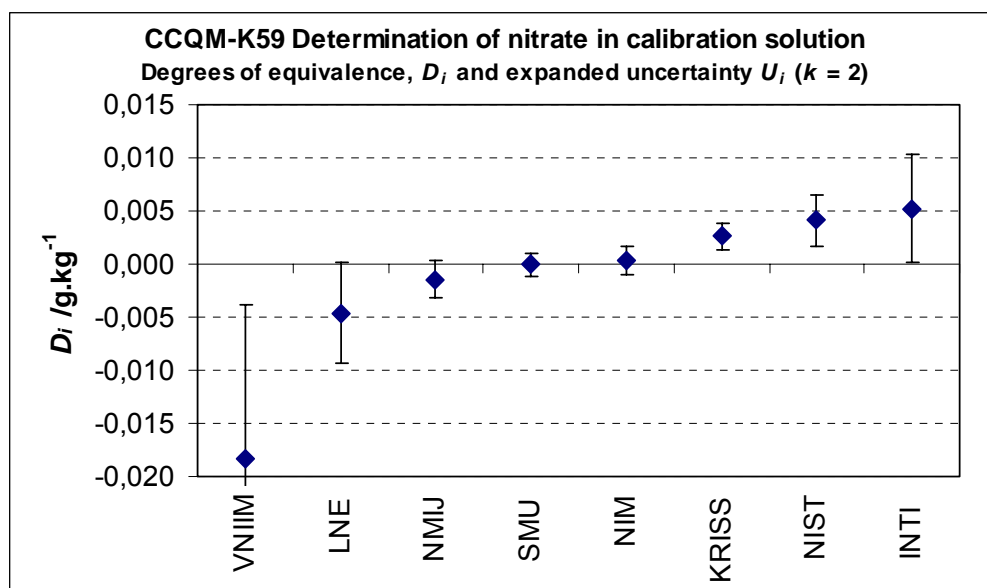| *Participant*	*Nitrate solution*		*Nitrite solution*	
	D_i /g kg^{-1}	U_i (k=2) /g kg^{-1}	D_i /g kg^{-1}	U_i (k=2) /g kg^{-1}
INTI	0,0052	0,0050	0,0041	0,0044
KRISS	0,0026	0,0012	0,0036	0,0025
LNE	-0,0046	0,0047	-0,0158	0,0068
NIM	0,0004	0,0013	0,0020	0,0022
NIST	0,0041	0,0025	-	-
NMIJ	-0,0014	0,0017	-0,0001	0,0027
SMU	0,0000	0,0011	0,0001	0,0024
VNIIM	-0,0184	0,0145	-0,0081	0,0107

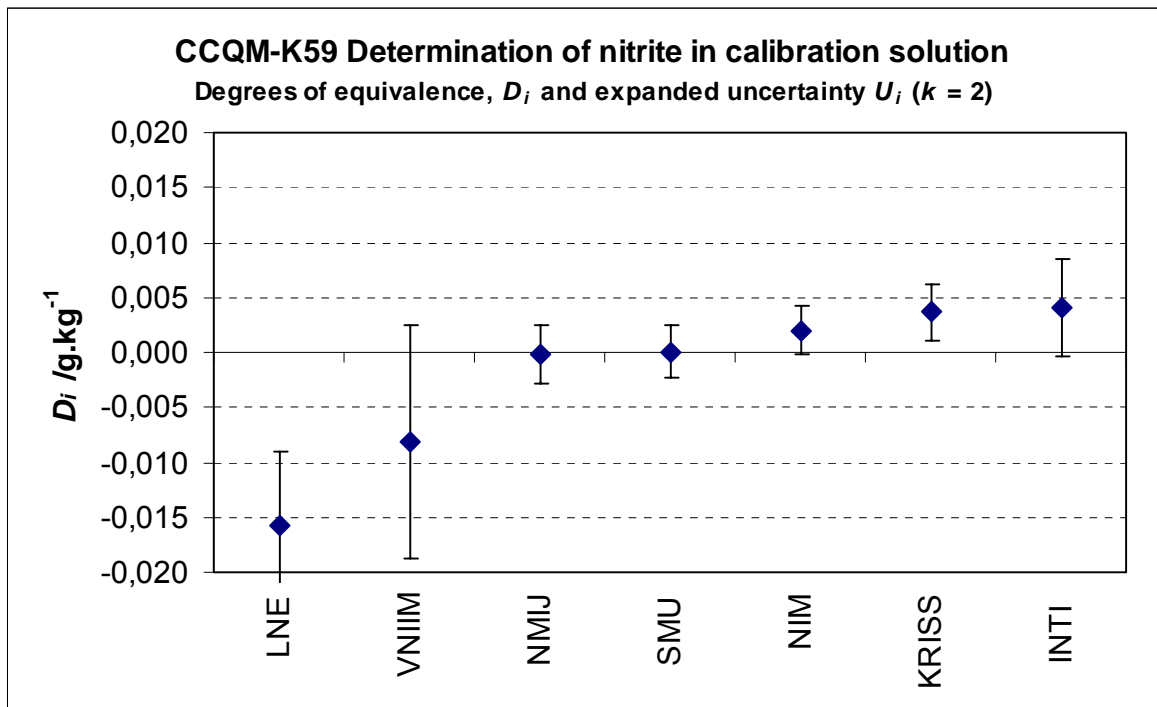Figure 3 Degrees of equivalence for nitrate calibration solution

Figure 4 Degrees of equivalence for nitrite calibration solution

8. Discussion

Compared to the previous comparisons on anion calibration solutions (CCQM-P32 and CCQM-K29) the results from this key comparison exhibit higher spread, but this corresponds to the different methods used in this comparison, calibration materials used and higher uncertainties claimed.

In one case a classical titration method was used to assay a solution used as a calibrant, which was in turn used as a standard in ion chromatography. The direct assay of the sample solution could lead to much smaller measurement uncertainty.

Table 6 Comparison of the spread of results with previous measurements on anion solutions

Analyte	Total results	Comparison	RSD between participants [%]
Chloride	16	P32	0.13
Phosphate	11	P32	0.26
Chloride	11	K29+K29.1	0.09
Phosphate	10	K29	0.10
Nitrite	7	K59	0.73
Nitrate	8	K59	0.75

Uncertainties

Large differences were observed in repeatability, as well as in magnitude and structure of uncertainties reported (Table 7 and 8). For nominally the same method, uncertainties differ by a

factor of 5. This is in part due to the differences in the methods themselves and their implementation, as can be seen from the standard deviation of the results obtained in the individual institutes – differences of almost two orders of magnitude occur. There are also differences in the uncertainty evaluation for similar methods; in some cases the evaluation slightly deviates from that of the GUM.

Table 7 Uncertainty contributions as stated by the participants for the nitrate solution

	RSD	$u_{r,B}$	$u_{r,A}$	Largest contributions in type B evaluation
LNE	0,25%	0,23%	0%	regression
NIM	0,04%	0,05%	0,01%	integration
NMIJ	0,11%	0,07%	0,04%	standard
NIST	0,21%	0,01%	0,12%	standard
INTI	0,35%	0,19%	0,16%	$NaNO_3$ purity
KRISS	0,08%	0,03%	0,04%	rep., standard
SMU	0,012%	0,04%	0,005%	coulometry, ion exchange
VNIIM	0,56%	0,46%	0,56%	standard solution, weighing

Table 8 Uncertainty contributions as stated by the participants for the nitrite solution

	RSD	$u_{r,B}$	$u_{r,A}$	Largest contributions in type B evaluation
LNE	0,50%	0,33%	0 %	regression
NIM	0,05%	0,06%	0,02%	standard, integration
NMIJ	0,08%	0,10%	0,03%	standard
NIST	x	x	x	x
INTI	0,21%	0,11%	0,17%	titration of NO_2 solution
KRISS	0,03%	0,08%	0,02%	standard
SMU	0,02%	0,08%	0,01%	amount content of $KMnO_4$ soln., chemical
VNIIM	0,25%	0,46%	0,25%	standard solution, weighing

In most cases the methods used are relative, requiring a standard of the same analyte. Therefore for properly designed exact matching or bracketing protocols (in the case of good repeatability) the results will depend mainly on sample preparation and quality of the standards used (Table 9). Deviations in negative direction can be expected if the solution used for calibration has higher concentration than expected (e.g. due to evaporation of the solution), the opposite can be caused e.g. by not accounting for water in the source salts when preparing the solutions. The information given in the reports is not exhaustive enough to extract this information.
It has to be noted that in the case of anion solutions the stability is not dependent solely on the concentration changes due to transpiration, as chemical or biological transformation of the anion can also lead to significant decrease of concentration. This is the case for the analytes in this comparison.

Table 9 Calibration materials used

Traceability based on values carried by	KNO_3 /$NaNO_3$	$NaNO_2$
CRM (known assay)	2	2
"pure compound"	4	2
other (e.g. titration solution)	1	2
commercial solution	1	1

If pure salts are used for calibration, it has to be cautioned again against assumptions, that high metallic purity means high assay. The producers do not claim this, although the users often have such impression. This can be demonstrated on the case of "Sodium nitrite, 99.999%", where specifications state "purity based on trace metal analysis" and titration assay is "98.0% (minimum) (with $KMNO_4$)".

9. Conclusions

This comparison showed that one has to be vary careful in the extrapolation to other analytes (how far the light shines statement), as the performance will vary due to different methods and standards used. For the current comparison, the scope statement can read as follows:
The results can be regarded as representative for nitrate and nitrite calibration solutions for concentrations used in this comparison (taking into account dilution used) and higher using the same methods as in this comparison.
Compared to the previous comparisons, there is not as good agreement as before. The selection of the references might be the crucial point for relative methods like ion chromatography. It is proposed to draw the attention to purity determination of salts, its limits and to alternative traceability routes.

References

[1] Cases,J.C., Revue de Chimie Minérale 10, 577 (1973)

[2] L. L. Lucas and M. P. Unterweger, Comprehensive Review and Critical Evaluation of the Half-Life of Tritium. J. Res. Natl. Inst. Stand. Technol. 105, 541 (2000)

[3] Müller J.W., Possible Advantages of a Robust Evaluation of Comparisons. J. Res. Natl. Inst. Stand. Technol. 105, 551-555 (2000)

[4] Duewer, D.L., A comparison of location estimators for interlaboratory data contaminated with value and uncertainty outliers, Accred Qual Assur 2008, DOI 10.1007/s00769-008-0360-3

Appendix A - Technical protocol
Key Comparison CCQM-K59
„Determination of nitrite and nitrate in calibration solutions"

Technical Protocol

1. Introduction
In 2003/4 the CCQM Inorganic Analysis Working Group (IAWG) organized a key comparison CCQM-K29 with anion calibration solutions. Chloride and phosphate were the analytes and the results have shown good performance of the participating institutes. At the CCQM Workshop on Comparability and Traceability in Food analysis, nitrites and nitrates were identified as priority analytes necessitating comparability. Furthermore, several methods used in the CCQM-P32 and CCQM-K29 comparisons cannot be used for these analytes. As anion calibration solutions are the base for their anion measurement, the comparability at highest level will be tested. The comparison was agreed at the IAWG meeting in April 2006 with SMU and NRC as coordinating laboratories, after the stability issues of the solutions were resolved.

Scope of the comparison (How far the light shines)
The comparison tests the capabilities and methods used for analysis of anionic solutions of nitrate and nitrite with mass fraction higher than about 0.5 g/kg for titration methods and higher than about 0,01 g/kg for chromatography methods.

2. Samples
Analytes/Matrix: The analytes in K59 are nitrate (NO_3^- from KNO_3), and nitrite (NO_2^- from $NaNO_2$) provided as monoanion solutions in water. The solution of about 1 g/kg (mass fraction of the anion) is prepared by weight. About 230 mL of solution is provided. The nitrate solution is not stabilized, the nitrite solution is stabilized with sodium hydroxide (approx. 0.0001 mol/kg). Purified reagent grade material is used for the solution preparation.
Packaging and labeling: 250 mL HDPE bottles are precleaned (24 h leaching) with ultrapure water and dried in a clean atmosphere. After bottling the samples are closed with a screw cap, sealed and welded in Mylar type foil to avoid transpiration during transport. Each sample is labeled with an individual sample code.
Distribution: Participants are expected to cover the transport costs of the samples. One bottle of each anion solution is dispatched to the participants by an adequate mail service. The participants will be informed by the pilot laboratory about the date of dispatching the samples. Participants are asked to **confirm the receipt of the sealed samples** by e-mail or fax. In case of any damage of the packaging or the samples the pilot laboratory should be informed. The integrity can be checked by weighing the samples (including the plastic bags) and comparing the mass with the original one (supplied by the coordinating laboratory).
Handling and storing instructions: The samples should be stored in refrigerator. To avoid transpiration the samples shall be kept in the aluminized bags until they are used. They shall be allowed to reach laboratory temperature and thoroughly homogenized before opening. The bottles should not be kept open longer than needed for taking the required sample aliquot. Participants are expected to handle the samples in a way that any contamination by air, the diluent or the equipment used is avoided.

3. Measurands
The measurands are the mass fractions of nitrate and nitrite, resp., in the sample solutions.

4. Reporting

The report should be sent to the coordinating laboratory before March 31, 2007, preferentially by e-mail. The coordinator will confirm the receipt of each report. If the confirmation does not arrive within 1 week, contact the coordinator to identify the problem.

Mass fraction (g/kg) of nitrate (NO_3^-) and nitrite (NO_2^-) should be reported, based on at least five individual measurements of each. Because K59 is a key comparison, only one final result per participant and anion can be reported. Each participant is allowed to report its result as an average value from different methods.

Calculation of the uncertainty should be done according to Guide to the Expression of Uncertainty in Measurement (GUM) and expressed as expanded uncertainty U (k = 2). This should be based on a complete uncertainty budget, including the assessment of all significant uncertainty sources, e.g. weighing, temperature, repeatability of measuring values, volume, calibration, interferences, integration, decomposition, blanks, etc.

A detailed description on all the applied methods of measurement is requested including all relevant equations used and the complete data for calculation of one of the results and reporting corrections e.g. of blanks and interferences.

A description of the used equipment (e.g. for ion chromatography instrument producer, type, column type, eluent type and concentration, suppression mode, detection), information about sample size and preparation, instrument calibration (model, number and concentrations of standards, measurement sequence, etc.), reference material used for calibration (origin, purity, assigned uncertainty) or any other material used during the analytical procedure should be reported, too.

An Excel file will be provided to facilitate reporting and evaluation of the results.

5. Methods of measurement

No measurement method is prescribed. The participants are free to choose one or more suitable methods of measurement, however the achieved expanded uncertainty is expected to be better than 0.5%.

6. Reference value

The reference value will be agreed at the Inorganic Analysis WG meeting.

7. Proposed time schedule

Deadline for registration: November 30, 2006
Sample distribution: 26 January 2007
Deadline for reporting results: **March 31, 2007**
Draft A report: April 2007
Final report: October 2007

8. Participants

This comparison is open only for NMIs and officially designated laboratories.

9. Correspondence

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Appendix B - *Solution preparation, weighing, uncertainty*

Source materials

Potassium nitrate was a triply recrystallised reagent grade material used at SMU for preparation of reference materials. A previous indirect analysis based on potassium gravimetric determination yielded assay expressed as mass fraction of potassium nitrate 99.95% ± 0.06%. Details of the certification procedure and data of impurities can be found in the certification report of CRM 10-2-09.

Sodium nitrite was a doubly recrystallised reagent grade material used at SMU for preparation of reference materials. Some impurities were quantified by ion chromatography.

List of significant impurities in the source materials quantified smaller than (mg/kg)

Impurity	KNO_3	$NaNO_2$
Calcium	4	?
Sodium	2	N/A
Potassium	N/A	?
Rubidium	10	?
Nitrite	<1	N/A
Sulfate	<5	<10
Ammonium	<2	?
Phosphate	<3	<30
Nitrate	N/A	110
Perchlorate	1	?
Chloride (+Br, I)	1	<10
Acetate	?	<30

N/A - not applicable – main component

? – not determined

Calculation of values based on preparation for CCQM-K59 solutions

balance type   Mettler AG285, PR1203

air density   1.169 kg m^{-3}

solution density used   1000 kg m^{-3}

Weighing of KNO_3 starting material and of aqueous KNO_3 solution:

KNO_3 density   2110 kg m^{-3}

balance reading for KNO_3 8.50169 g

balance reading for solution   5122.15 g

KNO_3 purity   0.9995 +- 0.0006

Calculated mass fraction of nitrate in CCQM-K59 solution

mass fraction $wNO_3 = mKNO_3 \cdot wKNO_3/m_{Soln}$ **1.01679 g/kg**

Weighing of $NaNO_2$ starting material and of aqueous $NaNO_2$ solution:

$NaNO_2$ density   2160 kg m^{-3}

balance reading for $NaNO_2$ 7.7528 g

balance reading for solution   5100.39 g

$NaNO_2$ purity (estimated)   0.999

Calculated mass fraction of nitrite in CCQM-K59 solution

mass fraction $wNO_2 = wNO_2 \cdot mNaNO_2/m_{Soln}$ **1.0119 g/kg**

The uncertainty budget is calculated according to GUM analogously to the CCQM-K29 key comparison. The following uncertainty contributions were considered:

Uncertainty component	Relative standard uncertainty – nitrate	Relative standard uncertainty – nitrite
Salt weighing	$1.1 \cdot 10^{-5}$	$1.2 \cdot 10^{-5}$
Solution weighing	$5.6 \cdot 10^{-6}$	$5.6 \cdot 10^{-6}$
Buoyancy corrections	$4 \cdot 10^{-6}$	$4 \cdot 10^{-6}$
Nitrate assay in the salt	$3 \cdot 10^{-4}$	$6.3 \cdot 10^{-5}$
Residual moisture in the salt	-	$8.7 \cdot 10^{-4}$
Evaporation, homogeneity	$1.3 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$
Combined relative uncertainty of mass fraction	**$3.3 \cdot 10^{-4}$**	**$8.8 \cdot 10^{-4}$**

Appendix C – Summary of methods used by the participants

NIST-USA
NO3 Analytical Method:
IC was used to determine nitrate in the K59 solution. The Dionex IC instrument and associated parameters include:
LC25 chromatography oven (35 degrees C)
EG40 eluent generator (isocratic, KOH fraction = 0.15)
ED50 electrochemical detector (35 degrees C, temperature compensation = 1.7 K^{-1})
GP50 gradient pump (1.00 mL min^{-1})
Injection volume = 25.0 µL
Ion-Pac AS11-SC Separation Column
Ion-Pac AG11-SC Guard Column
ASRS-Ultra 4 mm Suppressor (suppression current = 300 mA)
PeakNet Client software, v. 6.20

Calibration of the IC followed the same protocol used at NIST for high performance ICP-OES [Salit, Turk, Lindstrom, Butler, Beck, and Norman, "Single-Element Solution Comparisons with a High-Performance Inductively Coupled Plasma Optical Emission Spectrometric Method," *Anal. Chem.* **73** 4821-4829 (2001)]. Four primary standards were prepared gravimetrically from high-purity sodium nitrate of assessed purity and stoichiometry.
From each of the four primary standard solutions, two nominally 30 g aliquots were gravimetrically taken. Additionally, six nominally 6 g aliquots were gravimetrically taken from the K59 solution, and two nominally 6 g aliquots were gravimetrically taken from SRM 3185 Nitrate Anion Standard Solution, Lot No. 050517, which was used as a control sample. To each of the sixteen aliquots, an appropriate mass of chloride internal standard stock solution (30 g for the primary standards; 6 g for the K59 and control samples) was gravimetrically added, such that the expected ratio of the mass fractions of nitrate to chloride in all of the solutions would be equal. The solutions were then diluted using high-purity water (18.2 Mohm cm and passed through a 0.22 m filter), to bring the nitrate and chloride mass fractions to values suitable for introduction into the IC instrument (14 mg/kg nitrate, 5 mg/kg chloride).
The sixteen prepared solutions were injected once each into the IC in a randomized order. The same random order was repeated four times, for a total of five injections of each solution. The nitrate and chloride peak areas were downloaded into a Microsoft Excel workbook for processing. The processing included the application of drift correction to the observed nitrate to chloride peak area ratios, based upon the drift correction protocol used in high-performance ICP-OES [Salit and Turk, "A Drift Correction Procedure," *Anal. Chem.* **70** 3184-3190 (1998)

INTI – Argentina
INTI NO3
Description of the procedure and used equipment. **Ion chromatograph**: DIONEX DX 500, SOFTWARE Peak Net. Column type: AS 11. Eluent type: NaOH 21mM. Suppression mode: yes. Detection: conductimetric. **Balance**: Mettler H 35 AR and Sartorius BP 4100 S (Max. 4100 g, d= 0,01g). **Material used for calibration** - sodium nitrate, origin: Merck, art. 1.06537.0500 (lot.A 670737623), purity: > 99,5 %, used concentration: aprox. 1,0 g/kg, used purity: 99,8 weight percent (corrected in lab. for chloride and sulfate). **Procedure**: Quantitation is by measurement of peak area (C(x)=Ax*F*f(dil), where C(x) concentration of nitrate, Ax sample area, F response factor = concentration of standard/ area of standard) and f(dil) = dilution factor).
10-fold dilution, 1-point calibration

INTI NO2
Description of the procedure and used equipment. **Ion chromatograph**: DIONEX DX 500, SOFTWARE Peak Net. Column type: AS 11. Eluent type: NaOH 21mM. Suppression mode: yes. Detection: conductimetric. **Balance**: Mettler H 35 AR and Sartorius BP 4100 S (Max. 4100 g, d= 0,01g). **For titration** - type: redox, mode: gravimetric, Ox:standard potassium permanganate titrant (aprox. 0,1 N), Red: sodium oxalate (aprox. 0,05 N), end point detection method: visual, blanks: 0,02 g. **Material used for calibration** - standard reference material 40 h, sodium oxalate, reductometric standard, origin: NIST, purity: 99,972 ± 0,016 weight percent, used concentration: 3,3792 exp.-3 g/gsolution (0,0504meq./gsolution). **Procedure**: Quantitation is by measurement of peak area (C(x)=Ax*F*f(dil), where C(x) concentration of nitrite, Ax sample area, F response factor = concentration of standard/ area of standard) and f(dil) = dilution factor). Standardization of standard nitrite solution: To determine nitrite content, add a known excess of standard 0,1 N´KMnO4 solution, discharge permanganate color with a known quantity of standard reductant such as 0,05 N´ sodium oxalate, and back - titrate with standard permanganate solution.
10-fold dilution, 1-point calibration

VNIIM – Russia

VNIIM Nitrate
The procedure and used equipment: Capillary electrophoresis "Kapel 105", (Russia, OOO "Lumex") , the buffer: 7,0 mMol of Chromate - ion; 20 mMol of DEA; 2,0 mMol of ZTA-OH; capillary ID=75 mkm, L= 50 cm; input of sample – 300 mbar*c; running voltage –(-17kV); detection wavelength – 275 nm;
Concentration of calibration standard - 1000 mg/kg (u=0,6 %), linear calibration, 5 calibration standards (0,0010; 0,0044; 0,0109; 0,0221; 0,0432 g/kg), calibration coefficient -1,334; correlation factor – 0.999844

VNIIM Nitrite
The procedure and used equipment: Capillary electrophoresis "Kapel 105", (Russia, OOO "Lumex"), the buffer: 7,0 mMol of Chromate - ion; 20 mMol of DEA; 2,0 mMol of ZTA-OH; capillary: ID=75 mkm, L= 50 cm; input of sample – 300 mbar*c; running voltage –(-17kV); detection wavelength – 275 nm; 170-fold dilution
Concentration of calibration standard - 1000 mg/kg (U=0,6 %, P=0,95), linear calibration, 5 calibration standards (0,0011; 0,0044; 0,0111; 0,0223; 0,0434 g/kg), calibration coefficient - 1,362; correlation factor – 0.99996

KRISS – Korea

A. Ion Chromatography for Nitrite and Nitrate
 i. Equipment: Dionex ICS 90 with Anion Micro Membrane Suppressor (AMMS), DS5 Detection Stabilizer (Model DS 5) and Conductivity detector.
 ii. Analytical column: IonPac AG 14 + AS 14
 iii. Eluent: 1.0 mM NaHCO3/3.5 mM Na2CO3,
 iv. Regenerant: 50 mM H2SO4
 v. Sample size: 10 uL
 vi. Two point (bracketing) calibration; 10-fold dilution for nitrite
 vii. Gravimetrically prepared PRMs were used as reference solutions
 viii. Number of experiments for reproducibility: 5 for nitrite and 4 for nitrate
B. Source of reference materials for ion chromatography

i. Nitrite: NaNO2, Aldrich 563218 (Purity: 99.999 %)
ii. Nitrate: KNO3, Aldrich 542040 (Purity: 99.999 %)

NMIJ – Japan
NMIJ NO3
The nitrate ion in the calibration solution was analysed with an ion chromatographic analyser IC7000 (Yokogawa Analytical Systems). The conditions of instrument and measurement were as follows:
columns: ICS-A2G/ICS-A23; eluent: 3-mM sodium carbonate (1 mL/min); chemical suppression: 15-mM sulfuric acid (1 mL/min); detection: peak area of conductivity; injection volume: ca. 10 micro L; pretreatment: nothing; blank: nothing; calibration: bracket method with 5% concentration interval; density correction: nothing; repetition: 9; reference material: potassium nitrate (NMIJ primary material, purity 99.71%±0.18% (k=2.57)).
NMIJ NO2
The nitrite ion in the calibration solution was analysed with an ion chromatographic analyser IC7000 (Yokogawa Analytical Systems). The conditions of instrument and measurement were as follows:
columns: ICS-A2G/ICS-A23; eluent: 3-mM sodium carbonate (1 mL/min); chemical suppression: 15-mM sulfuric acid (1 mL/min); detection: peak height of conductivity; injection volume: ca. 10 micro L; pretreatment: nothing; blank: nothing; calibration: bracket method with 5% concentration interval; density correction: nothing; correction for coexisting sodium hydroxide: estimated (the mass fraction of NO2 in NO2 solution has been corrected from 1.01269 g/kg to 1.01177 g/kg); repetition: 9; reference material: sodium nitrite (NMIJ primary material, purity 99.57%±0.18% (k=2)).

NIM – China
NIM NO3
About 407mg high-purity Potassium nitrate was accurately weighted into the beaker and dissolved in 250mL water, then diluted to 20mg/kg; Weight accurately 2g sample solution and diluted the same concentration level as standard solution. Mass was corrected by buoyancy for each measurement. The determination was adopted as one-point calibration method, and the sample injection was between the same two standard solutions. Blank correction was done simultaneously. The concentration of the NO3- was calculated by the equation as below,

$$C = \frac{2A_x \times C_{std}}{(A_1 + A_2)} \times f$$

Where
    C: the concentration of NO3- in sample solution, mg/kg;
    Cstd: the concentration of NO3- in standard solution, mg/kg;
    A1: the peak area of standard solution before sample, mAU*min;
    A2: the peak area of standard solution before sample, mAU*min;
    Ax: the peak area of sample solution, mAU*min;
    f: dilution factor;
The anionic impurities and metal impurities of high-purity KNO3 were detected by ion chromatography and ICP-MS;
2. The Equipment and Reagent:
a) Ion chromatography: Model ICS3000, Dionex company;
b) Balance: Model XP205, Mettler Toledo company;

c) Potassium nitrate: 99.999%, ACROS company;
d) Sodium carbonate and sodium bicarbonate: G.R;
3. Parameters for ion chromatography:
a) Column: IonPac AG14A and AS14A-7μm (4×250μm);
b) Elute solution: 4.0mM Na2CO3 + 1.3mM NaHCO3;
c) Flow rate: 1.2 mL/min;
d) Column temperature: 30 ;
e) Inject volume: 33uL;
f) Detector: UV detector (210nm), conductive detector.

NIM NO2
About 375mg high-purity NaNO2 was weighted into the beaker and dissolved in 250mL water, then diluted to 20mg/kg; Weight 2g sample solution and diluted the same concentration level as standard solution. Mass was corrected by buoyancy for each measurement. The determination was adopted as one-point calibration method, and the sample injection was between the same two standard solutions. Blank correction was done simultaneously. The concentration of the NO2- was calculated by the equation as below,
(see equation for NO3)
Where,
    C: the concentration of NO2- in sample solution, mg/kg;
    Cstd: the concentration of NO2- in standard solution, mg/kg;
    A1: the peak area of standard solution before sample, mAU*min;
    A2: the peak area of standard solution before sample, mAU*min;
    Ax: the peak area of sample solution, mAU*min;
    f: dilution factor;
The anionic impurities and metal impurities of high-purity NaNO2 were detected by ion chromatography and ICP-MS;
2. The Equipment and Reagent:
a) Ion chromatography: Model ICS3000, Dionex company;
b) Balance: Model XP205, Mettler Toledo company;
c) Sodium nitrite: 99.999%, SIGMA-ALDRICH company;
d) Sodium carbonate and sodium bicarbonate: G.R;
3. Parameters for ion chromatography were: the same as for nitrate

LNE France
(NO2 and NO3)
The equipment used is a Dionex Ion Chromatograph instrument.
 It is composed of LC 25 chromatography oven, IC 25 ion chromatograph with conductivity detector, AS 40 automated sampler, Anion Atlas Electrolytic Suppressor, Ion Pac AG 14A guard column and Ion Pac AS 14A analytical column.
The eluent is composed of 8.0 mM Na2CO3 / 1.0 mM NaHCO3.
Prior to determinations, KNO3 and NaNO2 have been separately dried in an oven (120°C) during 24 hours (minimum) and then kept in desiccator.
 The quantification method chosen is respectively, nitrite and nitrate peak area, in μS.min.
 Anion mass is determined by comparison with four standard solutions prepared to bracket two by two the unknown solution.
 Nitrite sample is prepared by weighing 3ml of bottle N°16 completed to 100ml with ultrapure water (Millipore water - 18.2MΩ.cm) to obtain about 30mg/kg nitrite mass fraction solution.

A concentrated solution (2g/kg nitrite mass fraction) (m1/m2) is prepared with high purity NaNO2 salt (Its purity has been experimentally determined (P)). Aliquots of concentrated solution are weighed (m3) and completed to 100ml (m4), to prepare four standard solutions to bracket the sample solution, two by two (25mg/kg, 27.5mg/kg, 32.5 and 35mg/kg nitrite mass fraction solutions) .

Each sequence is composed of 52 injections: 1 H2O - 10 standard N°1- 10 standard N°2 - 10 sample - 10 standard N°3 - 10 standard N°4 - 1 H2O.

Five runs are independently led with new concentrated solutions and new dilutions of sample and new standard solutions.

The same protocol has been respected separately for nitrate.

Nitrate sample is prepared by weighing 3ml of bottle N°20.

Nitrate or nitrite mass fraction = Creg * fetalon * fidelite * fdilution

Cstandard : mass nitrate or nitrite in mg/kg of standard solution

Cstandard = MNO2/MNaNO2*m1/m2*P*m3/m4*E6

Cstandard = MNO3/MKNO3*m1/m2*P*m3/m4*E6

MNO2   : molar mass of NO2 in g/mol

MNaNO2 : molar mass of NaNO2 in g/mol

P   : purity of salt in kg/kg

MNO3   : molar mass of NO3 in g/mol

MKNO3   : molar mass of KNO3 in g/mol

m1   : mass of NaNO2 or KNO3 (salt) in g

m2   : mass of solution to dissolve NaNO2 or KNO3 in g (concentrated solution)

m3   : mass aliquot of concentrated solution in g

m4   : mass of solution to dilute aliquot in g

SMU - Slovakia

SMU NO3

Weighed amount of sample is passed through a ion-exchange column with strongly acid resin in H^+ cycle and eluted with water with conductivity detector. The eluent mass is recorded and an aliquot sample is taken for acid-base coulometric titration.

Equipment used for coulometry: High-accuracy coulometric system – Standard for amount of substance (Slovak National Standard No.22)

Ion chromatograph Dionex ICS 2500 with AS16 column was used do detect/determine interfering anion impurities.

SMU NO2

Nitrite is determined by injecting sample into ice-cooled solution of permanganate acidified with sulfuric acid and back titration of excess permanganate by Fe(II) solution with biamperometric detection. Permanganate content is determined by titration with Fe(II) solution, traceable to primary CRM of potassium dichromate A05 from SMU.

The weight titration is done using plastic disposable syringes and Mettler AG285 balance. Indication unit 8971 (Applied Precision) in combination with double pin platinum electrode is used for indication.