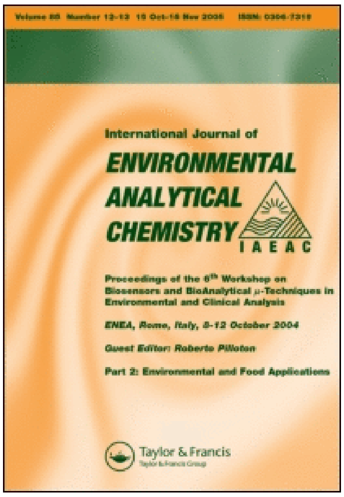

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Validation assessment about the determination of selected elements in groundwater by high-resolution inductively coupled plasma mass spectrometry (HR-ICPMS)

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Validation assessment about the determination of selected elements in groundwater by high-resolution inductively coupled plasma mass spectrometry (HR-ICPMS)

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A validation assessment of the determination of five elements (As, Cd, Cr, Cu and Fe) in groundwater by high-resolution inductively coupled plasma mass spectrometry (HR-ICPMS) is presented. The groundwater samples, which are used for the measurements of this validation assessment, have the following concentration ranges (As: 0.2–7.8 $\mu g\,L^{-1}$; Cd: 0.05–0.6 $\mu g\,L^{-1}$; Cr: 0.2–1 $\mu g\,L^{-1}$; Cu: 1.1–7.5 $\mu g\,L^{-1}$; Fe: 0.08–2.6 $mg\,L^{-1}$) and they are originated from different locations in The Netherlands. Besides the methodological aspects and the obtained analytical results, 10 relevant performance characteristics (limit of detection, recovery, repeatability, reproducibility, measuring range, trueness, lack of fit, expanded uncertainty of measurement, robustness and selectivity) are defined, calculated and discussed. The validated method is routinely applied in monitoring programs. This work can serve as a guideline for a complete validation assessment in environmental matrices.

Keywords: validation assessment; performance characteristics; elements; groundwater; high-resolution inductively coupled plasma mass spectrometry

1. Introduction

Since decade's groundwater is the preferred environmental matrix in provincial and national monitoring programs in The Netherlands, see, e.g. Dutch reports about groundwater monitoring. (Several Dutch reports on groundwater; mainly in Dutch. Available from <http://www.rivm.nl/milieuportaal/bibliotheek/rapporten/index.jsp?navigatieitem=tcm:115-38971&content_type=rapporten&navigatietype=onderwerpen>). Several parameters are routinely analysed in which the determination of elements plays an important role. Concentrations are used in databases and statistics to describe the quality of groundwater [1] and to determine changes of its quality. Furthermore, results obtained during a long period of years are used for explaining significant changes in relation to the environment as well as to the policy measures.

For the routine analysis of dissolved elements, inductively coupled plasma mass spectrometry (ICPMS) is the preferred method. Using, e.g. quadrupole based (Q)-ICPMS with applying interference corrections already leads for several elements to acceptable

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results. For five elements (As, Cd, Cr, Cu and Fe) it was found that the use of quadrupole (Q)-ICPMS without collision or reaction cell techniques did not always lead to acceptable results in terms of limits of detection (LOD).

Quality assurance for environmental analysis is a growing feature since the 1990s. The number of quality assurance guidelines and systems, which are implemented and enlarged nowadays, also illustrates this. It is a permanent process of new implementations of new analytical techniques. Using a new technique brings the need of validation of the analytical procedure. Validation means 'the confirmation by examination and provision of objective evidence that the particular requirements for a specified end-use are fulfilled' [2].

The process of method development and validation has a direct impact on the quality of analytical data and may therefore be an iterative process [3]. The limits of a method must be known and they are essential for a good interpretation of obtained results.

The analytical results are only estimates of the unknown true values. The extent of variation in analytical results in environmental matrices is quantified by the determination of method specific performance characteristics. These characteristics represent the performance of a method under different laboratory circumstances. Apart from developed methods, it is also possible to follow standards. For the general application of ICPMS to water samples, standards are also available [4,5]. Recently published standards always contain the performance characteristics. By using standards it is also necessary to monitor several laboratory internal performance characteristics because this allows the match of own results against results obtained in the fixed score of a standard. Within intercomparison studies performance characteristics are used to compare different laboratories. Also by the set-up of national [6] as well as international [7–10] standards performance characteristics play an important role. They determine the scope and the quality of a standard. Nevertheless performance characteristics also demonstrate the quality to an independent third party.

Before carrying out measurements it is important to define several criteria of the frame:

- The sample material (matrix) must be defined by, e.g. character, size and conditions. If interferences are known they must be clearly mentioned.
- The analyte, which is the particular quantity subject to measurement [11], must be defined, e.g. as concentration given as $\mu g\,L^{-1}$.
- The principle of measurement, i.e. the scientific basis for the measurement, must be described. In this study, it is HR-ICPMS applied for the determination of selected elements in groundwater.
- With respect to the results of the measurements a reference must be mentioned, e.g. the results are given as average of analysing a certain number of replicates.
- The test range (matrices/range of measurement), wherefore the method must be validated, must be described.

HR-ICPMS is applied in several research studies with natural waters, see examples in [12]. While the related validation assessment is seldom completely presented or carried out. For the determination of the elements (As, Cd, Cr, Cu and Fe) by HR-ICPMS there is also no international standard available. Therefore an analytical method was developed and its complete validation is presented in this study, which was performed in the frame of the quality system according to ISO 17025 [13].

2. Experimental

2.1 *Instrumentation and other materials*

The five-element-method is developed on the HR-ICPMS instrumentation ELEMENT2, Thermo Fisher, Bremen, Germany. The sample introduction system is also supplied by Thermo Fisher, details and instrumental operating conditions of HR-ICPMS are summarised in Table 1.

Cellulose nitrate membrane filters (0.45 µm) from Sartorius, Goettingen, Germany, are used for the filtration of the groundwater samples.

2.2 *Reagents, standards and reference materials*

Nitric acid (HNO_3), 65%, suprapur, is purchased from Merck, Darmstadt, Germany. Calibration standard solutions of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu) and iron (Fe) as well as solutions of the element used as internal standard rhodium (Rh) are made of single element stock solutions with a concentration of $1000\,\mu g\,mL^{-1}$ from Merck, Darmstadt, Germany. Deionised water (H_2O) is purified by a Millipore system (Milli-Q, 18.2 MΩcm). Certified reference materials 'SRM1640 (trace elements in natural water)' and 'CRM610 (trace elements in groundwater)' are supplied by C.N. Schmidt, Amsterdam, The Netherlands.

2.3 *Sampling and sample pre-treatment*

Directly after sample collection the groundwater samples are filtered in the field over 0.45 µm filters and acidified with HNO_3 to $pH < 2$. This procedure is in accordance with the standard ISO 5667-3 [14].

Prior to laboratory analysis, a simple pre-treatment of groundwater samples is applied by diluting the samples by factor of 5 with 0.7% HNO_3. With respect to 1 : 1 on-line mixing of the internal standard (also in 0.7% HNO_3), this leads to a total dilution factor of 10 in the measuring solution.

The dilution factor is the same as in a previous method with Q-ICPMS and also in agreement with comparable applications in natural waters where by at least a factor of 5 was used [12,15].

Table 1. Sample introduction system and instrumental operating conditions of HR-ICPMS (ELEMENT2).

Sample introduction system	
Nebulizer	PFA $100\,\mu L\,min^{-1}$
Operation mode	Pumped with on-line mixing of internal standard, 1:1
Spray chamber	Scott type
Cones	Nickel, type H
Instrumental operating conditions	
RF power	1290 W
Cool gas flow	$16\,L\,min^{-1}$ Ar
Auxiliary gas flow	$0.9\,L\,min^{-1}$ Ar
Sample gas flow	$1.11\,L\,min^{-1}$ Ar

2.4 *Measurement*

The elements selected for the determinations by HR-ICPMS are As, Cd, Cr, Cu and Fe. In the case of Cd, which often occurs in very low concentrations in groundwater, the higher sensitivity of HR-ICPMS is advantageous. It is known that the isotope signals of Cd are interfered by MoO. These interferences are not separable by HR-ICPMS because a resolution of >10,000 is required. Nevertheless, the abundance of Mo in groundwater as a potential interferent is low and therefore not investigated further. In the case of the As, Cr, Cu and Fe, HR-ICPMS allows the separation of several matrix- and plasma-based interferences that leads to a better performance of the method compared to Q-ICPMS. An overview about the main interferences is given in Table 2. Methodical parameters were optimised in respect to matrix- and plasma-based interferences as well as to sensitivity. The resulting best settings are given in Table 3. The quantification is carried out with an external calibration and correction by using an

Table 2. Selected isotopes and interferences.

Isotope	Interference (resolution for separation)
^{75}As	^{40}Ar^{35}Cl ($R = 7781$), ^{39}K^{36}Ar ($R = 7756$)
^{111}Cd	^{95}Mo^{16}O ($R = 32{,}332$)
^{52}Cr	^{40}Ar^{12}C ($R = 2375$), ^{40}Ca^{12}C ($R = 2353$), ^{36}Ar^{16}O ($R = 2367$)
^{63}Cu	^{40}Ar^{23}Na ($R = 2791$)
^{56}Fe	^{40}Ar^{16}O ($R = 2503$), ^{40}Ca^{16}O ($R = 2480$)

Table 3. Method and measuring parameters.

Low resolution mode ($R = 300$)	
Isotope (internal standard)	^{111}Cd (^{103}Rh)
Acquisition/'mass' window	120%
Search window	80%
Integration window	70%
Samples per peak	10
Medium resolution mode ($R = 4000$)	
Isotopes (internal standard)	^{52}Cr (^{103}Rh), ^{56}Fe (^{103}Rh), ^{63}Cu (^{103}Rh)
Acquisition/'mass' window	150%
Search window	70%
Integration window	60%
Samples per peak	20
High resolution mode ($R = 10{,}000$)	
Isotope (internal standard)	^{75}As (^{103}Rh)
Acquisition/'mass' window	150%
Search window	60%
Integration window	20%
Sample per peak	30
General parameters	
Acquisition mode	E-scan
Replicates per isotope	9

internal standard of Rh with a final concentration of 2.5 $\mu g\,L^{-1}$, which is on-line, added (see also Tables 1 and 3). Two compositions of standard solutions for external calibration are used, one for trace elements (TrEl) and one of macro element(s) (MaEl). Two-point-calibrations are applied while the highest concentration levels used for calibrations are TrEl with 10 $\mu g\,L^{-1}$ As, Cd, Cr and 50 $\mu g\,L^{-1}$ Cu, MaEl with 2000 $\mu g\,L^{-1}$ Fe.

2.5 *Definition of 10 performance characteristics*

The performance characteristics according to NEN 7777 [6] are grouped in Table 4. The performance characteristics are explained in detail in sections 2.5.1–2.5.10. Measurements, which deliver the data for the calculations of the performance characteristics, should be done together with the daily routine measurements. In practice, daily routine sample of the same matrix type show variability, e.g. with respect to sample heterogeneity and matrix composition. Therefore, a 'worst case approach' should be tested whereby eight, in origin, different samples of the same matrix type are analysed on eight different days. As a general overview this is given in Table 5. The aspects of the study 'validation of five selected elements (As, Cd, Cr, Cu and Fe) in groundwater' are given as examples.

2.5.1 *Limit of detection*

The limit of detection (LOD) is given as the lowest concentration of an element in the sample that can be measured with reasonable statistical certainty [11]. With respect to this presentation LOD is always used as methodical LOD and not as instrumental LOD. To obtain a realistic number for the LOD, the LOD is determined on reproducibility wherefore eight different test portions were analysed in different sequences (see also Table 5).

LOD is defined as follows

$$\mathrm{LOD} = 3 * s_{\mathrm{R}}$$

Table 4. Performance characteristics according to NEN 7777 [7].

Description	Performance characteristic
General performance characteristic	Measuring range (Expanded) uncertainty of measurement
Performance characteristics related to precision	Limit of detection Repeatability Reproducibility
Performance characteristics related to trueness	Trueness/freedom from bias Recovery Lack of fit (non-linearity) Robustness (for an individual influence variable) Selectivity (of an individual analye)
Non-quantitative defined performance characteristics	Robustness (as total) Selectivity (as total)

Table 5. Overview about the applied set-up for determining five performance characteristics (repeatability, reproducibility, limit of detection, trueness and lack of fit).

Sample (type)	Performance characteristic	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7	Day 8
Groundwater sample-1	Repeatability/reproducibility	xx	–	–	–	x	–	–	–
Groundwater sample-2	Repeatability/reproducibility	x	–	–	–	xx	–	–	–
Groundwater sample-3	Repeatability/reproducibility	–	xx	–	–	–	x	–	–
Groundwater sample-4	Repeatability/reproducibility	–	x	–	–	–	xx	–	–
Groundwater sample-5	Repeatability/reproducibility	–	–	xx	–	–	–	x	–
Groundwater sample-6	Repeatability/reproducibility	–	–	x	–	–	–	xx	–
Groundwater sample-7	Repeatability/reproducibility	–	–	–	xx	–	–	–	x
Groundwater sample-8	Repeatability/reproducibility	–	–	–	x	–	–	–	xx
LOD samples LOD-1, LOD-2	Repeatability/reproducibility	x	x	x	x	x	x	x	x
Reference materials e.g. SRM1640, CRM610	Trueness	x	x	x	x	x	x	x	x
Standards e.g. TrEl, MaEl	Lack of fit	x	x	x	x	x	x	x	x

Note: x = one replicate analysis: xx = duplicate analyses with repeatability circumstances.

with

$$s_R = \text{standard deviation of reproducibility}$$

For the determination of the LOD two samples (LOD-1, LOD-2) with concentrations in the range of the LOD of the analytes are analysed in each sequence.

2.5.2 *Recovery*

A sample in the matrix of interest is spiked with a known amount of the analyte. The fraction of the analyte, which is recovered by the analysis, is the recovery (*R*).

R is defined as follows

$$R = \frac{(\mathrm{aA} - \mathrm{a0})}{\Delta c}$$

with

aA = concentration of element in the sample after addition of standard spike solution.

In this case, 4.95 mL diluted sample +0.05 mL standard spike solution.

a0 = concentration of element in the sample after addition dilution solvent.

In this case, 4.95 mL diluted sample +0.05 mL 0.7% HNO_3.

Δc = theoretically added concentration of element A in aA.

In this case, standard spike solutions with Cd, Cr, As: 50 $\mu g\,L^{-1}$; Cu: 250 $\mu g\,L^{-1}$; Fe: 5000 $\mu g\,L^{-1}$.

In each sequence, spiking four different groundwater samples carries out four recovery-experiments.

2.5.3 *Variation coefficient of repeatability*

The variation coefficient of repeatability (vc_r) gives an indication of agreement between independent results of successively carried out identical measurements of the same analyte. The same operator using the same equipment within short intervals of time carries out the measurements in the same laboratory meaning in the same sequence of measurements [11].

vc_r is defined as follows

$$vc_r = \sqrt{\left(\frac{\sum_{i=n}^{n} ((x_{i1} - x_{i2})/(0.5(x_{i1} + x_{i2})))^2}{2n}\right)}$$

with

$x_{i1,2}$ = concentration of element from samples used for validation; duplicate measurement in same sequence

n = number of (all) measurements (in this case $n = 8$).

For the selection of samples and the timing of the measurements, see also Table 5.

Nevertheless, the determined result of vc_r will be more influenced by samples with low concentrations than by those with higher concentrations. Because of the fluctuations of measured signal (interpreted as *vc*), lower concentrations are greater. This effect is examined in detail for the reproducibility (see Refs. 4.1 and 4.2 of Table 7).

2.5.4 *Variation coefficient of reproducibility*

The variation coefficient of reproducibility (vc_{w}) gives an indication of agreement between results of measurements of the same analyte carried out under different circumstances, e.g. on different days, by different operators or in different laboratories [11]. For the calculation, the same formula is used as for the variation coefficient of repeatability (vc_{r}) (see Section 2.5.3; Ref. 3 of Table 7) while vc_{r} is replaced by vc_{w}.

2.5.4.1 *Variation coefficient of reproducibility (vc_w) at higher concentration level ($x \geq 50 * LOD$).* One laboratory-internal control sample, which is and should also in future measurements frequently be analysed routinely, is chosen with a higher concentration level of $x \geq 50 * \mathrm{LOD}$. This sample is analysed in each sequence. The results are used for the calculation of the variation coefficient of reproducibility ($vc_{\mathrm{w},x \geq 50*\mathrm{LOD}}$) according to Ref. 4 of Table 7.

2.5.4.2 *Variation coefficient of reproducibility (vc_w) at lower concentration level ($x < 50 * LOD$).* For the lower concentration level of $x < 50 * \mathrm{LOD}$ different groundwater samples ($n = 8$) are chosen. Especially, at the lower levels the vc_{w} is greater influenced than at higher levels of $x \geq 50 * \mathrm{LOD}$. For concentrations between $x = \mathrm{LOD}$ and $x = 50 * \mathrm{LOD}$ the $vc_{\mathrm{w},x<50*\mathrm{LOD}}$ is defined as follows:

$$vc_{\mathrm{w},x<50*\mathrm{LOD}} = \sqrt{\left((\mathrm{LOD}^2/3^2 * x^2) + vc^2_{\mathrm{w},x \geq 50*\mathrm{LOD}}\right)}$$

with

LOD = limit of detection of element
3 = with respect to the definition of $\mathrm{LOD} = 3 * s_{\mathrm{R}}$
x = concentration of element from samples used for validation

$vc_{\mathrm{w},x<50*\mathrm{LOD}}$ is strongly influenced by the first term, i.e. the LOD and the concentration of element in the chosen sample. The lower the x, the higher the value of $vc_{\mathrm{w},x<50*\mathrm{LOD}}$ will be. For a concentration exactly at the LOD the $vc_{\mathrm{w},x=\mathrm{LOD}}$ is given as 0.33. For higher levels the first term becomes smaller and therefore the whole term is given as the second term which is constant as $vc_{\mathrm{w},x \geq 50*\mathrm{LOD}}$ (see also Ref. 4.1 of Table 7).

2.5.5 *Measuring range*

The measuring range is determined by the limit of detection on the lower side and an upper limit; while the upper limit is given by the highest concentration of element in the used standard solution of calibration (in this case a standard solution of 'trace elements' (TrEl), respectively a standard solution of 'macro element' (MaEl)).

2.5.6 *Trueness/freedom from bias/accuracy*

The trueness (or freedom from bias or accuracy) (δ_{c}) is an indicator for the capacity of a method of measurement without systematic variation. It is indicating the closeness of agreement between the average value obtained from a large set of test results and an accepted reference value [11].

δ_c is defined as follows:

$$\delta_c = x_{avg} - c_{ref}$$

with

x_{avg} = average of measured concentration of element
c_{ref} = concentration of element in the certified reference material

In this case, the trueness is determined by analysing two standard reference materials:

SRM1640 (trace elements in natural water) and CRM610 (trace elements in groundwater).

SRM1640 is certified for all five elements, while in CRM610 the three elements As, Cd and Cu are certified.

2.5.7 *Lack of fit*

The lack of fit ($\delta_{c,fit}$) is defined as variation between the assumed relation between analyte and measurement signal.

$\delta_{c,\ fit}$ is defined as follows:

$$\delta_{c,fit} = x_{avg} - c$$

with

x_{avg} = average of measured concentration of element
c = concentration of element in the (certified) reference material

Analysing standard solution(s) of calibration as samples in each sequence tests the lack of fit. This could be carried out directly after the calibration. The results are used for the calculation wherefore it is claimed $\delta_{c,fit}$ must be lower than $2 * vc_{w,claim,x \geq 50*LOD}$.

2.5.8 *Expanded uncertainty of measurement*

The expanded uncertainty of measurement (U) is a parameter associating with the result of a measurement, which characterises the dispersion of the values that could reasonably be attributed to the analyte [11]. U is a characterisation of the results with respect to all known parameters, which may influence the obtained results. Therefore, it is stated that U is the product of a coverage factor (also named expansion factor) and the combined uncertainty (U_c). Different contributions influence the uncertainty. It must be distinguished between proportional and not proportional contributions. Proportional contributions are combined via the variation coefficients (*vc*'s). While contributions, which are independent from the value of the analyte, are combined via standard uncertainties.

U_c and U are defined as follows:

$$u_c^2 = \sum_i s_i^2 + \sum_i \delta_i^2$$

$$U = kU_c$$

In the case of the analysis of selected elements in groundwater, contributions of $vc_{\mathrm{w,claim}}$ and the recovery experiments are considered. Therefore U is defined as follows:

$$U = 2 * \sqrt{\left(vc^2_{\mathrm{w,claim}} + (R-1)^2 + \left(vc_{\mathrm{w,recovery}}\right)^2\right)}$$

with

s = standard deviation
δ = trueness (or freedom from bias or accuracy), lack of fit
k = coverage factor (also named expansion factor); in this case $k = 2$; which is related with a confidence interval of 0.95 (95%).
$vc_{\mathrm{w,claim}}$ = claimed vc_{w}; in this case as $vc_{\mathrm{w,claim},x \geq 50^*\mathrm{LOD}}$, at higher concentration level of $x \geq 50 * \mathrm{LOD}$ claimed for all elements with 5%, i.e. $vc_{\mathrm{w,claim,x \geq 50^*LOD}} = 0.05$; This is on the safer side and sufficient high with respect to the determined vc_{w}'s (see Ref. 1 of Table 7)
$R-1$ = mean of systematic error; with R = recovery ($n = 32$)
$vc_{\mathrm{w,recovery}}$ = vc_{w} of recovery experiments ($n = 32$)

2.5.9 *Robustness*

Robustness describes the changes of the measurement results caused by variation in performance, circumstances and quality of materials. Robustness is implicated in the reproduction and it is laid down on deliberate variations in method parameters [11] as well as on optimal laboratory conditions (e.g. 'clean room' conditions, stabile temperature). Depending on used reference robustness is also called ruggedness [16].

2.5.10 *Selectivity*

Selectivity is used as extent to which other substances interfere with the determination of a substance according to a given procedure [11].

In the case of the determination of selected elements by HR-ICPMS, the selectivity is given by set-up and using the measuring method. Wherefore, e.g. different resolution modes (LR, MR and HR) are used to control for interferences and to ensure the separation of interferences.

3. Results and discussion

3.1 *Selection of performance characteristics of measurement procedures in environmental matrices*

Depending on the purpose of the use of a method, different validation criteria – the performance characteristics – are chosen and grouped (see also Table 4). Nevertheless, for validations of a new method first additional instructions should be followed to select validation material, see Table 6.

As an example the validation of five selected elements (As, Cd, Cr, Cu and Fe) in groundwater is chosen. The measurements are carried out according to the same procedure whereof the main information is given in the next paragraph. Therefore, eight groundwater samples of different origins and with different compositions are chosen and are analysed on 8 days. They have the following concentration ranges: As: 0.2–7.8 μg L^{-1};

Table 6. Additional instructions for the selection of validation material.

Performance characteristic	Additional instruction. Use in order of preference
Reproducibility, Repeatability	1. Laboratory samples (daily routine) 2. Homogenised laboratory samples 3. Spiked and homogenised laboratory samples (daily routine)
Limit of detection	1. Laboratory samples (daily routine) in the range of LOD 2. Homogenised laboratory samples in the range of LOD 3. Homogenised laboratory samples (daily routine) spiked to range of LOD 4. Blank laboratory samples
Trueness	1. Representative certified reference material 2. Representative sample of an interlaboratory study 3. Recovery experiments as indicator for trueness, spiking must be representative to a laboratory sample(s)
Lack of fit (non-linearity)	Standards with the same matrix as calibration standards
Selectivity, robustness	Preparation of two identical samples from one laboratory sample, comparison of both analytical results, no significant influence on the analytical results should be demonstrable

Cd: 0.05–0.6 μg L^{-1}; Cr: 0.2–1 μg L^{-1}; Cu: 1.1–7.5 μg L^{-1}; Fe: 0.08–2.6 mg L^{-1}. Table 5 gives an overview about the recommendation of the combination of five performance characteristics (repeatability, reproducibility, limit of detection, trueness and lack of fit) on the one hand and a determination scheme on the other hand.

Standard methods have been developed and validated collaboratively by a group of experts. This development should include consideration of all of the necessary aspects of validation and related uncertainty. However, the responsibility remains firmly with the user to ensure that the validation documented in the method is sufficiently complete to fully meet their needs. Even if the validation is complete, the user will still need to verify that the documented performance characteristics can be met in their own laboratory [16]. Therefore, if an already existing standard should be applied and validated it may be sufficient to control only several aspects. Trueness and reproducibility must always be determined. If necessary, in addition, the limit of detection and the repeatability should be determined. For this kind of validation the analysis of reference material(s) is recommended and should lead to comparable results compared to the claims.

3.2 *Obtained performance characteristics for the determination of selected elements in groundwater by HR-ICPMS and interpretation*

Within quality assurance determining performance characteristics must validate each method, which should be routinely used. For an international or national standard performance characteristics must be controlled for the claims. It must be demonstrable that the routine use is not worse than the standard. All obtained results of validation must be in the range for calling the performance ‘in agreement with the standard’. For laboratory internal methods other aspects are important, i.e. the performance characteristics must be determined and consequently known as well as documented.

Table 7. Overview about results obtained by the validation of As, Cd, Cr, Cu and Fe in groundwater by HR-ICPMS.

Ref.	Element	Cd	Cr	Fe	Cu	As
	Measured isotope (resolution)	^{111}Cd (LR)	^{52}Cr (MR)	^{56}Fe (MR)	^{63}Cu (MR)	^{75}As (HR)
1	Limit of detection (LOD)					
	Aim* (μg L^{-1})	0.02	1	34	1.2	0.15
	Validation result (μg L^{-1})	0.05	0.07	1.9	0.17	0.08
	Reported limit (μg L^{-1})	0.05	0.1	10[a]	0.25	0.1
2	Recovery (R)					
	Average ($n=32$)	1.020	1.061	0.995	0.993	1.003
	Variation coefficient of recovery experiments ($vc_{\mathrm{w,recovery}}$)	0.053	0.049	0.050	0.023	0.049
3	Variation coefficient of repeatability (vc_{r})					
	vc$_{\mathrm{r}}$ of groundwater samples ($n=8$)	0.105	0.047	0.031	0.051	0.148
4	Variation coefficient of reproducibility (vc_{w})					
4.1	$vc_{\mathrm{w},x\geq 50*\mathrm{LOD}}$ of one control sample	0.026	0.014	0.020	0.029	0.020
4.2	$vc_{\mathrm{w},x\leq 50*\mathrm{LOD}}$ of different groundwater samples ($n=8$)	0.085	0.053	0.074	0.073	0.104
5	Measuring range					
	Minimal LOD (μg L^{-1})	0.05	0.1	10	0.25	0.1
	Maximal upper limit (μg L^{-1})	10	10	2000	50	10

6	Trueness/freedom of bias (δ_c)					
	● SRM1640					
	x_{avg} certified ($\mu g\,L^{-1}$)	22.79	38.6	34.3	85.2	26.67
	x_{avg}measured ($\mu g\,L^{-1}$)	23.48	40.07	30.32	88.85	27.33
	s ($\mu g\,L^{-1}$)	1.43	0.98	1.25	2.04	1.45
	vc	0.6	0.02	0.04	0.02	0.05
	δ_c ($\mu g\,L^{-1}$)	0.69	1.47	−3.98	3.65	0.66
	Deviation from certified value	0.03	0.04	−0.12	0.04	0.02
	Evaluation ($\pm 2 * vc_{w,claim,x \geq 50*LOD}$)	OK	OK	OK[b]	OK	OK
	● CRM610					
	x_{avg} certified ($\mu g\,L^{-1}$)	2.94	n.c.	n.c.	45.7	10.8
	x_{avg} measured ($\mu g\,L^{-1}$)	3.23	n.j.	n.j.	47.38	11.26
	s ($\mu g\,L^{-1}$)	0.13	n.j.	n.j.	1.46	0.49
	vc	0.04	n.j.	n.j.	0.03	0.04
	δ_c ($\mu g\,L^{-1}$)	0.29	n.j.	n.j.	1.68	0.46
	Deviation from certified value	0.10	n.j.	n.j.	0.04	0.04
	Evaluation ($\pm 2* vc_{w,claim,x \geq 50*LOD}$)	OK	n.j.	n.j.	OK	OK
8	Expanded uncertainty of measurement (U)					
	U with coverage factor 2, for ($x \geq 50 * LOD$)	0.15	0.19	0.14	0.11	0.14

Note: n.c. = not certified; n.j. = not judged.

[a] Based on results obtained with a former Q-ICPMS method. New LODs should be a factor of 2–10 better.

[b] With reference to practical relevance of groundwater samples.

Especially for own methods several performance characteristics are fixed, e.g. which limit of detection must be achieved. These performance characteristics are mainly given by national and international regulations for the matrix under investigation or by the necessity to achieve better or other performance characteristics in comparison to former used techniques.

The example of the determination of selected elements in groundwater by HR-ICPMS represents an own method. The obtained results for the performance characteristics are summarised in Table 7. All results are presented as averages and where necessary the correction for the dilution factor is already included. Judgments about obtained results and agreements with claims are also given in Table 7. For four of the five elements the validated LODs are significantly better than the aimed values. Only in the case of Cd the LOD is worse but still in an acceptable range. Regarding the performance characteristic of trueness all certified elements determined were in good agreement with the certified concentrations. With respect to the claims for the selected elements in groundwater by HR-ICPMS the validation was successfully performed. After the validation and approving the performance characteristics groundwater is successfully analysed by HR-ICPMS. This validated method lays the foundation of the analysis of a significant number of groundwater samples yearly. The results are routinely been assimilated in monitoring programs [1].

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