

Example in the Eurachem guide "Estimation of measurement uncertainty arising from sampling"

Dissolved iron in groundwater

Measurand				Uncertainty estimation		
Analyte & technique	Unit ¹	Sector & matrix	Sampling target	Purpose	Design	Statistics
Dissolved iron, ICP-AES ¹	mg/L	Environment, groundwater	The groundwater near one selected monitoring well in a groundwater body	Total uncertainty	Empirical duplicates used in validation and quality control	Range

1 Scope

The scope is determination of the total uncertainty of the measurement of dissolved iron in a sampling validation study and subsequent control of sampling uncertainty during monitoring.

2 Scenario

A groundwater body which is an important drinking water resource for the city of Århus, the second largest city of Denmark, has through surveillance monitoring been identified as at risk for deterioration of the quality due to intensive drinking water abstraction. An operational monitoring program shall now be established in order to control the trend in water quality development.

The groundwater body is in glacial outwash sand with Miocene sands and clays below and glacial till above. The geology at the site is complicated with several local aquifers (underground layer of water-bearing permeable rock, or permeable mixtures of unconsolidated materials) and aquitards (geological formation of layers comprised either of clay or on non-porous rock that restrict water flow from one aquifer to another). The groundwater body as identified is 2 km x 2 km x 10 m, starting 20-30 m below the surface. The natural quality of the groundwater is anaerobic without nitrate, with sulphate and reduced iron, but without hydrogen sulphide and methane. One of the threats to the groundwater body is oxygen intrusion into the aquifer as the result of the water abstraction and concomitant groundwater table draw down.

In the groundwater body, 9 wells had been sampled for chemical analysis during surveillance monitoring, and 6 wells are now available for sampling. In the operational monitoring plan, it was decided to aim at monitoring one well twice per year. The objective of the operational monitoring was set to having a 95% probability of recognising a 20% quality deterioration. It was decided to use dissolved iron as a target parameter that would be a sensitive indicator of aquifer oxidation (decreasing iron concentration with increasing oxidation) and with redox potential as supporting evidence. Oxygen, pH, electrical conductivity and redox potential were used as on-line indicators of sampling stability and sodium, calcium and chloride as general groundwater quality parameters. Only the two key parameters, dissolved iron and redox potential are discussed here.

¹ ICP-AES: inductively coupled plasma ionization with atomic emission spectroscopy detection and quantification

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Meeting the monitoring objective requires a measurement uncertainty including both sampling and analysis of not more than 10% (comparison of two means each for two samples, 95% confidence interval, two sided test) corresponding to an expanded measurement uncertainty of 20%. To ensure the compliance of the monitoring program with the stated objective, a sampling validation study was initially conducted including all wells available and based upon the results from this, a routine sampling quality control program was set up for implementation with the monitoring program for the selected monitoring well.

The properties of the groundwater body was summarised based upon previous monitoring activities (surveillance monitoring). In Table 1 is shown a summary for the two key parameters including variability in time and space as well as measurement (sampling and analytical) uncertainty.

Table 1 Key chemical parameters for 9 wells to the groundwater body, surveillance monitoring

	Redox potential mV	Dissolved iron mg/L
Mean	-123	1.11
Relative standard deviation	27%	56%
Main cause of uncertainty	Oxygen impact during sampling and on-line measurement	Filtering

The chemical data suggest that the groundwater composition is quite uniform over time and space with respect to the main components (data not shown, relative standard deviation 1.9-16%), whereas the variability is high for the redox parameters (oxygen, redox potential and dissolved iron). The expected main causes of uncertainty are indicated in the table for the two key parameters and the causes were controlled during sampling.

3 Sampling protocol

Sampling was done according to the Århus County groundwater monitoring protocol with permanent, dedicated pumps (Grundfos MP1) set in the middle of the screened interval of each well. Pump rates were 1-2 m³/L (well purging) with a 10% reduction just before sampling. Two of the 6 well were large diameter abstraction wells equipped with high yield pumps. These were pumped with 40-60 m³/L for well purging followed by pump rate reduction just before sampling. During well purging, the development in water quality was followed with on-line measurements of oxygen, pH, electrical conductivity and redox potential until stable readings and then, samples were taken. A field report was filled in during the sampling including also pump yields and pumping times, as well as water table measurements.

4 Study design – empirical

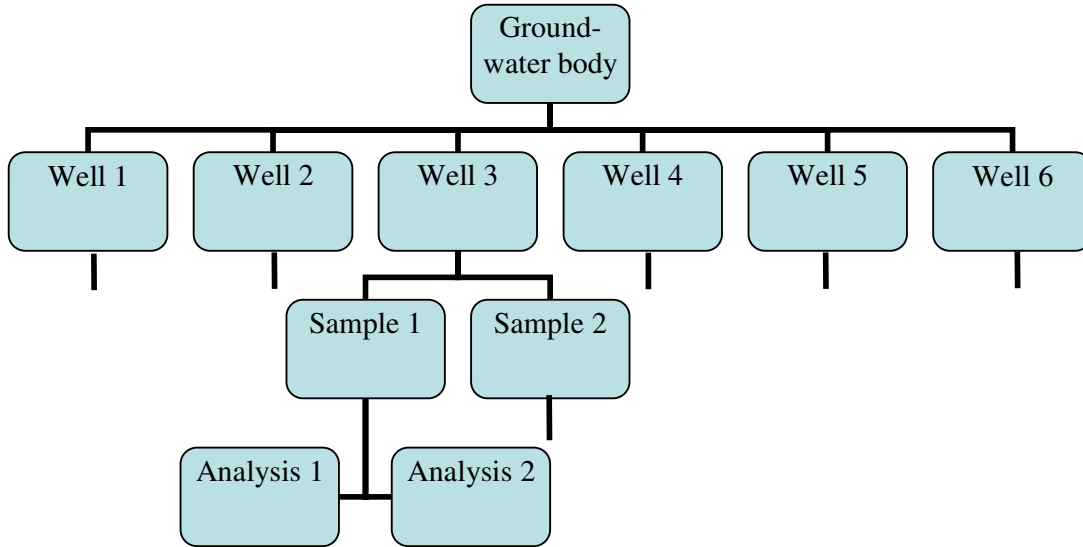
The empirical approach was selected for study design in order to provide estimates of heterogeneity in the groundwater body (between-target variation well to well and over time) and measurement uncertainty, split to show sampling uncertainty and analytical uncertainty.

4.1 Validation

The objective of the validation programme was to ensure that a measurement uncertainty meeting the set quality objective could be obtained and to describe the components of uncertainty in order to identify points of improvement, if required. The validation programme was set up with sampling of 6 wells, two independent samplings per well and 2 sub-samples per sample analysed, see Figure 1.

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Figure 1 Design outline for validation

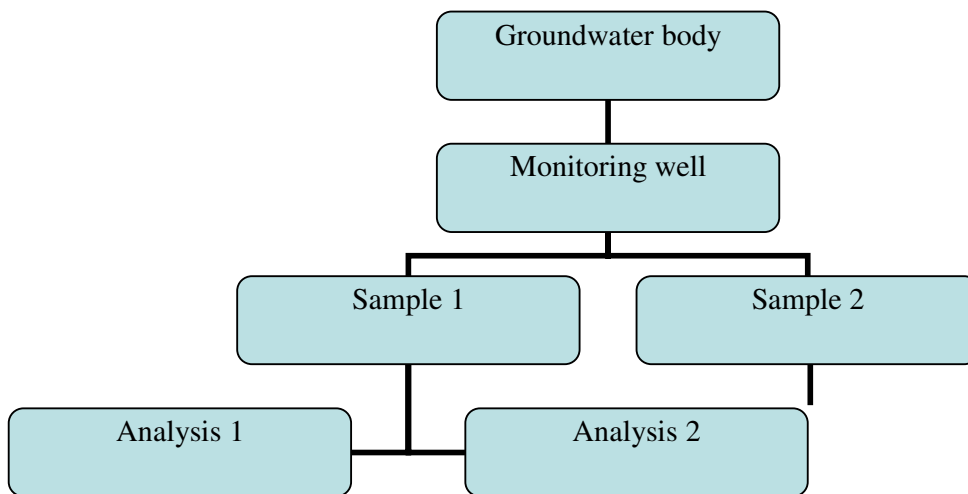


A total of 12 samples were taken and 24 sub-samples were sent for analysis in one sampling round as validation study.

4.2 Quality control

The objective of the quality control programme for the operational monitoring was to ensure that measurement uncertainty did not increase over time during the monitoring. The quality control programme was set up after careful evaluation of the results from the validation study. Quality control was designed to include duplicate sampling and each with duplicate analysis on one of the two annual sampling occasions of the monitoring programme, see Figure 2. Totally 6 sampling occasions with 12 samples and 24 sub-samples analysed were included in the first phase of the quality control programme.

Figure 2 Design outline for quality control, shown for one sampling occasion



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5 Sub-sampling and analysis

The sample pre-treatment and analytical set up for the two key parameters (redox potential and dissolved iron) are shown in Table 2.

Table 2 Pre-treatment and analytical programme

	Redox potential	Dissolved iron
Pre-treatment	On-line analysed	On-line filtered, preserved with nitric acid, laboratory analysed

5.1 Sub-sampling and sample pre-treatment

Duplicate online measurements/sub-samplings for laboratory analysis were done by taking out split sample streams and treating each stream independently. This means that the "analytical uncertainty" obtained with the duplicate design also included sub-sampling, pre-treatment, such as filtering, and transportation. An estimate of the analytical uncertainty alone could be obtained from the laboratory quality control data, see section 5.3.

Samples were on-line filtered excluding oxygen through 0.45 µm cellulose acetate membrane filters and sub-samples were preserved in the field for metal analysis by acidification with nitric acid. Sub-samples were stored in polyethylene containers in the dark at less than 10°C during transport to the analytical laboratory.

5.2 Field analysis

The sample stream was pumped through an on-line measuring array of a flow-through cell with sensors set up in series. The WTW sensor used for redox potential is described in Table 3.

Table 3 On-line sensor used for redox potential measurements

Parameter	Instrument	Cell	Instrument accuracy	Calibration and control
Redox potential	pH 340	Sensolyt Pt	±2mV	Daily service

No quality control was performed of on-line measurements in the field.

5.3 Laboratory analysis

Analyses were performed at an independent, accredited (ISO 17025) laboratory using accredited methods subject to the required quality assurance and analytical quality control. Methods and performance data from quality control are shown in Table 4.

Table 4 Methods and performance data from quality control for laboratory analyses

	Method	Within series re-peteability	Between series re-produceability	Total re-produceability	Total ex-panded un-certainty	Detection limit
Iron	ICP-AES	0.95%	4.2%	4.3%	8.6%	0.01 mg/L

The certified reference material (CRM) VKI Metal LL2, nominal 0.200 mg Fe/L was used for quality control with 101.9% recovery (mean for 92 control results).

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5.4 Calculation methods

The replicate data were treated using the range method (ISO 3085). For comparison, uncertainty estimates were calculated by analysis of variances (ANOVA) and robust ANOVA (rANOVA) using ROBAN version 1.0.1 (University of Newcastle upon Tyne, Imperial College and University of Sussex).

The applied calculations methods are demonstrated in section 6. The range calculations are easily done using standard spread sheets, and an example can be downloaded from <http://team.sp.se/analyiskvalitet/sampling/default.aspx>.

The occurrence of systematic sampling errors was not assessed quantitatively, but the consistency of the obtained results was used as a qualitative control of systematic errors. As an example, if dissolved iron was found above 0.1 mg/L in the same sample as oxygen was determined to be above 0.1 mg/L, this would indicate a systematic sampling and/or pre-treatment error. Similarly, redox potential and oxygen contents were checked to correspond in order to control systematic errors.

6 Results

The data set from the validation study is shown in Table 8 for dissolved iron with the range calculations. The calculations for redox potential in the validation study and for both dissolved iron and redox potential during quality control were done similarly.

The data from the validation study (6 different wells) using range calculations are shown in Table 5.

Table 5 Relative expanded uncertainty (% , coverage factor 2) for analysis, sampling and between-target (between wells) as obtained during validation using range calculations

Range calculations	Analyses	Sampling	Between-target
Redox potential	5.2%	15%	14%
Dissolved iron	2.1%	10%	70%

For comparison, the statistical estimates are shown in Table 6 as obtained using ANOVA and rANOVA.

Table 6 Relative expanded uncertainty (% , coverage factor 2) for analysis, sampling and between-target (between wells) as obtained for dissolved iron during validation using ANOVA and rANOVA calculations

Dissolved iron	Analyses	Sampling	Between-target
ANOVA	1.6%	9.6%	70%
rANOVA	1.8%	9.9%	72%

The statistical estimates obtained with the range statistics during quality control (6 sampling occasions) are shown in Table 7.

Table 7 Relative expanded uncertainty (% , coverage factor 2) for analysis, sampling and between-target (between occasions) as obtained during quality control using range calculations

	Analyses	Sampling	Between-target
Redox potential	18%	3.8%	23%
Dissolved iron	2.5%	3.6%	9.9%

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Table 8 Results and range calculations for the validation study, dissolved iron, basic data in bold, symbols used to describe calculations only (T: target, S: sample, A: analysis, R: absolute differences, r: relative differences, n: numbers)

Well number	S1A1 ²	S1A2	S2A1	S2A2	$R_1 = S1A1 - S1A2 $	$\overline{S1} = \frac{S1A1 + S1A2}{2}$	$r_1 = \frac{R_1 * 100}{\overline{S1}}$	$R_2 = S2A1 - S2A2 $	$\overline{S2} = \frac{S2A1 + S2A2}{2}$	$r_2 = \frac{R_2 * 100}{\overline{S2}}$	$\overline{S} = \frac{\overline{S1} + \overline{S2}}{2}$	$r = \frac{ \overline{S1} - \overline{S2} }{\overline{S}} * 100$
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	%	mg/L	mg/L	%	mg/L	%
99.474	0.815	0.834	0.912	0.893	0.019	0.825	2.30	0.019	0.903	2.11	0.864	9.03
99.468	1.80	1.83	1.94	1.93	0.030	1.82	1.65	0.010	1.94	0.517	1.88	6.40
99.469	1.69	1.68	1.79	1.77	0.010	1.69	0.593	0.020	1.78	1.12	1.73	5.48
99.916	2.62	2.61	2.83	2.84	0.010	2.62	0.382	0.010	2.84	0.353	2.73	8.07
99.327	1.66	1.63	1.58	1.59	0.030	1.65	1.82	0.010	1.59	0.631	1.62	3.72
99.371	1.52	1.53	1.47	1.50	0.010	1.53	0.656	0.030	1.49	2.02	1.51	2.66
							$\sum r_1 = 7.413$			$\sum r_2 = 6.750$	$\sum \overline{S} = 10.32$	$\sum r = 35.36$
Analysis					$r_A = \frac{7.413 + 6.750}{6 + 6} = 1.18$			$CV_A = \frac{r_A}{1.128} = 1.05$			$n_{r1} = 6$	$n_r = 6$
Sampling					$r_{S+A} = \frac{35.36}{6} = 5.89$			$CV_{S+A} = \frac{r_{S+A}}{1.128} = 5.22$			$CV_S = \sqrt{CV_{S+A}^2 - \frac{CV_A^2}{2}} = \sqrt{5.22^2 - \frac{1.05^2}{2}} = 5.17$	
Between-target					$S_{T+S+A} = \frac{10.32}{6} = 1.72$			$s_{T+S+A} = s_S^5 = 0.604$			$CV_{T+S+A} = \frac{s_{T+S+A}}{1.72} * 100 = 35.1$	
											$CV_T = \sqrt{CV_{T+S+A}^2 - \frac{CV_{S+A}^2}{2}} = \sqrt{35.1^2 - \frac{5.17^2}{2}} = 34.9$	

² S1A1: sample 1 analysis 1

³ The standard deviation can be obtained from the mean of relative differences between duplicate measurements by division with the statistical factor 1.128

⁴ The sum of relative variances is $CV_{S+A}^2 = CV_S^2 + \frac{CV_A^2}{2}$ with the factor 1/2 on CV_A^2 due to the mean of duplicate analyses being used

⁵ s: standard deviation with n-1 degrees of freedom as obtained from most standard calculators and spread sheets

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No groundwater samples had measurements of dissolved oxygen and dissolved iron above 0.1 mg/L, and the low redox potential measured (-110 to -200 mV) is consistent with the absence of oxygen (<0.1 mg/L) and the high dissolved iron concentrations (0.92 to 2.8 mg/L).

7 Comments

Overall, the validation data show that the variability in the aquifer (between-target) was dominating the total uncertainty for dissolved iron, whereas sampling and between target uncertainties were of the same size for dissolved iron. Analytical uncertainties were small (2-5%), and for dissolved iron comparable to the repeatability obtained in laboratory quality control (expanded uncertainty 2.1% as compared to 1.9%, respectively). If different wells were sampled, the sampling uncertainty was 10-15%.

For dissolved iron measured during validation, the use of ANOVA and rANOVA calculations did not provide statistical estimates more than slightly different from those obtained with the simple range calculations.

In the quality control scheme of monitoring, the variability between sampling occasions (between-target, 9.9%) was dominating the total uncertainty for parameters analysed as laboratory analysis (dissolved iron, 2.5% uncertainty), whereas the analytical uncertainty (18%) was almost as important as the between target uncertainty (23%) for on-line measurements (redox potential). The reason for the large contribution from on-line measurements is that during quality control, duplicate on-line measurements were done with two different instruments in contrast to the validation study done with one single instrument for both duplicate measurements. Accordingly, the analytical uncertainty (instrument to instrument variation) for redox potential was considerably larger in the quality control (18%) than in the validation study (5.2%). For dissolved iron, the analytical uncertainty was comparable in validation and in the subsequent quality control (2.1% and 2.5%, respectively). The sampling uncertainty was lower when sampling just one well at different occasions during quality control (3.6-3.8%) than when sampling different wells at the same time during validation (10-15%). The uncertainty between-target (variation from one sampling occasion to the next) during quality control was small for dissolved iron (9.9%), but larger for redox potential (23%).

If a continuous control of sampling uncertainty had been required, the control data could have been plotted in control charts in order to obtain an early warning of excessive uncertainty (random errors) for each sampling occasion.

The number of replicates (6) in this study was less than used in most cases and the risk of a decreased confidence in the uncertainty estimates should be considered in evaluation of the results.

The uncertainty contribution from sampling bias was only addressed through evaluation of the consistency of the measurements obtained from different, interrelated chemical parameters (oxygen, dissolved iron, redox) and the evaluation supported that sampling and sample pre-treatment had succeeded to avoid bias from oxygen impact and filter clogging.

8 Summary

The measurement uncertainty (% uncertainty with coverage factor 2) is summarised below for dissolved iron.

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The data show that the requirement for less than 20% expanded measurement uncertainty could be fulfilled for dissolved iron (sampling validation), and that the required measurement uncertainty was in reality achieved during the routine monitoring (sampling quality control). Furthermore, the data show that if an improvement of the certainty of monitoring was required, the obvious point of improvement would be increased monitoring density for dissolved iron (between-target uncertainty dominating), whereas improvement of the on-line measurement uncertainty could help for redox potential (large contribution of analysis uncertainty).

Dissolved iron in groundwater	Expanded uncertainty, coverage factor 2			Between-target variability
	Sampling	Analysis	Measurement	
Validation	10%	2.1%	10%	35% ⁶
Quality control	3.6%	2.5%	4.0%	9.9% ⁷

9 Acknowledgments

The work presented here has been supported by Nordic Innovation Centre, the Soil and Ground Water Contamination Committee of the Danish Council of Technical Sciences and Århus County, Denmark. Field work has skilfully been done by Mogens Wium, GEO.

⁶ In the validation study, between-target variability was between wells

⁷ In the quality control, between-target variability was between sampling occasions