Slovak Geol. Mag.,9, 2 – 3(2003), 157 – 159

The Evaluation of Precision and Trueness of Some Water Analysis Procedures in the Laboratories of Czech Geological Survey

LUDMILA DEMPÍROVÁ

Czech Geological Survey, Klárov 3, 118 21 Prague 1

Abstract. In the present contribution the practise of CGS laboratory in expressing precision and trueness of some water results is dealt with. Precision and trueness represent basic metrological parameters of an analytical method. For this evaluation, sets with QC samples or CRMs are used. Precision is characterized by standard deviation and relative standard deviation. Trueness is expressed by a difference from a true value and by recovery of a CRM.

The assessment steps are shown on the aluminium results acquired by atomic absorption spectrometry with electrotermic atomization, on pH measurement performed by a glass electrode, on conductivity measurements, on analysis of chlorides, nitrates and sulphates, determined by ion chormatography and on analysis of fluorides, determined by ion selective electrode.

Precision of conductivity measurements of rainfall samples is evaluated also by standard deviation and relative standard deviation calculated from duplicate samples rather than from QC samples.

The values of inner laboratory precision are compared with the precision values published in standard methods, relating to water quality in the Czech republic.

Key words: Analytical method, assessment of precision and trueness, criteria of an analytical method fit for purpose, suitability of a method for application.

Quality systems that are introduced in chemical laboratories, demand permanent check of analytical results. Practising checks on the calibration solutions and monitoring an error-free operation of an analytical instrumentation are desirable for an appropriate method control. Good proficiency information can be obtained from quality control (QC) samples as well as from different sorts of reference materials (RMs). Repeated measurements of samples (duplicates) belong to valuable assuarance outcomes, too.

Attention of a laboratory, paid to its controlling function, should lead to the declaration that the methods used by laboratory are of satisfactory accuracy. Quality assuarance (QA) measurements offer many repeatedly analysed QC samples that can be effectively evaluated and permit to make conclusions about trueness and precision of a method in use.

Trueness of a result can only be evaluated from a set of data with well defined mean value. Certified reference materials (CRMs) perfectly fulfill this requirement. Their assigned values are confirmed by a certificate issued by the certifying body. Reference values of QC samples can be derived from the mass and the volume, in which QC sample is dissolved.

An acceptable approach for assessing trueness is the expressing a difference of the analytical result and the certified value of a CRM. Further information about trueness of the results provides the value of recovery that is achieved by a tested analytical method on a CRM or a QC sample as well.

Table 1: Information data about QC samples used for precision trueness evaluation of some water analysis procedures

Element/ quality	Type of a sample	Laboratory mean value	Assigned value
Al	CRM BCR609 natural water	50.3 µg/L	47.7 µg/L
pH	CRM-buffer from Merck	6.86 pH	6.86 pH
Conductivity	CRM-conduct. std.from Alfa Aesar	725 µS/cm	718 µS/cm
Cl^-	Laboratory QC synthethic	2.66 mg/L	2.70 mg/L
NO^{3-}	Laboratory QC synthethic	6.55 mg/L	6.50 mg/L
SO_4^{2-}	Laboratory QC synthethic	16.49 mg/L	16.30 mg/L
F^-	Laboratory QC synthethic	0.67 mg/L	0.70 mg/L

The following equations (Standard Methods, 1998) are used for calculation a difference (% D)

$$\% D = \frac{found\ value - true\ value}{true\ value} * 100\% \quad (1)$$

and recovery (% Recovery) from values given by table 1

$$\% \text{ Recovery} = \frac{found\ value}{true\ value} * 100\% \quad (2)$$

The results of calculation are given in table 2.

Slovak Geol. Mag.,9, 2 – 3(2003), 157 – 159

Table 2: Error assessment in the control samples

Element/quality/ Analytical method	D %	Recovery %
Al/ET AAS	+ 5.5	105.5
pH/Glass electrode	± 0.0	100.0
Conductivity/CDM	+ 1.0	101.0
Cl^-/IC	- 1.5	98.5
NO_3^-/IC	+ 0.8	100.8
SO_4^{2-}/IC	+ 1.2	101.2
F/ISE	- 4.3	95.7

Legend: ET AAS – atomic absorption spectrometry with electrotermic atomization; CDM – conductivity meter; IC – ion chromatography; ISE – ion selective electrode.

Difference D (%) was calculated according to the formula (1), recovery according to (2).

The highest difference achieves +5.5% (determination of aluminium in water, see table 2), which at the same time corresponds to the recovery of 105.5% in the CRM BCR 609. If we regard ±5.0% difference as acceptable for good laboratory method performance then from this point of view the determination of Al by atomic absorption spectrometry with electrotermic atomization reaches the worse score.

The number of control data, the mean laboratory values in table 1 are calculated from, is between 20-40 elements. For quantifying precision of individual data sets, that contain repeated measurements of a specific QC sample, both standard deviation (3) or relative standard deviation (4) can be applied.

$$s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} \qquad (3)$$

$$\% RSD = \frac{s}{\bar{x}} * 100\ \% \qquad (4)$$

Standard deviation s is calculated according to the equation (3), relative standard deviation RSD according to (4).

The conclusions about laboratory methods precision that were used for the determination of Al, pH, conductivity, anions (Cl^-, NO_3^-, SO_4^{2-}) and fluorides (F^-) were drawn from the comparison with the data precision information of standard methods, that are valid in the Czech republic in the field of water analysis now (see table 4). Water examination methods of a laboratory can be regarded as standard methods suitably modified at laboratory conditions.

The laboratories of Czech geological survey achieve an european standard in water analysis in the determination of pH (method glass electrode) and in the determination of SO_4^{2-} (method ion chromatography) – see tables 3 and 4. For the rest of the examined methods, their precision parametres are slightly worse, but nevertheless, these precision parameters still meet the laboratory's requirement on the declared quality.

Table 3: Precision assessment in the sets of control samples

Element/quality	Analytical method	Std. deviation	Relative std. deviation
Al (50.3 µg/L)	ET AAS	*	12.0 %
pH (6.86)	Glass electrode	0.02 pH	*
Conductivity (725 µS/cm)	CDM	9.4 µS/cm	*
Cl^- (2.66 mg/L)	IC	*	2.6 %
NO_3^- (6.55 mg/L)	IC	*	2.4 %
SO_4^{2-} (16.49 mg/L)	IC	*	1.4 %
F (0.67 mg/L)	ISE	*	3.6 %

Legend: ET AAS-atomic absorption spectrometry with electrotermic atomization; CDM-conductivity meter; IC – ion chromatography; ISE – ion selective electrode. Methods are used for water examination in Czech geological survey.

Additional possibility how to get information about method precision from routine analytical work, is from the analysis of duplicates rather then from repeatedly reanalysed QC samples. Analysis of duplicates suit best for matrix samples. From the results of duplicate analysis standard deviation (5) and relative standard deviation (6) are computed as (Uncertainty and traceability, 2001)

$$s = \sqrt{\frac{\sum_{i=1}^{n} (x_{i1} - x_{i2})^2}{2n}} \qquad (5)$$

$$RSD\ (\%) = \sqrt{\frac{\sum_{i=1}^{n} (x_{i1} - x_{i2} / \bar{x}_i)^2}{2n}} * 100\% \qquad (6)$$

n is number of pairs, x_{i1}, x_{i2} the first and the second sample determination, $\bar{x}_i$ arithmetic mean of duplicates.

As a rule, the analysis of matrix samples gives results with worse precision. A good example of this effect is the conductivity measurement in rainfall water. The ionic strength of these samples is very small, which corresponds to the conductivity lower than 50 mS/cm. During the conductivity measurement, interfering effects, non removable by an operator, counteract. In table 5 the measurement results of these extremely low concentrated samples of 15 pairs of rainfall waters are presented.

Mean samples conductivity 29.4 mS/cm is an arithmetic mean of data in column 4. Standard deviation 1.4 mS/cm was computed after formula (5), relative standard deviation 7.1 % using formula (6).

For comparison: Conductivity remeasurements of QC sample (synthetically prepared from potassium chloride by company Alfa Aesar, molarity of KCl 0.005 $mol.dm^{3-}$) established mean value 725 mS/cm, s = 9.4 mS/cm, RSD = 1.3%. Sample matrix is a real cause of the larger variation of conductivity data in the rainfall samples therefore.

Table 4: Precision details of standard methods corresponding to the methods used in Czech geological survey for water analysis

Standard method	Element/standard analytical method	Sample	s/RSD (%)
ČSN EN ISO 5961	Cd – 0.91 µL / ET AAS	Waste water	RSD: 4.2-8.5 %
ČSN ISO 10 523	pH/range 3-10 pH / glass electrode	Drinking water	s: 0.01-0.05 pH
ČSN EN 27 888	Conductivity – 420 µS/cm / CDM	Natural water	s: 2.23 µS/cm
ČSN EN ISO 10304-1	Cl^- – 11.04 mg/L /IC NO_3^- – 5.37 mg/L /IC SO_4^{2-} – 20.02 mg/L /IC	Surface water Drinking water Synthetic water	RSD: 2.0 % RSD: 2.1 % RSD: 2.0 %
ČSN ISO 10 359-1	F^- – 0.531 mg/L / ISE	Synthetic water	RSD: 2.2 %

Table 5: The conductivity measurement (duplicates) in rainfall water. Unit: µS/cm.

n	x_{i1}	x_{i2}	Arithmetic mean	$\lvert x_{i1}-x_{i2}\rvert$
1	69.4	73.2	71.3	3.8
2	23.8	22.6	23.2	1.2
3	50.5	49.2	49.85	1.3
4	30.7	30.3	30.5	0.4
5	27.5	27.2	27.35	0.3
6	40.8	42.4	41.6	1.6
7	21.3	20.6	20.95	0.7
8	31.1	31.2	31.15	0.1
9	27.1	27.9	27.5	0.8
10	32.1	30.3	31.2	1.8
11	21.3	15.9	18.6	5.4
12	14.3	15.0	14.65	0.7
13	6.0	7.5	6.75	1.5
14	31.0	31.6	31.3	0.6
15	15.0	14.6	14.8	0.4

Summary

Permanent monitoring of precision and trueness practised on QC samples or certified reference materials, makes laboratory possible to obtain high degree of confidence and reliability in routine measurements. As a consequence of this finding, when carriyng out routine measurements, only single determination satisfies.

The size of precision and a difference from a true value of a CRM or a QC sample are parameters that decide about measurement accuracy. Both are inherent to measurement procedure in a full working range. For practical reasons it is desirable to determine them in separate experiments. Knowledge of both contributions to method accuracy is important and necessary in view of a laboratory and its clients, too.

The assessment steps applied in the procedures of this contribution, reflect final treatment of the results from reanalysed QC samples and CRMs. The steps chosen should be regarded as possible ones for correct method validation.

References

Standard Methods for the Examination of Water and Waste Water. Ed. by L.S.Clesceri, A.E.Greenberg, A.Eaton. 20th Edition, Apha, USA, 1998.

Uncertainty and Traceability of the Results from Spectroscopic Methods. Primary course texts. Spectroscopic Society of J. M. Marci, Prague 2001. P.85.