A worked example on MU evaluation by precision, accuracy and trueness

Method:

Determination of chloride ions in drinking water by ion chromatography (APHA Standard Method 4110)

Background:

The Water Service Laboratory BN has been conducting the anionic analyses (consisting of chloride, fluoride, sulfate and nitrate) in water by ion chromatographic technique for the past three years with a quality control check sample (CS) containing mixed anions in water analyzed in each batch of analysis consistently under intermediate precision conditions. The control data of these anions obtained have been monitored by plotting the results against time respectively on quality control charts. This worked example shows the evaluation of measurement uncertainty on one of the anions, i.e. chloride in water. The measurement uncertainties of other anions can be similarly estimated.

Certified reference material:

Using a branded CRM standard for IC with concentration 1000$\pm$2.2 *mg/L* chloride in water

Current working CRM as check sample (CS) after a series of successive dilutions: 5.00+0.18 *mg/L* chloride in water. This working CS has been found to be stable upon storage at room temperature ranging from 23°C to 26°C. In here, the standard uncertainty u_{Cref} = 0.18/2 = 0.09

Anderson-Darling (AD) statistic tests were carried out on both the sample standard deviation (s) and the moving range (MR) on the most recent 25 sets of CS data. The absolute moving range (MR) is given by:

$$|MR_i| = |x_{i+1} - x_i|$$

Note (1)

The AD test is to evaluate the normality (randomly distributed) and independence of these CS data, aiming to achieve the criteria for data normality and independency with both adjusted AD's, $A^{2*}(s)$ and $A^{2*}(MR)$ to be less than 1.00.

Note (2)

This AD statistic test can be carried out through its first principle using the AD equations mentioned below. It can also be easily done by using any statistical software. The confirmation of data normality can also be made by the Shapiro-Wilk test.

The AD equations used are:

$$A^2 = -\frac{\sum_{i=1}^{n}(2i-1)\left[\ln(p_i) + \ln(1-p_{n+1-i})\right]}{n} - n$$

or, after simplification to give:

$$A^2 = -\frac{AD}{n} - n$$

where, $$AD = \sum_{i=1}^{n}(2i-1)\left[\ln(p_i) + \ln(1-p_{n+1-i})\right]$$

and,

$$A^{2*} = A(1 + \frac{0.75}{n} + \frac{2.25}{n^2})$$

Where,

A^2 is AD normal distribution estimated statistic (against standard deviation *s*, and moving range *MR*)

A^{2*} is AD adjusted statistic value (against sample standard deviation *s*, and moving range)

p_i is the probability of data *i* to obey the normal probability distribution function

n is the total data in question（$n > 15$)

Raw data x_i obtained and their respective **moving range (MR)** calculated are summarized in Table 1 below:

No.	Original Data value	Moving Range	No.	Original Data value	Moving Range
i	I_i	$\|MR_i\|$	i	I_i	$\|MR_i\|$
1	5.122	/	14	5.131	0.234
2	4.989	0.133	15	5.03	0.101
3	5.054	0.065	16	4.971	0.059
4	4.941	0.113	17	4.975	0.004
5	5.102	0.161	18	5.032	0.057
6	5.144	0.042	19	5.006	0.026
7	5.036	0.108	20	5.323	0.317
8	4.995	0.041	21	4.848	0.475
9	5.105	0.11	22	4.967	0.119
10	5.093	0.012	23	5.005	0.038
11	5.156	0.063	24	5.158	0.153
12	4.856	0.3	25	5.122	0.036
13	4.897	0.041			

Upon Excel® calculation, the following statistical values were found:

$\bar{x}_i =$ 5.042 : s = 0.107,

$|\overline{MR}| = 0.117$: $s_{R'} = s_{MR} = 0.104$, where $s_{MR} = \frac{\overline{MR}}{1.128}$ *(See ISO 7870-2 Table 2)*

$A^2_s = 0.291$; $A^{2*}_s = 0.301$: $A^2_{MR} = 0.290$; $A^{2*}_{MR} = 0.299$

As both adjusted AD testing showed values <1.00, it was concluded that the 25 QC data collated were randomly distributed and independent to each other.

In fact, the XLSTAT statistical software also showed similar outcomes, as summarized below:

XLSTAT 2017.03.45028 - Normality tests - Start time: 2017/6/11 at 21:21:47 / End time: 2017/6/11 at 21:21:47 / Microsoft Excel 15.04693

Data: Workbook = A-D Calculation template - 25 data Chloride ion.xlsx / Sheet = Sheet1 / Range = Sheet1!$B$10:$B$35 / 25 rows and 1 column

Significance level (%): 5

Run again:

Summary statistics (Data):

Variable	*Observations*	*Obs. with missing data*	*Obs. without missing data*	*Minimum*	*Maximum*	*Mean*	*Std Dev*
I_i	25	0	25	4.848	5.323	5.042	0.107

Shapiro-Wilk test (I_i):

W	*0.966*
p-value (Two-tailed)	*0.537*
alpha	*0.05*

Test interpretation:

H0: The variable from which the sample was extracted follows a Normal distribution.
H1: The variable from which the sample was extracted does not follow a Normal distribution.
As the computed p-value is greater than the significance level alpha=0.05,
one cannot reject the null hypothesis H0.
The risk to reject the null hypothesis H0 while it is true is 53.71%.

Anderson-Darling test (I_i):

A2	*0.291*
p-value (Two-tailed)	*0.579*
alpha	*0.05*

Test interpretation:
H0: The variable from which the sample was extracted follows a Normal distribution.
Ha: The variable from which the sample was extracted does not follow a Normal distribution.
As the computed p-value is greater than the significance level alpha=0.05, one cannot reject the null hypothesis H0.
The risk to reject the null hypothesis H0 while it is true is 57.91%.

Evaluation of standard uncertainty components:

1. Intermediate precision $u_{R'}$ uncertainty contribution component

In here, the intermediate precision standard uncertainty $u_{R'} = s_{R'} = 0.104$.

2. Bias u_b uncertainty contribution component

Use the following bias equation for a single CS study:

$$u_b = \sqrt{b^2 + \frac{{s_b}^2}{n} + {u_{Cref}}^2}$$

where：

b – bias, i.e. the difference between mean result $\overline{x}$ 与 ARV (assigned reference value)。

s_b – standard deviation of the bias over *n* repeated analyses

u_{Cref} – standard uncertainty of the ARV, estimated from the certificate assigned value

Table 2 shows the differences of individual tested value from the working CRM standard solution with ARV concentration 5.00±0.18 *mg/L* Chloride

Original Data value	Bias=Value – ARV	Original Data value	Bias=Value – ARV
II_i	*Bias*	I_i	*Bias*
5.122	0.122	5.131	0.131
4.989	−0.011	5.03	0.03
5.054	0.054	4.971	−0.029
4.941	−0.059	4.975	−0.025
5.102	0.102	5.032	0.032
5.144	0.144	5.006	0.006
5.036	0.036	5.323	0.323
4.995	−0.005	4.848	−0.152
5.105	0.105	4.967	−0.033
5.093	0.093	5.005	0.005
5.156	0.156	5.158	0.158
4.856	−0.144	5.122	0.122
4.897	−0.103		

From the above bias data, Bias b = (5.042–5.00), s_b = 0.1067, n = 25, u_{Cref} = 0.09, and hence,

$$u_b = \sqrt{0.042^2 + \frac{0.1067^2}{25} + 0.09^2} = 0.1017$$

Note that s_b is actually the sample standard deviation, *s*.

Evaluation of the combined standard uncertainty and expanded uncertainty of the experiment

The combined standard uncertainty u_c :

$$u_c = \sqrt{{u_{R'}}^2 + {u_b}^2} = \sqrt{0.1037^2 + 0.1017^2} = 0.145 \quad mg/L$$

and,

the expanded uncertainty U for a mean chloride concentration in water of 5.042 mg/L was:

$U = 2 \times u_c$ = 0.290 mg/L with a coverage factor of 2 at 95% confidence.