Estimation of uncertainty in flame atomic absorption spectrophotometry

. Introduction

The concept of "uncertainty" is being introduced and applied to evaluate the reliability of analysis results. This Application News presents a sample of uncertainty calculation for flame atomic absorption spectrophotometry on calcium in mineral water.

Refer to the references at the end of this report for more details about the concept of uncertainty, the method of calculation for a variety of cases, and the statistical processing of measurement data.

Measurement procedure

The measurement procedure is outlined below.

The analysis solution was prepared by diluting the mineral water ten times (10mL/100mL).

The calibration curve method of analysis was employed.

A 10 ppm standard solution was created by diluting a commercial 1000μg/mL (ppm) standard solution 100 times (5mL/50mL→5mL/50mL). This was then further diluted to create six standards for calibration curve with 0, 0.4, 0.8, 1.2 1.6, and 2.0 ppm concentration.

Each analysis was conducted only once.

Additives were added to the analysis samples and standards to achieve 1 % hydrochloric acid and 0.1 % lanthanum concentration.

. Sources of uncertainty

The predicted sources of uncertainty in this analysis were as follows:

① uncertainty in sample dilution (tolerances of volumetric flasks and whole pipettes and operator's skill);
② uncertainty in the 1000 ppm standard;
③ uncertainty in the 10 ppm standard created from the 1000 ppm standard (tolerances of volumetric flasks and whole pipettes and operator's skill);
④ uncertainly in measurement.

Other additional causes of uncertainty can be suggested, including volume fluctuations due to temperature differences, time fluctuations in sensitivity, and interference from coexisting substances (chemical interference, optical interference, physical interference).

. Calculations

The calcium concentration C in mineral water (ppm) is calculated using expression (1).

$$C = Df \times F1 \times F2 \times Cm \quad (1)$$

Where,

Df is the dilution of the actual sample (=100mL/10mL)
F1 is the uncertainty coefficient in the 1000 ppm standard (=1000ppm/1000ppm)
F2 is the uncertainty coefficient in the 10 ppm standard (=1000ppm X (5mL/50mL) X (5mL/50mL)/10ppm)
C_m: Analysis sample concentration (= (Abs-b)/a)

The underlined numbers and letters can lead to uncertainty.

"Abs" is the absorbance of the unknown sample, "a" is the gradient of the calibration curve, and "b" is the calibration curve intercept.

Expressing the uncertainty as the product of the various factors in this way is convenient when comparing the size of the effect of each uncertainty factor.

The calibration curve coefficients "a" and "b" are calculated from expressions (2) and (3), using the method of least squares.

$$a = \sum_{i=1}^{k}(Cj-C)(Yi-Y)\} / \sum(Ci-C)^2 \quad (2)$$

$$b = Y - a \times C \quad (3)$$

Where,

C_i is the concentration of the standard;
C is the mean concentration of standards C_1 to C_k;
Y_i is the absorbance of standard C_i;
Y is the mean absorbance of standards C_1 to C_k.

The total standard uncertainty of the actual concentration (U_{total} (SD)) is calculated from expression (4), where the uncertainty of each factor in expression (1) is denoted as U_{Df} (SD), U_{F1} (SD), U_{F2} (SD), and U_{Cm} (SD).

$$U_{total}(SD) = \sqrt{U_{Df}(SD)^2/D_{f2} + U_{F1}(SD)^2/F_1^2 + U_{F2}(SD)^2/F_2^2 + U_{Cm}(SD)^2/C_m^2} \times C \quad (4)$$

Results and discussions

The individual standard uncertainties are calculated first.

To simplify the calculations, the standard uncertainty due to the whole pipette tolerance and operator's skill is taken as 0.5% volume and the volumetric flask tolerance and operator's skill is taken as 0.1% volume.

The certification for the 1000 ppm standard solution indicates ±6 ppm expanded uncertainty (95% reliability). Assuming a Gaussian distribution, this gives a standard uncertainty of the 1000 ppm standard solution of 6÷1.96 = 3.1 ppm.

$$U_{Df}(SD) = \sqrt{U_{100mL}(SD)^2/100^2 + U_{10mL}(SD)^2/10^2} \times 10$$
$$= 0.051$$

$$U_{F1}(SD) = U_{1000ppm}(SD)/1000$$
$$= 0.0031$$

$$U_{F2}(SD) = \sqrt{2 \times U_{50mL}(SD)^2/100^2 + 2 \times U_{5mL}(SD)^2/5^2} = 0.0072$$

The calibration curve method using linear expression approximation produces expression (5) to calculate the measured concentration $U_{cm}(SD)$:

$$U_{cm}(SD) = (S/a) \times \sqrt{1/k + 1/n + (C_m - C)^2/Sc} \qquad (5)$$

Where,

a is the calibration curve gradient;

$S = \sqrt{\text{(residual sum of squares)} / (k-2)}$;

k is the number of calibration curve points;

n is the number of measurements for the analyzed (unknown) sample;

Cm is the measured concentration (or mean value for repeated measurements);

$$Sc = \sum_{I=1}^{k} (Ci - C)^2$$

The measured data is shown in Table 1 and the calibration curve in Fig.1.

Table 1 Measured Data

Type	Set concentration (ppm)	Absorbance (mAbs)	Measured concentration (ppm)
Standard sample	0	0.2	
Standard sample	0.4	56.5	
Standard sample	0.8	111.3	
Standard sample	1.2	165.3	
Standard sample	1.6	218.8	
Standard sample	2.0	269.9	
Actual sample		249.1	1.830

0.1Abs=100mAbs

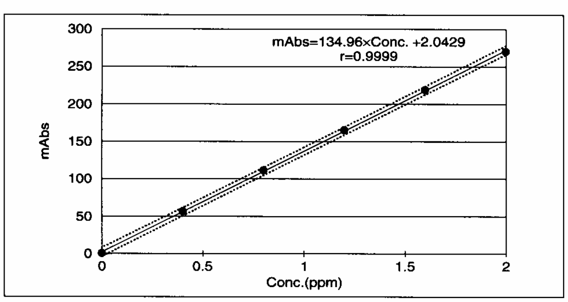

Fig.1 Calibration curve for calcium

Using expressions (2), (3), and (5) to calculate the standard uncertainty of the measured concentration from the measured data gives Ucm(SD) = 0.015.

The upper and lower broken lines in Fig. 1 represent the upper and lower limits with the expanded uncertainty (95% reliability) applied to the absorbance.

Substituting these values into expression (4) to calculate the total standard uncertainty of the actual concentration, gives:

$$U_{total}(SD) = \sqrt{U_{Df}(SD)^2/D_f^2 + U_{F1}(SD)^2/F_1^2 + U_{F2}(SD)^2/F_2^2 + U_{cm}(SD)^2/C_m^2} \times C$$
$$= \sqrt{0.051^2/10^2 + 0.0031^2/1^2 + 0.0072^2/1^2 + 0.015^2/1.83^2} \times 18.30$$
$$= \sqrt{0.000026 + 0.0000096 + 0.000052 + 0.000067} \times 18.30$$
$$= 0.23$$

The expanded uncertainty (95% reliability) is this value multiplied by the coverage factor of 2, giving 0.46, such that the analysis results are expressed as 18.30±0.46 ppm.

To compare the degree of contribution of each factor to U_{total} (SD), the expression was rewritten as the square of the relative standard uncertainty:

$$(U_{total}(RSD))^2 = (\underset{\text{(10x dilution)}}{26} + \underset{\text{(1000ppm standard)}}{9.6} + \underset{\text{(Preparation of 10ppm standard)}}{52} + \underset{\text{(Measurement)}}{67}) \times 10^{-6}$$

This expression shows that the major contributions to uncertainty in this example were from the uncertainty in dilution to 10 ppm and the uncertainty in measurement. Compared to these factors, the uncertainty in the 1000 ppm standard solution is negligibly small.

The major cause of uncertainty in dilution was the 0.5% volume tolerance of the whole pipette and the operator's skill.

On the other hand, the major cause of uncertainty in measurement could be the repeatability and calibration curve linearity on the instrument for a single sample.

References

(1)Eurachem-CITAC Second Edition, June 1999 (2)Hioki, Hamada, Kousaka, Kashiwadaira, Shimadzu Scientific Research Inc. Seminars, Abstracts "Accuracy Control and Uncertainty Evaluation in Analysis" (2000)

(3)J.C.Miller/J.N.Miller, "Compiling and Organizing Data" (1991)

(4)Ishikawa, Kume, Fujimori, Statistical Methods for Chemists and Chemical Technicians (2nd Edition), Tokyo Kagaku Dozin (1990)

SHIMADZU

SHIMADZU CORPORATION. International Marketing Division

3. Kanda-Nishikicho 1-chome, Chiyoda-ku, Tokyo 101-8448, Japan Phone: 81(3)3219-5641 Fax. 81(3)3219-5710 Cable Add.:SHIMADZU TOKYO

Printed in Japan 3295-12111-10A-IK