Example A1: Preparation of a Calibration Standard

Summary

Goal

A calibration standard is prepared from a high purity metal (cadmium) with a concentration of ca.1000 mg L^{-1}.

Measurement procedure

The surface of the high purity metal is cleaned to remove any metal-oxide contamination. Afterwards the metal is weighed and then dissolved in nitric acid in a volumetric flask. The stages in the procedure are shown in the following flow chart.

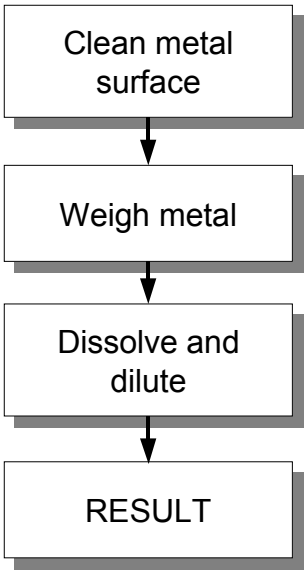


Figure A1. 1: Preparation of cadmium standard

Measurand

$$c_{Cd} = \frac{1000 \cdot m \cdot P}{V} \text{ [mg L}^{-1}\text{]}$$

where

c_{Cd} concentration of the calibration standard [mg L^{-1}]

1000 conversion factor from [mL] to [L]

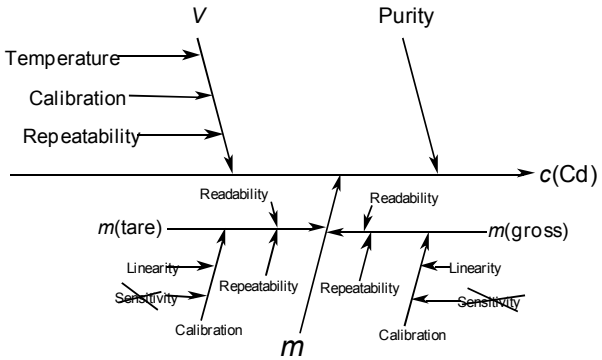
m mass of the high purity metal [mg]

P purity of the metal given as mass fraction

V volume of the liquid of the calibration standard [mL]

Identification of the uncertainty sources:

The relevant uncertainty sources are shown in the cause and effect diagram below:



Quantification of the uncertainty components

The values and their uncertainties are shown in the Table below.

Combined Standard Uncertainty

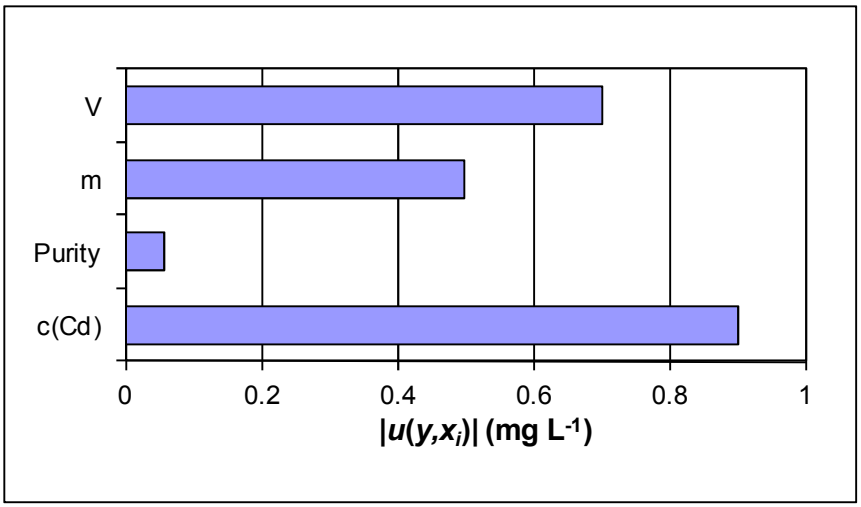
The combined standard uncertainty for the preparation of a 1002.7 mg L^{-1} Cd calibration standard is 0.9 mg L^{-1}

The different contributions are shown diagrammatically in Figure A1.2.

Table A1.1: Values and uncertainties

	Description	Value	Standard uncertainty	Relative standard uncertainty $u(x)/x$
P	Purity of the metal	0.9999	0.000058	0.000058
m	Mass of the metal	100.28 mg	0.05 mg	0.0005
V	Volume of the flask	100.0 mL	0.07 mL	0.0007
c_{Cd}	Concentration of the calibration standard	1002.7 mg L^{-1}	0.9 mg L^{-1}	0.0009

Figure A1.2: Uncertainty contributions in cadmium standard preparation



The values of $u(y,x_i) = (\partial y/\partial x_i).u(x_i)$ are taken from Table A1.3

Example A1: Preparation of a calibration standard. Detailed discussion

A1.1 Introduction

This first introductory example discusses the preparation of a calibration standard for atomic absorption spectroscopy (AAS) from the corresponding high purity metal (in this example $\approx$1000 mg L^{-1} Cd in dilute HNO_3). Even though the example does not represent an entire analytical measurement, the use of calibration standards is part of nearly every determination, because modern routine analytical measurements are relative measurements, which need a reference standard to provide traceability to the SI.

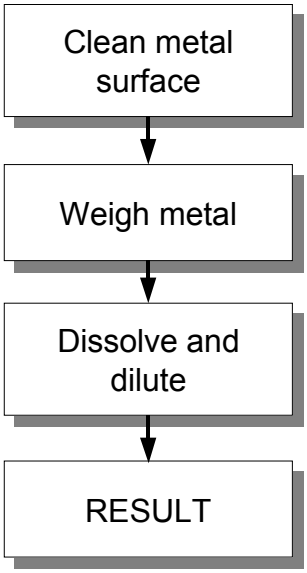
A1.2 Step 1: Specification

The goal of this first step is to write down a clear statement of what is being measured. This specification includes a description of the preparation of the calibration standard and the mathematical relationship between the measurand and the parameters upon which it depends.

Procedure

The specific information on how to prepare a calibration standard is normally given in a Standard Operating Procedure (SOP). The preparation consists of the following stages

Figure A1.3: Preparation of cadmium standard



The separate stages are:

i) The surface of the high purity metal is treated with an acid mixture to remove any metal-oxide contamination. The cleaning method is provided by the manufacturer of the metal and needs to be carried out to obtain the purity quoted on the certificate.

ii) The volumetric flask (100 mL) is weighed without and with the purified metal inside. The balance used has a resolution of 0.01 mg.

iii) 1 mL of nitric acid (65 g/100 g) and 3 mL of ion-free water are added to the flask to dissolve the cadmium (approximately 100 mg, weighed accurately). Afterwards the flask is filled with ion-free water up to the mark and mixed by inverting the flask at least thirty times.

Calculation:

The measurand in this example is the concentration of the calibration standard solution, which depends upon the weighing of the high purity metal (Cd), its purity and the volume of the liquid in which it is dissolved. The concentration is given by

$$c_{Cd} = \frac{1000 \cdot m \cdot P}{V} \text{ mg L}^{-1}$$

where

c_{Cd} concentration of the calibration standard [mg L^{-1}]

1000 conversion factor from [mL] to [L]

m mass of the high purity metal [mg]

P purity of the metal given as mass fraction

V volume of the liquid of the calibration standard [mL]

A1.3 Step 2: Identifying and analysing uncertainty sources

The aim of this second step is to list all the uncertainty sources for each of the parameters which affect the value of the measurand.

Purity

The purity of the metal (Cd) is quoted in the supplier's certificate as (99.99 ± 0.01) %. P is therefore 0.9999 ± 0.0001. These values depend on the effectiveness of the surface cleaning of the high purity metal. If the manufacturer's procedure is strictly followed, no additional uncertainty due to the contamination of the surface with metal-oxide needs to be added to the value given in the certificate.

Mass m

The second stage of the preparation involves weighing the high purity metal. A 100 mL quantity of a 1000 mg L^{-1} cadmium solution is to be prepared.

The relevant mass of cadmium is determined by a tared weighing, giving m= 0.10028 g

The manufacturer's literature identifies three uncertainty sources for the tared weighing: the repeatability; the readability (digital resolution) of the balance scale; and the contribution due to the uncertainty in the calibration function of the scale. This calibration function has two potential uncertainty sources, identified as the sensitivity of the balance and its linearity. The sensitivity can be neglected because the mass by difference is done on the same balance over a very narrow range.

NOTE: Buoyancy correction is not considered because all weighing results are quoted on the conventional basis for weighing in air [H.33] and the densities of Cd and steel are similar. Note 1 in Appendix G refers. The remaining uncertainties are too small to consider.

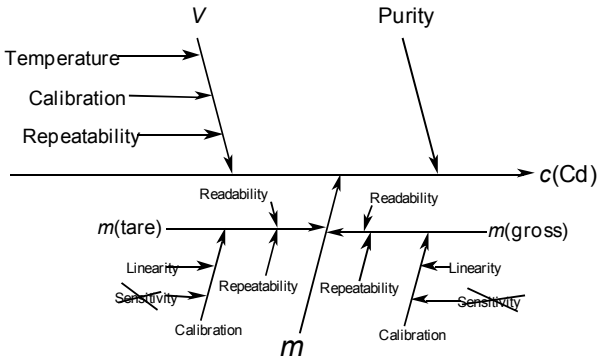
Volume V

The volume of the solution delivered by the volumetric flask is subject to three major sources of uncertainty:

- The uncertainty in the certified internal volume of the flask.
- Variation in filling the flask to the mark.
- The flask and solution temperatures differing from the temperature at which the volume of the flask was calibrated.

The different effects and their influences are shown as a cause and effect diagram in Figure A1.4 (see Appendix D for description).

Figure A1.4: Uncertainties in Cd Standard preparation



A1.4 Step 3: Quantifying the uncertainty components

In step 3 the size of each identified potential source of uncertainty is either directly measured, estimated using previous experimental results or derived from theoretical analysis.

Purity

The purity of the cadmium is given on the certificate as 0.9999 ± 0.0001. Because there is no additional information about the uncertainty value, a rectangular distribution is assumed. To obtain the standard uncertainty $u(P)$ the value of 0.0001 has to be divided by $\sqrt{3}$ (see Appendix E1.1)

$$u(P) = \frac{0.0001}{\sqrt{3}} = 0.000058$$

Mass m

The uncertainty associated with the mass of the cadmium is estimated, using the data from the calibration certificate and the manufacturer's recommendations on uncertainty estimation, as 0.05 mg. This estimate takes into account the three contributions identified earlier (Section A1.3).

NOTE: Detailed calculations for uncertainties in mass can be very intricate, and it is important to refer to manufacturer's literature where mass uncertainties are dominant. In this example, the calculations are omitted for clarity.

Volume V

The volume has three major influences; calibration, repeatability and temperature effects.

i) *Calibration*: The manufacturer quotes a volume for the flask of 100 mL ± 0.1 mL

measured at a temperature of 20 °C. The value of the uncertainty is given without a confidence level or distribution information, so an assumption is necessary. Here, the standard uncertainty is calculated assuming a triangular distribution.

$$\frac{0.1\,\text{mL}}{\sqrt{6}} = 0.04\,\text{mL}$$

NOTE: A triangular distribution was chosen, because in an effective production process, the nominal value is more likely than extremes. The resulting distribution is better represented by a triangular distribution than a rectangular one.

ii) *Repeatability*: The uncertainty due to variations in filling can be estimated from a repeatability experiment on a typical example of the flask used. A series of ten fill and weigh experiments on a typical 100 mL flask gave a standard deviation of 0.02 mL. This can be used directly as a standard uncertainty.

iii) *Temperature*: According to the manufacturer the flask has been calibrated at a temperature of 20 °C, whereas the laboratory temperature varies between the limits of ±4 °C. The uncertainty from this effect can be calculated from the estimate of the temperature range and the coefficient of the volume expansion. The volume expansion of the liquid is considerably larger than that of the flask, so only the former needs to be considered. The coefficient of volume expansion for water is 2.1×10^{-4} °C^{-1}, which leads to a volume variation of

$$\pm(100\times4\times2.1\times10^{-4}) = \pm0.084\,\text{mL}$$

The standard uncertainty is calculated using the assumption of a rectangular distribution for the temperature variation i.e.

Table A1.2: Values and Uncertainties

Description	Value x	$u(x)$	$u(x)/x$
Purity of the metal P	0.9999	0.000058	0.000058
Mass of the metal m (mg)	100.28	0.05 mg	0.0005
Volume of the flask V (mL)	100.0	0.07 mL	0.0007

$$\frac{0.084\,\text{mL}}{\sqrt{3}} = 0.05\,\text{mL}$$

The three contributions are combined to give the standard uncertainty $u(V)$ of the volume V

$$u(V) = \sqrt{0.04^2 + 0.02^2 + 0.05^2} = 0.07\,\text{mL}$$

A1.5 Step 4: Calculating the combined standard uncertainty

c_{Cd} is given by

$$c_{\text{Cd}} = \frac{1000\cdot m\cdot P}{V} \qquad [\text{mg L}^{-1}]$$

The intermediate values, their standard uncertainties and their relative standard uncertainties are summarised overleaf (Table A1.2)

Using those values, the concentration of the calibration standard is

$$c_{\text{Cd}} = \frac{1000\times100.28\times0.9999}{100.0} = 1002.7\ \text{mg L}^{-1}$$

For this simple multiplicative expression, the uncertainties associated with each component are combined as follows.

$$\frac{u_{\text{c}}(c_{\text{Cd}})}{c_{\text{Cd}}} = \sqrt{\left(\frac{u(P)}{P}\right)^2 + \left(\frac{u(m)}{m}\right)^2 + \left(\frac{u(V)}{V}\right)^2}$$

$$= \sqrt{0.000058^2 + 0.0005^2 + 0.0007^2}$$

$$= 0.0009$$

$$u_{\text{c}}(c_{\text{Cd}}) = c_{\text{Cd}}\times0.0009 = 1002.7\,\text{mg L}^{-1}\times0.0009$$

$$= 0.9\,\text{mg L}^{-1}$$

It is preferable to derive the combined standard uncertainty ($u_{\text{c}}(c_{\text{Cd}})$) using the spreadsheet method given in Appendix E, since this can be utilised even for complex expressions. The completed spreadsheet is shown in Table A1.3. The values of the parameters are entered in the second row from C2 to E2. Their standard uncertainties are in the row below (C3-E3). The spreadsheet copies the values from C2-E2 into the second column from B5 to B7. The result (c(Cd)) using these values is given in B9. The C5 shows the value of P from C2 plus its uncertainty given in C3. The result of the calculation using the values C5-C7 is given in C9. The columns D and E follow a similar procedure. The values shown in the row 10 (C10-E10) are the differences of the row (C9-

E9) minus the value given in B9. In row 11 (C11-E11) the values of row 10 (C10-E10) are squared and summed to give the value shown in B11. B13 gives the combined standard uncertainty, which is the square root of B11.

The contributions of the different parameters are shown in Figure A1.5. The contribution of the uncertainty on the volume of the flask is the largest and that from the weighing procedure is similar. The uncertainty on the purity of the cadmium has virtually no influence on the overall uncertainty.

The expanded uncertainty $U(c_{Cd})$ is obtained by multiplying the combined standard uncertainty with a coverage factor of 2, giving

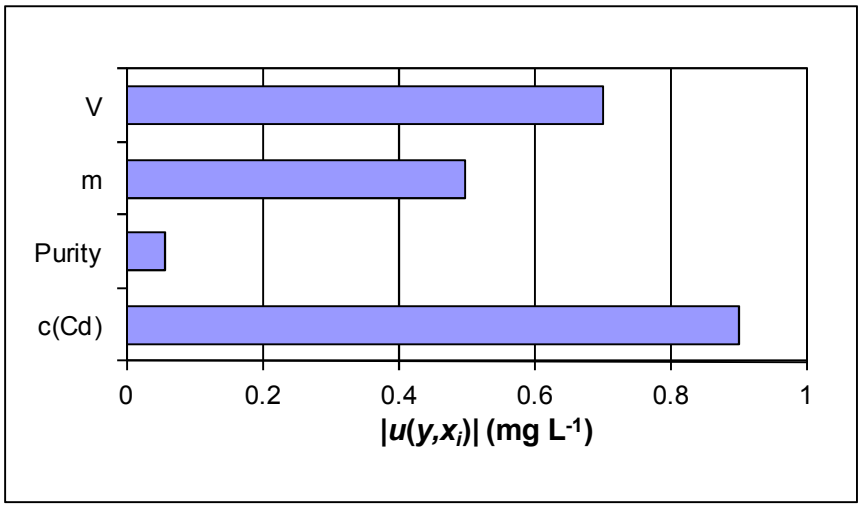
$$U(c_{Cd}) = 2 \times 0.9\,\text{mg l}^{-1} = 1.8\,\text{mg L}^{-1}$$

Table A1.3: Spreadsheet calculation of uncertainty

	A	B	C	D	E
1			P	m	V
2		Value	0.9999	100.28	100.00
3		Uncertainty	0.000058	0.05	0.07
4					
5	P	0.9999	0.999958	0.9999	0.9999
6	m	100.28	100.28	100.33	100.28
7	V	100.0	100.00	100.00	100.07
8					
9	c(Cd)	1002.69972	1002.75788	1003.19966	1001.99832
10	$u(y,x_i)$*		0.05816	0.49995	-0.70140
11	$u(y)^2$, $u(y,x_i)^2$	0.74529	0.00338	0.24995	0.49196
12					
13	u(c(Cd))	0.9			

*The sign of the difference has been retained

Figure A1.5: Uncertainty contributions in cadmium standard preparation



The values of $u(y,x_i) = (\partial y/\partial x_i).u(x_i)$ are taken from Table A1.3