Laboratory work 2
Preparation of liquid samples with a desired concentration of analyte and its uncertainty

Goal of the work: to learn preparation of liquid samples with a desired concentration of analyte and its uncertainty.

Types of Error

There are three types of limitations to measurements:

1) *Instrumental limitations*

Any measuring device can only be used to measure to with a certain degree of fineness. Our measurements are no better than the instruments we use to make them.

2) *Systematic errors and blunders*

These are caused by a mistake **which does not change** during the measurement. For example, if the platform balance you used to weigh something was not correctly set to zero with no weight on the pan, all your subsequent measurements of mass would be too large. Systematic errors do not enter into the uncertainty. They are either identified and eliminated or lurk in the background producing a shift from the true value.

3) *Random errors*

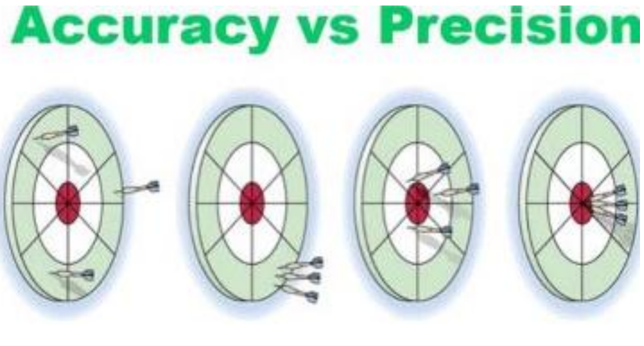
These arise from unnoticed variations in measurement technique, tiny changes in the experimental environment, etc. Random variations affect precision. Truly random effects average out if the results of a large number of trials are combined.

Precision vs. Accuracy

Measurements may be *accurate*, meaning that the measured value is the same as the true value; they may be *precise*, meaning that multiple measurements give nearly identical values (i.e., reproducible results); they may be both accurate and precise; or they may be neither accurate nor precise. The goal of scientists is to obtain measured values that are both accurate and precise.

- A precise measurement is one where independent measurements of the same quantity closely cluster about a single value that may or may not be the correct value.
- An accurate measurement is one where independent measurements cluster about the true value of the measured quantity.

Systematic errors are not random and therefore can never cancel out. They affect the accuracy but not the precision of a measurement.



A. Low-precision, Low-accuracy:
The average (the X) is not close to the center
B. Low-precision, High-accuracy:
The average is close to the true value
C. High-precision, Low-accuracy:
The average is not close to the true value
D. High-precision, High-accuracy.

Writing experimental numbers

Uncertainty of Measurements

Errors are quantified by associating an uncertainty with each measurement. For example, the best estimate of a length L is 2.59 cm, but due to uncertainty, the length might be as small as 2.57 cm or as large as 2.61 cm. L can be expressed with its uncertainty in two different ways:

1. *Absolute uncertainty*

Expressed in the units of the measured quantity: ***L = 2.59 ± 0.02 cm***

2. *Percentage uncertainty*

Expressed as a percentage which is independent of the units

Above, since 0.02/2.59 ≈1% we would write ***L = 7.7 cm ± 1%***

Significant figures

Experimental numbers must be written in a way consistent with the precision to which they are known. In this context one speaks of *significant figures* or digits that have physical meaning.

1. All definite digits and the first doubtful digit are considered significant.

2. Leading zeros are **not** significant figures.

Example: L = 2.31 cm has 3 significant figures. For L = 0.0231 m, the zeros serve to move the decimal point to the correct position. Leading zeros are not significant figures.

3. Trailing zeros are significant figures: they indicate the number's precision.

4. One significant figure should be used to report the uncertainty or occasionally two, especially if the second figure is a five.

Rounding numbers

To keep the correct number of significant figures, numbers must be rounded off. The discarded digit is called the *remainder*. There are three rules for rounding:

✓ **Rule 1**: If the remainder is less than 5, drop the last digit.

Rounding to one decimal place: 5.346 → 5.3

✓ **Rule 2**: If the remainder is greater than 5, increase the final digit by 1.

Rounding to one decimal place: 5.798 → 5.8

✓ **Rule 3**: If the remainder is exactly 5 then round the last digit to the closest even number.

This is to prevent rounding bias. Remainders from 1 to 5 are rounded down half the time and remainders from 6 to 10 are rounded up the other half.

Rounding to one decimal place: 3.55 → 3.6, also 3.65 → 3.6

Statistical analysis of small data sets

Repeated measurements allow you not only to obtain a better idea of the actual value, but also enable you to characterize the uncertainty of your measurement. Below are several quantities that are very useful in data analysis. The value obtained from a particular measurement is x. The measurement is repeated N times. Oftentimes in lab N is small, usually no more than 5 to 10. In this case, we use the formulae below:

Mean (x_{avg})	The average of all values of x (the "best" value of x)	$x_{avg} = \frac{x_1 + x_2 + \cdots + x_N}{N}$
Range (R)	The "spread" of the data set. This is the difference between the maximum and minimum values of x	$R = x_{max} - x_{min}$
Uncertainty in a measurement (Δx)	Uncertainty in a single measurement of x. You determine this uncertainty by making multiple measurements. You know from your data that x lies somewhere between x_{max} and x_{min}	$\Delta x = \frac{R}{2} = \frac{x_{max} - x_{min}}{2}$
Uncertainty in the mean (Δx_{avg})	Uncertainty in the mean value of x. The actual value of x will be somewhere in a neighborhood around x_{avg}. This neighborhood of values is the uncertainty in the mean	$\Delta x_{avg} = \frac{\Delta x}{\sqrt{N}} = \frac{R}{2\sqrt{N}}$
Measured value (x_m)	The final reported value of a measurement of x contains both the average value and the uncertainty in the mean	$x_m = x_{avg} \pm \Delta x_{avg}$

The average value becomes more and more precise as the number of measurements N increases. Although the uncertainty of any single measurement is always Δx, the uncertainty in the mean Δx_{avg} becomes smaller (by a factor of $1/\sqrt{N}$) as more measurements are made.

Statistical analysis of large data sets

If only random errors affect a measurement, it can be shown mathematically that in the limit of an infinite number of measurements ($N \to \infty$), the distribution of values follows a normal distribution (i.e. the bell curve on the Figure 4). This distribution has a peak at the mean value x_{avg} and a width given by the standard deviation σ.

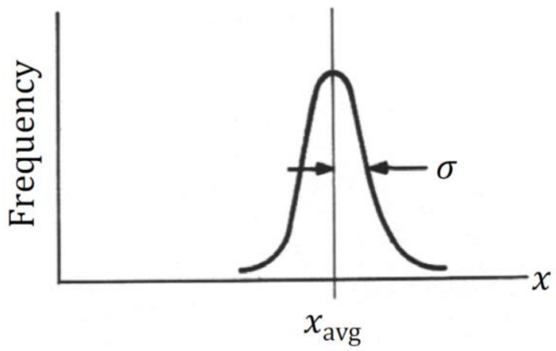


Figure 4. Normal distribution

Obviously, we never take an infinite number of measurements. However, for a large number of measurements, say, N~10-10^2 or more, measurements may be approximately normally distributed. In that event we use the formulae below:

Mean (x_{avg})	The average of all values of x (the "best" value of x). This is the same as for small data sets.	$x_{avg} = \frac{\sum_{i=1}^{N} x_i}{N}$
Uncertainty in a measurement (Δx)	Uncertainty in a single measurement of x. The vast majority of your data lies in the range $x_{avg} \pm \sigma$	$\Delta x = \sigma = \sqrt{\frac{\sum_{i=1}^{N}(x_i - x_{avg})^2}{N}}$
Uncertainty in the mean (Δx_{avg})	Uncertainty in the mean value of x. The actual value of x will be somewhere in a neighborhood around x_{avg}. This neighborhood of values is the uncertainty in the mean.	$\Delta x_{avg} = \frac{\sigma}{\sqrt{N}}$
Measured value (x_m)	The final reported value of a measurement of x contains both the average value and the uncertainty in the mean.	$x_m = x_{avg} \pm \Delta x_{avg}$

Most of the time we will be using the formulae for small data sets. However, occasionally we perform experiments with enough data to compute a meaningful standard deviation. In those cases, we can take advantage of software that has programmed algorithms for computing x_{avg} and σ.

Addition/Subtraction	$z = x \pm y$	$\Delta z = \sqrt{(\Delta x)^2 + (\Delta y)^2}$
Multiplication	$z = xy$	$\Delta z = \lvert xy \rvert \sqrt{\left(\frac{\Delta x}{x}\right)^2 + \left(\frac{\Delta y}{y}\right)^2}$
Division	$z = \frac{x}{y}$	$\Delta z = \left\lvert \frac{x}{y} \right\rvert \sqrt{\left(\frac{\Delta x}{x}\right)^2 + \left(\frac{\Delta y}{y}\right)^2}$
Power	$z = x^n$	$\Delta z = \lvert n \rvert x^{n-1} \Delta x$
Multiplication by a constant	$z = cx$	$\Delta z = \lvert c \rvert \Delta x$
Function	$z = f(x, y)$	$\Delta z = \sqrt{\left(\frac{\partial f}{\partial x}\right)^2 (\Delta x)^2 + \left(\frac{\partial f}{\partial y}\right)^2 (\Delta y)^2}$

Working procedure

Materials:

Volumetric flasks (25-100 mL): 15-30
Pipettes (1-5 mL, maybe 0.1 mL)
Analytical balances
Technical balances
Micropipette (100-1000 µL)

Task for laboratory work

Prepare liquid samples with desired concentration of solutes in water with desired uncertainties (uncertainties of glassware are shown in Tables 4-5):

1. Prepare solution with following concentration and its uncertainty from given solution of ethanol with concentration (95.4±0.4) vol.%:
    a. 10.0±0.2 ppm
    b. 1.50±0.03 mg/L
2. Prepare solution with following concentration and its uncertainty from given NaCl with >99% purity:
    a. 10.0±0.2 ppm (w/w)
    b. 20.0±0.3 mg/L
    c. 100±2 μg/L
    d. 50.0±0.1 mmol/L
    e. 50±1 ppb
3. Prepare solution with following concentration and its uncertainty from given NaH_2PO_4:
    a. 150±2 mmol/L
    b. 100±1 mmol/L
4. Prepare solution with following concentration and its uncertainty from given HCl (1.00±0.01) M:
    a. 50±1 mmol/L
5. Prepare solution with following concentration and its uncertainty from given solution of methanol (1.00±0.02) mg/L:
    a. 1.00±0.03 μg/L
    b. 30±1 ppb (v/v)
6. Prepare solution with following concentration and its uncertainty from given $K_2Cr_2O_7$ – 0.025-0.030 N (relative uncertainty <0.3%).
7. Prepare solution with following concentration and its uncertainty from given 0.100±0.001 N (relative uncertainty <0.3%) $Na_2B_4O_7 \cdot 10H_2O$ (V = 100 mL).

Table 4 - Uncertainties of glassware

Rated capacity	Permissible error				
	Cylinders		Graduated beakers	Volumetric flasks	
	1st class	2nd class		1st class	2nd class
5	0.10	0.10	-	0.025	0.05
10	0.10	0.20	-	0.025	0.05
25	0.25	0.50	-	0.04	0.08
50	0.25	1.00	2.50	0.06	0.12
100	0.50	1.00	5.00	0.10	0.20
200	-	-	-	0.15	0.30
250	1.25	2.00	5.00	0.15	0.30
300	-	-	-	0.20	0.40
500	2.50	5.00	12.50	0.25	0.50
1000	5.00	10.00	25.00	0.40	0.80
2000	10.00	20.00	-	0.60	1.20

Table 5 - Uncertainties of pipettes

Rated capacity	Smallest division of the scale	Permissible error of the volume	
		1st class	2nd class
0.5	0.01	0.005	-
1	0.01	0.006	0.01
2	0.02	0.01	0.02
5	0.05	0.03	0.05
10	0.1	0.05	0.1
25	0.1	0.1	-
	0.2	0.1	0.2