Chemometrics

MA4605

Ana-Maria Magdalina
ana-maria.magdalina@ul.ie

September 6, 2011

Components : 20 lectures, 10 lab sessions, 4 review classes
Assessments : 100% final examination

Recommended textbooks

- Peter Dalgaard (2002). Introductory Statistics with R. Springer
- Miller,J.N., Miller,J.C.(2005). Statistics and Chemometrics for Analytical Chemistry. Pearson-Prentince Hall, 5th Edition
- Statistics and chemometrics for analytical chemistry [electronic resource] / James N. Miller, Jane C. Miller.

Analytical problems

Modern analytical chemistry is overwhelmingly a **quantitative** science .
How much?

- boron in a distilled water sample
- albumin in a blood serum sample

Qualitative research requires quantitative measurements.

- This water sample contains boron.
- This water sample contains less than 1 μg ml^{-1} boron.

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No quantitative results are of any value unless they are accompanied by some estimate of the errors inherent in them.

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- If, however, investigations show that the error may amount to 10 units i.e. 104 ± 10, then it is quite likely that the true value is actually less than 100, in which case a new discovery is far from certain.
- Knowledge of the of the experimental error is crucial to proper interpretation of the results.

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- Is the values 25.39 ml an outlier?

Types of error

Experimental scientists make a fundamental distinction between

- gross
- random
- systematic errors.

  Gross errors lead to abandoning the experiment: instrument breakdown, accidentally discarding a crucial sample, discovering that a pure reagent is badly contaminated. Such errors are easy to recognize, so we focus on the other 2 types.

Random and systematic errors

To distinguish between random and systematic errors consider the experiment.

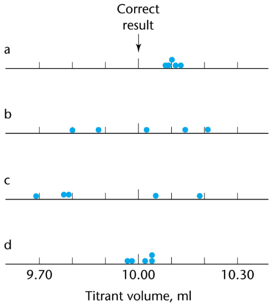
- Four students (A-D) each perform an analysis in which exactly 10.00 ml of exactly 0.1 M sodium hydroxide is titrated with exactly 0.1 M hydrochloric acid.
- Each student performs five replicate titrations, with the results shown in Table 1.1.

Table 1.1 Random and systematic errors

Student	Results (ml)					Comment
A	10.08	10.11	10.09	10.10	10.12	Precise, biased
B	9.88	10.14	10.02	9.80	10.21	Imprecise, unbiased
C	10.19	9.79	9.69	10.05	9.78	Imprecise, biased
D	10.04	9.98	10.02	9.97	10.04	Precise, unbiased

Graphical illustration

The results of experiment represented by dotplots:



Results characteristics

Random errors affect the precision of an experiment.

- Student A: random errors are small as results are very close to each other (precision).
- Student B: random errors are large as results are spread apart (poor precision).

Systematic errors cause all the results to be in error in the same direction(too high or too low).

- Student A: all results are too high compared to the true value of 10 (positively biased).
- Student B: results centered around the true value of 10(unbiased).

Student C: poor precision as values are spread apart and negatively biased.
Student D: good precision as values are close to each other and no bias as values are close the the true values of 10.

Random and systematic errors are independent of one another.
Random errors can never be eliminated, only minimized.
Systematics errors can be corrected by using standard method and materials.
A method that is precise but biased(Student A) can be converted to a method precise and unbiased(Student D) if the systematic errors are discovered and removed.

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- Methodological systematic errors such as this are very common.
- Solution: identify the problem areas before stating the experiment.

The rest of the course will deal with evaluating the random errors and we will assume the systematic errors are absent.