Instrumental methods of chemical analysis

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Introduction to instrumental analysis

The concept

1.Some external ***physical*** effect/force (electromagnetic radiation, heating, electrical voltage, etc.) is imposed onto the sample

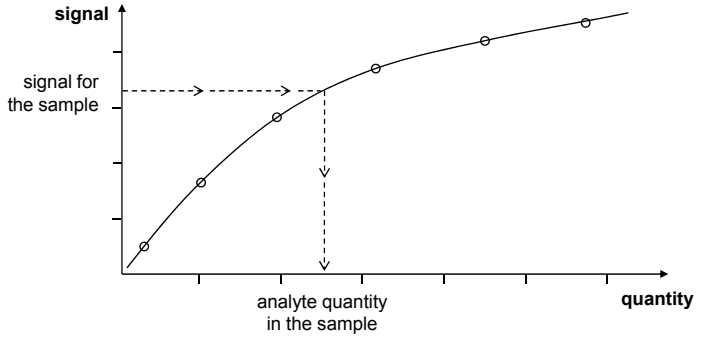
2.Induced changes (response) in the properties of the sample are detected by measuring an electric, mechanical, thermal or optical (***physical***) signal.

Consequently, ***instrumental analysis*** is often also referred to as ***physical analysis*** in contrast to ***chemical analysis***. Remember, that chemical/classical analytical methods (e.g. titration or gravimetry) rely on the stoichiometry of a chemical reaction so the measurement of the volume or mass of the reactants allow the direct calculation of the quantity of the analyte.

The application of physical methods always requires a ***calibration***.

Introduction to instrumental analysis
Calibration and calibration plots

Calibration is a process during which one records the instrumental response signal as a function of analyte concentration. The result is a ***calibration plot***. Such a plot (or the fitted mathematical function) can be used to determine the quantity of the analyte in a sample.



Introduction to instrumental analysis
Classification of methods

Classification of instrumental methods (according to the type of the physical effect applied or detected during analysis):

- electric current/voltage → **electroanalysis**
- electromagnetic radiation → **spectrochemistry**/radioanalysis
- separation processes → **chromatography**
- heat → thermoanalytical methods

Introduction to instrumental analysis
Pros and cons

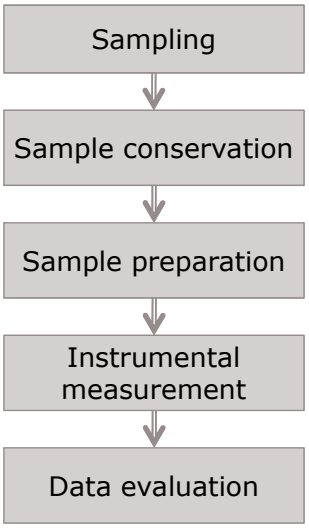
Advantages of instrumental methods over chemical ones:

- speed (can be automated, sample throughput is high)
- sensitivity (trace or ultra-trace analysis is possible)
- selectivity (accurate in the presence of many other components)
- reproducibility (reliable, objective)
- sample requirement is small (mL and mg or less can be handled)

Disadvantages:

- cost
- complexity
- maintenance

Introduction to instrumental analysis
General overview of the analytical process



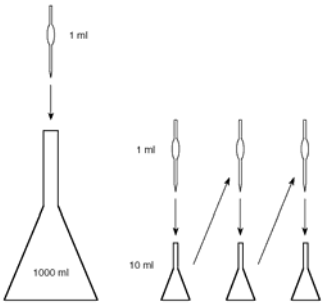
Representative versus point-like (e.g. $[Ca^{2+}]$ in a lake , or carbon in a steel sample)

Preservation of the chemical and physical status of a sample is always needed if the analysis is not performed immediately on site (e.g. danger of CO_2 or O_2 dissolution)

Purpose is to bring the sample into a form suitable for analysis (e.g. phase, concentration, etc.) (e.g. ceramics analysis by solution analytical methods after digestion) . Most time consuming.

Introduction to instrumental analysis
The approach to sample preparation

Sample preparation has a great effect on the performance of the total analysis process, therefore the general rule is that we use as little as possible sample preparation (both in terms of steps and also in terms of the endangering of the sample). One simple example is dilution … the other is sample digestion…



Introduction to instrumental analysis
Important terms

Important terms frequently used:

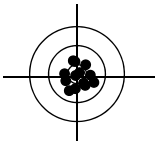
- accuracy and precision (standard deviation)
- sensitivity
- limit of detection and limit of determination
- linear dynamic range
- selectivity/resolution
- interference effects

Accuracy indicates how close the measured quantity of the analyte is to the true analyte quantity in the sample, and is usually expressed as the relative percent error.

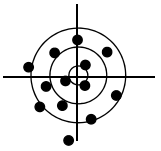
Precision characterizes the deviation of results from repeated analyses of the same sample. It is expressed as standard deviation or relative standard deviation (RSD%).

$$s = \sqrt{\frac{\sum_{i}^{n}\left(x_i - \bar{x}\right)^2}{n-1}}$$

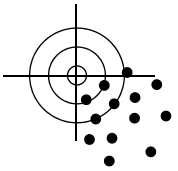
Introduction to instrumental analysis
Accuracy and precision – the target analogy



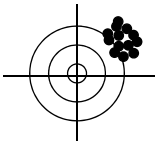
accurate and precise



accurate, but imprecise

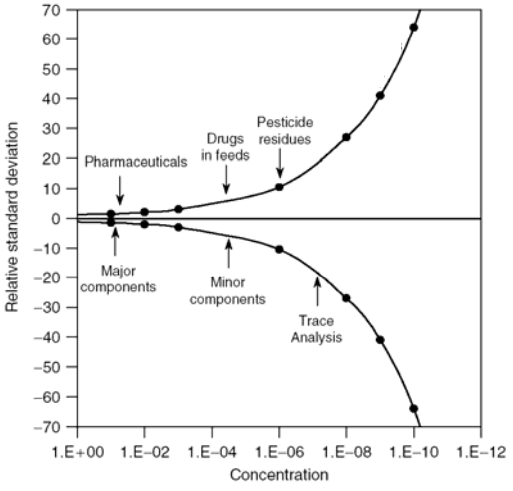


inaccurate and imprecise

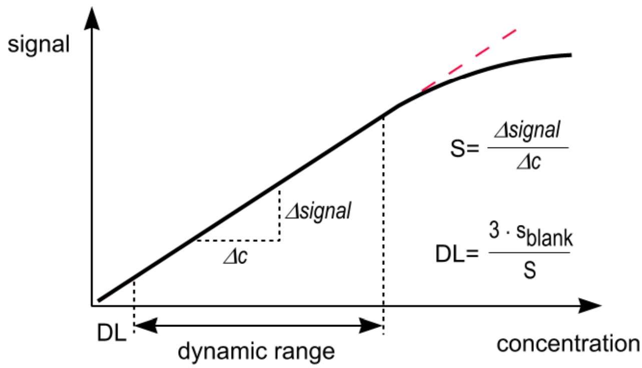


precise, but inaccurate

Introduction to instrumental analysis
Accuracy and precision – the target analogy



Introduction to instrumental analysis
Terms associated with calibration plots



$$S = \frac{\Delta signal}{\Delta c}$$

$$DL = \frac{3 \cdot s_{blank}}{S}$$

Detection limit (DL, LOD) is the minimum concentration (quantity) for which the signal can be reliably distinguished from the blank. This concentration level provides reliable detection! For quantitative determination, a concentration of 5-10 times DL is needed – this is the ***limit of determination/quantitation (LOQ)***.

Linear dynamic range is the concentration (quantity) range [illegible] (ca. 5% deviation [illegible])

Sensitivity (S) is the calibration plot derivative at a given concentration (quantity). In common cases, when the plot can be considered linear, this value is constant.

Introduction to instrumental analysis
Interference effects

Those components of a sample, which are not measured during analysis (***matrix***) or the macroscopic physical/chemical properties of the sample always have some indirect effect on the measurement results. These effects are called ***interference effects***. The nature and extent of these effects are different for different analytical methods. Three examples:

*The simplest case is that of inadequate resolution or **spectral interferences**, when e.g. spectral lines overlap.*

*In a clear solution, Hg^{2+} ions can be well measured by potentiometry and the data can also be used to estimate the total Hg content. Except, when e.g. Cl^- ions are also present in the matrix, because then chloro-complexes of Hg are formed and so the electrode will „detect” a lower concentration of total Hg than there actually is (the same is the case with e.g. Cu^{2+} and EDTA, etc.). This is an example for a **chemical interference effect**.*

*Nebulization, as a means of sample introduction into a spectroscopy, is a very popular method. It is easy to see that the viscosity, specific density or surface tension has an effect on the aerosol generation, which in turn influences the signal we detect. This is an example for **physical interference effects**.*

Introduction to instrumental analysis
Selectivity/resolution

In general, there are no „**specific**" measurement methods (chemical or instrumental) that are perfectly free from just any interference effects.

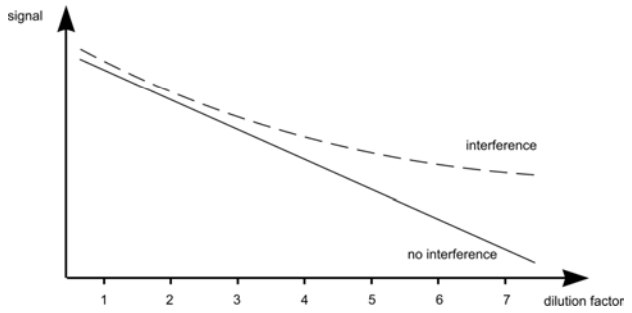
Selectivity is the term that characterizes the „robustness" of the methods against interferences and there are in fact large differences also between instrumental methods. For example, you will see that the selectivity of e.g. conductometry and UV-Vis spectrophotometry is quite poor. Other spectroscopic and chromatographic methods on the other hand can be very selective. Qualitatively, a method is more selective, if it has less interference effects and their influence is also smaller. One quantitative notion used to describe selectivity is ***resolution***. This is calculated in e.g. mass spectrometry as

$$R = \frac{m_1 + m_2}{2 \cdot \Delta m}$$

for when valley height is 5%...

Introduction to instrumental analysis
Non-spectral interferences – a simple check

When interference effects other than spectral interferences are present, accurate analysis becomes more difficult and advanced approaches are called for. Consequently, the first thing to do when the sample is in an unknown matrix is to check if there matrix effect at all. Assuming a suppressive interference effect, the check for matrix effects with solution samples is easy; you create a sequence of diluted subsamples and monitor the analytical signal in them.



Introduction to instrumental analysis
Matrix matched calibration

If there really are interference effects (other than spectral interferences), it means that your calibration will have to be done carefully, otherwise there will be a significant positive or negative error in the determination. *You can generally use on of three advanced calibration approaches* to handle the situation and eliminate/diminish the effect.

First alternative is ***matrix matched calibration.*** This can be done, if you know some preliminary information about the matrix (e.g. sample type, source, etc.). Then, you can simulate the matrix by preparing the calibration standards in this matrix.

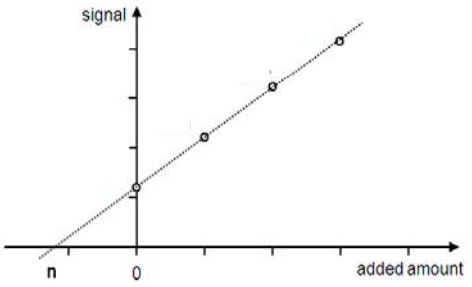
When using solid standards for calibration, this approach is easiest to use with ***certified reference materials.***

Introduction to instrumental analysis
Certified reference materials available (examples)

ORGANIC-RICH SOIL (extractable elements) BCR-700 17
OXIDE GLASS (15 ppm U) IRMM-540R 67
OXIDE GLASS (50 ppm U) IRMM-541 67
PCB STANDARD SOLUTION BCR-365 2
PEANUT BUTTER (aflatoxins low level) BCR-385R 33
PEANUT BUTTER (aflatoxins very low level) BCR-401R 33
PHARMACEUTICAL GLASS IRMM-435 53
PIG KIDNEY (CTC free) BCR-706 46
PIG KIDNEY (CTC incurred) BCR-707 46
PIG LIVER (CTC free) BCR-695 46
PIG LIVER (CTC incurred) BCR-696 46
PIG LIVER (vitamins) BCR-487 38
PIG MUSCLE (CTC free) BCR-697 46
PIG MUSCLE (CTC incurred) BCR-698 46
PLASTIC FILM (OVERALL MIGRATION IN OLIVE OIL (film A) BCR-537 40
PLASTIC FILM (OVERALL MIGRATION IN OLIVE OIL (film B) BCR-538 40
PLASTIC FILM (OVERALL MIGRATION IN OLIVE OIL (film C) BCR-539 40
POLYETHYLENE (40, 75, 200, 400 mg/kg Cd) VDA 001-004 67
POLYETHYLENE (high level) ERM-EC681k 67
POLYETHYLENE (LDPE) ERM-EC590 67
POLYETHYLENE (low level) ERM-EC680k 67
POLYPROPYLENE (PP) ERM-EC591 67
PORCINE MUSCLE (chloramphenicol blank) BCR-444 45
PORCINE MUSCLE (chloramphenicol positive) BCR-445 45

Introduction to instrumental analysis
Multiple standard additions calibration – the concept

The second approach is to use ***multiple standard additions*** calibration method. First, you divide (take) multiple subsamples of your orginal sample and spike them with a successively increasing amount of analyte. Then you create the additions plot (as seen below) and fit a straight line to the datapoints; the intercept of this line with the x-axis will tell you the amount of the analyte in the sample (*n*). Basically yo carry out calibration in your sample matrix.



Introduction to instrumental analysis
Multiple standard additions calibration – preconditions

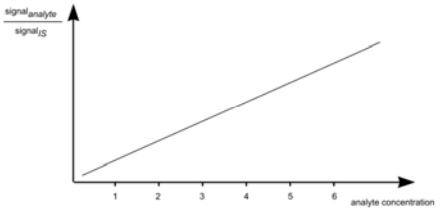
There are some preconditions that have to be considered for a successful use of this calibration approach:

- the signal should be linearly proportional with concentration
- addition plot has to have a reasonable slope
- always use more than one additions (more than two data points)
- dilution difference has to be kept at minimum, which dictates that
  - concentrated, low volume spikes have to be used, or
  - sample has to be diluted to a fixed volume
- the approach needs a larger than usual sample volume
- some preliminary knowledge about the concentration is needed

Introduction to instrumental analysis

The use of an internal standard

The third approach is to use an ***internal standard (IS)*** during calibration. Internal standard is a component which is „not present" in the samples, and whose physical/chemical properties is similar to that of the analyte. The concept is that you spike all samples and calibration standards with a fixed concentration of this IS, and then carry out calibration as usual, but consider the *signal ratio* for the analyte and IS as the analytical response.



If the internal standard is chosen correctly, this can provide an automatic correction for many physical and matrix effects, based on the assumption that the analyte and IS signals are affected the same way and that their signal is linearly proportional to their concentration.