7. Chemical Calculation

7.1 Dilutions and mixtures

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Very high analyte concentrations can be above the calibration line or even the linear range of the calibration line. If the element concentrations are higher than the linear range of the method, the extract has to be diluted. If the element concentration is "only" above the highest standard of the calibration line but within the linear range of the method, it has to be decided case by case. For element determination by ICP-OES, exceedances of the highest standard by a factor of four or five are normally unproblematic, as long as the concentrations are in the linear range. For higher exceedances it has to be decided if either an additional higher standard is set and the calibration line is extended or if the samples should be diluted. The setting of an extended calibration line is normally useful if a higher percentage of the samples is higher than the highest standard. A dilution of samples is normally useful if only some samples are higher. This decision should be made together with the technical assistant of the ICP-OES.

If samples have to be diluted, it has to be considered that it has to be **differentiated** between **dilution** and **mixtures** for specification of dilution factor and converting in "real" element concentrations.

- Definition of **mixture**:
    - If the specification of a dilution is referred to the **single components of a solution**, this has to be called a mixture and the so-called **dilution factor** for calculation of the "real" concentration is determined by **addition of single components**.

Example for the calculation of the dilution factor in a **mixture**:
It is necessary to dilute a sample for P determination. For this reason, a sample solution is mixed with ultra-pure water (RW) as followed: to 1 part sample 9 parts of water are added, that means 1 part sample + 9 parts water. This is called a mixture with 1 + 9. If both is added (1 + 9), the dilution factor is 10. With this dilution factor all measured element concentrations of the samples have to be multiplied to get the "real" element concentration in the sample.

If the sample solution is not only diluted by RW but also other solutions, all parts have to be added analogously. For example: 1 part of sample is mixed with 3 parts of a solution X and 5 parts of a solution Y, so the dilution factor is calculated as follows by addition: 1 + 3 + 5. This means a dilution factor of 9; therefore, the measurement value has to be multiplied by 9.

- Definition of a **dilution**:
  - A **dilution** in the narrow sense of the word means the ratio of the initial concentration to the end concentration. It is related to the **percentage of a component in the total solution**.

Example for the calculation of the dilution factor in a **dilution**:
At a dilution of 1 : 10, the 1 is the proportion in the total solution (10). The dilution factor for calculation of concentration is therefore 10 and not additive as in a mixture (1 + 10 = 11). That means, for example, in 10 ml of the total solution is 1 ml of the component. The tenth of the total solution is the sample. As a mixture it would be specified as 1 + 9.

Calculation of the dilutions of calibration standards for calibration lines

The calibration standards for a calibration line are made from so-called P stock solution by dilution. For calculation of necessary volumes of the P stock solution (in ml) the concentration of the P stock solution (in mg P L^{-1}), the end concentration of the calibration standards (in mg P L^{-1}) and the necessary volume of the calibration standards (in ml) is necessary.

<u>Given</u>:
X mg P per litre in the P stock solution e.g. 1 g P per litre

<u>Searched</u>:
Necessary ml of stock solution for 100 ml calibration standard for y mg P per litre e.g. 2 mg P; 4 mg P and 6 mg P per litre

<u>Solution steps (with example)</u>:

1. question: How many mg of P are in 1 ml of P stock solution?
For this calculation 1 litre is presented as 1000 ml and 1 g P as 1000 mg P for uniform units. This question can be solved by a ratio equation.

Abbreviations: stock sol. = stock solution vol = volume

Formula 1

$$\frac{a\ \text{mg P}}{10^{3}\ \text{ml stock sol.}} = \frac{x\ \text{mg P}}{1\ \text{ml stock sol.}}$$

Example: $\frac{1000 \text{ mg P}}{1000 \text{ ml}} = \frac{\text{x mg P}}{1 \text{ ml}}$

Converting to x mg of P means: 1 mg P per 1 ml stock solution

2. question: How many mg of P have to be in 100 ml calibration standard at a given concentration? This question can be solved by a ratio equation.

Formula 2

$$\frac{\text{b mg P in standard}}{\text{1000 ml standard}} = \frac{\text{y mg P}}{\text{vol ml standard}}$$

Example: $\frac{\text{2 mg P in standard}}{\text{1000 ml standard}} = \frac{\text{y mg P}}{\text{100 ml standard}}$

Converting to y

$$\frac{\text{vol standard ml} \times \text{b mg P in standard}}{\text{1000 ml standard}} = \text{y mg P}$$

Example: $\frac{\text{100 ml standard} \times \text{2 mg P in standard}}{\text{1000 ml standard}} = \text{0.2 mg P}$

That means 0.2 mg P are necessary for 100 ml of the standard.

3. question: If I have x mg P in 1 ml of stock solution and y mg P are necessary in the 100 ml standard, how many ml of stock solution are necessary?

Formula 3

$$\frac{\text{x mg P}}{\text{1 ml}} = \frac{\text{y mg P in standard}}{\text{z ml necessary stock sol.}}$$

Example: $\frac{\text{1 mg P}}{\text{1 ml}} = \frac{\text{0.2 mg P in standard}}{\text{z ml necessary stock sol.}}$

Converting to z means that 0.2 ml stock solution are necessary to set 100 ml standard with a concentration of 2 mg P per litre from a stock solution with 1 g P per litre.

Formulas can be brought together and so the calculation can be shortened.

For x mg P per 1 ml in formula 3 the stock solution concentration in mg P per 1000 ml (1 litre) of formula 1 can be inserted

That means:

$$\frac{\text{mg P in the stock sol.}}{\text{per 1000 ml stock sol.}} = \frac{\text{y mg P in standard}}{\text{z ml necessary stock sol.}}$$

Converting to z means:

$$\text{z ml necessary stock sol.} = \frac{\text{y mg P in standard} \times \text{per 1000 ml stock sol.}}{\text{mg P in stock sol.}}$$

For y mg P in the standard, formula 2, which is converted to y, is inserted, that means:

$$\text{z ml necessary stock sol.} = \frac{\text{standard vol ml} \times \text{b mg P in standard} \times \text{per 1000 ml stock sol.}}{\text{mg P in stock sol.} \times \text{per 1000 ml standard}}$$

Both "per 1000 ml" can be cancelled, that means:

$$\text{z ml necessary stock sol.} = \frac{\text{standard vol ml} \times \text{b mg P in standard}}{\text{mg P in stock sol.}}$$

Thus:

$$\text{necessary stock sol. (in ml)} = \frac{\text{standard vol. (in ml)} \times \text{P conc. in standard (in mg L}^{-1}\text{)}}{\text{P conc. in stock sol. (in mg L}^{-1}\text{)}}$$

For the calculation of the necessary volume of the stock solution the necessary standard volume (in ml) is multiplied with the searched P concentration in the standard (in mg P per litre) and divided by P concentration in the stock solution (in mg P per litre).

For our example this means:

$$\text{ml necessary stock sol.} = \frac{\text{100 ml standard} \times \text{2 mg P per l in standard}}{\text{1000 mg P per L in stock sol.}} = \text{0.2 ml stock sol.}$$

For both of the other standards 0.4 and 0.6 ml of the stock solution are necessary. After the pipetting of the stock solution in the volumetric flask the standards are filled by the necessary solution. It has to be paid attention that the stock solution has room temperature for the setting of standards, since the temperature changes the density and therefore, the volumes would be pipetted but not the necessary mass of the P!

For the **dilution of acids** or other chemicals the procedure is generally the same. Room temperature of the used chemicals is a prerequisite as well. Additionally, it has to be considered that first the water and subsequently the acid or base is filled into the flask! This means: after calculation of the necessary acid or base volume, the necessary water volume has to be calculated. A little bit less than the calculated water volume is filled into the volumetric flask. For a 1 litre volumetric flask that means for example 50 to 100 ml less water. After the water is filled the acid or base is added carefully. After cooling down of the solution the water is filled to the calibration mark. On bottles with concentrated acid the concentration is specified in % as well as in mol per litre. Therefore, it can be calculated for searched concentrations in % as well as in mol per litre.

The following calculation is possible:

$$\text{searched vol. of initial sol. (ml)} = \frac{\text{conc. of searched solution (M or \%)} \times \text{their necessary vol. (in ml)}}{\text{conc. of initial solution (M or \%)}}$$

General formula for dilution of solutions:

$$V_A = \frac{C_B \times V_B}{C_A}$$

V_A = searched volume of initial solution (e.g. in ml)
V_B = necessary volume of diluted solution (e.g. in ml)
C_A = concentration of initial solution (e.g. in mg element per litre)
C_B = concentration of diluted solution (e.g. in mg element per litre)

Example for dilution of an acid:
Initial acid conc. HCl: 37 % or 12 M per litre
searched: 1 litre 10 % HCl or 1 M HCl

solution for 10 % HCl:

$$\text{searched vol. of initial sol. (ml)} = \frac{10\ \% \times 1000\ \text{ml}}{37\ \%} = 270.27\ \text{ml}$$

For a 1 litre volumetric flask 270.27 ml conc. HCl are necessary. First, 600 to 700 ml water are filled into the volumetric flask. Subsequently, 270.72 ml of conc. HCl are added. After cooling down it has to be filled with water to the calibration mark.

Solution for 1 M HCl:

$$\text{searched vol. of initial sol. (ml)} = \frac{1\ \text{M} \times 1000\ \ \text{ml}}{12\ \text{M}} = 83.33\ \text{ml}$$

For a 1 litre volumetric flask 83.33 ml conc. HCl are necessary. First, 750 to 850 ml water are filled into the volumetric flask. Subsequently, 83.33 ml of conc. HCl are added. After cooling down it has to be filled with water to the calibration mark.

Detailed example: 1 litre of a 10 % HCl solution has to be made from conc. HCl (37 %). How many ml of the conc. HCl have to be pipetted into a 1 litre volumetric flask?

Given: 37 % HCl Searched: 1 litre of 10 % HCl

Shortened steps of solution analogous to setting of calibration standards:

- In a 37 % HCl are 37 ml HCl ions in 100 ml of the solution. That means that in 1 ml of the conc. HCl solution are 0.37 ml of HCl ions.
- If I want to make a 10 % HCl, there have to be 100 ml of HCl ions in 1 litre solution.

Question: How many ml of the conc. HCl are necessary to add 100 ml HCl ions into a 1 litre volumetric flask? This can be calculated by a ratio equation:

$$\frac{0.37\ \text{ml HCl}}{1\ \text{ml conc. HCl solution}} = \frac{100\ \text{ml HCl}}{x\ \text{ml conc. HCl necessary}}$$

Conversion to search x ml of the conc. HCl means:

$$x\ \text{ml conc. HCl necessary} = \frac{100\ \text{ml HCl} \times 1\ \text{ml conc. HCl solution}}{0.37\ \text{ml HCl}}$$

Therefore, 270.27 ml of conc. HCl are necessary and have to be given into the 1 litre volumetric flask and filled with water to get a 10 % HCl. However, first the water has to be added and subsequently the acid. First, estimate how many ml of water are approximately necessary to fill to 1 litre. 1000 ml necessary solution minus around 271 ml acid means 729 ml water. Fill 600 to 700 ml water and then the acid into the flask. After cooling down fill with water to calibration mark.

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