Using first and second derivative for determination of the inflexion point

When determining the inflexion point of curve, we search for the maximum value of the slope of curve, in other words the **maximum of the first derivative** that belongs to the inflexion point (IP). Also, the value of the **second derivative is equal to 0** at this point. Depending on the type of measurement IP can be named differently e.g. equivalence point (titration).

In this example we set variable ***A*** (it usually, but not necessarily, has constant increment e.g. time between the measurements or volume of added reagent) and variable ***B*** (measured quantity – pH, voltage etc.).

When computing the IP we usually use the **differential table** (see Tab. 1 with example data). Using two subsequent data points value of the **first derivative (*B´*)** can be calculated as:

$$B' = \frac{dB}{dA} = \frac{B_2 - B_1}{A_2 - A_1} \qquad \text{(Eq. 1)}$$

BEWARE! – B' value is not coupled to A_1 or A_2 (usual mistake) but to the A^* value:

$$A^* = \frac{A_1 + A_2}{2} \qquad \text{(Eq. 2)}$$

and it is arranged in between the two data point rows (see Tab. 1). Values of the **second derivative (*B´´*)** are computed out of the subsequent 1st derivative values in the same manner:

$$B'' = \frac{d^2B}{dA^2} = \frac{B_2' - B_1'}{A_2^* - A_1^*} \qquad \text{(Eq. 3)}$$

Again **BEWARE! –** B'' value is coupled to the A^{**} value:

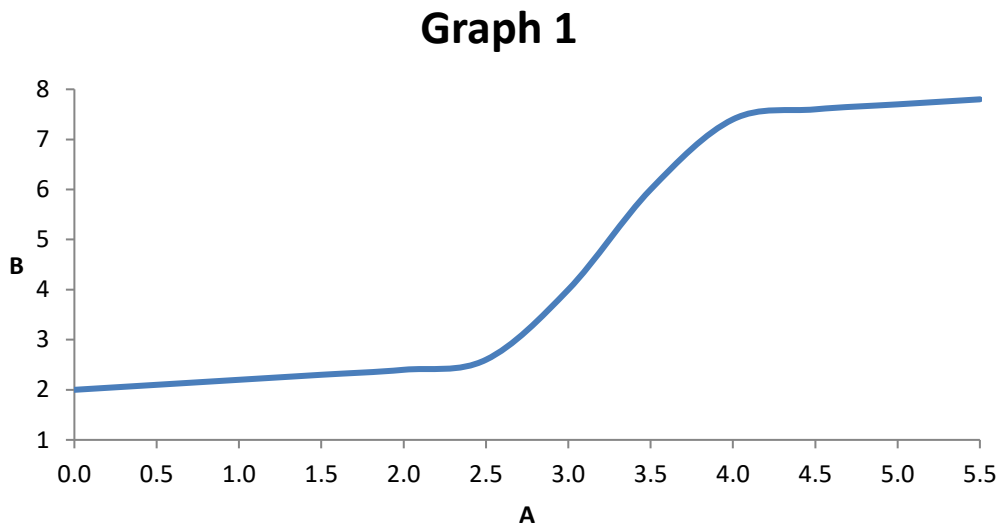
$$A^{**} = \frac{A_1^* + A_2^*}{2} \qquad \text{(Eq. 4)}$$

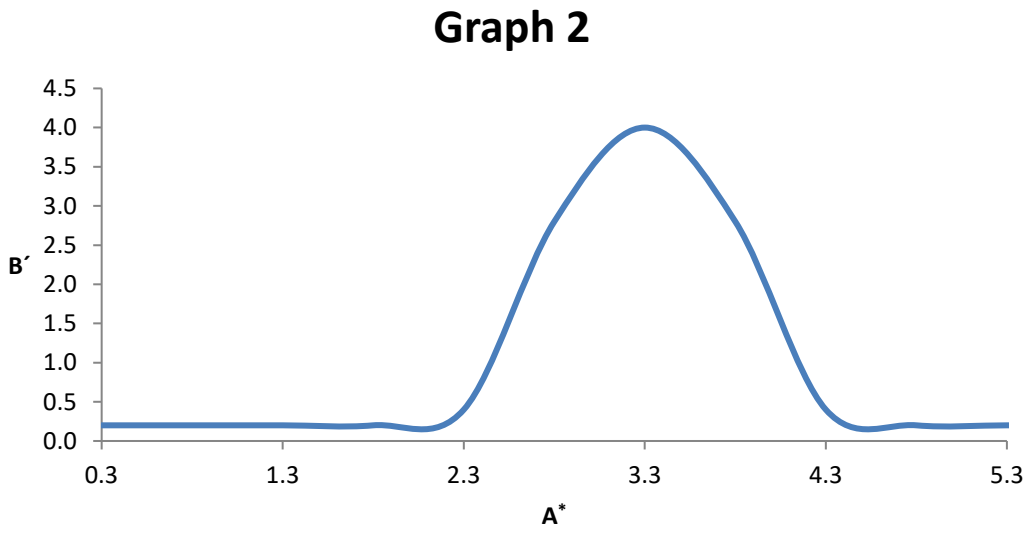
and it is arranged in between the two 1st derivative rows (e.g. on the same line with the original data points)

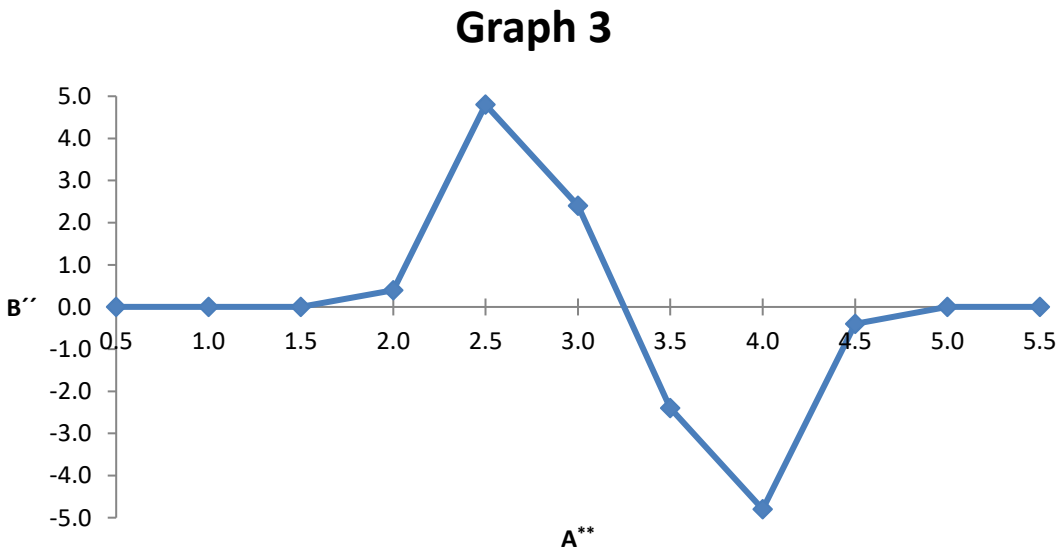
Tab. 1

Data points (**Graph 1**)		1st derivative curve points (**Graph 2**)		2nd derivative curve points (**Graph 3**)	
A	***B***	A^*	B'	A^{**}	B''
0.0	2.0				
		0.25	0.2		
0.5	2.1			0.5	0.0
		0.75	0.2		
1.0	2.2			1.0	0.0
		1.25	0.2		
1.5	2.3			1.5	0.0
		1.75	0.2		
2.0	2.4			2.0	0.4
		2.25	0.4		
2.5	2.6			2.5	4.8
		2.75	2.8		
3.0	4.0			3.0	2.4
		3.25	4.0		
3.5	6.0			3.5	-2.4
		3.75	2.8		
4.0	7.4			4.0	-4.8
		4.25	0.4		
4.5	7.6			4.5	-0.4
		4.75	0.2		
5.0	7.7			5.0	0.0
		5.25	0.2		
5.5	7.8				

Example graphs:







IP is found at the **intersection** of the **2nd derivative curve** and the ***x* axis** (Graph 3), i.e. at the point where **2nd derivative value equals 0**. Apart from graphic determination of the IP, its location can be also found computationally (**it is also <u>more precise</u>**). We take the last positive and the first negative value of B´´ and use them to compute the intersection between the A_1^{**} and A_2^{**} points:

$$A_{IP} = A_1^{**} + B_1^{''} \frac{A_2^{**} - A_1^{**}}{\left|B_1^{''}\right| + \left|B_2^{''}\right|} \qquad \text{(Eq. 5)}$$

→ using example data (blue in Tab. 1): $A_{IP} = 3 + 2.4 \frac{(3.5 - 3)}{\left|2.4\right| + \left|-2.4\right|} = \underline{3.25}$

If the derived data points are equidistantly spaced i.e. dA value is constant, it is possible to substitute derivatives by simple differentials (ΔB = B2 – B1), without the need of dividing them by the dA value. Computing the A^* and A^{**} value is also redundant. However it is still crucial to place the values of the 1st and 2nd derivative in between the proper rows, so that the 2nd derivative fits the proper initial A values. Misplacing of derivatives is a common mistake that leads to finding the wrong A value as it is shifted by the dA value. For this reason **<u>we strongly recommend you to compare the computed value with the graphic one.</u>**

Another way to simplify this process is to use only a few nearest data points around the IP. For this experimental data it would be sufficient to use only the A values between 2 and 4.5.

PROCEDURE

task 2 Potentiometric determination of dissociation constant

task 3 Nephelometry

- Calculate the differential table (such as a Tab. 1) for measured data using given equations (Eq. 1 – 4)
  A stands for **volume** in case of task 2 and **time** in case of task 3.
  B stands for **pH** in case of task 2 or **voltage** in case of task 3.
- Calculate the inflexion point using the values from differential table (Eq. 5).
- Construct the graphs of measured data and the 1st and the 2nd derivative (such as the graph 1, 2 and 3).
- Visually compare the computed value of IP with the graphic one.