Exercise: Potentiometric titration of halogenides

Simultaneous determination of iodide, bromide and chloride anions by potentiometric titration is based on the difference in the solubility of their respective silver salts. By titrating with a volumetric solution of silver nitrate, the least soluble AgI ($K_s = 10^{-16}$) is precipitated first, then AgBr ($K_s = 10^{-13}$) and finally AgCl ($K_s = 10^{-10}$). By titrating a sample containing all three halogenides, a potentiometric curve with three potential steps is obtained (Fig. 1)

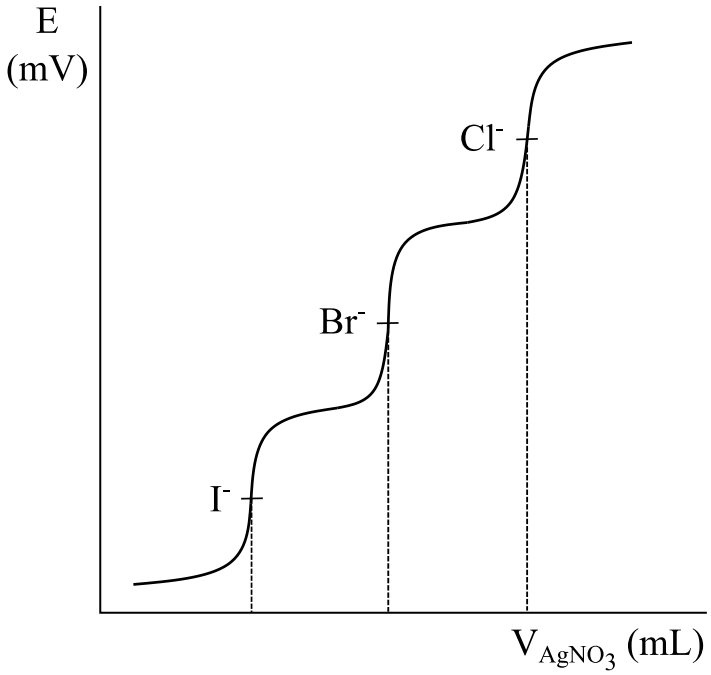


Figure 1 – Simultaneous potentiometric titration of iodide, bromide and chloride

The volume of the added titrant up until the first potential step corresponds to the amount of iodide, the difference of volumes between the first and the second potential step corresponds to the amount of bromide, and finally the difference of volumes between the second and the third potential step corresponds to the amount of chloride. Simultaneous determination of all three halogenides is feasible under certain conditions. Determination of iodide in the presence of chloride can be performed with ease. During the titration, a solution of barium nitrate is added to prevent the formation of colloid solution, which would cause a loss of sharpness of potential steps.

Instrumentation: combined silver indicator electrode with inner reference electrode, voltmeter with temperature sensor, magnetic stirrer, laboratory glassware, tweezers

Chemicals and solutions: silver nitrate solution c($AgNO_3$) = 0.03 M; barium nitrate solution c($Ba(NO_3)_2$) = 1% (CAUTION: highly toxic); potassium chloride standard solution c(KCl) = 0.01336 M; unknown sample solution; distilled water

Procedure:

Between each titration the electrode, the temperature sensor and the magnetic stirrer should be thoroughly cleaned with distilled water!

Standardization of the volumetric solution of silver nitrate

25 mL of *potassium chloride standard solution* is transferred to a beaker, followed by 5 mL of *barium nitrate solution*. The whole mixture is diluted with distilled water to a volume of approximately 70 mL. The solution, vigorously stirred, is titrated with *silver nitrate solution*. The titration is performed in duplicate. The first titration is performed by adding larger volume increments (1 mL) to estimate the equilibrium volume. During the second titration, the titrant is added in smaller volume increments (0.1 mL) near the equilibrium point (starting 1 mL before the expected equilibrium point; see also Table 1). The endpoint is determined by the general procedure for potentiometric titrations (see Endpoint determination in potentiometric titrations). The true concentration of the volumetric solution is then calculated.

Determination of iodide and chloride in an unknown sample

10 mL of *sample solution* is transferred into a beaker. Then 10 mL of *barium nitrate solution* are added and the whole mixture is diluted with distilled water to approximately 70 mL. The titration is performed analogically to the standardization titration, but it is done in triplicate. First titration serves to estimate the equilibrium volumes, then two titrations with smaller volume increments near the equilibrium points are performed. The amount of iodide and chloride in the sample is calculated using the volume of titrant in the equilibrium points (see Endpoint determination in potentiometric titrations).

Conclusion: The laboratory report should include the table of the measured potential values with the corresponding volumes of titrant, as well as the resulting potentiometric curve. The amount of iodide and chloride should be given in milligrams per 100 mL of sample.

Endpoint determination in potentiometric titrations

During the titration process, the change in potential per volume unit of added titrant is gradually increasing up to the equivalence point, where it reaches its maximum value. In case of symmetrical titration curves, the equivalence point corresponds to the inflexion point of the curve. The symmetry of the curve and its steepness (expressed as the value of the slope of $\Delta E/\Delta V$ in the equivalence point) depend on the properties of reactants, their concentrations and on the equilibrium constant of the corresponding chemical reaction. Near the equivalence point, it is useful to add the titrant in smaller volumes as it makes the determination more accurate. The equivalence point can be determined graphically (Fig. 2), or it can be calculated.

The easiest way to determine the value of the equivalence point by calculation is to calculate $\Delta E/\Delta V$ for each addition of the titrant. The equivalence point is then calculated as the mean value of two consecutive additions, where $\Delta E/\Delta V$ reaches maximum value.

More accurate calculation can be done using the second derivative $\Delta^2 E/\Delta V^2$. In the inflexion point, the second derivative is equal to zero. The zero value lies between the last positive and the first negative value of $\Delta^2 E$. The equivalence point is then calculated using an interpolation formula:

$$V_{eq} = V_1 + (V_2 - V_1)\frac{a}{a-b} \qquad \text{(x)}$$

where V_1 is the volume of the added titrant before the maximum value of $\Delta E/\Delta V$, V_2 is the volume of the added titrant after the maximum value of $\Delta E/\Delta V$, a is the last positive value of $\Delta^2 E/\Delta V^2$ (corresponding to the volume V_1), and b is the first negative value of $\Delta^2 E/\Delta V^2$ (corresponding to the volume V_2). An exemplary calculation is shown in Table 1.

Today, commercially available automatic titrators, often equipped with an autosampler, are operated by a computer and the whole titration process along with the endpoint determination are done automatically.

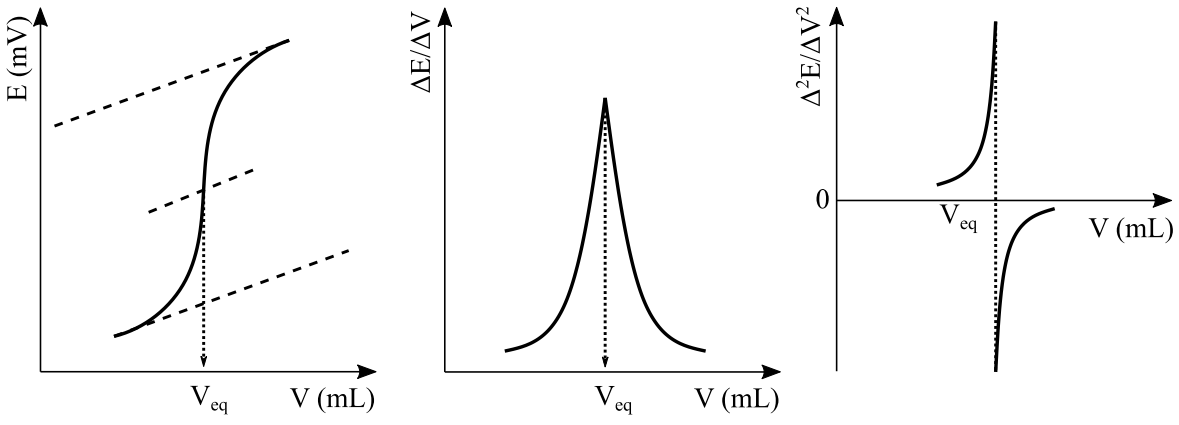


Figure 2 – Different approaches for equivalence point determination

Table 1 – Model titration data with calculation of the equilibrium point

V (mL)	E (mV)	$\Delta E/\Delta V$	$\Delta^2 E/\Delta V^2$	
10	126			
		13		
11	139		3	Calculation of the equilibrium point using the maximum value of $\Delta E/\Delta V$
		16		
12	155		44	$\frac{12.2 + 12.3}{2} = 12.25$ mL
		60		
12.1	161		120	
		180		
12.2	179		20	
		200		Calculation of the equilibrium point using the interpolation formula
12.3	199		-40	
		160		
12.4	215		-90	$12.2 + (12.3 - 12.2)\frac{20}{20 - (-40)}$
		70		
12.5	222		-42	$= 12.23$ mL
		28		
13	236		-16	
		12		
14	248			