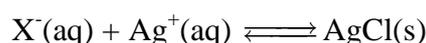


KJ 2051**Potentiometric titration of Cl⁻ and Br⁻**

By F.G. Banica, September 6, 2006

Goal: determination of title ions in a sample containing both of them.**Principles.** The sample solution will be titrated against a Ag⁺-containing solution. Ag⁺ reacts with halide ions (X⁻) to form sparingly soluble salts:

Solubility constants are 5.2×10^{-13} for AgBr and 1.8×10^{-10} for AgCl. Therefore, if the sample contains both Cl⁻ and Br⁻, AgBr precipitates first and Ag⁺ concentration increases gradually until all Br⁻ turns into AgBr. Then, Ag⁺ concentration increases suddenly to a higher level which is determined by AgCl solubility and AgCl starts to form. Ag⁺ concentration jumps again when AgCl precipitation was completed and free Ag⁺ ions accumulate in the solution (see Fig. 2).

It results that the progress of the titration can be monitored by checking Ag⁺ concentration. This can be accomplished by means of an indicator silver electrode. When dipped in a Ag⁺ containing solution, the electrode assumes an electric potential which is a function of Ag⁺ concentration according to Nernst equation:

$$(1) \quad E = E^0 + \frac{2.303RT}{F} \log_{10} [Ag^{+}] = E^0 - \frac{2.303RT}{F} pAg$$

Measurement of E provides therefore information about the change of Ag⁺ concentration during the titration. In order to perform E measurements, the indicator electrode should be combined with a reference electrode. Such an electrode contains as rule a concentrated KCl solution which can leak and contaminate the sample with additional amounts of Cl⁻, leading to a positive error in Cl⁻ determination. Contamination can be prevented if the reference electrode is dipped into another solution which is connected to the sample by means of an electrolyte bridge, like the Agar bridge (Fig. 1). The voltage of this cell will be measured by a mV-meter and plotted against the added silver nitrate volume to obtain the titration curve (Fig. 2) using either the initial data (upper curve) or its derivative (lower curve). Calculation of the derivative is illustrated by Fig. 3 (see on It's learning the Excel file with an example of calculation). The derivative provides a more reliable estimation of the equivalence volumes, (V_e).

In principle, the equivalence volume is proportional to the halide amount in the sample according to the stoichiometry of the chemical reaction:

$$(2) \quad m_X = V_{e,X} C_{AgNO_3} M_X \frac{V_{sample}}{V_{aliquot}}$$

Here, $V_{e,X}$ is the equivalence volume (in liter), C_{AgNO_3} is the concentration of silver nitrate (in mol/l) and M_X is the molar weight of the halogen (g/mol), $V_{aliquot}$ is the volume of the titrated aliquot (0.025 ml in this case) and V_{sample} is the overall volume of the sample.

However, a problem appears due to the relatively low difference in solubility between AgBr and AgCl. This makes AgCl precipitation to start up before the complete precipitation of AgBr was achieved and brings about a slight deviation from the stoichiometric ratio. In order to circumvent this problem, a standard solution will be first titrated in order to estimate the proportionality coefficients for Br⁻ and Cl⁻ (k_{Br} and k_{Cl} , respectively) as follows:

$$(3) \quad k_X = \frac{m_X}{V_{e,X}^s}$$

Here, m_X represent the amount of halide ion in the standard sample (in grams) whereas $V_{e,X}^s$ stands for the equivalence volumes determined with the standard sample. The above coefficients will be used to calculate the amount of halide in the unknown sample aliquot by means of the equivalence volume ($V_{e,X}^u$):

$$(4) \quad m_{X,u} = k_X V_{e,X}^u$$

The above value should be multiplied by ($V_{sample} / V_{aliquot}$) in order to find out the amount of halogen in the initial sample.

Experimental Procedure

1. Prepare first the agar bridge as follows.

4 g bacto-agar løses i 100 ml 1 M KNO₃ nær kokepunktet. Når blandingen er klar og fri for luftblærer, helles den øyeblikkelig i U-røret og settes bort til avkjøling og stivning.

250

2. Prepare the standard solution as follows: Add to an ~~150~~ ml beaker 15 ml 0.02 M KCl and 15 ml 0.02 M KBr solutions (use a buret for each solution), then 75 ml acetate buffer¹ (use a measuring cylinder). Perform the titration with 0.02 M AgNO₃ by means of the set-up depicted in Fig. 1. The solution should be stirred during the titration. Record the results (electrode potential vs. total added volume) in a table like that presented in Fig. 3. To begin with, add each time about 1 ml silver nitrate. When the potential variations are very high (i. e. in the region of the equivalence volume) add as small volumes as possible. Do not bother to adjust carefully the volume, but read it out very accurately.

3. The unknown sample is delivered in a calibrated flask of 250 ml. Made it up to the mark with pure water, stir the solution and transfer 25 ml to a 150 ml beaker. Add 75 ml acetate buffer and titrate the solution as before.

¹ The acetate buffer (0,1 M NaAc/HAc) maintains the pH at about 4.8. It prevents thus the interference of the hydroxyl ion which may react with Ag⁺ to form silver hydroxide.

Data processing and calculations

1. Plot the titration curves for the standard and unknown sample. See the file “Experiment No 2: Calculation example” on It’s learning for orientation. each graph should be plotted on a FULL A4 FORMAT in the Landscape disposition.
2. Find out the equivalence volumes.
3. Calculate the amount of each halogen ion in the unknown sample with no correction for co-precipitation (Equation (2)) and the deviations from expected values².
4. Calculate the proportionality coefficient by means of Equations (3).
5. Calculate the amount of Br (antall gram bromid-ikke KBr) and Cl (antall gram klorid-ikke KCl) in the whole unknown sample with correction for co-precipitation (Equation (4)) and the deviation from the expected values.
6. Report the amount and deviation for each halide ion calculated as in entry 3 and 5. Collect the results in a Table like Table 1 below. Compare the deviations and discuss the results.

IMPORTANT: Do not limit yourself to the present document when writing the theory part of your report! Go to the recommended literature and try to present your personal point of view.

Do not use the copy/paste computer functions! Do yourself everything that is included in the lab report.

Table 1. Results of Br⁻ and Cl⁻ determination by titration with silver nitrate

1) With no correction for co-precipitation (eqn. 2)	Amount, g	Cl	Br
	Expected, g		
	Deviation, %		
<hr/>			
2) With correction for co-precipitation (eqn. 4)	Amount, g		
	Deviation, %		

References

1. KJ 2051: Pensum og laboratoriekurs.
2. D.A. Skoog, D.M. West, F.J. Holler and S.R. Crouch, Fundamentals of Analytical Chemistry, Brooks/Cole, 2004, Sections 13F-1, 13F-2, 21 A,21B, 21 D-1, 21G (Introduction and 21G-1).

² Deviation(%) = 100(Found – E xpected) / Expected

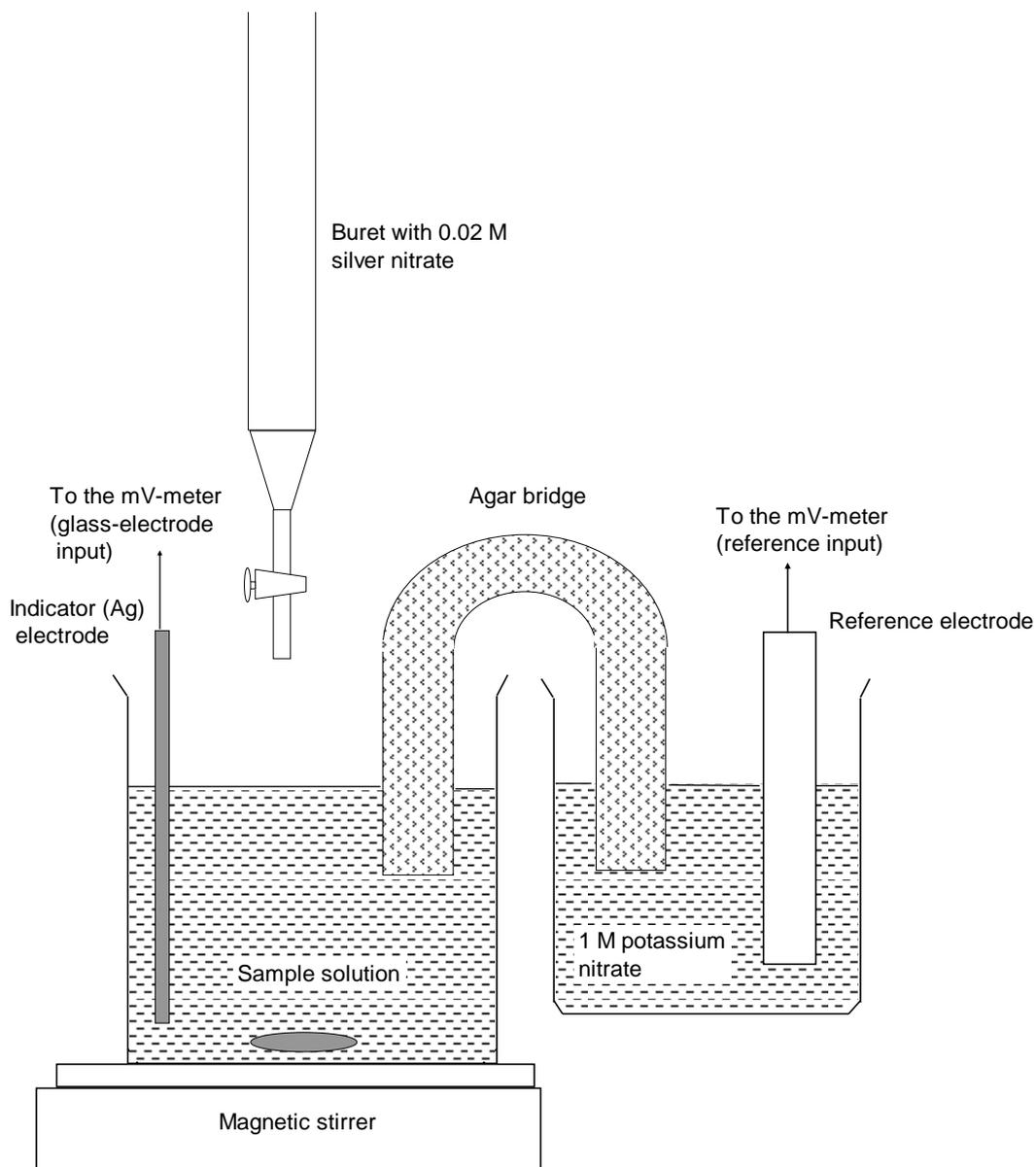
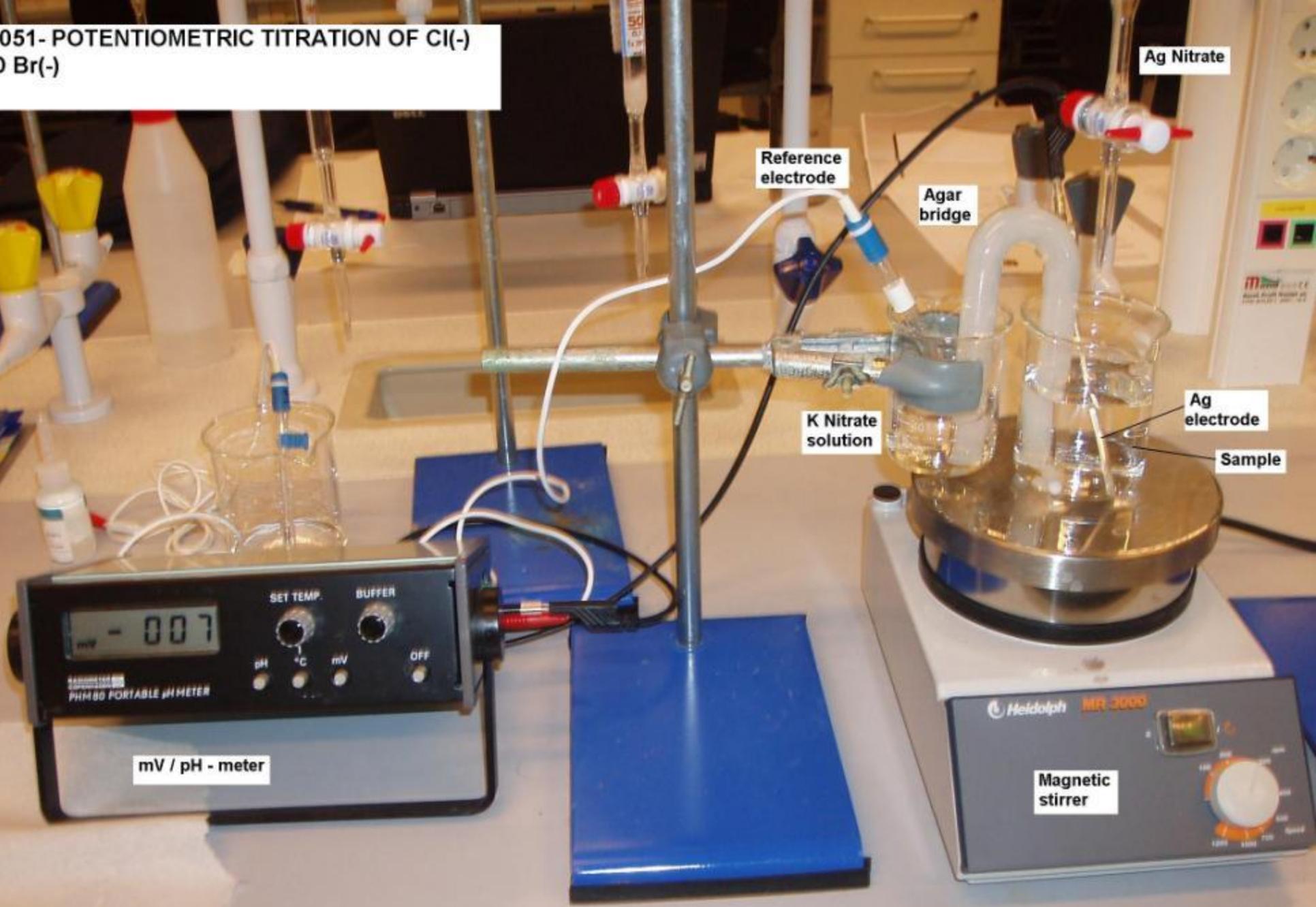


Fig. 1. Schematics of the experimental set-up for potentiometric titration by a silver nitrate solution.

**KJ2051- POTENTIOMETRIC TITRATION OF Cl(-)
AND Br(-)**



Ag Nitrate

Reference electrode

Agar bridge

K Nitrate solution

Ag electrode

Sample

SET TEMP. BUFFER
- 007
pH °C mV OFF
PHM 80 PORTABLE μ H METER
mV / pH - meter

Heldolph MR 3000
Magnetic stirrer

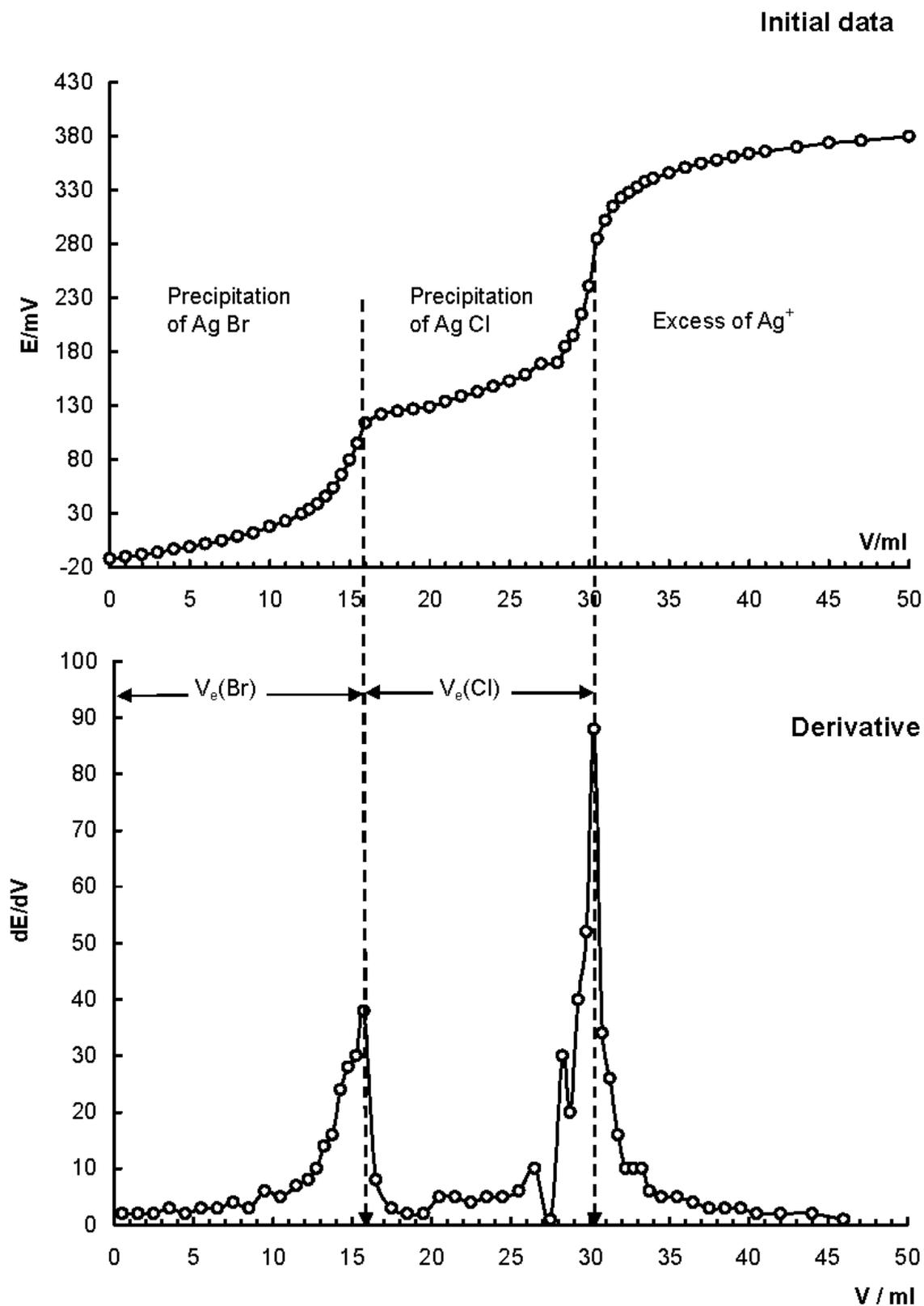


Fig. 2. Titration curve: initial data (up) and derivative (down).

1.Titrering av 15 ml KCl(0,02M) + 15 ml KBr(0,02M)				
Opprinnelig		Derivert		
V, ml	E, mV	V(mid),ml	dE/dV	
0	-12			
1	-10	0.5		2
2	-8	1.5		2
3	-6	2.5		2
4	-3	3.5		3
5	-1	4.5		2
6	2	5.5		3
7	5	6.5		3
8	9	7.5		4
9	12	8.5		3
10	18	9.5		6
11	23	10.5		5
12	30	11.5		7
12.5	34	12.25		8
13	39	12.75		10
13.5	46	13.25		14
14	54	13.75		16
14.5	66	14.25		24
15	80	14.75		28
15.5	95	15.25		30
16	114	15.75		38
17	122	16.5		8

Fig. 3. Calculation of the derivative curve data. See also the "Calculation example" file on It's learning.