KJ 2051

Fluoride determinations by an ISE

Theory and Procedure

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Theory

A cell with the following structure will be employed in this experiment (ISE stands for Ion Selective Electrode)

ISE | Test solution | Reference electrode

The cell voltage depends on fluoride activity (a) as follows:

(1) $E = E_0' + s(\log a)$

where E_0' and s are constants (s is the ISE sensitivity[1]). The activity is proportional to the concentration, c:

(2) $a = \gamma\, c$,

where γ is the activity coefficient of F^-. If the ionic strength[2] is kept constant (by adding an excess of indifferent electrolyte) γ will be independent on F^- concentration and can be included in the constant term E_0 in the following equation, which represents *the calibration function*:

(3) $E = E_0 + s \log c$

Here E is the cell voltage, c is fluoride concentration (M) and E_0 is a constant for a given pair of fluoride- and reference electrodes. The sensitivity can be calculated as the slope of the calibration function:

(4) $s = \Delta E \,/\, \Delta\left(\log c\right)$

Method No. 1 (Direct determination). Fluoride concentration will be calculated by means of calibration data (i.e. E_0 and s that were determined by means of a series of standard solution) and using the following equation:

(5) $\log c = (E_u - E_0)/s$

where E_u is the cell voltage for the unknown sample.

Method No. 2 (Standard addition): the voltage will be measured before (E_1) and after (E_2) adding V_a ml of standard solution (concentration c_a) to the unknown sample with the volume V and concentration c. It results, according to equation (3):

(6) $E_1 = E_0 + s \log c$

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[1] The theoretical sensitivity is $2.303RT/zF$, where R = gas constant; T = absolute temperature; z = ion charge; F = Faraday constant.

[2] Ionic strength depends on the concentration and charge of each ion in the solution and is defined as $\mu = 0.5\sum_i z_i^2 c_i$,

where z and c represent the charge and concentration of each ion, i.

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(7) $\quad E_2 = E_0 + s \log \dfrac{Vc + V_a c_a}{V + V_a}$

where the argument of the logarithm in equation (7) represents fluoride concentration after performing the standard addition. Equation (7) can be converted into a more convenient form if the following symbols are adopted:

(8) $\quad r = V /(V + V_a) \quad \text{and} \quad r_a = V_a /(V + V_a)$

It results thus:

(9) $\quad E_2 = E_0 + s \log\left(rc + r_a c_a\right)$

Equations (6) and (9) form a system with two unknowns: E_0 and c. This system can be solved to find c. If:

(10) $\quad f = (E_2 - E_1)/s,$

Then:

(11) $\quad \boxed{c = \dfrac{r_a c_a}{10^f - r}}$

This method is independent on E_0 and requires only the s value. But it is less accurate than Method No.1 because it relies on only one calibration measurement.

Interferences

At pH >5, the OH^- ion interfere by reacting with the ISE membrane along with F^-. Remember that the EIS can detect <u>free</u> F^- ions only. At pH< 5, F^- turns to HF or H_2F^{+-} that cannot be detected by the ISE. That is why, the pH should be adjusted to about 5 in order to avoid OH^- interference and F^- conversion to HF or H_2F^{+-}. If metal ions (such as Ca^{2+}, Al^{3+}, Fe^{3+} are present in the sample, F^- forms complex compounds and, in this form, it cannot be detected by the ISE. In order to prevent this reaction, a strong complexing agent (e.g. EDTA) should be present On the other hand, sample ionic strength should be similar to that of the standards (see Equations (1) to (3)).

In order to avoid such interferences, TISAB (Total Ionic Strength Adjustment Buffer) should be added to each sample or standard solution. TISAB solution contains three components: (1) a pH buffer to adjust the pH at about 5 (e.g. acetic acid - sodium acetate); (2) a metal ion binding component (e.g. citric acid or EDTA) to prevent F^- binding to metal ions; and (3) an inert salt (e.g. NaCl or KNO_3) which provides a background of constant ionic strength.

Procedure

1. Calibration. Prepare a standard solution by dissolving about 1 g NaF (accurately weighed) in 500 ml water (calibrated flask). Prepare 5 diluted standard solutions in volumetric flasks of 100 ml. To each flask add 10 ml TISAB solution (by a measuring cylinder) and different volumes of standard fluoride solution (by a burette) according to the Table 1. Add pure water to the mark. Transfer an aliquot of each solution to a dry beaker (of 100 to 150 ml), immerse the fluoride- and reference electrodes in the sample (gently stirred), read the cell voltage (E, mV) when it is stable and recorded it in Table l. Plot the E vs. $\log(c)$ graph and draw the calibration line by means of the least squares method (use Microsoft Excel). Record the **slope** and the **intercept** for of this line. Record also the *laboratory tempeature*.

Table 1. Calibration data

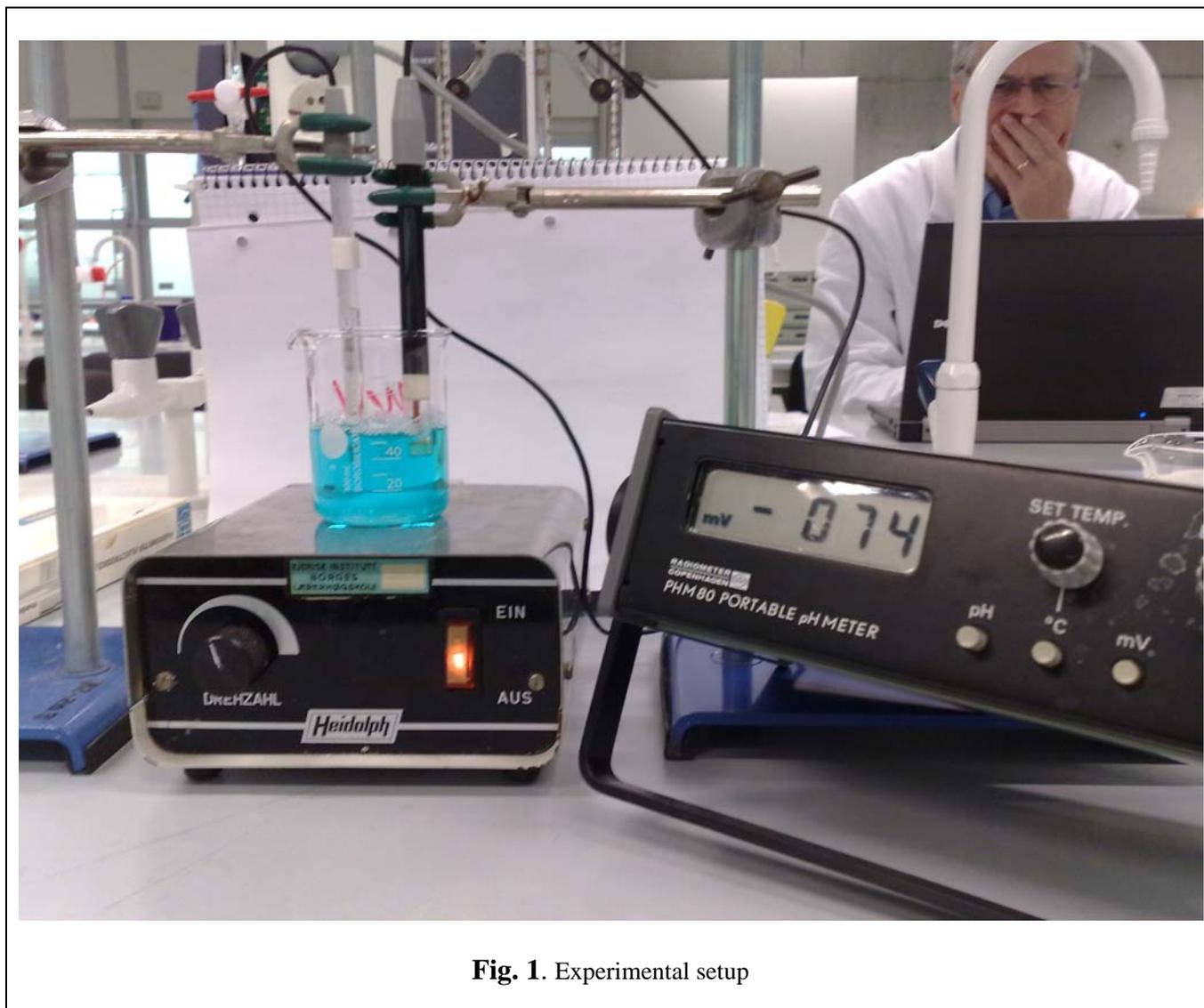| Standard No.	V_s / ml	c / M	log$c$	E / mV
1	0.5			
2	1.5			
3	5			
4	15			
5	50			

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Fig. 1. Experimental setup

2a. Determination of F⁻ in a synthetic sample

Method 1. Transfer 25 ml of the unknown sample (previously diluted to 250 ml) to a 100 ml volumetric flask; add 10 ml TISAB and pure water to the mark. Transfer accurately 50 ml of this solution to a dry beaker, immerse the electrodes and read out the voltage (E_u). Calculate fluoride content using equation (5).
Remark: an accurate measurement of the aliquot volume is necessary *only if* Method 2 is supposed to be employed next. Otherwise, the aliquot volume is meaningless.

Method 2. Add (by a burette) a small volume of standard solution to the above sample so that the voltage changes by 10 to 15 mV. Record accurately the added volume and the final potential. Calculate F⁻ concentration by equation (11).

2b. Determination of F⁻ in a real sample. The effect of the F⁻ chemical state

Take 50 ml mouth wash in a 100 ml flask. Add 10 ml TISAB and water to the mark.
Take an aliquot of the above solutions and find fluoride concentration by the method No. 1. Report the result as percent of fluoride in the original sample (assume that the sample density is 1). Calculate the deviation from the

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claimed content. Do not forget sample identification (name and supplier of the product)! For example, Colgate Total Mundskyl claims an F^- content of 0.011 %[3].

Repeat the above determination by using a TISAB solution which <u>does not contain citrate</u>. Assess the difference between the results and comment it.

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 own point of view.*

Results
Perform the calculation as shown in the Calculation example Excel file on it's learning.
Report the following values:
1. ISE sensitivity (theoretical value-s_t, see footnote 1; and experimental value, s), and s as percent of s_t, i.e $100s/s_t$.
2. Fluoride content in the unknown synthetic sample (in g) as determined by each of the above methods (deviation included for each method).
3. Fluoride content in the real sample (e.g. mouth wash) and its percent deviation from the claimed value, i.e. 100(found-claimed)/claimed).

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, Section 21D. Se also pp. 1097-1098 (on CD).

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[3] Fluoride content is sometimes available as ppm (parts per million, 1ppm = 1 mg/Kg). A diluted solution has a density close to that of pure water, therefore 1 ppm = 1 mg/liter.