Solid-state composite reference electrodes: Evaluation in different applications.

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Introduction

A chemical senor is an analytical device that converts chemical information (Presence of a particular ion, concentration of a certain substance, chemical activity, partial pressure…) into a useful signal. Chemical sensors have attracted much interest in the last years and their fields of application ranging from food industry and environmental monitoring to biomedical research. As a matter of fact, they offer many advantages over conventional analysis, namely their relatively low cost of manufacturing, simple design and possibility of miniaturization as well as fairly good metrological parameters such as sensitivity, measurement range, linearity and response time [1].

Among these devices, potentiometric sensors occupy an important place in the field of electrochemistry and they are still following the new trends of development in any research area given their ease of use comparing to other analytical instruments. For instance, potentiometric devices come in the first rank in the new emerging wireless sensing applications. They account for 21% of the published scientific works in the area of wireless sensors in the last decade [2].

Reference electrodes are a cornerstone of any potentiometric measurement. Yet, this research area remains behind ion-selective electrodes. Nevertheless, interest is growing in improving the performance of the existing reference electrodes and the development of novel reference electrodes in order to avoid problems related to the presence of the inner filling solution. These problems are, among others, maintaining the level of the inner filling solution, leaking of the inner filling solution to the sample, and having the reference electrode only in vertical position which limits the possibilities of effective and reliable field analysis. Solid-state reference electrodes might be a good alternative for eliminating these problems.

In this thesis, newly manufactured solid-state composite reference electrodes have been tested in different synthetic solutions as well as in real environmental and food samples with complex matrices in order to assess the possible influence of pH, solution composition, as well as the concentration and mobility of ions. Stability studies were also performed in order to evaluate the suitability of the studied solid-state composite reference electrodes for continuous, prolonged, and intensive usage.

Literature Review

1. Potentiometry

In most electrochemical measurements, both reference and working electrodes are essential. The working principle of potentiometric measurements is based on the fact that the potential of the working electrode depends on the concentration of the measured analyte, while the reference electrode must maintain a constant potential regardless of the composition of the sample of interest. What is measured is the potential difference (or the Electromotive Force, EMF) between the indicator (working) and the reference electrodes [3].

A typical set-up for potentiometric measurement using a conventional ion selective electrode (ISE) as the indicator electrode is shown in Figure 1 [Adapted from 4].

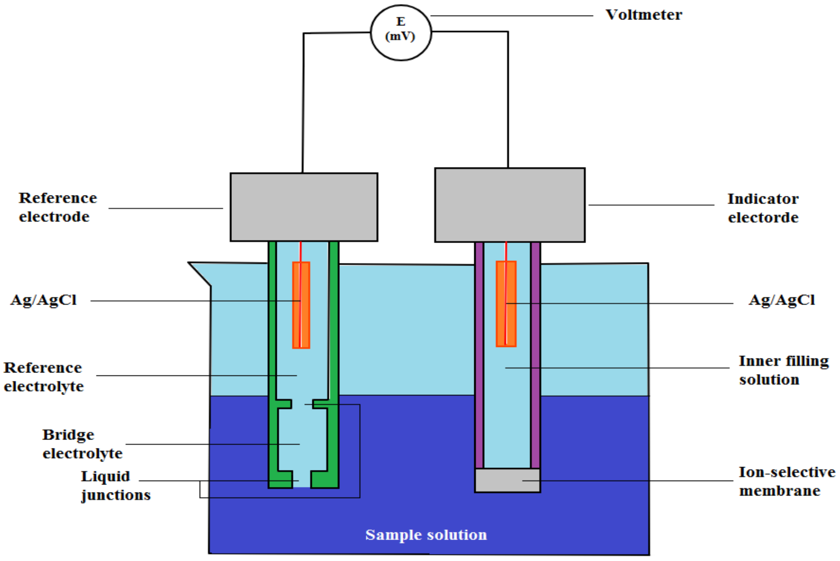


Figure 1. A typical set-up for potentiometric measurement.

The following equation gives the magnitude of the potential signal from an electrochemical cell where an ISE is used as the indicator electrode:

$$E_{\mathrm{cell}} = E_{\mathrm{ind}} - E_{\mathrm{ref}} + E_{\mathrm{j}} \qquad \text{(eq. 1)}$$

where E_{ind} and E_{ref} are the potentials of the ISE and the reference electrode, respectively.

E_{j} is a potential that is formed at the liquid junction between the internal filling solution of the reference electrode and the sample solution caused by the distinct diffusion mobilities of the ions in the area of that non-selective interface [5]. The liquid junction potential can be estimated by the Henderson equation [6]:

$$E_{\mathrm{j}} = \frac{\sum_{\mathrm{i}}^{\mathrm{n}} \frac{|\mathrm{z_i}|\mathrm{u_i}}{\mathrm{z_i}}[\mathrm{C_i}(\beta)-\mathrm{C_i}(\alpha)]}{\sum_{\mathrm{i}}^{\mathrm{n}} |\mathrm{z_i}|\mathrm{u_i}[\mathrm{C_i}(\beta)-\mathrm{C_i}(\alpha)]} \frac{\mathrm{RT}}{\mathrm{F}} \ln \frac{\sum_{\mathrm{i}}^{\mathrm{n}} |\mathrm{z_i}|\mathrm{u_i}\mathrm{C_i}(\alpha)}{\sum_{\mathrm{i}}^{\mathrm{n}} |\mathrm{z_i}|\mathrm{u_i}\mathrm{C_i}(\beta)} \qquad \text{(eq. 2)}$$

where z_i is the charge of the ion i, u_i is its mobility and C_i is its concentration.α and β represent the two different liquid phases. In this case, the internal filling of the reference electrode and the sample solution.

Although it cannot be completely eliminated, the liquid junction potential can be significantly reduced and kept constant by utilizing a salt bridge that contains an inner filling solution having a high concentration of cations and anions of very similar mobility. Such solutions can be potassium chloride (KCl), lithium acetate (LiOAc) or ammonium nitrate (NH_4NO_3) [5].

The working principle of the indicator electrode is based on the migration of ions from the sample solution that bind selectively with the specific sites of the ion-selective membrane. An electrical potential difference between the ISE and the reference electrode emerges. This resulting potential difference is linearly related to the logarithm of the activity of the ion of interest in the sample solution as illustrated by the Nernst equation [6]:

$$E_{\mathrm{cell}} = E^0 + \frac{\mathbf{RT}}{\mathbf{z_i F}} \ln \mathrm{a_i(aq)} \qquad \text{(eq. 3)}$$

where E_{cell} is the measured potential, E^{o} is the standard potential which depends on the properties of both working and reference electrodes, R is the universal gas constant, T is the absolute temperature, F is Faraday constant, z_i is the charge of the ion of interest i and a_i is the activity of the ion of interest in the solution. The term in bold characters defines the nernstian slope of a value of 59.2/z mV/decade at 25°C. Its value is negative for anions and positive for cations.

In practice, a solution generally contains different types of ions and as selective as the indicator electrode can be, one should take into account that the activity of some interfering ions might affect the activity of the target ion. Therefore, it is important to assess the selectivity of the indicator electrode which can be determined by the Nikolskii-Eisenman equation [6]:

$$E = \mathrm{Const} + \ S \log(a_i\,(aq) + \Sigma\, K_{i,j} a_j (aq)^{\frac{z_i}{z_j}} + DL) \qquad \text{(eq. 4)}$$

where Const is the intercept of the calibration plot which in the ideal case would be Eo of the measured cell,. S is the slope of the calibration plot which in the ideal case is the nernstian slope, $K_{i,j}$ is the selectivity coefficient, DL is the detection limit which is approximately 10^{-6} or 10^{-7} M [6], a_i is the activity of the primary ion (i), a_j is the activity of the interfering ions (j), z_i and z_j are the charges of the primary and interfering ions, respectively.

2. Reference electrodes

As discussed here above, the reference electrode plays as crucial role as an ISE in any potentiometric measurement. An ideal reference electrode should satisfy the following conditions [7]:

- It must be chemically and electrochemically reversible, i.e. it should have a stable potential, independent of the composition of the solution, which is governed by the Nernst equation.
- It must be a non-polarizable electrode.
- The thermal coefficient of potential should as small as possible.

Although no existing electrode fully complies with all three requirements, more and more electrodes are getting closer to the required ideal performance. In this part, the most prominent types of reference electrodes that were or still are in use will be reviewed. First, conventional reference electrodes will be addressed.

2.1. The Standard Hydrogen Electrode

The standard hydrogen electrode, which is considered as the primary standard reference electrode [7], follows the equilibrium equation mentioned here above:

$$\mathrm{H_2 + 2H_2O \rightarrow 2H_3\,O^+ + 2e^-} \qquad \text{(eq. 5)}$$

It is composed of a platinum wire or a sheet of platinum coated with platinum black and an internal filling solution of hydronium ions. The electrode requires a continuous flow of hydrogen gas [7].

Despite of its accurate and highly precise performance, its use is quite limited due its difficult handling. The used hydrogen must be of high purity giving the risk of poisoning of the platinum electrode by gases such as oxygen, hydrogen sulfide (H_2S), arsine (AsH_3), sulfur dioxide (SO_2), carbon monoxide (CO) and hydrogen cyanide (HCN). On the other hand, the use of this electrode is not well-adapted to the analysis of volatile substances than can be easily purged by the gas. Furthermore, metals are likely to be reduced at the electrode surface [8].

2.2. Mercury based electrodes

a. The Calomel (Hg/Hg_2Cl_2) Electrode

The calomel electrode was invented by Ostwald in 1890. It is an electrode of the second kind. More accurately known as the mercury/calomel electrode, it is made of a platinum wire which is in a mixture of mercury (Hg) and mercurous chloride (Hg_2Cl_2), commonly known as calomel. Moreover, an electrolyte solution of KCl or NaCl is added to this mixture [9]. The relevant half-cell reaction is:

$$\mathrm{Hg_2\,Cl_2(s) + 2e^- \rightarrow 2Hg(aq) + 2Cl^-} \qquad \text{(eq. 6)}$$

The main disadvantage of this electrode, like all mercury-based electrodes, is that mercury is highly toxic. In addition to that, measurements are unreliable at high temperatures [9].

b. The Mercury/Mercury (I) Sulphate Electrode

The Hg/Hg_2SO_4 electrode is used in a measurement where chloride must not be present. It plays a prominent role in experiments involving lead–acid batteries [10]. The electrode setup includes a platinum wire inserted into a mixture of liquid mercury and mercury sulphate (Hg_2SO_4). The electrolyte solution may consist of potassium sulphate (K_2SO_4) or mercury sulphate (Hg_2SO_4).The relevant half-cell equation is:

$$\mathrm{Hg_2SO_4(s) + 2e^- \rightarrow 2Hg(aq) + SO_4^{2-}} \qquad \text{(eq. 7)}$$

c. The Mercury/Mercuric Oxide Electrode

The Mercury/Mercuric Oxide Electrode is commonly used to analyse alkaline solutions [11]. The relevant equilibrium equation is:

$$\mathrm{HgO(s) + 2e^- + H_2O \rightarrow Hg(aq) + 2OH^-} \qquad \text{(eq. 8)}$$

2.3. The Silver/Silver Chloride Electrode

The silver/silver chloride (Ag/AgCl) electrode is the most widely used type of conventional reference electrode nowadays given the simplicity of its construction, the reproducibility of the potential and the fact that it does not contain any mercury. Its design is based on a silver wire that is electrochemically or thermally coated with fine silver chloride particles. The inner filling solution in which the coated wire is inserted is either KCl or NaCl [9]. The working principle of this electrode is based on the following half-cell reaction:

$$\mathrm{AgCl(s) + e^- \rightarrow Ag(s) + Cl^-} \qquad \text{(eq. 9)}$$

However, Ag/AgCl electrodes are sensitive to highly alkaline environments ($pH > 10$). Hydroxide ions moving from the sample solution into the electrode inner solution cause the formation of silver oxide and brown/black silver oxide (Ag_2O) instead of the AgCl coating resulting in a significant potential drift [9].

Other types of conventional electrodes such as the copper/copper sulphate ($Cu/CuSO_4$) electrode, pH-based reference electrodes, and the silver/silver sulphate (Ag/Ag_2SO_4) electrode are not in common use [7, 9].

2.4. Solid-state composite reference electrode

In order to avoid the drawbacks due to the inner filling solution, several attempts of developing solid-state reference electrodes for application in solution electrochemistry have been performed. For instance, a gel-like electrolyte [12] as well as a melted salt of potassium chloride [13] have substituted the inner filling solution. Furthermore, promising results were obtained by using a low-resistance material in the electrode junction [14] and even by manufacturing junction-less reference electrodes [15]. In addition, other alternatives such as lipophilic salts [16], conducting polymers [17] and carbon nanotubes [18] contributed to limiting the complications caused by the junction potential. However, the effectiveness of these trials is hindered by some intrinsic limitations such as the narrow pH operational range of junction-less reference electrodes [17]. As a result, conventional reference electrodes still have a better performance in terms of intensive and prolonged usage than solid-state reference electrodes [13].

Nevertheless, new analytical-quality solid-state composite reference electrodes have been introduced and showed comparable results to the traditional reference electrodes [20, 21]. As shown in Figure 2, the Solid-State Composite (SSC) reference electrode is based on a silver/silver chloride reference element enclosed in a polymeric matrix (e.g. polyvinyl acetate) mixed with an inorganic salt (potassium chloride). This composite is the inorganic salt storage material while being in contact with the sample solution.

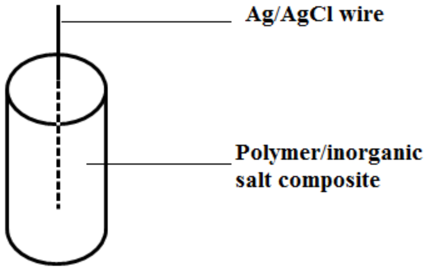


Figure 2. Schematic illustration of the solid-state composite reference electrode.

Whether prepared by injection moulding or chemical polymerization, solid-state composite reference electrodes present a promising alternative to the conventional reference electrodes given the numerous advantages they offer, mainly [20, 21]:

- They have excellent potential stability.
- They have a very low leakage of inorganic salt.
- They are cheap to manufacture and are maintenance-free by eliminating the liquid component from the electrode structure.

- They are robust as they benefit of the physical properties of the used polymers.
- They offer the possibility to operate in other positions than the upright one.

In addition to that, the SSC reference electrode has been successfully tested in an all-solid-state electrochemical device used for potentiometric measurements giving a close response to the theoretical one in both anionic and cationic selective platforms. Furthermore, when the solid state reference electrode was used separately from the platform to analyse a river water sample, the stability of the potential of the tested indicator electrodes was superior to when using a commercial conventional reference. This was explained by the junction clogging of the traditional reference electrode due to the high sediment content of the river water [19].

3. Electrochemical impedance

When a potential difference is applied to a system, the resistance of this system is equal to the potential/current ratio. In the case of applying an alternating current (variable potential) to a system, the same ratio is called impedance [22].

In an electrochemical impedance spectroscopy (EIS) experiment where potential is controlled, the studied system is kept at fixed DC potential (E_{dc}) and a small amplitude sinusoidal excitation signal E (ω) (eq.10) is superimposed on the direct current potential. The occurring sinusoidal alternating current I (ω) is subsequently measured (eq. 11).

$$\mathrm{E}(\omega) = \mathrm{E}\sin(\omega \mathrm{t}) \qquad \text{(eq. 10)}$$

$$\mathrm{I}(\omega) = \mathrm{I}\sin(\omega \mathrm{t} + \Phi) \qquad \text{(eq.11)}$$

In equations 10 and 11, $\omega=2\pi$ f is the angular frequency. In equation 11, Φ is the phase shift between the applied signal and the resulting response. If $\Phi = 0°$, the phase shift is that of a pure resistor. $\Phi = 90°$ is a characteristic of a pure capacitor. $\Phi = 45^{\circ}$ in the case of a Warburg impedance due to diffusion limitation.

The frequency of the potential is varied over several decades and the impedance of the system, which is the E (ω)/ I (ω) ratio, is measured as a function of the frequency [23].

The impedance of a system is usually presented as a vector having a real (Z') and an imaginary (-Z'') component at each frequency in the so-called Nyquist plot (complex-plane impedance plot) as given in Figure 3 [3, 23].

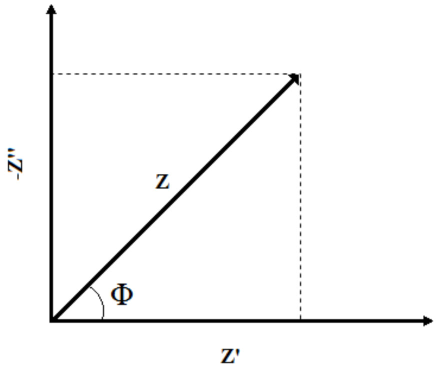


Figure 3. Presentation of the impedance Z in the Nyquist plot. Φ is the phase shift between the applied signal and the resulting response

EIS is a powerful tool to obtain several kinds of information, mainly [24]:

- The resistive behaviour of a given system: electrolyte resistance, polarization resistance, charge transfer resistance.
- The capacitive behaviour of a given system: double layer capacitance, coating capacitance.
- Information about diffusion phenomena.

When compared to other electrochemical methods, EIS presents many advantages [24]:

- Ability to discriminate between several simultaneous electrochemical reactions.
- Possibility to operate in low conductivity environments.
- Higher information content than in a DC technique or any single frequency measurement.
- Use of very small amplitude of signal without disrupting the measured properties.

Materials and Methods

1. Materials

1.1. Chemicals and reagents

All chemicals and reagents used were of analytical reagent grade.

- Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$), Baker Analyzed®, p.a. of ≥ 99.0%, J.T Baker, Holland.
- Deionized water (ELGA, 18.2 MΩ cm)
- Hydrochloric acid 30% (HCl), Suprapur®, Merck, Germany.
- Orion application solutions: pH buffers 4.01, 7.00 and 10.01, Thermo Scientific, USA.
- Potassium chloride (KCl), p.a. of ≥99.0%, Fluka, Switzerland.
- Potassium hydroxide (KOH) Pellets G.R. for analysis, p.a of ≥ 85.0 %, Merck, Germany.
- Sodium bicarbonate ($NaHCO_3$), p.a. of ≥ 99.5%, Sigma, USA.
- Sodium bromide (NaBr), Baker Analyzed®, p.a. of ≥ 99.0%, J.T Baker, Holland.
- Sodium chloride (NaCl), p.a. of 99.73%, Fischer Scientific, United Kingdom.
- Sodium hydroxide (NaOH) Pellets G.R. for analysis EMSURE® ISO, p.a. of 99.0 %, Merck, Germany.

1.2. Instrumentation and softwares

- Injection moulder (JKV 105-2/100, Finland).
- Galvanostat (Coulometer type E211, Switzerland).
- EMF 16 Precision Electrochemistry Interface (Lawson Labs. Inc., USA).
- Autolab PGSTAT20 (Metrohm, The Netherlands).
- Lauda E100 Ecoline 20 Liter Circulating Heating Water Bath (Lauda-Brinkmann, USA).
- Glass thermometer (Widder, Germany).
- EMF Suite 2.0 (Lawson Labs. Inc., USA).
- Origin 9.0 (OriginLab Corporation, USA).

1.3. Electrodes

a. Commercial electrodes

- Ca-ISE, 6.0508.100 Metrohm, Switzerland.
- Na-ISE, 6.0508.100 Metrohm, Switzerland.
- Silver/silver chloride (Ag/AgCl) reference electrode 6.0733.100 Metrohm S/J, Reference electrolyte c (KCl) = 3 mol/l,Switzerland.
- Silver/silver chloride (Ag/AgCl) reference electrode: RL 100 D/J, Reference electrolyte c (KCl) = 3 mol/l, outer filling c (KCl) =1 mol/l, Elmetron, Poland.
- Orion: 800500U Ross Ultra D/J, Thermo Scientific, USA.
- Orion 8101BNWP pH electrode, Thermo Scientific, USA.
- Orion 9417BN Chloride ion-selective electrode (Cl-ISE), Thermo Scientific, USA.
- Orion 9300BN Potassium ion-selective electrode (K-ISE), Thermo Scientific, USA

b. SSC reference electrodes

SSC reference electrodes prepared by injection moulding

The protocol for manufacturing SSC reference electrodes by injection moulding was adapted from previous works [21] with minor changes. The Ag/AgCl reference wire was galvanostatically prepared by chlorination of a silver wire (99.99 %, 1.6 mm diameter), in a 1 M KCl solution, by passing a current of 0.1 mA for 3 hours using a galvanostat (Coulometer type E211,Switzerland). Drying potassium chloride was undertaken for 30 min at 450 °C and KCl placed in a desiccator for cooling. A KCl powder with particles having diameters varying between 1 to 300 µm was obtained by grinding with a mortar. Polypropylene powder and dry KCl were thoroughly mixed. The composite resin (Polypropylene + KCl) was prepared by Premix Oy.

The form for the injection moulding consisted of two aluminium blocks that contained two cavities for the body of reference electrode, two smaller cavities for the Ag/AgCl reference element and an inlet and outlet as shown in Figure 4. The injection moulder (JKV 105-2/100, Finland) was manually controlled. Pellets of polypropylene/KCl composite resin were placed in the injection moulder. Prior to injection, the Ag/AgCl wire was placed in the form. The polymer/salt granules were injected at 170 °C. The melted granules filled the injection moulding form getting hard while cooling down. The electrodes were subsequently conditioned in 0.1M KCl solution. Five SSC electrodes prepared by injection moulding were used in the study. They will be referred to as IM1 to IM5.

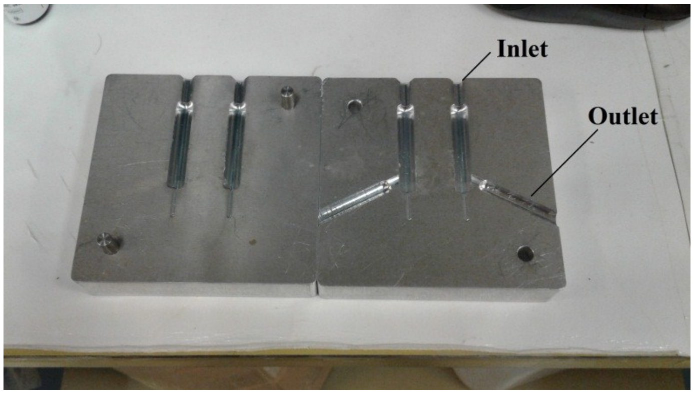


Figure 4. Photograph of the mould used in the injection moulding of SSC reference electrode.

SSC reference electrodes prepared by chemical polymerization

The protocol for manufacturing SSC reference electrodes by chemical polymerization was from previous works [20]. The preparation of the Ag/AgCl reference element was performed by the chlorination of a silver wire (99.99%, 1 mm diameter) galvanostatically in 1M KCl solution by passing a current of 0.1 mA for 3 hours using a galvanostat (Coulometer type E211, Switzerland).

Potassium chloride was dried for 30 minutes at 450–500°C, and then ground in a mortar to get a powder. In a plastic vial were mixed the salt powder, polyvinyl acetate powder, vinyl acetate monomer, and the photo-initiator 2,2-Dimethoxy-2-phenylacetophenone (DMPP). The polymerization was executed using a UV lamp (NAIL-EON, Germany) which delivers 36 watts UV (365 nm) light. Before the hardening of the polyvinyl acetate/potassium chloride (PVAc/KCl) composite, the Ag/AgCl wire was inserted into the centre of the plastic vial keeping a suitable distance from the bottom of the vial. The polymerization proceeded until the composite was sufficiently hard. The bottom of the vial was cut and the surface of the polymeric matrix was exhibited. The electrodes were subsequently conditioned in 0.1M KCl solution. Five SSC electrodes prepared by chemical polymerization were used in the study. They will be referred to as CP1 to CP5.

1.4. Samples

a. Water samples

The water sample was collected from two different locations in the vicinity of Turku, Finland:

Halistenkoski, which is a part of Aura River (Figures 5a, 5b) and Savijoki stream (Figures 6a, 6b) that goes to the Aura River. Both of these streams are joining the Aura River. Table 1 summarizes details of the sampling procedure. Water samples were stored in the fridge at 4°C prior to analysis. The measurement was performed four days after the sampling.

Table 1. Details of river water sampling procedure

Sample	Location	Date and time	Temperature	Water temperature	Sampling point	Sampling depth
RW1	Halistenkoski	16-05-2018, 9:45	28°C [25]	18°C	The shore	20 cm
RW2	Savijoki	16-05-2018, 10:15	28°C [25]	14°C	River-bed	30 cm

Figure 5. (a) Geographical location of the first sampling location (Google Maps, 2018) (b) Sampling procedure.

Figure 6. (a) Geographical location of the second sampling location (Google Maps, 2018) (b) Sampling procedure.

b. Food samples

Food samples consisted of five food preparations purchased from the local supermarket. The food samples and their salt content are described in Table 2. Samples were stored in the fridge at 4°C for 2 days prior to the analysis.

Table 2. Food samples and their salt contents.

Food sample and description	Salt content (g NaCl/100g)	Na$^+$ content (g/100g)	Cl$^-$ content (g/100g
Sample 1: Red Wine Sauce	1.10	0.43	0.67
Sample 2: Basic Sauce	0.75	0.30	0.45
Sample 3: Baby food (Salmon flavor)	0.06	0.02	0.04
Sample 4: Baby food (Reindeer flavor)	0.03	0.01	0.02
Sample 5: Powdered soup (Mushroom flavor)	0.88	0.35	0.53

Na$^+$ and Cl$^-$ contents were recalculated as follows:

1mol NaCl = (1 mol Na + 1 mol Cl) = (22.99 g + 35.45g) = 58.44g.

Mass percent of Na in NaCl = (22.99g/58.44g) × 100 = 39.34%.

Mass percent of Cl in NaCl = (35.45g/58.44g) × 100 = 60.66%.

For sample 1, NaCl content is 1.10g /100g.

Therefore Na$^+$ content in sample 1 is 39.34% ×1.10g/100g = 0.43g/100g.

And Cl^- content in sample 1 is 60.66% × 1.10g/100g = 0.67g/100g.

2. Methods

2.1. Testing of SSC reference electrodes stability

The stability of electrodes was studied for 25 weeks and 12 weeks for IM SSC and CP SSC reference electrodes, respectively. The five SSC reference electrodes of each type were immersed in an unstirred solution of 10^{-1} M KCl and the potential readings were recorded for five minutes against the Elmetron reference electrode using the 16-channel milli-voltmeter (Lawson Labs. Inc., Malvern, PA, USA). No stirring was applied to the solution in order to mimic the physical state of the sample as it occurs in nature. Potential values were obtained every two seconds and were subsequently plotted vs. time using EMF Suite 2.0.

2.2. Electrochemical impedance spectroscopy (EIS)

The impedance of electrodes was tested for 25 weeks and 12 weeks for IM SSC and CP SSC reference electrodes, respectively. Impedance measurements SSC reference electrodes were performed using glassy carbon electrode as a counter electrode, Metrohm single junction as a reference electrode.

The reference electrode was connected to the blue terminal of Metrohm Autolab PGSTAT20 (The Netherlands) while the glassy carbon counter electrode and the working electrode were connected to the black and red terminals, respectively. The electrodes were immersed in a 10^{-1} M KCl solution without stirring or purging with inert gas. The frequency was scanned from 500 kHz to 0.1 Hz by recording 55 measuring points. The used excitation potential amplitude was E_{ac} = 10 mV and E_{dc} = 0 V. The Nyquist plot was recorded for every impedance measurement.

2.3. Multi-solution protocol

The multi-solution protocol (MSP) was carried out in order to investigate the effect of the nature and the concentration of the electrolyte solution on the response of the selected commercial and SSC reference electrodes. The idea behind this protocol is to test the versatility and robustness of the SSC reference electrodes and whether the tested electrodes have a constant potential regardless of the solution they are tested in. The electrode response was monitored in the presence of different cations (K^+, Na^+, Ca^{2+}) and anions (Cl^-, Br^-). In addition to that, the effect of the solution ionic strength on the electrode was investigated by measuring the electrode potential in equi-transferent (KCl) and non-equitransferent ($CaCl_2$) solutions with different concentrations. Furthermore, the pH effect was studied by performing the measurement in acidic (HCl) and basic (NaOH) solutions. The potential of the ten SSC electrodes was recorded for five minutes against the Orion Ross Ultra double junction reference electrode. The electrodes were rinsed with deionized water (ELGA, 18.2 MΩ cm) between each measurement. Potential values were obtained every two seconds and were subsequently plotted vs. time. The obtained potential values were normalised taking the first recorded potential reading as a reference value. Two sequences of different solutions were used during the multi-solution protocol.

The solutions of the first protocol consisted of solutions of high and low concentrations (especially of strong acids and bases) and were used in the following order: 10^{-1} M KCl, 10^{-1} M $CaCl_2$, 10^{-4} M $CaCl_2$, deionized water, 10^{-1} M HCl, 10^{-4} M HCl, deionized water, 10^{-1} M NaOH, and 10^{-4} M NaOH. This will be addressed to as MSP 1.

The second protocol contained the ensuing sequence of solutions as previously described [20,21]: 3 M KCl, deionized water, 10^{-2} M NaCl, 10^{-2} M KCl, 10^{-1} M KCl, 10^{-2} M HCl, deionized water, 3 M KCl, 10^{-1} M NaCl, 10^{-2} M HCl, 10^{-1} M NaBr, 10^{-1} M $NaHCO_3$, 10^{-3} M KOH, 10^{-2} M HCl, 3 M KCl. This will be addressed to as MSP 2.

2.4. Calibration measurements

Calibrations of the different ISEs used in the sample measurement were performed by recording their potentials against each of the SSC electrodes as well as the Orion Ross Ultra double junction reference electrode in a freshly prepared solution without stirring. The electrodes were rinsed with deionized water between each measurement. Potential values were obtained every two seconds and were subsequently plotted vs. time. The calibrations were performed at 5°C, 14°C, 18°C and room temperature (22 ±1°C). Calibration solutions were made by sequential dilutions except for pH where buffers were used. Table 3 summarizes the used calibration solutions and the calibration range.

Table 3. Calibration measurements parameters

Target Ion	Calibration solution	Calibration range	Calibration points
K^+	KCl	10^{-1} – 10^{-6} M	6
Na^+	NaCl	10^{-1} – 10^{-5} M	5
Cl^-	NaCl	10^{-1} – 10^{-5} M	5
Ca^{2+}	$CaCl_2$	10^{-1} – 10^{-5} M	5
H^+	pH buffers	4.01 – 10.01	3

2.5. Sample measurements

Concentrations of the target ions (K^+, Na^+, Cl^-, Ca^{2+} and H^+) were measured in both water samples as well as in the five food samples by dipping the five ISEs and recording their potential against each of the SSC reference electrodes and Orion Ross Ultra double junction commercial reference. Food samples were thoroughly mixed before sampling and no stirring of the samples was performed during measurements. No further sample preparation was undertaken except for the powdered soup that was dissolved in 200 mL of boiling water before let to cool down at room temperature. The electrodes were rinsed with deionized water between each measurement. Potential readings were obtained every two seconds and were plotted vs. time afterwards. Measurements were carried out in triplicate. Table 4 shows the temperatures at which the measurements were made.

Table 4. Temperatures at which the samples were analyzed

Sample	Temperatures (°C)
River water 1 (RW 1)	5, 18, Room temperature (22 ± 1°C)
River water 2 (RW 2)	5, 14, Room temperature (22 ± 1°C)
Food samples	Room temperature (22 ± 1°C)

Results and Discussion

1. Potentiometric measurement for stability testing of the electrodes

The IM SSC electrodes showed a stable potential between 2 and 4 weeks of conditioning as shown in Table 5 and Appendix 1. IM1 had 0.08 mV difference between the highest and lowest recorded potential values after 2 weeks of conditioning in 10^{-1} M KCl. CP SSC electrodes were fairly stable after 2 weeks of conditioning time (Table 6, Appendix 1). CP1 exhibited a potential difference of 0.34 mV during the measurement time after 2 weeks from manufacturing. IM SSC and CP SSC reference electrodes exhibited an excellent long-term stability after 25 and 12 weeks, respectively. No fluctuations were observed (Figure 7). Potentials recorded were between -3.15 mV (IM2) and -5.11 mV (IM4) against the commercial reference electrode for IM SSC electrodes and ranging from -3.14 mV (CP4) to -8.11 mV (CP1) for the CP SSC electrodes against the same commercial reference electrode.

Table 5. Potentiometric readings during stability testing of IM1 vs. Elmetron reference electrode in 10^{-1} M KCl solution.

Conditioning Time (weeks)	End EMF (mV)	Highest EMF (mV)	Lowest EMF (mV)	EMF difference (mV)
0	-0.17	65.14	-21.71	86.84
1	1.51	2.56	1.39	1.17
2	0.08	-0.01	-0.09	0.08
3	0.45	0.48	0.43	0.05
4	-0.09	0.03	-0.09	0.12
5	0.64	1.12	0.53	0.59
6	0.16	0.99	0.12	0.87
7	0.53	1.27	0.56	0.71
8	1.24	1.31	0.89	0.42
9	0.28	0.55	0.18	0.37
10	-1.04	-0.88	-1.04	0.16
11	-1.77	-1.73	-1.78	0.05
12	-2.35	-2.35	-2.39	0.04
13	-2.75	-2.73	-2.77	0.04
14	-3.01	-2.99	-3.05	0.06
15	-3.46	-3.46	-3.48	0.02
16	-3.82	-3.82	-3.86	0.04
17	-4.17	-4.14	-4.17	0.03
18	-4.19	-4.18	-4.22	0.04
19	-4.22	-4.20	-4.23	0.03
20	-4.08	-4.07	-4.10	0.03
21	-4.25	-4.25	-4.26	0.01
22	-4.16	-4.15	-4.18	0.03
23	-4.02	-4.00	-4.03	0.03
24	-4.23	-4.22	-4.25	0.03
25	-4.01	-4.01	-4.04	0.03

Table 6. Potentiometric readings during stability testing of CP1 vs. Elmetron reference electrode in 10^{-1} M KCl solution.

Conditioning Time (weeks)	End EMF (mV)	Highest EMF (mV)	Lowest EMF (mV)	EMF difference (mV)
0	-3.74	33.21	-19.73	52.94
1	-5.48	-4.20	-5.98	1.78
2	-3.64	-3.47	-3.81	0.34
3	-5.77	-5.69	-5.82	0.13
4	-8.16	-8.09	-8.17	0.08
5	-8.03	-8.01	-8.07	0.06
6	-7.95	-7.93	-7.98	0.05
7	-8.24	-8.22	-8.28	0.06
8	-8.12	-8.12	-8.16	0.04
9	-8.03	-8.01	-8.05	0.04
10	-8.16	-8.11	-8.16	0.05
11	-8.14	-8.12	-8.18	0.06
12	-8.11	-8.11	-8.13	0.02

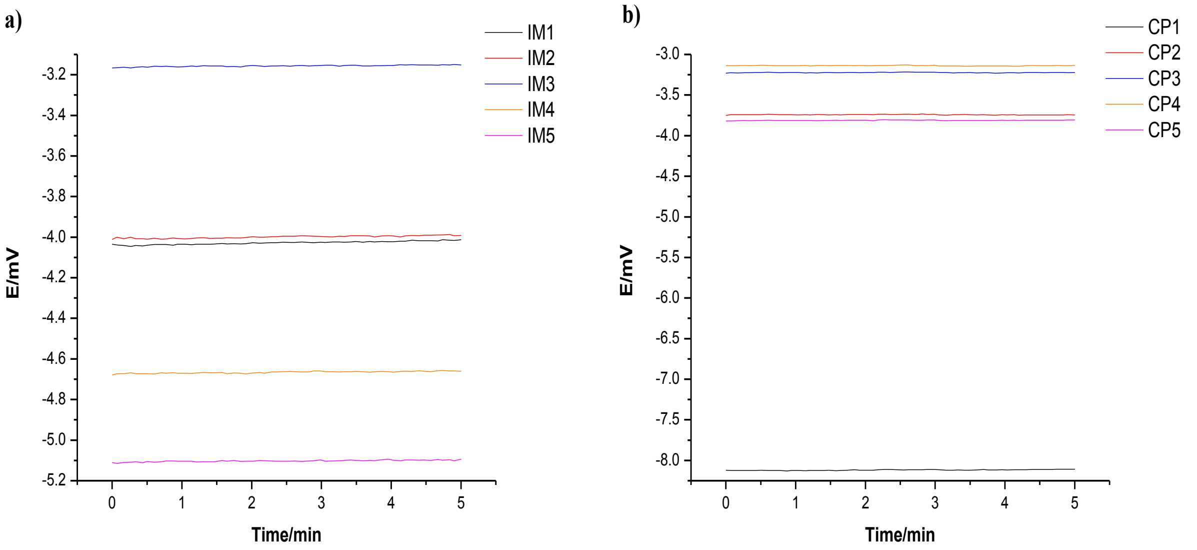


Figure 7. (a) Potentiometric readings during IM SSC electrodes' stability testing vs. Elmetron in 10^{-1} M KCl solution after 25 weeks of conditioning in 10^{-1} M KCl solution. (b) Potentiometric readings CP SSC electrodes' stability testing vs. Elmetron in 10^{-1} M KCl solution after 12 weeks of conditioning in 10^{-1} M KCl solution.

2. Multi-solution Protocol

In MSP1, the drastic variation in pH of the solution (i.e. hydrochloric acid as a strong acid and sodium hydroxide as a strong base) had a bigger influence on the response of the electrodes than the change in cations or anions or the change in the ionic strength of the solution (+5 mV in 10^{-1}

M HCl and –6 mV for 10^{-1} M NaOH, Figure 8).That was especially noticed on the IM set of electrodes. It is possible that these two variations come from the commercial reference electrode since all SSC electrodes showed the same potential difference. In Figure 8, points at solutions 2, 3 and 4 are disjoint., That could be attributed to small differences in the response of the SSC as it is the case in the 10^{-4} M $CaCl_2$ solution. In MSP 2 (Figure 9), the potential stability in all solutions, except for 10^{-2} M HCl and 10^{-3} M KOH (+4 mV and -5 mV, respectively), was found to be fairly good (± 1mV in most solutions). Hence, the IM SSC reference electrodes were found to be more sensitive to harsh pH changes than CP SSC. Apart from that, all SSC reference electrodes combined were performing well in other solutions.

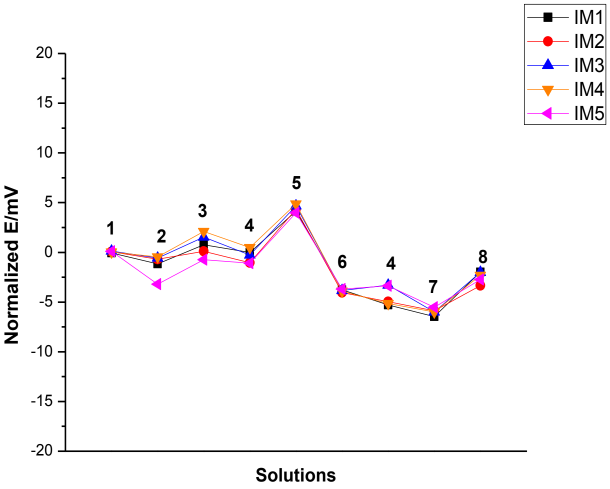


Figure 8. MSP test carried out for five identical IM SSC reference electrodes vs Orion commercial reference electrode in the following solutions: (1) 10^{-4} M KCl, (2) 10^{-1} M $CaCl_2$, (3) 10^{-4} M $CaCl_2$, (4) deionized water, (5) 10^{-1} M HCl, (6) 10^{-4} M HCl, (7) 10^{-1} M NaOH, (8) 10^{-4} M NaOH.

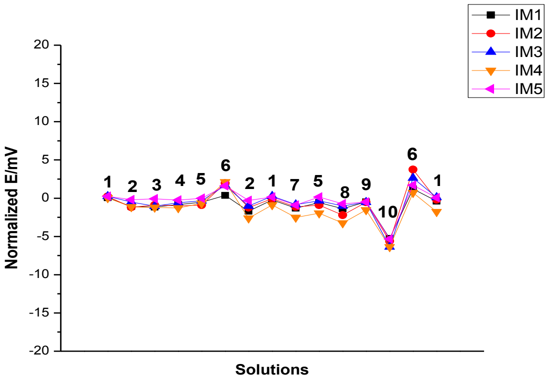


Figure 9. MSP test carried out for five identical IM SSC reference electrodes vs Orion commercial reference electrode in the following solutions: (1) 3 M KCl, (2) deionized water, (3) 10^{-2} M NaCl, (4) 10^{-2} M KCl, (5) 10^{-1} M KCl, (6) 10^{-2} M HCl, (7) 10^{-1} M NaCl, (8) 10^{-1} M NaBr, (9) 10^{-1} M $NaHCO_3$, and (10) 10^{-3} M KOH.

Regarding the CP SSC reference electrodes, they showed a relatively better stability when compared to IM electrodes especially in acidic and basic media. In MSP1, potential variations had amplitudes varying between + 2.04 mV and -1.77 mV as can be seen in Figure 10. In MSP2, results were comparable to previous studies [20]. All CP SSC reference electrodes demonstrated excellent stability with all the tested solutions (± 2 mV) as shown in Figure 11.

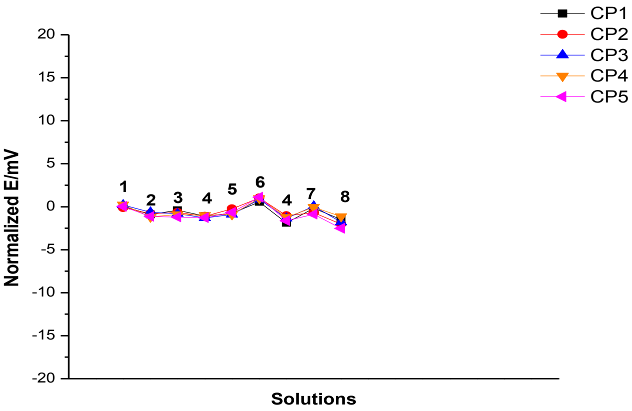


Figure 10. MSP test carried out for five identical CP SSC reference electrodes vs Orion commercial reference electrode in the following solutions: (1) 10^{-4}M KCl, (2) 10^{-1} M $CaCl_2$, (3) 10^{-4}M $CaCl_2$, (4) deionized water, (5) 10^{-1}M HCl, (6) 10^{-4}M HCl, (7) 10^{-1}M NaOH, (8) 10^{-4}M NaOH.

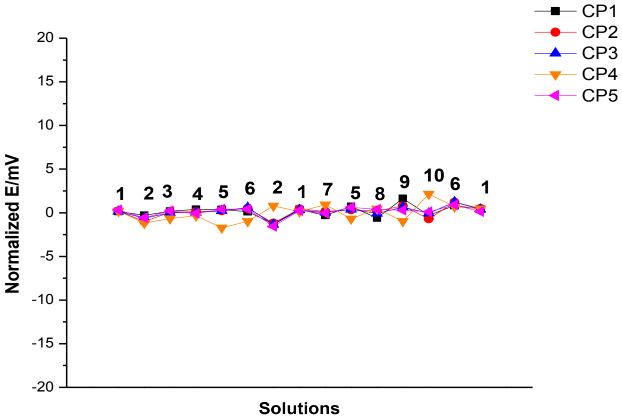


Figure 11. MSP test carried out for five identical CP SSC reference electrodes vs Orion commercial reference electrode in the following solutions: (1) 3 M KCl, (2) deionized water, (3) 10^{-2} M NaCl, (4) 10^{-2} M KCl, (5) 10^{-1}M KCl, (6) 10^{-2} M HCl, (7) 10^{-1} M NaCl, (8) 10^{-1} M NaBr, (9) 10^{-1} M $NaHCO_3$, and (10) 10^{-3} M KOH.

3. Electrochemical Impedance Spectroscopy

As seen in Tables 7 and 8, IM1 and CP1 showed an acceptable impedance value after 3 and 2 weeks of conditioning in 10^{-1} M KCl solution, respectively. The recorded impedance values for all the other electrodes can be found in Appendix 2. Individual impedance fluctuations during the whole analysis duration were negligible. Hence, all the used SSC electrodes were proven to be suitable for long-term usage.

Table 7. Recorded impedance values for IM1 during the whole analysis duration.

Conditioning Time (weeks)	Impedance value
0	GΩ range
1	5.1 MΩ
2	56 KΩ
3	9 KΩ
4	10 KΩ
5	12 KΩ
6	10 KΩ
7	10 KΩ
8	8 KΩ
9	6.7 KΩ
10	6.2 KΩ
11	5.4 KΩ
12	5.1 KΩ
13	4.9 KΩ
14	4.3 KΩ
15	3.6 KΩ
16	3.1 KΩ
17	2.7 KΩ
18	2.7 KΩ
19	2.7 KΩ
20	2.7 KΩ
21	2.6 KΩ
22	2.7 KΩ
23	2.6 KΩ
24	2.6 KΩ
25	2.6 KΩ

Table 8. Recorded impedance values for CP1 during the whole analysis duration.

Conditioning Time (weeks)	Impedance Value
0	GΩ range
1	14.2 KΩ
2	8.5 KΩ
3	7.4 KΩ
4	7.0 KΩ
5	6.7 KΩ
6	5.0 KΩ
7	4.2 KΩ
8	4.2 KΩ
9	2.8 KΩ
10	2.9 KΩ
11	2.8 KΩ
12	2.7 KΩ

4. Calibration measurements

4.1. K-ISE

The K-ISE had a slope close to the Nernstian slope (59.2 mV/decade). Slope values varied between 57.7 and 58.2 mV/decade in the linear part of the calibration curve when IM SSC references electrodes were used (Table 9). Additionally, slope values were similar when using CP SSC references electrodes ranging between 57.8 and 58.3 mV/decade (Table 10). All the SSC reference electrodes slightly outperformed the conventional reference electrode that resulted in a slope of 57.7 mV/decade for the K-ISE. The standard potentials recorded were of good stability varying from 103.2 mV to 114.3 mV. For the commercial reference electrode (Orion) the standard potential was -144.8 mV because it is not an Ag/AgCl reference electrode. This difference was observed in the calibrations of all the other ISEs. (Tables 9 and 10). The calibration data for the other SSC electrodes at different temperatures can be seen in Appendix 3.

Table 9. Calibration data for the K-ISE at room temperature (22 ± 1°C) in KCl solutions using the reference electrodes prepared by IM and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the K-ISE (M)
IM 1	58.2	110.4	10^{-1} - $10^{-4.5}$
IM 2	57.9	107.3	10^{-1} - $10^{-4.5}$
IM 3	57.9	108.5	10^{-1} - $10^{-4.5}$
IM 4	58.0	109.1	10^{-1} - $10^{-4.5}$
IM 5	57.7	114.3	10^{-1} - $10^{-4.5}$
Orion	57.7	-144.8	10^{-1} - 10^{-5}

Table 10. Calibration data for the K-ISE at room temperature (22 ± 1°C) using KCl solutions the reference electrodes prepared by CP and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the K-ISE (M)
CP 1	58.1	103.9	10^{-1} - $10^{-4.5}$
CP 2	57.9	110.1	10^{-1} - $10^{-4.5}$
CP 3	57.8	109.4	10^{-1} - $10^{-4.5}$
CP 4	58.2	108.1	10^{-1} - $10^{-4.5}$
CP 5	58.3	103.2	10^{-1} - $10^{-4.5}$
Orion	57.7	-144.8	10^{-1} - 10^{-5}

It is important to point out that the detection limit of the K-ISE increased from 10^{-5} M (with the conventional reference electrode) to $10^{-4.5}$ M while using the SSC reference electrodes due to a possible leakage of potassium ions from the SSC reference electrodes that contaminate the sample solution at low concentrations. The potential drift (of approximately 17 mV in 5 minutes) observed in the presence on an IM SSC reference electrode (Figure 12) confirms this hypothesis. This phenomenon might be due to the porous contact surface of the IM SSC electrodes as shown in Figure 13. Similar explanation is valid for CP SSC reference electrodes.

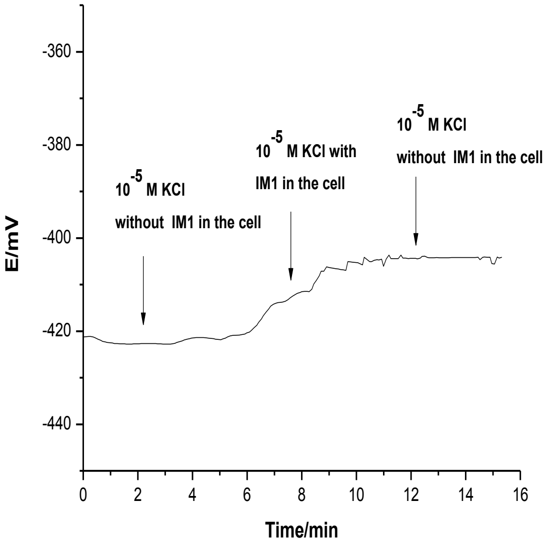


Figure 12. Potential recorded of K-ISE vs. Orion reference electrode with and without the IM electrode in 10^{-5}M KCl solution.

Figure 13. Porous surface of IM SSC electrode

4.2. Na-ISE

The Na-ISE reached a slope of 58.1 mV/decade at 22 ± 1 °C in the linear part of the calibration in the presence of the conventional reference electrode. When IM SSC and CP SSC reference electrodes were used, the slope was ranging between 57.9 and 58.2 mV/decade and from 57.8 to 58.5 mV/decade, respectively. Likewise, the standard potential of the different SSC reference electrodes was found to be comparable with a variation between 143.3 mV and 151.4 mV (Tables 11 and 12). The calibration data for the other SSC electrodes at different temperatures can be seen in Appendix 5.

Table 11. Calibration data for the Na-ISE at room temperature (22 ± 1°C) using the reference electrodes prepared by IM and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Na-ISE (M)
IM 1	58.2	149.2	10^{-1} - 10^{-4}
IM 2	57.9	149.8	10^{-1} - 10^{-4}
IM 3	58.1	149.9	10^{-1} - 10^{-4}
IM 4	57.9	149.2	10^{-1} - 10^{-4}
IM 5	57.9	151.4	10^{-1} - 10^{-4}
Orion	58.1	-103.3	10^{-1} - 10^{-4}

Table 12. Calibration data for the Na-ISE at room temperature (22 ±1°C) using the reference electrodes prepared by CP and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Na-ISE (M)
CP 1	58.0	143.3	10^{-1} - 10^{-4}
CP 2	58.5	147.3	10^{-1} - 10^{-4}
CP 3	58.0	148.3	10^{-1} - 10^{-4}
CP 4	57.8	148.5	10^{-1} - 10^{-4}
CP 5	57.9	147.9	10^{-1} - 10^{-4}
Orion	58.1	-103.3	10^{-1} - 10^{-4}

Unlike the calibration of the K-ISE, no contamination of the sample was observed. Hence, there was no change in the limit of detection when SSC reference electrodes were used.

4.3. Cl-ISE

Similarly to K^+ and Na^+, Cl-ISE showed equivalent slopes at 22 ± 1 °C in the linear part of the calibration in the three setups. As a matter of fact, the slope value was between -56.1 and -56.7 mV/decade for IM SSC reference electrodes, between -56.0 and -56.7 mV/decade for CP SSC reference electrodes while it was equal to -56.3 mV/decade in the presence of the commercial reference electrode. Furthermore, standard potentials of the SSC electrodes were between 19.4 mV and 28.8 mV (Tables 13 and 14). The linear range of the calibration was the same for SSC and the conventional reference electrodes. The calibration data of the remaining SSC electrodes at different temperatures can be visualized in Appendix 7.

Table 13. Calibration data for the Cl-ISE at room temperature (22 ± 1 °C) using the reference electrodes prepared by IM and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Cl-ISE (M)
IM 1	-56.1	28.8	10^{-1} - 10^{-4}
IM 2	-56.5	27.5	10^{-1} - 10^{-4}
IM 3	-56.7	26.6	10^{-1} - 10^{-4}
IM 4	-56.7	26.2	10^{-1} - 10^{-4}
IM 5	-56.1	27.9	10^{-1} - 10^{-4}
Orion	-56.3	-228.9	10^{-1} - 10^{-4}

Table 14. Calibration data for the Cl-ISE at room temperature (22 ± 1 °C) using the reference electrodes prepared by CP and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Cl-ISE (M)
CP 1	-56.0	19.4	10^{-1} - 10^{-4}
CP 2	-56.3	20.5	10^{-1} - 10^{-4}
CP 3	-56.5	23.3	10^{-1} - 10^{-4}
CP 4	-56.4	24.0	10^{-1} - 10^{-4}
CP 5	-56.7	21.6	10^{-1} - 10^{-4}
Orion	-56.3	-228.9	10^{-1} - 10^{-4}

4.4. Ca-ISE

For the Ca-ISE calibration, the Nernstian response in the linear part of the calibration curve was slightly improved with the usage of SSC reference electrodes (from 27.9 to 28.2 mV/decade and from 28.1 to 28.3 mV/decade for IM SSC and CP SSC, respectively) than that with the usage of the conventional reference electrode (27.7 mV/decade) as illustrated in Tables 15 and 16. Furthermore, the standard potentials of the SSC reference electrodes were comparable and ranging from 93.9 mV to 105.5 mV. An identical linear range of the calibration was observed for all the tested electrodes. Appendix 9 contains the calibration data of the other SSC electrodes at different temperatures.

Table 15. Calibration data for the Ca-ISE at room temperature (22 ± 1 °C) using the reference electrodes prepared by IM and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Ca-ISE (M)
IM 1	28.0	103.9	10^{-1} - 10^{-4}
IM 2	28.0	103.9	10^{-1} - 10^{-4}
IM 3	28.2	103.7	10^{-1} - 10^{-4}
IM 4	27.9	103.3	10^{-1} - 10^{-4}
IM 5	28.1	104.8	10^{-1} - 10^{-4}
Orion	27.7	-152.1	10^{-1} - 10^{-4}

Table 16. Calibration data for the Ca-ISE at room temperature (22 ± 1°C) using the reference electrodes prepared by CP and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Ca-ISE (M)
CP 1	28.3	93.9	10^{-1} - 10^{-5}
CP 2	28.3	95.0	10^{-1} - 10^{-5}
CP 3	28.1	102.9	10^{-1} - 10^{-5}
CP 4	28.3	105.5	10^{-1} - 10^{-5}
CP 5	28.3	105.2	10^{-1} - 10^{-5}
Orion	27.7	-152.1	10^{-1} - 10^{-5}

4.5. pH electrode

As for the previous four ions, the slopes observed when using SSC reference electrodes were equivalent to the one displayed after the use of the conventional reference electrode (from 56.7 to 57.1 mV/decade, from 57.2 to 57.4 mV/decade and 56.8 mV/ decade for IM SSC, CP SSC and the traditional reference electrode, respectively). The measured standard potentials for the SSC reference electrodes were also comparable fluctuating between 637.4 and 642.2 mV (Tables 17 and 18). In addition to that, the linear range was identical for all tested reference electrodes. The calibration data of the other tested reference electrodes is available in Appendix 11.

Table 17. Calibration data for the pH electrode at room temperature (22 ±1 °C) using the reference electrodes prepared by IM and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Calibration range
IM 1	56.7	639.2	4.01 – 10.01
IM 2	56.9	639.3	4.01 – 10.01
IM 3	56.7	639.3	4.01 – 10.01
IM 4	56.7	638.4	4.01 – 10.01
IM 5	57.1	642.2	4.01 – 10.01
Orion	56.8	385.7	4.01 – 10.01

Table 18. Calibration data for the pH electrode at room temperature (22±1 °C) using the reference electrodes prepared by CP and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Calibration range
CP 1	57.4	637.4	4.01 – 10.01
CP 2	57.3	640.5	4.01 – 10.01
CP 3	57.3	641.9	4.01 – 10.01
CP 4	57.2	640.8	4.01 – 10.01
CP 5	57.4	638.9	4.01 – 10.01
Orion	56.8	385.7	4.01 – 10.01

4.6. Effect of the temperature on the nernstian slope

The change of temperature affected the Nernstian response of the K-ISE. The nernstian slope was decreasing as the temperature goes lower as seen in Figure 14 and Appendix 4. The experimental Nernstian ratio (eq 12) should be equal to the temperature ratio that is expressed by equation 13:

$$\text{Experimental Nernstian ratio} = \frac{\text{Nernstian slope measured at higher temperature (mV/decade)}}{\text{Nernstian slope measured at lower temperature (mV/decade)}} \quad \text{(eq 12)}$$

$$\text{Theoretical Nernstian ratio} = \text{Temperature ratio} = \frac{\text{Higher temperature (K)}}{\text{Lower temperature (K)}} \quad \text{(eq 13)}$$

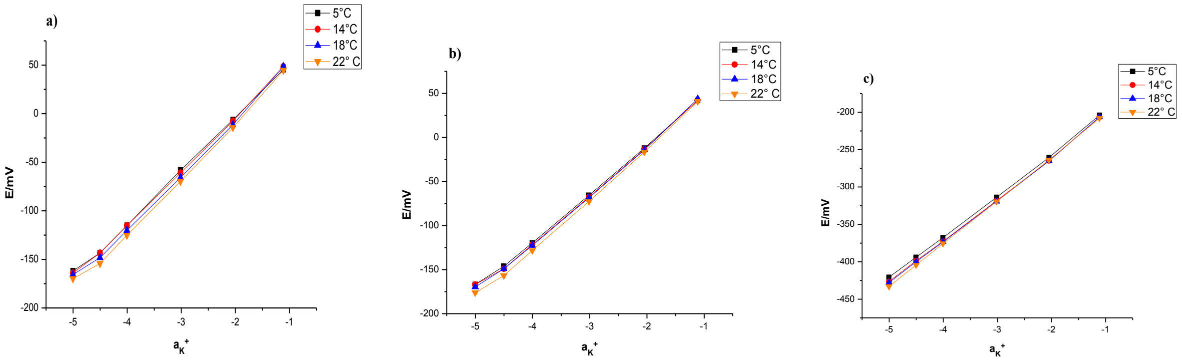


Figure 14. Calibration curves for K-ISE vs. (a) IM1 SSC, (b) CP1 SSC and (c) Orion reference electrodes

Table 19 shows a comparison between theoretical and experimental Nernstian ratios for K-ISE calibration. The Nernstian ratios of the other SSC electrodes are in Appendix 4.

Table 19. Theoretical and experimental nernstian ratios for K-ISE calibration.

Temperature change	From 5 °C to 14 °C	From 14 °C to 18 °C	From 18 °C to 22 °C
Theoretical nernstian ratio	1.03	1.01	1.01
Experimental nernstian ratio IM1	1.01	1.02	1.01
Experimental nernstian ratio CP1	1.01	1.02	1.01
Experimental nernstian ratio Orion	1.01	1.02	1.01

Theoretical and experimental nernstian ratios were found to be very comparable for all tested reference electrodes. All these findings are valid for the other ISEs (Appendix 4, 6, 8, 10, 12).

5. Sample measurements

5.1. River water samples

River water samples were analyzed by direct potentiometry for all five target ions using commercial and SSC reference electrodes. For comparison purposes, the same samples were analyzed in Lounais-Suomen Vesi ja Ympäristötutkimus Oy (LSVY) laboratory. Cl^- was determined by ion chromatography according to the method SFS-EN ISO 10304-1. K^+, Na^+ and Ca^{2+} were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) by the method SFS-EN ISO 11885. Finally, pH was determined by potentiometry according to the Method SFS 3021.

Tables 20 and 21 summarize the concentrations of the five target ions in RW1 and RW2, respectively. The measured concentrations of all ions were in accordance with those obtained by the direct potentiometric measurement method. For instance, in RW1, potassium measured concentrations ranged from 1.59 mg/l to 1.62 mg/l using SSC reference electrodes while the external laboratory analysis showed a value of 1.60 mg/l. Results of other potentiometric analyses conducted at different temperatures showed similar concentrations to those measured at room temperature. These results can be consulted in Appendix 13.

Table 20. Ions concentration measured in RW1 at room temperature (22 ± 1 °C) using SSC, commercial reference electrodes and laboratory analysis.

Reference Electrode	K^+ concentration (mg/l)	Na^+ concentration (mg/l)	Cl^- concentration (mg/l)	Ca^{2+} concentration (mg/l)	pH
IM1	1.61 ± 0.05	7.06 ± 0.24	9.62 ± 0.13	9.73 ± 0.25	7.46 ± 0.00
IM2	1.59 ± 0.02	7.10 ± 0.16	9.56 ± 0.09	9.54 ± 0.15	7.47 ± 0.01
IM3	1.59 ± 0.04	7.13 ± 0.31	9.45 ± 0.22	9.39 ± 0.13	7.46 ± 0.01
IM4	1.60 ± 0.05	7.19 ± 0.32	9.40 ± 0.12	9.97 ± 0.19	7.47 ± 0.01
IM5	1.58 ± 0.04	7.10 ± 0.24	9.58 ± 0.11	9.53 ± 0.36	7.50 ± 0.02
CP1	1.60 ± 0.01	7.28 ± 0.25	9.55± 0.12	9.71 ± 0.17	7.51 ± 0.00
CP2	1.60 ± 0.04	7.13 ± 0.18	9.65 ± 0.13	9.50 ± 0.26	7.53 ± 0.01
CP3	1.59 ± 0.03	7.21 ± 0.11	9.57± 0.18	9.73 ± 0.07	7.48 ± 0.01
CP4	1.59 ± 0.04	7.03 ± 0.16	9.58 ± 0.27	9.56 ± 0.15	7.47 ± 0.01
CP5	1.62 ± 0.03	7.10 ± 0.13	9.52 ± 0.10	9.67 ± 0.25	7.48 ± 0.00
Orion	1.60 ± 0.02	7.14 ± 0.27	9.62 ± 0.14	9.51 ± 0.19	7.51 ± 0.01
External laboratory	1.60	7.20	9.10	9.30	7.50

Concentrations are reported as the average of 3 repetitions ± standard deviation except for the external laboratory results.

Table 21. Ions concentration measured in RW2 at room temperature (22 ± 1 °C) using SSC, commercial reference electrodes and ICP-OES.

Reference Electrode	K^+ concentration (mg/l)	Na^+ concentration (mg/l)	Cl^- concentration (mg/l)	Ca^{2+} concentration (mg/l)	pH
IM1	2.06 ± 0.11	10.05 ± 0.21	9.84 ± 0.16	13.72 ± 0.33	7.72 ± 0.02
IM2	1.99 ± 0.05	10.27 ± 0.26	9.74 ± 0.13	13.73 ± 0.14	7.71 ± 0.02
IM3	2.02 ± 0.05	10.24 ± 0.13	9.73 ± 0.38	13.40 ± 0.13	7.72 ± 0.02
IM4	2.09 ± 0.07	10.17 ± 0.47	9.72 ± 0.12	13.73 ± 0.22	7.71 ± 0.03
IM5	2.09 ± 0.02	10.14 ± 0.28	9.71 ± 0.18	13.55 ± 0.21	7.72 ± 0.02
CP1	2.10 ± 0.04	10.17 ± 0.22	9.75 ± 0.10	13.56 ± 0.23	7.70 ± 0.02
CP2	2.07 ± 0.04	10.16 ± 0.34	9.76 ± 0.12	13.53 ± 0.41	7.73 ± 0.01
CP3	2.07 ± 0.01	10.32 ± 0.27	9.78 ± 0.10	13.15 ± 0.48	7.69 ± 0.02
CP4	2.08 ± 0.01	10.22 ± 0.25	9.63 ± 0.10	13.65 ± 0.17	7.69 ± 0.02
CP5	2.08 ± 0.04	10.15 ± 0.32	9.84 ± 0.22	13.67 ± 0.23	7.72 ± 0.02
Orion	2.13 ± 0.01	9.99 ± 0.49	9.91 ± 0.23	13.70 ± 0.14	7.69 ± 0.00
External laboratory	2.10	10.00	10.00	14.00	7.70

Concentrations are reported as the average of 3 repetitions ± standard deviation except for the external laboratory results.

5.2. Food samples

Ion concentrations measured in the five food samples are reported in Tables 22, 23, 24, 25 and 26 as well as Appendix 14.The concentrations of measured ions were comparable in the five food samples.Nevertheless, these values were somewhat far from the indicated values of the manufacturer which include sodium and chloride. For example, the Na^+ contents measured using SSC and the commercial reference electrode were varying from 0.17 to 0.21 g/100g in food 1 while it amounts to approximately the double of that value in the manufacturer's claim in Food 1 (0.43 g/100g). Similarly, there was a significant discrepancy in Na+ content in Food 2 with differences ranging between 0.13 and 0.15 g/100g which represent almost 30% of the manufacturer's claimed value. For all remaining samples, differences in Na^+ content between the results of the potentiometric method and the label specifications were minor to non-existent especially in samples 3 and 4, where the Na^+ content was low.

Regarding Cl^- content, differences between measured values and the label's specifications were major except for food 4. In fact, measured values were two to three times less than the specified concentration for samples 2 and 3, respectively. For sample 5, the difference between obtained and described values was relatively the lowest (excluding sample 4) with discrepancies ranging between 0.09 g/100g for CP 1 and 0.20 g/100g while using the commercial reference electrode. A possible explanation of these differences lies in the absence of sample preparation such as dilution or sample digestion or any other pre-treatment of all the foods which might be the cause of interferences. Nevertheless, the performance of the SSC reference electrodes seems to be reproducible and similar to that of the commercial reference electrode in all the measured target ions.

Table 22. Ion concentrations measured in red wine sauce using IM 1, CP1 and Orion as reference electrodes compared to the label specifications.

Electrode	Na^+ (g/100g)	Cl^- (g/100g)	K^+ (g/100g)	Ca^{2+} (g/100g)	pH
IM1	0.17	1.03	0.08	0.00082	4.93
CP1	0.19	0.97	0.07	0.00080	4.90
Orion	0.21	1.07	0.06	0.00095	4.98
Label	0.43	0.67	-	-	-

The label specification is presented as g NaCl/100g of food.

Table 23. Ion concentrations measured in basic sauce using IM 1, CP1 and Orion as reference electrodes compared to the label specifications.

Electrode	Na^+ (g/100g)	Cl^- (g/100g)	K^+ (g/100g)	Ca^{2+} (g/100g)	pH
IM1	0.43	0.93	0.09	0.00024	6.04
CP1	0.43	0.87	0.09	0.00026	6.01
Orion	0.45	0.94	0.08	0.00022	6.05
Label	0.30	0.45	-	-	-

The label specification is presented as g NaCl/100g of food.

Table 24. Ion concentrations measured in baby food (Salmon flavour)using IM 1, CP1 and Orion as reference electrodes compared to the label specifications.

Electrode	Na^+ (g/100g)	Cl^- (g/100g)	K^+ (g/100g)	Ca^{2+} (g/100g)	pH
IM1	0.01	0.12	0.09	0.00038	5.69
CP1	0.01	0.09	0.09	0.00037	5.71
Orion	0.01	0.11	0.10	0.00040	5.67
Label	0.02	0.04	-	-	-

The label specification is presented as g NaCl/100g of food.

Table 25. Ion concentrations measured in baby food (Reindeer flavour)baby using IM 1, CP1 and Orion as reference electrodes compared to the label specifications.

Electrode	Na^+ (g/100g)	Cl^- (g/100g)	K^+ (g/100g)	Ca^{2+} (g/100g)	pH
IM1	0.01	0.03	0.11	0.00031	5.55
CP1	0.01	0.02	0.14	0.00034	5.59
Orion	0.01	0.03	0.10	0.00032	5.63
Label	0.01	0.02	-	-	-

The label specification is presented as g NaCl/100g of food.

Table 26. Ion concentrations measured in powdered soup using IM 1, CP1 and Orion as reference electrodes compared to the label specifications.

Electrode	Na^+ (g/100g)	Cl^- (g/100g)	K^+ (g/100g)	Ca^{2+} (g/100g)	pH
IM1	0.39	0.68	0.02	0.00068	6.56
CP1	0.43	0.62	0.01	0.00072	6.58
Orion	0.36	0.73	0.02	0.00070	6.64
Label	0.35	0.53	-	-	-

The label specification is presented as g NaCl/100g of food.

Conclusion

In this study, solid-state composite SSC reference electrodes were manufactured by injection moulding and chemical polymerization. A simple, sample preparation-free and fast potentiometric sensing method based on the use of these SSC reference electrodes was extensively tested in river water and different food samples as well as in synthetic solutions of different ionic strengths and pH. It is evident that SSC reference electrodes were on par or even slightly better than the conventional reference electrodes except in synthetic 10^{-5}M of potassium chloride where a leakage of potassium to the sample solution was observed especially from the SSC reference electrodes prepared by injection moulding. An effective solution might be the change of the design of the electrodes in a way that reduces the electrode/sample solution contact surface.

In the multi-solution protocol, it was observed that SSC reference electrodes prepared by injection moulding were found to be sensitive in concentrated acidic and basic solutions (+5 mV in 10^{-1} M HCl and -6mV in 10^{-1} M NaOH, +4 mV and -5 mV and 10^{-2} M HCl and 10^{-3} M KOH respectively). On the other hand, SSC reference electrodes prepared by chemical polymerization showed an excellent stability in all tested solutions with a potential variation limited to ±2 mV.

The stability of all the tested SSC reference electrodes was continuously evaluated by electrochemical impedance spectroscopy and all electrodes were having a low impedance value starting from the third and the first conditioning week for IM and CP reference electrodes, respectively. The SSC reference electrodes kept their low resistance until the end of the experimental analysis. Hence, the long-term stability of the SSC electrodes can be considered as excellent and that these electrodes are suitable for continuous, prolonged, and intensive usage.

Furthermore, ion concentration measurements of the five target ions in river water samples were very comparable to those of the external laboratory analysis made by the ICP-OES standard method. Nevertheless, the same potentiometric method gave different results from the values of salt content claimed by the manufacturers in food samples. Evidently, a confirmatory analysis with ICP-OES is required in order to assess the importance of the sample preparation in the accuracy of the final results.

References

[1] Szulczynski, B., Gebicki, J. (2017). Currently Commercially Available Chemical Sensors Employed for Detection of Volatile Organic Compounds in Outdoor and Indoor Air. *Environments*, 4, 21.

[2] Kassal, P., Steinberg, M.D., Murković Steinberg, I. (2018). Wireless chemical sensors and biosensors: A review. *Sensors and Actuators B: Chemical*, 266, 228-245.

[3] Bard A.J., Faulkner L.R. (2001). *Electrochemical Methods: Fundamentals and Applications* (Wiley, New York), 2nd Ed.

[4] Lindner, E.1., Pendley, B.D., (2013). A tutorial on the application of ion-selective electrode potentiometry: An analytical method with unique qualities, unexplored opportunities and potential pitfalls; Tutorial. *Anal Chim Acta*. **762***:*1-13

[5] Vanamo, U. (2015). *Solid-State Reference and Ion-Selective Electrodes - Towards Portable Potentiometric Sensing.* (PhD Thesis).

[6] Bobacka J., Ivaska A., Lewenstam A., (2008). Potentiometric Ion Sensors. *Chem. Rev.,* **108** 329−351.

[7] Kahlert, H., (2010). Reference electrodes *In Electroanalytical Methods, 2nd ed.*, pp 291-308. Springer-Verlag Berlin Heidelberg.

[8] Von Smolinski, A.W., Moore, C.E., Jaselskis, B. (1989). The Choice of the Hydrogen Electrode as the Base for the Electromotive Series In *Electrochemistry, Past and Present* pp 127–141. American Chemical Society.

[9] Inzelt, G., Lewenstam, A., Scholz, F. (2013). *Handbook of Reference Electrodes (Eds.).* Springer-Verlag.

[10] Ruetschi, P. (2003) Silver–silver sulfate reference electrodes for lead-acid batteries. *Journal of Power Sources,* **113**, 363–370.

[11] Corti, K. H., Fernández-Prini, R. (1982). Behaviour of the mercury, mercuric oxide electrode in alkaline solutions in the temperature range**,** *Journal of the Chemical Society, Faraday Transactions,* **78,** 545-554.

[12] Ciobanu, M., Wilburn, J. P., Buss, N. I., Ditavong, P., Lowy, D. A. (2002). Miniaturized Reference Electrodes Based on Ag/AgiX Internal Reference Elements. I. Manufacturing and Performance. *Electroanalysis*, **14**, 989–997.

[13] Vonau, W. Oelssner, W. Guth, U., Henze, J. (2010). An all-solid-state reference electrode. *Sens. Actuators B*, **144**, 368–373.

[14] Diamond, D., McEnroe, E., McCarrick M., Lewenstam, A. (1994). Evaluation of a new solid-state reference electrode junction material for ion-selective electrodes. *Electroanalysis*, **6**, 962–971.

[15] Cicmil, D., Anastasova, S., Kavanagh, A., Diamond, D., Mattinen, U., Bobacka, J., Lewenstam A. Radu, A. (2011). Ionic liquid-based, liquid-junction-free reference electrode. *Electroanalysis*, **23**, 1881–1890.

[16] Anastasova-Ivanova, S., Mattinen, U., Radu, A., Bobacka, J., Lewenstam, A., Migdalski, J., Danielewski M., Diamond, D. (2010). Development of miniature all-solid-state potentiometric sensing system. *Sens. Actuators B*, **146**, 199–205.

[17] Blaz, T., Migdalski J., Lewenstam, A. (2005). Junction-less reference electrode for potentiometric measurements obtained by buffering pH in a conducting polymer matrix. *Analyst*, **130**, 637–643.

[18] Rius-Ruiz, F. X., Kisiel, A., Michalska, A., Maksymiuk, K., Riu J., Rius, F. X. (2011). Solid-state reference electrodes based on carbon nanotubes and polyacrylate membranes *Anal. Bioanal. Chem*., **399**, 3613–3622.

[19] Mousavi, Z., Granholm, K., Sokalski, T., Lewenstam, A. (2015). All-solid-state electrochemical platform for potentiometric measurements. *Sensors and Actuators B: Chemical*, **207**, 895-899.

[20] Mousavi, Z., Granholm, K., Sokalski, T., Lewenstam, A. (2013). An analytical quality solid-state composite reference electrode. *Analyst,* **138**, 5216-5220.

[21] Granholm, K., Mousavi, Z., Sokalski, T., Lewenstam, A. (2014). *"*Analytical quality solid-state composite reference electrode manufactured by injection moulding*" J Solid State Electrochem,* **18**, 607-612.

[22] Wang, J. (2006). *Analytical Electrochemistry 3rd Edition*, New Jersey, USA: John Wiley & Sons, Inc.

[23] Mousavi, Z. (2009). *Ion Sensing Based on the Conducting Polymer Poly(3,4-ethylenedioxythiophene*. (PhD Thesis).

[24] Southampton Electrochemistry Group. (2001). *Instrumental Methods in Electrochemistry,* Ellis Horwood, Chichester, **12**, 251-270.

[25] Weather of Turku (2018, May 16). *AccuWeather*. Retrieved from https://www.accuweather.com/en/fi/turku/134768/mayweather/134768?monyr=5/1/2018&view=table on 26th of May 2018.

Appendix

Appendix 1

Table 1. Potentiometric readings during stability testing of IM 2 SSC reference electrode vs. Elmetron reference electrode in 10^{-1} M KCl solution.

Conditioning Time (weeks)	End EMF (mV)	Highest EMF (mV)	Lowest EMF (mV)	EMF difference (mV)
0	-18.03	19.29	-66.02	85.31
1	6.98	36.66	-13.91	50.57
2	-0.34	-0.02	-0.91	0.89
3	-1.15	-1.12	-1.22	0.10
4	-0.06	-0.05	-1.06	1.01
5	0.03	0.15	-0.96	1.11
6	0.17	0.32	2.03	1.71
7	-0.14	1.56	0.19	1.37
8	-0.42	-0.34	-2.01	1.67
9	-1.16	-0.79	-2.18	1.39
10	-1.87	-1.73	-2.26	0.53
11	-2.31	-2.28	-2.32	0.04
12	-2.66	-2.64	-2.69	0.05
13	-3.14	-3.14	-3.18	0.04
14	-3.47	-3.45	-3.49	0.04
15	-3.61	-3.60	-3.64	0.04
16	-3.82	-3.82	-3.86	0.04
17	-3.97	-3.96	-4.00	0.04
18	-3.98	-3.97	-4.02	0.05
19	-3.99	-3.98	-4.01	0.03
20	-3.86	-3.86	-3.93	0.07
21	-3.88	-3.87	-3.90	0.03
22	-3.92	-3.92	-3.98	0.06
23	-3.96	-3.96	-4.01	0.05
24	-3.99	-3.96	-3.99	0.03
25	-3.97	-3.97	-3.99	0.02

Table 2. Potentiometric readings during stability testing of IM 3 SSC reference electrode vs. Elmetron reference electrode in 10^{-1} M KCl solution.

Conditioning Time (weeks)	End EMF (mV)	Highest EMF (mV)	Lowest EMF (mV)	EMF difference (mV)
0	0.17	0.20	0.16	0.04
1	1.29	1.38	1.29	0.09
2	0.84	0.86	0.76	0.09
3	1.34	1.37	1.33	0.04
4	1.48	1.62	1.48	0.14
5	1.95	2.23	1.85	0.38
6	1.88	2.88	1.86	1.02
7	2.24	2.45	0.53	1.92
8	3.10	3.27	0.22	3.05
9	2.18	2.97	2.53	0.44
10	1.16	2.14	1.82	0.32
11	0.13	0.18	0.13	0.05
12	-0.22	-0.16	-0.23	0.07
13	-0.68	-0.66	-0.7	0.04
14	-1.23	-1.18	-1.23	0.05
15	-2.04	-2.00	-2.05	0.05
16	-2.68	-2.67	-2.7	0.03
17	-3.07	-3.05	-3.07	0.02
18	-3.11	-3.1	-3.13	0.03
19	-3.12	-3.09	-3.12	0.03
20	-3.16	-3.15	-3.17	0.02
21	-3.18	-3.17	-3.19	0.02
22	-3.16	-3.15	-3.17	0.02
23	-3.14	-3.14	-3.16	0.02
24	-3.16	-3.13	-3.16	0.03
25	-3.15	-3.14	-3.15	0.01

Table 3. Potentiometric readings during stability testing of IM 4 SSC reference electrode vs. Elmetron reference electrode in 10^{-1} M KCl solution.

Conditioning Time (weeks)	End EMF (mV)	Highest EMF (mV)	Lowest EMF (mV)	EMF difference (mV)
2	3.74	57.51	-23.48	80.99
3	1.30	1.34	1.25	0.09
4	1.84	3.71	0.41	3.30
5	6.57	7.06	5.19	1.87
6	4.19	7.87	2.48	5.39
7	2.77	3.34	2.13	1.21
8	0.60	1.31	0.56	0.75
9	-1.01	-0.34	-2.01	1.67
10	-2.11	-1.53	-2.28	0.75
11	-2.47	-2.01	-2.87	0.86
12	-2.65	-2.07	-2.89	0.82
13	-2.89	-2.16	-2.91	0.75
14	-3.28	-3.17	-3.88	0.71
15	-3.74	-3.28	-3.78	0.50
16	-4.39	-4.37	-4.47	0.10
17	-4.42	-4.38	-4.46	0.08
18	-4.58	-4.56	-4.62	0.06
19	-4.62	-4.57	-4.66	0.09
20	-4.63	-4.58	-4.67	0.09
21	-4.72	-4.71	-4.78	0.07
22	-4.70	-4.69	-4.73	0.04
23	-4.68	-4.66	-4.72	0.06
24	-4.73	-4.70	-4.74	0.04
25	-4.66	-4.64	-4.66	0.02

Table 4. Potentiometric readings during stability testing of IM 5 SSC reference electrode vs. Elmetron reference electrode in 10^{-1} M KCl solution.

Conditioning Time (weeks)	End EMF (mV)	Highest EMF (mV)	Lowest EMF (mV)	EMF difference (mV)
2	8.63	59.73	-13.70	73.43
3	1.18	8.65	1.12	7.53
4	-0.45	-0.33	-0.45	0.12
5	-0.25	-0.19	-0.25	0.07
6	-0.52	-0.52	-0.56	0.04
7	-1.46	-1.34	-1.48	0.14
8	-1.86	-1.73	-1.95	0.22
9	-1.47	-1.44	-1.50	0.06
10	-1.96	-1.88	-1.97	0.09
11	-2.33	-2.28	-2.35	0.07
12	-2.54	-2.50	-2.68	0.18
13	-2.79	-2.68	-2.79	0.11
14	-2.81	-2.76	-2.90	0.14
15	-3.00	-2.93	-3.00	0.07
16	-3.30	-3.30	-3.37	0.07
17	-4.12	-4.04	-4.13	0.09
18	-4.68	-4.60	-4.65	0.05
19	-5.01	-4.98	-5.03	0.05
20	-4.99	-4.96	-5.02	0.06
21	-5.06	-5.02	-5.06	0.04
22	-5.09	-5.07	-5.09	0.02
23	-5.04	-5.04	-5.07	0.03
24	-5.06	-5.05	-5.08	0.03
25	-5.10	-5.09	-5.11	0.02

Table 5. Potentiometric readings during stability testing of CP2 SSC reference electrode vs. Elmetron reference electrode in 10^{-1} M KCl solution.

Conditioning Time (weeks)	End EMF (mV)	Highest EMF (mV)	Lowest EMF (mV)	EMF difference (mV)
0	1.48	15.93	-42.12	58.04
1	-1.53	0.30	-2.30	2.60
2	1.18	1.35	1.00	0.35
3	-2.75	-2.53	-2.81	0.28
4	-3.66	-3.61	-3.75	0.14
5	-3.78	-3.72	-3.80	0.08
6	-3.82	-3.77	-3.83	0.06
7	-3.74	-3.68	-3.75	0.07
8	-3.80	-3.77	-3.81	0.04
9	-3.76	-3.74	-3.78	0.04
10	-3.77	-3.77	-3.80	0.03
11	-3.80	-3.76	-3.81	0.05
12	-3.75	-3.73	-3.75	0.02

Table 6. Potentiometric readings during stability testing of CP3 SSC reference electrode vs. Elmetron reference electrode in 10^{-1} M KCl solution.

Conditioning Time (weeks)	End EMF (mV)	Highest EMF (mV)	Lowest EMF (mV)	EMF difference (mV)
0	0.07	44.60	-4.74	49.34
1	-1.99	-0.81	-3.11	2.30
2	0.20	0.37	0.01	0.36
3	-1.84	-1.81	-1.97	0.16
4	-3.22	-3.17	-3.30	0.13
5	-3.26	-3.20	-3.34	0.14
6	-3.31	-3.25	-3.37	0.12
7	-3.28	-3.27	-3.32	0.05
8	-3.31	-3.30	-3.34	0.04
9	-3.27	-3.22	-3.28	0.06
10	-3.26	-3.24	-3.28	0.04
11	-3.28	-3.28	-3.30	0.02
12	-3.22	-3.21	-3.22	0.01

Table 7. Potentiometric readings during stability testing of CP4 SSC reference electrode vs. Elmetron reference electrode in 10^{-1} M KCl solution.

Conditioning Time (weeks)	End EMF (mV)	Highest EMF (mV)	Lowest EMF (mV)	EMF difference (mV)
0	0.45	23.81	-16.29	40.10
1	-1.20	0.20	-2.36	2.56
2	0.45	0.69	0.30	0.39
3	-1.07	-1.01	-1.12	0.11
4	-3.08	-3.05	-3.14	0.09
5	-3.11	-3.09	-3.12	0.03
6	-3.15	-3.12	-3.17	0.05
7	-3.18	-3.16	-3.20	0.04
8	-3.12	-3.12	-3.14	0.02
9	-3.14	-3.11	-3.16	0.05
10	-3.13	-3.07	-3.13	0.06
11	-3.18	-3.14	-3.21	0.07
12	-3.14	-3.13	-3.15	0.02

Table 8. Potentiometric readings during stability testing of CP5 SSC reference electrode vs. Elmetron reference electrode in 10^{-1} M KCl solution.

Conditioning Time (weeks)	End EMF (mV)	Highest EMF (mV)	Lowest EMF (mV)	EMF difference (mV)
0	0.19	24.24	-13.75	37.99
1	-1.84	-1.09	-2.96	1.86
2	-0.21	0.49	-0.55	1.04
3	-1.77	-1.53	-1.87	0.34
4	-3.05	-2.88	-3.07	0.19
5	-3.88	-3.77	-3.87	0.10
6	-3.81	-3.74	-3.85	0.11
7	-3.87	-3.82	-3.89	0.07
8	-3.84	-3.82	-3.87	0.05
9	-3.88	-3.85	-3.89	0.04
10	-3.85	-3.82	-3.86	0.04
11	-3.81	-3.79	-3.85	0.06
12	-3.81	-3.81	-3.82	0.01

Appendix 2

Table 1. Recorded impedance values for IM2 SSC reference electrode during the whole analysis duration.

Conditioning Time (weeks)	Impedance Value
0	GΩ range
1	GΩ range
2	6.1 MΩ
3	71.0 KΩ
4	63.1 KΩ
5	64.2 KΩ
6	65.5 KΩ
7	64.2 KΩ
8	64.6 KΩ
9	65.4 KΩ
10	64.7 KΩ
11	65.6 KΩ
12	60.1 KΩ
13	60.9 KΩ
14	60.4 KΩ
15	60.6 KΩ
16	60.2 KΩ
17	60.3 KΩ
18	60.4 KΩ
19	60.2 KΩ
20	60.3 KΩ
21	60.4 KΩ
22	60.0 KΩ
23	60.0 KΩ
24	60.0 KΩ
25	60.2 KΩ

Table 2. Recorded impedance values for IM3 SSC reference electrode during the whole analysis duration.

Conditioning Time (weeks)	Impedance Value
0	GΩ range
1	62.0 KΩ
2	34.0 KΩ
3	17.0 KΩ
4	17.0 KΩ
5	14.0 KΩ
6	16.0 KΩ
7	14.0 KΩ
8	13.0 KΩ
9	8.0 KΩ
10	6.0 KΩ
11	5.2 KΩ
12	5.4 KΩ
13	5.6 KΩ
14	5.1 KΩ
15	4.7 KΩ
16	4.4 KΩ
17	4.2 KΩ
18	3.7 KΩ
19	3.6 KΩ
20	3.7 KΩ
21	3.6 KΩ
22	3.6 KΩ
23	3.7 KΩ
24	3.6 KΩ
25	3.7 KΩ

Table 3. Recorded impedance values for IM4 SSC reference electrode during the whole analysis duration.

Conditioning Time (weeks)	Impedance Value
2	GΩ range
3	GΩ range
4	83.5 MΩ
5	63.6 MΩ
6	53.5 MΩ
7	32.9 MΩ
8	17.5 MΩ
9	28.7 MΩ
10	22.2 MΩ
11	13.7 MΩ
12	8.3 MΩ
13	4.2 MΩ
14	2.4 MΩ
15	920.0 KΩ
16	350.7 KΩ
17	215.8 KΩ
18	195.2 KΩ
19	87.6 KΩ
20	48.2 KΩ
21	46.7 KΩ
22	45.9 KΩ
23	45.3 KΩ
24	45.2 KΩ
25	45.3 KΩ

Table 4. Recorded impedance values for IM5 SSC reference electrode during the whole analysis duration.

Conditioning Time (weeks)	Impedance Value
2	GΩ range
3	GΩ range
4	400.6 KΩ
5	305.7 KΩ
6	26.3 KΩ
7	27.0 KΩ
8	17.9 KΩ
9	28.5 KΩ
10	27.9 KΩ
11	27.2 KΩ
12	28.4 KΩ
13	25.8 KΩ
14	25.3 KΩ
15	25.6 KΩ
16	25.4 KΩ
17	26.3 KΩ
18	26.3 KΩ
19	25.7 KΩ
20	25.4 KΩ
21	28.3 KΩ
22	28.0 KΩ
23	25.9 KΩ
24	23.4 KΩ
25	23.4 KΩ

Table 5. Recorded impedance values for CP2 SSC reference electrode during the whole analysis duration.

Conditioning Time (weeks)	Impedance Value
0	GΩ range
1	22.3 KΩ
2	12.8 KΩ
3	7.9 KΩ
4	7.5 KΩ
5	6.6 KΩ
6	5.9 KΩ
7	4.8 KΩ
8	4.3 KΩ
9	3.1 KΩ
10	3.2 KΩ
11	2.8 KΩ
12	2.8 KΩ

Table 6. Recorded impedance values for CP3 SSC reference electrode during the whole analysis duration.

Conditioning Time (weeks)	Impedance Value
0	GΩ range
1	34.2 KΩ
2	18.5 KΩ
3	11.5 KΩ
4	9.6 KΩ
5	7.5 KΩ
6	5.8 KΩ
7	4.9 KΩ
8	4.2 KΩ
9	3.8 KΩ
10	3.9 KΩ
11	3.8 KΩ
12	3.7 KΩ

Table 7. Recorded impedance values for CP4 SSC reference electrode during the whole analysis duration.

Conditioning Time (weeks)	Impedance Value
0	GΩ range
1	13.5 KΩ
2	10.7 KΩ
3	8.2 KΩ
4	8.0 KΩ
5	7.2 KΩ
6	6.4 KΩ
7	6.2 KΩ
8	5.2 KΩ
9	4.8 KΩ
10	4.6 KΩ
11	4.8 KΩ
12	4.6 KΩ

Table 8. Recorded impedance values for CP5 SSC reference electrode during the whole analysis duration.

Conditioning Time (weeks)	ImpedanceValue
0	GΩ range
1	12.8 KΩ
2	8.9 KΩ
3	8.4 KΩ
4	7.1 KΩ
5	6.4 KΩ
6	6.4 KΩ
7	6.5 KΩ
8	4.2 KΩ
9	3.8 KΩ
10	3.9 KΩ
11	3.8 KΩ
12	3.9 KΩ

Appendix 3

Table 1. Calibration data for the K-ISE at 5°C using the reference electrodes prepared by IM and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the K-ISE (M)
IM 1	55.6	107.8	10^{-1} - $10^{-4.5}$
IM 2	56.3	108.9	10^{-1} - $10^{-4.5}$
IM 3	55.4	107.9	10^{-1} - $10^{-4.5}$
IM 4	55.6	108.5	10^{-1} - $10^{-4.5}$
IM 5	55.4	111.1	10^{-1} - $10^{-4.5}$
Orion	55.4	-144.9	10^{-1} - 10^{-5}

Table 2. Calibration data for the K-ISE at 5°C using the reference electrodes prepared by CP and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the K-ISE (M)
CP 1	55.5	102.6	10^{-1} - $10^{-4.5}$
CP 2	55.4	104.6	10^{-1} - $10^{-4.5}$
CP 3	55.7	105.4	10^{-1} - $10^{-4.5}$
CP 4	55.5	103.9	10^{-1} - $10^{-4.5}$
CP 5	55.4	104.9	10^{-1} - $10^{-4.5}$
Orion	55.4	-144.9	10^{-1} - 10^{-5}

Table 3. Calibration data for the K-ISE at 14°C using the reference electrodes prepared by IM and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the K-ISE (M)
IM 1	56.3	109.5	10^{-1} - $10^{-4.5}$
IM 2	56.7	110.6	10^{-1} - $10^{-4.5}$
IM 3	56.5	107.3	10^{-1} - $10^{-4.5}$
IM 4	56.8	109.9	10^{-1} - $10^{-4.5}$
IM 5	56.5	112.1	10^{-1} - $10^{-4.5}$
Orion	56.0	-147.6	10^{-1} - 10^{-5}

Table 5. Calibration data for the K-ISE at 14°C using the reference electrodes prepared by CP and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^0) (mV)	Linear range of the K-ISE (M)
CP 1	56.2	103.2	10^{-1} - $10^{-4.5}$
CP 2	57.0	108.2	10^{-1} - $10^{-4.5}$
CP 3	56.3	105.3	10^{-1} - $10^{-4.5}$
CP 4	56.5	105.7	10^{-1} - $10^{-4.5}$
CP 5	56.1	104.4	10^{-1} - $10^{-4.5}$
Orion	56.0	-147.6	10^{-1} - 10^{-5}

Table 6. Calibration data for the K-ISE at 18°C using the reference electrodes prepared by IM and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^0) (mV)	Linear range of the K-ISE (M)
IM 1	57.5	109.5	10^{-1} - $10^{-4.5}$
IM 2	57.3	111.9	10^{-1} - $10^{-4.5}$
IM 3	57.0	107.8	10^{-1} - $10^{-4.5}$
IM 4	57.3	108.2	10^{-1} - $10^{-4.5}$
IM 5	56.8	113.3	10^{-1} - $10^{-4.5}$
Orion	56.5	-146.8	10^{-1} - 10^{-5}

Table 7. Calibration data for the K-ISE at 18°C using the reference electrodes prepared by CP and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^0) (mV)	Linear range of the K-ISE (M)
CP 1	57.6	104.2	10^{-1} - $10^{-4.5}$
CP 2	57.3	109.1	10^{-1} - $10^{-4.5}$
CP 3	56.9	107.3	10^{-1} - $10^{-4.5}$
CP 4	57.2	106.6	10^{-1} - $10^{-4.5}$
CP 5	56.9	103.7	10^{-1} - $10^{-4.5}$
Orion	56.5	-146.8	10^{-1} - 10^{-5}

Appendix 4

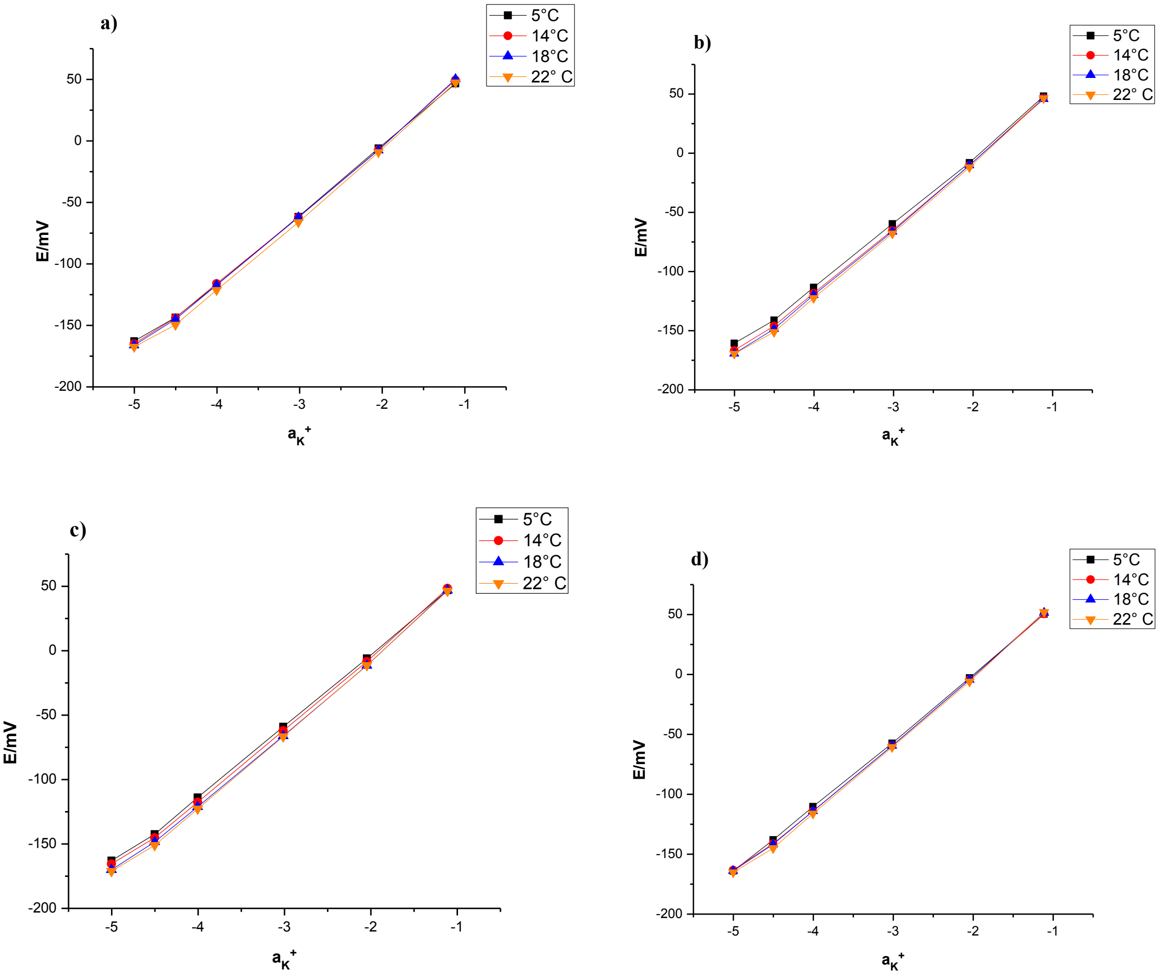


Figure 1. Calibration curves for K-ISE vs. (a) IM2 SSC, (b) IM3 SSC, (c) IM4 SSC and (d) IM5 SSC reference electrodes.

Table 1. **Theoretical and experimental nernstian ratios for K-ISE calibration.**

Temperature change	From 5 °C to 14 °C	From 14 °C to 18 °C	From 18 °C to 22 °C
Theoretical nernstian ratio	1.03	1.01	1.01
Experimental nernstian ratio IM2	1.02	1.01	1.02
Experimental nernstian ratio IM3	1.03	1.02	1.01
Experimental nernstian ratio IM4	1.04	1.02	1.02
Experimental nernstian ratio IM5	1.02	1.01	1.01

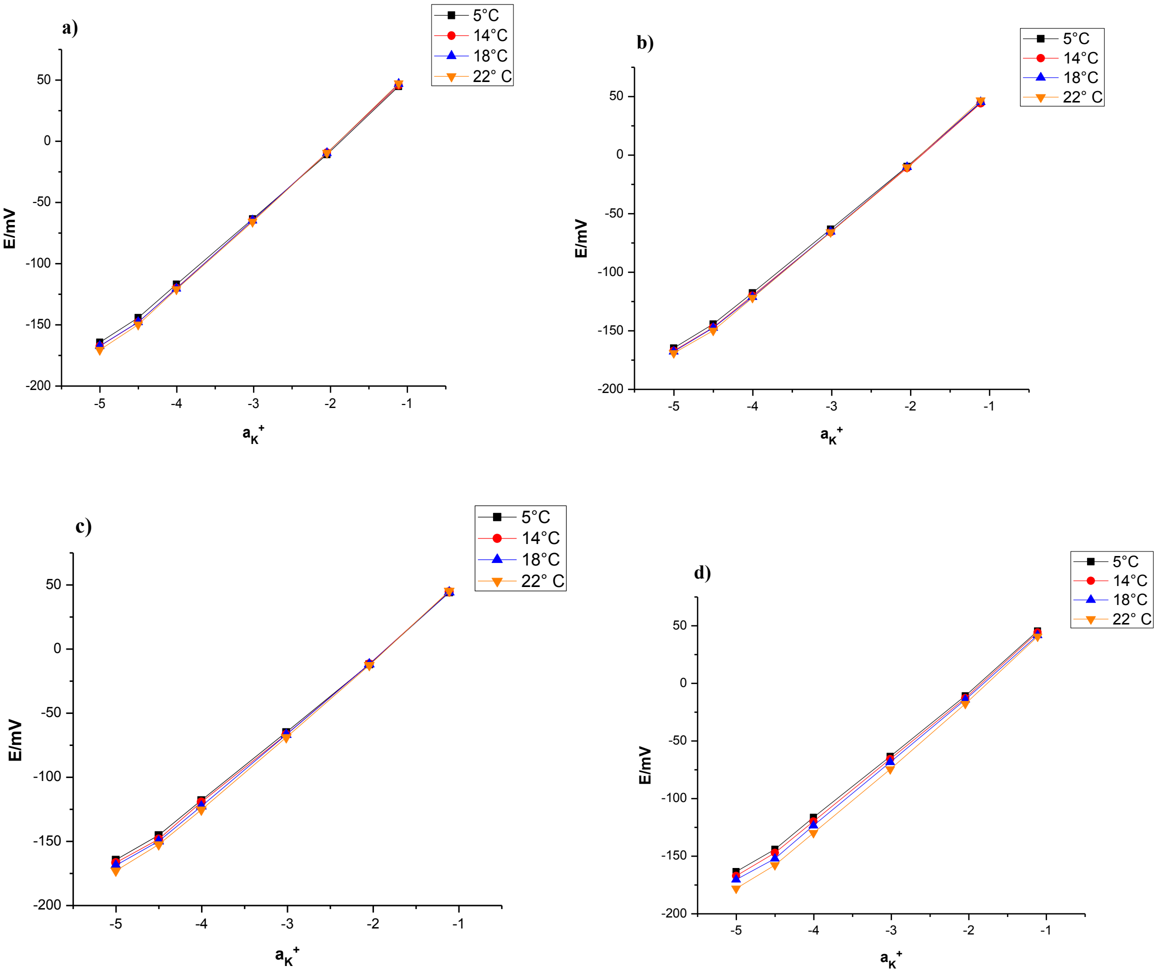


Figure 2. Calibration curves for K-ISE vs. (a) CP2 SSC, (b) CP3 SSC, (c) CP4 SSC and (d) CP5 SSC reference electrodes.

Table 2. Theoretical and experimental nernstian ratios for K-ISE calibration.

Temperature change	From 5 °C to 14 °C	From 14 °C to 18 °C	From 18 °C to 22 °C
Theoretical nernstian ratio	1.03	1.01	1.01
Experimental nernstian ratio CP2	1.03	1.02	1.02
Experimental nernstian ratio CP3	1.04	1.01	1.01
Experimental nernstian ratio CP4	1.02	1.01	1.02
Experimental nernstian ratio CP5	1.03	1.01	1.01

Appendix 5

Table 1. Calibration data for the Na-ISE at 5°C using the reference electrodes prepared by IM and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Na-ISE (M)
IM 1	53.9	147.1	10^{-1} - 10^{-4}
IM 2	53.5	144.5	10^{-1} - 10^{-4}
IM 3	54.3	145.3	10^{-1} - 10^{-4}
IM 4	54.3	145.7	10^{-1} - 10^{-4}
IM 5	54.2	146.0	10^{-1} - 10^{-4}
Orion	53.9	-109.0	10^{-1} - 10^{-4}

Table 2. Calibration data for the Na-ISE at 5°C using the reference electrodes prepared by CP and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Na-ISE (M)
CP 1	53.8	137.4	10^{-1} - 10^{-4}
CP 2	54.7	138.2	10^{-1} - 10^{-4}
CP 3	54.4	143.1	10^{-1} - 10^{-4}
CP 4	53.9	142.6	10^{-1} - 10^{-4}
CP 5	53.7	140.4	10^{-1} - 10^{-4}
Orion	53.9	-109.0	10^{-1} - 10^{-4}

Table 3. Calibration data for the Na-ISE at 14°C using the reference electrodes prepared by IM and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Na-ISE (M)
IM 1	56.2	152.3	10^{-1} - 10^{-4}
IM 2	54.8	148.5	10^{-1} - 10^{-4}
IM 3	56.1	149.5	10^{-1} - 10^{-4}
IM 4	55.5	151.5	10^{-1} - 10^{-4}
IM 5	55.7	150.2	10^{-1} - 10^{-4}
Orion	55.1	-103.5	10^{-1} - 10^{-4}

Table 4. Calibration data for the Na-ISE at 14°C using the reference electrodes prepared by CP and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Na-ISE (M)
CP 1	56.2	143.1	10^{-1} - 10^{-4}
CP 2	55.5	139.7	10^{-1} - 10^{-4}
CP 3	56.7	147.8	10^{-1} - 10^{-4}
CP 4	55.6	147.3	10^{-1} - 10^{-4}
CP 5	56.7	147.3	10^{-1} - 10^{-4}
Orion	55.1	-103.5	10^{-1} - 10^{-4}

Table 5. Calibration data for the Na-ISE at 18°C using the reference electrodes prepared by IM and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Na-ISE (M)
IM 1	57.1	148.9	10^{-1} - 10^{-4}
IM 2	56.9	150.6	10^{-1} - 10^{-4}
IM 3	56.3	149.0	10^{-1} - 10^{-4}
IM 4	56.6	150.4	10^{-1} - 10^{-4}
IM 5	56.2	150.7	10^{-1} - 10^{-4}
Orion	56.1	-104.5	10^{-1} - 10^{-4}

Table 6. Calibration data for the Na-ISE at 18°C using the reference electrodes prepared by CP and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Na-ISE (M)
CP 1	57.4	141.9	10^{-1} - 10^{-4}
CP 2	56.8	143.8	10^{-1} - 10^{-4}
CP 3	56.5	149.7	10^{-1} - 10^{-4}
CP 4	56.5	149.1	10^{-1} - 10^{-4}
CP 5	56.2	147.8	10^{-1} - 10^{-4}
Orion	56.1	-104.5	10^{-1} - 10^{-4}

Appendix 6

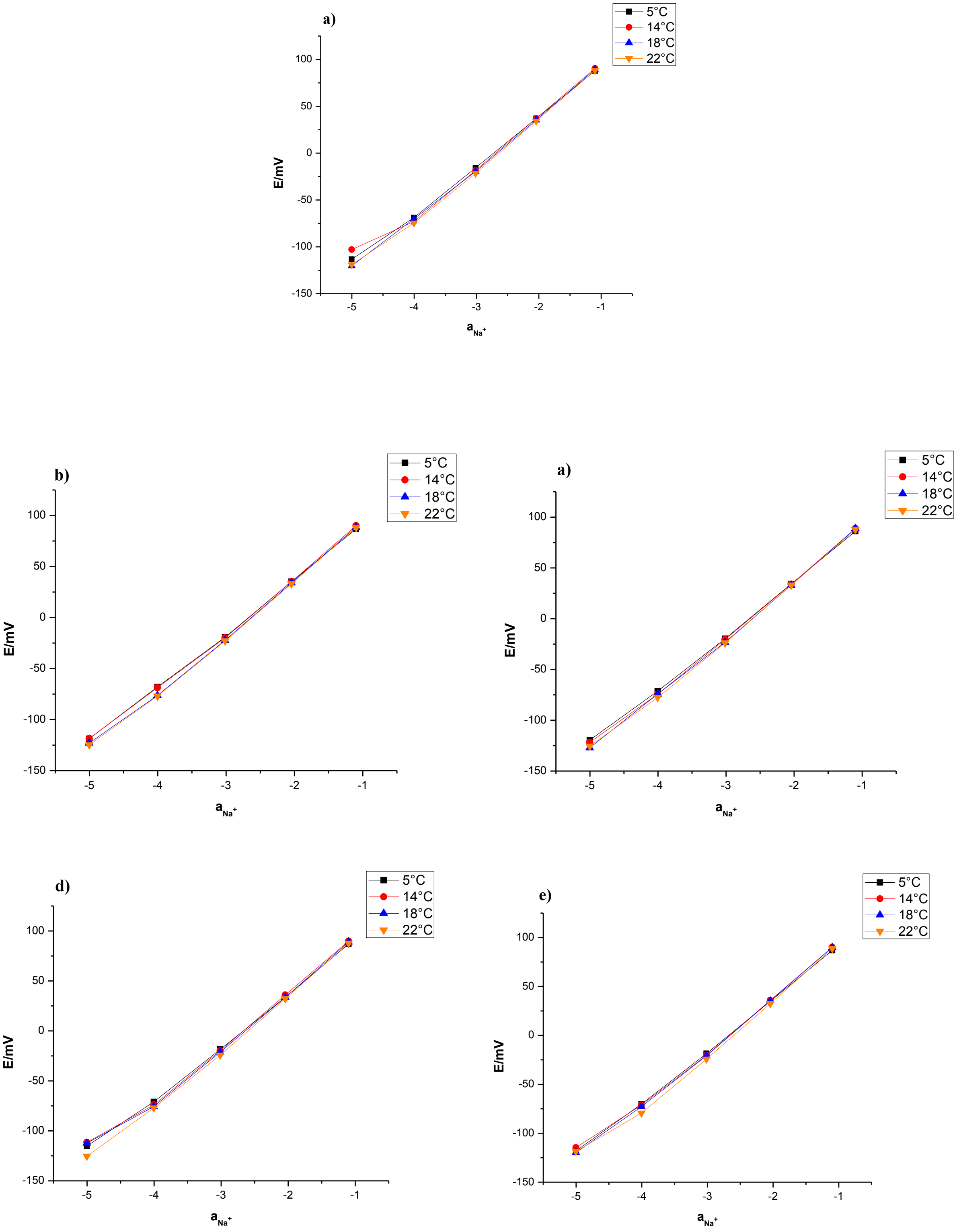
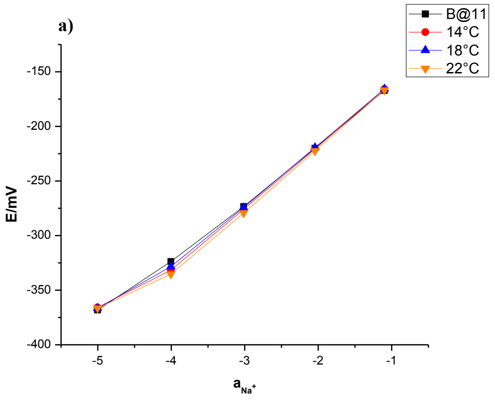
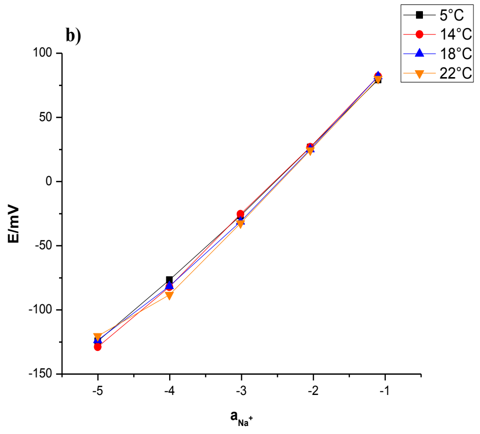


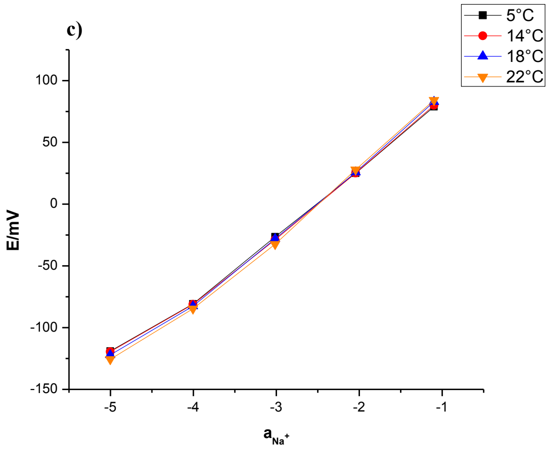
Figure 1. Calibration curves for Na-ISE vs. (a) IM1 SSC (b) IM2 SSC, (c) IM3 SSC, (d) IM4 SSC and (e) IM5 SSC reference electrodes.

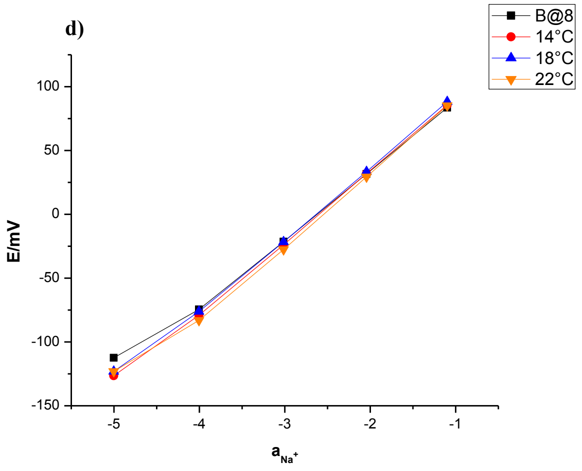
Table 1. Theoretical and experimental nernstian ratios for Na-ISE calibration.

Temperature change	From 5 °C to 14 °C	From 14 °C to 18 °C	From 18 °C to 22 °C
Theoretical nernstian ratio	1.03	1.01	1.01
Experimental nernstian ratio IM1	1.04	1.02	1.02
Experimental nernstian ratio IM2	1.02	1.01	1.01
Experimental nernstian ratio IM3	1.02	1.02	1.01
Experimental nernstian ratio IM4	1.04	1.00	1.01
Experimental nernstian ratio IM5	1.03	1.02	1.02









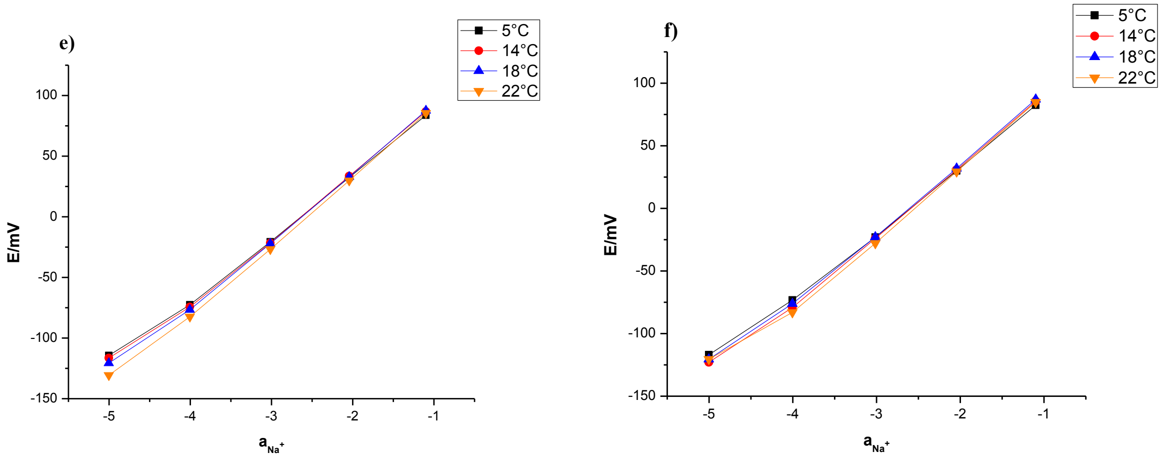


Figure 2. Calibration curves for Na-ISE vs. (a) Orion , (b) CP1 SSC, (c) CP2 SSC and (d) CP3 (e) CP4 SSC (f) CP5 SSC reference electrodes.

Table 2. **Theoretical and experimental nernstian ratios for Na-ISE calibration.**

Temperature change	From 5 °C to 14 °C	From 14 °C to 18 °C	From 18 °C to 22 °C
Theoretical nernstian ratio	1.03	1.01	1.01
Experimental nernstian ratio CP1	1.04	1.02	1.01
Experimental nernstian ratio CP2	1.03	1.02	1.01
Experimental nernstian ratio CP3	1.03	1.00	1.01
Experimental nernstian ratio CP4	1.02	1.01	1.02
Experimental nernstian ratio CP5	1.04	1.01	1.01
Experimental nernstian ratio Orion	1.02	1.02	1.04

Appendix 7

Table 1. Calibration data for the Cl-ISE at 5°C using the reference electrodes prepared by IM and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Cl-ISE (M)
IM 1	-53.0	24.0	10^{-1} - 10^{-4}
IM 2	-53.1	23.5	10^{-1} - 10^{-4}
IM 3	-53.3	22.3	10^{-1} - 10^{-4}
IM 4	-53.0	24.1	10^{-1} - 10^{-4}
IM 5	-53.7	22.1	10^{-1} - 10^{-4}
Orion	-53.4	-230.1	10^{-1} - 10^{-4}

Table 2. Calibration data for the Cl-ISE at 5°C using the reference electrodes prepared by CP and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Cl-ISE (M)
CP 1	-53.4	16.6	10^{-1} - 10^{-4}
CP 2	-53.0	14.6	10^{-1} - 10^{-4}
CP 3	-53.3	19.5	10^{-1} - 10^{-4}
CP 4	-53.4	19.6	10^{-1} - 10^{-4}
CP 5	-53.4	19.8	10^{-1} - 10^{-4}
Orion	-53.4	-230.1	10^{-1} - 10^{-4}

Table 3. Calibration data for the Cl-ISE at 14°C using the reference electrodes prepared by IM and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Cl-ISE (M)
IM 1	-54.8	27.0	10^{-1} - 10^{-4}
IM 2	-54.6	28.0	10^{-1} - 10^{-4}
IM 3	-54.0	25.9	10^{-1} - 10^{-4}
IM 4	-54.4	26.8	10^{-1} - 10^{-4}
IM 5	-54.3	28.7	10^{-1} - 10^{-4}
Orion	-54.8	-229.9	10^{-1} - 10^{-4}

Table 4. Calibration data for the Cl-ISE at 14°C using the reference electrodes prepared by CP and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Cl-ISE (M)
CP 1	-55.1	25.7	10^{-1} - 10^{-4}
CP 2	-54.3	16.9	10^{-1} - 10^{-4}
CP 3	-54.9	23.2	10^{-1} - 10^{-4}
CP 4	-55.0	25.5	10^{-1} - 10^{-4}
CP 5	-54.7	22.6	10^{-1} - 10^{-4}
Orion	-54.8	-229.9	10^{-1} - 10^{-4}

Table 5. Calibration data for the Cl-ISE at 18°C using the reference electrodes prepared by IM and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Cl-ISE (M)
IM 1	-55.7	28.6	10^{-1} - 10^{-4}
IM 2	-55.6	27.2	10^{-1} - 10^{-4}
IM 3	-56.2	24.5	10^{-1} - 10^{-4}
IM 4	-55.8	25.1	10^{-1} - 10^{-4}
IM 5	-55.4	28.4	10^{-1} - 10^{-4}
Orion	-55.0	-224.0	10^{-1} - 10^{-4}

Table 6. Calibration data for the Cl-ISE at 18°C using the reference electrodes prepared by CP and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Cl-ISE (M)
CP 1	-55.4	19.6	10^{-1} - 10^{-4}
CP 2	-55.5	20.1	10^{-1} - 10^{-4}
CP 3	-55.3	26.8	10^{-1} - 10^{-4}
CP 4	-55.3	27.7	10^{-1} - 10^{-4}
CP 5	-55.0	26.7	10^{-1} - 10^{-4}
Orion	-55.0	-223.9	10^{-1} - 10^{-4}

Appendix 8

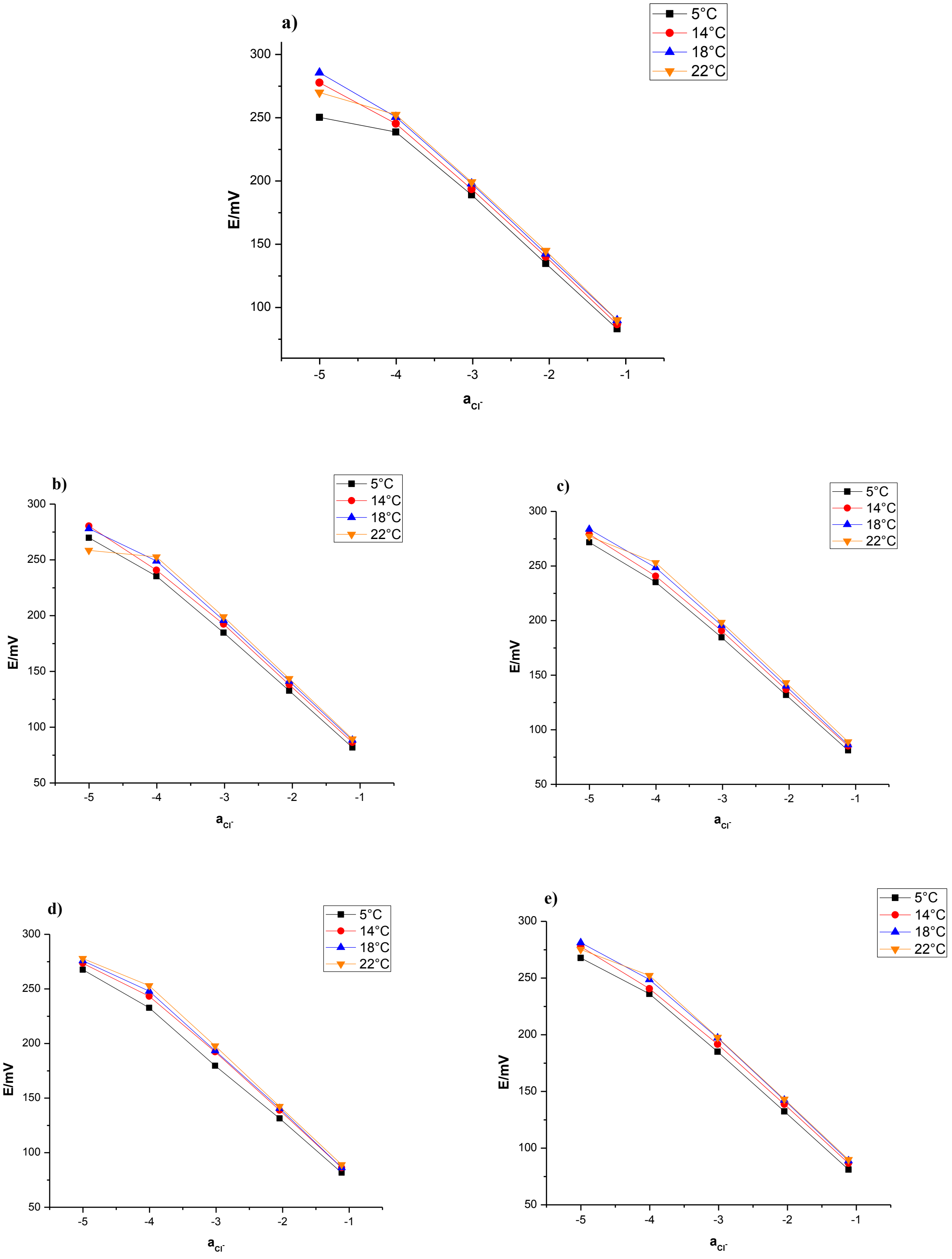
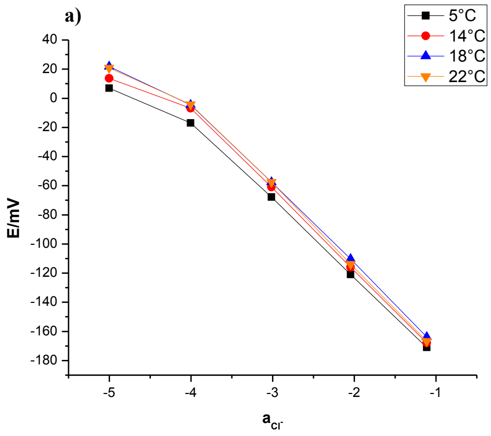
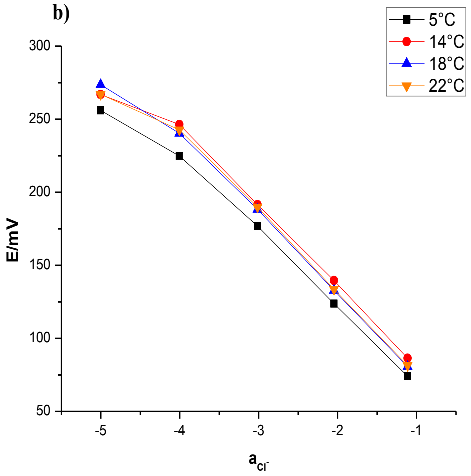


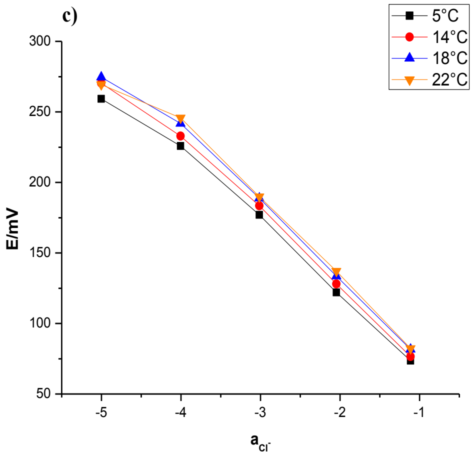
Figure 1. Calibration curves for Cl-ISE vs. (a) IM1 SSC (b) IM2 SSC, (c) IM3 SSC, (d) IM4 SSC and (e) IM5 SSC reference electrodes.

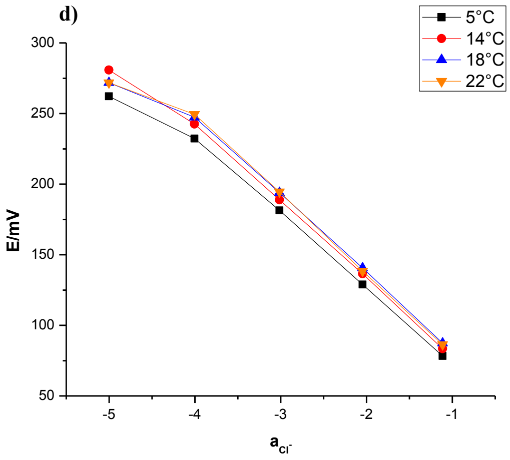
Table 1. Theoretical and experimental nernstian ratios for Cl-ISE calibration.

Temperature change	From 5 °C to 14 °C	From 14 °C to 18 °C	From 18 °C to 22 °C
Theoretical nernstian ratio	1.03	1.01	1.01
Experimental nernstian ratio IM1	1.03	1.02	1.01
Experimental nernstian ratio IM2	1.02	1.01	1.01
Experimental nernstian ratio IM3	1.04	1.00	1.01
Experimental nernstian ratio IM4	1.03	1.02	1.02
Experimental nernstian ratio IM5	1.03	1.01	1.03









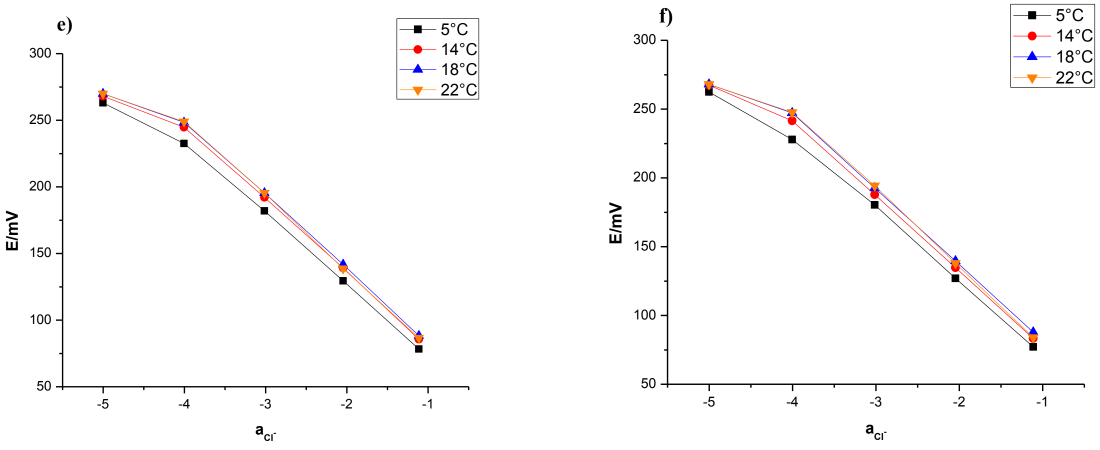


Figure 2. Calibration curves for Cl-ISE vs (a) Orion , (b) CP1 SSC, (c) CP2 SSC and (d) CP3 (e) CP4 SSC (f) CP5 SSC reference electrodes.

Table 2. Theoretical and experimental nernstian ratios for Cl-ISE calibration.

Temperature change	From 5 °C to 14 °C	From 14 °C to 18 °C	From 18 °C to 22 °C
Theoretical nernstian ratio	1.03	1.01	1.01
Experimental nernstian ratio CP1	1.03	1.01	1.01
Experimental nernstian ratio CP2	1.01	1.01	1.03
Experimental nernstian ratio CP3	1.04	1.01	1.00
Experimental nernstian ratio CP4	1.03	1.02	1.01
Experimental nernstian ratio CP5	1.03	1.00	1.01
Experimental nernstian ratio Orion	1.03	1.00	1.02

Appendix 9

Table 1. Calibration data for the Ca-ISE at 5°C using the reference electrodes prepared by IM and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Ca-ISE (M)
IM 1	26.4	98.1	10^{-1} - 10^{-4}
IM 2	26.4	98.0	10^{-1} - 10^{-4}
IM 3	26.4	98.1	10^{-1} - 10^{-4}
IM 4	26.4	98.6	10^{-1} - 10^{-4}
IM 5	26.8	100.0	10^{-1} - 10^{-4}
Orion	26.6	-152.7	10^{-1} - 10^{-4}

Table 2. Calibration data for the Ca-ISE at 5°C using the reference electrodes prepared by CP and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Ca-ISE (M)
CP 1	26.6	87.3	10^{-1} - 10^{-4}
CP 2	26.6	89.5	10^{-1} - 10^{-4}
CP 3	26.6	99.5	10^{-1} - 10^{-4}
CP 4	26.6	99.0	10^{-1} - 10^{-4}
CP 5	26.8	99.7	10^{-1} - 10^{-4}
Orion	26.6	-152.7	10^{-1} - 10^{-4}

Table 3. Calibration data for the Ca-ISE at 14°C using the reference electrodes prepared by IM and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Ca-ISE (M)
IM 1	27.1	100.9	10^{-1} - 10^{-4}
IM 2	27.1	101.1	10^{-1} - 10^{-4}
IM 3	27.1	100.5	10^{-1} - 10^{-4}
IM 4	27.2	101.2	10^{-1} - 10^{-4}
IM 5	27.0	102.0	10^{-1} - 10^{-4}
Orion	26.9	-153.4	10^{-1} - 10^{-4}

Table 4. Calibration data for the Ca-ISE at 14°C using the reference electrodes prepared by CP and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Ca-ISE (M)
CP 1	27.2	90.9	10^{-1} - 10^{-4}
CP 2	27.1	91.2	10^{-1} - 10^{-4}
CP 3	27.1	100.7	10^{-1} - 10^{-4}
CP 4	27.0	102.1	10^{-1} - 10^{-4}
CP 5	27.2	102.7	10^{-1} - 10^{-4}
Orion	26.9	-153.4	10^{-1} - 10^{-4}

Table 5. Calibration data for the Ca-ISE at 18°C using the reference electrodes prepared by IM and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Ca-ISE (M)
IM 1	27.6	103.0	10^{-1} - 10^{-4}
IM 2	27.5	102.5	10^{-1} - 10^{-4}
IM 3	27.4	101.8	10^{-1} - 10^{-4}
IM 4	27.5	102.5	10^{-1} - 10^{-4}
IM 5	27.6	103.8	10^{-1} - 10^{-4}
Orion	27.5	-152.7	10^{-1} - 10^{-4}

Table 6. Calibration data for the Ca-ISE at 18°C using the reference electrodes prepared by CP and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Linear range of the Ca-ISE (M)
CP 1	27.6	92.3	10^{-1} - 10^{-4}
CP 2	27.6	93.3	10^{-1} - 10^{-4}
CP 3	27.6	102.1	10^{-1} - 10^{-4}
CP 4	27.6	103.8	10^{-1} - 10^{-4}
CP 5	27.6	103.1	10^{-1} - 10^{-4}
Orion	27.5	-152.7	10^{-1} - 10^{-4}

Appendix 10

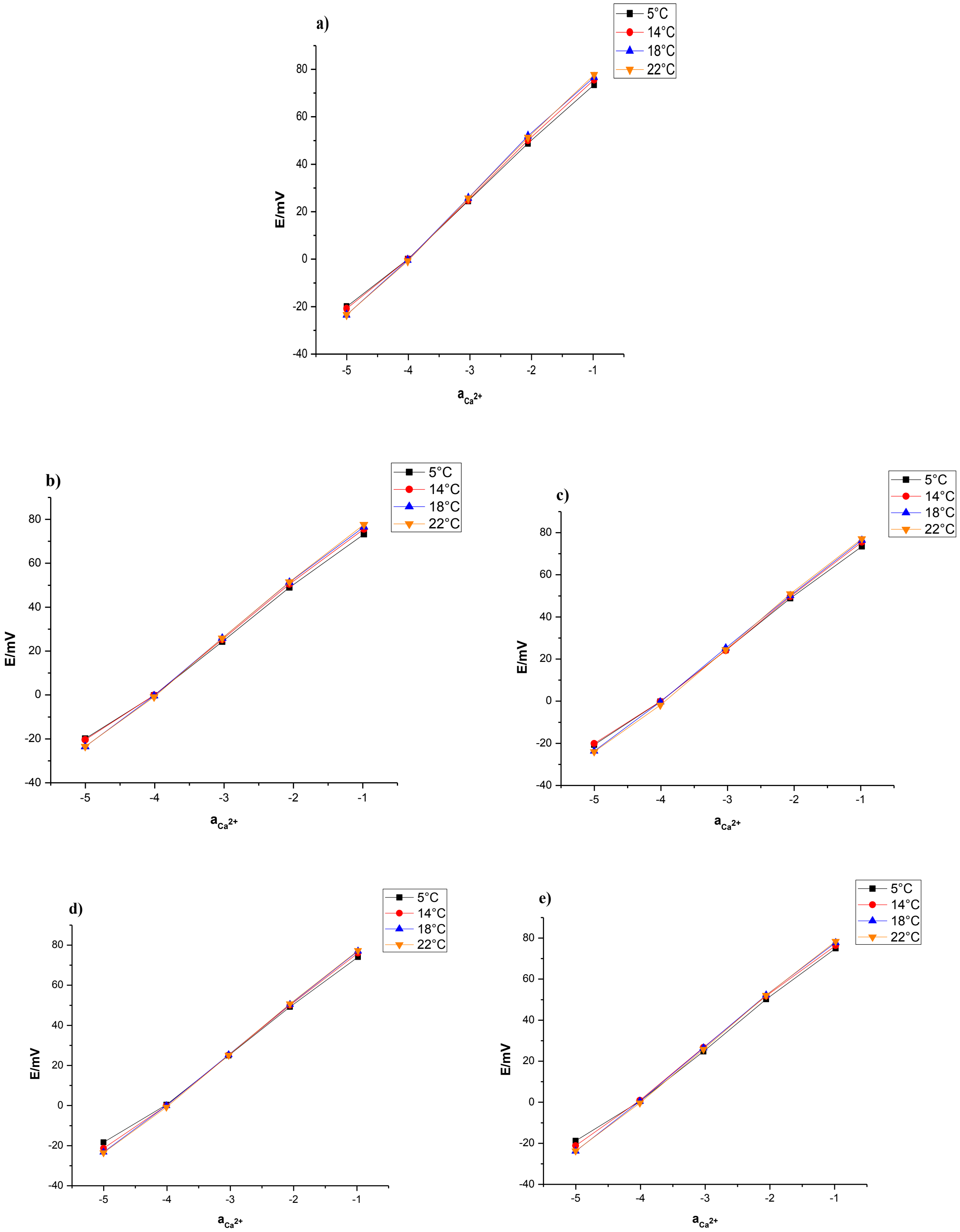
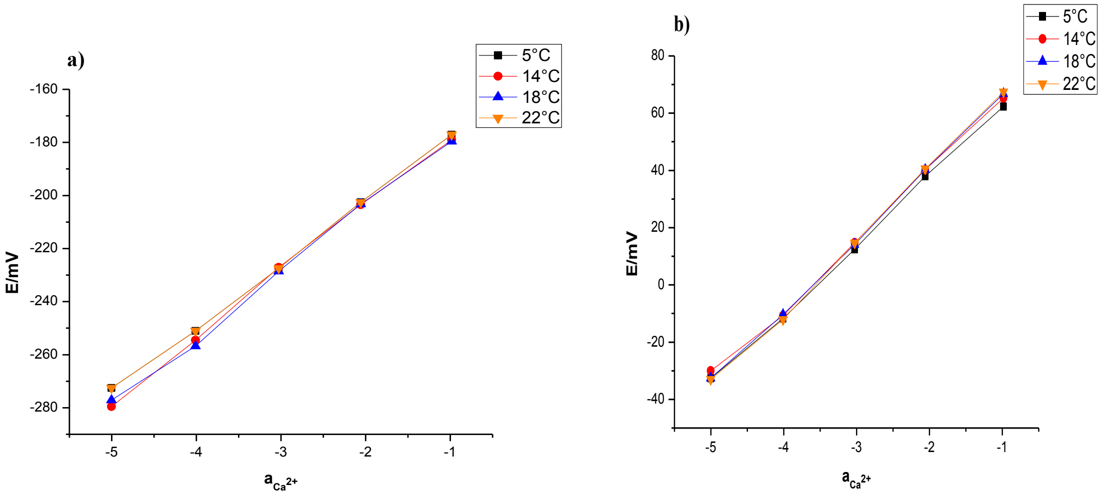


Figure 1. Calibration curves for Ca-ISE vs. (a) IM1 SSC (b) IM2 SSC, (c) IM3 SSC, (d) IM4 SSC and (e) IM5 SSC reference electrodes.

Table 1. Theoretical and experimental nernstian ratios for Ca-ISE calibration.

Temperature change	From 5 °C to 14 °C	From 14 °C to 18 °C	From 18 °C to 22 °C
Theoretical nernstian ratio	1.03	1.01	1.01
Experimental nernstian ratio IM1	1.03	1.02	1.01
Experimental nernstian ratio IM2	1.03	1.02	1.00
Experimental nernstian ratio IM3	1.01	1.01	1.01
Experimental nernstian ratio IM4	1.04	1.01	1.01
Experimental nernstian ratio IM5	1.02	1.02	1.01



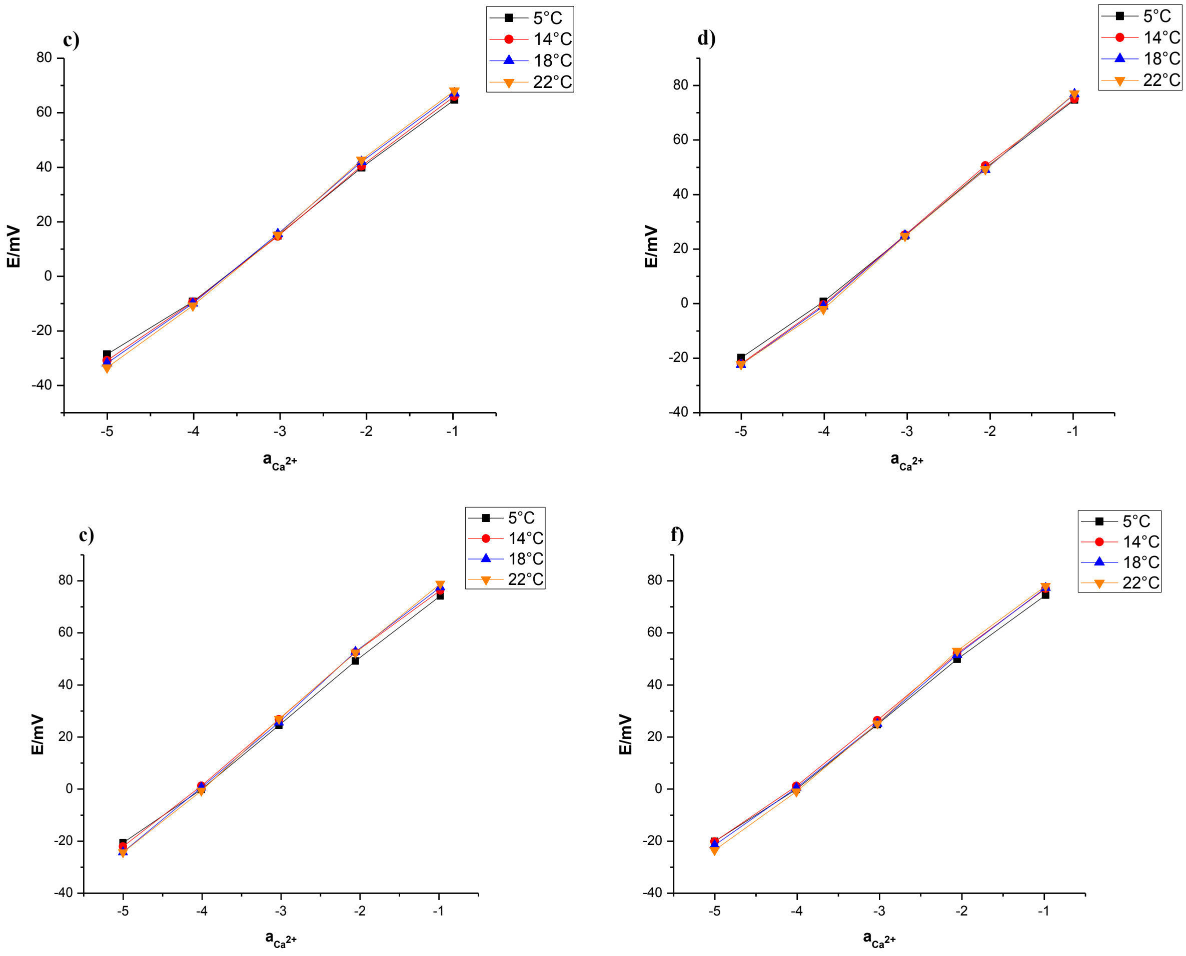


Figure 2. Calibration curves for Ca-ISE vs. (a) Orion, (b) CP1 SSC, (c) CP2 SSC and (d) CP3 (e) CP4 SSC (f) CP5 SSC reference electrodes.

Table 2. **Theoretical and experimental nernstian ratios for Ca-ISE calibration.**

Temperature change	From 5 °C to 14 °C	From 14 °C to 18 °C	From 18 °C to 22 °C
Theoretical nernstian ratio	1.03	1.01	1.01
Experimental nernstian ratio CP1	1.02	1.01	1.02
Experimental nernstian ratio CP2	1.02	1.02	1.01
Experimental nernstian ratio CP3	1.01	1.01	1.02
Experimental nernstian ratio CP4	1.03	1.01	1.02
Experimental nernstian ratio CP5	1.03	1.01	1.02
Experimental nernstian ratio Orion	1.04	1.00	1.01

Appendix 11

Table 1. Calibration data for the pH electrode at 5°C using the reference electrodes prepared by IM and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Calibration range
IM 1	54.5	623.6	4.01 – 10.01
IM 2	54.7	625.1	4.01 – 10.01
IM 3	54.1	619.4	4.01 – 10.01
IM 4	54.4	619.0	4.01 – 10.01
IM 5	54.2	621.6	4.01 – 10.01
Orion	54.9	373.7	4.01 – 10.01

Table 2. Calibration data for the pH electrode at 5°C using the reference electrodes prepared by CP and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Calibration range
CP 1	54.2	617.3	4.01 – 10.01
CP 2	54.6	621.3	4.01 – 10.01
CP 3	54.9	625.4	4.01 – 10.01
CP 4	54.9	626.0	4.01 – 10.01
CP 5	54.9	624.3	4.01 – 10.01
Orion	54.9	373.7	4.01 – 10.01

Table 3. Calibration data for the pH electrode at 14°C using the reference electrodes prepared by IM and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Calibration range
IM 1	55.7	629.8	4.01 – 10.01
IM 2	55.6	631.3	4.01 – 10.01
IM 3	55.3	629.5	4.01 – 10.01
IM 4	55.6	630.9	4.01 – 10.01
IM 5	55.6	631.3	4.01 – 10.01
Orion	55.6	378.6	4.01 – 10.01

Table 4. Calibration data for the pH electrode at 14°C using the reference electrodes prepared by CP and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Calibration range
CP 1	55.6	625.3	4.01 – 10.01
CP 2	55.5	629.2	4.01 – 10.01
CP 3	55.5	629.4	4.01 – 10.01
CP 4	55.5	630.0	4.01 – 10.01
CP 5	55.4	628.4	4.01 – 10.01
Orion	55.6	378.6	4.01 – 10.01

Table 5. Calibration data for the pH electrode at 18°C using the reference electrodes prepared by IM and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Calibration range
IM 1	56.3	635.2	4.01 – 10.01
IM 2	56.2	634.6	4.01 – 10.01
IM 3	56.0	634.7	4.01 – 10.01
IM 4	56.2	634.5	4.01 – 10.01
IM 5	56.1	636.2	4.01 – 10.01
Orion	56.3	383.2	4.01 – 10.01

Table 6. Calibration data for the pH electrode at 18°C using the reference electrodes prepared by CP and the commercial reference electrode.

Reference electrode	Slope (mV/decade)	Standard potential (E^o) (mV)	Calibration range
CP 1	56.1	628.7	4.01 – 10.01
CP 2	56.3	633.6	4.01 – 10.01
CP 3	56.1	634.0	4.01 – 10.01
CP 4	56.0	633.6	4.01 – 10.01
CP 5	56.1	634.5	4.01 – 10.01
Orion	56.3	383.2	4.01 – 10.01

Appendix 12

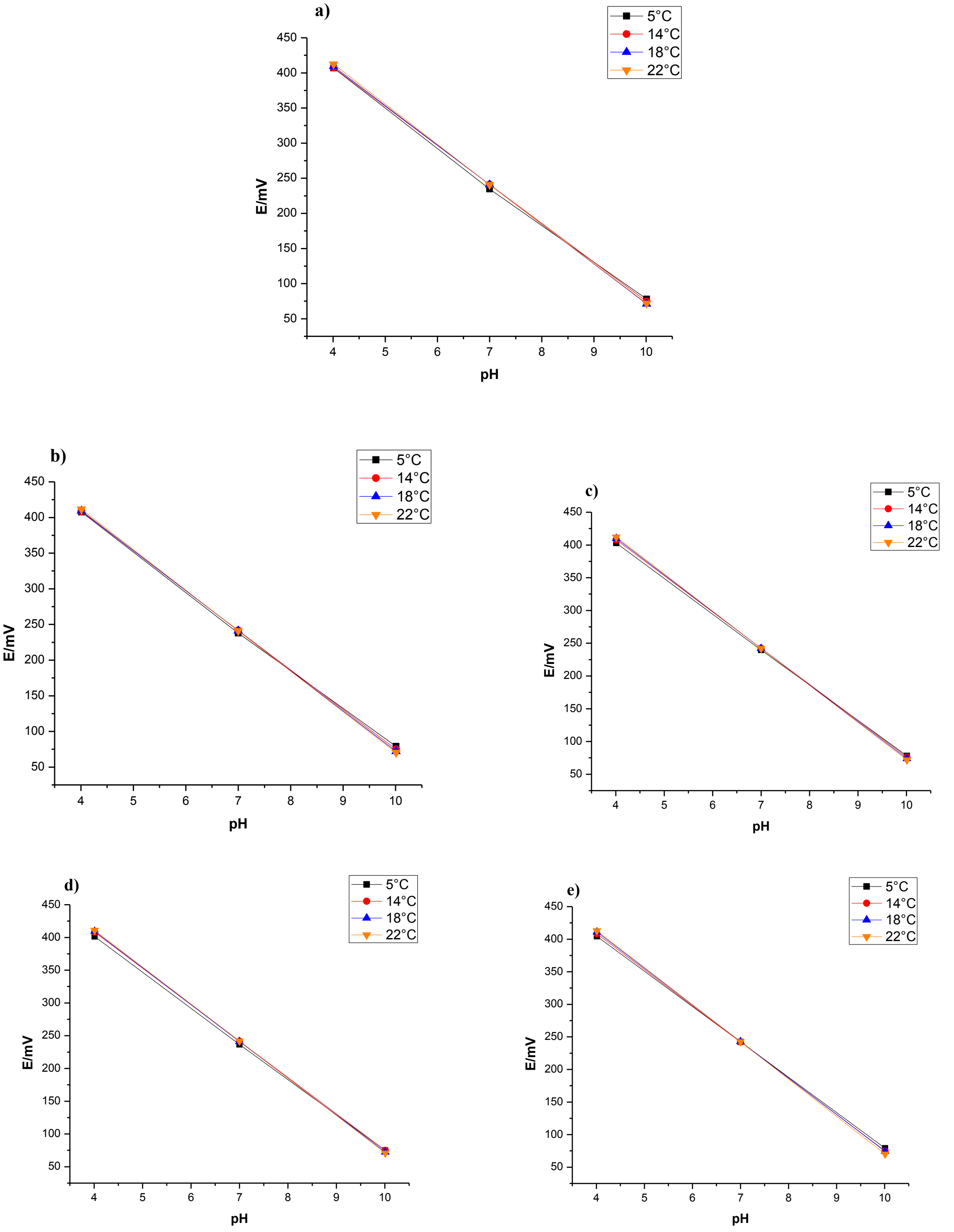
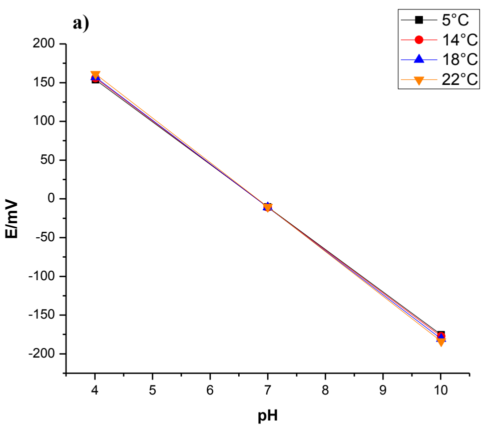
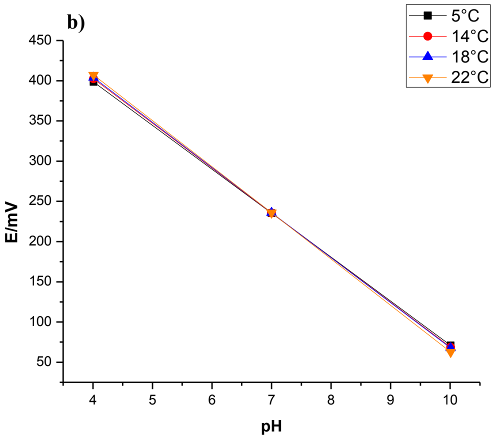


Figure 1. Calibration curves for the pH electrode vs. (a) IM1 SSC (b) IM2 SSC, (c) IM3 SSC, (d) IM4 SSC and (e) IM5 SSC reference electrode.

Table 1. Theoretical and experimental nernstian ratios for the pH electrode calibration.

Temperature change	From 5 °C to 14 °C	From 14 °C to 18 °C	From 18 °C to 22 °C
Theoretical nernstian ratio	1.03	1.01	1.01
Experimental nernstian ratio IM1	1.03	1.01	1.01
Experimental nernstian ratio IM2	1.01	1.01	1.01
Experimental nernstian ratio IM3	1.03	1.00	1.00
Experimental nernstian ratio IM4	1.02	1.02	1.02
Experimental nernstian ratio IM5	1.03	1.01	1.01





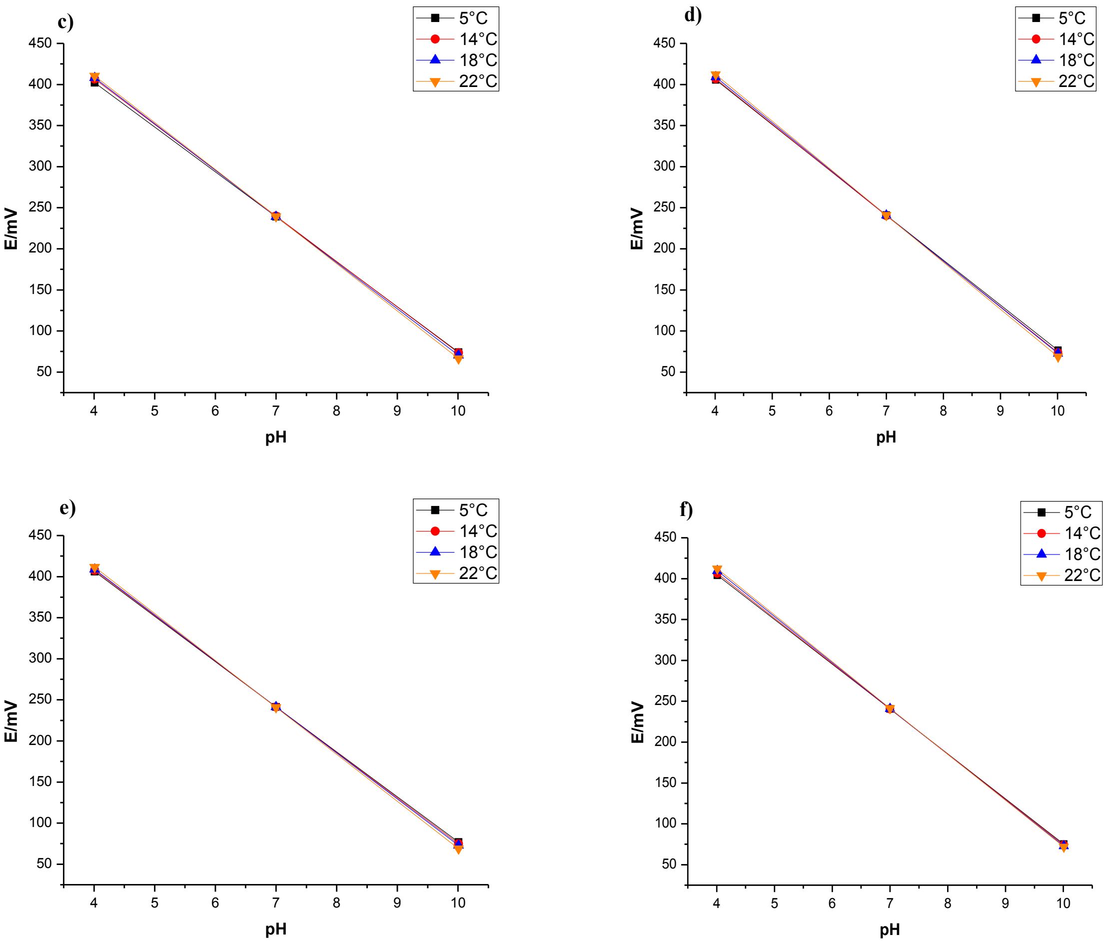


Figure 2. Calibration curves for the pH electrode vs. (a) Orion, (b) CP1 SSC, (c) CP2 SSC and (d) CP3 (e) CP4 SSC (f) CP5 SSC reference electrodes.

Table 2. **Theoretical and experimental nernstian ratios for the pH electrode calibration.**

Temperature change	From 5 °C to 14 °C	From 14 °C to 18 °C	From 18 °C to 22 °C
Theoretical nernstian ratio	1.03	1.01	1.01
Experimental nernstian ratio CP1	1.03	1.01	1.02
Experimental nernstian ratio CP2	1.03	1.01	1.01
Experimental nernstian ratio CP3	1.03	1.03	1.01
Experimental nernstian ratio CP4	1.02	1.01	1.02
Experimental nernstian ratio CP5	1.04	1.02	1.01
Experimental nernstian ratio Orion	1.01	1.01	1.01

Appendix 13

Table 1. Ions concentration measured in RW1 at 5°C using IM and commercial reference electrodes.

Concentrations are reported as the average of 3 repetitions ± standard deviation except for the external laboratory results.

Reference Electrode	K$^+$ concentration (mg/l)	Na$^+$ concentration (mg/l)	Cl$^-$ concentration (mg/l)	Ca^{2+} concentration (mg/l)	pH
IM1	1.61 ± 0.03	7.18 ± 0.16	9.58 ± 0.31	9.53 ± 0.19	7.77 ± 0.03
IM2	1.62 ± 0.05	7.17 ± 0.16	9.57 ± 0.09	9.75 ± 0.05	7.80 ± 0.03
IM3	1.61 ± 0.01	7.32 ± 0.18	9.42 ± 0.11	9.78 ± 0.13	7.81 ± 0.01
IM4	1.57 ± 0.02	7.01 ± 0.27	9.59 ± 0.13	9.62 ± 0.19	7.78 ± 0.01
IM5	1.60 ± 0.02	6.86 ± 0.10	9.56 ± 0.14	9.61 ± 0.22	7.76 ± 0.01
Orion	1.60 ± 0.02	6.80 ± 0.44	9.60 ± 0.08	9.42 ± 0.19	7.78 ± 0.01

Table 2. Ions concentration measured in RW1 at 18°C using IM and commercial reference electrodes.

Reference Electrode	K$^+$ concentration (mg/l)	Na$^+$ concentration (mg/l)	Cl$^-$ concentration (mg/l)	Ca^{2+} concentration (mg/l)	pH
IM1	1.63 ± 0.06	7.13 ± 0.14	9.41 ± 0.27	9.55 ± 0.38	7.60 ± 0.02
IM2	1.61 ± 0.06	7.28 ± 0.16	9.57 ± 0.09	9.52 ± 0.21	7.59 ± 0.02
IM3	1.61 ± 0.04	7.10 ± 0.22	9.52 ± 0.15	9.30 ± 0.20	7.61 ± 0.02
IM4	1.61 ± 0.03	7.07 ± 0.19	9.57 ± 0.24	9.57 ± 0.31	7.58 ± 0.01
IM5	1.60 ± 0.02	7.14 ± 0.38	9.55 ± 0.16	9.55 ± 0.17	7.61 ± 0.02
Orion	1.60 ± 0.02	7.17 ± 0.31	9.50 ± 0.15	9.53 ± 0.30	7.56 ± 0.01

Concentrations are reported as the average of 3 repetitions ± standard deviation except for the external laboratory results.

Table 3. Ions concentration measured in RW1 at 5°C using CP and commercial reference electrodes.

Reference Electrode	K$^+$ concentration (mg/l)	Na$^+$ concentration (mg/l)	Cl$^-$ concentration (mg/l)	Ca^{2+} concentration (mg/l)	pH
CP1	1.60 ± 0.02	6.56 ± 0.24	9.67 ± 0.26	9.61 ± 0.16	7.81 ± 0.01
CP2	1.62 ± 0.01	7.58 ± 0.12	9.46 ± 0.17	9.78 ± 0.07	7.80 ± 0.02
CP3	1.61 ± 0.01	7.36 ± 0.35	9.65 ± 0.31	9.63 ± 0.25	7.80 ± 0.02
CP4	1.60 ± 0.03	7.06 ± 0.16	9.65 ± 0.31	9.77 ± 0.27	7.77 ± 0.01
CP5	1.60 ± 0.02	7.34 ± 0.28	9.57 ± 0.19	9.50 ± 0.13	7.77 ± 0.01
Orion	1.60 ± 0.02	6.80 ± 0.44	9.60 ± 0.08	9.42 ± 0.19	7.78 ± 0.01

Concentrations are reported as the average of 3 repetitions ± standard deviation except for the external laboratory results.

Table 4. Ions concentration measured in RW1 at 18°C using CP and commercial reference electrodes.

Reference Electrode	K^{+} concentration (mg/l)	Na^{+} concentration (mg/l)	Cl^{-} concentration (mg/l)	Ca^{2+} concentration (mg/l)	pH
CP1	1.64 ± 0.04	7.21 ± 0.30	9.58 ± 0.10	9.72 ± 0.25	7.58 ± 0.01
CP2	1.62 ± 0.06	7.23 ± 0.25	9.61 ± 0.06	9.46 ± 0.15	7.58 ± 0.01
CP3	1.62 ± 0.03	7.10 ± 0.28	9.49 ± 0.15	9.64 ± 0.19	7.58 ± 0.01
CP4	1.62 ± 0.03	7.30 ± 0.36	9.75 ± 0.15	9.69 ± 0.23	7.59 ± 0.02
CP5	1.58 ± 0.02	7.14 ± 0.22	9.55 ± 0.24	9.55 ± 0.09	7.57 ± 0.02
Orion	1.60 ± 0.02	7.17 ± 0.31	9.50 ± 0.15	9.53 ± 0.30	7.56 ± 0.01

Table 5. Ions concentration measured in RW2 at 5°C using IM and commercial reference electrodes.

Reference Electrode	K^{+} concentration (mg/l)	Na^{+} concentration (mg/l)	Cl^{-} concentration (mg/l)	Ca^{2+} concentration (mg/l)	pH
IM1	2.01 ± 0.03	9.25 ± 0.14	9.85 ± 0.18	13.60 ± 0.26	8.11 ± 0.03
IM2	1.97 ± 0.01	9.27 ± 0.30	9.99 ± 0.19	13.64 ± 0.13	8.10 ± 0.02
IM3	2.01 ± 0.03	9.33 ± 0.32	9.91 ± 0.26	13.42 ± 0.10	8.09 ± 0.02
IM4	2.03 ± 0.03	9.34 ± 0.30	9.91 ± 0.18	13.27 ± 0.40	8.03 ± 0.01
IM5	2.08 ± 0.03	9.55 ± 0.53	9.84 ± 0.22	13.47 ± 0.10	8.11 ± 0.02
Orion	1.97 ± 0.02	9.55 ± 0.26	9.84 ± 0.26	13.16 ± 0.16	8.10 ± 0.01

Concentrations are reported as the average of 3 repetitions ± standard deviation except for the external laboratory results.

Table 6. Ions concentration measured in RW2 at 14°C using IM and commercial reference electrodes.

Reference Electrode	K^{+} concentration (mg/l)	Na^{+} concentration (mg/l)	Cl^{-} concentration (mg/l)	Ca^{2+} concentration (mg/l)	pH
IM1	1.93 ± 0.02	9.67 ± 0.50	9.77 ± 0.15	13.48 ± 0.09	7.90 ± 0.01
IM2	2.00 ± 0.02	9.53 ± 0.39	9.81 ± 0.13	13.62 ± 0.14	7.90 ± 0.01
IM3	2.02 ± 0.04	9.73 ± 0.19	9.86 ± 0.20	13.30 ± 0.27	7.92 ± 0.01
IM4	1.96 ± 0.05	9.53 ± 0.46	9.75 ± 0.16	13.42 ± 0.34	7.91 ± 0.02
IM5	2.02 ± 0.05	9.84 ± 0.39	9.88 ± 0.14	13.34 ± 0.09	7.91 ± 0.02
Orion	2.02 ± 0.07	9.96 ± 0.62	9.83 ± 0.13	13.44 ± 0.32	7.89 ± 0.01

Concentrations are reported as the average of 3 repetitions ± standard deviation except for the external laboratory results.

Table 7. Ions concentration measured in RW2 at 5°C using CP and commercial reference electrodes.

Reference Electrode	K^{+} concentration (mg/l)	Na^{+} concentration (mg/l)	Cl^{-} concentration (mg/l)	Ca^{2+} concentration (mg/l)	pH
CP1	2.00 ± 0.04	9.45 ± 0.18	9.74 ± 0.13	13.43 ± 0.19	8.10 ± 0.03
CP2	2.00 ± 0.03	9.75 ± 0.11	9.81 ± 0.21	13.32 ± 0.38	8.13 ± 0.01
CP3	2.03 ± 0.02	9.47 ± 0.15	9.72 ± 0.14	13.57 ± 0.42	8.09 ± 0.01
CP4	2.04 ± 0.02	10.12 ± 0.21	9.72 ± 0.14	13.26 ± 0.23	8.10 ± 0.02
CP5	2.01 ± 0.01	9.59 ± 0.31	9.84 ± 0.17	13.73 ± 0.22	8.08 ± 0.02
Orion	1.97 ± 0.02	9.55 ± 0.26	9.84 ± 0.26	13.16 ± 0.16	8.10 ± 0.01

Concentrations are reported as the average of 3 repetitions ± standard deviation except for the external laboratory results.

Table 8. Ions concentration measured in RW2 at 14°C using CP and commercial reference electrodes.

Reference Electrode	**K $^{+}$ concentration (mg/l)**	**Na $^{+}$ concentration (mg/l)**	**Cl $^{-}$ concentration (mg/l)**	**Ca $^{2+}$ concentration (mg/l)**	**pH**
CP1	2.09 ± 0.04	9.50 ± 0.37	9.72 ± 0.06	13.34 ± 0.32	7.90 ± 0.01
CP2	2.08 ± 0.03	9.98 ± 0.75	9.84 ± 0.13	13.26 ± 0.29	7.89 ± 0.01
CP3	2.03 ± 0.04	10.03 ± 0.21	9.88 ± 0.09	13.43 ± 0.19	7.89 ± 0.01
CP4	2.00 ± 0.02	10.16 ± 0.37	9.87 ± 0.20	13.76 ± 0.19	7.91 ± 0.01
CP5	2.02 ± 0.04	10.07 ± 0.08	9.83 ± 0.10	13.03 ± 0.39	7.90 ± 0.01
Orion	2.02 ± 0.07	9.96 ± 0.62	9.83 ± 0.13	13.44 ± 0.32	7.89 ± 0.01

Concentrations are reported as the average of 3 repetitions ± standard deviation except for the external laboratory results.

Appendix 14

Table 1. Ion concentrations measured in red wine sauce using IM and CP as reference electrodes compared to the label specifications.

Electrode	Na^+ (g/100g)	Cl^- (g/100g)	K^+ (g/100g)	Ca^{2+} (g/100g)	pH
IM2	0.23	0.99	0.08	0.00077	4.96
IM3	0.25	1.02	0.11	0.00082	4.88
IM4	0.27	0.86	0.07	0.00084	4.97
IM5	0.30	0.89	0.08	0.00092	5.02
CP2	0.29	0.82	0.09	0.00081	4.87
CP3	0.31	0.87	0.09	0.00075	4.92
CP4	0.32	0.77	0.08	0.00073	4.86
CP5	0.31	0.96	0.09	0.00085	4.99
Label	0.43	0.67	-	-	-

The label specification is presented as g NaCl/100g of food.

Table 2. Ion concentrations measured in basic sauce using IM and CP as reference electrodes compared to the label specifications.

Electrode	Na^+ (g/100g)	Cl^- (g/100g)	K^+ (g/100g)	Ca^{2+} (g/100g)	pH
IM2	0.43	0.87	0.07	0.00028	6.00
IM3	0.41	0.94	0.06	0.00026	6.04
IM4	0.40	0.87	0.09	0.00031	6.08
IM5	0.45	0.94	0.07	0.00028	6.07
CP2	0.49	0.84	0.08	0.00028	5.98
CP3	0.46	0.84	0.07	0.00026	6.01
CP4	0.46	0.84	0.08	0.00025	6.08
CP5	0.44	0.88	0.08	0.00026	6.06
Label	0.30	0.45	-	-	-

The label specification is presented as g NaCl/100g of food.

Table 3. Ion concentrations measured in baby food (Salmon flavour) using IM and CP as reference electrodes compared to the label specifications.

Electrode	Na^+ (g/100g)	Cl^- (g/100g)	K^+ (g/100g)	Ca^{2+} (g/100g)	pH
IM2	0.01	0.08	0.08	0.00035	5.74
IM3	0.01	0.09	0.09	0.00038	5.68
IM4	0.01	0.09	0.09	0.00034	5.74
IM5	0.02	0.08	0.08	0.00039	5.68
CP2	0.02	0.09	0.07	0.00039	5.66
CP3	0.02	0.10	0.08	0.00043	5.62
CP4	0.02	0.08	0.08	0.00037	5.77
CP5	0.01	0.08	0.09	0.00044	5.65
Label	0.02	0.04	-	-	-

The label specification is presented as g NaCl/100g of food.

Table 4. Ion concentrations measured in baby food (Reindeer flavour) using IM and CP as reference electrodes compared to the label specifications.

Electrode	Na^+ (g/100g)	Cl^- (g/100g)	K^+ (g/100g)	Ca^{2+} (g/100g)	pH
IM2	0.02	0.03	0.12	0.00032	5.53
IM3	0.01	0.02	0.13	0.00042	5.58
IM4	0.01	0.02	0.14	0.00034	5.62
IM5	0.02	0.02	0.13	0.00034	5.60
CP2	0.01	0.02	0.13	0.00030	5.63
CP3	0.01	0.02	0.10	0.00037	5.61
CP4	0.01	0.02	0.14	0.00034	5.63
CP5	0.01	0.02	0.13	0.00038	5.69
Label	0.01	0.02	-	-	-

The label specification is presented as g NaCl/100g of food.

Table 5. Ion concentrations measured in powdered soup using IM and CP as reference electrodes compared to the label specifications.

Electrode	Na^+ (g/100g)	Cl^- (g/100g)	K^+ (g/100g)	Ca^{2+} (g/100g)	pH
IM2	0.43	0.63	0.02	0.00069	6.57
IM3	0.36	0.69	0.03	0.00073	6.55
IM4	0.42	0.67	0.01	0.00072	6.58
IM5	0.33	0.72	0.01	0.00073	6.60
CP2	0.42	0.66	0.01	0.00063	6.52
CP3	0.38	0.70	0.02	0.00066	6.59
CP4	0.40	0.64	0.01	0.00072	6.52
CP5	0.38	0.72	0.02	0.00080	6.66
Label	0.35	0.53	-	-	-

The label specification is presented as g NaCl/100g of food.