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Determining detection limits of aqueous anions using electrochemical impedance spectroscopy

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Abstract

Background: Pulsed amperometric detection is a relatively new method for detection of ions and especially non-electrolytes such as carbohydrates in aqueous solutions. Pulsed amperometric detection relies on a redox reaction while electrochemical impedance simply measures the real and capacitive resistant of the solution. There is a correlation between the real impedance of a solution and the ionic strength of the solution.

Method: This work explores measuring real impedance of pure water as a function of temperature from 25.0 to 60.0 °C to determine the relationship between impedance and temperature. Maintaining temperature at 25.0 °C, solutions of sodium chloride, potassium carbonate, sodium sulfate acetate and bicarbonate have been measured using impedance spectroscopy.

Results: Regression analysis shows that measuring anions using impedance spectroscopy and simple stainless steel cylinders that detection limits at the parts per trillion (ppt) level are possible. There was no statistical difference when comparing impedance values of the same concentration of acetate and chloride in solution, showing real impedance is not dependent on ion size. However, ions with higher charge do result in lower impedance measurements.

Conclusions: This work establishes the use of simple, small, robust stainless steel cylinders and impedance measurements following separation for the identification and quantification of ions in solution.

Keywords: Impedance Spectroscopy, Anions, Stainless Steel Cylinders, Detection Limit

Background

Electrochemical techniques such as conductivity, pulsed amperometry, and impedance have been used to quantify metal ions and even non-electrolytes (Bansod et al., 2017; Mefteh et al., 2015; Shervedani and Seyed, 2006; Zazoua et al., 2008; Gabrielli et al., 2004). Conductivity measures the resistance across two parallel plates using an alternating voltage with a frequency of 1–3 kHz. In pulsed amperometric detection, the analyte is oxidized and reduced at an electrode with a fixed potential and the current is measured. This detection technique involves using a silver/silver chloride reference electrode that is recommended to be replaced every 6 months (Rohrer, 2013). Pulsed amperometric detection has been used following ion exchange to find the concentration of compounds such as aldehydes and common sugars with detection limits ranging from 1 to 3 parts per million (ppm) (Rocklin, 1985). EIS is a technique in which a voltage sine wave is applied with known amplitude over a frequency range. The impedance (Z) can then be determined by Eq. (1) (Huang et al., 2009):

$$Z = \frac{R_1}{1 + j2\pi f R_1 C_1} \tag{1}$$

where R_1 is the resistance of the solution, j is imaginary number i, f is the frequency and C is capacitance. Solving this equation results in an imaginary impedance ($-Z''$) which can be plotted vs. the real impedance (Z') resulting in a semicircle referred to as a Nyquist plot. Sample data available by downloading and using the EIS Spectrum Analyzer Software is plotted and shown in Fig. 1 (Bondarenko and Ragoisha, 2005).

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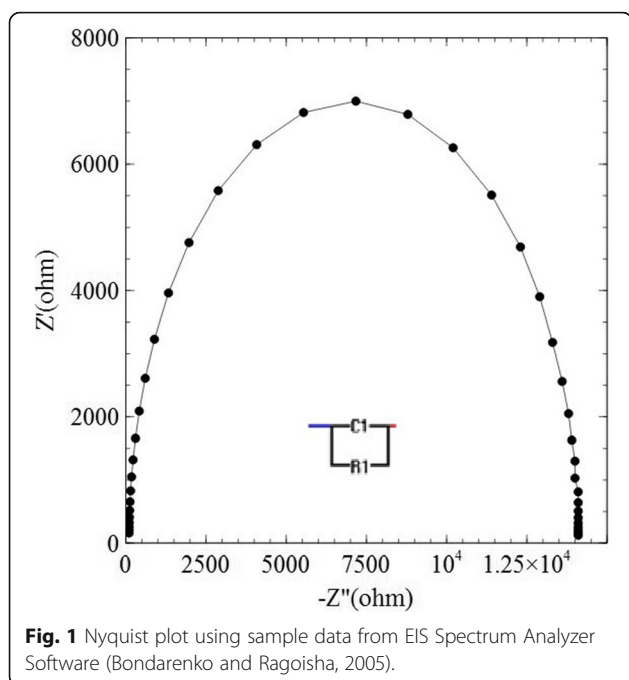East Tennessee State University, 325 Treasure Lane, Johnson City, TN 37601, USA

Fig. 1 Nyquist plot using sample data from EIS Spectrum Analyzer Software (Bondarenko and Ragoisha, 2005).

A circuit composed of a resistor and capacitor in series parallel will result in a semicircle Nyquist Plot. For the example, in Fig. 1, the circuit is best fit using a resistor and capacitor in parallel (RC circuit) as shown in the center of Fig. 1. Both a resistor and capacitor in parallel are required to obtain a real impedance measurement. Using EIS Spectrum Analyzer software, the imaginary and real impedance can be determined as shown in Fig. 2 resulting in values of 9.8574×10^{-8} F and 14,008 Ω for
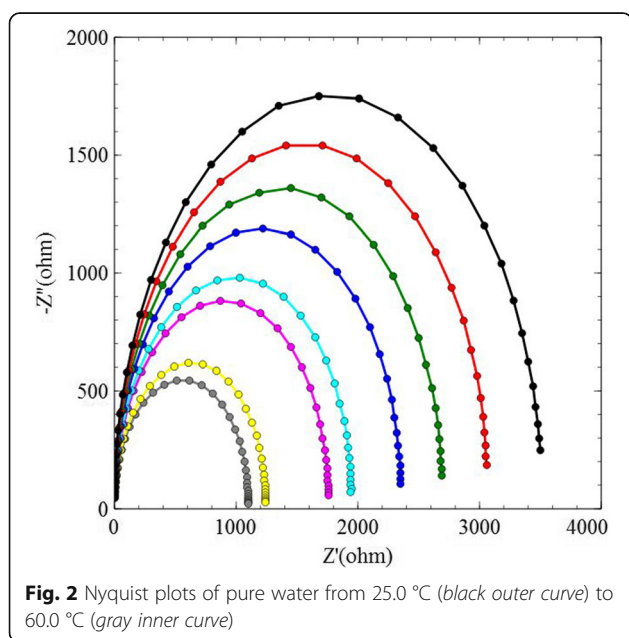
capacitance and resistance with absolute errors of 5.1 and 4.7%, respectively.

The use of co-axial electrodes with simple Electrochemical Impedance Spectroscopy (EIS) measurements is a method that has been developed as a sensor (Szypłowska et al., 2013). However, the detection limit was not determined. This method using stainless steel plates has been applied in determining lithium (Adriana and Vannucci, 2008). Heavy metals such as mercury ions have been determined by EIS with a reported 20 parts per trillion (ppt) detection limit using nanoparticle modified electrodes including DNA (Bansod et al., 2017; Zhang et al., 2017). Silver ions have also been determined using modified electrodes and have detection limits ranging from 0.01 to 170 nM (Yang et al., 2015). Thin films have been developed that are even selective for calcium (Aicher et al., 2017). In these cases, modified electrodes or stainless steel parallel plates with precisely known dimensions are used as a measuring cell that contains the liquid.

This work uses real impedance to quantify how the real impedance of pure water changes as a function of temperature. Solutions having low ionic strengths were measured experimentally to determine the detection limit of anions in water using impedance spectroscopy. Acetate, chloride, cyanide, carbonate, sulfate, and bicarbonate were measured experimentally to determine the effect of ion charge and size on the impedance measurement at 25.0 °C. This data is useful in the development of a simple robust method using stainless steel cylinders and impedance measurements being applicable to water-quality-monitoring technologies with detection limits at the parts per trillion (ppt) level.

Methods

Deionized water was routed to a Millipore Direct QUV 3 system resulting in 18.2 MΩ water and used to prepare and measure all solutions. Temperature was measured using a Vernier temperature probe. Salts were used as received. A stock solution of each salt solution was prepared and serial dilution was carried out to obtain the desired

Fig. 2 Nyquist plots of pure water from 25.0 °C (*black outer curve*) to 60.0 °C (*gray inner curve*)

Table 1 Real impedance values (Ω) of pure water as a function of temperature (°C)

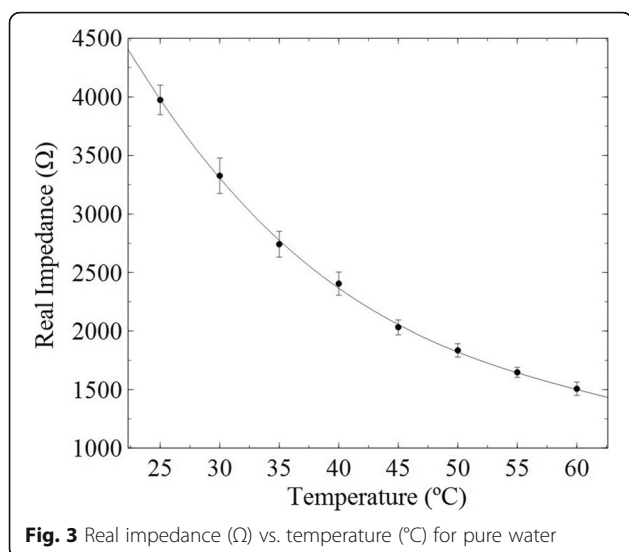| Temperature (°C)	Real impedance (Ω)	Error (±Ω)
25.0	3482	139
30.0	3070	92
35.0	2694	81
40.0	2359	71
45.0	1947	58
50.0	1753	53
55.0	1237	37
60.0	1092	33

Fig. 3 Real impedance (Ω) vs. temperature (°C) for pure water

molarity. Molarity values were converted to ppm. A simple stainless steel probe from Brookhaven Instruments of proprietary dimensions was utilized for impedance spectroscopy of the solutions. The probe consists of an inner and outer cylinder separated by Teflon posts. The testing probe is put directly into the test solution in a glass cell. AC impedance spectroscopy was then conducted using an initial voltage of 0.2 and 0.7 V amplitude. Real and imaginary impedance data was collected over a range of 1 to 100 kHz generating a Nyquist plot. Pure water was used to collect Nyquist plots over a temperature range of 25.0 to 60.0 °C. Each spectrum was converted to a text file and imported into the EIS Spectrum Analyzer Software to fit the Nyquist plot to find the real impedance values and error for the equivalent circuit shown in Fig. 1. AC impedance spectroscopy was used to measure standard solutions of chloride, acetate, bicarbonate, carbonate, and sulfate ranging from 0.06 to 6000 parts per billion (ppb) depending on the anion. Solutions of 0.6 ppm acetate, chloride, sulfate, carbonate, and bicarbonate were measured at 25.0 °C to compare the effect of ion size and charge on impedance measurements.

Results and discussion

Pure water and temperature dependence

The impedance spectroscopy of pure water was measured from 25.0 to 60.0 °C. Figure 2 below shows the resulting Nyquist plots. Data for every Nyquist plot was fit using EIS software which performed regression analysis resulting in the real resistance, error and R^2 of the fit. Attempts were made to use other circuit configurations. The best R^2 values were obtained using one resistor and one capacitor in parallel to represent the solution and two stainless steel cylinders as shown in Fig. 1. Measurements of pure water from 25.0 to 60.0 °C resulted in typical semi-circular Nyquist plots shown in Fig. 2.

Table 1 below shows the real resistance values and error obtained measuring pure water from 25.0 to 60.0 °C.

Interestingly, the change in real impedance as a function of temperature is not linear as one might expect. Real impedance plotted as a function of temperature results in a cubic polynomial as shown in Fig. 3.
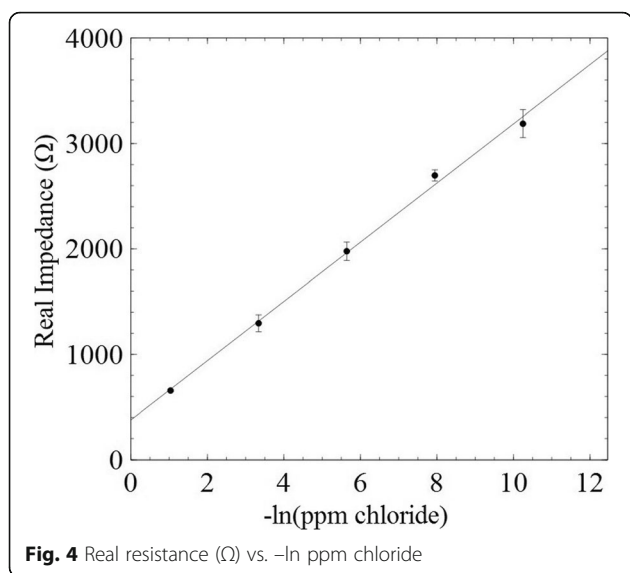
The polynomial fit for plot of Ω vs. T (°C) is:

$$\Omega = -0.0287(°C)^3 + 5.423(°C)^2 - 367.45(°C) + 10,223 \qquad (2)$$

where y is real impedance (Ω) and x is temperature in degrees celsius. The polynomial fit results in an R^2 value of 0.9993. Interestingly, permittivity of pure water as a function temperature is also a third order polynomial (Malmberg and Maryott, 1956). This is not unexpected as permittivity is an extensive property that is dependent on resistance. Because impedance is a function of temperature and ionic strength, varying concentrations of sodium chloride, sodium acetate, sodium sulfate, and sodium cyanide were measured at 25.0 °C separately to calibrate the impedance measurement for quantifying anions. The effect of ion charge and size were also explored. The detection limit was calculated to determine the feasibility of using impedance spectroscopy as a detector at ppt levels following separation by methods such as ion exchange.

Table 2 The ppb amounts of prepared standard anion solutions, real resistance determined by fitting the Nyquist plot and error measured at 25.0 °C

Chloride ppb	Ω	Bicarbonate ppb	Ω	Carbonate ppb	Ω	Acetate ppb	Ω	Sulfate ppb	Ω
3545	68.4 ± 0.3	6102	237 ± 5	600	574 ± 31	590.4	699 ± 8	5960	72 ± 1
354.5	656 ± 19	610.2	907 ± 103	60	906 ± 40	59.04	1219 ± 21	596.0	577 ± 34
35.45	1431 ± 131	61.02	2177 ± 78	6	1181 ± 27	5.904	2203 ± 28	59.60	1689 ± 89
3.545	1977 ± 219	6.102	2363 ± 52	0.6	2000 ± 26	0.5904	2401 ± 119	5.960	2165 ± 48
0.3545	2697 ± 87			0.06	2695 ± 83			0.5960	2518 ± 52

Fig. 4 Real resistance (Ω) vs. –ln ppm chloride

Detection limit for anions

As expected, when an ionic compound is dissolved in water, the resistance of the solution decreases. Resistance increases with decreasing concentration of the dissolved salt eventually reaching a value similar to pure water.

Serial dilutions of standard stock solutions of anions were prepared, and the real resistance from the fit of Nyquist plots were determined at 25.0 °C. Table 2 shows the real resistance values determined from fitting the Nyquist plots and error for ppb solutions of anions at 25.0 °C.

A plot of the real resistance in ohms against concentration results in a log plot. To make the data linear, the real impedance (Ω) is plotted against the negative natural logarithm of ppm according to Eq. (3):

$$\Omega = \text{-}\ln(\text{ppm}) + b \tag{3}$$

The calibration plot for chloride at 25.0 °C is shown in Fig. 4.

Within error, all calibration plots are linear. Very low concentrations correspond to –ln values that are not zero. In other words, solutions with low ppm chloride result in high impedance values in this plot. The text book method for determining the detection limit must be modified to subtract three times the standard

deviation (3 s) from the impedance of pure water and take the negative antinatural logarithm of this value to obtain the detection limit in ppt. Eq. 4 shows this calculation:

$$\text{Detection limit} = e^{\text{-}\left(\frac{3,853\Omega\text{-}3s}{m}\right)}\left(1 \times 10^6\right) \text{ppt} \tag{4}$$

This equation takes three times the standard deviation, s, of impedance measurements using a 355 ppb solution of chloride (321 Ω), subtracts this from the real resistance of pure water (3853 Ω), subtracts the intercept, divides by the slope and taking the negative anti-natural logarithm and multiplies by 1×10^6 resulting in a detection limit of 13 ppt for chloride. The detection limit for chloride and other anions are below the maximum contaminant levels established by the EPA. The detection limits, slopes, and errors for anions determined are listed in Table 3.

Effect of ion charge and size

One possible impact on the real resistance of the solution is size of ions and ionic charge. To determine if there is an effect of ion size and charge on real impedance, 0.6 ppm solutions of different anions were measured at 25.0 °C. Table 4 shows the real impedance for these solutions.

Using Table 4 and comparing chloride and acetate, there is only a statistical difference of 21 Ω, making the impedance response to chloride and acetate nearly identical. Both sulfate and carbonate having a charge of (2-) resulted in real impedance values less than ions with a charge of (1-). Bicarbonate has the same charge as chloride and acetate, (1-), and has a real impedance 150 Ω higher. This is attributed to bicarbonate behaving as an ampholyte in pure water. This table clearly shows that charge of ion in solution has a much greater influence on impedance.

Advantages and disadvantages of impedance detection and future work

This work shows that impedance measurements are capable of detecting ions with similar detection limits as pulsed amperometry. The main advantage to using impedance spectroscopy is detection of ions at the ppb level without using a reference electrode. Thermoscientific note 21 recommends replacing the silver/silver chloride reference electrode every 6 months (Rohrer, 2013). Using

Table 3 Detection limit, calibration and goodness of fit for anions measured at 25.0 °C

Ion	Detection limit (ppt)	Detection limit (nM)	Slope (Ω^{-1})	Error (± Ω^{-1})	Intercept (Ω)	Error (±Ω)	R^2 correlation
Carbonate	16	0.02	232	18	362	111	0.9942
Bicarbonate	129	2.1	309	6	779	19	0.9998
Chloride	13	0.4	296	6	330	29	0.9996
Acetate	128	2.1	325	35	583	118	0.9943
Sulfate	2.0	0.02	180	15	1201	83	0.9965

Table 4 Real impedance values (Ω) of 0.6 ppm solutions of anions at 25.0 °C

Ion	Real impedance(Ω)	Error (±Ω)
Carbonate	573	31
Bicarbonate	850	12
Chloride	656	23
Acetate	698	8
Sulfate	472	39

impedance measurements requires no reference electrode, thus reducing the instrument and maintenance costs for detection of ions in solution. The obvious disadvantages to this method are the ability to distinguish between different ions, software required to determine the real impedance of the sample, and finally using that information to determine concentration in parts per million. Work is currently underway to circumvent these disadvantages by developing inner and outer cylinders in a microfluidic device in line with anion or cation exchange resin for separation. Circuitry is also being developed to provide stand alone output values in ppb using an LCD screen. Once the circuitry is developed the system will be calibrated and is expected to be published or patented.

Conclusions

Impedance spectroscopy was utilized to determine the temperature dependence of impedance measurements. As such, 25.0 °C was chosen for measurements of electrolytes and non-electrolytes in solution. Anions were used to calibrate the detection method and found that detection limits to be at the ppb level. Comparing the impedance of similar concentrations of chloride and acetate, ion size had little to no effect on impedance measurements. However, when comparing chloride to carbonate or sulfate, impedance measurements are clearly lower for ions of higher charge. This work shows the promise and possibility of detecting and quantifying ions using retention time and impedance measurements at ppt levels following separation by ion exchange. This can be accomplished using simple robust stainless steel cylinders and electrochemical impedance measurements.

Abbreviations
EIS: Electrochemical Impedance Spectroscopy; Z: Impedance; PPB: Parts per billion; PPT: Parts per trillion; PPM: Parts per million

determined at 25.0 °C. The detection limits were found to be at part per trillion levels which is less than maximum contaminant levels. This work then serves as the basis of our continuing work to develop a simple inexpensive and robust method for detection and quantification of ions following separation methods by using a simple impedance measurement.

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