

# Using multi-frequency electrical conductivity measurement to determine the selective salinity in a two-component salt solution

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Received: January 12<sup>th</sup>, 2023; Accepted: April 27<sup>th</sup>, 2023; Published: July 19<sup>th</sup>, 2023

**Abstract.** Digital technologies can help farmers produce safe, sustainable, high-quality food while contributing to the fight against effects of abiotic and edaphic factors. Due to digitalization, a paradigm shift occurred in agriculture, which boosted sensor technology's rapid development, especially soil sensors. Using sensors and the digital knowledge of soil properties, farmers can better understand the needs of the fields and cultivated plants on a micro-scale, thereby saving resources and putting less strain on our environment. The relative salinity of our soils is an important aspect because of the impact on production costs and yield. The future of site-specific crop production is moving towards a sensor-based on-the-go measurement approach because obtaining important soil characteristics quickly and cheaply is still one of the biggest challenges in precision agriculture today. Measuring soil electrical conductivity (EC) could offer an opportunity to overcome these limitations if the different salt components of soil could be separated by analytical methods. In our study, we present a calibration model based on conductometry with which the selective potassium and calcium content can be determined in the laboratory under controlled conditions. Solutions containing  $K^+$  and  $Ca^{2+}$  cations in the concentration determined in the experimental model were mixed and measured by changing the frequency of the measuring current. In this study, measurements proved that a mathematical relationship can be used to describe the relationship between the composition and concentration of the two-component solution, the measurement frequency and the conductivity. The potassium (K) and calcium (Ca) content of the solution can be separated from each other, and a regression calibration curve can be recorded, from which the proportion of potassium and calcium in the given solution can be determined as a function.

**Key words:** multi-frequency, electrical conductivity, soil salinity, digital agriculture, soil sensor.

## INTRODUCTION

Today, sensor technology is one of the fastest-growing areas of technology. A sensor is a device that can detect a change in the physical or chemical environment,

which then converts it into electrical signals, both electric current and voltage. The precision agriculture mainly relies on real-time monitoring of soil conditions using information technology and GPS technology and then analysing and managing the spatial-temporal variability of soil and field crops (Lu et al., 2022). This information helps make the decision on the precision application of crop inputs including water and fertilizer. It can improve efficiency and reduce the losses of water and fertilizer (Popp et al., 2018). With the correct and sensible use of sensor technology, farmers can better understand their crops and soils while conserving resources and at the same time saving resources and reducing their impact on the environment (Horváth & Schmitz, 2019).

Due to increases in the cost of fertilizer production inputs—predominantly nitrate (N), phosphate (P), and potassium (K) those in agriculture are looking for ways to optimize plant yield while minimizing the application and consumption of fertilizer (USDA, 2022). Since these macro-nutrients vary even on a small scale throughout a cultivated field, numerous researchers have attempted to develop an on-the-go sensing apparatus that can map the presence of these chemicals in situ so that this map, once overlaid with parameters such as pH, electrical conductivity (EC), crop yield, and mechanical properties of the soil, can give a precise spatially varying prescription for fertilizer application (Sinfield et al., 2010).

The global Agricultural Sensors market was valued at USD 1,505.4 million in 2020 and is expected to reach USD 3,200.8 million by the year 2028, at a CAGR of 11.04% (ICT - Agricultural Sensor Market Analysis, 2020). Smart Sensors allow farmers to maximize yields using minimal reserves such as fertilizer, water, and seeds. By utilizing sensors and mapping fields, farmers can commence realizing their crops at a micro-scale, conserve resources, and lessen influences on the ecosystem. The modern age of Precision Agriculture (PA) is often linked to the announcement by US President Ronald Reagan in 1983 that would allow global positioning systems (GPS) for civilian use (Lowenberg-DeBoer & Erickson, 2019). Once farmers were able to map their crop fields accurately, they could monitor and use fertilizer and weed treatments only to parts that required it. During the 1990s, early precision agriculture users implemented crop yield monitoring to create fertilizer and pH correction suggestions (Schriber, n.d.). Usually, sensor networks have a base station known as a sink and several other sensors too, which sense and transmit the signals along with sending information to other nodes. Weather stations are self-contained units placed at various sites throughout growing fields. These stations have a mixture of sensors suitable for the local crops and climate. Data such as air temperature, soil temperature at various depths, dew point temperature, wind direction, relative humidity, rainfall, leaf wetness, chlorophyll, wind speed, solar radiation, and atmospheric pressure are measured and recorded at predetermined intervals (ICT - Agricultural Sensor Market Analysis, 2020).

For sensor measurement, the following sensor groups can be found in crop production: crop sensors, environment sensors, function monitoring sensors and soil sensors. From the growth of forecast solutions using sensors, it is very easy to recognize that the future of site-specific crop production is moving towards a sensor-based approach because obtaining important soil characteristics quickly and cheaply is still one of the biggest challenges in precision agriculture today. Several researchers and manufacturers are trying to develop on-the-go soil sensors to directly measure the mechanical, physical, and chemical properties of the soil (Adamchuk et al., 2004). The disadvantage of the practical use of the increasingly widespread ground sensors is that

they are less accurate than individual sampling and laboratory tests, but the advantage is that they are suitable for rapid measurement and are therefore cheaper in practice (Hajdú, 2018). In the future, mechanized soil testing and nutrient mapping solutions will become widely available using faster and more cost-effective measurement tools. To implement sustainable agricultural and environmental management, a better understanding of the soil at increasingly precise scales is needed. Conventional soil sampling and laboratory analyses cannot provide this information because they are slow and expensive (Adamchuk et al., 2010).

Soil properties often vary significantly within a field, and one of the challenges in precision agriculture is collecting enough soil data to accurately delineate this variability. Soil electrical conductivity (EC) has become a widely used tool for mapping soil variability within fields. Soil EC measurements are typically correlated with soil texture, moisture, and salinity. Soil texture is an important factor in crop yields because it relates to water-holding capacity, cation-exchange capacity, rooting depths, drainage, and other properties that impact crop production (Lund, 2008).

Conductometry is an analytical method based on the measurement of the electrical conductivity of solutions. In analytical chemistry, the electrical conductivity of electrolyte solutions is measured by conductometric methods, and analytical information is derived from this and its changes due to chemical reactions. The conductivity of materials (measured in siemens, S) is the reciprocal of their electrical (ohmic) resistance (R) (the unit is ohm,  $\Omega$ ). Electrical conduction requires the presence of charge carriers (e.g., electrons or anions and cations) that can move under the action of the electric field (Krupička et al., 2015). The ion migration in the solution due to the electric field is the reason for the electrical conduction of the solutions. Based on this, electrical conductors and insulators are to be distinguished. Pure (distilled) H<sub>2</sub>O contains only very small charge carriers in the concentration  $[H^+] = [OH^-] \approx 10^{-7} \text{ mol L}^{-1}$  corresponding to autoproteolysis, conducts electricity only to a very small extent, therefore it can be considered as an insulator. However, the concentration of cations and anions in aqueous solutions of electrolytes can be significant, making them mostly conductive depending on the degree of electrolytic dissociation. Each ion in the solution makes some contribution to the conduction value. These are inseparable, so conductometry is not suitable for the selective measurement of individual ions, i.e., it is not an ion-specific method (Galbács et al., 2015). Therefore, its analytical application is limited to the study of systems that

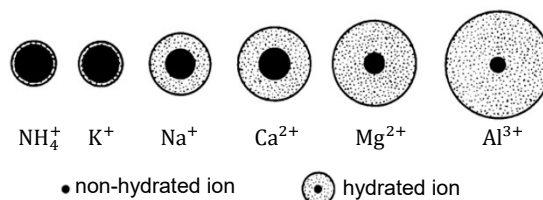
- contain only a single electrolyte (so the contribution of the ‘background’ is negligible) or
- chemical reactions take place in them, during which the mobility of the ions that make up the system changes significantly (compared to non-zero ‘background’) (Galbács et al., 2015).

Various inorganic salts, organic matter and gases are dissolved in the soil moisture. Dissolved mineral salts are dissociated into positively and negatively charged ions and the ions are surrounded by a hydrate shell. The following ions are predominantly present in the soil solution:

- Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup> and in some soils Al<sup>3+</sup>, Fe<sup>3+</sup> or Fe<sup>2+</sup> (cations);
- HCO<sub>3</sub><sup>3-</sup>, CO<sub>3</sub><sup>2-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>3-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>4-</sup>, HPO<sub>4</sub><sup>2-</sup> (anions).

Most of the dissolved organic compounds are organic acids and low molecular weight humic substances, with CO<sub>2</sub> and O<sub>2</sub> being the most significant dissolved gases. Soluble substances in the soil are mostly products of weathering and soil formation, but salts also enter the soil solution with groundwater close to the surface. In addition, fertilizers and compounds applied to irrigation water in agricultural areas modify the salinity of the soil (Stefanovits et al., 2005).

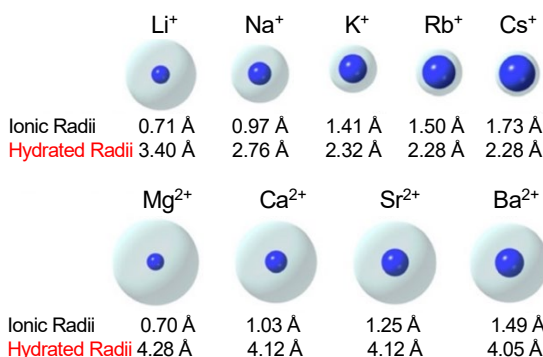
The interaction between solvated ions and water has been a subject of great interest due to its importance in various chemical, biological, and environmental processes (Waluyo et al., 2011). Various studies have explored aqueous solutions of ions, both in the bulk (Ohtaki & Radnai, 1993; Marcus, 2009) and at interfaces (Ghosal et al., 2005; Jungwirth & Tobias, 2006; Craig & Henry, 2009). The size of the hydrate shell in aqueous solution is illustrated in Fig. 1. The smaller the diameter of the dehydrated cation and the larger its charge is, the thicker the hydrate sphere in aqueous solution is which also affects the mobility of hydrated ions (Fig. 1). K is the most mobile element in the soil and as such readily available within the rhizosphere for plants uptake, however, care must be taken to avoid it leaching out of the vadose zone of the soil because of its high mobility (Dayo-Olagbende & Ewulo, 2021).



**Figure 1.** The size of the aqueous hydrate cover for each element in the soil (Stefanovits et al., 2005).

In fact, the common cations in soil have a wide range of sizes, as shown in Fig. 2. Rengasamy (1998, 2016) showed that the dispersive effect of Na is greater than that of K, and that the flocculating effect of Ca is greater than that of Mg. Conventionally, these cations have been called base or base-forming cations. Hydrated radii are critical to the composition of soil (see Fig. 2).

The soil salinization is one of the critical global problems threatening land productivity (Hossain, 2019). Plant responses to salt and water stress have much in common. Salinity reduces the ability of plants to take up water, and this quickly causes reductions in growth rate, along with a suite of metabolic changes identical to those caused by water stress (Munns, 2002). In more than 100 countries around the world, saline soils cover more than 1,125 million hectares of land (Wicke et al., 2011). The salinity It is increasing at about 1–2% annually and is projected that 50% of the available arable lands can be affected by soil salinity by 2050 and would pose a serious threat to the sustainable development of global agriculture (Massoud, 1981).



**Figure 2.** The ionic and hydrated radii (effective sizes) in angstroms, of some of the common ions (Luo et al., 2019).

Geoelectrical methods have shown their capability to detect spatial variation of important physico-chemical soil parameters in an efficient way. However, relationships between the electrical parameters (electrical conductivity or resistivity) and other soil properties are not always consistent over different fields. This can, to some extent, be due to the characteristics of instruments used for soil mapping (Dabas et al., 2009). It is obvious that the measurement of electrical conductivity (EC) is one of the in-situ tools for soil testing required for precision farming and accordingly there is a large-scale literature on the development of EC detectors. These detectors typically and traditionally have 4 electrodes (Li et al., 2006; Seifi et al., 2010; Pei et al., 2012). The traditional current-voltage four-electrode method fits for in-situ measuring and can be aimed at developing an in-situ soil EC detector with low price, easy operation, high measurement precision, integral control procedures and data processing procedures (Pei et al., 2012). Apparent soil electrical conductivity is one of the simplest, least expensive soil measurements to obtain useful information about soil characteristics, which have a vital role in precision agriculture (Seifi et al., 2010).

The use of sensors for the assessment of the EC of soils offers a way to overcome these constraints. These sensors are based on three electromagnetic phenomena, namely, electrical resistivity, electromagnetic induction, and reflectometry (Visconti & de Paz, 2016). Multi-frequency (MF) and multi-coil (MC) are the two types of commercially available electromagnetic induction sensors. Although the working principles are similar, their theoretical and effective depth of investigation and their resolution capacity can vary. Given the recent emphasis on non-invasive mapping of soil properties, the selection of the most appropriate instrument is critical to support robust relationships between EC and the targeted properties. The performance of the MC sensor was less affected by variable weather conditions, providing overall stronger correlations to both, temporally stable or variable soil properties (Aldorff et al., 2020). The electrical conductivity of soil is dependent on various factors including soil properties, moisture content, and the presence of dissolved salts. In the field, these factors can vary significantly across different soil types, depths, and locations. As a result, understanding the relationship between EC and soil properties is crucial for effective soil management and precision agriculture (Adamchuk et al., 2004; Johnson et al., 2005; Kim & Park, 2021).

The goal of this study was to prove that measurements of K and Ca in a solution based on electrical conductivity can be separated by reasonably changing the measurement frequency which is being developed within the framework of Hungarian University of Agriculture and Life Sciences, Institute of Technology. The methodology development focuses on how to replace slow, complex, and relatively expensive laboratory determination of salinity with as many on-the-go measurements as possible. Current knowledge, conductivity tests with soil sensors alone are not sufficient to infer the salinity properties of a given field. The measurement is affected by the unequal distribution of different nutrients, different pH conditions, different particle compositions, differences in organic matter content or even temperature (Corwin & Lesch, 2005).

The objective of our study is to test the conductivity of a mixture of salts dissolved in distilled water at a known concentration with an alternating frequency instrument, as opposed to commercially available static frequency measuring conductometers. We looked at whether, using different frequencies to measure the conductivity, we could infer the measurement technique and concentration of individual ions, or perhaps the relative

amount of the various ions, or its change. During the measurement, the effect of the cations of dissolved salts found in soil moisture under natural conditions were examined.

## MATERIALS AND METHODS

The measurements were performed in the Laboratory of Institute of Technology, in Hungarian University of Agriculture and Life Sciences. The laboratory temperature was maintained at a constant 22 °C. The solutions were used for the measurement at 22 °C. In this study the effect of the cations of the dissolved salts were examined in mixture under natural conditions. The salts and chlorides are very soluble in water, therefore the chlorine salts of K<sup>+</sup> and Ca<sup>2+</sup> cations were considered for this experiment. Approximately 1 M concentration (1 M = 1 mol dm<sup>-3</sup>) stock solutions were prepared from salts and used in 50 mL units. The salts described in Table 1 were used the following two component solutions:

- 100% KCl - 0% CaCl<sub>2</sub>
- 80% KCl - 20% CaCl<sub>2</sub>
- 60% KCl - 40% CaCl<sub>2</sub>
- 50% KCl - 50% CaCl<sub>2</sub>
- 40% KCl - 60% CaCl<sub>2</sub>
- 20% KCl - 80% CaCl<sub>2</sub>
- 0% KCl - 100% CaCl<sub>2</sub>

The system was rinsed with distilled H<sub>2</sub>O between the measurements, so that any ions left on the electrode during the previous measurement do not contaminate the subsequent solutions.

**Table 1.** The properties of salts

Solution	CAS	Molar mass (g mol <sup>-1</sup> )	Description	Properties	Energy of solvation
KCl	7447-40-7	74.550	Potassium Chloride	white crystals	endothermic
CaCl <sub>2</sub>	10043-52-4	110.980	Calcium Chloride	white, small plate	strongly exothermic

### Hardware specification

Elements of the measuring circuit as in Fig. 3:

1. SOURCETRONIC ST2829C

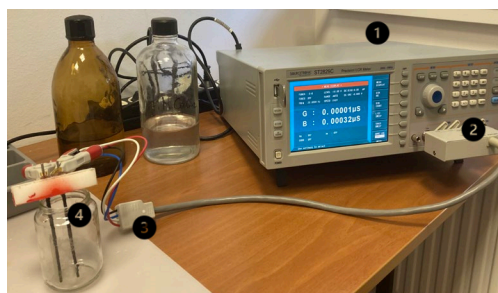
Precision LCR meter with USB stick recording the data;

2. SOURCETRONIC ST26011B

Test Fixture: the resolution of the instrument is 0.00001nS, the basic accuracy is 0.05%. During the measurement, the voltage of the electrodes is 10V DC. The output impedance of the instrument was 100Ω;

3. Measuring cup (100 mL) to store the input solution;

4. Measuring electrodes 2 pcs, Ø2 mm, length: 80 mm full length insulated, uninsulated part length 5 mm, probe distance 12 mm, material is stainless steel.

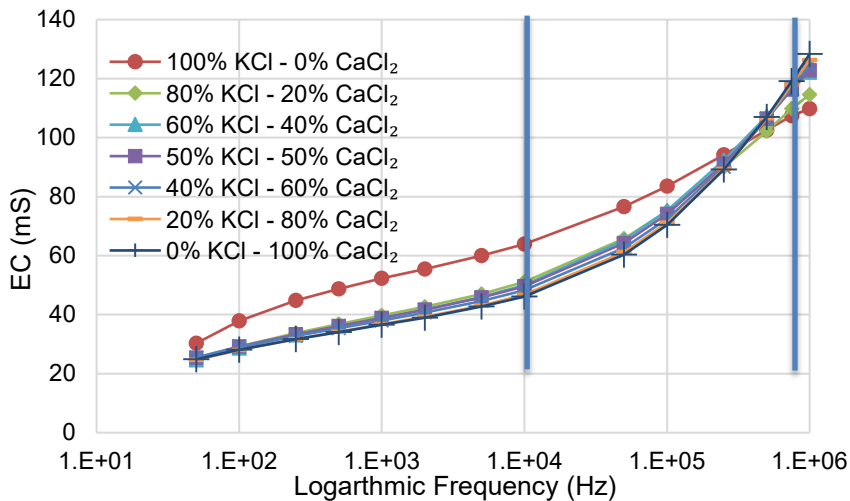


**Figure 3.** The measuring circuit.

The LCR meter measured the electrical conductivity (G in Siemens) between the two stainless steel electrodes placed in the ground paste in an endless series at a predetermined program frequency and restarted the measurement in an endless cycle upon completion of the measurement sequence. The SOURCETRONIC ST2829C Precision LCR meter used in this study allows for the simultaneous recording of several frequencies. However, selection of too many frequencies reduces the strength of each frequency signal and consequently lowering the resolution. Based on our previous studies, we selected 14 frequencies, covering the frequency range recommended by the manufacturers (Altdorff et al., 2020). The frequency values used for the measurements were recorded in the range of 50, 100, 250, 500, 1,000, 2,000, 5,000, 10,000, 50,000, 100,000, 250,000, 500,000, 750,000, 1,000,000 Hz. Each EC measurement in each frequencies were repeated ten times. Functional analyzes were performed using Microsoft Excel and Microcal Origin software.

### Statistical analysis

First, we measured the EC values of the different mixed solutions at the set frequencies. The results of the measurements are presented in Fig. 4.



Cation ratio in the solution	Frequency (Hz)															
	5.E+01	1.E+02	3.E+02	5.E+02	1.E+03	2.E+03	5.E+03	1.E+04	5.E+04	1.E+05	3.E+05	5.E+05	8.E+05	1.E+06		
100% KCl - 0% CaCl <sub>2</sub>	30.30	37.85	44.84	48.73	52.25	55.40	59.99	63.92	76.62	83.58	94.16	102.49	107.46	109.83		
80% KCl - 20% CaCl <sub>2</sub>	24.72	29.25	33.78	36.80	39.69	42.61	46.99	51.07	65.81	75.06	89.89	102.18	109.80	114.60		
60% KCl - 40% CaCl <sub>2</sub>	24.64	28.70	33.07	35.98	38.81	41.67	45.98	50.04	65.20	75.31	92.34	107.26	116.64	122.13		
50% KCl - 50% CaCl <sub>2</sub>	25.44	29.25	33.36	36.15	38.88	41.63	45.78	49.64	64.20	74.06	91.12	106.43	116.33	122.77		
40% KCl - 60% CaCl <sub>2</sub>	25.42	28.97	32.80	35.42	38.02	40.65	44.63	48.34	62.66	72.52	90.05	106.17	116.87	124.50		
20% KCl - 80% CaCl <sub>2</sub>	24.62	28.06	31.75	34.22	36.75	39.28	43.14	46.79	61.17	71.23	89.42	106.53	117.98	126.33		
0% KCl - 100% CaCl <sub>2</sub>	24.86	28.15	31.73	34.10	36.54	39.00	42.78	46.15	60.33	70.43	89.14	106.97	119.16	128.33		

**Figure 4.** Comparison of EC measurements of different mixtures at logarithmic frequency.

It is clearly visible in the figure that

- Increasing EC values are obtained as the frequency increases,
- The conductivity of the solution containing the K<sup>+</sup> cations differs from that of the solution containing the Ca<sup>2+</sup> cations, because the sizes of the hydrated cations are

significantly different from each other and thus they move at different speeds in the medium of the given viscosity under the influence of a given electric field,

- According to our experience, up to a frequency of 104 Hz, the change in EC due to the change in frequency is linear and does not differ significantly for solutions containing different proportions of Ca and K ions. However, in the 10 kHz and 750 kHz frequency range, the measured electrical conductivity depends on the calcium/potassium ion ratio of the solution.

In the frequency range of 10 kHz and 750 kHz, the functions were transposed and statistical analyses, performed function tests for the conductivity values measured as a function of the concentration of the solutions in the case of different measurement frequencies. (Fig. 5).

In this study exponential functions were used in the following form as fitted functions (Mitscherlich, 1909; Mitscherlich, 1928):

$$f(x) = y_0 + Ae^{-\frac{x}{t}} \quad (1)$$

where  $y_0$  – the conductivity extrapolated to zero frequency, i.e. the starting point of the system;  $A$  – shows the rate of change and  $t$  – the frequency constant. The parameters of the equations of the fitted curves obtained in this way are summarized in Table 2:

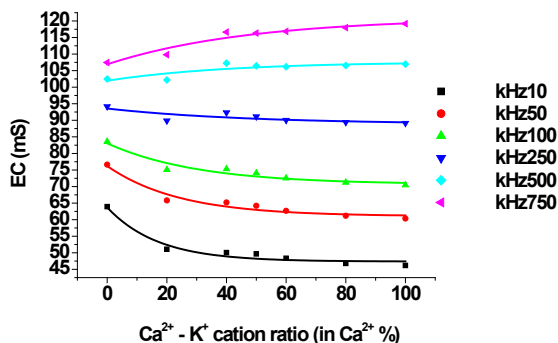
The coefficient of determination, apart from two measurements, gave  $R^2$  values ranging 0.88 to 0.93, which is adequate. For 250 kHz and 500 kHz measurements, a linear fit is more appropriate.

$$f(x) = A + Bx \quad (2)$$

Table 3 shows the parameters calculated by linear fitting.

First, the starting point of the functions ( $y_0$ ) was analyzed where the conductivity extrapolated to the zero frequency (direct current), as a function of the measurement frequencies and fitted an exponential function to the points. The result of the function test can be seen in Fig. 6.

The fitted function shows that the initial values of the K - Ca ratios differ significantly, in a way that can be described by a function, if different measurement frequencies are reasonably used.



**Figure 5.** Comparison of EC measurements of different mixes and function fitting for measurements made at different frequencies.

**Table 2.** Parameters of exponential function fitting and coefficient of determination

Parameters	$y_0$	A	t	$R^2$
10 kHz	47.36	16.34	16.97	0.9329
50 kHz	61.04	15.15	24.23	0.9124
100 kHz	70.64	12.42	30.47	0.8699
250 kHz	88.82	4.74	37.85	0.3990
500 kHz	107.69	-5.74	41.03	0.5246
750 kHz	120.99	-14.08	47.64	0.8800

**Table 3.** The parameters of the linear function fitting and the coefficient of determination for the measurements made at 250 kHz and 500 kHz

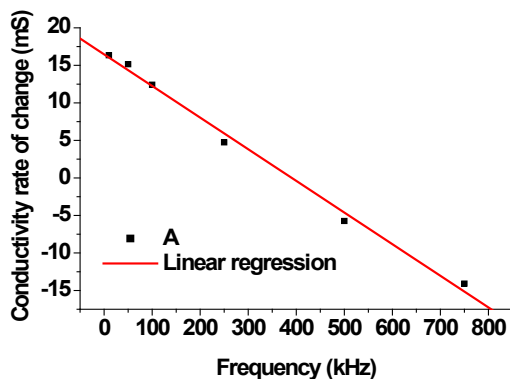
Parameters	A	B	$R^2$
250 kHz	92.93	-0.04	0.5929
500 kHz	102.97	-0.04	0.6084



Then the difference ( $A$ ) of the starting points of the functions extrapolated to zero frequency (to infinity), i.e. the degree of change, was plotted as a function of frequency and a linear function was fitted to the points. The result of the function test can be seen in Fig. 7.

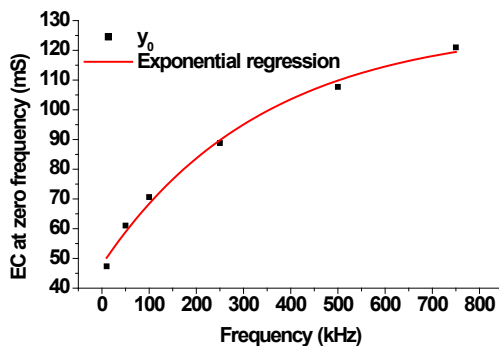
This fitted function also shows that the measurements of mixtures with different K - Ca ratios differ significantly, in a way that can be described by a function, if variable measurement frequencies are used. Solving the fitted function to zero reveals that the value of the EC changes at the frequency of 392.11 kHz is zero at this selected frequency, in the interpretation of Fig. 5, the drawn function will be horizontal at this frequency, the EC value does not change by changing the composition of the mixture. Therefore, the frequency range of the experiment was correctly determined.

In the next step, the frequency constant ( $t$ ) was analysed. The  $t$  parameter or *frequency constant* shows the frequency change during which the deviation of the conductivity from the asymptotic value decreases for the  $e$  exponent. The result of the analysis is illustrated in Fig. 8.



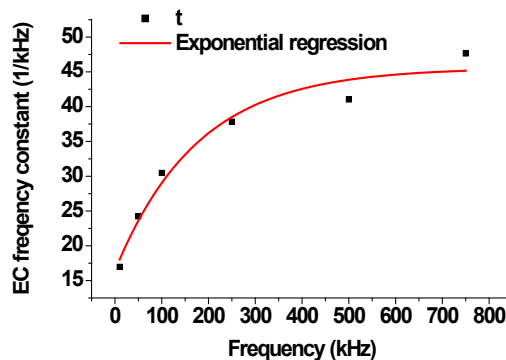
Parameters	Value	Error	Unit
A	16.469	0.628	-
B	-0.042	0.002	-
$R^2$	0.974	-	-

**Figure 7.** The values of the degree of change as a function of the measurement frequencies and the fitting of the linear function.



Parameters	Value	Error	Unit
$y_0$	128.30	6.57	mS
A	-80.42	5.82	mS
$t$	339.68	69.33	1/%
$R^2$	0.99	-	-

**Figure 6.** The values of conductivity extrapolated to zero frequency as a function of measurement frequencies and fitting of the exponential function.



Parameters	Value	Error	Unit
$y_0$	45.58	2.38	mS
A	-29.16	2.87	mS
$t$	176.62	53.67	1/%
$R^2$	0.94	-	-

**Figure 8.** The values of the frequency constant as a function of the measurement frequencies and the fitting of the exponential function.

With the fitted function, it was again proven that the EC values measured for K - Ca ratio mixtures differ significantly, in a way that can be described by the function, if variable measurement frequencies were used. Therefore, EC measurement at variable frequencies can be a suitable tool for determining the concentration of solutions containing  $K^+$  -  $Ca^{2+}$  cations. As a variable frequency, the kHz frequency range seems to be the most appropriate measurement range.

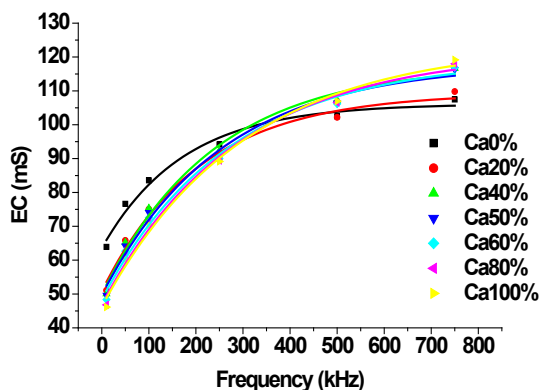
## RESULTS AND DISCUSSION

Current study focused on how to replace slower, more complex, and thus relatively expensive laboratory determination of salinity with as many on-the-go measurements as possible. The dependence of soil EC on soil properties in the field is important because it provides valuable information about soil salinity, water content, texture, and structure. This information can be used to make informed decisions about soil management and crop production (Friedman, 2005; Corwin & Lesch, 2005). Our current approach provides framework, guidance of further analyses and finally laboratory background for further development of on-the-go soil sensors based on EC measurement.

The commonly used frequency range for EC determination in the field is about 100 Hz to several kHz, because at lower frequencies, electrode polarization interferes with the readings and at higher frequencies (kilo- to megahertz), the phenomenon of termed dispersion may occur. Furthermore, high-frequency conductivity meters are expensive (Friedman, 2005). At low frequencies, i.e. below 1 MHz, capacitance and electrolytic effects on the measurement electrodes and besides, amplifier distortions, are avoided, while resistive effects overwhelmingly contribute to the signal like in a purely direct current (DC) measurement (Johnson, 2007; Groom, 2008; Visconti & de Paz, 2016).

Most of the electromagnetic induction (EMI) sensors operate in the low-frequency range below 300 kHz (Špikić et al., 2022). In contrast to low-frequency EMI, high-frequency electromagnetic induction (HFEMI) sensors operate in the frequency range between 300 kHz and 30 MHz (Stewart et al., 1994). The principle of a series of measurements with varying frequency values was motivated by the assumption that different ions of different sizes exhibit different conductivity as a function of frequency variation, thus providing the possibility of selective detection. As we wanted to investigate both low and mid frequency EC responses and the upper limit of the available laboratory equipment was 1 MHz we decided to use the 10 logarithm based measurements. The measurement results confirmed this theory, see Fig. 9.

This study investigated on how to determine the  $K^+$  and  $Ca^{2+}$  cation concentration in a two-component KCl – CaCl<sub>2</sub> solution. One measurement is defined as a full set,



**Figure 9.** Comparison of measurements of different two components mixtures as a function of frequency.

measurement over the entire frequency range then two non-independent variables, a frequency sequence and the EC values corresponding to the frequencies will be the output parameters of a given measurement. These sequences were used to separate the components of a two-component solution. In order to do this, it was necessary to determine a calibration curve, which explicitly gives the concentration of one of the components in the unknown solution.

If we take the original Fig. 4 again, which shows the EC values as a function of measurement frequency for the different solutions but now focuses only on the frequency range 10 kHz to 750 kHz and fits the measurement points with exponential regression according to Function 1, we get the plot shown in Fig. 9.

The fitting parameters of the exponential functions are summarized in Table 4.

**Table 4.** Fitting parameters of the functions and the coefficient of determination

Mixed solutions - contents	$y_0$	A	t	$R^2$
100% KCl - 0% CaCl <sub>2</sub>	106.17613	-42.62836	172.20536	0.98492
80% KCl - 20% CaCl <sub>2</sub>	109.38066	-58.54349	207.90067	0.99916
60% KCl - 40% CaCl <sub>2</sub>	117.57815	-67.63566	237.28209	0.94130
50% KCl - 50% CaCl <sub>2</sub>	118.03697	-68.38452	253.19429	0.99186
40% KCl - 60% CaCl <sub>2</sub>	119.55523	-71.11624	270.70152	0.99247
20% KCl - 80% CaCl <sub>2</sub>	121.59095	-74.66261	284.33045	0.99302
0% KCl - 100% CaCl <sub>2</sub>	123.8331	-77.5342	299.80215	0.99362

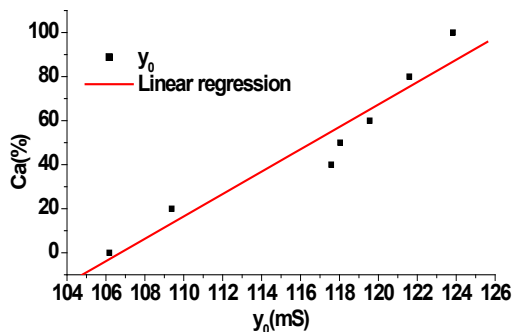
The coefficient of determination is very strong, as even the smallest coefficient shows values above 0.94, so the fits are good. Based on the previous statistical analysis, we created a calibration curve where the Ca concentration can be determined as a function of the values of conductivity ( $y_0$ ) extrapolated to zero frequency. For this, the  $y_0$  displayed the values in a  $y_0$  – Ca% coordinate system and plotted a linear regression curve for the points (Fig. 10).

Finally, by adding a calibration curve of the two-component solution, which gave the relationship between the two parameters described by a linear function (Ca<sup>2+</sup> concentration and the exponential frequency constant) and describes the statistical reliability of this relationship ( $R^2 = 0.96$ ) in the examined range (Fig. 11).

The linearly fitted calibration function:

$$f(x) = -135.049 + 0.75x \quad (3)$$

Knowing this function, the Ca% can be calculated in two steps from the EC values measured at the given frequencies in one measurement sequence. Calculation method is a solution containing K<sup>+</sup> and Ca<sup>2+</sup> cations of unknown composition, on which, in the case of this experiment, electrical conductivity is measured at 6 known frequencies, where:



Parameters	Value	Error	Unit
A	107.53	1.404	-
B	0.181	0.023	-
$R^2$	0.919	-	-

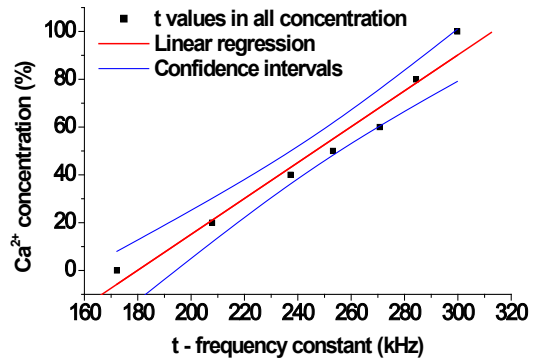
**Figure 10.** The Ca content in the Ca – K ion mixture as a function of the conductivity ( $y_0$ ) extrapolated to zero frequency.

1. The EC values in one sequence are plotted on the measurement frequencies according to Fig. 9 and

2. one-parameter exponential function to be fitted to the measurement points by Mitscherlich equation (Mitscherlich, 1909; Mitscherlich, 1928) according to Fig. 9.

3. then the obtained parameter  $t$  is inserted into Function 3 and the equation is solved to obtain the ratio of the  $\text{Ca}^{2+}$  component of the two-component solution compared to the total amount of  $\text{K}^+ - \text{Ca}^{2+}$  ions.

Our current approach provides framework and laboratory background for further development.



**Figure 11.** The frequency constant ( $t$ ) is a function of the  $\text{Ca}^{2+}$  concentration of the two-component solution.

## CONCLUSIONS

With the spread of soil sensors, it is possible to measure soil properties on-the-go, so growers can get immediate information about the state of the most important resource, the soil, which can save resources and reduce the impact on the environment. The use of soil sensors enables rapid, immediate and cost saving soil testing and nutrient mapping solutions.

This study was looking for the answers to whether one of the simplest and cheapest measurement methods, i.e. the new approach to measuring the electrical conductivity as a parameter of the soil, offers the possibility to measure selective salinity in the laboratory. In this it was demonstrated that it is possible to determine the selective salinity of a two-component solution containing  $\text{K}^+$  and  $\text{Ca}^{2+}$  cations by measuring electrical conductivity at a variable frequency, and we also determined which frequency range is relevant from the point of view of measurability as functions published in the results.

It was evident that a calculation model can provide guidance for calculating the selective salinity of two component solution in laboratory conditions using the analytical application of conductometry. The model shows that by consistently changing the measurement frequencies, the selective salinity can be determined by EC measurement under laboratory conditions.

**ACKNOWLEDGEMENTS.** The authors would like to acknowledge the Hungarian University of Agriculture and Life Sciences, Institute of Technology for the financial support and for providing facilities and infrastructure that enabled this research to be conducted.

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