EXAMINATION OF CHARACTERISTICS DETERMINING THE CONDITION AND CULTIVABILITY OF SOILS

Doctoral (PhD) theses

by

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1. INTRODUCTIONS, OBJECTIVES

1.1. Introduction

The number of inhabitants of our planet is constantly growing, practically tripling in the 20th century, and already reached six billion at the turn of the millennium. The United Nations predicts that there will be 9.7 billion people on Earth in 2050, which is how many people agriculture will need to feed. Looking at the trends, we can conclude that, to keep pace, agricultural production would need to grow by 50 – 100 % over a few decades. There can be unforeseeable social consequences if supply fails to keep pace with demand. Therefore, consumables should be used more consciously and wisely to achieve maximum effect with them. To meet these challenges in the future, a global agricultural strategy is needed that emphasises that the necessary productivity gains must contribute to meeting the needs of producers and consumers in such a way as to preserve the environmental, economic and social sustainability of agriculture for future generations. The digitalisation of agriculture plays a key role in achieving the sustainability goal.

1.2. Objectives

The study of the Electrical Conductivity (EC) of soil solutions has long been a tool in precision agriculture. While studying the literature, it came to my attention that researchers consider it a fact that measuring electrical conductivity is not an ion-selective method due to its additivity, so they consider it a suitable tool only for detecting the total salinity of the soil in practice. I also found that research and measuring instruments used in practical metrology do not deal extensively with a very important electrical metrology parameter, the frequency of the measuring current. Therefore, with my investigations I wanted to prove:

- The electrical conductivity of soil selectively enriched with one known concentration of electrolyte at a time depends on the frequency of the measuring current, and the EC response functions of different electrolytes differ. Thus, solutions containing different cations behave differently in the same environment with the same measurement parameters. To investigate this, I measure the electrical conductivity on a soil with known properties, using a constant frequency series, while the soil sample solution of known concentrations of K and Ca salts and compare the response functions obtained.

- A change in the measurement frequency affects the measuring circuit and changes the measurement output, i.e. the electrical conductivity. There is a significant correlation between the easily measured EC

value of the soil(paste) and the relative salinity of the soil. In my experiments, I investigate whether, by measuring the electrical conductivity of a soil sample soaked with a cationic solution of different concentrations at a given frequency series, a correlation can be found between the measured EC value at the measurement frequency and the known concentration.

- Conductometry, as is the measurement of electrical conductivity, can be a measurement and mathematical methodology for ion-selective measurement of solutions because there is a mathematical method for describing the proportion of K^+ and Ca^{2+} components in a known solution by reasonably varying the measurement frequency of EC and the proportion of each component can be described by a function.

2. MATERIAL AND METHOD

2.1. The background of the measurements

From the literature I learned that the measurement of electrical conductivity is not suitable for ion-selective measurement, so currently its analytical application is limited to the study of systems that contain only a single electrolyte, so the contribution of the "background" is negligible. Therefore, in my investigations I wanted to know whether

- **Single-phase soil solution.** What happens in the soil if I measure the electrical conductivity of the selectively electrolyte-enriched soil by changing the frequency of the current during the measurement? I wanted to find out how the measurement frequency affects the model and whether there is a significant relationship between the easily measurable EC value of the soil(paste) and the relative salinity if I change the frequency of the measuring current during the measurements. Therefore, **using a constant series of frequencies, I examined the conductivity of a soil with known properties at different frequencies, while washing the soil sample with an aqueous solution of K and Ca salts**. The electrical conductivity of a soil sample soaked with cationic solution of different concentrations was examined by measuring a predetermined given frequency series, and correlations were sought between the measured EC value, the measurement frequency, and the known concentration.

- Two-phase/two-component solution. It was investigated whether the K^+ and Ca^{2+} cation concentrations in a solution could be separated by electrical conductivity measurements by rationally changing the measurement frequency. In contrast to commercially available static frequency measuring conductors, AC frequency measurements were used to examine the conductivity of the salt mixture dissolved in distilled water of known concentration. I measured whether I could infer the concentration of each cation, or the relative number of different ions and their changes, using different frequencies to measure conductivity.

The measurements were made in the Gödöllő Laboratory of the Hungarian University of Agriculture and Life Sciences Technical Institute. The temperature in the lab was set at a constant 22 °C. The solutions used and the soil were used during the measurement at a temperature of 22 °C.

2.2. Characterisation of the soil used

For the experiments with soil paste, a neutral soil with no detectable $CaCO_3$ content was chosen as a model soil $pH_{H_2O} = 7.16$. The soil sample was collected from the area of the MATE Training Farm in Gödöllő-Szárítópuszta from 0-20 cm layer of arable land (47° 35' 47.65" N, 19° 21' 18.54" E) from an altitude of 232 m above sea level. The soil texture was sand with < 0.5 % organic matter.

2.3. The solutions used

During my measurements, I wanted to investigate the concentration of cations of salts dissolved in soil moisture under natural conditions. For my measurements, I chose salts, the rational replacement of which is a topical and costly issue during the cultivation of cultivated crops.

- **Potassium** - salts, and chlorides dissolve well in water, so I chose chlorine salts of the K^+ cation for the experiment. I prepared stock solutions with a concentration of 1 M (1 M = 1 mol dm^{-3}) from potassium chloride (KCl), ACS Reagent, 99.0 - 100.5 % CAS: 7447-40-7. These solutions were further diluted with the dilution series: 1 M; 0.66 M; 0.5 M; 0.33 M and distilled water, i.e. 0 M, was the reference measurement. Between measurements, I always washed the system with distilled water so that the ions remaining on the electrode during the previous measurement would not cause measurement errors.

- **Calcium** - these ions had to be added into the soil solution in the form of water-soluble salts. Salts and chlorides dissolve well in water, so chlorine salts of the Ca^{2+} cation ($CaCl_2$) were chosen for the experiment. I prepared stock solutions with a concentration of 1 M (1 M = 1 mol dm^{-3}) from calcium chloride, 99.0 - 103.0 %, CAS: 10043-52-4. These solutions were further diluted with a dilution series, similar to the KCl solution, of 1 M; 0.66 M; 0.33 M and distilled water as is 0 M. Between measurements, the system was washed with distilled water to ensure that the ions remaining on the electrode during the previous measurement did not cause measurement errors.

- **Two-phase mixture solution,** in my experiments I investigated the effect of cations of dissolved salts under natural conditions, in a mixture. Salts and chlorides dissolve well in water, so chlorine salts of K^+ and Ca^{2+} cations were used in the experiment. Stock solutions with a concentration of approximately 1 M (1 M = 1 mol dm^{-3}) were

prepared from the salts and the solutions were used in 50 ml units. I used the salts described in Table 1.

Table 1 Parameters of the salts in the test

Solution	CAS	Molar mass (g mol^{-1})	Name	Features
KCl	7447-40-7	74.550	potassium chloride	white crystals
CaCl$_2$	10043-52-4	110.980	calcium chloride	white, small plate

- The following two-component solutions were prepared and used for measurements:

    o 100 % KCl – 0 % CaCl$_2$.

    o 80 % KCl – 20 % CaCl$_2$

    o 60 % KCl – 40 % CaCl$_2$

    o 50 % KCl – 50 % CaCl$_2$

    o 40 % KCl – 60 % CaCl$_2$

    o 20 % KCl – 80 % CaCl$_2$

    o 0 % KCl – 100 % CaCl$_2$

Between measurements, I rinsed the measuring instruments with distilled water so that the ions remaining on the electrodes during the previous measurement would not contaminate the solutions of the next measurement.

2.4. Specification of measuring circuits

2.4.1. Measuring scope of measurements with soil paste

I built the measuring circuit shown in Fig. 1, the elements of which are:

- SOURCETRONIC ST2829C precision LCR meter with USB memory
- SOURCETRONIC ST26011B linkage
- KSP-F01A peristaltic dosing pump
- 500 ml measuring cup (scaled up to 50 ml) for input solution storage
- Measuring cylinder $\varnothing$61 mm × 137 mm.

- Measuring electrodes 2 pcs, $\varnothing$2 mm, length: 80 mm total length insulated, length of uninsulated part 5 mm, scope distance 12 mm, material stainless steel

- Piping inner $\varnothing$3 mm

- Tray with hoist

Fig. 1 The measuring circuit for experiments with soil paste

2.4.2. *Measuring circuit for testing two-phase solutions*

For the measurement of the mixture solution, I simplified and used a measuring circuit as shown in Figure 1 to measure the premixed solutions. The elements of the measuring circuit as shown in Fig. 2:

1. SOURCETRONIC ST2829C precision LCR meter with USB memory

2. SOURCETRONIC ST26011B linkage

3. Measuring electrodes 2 pcs, $\varnothing$2 mm, length: 80 mm total length insulated, length of uninsulated part 5 mm, scope distance 12 mm, material stainless steel

4. 100 ml measuring cup

Fig. 2 Conversion of the measuring circuit to the two-phase solution

2.4.3. The SOURCETRONIC ST2829C precision LCR meter

The principle of operation of the SOURCETRONIC ST2819C high precision LCR meter is to provide a constant excitation at the output via a four-wire measuring system and to detect the response function from the ground sensor. SOURCETRONIC ST2829C measured electrical conductivity (G, Siemens) between two stainless steel electrodes placed in the earth paste on a pre-programmed frequency sequence and then restarted the measurement cycle at the end of the measurement series. The SOURCETRONIC ST2829C precision LCR meter allows you to record several frequencies in series in one measurement cycle. I considered a measurement to be the completion of an entire measurement sequence. However, selecting too many frequencies reduces the strength of each frequency signal and, consequently, reduces the resolution. For my measurements, I programmed 14 characteristic frequencies into the device, which covers the frequency range recommended by manufacturers. The frequency values used for measurements are: 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.

The measuring instrument is extremely sensitive to interference signals from the environment, so a special measurement method has been developed to eliminate them. The four-wire measurement method for eliminating interfering (capacitive) signals is shown in Fig. 3.
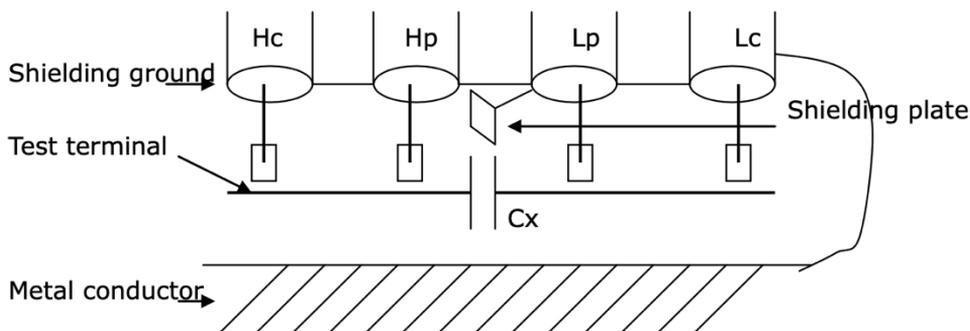
Fig. 3 Method of measurement to eliminate interference

In the rest of my thesis, I refer to the G-conductance value as the EC value.

2.5.   Process of data processing

2.5.1. *Measurement of a single-phase solution in soil paste*

First, I compiled the measuring circuit shown in Fig. 1 for my examination. I started each new measurement by calibrating the KSP-F01A peristaltic dosing pump. I set the pump fluid delivery to 0.5 g s^{-1}. Before starting each measurement with a new solution, the soil paste was washed in the measuring cylinder with at least 300 ml of distilled water so that the remaining ions after the previous measurement did not affect the measurement results. During the measurements, the premixed concentration solution was pushed by the KSP-F01A peristaltic dosing pump through the dosing head into the measuring cylinder at the entry point formed at the bottom of the measuring cylinder pre-filled with soil.

At each concentration, with each solution, measurements were carried out by triple repetition, adding solution as 300 ml and each filling was followed by washing and neutralization with at least 300 ml of distilled water. If during the washing of the soil paste the measured EC value did not fall below 0.1 mS, I continued washing with distilled water added as an additional 100 ml. The measurements were documented for the reproducibility of the experiments.

The *.csv* file obtained as a result of the measurement was processed using the spreadsheet editor program, Microsoft Excel. After uploading the file into Excel, I converted it and created the database for data processing. From the raw database I made a statement, which is a matrix that obviously arranges the G value of the previous tabular database for the given parameter, in this case the measurement frequencies. A record is a measurement on a full measurement sequence (the entire frequency measurement series). From the database thus formed, a diagram characteristic of the measurement can be made, which is shown in Fig. 4. The diagram shows that for a given

concentration, I repeated 3 times at each measurement frequency by washing the measuring circuit with distilled water between measurements.
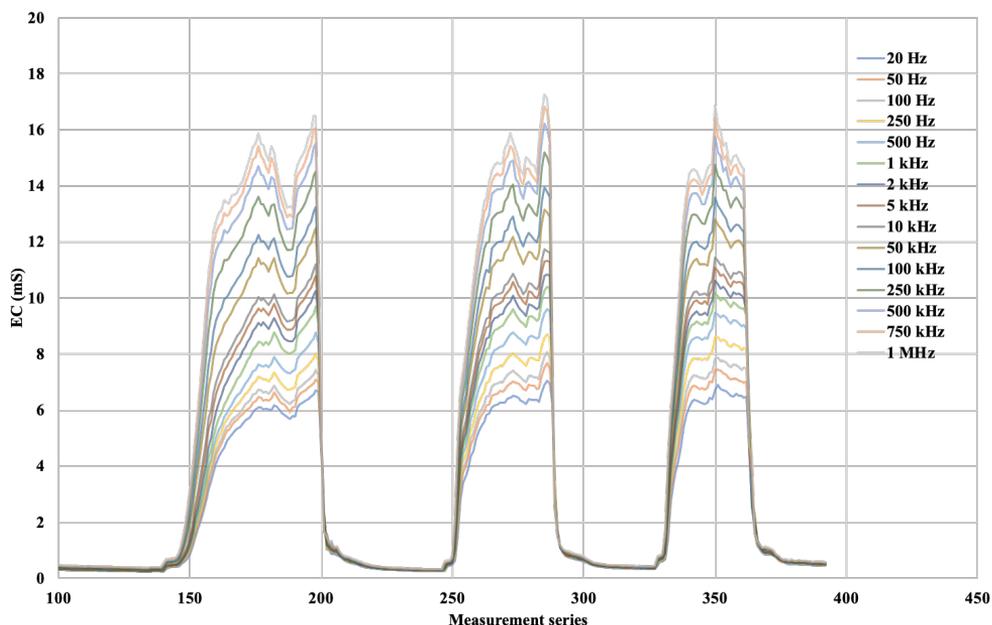
Fig. 4 Diagram of EC value per soil solution measurement sequence

I created the variance analysis of the records from the Pivot. Only those measurement values where the change on the next sequence did not exceed 5 % ($\Delta < 5$ %) were included in the calculation of the arithmetic mean. I determined the frequency-dependent arithmetic averages of the entire measurement. After performing the calculations, it was possible to analyse the calculated values, which will be presented in Chapter 3.1. The functional analyses were evaluated in Microcal Origin software.

2.5.2. Measurement of a two-phase mixture solution

First, I compiled the measuring circuit shown in Fig. 2 for my examination. Before starting each measurement with a new solution, the measuring cup was washed with distilled water so that the remaining ions after the previous measurement did not affect the measurement results. Stock solutions with a concentration of approximately 1 M (1 M = 1 mol dm^{-3}) were prepared from the salts and the solutions were used in 50 ml units. All measurements were made with each two-component mixture solution in at least a tenfold measurement sequence (measurement series). The measurements were documented in a measurement report due to the reproducibility of the experiments.

The *.csv* file obtained as a result of the measurement was processed using the spreadsheet editor program, Microsoft Excel. After uploading the file into Excel, I converted it and created the database for data processing. From the raw database I created a report, which is a matrix that computes the G value of the previous database for the given parameter, in this case the measurement frequencies. A record is a measurement on a single measurement sequence (the entire frequency measurement sequence). During data processing, I noticed that all measurements made with a frequency of 20 Hz show the negative value, so I removed 20 Hz from the study.

From the database edited, a diagram characteristic of the measurement can be created, which is shown in Fig. 5. The diagram shows that I ran at least 10 measurement sequences as is 10 measurement sequences, with the given mixture solution.
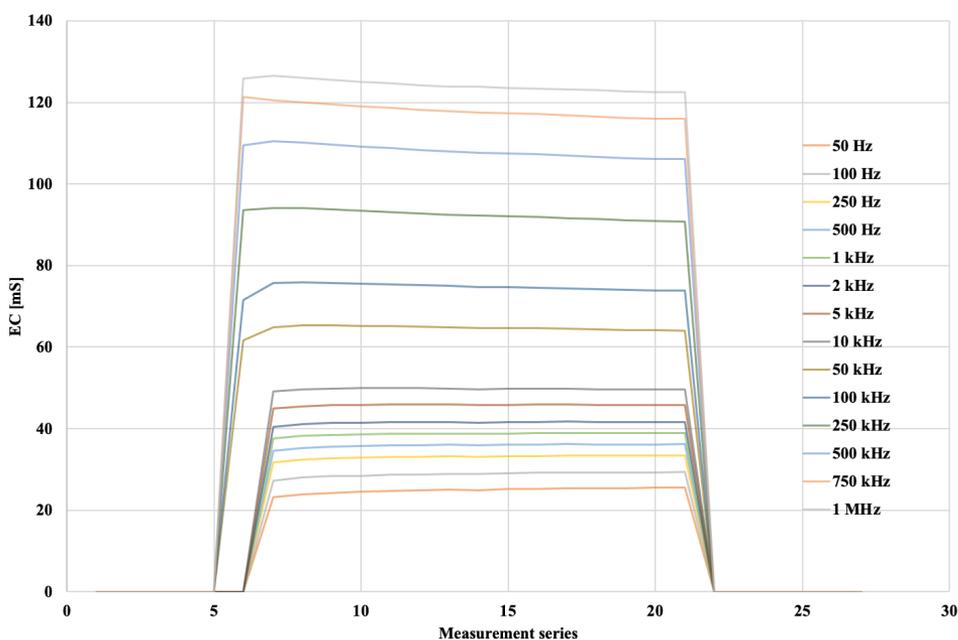
Fig. 5 Diagram of EC value per measurement sequence of 50 % KCl – 50 % CaCl$_2$ mixture solution

From the measurements, I selected the last 5 complete measurement sequences and averaged the measurement values by frequency. I determined the frequency-dependent arithmetic averages of the entire measurement. After performing the calculations, it was possible to analyse the calculated values, which will be presented in Chapter 3.2. The functional analyses were evaluated in Microcal Origin software.

3. RESULTS

3.1. Determination of cation content of single-phase soil solutions

For the detection of the cation content, the reference EC saturation curves characteristic of the given soil, were first determined by measurements performed in the laboratory with predetermined solution concentrations using the procedure described in subsection 2.5.1.

3.1.1. Determination of potassium reference functions by laboratory measurement

After cleaning and processing the data, it was possible to analyse the measurement results of the processed data by cation, concentration, and measurement frequency. Figure 6 shows that EC increases with an increase in concentration in some function context, and it can be clearly seen that even if the measurement frequency is increased, the EC value still increases.
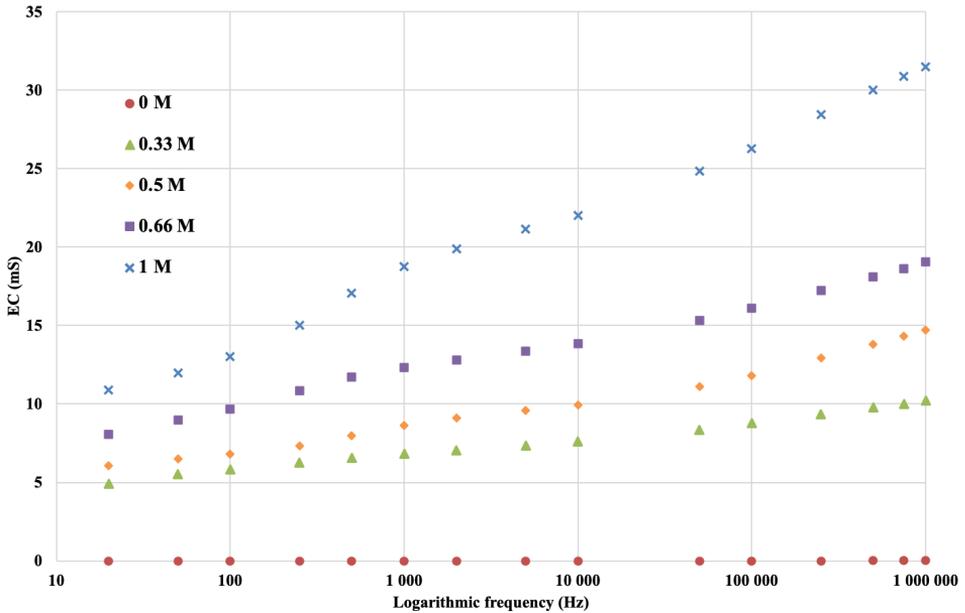
Fig. 6 EC as a function of logarithmic measurement frequency for soil solutions soaked with different concentrations of KCl

In Fig. 7, the EC measurement results of solutions of different concentrations are plotted on a linear scale as a function of frequency. I was able to fit strictly monotonously increasing power functions to the obtained points, which have a coefficient of determination $R^2 > 0.98$, so they show a tight fit.

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The potassium (K^+) cation reference functions for the set measurement model with a very good fit are as follows:

- For 1 M solution, such $f(x) = 8.8789x^{0.0949}$ that $R^2 = 0.981$

- For solution 0.66 M, $f(x) = 7.0164x^{0.0733}$ $R^2 = 0.9875$

- For a solution of 0.5 M, such $f(x) = 4.7791x^{0.0806}$ that $R^2 = 0.9961$

- For solution 0.33 M, $f(x) = 4.34x^{0.0619}$ $R^2 = 0.9947$

- 0 M solution, as is with distilled water, such $f(x) = 5E-09x + 0.0035$ that $R^2 = 0.9307$
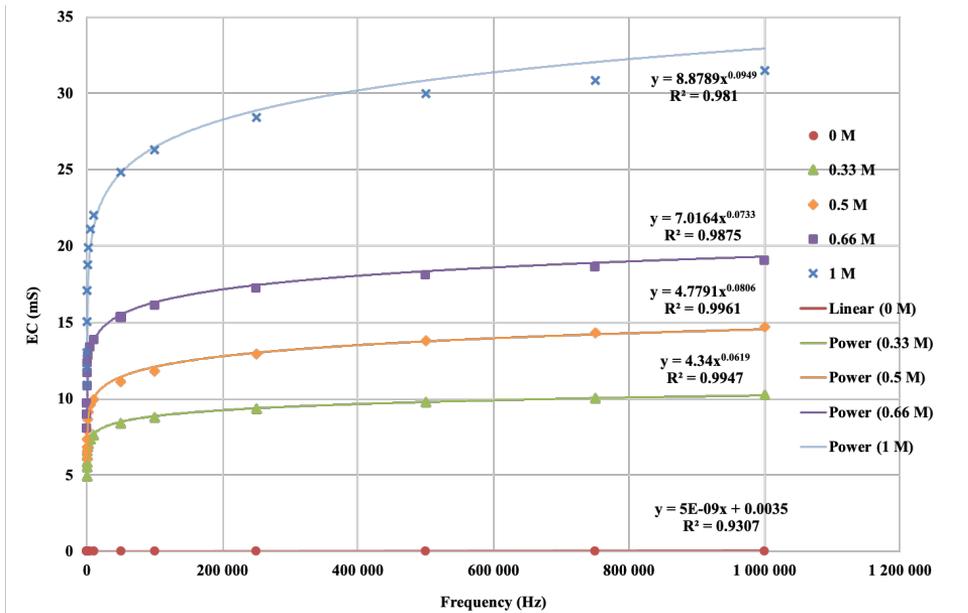
Fig. 7 EC saturation curve for soil solutions of different K^+ concentrations

3.1.2. Determination of calcium reference functions by laboratory measurement

I followed the same calculation method to produce the database that I had previously shown for measurements with potassium. After performing the calculations, it became possible to record the measurement results of the calculated data series by ion, concentration, and measurement frequency. Fig. 8 not only shows that EC increases with an increase in concentration in some function context, but it can also be clearly seen that if the measurement frequency is increased, the EC value still increases, and especially high measurement frequencies are suitable for detecting Ca content at higher concentrations.

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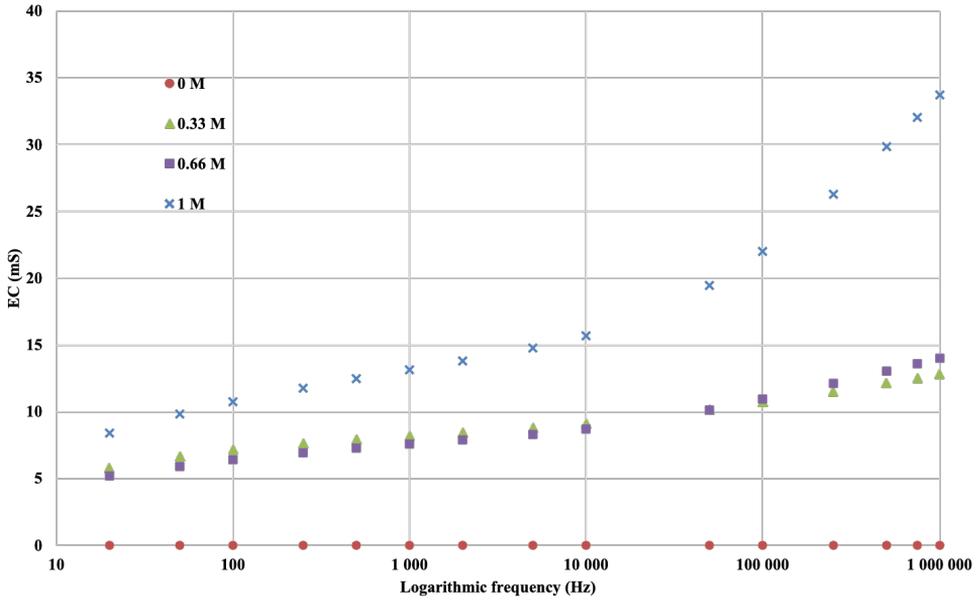
Fig. 8 EC as a function of logarithmic measurement frequency for soil solutions soaked with different concentrations of CaCl2

In Fig. 9, the EC measurement results of solutions of different concentrations are plotted on a linear scale as a function of frequency. To the obtained points I fitted strictly monotonously increasing power functions with a coefficient of determination $R^2 > 0.97$, so they show a tight fit.

The calcium (Ca^{2+}) cation reference functions for the established measurement model with a very good fit are as follows:

- For solution 1 M, such $f(x) = 5.782x^{0.121}$ that $R^2 = 0.9753$

- For solution 0.66 M $f(x) = 4.1613x^{0.0858}$, $R^2 = 0.9919$

- For solution 0.33 M, $f(x) = 5.0884x^{0.066}$ such that $R^2 = 0.991$

- 0 M solution as is distilled water, such that $f(x) = 5E - 09x + 0.0035$ where $R^2 = 0.9307$, which is obviously the same as in the previous series of measurements with potassium.

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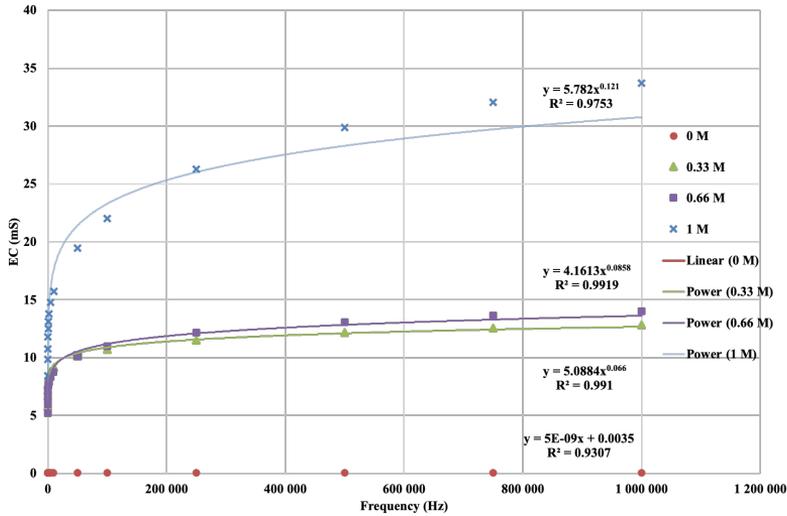
Fig. 9 EC saturation curve plotted on a natural scale for soil solutions with different Ca^{2+} concentrations

3.1.3. Comparison of potassium and calcium reference functions

The following Table 2 shows a comparison of the reference functions.

Table 2 Comparison of reference functions

Concentration	K^+	Ca^{2+}
1 M	$f(x) = 8.8789x^{0.0949}$	$f(x) = 5.782x^{0.121}$
0.66 M	$f(x) = 7.0164x^{0.0733}$	$f(x) = 4.1613x^{0.0858}$
0.5 M	$f(x) = 4.7791x^{0.0806}$	
0.33 M	$f(x) = 4.34x^{0.0619}$	$f(x) = 5.0884x^{0.066}$
0 M	$f(x) = 5E - 09x + 0.0035$	$f(x) = 5E - 09x + 0.0035$

My measurements clearly proved that when measuring the electrical conductivity of a soil paste enriched selectively with one known concentration of electrolyte at a time, by cleverly changing the frequency of the measuring current, the response functions of EC will be different from electrolyte to electrolyte. When comparing response functions at the same solution concentration, it can be concluded that the responses of solutions to varying measurement frequencies exhibit different behaviour because the exponents of strictly monotonously increasing power functions differ from one concentration pair to another. The difference in exponents explains the different behaviour of cations. Therefore, potassium and calcium solutions of

the same concentration behave differently in the same environment with the same measurement parameters, since hydrated cations differ significantly in size, so they move at different speeds in a medium of the same viscosity under the influence of a given electric field.

3.1.4. Determination of the cation concentration of an unknown single-phase soil solution

Previously, I determined the reference functions of potassium and calcium electrolytes by measurements, therefore I determined what EC values the response function returns at variable frequency measured on the entire measurement sequence. If I know the composition of the single-phase soil solution, I can mathematically determine the concentration of the single-phase soil solution based on the reference functions taken. I developed two possible mathematical methods for this solution: Determination of solution concentration by (i) interpolation of reference values and (ii) interpolation of regression functions of reference values.

3.2. Determination of cation ratio of two-phase soil solutions

3.2.1. Variable frequency EC measurement as a measuring tool

First, I performed a function test to prove that variable frequency EC measurements can be used as a tool to determine the concentration of biphasic solutions. In the process described in subsection 2.5.2., EC values have been generated from mixed solutions at the set frequencies. The results of the measurements were plotted as a function of logarithmic frequency in Fig. 10. The EC values for the cation concentration of the solutions are summarized in Table 3.
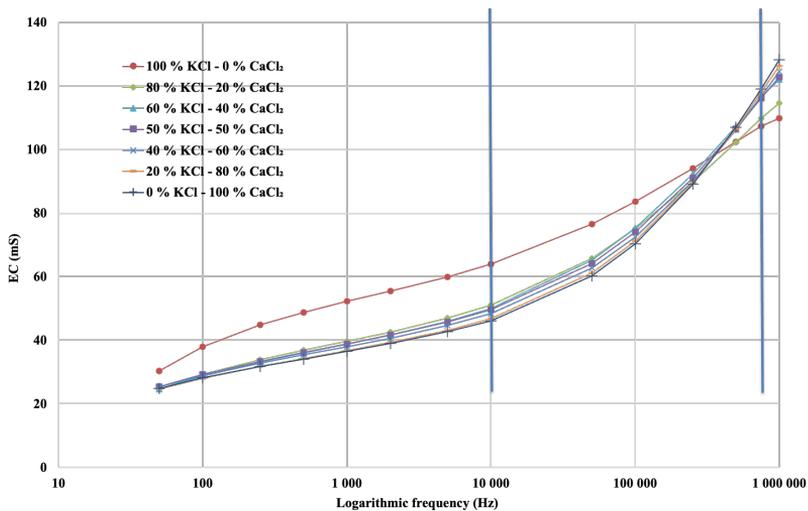
Fig. 10 Comparison of EC measurements of different mixtures

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It is clear from the measurement results that:

- As the measurement frequency increases, the value of EC increases.

- The conductivity of a solution containing K^+ cations differs from that of a solution containing Ca^{2+} cations, since the hydrated cations differ significantly in size, so they move at different speeds in a given viscosity medium under the influence of a given electric field.

- Up to a frequency of 10^4 Hz, the EC change due to frequency change is linear and does not differ significantly for solutions containing different ratios of Ca and K ions. However, in the frequency range of 10 kHz to 750 kHz, the measured electrical conductivity depends on the calcium/potassium ion ratio of the solution.

Table 3 Measurement results

Frequency (Hz)	EC for the cation concentration of the solutions (mS)						
	100 % KCl - 0 % $CaCl_2$	80 % KCl - 20 % $CaCl_2$	60 % KCl - 40 % $CaCl_2$	50 % KCl - 50 % $CaCl_2$	40 % KCl - 60 % $CaCl_2$	20 % KCl - 80 % $CaCl_2$	0 % KCl - 100 % $CaCl_2$
50	30.30	24.72	24.64	25.44	25.42	24.62	24.86
100	37.85	29.25	28.70	29.25	28.97	28.06	28.15
250	44.84	33.78	33.07	33.36	32.80	31.75	31.73
500	48.73	36.80	35.98	36.15	35.42	34.22	34.10
1 000	52.25	39.69	38.81	38.88	38.02	36.75	36.54
2 000	55.40	42.61	41.67	41.63	40.65	39.28	39.00
5 000	59.99	46.99	45.98	45.78	44.63	43.14	42.78
10 000	63.92	51.07	50.04	49.64	48.34	46.79	46.15
50 000	76.62	65.81	65.20	64.20	62.66	61.17	60.33
100 000	83.58	75.06	75.31	74.06	72.52	71.23	70.43
250 000	94.16	89.89	92.34	91.12	90.05	89.42	89.14
500 000	102.49	102.18	107.26	106.43	106.17	106.53	106.97
750 000	107.46	109.80	116.64	116.33	116.87	117.98	119.16
1 000 000	109.83	114.60	122.13	122.77	124.50	126.33	128.33

In the 10 kHz and 750 kHz frequency range, statistical analyses and function tests were performed for conductivity values measured as a function of the concentration of solutions at different measurement frequencies (Fig. 11).
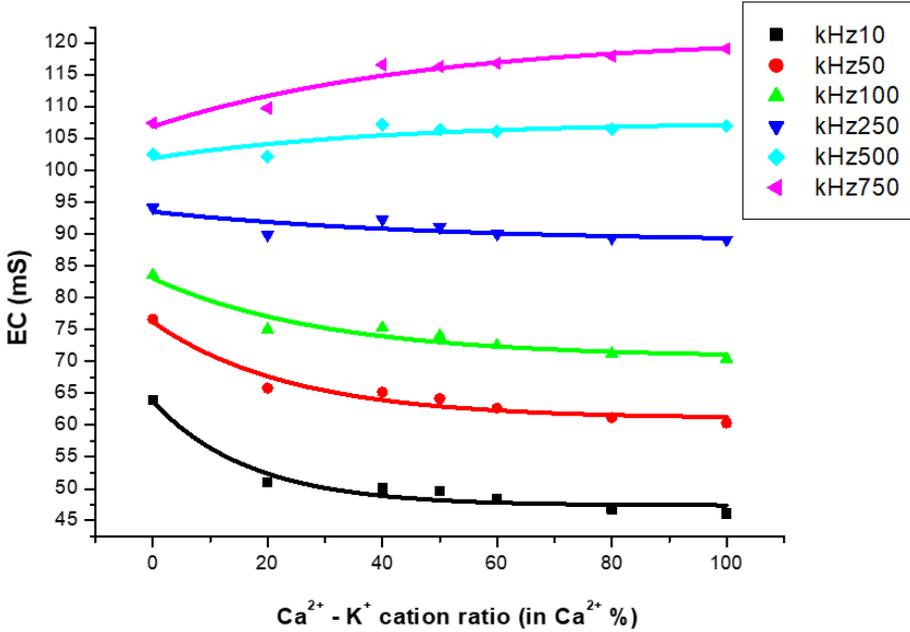
Fig. 11 Comparison of measurements and function matching

In my thesis I used exponential functions as fitted functions in the following form, and I performed a parametric analysis of this function as proof:

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

where y_0 - conductivity extrapolated to zero frequency, that is, to the starting point of the system; A - shows the rate of change, and t - is the frequency constant. The parameters of the equations for the resulting fitted curves are summarised in Table 4:

Table 4 Parameters and coefficient of determination of the fitting of the exponential function

Measuring frequency	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

Results

The coefficient of determination (R^2) gave values between 0.8699 and 0.9329, apart from two measurements, which is adequate. For measurements at 250 kHz and 500 kHz, linear fitting is more suitable.

$$f(x) = A + B \tag{2}$$

Table 5 shows the parameters calculated by linear fitting.

Table 5 Linear function matching parameters and coefficient of determination for measurements at 250 kHz and 500 kHz.

Measuring frequency	A	B	R2
250 kHz	92.93	-0.04	0.5929
500 kHz	102.97	-0.04	0.6084

First, I analysed the starting point of the functions (y_0), where the conductivity was extrapolated to zero frequency, as a function of the measured frequencies. I fitted an exponential function to the points. The result of the function analysis with the function parameters is shown in Fig. 12.
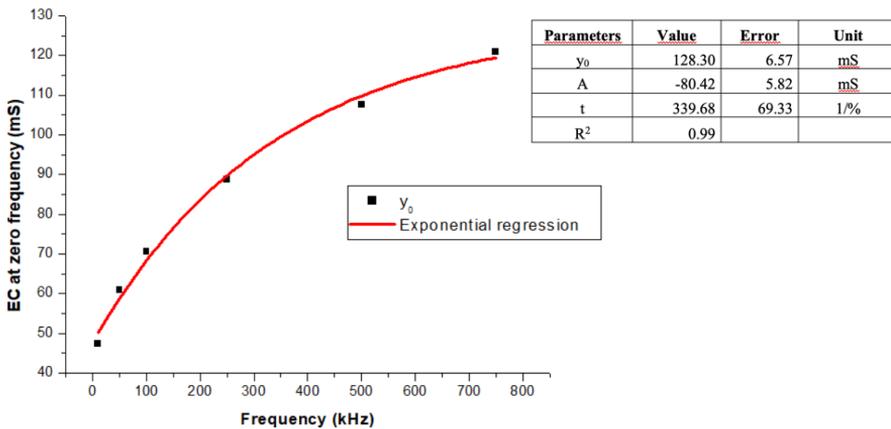
Fig. 12 Conductivity extrapolated to zero frequency as a function of measurement frequencies and matching of exponential function

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 reasonably different measurement frequencies are used. Then I plotted the difference (A) between the extrapolated starting points of the functions to null frequency (infinity), as is the rate of change as a function of the measurement frequency. I fitted a linear function to the points. The result of the function test is shown in Fig. 13.
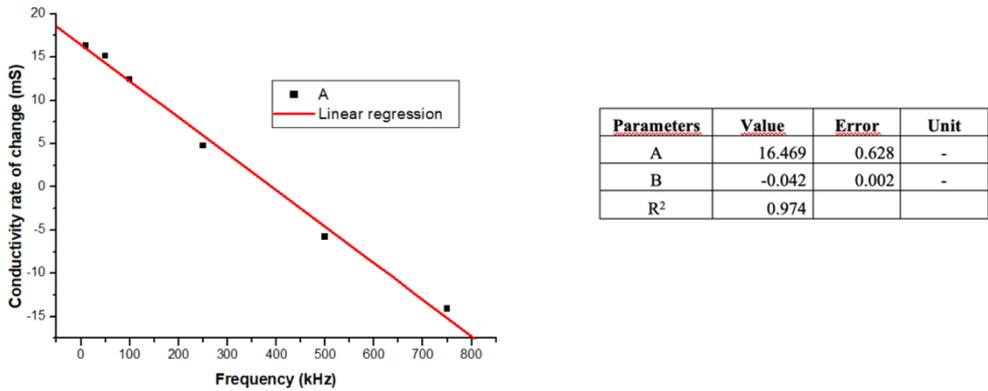
Fig. 13 Values of the rate of change as a function of measurement
frequencies and linear function fitting

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

The fitted function shows that the measurements of mixtures with different K to Ca ratios differ significantly from each other in a function-describable way when a variable measurement frequency is used. Solving the fitted function to zero, it turns out that the value of EC **takes on zero at the frequency of 392.11 kHz.** In the interpretation of Fig. 11, the function drawn will be horizontal at this frequency, the value of EC will not change with the change in the composition of the mixture. **Therefore, the frequency range of the experiment was determined correctly.**

In the next step, the frequency constant (t) was analyzed. The parameter t or frequency constant represents the change in frequency during which the deviation of conductivity from the asymptotic value decreases for exponent e. The result of the analysis is illustrated in Fig. 14.

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		
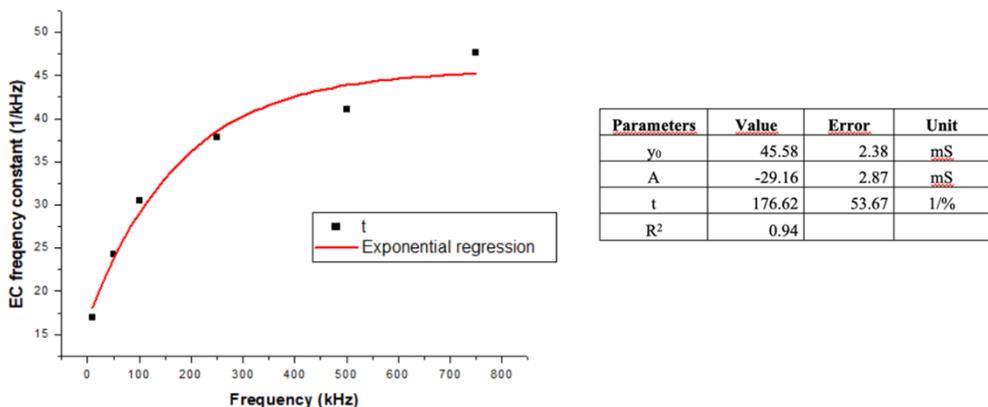
Fig. 14 Values of the frequency constant as a function of the measurement
frequencies and fitting of the exponential function

3.2.2. Mathematical method - the calibration function

With the fitted function, I proved again that the EC values measured in the ratio of K to Ca differ significantly in a way that can be described by a function if EC measurement with variable measurement frequency is used. **Variable frequency EC measurement is therefore 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 suitable measurement range.

One of the objectives of my thesis focuses on how to replace the slower, more complex, and therefore relatively expensive laboratory salinity determination with as many field measurements as possible. The dependence of soil EC value 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. My current approach can provide a framework, guidance for further analyses and laboratory background for the further development of on-the-go soil sensors based on EC measurement.

In my thesis I investigated how to determine the K^+ and Ca^{2+} cation concentrations in a two-component KCl - $CaCl_2$ solution. I interpreted a measurement on a complete set measurement sequence, i.e. frequency series, then the two non-independent variables, a frequency series and the EC values corresponding to the frequencies will be the output parameters of the given measurement. **These sequences were used to separate the components of a two-component solution. To do this, a calibration curve had to be determined specifically indicating the concentration of one of the components in the unknown solution.**

If we revisit the initial measurement shown in Fig. 10, which shows the EC values of different solutions as a function of the measurement frequency, but now concentrate only on the frequency range between 10 kHz and 750 kHz and match the measurement points by exponential regression according to Function 1, we get the figure shown in Fig. 15. The fitting parameters of exponential functions are summarised in Table 6.
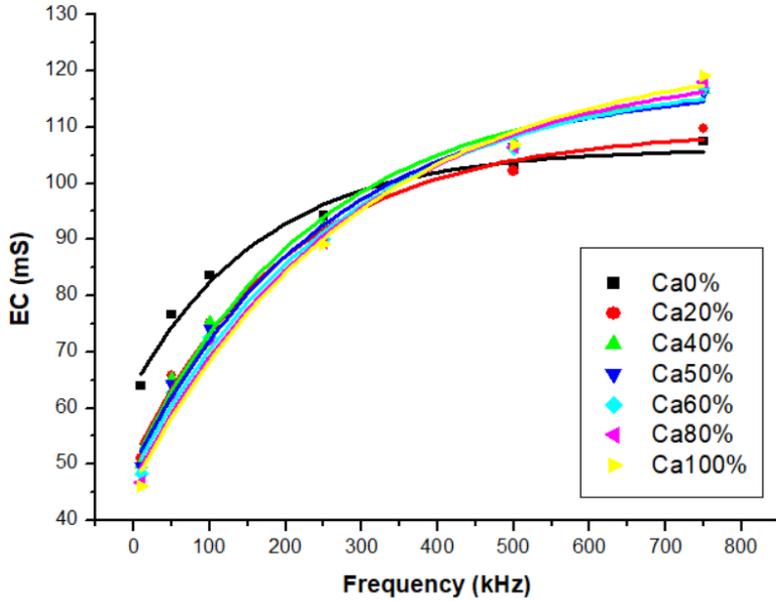
Fig. 15 Comparison of measurements of different two-component mixtures as a function of frequency

Table 6 Fit parameters of functions and coefficient of determination

Solution	y_0	A	t	R^2
100 % KCl – 0 % CaCl₂	106.17613	-42.62836	172.20536	0.98492
80 % KCl – 20 % CaCl₂	109.38066	-58.54349	207.90067	0.99916
60 % KCl – 40 % CaCl₂	117.57815	-67.63566	237.28209	0.94130
50 % KCl – 50 % CaCl₂	118.03697	-68.38452	253.19429	0.99186
40 % KCl – 60 % CaCl₂	119.55523	-71.11624	270.70152	0.99247
20 % KCl – 80 % CaCl₂	121.59095	-74.66261	284.33045	0.99302
0 % KCl – 100 % CaCl₂	123.8331	-77.5342	299.80215	0.99362

The coefficient of determination is very strong, since even the lowest coefficient shows values above 0.94, so the fit of the regression curves is correct. With the help of the functions of the fitted curves, I created the calibration curve of the two-component solution Ca - K by taking the Ca^{2+} *concentrations* as a function of the exponential *t - frequency constants* derived from the previously described alignments and fitting a linear function to the obtained points. The coefficient of determination of the linearly fitted function describing the relationship between the two parameters is $R^2 = 0.966$, so the function fits well and is statistically reliable in the examined range (Fig. 16).

Parameter	Value	Error	Unit
A	-135.049	15.747	-
B	0.750	0.063	-
R^2	0.966		-
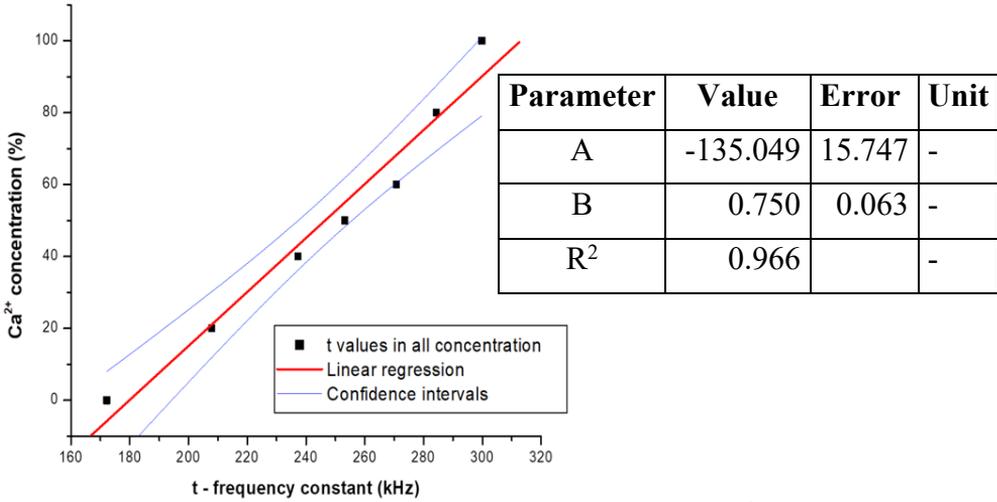
Fig. 16 The frequency constant (t) is a function of the Ca^{2+} concentration of the two-component solution

Therefore, the formula for the linearly fitted calibration function is:

$$f(x) = -135.049 + 0.75x \tag{3}$$

Knowing the calibration function, *Ca% can* be calculated in two steps at given frequencies from EC values measured in a series of measurements on one measurement sequence. The calculation method is suitable for determining the component ratios of a solution containing K^+ and Ca^{2+} cations of unknown composition, where in the present experiment electrical conductivity was measured at 6 known frequencies. The mathematical solution:

- The EC values are plotted in a measurement sequence as shown in Fig. 15.

- A one-parameter exponential function is fitted to the measurement points using the Mitscherlich equation according to Function 1 as shown in Fig. 15.

- With the obtained parameter t the Function 3 to be solved, so I get the ratio of the Ca^{2+} component of the two-component solution to the total amount of K^+ - Ca^{2+} cations.

4. NEW SCIENTIFIC RESULTS

Thesis#1 - My lab studies have shown that soil solutions containing single-phase potassium and single-phase calcium ions show an increasing electrical conductivity (EC) value by increasing the measurement frequency, as shown in Fig. 17.
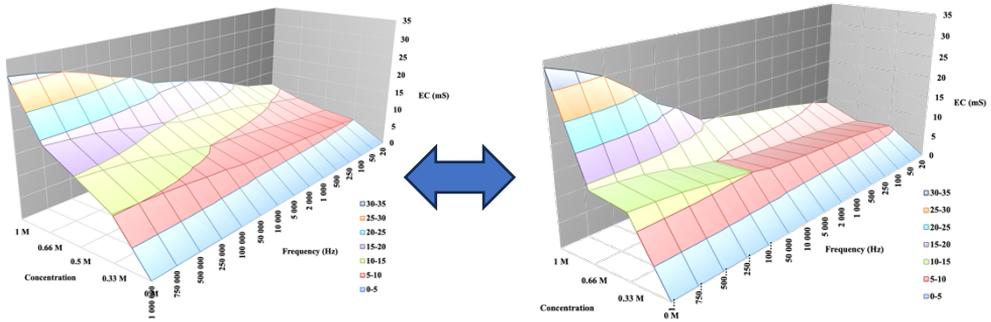
Fig. 17 EC and concentration in soil and as a function of measurement frequency – comparison between K and Ca

It can be clearly seen from the diagrams that for soil solutions with concentrations in the range of 0.33 – 1.0 M, the output value of the measurement, as is the EC value, increases proportionally with the increase in the measurement frequency at the same solution concentration. Furthermore, the higher the ion concentration of the solution, the saltier the solution, the higher the value of EC that can be calculated from the response function.

Thesis#2 - My measurements clearly proved that when measuring the electrical conductivity of a soil paste selectively enriched with one known concentration of electrolyte at a time, by rationally changing the frequency of the measuring current, the response functions of EC will differ from electrolyte to electrolyte. So, potassium and calcium solutions of the same concentration behave differently in the same environment with the same measurement parameters.

For soil solutions with concentrations in the range of 0.33 – 1.0 M for a given test frequency range, I determined the typical potassium (K^+) and calcium (Ca^{2+}) cation reference functions (Fig. 7 and 9), which can be described by a power function, and which are clearly different, as shown in Fig. 18.
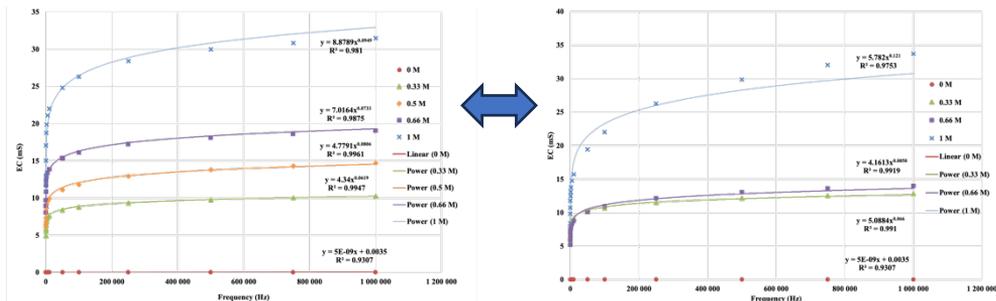
Fig. 18 The reference functions for potassium (K$^+$) and calcium (Ca^{2+}) differ

The reference functions were presented and compared itemized in Table 2.

Thesis#3 - With my laboratory tests I have established that conductometry, as a measurement method, can be used for ion-selective measurement using variable frequency values in the appropriately chosen frequency range, under given conditions. This was confirmed by a biphasic test on a solution containing potassium and calcium ions. For the tested two-phase solution, I determined the test frequency range, which is between 10 kHz and 750 kHz.

It was found that the conductivity of a solution containing K$^+$ cations differ from that of a solution containing Ca^{2+} cations, using the recognition that the hydrated cations differ significantly in size. Thus, under the influence of a given electric field, different ions move at different speeds in a medium of a given viscosity.

Thesis#4 - I developed a mathematical model and method for determining the concentration ratio of a two-component solution. I investigated how to determine the K$^+$ and Ca^{2+} cation concentrations in a two-component KCl - CaCl$_2$ solution. I interpreted a measurement on a complete set measurement sequence, as is frequency series, then the two non-independent variables, a frequency series and the EC values corresponding to the frequencies will be the output parameters of the given measurement. These sequences were used to separate the components of a two-component solution. For this, a calibration curve was determined, which specifically gives the concentration of one of the components in the solution of unknown composition. I found that the concentration ratio was determined by

$$f(x) = -135.049 + 0.75x$$

calibration function. Knowing this, Ca % can be calculated in two steps at given frequencies from EC values measured in a series of measurements on one measurement sequence. The calculation method is suitable for determining the component ratios of a solution containing K$^+$ and Ca^{2+} cations of unknown composition.

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5. CONCLUSIONS AND PROPOSALS

My research contains new scientific results that can be used in several areas. During my research work, my experiments and developments in metrology using the principle of electrical conductivity with solutions proved that electrical conductivity as a measurement technique has a place in current precision agricultural practice and there are further development opportunities in this field.

To break out of the previous paradigms, I developed a laboratory measurement methodology. My thesis details the development of a new laboratory measurement methodology, which measures the electrical conductivity of soil saturated with cations. My research showed that by rationally changing the measurement frequency of electrical conductivity, the ratio of cations in a two-component solution can be determined. Further development of this measurement principle will enable the development of more efficient, faster, and cheaper soil sensors for site-specific agricultural applications. This saves resources and reduces the environmental impact of cultivation and nutrient supply. Using such soil sensors, soil properties can be measured on-the-go, which allows immediate information on soil condition. This new method offers the possibility to determine the nutrient content of the soil, even on-the-go on the machine-machine connection in real time.

My thesis also highlights that a novel approach to measuring electrical conductivity may be suitable for measuring selective salinity in the laboratory. By varying the frequency and applying mathematical models, the selective salt content of solutions containing different cations can be determined.

I defined and developed a calculation model that provides a mathematical background for calculating the selective salinity of soil under laboratory conditions using conductometry analytically.

My conclusions point to the fact that the results of my research contribute to increasing the efficiency of precision agricultural practices and offer new possibilities in soil testing with a novel approach to electrical conductivity as a measurement method.

Based on my research work presented in my thesis, I propose to extend the relationships established based on my measurements with K^+ and Ca^{2+} cations to include other elements of the lyotropic series, such as the inclusion of Mg^{2+} and Na^+ cations and cation combinations in the study. To create a practical "black box", as is measurement method, I consider it worthwhile to develop calibration functions on several soil types with my method and to refine the algorithm in order to create a general model that corresponds to Hungarian

precision agricultural practice. As a next step, I propose to install the algorithm developed in the laboratory on a field tool suitable for electrical conductivity measurement and further refine the model under field conditions so that the variable frequency measurement principle can be applied in practice.

6. SUMMARY

The approaches of my research proved that measuring technology using electrical conductivity, which has been used in agricultural practice for several decades, also has potential for development. Challenging fact-based principles by using a new approach could open up opportunities for improvements in the use of electrical conductivity across a broader spectrum in precision agricultural practice.

In my doctoral dissertation, on the one hand, I develop a new laboratory measurement method and prove that when saturating the soil with solutions containing cations, the electrical conductivity of the soil develops according to different functions depending on the measurement frequency. Furthermore, I show that by rationally changing the measurement frequency of electrical conductivity in a two-component solution, the ratio of cations can be determined by measuring electrical conductivity. From the obtained results I draw the appropriate conclusions and give a mathematical model for determining the cation ratio in solution using laboratory experimental method. The relationships revealed by my work help to develop an on-the-go measurment device that can be used in precision agriculture practice to determine the nutrient content of the soil by measuring electrical conductivity.

With the spread of soil sensors, it is possible to measure soil properties on-the-go, so growers can get instant 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 fast, immediate, and cost-effective soil analysis and nutrient mapping solutions.

In my present thesis I was looking for the answer to whether one of the simplest, most popular and at the same time the cheapest measurement methods, i.e. the measurement of electrical conductivity, provides an opportunity for the laboratory measurement of selective salinity with a novel approach and a rethought measurement technique. My experiments proved that there is a relationship between soil salt concentration, measurement frequency and measured EC that can be described by a function. By increasing the frequency, the measured EC value of the soil saturated with solutions of a given concentration changed according to the functions published in the results, so saturating the soil with solutions containing the same concentrations of cations (K^+ and Ca^{2+}) gives different EC functions depending on the measurement frequency.

I also developed a calculation model that can guide the calculation of selective salinity of soil under laboratory conditions using conductometry analytically. The model shows that by consistently varying the measurement frequencies,

the selective salinity of a known soil can be determined under laboratory conditions by EC measurement. For solutions containing cations of the same concentration, EC is saturated according to different functions depending on the measuring frequency.

My thesis also sought to answer the question whether the novel approach to measuring electrical conductivity provides an opportunity for the measurement of selective salinity in the laboratory. I proved and mathematically derived that it is possible to determine the selective salt content of a two-component solution containing K^+ and Ca^{2+} cations by measuring electrical conductivity at variable frequency, and I also determined which frequency range is relevant for the functions published in the results from the point of view of measurability and gave the calibration function for phase separation. It became apparent that a computational model provides guidance for calculating the selective salt content of a two-component solution under laboratory conditions using conductometry analytically. The model shows that by consistently varying the measurement frequencies, selective salinity can be determined under laboratory conditions by EC measurement.

7. KEY PUBLICATIONS RELATED TO THE THESIS

Peer-reviewed article in foreign language

1. **HORVÁTH, J.**, KÁTAI, L., SZABÓ, I. (2024): Compatibility analysis of the soil calcium content by multifrequency ec sensors. *International Journal of Research - GRANTHAALAYAH*, 11(12), 175–187 p. https://doi.org/10.29121/granthaalayah.v11.i12.2023.5437
2. **HORVÁTH, J.**, KÁTAI, L., CZINKOTA, I., SZABÓ, I. (2023): Using multi-frequency electrical conductivity measurement to determine the selective salinity in a two-component salt solution. *Agronomy Research* 21(3), 1228–1142 p. *https://doi.org/10.15159/ar.23.069*
3. **HORVÁTH, J.**, KÁTAI, L., SZABÓ, I. (2023): Analysis of the Soil Selective Potassium Content, using Multifrequency EC Sensors. *Acta Polytechnica Hungarica*, 20(7), 231–248 p. *https://doi.org/10.12700/APH.20.7.2023.7.13*
4. **HORVÁTH, J.**, KORZENSZKY, P., KÁTAI, L., SZABÓ, I. (2022): On the go soil sensor development in AGIT FIEK programme. *Mechanical Engineering Letters: R And D: Research And Development*, 23, 33–48 p.
5. **HORVÁTH, J.**, SCHMITZ, B. (2019): Digitalisation in agriculture – From the perspective of a global agricultural machinery producer. *Hungarian Agricultural Engineering*, 36, 63–68 p. *https://doi.org/10.17676/HAE.2019.36.63*

Peer-reviewed article in Hungarian language

6. **HORVÁTH, J.**, KÁTAI, L. SZABÓ, I. (2021): Menet közbeni talajszenzorok a precíziós mezőgazdaságban. *Mezőgazdasági technika*, 62(10), 2–5 p.
7. SZABÓ, I., **HORVÁTH, J.** (2020): Ikervélemény – Dr. Szabó István és Horváth János. *Agronapló*, 24, 72–74 p.

International Conference Abstract

8. **HORVÁTH, J.**, SZABÓ, I., KÁTAI, L. (2021): Evaluation of multi-frequency electrical conductivity measurements to determine the soil nutrient cation concentration. In 12th International Conference on Biosystems Engineering 2021: Book of abstracts.