

Application Note 20. Increasing accuracy of repeated EIS measurements for detecting weak emissions

Other documents, related to this topic:

- **User Manual:** CYBRES EIS Differential Impedance Spectrometer for electrochemical and electrophysiological analysis of fluids and organic tissues
- **Application Note 18.** Online system for automatic detection of remote interactions based on the CYBRES MU EIS impedance spectrometer, 2017
- S.Kernbach, I.Kuksin, O.Kernbach, **On accurate differential measurements with electrochemical impedance spectroscopy**, WATER 8, 136-155, (arXiv:1607.07292), 2017

This description is valid for the following versions: EIS firmware 1183.x, client program 1.20.x

Abstract. This application note describes the methodology of EIS measurements, related to detection and characterization of weak emissions possessing non-electromagnetic, non-acoustic, non-thermal and non-mechanical nature. The “shape effect” is used as a test source of such emission. The proposed approach with the source of emission (the generator “Contur”) and the detector (CYBRES EIS spectrometer) can be applied for demonstration purposes, where the local or non-local impact is reliably detected by the impedance measurements, for performing replication experiments with a high degree of repeatability and for validation of measurements related to weak emissions of different origin. Very small changes of conductivity on the level of 10^{-9} - 10^{-11} S/cm require an accurate handling of systematic and random inaccuracies during measurements, and strict following the experimental methodology.

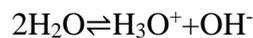
Table of content

1.	Chemistry and physics of EIS measurements: differential approach	1
2.	Which requirements should satisfy the measurement equipment for sensing weak emissions?.....	3
3.	Validation of systematic and random inaccuracy of EIS measurements	3
3.1.	Fluid’s degasification	3
3.2.	Right frequency and temperature parameters	4
3.3.	Impact of external temperature on measurements with thermostabilization of samples.....	5
3.4.	Repeatability of measurements before the exposure	7
3.5.	Saturation of sensors	8
4.	Test measurements with the generator “Contur”	9
5.	Methodology of EIS measurement I: differential impact without thermostabilization.	10
6.	Methodology of EIS measurement II: common impact with thermostabilization.	13
7.	Methodology of EIS measurements III: external exposure	16
8.	How to assess the positive results of measurements	20
9.	Typical problems	21
10.	Disclaimer.....	22
11.	Literature.....	23

1. Chemistry and physics of EIS measurements: differential approach

The electrical conductivity of a solution generally depends on the number of ions and the ionic mobility; the more ions a solution contains, the higher its electrical conductivity. Different parameters of fluids such as the self-ionization constant, hydration, temperature, viscosity, and different processes, related to

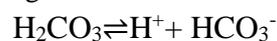
degasification, ion-ion and ion-dipole interactions, electric fields in fluids, polarization of electrodes, electrochemical reactions with dissolved ions, and other phenomena also impact the electrical conductivity. In order to make electrochemical measurements stable and to avoid electrochemical reactions it is recommended to perform experiments with bi-distilled, distilled or demineralized water. The conductivity of pure water depends mainly on two factors: self-ionization and dissolving of atmospheric CO₂ in water. The self-ionization is an ionization reaction in pure water, in which a water molecule, H₂O, deprotonates (loses the nucleus of one of its hydrogen atoms) to become a hydroxide ion, OH⁻. The hydrogen nucleus, H⁺, immediately protonates another water molecule to form hydronium, H₃O⁺



Exposing the pure water to air, the atmospheric CO₂ rapidly dissolves in water to form carbonic acid H₂CO₃



which is unstable and dissociates according to:



Ions H⁺ and HCO₃⁻ are the source of increasing the conductivity upon exposure of water to air. Depending on the actual atmospheric CO₂ concentration, the increase of the water conductivity is about ~0.8-1.5 μS/cm [1,2,3]. Self-ionization and dissolving of CO₂ are nonlinear, depending mostly on temperature and mechanical distortions applied to fluids.

From the physical side, the **conductivity** κ represents the ability of a fluid to conduct electricity and is measured in Siemens per metre (S/m). It is reciprocal of **resistivity** τ that is measured in Ohm-metre (Ω·m) and represents the value of how strongly a material opposes the flow of electric current. **Impedance** $Z(\omega)$ is a complex value (composed from the **resistance** R and the **reactance** X) depending on the **frequency** ω and is measured in Ohm; its magnitude represents the ratio of the voltage amplitude to the current amplitude in the fluidic cell; the phase of impedance is the phase shift by which the current lags the voltage. EIS measurements frequently use the **RMS Impedance** that have the same meaning as the magnitude, but calculated in different way. The reciprocal of impedance denotes **the admittance** Y , measured in Siemens. The **cell constant** C (the SI unit - m⁻¹) defines the ratio of distance between electrodes to the area of the electrodes measured from the determined resistance of a solution of known specific conductance. The resistivity in case of a complex impedance Z is defined by

$$\tau = Z * C^{-1}$$

and correspondingly for the conductivity

$$\kappa = Z * C.$$

The EIS measurements use sometimes the Z value only, it needs to remember, in order to calculate the conductivity these values should be multiplied by the cell constant C for the used electrodes.

The differential EIS measurement is performed in two containers that have equal chemical, temperature, electrical and mechanical conditions. Such a measurement scheme allows compensating nonlinearities; moreover, it allows comparing a long-term electrochemical behaviour of two fluids under equal environmental and fluidic conditions. Since weak emissions, which have non-electromagnetic, non-acoustic, non-thermal and non-mechanical character, change a rate of electrochemical processes (see the explanation in Sec.8), such a direct comparison of impacted and non-impacted samples enables identifying the fact of exposure to these emissions and performing their characterization. Carrying out accurate measurements require understanding the methodology, the sources of inaccuracies and setting up the parameters of EIS spectrometer.

2. Which requirements should satisfy the measurement equipment for sensing weak emissions?

Conductivity of purified water is about $1\text{-}5\mu\text{S}/\text{cm}$, the standard ISO 3696 (1987) defines maximum contaminant levels of purified water in the grade 1 as $0.1\mu\text{S}/\text{cm}$ at $25\text{ }^\circ\text{C}$, which is equivalent to the resistivity of $10\text{ M}\Omega\cdot\text{cm}$ at $25\text{ }^\circ\text{C}$. Assume that in the EIS measurement III (see Sec.7) the weak emission changes resistivity from $0.5\text{ M}\Omega\cdot\text{cm}$ to $0.51\text{ M}\Omega\cdot\text{cm}$ and then to $0.52\text{ M}\Omega\cdot\text{cm}$. This corresponds to changes in conductivity from $2\mu\text{S}/\text{cm}$ to $1.9607\mu\text{S}/\text{cm}$ and $1.9230\mu\text{S}/\text{cm}$ correspondingly. Changes detected in continuous mode measurements (see Sec. 5 & 6) are even smaller – deviations about $\Delta=20\text{-}200\Omega\cdot\text{cm}$ from the trend $0.5\text{ M}\Omega\cdot\text{cm}$ corresponds to conductivity change about $\Delta=800\text{-}80\text{ pS}/\text{cm}$ from the trend $2\mu\text{S}/\text{cm}$. In other words, in order to detect these changes the resolution of measurement equipment should be in the range of nano-/pico-Siemens/cm with very low measurement noise¹.

Secondly, the electrochemical changes under weak emissions occurs very slow, in several cases the rate of changes is about $20\text{-}200\Omega\cdot\text{cm}$ per hour for distilled water (see Sec.5 & 6). The measurement equipment should be capable of long-term measurements under stable conditions. Typically, the conductivity meters perform so-called “compensated” measurements, which are made by assuming a linear increase of conductivity versus temperature. These devices measure the temperature of fluid and calculate a correction. However, the true dependency is nonlinear, moreover it depends on the chemicals dissolved in water. Thus, long-term and/or accurate measurements require stabilizing the temperature and keeping it stable during all long-term measurements.

Finally, due to electrode polarization effect, two-electrode devices measure the conductivity by alternating current that is typically fixed at $1\text{-}3\text{ kHz}$. The measurement calibration (that also includes the cell constant) is performed at this frequency. However, the measurements of effects created by weak emissions require performing measurements at different frequencies. The EIS measurement devices should be capable of setting the frequency, as demonstrated by experiments, between 10 Hz and 100 kHz .

3. Validation of systematic and random inaccuracy of EIS measurements

Systematic and random inaccuracy of EIS measurements occurs due to variation of experimental conditions in both containers, among them the temperature, the rate of CO_2 dissolving, introduction of mechanical/electromagnetic distortions during measurements and chemical contaminations of samples. The systematic inaccuracy depends primarily on the EIS approach, whereas the random inaccuracy depends on the way how a particular experiment is prepared and performed. Thus, it is recommended to perform a series of validation experiments to assess and to decrease the inaccuracy of measurements related to weak emissions.

3.1. Fluid’s degasification

Degasification is the removal of dissolved gases from water or aqueous solutions. When increasing the temperature of fluids (e.g. by inserting containers in thermostat), the gases build a bubble for-



Figure 1. Building of gas bubbles on electrodes.

¹ Most standard conductometers measure in the range $0\text{-}9999\mu\text{S}/\text{cm}$, whereas the resolution in the low-range area is $1\mu\text{S}/\text{cm}$.

mation at solid-liquid interfaces (e.g. electrodes), see Figure 1. These gas bubbles change the area of surface electrodes that contact with water and impact the electrical conductivity measurements. Thus, any time when a fluid container is inserted into thermostat and the thermostat reached the set temperature, the bubbles should be removed from surfaces. The simplest way to do it is to remove electrodes from the container for a short time and then to insert them again. In continuous measurement mode, the removal of gas bubbles can be skipped when only a temporal EIS dynamics is of interest.

3.2. Right frequency and temperature parameters

Proper setting the frequency and temperature is important for stability of long-term EIS measurements. The thermostat temperature should be set in regard to environmental temperature, the general rule: the lower is the temperature, the less is the degasification and the less time is required to warm up the containers. However, at a too low temperature the thermostats are not capable to maintain the required set temperature. Thus, the difference about 4°-5°C should be maintained between environmental and thermostat temperatures.

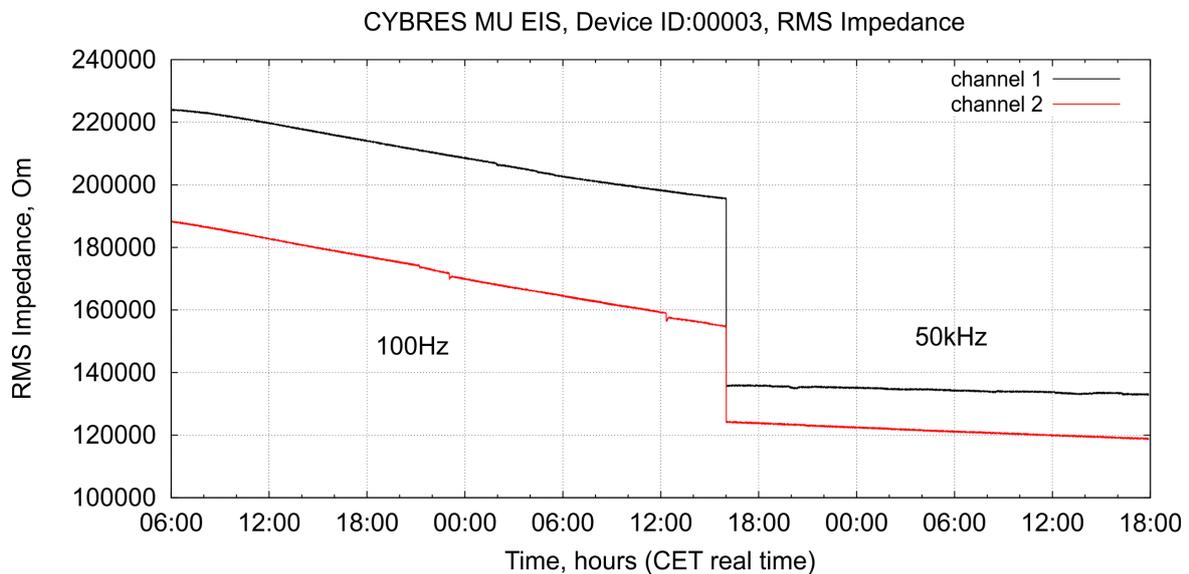


Figure 2. Decreasing of RMS impedance at frequencies of 100Hz and 50kHz during 60 hours of measurement (the continuous mode measurements).

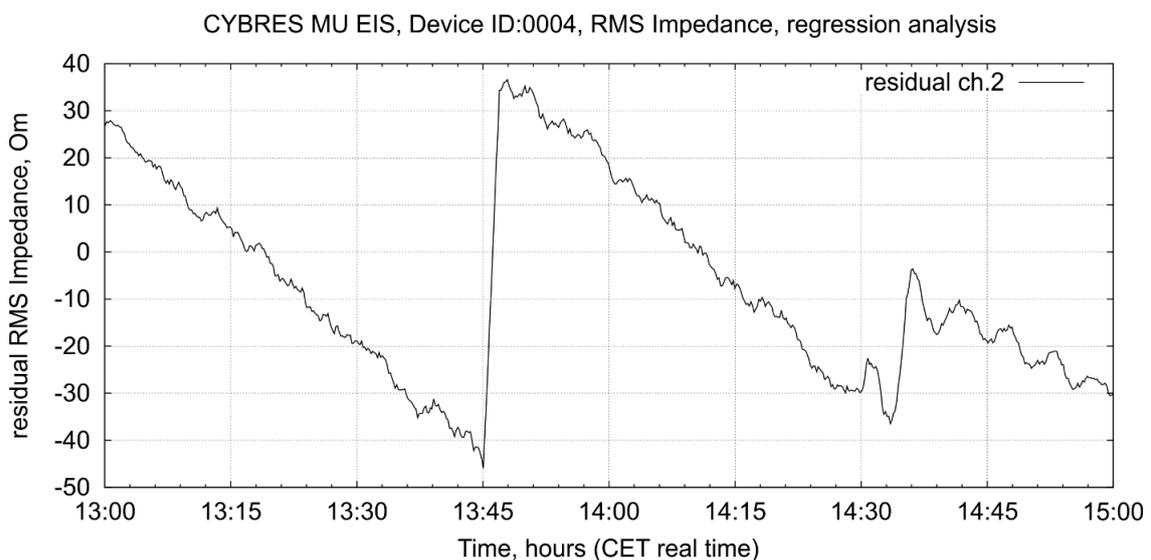


Figure 3. Appearance of spikes in long-term dynamics.

The frequency impacts several EIS processes, among them the degradation of impedance by saturation of water by ions. The long-term behaviour of RMS Impedance at 100Hz and 50 kHz is shown in Figure 2. The higher is the frequency, the lower is the degradation of impedance (and thus the resistivity and conductivity). The level of measurement noise also depends on frequency. The lower is the frequency, the less noise contains the measured signal.

Another issue that occurs only in a long-term measurements is the AC electrolyse, the critical current density varies among others with the frequency: the higher the frequency the higher the critical current density [4,5]. This effect explains the appearance of spikes, shown in Figure 3. To remove spikes, it needs to decrease the applied voltage and/or to increase frequency. It is also recommended to use only a short frequency range in impedance spectroscopy mode for such measurements, e.g. 5kHz-6kHz (min.-max.) with step of 50Hz. Setting of frequency/temperature in the client program is shown in Figure 4.

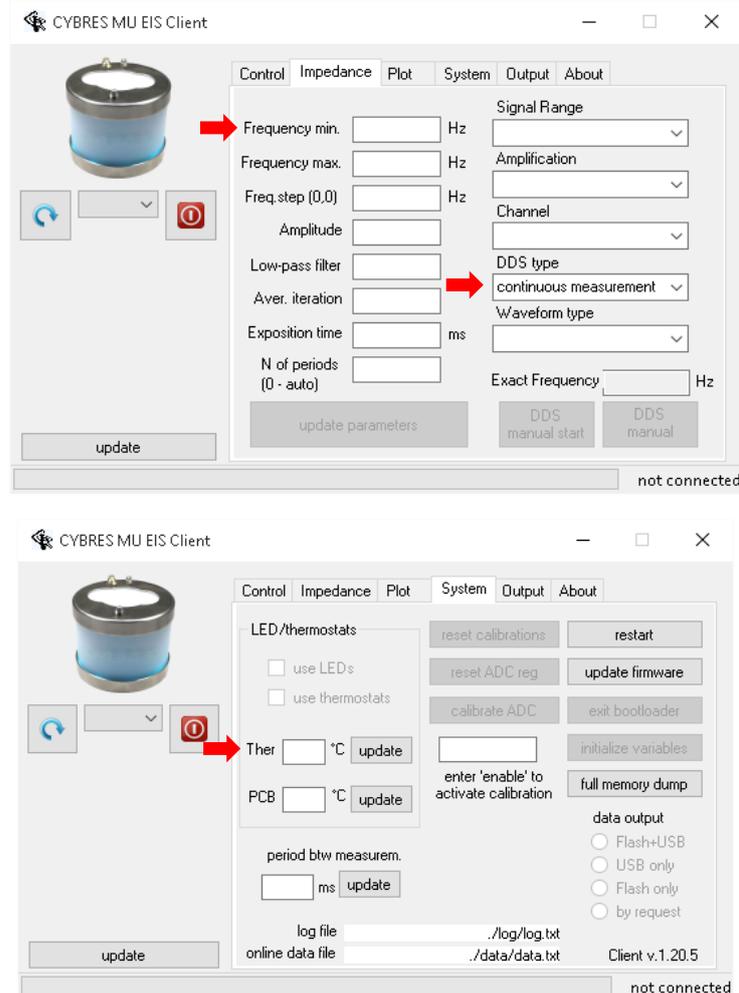


Figure 4. Setting the frequency and thermostat temperature in the client program (in continuous mode measurement).

3.3. Impact of external temperature on measurements with thermostabilization of samples

When the thermostat is on and fluidic samples are inserted in the EIS spectrometer, the EIS measurements do not depend essentially on the external temperature, provided it changes slowly enough so that thermostat can compensate this change. Figure 5 shows experimental data, where the external tempera-

ture was increased on $\sim 0.35^{\circ}\text{C}$ during 70 minutes. Variation of the thermostats temperature was about 0.008°C , the corresponding changes of RMS impedance was about 3-4 Om on both channels.

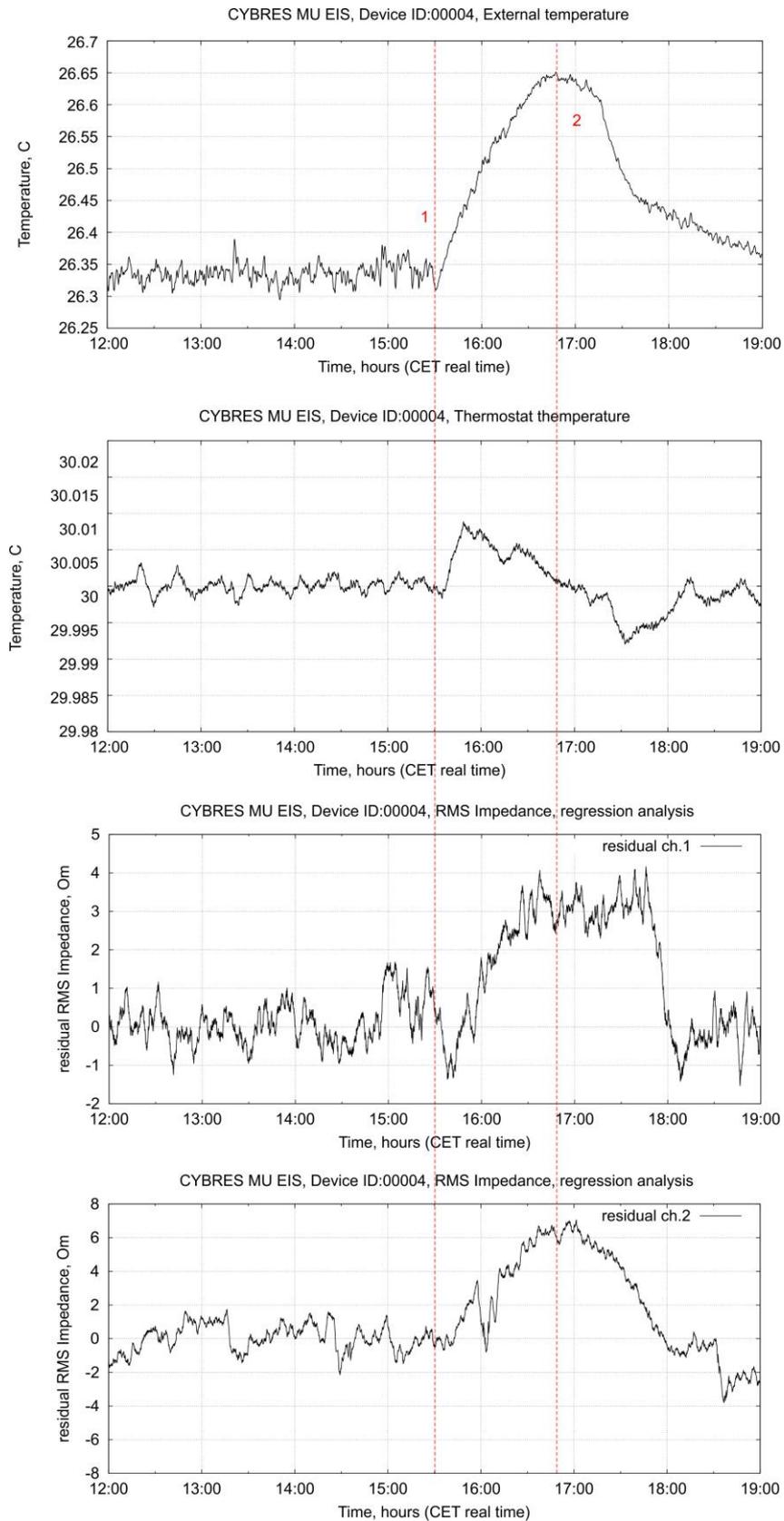


Figure 5. Example of measurements with variation of external temperature.

3.4. Repeatability of measurements before the exposure

The differential measurements rely on the fact that fluids, conditions in both containers are similar and do not change during measurements. Any difference introduced during the measurements will increase the inaccuracy. It is recommended to have the same level of fluid in the containers (full containers with 15ml), make sure that electrodes are positioned in the middle of containers. Mechanical distortions during measurements should be avoided. It is recommended to leave enough time for achieving the set temperature (30-60 minutes) when the thermostat is used. The accuracy of repeatability of measurements before exposure in such conditions is about $\pm 4 \text{ Om}$ per channel in the impedance spectroscopy mode (see Sec. 7 for repeatability after the exposure), provided all measurements are conducted immediately after each other, the gas bubbles are removed and the voltage is set to a minimal level.

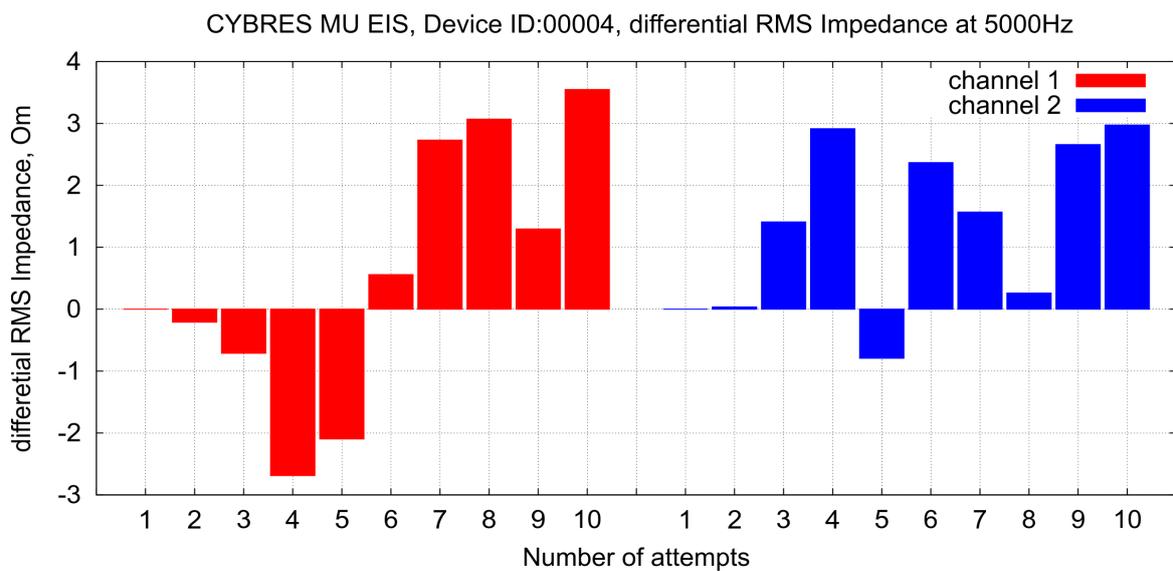


Figure 6. Ten repeated measurements before exposure conducted immediately after each other in impedance spectroscopy mode. The first measurement is subtracted from further measurements.

However, the measurements conducted with time intervals between measurements will differ from each other. The reasons are the ionic processes in fluid related to self-ionization and dissolving of CO_2 , as well as temperature-related degasification. Figure 7 shows an example of such measurements; a degradation of impedance is also well visible in Figure 2.

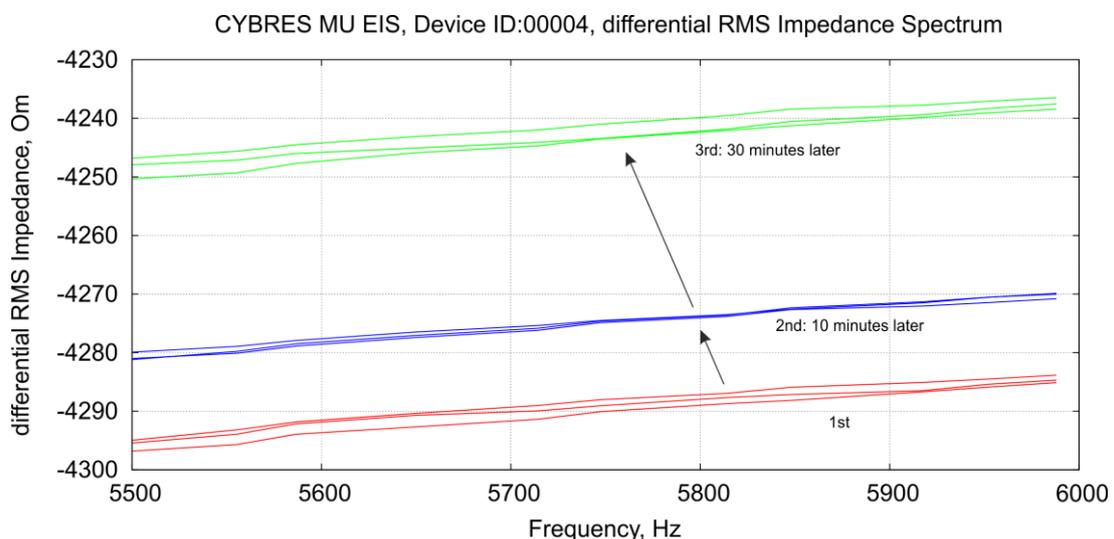


Figure 7. Measurements performed with time intervals 10 and 30 minutes before exposure in the impedance spectroscopy mode.

After some transient time, the rate of degradation becomes stable in separate channels and also in differential channel. This enables performing very accurate measurements in continuous measurement mode when the trend is approximated by a linear regression and residual curves demonstrate a deviation from the trend after the exposure. This approach is utilized in Sec. 5 and 6 as well as in the measurements shown in the Application Note 18. It needs also to note that the EIS is an invasive measurement approach, it impacts the electrochemical properties: the frequency difference is shown in Figure 2, the impact of sampling rate is shown in Figure 8.

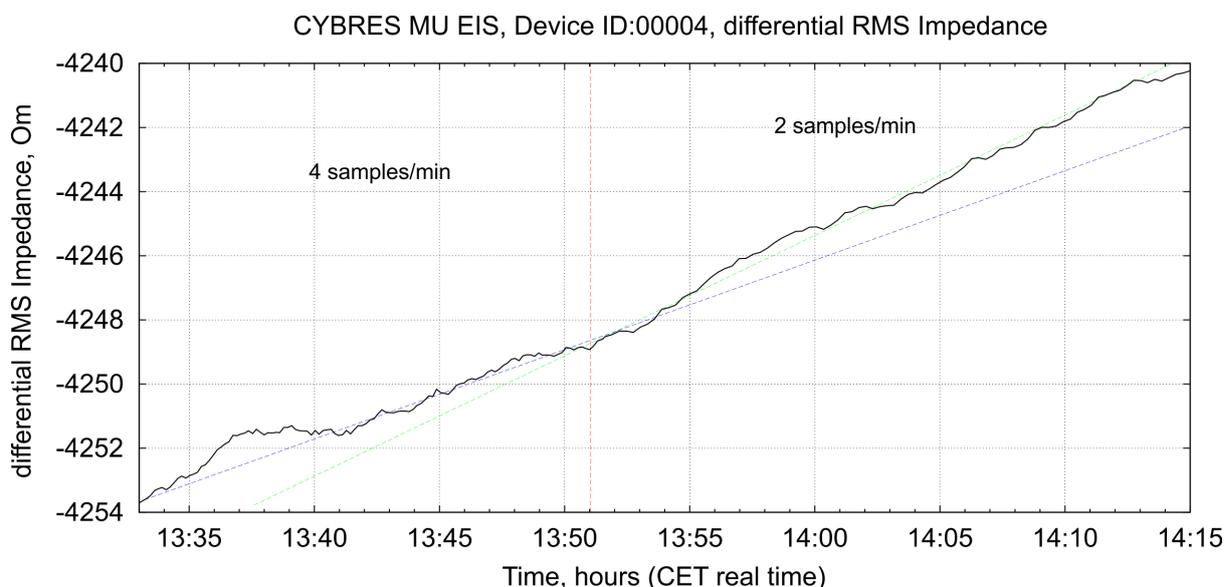


Figure 8. Change of differential RMS impedance before the exposure in continuous measurement mode with two different sampling rates.

Thus, the general recommendation for performing accurate measurements is to decrease the voltage applied to the fluidic cell (up to an acceptable level of noise) and to reduce the time of active measurements (e.g. by performing only one frequency scan). All parameters should be kept unchanged during measurements. The measurements with external exposure of sample, described in Sec. 7, are more tricky, since it needs to estimate the trend of degradation before and after the exposure (see the description of double differential methodology in Sec. 7).

3.5. Saturation of sensors

After performing multiple repeated measurements, almost all types of fluidic and semiconductor sensors can become saturated and decrease the sensitivity to weak emissions. The origin of this phenomenon is not fully understood, it is assumed that a part of emissions is to some extent “accumulated” on the measurement equipment. The saturation is one of reasons why sensors are assumed to have a probabilistic nature and measurements of weak emissions are always performed by several independent sensors in parallel. When the sensor does not react on several exposures during one measurement, water should be removed from containers and the device should be switched off for a while. After this “resting time” the device is ready again for measuring weak emissions. During the “resting time”, another measurement device in different location can be used.

4. Test measurements with the generator “Contur”

For performing test measurements, the source of weak emission is required. In many cases the “shape effect” can satisfy the requirements imposed on such a test source. The generator “Contur” consists of a series of cone-shaped geometric structures. It is a passive device without any sources of electromagnetic emissions, see Figure 9.

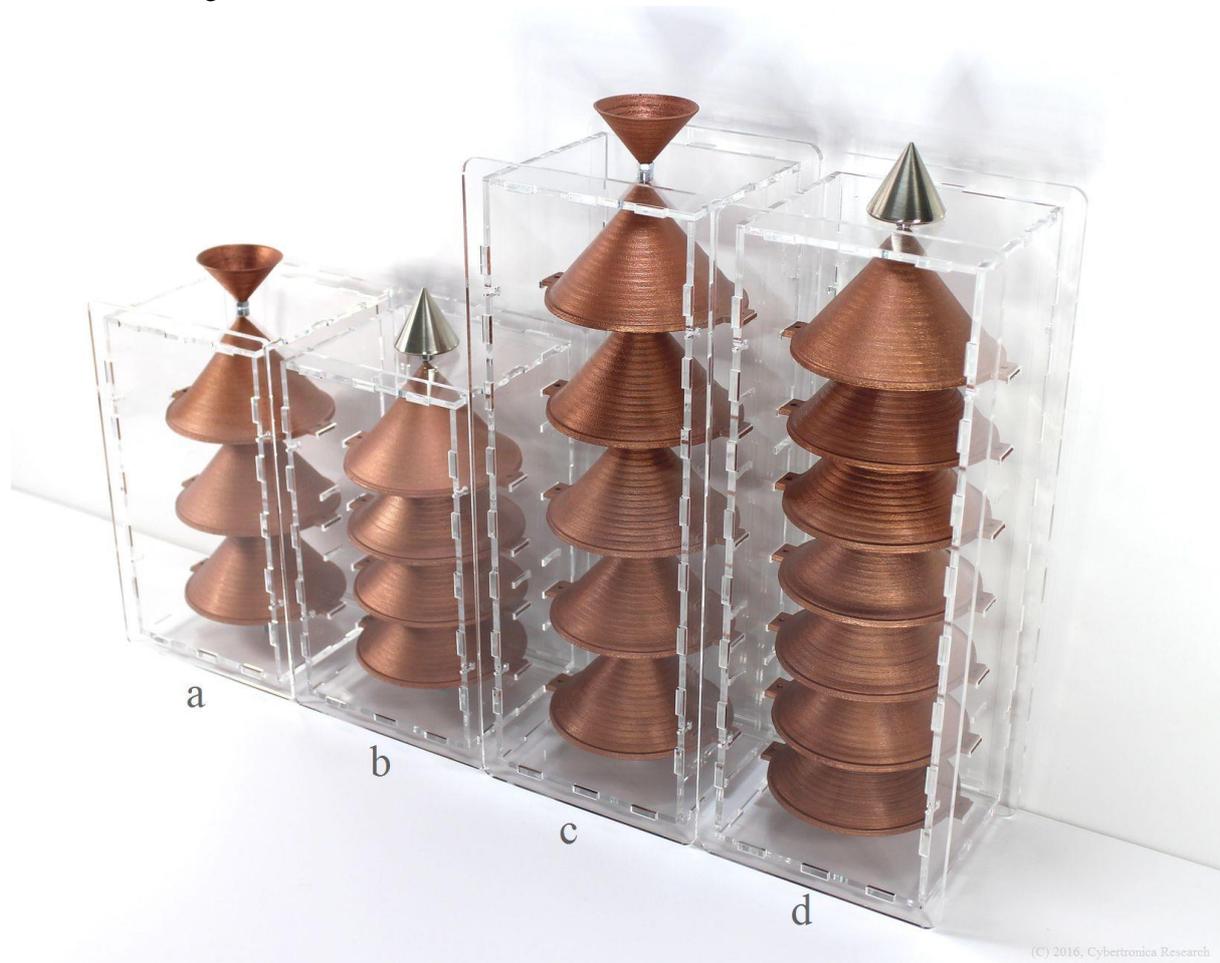


Figure 9. Different versions of the generator “Contur”.

As demonstrated by experiments, the geometric shapes can produce several effects associated phenomenologically with weak emissions. In particular, the fluid exposed by this emission changes the magnitude and phase of impedance (these changes are well visible also in real/imaginary parts, the Nyquist plot and the RMS impedance). Thus, the impact of weak emissions can be demonstrated with a high rate of repeatability, when the control and experimental samples are kept in equal conditions, but the experimental samples will be additionally exposed by the “Contur”. It needs to note, that the “intensity” of weak emission from “Contur” depends on environment (since it is in fact a passive “concentrator-amplifier”). In several cases an additional source of emission is required, see the experiment in Figure 16. Thus, the exposition time should be selected experimentally, usually a minimal time is about 30-60 minutes, and a maximal time can be on the levels of weeks. For exposition it is enough to install the experimental samples in (or above) the top cone. In practical cases the generator “Contur” can be replaced by another source of emission. The measured objects – when it needs to measure whether an object does emit some weak emission and to characterize it -- are used instead the generator in all three typical measurement schemes, described in the next sections.

5. Methodology of EIS measurement I: differential impact without thermostabilization.

This measurement scheme uses the impact that is produced only on one channel during measurements. The experimental setup is shown in Figure 10. The EIS spectrometer is placed on the platform so that both containers are possibly far away from each other. One container is placed on such a way that the “Contur” can be installed under the container and also removed without mechanical distortion of fluids. Make sure that the experimental container and the generator are separated by a metal (we used a multi-layer aluminium foil as shown in Figure 11), this allows avoiding possible electrostatic phenomena, produced by metallic parts (e.g. the top conus) of the generator.

1. **Preparation.** Use bi-distilled, distilled or demineralized water. Make sure that both containers are clean; wash the containers with distilled water before experiments. Leave the water in the same room to equalize the temperature. The room with EIS spectrometer should be closed, without sunlight, any active EM emitters.
2. Set the frequency in continuous measurement mode. **Start the measurements.** Wait until the RMS impedance data become more or less linear for 30-60 minutes (usually it happens after 2-5 hours after begin of measurements). Do not start the step 3 when EIS curves have large nonlinearities.
3. **Experimental impact.** Insert the generator “Contur” under the experimental container for 30-60 minutes. Make sure that an experimenter enters the room only for a short time and no mechanical distortion is produced.



Figure 10. Experimental setup for differential exposure by “Contur”

Results of several such measurements are shown in Figure 12 and Figure 13. It is well visible that the experimental channel changes the trend, whereas the control channel still follows the previous trend. Attention should be paid to avoid the temperature impact on fluids during measurements (e.g. the “Contur” should have the same room temperature).

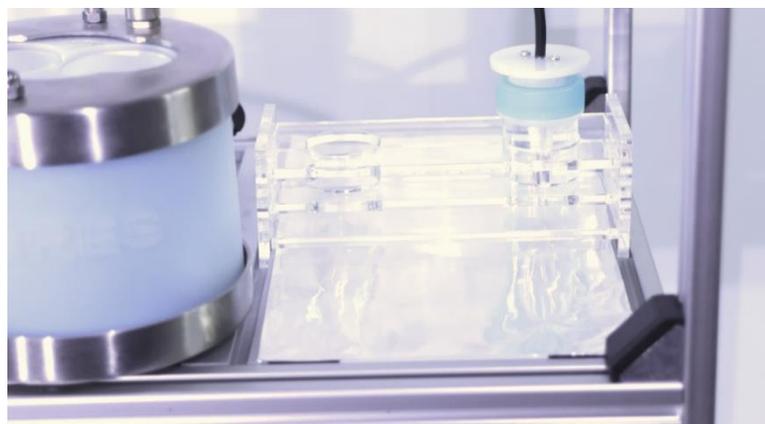


Figure 11. Aluminium foil below the experimental container.

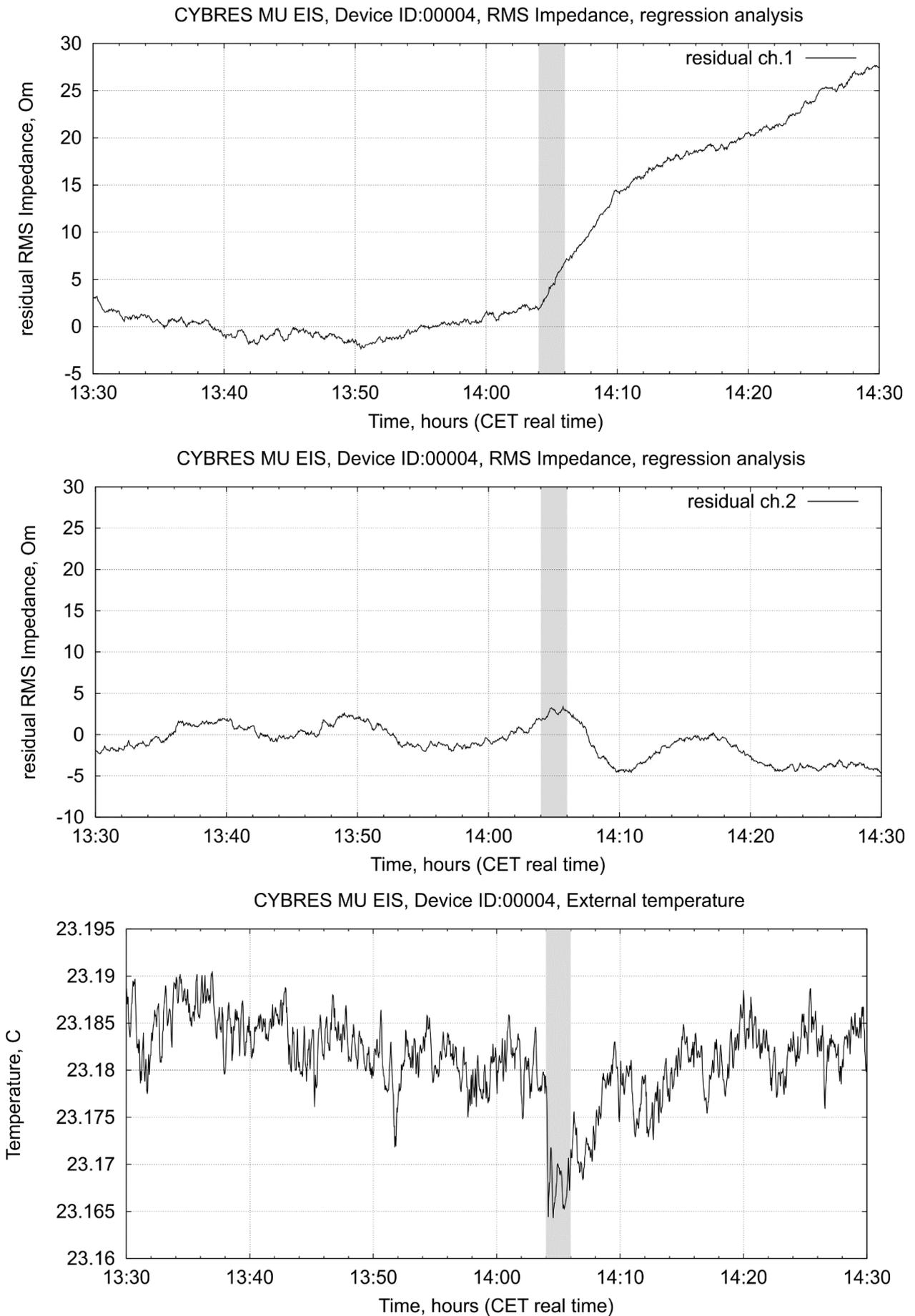


Figure 12. Example of data with differential impact on channels (continuous measurement mode at 5kHz).

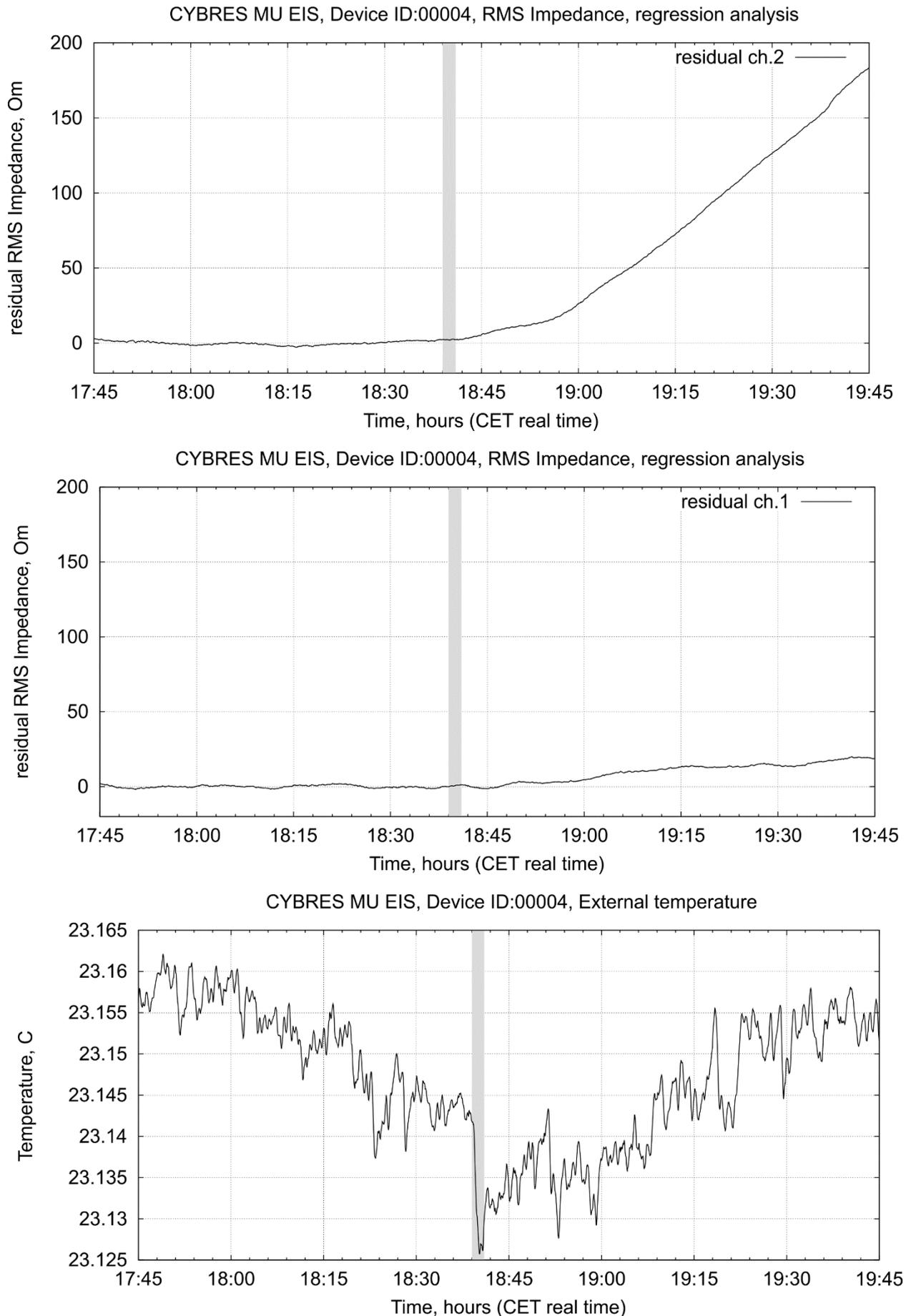


Figure 13. Example of data with differential impact on channels (continuous measurement mode at 5kHz).

6. Methodology of EIS measurement II: common impact with thermostabilization.

This measurement scheme uses the impact that is produced on two channels during measurements. This approach is useful for measuring local and non-local impacts. For non-local case, please follow the Application Note 18 “Online system for automatic detection of remote interactions based on the CYBRES MU EIS impedance spectrometer”. In the local case the EIS spectrometer is placed on the platform, both containers with fluid are inside the thermostat. The experimental setup is shown in Figure 14. The top conus of the generator “Contur” should be focused on the middle of the EIS spectrometer (the high of the platform should allow installing and removing the generator without mechanical distortion of the fluids). In this case the impact is produced on the both fluids and also on the electronic components.

1. **Preparation.** Use bi-distilled, distilled or demineralized water. Make sure that both containers are clean; wash the containers with distilled water before experiments. Leave the water in the same room to equalize the temperature. The room with EIS spectrometer should be closed and without human personal, without sunlight, any active EM emitters.
2. **Warming up.** Insert electrodes and install containers into the EIS spectrometer for 30 min.
3. **Remove gas bubbles** by taking out electrodes from containers for a short time and putting them again. Wait until the temperature is stabilized again. This step can also be removed when no repeated measurements are planned.
4. Set the frequency in *continuous measurement mode*. **Start the measurements.** Wait until the RMS impedance data become more or less linear for 30-60 minutes (usually it happens after 2-5 hours after begin of measurements). Do not start the step 3 when EIS curves have large nonlinearities.
5. **Experimental impact.** Insert the generator “Contur” under the experimental container for 30-60 minutes. Make sure that no mechanical distortions are produced.

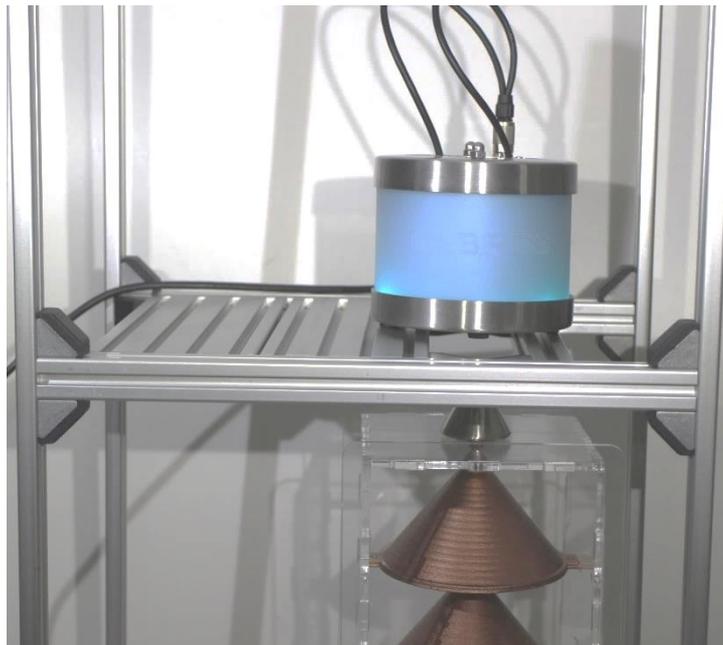


Figure 14. Setup with common impact on both channels.

Results of several such measurements are shown in Figure 15 and Figure 16. In this case the change of trend is observed on both channels. Since the samples are thermostabilized, this measurement scheme is more stable to environmental variations of temperature, for instance a human personal can be present during the measurement. Due to usage of porous materials in the EIS spectrometer, the response is slower (i.e. it appears after some time) and it is weaker compared with the case of open containers. As already mentioned, an additional source of emission is sometimes required (in the experiment in Figure 16 a human experimenter entered the laboratory, the setup was in a closed box, the distance btw. the device and operator about 1.5-2 meters).

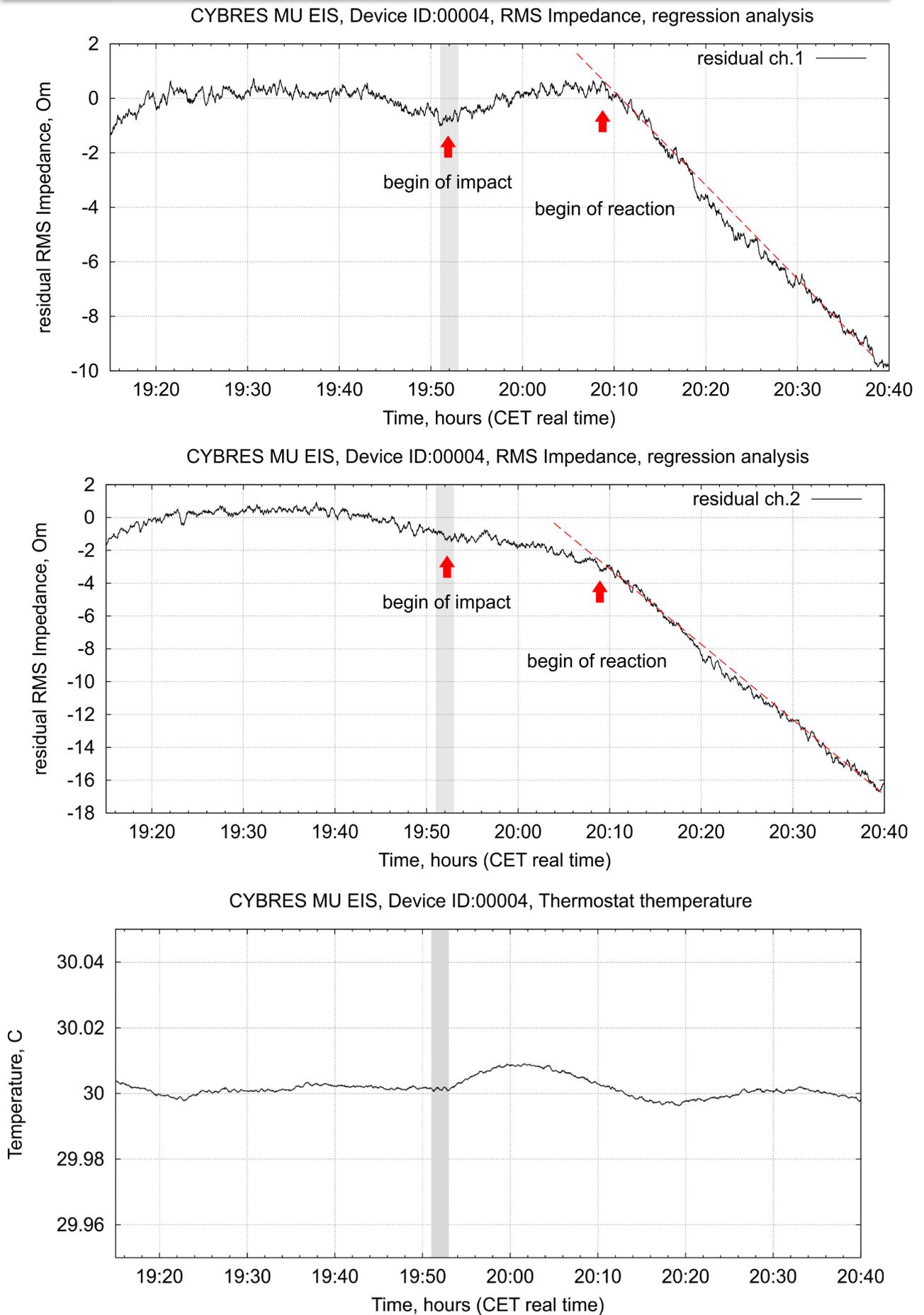


Figure 15. Example of data with common impact on channels (the continuous measurement mode at 5kHz).

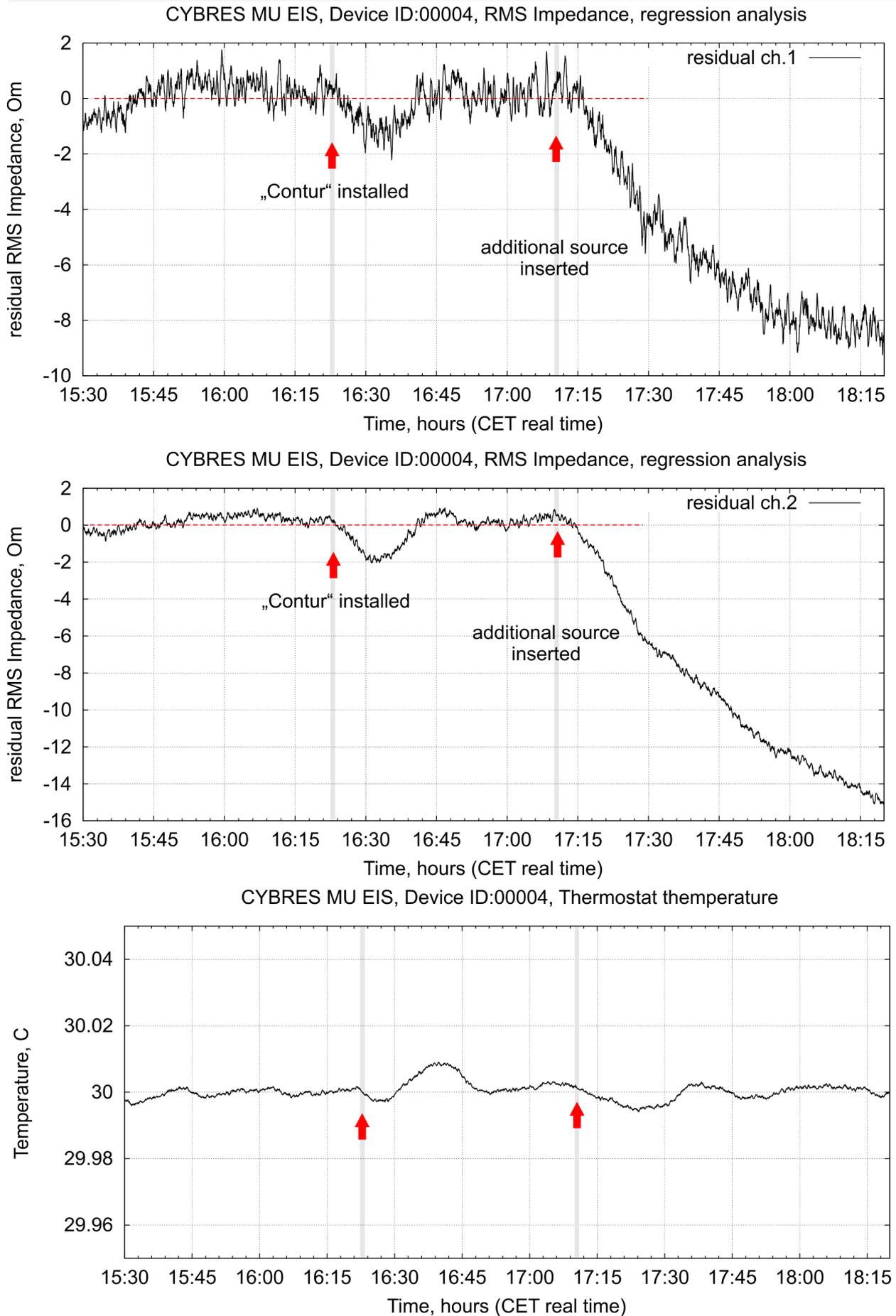


Figure 16. Example of data with common impact on channels (the continuous measurement mode at 5kHz).

7. Methodology of EIS measurements III: external exposure

This measurement scheme assumes two independent measurements: before the exposure and after the exposure. The impact on experimental samples can be produced everywhere by any source of emission. This approach has advantages when the source of emission is large or not movable, e.g. for measuring the geological situation in a specific location. However, it has also a larger random inaccuracy produced primarily by different rate of CO₂ absorption caused by different mechanical distortions of control and experimental samples. Thus, the main principle of this measurement scheme is a careful handling of control and experimental samples, the containers should be always closed and stored in the same vertical positions, as e.g. shown in Figure 17. In order to avoid repeated removal and insertion of samples in the thermostat, it is recommended to use two pairs of samples of the same fluid: the first pair for the measurement “before exposure”, and the second pair for the measurement “after exposure” (exposed is only one “experimental sample” from the second pair), see Figure 22.

The analysis is also more complex compared to the previous schemes. It is based on the following observation. As mentioned in Sec. 3.4 (see e.g. Figure 7) EIS measurements degrade over time. However, the rate of changes in both samples remains comparable as long as these samples (always pairwise) were treated in comparable way. Figure 18 shows two independent measurements with two pairs of samples: the first pair was measured, after this, the second pair was measured. It is well visible that absolute values are different, however the rate of differential changes remain comparable (within 40-50 Om per hours).



Figure 17. External exposure of experimental sample by the generator "Contur"

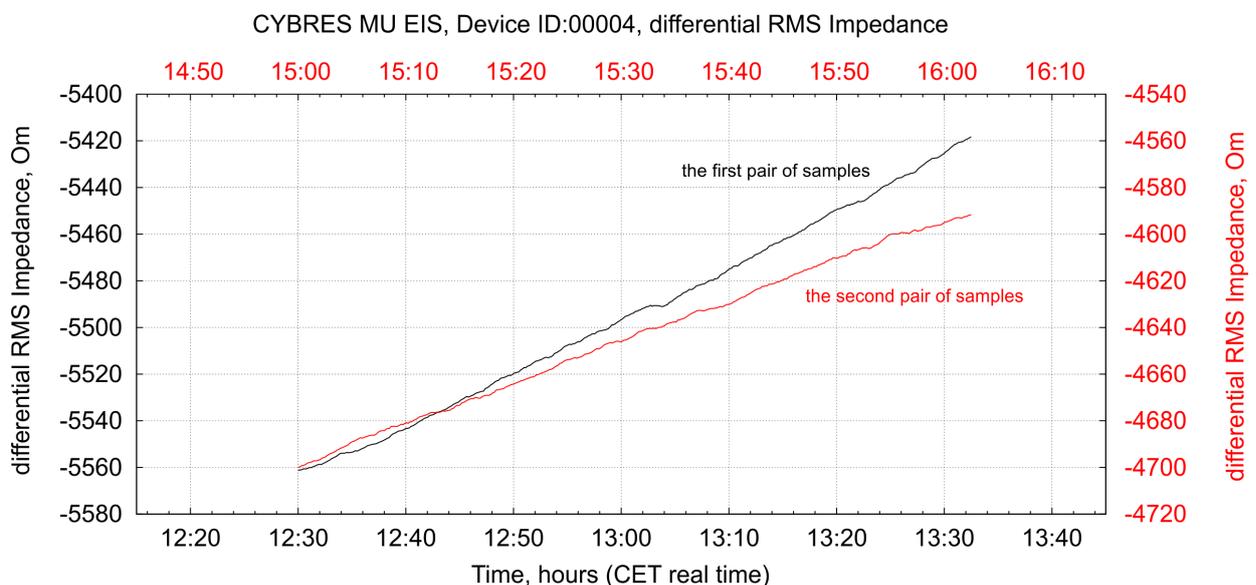


Figure 18. Two differential measurements of 60 minutes from two different pair of water samples.

For comparison, Figure 19 shows the differential measurement of a pair of samples, where one sample was exposed by the “Contur” during 20 hours. We observe that the experimental channel changed not only the RMS impedance values, but also the gradient of changes. This is well visible in the differential curve in relation to non-impacted samples from Figure 18.

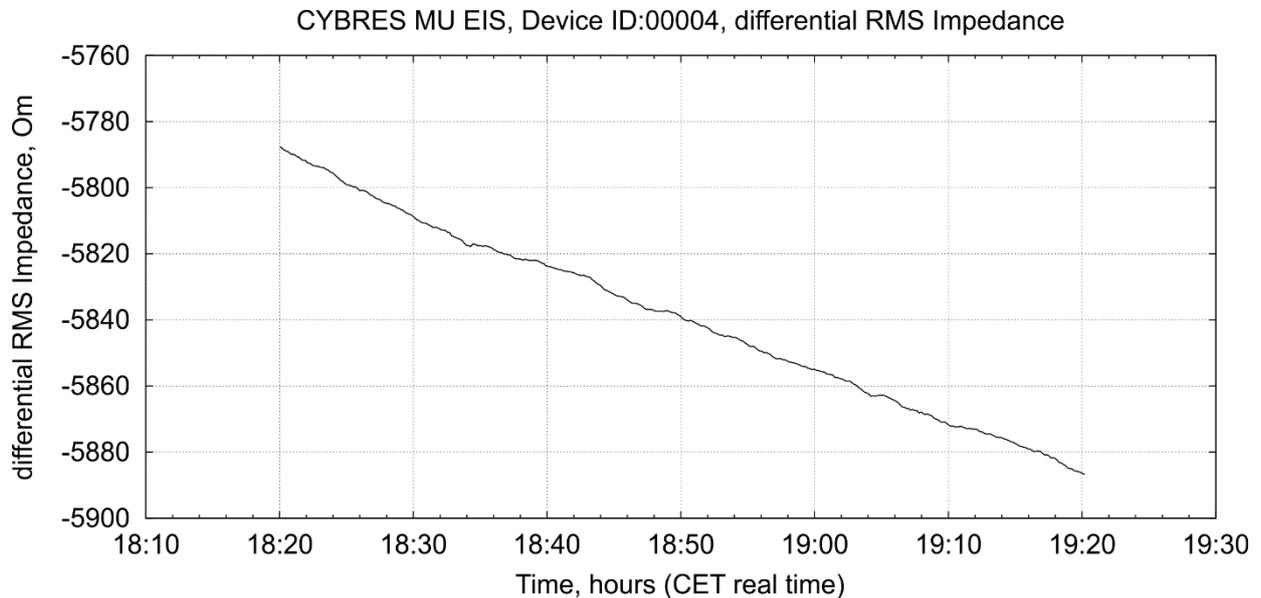


Figure 19. Differential measurement of 60 minutes of two samples, one of them was exposed by “Contur” during 20 hours.

The most measurements indicate that the rate of changes in experimental fluid after the impact is larger, see Figure 21. However, this behaviour is assumed to be characteristic for one specific type of weak emissions, in some cases the rate of changes can be slowed down. Thus, the reliable indicator of impact is the difference (over the noise level) between the control pair of samples and the experimental pair of samples. The dynamics of changes is convenient to represent as a bar diagram, where the first measurements are set to zero, see Figure 20.

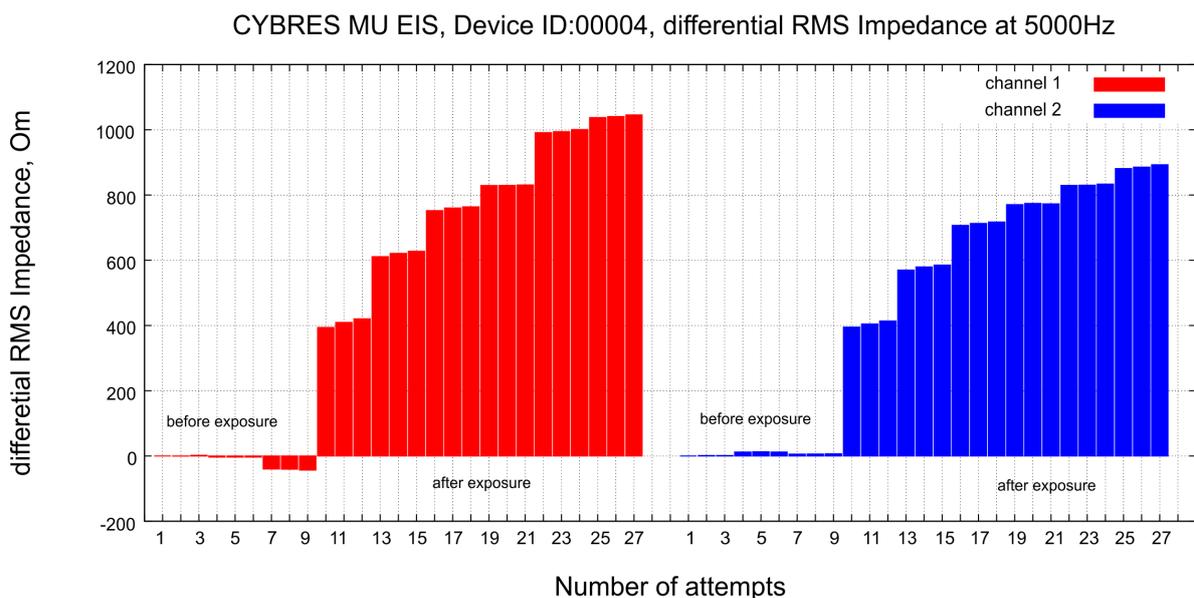


Figure 20. Bar diagram of 9 measurements with the interval of 10 minutes (each measurement is repeated 3 times).

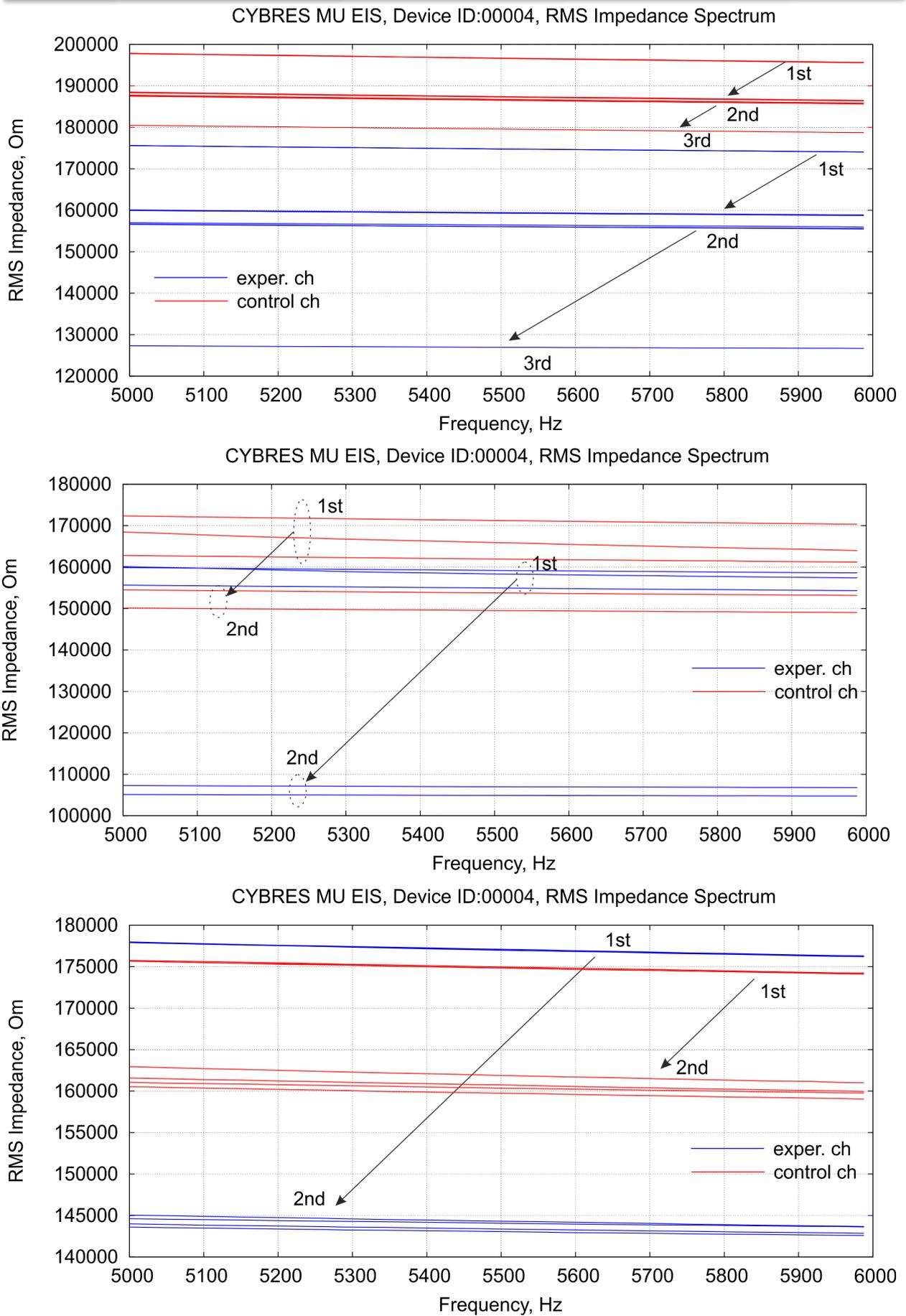


Figure 21. Result of three experiments with external exposure of samples. Different rate of change in experimental fluid is observed.

In fact the representation from Figure 20 can be improved in a number of ways: 1) it does not need to show the zero measurements, 2) repetitive measurements at one time (usually three such measurements are performed immediately after each other) do not make any essential sense, and, finally 3) it is enough to make only two measurements from each pairs at e.g. 0 and 60 minutes. Thus, the methodology – it represents a kind of double differential measurement methodology – is shown in Figure 22 and produces a bar diagram shown in Figure 23 (as a final result).

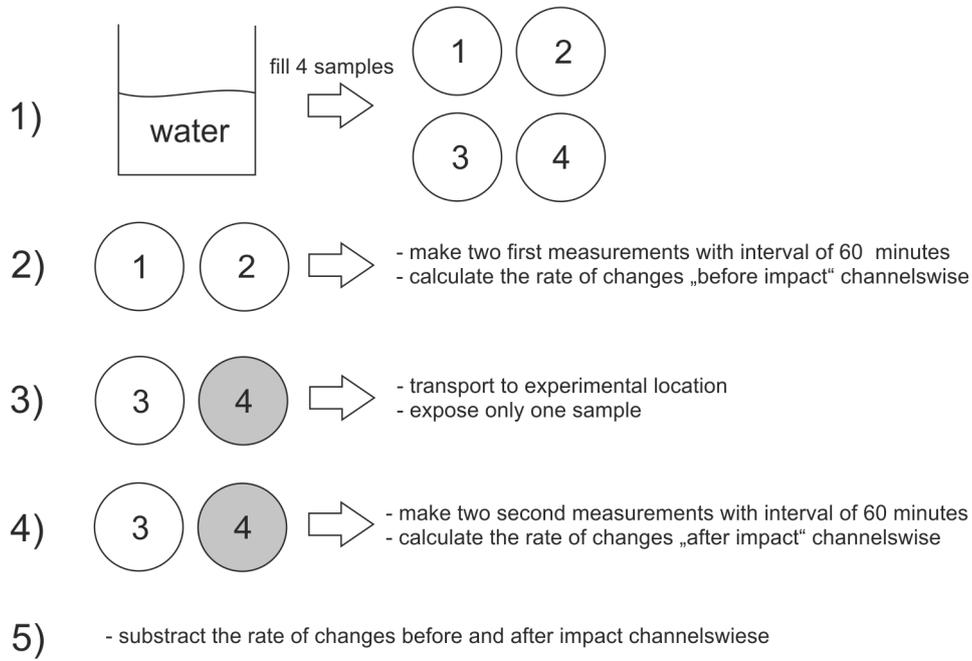


Figure 22. The double differential methodology of EIS measurements III with external exposure of samples.

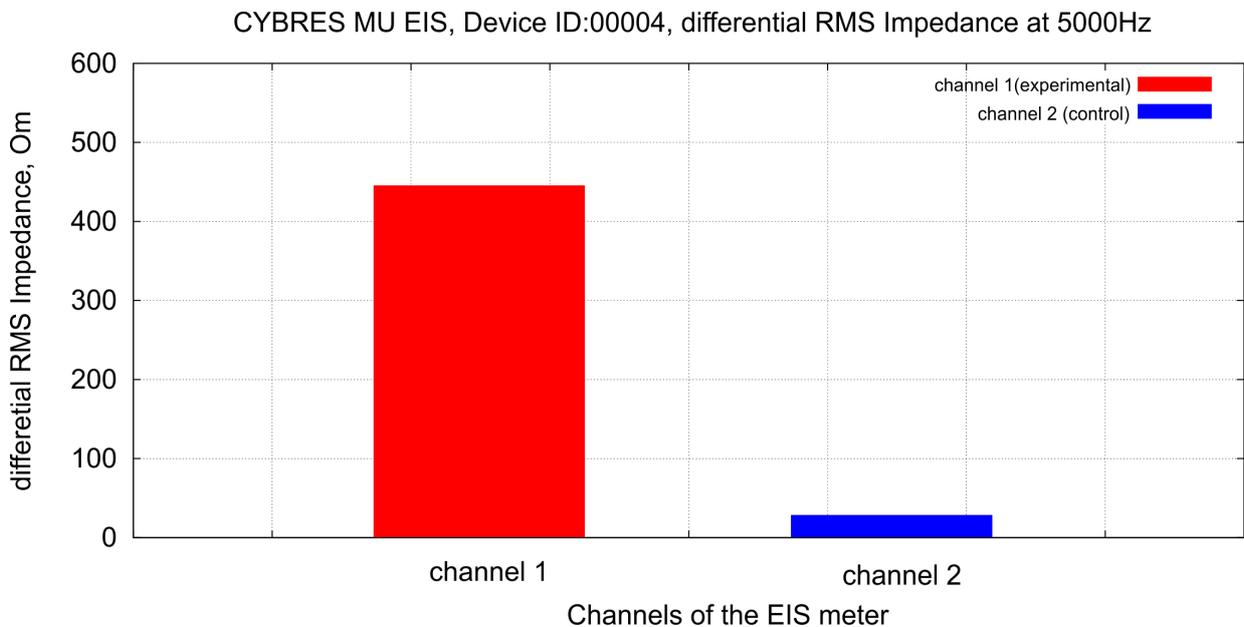


Figure 23. The bar diagram of the experimental (exposed by “Contur”) and control channels, see Figure 22 for explanation of double differential measurement methodology.

The following steps summarize this methodology:

1. **Preparation.** Use bi-distilled, distilled or demineralized water. Make sure that all four containers are clean; wash the containers with distilled water before experiments. Set up the thermostat temperature on 4°-5°C higher than the environmental temperature.
2. **Warming up.** Insert electrodes and install containers 1 and 2 into the EIS spectrometer for 30-60 min.
3. **Remove gas bubbles** by taking out electrodes from containers for a short time and putting them again. Wait until the temperature is stabilized again.
4. Set the frequency. It is recommended to use only one frequency for these measurements, in this case set the minimal frequency on e.g. 5000 and the maximal frequency on 5001 with step 10, this will produce only one sweep at 5kHz. **Run the first measurement in the spectroscopy mode** and repeat it after 60 minutes.
5. **Experimental impact.** Remove containers 1 and 2 from the EIS spectrometer. Transport containers 3 and 4 into experimental location (containers should undergo similar mechanical distortions). Leave one (control) container on the holder, set up another (experimental) container into the upper cone of the generator “Contur” (or into another source of emission). Make a long exposure time.
6. Repeat the steps 2 and 3 for the containers 3 and 4.
7. **Run the second measurement in the spectroscopy mode** and repeat it after 60 minutes.
8. Use bar diagram option to process and to plot the result (see Figure 23).

Note, this approach demonstrates suitable results only when all samples pairwise are treated more or less equally from mechanical point of view and the impact created by weak emissions is large enough (e.g. by a longer exposure time). For sensing weaker impacts the methodology of EIS measurements I or II should be used.

8. How to assess the positive results of measurements

The weak emission impacts a dynamics of chemical and physical processes in experimental fluids, which becomes visible as changes of pH, conductivity, electrochemical stability or other parameters. It is important to note, that the weak emission impacts primarily a temporal dynamics of processes, and changes of measured parameters are only the secondary indicators. The origin of these “weak emissions” is currently unknown, it seems that many natural and artificial sources of “weak emissions” exist in environment and in laboratory. Thus, it is important to use the place for performing experiments that indicates minimal perturbations of dynamics during the background measurement. Before introducing an experimental impact by the selected source of emission, the background dynamics should be recorded with a minimal number of nonlinearities, otherwise the impact will be not recognizable. In most cases in the continuous measurement mode, the impact is demonstrated as a change of trend. The maximal amplitude of deviation from the trend and the delay between start of exposure and start of response indicate the intensity of impact. The general rule for impact recognition in EIS methodology I & II is that changes after exposure should be 2x-3x larger than the variations during background recording. The EIS methodology III has a larger variation of EIS background recording, it needs to take into account the difference between experimental and control channels that should be also 2x-3x larger than the variation of 40-50 Om per hour (in order to obtain the resistivity/conductivity values, the impedance should be multiplied/divided on the Cell constant for given electrodes).

It needs to remember that weak emissions impact not only the fluids, but also electronic components, especially semiconductor sensors. Figure 24 shows the dynamics of external temperature from the

experiment in Figure 16, recorded by a semiconductor sensor. It is well visible that a noise during the exposure was larger than before and after the exposure. Thus, observing dynamics of additional sensors helps in identifying the impact.

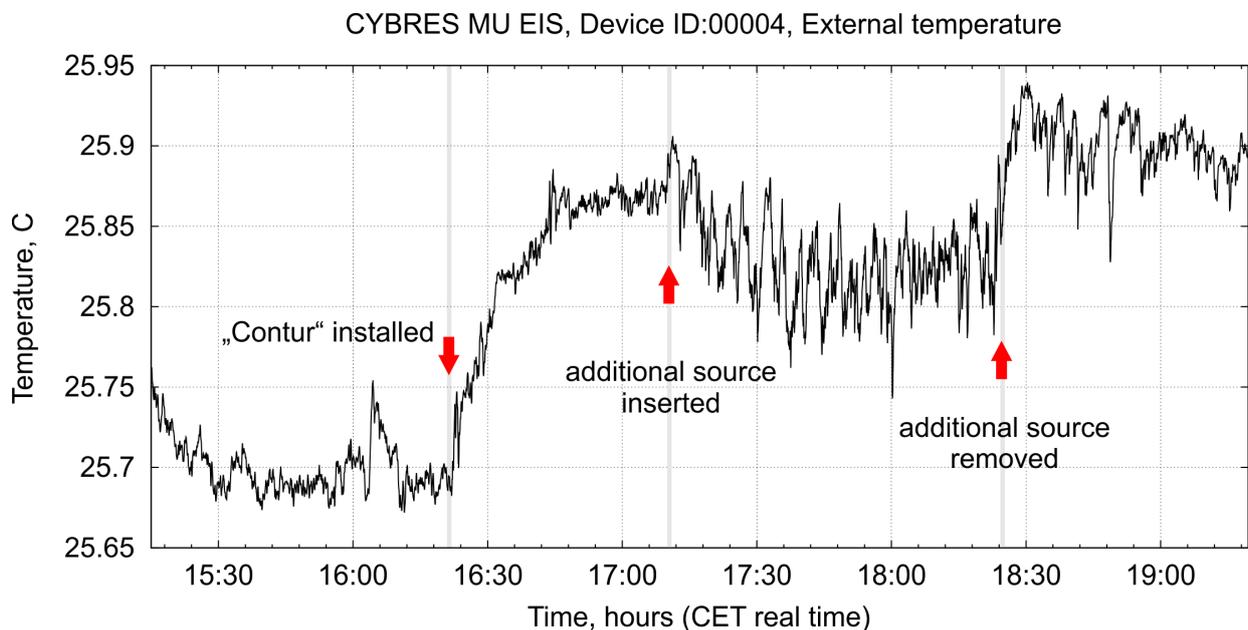


Figure 24. Dynamic of external temperature from the experiment in Figure 16, recorded by a semiconductor sensor.

Important: the EIS measurements allow only detecting and characterizing the fact of exposure by weak emissions. This approach is useful in cases when the presence of emission should be detected or confirmed and correspondingly some conclusions about possible effects can be drawn. However, this method is not suitable for detecting any biological effects (e.g. stimulation or inhibition) or specific “information phenomena” (e.g. imprinting effects).

9. Typical problems

It needs to be remembered that effects of weak emissions appear on the level of 10^{-9} - 10^{-11} S/cm with relatively slow dynamics. Moreover, the nature of this emission is not fully understood at the moment, thus a large number of unexpected effects can appear. Based on the performed experiments, two major issues are identified: too low level of weak emission (under the sensitivity threshold of sensors) and additional distortions that increase the noise level of EIS measurements.

1. **Mechanical distortions.** Make sure that containers are not exposed to unnecessary mechanical distortions, vibrations or shaking during measurement, warming or exposing/holding phases.
2. **Electromagnetic distortions.** Make sure that control and experimental samples are contained in equal electromagnetic conditions, these include light, high frequency emission from mobile phones/WiFi routers or from other sources of emission.
3. **Thermal distortions.** Make sure, that both containers are equally warmed up and cooled down. Avoid warming up only one container, e.g. by keeping it in the hand for a long time or inserting an object (e.g. the generator “Contur”) with a different temperature in experiments without thermal stabilization.

4. **Amplification of the weak emission level.** Many passive source of emission (e.g. different stickers, modulators and similar, see Figure 25) needs an active emitter and/or using the shape effect to “concentrate” the emission as well as long exposition times. Generally, the EIS methodology I is the most suitable (as the most accurate approach) for such measurements.



Figure 25. Example of EIS measurements (with the methodology I) that require long exposure times and/or presence of active source of emission.

5. **Preparation and storage of water samples.** The original water for all samples and the control samples should be stored in places away from source of weak emissions. In many cases the reason for failed attempts was not proper storage of control samples (which become more “activated” than the experimental ones). It is a good strategy to store control samples close to the measurement equipment, whereas the experimental sample will be exposed away from the equipment.
6. Make sure that all measurements for a single experiment are performed with the same setting of the EIS spectrometer, with the same handling/preparation of water samples, moreover a short time for one experiment allows avoiding undesired effects (related e.g. to impact of different environmental emissions).

As a result of not keeping the conditions, the experimental impact can be not recognizable from distortions. When it happened, it is recommended to improve the methodology and to repeat measurements as described in the previous sections.

10. Disclaimer

These measurements mean open-science approach of experimental nature. Its experimental character in relation to methodology, equipment or accuracy should be always considered. Remember, a single measurement has a probabilistic nature. Before drawing any conclusions, a statistically significant number of attempts (>30) should be undertaken. CYBRES reserves the right to make any changes of any product without further notice. Product information is current as of publication date. Production processing does not necessarily include testing of all parameters. CYBRES assumes no liability for applications assistance, Buyers are responsible for their applications using CYBRES products. To minimize the risks associated with Buyers' applications, Buyers should provide adequate operating safeguards. CYBRES does not assume any liability arising out of the application or use of any product, and specifi-

cally disclaims any and all liability, including without limitation special, consequential or incidental damages. 'Typical' parameters described in specifications can and do vary in different applications and actual performance may vary over time. All operating parameters must be validated for each customer application by customer's technical experts. CYBRES products are not designed, intended, or authorized for use in applications intended to support or sustain life, or for any other application in which the failure of the product could create a situation where personal injury or death may occur.

11. Literature

- [1] Truman S. Light, Elizabeth A. Kingman, and Anthony C. Bevilacqua, The conductivity of low concentrations of CO₂ dissolved in ultrapure water from 0-100°C, 209th American Chemical Society National Meeting, Anaheim, CA, April 2-6, 1995
- [2] Börner, Jana H. and Herdegen, Volker and Repke, Jens-Uwe and Spitzer, Klaus, The impact of CO₂ on the electrical properties of water bearing porous media – laboratory experiments with respect to carbon capture and storage, *Geophysical Prospecting*, 61, 446–460, 2013
- [3] Wang, Hongbo, Zeuschner, Janek, Eremets, Mikhail, Troyan, Ivan, Willams, Jonathan, Stable solid and aqueous H₂CO₃ from CO₂ and H₂O at high pressure and high temperature, *Scientific Reports*, 6:19902, DOI: 10.1038/srep19902, 2016
- [4] J. W. Shipley, The alternating current electrolysis of water, *Canadian Journal of Research*, 1929, Vol. 1, No. 4 : pp. 305-358, 10.1139/cjr29-020, 2011
- [5] Parantap Nandi, Effect of alternating current on electrolytic solutions, *IOSR Journal of Engineering*, 3(8), 51-59, 2013