

# Reliable detection of weak emissions by the EIS approach

S.Kernbach\*, O.Kernbach\*

**Abstract**—This work<sup>1</sup> describes the methodology of EIS<sup>2</sup> 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 (EIS spectrometer) can be applied for demonstration purposes, where the local or non-local impact is reliably detected by changes of impedance. Statistically significant number of measurements demonstrated 93,3% repeatability of results. This allows performing replication, laboratory and industrial measurements related to weak emissions of different origin by well accepted approach. 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.

## I. 1. CHEMISTRY AND PHYSICS OF EIS MEASUREMENTS: DIFFERENTIAL APPROACH

Measurements of electrochemical parameters of water, starting from pioneer works of V.A.Sokolova [2] in the early 80s, A.V.Bobrov [3] and S.V.Zenin [4], as well as numerous works [5], [6], [7], [8], [9], [10], [11] indicate the differential impedance measurement as a recognized technique for detecting and measuring the effects of 'weak emissions'. This research has already reached the stage of mature technology and related devices are on the market. This work has an experimental and methodological nature with the goal to show the EIS schemes and methodologies of measurement (for e.g. passive objects, active generators, geobiological measurements), which have a high (>90%) repeatability.

The EIS measures the frequency response of electrical conductivity of an aqueous solution that 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, polarization of electrodes, electrochemical reactions with dissolved ions also impact the electrical conductivity [12]. In order to make electrochemical measurements stable, it is recommended to perform

\*Cybertronica Research, Research Center of Advanced Robotics and Environmental Science, Melunerstr. 40, 70569 Stuttgart, {serge.kernbach, olga.kernbach}@cybertronica.co

<sup>1</sup>This work represents the extended version of [1].

<sup>2</sup>Electrochemical Impedance Spectroscopy

experiments with distilled water. The conductivity of pure water depends mainly on two factors: self-ionization and dissolving of atmospheric  $CO_2$  in water. The self-ionization is an ionization reaction, in which a molecule  $H_2O$  loses the nucleus of one of its hydrogen atoms to become a hydroxide ion  $OH^-$ . The hydrogen nucleus  $H^+$  protonates another water molecule to form the hydronium  $H_3O^+$ :



Exposing the pure water to air, the atmospheric  $CO_2$  rapidly dissolves in water to form carbonic acid  $H_2CO_3$ :



which is unstable and dissociates according to:



$H^+$  and  $HCO_3^-$  are the source of increasing the conductivity upon exposure of water to air [13]. Depending on the actual atmospheric  $CO_2$  concentration, the increase of the water conductivity is about 0.8-1.5  $\mu$  S/cm [14], [15]. Self-ionization and dissolving of  $CO_2$  are nonlinear, depending mostly on temperature and mechanical distortions applied to fluids. The explanation for self-ionization was proposed in [16] – random thermal fluctuations in molecular motions occasionally produce an electric field that is strong enough to break an oxygen-hydrogen bond, resulting in appearance of  $OH^-$  and  $H_3O^+$ . Changing the rate of self-ionization by probabilistic mechanisms in Boltzmann distribution represents one of possible explanations for changes of conductivity (and pH) under weak emissions. In this scenario, interactions on microscopic level related to weak emissions are averaged in multi-body molecular systems and measured as changes of macroscopic parameters.

On the physical side, the conductivity  $\kappa$  represents the ability of a fluid to conduct electricity and is measured in Siemens per metre (S/m). It is reciprocal of resistivity  $\tau$  that is measured in Ohm-metre (O·) 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  $\omega$  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.

For measuring the impedance, the EIS meter uses an auto-balancing bridge [17], where a test system is excited by the voltage  $V_V$ , see Fig. 1. The signal waveform for  $V_V$

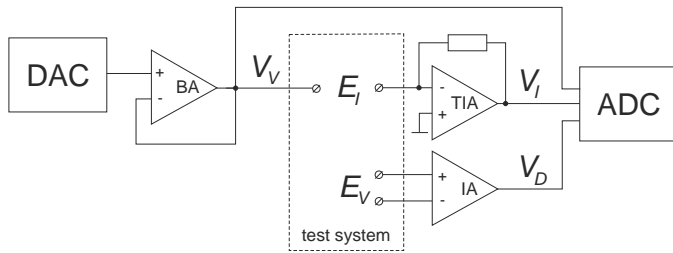


Fig. 1. The EIS measurement scheme, see descriptions in text.

is generated by DAC and is buffered by the amplifier. The flowing current  $I$  through the test system is converted into a voltage  $V_I$  by the transimpedance amplifier. Synthesis of the signal  $V_V$  occurs by Direct Digital Synthesis with 32-bit frequency resolution, the signals are digitalized by two synchronous 1.2 msp/s ADCs for simultaneous sampling of  $V_V$  and  $V_I$  signals. The EIS meter uses an external analog circuitry for impedance matching. The electrode pair  $E_I$  is utilized for the current sensing  $V_V \rightarrow V_I$  (so-called two electrode system). Another electrode pair  $E_V$  is used to sense a differential potential with the instrumental amplifier, this represents so-called four electrode system. MU EIS allows using harmonic and non-harmonic signals  $V_V$  for driving an electrochemical system (e.g. for fast EIS). The EIS spectrometer does not use the window functions, this allows avoiding specific errors of this approach [18], [19]. The potential input with  $E_V$  electrodes has a high input impedance (input bias current is about  $\pm 70$  pA), this enables sensing of bio-potentials in electrophysiological measurements. In such applications, the current flowing through the test system can be also used for electro-stimulation purposes. EIS approach involves the RMS impedance that have the same meaning as the magnitude, but calculated in different way [9].

EIS measurements have to consider the cell constant  $C$  (the SI unit -  $m^{-1}$ ) that defines the ratio of distance between electrodes to the area of the electrodes measured from the determined resistance of a solution with known conductance. The resistivity in case of a complex impedance  $Z$  is defined by

$$\tau = Z * C^{-1} \quad (4)$$

and correspondingly for the conductivity

$$\kappa = Z * C. \quad (5)$$

The EIS measurements indicate sometimes the  $Z$  value only, 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, see Fig. 2. Such a measurement scheme allows compensating nonlinearities; moreover, it allows comparing a long-term electrochemical behaviour of two fluids in equal conditions. Since weak emissions, which have non-electromagnetic, non-acoustic,



Fig. 2. The CYBRES EIS spectrometer.

non-thermal and non-mechanical character, change a rate of electrochemical processes (see the explanation in Sec.VIII-A), 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 EIS measurements require understanding the methodology and sources of inaccuracies.

This paper is organized as follows: sections II, III, IV are devoted to errors and technical aspects of measurements. Sections V, VI, VII, describe three measurement methodologies, analysis of statistically significant number of repetitions is shown in the section VIII. Conclusion in section X finalizes the paper.

## II. WHICH REQUIREMENTS SHOULD SATISFY THE MEASUREMENT EQUIPMENT FOR SENSING WEAK EMISSIONS?

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

Electrochemical changes under weak emissions occur slow, in several cases the rate of changes is about  $20-200 \Omega \cdot cm$  per hour for distilled water (see Sec. V, VI). The measurement equipment should be capable of long-term measurements under stable conditions. Typically, the conductivity meters perform so-called 'compensated'

measurements, these devices measure the temperature of fluid and calculate a correction of conductivity. However, the true dependency is nonlinear, moreover it depends on temporal dynamics of conductivity [13], [14], [20]. 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 1-3 kHz. Calibration (including the cell constant) is performed at this frequency. However, the effects created by weak emissions indicated different frequency characteristics, therefore measurements should be performed at different frequencies, as demonstrated by experiments, between 10Hz and 100kHz.

### III. 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, mechanical/electromagnetic distortions 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.

#### A. 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 formation at solid-liquid interfaces, see Fig. 3. These gas bubbles change the area of electrodes

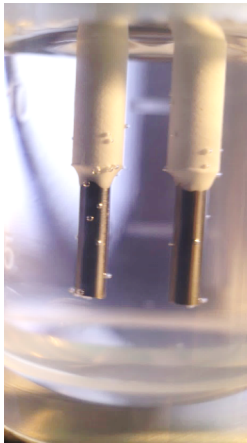


Fig. 3. Building of gas bubbles on electrodes.

that contact with water and impact the electrical conductivity measurements (especially micro-bubbles [21]). Thus, any time when a fluid container is inserted into the thermostat and it reached the set temperature, the bubbles should be removed. The simplest way to do it is to remove

electrodes from the container for a short time. Removal of bubbles influences the absolute values of impedance, the rate of degradation remains in fact unchanged, see Fig. 4. In continuous measurement mode, the removal of

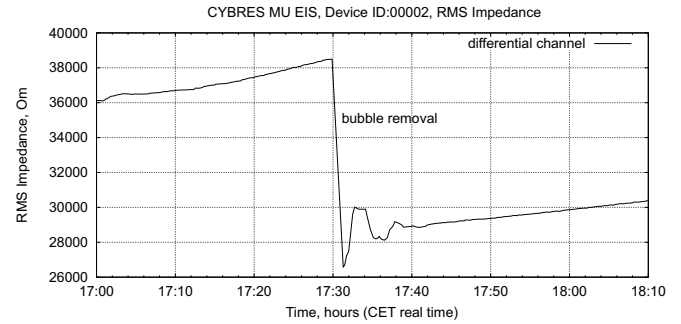
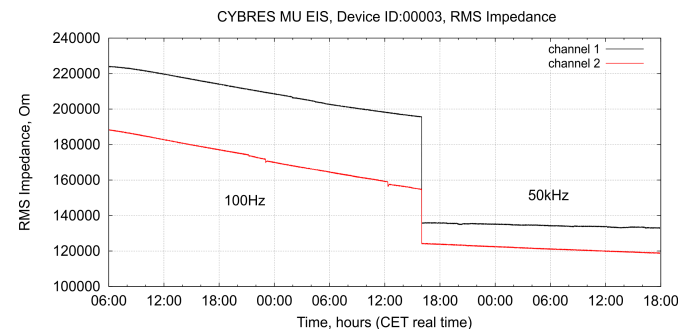


Fig. 4. Dynamics of differential channel before and after removal of bubbles.

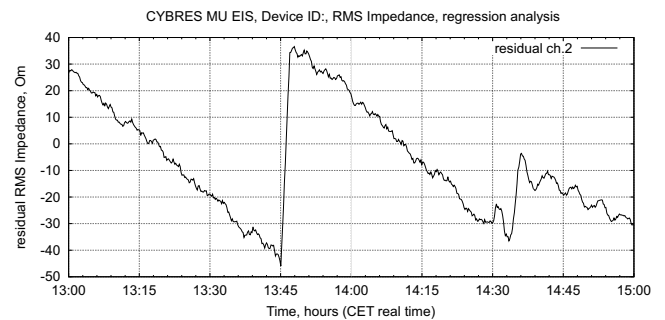
gas bubbles can be skipped when only a temporal EIS dynamics is of interest and a small inaccuracy of gradient measurement can be neglected, e.g. in the express-test, see Sec. IX.

#### B. Right frequency and temperature parameters

Proper setting the frequency and temperature is important for stability of long-term EIS measurements. The



(a)



(b)

Fig. 5. (a) Decreasing of RMS impedance at frequencies of 100Hz and 50kHz during 60 hours of measurement (the continuous mode measurements); (b) Appearance of spikes in long-term dynamics.

thermostat temperature should be set in regard to environment, 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, thermostats at a too low set temperature become unstable. Thus, the difference about  $4^{\circ}$ - $5^{\circ}$  should be maintained between environmental and thermostat temperatures.

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 Fig. 5(a). The higher is the frequency, the lower is the rate of degradation. The level of

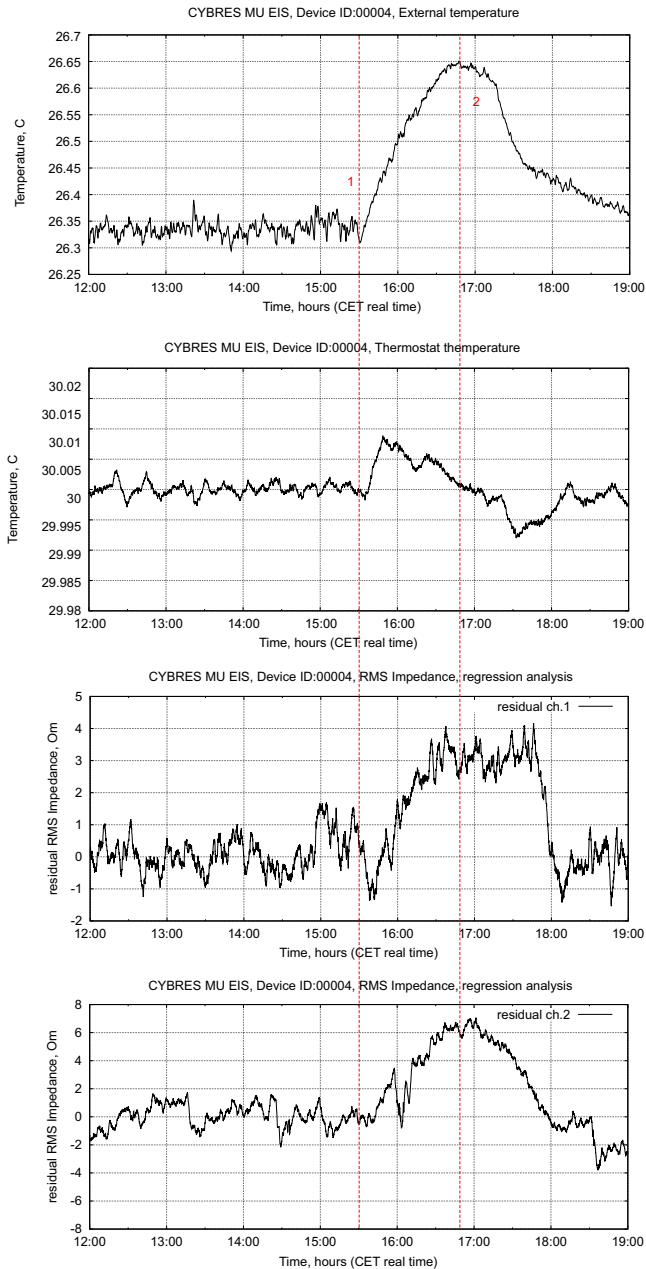


Fig. 6. Example of measurements with variation of external temperature.

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 [22]. The critical current density varies among others with the frequency [23]. This effect explains the appearance of spikes, shown in Fig. 5(b). To remove spikes, it needs to decrease the applied voltage and/or to increase the frequency.

### C. Impact of external temperature on measurements with thermostabilization of samples

When the thermostat with fluidic samples is on, the EIS measurements do not depend essentially on the external temperature, provided it changes slowly enough so that thermostat can compensate this change. Figure 6 shows experimental data, where the external temperature was increased on  $0.35^{\circ}\text{C}$  during 70 minutes. Variation of the thermostats temperature was about  $0.008^{\circ}\text{C}$ , the corresponding changes of RMS impedance was about 3-4 Om on both channels.

### D. Repeatability of measurements before the exposure

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

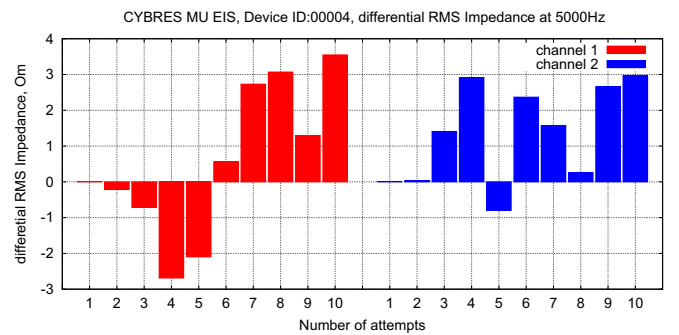


Fig. 7. Ten repeated measurements before exposure conducted immediately after each other in impedance spectroscopy mode. The first measurement is subtracted from further measurements.

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  $\text{CO}_2$ , as well as temperature-related degasification. Figures 5(a), and 8 show examples of such measurements, see also the Sec.VIII-B.



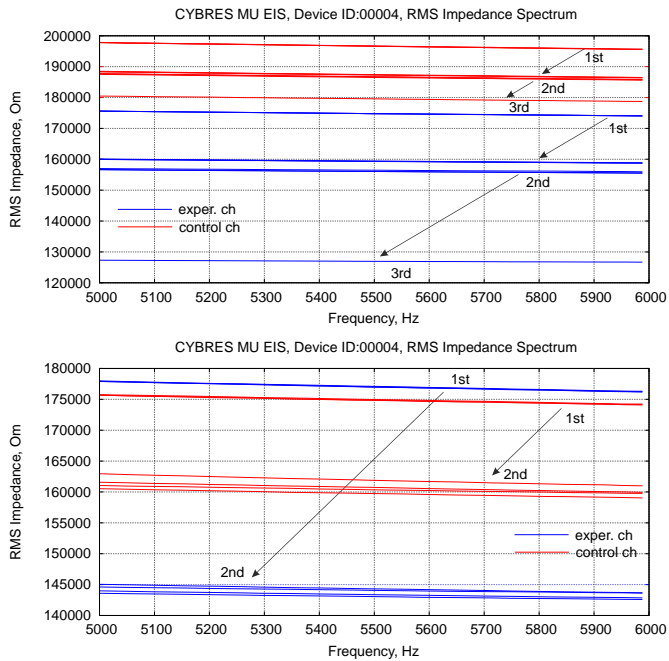


Fig. 8. Experimental results with external exposition of samples, different rate of changes is observed in experimental and control (without exposition of samples) channels

After some transient time, the rate of degradation becomes stable. This enables performing 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. V and VI as well as in non-local measurements shown in [24]. It needs to note that the EIS is an invasive approach, it impacts the electrochemical properties of fluids. For instance, the impact of different frequencies is shown in Fig. 5(a), the impact of sampling rate is shown in Fig. 9.

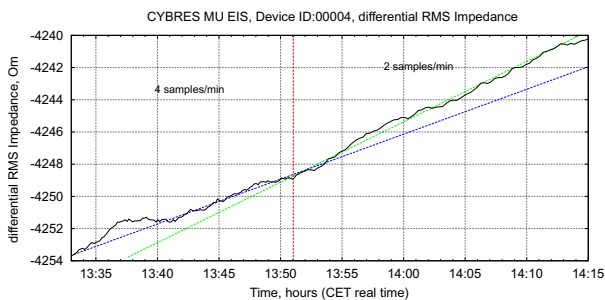


Fig. 9. Change of differential RMS impedance before the exposure in continuous measurement mode with two different sampling rates.

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

approach with external exposure of samples, described in Sec. VII, requires estimating the trend of degradation before and after the exposure (see the description of double differential methodology in Sec. VII).

#### E. Saturation of sensors

After performing multiple repeated measurements, 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 equipment. The saturation is one of reasons why sensors are assumed to have a probabilistic nature and measurements of weak emissions should be performed by several independent sensors in parallel. When the sensor does not react on a few 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 measurements.

#### IV. 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 emission, see Fig. 10.



Fig. 10. 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 exposed fluid changes the magnitude and phase of impedance. 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'. The 'intensity' of weak emission from 'Contur' depends on environment (since it is in fact a passive 'amplifier'). In several



Fig. 11. (a) Experimental setup for differential exposure by 'Contur'; (b) Aluminium foil below the experimental container.

cases an additional source of emission is required, and/or the generator should remain in experimental location a few days before experiments, see the experiment in Sec. VIII-B. The installation place and exposition time should be selected experimentally (the time varies between 30 minutes and a few weeks). For exposition it is enough to install samples in (or above) the top cone, see Fig. 16(b).

#### V. METHODOLOGY OF EIS MEASUREMENT I: DIFFERENTIAL IMPACT WITHOUT THERMOSTABILIZATION

This scheme uses the impact produced only on one channel during measurements. The experimental setup

is shown in Fig. 11(a). 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 and removed without mechanical distortion of fluids. The experimental container and the generator are separated by a metal

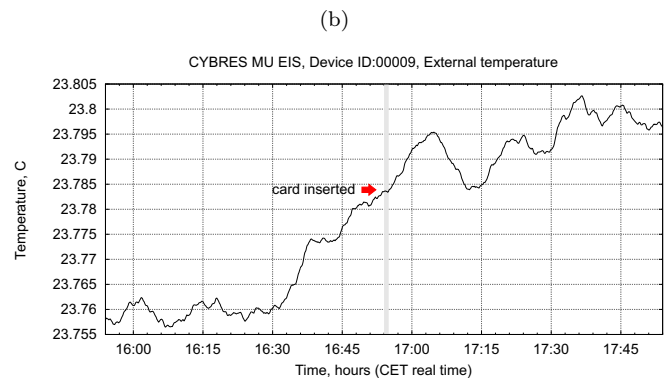
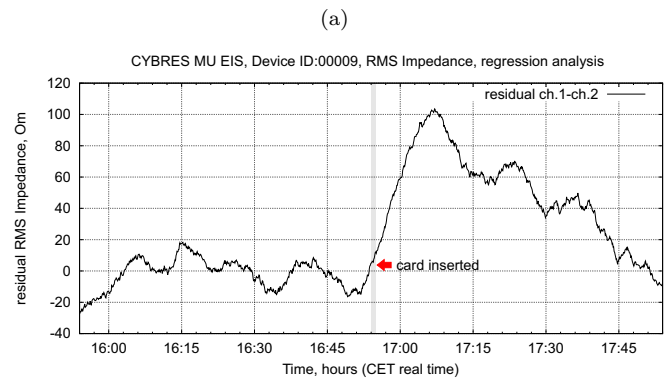
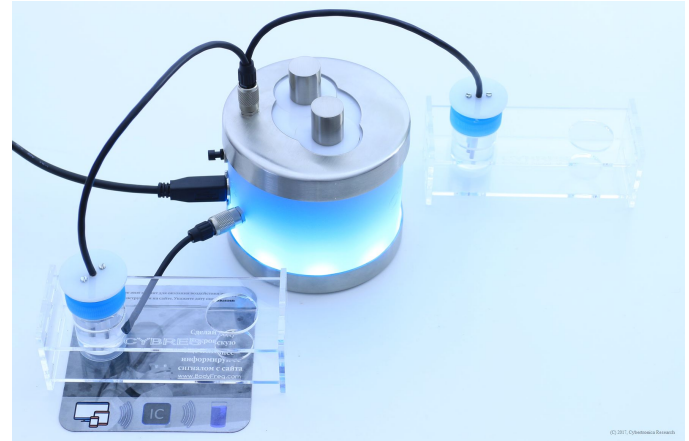


Fig. 12. (a) Example of EIS measurements with the methodology I and passive objects. The external temperature sensor is placed on the experimental container; (b) Regression analysis of RMS impedance with passive object under experimental channel (continuous measurements at 5 kHz mode); (c) Fluctuations of ambient temperature during measurement.

foil as shown in Fig. 11(b), this allows avoiding possible electrostatic phenomena, produced by metallic parts (e.g. the top conus) of the generator. The methodology of this approach is the following:

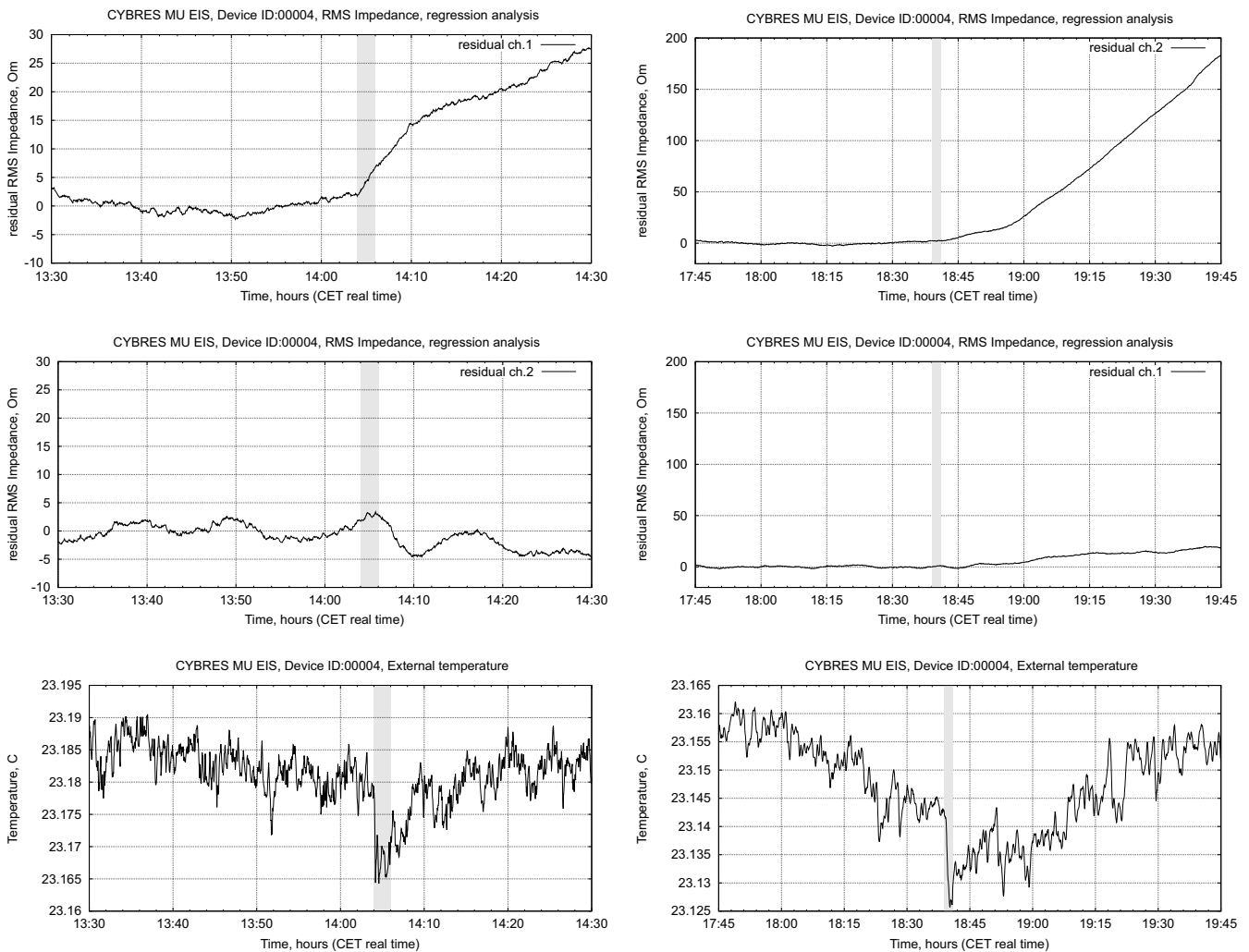


Fig. 13. Two examples of data with differential impact on channels (continuous measurement mode at 5kHz).

**1. Preparation** (this is a common step for all measurement schemes). 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 and any EM emitters.

**2. Background measurements.** Set the frequency in continuous measurement mode and start 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.

Results of several such measurements are shown in Fig. 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). It makes sense to place the external temperature sensor on experimental containers as shown in Fig. 12(a).

This measurement scheme is the most sensitive, since water samples are placed directly on the measured object. In particular it is well suited for measuring so-called 'activators' (various labels, cards, holders, etc.), see Fig. 12(a). These objects are placed under the experimental channel. Results of one of such measurements are shown in Fig. 12, a statistically significant number of attempts with different objects will be shown in a separate paper.

## VI. METHODOLOGY OF EIS MEASUREMENT II: COMMON IMPACT WITH THERMOSTABILIZATION

This scheme uses the impact produced on two channels and is useful for measuring local and non-local impacts. For non-local case, follow the document [24]. 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 Fig. 15. The top conus of the generator 'Contur' should be focused on the middle of the EIS spectrometer (the high of the platform should allow

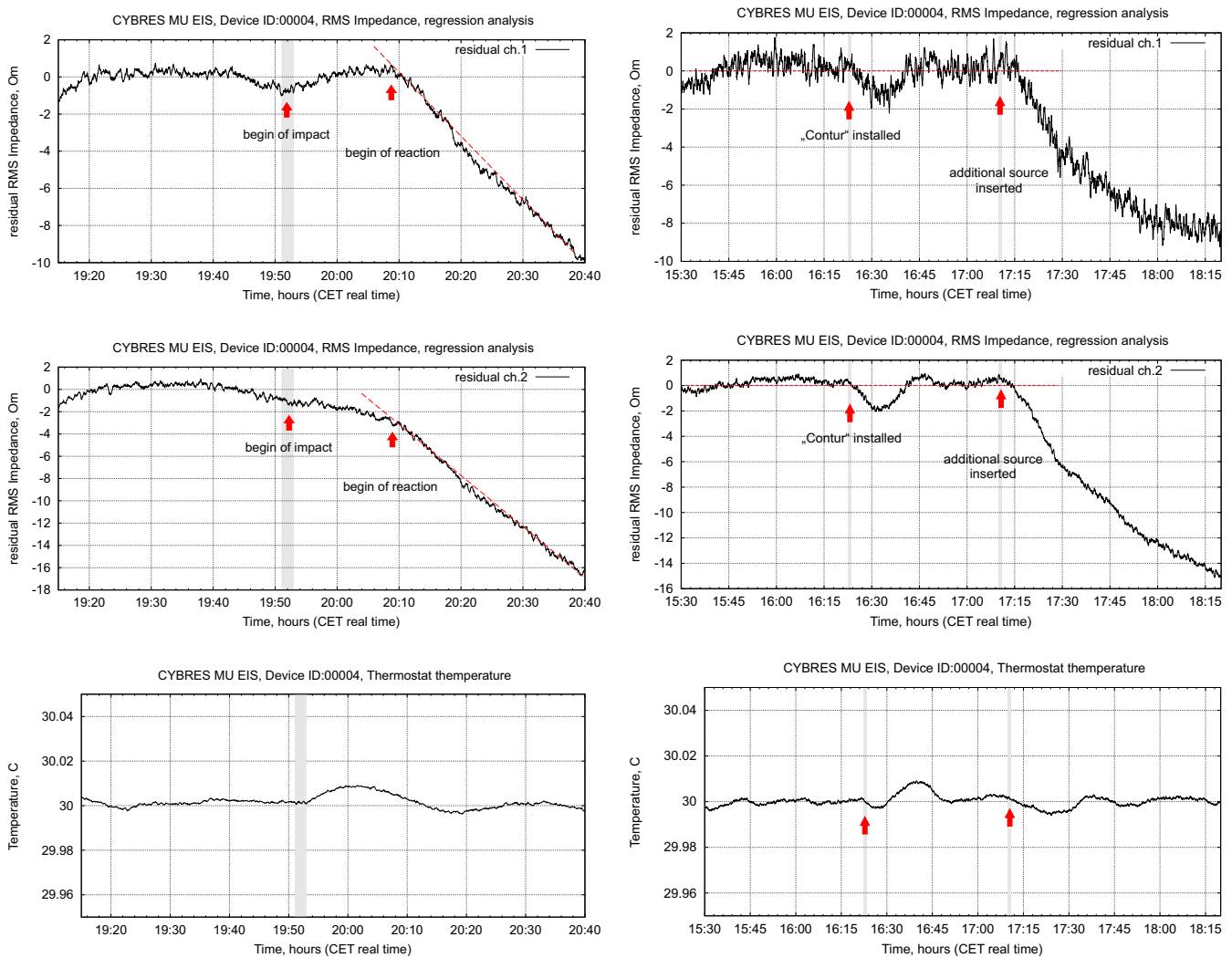


Fig. 14. Two examples of experiments with methodology II and with common impact on channels (the continuous measurement mode at 5kHz).

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. The methodology of this approach is the following:

1. **Preparation** (see the methodology I).
2. **Warming and degasation.** Insert the containers in the EIS spectrometer for 30-40 minutes. Remove air bubbles and wait until the temperature stabilizes again.
3. **Background measurements.**
4. **Experimental impact.** Insert the generator 'Contur' under the experimental container for 30-60 minutes without mechanical distortions of fluids.

Results of several such measurements are shown in Fig. 14. In this case the change of trend is observed in both channels. Since the samples are thermostabilized, this scheme is more stable to variations of temperature. 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

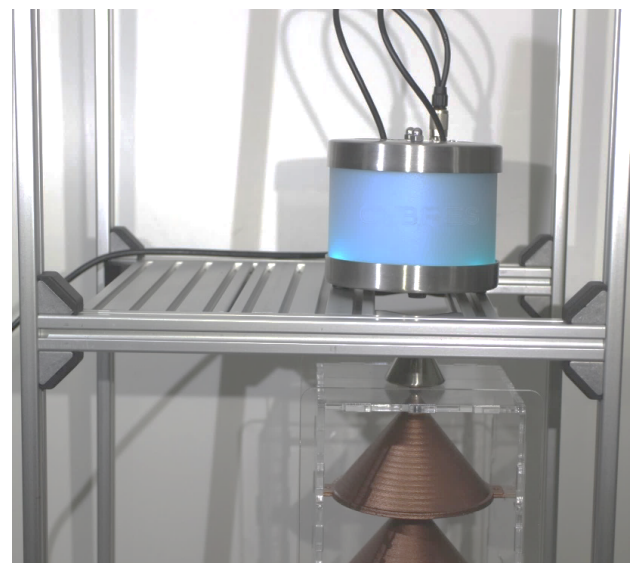


Fig. 15. Setup for the methodology II with common impact on both channels.



is sometimes required. For this measurement schemes, special electrodes with the input cone are developed, see Fig. 16(a).

VII. METHODOLOGY OF EIS MEASUREMENTS III: EXTERNAL EXPOSURE

This scheme assumes two independent measurements before 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 unmovable, e.g. for measuring a geo-biological situation in specific location. However, it

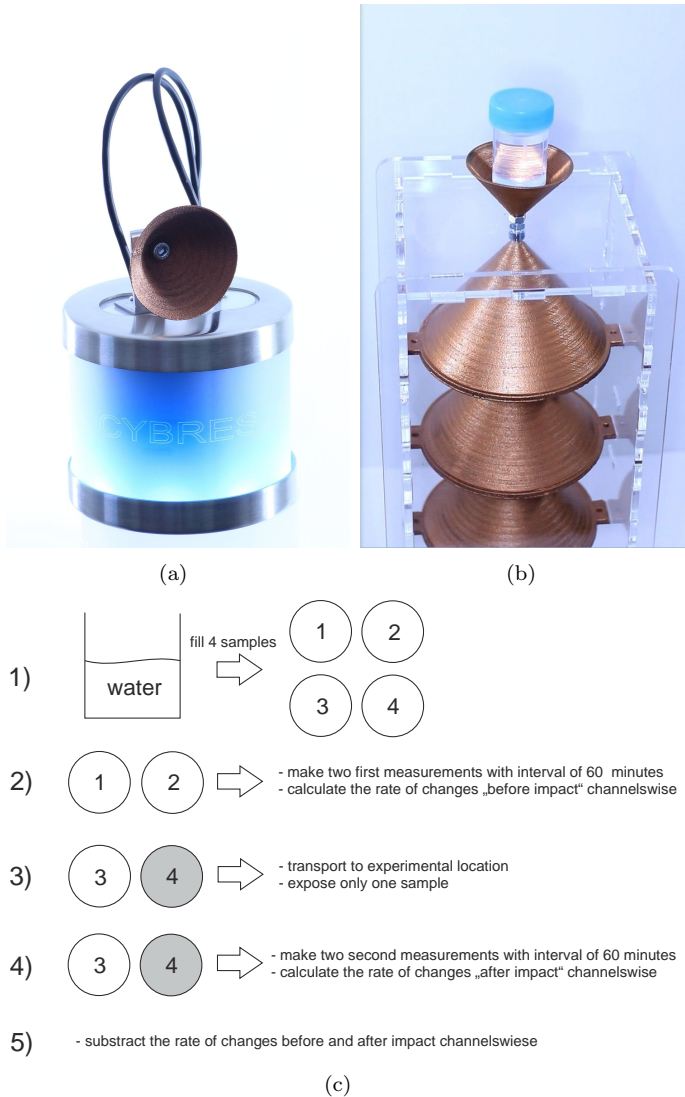


Fig. 16. (a) EIS spectrometer with the input cone in experimental channel; (b) External exposure of experimental sample by the generator 'Contur' with the methodology III; (c) Explanation of the double differential methodology of EIS measurements III with external exposure of samples.

has also a large random inaccuracy produced primarily by different mechanical distortions of control and experimental samples. Thus, this measurement scheme assumes a careful handling of samples, the containers should be

always closed and stored in the same vertical positions, as e.g. shown in Fig. 16(b). 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 Fig. 16(c). This approach represents a kind of double differential measurement methodology.

The analysis is also more complex compared to the previous schemes. It is based on the following observation. As mentioned in Secs. III and V, the EIS parameters degrade over time. However, the rate of changes in both samples remains comparable as long as these samples (always pairwise) were treated in a comparable way. Fig. 17(a) shows EIS data of two pairs of samples measured after each other. It is well visible that absolute values are different, however the rate of differential changes remain comparable.

Figure 17(b) shows the differential measurement of a pair of samples, where one sample was exposed by the 'Contur' during 20 hours. The experimental channel changed not only the values of RMS impedance, but also the gradient of changes compared to non-impacted samples from Fig. 17(a). Thus, the difference (over the noise level)

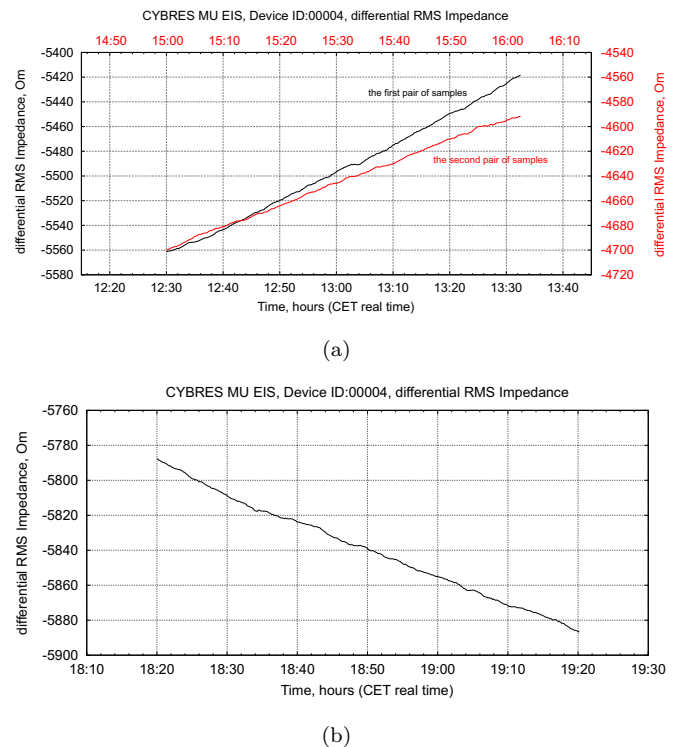


Fig. 17. (a) Two differential measurements of two different pair of water samples without exposure; (b) Differential measurement of two samples, one of them was exposed by the 'Contur' during 20 hours.

between the control and experimental pairs of samples represent a reliable indicator of an impact. There is a transient process, when the conductivity passes through a

maximum and the gradient changes its sign [20]. Therefore it is important to carry out all phase of measurements (heating, bubbles removal, measurement) **at the same time for control and experimental samples**. The starting point is the insertion of samples in a thermostat. The dynamics of changes is convenient to represent in the form of bar diagrams as a difference between first and last measurements, see Fig. 18.

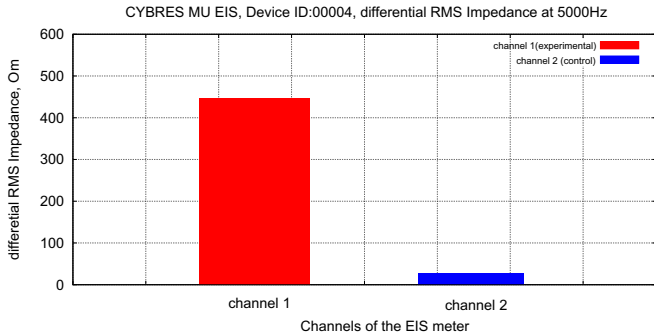


Fig. 18. Representation of results by the bar diagrams: each bar represents the rate (in differential terms) of degradation in corresponding channel. The difference in two and more time points to impact.

The following steps summarize this methodology:

1. **Preparation** with containers 1,2,3,4.
2. **Warming and degassing** the containers 1 and 2.
3. **Background measurement** with containers 1 and 2. Perform the first measurements and repeat it after 60 minutes.
4. **Experimental impact**. Remove the containers 1 and 2 from the EIS spectrometer. Containers 3 and 4 can be moved to the experimental site (both containers must pass similar mechanical disturbances). Leave the control container on the holder and install the experimental container in the upper cone of the generator 'Contur' (or another source of emission).
5. Repeat the steps 2 and 3 for the containers 3 and 4.
6. Perform the second measurement in the spectroscopy mode and repeat it 60 minutes after. Plot the result with the option 'bar diagram' (see Fig. 18).

This approach demonstrates appropriate results only when all samples are treated pairwise 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.

## VIII. STATISTICALLY SIGNIFICANT MEASUREMENTS

### A. 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. Changes of measured parameters are only the secondary macroscopic indicators of impact that happens on a microscopic level, i.e. the

described schemes perform indirect measurements. 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.

**The general rule for impact recognition in all EIS methodologies is that the changes after exposure (or experimental samples) should be at least 2x larger than the variations during background recording (or control samples without impact).** The impact in continuous measurement mode (the methodology I & II) 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. EIS methodology III is based on the rate of degradation in experimental and control channels. Here, the difference in the slope of a trend indicates the intensity of impact.

Let  $C_1$  and  $C_2$  be the values of RMS impedance of the control channel at the time points  $t_1 = 0$  and  $t_2 = 60$  minutes. By analogy,  $E_1$   $E_2$  are the values of RMS impedance of the experimental channel at the same time points. Define

$$\Delta_C = C_1 - C_2, \quad (6)$$

$$\Delta_E = E_1 - E_2, \quad (7)$$

then  $\frac{\Delta_E}{\Delta_C}$  determines the relation between experimental and control channels and the following expression determines the boundary of negative measurement (where the effect of weak emission is not registered):

$$2 > \frac{\Delta_E}{\Delta_C} > 0,5 \quad (8)$$

The result, which violates (8), is considered as positive. Since (8) does not include the time, due to small differences in the preparation of samples, EIS parameters of unexposed liquids can 'drift' from each other and become 'positive' in sense of (8). Therefore, the time  $\Delta t = t_2 - t_1$ ,

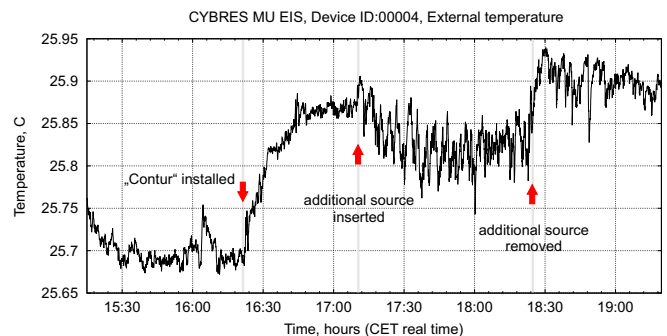


Fig. 19. Dynamic of external temperature from the experiment in Fig. 14, recorded by a semiconductor sensor.

needed to calculate (6), is selected experimentally. Not properly chosen  $\Delta t$  can lead to a negative result even in case of exposed samples, see. Fig. 21.

The weak emissions impact not only fluids, but also semiconductor sensors. Fig. 19 shows the dynamics of external temperature from the experiment in Fig. 14, 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.

### B. Methodology of repeated measurements

For accumulating sufficient statistical data for the measurement methodology III, the following approach was utilized. Several generators 'Contur' and EIS spectrometers are installed in the laboratory. All 'Conturs' are placed close to external wall of the building (sun side) at about 1 meter from each other. This position was free from electrical power lines, all WiFi emitters are off, the intensities of AC electric/magnetic fields do not vary over 5V/m and 10nT. The EM power in frequency range 50Mhz-2Ghz was measured close to 'Conturs', no anomalies are detected in the intensity of EM fields. Additionally, the index of geomagnetic activity  $A_p$  (sum of two values between 9.00 and 15.00) was recorded, data are obtained from the Helmholtz center in Potsdam ([www.gfz-potsdam.de/en/kp-index/](http://www.gfz-potsdam.de/en/kp-index/)). EIS meters are located on the table close to each other, different electrodes are utilized during measurements. Experiments are performed by two operators, they start at the same time and follow the same procedure:

1) 8 or 12 water containers (samples) are filled with distilled water, all containers remain always on the table close to each other.

2) Three randomly selected samples are installed on the top conus, as shown in Fig. 16(b).

3) The control pair of samples (randomly selected from all containers) is measured by three EIS spectrometers at 5kHz. Measurements in continuous mode takes 2-3 hours.

4) After this, the experimental containers are taken from the 'Conturs' and the step 3 was repeated with the experimental pair of samples. Experimental container was always installed in the channel 2.

For each attempt, the initial value and the difference are recorded, Table I shows the obtained results. At beginning and end of measurements several control experiments (the same procedure, but the water samples are not exposed) have been carried out. Fig. 20 shows typical results of these measurements – the experiment 22.02.17.

Firstly, the high repeatability of results (qualitatively assessed as 'yes' – 'no') is well visible, only two negative results (6.7%) were obtained from 30 measurements. This corresponds to 93.3% of repeatability. The first negative result was obtained when one 'Contur' was placed in a new location. Apparently, passive generators require some time before operation. We are interested in the second negative result obtained on 02.13.17, graphs are shown in Fig. 21. Here the control channel (N1) has the same inclination of the trend in the first and second pair of liquids. The experimental channel (N2) shows the beginning of

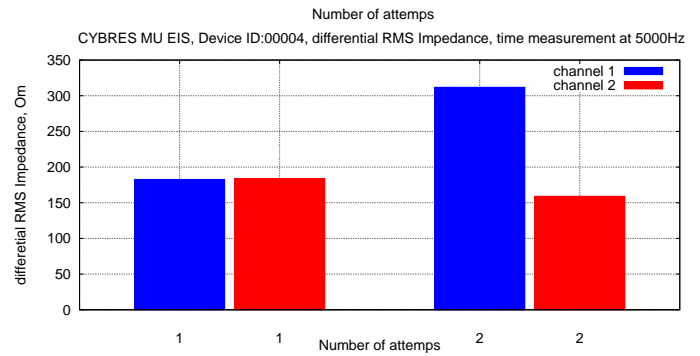


Fig. 20. The bar diagram of differential results (calculated based on 20 last samples, about 6 minutes) in the experiment on 22.02.17. The first attempt is the control measurement without exposure (similar dynamics of channels), the second attempt – one sample was exposed (substantial difference between the channels). This diagram can be considered as an express-test for this experiment, see Sec. IX.

different trends 'up' and 'down', but only the initial part of curves was recorded, where these changes are small. This situation is already mentioned in the context of relations

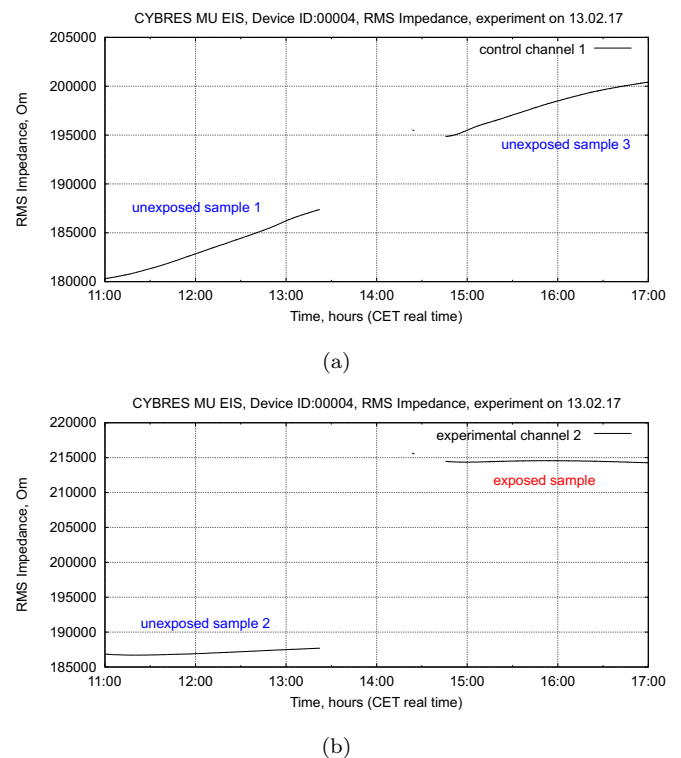


Fig. 21. Dynamics of the experiment on 13.02.17 with negative result due to wrongly selected  $\Delta t$ ; first the control pair of fluid was measured, after the experimental pair; exposed was only one sample from experimental pair; (a) control channel (all sample are unexposed), (b) experimental channel (only one sample was exposed in the second measurement).

(8) – the time interval  $\Delta t$  between repeated measurements can influence the detection of impact.

Secondly, measurement results of control pairs (without impact) differ from each other across the experiments. The

TABLE I  
 TABLE OF PERFORMED EXPERIMENTS,  $A_p$  SUMMED INDEX OF GEOMAGNETIC ACTIVITY FROM 9.00 TO 15.00 (EACH DAY),  
 PARAMETERS  $C_1$ ,  $E_1$ ,  $\Delta_C$ ,  $\Delta_E$  ARE CALCULATED AS SHOWN IN SEC. VIII-A.

N	Date	EIS ID	Cont. $C_1$	Cont. $\Delta_C$	Exp. $E_1$	Exp. $\Delta_E$	$\frac{\Delta_E}{\Delta_C}$	$A_p$	Comments
1c	04.02.17	4	-5560	-140	-4700	-110	0,78	13	control without impact
1	04.02.17	4	-5560	-140	-5790	+100	-0,74	13	
2	06.02.17	4	-4180	-60	-4620	+20	-0,33	15	
3	07.02.17	4	-9800	-140	-8990	-870	6,21	15	
2c	07.02.17	2	-10500	-650	-30300	-1200	1,84	15	control without impact
4	08.02.17	4	-3650	-1550	-8200	-450	0,29	10	
3c	08.02.17	4	-8200	-450	-8125	-525	1,16	10	control without impact
5	08.02.17	2	4600	-1200	9500	-1500	1,25	10	negative result*
4c	08.02.17	2	9500	-1500	14900	-2100	1,4	10	control without impact
6	09.02.17	2	27500	-2750	27200	300	-0,11	9	
7	09.02.17	3	15100	1100	23600	-1300	-1,18	9	
8	09.02.17	4	2900	-800	-36000	1600	-2,0	9	
9	10.02.17	4	3650	100	-38300	1700	17	14	
10	10.02.17	2	-5750	400	-87150	-450	-1,16	14	
11	13.02.17	4	-6500	-2500	-19500	-2900	1,16	5	negative result
12	13.02.17	2	3000	6000	26750	-2500	-0,41	5	
13	14.02.17	4	6300	1500	-8000	-6500	-4,33	0	
14	14.02.17	2	-7200	-1600	32000	14000	-8,75	0	
15	15.02.17	4	10000	5500	13500	2150	0,39	2	
16	15.02.17	2	-3000	7000	17500	3500	0,5	2	
17	19.02.17	2	-200	2500	10400	400	0,16	19	
18	19.02.17	4	31500	5500	19000	2250	0,40	19	
19	20.02.17	2	17000	-7500	2780	-120	0,016	15	
20	20.02.17	4	135600	-1000	9400	-2100	2,1	15	
21	21.02.17	2	-12500	3750	-4500	-2700	-0,72	4	
22	21.02.17	4	1350	350	14950	850	2,42	4	
23	22.02.17	2	-2400	600	7750	2000	3,33	8	
24	22.02.17	4	23450	950	9500	2300	2,42	8	
25	23.02.17	2	-4500	3500	5480	-100	0,03	22	
26	23.02.17	4	52250	-3500	19100	-800	0,22	22	
27	24.02.17	2	13000	-5500	3300	800	0,14	44	
28	24.02.17	4	21900	-2200	1600	700	0,31	44	
29	25.02.17	2	-300	600	11550	-400	-0,66	4	
30	25.02.17	4	24250	3750	16450	350	0,09	4	
5c	26.02.17	9	-2400	-1800	-25500	-1750	0,97	2	control without impact
6c	26.02.17	3	11200	-1400	14250	-2150	1,53	2	control without impact
7c	26.02.17	4	14500	-350	27400	-400	1,14	2	control without impact
8c	27.02.17	9	-4920	120	-5160	120	1,0	8	control without impact
9c	27.02.17	3	-3350	900	1600	500	0,55	8	control without impact
10	04.03.17	2	6650	-550	7100	-900	1,63	30	control without impact
11	04.03.17	4	5550	-200	2900	-120	0,6	30	control without impact
12	05.03.17	4	15200	600	3200	700	1,16	24	control without impact

\* – the generator 'Contur' is placed in a new location

reason lies in variations of liquid preparation (mechanical impact during dispensing, the liquid storage space), and performing a particular experiment (used electrodes, removal of bubbles). There exists a natural variation of EIS data, this fact was already mentioned e.g. in [7].

When comparing the results with the index of geomagnetic activity  $A_p$ , it can be assumed that a large  $A_p$  increases the probability of significant changes in conductivity, but we failed to establish a clear correlation between variations of conductivity and the value of  $A_p$ .

## IX. EXPRESS-ANALYSIS

An interesting effect was discovered during preparation of control measurements shown in Table I. Plastic con-

tainers (made from an organic polymer – Polypropylene ( $C_3H_6$ )<sub>n</sub>), which are used in experimental channels of previous experiments, change properties of fluids even after finishing these experiments.

Figure 22 shows two graphs of the same control experiment (without exposure). Preparation of containers and liquids was the same for all channels, but the first attempt used plastic containers, which have been used previously. Figure 22(a) shows the first 30 minutes of recording the RMS impedance at 5 kHz. The dynamics of both channels is different, this behaviour was not changed after degassing or heating the containers. In the second attempt the liquids are poured into new containers on the same device with the same set of electrodes. Dynamics of both channels is



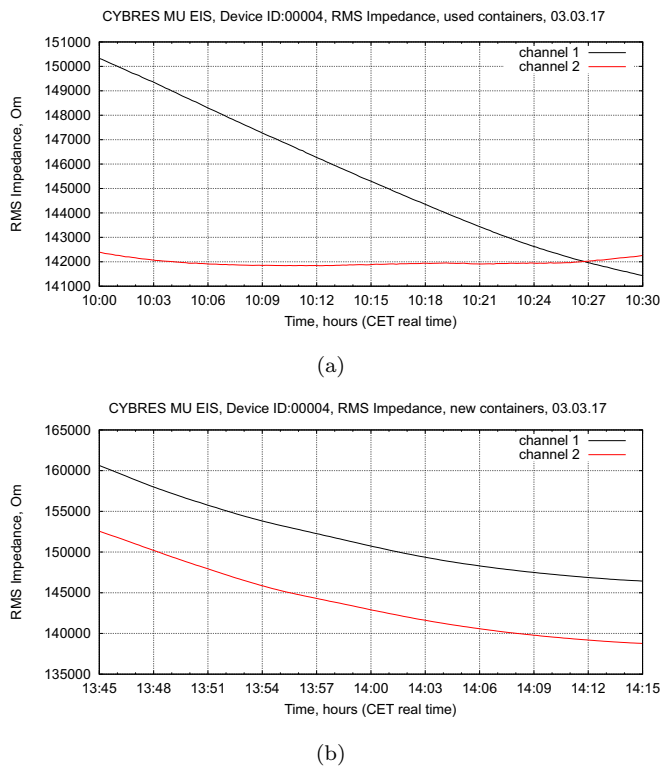


Fig. 22. The first 30 minutes of RMS impedance measuring at 5kHz (in the initial stage of temperature stabilization before degassing, the same device and the same set of electrodes was used); (a) fluids in both channels are poured into used containers; (b) liquids in both channels are poured into new containers.

similar in this case, see 22(b), that is typical for all control experiments. Representation of data from Fig. 22 as bar diagrams is shown in Fig. 23.

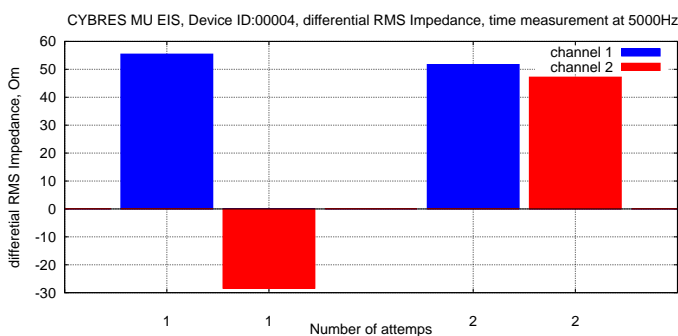


Fig. 23. Bar diagram of differential results for last five samples (about one minute of measurement), shown in Fig. 22. The difference between channels in the first attempt (from Fig. 22(a)) is well visible, whereas the second attempt (from Fig. 22(b)) indicates a comparable dynamics of channels.

This experiment was repeated several times with similar results – some containers changes properties of liquids. Chemical pollution as a possible explanation for this phenomenon is rejected because all containers are used only with distilled water, moreover, they are cleaned with distilled water at beginning of each experiment. The tem-

perature factor is also irrelevant due to achieving uniform temperature in the thermostat. Given that the 'weak emission' influences the rate of electrochemical changes, the possible explanation can indicate an information phenomenon associated e.g. with the 'after-effect' in used containers.

This technique shows that a similar EIS dynamics in both channels points to similar properties of liquids, even in the first minutes of measurement. Thus, the first 3-5 minutes of differential EIS measurements are sufficient for express-analysis to determine whether the fluid is exposed to 'weak emission', e.g. from some imprinting effects, the influence of an operator, info-cards, or 'passive modifiers'. This method is suitable for qualitative analysis or for demonstration in field conditions, where the time represents the most important factor.

## X. CONCLUSION

The impact of 'weak emission' is detected on the level of  $10^{-9} - 10^{-11}$  S/cm with relatively slow dynamics. EIS measurements can detect and characterize only the presence of 'weak emission'. This method is not suitable for detection of biological effects (e.g., stimulation or inhibition). Since the *measurement of 'weak emissions' has the probabilistic nature*, a sufficient number of repeated experiments should be carried out. The origin of these emissions is not fully understood, the performed experiments indicated the importance of the following issues:

**1. Mechanical distortions.** Containers should not be exposed to unnecessary mechanical distortions, vibrations, warming during exposing/holding phases of measurements.

**2. Electromagnetic distortions.** Control and experimental samples should be 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.** Both containers should be equally warmed up and cooled down. Avoid warming up only one container, e.g. by keeping it in the hand or by inserting an object with different temperature (in experiments without thermal stabilization).

**4. Amplification of the emission level.** Many passive source of emission needs an active emitter and/or long exposition times. Generally, the EIS methodology I is the most suitable for such measurements.

**5. Preparation and storage of water samples.** The original water for all samples and the control samples should be stored in places away from sources of weak emissions. It is a good strategy to store control samples close to the measurement equipment, whereas the experimental samples are exposed away from the equipment.

**6. Short measurement time** for one experiment allows avoiding undesired effects related e.g. to impact of different environmental emissions.

Regarding the measurement techniques, EIS methodology I and II appeared as the most accurate method, EIS methodology III requires the double differential method

to obtain repeatable results. Analysis of control measurements in Table I shows that liquids are exposed to multiple 'natural influences'. Sharp corners, the combination of objects near the storage location, metal objects can form the shapes effect and affect the fluids. We draw attention to the fact that the storage and the 'after-effect' can affect fluids, especially the bottled liquids.

Interesting phenomena are demonstrated by measuring the passive objects or modifiers, as shown in Fig. 12(a). Apparently, the 'effect of modifiers' is to some extent similar to the 'shape effect'. The systematic investigation of these objects will be undertaken in the next paper.

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