

CONSIDERATIONS ON THE ACCURACY OF MEASUREMENTS OF ELECTRICAL CONDUCTIVITY OF LIQUIDS

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Abstract: The purpose of this paper is the presentation of new requirements created by contemporary applications of electrolytic conductivity measurements, the main factors limiting accuracy of such measurements and also discussion of the means enabling minimization of effects caused by these factors. Recently observed demand for accurate microscale conductivity measurements, mainly in biomedical engineering, involves new features required from the conductivity sensors and co-operating electronics: miniaturization, robustness, low price (mass produced, disposable devices). Consequently, a new approach in designing such instrumentation is required.

Keywords: electrolytic conductivity, cell constant, electrode polarization, microscale measurement, miniature sensor

1. INTRODUCTION

Most of the liquids conducting electrical current are electrolytic solutions, i.e. ionic conductors. They are also the main component of all live organisms, hence the great practical importance of conductometry. The area of its traditional applications has recently considerably extended over many new applications: biological, medical, industrial, objects of daily use, etc. Many new conductometry based devices, like chemical micro-analyzers, electrical diagnostic devices, biosensors and electrical resistance tomography systems have been developed.

New applications create new requirements, especially for much better spatial resolution, smaller sample volumes and wider range of measuring frequencies [1,2,3] (although basic conductivity measurement is carried out usually at one frequency, investigations are often performed over a wide range of frequency – to minimize the influence of the electrode polarization or to distinguish specific features of matter, e.g. in impedance spectroscopy of biological tissues), etc. This involves new features required from the sensors: miniaturization, robustness, low price (mass produced, disposable devices), and new conditions of their use – multi-frequency and multi-point measurements in variable environments, very low level of measuring signals, etc. Very often absolute values of the conductivity are required (not relative changes only) for distinguishing particular objects (type of electrolyte dissolved, type of tissue examined, etc.). That indicates an increasing demand

for new designs and new technologies for manufacturing the sensors. Therefore a new look at the problem of accuracy of measurements of electrical conductivity of liquids seems to be necessary. Because of the author's present interests the considerations presented are oriented towards biomedical applications.

2. PRINCIPLES OF MEASUREMENT

Electrical conductivity κ of a conductor characterizes its ability to conduct electric current and is defined as the ratio of the density J of the current flowing through the conductor to the electric field strength E generating this current, i.e. $\kappa = J/E$. It is determined indirectly, from the solution resistance or conductance, using a suitable conductivity sensor – the principle is illustrated in fig. 1. [1].

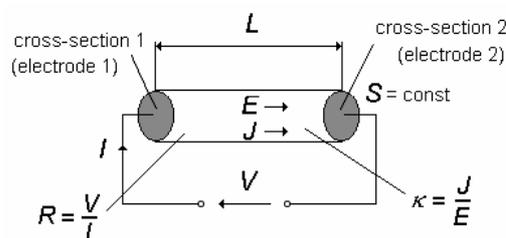


Fig. 1. Illustration of the principle of measurement of electrical conductivity

The basic parameter of all conductivity sensors is the so called “cell constant” K – a scale factor dependent on the geometry of the sensor and the current paths (often affected by the overall geometry and volume of the sample), necessary for calculating the conductivity from the resistance or conductance of the sensor. Considering a volume of solution bounded by two parallel cross-sections, 1 and 2 (fig. 1), its resistance R_{12} determined as the ratio of the voltage drop V to the current I can be calculated from equation (1) where κ is the conductivity and L and S are, respectively, the length and the cross-section of the currents paths:

$$R_{12} = \frac{V}{I} = \frac{1}{\kappa} \cdot \frac{L}{S} = \frac{K}{\kappa} \quad (1)$$

Hence the cell constant is

$$K = \kappa \cdot R_{12} = \frac{L}{S} \quad (2)$$

If the cross-sections of the current paths are not uniform along their lengths (fig. 2), integral expressions are required. Then:

$$K = \int_0^L \frac{1}{S(l)} dl \quad (2b)$$

The conductivity determined in the described way is an average value over the whole volume of the specimen measured by the sensor. Local conductivity measurements require applying sensors of appropriately small size. Miniature sensors of size of the order of tens to hundreds micrometers are available now.

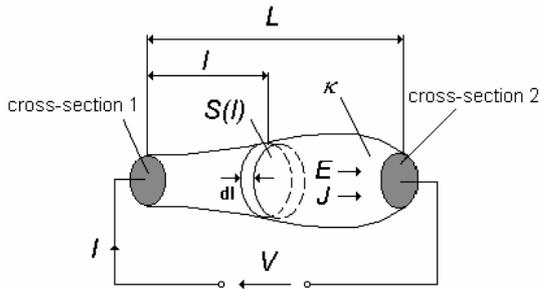


Fig. 2. Illustration of the integral definition of the cell constant of conductivity sensor [1]

The most popular is the two-electrode method of measurement – the same pair of electrodes, 1 and 4 in fig. 3, is used for exciting the current flow I and for measuring the voltage drop V_1 . The ratio V_1/I is identified then with the resistance R_e of the solution. In reality the voltage V_1 contains also the voltage drops V_p across the electrode impedances (polarization impedances) – as shown in fig. 3. Therefore the resistance measured in this way is always greater than the bulk solution resistance. This is the so called “polarization error”. Analyzing the potential distribution along the current paths (fig. 3) one can observe that the regions adjacent to the electrodes exhibit much greater potential gradient than the bulk of the solution. Polarization error can be eliminated (in theory) or minimized (in practice) applying a differential [4] or four-electrode method of measurement [1,2]. The second one is more effective and hence much more popular. In the four-electrode method an additional pair of electrodes, 2 and 3 – in fig. 3, is inserted into the bulk solution – to the region of linear potential gradient. The potential electrodes should not disturb the original distribution of the potential, hence they must be sufficiently small and the voltage drop V_2 should be measured with negligible (in theory zero) current. The ratio V_2/I is then accurately equal to the bulk solution resistance, free of polarization effects.

The cell constant defined in the way illustrated in fig. 2 has a general meaning and can characterize all types of conductivity sensors, two-electrode and four-electrode ones as well as electrodeless sensors, e.g. inductive ones in which the electric field is excited in the volume bounded by the cross-sections 1 and 2 using electromagnetic coupling.

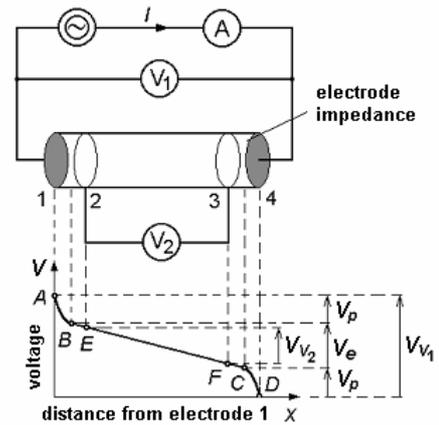


Fig. 3. Illustration of two- and four-electrode method of measurement and distribution of the potential along the conductivity sensor (electric field close to uniform assumed) [1]

It is assumed that the cell constant has, for a given sensor, at a given temperature, a certain and invariable value. In reality it can exhibit variations depending on many factors: occurrence of current paths spreading out of the sensor (stray electric field), the value of the measured conductivity of the liquid and the measuring frequency (effects of electrode polarization at lower frequencies and parasitic stray capacitances at higher frequencies) [1,5], etc. Consequently, the majority of usable conductivity sensors require experimental determination of their cell constant value at the conditions close to the expected application [1].

The recommended method of calibration is based on the measurement of electrical resistance of the cell filled up with the standard solution [6]. Such calibration has a serious disadvantage – it is strongly disturbed by temperature changes, similar to all measurements of electrolytic conductivity. Free of this disadvantage are absolute measurements of conductivity, performed by cells of calculable constant [5,7]. Until now such sensors are rather seldom applied as usable ones and they have not been realized yet in a miniature form.

2. MAIN FACTORS LIMITING ACCURACY OF CONDUCTOMETRIC MEASUREMENTS

The main sources of errors and uncertainties in measurements of electrical conductivity of liquids (electrolytic conductivity) are: inaccurate determination of the cell constant value, strong influence of temperature on the measured solution conductivity, electrode polarization and also instrumental errors, including residual and parasitic effects [1,5].

2.1. Influence of temperature

Electrical conductivity of all electrolytic solutions is strongly dependent on temperature (fig. 4) – its value increases 1%–3% per degree celsius, or even more. Usually it is necessary to convert results obtained at different temperatures to a standard reference temperature (usually 25°C, this is so called “temperature compensation”) – only then are the conductivity values comparable. Such a procedure is not easy because various solutions have

different temperature characteristics. Lack of or inexact temperature compensation can be a source of very serious errors [1].

For instance, skin temperature can vary in the order of 10°C from the core body temperature and is strongly dependent on the depth, and therefore the temperature at the point of measurement needs to be known. This requires the application of a miniature temperature sensor integrated with the conductivity sensor [2].

A significant source of the temperature error can be self-heating caused by excessive power dissipation in the sensor, resulting from the measuring current applied, essential particularly when the sensor has a closed vessel and heat exchange with surroundings is poor.

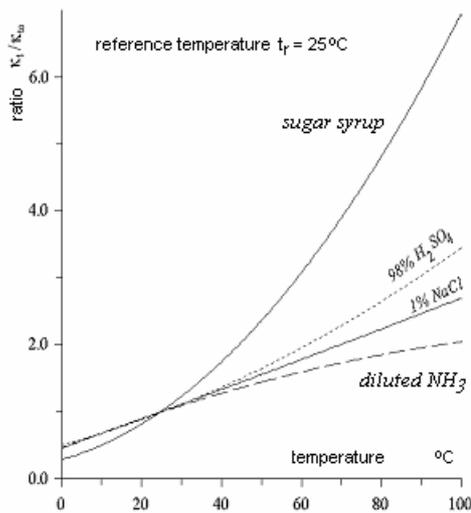


Fig. 4. Influence of temperature on the conductivity of some aqueous solutions (the vertical axis presents the ratio of conductivities at actual and reference temperature) [1]

2.2. Influences of electrode polarization

The total impedance of the two-electrode conductivity sensor can be presented as a sum of the resistance of the bulk electrolyte solution R_e (measurand) and two electrode impedances Z_E consisting of double layer capacitances C_{DL} , Warburg impedances (diffusion impedances) Z_W and Faraday resistances (chemical reactions resistances) R_F , where Z_W and R_F are frequency dependent – a suitable equivalent circuit is shown fig. 5a [8,1] (electrode impedances can be considered as linear ones only in the range of small electrical signals). Transforming this circuit to a serial form (fig. 5b) one can show that the measured sensor resistance R_S is a sum of the solution resistance R_e and two frequency dependent polarization resistances R_p .

The major problem is how to arrange the measurement to extract accurately the measurand R_e from the measured resistance R_S . It can be achieved minimizing the contribution of the polarization resistances or applying the four-electrode method of measurement. Often both these approaches are necessary.

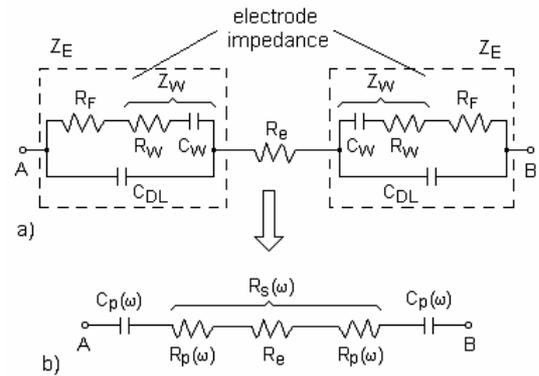


Fig. 5. Equivalent circuit of a two-electrode conductivity sensor (a) and its transformation to the serial form (b); $R_p(\omega)$ and $C_p(\omega)$ are the equivalent serial resistance and capacitance of polarization [1]

To avoid chemical reactions at the electrodes and to minimize the polarization impedances, conductivity measurements are usually performed using nearly ideal polarized electrodes (such as electrodes made from platinum or gold), excited with alternating current (AC) of sufficiently high frequency. But even then the electrode polarization can considerably effect the measured sensor resistance and hence worsen the accuracy of determining the electrolytic conductivity. Exemplary values of the polarization resistance r_p per unit of the area of one electrode, measured by the author [1], are presented in fig. 6 and 7. These results confirm that the polarization resistance strongly depends on the material, porosity of the electrode surface, the measuring frequency and the measured conductivity (it can depend also on the kind of the measured electrolyte, which is not presented there). Porous electrodes have low polarization impedance but they are unacceptable in most of biological, medical and food industry applications whereas suitable for such applications are smooth metal electrodes that have higher values for this impedance. The results obtained by the author are in good agreement with those presented later in [9] – fig. 8 (this figure presents also the results of measurements of the polarization capacitance c_p per unit of the area of one electrode, which determines the sensor reactance).

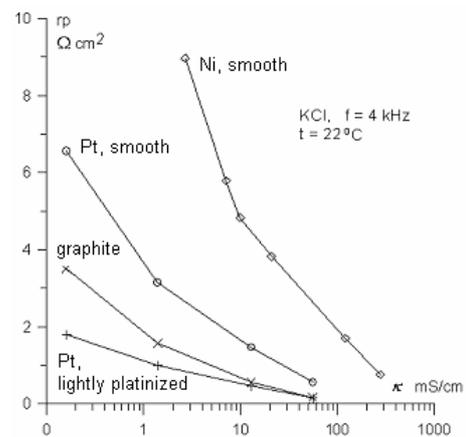


Fig. 6. Polarization resistance per unit for one electrode surface made up of different materials, as a function of conductivity [1]

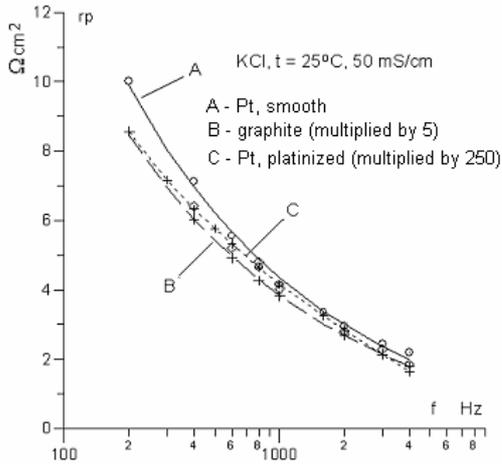


Fig. 7. Polarization resistance per unit for one electrode surface made up of different materials, as a function of frequency [1]

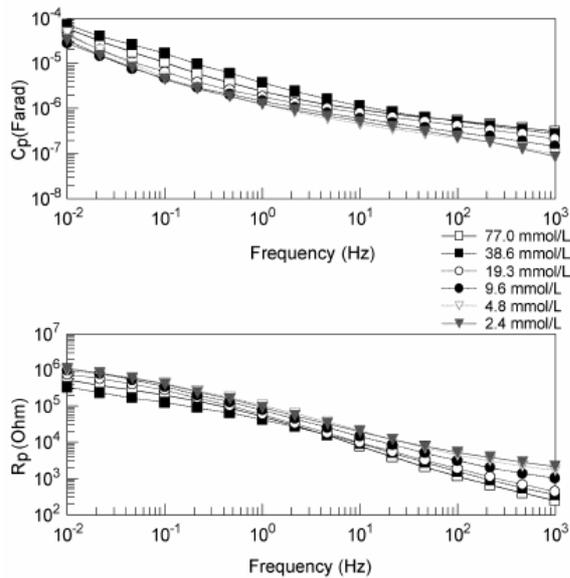


Fig. 8. Polarization impedance for one platinum electrode surface (0.07 cm^2) in 2-77 mmol/l NaCl solutions [9]

Influences of the electrode polarization manifest themselves also in the four-electrode method of measurement. At least three harmful effects can be observed: increase in the impedance of the current electrodes, increase in the impedance of the potential electrodes and variations of the cell constant resulting from the finite size of the potential electrodes. The first effect means the necessity of applying a higher voltage for supplying the current electrodes, the second one – necessity of applying the differential input voltmeter of high input impedance and large CMMR (Common Mode Rejection Ratio) value. These problems are commonly well known [2] unlike the effect of the finite size of the potential electrodes – which therefore needs more detailed explanation here [1].

Two identical potential electrodes, made up of the same material, should generate identical distortions of the potential distribution and hence compensate each other. However, in practice, it is difficult (if at all possible) to ensure the identity of the electrodes. Potential electrodes of large size and large electrode impedances can produce the

potential difference depending on the measuring frequency and on properties (type, concentration) of the measured solution – and therefore the cell constant of such sensor is a function of these factors. This effect was modelled by the author for the four-electrode sensor having stainless steel potential electrodes of width $w = 0.5 \text{ cm}$ and 3.6 cm interelectrode distance, using FEM (Finite Element Method) [1]. The results of this modelling are presented in fig. 9, in comparison with the results of experiments obtained for two identically manufactured copies of the sensor (A and B in fig. 9). Two methods of FEM modelling were applied: the relative method and the combined one (energy method plus relative one). Modelling was performed as a function of the ratio of the polarization resistance to the solution resistance, i.e. R_p/R_e , for different widths w of the potential electrodes. Different values of the R_p/R_e ratio were obtained by changing the measuring frequency. The results presented in fig. 9 demonstrate clearly the previously mentioned influence of the finite size of the potential electrodes on the cell constant value. For the real sensor, with the potential electrodes 0.5 cm wide, the observed variations of the cell constant can be even 10%. Only the sensor with dimensionless potential electrodes has its cell constant value invariant and proportional to the interelectrode distance. That confirms theoretical expectations that it is advantageous to minimize the size of the potential electrodes.

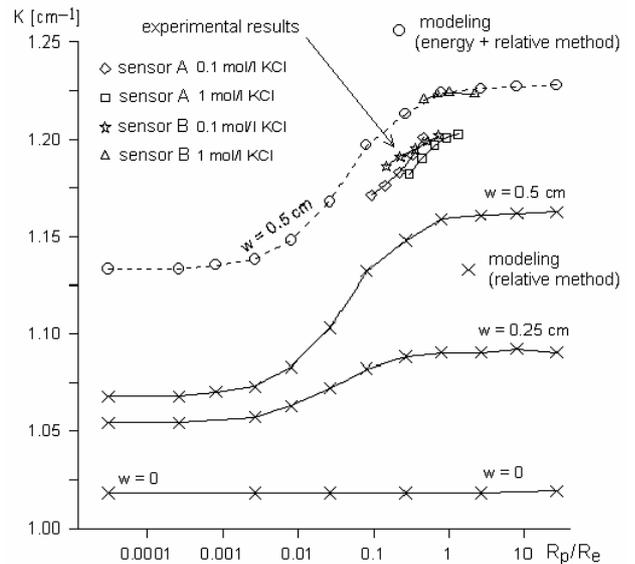


Fig. 9. Variations of the cell constant of the four-electrode conductivity sensor versus the ratio R_p/R_e and the width of the potential electrodes – comparison of the modeled and measured values [1]

3. PROBLEMS ASSOCIATED WITH MINIATURIZATION OF SENSORS

3.1. Polarization error in miniature sensors

Miniaturization of the conductivity sensors requires a cautious approach to their design. Because the measured conductivity is equal to

$$\kappa = \frac{K}{R} \quad (3)$$

the error of its determination, resulting from polarization, can be calculated as

$$\Delta\kappa_p = \frac{K}{R_e + 2R_p} - \frac{K}{R_e} = K \frac{-2R_p}{R_e(R_e + 2R_p)} \quad (4)$$

The relative value of this error is

$$\delta\kappa_p = \frac{\Delta\kappa_p}{\kappa} = -\frac{2R_p}{R_e} = -\frac{2V_p}{V_e} \quad (5)$$

One electrode of surface area S and unit polarization resistance r_p has its polarization resistance

$$R_p = \frac{r_p}{S} \quad (6)$$

therefore the measured sensor resistance is

$$R_s = R_e + 2R_p = \frac{K}{\kappa} + 2 \frac{r_p}{S} = \frac{L}{S \cdot \kappa} + 2 \frac{r_p}{S} \quad (7)$$

and then

$$\delta\kappa = -2 \frac{r_p}{L} \cdot \kappa \quad (8)$$

An important conclusion arises from formula (8) – miniature two-electrode conductivity sensors of the “classic” design (i.e. with the electric field distribution close to uniform) cannot be used for measurement of highly conducting solutions. Assuming electrodes of a given polarization resistance r_p per unit of the area, too small a length L of the current paths makes impossible the reduction of the error caused by electrode polarization to a reasonable value – this is a problem of impossibility of designing such sensors of sufficiently high value of the cell constant and, simultaneously, of sufficiently large electrodes.

Example: considering 0.01 mol/l NaCl aqueous solution at 25°C, measured at frequency 4 kHz using two polished platinum electrodes of unite polarization resistance 4 Ωcm^2 , from formula (8) we obtain $\delta\kappa = -0.8\%$ for $L = 1$ cm and $\delta\kappa = -80\%$ for $L = 0.01$ cm (100 μm). For better conducting solutions the situation will be worse. Therefore, when using the miniature sensor under these conditions, application of the four-electrode method is required. Of course, increasing the frequency will reduce the polarization error.

A possible and feasible solution is applying sensors of such a design that their cell constant value depends on the non-uniform distribution of the electric field rather than on their geometric dimensions. Examples of such designs, in the form of two- and four-electrode planar interdigitated sensors, feasible to manufacture as thin or thick film devices, are discussed in detail in [2] and are shown schematically in fig. 10. The cell constant of such sensors can be estimated theoretically or modelled with an accuracy of the order of 20-30 % [10,2]. The planar conductivity sensors mentioned operate with the “open” (stray) electric field and therefore they have to be used in a sufficiently large volume of the medium if the absolute value of the conductivity has to be determined. When this volume is limited, the application of suitable electrical shields concentrating the lines of the field (current paths) is advisable [1].

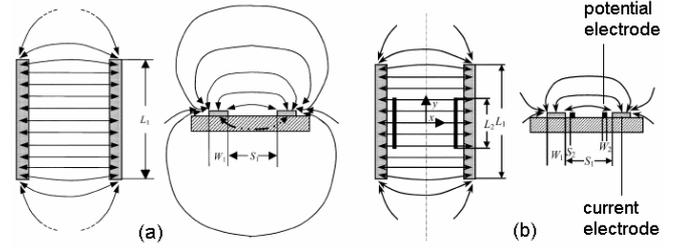


Fig. 10. Top view and side view of planar two-electrode (a) and four-electrode (b) conductivity sensor [2]

At present there are known conductivity sensors, the electrodes of which are provided with a thin insulating film, e.g. from Ta₂O₅. The specific nature of the Ta₂O₅–solution interface provides the electrode with a stable and relatively low impedance [10]. Insulation coating also protects electrodes against dirt, is easy for washing and drying, etc. – however it requires application of higher measuring frequencies

3.2. Instrumental errors

Most of instrumental errors occurring in the conductivity measurements performed using classic “large” conductivity sensors (dimensions in centimetres) will occur when using miniature ones (dimensions of order 10-100 μm), usually more intensively.

Very small electrode surfaces significantly increase electrode impedances. At lower measuring frequencies the current applied to the supplying (current) electrodes produces a much higher voltage drop at the sensor, hence much higher power is dissipated in it and a noticeable effect of self-heating can occur. Simultaneously, the maximum acceptable power dissipation is limited then by the very small dimensions of the sensor. This problem applies to the two- and four-electrode sensors. Hence the measuring current has to be adequately limited. Currents of the order of 10 μA or even lower are applied (higher currents are also undesirable because they could produce excessive current density at the supplying electrodes). Consequently, the measured voltage drops are very low and very good quality, high-gain and low-noise amplifiers are required.

Very high impedances of the current and potential electrodes involve also a necessity of increasing considerably the input impedance and CMMR of the input amplifier used for measurement of the voltage occurring between the potential electrodes. Simultaneously, at higher frequencies a stronger influence of the parasitic stray capacitances can be observed (smaller distances between the leads, thinner insulation, etc. can considerably increase these capacitances). That gets worse given the high frequency characteristics of such measurements.

4. SUMMARY

A demand for accurate microscale conductivity sensors, robust and low-cost (disposable) can be observed in contemporary applications of electrolytic conductivity measurements. It requires a new approach in designing conductometric instrumentation, mainly with regard to the

miniature conductivity sensors but also concerning the co-operating electronics. Such sensors, in the form of two- and four-electrode planar interdigitated ones, feasible to manufacture as thin or thick film devices and integrated with temperature sensors have been developed.

Application of the four-electrode method of measurement is a recognized remedy for avoiding the influence of the electrode polarization in the microscale measurements but it must be applied carefully to avoid (minimize) residual and parasitic effects, especially when the measurements are carried out across a wide range of frequencies.

The problem of the absolute measurement of local conductivities is still unsolved – miniature, well calculable conductivity sensors are still unavailable.

Miniaturization of the electrodeless conductivity sensors is at present not feasible to the same extent as for the electrode ones, however it would be very advantageous for many reasons, e.g. nonoccurrence, in principle, of polarization influences, the possibility of non-invasive local measurements at different depths, etc.

The subject as stated in the title of this paper is too wide for presentation in full in the space available here and therefore this paper should be regarded as an introduction to the problem – further details will be provided in subsequent publications.

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