IMPROVEMENT OF THE SPECIFIC CONDUCTIVITY MEASUREMENTS TRACEABILITY TO PRIMARY STANDARDS OF RESISTANCE, LENGTH AND TEMPERATURE

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Dependence of the specific conductivity measurements on resistance standard, length standard and temperature standard is analyzed. Results of conductivity measurement traceability improving are given. Appropriate constructions of the cell and resistive measuring systems are discussed.

Introduction. Accuracy of absolute specific conductivity measurements today isn't sufficient for many applications. For example, oceanological thermoconductivity measurements have to have very high accuracy (uncertainty less than (0,001–0,002 %). That's why up to now there is no good traceability of ocean measurements to the best primary conductivity standards [1, 2].

Conductivity unit traceability. To reproduce specific resistance or conductivity unit we usually measure resistance (conductivity) of the sample, having well determined dimensions – length and surface of its cross-section. If properties of the material to be measured depend on temperature, the equation below describe result of measurement:

$$g(T_0) = G_x(T)*L/S\ (1+\Sigma\ a_n\ (T-T_o)^n)\quad (S/m),$$

where $g(T_0)$ – specific conductivity for temperature T_0; L and S, – sample length and cross-section surface; T – sample temperature during the measurement.

In conductivity measurements L and S usually are determined by length and inner diameter of the tube, forming the measured solution sample.

Last equation show that measuring system has to measure the following main parameters:

- complex solution conductivity $G_x(T_o)$;
- solution temperature;
- tube dimensions – length L and inner diameter D.

To achieve good accuracy these measurements has to be well traced to three primary standards:

- primary standard of conductivity (RPS);
- primary standard of length (LPS);
- primary standard of temperature (TPS).

Diagram, shown on fig. 1, demonstrate the complex of traces between primary conductivity standard and whole complex of other standards. By this diagram calculated conductivity cell CC has to have dimensions, traced to length primary standard LPS. Uncertainty of this action has to be less than $3\text{-}5*10^{-6}$. Conductivity measuring system CMS measures cell Complex conductivity. Inner resistive standard G_o of the GMS has to be traced to primary resistive standard with uncertainty less than $2\text{-}4*10^{-6}$. In case of cell capacitance measurement GMS has to be traced to the standards of capacitance or frequency ω as well. For accurate temperature measurements usually platinum resistive thermometer (PRS) is used. The temperature measuring system TMS measure resistance of PRS, so that uncertainty of temperature measurement don't decrease $(2\text{-}\ 5*10^{-4})\ ^oK$. To get such accuracy inner resistive standard of TMS has to be traced to RPS with accuracy better than $1\text{–}1.5*10^{-6}$. PRS itself has to be traced to primary temperature standard TPS with uncertainty not worse than $(2\text{-}\ 5*10^{-4})\ ^oK$.

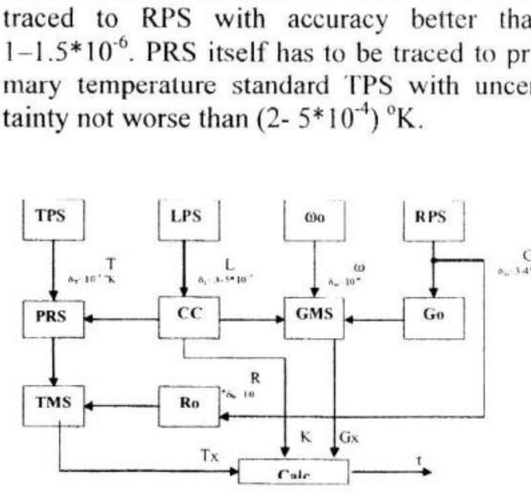


Fig. 1

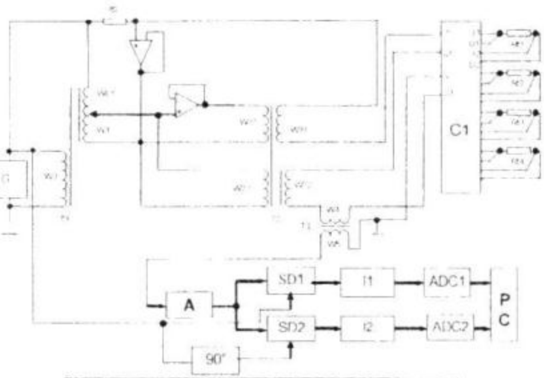
Described system of tracing could ensure enough accuracy of conductivity measurement. Unfortunately, there we meet the lots of problems.

a) It is very difficult to calibrate the cell dimensions with low uncertainty (firstly – inner diameter). In addition, uncertainty of inner diameter measurement determines uncertainty of cell constant calculation with coefficient 2.

b) It is very difficult to measure the conductivity (or resistance) of the cell in wide range of measurement, because of the cell and measuring devise itself have to be highly protected (equivalent diagram of the cell show that measuring sample is connected to measuring circuit through great impedances up to 10 kOhm or more). Stray capacitances of the cell and connecting cables cause increasing uncertainty of the complex conductivity measurement as well.

c) Thermometric measuring system and platinum resistive standard has to have good accuracy of temperature measurement. And here remains the thermodynamic problems as well.

Possible decision of the problems.



$$R_x = R_n \cdot \frac{W_3}{W_2} \times \left(\frac{W_3}{W_n} + \mathrm{Re}\left(\left(\frac{W_{11}}{W_n}\right)_x \times \frac{\dot{U}_n}{\dot{U}_x - \dot{U}_n}\right) \right)$$

Fig. 2

Fig. 2 show the circuit diagram used for conductivity cell and thermometer sensor parameter measurements. It is the transformer bridge, where the object of measurement is connected to measuring circuit by commutator. This bridge ensures good protection of the cell and measuring circuit. Thermostated inner resistive standard has stability better than 10^{-6}. Measurement sensitivity is better than 10^{-7}. Experimental investigations of this bridge have shown that it has enough good metrologic parameter for conductivity unit reproduction taking into account demanded accuracy of the temperature measurements. Inner bridge standard is calibrated by outer resistive standard traced to resistive primary standard. Platinum temperature sensors are traced to primary temperature standard, using developed bridge.

To get high accuracy of the cell constant determination we developed new cell constructions.

One of these cell need for its calibration measurements of length and surface. But to measure the surface we need the measurement of outer diameter only. This cell construction is shown on fig. 3. It consists of two flat plates, caring out the potential electrode (on lower plate) and current electrode together with protecting electrode (on upper plate).

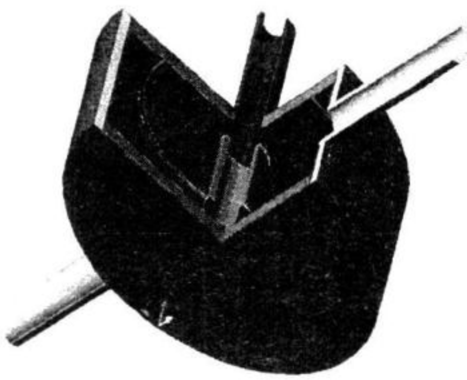


Fig. 3

Between these two electrodes the tube is set. This one carry out on its button ends two thin film potential electrodes, covered by thin film isolation. The constant K of this cell can be easily calculated by equation:

$$K = 4L/\pi(D^2 - d^2) = 4L/\pi D^2 (1 - d^2/D^2),$$

where D diameters of central current electrode; d =outer diameter of central tube; L = distance between potential electrodes.

Last equation shows, that cell constant depends on the outer dimensions only. These ones could be measured by greater accuracy than inner diameter. But it needs three measurements to determine its constant as earlier. It means that uncertainty of the length measurements enter in common uncertainty of specific conductivity measurements multiplied on 3. The constant K of this cell is rather low because of usually the current electrode surface is big and distance between potential electrodes – low.

To measure temperature the platinum thermometer, set into central tube, is used. It ensure good thermal contact between thermometer and solution.

Another construction of the calculated cell is shown on the fig. 4. In this construction the potential electrode is set between adjoining current electrodes divided onto two parts.

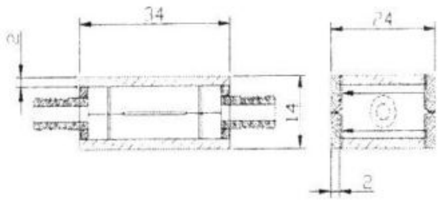


Fig. 4

The same principle is used in the cell, shown on fig. 5. Here the potential and current electrodes are formed as platinum thin film, covering flat electrodes. Potential electrodes are formed as very narrow strip (width around 1–2 μm) set in the middle of adjoining current electrode in such way that gap between them not decrease 2–3 μm. Such cell is useful for conductivity measurements in wide frequency range.

Fig. 5

By its dimensionality, specific conductivity has dimension S/m, i.e. length enter one time only. It means, the cell constant could be determines by one measurement of the length only. To create the cell which could be calibrated by one measurement only the Van der Pauw theorem [4] could be used. This theorem shows how to determine specific resistance by two measurements of resistance and is related to measurement of thin film specific resistance.

Investigators have made earlier attempts to use this theorem for conductivity measurements [5]. Unfortunately these attempts haven't been successful of different reasons.

The conductivity cells, having construction, based on Van der Pauw theorem, are shown on fig. 6 and fig. 7. These two constructions are similar and differ in the used technology only. Construction consists of four prisms, set in such way, that they create central square. This square is covered by two covers – lower and upper (upper one isn't shown on the fig. 6). These four prisms create the central inner square and four lateral ones. Four narrow gaps connect last squares with central one. The surface of lateral squares is covered by platinum. The four thermometric sensors having cylindrical form and covered by platinum are set in the lateral square. This platinum thin film on the thermometric sensors, together with platinum film, covering surface of lateral squares and appropriate gaps between lateral and central squares serves as conductivity electrodes. Solution to be measured fill up the central square through two lateral squares and run out through two another lateral squares.

All prisms and covers have to be manufactured from quartz or another similar stable material, having good isolating properties.

Two resistances of the cell are measured:

– when two adjoining electrodes are used as current one and another ones – as potential electrodes ($R_{AB,CD}$);

– when two another adjoining electrodes are used as current one and next ones – as potential electrodes ($R_{BC,DA}$).

Using these data and the formula given below accurate specific conductivity can be calculated.

The cell constant in this case is equal to tickness of the prisms. This value can be accurately measured. Van der Pauw theorem permits to calculate specific conductivity of the solution using equations:

$$\rho = \frac{\pi L}{\ln 2} \frac{(R_{12,34} + R_{23,41})}{2} f(\frac{R_{12,34}}{R_{23,41}}),$$

$$f(\frac{R_{12,34}}{R_{23,41}}) \approx 1 - A(\frac{R_{12,34} - R_{23,41}}{R_{12,34} + R_{23,41}})^2 - A^2\left(1 - \frac{2}{3}A\right)\left[\frac{R_{12,34} - R_{23,41}}{R_{12,34} + R_{23,41}}\right]^4$$

$$A = \frac{\ln 2}{2}.$$

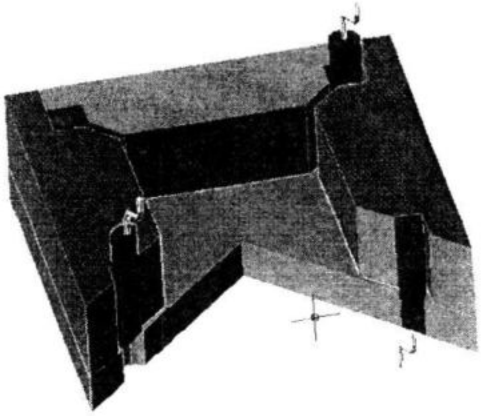


Fig. 6

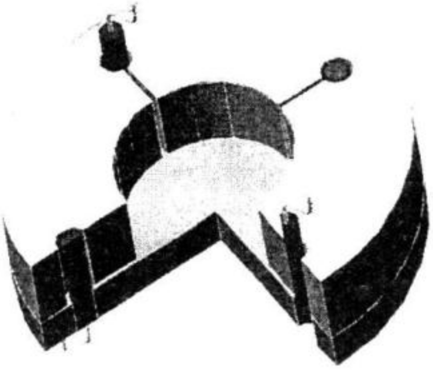


Fig. 7

When $R_{12,34} = R_{23,41} = R_s$ and prisms thickness is L formula above can be simplified

$$\rho = \pi L R_s / \ln 2.$$

From this formula specific conductivity χ of the solution could be written

$$\chi = \ln 2 / \pi L R_s.$$

The temperature in this cell is measured directly in the solution in four points simultaneously. It permits to get not simply temperature of the solution, but its nonuniformity as well. Average of the results of temperature measurement sufficiently increases the accuracy of such measurements.

To create the additional and central spaces here are drilled five holes, connected by gaps.

One of most important requests to measuring circuit consists in influence of the resistance R_G of the solution, which fill gaps. This resistance enter in measuring circuit as common interference. Analysis show that interference resistance ratio to measured vertical or horizontal resistance is given by formula

$$\frac{R_G}{R_S} = \frac{l}{\Delta} \frac{\pi}{\ln 2}.$$

Ratio of the gap wideness Δ the its length l usually is not lower than 3.

In this case the ratio R_G/R_S could achieve 10. If we want to measure R_S with uncertainty, which don't decrease 10^{-5} influence of the interference resistance R_G have to be excluded in 10^6 times. It is the problem, which has to be taken into account during the constructing of the measuring circuit.

Preliminary conductivity measurements using prototype of last cell tip, manufactured from plexiglass, have shown good results (uncertainty less than 300 ppm).

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