Hydrogen sensor development

Tomáš Moucha[1], Václav Linek[1], Adam Bouřa[2], Tomáš Kracík[1]

[1]University of Chemistry and Technology, Prague, Chemical Engineering Dep., Technická 5, 166 28 Praha 6, Czech Republic; tel: +420220443297, e-mail: mouchat@vscht.cz
[2]Czech Technical University in Prague, Faculty of Electrical Engineering, Department of Microelectronics, Technicka 2, 166 27 Prague 6, Czech Republic

1. Summary

In the era of the expansion of hydrogen use, its concentration measurement becomes more important. We further focus on one of the H_2 concentration measurement purposes. To keep optimal process conditions in the primary cooling circuit of nuclear power plants, various chemical species are dosed in. Among the species the concentration of which is monitored in primary coolant, belong oxygen and hydrogen. While a plenty of companies offer oxygen sensors suitable for the measurement in rimary coolant, the hydrogen sensor, really selective to H_2 concentration, is offered by only one company. It is worth, therefore, accomplishing the development of hydrogen sensor, which begun at UCT Prague at 1990's and, after several successful measurements in nuclear power plant, interrupted due to fateful events in the research team. We introduce here the results of the first part of contemporary work of the Mass transfer laboratory based on new technologies but using the experience from 1990's. Having at disposal modern functional sample to measure both oxygen and hydrogen concentrations we would like to cooperate with an industrial partner to finalize the development of prototypes and start the production of monitoring units.

2. Introduction

The need for hydrogen concentration measurement is associated with the hydrogen dosing into the primary circuit in new nuclear power plants (NPP) (as an alternative to the dosing of ammonia and hydrazine). This way is used in some contemporary NPPs of the former "western" countries, while in the NPPs of the former Soviet bloc, ammonia and hydrazine were only dosed. Now, for instance, in The Czech Republic the hydrogen dosage is also planned for new blocks which are to be built. It is, therefore, desirable to have measuring device that is available to provide a feedback in the regulation of hydrogen dosing without any time delay. According to the statement of potential users in energy industry, there is currently no choice on the market in sensors for monitoring the concentration of hydrogen in liquids. In connection with stricter standards for the reduction of corrosion risks in power generation technologies, it is increasingly important to accurately measure in the primary coolant not only the low concentrations of oxygen (fractions of thousandths of air oxygen solubility) but also hydrogen concentrations (up to 3 bars).

Having long-term experience in developing the measurement device for oxygen concentration in NPP primary coolant, we focuse now on the development of hydrogen concentration measurement unit.

The aim of our contemporary work is also to develop the electronics with very low noise level in order to obtain accurate data even when measuring values corresponding with the fractions of per mille of the measuring range. Newly developed apparatus built using modern components, will allow precise measurements of both hydrogen and oxygen, and in the case of oxygen, wider range of applications can be considered, for instance, oxygen saturation of blood or in the area of geological research of groundwater.

3. The principle of the sensor

The hydrogen, amperometric, sensor connected to constant polarization voltage provides a current signal proportional to the concentration of hydrogen in front of the membrane covering the electrode. Hydrogen is transported to the electrode by diffusion through the membrane, with zero hydrogen concentration maintained at the surface of the electrode in the optimum operating mode. The probe operating at the limiting diffusion current provides a linear response to the hydrogen concentration in front of the membrane. The sensor is characterized by a quick response to a step change in hydrogen concentration in front of the membrane (with a first-order response time constant of about 0.2 s^{-1}). The sensor electrodes are located in the common electrolyte-filled compartment. When the electrolyte compartment is properly filled and closed, the probe signal is insensitive to the changes in total pressure in the measured environment (when a constant value of hydrogen partial pressure is maintained).

4. State-of-the-art

The first version of our dissolved hydrogen measurement device, H-meter, was developed in 1990's. The development had been conducted in Mass Transfer Lab at Prague Institute of Chemical Technology (today University of Chemistry and Technology Prague). Several pieces were tested in Czech and Slovak nuclear power plants (NPP Temelin, NPP Dukovany and NPP Jaslovske Bohunice). The tests in 1990's brought the following results.

4.1. Long-term stability tests

The device had been tested for long-term stability in Mass Transfer Laboratory at UCT Prague, the results of which are presented in Figure 1. We can see 2 months' record of the relative H-meter signal **S** when hydrogen concentration in gas phase is measured. Pure hydrogen flows through a measuring cell with the output open to the atmosphere. The fluctuations of the signal correspond with barometric pressure changes (relative values **P**). The pressure-normalized signal **S**/**P** confirms the H-meter reading is stable within the range of 2 % data scatter. In addition, the comparison of **P** and **S** time profiles shows the decay of H-meter signal by 2% approximately, which should be eliminated by the improvement of the long-term stability of the sensor.

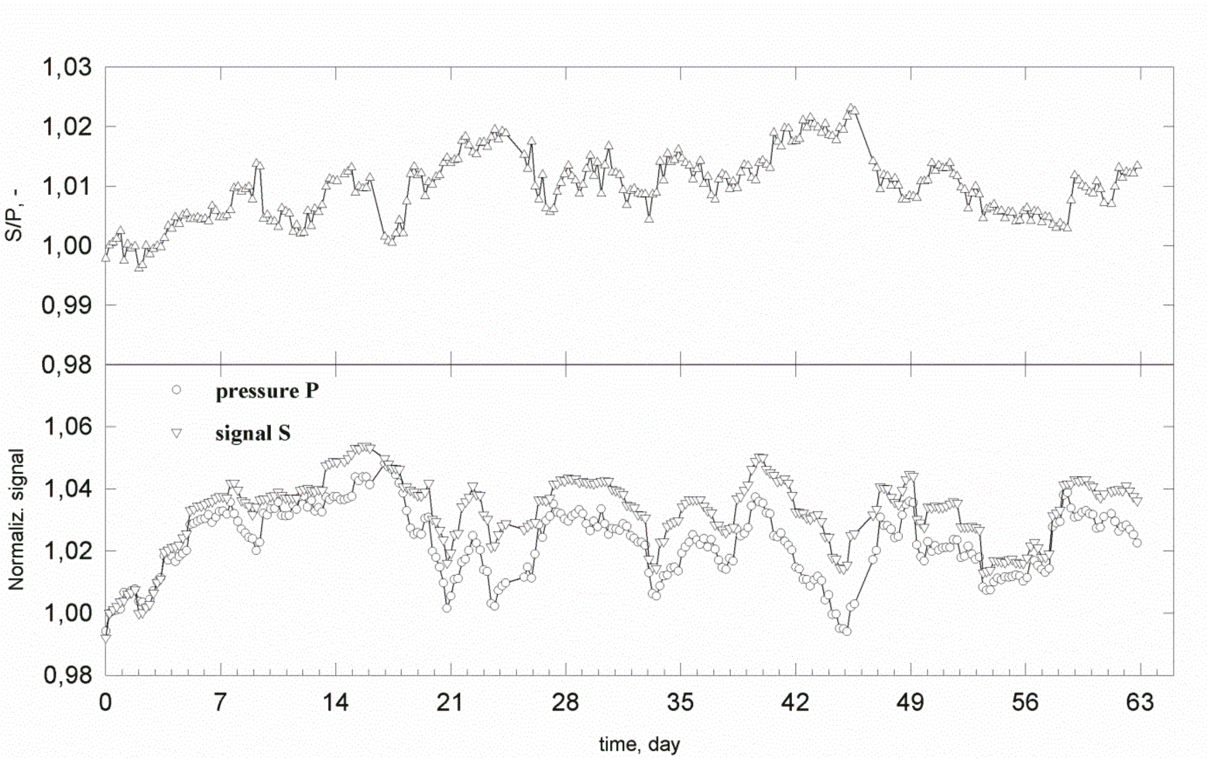

Figure 1: Long-term record of H-meter output during the measurement in gas phase

4.2. Operational tests in nuclear power plant

Measurements were conducted in the NPP Dukovany from the 14th to 22nd September 1999 in RCH305 sampling line. The dissolved hydrogen concentration was recorded simultaneously by two independent devices, to which the sampled primary loop coolant was fed by stainless steel tubes:

i) standard Orbisphere unit Type No. 26415 with dissolved hydrogen sensor Type No. 2231 using 29015A membrane and

ii) H-meter developed at UCT Prague connected to control unit by ASSET for measurement of dissolved hydrogen in the range 0 - 60 Nml/l calibrated by gaseous hydrogen at atmospheric pressure.

Figure 2 shows the data, including sampled liquid temperature, measured in the timespan of 8 days. We can see both devices` data agreement in the range of 5 %. Even if the temperature of the sampled water fluctuated significantly, both devices gave practically the same hydrogen concentrations. It is apparent that both devices properly compensate the temperature effect on the probe signal. In addition, it is seen that H-meter's probe is of significantly shorter response time (time constant about 4.3 s), which enables the usage of H-meter to timely determine an explosive mixture during coolant exchange procedure (oxygen desorption into hydrogen atmosphere)

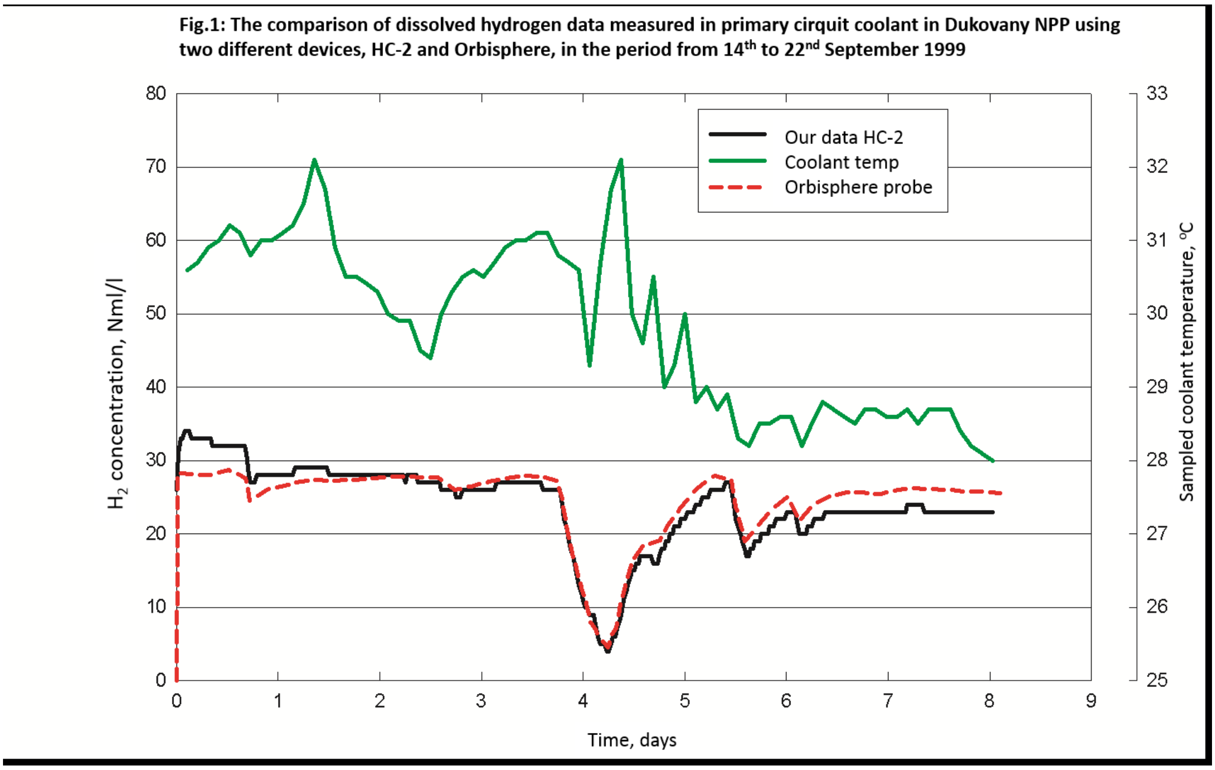

Figure 2: primary coolant hydrogen concentration measured in NPP Dukovany (the legend HC-2 refers to H-meter produced at UCT Prague)

This measurement showed the H-meter ability to measure hydrogen concentration under real operating conditions in NPP primary circuit. Nevertheless, the H-meter signal decay is still seen, which should be fixed during the final period of H-meter development.

The 1990's design of H-meter and the probe are shown in Figures 3 and 4.

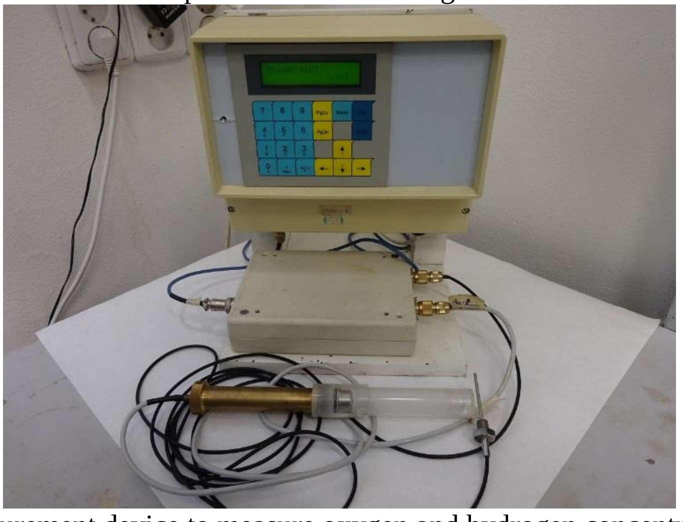

Figure 3: 1990's measurement device to measure oxygen and hydrogen concentration


Figure 4: hydrogen sensor - detailed view of the membrane covered anode and thermometer

5. Contemporary experimental set-up

The sensor has a cylindrical shape with a diameter of 19 mm and a length of 220 mm, with the outer part made of plexiglass. The probe anode is made of a glass stem with a sealed platinum gold-plated contact covered by a polymeric membrane. A silver cathode is placed inside the probe, and the space between the anode and the cathode is filled with a potassium chloride solution. The probe connected to constant polarization voltage provides a current signal proportional to the concentration of hydrogen in front of the membrane. The sensor usually provides a very low current signal (units to fragments of nanoampers; nA), and it is therefore the task of the development of electronics to prevent signal noise in the analog section. Proper shielding and signal processing should be implemented to receive accurate and reliable signal output.

The electronics consists of several sub-circuit blocks that are centrally controlled by an ARM processor from the STM32 family. The electronics contains a block for setting the DC polarization voltage for the sensor in the range of 0 to 2 V, with accuracy better than 1 mV. A low-noise operating amplifier with sufficient current capacity is used to supply the sensor with a current up to 10 mA. The current from the sensor is sensed by the block with a current-to-voltage converter. Due to the magnitude of currents in the nA lines, great emphasis is placed on the converter. The converter is designed with high gain, but it must also be unconditionally stable, i.e. resistant to self-oscilations. It must also be resistant to external interference, which is ensured by sufficient shielding of the circuit and the sensor itself. For further treatment of the sensor signal, the electronics is prepared to include temperature and pressure sensor inputs. It also operates the display unit, keyboard and the data transfer to a PC using USB interface (UART FT232 converter). Figure 5 shows the first version of the new control unit.

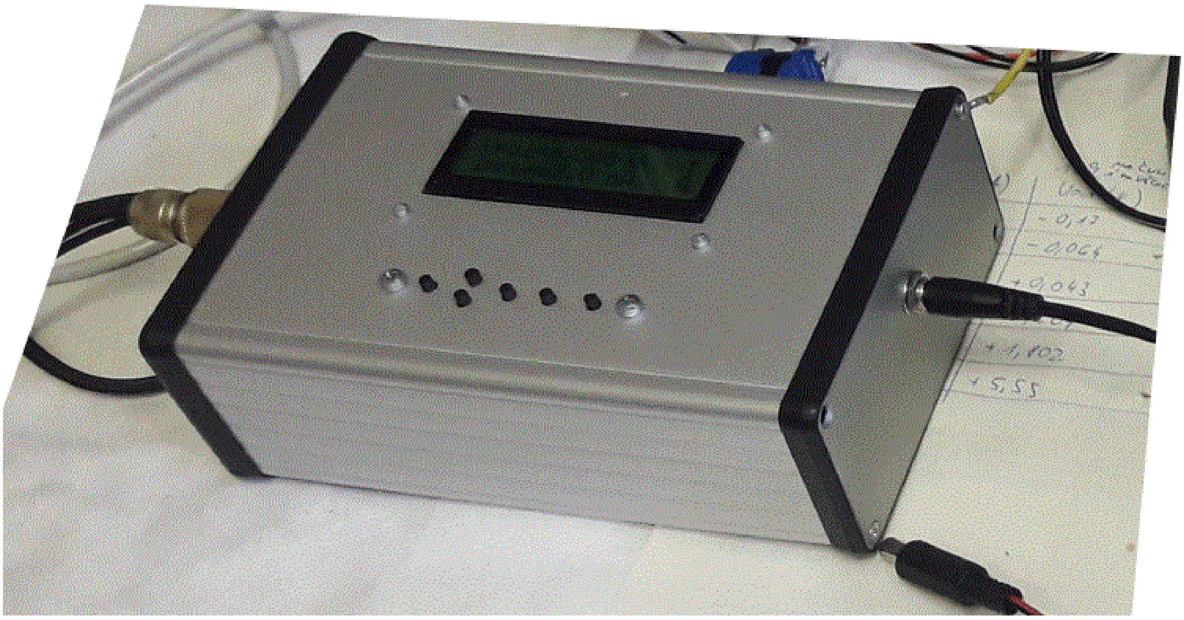

Figure 5: Control unit developed for H-meter

6. Results of the first period tests

After assembling the electronics on a laboratory bench from standard components, and testing the function and levels of noise, the parametric sensitivity of the output signal on the properties of the sensor was tested. After assembling the electronics integrated into the size of a functional sample and testing the quality of basic functions such as feedback sensitivity, noise dependence and electronic magnification settings, first information about hydrogen sensors behaviour were collected.

6.1. Polarograms

Using new prepared sensors, we tested first, when a polarographic plato exists, in which the limiting diffusion current occurs. In this plato the linearity of the sensor with the hydrogen concentration is expected. We found the platos between approximately 0.2 and 0.4 Volts of polarization voltage, as shown in Figure 6.

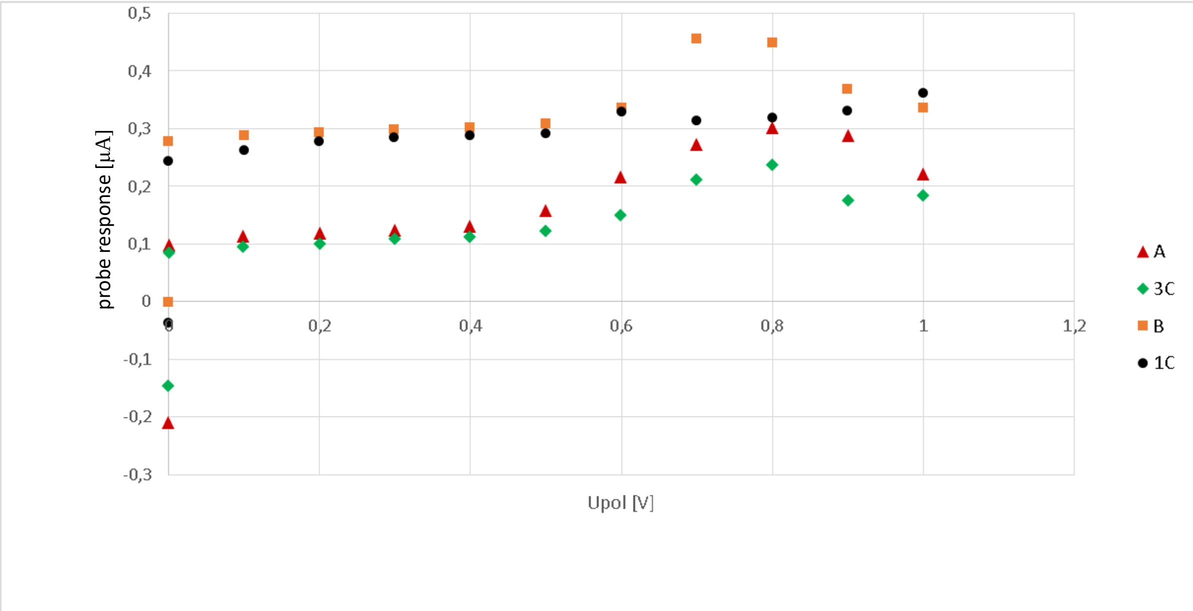

Figure 6: polarograms of the first hydrogen sensors with work marking A, 3C, B and 1C

6.2. Linearity

Using the polarization voltage corresponding with the plato, several sensors have been tested for their reading linearity with hydrogen partial pressure, as shown in Figure 7

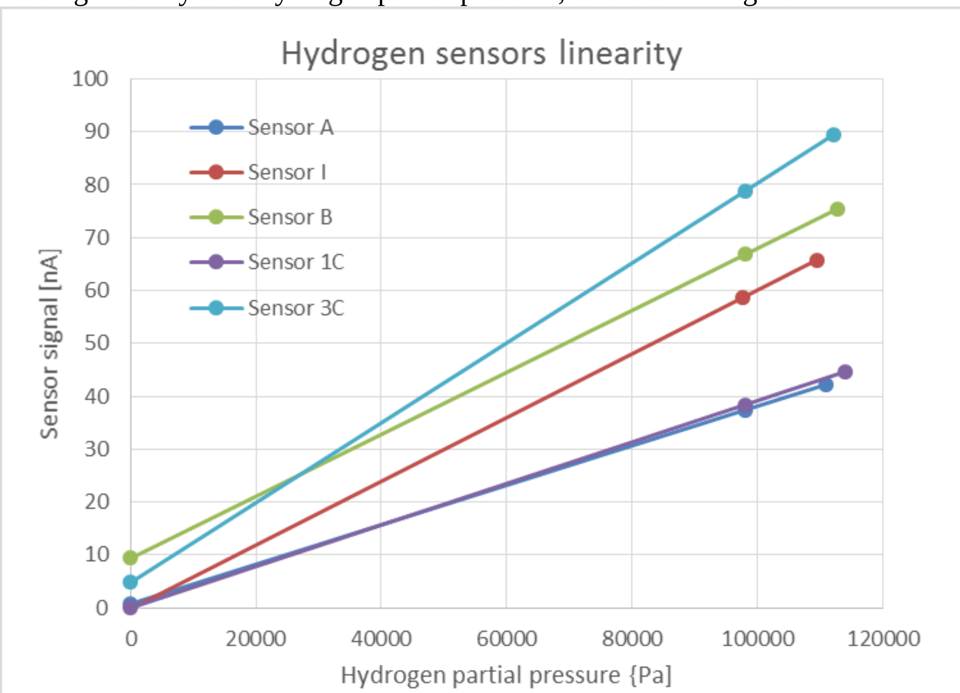

Figure 7: linear dependencies of hydrogen sensors on hydrogen partial pressure

The linearity data were obtained by the exposure of the hydrogen probes gradually to nitrogen stream, hydrogen stream at atmospheric pressure and hydrogen stream at elevated pressure realized by introducing the measuring cell output into a manostat.

6.3. Long-term stability and temperature dependency

During the long-term stability tests, together with H-sensors signal, we also recorded the measuring cells temperature and obtained the data enabling to quantify the temperature dependency of hydrogen concentration signal. An example of such data shows Figure 8.

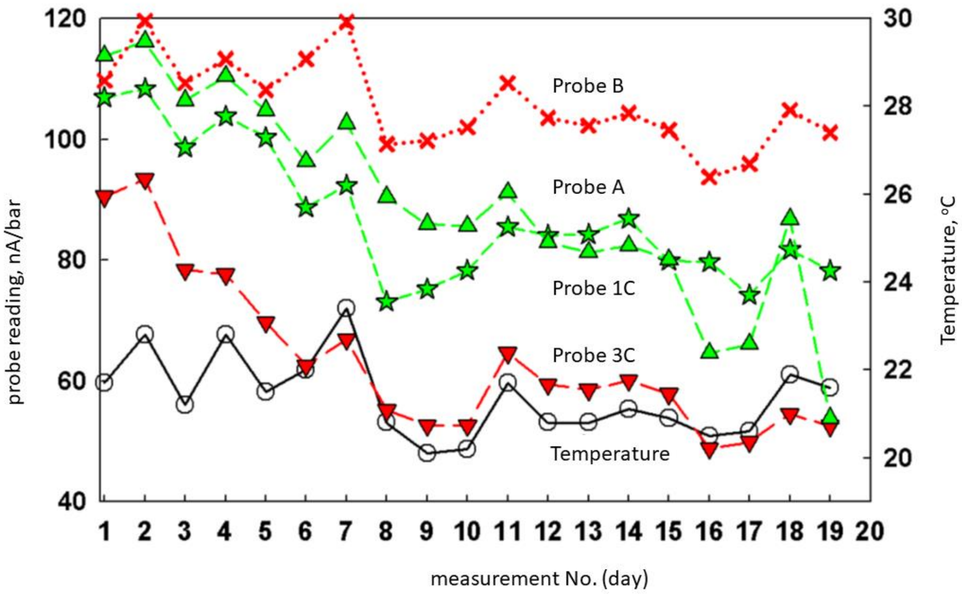

Figure 8: H-sensors signal records illustrating their temperature dependencies, which are quantified now

Further, the long-term stability of the sensors is tested and within the period of more than 100 days the signal stability in the range of 15% is being reached in most cases as **Figure 9** illustrates.

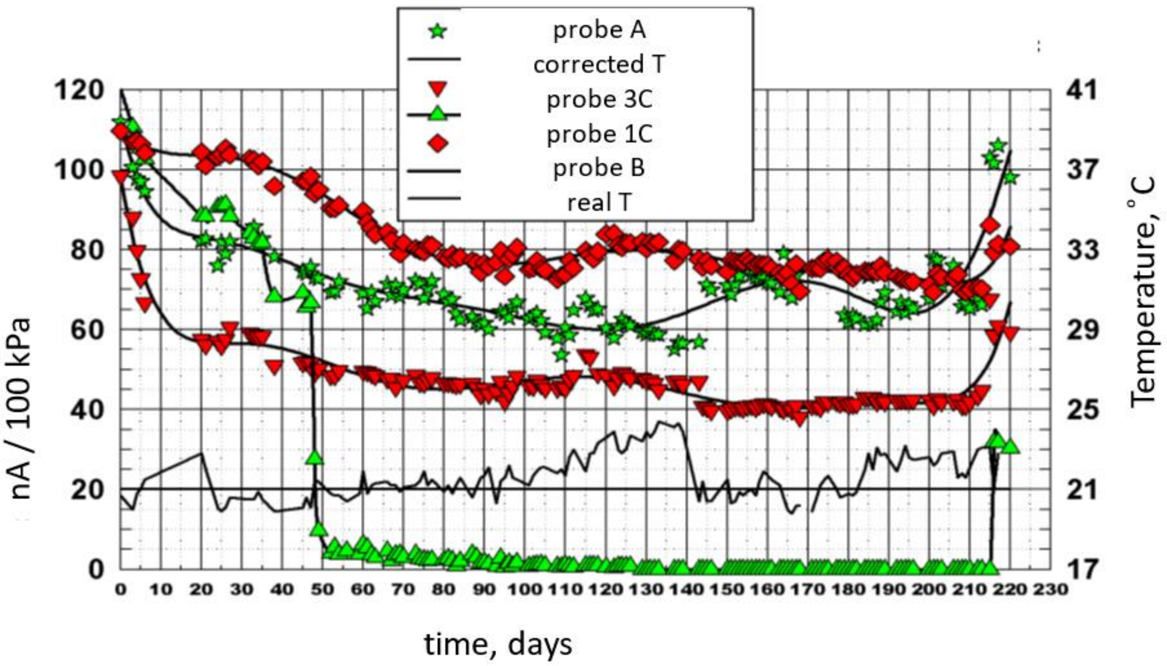

Figure 9: H-sensors signal records illustrating their long-term stability after the initial maturing period, which also includes the signal corrections to temperature fluctuation and polarization voltage change in the end.

7. Conclusions

The first version of new electronics for the control unit of hydrogen concentration measuring device has been developed, built and verified. The polarograms of the first series of hydrogen sensors produced at UCT Prague have been measured, which showed the existence of polarographic platos corresponding with hydrogen electrochemical reaction. The sensors' reading linearity with hydrogen partial pressure has been verified and the data for the quantification of temperature dependency of the sensors' reading were obtained. These preliminary results promise that modern hydrogen sensors can be successfully developed in the Mass Transfer Laboratory at UCT Prague, which will be suitable for hydrogen concentration monitoring in nuclear power plants. We are looking for an industrial partner to finalize the prototype development and to commercialize the product.

8. Acknowledgements

Financial Support by Specific University Research (MSMT No. 21-SVV/2019) and by European Regional development Fund-Project **ORGBAT** No.CZ.02.1.01/0.0/0.0/16_025/0007445 are gratefully acknowledged. The research has also been supported by the project 7D Eurostars grant n° 7D19001 - SACON - Smart Access Control for Smart Buildings.