

# INITIAL RESULTS OF QCM USING FOR HEAVY METALS DETERMINATION IN WATER

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*Abstract* - The electric current can deposit heavy metal ions on the surface of quartz crystal microbalance (QCM) electrode as it is connected to the minus of electric source. The kind of metal deposition from water solution depends on electrode voltage correctly to electrochemical series of metals. The gradual increase of voltage results in progressive deposition of next metal correctly to electrochemical series. The metal deposition results in decrease of resonant frequency of QCM sensor. The inverted process is also possible. The initial deposition of metals and gradual dissolution of them by reverse direction of current results in increase of sensor resonant frequency. The QCM sensitivity is very high. The frequency measurement resolution below 1 Hz, for 10 MHz sensor, results in mass resolution below 3ng. It makes possible ions concentration measurement with resolution below 50µg/L. In Tele and Radio Research Institute the laboratory measurement stand for determination of heavy metal ions concentration was elaborated. The experimental measurements of ions concentration were carried out for Cu and Ni ions in cooperation with Institute of Meteorology and Water Management. The results of these investigations showed possibility to distinguish the kind of metals and determination in range 50 – 10000 µg/L. The results obtained are very promising for analytical measurements.

## 1. INTRODUCTION

The natural water, drinking water and wastes contains different kinds of metal ions in very low concentration from few nanograms to milligrams per liter. Some of them as Na, K, Ca, Fe, are necessary for proper function of human body. Some of them included to so called microelements in low amount are profitable for human organism but in higher amount are poisons. Belong to them the metals as Ba, Cr, Zn and Cu. There are existing another metals which are cumulating in human organism poisons detrimental in any amount. Belong to them Pb, As, Cd, Hg [1,2]. The national and international standards determine acceptable amount of these metals in drinking water. Concentration of metals in water is one of criteria of natural water purity classification. The natural water classes dependence on metal ions concentration according to Polish national standard is presented in Table 1.

TABELE 1

THE WATER CLASSES DEPENDENCE ON METAL IONS CONCENTRATION [3]

Element or ion	Units	Class of purity		
		I	II	III
Cr <sup>+6</sup>	mg/dm <sup>3</sup>	0,05		
Cr <sup>+3</sup>	-,-,-	0,05	0,1	0,1
Zn	-,-,-	0,2		
Cd	-,-,-	0,005	0,03	0,1
Mn	-,-,-	0,1	0,3	0,8
Cu	-,-,-	0,05		
Ni	-,-,-	1,0		
Pb	-,-,-	0,05		
Hg	-,-,-	0,001		
Ag	-,-,-	0,01		
Fe	-,-,-	1,0		

Acceptable concentration of metals in drinking water is presented in tab.2.

TABELE 2.  
ACCEPTABLE CONCENTRATION OF METALS IN DRINKING WATER[3]

<i>Metal or ion</i>	<i>Concentration[mg/dm<sup>3</sup>]</i>
Cr <sup>+6</sup>	0,003
Cr total	0,05
Cd	0,003
Cu	1
Ni	0,02
Pb	0,01
Hg	0,01
Ag	0,01

## 2. THE PROPOSED METHOD

The electrolysis of water solutions of salts causes metals deposition on cathode. The electric current can deposit heavy metal ions on the surface of quartz crystal vibrator electrode immersed in water solution as it is connected to the minus of electric source. The kind of metal deposition from water solution depends on electrode voltage correctly to electrochemical series of metals. The gradual increase of voltage results in progressive deposition of next metal correctly to electrochemical series. The metal deposition results in decrease of resonant frequency of quartz sensor. The inverted process is also possible. The initial deposition of metals and gradual dissolution of them by reverse direction of current results in increase of sensor resonant frequency. The mass of deposited, or dissolved metal will be expressed by equation:

$$m = k \cdot i \cdot t \quad (1)$$

where : m – mass of metal deposited on electrode, k – coefficient of mass deposition, i – current on electrode, t – time of current flow

The mass of metal deposited on quartz crystal electrode will result in frequency diminishing in accordance to equations[4]:

$$m = h_{\text{met}} \cdot \rho_{\text{met}} \cdot A \quad (2)$$

$$\Delta f = \frac{h_{\text{met}} \cdot \rho_{\text{met}} \cdot f_{\text{met}}}{\rho_q \cdot h_q} \quad (3)$$

where : A –electrode area,  $h_{\text{met}}$  – electrode thickness,  $\rho_{\text{met}}$  – electrode material density,  $h_q$  – quartz plate thickness,  $\rho_q$  – quartz density

The current in water solution depends on ions concentration according to equation[5]:

$$i_g = \frac{nFAC_{\text{ox}}^0 \sqrt{D}}{\sqrt{\pi \cdot t}} \quad (4)$$

where:  $i_g$  – current maximum, F –Faraday constant,  $C_{\text{ox}}^0$  - ions concentration, D – diffusion coefficient, A –electrode area, t –time of process, n –ion valence

Presented above equations show the resonant frequency of quartz resonator dependence on ions concentration in solution.

The metal deposition on cathode voltage depends on electrochemical potential of ions. The electrochemical potentials of metals are presented in Tab.3.

TABLE 3  
THE ELECTROCHEMICAL POTENTIALS OF SELECTED METALS [6]

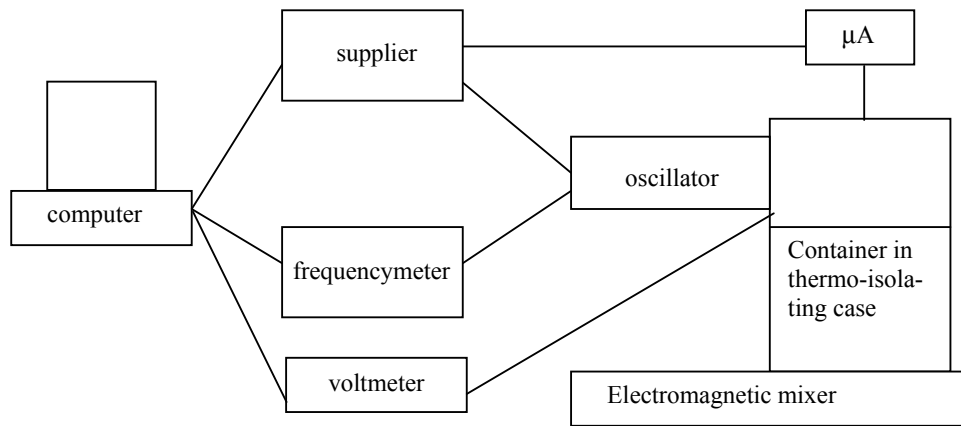
<i>Name of element</i>	<i>Symbol of element</i>	<i>Potential[V]</i>	<i>Reaction on cathode</i>
Manganese	Mn	-1,05	$\text{Mn}^{+2} + 2\text{e} \rightarrow \text{Mn}$
Zinc	Zn	-0,76	$\text{Zn}^{+2} + 2\text{e} \rightarrow \text{Zn}$
Chromium	Cr	-0,71	$\text{Cr}^{+3} + 3\text{e} \rightarrow \text{Cr}$
Iron	Fe	-0,44	$\text{Fe}^{+2} + 2\text{e} \rightarrow \text{Fe}$
Cadmium	Cd	-0,40	$\text{Cd}^{+2} + 2\text{e} \rightarrow \text{Cd}$
Cobalt	Co	-0,28	$\text{Co}^{+2} + 2\text{e} \rightarrow \text{Co}$
Nickel	Ni	-0,24	$\text{Ni}^{+2} + 2\text{e} \rightarrow \text{Ni}$
Tin	Sn	-0,14	$\text{Sn}^{+2} + 2\text{e} \rightarrow \text{Sn}$
Lead	Pb	-0,13	$\text{Pb}^{+2} + 2\text{e} \rightarrow \text{Pb}$
Antimony	Sb	+0,20	$\text{Sb}^{+3} + 3\text{e} \rightarrow \text{Sb}$
Bismuth	Bi	+0,23	$\text{Bi}^{+3} + 3\text{e} \rightarrow \text{Bi}$
Copper	Cu	+0,37	$\text{Cu}^{+2} + 2\text{e} \rightarrow \text{Cu}$
Mercury	Hg	+0,85	$\text{Hg}^{+2} + 2\text{e} \rightarrow \text{Hg}$

Applying proper potential to electrodes it is possible to obtain deposition of selected metals. By gradual change of this potential one can deposit successive metals and determine their concentration in solution.

### 3. EXPERIMENTAL RESULTS

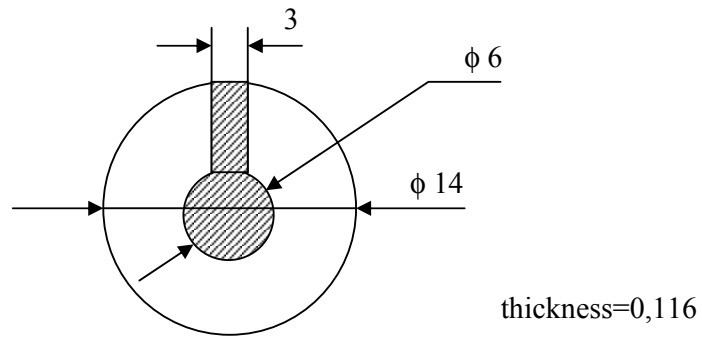
#### 3.1. Design of laboratory stage

The laboratory stage has to be computer controlled. It consist of polypropylene container with volume about 80 cm<sup>3</sup> with gold working electrode, platinum reference electrode, quartz resonator in special case. The container is located on magnetic mixer. The quartz resonator electrodes are connected to special oscillator. The frequency of oscillator is measured by frequency meter. The gold working electrode and the quartz resonator electrode immersed in solution are connected by ammeter to precise voltage supplier. The electrode of quartz resonator and reference platinum electrode are connected to voltmeter. The supplier and the frequency meter are controlled by computer. The data from voltmeter and frequency meter are send to computer. The block diagram of elements of stage and connections between them are presented in fig.1.



**Fig.1. The block diagram of laboratory stage**

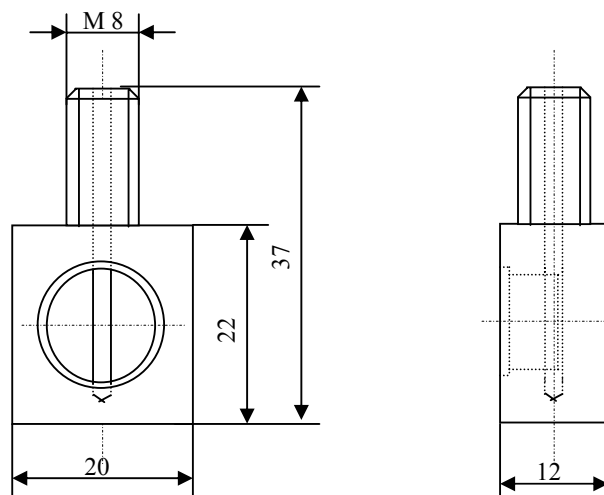
As the mass sensor was used 10 MHz AT-cut quartz crystal vibrator mounted in polycarbonate holder using silicone adhesive. The quartz crystal electrode shape is presented in fig.2.

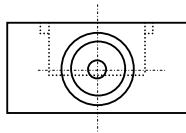


Front and back electrode shape the same

**Fig. 2. The quartz vibrator electrode shape**

The holder construction is presented in fig.3.



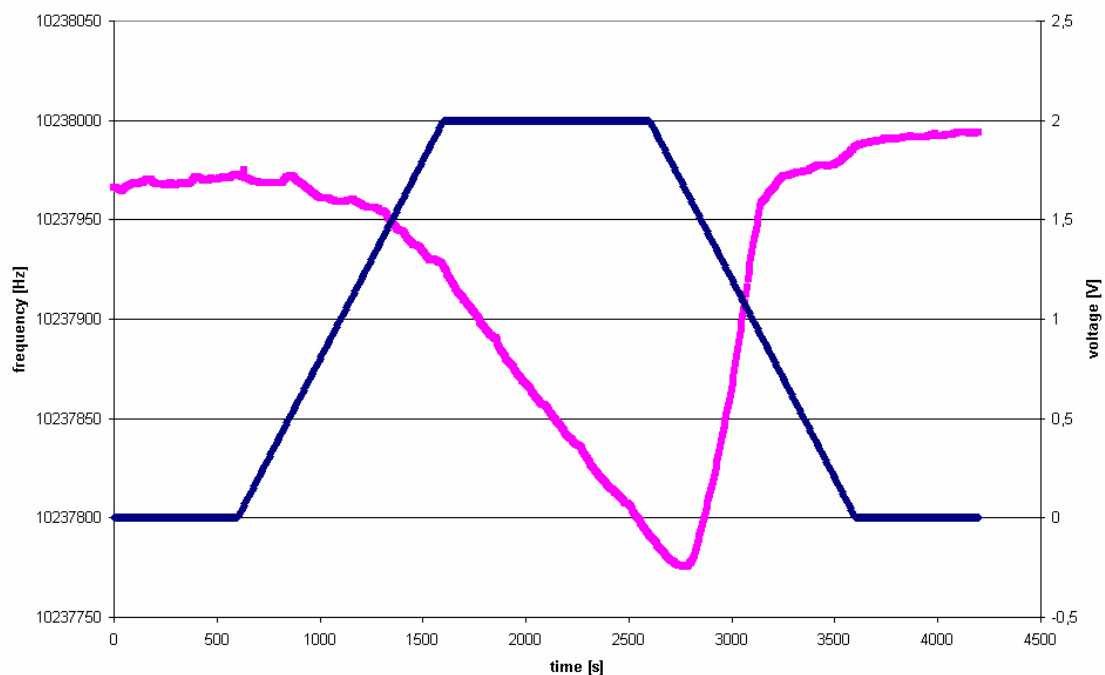


**Fig 3.** *The quartz crystal holder construction*

### 3.2. The measurement cycle determination

At the beginning it was decided the graduated voltage increase till the perceptible frequency diminish will be noticed. Next keeping this voltage till the frequency will stabilize. But the first experiments showed this process to long. For copper concentration in solution  $100\mu\text{g/L}$  it was over 10 hours. It was changed for linear voltage increase to initially determined value. The frequency change and the voltage between quartz crystal electrode and reference platinum electrode were observed. The voltage increase speed was changed in range from  $0,01\text{V/1s}$  to  $0,01\text{V/12s}$ . The pH factor of solution was changed in range  $2\div 7$ .

The example of registered frequency and electrode voltage for copper  $2\text{ mg/L}$  solution with pH  $2,0$ . Is presented in fig 4.



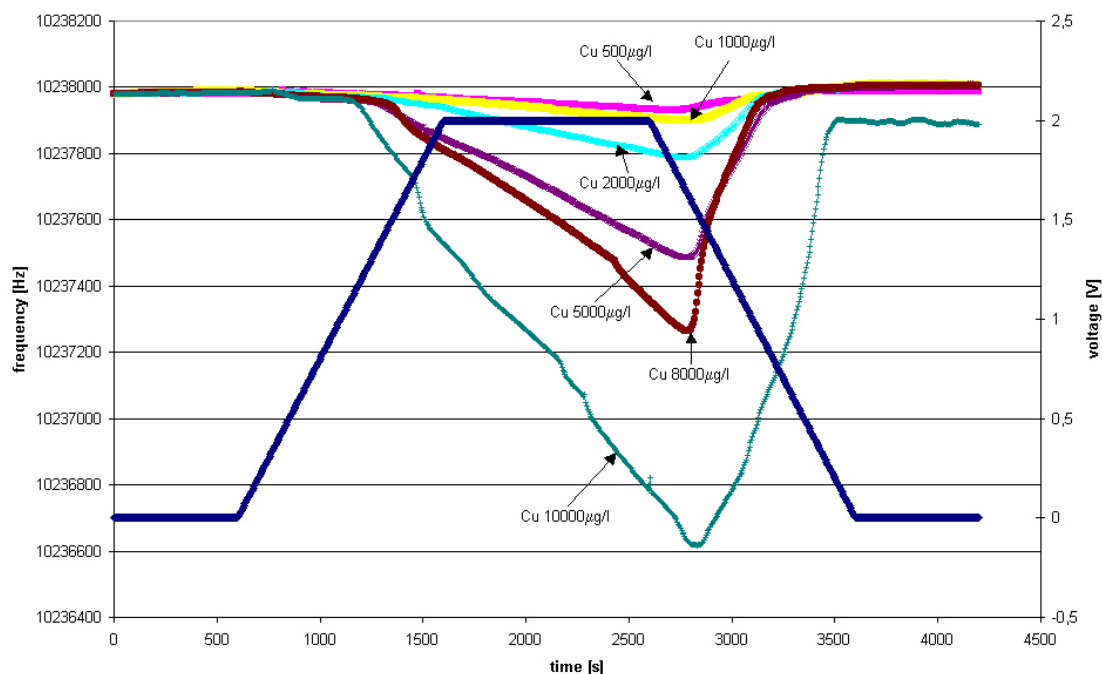
**Fig.4.** *Frequency change during voltage application*

The rapid solving the copper layer from electrode as the voltage was lower than  $1,5\text{V}$  was observed.

### 3.3. The results of seperated ions concentration determination

For this experiment the nitrides of copper, lead and nickel in deionized water solutions were used. The pH factor was stabilized by adding  $\text{HNO}_3$  or  $\text{NH}_4\text{OH}$  solutions.

The results for copper in the range of ions concentration  $0,10\div 10\text{ mg/L}$  are presented in fig.5.

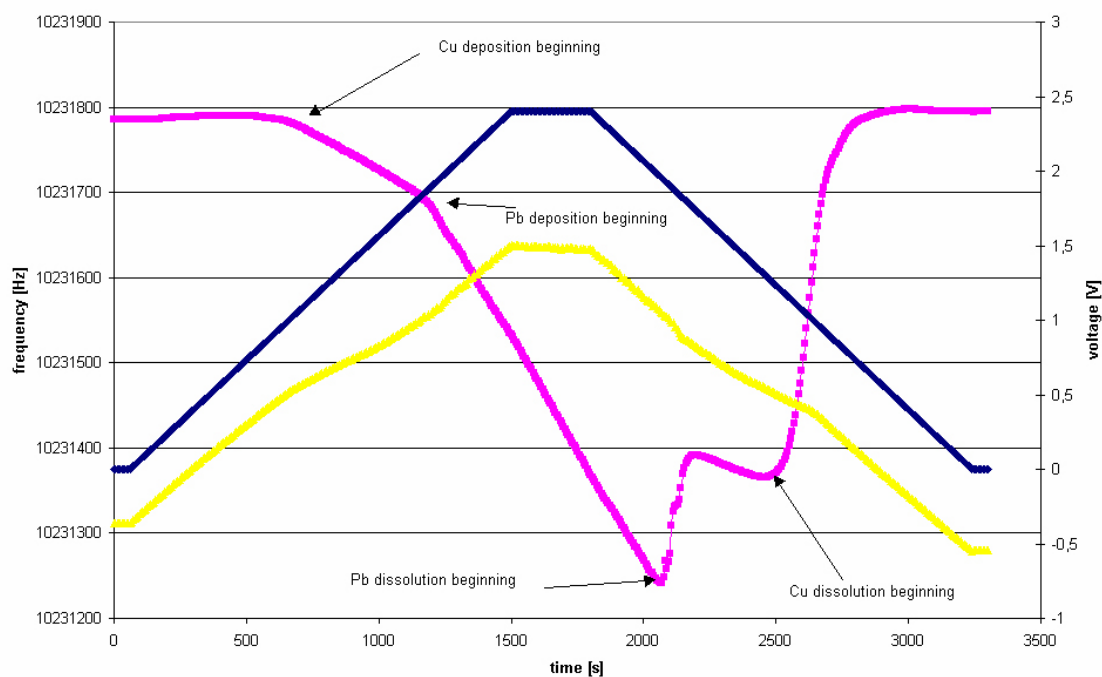


**Fig.5. Copper concentration dependence on frequency changes of mass sensor**

Similar results were obtained for lead. By changes of pH factor and velocity of voltage increase it was possible to obtain the concentration of copper resolution below  $40 \mu\text{g/L}$ . In the case of lead the resolution of  $100 \mu\text{g/L}$  was obtained. In the case of nickel the result was very difficult for interpretation.

### 3.4. The results of ions mixture concentration determination

The experiment was carried out for copper and lead ions with concentration of  $1 \text{ mg/L}$ . The results are presented in fig.6.



**Fig.6. Lead and copper water solution characteristic**

.It was significant difference between shape of frequency changes during process in the case of one ion and mixed ions existence in solution. The voltage of solving both ions are different and it is easy on the basis of this voltage value determination the kind of ion

**5. Conclusions**

In this paper there are presented the initial results of investigation of new method of heavy metals ions determination in water solutions. The results are worse as initially predicted on the basis of theoretical calculation. In the paper there were not described all results of measurements. It was too short time for determining all parameters of process and optimization parameters for any ion of heavy metals but the investigations will be continued. Presented investigations showed only possibility of quartz sensor utilization for these ions determination in water solutions.

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