ORIGINAL PAPER

QUARTZ CRYSTAL MICROBALANCE: NANO-SENSOR FOR CYANIDE DETECTION

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Abstract. *The extremely high level of potassium cyanide toxicity makes its effects to be important even in low concentrations. Quartz crystal microbalance (QCM) allows the determination of these values due to the high sensitivity of resonant crystal frequency. The sensitivity of the method increases with the alkaline pH values and for this reason in this study it has used two sets of solutions with pH 9 and 12. The obtained experimental results lead to the conclusion that the QCM method can be successfully used to obtain an accurate quantitative and qualitative analysis of cyanides in drinking water in real time.*

Keywords: *quartz crystal microbalance, cyanide, sensor.*

1. INTRODUCTION

Cyanides include a wide range of compounds with high or less complexity, but all contain a CN^- ions or groups (inorganic, respectively organic compounds). In this respect, the humans are exposed to the natural sources but mostly to anthropogenic sources (chemical manufacturing and processing industries, such as metallurgical industries and metal plating, and extraction of gold and silver from low-grade ores, the volatilization from cyanide wastes disposed of in landfills and waste ponds, emissions from municipal solid waste incinerators, biomass burning, fossil fuel combustion, including vehicle emissions, fumigation operations, and the production of coke or other coal carbonization procedures) [1].

The principal features of the toxicity profile for cyanide are its high acute toxicity by all routes of administration, with a very steep and rate-dependent dose–effect curve, and chronic toxicity, probably mediated through the main metabolite and detoxification product, thiocyanate. The toxic effects of cyanide ion in humans and animals are generally similar and are believed to result from inactivation of cytochrome oxidase and inhibition of cellular respiration and consequent histotoxic anoxia [1].

The recent methods used for cyanides detection include usual methods, such as, visual detection, spectrophotometric, colorimetric, fluorimetric, electrochemical techniques, but today especially, capillary electrophoresis, chemiluminescence, atomic absorption spectrometry, and gas chromatography-mass spectrometry are applied [2].

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Some of detection methods present a number of disadvantages such as requiring large sample sizes, long analysis times, high detection limits, and poor precision, largely due to interferences. The current methods involve laborious preparation stages and require significant special skill and training [3].

The proposed method to determine and to monitory the cyanide concentration in drinking and fresh waters is based on the piezoelectric sensor.

Quartz Crystal Microbalance (QCM) has found numerous applications in many fields including thin-film measurement, chemical analysis, gas sensor, humidity sensor and biosensor [5]. Especially, the development of QCM systems for use in fluids or with viscoelastic deposits has dramatically increased the interest towards this technique [6].

QCM has many advantages over the traditional sensing methods such as high sensitivity (up to nanograms level), noninvasiveness, long-term measurements, and free labels. It has a wide detection range from a monolayer of small molecules to much greater masses-even complex arrays of whole cells.

The focus of this study is to provide a single analytical sensor for cyanide studies. The developed detection system provides rapid cyanide determinations with little sample preparation or instrument supervision [4].

2. EXPERIMENTAL

The high sensitivity and the real-time monitoring of mass changes on the sensor crystal make Quartz Crystal Microbalance (QCM) a very attractive technique for a large range of applications. The quartz crystal microbalance is an extremely sensitive sensor capable to measure the mass changes in the nanogram/cm^2 range with a wide dynamic range extending into the 100 μg/cm^2 range. The sensibility depends by the detector area and the type of solid electrode in contact with the fluids [5-7].

The experiment is performed with a QCM200 (Stanford Research Systems) equipped with a controller, oscillator QCM25, crystal support, flow cell (Fig. 5), peristaltic pump (Fig. 6), and SRFQCM200 software, under LabView, as well.

The QCM sensor is composed by a quartz plate covered with metal electrodes. The used standard sensor crystal (Fig. 1) consists of a thin disk at 5-15 MHz resonant frequency, AT-cut (Fig. 2), α-quartz with circular electrodes patterned on both sides (Fig. 3).

Fig. 1. Quartz crystal.

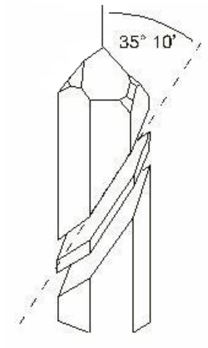


Fig. 2. AT-cut mode.

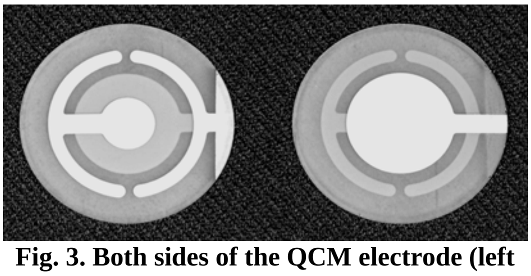


Fig. 3. Both sides of the QCM electrode (left side – in contact with the oscillator and right side – in contact with the liquid).

Quartz Crystal Microbalance technique was chosen for cyanide ions analyses because of obvious advantages, such as: very fast analysis, the results are shown in real-time, require a small quantity of sample, present a higher limit of detection etc. The prepared samples are passed from the flow cell (Figs. 4 and 5) and if the sample has cyanide, the CN$^-$ will remove a gold quantity from the surface of Chromium-Gold (CrAu) electrode in according with reaction (1).

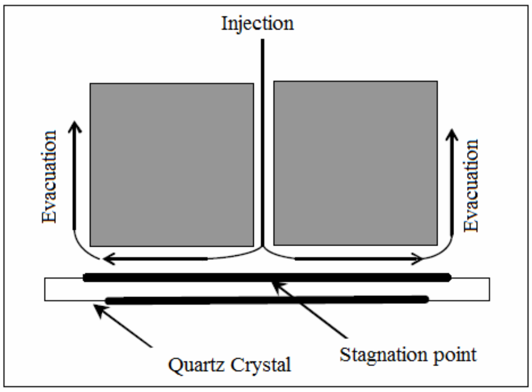


Fig. 4. Schematic representation of the Flow Cell.

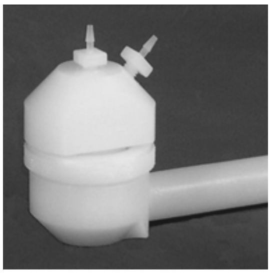


Fig. 5. Flow cell.

Fig. 6. Peristaltic pump.

Therefore the sensor response is a frequency shift directly proportional with mass of gold removed, according with *Elsner reaction* [8]:

$$4Au + 8CN^{-} + 2H_2O + O_2 \rightarrow 4Au\left(CN\right)_2^{-} + 4OH^{-} \qquad (1)$$

The higher or lower pH value of the solution influences the measured data. For this reason, must be adjust the pH of the solution to a well determined value.

Another factor which influences the measured data is the flow rate. It is recommended to set a flow rate less than 0.5 mL/min.

It is known that cyanide may exist in aqueous solutions in a variety of forms including hydrocyanic acid (HCN) and cyanide ion (CN^-). Hydrogen cyanide and free cyanide ion are in equilibrium in aqueous solution according to the following equation [9]:

$$\mathrm{CN^{-} + H_2O \rightarrow HCN + OH^{-}} \qquad (2)$$

The sample preparation involves dissolution of potassium cyanide (KCN) in distilled water at different concentrations such as 0; 0.2; 0.5; 1 and 2 ppm. The 9 and 12 pH values of the samples were corrected with KOH (20%). It is chosen these values of pH for study because for the pH values 9 and 12 was obtained a good repeatability (Fig. 7) in according with literature data [3].

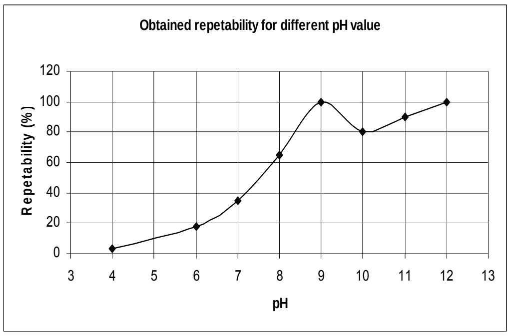


Fig. 7. Repeatability of measurements for different value of pH.

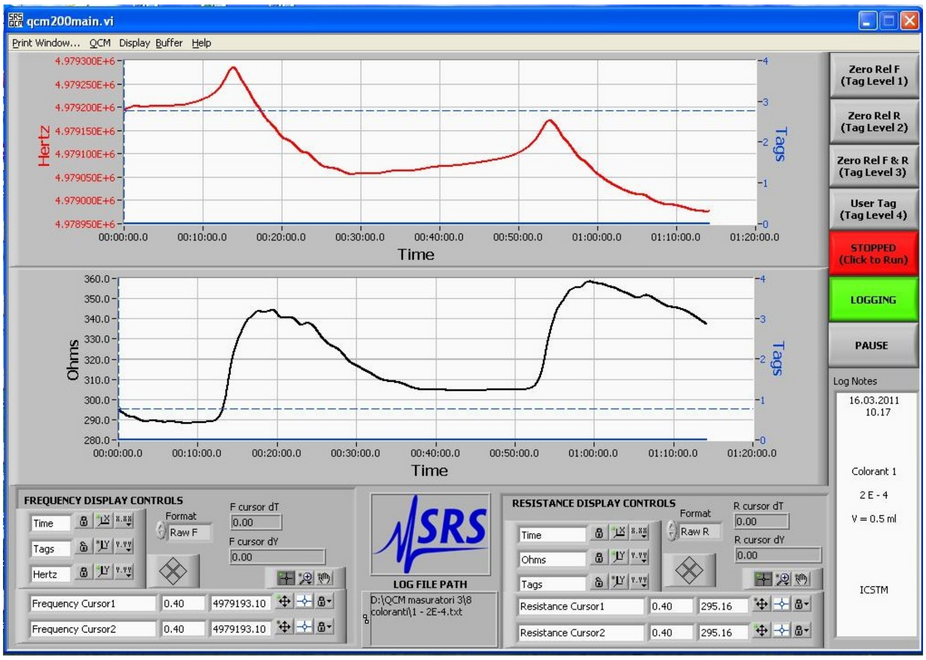
Therefore, it was measured the frequency shift for all 10 samples, for 5 minutes with 0.2 mL/min flow rate. After measurements it was calculated the inhibition coefficient (I_x) with the equation (3):

$$I_x = \frac{\Delta F_0 - \Delta F_x}{\Delta F_0} \tag{3}$$

where: ΔF_0 is the frequency shift in the absence of cyanide and ΔF_x is the frequency shift in the presence of cyanide.

3. RESULTS AND DISCUSSION

The SRSQCM200 software display in real-time the frequency shift and the resistance shift on the computer monitor (Fig. 8). The frequency shifts for analyzed samples are presented in Figs. 9 and 10. Calibration data, presented in Fig. 11 (cyanide analysis at pH 9), show a good linearity over a large range of concentrations with the squared linear correlation coefficient of 0.91798 and an error about 17.72%.



Log Notes
16.03.2011
10.17

Colorant 1

2 E - 4

V = 0.5 ml

ICSTM

Time
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Hertz
Format: Raw F
F cursor dT: 0.00
F cursor dY: 0.00

Frequency Cursor1	0.40	4979193.10
Frequency Cursor2	0.40	4979193.10

LOG FILE PATH: D:\QCM masuratori 3\8 coloranti\1 - 2E-4.txt

Time
Ohms
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Format: Raw R
R cursor dT: 0.00
R cursor dY: 0.00

Resistance Cursor1	0.40	295.16
Resistance Cursor2	0.40	295.16

Fig. 8. Image captured from display.

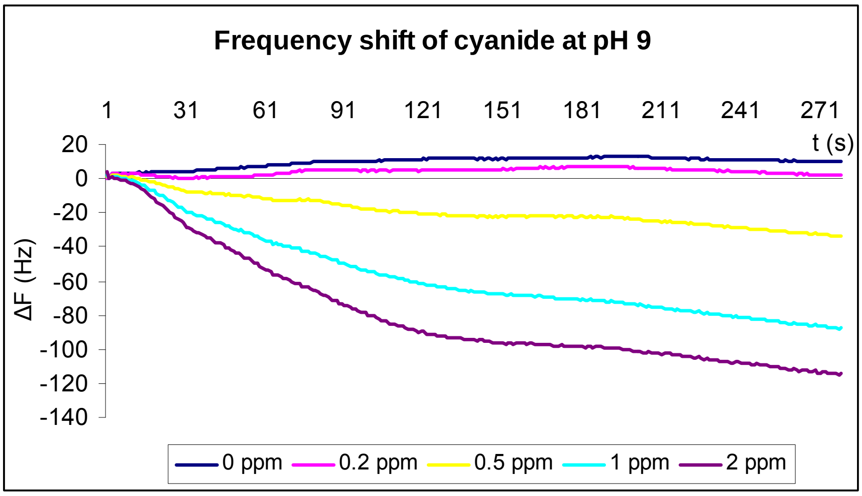

Fig. 9. Frequency shift of cyanide at pH 9.

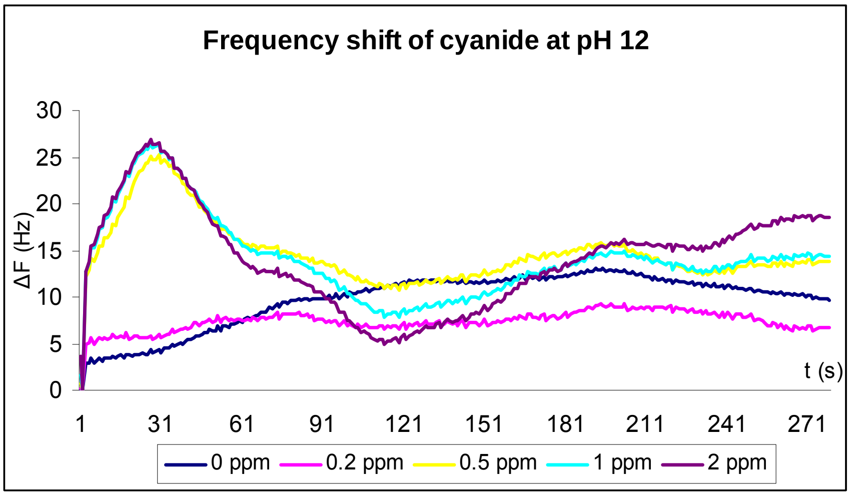

Fig. 10. Frequency shift of cyanide at pH 12.

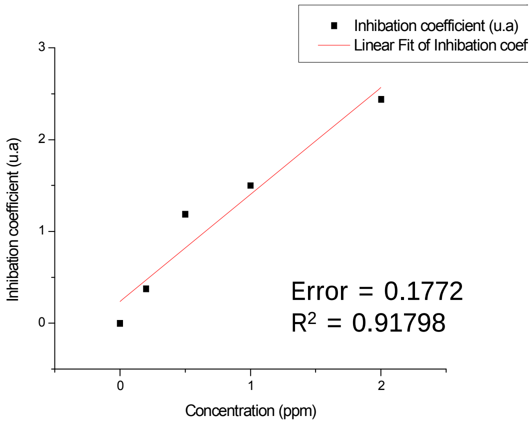

Fig. 11. Calibration curve for cyanide at pH 9.

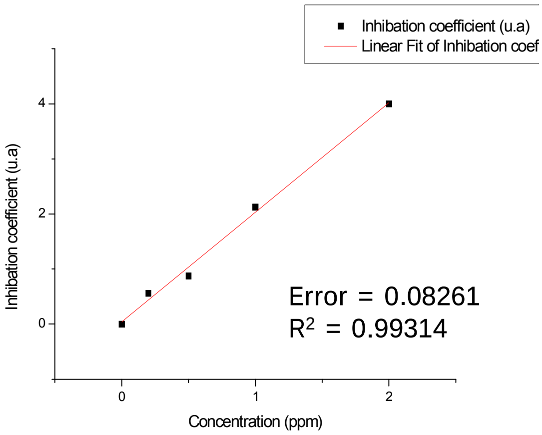

Fig. 12. Calibration curve for cyanide at pH 12.

The linearity of cyanide analysis at pH 12 (Fig. 12), is much better than the first case (pH 9), concerning the squared linear correlation coefficient (R^2=0.99314) and the error (8.26%).

Therefore, the variation of signal with pH demonstrates that whatever the chosen pH value for analysis, must to be constant to be obtain accurate results.

Moreover, this study confirms that the system has the ability to be incorporated into an automated, online, real-time monitoring system for both immediate response and continuous monitoring. This system offers a unique opportunity for user customization to various applications.

The parameters which affected the performance and sensitivity of the system can be easily adjusted in order to produce optimal analysis times and reproducibility, depending on individual requires of the desired analysis. Reliable analysis of aqueous cyanide in the ppm concentration range can be obtained in less than 5 min and this is a very important advantage for the analysis.

4. CONCLUSIONS

This is the first part of the study because research has continued to analyze the amount of gold bounded in cyano-auric complex by Atomic Absorption Spectrometry with graphite furnace. If prepared solutions contain gold at ppm or ppb concentration can be explained if in drinking or fresh water exist cyanide ions and consequently is a danger for life.

In this paper, was presented a cyanide detection method suitable for drinking and fresh water, which offers many operational advantages that should allow it to be a widely accepted routine monitoring system.

The analytical device is simple to operate and does not require special analyst skills. When following the described methodology, little or no sample preparation other than pH adjustment is required.

The system is primarily sensitive to the same aqueous cyanide species that exhibit toxicity to aerobic organisms. This correlation makes the sensor especially attractive for applications aimed at safety and security. However, the QCM method is faster and needs a little sample volume.

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