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Easy detection of chloroform in drinking water by quartz crystal microbalance sensor

İçme sularındaki kloroformun kuvars kristal mikroterazi sensör ile kolay tespiti

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Abstract

In this study, two different surface modification methods have been tested for easy detection of chloroform, which is harmful to human health in case of excess in the mains water, with a Quartz Crystal Microbalance (QCM) sensor. In the first coating method, acidic and basic solutions of 3-mercaptopropyltrimethoxysilane (MPS) in ethyl alcohol were applied respectively. In the second coating method; Acidic MPS was applied in the first step and then surface modification was completed using 2-mercaptoethanol (ME). In Coating-1, average frequency shifts of -180(±30) Hz, -200(±40) Hz and +40(±10) Hz were recorded for acidic MPS, basic MPS and 10 ng mL chloroform, respectively. In Coating-2, chloroform molecules formed covalent bonds with thiol groups and the mean frequency shifts obtained for acidic MPS, ME and 10 ng / mL chloroform were -180(±30) Hz, -80(±15) Hz, and -70(± 8) Hz, respectively. According to empirical results, coating-2 method provided a better surface modification than coating-1 method. Resonance frequency shifts of -2.5(±1), -12(±4), -70(±8) and -356(±87) Hz respectively were obtained at chloroform concentrations of 0.1, 1, 10, and 100 ng/mL by using QCM sensor modified with MPS + ME.

Keywords: *Chloroform, Quartz crystal Microbalance, Surface modification, Drinking water, Biosensor*

Özet

Bu çalışmada, şebeke suyunda fazla bulunması halinde insan sağlığına zararlı olan kloroformun Kuvars Kristal Mikroterazi (QCM) sensör ile kolay tespiti için iki farklı yüzey modifikasyonu yöntemi denenmiştir. İlk kaplama yönteminde, 3-Merkaptopropiltrimetoksisilan'ın (MPS) etil alkol içerisinde sırasıyla asidik ve bazik solüsyonları uygulanmıştır. İkinci kaplama yönteminde ise; ilk aşamada asidik MPS uygulanmış ve daha sonra 2-Merkaptoetanol (ME) kullanılarak yüzey modifikasyonu tamamlanmıştır. Kaplama-1'de, asidik MPS, bazik MPS ve 10 ng/mL kloroform için sırasıyla -180(±30) Hz, -200(±40) Hz ve +40(±10) Hz ortalama frekans kaymaları kaydedilmiştir. Kaplama-2'de, kloroform molekülleri tiyol grupları ile kovalent bağlar oluşturmuş ve asidik MPS, ME ve 10 ng/mL kloroform için elde edilen ortalama frekans kaymaları sırasıyla -180(±30) Hz, -80(±15) Hz ve -70(±8) Hz olmuştur. Ampirik sonuçlara göre, kaplama-2 yöntemi, kaplama-1 yönteminden daha iyi bir yüzey modifikasyonu sunmuştur. MPS + ME ile modifiye edilmiş QCM sensör kullanarak, 0.1, 1, 10 ve 100 ng/mL kloroform konsantrasyonlarında, sırasıyla -2.5(±1), -12(±4), -70(±8) ve -356(±87) Hz rezonans frekansı kaymaları elde edilmiştir.

Anahtar kelimeler: *Kloroform, Kuvars kristal mikroterazi, Yüzey modifikasyonu, İçme suyu, Biyosensör*

1 Introduction

Chlorine is the most preferred disinfectant for water sources. Unfortunately, such unwanted chemicals, typically known as disinfection byproducts (DBPs), pollute drinking water. Trihalomethanes (THMs), a group of four organic chemicals, are a product of the reaction of disinfectants (such as chlorine) with. inorganic and organic matter in water. The constituents of THM are bromodichloromethane (BDCM), tribromomethane (bromoform), trichloromethane (chloroform) and dibromochloromethane (DBCM) [1]. THM, the most common form of chloroform, is formed when chlorine that was initially meant for water treatment reacts with the organic compounds present in a water sample.

Since chloroform is known to be poisonous, genetic mutation and cancer causing, significant health problems are produced by municipal waters over-treated with this agent. There are both temporal and persistent adverse effects of chloroform. Damages associated with the reproductive and nervous system have been reported for high exposure to chloroform. The carcinogenic effects of chloroform have been shown in several studies, including human lesions, skin and lung diseases, when exposed to chloroform through drinking water or inhalation [2-4]. It is critical to make a specific measurement and quantify it quickly and easily.

The Environmental Protection Agency (EPA) listed the cancerogenic chemical as Group B2 in 2003 and recorded the maximum appropriate amount of 22 ng/mL. The most chosen techniques for the qualitative and quantitative evaluation of chloroform within detection limits of 0.1-0.002 µg/L, 0.23-0.45 µg/L, 0.02 µg/L are gas chromatography, solvent extraction [5], membrane isolation and electrolytic conductivity detector techniques [6]. Nevertheless, in order to improve sensitivity and avoid interference, these methods require sophisticated planning and the use of additional chemical agents.

Different analytical approaches are currently also available, such as high-pressure liquid chromatography (HPLC) with 1 to 100 ng/mL of detection range [7], and gas chromatography / electron capture detectors (GC / ECD) with 0.02 [8] - 0.1 ng/mL of detection limits [9]. However, these approaches require highly trained professionals, complicated systems, and costly instrumentation. The application of these approaches to a quick and systematic field study is therefore considerably difficult [10, 11].

The most readily available high-precision under-development approaches relative to commercial methods are electro-chemical analysis [12], optic techniques [13], surface plasmon resonance (SPR) sensor [14] and nanoparticle-based sensors [15]. Among the several detection methods

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published, Quartz Crystal Microbalance (QCM), which is a piezoelectric mass sensor, was chosen to determine the most optimal surface functionalization technique for the detection of chloroform in drinking water.

QCM is one of the most suitable sensor systems for the real-time, rapid and early identification of chloroform in municipal water treatment facilities with high precision, lower price and sensitive detection in the ng/mL range employing promising surface modification techniques.

A commercially available procedure, such as QCM, which is commonly recognized as an efficient method of detection for the detection of chloroform at very low concentrations in drinking water samples, may indicate the most suitable surface alteration for the determination of chloroform. It also has the ability to eventually enable the development of an electrochemical in situ detection sensor.

As a consequence, the fact that chloroform is a world-class carcinogen that impacts the wellbeing of hundreds of millions of people around the world makes the high-level exposure of chloroform in drinking water an immediate concern to the public health. This study uses the QCM sensor to assess chloroform levels, an appropriate candidate with fast, real-time, specific and early sensing properties because of the long-term cancer causing properties associated with health and long-term health effects. It is also aimed at evaluating the most effective approach for surface alteration. In parallel, morbidity and mortality rates due to acute and chronic chloroform toxicity will decrease dramatically due to the fast and precise detection potential of chloroform.

2 Materials and method

Two different methods were used for coating (Table 1.). Surface functionalization for chloroform detection on the gold surface is carried out in an acidic medium using 3-Mercaptopropyl trimethoxysilane (MPS - 95%, Sigma-Aldrich) while MPS (95%, Sigma-Aldrich), 2-Mercaptoethanol (ME-99%, Merck) were applied in basic medium; and all the steps of surface modification and chloroform (99,5%, Merck) detections were electrically monitored. Measurements were taken using the Gamry eQCM 10M instrument (Gamry Instruments, Warminster, United States). Circular, symmetrical quartz crystals of equal diameter (4mm) on both surfaces with AT-cut, gold-plated with a basic resonance frequency of 5 MHZ are used.
In the pre-preparation step, chemicals were added in the ratio of 33 % DIW (V/V) + 33 % Sulphuric acid (V/V) (97 %, Sigma Aldrich) + 33 % Hydrogen Peroxide (V/V) (35 %, Merck) to prepare a piranha solution.

Table 1. Tested surface modification methods

Coating #	First Modification	Second Modification	Analyte
1	Acidic MPS	Basic MPS	Chloroform
2	Acidic MPS	ME	Chloroform

The prepared piranha solution was taken into a 5 mL beaker, and the surface of the sensor was organically cleaned in a beaker for 5 minutes. Next, the sensor was then passed through deionized water and ethyl alcohol, respectively.

Coating-I step was carried out after completion of the cleaning step. This stage initially involved the application of 3-Mercaptopropyltrimethoxysilane (MPS) in an acidic medium. MPS was subsequently applied in a basic medium. Afterwards, surface modification was carried using 2-Mercaptoethanol (ME). In both coating methods, the sensor surface was activated using MPS hydrolysis at pH=4.5 and condensation at pH=9.0.

The thiol groups of MPS in acidic ethanol solution are bonded onto the QCM gold surface through the thiol-gold interaction. The methoxy groups on the captured MPS molecules and free MPS molecules are hydrolyzed (exchange of a silane group with a silanol) in aqueous ethanol solution with a pH of 9.0. The hydroxyl groups condense among themselves in the coating process to form a layer on the gold surface. The condensation of hydroxyl groups on free MPS molecules and hydroxyl groups on this layer continues and an upper layer of thiol groups is formed on the surface (Figure 1.a). The sensor surface was exposed to chloroform molecules in both experiments.

In Coating-II a combination of acidic MPS coating and ME connection was used. The hydroxyl groups on the surface MPS molecules begin to condense with the hydroxyl group of the next bonding ME molecule and this condensation forms a tight coating on the surface of the gold (Figure 1.b).

The prepared solution was applied to the sensor surface for 30 min using a closed loop flow with a peristaltic pump at a flow rate of 200 µL/min. Each experiment was carried out repeatedly for a minimum of 3 times to obtain the average and standard deviations of the frequency shift. The experimental setup and block diagram of the coating stages are given in Figure 1.c and 1.d, respectively.

As a target, 0.1, 1, 10, and 100 ng/mL of Chloroform sample solutions were prepared by using a 500 mL drinking water brand from Turkish bottled drinking water market. The experiments for investigating the coating quality were carried out by using 10 ng/mL Chloroform samples. In the dose-response experiments after the determination of the best coating, four different concentrations of Chloroform were used in at least 3 repetitive trials for each concentration.

3 Results and Discussion

The most commonly used methods for functionalization of sensor surfaces include covalent bonding and adsorption. There severally demonstrated practical application of detection with adsorption for numerous sensors [16, 17].

In the study, it is aimed to produce chloroform determination in drinking water On-site, reliable, sensitive solution suitable for surface modification and produces results within a short detection time (30 minutes) under non-specific binding for chloroform determination in drinking water. For this purpose, the studies are divided into two parts. The first part consists of conducting experiments and recording the results; the second part is the processing of the data. The processing of the data for Coating-I and Coating-II was performed separately

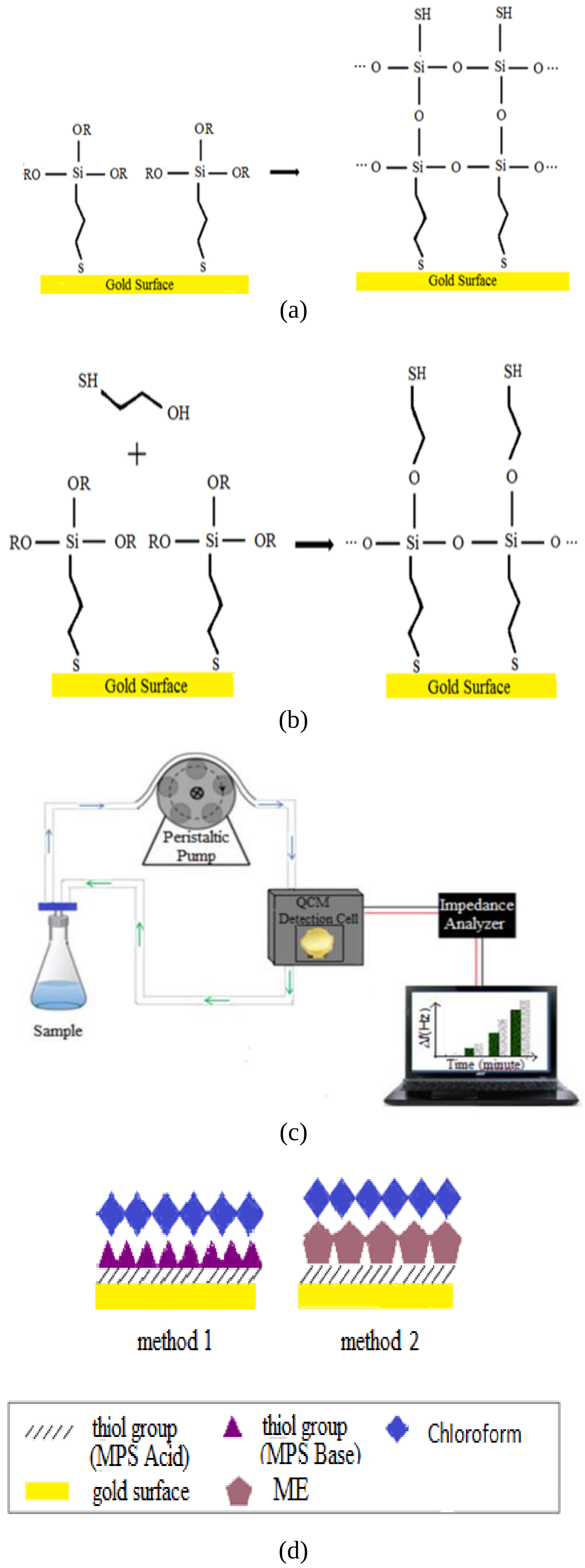

Figure 1. Illustrations of a) coating-1, b) coating-2, c) the detection setup, and d) the surface modification methods

Coating-1 is dependent on the acidic and basic MPS coating of the gold surface. In this study, the development of thiol groups after basic MPS coating for the capture of chloroform was taken as a basis. In the basic coating solution, the hydrolyzed MPS molecules form a solid, self-assembled monolayer and end up with sidewards compact OH groups and vertical non-compact OH groups on the gold surface [18]. Due to the pH sensitivity of MPS, if the appropriate pH can not be balanced, it can form a mobile surface structure, resulting in less surface thiol groups [19]. To remove irregularities due to the higher pH and temperature sensitivity of MPS, acidic MPS immobilization was carried out in Coating-2 as a monolayer on the floor. Then, easy ME at pH = 9.0 was used to form properly oriented thiol groups on the sensor surface.

The test results of the coatings are given in Figure 2 and Figure 3, respectively. The coating-I procedure, which recorded the average frequency shifts of 180 (± 30) Hz, 200 (± 40) Hz and 40 (± 10) Hz for acidic MPS, basic MPS and chloroform, respectively. Also, it was observed that the chloroform molecules failed to bond with the thiol groups leading to an inverse and undesirable shift. For the coating-II experiments, the chloroform molecules formed covalent bonds with the thiols groups, and the recorded average frequency shifts for acidic MPS, ME and chloroform were 180 (± 30) Hz, 80 (± 15) Hz and 70 (± 8) Hz, respectively. It was confirmed that these numerical values observed when the resonance frequencies for both coatings were calculated using the Sauerbrey Equation, yielded very concordant results. Additionally, from our experimental results, coating-II method offered a better gold surface modification than coating-I method for the QCM sensor.

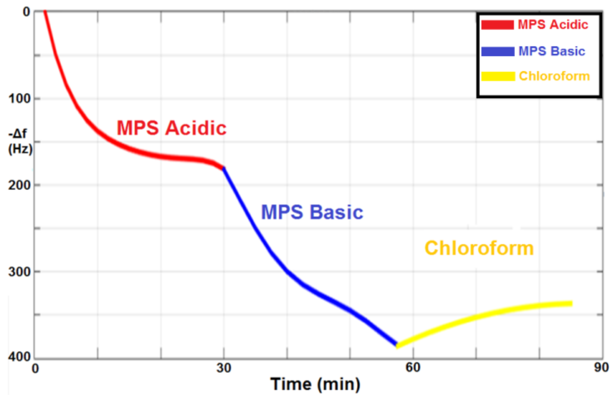

Figure 2. Frequency changes of Coating-I steps and Chloroform detection

The influence of receptors on chloroform detection during the control and detection process in erratic and fluctuating frequency changes was examined by surface modification assays (Coating 1, 2). Chloroform binding to the surface has improved the efficacy of identification. With sufficient receptor orientation, ME provides a higher detection sensitivity level. When unpaired two-tailed t-Test was applied to the results of chloroform detections, Coating 2 indicated a significant preference for chloroform detection (M = 70, SD = 8) than Coating 1 (M = 40, SD = 10), $t(4) = 4.0575$, $p < .001$

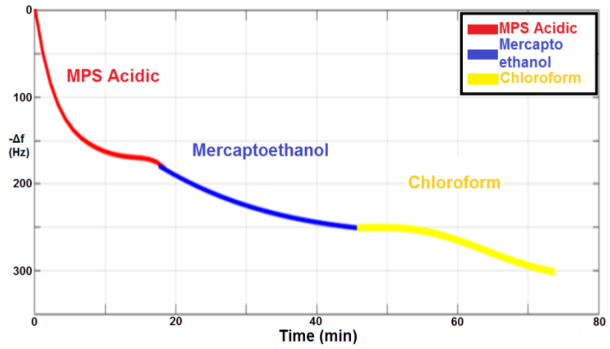

Figure 3. Frequency changes of Coating-II steps and Chloroform detection

In Figure 4, it has been reported that 0,1 (±0.02) Hz frequency shift for the absence of chloroform, 2.5 (±1) Hz frequency shift for 0,1 ng/mL mL of chloroform, 12 (±4) Hz frequency shift for 1 ng/mL of chloroform, 70 (±8) Hz frequency shift for 10 ng/mL of chloroform, and 356 (±87) Hz frequency shift for 100 ng/ mL of chloroform were observed in the dose response experiments in drinking water. When unpaired two-tailed t-Test was applied to the dose-response results of chloroform detections for the negative control and the lowest concentration, the result of 0.1 ng/mL chloroform indicated a significant preference for chloroform detection (M = 2.5, SD = 1) than the negative control (M = 0.1 , SD = 0.02), t(4) = 4.1561, $p < .001$.

The other approaches, with the exception of Nie et al. (2015) [20], include complicated, tricky, and time-consuming chemical surface alteration procedures. In light of the performance of our surface modification technique, the limit of detection and linear range of this analysis can be further strengthened by using a sensor platform with a wider detection range.

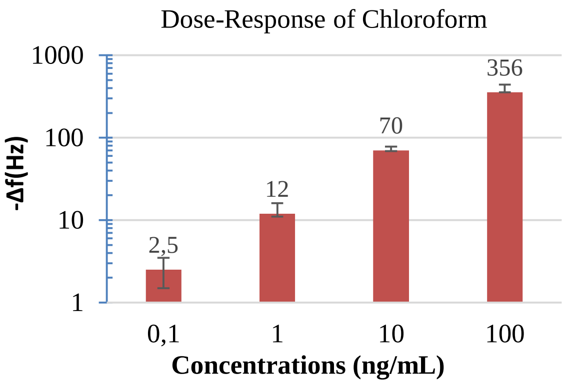

Figure 4. Dose-response results with average resonance frequency changes of Chloroform detection with Coating 2

4 Conclusion

In summary, for sensitive chloroform detection in the detection limit range between 0.1 and 100 ng / mL, we have created a new methodology for gold surface functionalization that is simple, fast and durable. Coating-2 exhibited superlative quality and sensitivity in drinking water among the two distinct coating processes studied.

Since MPS is pH sensitive, if the required pH can not be set, it builds an elastic surface morphology, which results in far less surface thiol groups after coating-1. Few changes in resonance frequency confirm that chloroform molecules are not easily bound by acidic MPS and simple MPS coating, whereas frequency shifts indicate surface bonding. In contrast with the other method, coating-1, the ME technique with higher reliability and response was found to be the most efficient method for the precise determination of chloroform in drinking water samples. Therefore, a novel chloroform determination approach that sensitively detects in a much shorter period can be established for field analysis by the combination of the surface functionalization technique reported in this study and a sensing technology with a broad linear range. Furthermore, this chloroform assessment method may be used for studies in the future from different water supplies exposed to excess amounts of chloroform.

Similarity score (iThenticate): %19

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