Selective determination of potassium ions by SPR based molecularly imprinted sensor

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Abstract. Novel potassium ions imprint polymer sensor were successfully prepared by applying a facile combination of a reversible addition chain transfer mechanism (RAFT) and surface plasmon resonance (SPR). UV photopolymerization in synergy with 2-methyl-2-[(dodecylsulfanylthiocarbonyl)sulfanyl]propanoic acid (DDMAT) as a chain transfer reagent was employed for film synthesis on an SPR sensor chip for the detection of potassium ions using ethylene glycol dimethacrylate (EGDMA) as a cross linker. The modified surface of the sensor was characterized by contact angle measurements, frontier transfer infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The results of potassium ion imprint polymer film showed a high adsorption capacity and excellent selectivity in comparison to other analogues and non-imprinted polymer (NIP) film. Through 5 adsorption–desorption cycles, the high recoverability of MIP film was confirmed. Consequently, within the concentration range of 10^{-15}-10^{-5} mol/L, the coupling angle change of SPR versus the negative logarithm of concentration showed excellent linearity: R^2 = 0.98. Based on a linear equation, MIPs showed excellent values for the limit of detection (1.6x10^{-16}M). Furthermore, it was also used to detect potassium ions in real sample, and in the tap water it showed high recovery and low detection limit. Hence, potassium ions imprint polymer film in combination with an SPR sensor chip demonstrated potential applications for rapid and highly effective sensing even in tap water.

1. Introduction
Potassium; main cation in intracellular fluid is vital element which plays an important role in animals and plants. Potassium ion is the main cation in the intracellular fluid. 98% of potassium in the body is present in the cells, and both myocardium and neuromuscular need a relatively constant potassium concentration to maintain normal stress. [1] Potassium ions are related to many physiological and pathophysiological processes in the human body, too much or too little potassium can cause diseases [2]. Increase in K^+ ion concentration triggers abnormal heart beat and arrhythmias. [3,4] Whereas decrease in k ion concentration can cause various nervous disorders along with mental instability. [5] Therefore, it is necessary to find a fast, simple and sensitive method to measure the potassium ion level.

Currently, there are many ways to detect potassium e.g. electrochemical method,[6-9] colorimetric detection method, [10] fluorescent method, [11,12] and responsive hydrogel method.[13,14] Although each method has its own advantages, but some problem do exist such as complicated production process, high cost, and low sensitivity and so on.

Generally, Molecularly Imprinted Polymer (MIP) is made by copolymerizing the functional monomer and cross-linker with the target analyte as a template molecule.[15] Then removal of the
template molecules from the polymer will expose the cavities which are complementary not only in size and shape but also in the interaction point and the coordination range of the template molecules.[16] Therefore, MIP has the advantages of simple synthesis, pre-designed recognition and high selectivity along with has a wide range of applications.[17] In contrast, ion-imprinted polymers (IIP) are similar to MIP and retain all the advantages of MIP, but their templates are ions or ion complexes.[18-20] Previously, similar work has been reported in literatures to make ion-imprinted polymers in order to selectively recognize Hg^{2+}, Cd^{2+}, Rb^+, Zn^{2+}, K^+.[21-26]

Based on the advantages of MIP, it has received continuous attention and has been widely used in solid-phase as well as micro-solid-phase extraction, chromatography science and chemical biosensor research. Surface Plasmon Resonance (SPR) sensors are popular because of high sensitivity, simple sample preparation, low cost, fast measurement ability, high repeatability, the ability to monitor dynamic behavior, no label detection and non-destructive detection.[27] At present, there is considerable work on SPR sensor, using SPR optical detector to detect various substances,[28,29] explosives,[30] hormones,[31] and metal ions.[32-35] Facile combination of MIP and SPR lead to effective design of chemical sensors which is evidenced by past research.[36-39]

Although there have been many reports on potassium imprints,[25,26] precipitation polymerization method was used in their research. This method is complicated and time-consuming, and it is difficult to achieve high efficiency and rapid detection. And there are some articles using SPR to detect ions,[32-35] there are fewer articles using MIP and SPR to detect potassium ions. In addition, the polymerization method used to prepare potassium ion imprint polymers in present work is reversible addition-fragmentation chain transfer polymerization (RAFT). Compared with Atom Transfer Radical Polymerization (ATRP), RAFT polymerization has the advantages of mild reaction conditions, a wide range of functional monomers and can synthesize well-defined compounds. Conversion, it can be used for a variety of free radical reactions, precipitation polymerization, emulsion polymerization and suspension polymerization.[40]

Therefore, the purpose of this work is to develop a novel technique with the combination of ion-imprinted polymers and SPR to detect potassium ion in water. The selective recognition of crown ether was introduced into the polymer network, to preconcentration with K^{+} ion coordination were used as the template. Here, 2-Methyl-2-[dodecylsulfanylthiocarbonylsulfonyl] propanoic acid (DDMAT) is used as a free radical initiator and chain transfer agent, methacrylic acid (MAA) and ethylene glycol dimethacrylate (EGDMA) are used as functional monomers and crosslinker monomers, respectively. The copolymerization was carried out by using RAFT polymerization method with K^{+}: 18-C-6 as a template. After the completion of polymerization, K^{+} ions were removed and potassium ion-imprinted polymer (potassium-IIP) on SPR sensor chip was obtained to detect potassium ions in water. The proposed sensor has simple preparation method, high sensitivity with low detection limit of 1.6x10^{-16}. 
2. Materials and Methods

2.1. Materials
Potassium nitrate, and nitric acid were purchased from Xilong Science Co., Ltd. (China). Methacrylic acid (MAA) was purchased from Tianjin Fuchen Chemical Reagent Factory. 18-crown-6 and ethylene glycol dimethacrylate (EGDMA) were purchased from Aladdin Biochemical Co., Ltd. (China). 95% β-mercaptoethylamine, 2-Methyl-2-[(dodecylsulfanylthiocarbonylsulfanyl)sulfanyl] propanoic acid (DDMAT) and N,N0-dicyclohexylcarbodiimide (DCC) were obtained from Macklin Biochemical Co., Ltd. (China). Acetonitrile, ethanol and acetic acid were of analytical grade and purchased from Beijing Yinhetianhong Fine Chemicals Company. MAA and EGDMA were distilled under reduced pressure before use.

2.2. Apparatus
A Nicolet 6700 FT-IR spectrometer (Thermo Scientific, U.S.A.) with a photoelastic modulation module (PEM) was used for MIP and NIP films' detection. The contact angles of the surfaces were measured with the sessile drop method using a contact angle instrument (Powerreach, JC2000C, Shanghai Zhongchen Digital Technical Apparatus Co., China) by adding a drop of water each on the surface of MIP and NIP films. Scanning electron microscope (SEM) images of films' surfaces were obtained by Zeiss SUPRATM55 SAPPHIRE (Germany) apparatus. The SPR setup (home-built) is based on a Kretschmann configuration with a 632.8 nm laser source. The SPR substrate consisted of a glass slide (LaSFN9, refractive index =1.845) with a metal layer (Au, 50 nm in thickness). UV irradiation was carried out using a LED light source (λ=365 nm, irradiation power of 3 W cm\(^{-2}\)).

2.3. Preparation of potassium-IIP and non-imprinted polymer (NIP) film
First of all, modification of Au-chips was made. An Au-coated chip (50 nm) was placed in a solution of mercaptomethylamine (5 mmol) and ethanol for 24 h. Then, the chip was mixed with a solution of 1 mmol DDMAT and 2 mmol DCC in 40 mL of acetonitrile and left for 24 h. Afterwards, The chip was washed with acetonitrile and dried under a stream of nitrogen. Next, 25 mmol (0.0051 g) of K\(^+\) and 25 mmol of 18-crown-6 ether (0.0132 g) were added to a 2 ml mixed solution of acetonitrile and water (19: 1), stirred continuously for 30 minutes, and then add MAA (34 μL) to the solution. After three
hours, cross-linker (EDGMA 94μL) and the chain transfer reagent (DDMAT 0.0075mg) were added to the prepolymerization solution, placed in ultrasonication for 10 min and afterwards nitrogen purging was made for 5 minutes. The reaction mixture was injected to SPR making a cell, irradiated with ultraviolet light (wavelength 365 nm, radiant power 3 W cm$^{-2}$), polymerized in situ, and the reaction was monitored in real time. After the completion of polymerization, 1.0 M nitric acid aqueous solution was introduced as the washing solution to remove potassium ions. Same procedure was followed for NIP film formation except for the addition of potassium ions.

2.4. Real-time detection and kinetic studies

After preparation of potassium ion imprinted chip, real time monitoring was made in SPR. Different adsorption solutions ranging from $10^{-15}$-$10^{-5}$mol/L in distilled water were prepared and analyzed in SPR. SPR monitors the change of its light intensity value in real time. Afterwards, the detector was applied to tap water in order to evaluate the stability.

3. Results and Discussion

3.1. Choice of eluent

![Figure1. Influence of different HNO$_3$ concentration on the elution of K$^+$ from the potassium-IIP. (A) 0.75M, (B) 1.50M, (C) 1.0 M](image)

In the previous research, it was pointed out that nitric acid can efficiently extract potassium ions when preparing potassium ion imprinted polymers, so we also chose nitric acid as the eluent in this study.$^{[25]}$ In order to find the appropriate concentration, three concentrations of 0.75M, 1.0M and 1.5M were used as eluents. Lower concentration of nitric acid caused no obvious difference as shown in Figure 1a, whereas, higher concentration deformed SPR signal which denoted structure destruction of the chip. Therefore, in this study, 1.0M nitric acid was selected as the eluent for further research.
3.2. FT-IR analysis

FTIR analyses were made to observe functional groups on the surface of film. The infrared spectra of the polymer containing potassium ions, the polymer without potassium ions after washing, and the polymer without potassium ions (NIP) are shown in Figure 2. It can be seen from the figure that the a), b), c) curves have similar characteristic peaks, and it means that different materials have similar main chain structures. It means that the crown ether is fixed on the ion-imprinted film, and the crown ether was not washed off during the washing process. The peaks around 1169cm⁻¹ are C-O vibration peaks; the peaks around 1263cm⁻¹ are anti-symmetric vibrations of the C-O-C group; the peaks around 1450cm⁻¹ are methylene anti-symmetrical vibrations and flexural vibrations; The peak around 1733.5cm⁻¹ is the characteristic peak of C = O group stretching vibration. These results indicated the formation of potassium-MIP and NIP chips successfully.

3.3. Contact Angle analysis

Contact angle measurement was made to investigate the hydrophobic character of the film in Figure 3. Contact angles of the gold film surface modified with mercaptoethylamine, the gold film surface modified with DDMAT-mercaptoethylamine, and the gold film surface grafted with potassium-IIP were measured as 74.6°, 41.74°, 76.4°, 59.84°, respectively. After the modification of mercaptoethylamine, the contact angle becomes smaller and the hydrophilicity is enhanced, mainly because the -SH group in mercaptoethylamine self-assembles with the gold film, and the -NH₂ side is on the exterior part, which is more hydrophilic. Moreover, the chain transfer reagent is subsequently modified based on the first step, after DCC condensation, its alkyl chain is in outside, has a certain degree of hydrophobicity, and the contact angle increases. Afterwards, contact angle after second step of modification, showed enhanced hydrophilicity, proving that the potassium ion imprinted film we prepared has a certain degree of hydrophilicity.
3.4. Morphological study
The surface morphology of K⁺ ion imprinted polymer (potassium-IIP) and non-imprinted polymer (NIP) was observed by scanning electron microscope, as shown in the figure 4. It can be seen from the Figure 4 a, the surface of potassium-IIP is rough which can be attributed to the removal of template molecules after washing. The NIP surface is smoother as shown in Figure 4 b. Hence, SEM microphotographs indicated the successful fabrication of potassium ion imprinted film on the surface of SPR sensor chip.

3.5. SPR performance test

3.5.1. Preparation of potassium ion- imprinted polymers
The process of film formation is monitored in real time by the SPR. The kinetics of the film formation process is shown in the Figure 5 (A). After reaction solution was passed in, the light intensity rapidly decreases due to the change in refractive index. After the reaction solution fills the entire sample cell, the solution is allowed to stand still, and the LED lamp is irradiated to the reaction solution. Until down to the lowest value and stop the reaction. The resonance angles in acetonitrile before and after grafting the potassium ion-imprinted film were 58.31° and 69.27°. Distilled water was then passed in, and after the membrane was stabilized, a fine scan in water gave a resonance angle of 67.94°. After that, 1.0 M HNO₃ washing was ensured for 15 min. The elution kinetics and the changes in the angle...
diagram before and after the elution are shown in the Figure 5 (C) and Figure 5 (D). The light intensity is decreased by 5.9% and the angle decreased by 0.15° during elution, which may be caused by the elution of potassium ions.

Figure 5. (A) The potassium-IIP film polymerization; (B) the angles before in acetonitrile and after polymerization in acetonitrile and water; (C) The elution kinetics curve during washing process; (D) the angles before and after washing in water.

3.5.2. Adsorption process by potassium ion-imprinted polymers

In order to evaluate the adsorption performance of the K⁺ ion imprinted film, a series of potassium ion solutions were prepared in distilled water and analyzed by sensor from $10^{-15}$ mol/L to $10^{-5}$ mol/L. SPR records its kinetics in real time. Each sample is adsorbed for 15 minutes, and then distilled water is passed to make the curve flatten. The adsorption kinetics is shown in the Figure 6 (B). With the addition of adsorption solution, the intensity of the reflected light on the surface of ion imprinted film is increased. This is probably because of the interaction of potassium ions with imprinted recognition cavities. In the range of $10^{-15}$-$10^{-5}$ mol/L, the change in reflectivity has a linear relationship with the potassium ion concentration. The linear equation is $y = 0.1971x + 3.262$ with the correlation coefficient of $R^2 = 0.9964$. The limit of detection which is calculated by a linear fitting curve is $1.6 \times 10^{-16}$. The points of the calibration curve are determined by the average of three measurements of the sample, and the LOD is three times the average of the measurements of the three blank samples. In Table 1, compared with others work, combine MIP with SPR (this work) have the lower LOD.

Table 1. Comparison of this study with other studies

| Detection method | Contact time | LOD | Reuse NO. | Ref. |
|------------------|--------------|-----|-----------|------|
| K⁺-imprinted nanoparticles and flame photometry to detect the potassium | 10min | 4.62 ng/L | multiple | 26 |
| Valinomycin doped chitosan-graphene oxide (C–GO–V) thin film and surface plasmon resonance (SPR) system for potassium ion (K⁺) detection | 10min | 0.001 ppm(0.02557 μM) | -- | 33 |
A self-assembled monolayer of calix[4]crown-5 derivative (calix[4]crown) modified gold chip based on surface plasmon resonance (SPR).

Square-wave voltammetry (SWV) aptasensor and useredox couple [Fe(CN)₆]³⁻/⁴⁻ as a redox probe to detect potassium ions (K⁺)

Colorimetric method for the detection of potassium ions based on gold nanoparticles modified with aminobenzo-18-crown-6

Detect potassium ion based on graphene field-effect transistors with surface plasma pretreatment

Self-assembled monolayer of 4-aminobenzo-18-crown-6 ether with electrochemical method

K⁺ ion-imprinted polymer film and SPR

| Method                        | Time (min) | Initial Concentration | Adsorption  |
|-------------------------------|------------|-----------------------|-------------|
| Square-wave voltammetry (SWV)| 10         | 1.0 × 10⁻¹² M         | --          |
| Colorimetric method           | 30         | 0.13 pM               | --          |
| Detect potassium ion based    | 20         | 5.24 μM               | --          |
| on graphene field-effect      | --         | 5.8 × 10⁻¹⁴ M         | --          |
| transistors with surface      | 60         | 0.1 mM                | --          |
| plasma pretreatment           | --         | 1.6 × 10⁻¹⁶ M         | multiple    |

3.5.3. Selective characterization

The Figure 7 shows the selectivity of potassium-IIP film towards potassium ions analogues as Li⁺, Na⁺, Mg²⁺, Ca²⁺. Sample solutions of these four ions was prepared in distilled water at a concentration of 10⁻⁷ mol/L and allowed to interact with potassium-IIP for 15 min. Each sample was tested 3 times. Compared with other ions, potassium-IIP film has a higher adsorption value for K⁺. The reason might be the pores on the prepared molecularly imprinted membrane fit the K⁺ structure and can be better combined. Since most of the crown ether molecules are still very soft, their structure can be adjusted to suit the size of the complex ions.[42] Although 18-crown-6 itself can also form complex with other ions but the crown ether structure is compatible with potassium ions in the reaction. The cavities formed after the potassium ions were eluted have better coordination with potassium ions, and weak binding ability with other ions. For comparison, the NIP film also applied to detect these four ions, and the results are shown in the Figure 7. Therefore, it can be seen from the Figure 7 that our potassium-IIP has good selectivity for potassium ions.

Figure 6. (A) Angular reflectivity spectra of potassium-IIP: (1) after washing rebinding of K⁺ at concentrations of (2) 10⁻¹⁵ mol/L, (3) 10⁻¹³ mol/L, (4) 10⁻¹¹ mol/L, (5) 10⁻⁹ mol/L, (6) 10⁻⁷ mol/L and (7) 10⁻⁵ mol/L. Inset: A graph of the enlarged part of resonance angles. (B) The rebinding kinetics of K⁺ ion-imprinted polymer film and SPR.
from $10^{-15}$ to $10^{-5}$ mol/L. (C) Calibration curve obtained for the detection of $\text{K}^+$ in water. The error bars represent the standard deviation of measurements for detect one sample 3 times.

3.5.4. Characterization of stability and repeatability

The stability and repeatability of the films were further characterized. After storing the chip under standard conditions of temperature and pressure for 54 days, stability was evaluated by using $10^{-15}$ mol/L potassium ion sample solution. The results showed that after 54 days of storage, the reflected light intensity value of the potassium-IIP film was 89% of the initial value. Five adsorption-desorption cycles were performed on the adsorption solution of 15 mol/L concentration. Each adsorption was performed for 15 min and then distilled water was passed until the light intensity dropped to the initial value, then the next adsorption experiment was performed. The results of five consecutive experiments as shown in the Figure 8(C), it can be seen from the figure that although it is difficult to reach the initial value at the time of elution, a better adsorption effect can still be achieved at the next adsorption. This result shows that the SPR sensor based on the potassium ion imprinted film has good reproducibility and stability.

3.5.5. Testing in real samples

The prepared chip is used for real sample to detect potassium ions. Prepare a higher concentration of potassium ion sample solution with distilled water, and then dilute to a series of sample solutions with tap water. SPR monitored the film's adsorption performance in tap water, and the results are shown in the Table 2. This result indicates that the prepared sensor can be used for the detection of actual samples and has a good recovery rate.

Figure 7. The SPR response for the adsorption of $\text{K}^+$, $\text{Na}^+$, $\text{Li}^+$, $\text{Mg}^{2+}$, $\text{Ca}^{2+}$ (each at $10^{-7}$ mol/L) on the potassium-IIP and NIP film. The error bars represent the standard deviation of measurements for detect one sample 3 times.
Figure 8. (A) the reflectivity changes: rebinding $10^{-15}\text{mol/L K}^+$ after storing for 0 day and 52 days. The error bars represent the standard deviation of measurements for detect one sample 3 times. (B) the rebinding kinetics of rebinding $10^{-15}\text{mol/L K}^+$ after storing for 0 day, 52 days and (C) Reproducibility of the potassium-IIP film (5 times for rebinding and washing $10^{-15}\text{mol/L K}^+$).

Table 2. Relevant parameters detected in real sample

| Sample    | Linear range | Linearity($R^2$) | Slope   | Intercept | LOD(mol/L) | Recovery (%) (3 times) |
|-----------|--------------|------------------|---------|-----------|------------|------------------------|
| Tap water | $10^{-11}$-$10^{-5}$ | 0.9999          | 0.2264  | 3.369     | $10^{-13}$  | 88                     |

4. Conclusion

Novel potassium ion imprinted film was successfully prepared, via a facile combination of RAFT and SPR by using EGDMA as a cross linker and DDMAT as a chain transfer agent in the presence of UV light, for the excellent detection of potassium ions. The method proposed in this work is very sensitive to the detection of potassium ions, the limit of detection is $1.6\times10^{-16}\text{M}$, and the prepared chip has excellent stability. After 54 days of storage, it can still have a good adsorption effect. Five consecutive adsorption-desorption experiments indicate good repeatability. Furthermore, the developed sensor was successfully applied to detect potassium ions in the presence of tap water. Lower detection limits and applications in real samples describe the potential practical application of this method.

Obviously, the potassium-imprinted polymer film-SPR sensor introduced in this paper has the advantages of short response time, simple preparation, high precision, good selectivity, low detection limit and so on. And this can push forward the development of molecular imprinting techniques.

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