Using Ionic Polymer Metal Composite (IPMC) based Devices for Naked-eye Sensing of Thiocyanate Ion (SCN⁻)

Abstract
This work introduces the concept of a novel thiocyanate ion (SCN⁻) detecting device. We show proof-of-principle of the device, namely IPMC film prepared by surface modification of the ionic-polymer film. In this work, naked-eye detection of thiocyanate ion (SCN⁻) by using iron exchanged ionic polymer-metal composites (IPMC) strip has been achieved. It was successfully applied to direct determination of thiocyanate at micro-molar level in water samples. The response time of the sensor in whole concentration ranges is very short (<10 s). The response of the sensor is independent on the pH range of 2-10.

Keywords: Ionic Polymer; Metal Composite; Thiocyanate; Flurometric; Potentiometric

Introduction
Thiocyanate (SCN⁻), a metabolite of cyanide detoxification is produced endogenously in the liver [1], and it is abundance in physiological fluids like saliva, breast milk [2]. However, the concentration of thiocyanate in physiological fluids, particularly in saliva, depends on the smoking habits [3]. For non-smokers, the saliva thiocyanate concentration lies in the range 0.5-2 mm, whereas, it could be as high as 6 mm for typical occupational smokers [4]. If the content of thiocyanate ion is a little higher in the body than normal, the protein dialysis will be affected and it may even result in coma. Many methods, such as spectrophotometric [5], voltammetric [6], chromatographic [7], potentiometric [8] and fluorometric [9] have been developed for the determination of SCN⁻. However, most of them are time consuming or costly or require sophisticated instrumentation, which prevent them from being used for on-site analyses and field tests. As such, development of devices and methods offering various advantages such as simplicity, relatively fast response, low cost, wide linear dynamic range and ease of preparation and procedures for precise determination of thiocyanate is of current research interest [10-14], particularly in the context of monitoring the cyanide exposure, especially from tobacco smoking. In this paper we report the possibility of using ionic polymer metal composites (IPMC) towards naked-eye detection of thiocyanate in aqueous sample based on the formation of a red color Fe-SCN adduct [15].

Experimental
Reagents and chemicals
All reagents and chemicals used were of A.R grade and used as received. The pH of solutions was adjusted with sodium hydroxide or hydrochloric acid solution as appropriate. All other reagents used were of analytical reagent grade. Double distilled water was used throughout the experiments. A 0.1M stock solution of thiocyanate was prepared by dissolving an appropriate, accurate amount of KSCN. The standard 0.1 mm to 100 mm solutions of thiocyanate were prepared daily by sequential dilution of the appropriate stock solution with doubly distilled water.

Fabrication of IPMC based sensor
A piece of Nafion117 membrane (2" x 2") of 0.2 mm thickness was subjected for pretreatment processes in 3% hydrogen peroxide (H₂O₂) for elimination of organic impurities. Subsequently, this piece was further treated in 1.0 M sulfuric acid (H₂SO₄) at 80°C for removal of metallic impurities. Then this pretreated polymer membrane sample was immersed in a solution of FeCl₃ (0.02 M) at room temperature for 24 h to allow Fe³⁺ to diffuse through the ion-exchange process, and then washed several times with multi-distilled water.
Results and discussion

Development of bio-mimetic smart devices using ionic polymer-metal composites (IPMCs) has gained current importance [16]. IPMCs consist of a ion exchange electroactive polymer membrane and thin conductive metal electrodes chemically deposited on both sides of the membrane. Although many ion-exchanged polymers have been studied, Nafion™, a fluorocarbon polymer with linear backbone shown in Figure 1 with no cross linking and attached with fixed ionic groups (-SO₃⁻ for cation exchange), has been shown to be a viable material [1]. The noble metals such as gold or platinum can be electrode materials to improve surface conductivity (Figure 1). We have been engaged in developing actuators and sensors using IPMCs [17,18]. Very recently we have reported results of the actuation and sensing studies of a five-fingered miniaturized robotic hand fabricated by using IPMC [18]. In the present work we explored the possibility of using IPMC strip as a device for detection of thiocyanate (SCN⁻). The Fe³⁺-exchanged IPMC strip prepared by exchanging Fe³⁺ ions was applied to detect thiocyanate ions in pure water solution. The rational strategy as shown schematically in Scheme 1 for the naked-eye detection of thiocyanate in aqueous sample without any spectroscopic instrumentation is based on the formation of a red coloured Fe-SCN species on to the surface of the IPMC strip (Scheme 1). Addition of 10 µL (using micro-pipette) of the aqueous test solution of SCN⁻ onto the surface of Fe³⁺-exchanged IPMC strip immediately resulted in the formation of red spot on to the yellowish strip. One the spots got dried (within few seconds) photograph of the strips were taken using a Canon Camera, and Microsoft Paint software was used as a imaging treatment program. In Figure 2 shown is the pictorial change in the intensity of the color with the change in the concentration of SCN⁻ in solution (Figure 2). Clearly, the IPMC based device allow naked-eye detection SCN⁻ in aqueous solution at a low limit of 0.5 mM, thus provides a practical means to inspect thiocyanate anion concentrations in the wilderness.

Conclusion

In conclusion, results of our studies show that the Fe³⁺-exchanged IPMC strip could be able to detect thiocyanate anion in aqueous solution at a low limit of 0.5 mM. This method may offer a new cost-effective, rapid and simple solution to the inspection of SCN⁻ ion in saliva and environmental aqueous samples. The obvious color change induced by thiocyanate can be easily observed by the naked eye, suggesting excellent applicability as a good probe to distinguish between smokers and non-smokers in the undeveloped regions.

Acknowledgments

This work was carried out under the financial support from CSIR, New Delhi (Project No. ESC 0203). DC is thankful to Dr. P Pal Roy, Director, of this institute for his encouragement to this work.
References

1. Wrobel M, Jurkowska H, Sliwa L, Srebro Z (2004) Toxicol Mech Methods 14: 331.
2. Fragoso MA, Fernandez V, Forteza R, Randell SH, Salathe M, et al. (2004) Journal of Physiol. 561: 183
3. Pettigrew AR, Logan RW, Willocks J (1977) Journal of Obstet Gynecol. 84: 31.
4. Valdes MG, Diaz-Garcia ME (2004) Crit Rev Anal Chem 34: 9.
5. Lundquist P, Kagedal B, Nilsson L (1995) European Journal of Clinical Chem and Clinical Biochem. 33: 343.
6. Cox JA, Gray T, Kulkarni KR (1988) Analytical Chem 60: 1710.
7. Li J, Wang Y, Liang L (2010) Chin J Chromatography 28: 422.
8. Ardakani MM, Karimi MA, Mazidi R, Naeimi H, Rabiei K (2007) Can J Analytical Sci Spectroscopy 52: 233.
9. Zhang Y, Wang H, Yang RH (2007) Bio-Sensors 7: 410.
10. Saussereau E, Goulle JP, Lacroix C (2007) Journal of Analytical Toxicol 31: 383.
11. Kanthale P, Kumar A, Upadhyay N, Lal D, Rathod G (2015) Food Sci Technol 52: 1698.
12. Badri A, Pouladsaz P (2011) Int. Journal of Electrochemical Sci. 6: 3178.
13. Zhang Z, Zhang J, Qu C, Pan D, Chen Z (2012) Journal of Analyst. 137: 2682.
14. Pena-Pereira F, Lavilla I, Bendicho C, Talanta (2016) Paper-based analytical device for instrumental-free detection of thiocyanate in saliva as a biomarker of tobacco smoke exposure 147: 390-390.
15. Laurence GC (1956) Trans. Faraday Soc 62: 236.
16. Bhandari B, Lee G, Ahn S (2012) Int J Precis Eng Manuf 13: 141-163.
17. Chatterjee D (2009) Ind J Chem (A) 48: 1201-1203.
18. Chatterjee D, Hanumaiah N, Bahramzadeh Y, Shahinpoor M (2013) Adv Mat Res 740: 492-495.