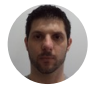
Optical Chemosensor for the Detection of Cyanide in Water Based On Ethyl(hydroxyethyl)cellulose Functionalized with Brooker's Merocyanine

ARTICLE *in* ANALYTICAL CHEMISTRY · MAY 2014

Impact Factor: 5.64 · DOI: 10.1021/ac501233x · Source: PubMed

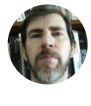
4 AUTHORS:

Leandro Guarezi Nandi
Federal University of Santa Catarina
15 PUBLICATIONS **45** CITATIONS
SEE PROFILE



Celso Rodrigo Nicoleti
Federal University of Santa Catarina
10 PUBLICATIONS **36** CITATIONS
SEE PROFILE

Ismael C Bellettini
Federal University of Santa Catarina
14 PUBLICATIONS **67** CITATIONS
SEE PROFILE



Vanderlei Gageiro Machado
Federal University of Santa Catarina
67 PUBLICATIONS **761** CITATIONS
SEE PROFILE

analytical chemistry

Letter

pubs.acs.org/ac

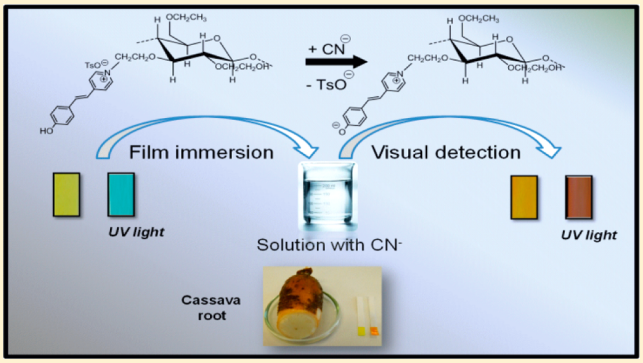
Optical Chemosensor for the Detection of Cyanide in Water Based On Ethyl(hydroxyethyl)cellulose Functionalized with Brooker's Merocyanine

Leandro G. Nandi, Celso R. Nicoleti, Ismael C. Bellettini, and Vanderlei G. Machado*

Departamento de Química, Universidade Federal de Santa Catarina, UFSC, CP 476, Florianópolis, Santa Catarina 88040−900, Brazil

Supporting Information

ABSTRACT: Ethyl(hydroxyethyl)cellulose was functionalized with Brooker's merocyanine. The modified polymer was easily transformed in a film, which could be used as a highly selective chromogenic and fluorogenic chemosensor for the detection of cyanide in water, with detection limits of 1.9×10^{-5} and 1.0×10^{-7} mol L^{-1}. The film was successfully applied to the detection of cyanide in cassava (*Manihot esculenta* Crantz) roots, which are a well-known source of endogenous biological cyanide.



The field of the recognition and detection of anions has increased in importance in recent years due to the very important role developed by these species in chemical and biological processes.[1−13] A very attractive anion in terms of detection is CN^-,[14,15] which is lethal in very small concentrations because it binds strongly to the active site of cytochrome-oxidase, causing a decrease in the oxidative metabolism.[14−16] CN^- is used in various industrial activities, such as, metallurgy, mining, and fabrication of polymers, and is delivered through hydrolysis from some fruit seeds and roots.[14−16] Some warfare neurotoxic compounds release CN^- through hydrolysis.[17] Many chromogenic and fluorogenic chemosensors have been designed for CN^-.[16,18−22] Among the strategies used to construct CN^- detection devices, many research groups have synthesized optical polymer chemosensors.[23] These systems exhibit various advantages, such as good mechanical properties and the ability to operate in organic and aqueous solutions and as solid insoluble materials, as well as having the possibility to be used for the naked-eye and quantitative detection of the analyte in water.

Our research group has studied chromogenic chemosensors for CN^-, based on an acid−base strategy, using phenols whose conjugated bases are dyes.[24−27] More specifically, the deprotonation of the phenolic moiety of the chemosensor in organic solvents by the presence of the basic anion, such as CN^-, generates the corresponding phenolate, which makes the colored solution. The addition of small amounts of water to the medium makes the system highly selective to CN^-,[24−27] but these chemosensors are unable to detect this anionic species in water. Herein, we describe an efficient, simple, and low cost strategy for the detection of CN^-, which is based on the covalent anchorage of 1-methyl-4-[(1-oxocyclohexa-2,5-dienylidiene)ethylidene]-1,4-dihydropyridine (Brooker's merocyanine, BM), a solvatochromic dye, in ethyl(hydroxyethyl)-cellulose (EHEC), in order to provide an anionic detection device exhibiting as main properties high sensitivity and specific selectivity for CN^- in water. BM and its derivatives have been used previously in functional polymeric devices, covalently anchored on poly(*N*-isopropylacrylamide)[28] and poly[4(5)-vinylimidazole],[29] to investigate the physicochemical properties of polymeric systems in solution. The synthesis of the decorated polymer is described in Scheme 1.

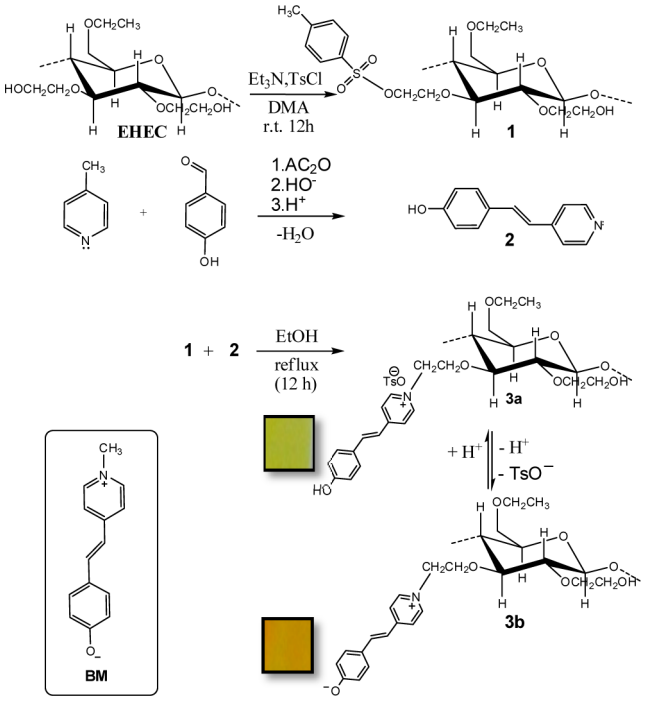
First, EHEC was tosylated to give polymer **1** and, in parallel, 4-methylpyridine was condensed with 4-hydroxybenzaldehyde to yield compound **2**.[28] Polymer **1** was easily transformed in thin films through dissolution in water, shedding the resulting solution on a Petri dish, followed by the evaporation of the solvent. In the next step, a film of **1** was refluxed in the presence of **2** in ethanol to give the polymer **3a**, which was characterized by thermogravimetric analysis and infrared spectrophotometry. The prepared film was left in water, and it was observed that the dye was not delivered to the aqueous environment even after several days, which is in contrast to the observation of other films prepared by the simple physical mixture of EHEC with BM, in which the dye is rapidly delivered to water.

The pK_a value for the protonated BM unit in the film of **3a** was determined to be 9.84 ± 0.02. This value is higher than the value previously determined by Jencks and Davidson for protonated BM in aqueous solution (8.6).[30] The observed

Received: April 4, 2014
Accepted: May 7, 2014
Published: May 7, 2014

   dx.doi.org/10.1021/ac501233x | *Anal. Chem.* 2014, 86, 4653−4656

Scheme 1. Synthesis of the EHEC Functionalized with BM, Showing Its Protonated (3a) and Deprotonated Form (3b)



increase in the pK_a suggests that the microenvironment of BM in the polymer is protected from the bulk water. The solvatofluorochromic properties of BM have been reported in the literature,[28,31] and this dye can act as a probe, with the ability to report the polarity of its microenvironment. Table 1 shows the wavelengths of maximum absorption and the fluorescence emission intensity for protonated and deprotonated BM and for the films of **3a** and **3b** in aqueous solution. The deprotonation of BM in aqueous solution leads to the appearance of the solvatochromic band at λ_{max} = 444 nm. Interestingly, the deprotonation of the dye units in the film leads to the appearance of the solvatochromic band of the dye at λ_{max} = 468 nm. This bathochromic shift of $\Delta\lambda_{max}$ = +24 nm suggests that the dye is in a less polar environment in the film.[28,31]

Table 1. Maximal Wavelengths of Absorption and Fluorescence Emission Intensity for Protonated and Deprotonated BM and for the Film of 3a and 3b in Aqueous Solution[a]

compound	λ_{max} (nm) protonated	λ_{max} (nm) deprotonated	λ_{max}^{fl} (nm) protonated	λ_{max}^{fl} (nm) deprotonated
BM	374	444	505	573
3	384	468	500	578

[a]The deprotonation was made by adding tetra-*n*-butylammonium hydroxide aqueous solution to each flask containing 2 mL of water.

Figure 1A shows films of **3a** before and after immersion in aqueous solutions of various anions. The film of **3a** is yellow and of **3b** (obtained after immersion in an aqueous HO^- solution) is orange in color. Of the several anion solutions studied, only CN^- is able to change the color of the film to orange, which is sufficiently basic to deprotonate the dye, forming **3b**. The studies performed allowed the verification that the films of **3a** are applicable for the detection of CN^- within a pH range of 7.4−8.8. Since BM is fluorescent,[31] the same system was exposed to UV light after immersion in the solutions (Figure 1B), and it is possible to observe that the blue fluorescent color of the film corresponding to **3a** is changed only if the dye is deprotonated to **3b**, which has a pale red color.

Figure 2A shows the UV−vis spectrum of the film of **3a**, which exhibits a band with maximum wavelength (λ_{max}) at 380 nm. The immersion of the film in a CN^- aqueous solution shows the occurrence of another band with λ_{max} = 468 nm, while the other anions did not cause any spectral alteration. The fluorescence spectrum of the film showed a maximum in the emission intensity at 500 nm (Figure 2B), which disappeared only after immersion of the film in the CN^- solution, simultaneously with the appearance of another

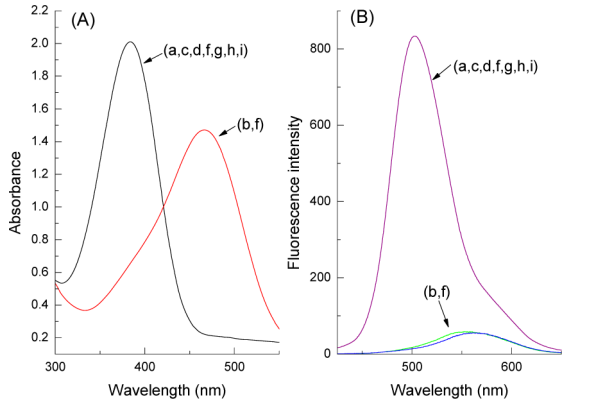


Figure 2. (A) UV−vis and (B) fluorescence spectra for films of (a) **3a** and (b) **3b** and **3a** in the presence of (c) HSO_4^-, (d) $H_2PO_4^-$, (e) NO_3^-, (f) CN^-, (g) CH_3COO^-, (h) F^-, (i) Cl^-, (j) Br^-, and (k) I^- in water [c(anion) = 6.0 × 10^{-4} mol L^{-1}].

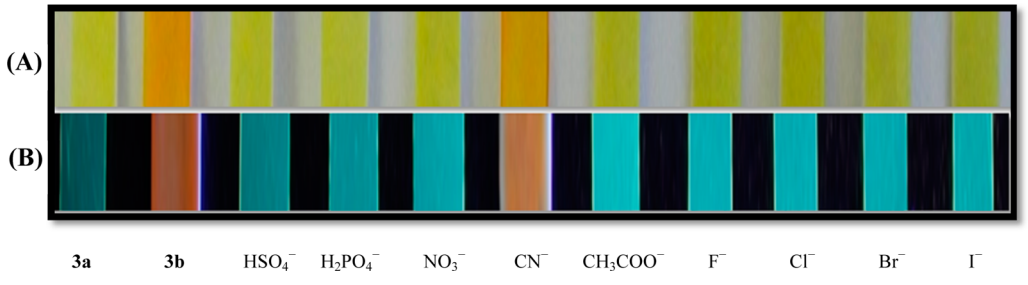


Figure 1. (A) Films of **3a**, **3b**, and **3a** after immersion in aqueous solutions containing HSO_4^-, $H_2PO_4^-$, NO_3^-, CN^-, CH_3COO^-, F^-, Cl^-, Br^-, and I^- [c(anion) = 6.0 × 10^{-4} mol L^{-1}]. (B) The same films exposed to a UV lamp (365 nm).

dx.doi.org/10.1021/ac501233x | *Anal. Chem.* 2014, 86, 4653−4656

emission band with maximum at 560 nm and having a very small intensity.

UV−vis spectra of the films of **3a** were recorded after 5 min of immersion in solutions with increasing concentrations of CN^- (Figure 3A), and it was observed that the band at λ_{max} =

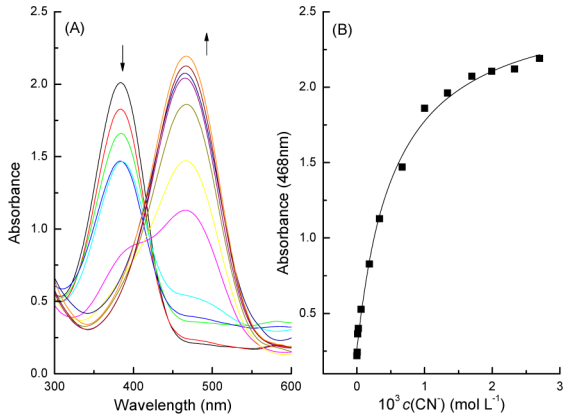


Figure 3. (A) UV−vis spectra of the film of **3a** after immersion in water containing increasing concentrations of CN^- at 25 °C. (B) Curve of the variation in the absorbance at 468 nm of the film with the addition of increasing amounts of CN^-.

380 nm disappeared simultaneously with the appearance of another band at λ_{max} = 468 nm. A plot of the absorbance values at 468 nm as a function of $c(CN^-)$ (Figure 3B) shows a behavior typical of a 1:1 stoichiometry considering the anion and the dye units anchored in the polymer. A fitting of the experimental data[32] gave a binding constant of (1.82 ± 0.22) × 10^3 L^1 mol^{-1}. An analysis of the linear segment of the titration curve gave a detection limit of 1.9 × 10^{-5} mol L^{-1} and a quantification limit of 6.2 × 10^{-5} mol L^{-1}.[33,34]

Figure 4A shows the influence of the $c(CN^-)$ on the fluorescence spectrum of the film, and it is observed that the

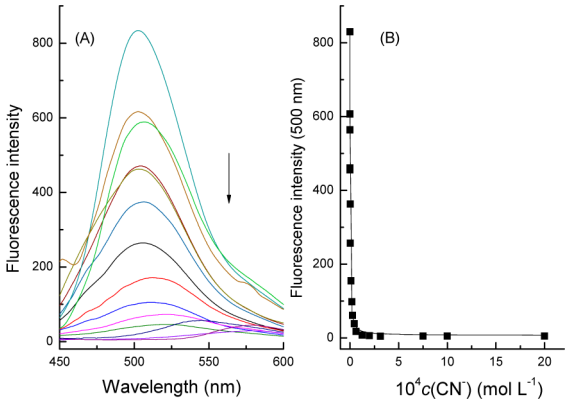


Figure 4. (A) Emission spectra of the film of **3a** after immersion in water containing increasing concentrations of CN^- at 25 °C. (B) Curve of the variation in the fluorescence emission intensity at 500 nm of the film with the addition of increasing amounts of CN^-.

emission band corresponding to the film of **3a**, with λ_{max} = 500 nm, has its intensity reduced until its complete disappearance with the increase in the $c(CN^-)$. The corresponding titration curve, obtained by collecting the emission fluorescence intensities at 500 nm for each $c(CN^-)$ after 5 min of immersion of the film, is presented in Figure 4B, and it is possible to observe that this detection system is highly sensible to the presence of CN^- in water. The analysis of the linear segment of the titration curve provides detection and quantification limits of 1.0 × 10^{-7} and 3.2 × 10^{-7} mol L^{-1}, respectively. A fitting of the experimental data[32] gave a binding constant of (4.20 ± 1.59) × 10^5 L^1 mol^{-1}.

The fluorophore units in **3a** are distributed in microenvironments of different polarities, and the units found in a microenvironment more protective of water molecules have a higher quantum yield than those with more contact with the solvent. This explains the fact that the film after immersion in water has emission intensity much higher than protonated BM in water. The binding constant value determined using fluorescence data, higher than that determined using the UV−vis technique, may reflect the fact that the ability of the polymer to shield the fluorophore from the solvent makes the system largely sensible to the presence of the anionic species.

The applicability of the film of **3a** for the detection of CN^- was verified in a practical situation. The roots of cassava (*Manihot esculenta* Crantz) are a well-known source of endogenous biological cyanide.[35] Therefore, aqueous extracts of these roots were prepared according to a procedure reported in the literature.[36] Subsequently, films of **3a** were immersed for 5 min in the extracts. Figure 5A shows the UV−vis spectrum

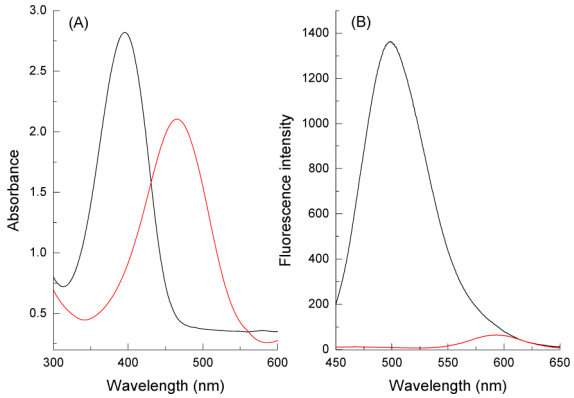


Figure 5. (A) UV−vis spectra and (B) emission spectra for the film of **3a** (black −) before and (red −) after its immersion in the diluted crude aqueous cassava solution.

for the film of **3a**, where it can be observed that the band at λ_{max} = 380 nm disappears after its immersion in the extract, simultaneously with the appearance of the band at λ_{max} = 468 nm, typical of the deprotonated dye. The absorbance value obtained at 468 nm was used to determine the concentration of CN^- in the cassava roots, which was 132.0 ± 8.4 mg/kg. A similar study was carried out using the fluorescence technique (Figure 5B), and the disappearance of the emission band at λ_{max} = 500 nm was noted after the immersion of the film in the extract. The fluorescence data allowed the concentration of CN^- in the root to be estimated as 109.3 ± 4.2 mg/kg.[36] A sample of cyanide-free cassava was assayed and gave a negative result.

In summary, the functionalization of EHEC allowed the obtainment of a film which is highly selective as a chromogenic and fluorogenic chemosensor for the detection of CN^- in water. The role of the polymeric chain, protecting the sensing unit from the medium, explains the ability of this ensemble to sense very small concentrations of CN^- in water, which is not possible if only protonated BM is used in water. The versatility

dx.doi.org/10.1021/ac501233x | *Anal. Chem.* 2014, 86, 4653−4656

of the strategy presented herein was demonstrated by the applicability of the film of **3a** to the detection of CN^- in water and in cassava roots. Finally, it is important to emphasize that the fluorescent chemosensor studied exhibits detection and quantification limits much lower than the maximum level of $c(CN^-)$ allowed by World Health Organization in potable water, which is 1.7 μmol L^{-1}.[37]

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, procedures, and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: vanderlei.machado@ufsc.br. Tel.: +55 48 3721 4542.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Brazilian Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (Capes), and UFSC. The authors also acknowledge Akzo Nobel Surface Chemistry AB (Stenungsund, Sweden) for donating the EHEC.

■ REFERENCES

(1) Martínez-Máñez, R.; Sancenón, F. *Chem. Rev.* **2003**, *103*, 4419−4476.
(2) Suksai, C.; Tuntulani, T. *Chem. Soc. Rev.* **2003**, *32*, 192−202.
(3) Suksai, C.; Tuntulani, T. *Top. Curr. Chem.* **2005**, *255*, 163−198.
(4) Kubik, S.; Reyheller, C.; Stüwe, S. *J. Inclusion Phenom. Macrocyclic Chem.* **2005**, *52*, 137−187.
(5) Callán, J. F.; de Silva, A. P.; Magri, D. C. *Tetrahedron* **2005**, *61*, 8551−8588.
(6) Gunnlaugsson, T.; Glynn, M.; Tocci, G. M.; Kruger, P. E.; Pfeffer, F. M. *Coord. Chem. Rev.* **2006**, *250*, 3094−3117.
(7) Anslyn, E. V. *J. Org. Chem.* **2007**, *72*, 687−699.
(8) Zimmermann-Dimer, L. M.; Machado, V. G. *Quim. Nova* **2008**, *31*, 2134−2146.
(9) Cho, D. G.; Sessler, J. L. *Chem. Soc. Rev.* **2009**, *38*, 1647−1662.
(10) Gale, P. A. *Chem. Soc. Rev.* **2010**, *39*, 3746−3771.
(11) Moragues, M. E.; Martínez-Máñez, R.; Sancenón, F. *Chem. Soc. Rev.* **2011**, *40*, 2593−2643.
(12) Wenzel, M.; Hiscock, J. R.; Gale, P. A. *Chem. Soc. Rev.* **2012**, *41*, 480−520.
(13) Yang, Y.; Zhao, Q.; Feng, W.; Li, F. *Chem. Rev.* **2012**, *113*, 192−270.
(14) Lv, J.; Zhang, Z. J.; Li, J. D.; Luo, L. R. *Forensic Sci. Int.* **2005**, *148*, 15−19.
(15) Nelson, L. *J. Emerg. Nurs.* **2006**, *32*, S8.
(16) Zelder, F. H.; Männel-Croisé, C. *Chimia* **2009**, *63*, 58−62.
(17) Agatemor, C. *Electron. J. Environ. Agric. Food Chem.* **2009**, *8*, 189−194.
(18) Isaad, J.; Salaünb, F. *Sens. Actuators, B* **2011**, *157*, 26−33.
(19) Isaad, J.; Achari, A. E. *Tetrahedron* **2011**, *67*, 4939−4947.
(20) Guan, R.; Chen, H.; Cao, F.; Cao, D.; Deng, Y. *Inorg. Chem. Commun.* **2013**, *38*, 112−114.
(21) Shi, B. B.; Zhang, P.; Wei, T. B.; Yao, H.; Lin, Q.; Zhang, Y. M. *Chem. Commun.* **2013**, *49*, 7812−7814.
(22) Gotor, R.; Costero, A. M.; Gil, S.; Parra, M.; Martínez-Máñez, R.; Sancenón, F.; Gaviña, P. *Chem. Commun.* **2013**, *49*, 5669−5671.
(23) García, J. M.; García, F. C.; Serna, F.; de la Peña, J. L. *Polymer Rev.* **2011**, *51*, 341−390.
(24) Zimmermann-Dimer, L. M.; Reis, D. C.; Machado, C.; Machado, V. G. *Tetrahedron* **2009**, *65*, 4239−4248.
(25) Zimmermann-Dimer, L. M.; Machado, V. G. *Dyes Pigm.* **2009**, *82*, 187−195.
(26) Marini, V. G.; Torri, E.; Zimmermann, L. M.; Machado, V. G. *Arkivoc* **2010**, 146−162.
(27) Nicoleti, C. R.; Marini, V. G.; Zimmermann, L. M.; Machado, V. G. *J. Braz. Chem. Soc.* **2012**, *23*, 1488−1500.
(28) Koopmans, C.; Ritter, H. *J. Am. Chem. Soc.* **2007**, *129*, 3502−3503.
(29) Mikeš, F.; Štrop, P.; Tuzar, Z.; Labský, J.; Kálal, J. *Macromolecules* **1981**, *14*, 175−180.
(30) Davidson, S. J.; Jencks, W. P. *J. Am. Chem. Soc.* **1969**, *91*, 225−234.
(31) Cavalli, V.; da Silva, D. C.; Machado, C.; Machado, V. G.; Soldi, V. *J. Fluoresc.* **2006**, *16*, 77−86.
(32) Valeur, B.; Pouget, J.; Bourson, J.; Kaschke, M.; Ernsting, N. P. *J. Phys. Chem.* **1992**, *96*, 6545−6549.
(33) Skoog, D. A.; West, D. M. *Fundamentals of Analytical Chemistry*; Saunders College Publishing: Philadelphia, 1982.
(34) Isaad, J.; El Achari, A.; Malek, F. *Dyes Pigm.* **2013**, *97*, 134−140.
(35) Cardoso, A. P.; Mirione, E.; Ernesto, M.; Massaza, F.; Cliff, J.; Haque, M. R.; Bradbury, J. H. *J. Food Compos. Anal.* **2005**, *18*, 451−460.
(36) Männel-Croisé, C.; Probst, B.; Zelder, F. *Anal. Chem.* **2009**, *81*, 9493−9498.
(37) *Background Document for Development of WHO Guidelines for Drinking-Water Quality*; World Health Organization: Geneva, Switzerland, 2007.