sensors

Amperometric Sensor Used for Determination of Thiocyanate with a Silver Nanoparticles Modified Electrode

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Abstract: A novel electrode modified with silver nanoparticles was fabricated. It is found that the reducibility of silver nanoparticles is higher than for bulk silver by comparing a silver nanoparticles modified electrode with a silver micro-disk electrode. When SCN^- was added, a new oxidation peak occurred and the anodic peak current of silver nanoparticles decreased. The new anodic peak current is proportional to the thiocyanate concentration in the range of $5.0 \times 10^{-7} \sim 4.0 \times 10^{-4}$ mol/L in pH 6.0 NaH_2PO_4-Na_2HPO_4 buffer solutions (PBS). The detection limit (S/N=3) is 4×10^{-8} mol/L. This method has been applied to the determination of saliva (smoker and non-smoker).

Keywords: Silver nanoparticles, modified electrode, thiocyanate determination.

Introduction

Metal and semiconductor nanoparticles have received considerable attention in recent years. They have unique chemical, electrical and optical properties due to their size-dependent properties and quantum-size effect. They are very promising for practical applications in diverse fields such as electronic nanodevices, molecular catalysts, multifunctional reagent and biosensors [1-6]. Nanoparticles are very different from their bulk materials in their electronic, optical and catalytic properties originated from their quantum-scale dimensions [2,7]. As nano-sized Ag is largely different from its bulk counterpart, it would be promising to utilize the self-assembly technique of Ag nanoparticles for a sensing application.

Thiocyanate usually exists in industrial wastewaters, pesticides residues and organism metabolites. It is also present in low concentrations in human serum saliva, and urine. High concentrations of this ion arise from tobacco smoke and clinical studies have shown that the saliva thiocyanate concentration is higher for smokers than for non-smokers. So, the level of thiocyanate is considered to be a good probe for distinguishing between smokers and non-smokers [8]. If the content of SCN^- is a little higher in the body than normal, the protein dialysis will be affected and it may even result in coma. Therefore, the determination of the SCN^- concentration at low levels is important. Several SCN^--selective electrodes, based on a variety of carriers such as organometallic compounds and metalloporphyrin derivatives, have been reported over the past years [9-13]. Because some of these are complicated, laborious to perform, require toxic reagents, etc. it is essential to look for new materials with high sensitivity and efficiency for the detection of SCN^-.

In this article, we prepare a Ag nanoparticles modified glassy carbon (GC) electrode. Compared with a silver micro-disk electrode we found that silver nanoparticles have a higher reducibility than bulk silver. Chuan-yi Wang et al. [14] have investigated the adsorption of SCN^- on colloidal Ag particles and the accompanying optical effects. In our experiment, we discuss the electrochemical phenomenon of an Ag nanoparticles modified electrode with SCN^-. It is found that when SCN^- was added to the solution, a new oxidation peak occurred due to the formation of an Ag^+-SCN^- complex and the anodic peak current of silver nanoparticles is decreased. This new anodic peak current increases when the concentration of SCN^- is increasing. We suggest that the following electrode processes took place during the cyclic sweep:

$$Ag \rightleftharpoons Ag^+ + e^- \tag{1}$$

$$Ag^+ + nSCN^- \rightleftharpoons Ag(SCN)_n^{1-n} \tag{2}$$
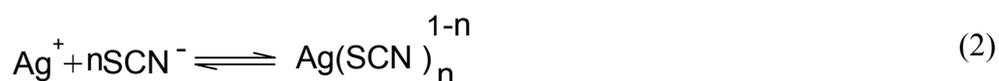
We investigated this phenomenon and found out that the anodic peak current was proportional to the concentration of thiocyanate in the range from 5.0×10^{-7} to 4.0×10^{-4} mol/L in 0.1 mol/L, pH 6.0 (PBS). The limit of detection was 4×10^{-8} mol/L. The limit of detection is better than for some reported electrodes [13] and is several orders of magnitude lower than the thiocyanate concentration in biological samples [8]. Thus, this modified electrode makes it possible to determine thiocyanate in practical samples. We apply this electrode to investigate saliva of smokers and non-smokers and the results are presented. The sensor is a new application of Ag nanoparticles.

Experimental

Instrumentations

Transmission electron microscopy (TEM) measurements were conducted with a Hitachi-600 transmission electron microscope (Japan, Hitachi). All electrochemical measurements were performed with a CHI660A electrochemical workstation (CHInstruments, Austin, Texas, USA). A conventional three-electrode system was used for voltammetric determination consisting of a silver micro-disk electrode (20 μm in diameter) or Ag nanoparticles modified GC electrode (diameter 2.0 mm) as working electrode, a saturated calomel electrode (SCE) with a salt bridge filled with 1 mol/L KNO_3 solution to avoid Cl^- leaking into the working solution as reference electrode, and a platinum wire as counter electrode.

Reagents

Silver nitrate ($AgNO_3$), sodium borohydride ($NaBH_4$) and other reagents used in this investigation were of analytical grade and were used without further purification. PBS was prepared from NaH_2PO_4 and Na_2HPO_4 (0.1 mol/L) and the pH was adjusted with 0.1 mol/L H_3PO_4 and 0.1 mol/L NaOH solutions. All aqueous solutions used in this experiment were double-distilled with a quartz apparatus. Oxygen was removed by purging with high-purity nitrogen for 10 min., and a nitrogen atmosphere was kept over the solution during measurements. All electrochemical experiments were carried out at room temperature.

Preparation of oleate-stablized silver nanoparticles

The oleate-stabilized silver nanoparticles were synthesized by $NaBH_4$ reduction [15]. Figure 1(a) shows the characteristic UV-vis absorption of the hydrosol of oleate-capped silver nanoparticles. The extinction band appeared at 414 nm with a full width at half-maximum of 79 nm, characteristic of rather monodispersed small silver particles. The nanoparticles were examined by TEM as shown in Figure 1(b). Statistical analysis gives a mean diameter (D) of 21.6 nm.
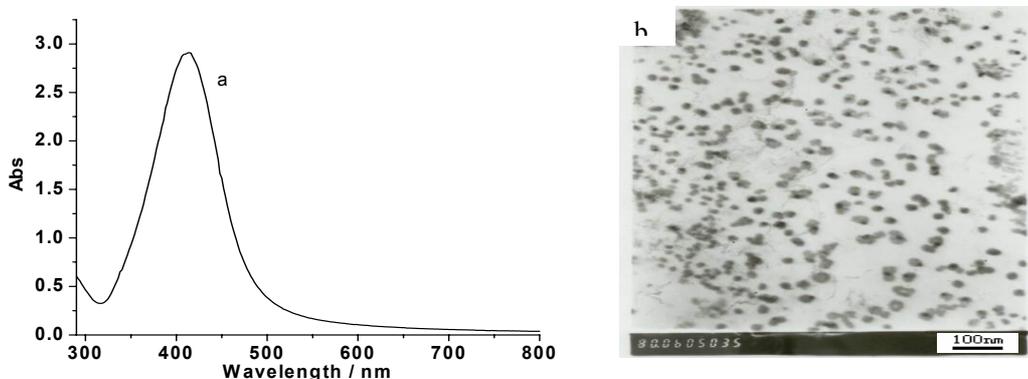

Figure 1. (a) UV-vis spectrum of the silver nanoparticles capped by oleate and (b) TEM of Ag nanoparticles.

Preparation of Ag nanoparticles modified GC electrode

Before modification, the bare GC electrode of 2.0 mm diameter was polished successively with an Al_2O_3 (0.3 and 0.05 μm) slurry on empery paper and sonicated in HNO_3, acetone and double-distilled water for 10 min., respectively. Then, the polished electrode was immersed into the as-prepared nano-sized Ag colloid solution for 30 min. After evaporation of the solvent water, the Ag nanoparticles modified GC electrode was obtained.

Results and discussion

Comparison with silver micro-disk electrode

Figure 2 shows the two cyclic voltammograms of the Ag nanoparticles modified electrode and the silver micro-disk electrode, respectively, as working electrode in PBS. It is found that the cathodic and anodic peak potential is 349 mV and 629 mV at the Ag nanoparticles modified electrode. The redox potential here is lower than that at the bulk electrode, which is 700 mV and more than 800 mV, respectively. This obviously reveals that the reducibility of the silver nanoparticles is better than for the bulk silver.
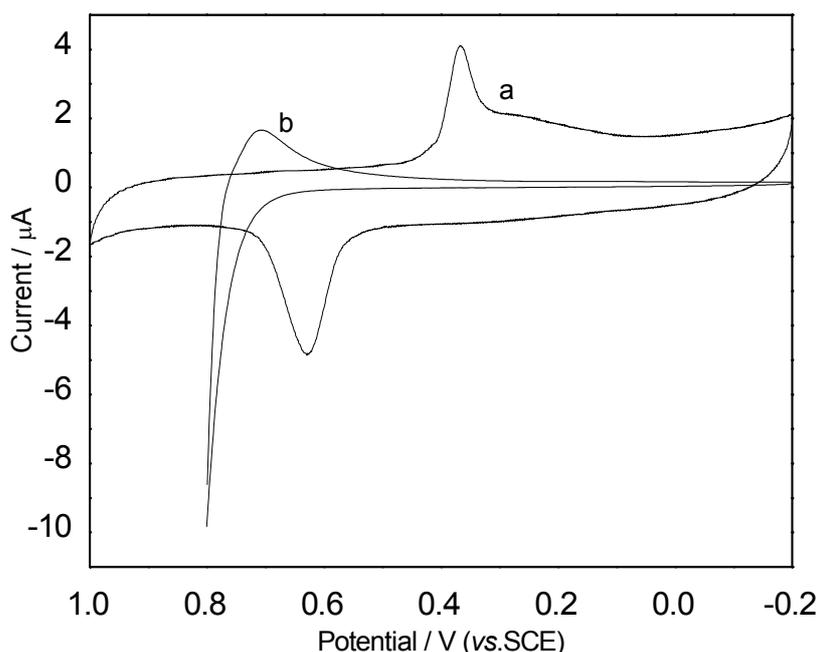

Figure 2. Cyclic voltammograms at (a) silver nanoparticles modified electrode and at silver micro-disk electrode (b) in 0.1 mol/L PBS (pH 6.0); scan rate: 80 mV/s; scan from 1.0 (a) or 0.8 (b) to –0.2 V.

Electrochemical behaviour of SCN⁻ at Ag nanoparticles modified electrode

Cyclic voltammetric (CV) experiments were performed at silver nanoparticles modified GC electrode in PBS and a couple of redox peaks were observed, as shown in Fig. 3(a). When SCN⁻ was added to the solution, a new oxidation peak occurred due to the formation of a Ag^+-SCN⁻ complex and the anodic peak current for the of silver nanoparticles decreased. The new anodic peak current increased with the concentration of SCN⁻ increasing. Based on this phenomenon, the determination of

SCN⁻ with this modified electrode should be possible. Because the anodic peak potential changed more obviously, it has been chosen for investigation.
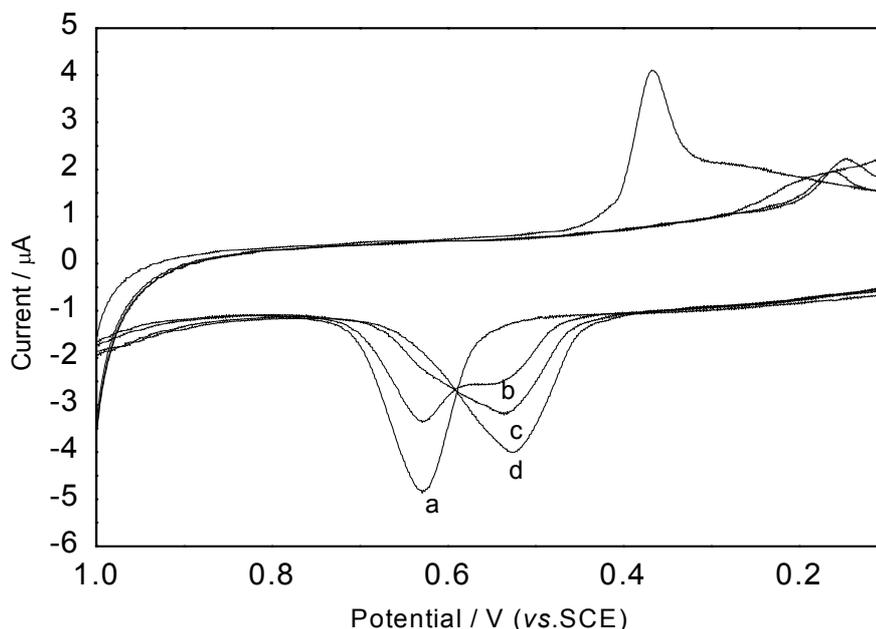

Figure 3. CV curve of SCN⁻ of different concentrations at silver nanoparticles modified electrode. (a) 0; (b) 5.0×10^{-5}; (c) 10×10^{-5}; (d) 15×10^{-5} mol/L SCN⁻ in 0.1 mol/L PBS (pH 6.0); scan rate: 80 mV/s.

Choosing of supporting electrolyte

For optimizing the determination conditions of SCN⁻, a number of buffer systems were tested including 0.1 mol/L HAc-NaAc, PBS, Tris-HAc, potassium acid phthalate, and sodium citrate. In general, a somewhat higher sensitivity and better peak shape were obtained in PBS. Thus, measurements were carried out in 0.1 mol/L PBS. Another reason to choose PBS as supporting electrolyte is that it is similar to the environment of SCN⁻ in organism.

Effect of solution pH

The effect of pH on the response of SCN⁻ at the modified electrode was investigated with pH 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5 and 7.0, respectively. The results showed that the peak currents increased with the increasing pH until it reached 6.0. Then the anodic and cathodic peak currents decreased with increasing pH value. Therefore, 0.1 mol/L, pH 6.0, PBS as supporting electrolyte has been chosen in the following experiments.

Effect of the scan rate

The relationship between the peak current and the scan rate is shown in Figure 4. In this investigation it is found that scan rates from 20 to 180 mV/s show a linear response on the peak current at the modified electrode in the presence of SCN⁻. The result indicated that the electron-transfer reaction was controlled by adsorption. In order to identify the electrode-reaction process, a continuous

CV experiment was carried out. It is found from continuous cyclic voltammograms that the peak current of the first CV was more than that of the second one and after the third CV, the peak current tended to be stable, which also revealed that the adsorptive process controlled the process of electrode reaction. Therefore, the contribution of adsorption plays a more important role in the electrode process.
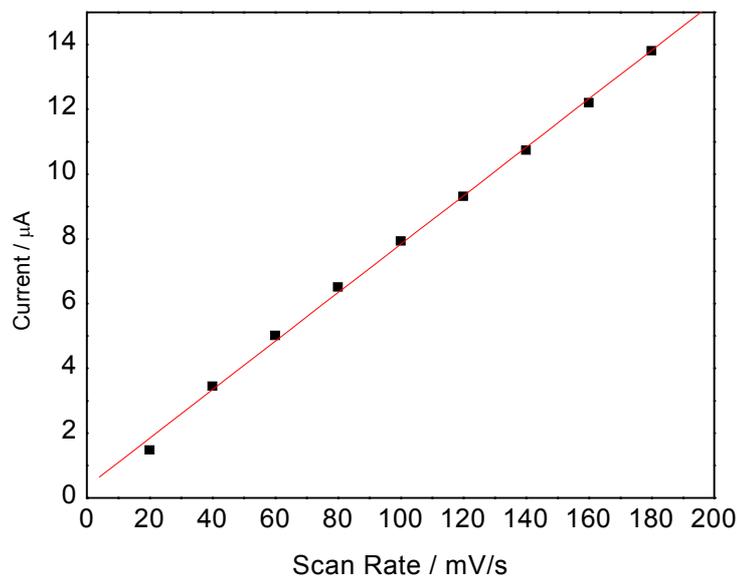

Figure 4. Relationship between scan rate and oxidation peak current in 1.5×10^{-5} mol/L SCN$^-$ at the Ag nanoparticles modified GC electrode in 0.1 mol/L PBS (pH 6.0).

Reproducibility and stability of the modified electrode

6.0×10^{-5} mol/L thiocyanate with the same electrode has been determined for eight times. It was found that the relative standard deviation (RSD) of 8 times successive scans was just 4.5% indicating that the modified electrode has an excellent reproducibility. The stability of the modified electrode was also investigated. The modified electrode had been stored at 4 °C for a week and the response current was almost the same for the determination of SCN$^-$.

Determination of thiocyanate

The determination of SCN$^-$ at the Ag nanoparticles modified GC electrode was performed with differential pulse voltammetry (DPV). The anodic peak current was selected as analytical signal. The results showed that the peak current was proportional to the concentration over a certain range of concentration (as shown in Figure 5).
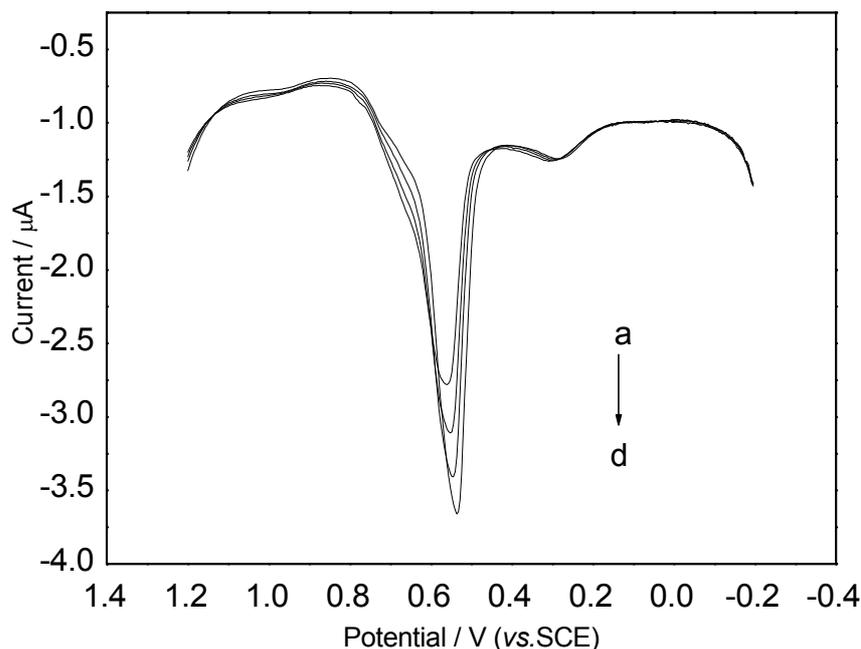
Figure 5. DPV of SCN⁻ on Ag nanoparticles modified electrode. The concentration of SCN⁻: (a) 9; (b) 12; (c) 15; (d) 18 μmol/L.

In the range of $5.0 \times 10^{-7} \sim 7.0 \times 10^{-6}$ mol/L, the linear regression equation is $I_P(\mu A)=3.83+0.19*C_{SCN^-}(\mu mol/L)$ (r = 0.9995) and in the range of 7.0×10^{-6}- 4.0×10^{-4} mol/L, the equation is $I_p(\mu A)=1.8692+0.0724*C_{SCN^-}(\mu mol/L)$ (r = 0.9958). The detection limit (S/N=3) is 4×10^{-8} mol/L.

Interference study

We have studied about 20 kinds of ions interference with SCN⁻ (with 5×10^{-6} mol/L SCN⁻, the deviation of the determination is within 10%). We found that 1000 times higher SO_4^{2-}, 2000 times higher Na^+ and NO_3^-, 200 times higher Mg^{2+} and Mn^{2+}, 100 times higher Al^{3+} and $C_2O_4^{2-}$, 50 times higher Zn^{2+}, Ca^{2+} and Cd^{2+}, 10 times higher F⁻, $S_2O_3^{2-}$, 1 times higher I⁻, Br⁻ and Cl⁻ and 200 times higher caffein concentrations did not interfere with the determination of SCN⁻.

Analytical Application

The injection of thiocyanate was analysed by standard addition method using the proposed analytical methods described above. We investigated the saliva of five smokers and non-smokers, respectively. The results were shown in Table 1. The results show that the proposed methods could be efficiently used for the determination of thiocyanate in practical samples.

The accuracy of the proposed method was further validated by comparison of the found values with those estimated by the reference methods for SCN⁻ [16]. The results are shown in Table 2. The experimental results verified the accuracy of the propose method as good.

Table 1. Determination of thiocyanate in practical samples.

Samples	Content of SCN⁻	SCN⁻ added	SCN⁻ found
Saliva (smoker)	21.3	15	36.6
Saliva (non-smoker)	10.9	15	26.7

Table 2. Accuracy of the proposed method.

Samples Saliva	SCN⁻ found (μmol/L)		Error relative %
	Proposed method	Reference method	
Non-smokers	10.9	10.4	+4.6
Smokers	21.3	22.1	-3.7

Conclusions

The present work reveals the fact that nano-sized Ag is largely different from the bulk counterpart and it shows a surprisingly high electro-reductive activity. The electrode can detect SCN⁻ at the sub-micromolar level. The potential application of a nano-sized Ag modified electrode for the fabrication of a voltammetric SCN⁻ sensor is demonstrated for the first time in electrochemistry. The proposed method can be applied for the detection of SCN⁻ in practical samples. It shows excellent sensitivity, good selectivity and antifouling properties.

Acknowledgements

Reference

1. Raj, C.R.; Okajima, T.; Ohsaka, T. Gold nanoparticles arrays for the voltammetric sensing of dopamine. *J. Electroanal. Chem.* **2003**, 543(2), 127.

2. Israel, L.B.; Kariuki, N.N.; Li, H.; Maye, M.M.; Luo, J.; Zhong, C.J. Electroactivity of Cu^{2+} at a thin film assembly of gold nanoparticles linked By 11-mercaptoudecanoic acid. *J. Electroanal. Chem.* **2001**, 517, 69.

3. Grabar, K.C.; Freeman, R.G.; Hommer, M.B.; Natan M.J. Preparation and characterization of Au colloid monolayers. *Anal. Chem.* **1995**, 67, 735.

4. Leibowitz, F.L.; Zheng, W.; Maye, M.M.; Zhong, C.J. Structures and properties of nanoparticles thin films formed via a one-step exchange-cross-linking-precipation route. *Anal. Chem.* **1999**, 71, 5076.

5. Doron, A.; Katz, E.; Willner, I. Organization of Au colloids as monolayer films onto ITO glass surface: Application of the metal colloid films as base interfaces to construct redox-active monolayers. *Langmuir* **1995**, 11, 1313.

6. Brown, K.R.; Fox, A.P.; Natan, M.J. Morphology-dependent electrochemistry of cytochrome C at Au colloid-modified SnO_2 electrodes. *J. Am. Chem. Soc*. **1996**, 118, 1154.

7. Alivisatos, A.P. Semiconductor clusters, nanocrystals and quantum dots. *Science* **1996**, 271, 933.

8. Glatz, Z.; Novakova, S.; Sterbova H. Analysis of thiocyanate in biological fluids by capillary zone electrophoresis. *J. Chromatogr. A*. **2001**, 916, 273.

9. Wuthier, U.; Pham, H.V.; Zund, R.; Welti, D.; Funck, R.J.J.; Bezegh, A.; Ammann, D.; Pretsch, E.; Simon,W. Tin organic compounds as neutral carriers for anion selective electrodes. *Anal. Chem.* **1984**, 56, 535.

10. Florido, A.; Bachas, L.G.; Valiente, M.; Villaescusak, I.; Florido, A. Anion-selective electrodes based on a gold(III)-triisobutylphosphine sulfide complex. *Analyst*, **1994**, 119, 2421.

11. Chaniotxkis, N.A.; Chasser, A.M.; Meyerhoff, M.E. Influence of porphyrin structure on anion selectivities of manganese(III) porphyrin based membrane electrodes. *Anal. Chem.* **1988**, 60, 185.

12. Gao, D.; Li, J.Z.; Zheng, R.Q. Metalloporphyrin derivatives as neutral carriers for PVC membrane electrodes. *Anal. Chem.* **1994**, 6, 224.

13. Ganjali, M.R.; Poursaberi, T.; Basiripour, F.; Salavati-Niassari, M.; Yousefi, M. Shamsipur, M. Highly selective thiocyanate poly(vinyl chloride) membrane electrode based on a cadmium–schiff's base complex. *Fresenius. J. Anal. Chem.* **2001**, 370, 1091.

14. Wang, C.Y.; Liu, C.Y.; Wang, M.; Shen, T. Spectroscopic studies of thiocyanate in silver hydrosol and the influence of halide ions. *Spectrochimica Acta Part A*. **1999**, 55, 991.

15. Wang, W.; Efrima, S.; Regev, O. Directing oleate stabilized nanosized silver colloids into organic phases. *Langmuir* **1998**, 14, 602.

16. Lahti, M.; Vilpo, J.; Hovinen, J. Determination of thiocyanate within physiological fluids and environmental samples: Current practice and future trends. *J. Chem. Educ*. **1999**, 76, 1281.