

Application of bismuth-film modified glassy carbon electrode for solid-phase extraction of sudan I

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ABSTRACT

A sensitive electrochemical sensor for detection of sudan I was developed based on solid-phase extraction (SPE) at bismuth-film modified glassy carbon electrode. SPE of sudan I may be due to the physical adsorption between sudan I and the bismuth film. The properties of the bismuth-film electrode (BiFE) designed for detection Sudan I were examined by scanning electron microscopy (SEM), electrochemical impedance and voltammetry. The various bismuth plating solutions containing Cl^- , Br^- and I^- respectively, were tested in bismuth-film generation. It has been found that the plating solution only containing Br^- ensures the finest quality bismuth film for analytical purposes. Other operational parameters such as extraction time, pH of the electrolytic and sample solution, and co-solvents have been optimized. Under the optimum experimental conditions, the stripping voltammetric response was proportional to the concentration of sudan I ranging from 0.1 to 10 μM . The detection limit was 0.05 μM . Copyright © 2012 VBRI Press.

Keywords: Bismuth-film electrode; solid-phase extraction; cathodic stripping voltammetry; Br^- ; Sudan I.



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Introduction

Since the year 2000, bismuth-film electrodes (BiFEs) have become an attractive new subject of electroanalytical research as a potential replacement for common mercury-based electrodes, such as the mercury-film electrode and hanging mercury drop electrode [1]. Bismuth is an environmental friendly element, with very low toxicity and advantageous electrochemical properties, such as high hydrogen over-potential, limited oxygen interference or the ability to form fused or low-temperature alloys with heavy metals [2], very similar to those attained when using mercury electrodes. However, only few reports have focused on determination of organic compounds using BiFEs. There are reports of amperometric detection of 2-nitrophenol and 4-nitrophenol [3], methyl parathion [4], tetracycline [5], voltammetric detection of metamitron [6], thiamethoxam [7], and AdSV detection of daunomycin [8]. Recently, BiFEs have been applied to detect metallothionein [9].

BiFEs can be deposited electrochemically at constant potential either in situ or ex situ by pre-deposition. It was observed that the addition of complexing Br^- into the modification solution is beneficial for the ex situ preparation of a bismuth film [10]. This deposition route, reported for the first time by Krolicka et al. [10], has

provided BiFEs of higher (physical) stability and enhanced reproducibility of measurements associated with the electrochemical stripping analysis. Recently, it suggested that the introduction of Br^- during ex situ preparation of bismuth films enhances the stability of ex situ BiFEs, without adversely affecting their conductivity and electrochemical characteristics [11].

Interestingly, we found that Sudan I can be strongly adsorbed onto BiFE surface. The force that holds Sudan I at BiFEs is not well understood, but the obvious voltammetric signals indicate that the main force is adequate strong. Motivated by these results, in this paper we developed an electrochemical sensor for sudan I based on solid-phase extracation (SPE) at BiFEs. The determination of sudan I included two main steps: (A) sudan I adsorption; (B) electrochemical stripping detection of adsorbed Sudan I. The electrochemical characterization and cathodic stripping voltammetric performance of bound sudan I were evaluated using cyclic voltammetric and square-wave voltammetric (SWV) analysis. The promising SPE and stripping voltammetric performances open new opportunities for fast, simple, and sensitive analysis of sudan I.

Experimental

Reagents

The bismuth (III) ion stock solution (1000 mg/L in 5 wt% nitric acid) was purchased from Sigma-Aldrich (St Louis, USA). Sudan I was purchased from (Augsburg, Germany). Sudan I is a rodent carcinogen and the wastes containing these compounds were collected in a specific container. Appropriate personal protective equipment was utilized to minimize skin and eye contact and the potential for accidental inhalation or ingestion. Stock solution of 8×10^{-4} mol/L Sudan I was prepared by dissolving an appropriated amount in ethanol. Acetate buffer (0.2 M), KCl, KBr, KI, ethanol, and other reagents used were of analytical reagent grade. Aqueous solutions were prepared with double-distilled water.

Apparatus

Scanning electron microscopy (SEM) was carried out on a JEOL JSM-5900 LV machine. Cyclic and cathodic stripping voltammetric measurements were performed on CHI-660C workstation (Shanghai, China). A bare glassy carbon electrode (GCE) or a bismuth-film modified GCE (BiF/GCE) served as working electrode, with a saturated calomel electrode (SCE) and a platinum wire as reference and auxiliary electrode, respectively. Electrochemical impedance experiments were carried out in the same electrochemical cell. Impedance measurements were performed at a potential of -1.0 V with frequencies ranging from 100 kHz to 0.1 Hz and a sinusoidal voltage perturbation of amplitude 5 mV.

Preparation of BiF/GCE

A GCE (3-mm diameter) was polished carefully to a mirrorlike with 0.3-, 0.1- and 0.05- μm alumina slurry and sequentially sonicated for 3 min in ethanol and water. Bismuth film was formed by ex situ deposition on GCE at

constant applied potential. In detail, the bismuth film was deposited from a separate acetate buffer solution (pH 4.5) (ex situ deposition) in the presence of dissolved oxygen, containing 0.25 mg/mL Bi (III) by electrolysis at -1.0 V vs. SCE for 80 s while stirring the solution. BiF/GCE in the presence of Br^- was prepared similarly from an acetate buffer solution (pH 4.5) containing 0.125 mg/mL bismuth (III) and 0.125 mg/mL KBr at -0.3 V vs. SCE for 80 s. For BiF/GCE in the presence of Cl^- or I^- , only KBr was replaced with KCl or KI, respectively.

Electrochemical stripping detection based on SPE

A BiF/GCE prepared with Br^- was dipped into a stirring 0.2 mol/L acetate solution containing 20% (v/v) ethanol and the desired concentrations of Sudan I for a given time period, washed with distilled water carefully, and transferred to a 2-mL electrochemical cell containing 0.2 M acetate solution. SWV measurements were performed from -0.3 to -0.9 V with a step potential of 4 mV, an amplitude of 20 mV, and a frequency of 25 Hz. Electrochemical measurements were carried out in nondeoxygenated solutions, and were performed at room temperature.

Regeneration of electrode surface

After the electrochemical stripping measurement, multiple successive SWV scanning was used to remove the bound Sudan I until the cathodic stripping peak disappeared. The electrode was washed with distilled water for the next measurement. And the renewal of the BiF/GCE required only a simple two-step electrochemical procedure resulting in repeatedly identical fresh bismuth film surface.

Sample preparation

The ketchup sample possibly contained Sudan I was obtained from a local market. The ketchup sample was treated as follows: 10.0 g ketchup was exactly weighed, and then 20 mL ethanol was added into. After 20-min ultrasonication, the mixture was filtrated and the liquid phase was collected in a 100-mL volumetric flask. The treatment was repeated three times, and the filtrate extract was diluted to volume with ethanol. the spiked sample solution was prepared as the same method after adding known-amount of Sudan I standard.

Results and discussion

SEM images

Fig. 1 shows the SEM images of BiF/GCE prepared without Br^- (a) and with Br^- . It is evident that the bismuth film, which was grown without Br^- (a), exhibits relatively large and sparse bismuth crystals. The surface of bismuth films in the absence of Br^- was rougher and bigger bismuth crystals were observed in comparison with those prepared with Br^- . The deposition protocol in the presence of Br^- yielded a denser growth of smaller bismuth crystals, which were distributed uniformly on the surface of the substrate GCE. This phenomenon can be ascribed, and is also consistent with earlier observation [12], to different stabilities of bismuth hydroxo- and halogen-complexes, which affect the deposition of bismuth film. The order of bismuth halogen-complexes' stabilities is $\text{I}^- > \text{Br}^- > \text{Cl}^-$

[12]. Since we found that Cl^- , Br^- and I^- could be adsorbed onto the surface of bismuth film during plating and I^- can cause a serious problem of undesired adsorption, here we selected Br^- to form a more uniform bismuth film.

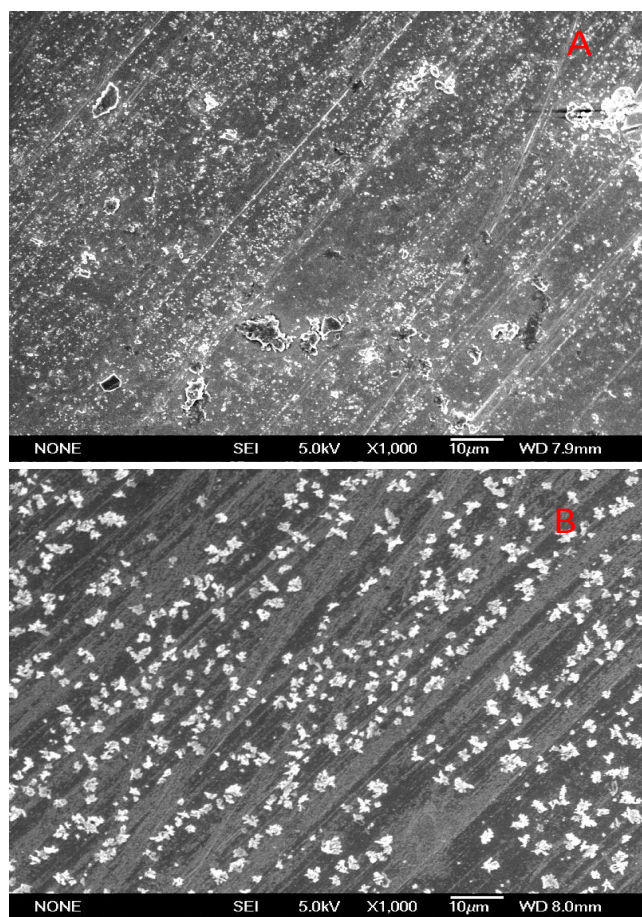


Fig. 1. SEM images of BiF/GCE prepared without Br^- (a) and with Br^- in the preparation solution.

Electrochemical impedance spectra

Fig. 2A shows impedance spectra recorded at BiF/GCE prepared with Br^- (curve a), GCE (curve b), BiF/GCE prepared with Cl^- (curve c), BiF/GCE prepared with I^- (curve d), and at BiF/GCE prepared without halogen ions (curve e). The peak of BiF/GCE prepared with Br^- shifted to much higher frequency ($\lg f = 0.3$) due to the facile charge transfer compare to that on GCE ($\lg f = -0.7$), BiF/GCE prepared with I^- ($\lg f = -0.3$), without halogen ions ($\lg f = -0.2$) and prepared with Cl^- ($\lg f = 0$). It is the direct evidence of successful deposition of a uniform bismuth film prepared in the presence of Br^- .

Fig. 2B shows the cyclic voltammograms of different electrodes. No peak was observed at bare GCE (curve a), BiF/GCE prepared without Br^- (curve b) and BiF/GCE prepared with Br^- (curve c) in 0.2 M acetate buffer (pH 4.5). The bare GCE showed very low background current, while the BiF/GCE prepared without Br^- displayed much larger current, and the BiF/GCE prepared with Br^- displayed the largest current, confirming the modification of the bismuth film onto the GCE and a more uniform

bismuth film prepared in the presence of Br^- since the modification of bismuth film increased the electrode area, and thus increased the interfacial capacitance of the prepared BiF/GCE. After SPE of Sudan I, small reduction peaks were observed on GCE (curve d) and BiF/GCE prepared without Br^- (curve e) at -680 mV and -620 mV, respectively. Obviously, a well-defined reduction peak and positive direction-shifted reduction potential was observed at -570 mV on BiF/GCE prepared with Br^- (curve f). This result indicated that the presence of Br^- most significantly facilitated forming a more uniform bismuth film, which provided a conductive pathway to electron transfer and thus promoted electron transfer reactions at a higher potential. With increasing the scan rates, the peak currents increased and the peak potential shifted slightly (**Fig. 2C**), indicating a typical surface-controlled electrode process. The cathodic peak current was linear to the scan rate over the investigated range from 5 to 300 mV/s, with a correlation coefficient of 0.9976 (inset in **Fig. 2C**).

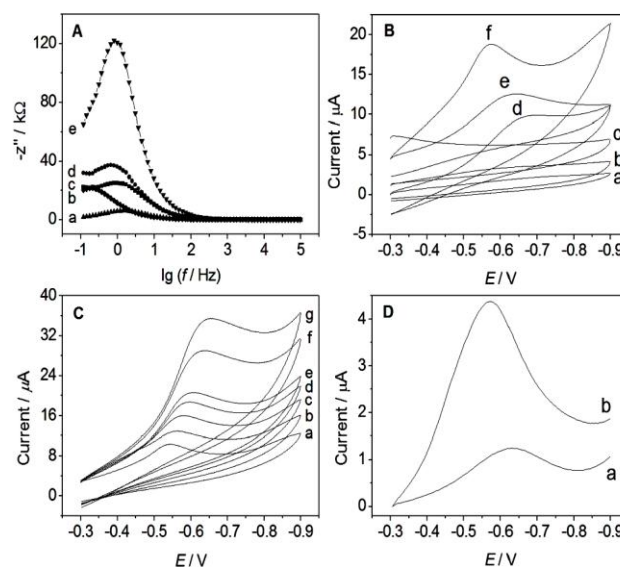


Fig. 2. (A) Electrochemical impedance spectra of BiF/GCE prepared with Br^- (a), GCE (b), and BiF/GCE prepared with Cl^- (c), with I^- (d) and without halogen ions (e) in 0.2 M acetate buffer (pH 4.5). (B) Cyclic voltammograms of GCE (a), BiF/GCE without Br^- (b) and with Br^- (c) in 0.2 M acetate buffer (pH 4.5), and (d), (e) and (f) are corresponding responses after 3-min extraction from a sample solution containing 10^{-5} M Sudan I. Scan rate: 50 mV/s. (C) Cyclic voltammograms of BiF/GCE after extraction of Sudan I at different scan rates. 5 (a), 10 (b), 20 (c), 50 (d), 100 (e), 200 (f), 300 (g) mV s^{-1} . Inset is the relationship between scan rates and peak currents. (D) SWV responses of BiF/GCE in 0.2 M acetate buffer (pH 4.5) with 3-min extraction from sample solution containing 10^{-6} M Sudan (a) and without pre-concentration (b). SWV conditions: scanning potential range, -0.3 to -0.9 V; frequency, 25 Hz; increasing potential, 4 mV.

Electrochemical behavior of Sudan I at BiF/GCE

SWV is widely used in electrochemical determination because of high sensitivity and excellent resolution. **Fig. 2D** shows the SWV responses in acetate buffer (0.2 M, pH 4.5) after 3-min extraction from Sudan I solution to the BiF/GCE (curve a). In comparison with the direct measurement in sample solution (curve b), SPE resulted in a significant enhancement of the current response.

Optimization of experimental conditions for the preparation of BiF/GCE

Since the composition of plating electrolyte could influence the quality of bismuth coating, the addition of Cl^- , Br^- and I^- in the preparation solution was studied. As shown in **Fig. 3A**, no peak was observed at the BiF/GCE prepared with Br^- (curve a) in 0.2 M acetate buffer (pH 4.5). After 3-min SPE in Sudan I sample solution, small reduction peaks on BiF/GCE prepared with I^- (curve b), bare GCE (curve c), BiF/GCE prepared without halogen ions (curve d) and BiF/GCE prepared with Cl^- (curve e) were observed. However, the reduction peak current of Sudan I increased significantly on the BiF/GCE prepared with Br^- , and the peak potential of the reduction peak (-560 mV) shifted ~ 110 mV to a positive direction compared with that on GCE (curve f). These results indicated that the addition of complexing Br^- into the modification solution is beneficial for the ex situ preparation of a bismuth film in connection with its electrochemical stripping operation. Therefore, BiF/GCE prepared with Br^- was used for the detection of Sudan I.

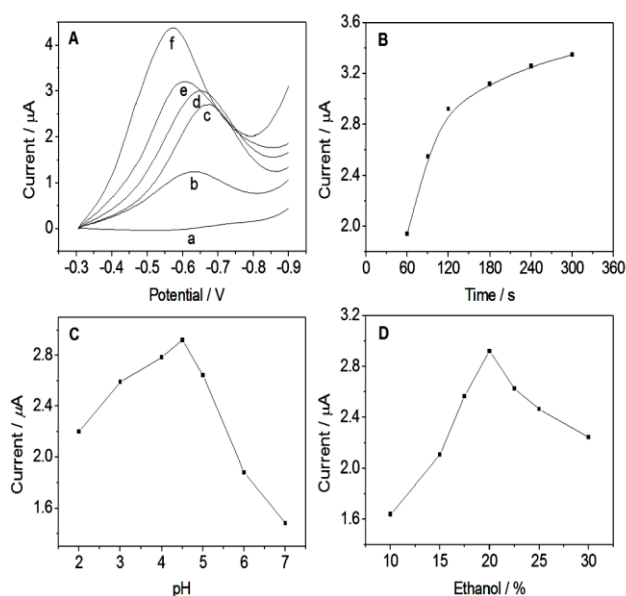


Fig. 3. Effect of the composition of plating electrolyte (A), extraction time (B), pH (C) and the content of ethanol (D) on the stripping responses of adsorbed Sudan I.

The effect of extraction time was another factor on the stripping peak current (**Fig. 3B**). The peak currents increase rapidly with the accumulation time at first and then slowly down after 3 min. The rapid and highly effective accumulation was attributed to the strong interaction between BiF/GCE and Sudan I. Thus, 3 min of extraction time was employed.

The effect of the pH in sample solution on SPE was further studied. The result revealed that pH 4.5 was the best pH for SPE (**Fig. 3C**). It is most likely due to the stability of BiF/GCE at pH 4.5, which results in a higher affinity of Sudan I to BiF/GCE. Therefore, pH 4.5 was used for further measurements.

The influence of ethanol in different volume ratio in sample solution on the stripping peak current of Sudan I

was investigated. The cathodic currents gradually increased with increasing the content of ethanol and reached a maximum at 20%, as shown in **Fig. 3D**. Further increase of the ratio of ethanol led to a decrease in the response. The decrease of the stripping current can be understood by considering the “squeezing out” effect [13]. Therefore, 20% ethanol was used to prepare the sample solution for SPE.

Analytical performance

Fig. 4 displayed the SWV response of adsorbed Sudan I by SPE process at BiF/GCE prepared with Br^- . Well-defined peaks proportional to the concentration of the corresponding Sudan I were observed covering the concentration range from 0.1 to 10 μM. The linear regression equation is $I (\mu\text{A}) = 0.1169 C + 0.8321$, with a correlation coefficient of 0.9986. A detection limit of 0.05 μM was obtained based on signal-to-noise ratio equal to 3. It is comparable with that reported so far at montmorillonite calcium modified carbon paste electrode [14], and much lower than that of 7.1×10^{-7} M at activated GCE [15]. The relative standard deviation was 5.2% for ten replicate determination of 1.0×10^{-6} M Sudan I, indicating an acceptable reproducibility.

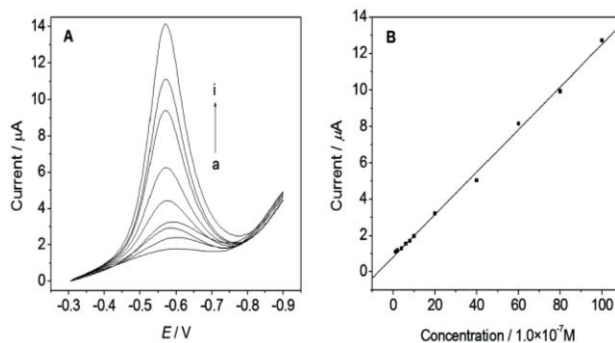


Fig. 4. (A) SWV responses of adsorbed Sudan I at BiF/GCE prepared with Br^- . The concentrations are 0.1 (a), 0.4 (b), 0.6 (c), 1.0 (d), 2.0 (e), 4.0 (f), 6.0 (g), 8.0 (h), 10 (i) μM, respectively. (B) Calibration curve.

Interferences arising from many foreign species (especially contained in ketchup sample) that are expected to coexist in solution were used to evaluate the selectivity of the determination of Sudan I at BiF/GCE. The results suggested that the natural pigments (lycopene and β -carotene) in ketchup did not interfere with the detection of Sudan I, because of the marked difference of electrochemical characteristics between pigments mentioned above and Sudan I. Some metal ions such as Fe^{3+} , Cu^{2+} , Al^{3+} , Ca^{2+} , Ba^{2+} , Mg^{2+} , Zn^{2+} almost did not influence the determination of Sudan I. While some surfactants such as cetyltrimethyl ammonium bromide and TritonX-100 produced obvious interferences. It is due to the fact that the adsorption capability of surfactants to bismuth film is much stronger than Sudan I [16].

To further demonstrate the practicality of the proposed method, the recovery test was studied by adding different amounts of Sudan I into prepared ketchup samples. Results were summarized in **Table 1**. The recoveries were from

97.4 to 103.3 %. The results indicated that the proposed method is highly accurate can be used for direct analysis of relevant samples.

Table 1. Recovery study of Sudan I in ketchup samples (n=5).

Sample	Known (1.0×10^{-7} M)	Found (1.0×10^{-7} M)	Recovery (%)
	1.00	1.06	103.3
2	2.00	2.04	102.0
3	5.00	4.97	99.4
4	10.0	9.86	98.6
5	50.0	50.2	100.4
6	100	97.4	97.4

Conclusion

A sensitive method for electrochemical stripping analysis of Sudan I has been demonstrated. The bismuth film, served as a selective “sorbent”, is able to extract Sudan I rapidly and effectively. A significantly enhanced stability of an ex-situ prepared BiFE under its electrochemical stripping operation attributed to a more uniform bismuth film formation in the presence of Br⁻. The combination of SPE with BiFE and SWV allows fast, sensitive, and selective determination of Sudan I.

Reference

- Wang, J.; Lu, J.; Hočevár, S.B.; Farias, P.A.M. *Anal. Chem.* **2000**, 72, 3218-3222.
DOI: [10.1021/ac000108x](https://doi.org/10.1021/ac000108x)
- Economou, A. *Trends in Anal Chem.* **2005**, 24, 334-340.
DOI: [10.1016/j.trac.2004.11.006](https://doi.org/10.1016/j.trac.2004.11.006)
- Hutton, E.A.; Ogorevc, B.; Smyth, M.R. *Electroanalysis* **2004**, 19, 1616-1621.
DOI: [10.1002/elan.200402979](https://doi.org/10.1002/elan.200402979)
- Du, D.; Ye, X.P.; Zhang, J.D.; Liu, D.L. Cathodic electrochemical analysis of methyl parathion at bismuth-film modified glassy carbon electrode. *Electrochim. Acta* **2008**, 53, 4478-4484.
DOI: [10.1016/j.electacta.2008.01.023](https://doi.org/10.1016/j.electacta.2008.01.023)
- Sattayasamitsathit, S.; Thavarungkul, P.; Kanatharana, P. *Electroanalysis* **2007**, 19, 502-505.
DOI: [10.1002/elan.200603726](https://doi.org/10.1002/elan.200603726)
- Arribas, A.S.; Bermejo, E.; Chicharro, M.; Zapardiel, A. *Electroanalysis* **2006**, 18, 2331-2336.
DOI: [10.1002/elan.200603666](https://doi.org/10.1002/elan.200603666)
- Guzsvány, V.; Kádár, M.; Gaál, F.; Bjelica L.; Tóth K. *Electroanalysis* **2006**, 18, 1363-1371.
DOI: [10.1002/elan.200603540](https://doi.org/10.1002/elan.200603540)
- Bučková, M.; Gründler, P.; Flechsig, G.U. *Electroanalysis* **2005**, 17, 440-444.
DOI: [10.1002/elan.200403178](https://doi.org/10.1002/elan.200403178)
- Yang, M.; Zhang, Z.; Hu, Z.; Li, J. *Talanta* **2006**, 69, 1162-1165.
DOI: [10.1016/j.talanta.2005.12.041](https://doi.org/10.1016/j.talanta.2005.12.041)
- Krolicka, A.; Bobrowski, A.; Kalcher, K.; Mocak, J.; Svancara, I.; Vytras, K. *Electroanalysis* **2003**, 15, 1859-1863.
DOI: [10.1002/elan.200302763](https://doi.org/10.1002/elan.200302763)
- Hočevár, S.B.; Daniele, S.; Bragato, C.; Ogorevc, B. *Electrochim. Acta* **2007**, 53, 555-560.
DOI: [10.1016/j.electacta.2007.07.035](https://doi.org/10.1016/j.electacta.2007.07.035)
- Svancara, I.; Baldrianova, L.; Vlcek, M.; Metelka, R.; Vytras, K. *Electroanalysis* **2005**, 17, 120-126.
DOI: [10.1002/elan.200403061](https://doi.org/10.1002/elan.200403061)
- Väärtnõu, M.; Lust, E. *J. Electroanal. Chem.* **2006**, 587, 220-225.
DOI: [10.1016/j.jelechem.2005.11.019](https://doi.org/10.1016/j.jelechem.2005.11.019)
- Lin, H.G.; Li, G.; Wu, K.B. *Food Chem.* **2008**, 107, 531-536.
DOI: [10.1016/j.foodchem.2007.08.022](https://doi.org/10.1016/j.foodchem.2007.08.022)
- Du, M.J.; Han, X.G.; Zhou, Z.H.; Wu, S.G. *Food Chem.* **2007**, 105, 883-888.
DOI: [10.1016/j.foodchem.2006.12.039](https://doi.org/10.1016/j.foodchem.2006.12.039)
- Wang, J.; Deo, R.P.; Thongngamdee, S.; Ogorevc, B. *Electroanalysis* **2001**, 13, 1153-1156.
DOI: [10.1002/1521-4109\(200110\)13<1153::AID-ELAN1153>3.0.CO;2-1](https://doi.org/10.1002/1521-4109(200110)13<1153::AID-ELAN1153>3.0.CO;2-1)

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