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ORIGINAL PAPER

Voltammetric sensor for glutathione determination based on ferrocene-modified carbon paste electrode

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Abstract The electrocatalytic oxidation of glutathione (GSH) has been studied at the surface of ferrocene-modified carbon paste electrode (FMCPE). Cyclic voltammetry (CV), double potential step chronoamperometry, and differential pulse voltammetry (DPV) techniques were used to investigate the suitability of incorporation of ferrocene into FMCPE as a mediator for the electrocatalytic oxidation of GSH in buffered aqueous solution. Results showed that pH 7.00 is the most suitable for this purpose. In the optimum condition (pH 7.00), the electrocatalytic ability of about 480 mV can be found and the heterogeneous rate constant of catalytic reaction was calculated as $k'_h = 1.83 \times 10^{-1}$cm s^{-1}. Also, the diffusion coefficient of glutathione, D, was found to be 3.61×10^{-5} cm^2 s^{-1}. The electrocatalytic oxidation peak current of glutathione at the surface of this modified electrode was linearly dependent on the GSH concentration and the linear analytical curves were obtained in the ranges of 3.2×10^{-5} M–1.6×10^{-3} M and 2.2×10^{-6} M–3.5×10^{-3} M with cyclic voltammetry and differential pulse voltammetry methods, respectively. The detection limits (3σ) were determined as 1.8×10^{-5} M and 2.1×10^{-6} M using CV and DPV, respectively. Finally, the electrocatalytic oxidation of GSH at the surface of this modified electrode can be employed as a new method for the voltammetric determination of glutathione in real samples such as human plasma.

Keywords Ferrocene · Carbon paste electrode · Glutathione · Electrocatalysis · Cyclic voltammetry · Differential pulse voltammetry

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Introduction

Glutathione as a biological compound containing thiol groups is found in most living cells from microbes to higher organisms in the oxidized (GSSG) and reduced (GSH) forms. Its concentration levels are dependent upon the activity of glutathione reductase enzyme, which appears to be as ubiquitous in natural as GSH [1]. GSH is a non-protein tripeptide composed of the amino acids which are synthesized in two steps: catalyzation by γ-glutamyl-cysteine synthetase and GSH synthetase followed by degradation into cysteinyl-glycine by γ-glutamyltranspeptidase [2]. GSH as a major intracellular thiol compound plays an important role in many biological processes such as intracellular reduction–oxidation metabolic cycles, transportation, protein synthesis, catabolism, and metabolism [3, 4]. GSH may act as an enzyme cofactor [5], a detoxification agent in the case of high concentrations of poisonous heavy metals [6], a protective agent against irradiation damage [7], important physiological function to maintain the integrity of red blood cells [8], or antioxidant, scavenger of oxygen-derived free radicals [2]. The studies also indicated that changes of GSH concentration in biological bodies may lead to diseases like occlusive vascular disease, leukemia, diabetes, acquired immunodeficiency syndrome, cataract, heart attack, AIDS, and hemolytic anemia [9–12].

As a consequence of the widespread involvement of GSH for many biological functions, much effort has been made to develop sensitive and selective methods for its detection. Many chemical and instrumental techniques have been reported for the determination of GSH, which are divided into titrimetry [13], spectrophotometry [14–16], spectrofluorimetry [17–20], high-performance liquid chromatography [21–24], capillary zone electrophoresis [25], ^{1}H NMR [26], and enzymatic methods [27]. However, most

of them suffer from the difficulties at sample preparation, the necessity of derivatization or lack of sufficient sensitivity, all of which limit their utility. Compared to the other techniques, electroanalytical methods have the advantages of simplicity, low expense, and high sensitivity. The electron transfer reaction of GSH at bare common electrodes such as carbon, platinum, gold, and silver is a slow process with required high over-potential, except the mercury electrode [28–30]. Mercury is apparently not ideal for use as sensor due to its toxicity. In addition, strong adsorption of GSH at the surface of the noble metallic electrodes makes GSH detection unsatisfactory, resulting in serious blocking and fouling of these electrodes [31].

In order to solve those problems mentioned above, much works have been done to develop the chemically modified electrodes for determination of GSH. A series of modified electrodes base on enzymes such as GSH oxidase [32], GSH peroxidase [33, 34], and tyrosinase [35]; organ-metallic compounds [36–39]; organic compounds [38, 40]; and TTF–TCNQ complex [41]. However, some authors have emphasized the instability of the attached materials on the electrodes as a problem arising in the utilization of chemically modified electrodes (CMEs) [42]. It seems that the incorporation of electrocatalysts into the electrode matrix can, even partly, help to solve these problems, and carbon paste electrodes (CPEs), due to their ease and speed of construction, obtaining a new reproducible surface, low residual current compared to the other solid electrodes, porous surface, compatibility with various types of modifiers, and low cost, have been widely used as a suitable matrix for preparation of CMEs [43–46].

On the other hand, ferrocene and its derivatives, due to their good stability in solution, rapid responses to many electroactive substances, being pH-independent, stable in both oxidized and reduced forms, unreactive with oxygen, regenerated at low potential, and having fast electron transfer, are the most successful mediators. Therefore, we prepared some ferrocene-derived CMEs and applied for electrocatalytic determination of some biological compounds [47, 48].

In this paper, we suggest a voltammetric sensor for GSH determination based on the use of ferrocene as a mediator into the carbon paste electrode matrix. Therefore, the suitability of this modified electrode in the electrocatalytic determination of glutathione is demonstrated by cyclic voltammetry and differential pulse voltammetry.

Experimental

Apparatus and reagents

The electrochemical experiments were carried out using a potentiostat/galvanostat (BHP 2061-C Electrochemical Analysis System, Behpajooh, Iran) coupled with a Pentium III personal computer connected to a HP laser jet 6L printer, and experiments were performed in a three-compartment cell. A platinum wire was used as the auxiliary electrode. The ferrocene-modified carbon paste electrode (FMCPE) was used as the working electrode. The reference electrode was $Ag|AgCl|KCl_{sat}$ (Metrohm). Also, a pH-meter (Ion Analyzer 250, Corning) was used to read the pH of the buffered solution.

The solvent used for the electrochemical studies was twice-distilled water. Buffer solutions were prepared from orthophosphoric acid and its salts were in the pH range 2.00–10.00. High-viscosity paraffin (density=0.88 g cm^{-3}) from Fluka was used as the pasting liquid for the carbon paste electrode. Graphite powder (particle diameter= 0.1 mm) from Merck was used as the working electrode substrate. Ferrocene and glutathione (from Fluka) were used as received. All other reagents were of analytical grade.

Fabrication of modified and unmodified carbon paste electrodes

A 1% (*w*/*w*) ferrocene-spiked carbon powder was made by dissolving the given quantity of ferrocene in diethyl ether and hand-mixing with 99 times its weight of graphite powder with a mortar and pestle. The solvent was evaporated by stirring the 1:1 (*w*/*w*) mixture of 1 % ferrocene-spiked carbon powder and paraffin oil was blended by hand-mixing and the resulting paste was inserted in the bottom of a glass tube (with internal radius 3.0 mm). The electrical connection was implemented by a copper wire lead fitted into a glass tube. A carbon paste electrode without ferrocene was used as a blank to determine the background current.

Results and discussion

Electrochemical behavior of FMCPE

We have recently constructed FMCPE by incorporation of ferrocene into carbon paste matrix and studied its electrochemical properties in buffered aqueous solution by cyclic voltammetry. The experimental results show that well-defined and reproducible anodic and cathodic peaks (with E_{pa}=0.320 V and E_{pc}=0.214 V vs. $Ag|AgCl|KCl_{sat}$) related to oxidation and reduction of Fc/Fc^{+} redox couple with quasi-reversible behavior [49]. The redox process of Fc/Fc^{+} is not dependent on the pH of aqueous solution.

It is known that pH has a critical influence on the oxidation of GSH [50], whereas the electrochemical behavior of Fc^{+}/Fc redox couple is independent of pH. Thus, the effect of pH on the electrochemical properties of GSH in buffered solutions with different pH values (1.00 to 9.00) was also investigated

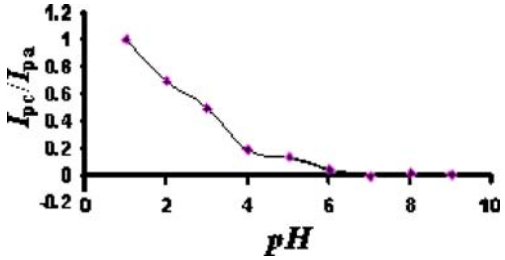


Fig. 1 Current–pH curve for electrooxidation of 1.0 mM GSH in 0.1 M phosphate buffer solution with various pH values at the surface of FMCPE at a scan rate of 10 mV s^{-1}

at the surface of FMCPE by cyclic voltammetry. It was found that electrocatalytic oxidation was more favored under neutral conditions than in acidic medium. This appears as a gradual growth in the anodic peak current and a simultaneous decrease in the cathodic peak current in the FMCPE cyclic voltammograms. Therefore, pH 7.00 was chosen as the optimum pH for electrocatalysis of GSH at the surface of FMCPE (Fig. 1).

Electrocatalytic oxidation of GSH at the FMCPE

The cyclic voltammograms obtained for FMCPE and an unmodified carbon paste electrode in a phosphate buffer solution (pH 7.00) in the presence (0.48 mM) and absence of GSH are shown in Fig. 2. The oxidation of glutathione at the bare CPE occurred irreversibly with a peak potential 840 mV vs. $Ag|AgCl|KCl_{sat}$ (curve b); in the absence of GSH, no peak appears (curve a). The anodic peak that is observed for FMCPE in the absence of GSH increased greatly in 0.48 mM of GSH solution, while the corresponding cathodic peak disappeared on the reverse scan (curves c and d). The reaction can be defined in Scheme 1, whereby the electrogenerated Fc^+ at the FMCPE surface catalyzes the oxidation

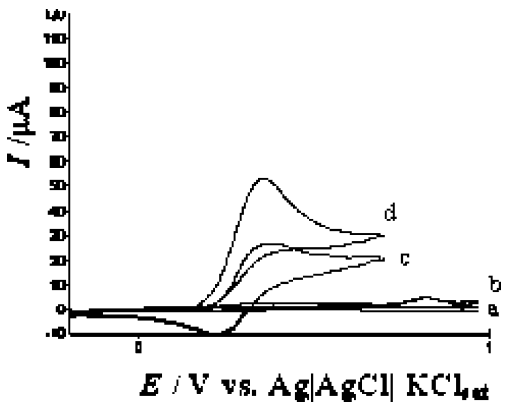
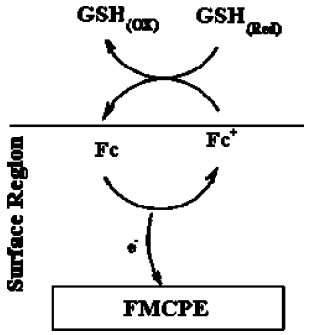


Fig. 2 Cyclic voltammograms of (*a*) CPE in 0.1 M phosphate buffer solution (pH 7.00) at a scan rate of 10 mV s^{-1} and (*b*) as *a* in the presence of 0.48 mM GSH, (*c*) as *a* and (*d*) as *b* at the surface of FMCPE

Scheme 1 Electrocatalytic oxidation of GSH at FMCPE



of GSH. The Fc^+ then undergoes a catalytic reduction by GSH back to Fc, which can then be electrochemically reoxidized to produce an enhancement in the oxidation current. The kinetic mechanism of this electrocatalyzed (EC') reaction process remains unexplained due to the oxidation processes of Fc and GSH having similar voltages at FMCPE. Therefore, the oxidation of GSH at the surface of FMCPE is shifted about 480 mV to less positive potential.

Effect of scan rate on electrocatalysis of GSH

The effect of the potential scan rates on the electrocatalytic property of FMCPE toward GSH was studied by cyclic voltammetry (Fig. 3). These results show that the catalytic effect of the mediator appeared at scan rates lower than 200 mV s^{-1}. It can also be noted from Fig. 3 that, with an increasing scan rate, the electrooxidation peak potential of GSH shifts to more positive potentials, suggesting a kinetic limitation in the reaction between Fc^+ and GSH. In addition the cathodic current would increase with increasing scan rate, because in short time-scale experiments there is not enough time for catalytic reaction to take place completely.

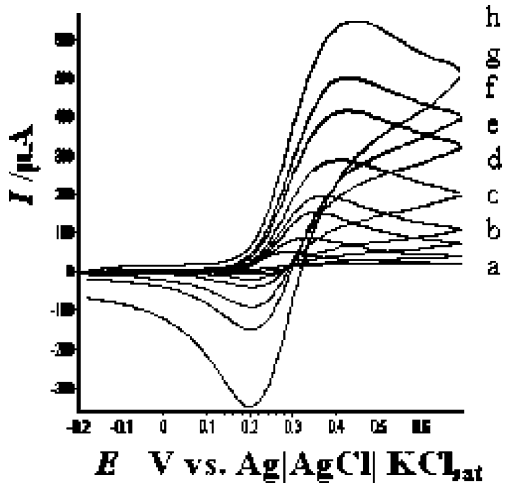


Fig. 3 Cyclic voltammograms of 0.5 mM GSH at various scan rates: (*a*) 10, (*b*) 20, (*c*) 50, (*d*) 100, (*e*) 200, (*f*) 500, (*g*) 1,000, and (*h*) 2,000 mV s^{-1} in 0.1 M phosphate buffer solution (pH 7.00)

However, the oxidation current of GSH increased linearly with the square root of the scan rate of potentials ($y = 14.817x + 20.803, R^2 = 0.9984$), demonstrating a diffusion-controlled electrochemical process.

Chronoamperometric measurements

Double step potential chronoamperometry as well as other electrochemical methods was employed for investigation of electrochemical processes at chemically modified electrodes [51, 52]. Therefore, double step potential chronoamperometric behavior of unmodified and modified carbon paste electrodes was examined in the absence and presence of various concentrations of GSH in aqueous buffered solution (pH 7.00) by setting the working electrode potential at 0.450 V (at the first potential step) and 0.00 V (at the second potential step) vs. Ag|AgCl|KCl_{sat} (Fig. 4a). As can be seen, there is not any net cathodic current corresponding to the reduction of ferricinium ion in the presence of GSH, when the potential is stepped from 0.40 to 0.00 V vs. Ag|AgCl|KCl_{sat}.

A plot of I versus $t^{-1/2}$ for a FMCPE in the presence of GSH given to be a straight line (Fig. 4b), the slope of such lines can be used to estimate the diffusion coefficient (D) of glutathione in the range 2.0–2.5 mM. The mean value of D was found to be 3.61×10^{-5} cm^2 s^{-1}. Therefore, the results show that a mediator at the surface of FMCPE can catalyze the oxidation of glutathione.

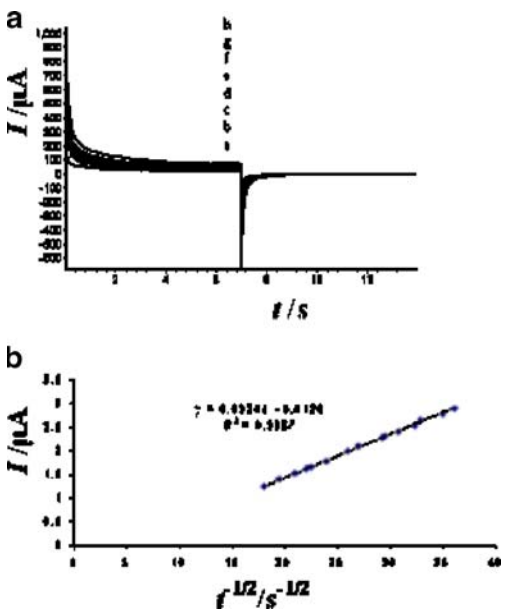


Fig. 4 **a** Chronoamperograms obtained at the FMCPE in the (*a*) absence and presence of (*b*) 0.5, (*c*) 0.7, (*d*) 1.0, (*e*) 1.5, (*f*) 2, (*g*) 2.5, and (*h*) 3.0 mM of GSH in 0.1 M phosphate buffer solution (pH 7.00). First and second potential steps were 0.450 and 0.000 V vs. Ag | AgCl | KCl_{sat}. **b** Cottrell plot for curve *b* in **a**

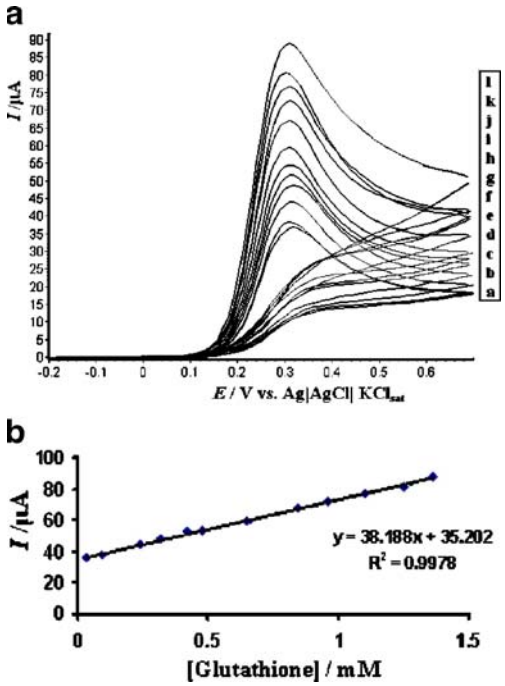


Fig. 5 **a** Cyclic voltammograms of GSH at various concentrations: (*a*) 0.03, (*b*) 0.09, (*c*) 0.24, (*d*) 0.32, (*e*) 0.42, (*f*) 0.48, (*g*) 0.65, (*h*) 0.84, (*i*) 0.96, (*j*)1.1, (*k*), 1.25 and (*l*) 1.36 mM at the surface of FMCPE in 0.1 M phosphate buffer solution (pH 7.00) at a scan rate of 10 mV s^{-1}. **b** Plot of electrocatalytic peak currents (from CV of **a**) vs. the GSH concentrations

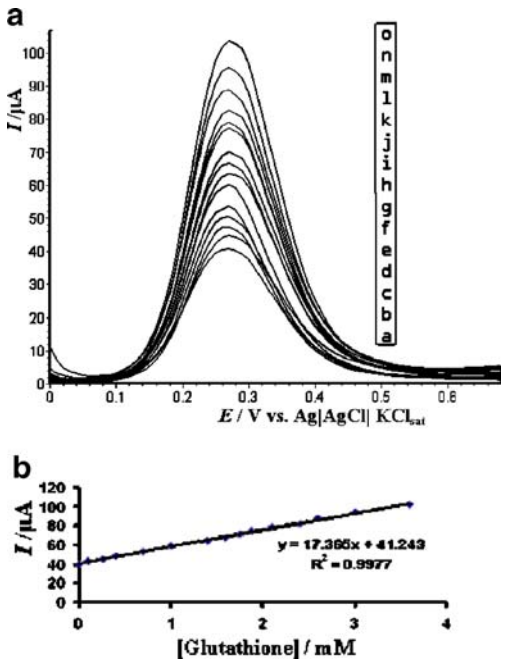


Fig. 6 **a** Differential pulse voltammograms at the FMCPE (*a*) absence and presence of (*b*) 0.0001, (*c*) 0.1, (*d*) 0.26, (*e*) 0.4, (*f*) 0.7, (*g*) 0.1, (*h*) 1.4, (*i*) 1.6, (*j*) 1.75, (*k*) 1.88, (*l*) 2.1, (*m*) 2.4, (*n*) 2.6, and (*o*) 3.00 mM of GSH in 0.1 M phosphate buffer solution (pH 7.00). **b** Plot of electrocatalytic peak currents (from DPV of **a**) vs. the GSH concentrations

The rate constant for the chemical reaction between GSH and redox sites in FMCPE, K'_h, can be evaluated by chronoamperometry according to the method described in [53]:

$$I_C/I_L = \pi^{1/2}\gamma^{1/2} = \pi^{1/2}(k_h C_b t)^{1/2} \quad (1)$$

where I_C is the catalytic current of FMCPE in the presence of GSH and I_L is the limited current in the absence of GSH, γ is the argument of the error function, C_b is the bulk concentration of GSH, mol cm^{-3}, and k_h and t are the catalytic rate constant (cm^3 mol^{-1} s^{-1}) and time elapsed (s), respectively. The above equation can be used to calculate the rate constant of the catalytic process, k_h. From the slope of I_C/I_L versus $t^{1/2}$ plot, the value of k_h can be simply calculated for a given concentration of substrate. The value of k_h was calculated as 5.1×10^3 M^{-1} s^{-1} using the slope of I_C/I_L–$t^{1/2}$ plot. This value of k_h explains as well as the sharp feature of the catalytic peak observed for catalytic oxidation of GSH at the surface of FMCPE. On the other hand, the surface coverage, Γ, of a modified electrode prepared at optimum conditions was obtained from the equation $\Gamma = Q/nFA$, where Q is the charge obtained by integrating the anodic peak under the background correction, A is the geometric area of the electrode, and other symbols have their usual meanings. The calculated value of Γ was 3.23×10^{-8} mol cm^{-2} at pH 7.00. Using this value of coverage, the heterogeneous rate constant of catalytic reaction was calculated as $k'_h = 1.83\times10^{-1}$ cm s^{-1}.

Electrocatalytic determination of glutathione

The electrocatalytic oxidation peak current of GSH at the surface of FMCPE can be used for the determination of GSH in solution. Therefore, cyclic voltammetry and differential pulse voltammetry experiments were performed using FMCPE in phosphate buffer solution containing various concentrations of glutathione. The results show that the electrocatalytic peak current of GSH oxidation at the surface of FMCPE was linearly dependent on the GSH concentrations, and the range of this linearity depended on the amount of mediator in the electrode matrix. The mediated oxidation peak currents of GSH at the surface of a FMCPE was proportional to the concentration of the GSH within the ranges 3.2×10^{-5} M–1.6×10^{-3} M (with a correlation coefficient of 0.9978) and 2.2×10^{-6} M–3.5×10^{-3} M (with a correlation coefficient of 0.9977) in cyclic voltammetry (Fig. 5a,b) and differential pulse voltammetry (Fig. 6a,b), respectively. The detection limits (3σ) were 1.8×10^{-5} M and 2.1×10^{-6} M. These values are comparable with the values obtained by other research groups (Table 1). Thus, the catalytic oxidation of glutathione can readily be applied to the determination of GSH.

Determination of glutathione in real samples

In order to demonstrate the electrocatalytic oxidation of GSH in real samples, we have examined this ability in the voltammetric determination of GSH in human plasma by using the standard addition method. In this method, we added a known amount of GSH to buffer phosphate solution (pH 7.00) containing a deliberated amount of plasma. The concentration of GSH in human plasma was obtained as 0.085 mM.

Conclusion

The experimental results reported above demonstrate that ferrocene incorporated into carbon paste matrix can act as mediator for the electrocatalytic oxidation of GSH in aqueous solution with optimum pH 7.00. It has been shown by cyclic voltammetry that the electrocatalytic oxidation of GSH at the surface of FMCPE occurs at a potential about 480 mV less positive than is the case for bare CPE. The heterogeneous rate constant, k'_h, of catalytically coupled reaction between the electrogenerated Fc^+ and GSH was estimated as $=1.83\times10^{-1}$ cm s^{-1}.

The electrocatalytic oxidation peak current of GSH at the surface of FMCPE showed a linear dependence on the GSH

Table 1 Comparison of the efficiency of some modified electrodes in the determination of glutathione

Electrode	Modifier	pH	LOD (μM)	LDR (μM)	Reference substrate
GC	Well-aligned/CNT	7.00	0.2	0.4–16.4	[31]
GC	PQQ/PPy[a]	8.42	13.2	–	[54]
Carbon paste	TTF-TCNQ[b]	7.00	0.3	5–340	[41]
Carbon paste	Ferrocene[c]	7.00	1.4	2.2–3500	This work
	Ferrocene[d]		12	32–1600	

[a] Pyrroloquinoline quinine into polypyrrole
[b] Tetrathiafulvalene (TTF)–tetracyanoquinodimethane
[c] With differential pulse voltammetry
[d] With cyclic voltammetry

concentration and linear analytical curves were obtained in the range 3.2×10^{-5} M to 1.6×10^{-3} M (with a detection limit equal to 1.8×10^{-5} M) and 2.2×10^{-6} M to 3.5×10^{-3} M (with a detection limit equal to 2.1×10^{-6} M) in cyclic voltammetry and differential pulse voltammetry, respectively. Finally, the electrocatalytic oxidation of GSH at the surface of this modified electrode can be employed as a new method for the voltammetric determination of glutathione in real samples such as human plasma.

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