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Potentiometric Determination of *N*-(2–Mercaptopropionyl)-glycine Using an Electrode with AgI-based Membrane

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Potentiometric methods for determination of *N*-(2–mercaptopropionyl)-glycine (MPG) using a commercial indicator electrode with AgI-based membrane are described. Heterogeneous and homogeneous chemical reactions important for the response of the sensor are discussed. For direct potentiometric measurements, equilibrium potentials recorded under continuous addition of standard MPG solution into 0.1 mol L^{-1} $HClO_4$ as the background solution were considered relative to pMPG. Linear response with a slope of 59 ± 0.7 mV was obtained in the concentration range from 2.0×10^{-5} to 1.5×10^{-3} mol L^{-1}. In the »kinetic« potentiometric experiment, the relationship between the potential change and the concentration of MPG was found to be linear for more than a one-decade range of the amount of MPG. The best analytical results were achieved using the potentiometric titration method. This method with 0.1 mol L^{-1} $HClO_4$ as the background solution is recommended for the determination of MPG in pharmaceutical preparations.

Keywords
N-(2–mercaptopropionyl)-glycine
direct potentiometry
kinetic potentiometry
potentiometric titration

INTRODUCTION

N-(2–mercaptopropionyl)-glycine (MPG), also named tiopronin, is a synthetic aminothiol antioxidant. It is used in treatment of cystinuria,[1,2] rheumatoid arthritis, liver and skin disorders,[3] and as an antidote to heavy metal poisoning. Recent studies have shown that MPG can function as a chelating, cardioprotecting and radioprotecting agent.[4,5] Along with its desired effects, it may cause some side effects such as muscle pain, yellow skin or eyes, sore throat or fever, changes in taste and smell, *etc*. Moreover, this drug produces a dose-related nephrotic syndrome.[6] Therefore, sensitive determination of MPG in biological samples and pharmaceutical preparations is highly desirable.

A number of spectrometric,[7–9] fluorimetric,[10,11] chemiluminescence[12–15] and chromatographic methods[16–20] have been developed for MPG determination. All these techniques are highly efficient but very expensive and their application is rather complicated. Electrochemical methods are popular for many applications because the procedures are simple and fast, and the cost is low. Recently, Siangproh and co-workers[21] reported MPG determination in commercial tablets using cyclic voltammetry.

In this paper, a novel, simple, sensitive and affordable potentiometric methods for determination of MPG in solution as well as in pharmaceutical preparations is presented. The proposed procedure is based on MPG reaction with silver (I) using an indicator electrode with AgI–based membrane. Response of the applied chemical

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sensor to MPG (also designated RSH) is explained by the formation of sparingly soluble RSAg in the reaction solution and/or on the exposed surface of the sensor. In addition, a method for MPG determination in commercially available tablets by potentiometric titration in an aqueous solution (0.1 mol L^{-1} $HClO_4$, pH = 1) with standard solution of silver nitrate is described.

EXPERIMENTAL

Apparatus

All potentiometric studies were carried out with a millivoltmeter Iskra Model MA 5740, coupled to a personal computer. A double-walled, thermostated reaction vessel, maintained at 25 ± 0.1 °C was used. Cell potentials were measured with an indicator electrode with AgI–based membrane (Orion 9453) *versus* a double-junction reference electrode (Orion 90-02-00), with 10 % potassium nitrate solution as the outer filling solution. The selective electrode was dry-stored between measurements and overnight. Before each set of measurements, the ion-selective membrane was polished with a special polishing strip (Orion 94-82-01). During measurements, the solution was stirred using a Teflon-coated magnetic bar. Stirring speed and electrode distance were kept constant throughout all measurements.

Reagents

All chemicals were of analytical-reagent grade and solutions were prepared in MilliQ deionized water. MPG (0.01 mol L^{-1}) stock solution was prepared by dissolving an appropriate amount of MPG (Sigma-Aldrich) in 0.1 mol L^{-1} perchloric acid (Merck, Suprapur) and stored in a dark bottle at 4 °C. Working solutions of lower concentration were prepared daily by appropriate dilution of the stock standard solution with 0.1 mol L^{-1} perchloric acid.

Silver nitrate (0.1 mol L^{-1}) stock solution was prepared by diluting a titrisol of silver nitrate solution (Kemika) to 1 L with water, and was kept in the dark. The solution was standardized by potentiometric titration with sodium chloride (0.1 mol L^{-1}) using an indicator electrode with AgI–based membrane (Orion 9453). Working solutions of silver nitrate were prepared daily from the standard solution.

The applied basic buffer solution (pH = 2) was prepared by mixing acetic, boric and phosphoric acids of final concentrations 4×10^{-2} mol L^{-1}. Buffer solutions with higher pH values were prepared by mixing the basic buffer solution with sodium hydroxide solution, c = 2.0 mol L^{-1}. The appropriate pH value was checked using a Metrel (HEC 0102) pH glass electrode.

The MPG containing drug, Captimer, was obtained from MIT Gesundheit GmbH, Germany. At least 10 tablets were weighed to obtain the mean weight per tablet. An accurately weighed tablet was left overnight in 50.00 mL $HClO_4$, c = 0.1 mol L^{-1}, partly dissolved, and then crushed. The obtained suspension was filtrated through filter paper (Blue ribbon, S&S, Germany). Solid residue on the filter paper was washed with ca 40 mL of perchloric acid. The filtrate was collected in a calibrated flask, and diluted to 100 mL with perchloric acid.

Procedure

Direct Potentiometric Measurements. – The response of the cell with the indicator electrode with AgI–based membrane to the Ag^+ ion was measured by serial dilution of the standard 0.1 mol L^{-1} $AgNO_3$ solution with 0.1 mol L^{-1} $HClO_4$ solution. The potential response of the indicator electrode to MPG was recorded under standard addition. Before addition of MPG, 50.0 mL 0.1 mol L^{-1} perchloric acid and 10 μL 0.01 mol L^{-1} silver nitrate were added, as a background solution, into the thermostated reaction vessel. In the other experiment, the background solution consisted of 50.0 mL buffer solution (pH = 3) and 10 μL 0.01 mol L^{-1} silver nitrate. The potential–time response of the electrode was measured in a regular analytical setup. The background solution was stirred and monitored under successive additions of known quantities of MPG. The potential values were taken after a steady–state potential had been established.

Potentiometric Titration. – Potentiometric titration studies were carried out in the manner of conventional potentiometric titrations. Unless otherwise indicated, the total ionic strength and pH were kept constant by addition of 0.1 mol L^{-1} $HClO_4$ solution. During the potentiometric titration studies, the titrant was delivered in 0.05–0.10 mL steps, using a Hirschmann micropipette. The end-point volume was calculated mathematically from the second derivative data.

From the collected data, the concentration of MPG in sample solution and the solubility product of RSAg were calculated.

»Kinetic« Determination. – 50 mL of 0.1 mol L^{-1} $HClO_4$ was accurately pipetted into a reaction vessel and 1 mL of $AgNO_3$, $c = 5 \times 10^{-4}$ mol L^{-1}, was added. During measurements, the solution was stirred with a Teflon–coated magnetic bar at a suitable steady rate to avoid splashing and bubbling. After the steady–state potential had been reached, 1 mL of solution containing different amounts of MPG was introduced into the cell. The change in potential with time (1 minute intervals) was recorded for each solution. After each experiment, the reaction vessel and the electrodes were washed with dilute nitric acid and distilled water. Between the sets of experiments, the sensing membrane of the electrode was polished. Before the next run, the electrode was soaked in 1×10^{-3} mol L^{-1} Ag^+ and 1×10^{-3} mol L^{-1} I^- ion solutions for 10 minutes and washed twice with water.

RESULTS AND DISCUSSION

In this experiment, the indicator electrode with AgI–based membrane used in combination with a reference electrode responds primarily to the activity of Ag^+ ions in the solution or on the phase boundary surface membrane/solution, according to the Nernst equation:

$$E = \text{constant} + S \log a_{Ag^+} \quad (1)$$

The silver ion activity can be replaced with its concentration multiplied by its activity coefficient:

$$E = \text{constant} + S \log [Ag^+] \cdot y_{Ag^+} \quad (2)$$

In a solution with constant ionic strength, a practical equation can be written:

$$E = E_1 + S \log [Ag^+] \quad (3)$$

Constants E_1 (539.4 mV) and S (52.8 mV) were determined by experiment (Table I).

Table I. Values of E_1 and S calculated from experiments when the response of the cell was recorded by serial dilution of Ag^+ solution with 0.1 mol L^{-1} $HClO_4$, as the background solution

No. of experiment	E_1 / mV	S / mV
1	540.2	51.7
2	530.3	51.1
3	547.6	55.7
Mean ± SD	539.4 ± 8.7	52.8 ± 2.5

When a sample of MPG (also designated RSH) is added into reaction solution in a concentration sufficiently high to cause precipitation of RSAg, the concentration of Ag^+ ions will decrease. Since RSAg is a less soluble salt than AgI (see below), in the second step when all Ag^+ is precipitated with RSH, a new compound can be formed on the membrane surface.[22] Now the reaction solution contains insoluble RSAg and RSH in excess and the following equilibriums exist in solution:

$$RSAg\ (s) \leftrightarrows RS^- + Ag^+ \quad (4)$$

$$RSH \leftrightarrows RS^- + H^+ \quad (5)$$

The response of the membrane to MPG (RSH) can be understood by writing the expression for the solubility product for RSAg, $K_{sp,RSAg}$, and including this term in Eq. (3):

$$E = E_1 + S \log \left(\frac{K_{sp,RSAg}}{[RS^-]} \right) \quad (6)$$

Solving Eq. (6), we can write:

$$E = E_2 - S \log [RS^-] \quad (7)$$

Value for $K_{sp,RSAg}$ determined in the potentiometric titration experiment was used for the calculation constant, E_2.

When pH is fixed and known, we can write:

$$E = E_2 - S \log (c_{RSH} \cdot \alpha_{RS^-}) \quad (8)$$

Using Eq. (5), α_{RS^-} can be analyzed and expressed as:

$$\frac{[RS^-] \cdot [H^+]}{[RSH]} = K_a \quad \{K_a = 1.82 \times 10^{-9}\}^{23} \quad (9)$$

$$\alpha_{RS^-} = \frac{[RS^-]}{c_{RSH}} = \frac{[RS^-]}{[RS^-] + [RSH]} \quad (10)$$

$$\alpha_{RS^-} = \frac{K_a}{K_a + [H^+]} \quad (11)$$

Inclusion of α_{RS^-} in Eq. (8) gives:

$$E = E_3 - S \log c_{RSH} \quad (12)$$

Eq. (12) was used for calculation of the theoretical potential response of the used cell to analytical concentration of MPG in 0.1 mol L^{-1} $HClO_4$ solution (Figure 1).

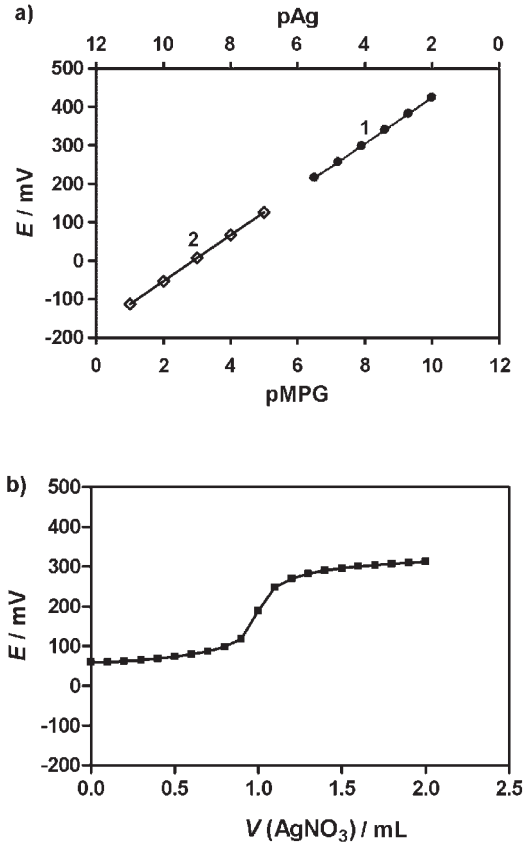

Figure 1. (a) Response of the cell with AgI–based membrane to Ag^+ ion in 0.1 mol L^{-1} $HClO_4$ solution (1), relationship between analytical concentration of MPG and the calculated potential of the cell using Eq. (12) (2). (b) Potentiometric titration curve for the titration of MPG in 0.1 mol L^{-1} $HClO_4$.

Calculation of the Concentration Solubility Product Constant

In the potentiometric titration experiment, before the equivalence point, the concentration of RSH is much higher than Ag^+. Reaction: $RS^- + Ag^+ \rightarrow RSAg$ (s) has been completed and the precipitate solubility is determined by the concentration of free RS^- remaining in the solution. Concentration of Ag^+ in equilibrium with this much MPG can be calculated by using Eq. (3) and the experimental potential values collected during the potentiometric titration experiment. If the concentration values of MPG remaining in the solution are known, the concentration solubility product constant of silver MPG can be calculated:

$$K_{\mathrm{sp,RSAg}} = [\mathrm{Ag}^+] \cdot c_{\mathrm{RSH}} \cdot \alpha_{\mathrm{RS^-}} \qquad (13)$$

In 0.1 mol L^{-1} $HClO_4$ solution, α_{RS^-} can be calculated using Eq. (11).

The calculated mean value ± standard deviation (SD) of the solubility product of silver MPG in 0.1 mol L^{-1} $HClO_4$ was $(1.46 \pm 0.97) \times 10^{-20}$. This mean value was calculated from 30 experimental points recorded during three independent experiments. This value is very close to the previously determined solubility product of silver penicillamine.[24]

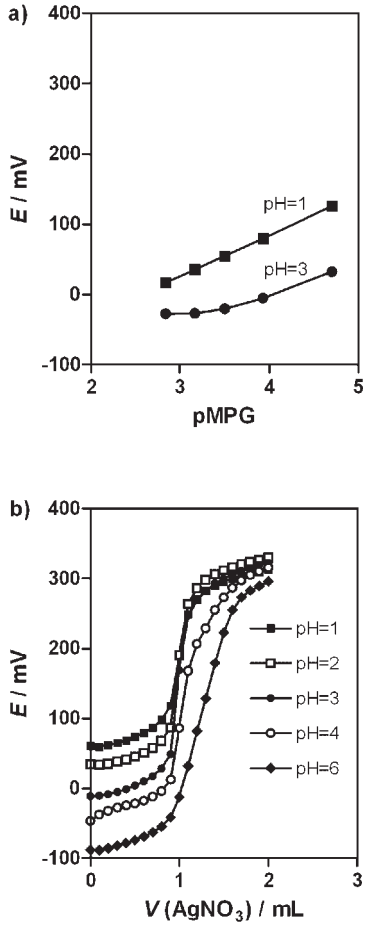

Figure 2. Influence of pH on (a) direct potentiometric measurements, and (b) potentiometric titration.

Influence of pH on Potentiometric Experiments

Figure 2 provides titration curves of MPG in solution buffered to various pH levels. It can be seen from Figure 2b that an adequate end-point in the titration of MPG requires a pH from 1 up to 3. At higher pH, end points were reached in a larger volume of titrant. When the direct potentiometric experiment was applied (Figure 2a), the response of the electrode to MPG was linear at pH = 1. Experimental slope of 59 ± 0.7 mV was obtained in good agreement with the theoretical value. At pH = 3, however, its response to MPG was neither Nernstian nor linear. In addition, at pH = 1, a parallel drift of potential response between two sets of measurements was recorded.

Influence of pH on the potentiometric titration curves can be explained by the following consideration. As shown by Eq. (6), the potential before equivalence point was determined with the solubility product constant of RSAg precipitate and the concentration of MPG. The precipitate solubility may increase dramatically in the presence of reagents that form complexes with an anion or cation of the precipitate. The cause of increase/decrease in solubility of RSAg in solutions with different pH is shown by the following equilibria:

$$\begin{array}{ccc} \mathrm{RSAg(s)} \leftrightarrows \mathrm{RS^-} & + & \mathrm{Ag^+} \\ + & & + \\ \mathrm{H_2O} & & x\mathrm{H_2O} \\ \downarrow\uparrow & & \downarrow\uparrow \\ \mathrm{RSH + OH^-} & & \mathrm{Ag(OH)}_x^{(1-x)+} + \mathrm{H^+} \end{array} \qquad (14)$$

RS^- form may be treated as the anionic part of a monoprotonic weak acid and its concentration is shown by the following equilibrium with an appropriate constant:

$$\mathrm{RS^- + H_2O} \rightleftharpoons \mathrm{RSH + OH^-}$$

$$K_{\mathrm{b}} = \frac{[\mathrm{RSH}] \cdot [\mathrm{OH^-}]}{[\mathrm{RS^-}]} = \frac{K_{\mathrm{w}}}{K_{\mathrm{a}}} \qquad (15)$$

Eq. (14) requires a new conditional solubility product constant accounting for the fact that only some of MPG is in the RS^- form and only some of the silver, theoretically not bound to RS^-, is in the Ag^+ form.

$$K''_{\mathrm{sp,RSAg}} = \frac{K_{\mathrm{sp,RSAg}}}{\alpha_{\mathrm{RS^-}} \cdot \alpha_{\mathrm{Ag^+}}} \qquad (16)$$

For any pH values, α_{RS^-} can be calculated using Eq. (11).

Ag^+ ions take part in the hydrolysis process only in a strong alkaline solution. For different pH of the experiment, α_{Ag^+} values were practically equal to one.

In contrast, α_{RS^-} is strongly influenced by the solution pH and increases from 1.82×10^{-8} (pH = 1) to 1.82×10^{-3} (pH = 6). The calculated conditional solubility product constant of RSAg and Ag^+ concentration decrease with increasing pH. Ag^+ concentration decreases because of the increase in RS^- concentration. The foregoing statements are in agreement with experimental results before the equivalence point (Figure 2b).

Potentiometric Titration

Reproducible results for MPG were obtained when the titration was carried out in 0.1 mol L^{-1} $HClO_4$ as background solution. A white precipitate containing MPG and silver in a 1:1 ratio was formed during titration in acidic media (pH = 1–3).

The titration of MPG with silver performed in a less acidic medium (pH = 4 or 6; Figure 2b) was non-stoichiometric. Our results show that titration is possible for MPG amounts from 0.4 to 1.0 mg (Figure 3; Table II) and from 1.0 to 3.0 mg (Table III). Amounts outside this range were also investigated, but with low accuracy of the results. Titration in mixtures of water and organic solvents, such as ethanol and *tert*-butanol, was also achieved but without any particular advantage.

»Kinetic« Measurements

Addition of various amounts of MPG to (0.1 mol L^{-1} $HClO_4$) silver solution alters the concentration of Ag^+ in the solution and the potential of the cell according to Eqs. (6) and (12) (Figure 4).

For all MPG concentrations, the voltage differences, ΔE, for 2 and 10 min time intervals were calculated (Figure 5). The relationship between the potential change (for 2 min) and the MPG concentration was found to be linear for more than one-decade range of the amount of MPG. It should be stressed that this linear or analytical range was found when the response of the electrode was unstable and voltage differences were calculated with non-steady-state potentials recorded 2 min after the addition of MPG. For these measurements, the analytical signal, ΔE, was taken in the kinetic region of the reaction.

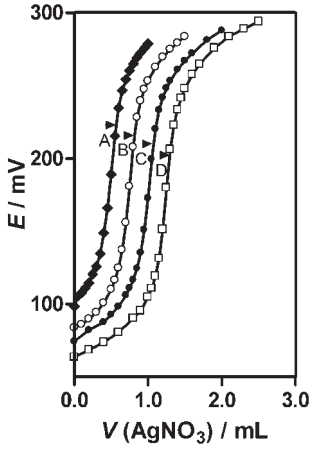

Figure 3. Potentiometric titration curves for titration of various amounts of MPG with 5 mmol L^{-1} silver nitrate: (A) 2.50; (B) 3.75; (C) 5.00; and (D) 6.25 μmol of MPG in 0.1 mol L^{-1} $HClO_4$ (pH = 1) (arrows denote end-points).

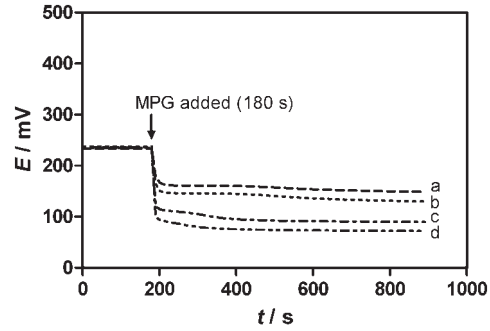

Figure 4. Dynamic response curves of the cell with the indicator electrode with AgI based membrane after adding 1 mL of MPG solution (t = 180 s) to the reaction solution containing 50 mL 0.1 mol L^{-1} $HClO_4$ and 1 mL 5.0×10^{-4} mol L^{-1} $AgNO_3$. $c(MPG)_{added}$ = (a) 7.5×10^{-4}; (b) 1.0×10^{-3}; (c) 2.5×10^{-3}; (d) 5.0×10^{-3} mol L^{-1}.

Table II. Results of the potentiometric titration of MPG with silver nitrate. Mean values ± SD of four determinations are given for each amount of MPG

MPG taken	MPG found	Recovery
mg	mg	%
0.410	0.4245 ± 0.0007	103.54 ± 0.17
0.614	0.6172 ± 0.0056	100.48 ± 0.91
0.816	0.8155 ± 0.0014	99.38 ± 0.17
1.020	0.9961 ± 0.0049	97.65 ± 0.48

The investigated »kinetic« method provides a simple and rapid technique for the determination of MPG in aqueous solution. However, when applied to the MPG determination in pharmaceutical preparations, it gave poor reproducibility.

Applications

The proposed potentiometric titration method was applied to the determination of MPG in pharmaceutical preparations. The results obtained and the labelled contents are summarized in Table III. There were no significant differences between labelled contents and those obtained by the proposed method. Recovery studies were performed by adding a known amount of MPG to the sample before the recommended determination by potentiometric titration in 0.1 mol L^{-1} $HClO_4$. Recoveries ranged from 97–103 %. Table III also summarizes recovery results.

Table III. Determination of MPG in pharmaceutical preparations and recovery experiments

Sample[a]	Amount / mg		Added	Recovered ± SD	Recovery ± SD
	Label	Found ± SD	mg	mg	%
		(n = 5)			(n = 3)
Captimer® (pills)	100	101.5 ± 3.4	50	51.7 ± 0.9	103.4 ± 1.8
			100	99.3 ± 1.6	99.3 ± 1.6
			150	145.3 ± 2.1	96.8 ± 1.4
			200	193.4 ± 3.0	96.7 ± 1.5

[a] Sample (Captimer) ingredients: 100 mg MPG, excipient. Captimer is the trademark of MPG manufactured by MIT Gesundheit GmbH (Kleve, Germany).

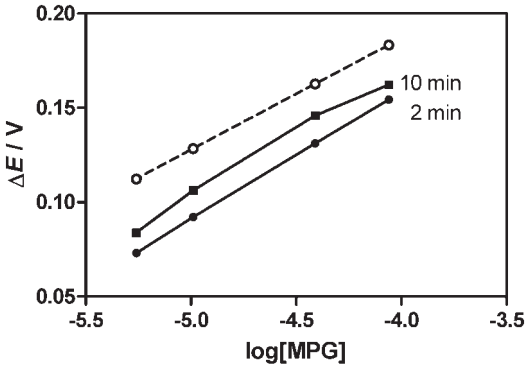

Figure 5. Relationship between the voltage difference (ΔE) and the concentration of MPG in reaction solution. Voltage differences were calculated for 2 and 10 min intervals after MPG addition. Theoretical values for each concentration of MPG (dotted line) were calculated by Eq. (6).

The proposed method for analysis of MPG in pharmaceutical preparations has the following limitations: MPG cannot be determined in non-aqueous solutions or if the reaction solution has pH > 3.

CONCLUSIONS

The potentiometric methods described in this work are simple, economic and rapid techniques for the determination of MPG. The potential response of the indicator electrode with AgI based membrane to MPG is based on the reversible chemical reactions involving the RSAg compound on the exposed surface of the sensor. When the direct potentiometric method was applied, a linear response was obtained in the concentration range from 2.0×10^{-5} to 1.5×10^{-3} mol L^{-1}. The kinetic potentiometric method makes it possible to determine MPG in the concentration range from 5.0×10^{-3} to 7.5×10^{-4} mol L^{-1}. The best accuracy and reproducibility were achieved with the potentiometric titration method. This method, involving 0.1 mol L^{-1} $HClO_4$ as the background solution, was applied to determination of MPG in pharmaceutical preparations.

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REFERENCES

1. F. Barbey, D. Joly, P. Rieu, A. Mejean, M. Daudon, and P. Jungers, *J. Urol.* **163** (2000) 1419–1423.
2. G. K. Chow and S. B. Streem, *J. Urol.* **156** (1996) 1576–1578.
3. D. Jarrar, P. Wang, W. G. Cioffi, K. I. Bland, and I. H. Chaudry, *J. Trauma* **49** (2000) 879–885.
4. A. Garner, Z. Jamal, and T. F. Slater, *Int. J. Radiat. Biol. Relat. Stud. Phys. Chem. Med.* **50** (1986) 323–335.
5. S. I. Ayene, R. K. Kale, and P. N. Srivastava, *Int. J. Radiat. Biol. Relat Stud. Phys. Chem. Med.* **53** (1988) 629–639.
6. S. Lecoules, C. Duvic, M. Herody, and G. Nedelec, *Presse Med.* **28** (1999) 273–275.
7. M. A. Raggi, M. R.Cesaroni, and A. M. Di Pietra, *Farmaco [Prat.]* **38** (1983) 312–316.
8. M. A. Raggi, L. Nobile, V. Cavrini, and A. M. Di Pietra, *Boll. Chim. Farm.* **125** (1986) 295–297.
9. M. S. Garcia, C. Sanchez-Pedreno, M. I. Albero, and V. Rodenas, *J. Pharm. Biomed. Anal.* **11** (1993) 633–638.
10. T. Perez-Ruiz, C. Martinez-Lozano, V. Tomas, and C. Sidrach de Cardona, *J. Pharm. Biomed. Anal.* **15** (1996) 33–38.
11. T. Perez-Ruiz, C. Martinez-Lozano, V. Tomas, and G. Lambertos, *Microchem. J.* **44** (1991) 72–77.
12. J. Lu, C. Lau, S. Yagisawa, K. Ohta, and M. Kai, *J. Pharm. Biomed. Anal.* **33** (2003) 1033–1038.
13. Y. Zhao, W. R. G. Baeyens, X. Zhang, K. Nakashima, A. C. Calokerinos, and G. Van der Weken, *Biomed. Chromatogr.* **11** (1997) 115–116.
14. T. Perez-Ruiz, C. Martinez-Lozano, W. R. G. Baeyens, A. Sanz, and M. T. San Miguel, *J. Pharm. Biomed. Anal.* **17** (1998) 823–828.
15. P. Vinas, G. Lopez, and J. A. Martinez Gil, *J. Pharm. Biomed. Anal.* **11** (1993) 15–20.
16. S. Penugonda, W. Wu, S. Mare, and N. Ercal, *J. Chromatogr., B: Anal. Technol. Biomed. Life Sci.* **807** (2004) 251–256.
17. K. Matsuura, K. Murai, Y. Fukano, and H. Takashina, *J. Pharm. Biomed. Anal.* **22** (2000) 101–109.

18. K. Matsuura and H. Takashina, *J. Chromatogr.* **616** (1993) 229–234.
19. V. Springolo, W. Bertani, and G. Coppi, *J. Chromatogr.* **232** (1982) 456–460.
20. B. Kagedal, M. Carlsson, and T. Denneberg, *J. Chromatogr.* **380** (1986) 301–311.
21. W. Siangproh, N. Wangfuengkanagul, and O. Chailapakul, *Anal. Chim. Acta* **499** (2003) 183–189.
22. Nj. Radić and J. Komljenović, *Acta Chim. Slov.* **52** (2005) 450–454.
23. M. Filella and D. R. Williams, *Inorg. Chim. Acta* **106** (1985) 49–57.
24. Nj. Radić, J. Komljenović, and D. Dobčnik, *Croat. Chem. Acta* **73** (2000) 263–277.
25. J. Inczedy, *Analytical Applications of Complex Equilibria*, Ellis Horwood, Chichester, 1976, p.323.

SAŽETAK

Potenciometrijsko određivanje *N*-(2–merkaptopropionil)-glicina primjenom indikatorske elektrode s membranom na osnovi AgI

Lea Kukoč Modun i Njegomir Radić

Opisane su potenciometrijske metode za određivanje *N*-(2–mercaptopropionil)-glicina (MPG) primjenom komercijalne indikatorske elektrode s membranom na osnovi AgI. Raspravljene su heterogene i homogene kemijske reakcije važne za odziv senzora. Kod izravnog potenciometrijskog mjerenja ravnotežni potencijali, zabilježeni pri uzastopnim dodatcima standardne otopine MPG u 0,1 mol L^{-1} $HClO_4$ otopinu, prikazani su u odnosu na pMPG. Linearni odziv s nagibom od 59 ± 0,7 mV dobiven je u koncentracijskom području od $2{,}0 \times 10^{-5}$ mol L^{-1} do $1{,}5 \times 10^{-3}$ mol L^{-1}. Odnos između promjene potencijala i koncentracije MPG, kod »kinetičkog« potenciometrijskog eksperimenta, bio je linearan za više od deseterostruke promjene koncentracije MPG. Najbolji analitički rezultati postignuti su metodom potenciometrijske titracije. Ova metoda u 0,1 mol L^{-1} $HClO_4$ otopini preporučuje se za određivanje MPG u farmaceutskim pripravcima.