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A sub-second fast Fourier transform-adsorptive voltammetric technique for the nano-level determination of guthion at a gold microelectrode in flowing solutions

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Abstract

This research demonstrates the quick guthion monitoring with the help of a sensitive method called fast Fourier transformation continuous cyclic voltammetry (FFTCV). Fortunately, FFTCV illustrates the benefits of precision, determination speed, cost-effectiveness, accuracy and simplicity, in comparison with formerly reported techniques.

In particular, this method was applied to a gold microelectrode in flowing solutions to detect the guthion concentration in its formulations. The effects of several parameters were examined regarding the sensitivity of the method. After a series of experiments, the detection limit of the method was found to be equal to1.27 pg/mL, when the optimum conditions were imposed, which is a scan rate value of 40 V/s, an accumulation time of 0.4 s, an accumulation potential of 0 mV and a pH value of 2. During the measurements performance, the integration range of currents included all the potential scan ranges, even the oxidation and reduction of the Au surface electrode, for the achievement of a sensitive determination. Then, the potential waveform, consisting of the potential steps for cleaning, accumulation and the step for the potential ramp, was applied to an Au disk microelectrode in a continuous way.

It is also important to refer to the positive points, presented only by the use of this technique. Firstly, it is no longer necessary to remove the oxygen from the test solution. Furthermore, the quick determination of any such compound in many chromatographic methods is possible. Thirdly, the corresponding detection limit is of nanomolar level.

Keywords: Guthion; Ultramicroelectrode; Continuous cyclic voltammetry; Flow injection analysis; Fast Fourier transformation

1. Introduction

The extensive use of pesticides to enlarge the production in agriculture has lead to growing input of these pollutants into environment over the last decades. Organophosphorus (OP) pesticides are among most wide spread pollutants used for pest control with many applications, but with the growing importance as insecticides, acaricides, nematocides and helmithicides.

Azinphosmethyl or guthion (*O*,*O*-dimethyl-*S*-[4-oxo-(1,2,3-benzotriazin-3(4*H*)-yl-methyl]phosphorodithioate) is one of this pesticides with a molecular weight of 317.33, a melting point of 73–75 °C and a water solubility value of 20 ppm at 25 °C. Under the sunlight or in the water, this compound decomposes to *N*-methylbenzazimide, benzazimide, anthranilic acid, azinphosmethyloxon and other compounds [1,2]. Among these degradation products, the oxygen analogues are the most toxic.

The present methods for the determination of this compound residues include MAP-GC (microwave assisted process-GC) [3], colorimetric [4,5], fluorimetric [6], capillary gas chromatographic-NPD [7], HPLC-membrane separation [8], and GC/MS [9] procedures. These methods are time consuming because of the lengthy extraction, column cleanup and/or derivatization steps. The HPLC procedures are not readily applicable to fruit and vegetable [10–13].

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In pharmaceutical, biomedical and food analysis, a tendency can be observed towards the development of miniaturized and fast methods to achieve a highly sensitive determination. Recently, stripping voltammetric methods were used in the determination of heavy metal ions and some organic compounds in flowing solutions with a parts-per-billion sensitivity range. Indeed, application of such techniques needs fast analyte accumulation and fast potential sweeping, which is not appropriate for large electrodes [14,15]. So the UMEs (ultra-micro electrodes) introduction has encouraged the use of voltammetric techniques. For example, they demonstrate steady state currents, higher sensitivity caused by the increased mass transport and application to highly resistant solutions. Additionally, UMEs have been applied as sensors in various techniques such as flow injection analysis [16,17], cardiovascular monitoring and organic compounds analysis [18–20]. Nonetheless, this study aims to present a novel method for the prompt determination of guthion ultra trace amounts in its pure and preparation solutions.

2. Experimental

2.1. Reagents

The used reagents to prepare the eluent solution for the flow injection analysis were obtained from the Merck Chemicals. The guthion standard solution was a gift from the Graduate Faculty of Environment. Also, all solutions were prepared in double-distilled deionized water with the help of the analytical grade reagents, filled with the background electrolyte solution and used without the removal of the dissolved oxygen.

2.1.1. Background electrolyte (BGE)

For the preparation of the running buffer or BGE, 8.7 mL of phosphoric acid (85%, w/v) were added into a 1000 mL volumetric flask. Afterwards, the resulting solution was diluted to a constant volume with distilled water. The pH was adjusted to the value of 2.3 with sodium hydroxide. All solutions were freshly prepared and filtered, using a Millipore filter (0.45 μm) each day.

2.1.2. Standards and sample solutions

2.1.2.1. Standard stock solutions. A guthion standard stock solution (20 μg/mL) was prepared in the running buffer. This solution was light-protected from using foil and was freshly prepared each day.

2.1.2.2. Standard solutions for FIA (flow injection analysis). Aliquots of the guthion standard stock solution were dispensed into 10 mL volumetric flasks. These flasks were filled up with the running buffer until a final concentration range of 4–69,800 pg/mL is reached.

2.2. Electrode preparation

Gold UMEs (with a diameter of 12.5 μm) were prepared by sealing metal micro-wires (Good Fellow Metals Ltd., UK) into a soft glass capillary. The capillary was then cut perpendicularly to its length to expose the wire. Electrical contacts were made using silver epoxy (Johnson Matthey Ltd., UK). Before each experiment the electrode surface was polished for 1 min, using extra fine carborundum paper and then for 10 min with 0.3 μm alumina. Prior to being placed in the cell, the electrode was washed with water. In all measurements, an Ag (s)|AgCl (s)|KCl (aq, 1 M) reference electrode was used. The auxiliary electrode was made of a Pt wire, 1 cm in length and 0.5 mm in diameter.

2.3. Sample preparation assay

A suitable amount of guthion standard crystalline solid was finely powdered and portions equivalent to 10 mg of guthion were accurately weighed and transferred into an 1000 mL volumetric flask. Afterwards, 500 mL of distilled water were added to this flask, shaken completely to dissolve and mixed well.

Suitable aliquots from this solution were filtered through a Millipore filter (0.45 μm Chrom Tech Nylon_66). Then, 1 mL of the filtered solution was diluted with distilled water in an 1000 mL volumetric flask. Eventually, 1 mL of the resulting solution was added to a 10 mL flask and filled up with 0.05 mol/L phosphoric acid, reaching an initial concentration of 1 ng/mL.

2.4. Flow injection setup

In Fig. 1, the electrochemical cell of the flow injection analysis is illustrated. For this analysis, a six roller peristaltic pump (LKB 2115 Miltiperpex Co.) and a four-way injection valve (Supelco Rheodyne Model 5020) with a 50-μL sample injection loop were used. Moreover, a plastic syringe was used for the introduction of the solutions into the sample loop. The flow rate of the eluent solution during the experiments was set to 3 mL/min and the cell volume was 100 μL.

2.5. Validation

The validation parameters of the method included the selectivity, limit of quantitation (LOQ), limit of detection (LOD), robustness, accuracy precision, recovery and linearity [21–23].

Linear regression analysis was applied along with the help of the least square regression method for the evaluation of the lin-

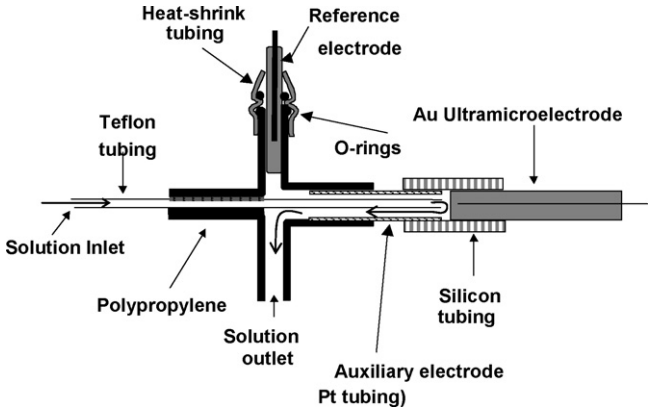

Fig. 1. Diagram of the electrochemical cell.

earity [24,25]. For the concentration range of 4–69,800 pg/mL ($n=5$), the calibration curves which were constructed for guthion were linear. The peak areas of guthion were plotted versus its concentration and, afterwards, linear regression analysis was carried out on the resultant curve.

The LOQ and LOD were calculated from the signal-to-noise ratios, being based on the analytical responses of the background noise for 10 and 3 times, respectively [26].

The precision assessment was performed in accordance with repeatability and reproducibility. Repeatability was investigated by injecting nine replicate samples of each of the 4, 1000 and 69,800 pg/mL standards.

For the accuracy assessment of the method, replicate ($n=6$) peak areas of three accuracy standards (4, 1000 and 69,800 pg/mL) were interpolated from a calibration curve, which was prepared as previously reported. Additionally, the relevant error percentage and accuracy were calculated in each case.

2.6. Data acquisition and processing

For the data acquisition, a setup of a PC PIV Pentium 900 MHz microcomputer, equipped with a data acquisition board (PCL-818HG, Advantech. Co.), and a custom made potentiostat were used. All data acquisition and data processing programs were developed in Delphi 6® program environment.

In Fig. 2, the applied waveform potential diagram during the cyclic voltammetric measurements is shown. Three parts are evident in the potential waveform: (a) potential steps, E_{c1} and E_{c2} (which are used for the oxidation and reduction of the electrode surface, respectively), during which the electrochemical cleaning of the electrode surface takes place, (b) E_c, where the analyte accumulation takes place and (c) the potential ramp, where the current measurements occur.

In this method, the signal calculation is measured by the integration of the net current changes over the scanned potential range. It must be noted that, in this case, the current changes (result of the injected analyte) at the voltammogram can be caused by various processes, which happen on the electrode surface. Those processes include: (a) oxidation and reduction of the adsorbed analyte and (b) oxidation and reduction inhibition of the electrode surface by the adsorbed analyte. Indeed, in order to see the influence of the adsorbed analyte on the oxidation and reduction peaks of the gold surface, the scan rate must be set at high rates (e.g., >20 V/s).

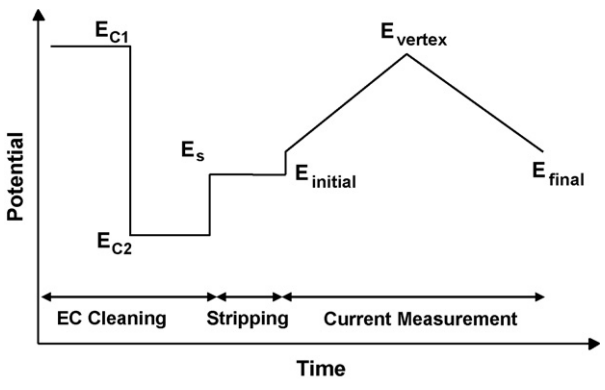

Fig. 2. Applied potential waveform diagram.

During the scan, some of the adsorbed analyte molecules are desorbed. Depending on the rate of those processes and the scan rate, the amount of the desorption analyte molecule (during the scan) can be changed. All the same, the adsorbed analyte molecules have not been yet removed from the electrode surface, leading to the red/ox inhibition of the electrode surface. Then, the ΔQ calculation is performed in agreement with all the current changes at the CVs (cyclic voltammograms) [27–35]. Nonetheless, the selectivity and sensitivity of the analyte response, expressed in terms of ΔQ, strongly depends on the selection of the integration limits.

At this point of the study, the application of a special digital filtration should be mentioned. Initially, an electrode CV was recorded. Then, FFT (fast Fourier transformation) was applied on the collected data and the existing high frequency noises were indicated. Based on this information, the cutoff frequency of the analog filter was set at a certain value (where the noises were removed from the CV).

Several potential waveforms were investigated in order to obtain a reproducible electrode surface (or a stable background signal), given that the crystal structure of a polycrystalline gold electrode greatly depends on the condition of the applied potential waveform [36]. Actually, the application of cyclic voltammetry for the determination of electroactive compounds mainly faces low stability of the background signal, because of the changes taking place in the surface crystal structure during the oxidation and reduction of the electrode in each potential cycle. After the examination of various potential waveforms, the best potential waveform, providing a stable background during the measurement, was the one depicted in Fig. 2. It has been already stated that the potential waveform was continuously applied during an experiment run, where the collected data were filtered by the FFT method, before their use in the signal calculation.

The starting point for the electrochemical oxidation process of the gold surface is the hydroxyl ion electrosorption. In fact, at more positive potentials, it results in the gold oxide formation, undergoing structural rearrangement [37]. Another way to initiate the surface oxidation is the water molecule adsorption where AuOH is formed at a more positive potential, leading to a two-dimensional phase formation of the gold oxide:

$$Au(H_2O) \rightarrow AuO + 2e + 2H^+ \quad (1)$$

Fig. 3a and b presents an example of the recorded CVs. The former (Fig. 3a) depicts a CV sequence recorded during the flow analysis for the drug determination. The injection volume was 50 μL of 5.0×10^{-6} mol/L guthion (in 0.05 mol/L H_3PO_4) into the eluent solution containing 0.05 mol/L H_3PO_4. At the graph, the time axis represents the time of the flow injection experiment. When guthion is not present, the shape of the CV curves is typical for a polycrystalline gold electrode in acidic media [38]. The latter (Fig. 3b) illustrates the absolute current changes in the CVs curves, after the subtraction of the four CVs average background (in the absence of the analyte). Consisting of a bet-

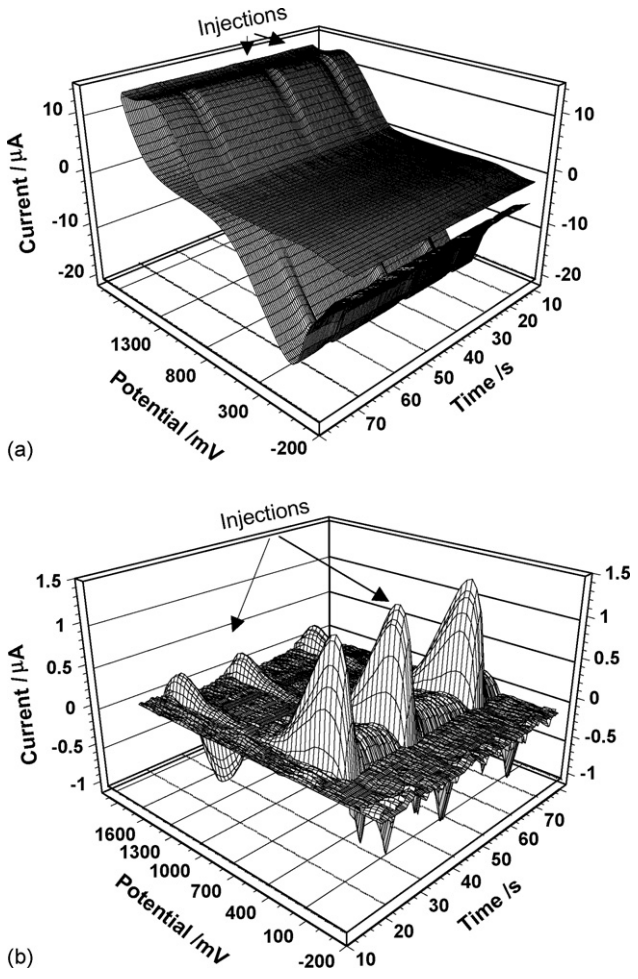

Fig. 3. (a) Cyclic voltammogram at a Au ultramicroelectrode, recorded during a flow-injection experiment. Each scan was preceded by a conditioning of 100 ms (at 1600 mV) and 100 ms (at 300 mV), respectively. These CVs are recorded at the optimum condition and flow rate. (b) Curves result from the subtraction of a CV average (in the absence of the analyte) from the CV test in (a).

ter way of presenting the electrode response, it provides more details about the adsorbed ion effect on the CV currents. Actually, the curves show that the current changes mainly take place at the potential regions of the oxidation and reduction of gold. The oxide formation process becomes severely inhibited, when the electrode–solution interface is exposed to guthion, which can be adsorbed on the electrode. In detail, the surface process inhibition causes significant change in the currents at the potential region and, as a consequence, the profound changes in the shape of the CVs take place. In chromatographic analysis, where a mixture of compounds presents in the sample, the universality of the detector is beneficial.

In general, the thermodynamic and kinetic parameters of adsorption, the mass transport rate and the electrochemical behavior of the adsorbed species influence the analyte response. Regarding the free energy and the adsorption rate, they depend on the electrode potential, the electrode material and, to some extent, on the choice of the concentration and the type of the supporting electrolyte. As a result, for the achievement of the detector maximum performance, the effect of the experimental parameters (such as the pH of the supporting electrolyte, the potential, the accumulation time and the potential scan rate) must be examined and optimized.

3. Result and discussions

3.1. Experimental parameter optimisation

Additionally, the pH effect of the eluent on the detector performance was examined. The corresponding results are demonstrated in Table 1, explaining that the best S/N ratio was obtained between the pH values of 2–3. Moreover, it is illustrated that, at pH values higher than 9, the noise level in the baseline (ΔQ versus time) is higher up to 12%, compared with that of the acidic solution.

For the investigation of the scan rates influence and the eluent flow rate on the sensitivity of the detector response, solutions were injected having a guthion concentration of 2.0×10^{-9} mol/L. Afterwards, the detector responses to the injected sample were recorded at different scan rates (from 5 to 100 V/s) and eluent flow. These results are presented in Fig. 4, exhibiting the maximum sensitivity at the scan rate of 40 V/s and flow rate of 3 mL/min.

The sweep rate effects affect the detection performance in a triple manner. The first influence concerns the speed in data acquisition. The second one is the kinetic factors of the guthion adsorption and the third one is the eluent flow rate, which controls the time window of the solution zone in the detector.

Table 1
pH effect on the ultra-microelectrode response

pH	S/N
2.1	160
4	150
6	140
8	135
10	128
12	132

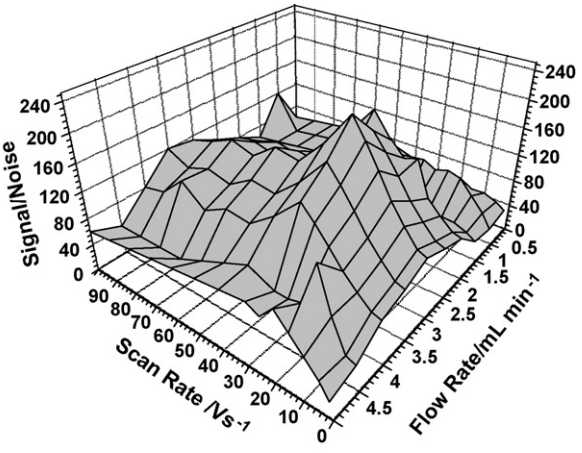

Fig. 4. The sweep rate effect on the response of the Au electrode (with a radius of 12.5 μm) to the injection of 2.0×10^{-9} mol/L guthion in 0.05 mol/L H_3PO_4 and the effect of the flow rate.

In addition, the main reason for the application of high scan rates is desorption prevention of the adsorbed guthion during the potential scanning (because under this condition, the inhibition outcome of the adsorbed guthion on the oxidation process can take place).

Certainly, the application of high scan rates is required for the use of this detection method in conjunction with fast separation techniques, such as capillary electrophoresis. Furthermore, the sweep rate consists of a crucial factor for the sensitivity of the method. As a consequence, the way that it influences the method sensitivity should be inspected. The employment of high sweep rates leads to the detection of the adsorbed analyte amount on the electrode surface, since the potential scanning step is short in comparison with the accumulation period. Another significant factor is the time when the guthion accumulation occurs at a potential that is greater or smaller than E_i. Basically because of the adsorption kinetic factors as well as the instrumental limitations, the potential sweep rate comprises the determining factor, defining the sensitivity of the detection system.

Obviously, the measurement sensitivity is greatly influenced by the changes in the parameters, which are related to the adsorption process and they are affecting the applied potential, the time and the potential of accumulation. For that reason, the influence of the accumulation potential and time on the response of the method for the injection of a solution of 2.0×10^{-9} mol/L guthion in 0.05 mol/L H_3PO_4, was studied. In Fig. 5, the detector response is depicted over the accumulation potential ranges from −200 to 800 mV and the accumulation time range from 0.1 to 0.9 s. It is evident that the optimum conditions to be chosen are accumulation potential of 0 mV and accumulation time of 400 ms.

It has been already stated that the gold ultra-microelectrode surface is small and in a short time the electrode surface can be saturated. Assuming that an appropriate potential is selected, the guthion accumulation takes place on the electrode during the accumulation step. In fact, the existing differences in the kinetics of the electron transfer and mass transport result in diverse values for the saturation time of the various compounds.

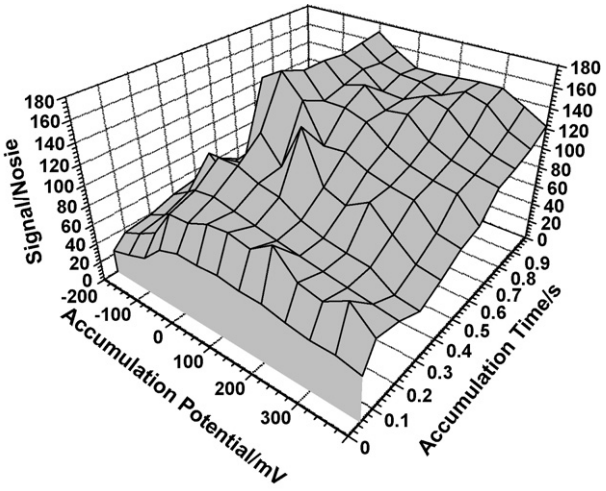

Fig. 5. The accumulation effects of potential and time on the electrode response to the injection of 2.0×10^{-9} mol/L guthion in 0.05 mol/L H_3PO_4.

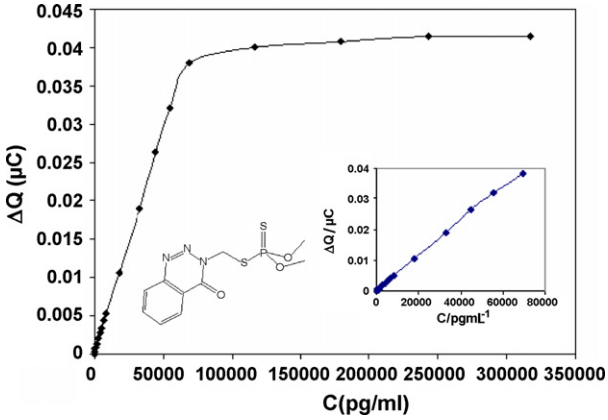

Fig. 6. Calibration curves obtained for guthion on the Au electrode in 0.05 mol/L H_3PO_4.

3.2. Linearity

The results of the analysis provide a correlation coefficient with a value of $R = 0.9965$ with %R.S.D. values, ranging from 0.35 to 4.1% across the studied concentration range. Typically, the regression equation for the calibration curve was found to be $Y = 0.8487X - 4.2041$. Fig. 6 presents the obtained calibration graph from the monitoring of guthion in a 0.05 mol/L H_3PO_4.

3.3. LOQ and LOD

In the end, the LOQ was found to be 4 pg/mL with a resultant %R.S.D. value of 0.28% ($n = 5$). In addition, the LOD was equivalent to 1.27 pg/mL.

3.4. Precision

The final mean concentrations were found to be 4.11, 1013 and 69,850 with associated %R.S.D. values of 3.6, 1.78 and 0.31, respectively. The inter-day precision was assessed by injecting the same three concentrations for 3 consecutive days, resulting in mean guthion concentrations of 4.15, 1021 and 69,950 pg/mL with associated %R.S.D. values of 3.73, 3.41 and 2.32%, respectively.

3.5. Accuracy

The resultant concentrations were 4.15 ± 0.14, 1014.5 ± 17.92 and $69{,}410 \pm 228$ pg/mL with relevant error percentage of 3.7, 1.56 and 0.54%, respectively.

3.6. Ruggedness and recovery

Following accuracy, the ruggedness of the method was estimated. For this aim, a comparison was performed between the intra- and inter-day assay results for guthion, undertaken by two analysts. The %R.S.D. values for intra- and inter-day assays of guthion in the cited samples were performed in the same laboratory by the two analysts. The result showed that they did

Table 2
Influence of the changes in the experimental conditions on the FIA system performance

Parameter	Modification	Guthion (%recovery)
pH	1.8	101.3
	2	101.9
	2.3	100.1
	3.0	100.3
Flow rate (mL/min)	2.8	101.5
	3.0	101.0
	3.2	99.9
Buffer composition (M)	0.04	99.8
	0.05	101.7
	0.06	101.3
Laboratory temperature (°C)	20	100.6
	25	99.7
	30	100.5

Table 3
Detection limit comparison of methods

Method	Detection limit (pg/mL)	Reference
GC-MAP	186×10^6	[3]
GC/MS	12,500	[9]
FFTCV	1.27	This work

not exceed 4.5%; in this way, the ruggedness of the method is illustrated.

The robustness was also examined while the parameters values (the pH of the eluent, the flow rate, the buffer composition and the laboratory temperature) were being slightly changed [39]. According to Table 2, the guthion recovery percentages were satisfactory in most cases, without presenting any important changes during the alteration of the critical parameters.

3.7. Sensitivity comparison of the detection methods

Finally, the sensitivity (detection limit) of this method is compared with those of the previously reported methods in Table 3. Obviously, the detection limit of this method is about 10,000 times lower than that of the gas chromatography method.

4. Conclusion

In this work it is demonstrated that the concentration of guthion in flowing solution can be measured indirectly via monitoring the current changes at oxidation and reduction of the electrode surface. In this method the S/N ratio is enhanced by using of fast Fourier transform of the analyte and signal integration. Also, for improving the sensitivity, the method take advantage of adsorption of the analyte on the Au microelectrode and the influence of adsorbed possible impurity in the eluent was removed by background subtraction. FFTCV can be considered as a new sensitive, accurate and fast method for determination of drugs and some pesticides, with ability of adsorption gold surface, in chromatographic systems, such as HPLC and capillary electrophoresis. However, in order to obtain better sensitivity for a specific target, experimental parameters should be optimized. Finally, such detection limit (in nanomolar level), make the method suitable for bio-analysis. The detection limit of the proposed method is about 10,000 times lower than that of the most sensitive reported method.

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References

[1] T.T. Liang, E.P. Lichtenstein, Effects of and leaf surfaces on photodecomposition of (C-14) azinphosmethyl, J. Agric. Food Chem. 24 (1976) 1205–1210.
[2] T.T. Liang, E.P. Lichtenstein, J. Econ. Entomol. 65 (1972) 315.
[3] L. Sánchez, M.D. Mingorance, A. Peña, Microwave assisted process for methidathion in water samples for physicochemical studies, Analyst 125 (2000) 1199.
[4] Official Methods of Analysis, vol. 29, Association of Official Analytical Chemist, Washington, DC, 1975, p. 102.
[5] W.S. Cox, J. Assoc. Off. Agric. Chem. 46 (1963) 229.
[6] J.M. Adams, C.A. Anderson, J. Agric. Food Chem. 14 (1966) 53.
[7] L. Rastrelli, K. Totaro, F. Simone, Determination of organophosphorus pesticide residues in Cilento (Campania, Italy) virgin olive oil by capillary gas chromatography, Food Chem. 79 (2002) 303.
[8] R. Carabias-Martınez, E. Rodrıguez-Gonzalo, P.H. Paniagua-Marcos, J. Hernandez-Mendez, Analysis of pesticide residues in matrices with high lipid contents by membrane separation coupled on-line to a high-performance liquid chromatography system, J. Chromatogr. A 869 (2000) 427.
[9] M.B. Kralj, P. Trebše, M. Franko, Oxidation as a pre-step in determination of organophosphorus compounds by the AChE-TLS bioassay, Acta Chim. Slov. 53 (2006) 43.
[10] R.A. Hoodless, J.A. Sidwell, J.C. Skinner, R.D. Treble, J. Chromatogr. 166 (1978) 279.
[11] G. Szalontai, High-performance liquid-chromatography of organophosphorus insecticides, J. Chromatogr. 124 (1976) 9–16.
[12] S. Lin, C. Chen, S.D. Murphy, R.M. Caprioli, Quantitative high-performance liquid-chromatography and mass-spectrometry for the analysis of the in vitro metabolism of the insecticide azinphosmethyl (guthion) by rat-liver homogenates, J. Agric. Food Chem. 28 (1980) 85–88.
[13] J. Kvalvag, D.E. Ott, F.A. Gunther, Liquid-chromatographic determination of azinphosmethyloxon in foliar dislodgeable residues and in soil surface dusts from an azinphosmethyl-treated orange grove, J. Assoc. Off. Anal. Chem. 60 (1977) 911–917.
[14] P.T. Kissinger, W.R. Heineman, Laboratory Techniques in Electroanalytical Chemistry, Marcel Dekker, New York, 1984.
[15] S.F.Y. Li, Capillary Electrophoresis: Principles, Practice and Applications, Elsevier, Amsterdam, 1992.
[16] M. Paeschke, F. Dietrich, A. Ulig, R. Hintsche, Voltametric multichannel measurements using silicon fabricated microelectrode arrays, Electroanalysis 8 (1996) 891–898.
[17] T. Dimitrakopoulos, P.W. Alexander, D.B. Hibbert, Serial array of ISEs for use in a portable battery-powered flow injection analyzer, Electroanalysis 8 (1996) 438–442.
[18] R. Hintsche, M. Paeschke, U. Wollenberger, U. Schnakenberg, B. Wagner, T. Lisec, Microelectrode arrays and application to biosensing devices, Biosens. Bioelectron. 9 (1994) 697–705.
[19] G. Sreenivas, S.S. Ang, I. Fritsch, W.D. Brown, G.A. Gerhardt, D. Woodward, Fabrication and characterization of sputtered-carbon microelectrode arrays, J. Anal. Chem. 68 (1996) 1858–1864.

[20] V. Cosofret, M. Erdosy, T.A. Johnson, R.P. Buck, R.B. Ash, M.R. Neuman, Microfabricated sensor arrays sensitive to pH and K^+ for ionic distribution measurements in the beating heart, Anal. Chem. 67 (1995) 1647–1653.
[21] J. Ermer, Validation in pharmaceutical analysis. Part I. An integrated approach, J. Pharm. Biomed. Anal. 24 (2001) 755–767.
[22] G.A. Shabir, Validation of high-performance liquid chromatography methods for pharmaceutical analysis: understanding the differences and similarities between validation requirements of the US Food and Drug Administration, the US Pharmacopeia.
[23] United States Pharmacopeia 28-NF 23, United States Pharmacopeial Convention Inc., Rockville, MD, 2005, p. 2748.
[24] J.C. Miller, J.N. Miller, Statistics for Analytical Chemistry, vol. 22, Ellis Horwood, Chichester, 1984, p. 82.
[25] Z. Al-Kurdi, T. Al-Jallad, A. Badwanamd, A.M.Y. Jaber, High performance liquid chromatography method for determination of methyl-5-benzoyl-2-bezimidazole carbamate (mebendazole) and its main degradation product in pharmaceutical dosage forms, Talanta 50 (1999) 1089–1097.
[26] Proceedings of the Internatioal Conference on Harmonisation (ICH), Topic Q2 B: Validation of Analytical Procedures: Methodology, The European Agency for the Evaluation of Medicinal Products, Geneva, 1996.
[27] M.R. Ganjali, P. Norouzi, M. Ghorbani, A. Sepehri, Fourier transform cyclic voltametric technique for monitoring ultratrace amounts of salbutamol at gold ultra-microelectrode in flowing solutions, Talanta 66 (2005) 1225–1233.
[28] P. Norouzi, M.R. Ganjali, P. Matloobi, Sub-second adsorption for sub-nanomolar monitoring of metoclopramide by fast stripping continuous cyclic voltametry, Electrochem. Commun. 7 (2005) 333–338.
[29] P. Norouzi, G.R. Nabi Bidhendi, M.R. Ganjali, A. Sepehri, M. Ghorbani, Sub-second accumulation and stripping for pico-level monitoring of amikacin sulphate by fast Fourier transform cyclic voltametry at a gold ultra-microelectrode in flow-injection systems, Microchem. Acta 152 (2005) 123–129.
[30] P. Norouzi, M.R. Ganjali, M. Ghorbani, A. Sepehri, Novel method for fast determination of ultra trace amounts of timolol maleate by continuous cyclic voltametry at Au microelectrode in flow-injection systems, Sens. Actuators B 110 (2005) 239–245.
[31] P. Norouzi, M.R. Ganjali, T. Alizadeh, P. Daneshgar, Fast Fourier continuous cyclic voltammetry at gold ultramicroelectrode in flowing solution for determination of ultra trace amounts of penicillin G, Electroanalysis 18 (2006) 947–954.
[32] P. Norouzi, M.R. Ganjali, P. Daneshgar, Fast Fourier transform continuous cyclic voltammetry development as a highly sensitive detection system for ultra trace monitoring of thiamine in tablets, Anal. Lett., in press.
[33] P. Norouzi, M.R. Ganjali, L. Hajiaghababaei, Fast monitoring of nanomolar level of gentamycine by fast Fourier transform continuous cyclic voltammetry in flowing solution, Anal. Lett. 39 (2006) 1941.
[34] P. Norouzi, S. Shirvani-Arani, P. Daneshgar, M.R. Ganjali, Sub-second adsorptive fast Fourier transform coulometric technique as a novel method for the determination of nanomolar concentrations of sodium valproate in its pharmaceutical preparation in flowing solution systems, Biosens. Bioelectron., in press.
[35] P. Norouzi, M.R. Ganjali, S. Shirvani-Arani, A. Mohammadi, Novel method for the fast determination of ultra trace amount of nortriptyline in its pharmaceutical formulations by fast Fourier transform continuous cyclic voltammetric technique at Au microelectrode in flowing solutions, J. Pharm. Sci. 95 (2006) 1.
[36] R.M. Wightman, D.O. Wipf, Voltammetry at ultramicroelectrodes, in: A.J. Bard (Ed.), Electroanalytical Chemistry, vol. 15, Marcel Dekker, New York, 1989.
[37] J. Lipkowski, L. Stolberg, Adsorption of Molecules at Metal Electrodes, VCH, New York, 1992.
[38] J.O.M. Bockris, B.E. Conway, E. Yeager, Comprehensive Treatise of Electrochemistry, Plenum, New York, 1980.
[39] Y.V. Heyden, A. Nijhuis, J. Smeyers-Verbeke, B.G.M. Vandeginste, D.L. Massaret, Guidance for robustness tests in method validation, J. Pharm. Biomed. Anal. 24 (2001) 723–753.