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Development of an electrochemical caffeine sensor for PAT Application in the Food and Beverage Industry

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This work reports on the development of an electrochemical sensor for on-line caffeine detection using screen printed graphite electrodes. The effects of solution pH and pre-treatment procedures on electrode performance have been discussed, as well as the modification of the electrode surface for increased electrode sensitivity. Successful caffeine determination in soft drink samples is described. The results indicate the potential of electrochemical sensors to compare and compete with the current off-line methods of caffeine analysis, such as HPLC, allowing for both a reduction in time and cost of product quality analysis. The successful performance of the screen printed electrode, as well as its low cost and small dimensions, will allow for efficient integration into a multi-parameter device for on-line quality control analysis.

Keywords—caffeine; electrochemical detection; process analytical technology; screen printed electrodes; food and beverage

I. INTRODUCTION

In September 2004, the United States Food and Drug Administration (FDA) introduced a Process Analytical Technology (PAT) initiative for industries, which aimed at supporting the voluntary growth and implementation of innovative industrial development, manufacturing, and quality assurance [1]. The PAT approach involves multivariate data collection through the application of a variety of analytical methodologies in- line, on- line or at- line allowing for timely measurements of the product attributes throughout the manufacturing process. This allows manufacturers to use the data obtained to increase the level of process understanding and control. By using a Quality by Design (QbD) approach to manufacturing, the quality of the products is incorporated by process design and not by post-production quality testing.

Food and beverage quality and safety have become of significant importance over the past decade and assuring the highest standards of process control is a key priority [2-5]. As with the pharmaceutical industry, the food industry faces high regulatory standards regarding the quality control, safety and traceability of their production processes. All of these factors have emphasised the need for reliable techniques to evaluate the food quality in a rapid, cost effective and reproducible way. Through the introduction of PAT to manufacturing processes, the food and beverage industry is gradually moving from inferential monitoring and control toward continuous measurement of core quality parameters. As a method of reducing the cost and time of quality control analysis, increased interest has been given to the implementation of integrated devices. These systems consist of the integration of several analytical techniques into a single, easy to use device which can be used to determine many quality control parameters simultaneously [6-9]. In recent years, microelectrodes fabricated using screen printing or thick film techniques have seen an increased use in these systems, as they can be produced in large quantities at very low costs per unit, maintaining high levels of reproducibility. Carbon-based materials are commonly used in electrochemical analysis due to their long-term chemical stability, fast electron mobility, good electrical conductivity, rich surface chemistry, as well as their usefulness over the wide potential range of the anodic and cathodic areas of the instrumentation [10]. Screen printed carbon-based electrodes have been used in this project to determine the caffeine levels of soft drink beverage solutions, using electrochemical analysis.

Caffeine (1, 3, 7 trimethylxanthine) is an active alkaloid, naturally produced by plants and a constituent in beverages such as tea, coffee and soft drinks. The quantification of caffeine in both beverage and pharmaceutical products is mainly of pharmaceutical and alimentary interest and requires the development of rapid, reliable and accurate analytical methods, suitable for detecting caffeine in a specific matrix under the influence of interfering agents. Thus, the development of dependable analytical techniques for the determination and evaluation of caffeine is an active field of research. Electrochemical methods offer many practical advantages over separation techniques for the detection of caffeine including suitability for real time analysis, low cost instrumentation, possibility of miniaturisation, simplicity in operation and reduced sensitivity to matrix effects and external influences [11-13]. Electrochemical methods for the detection of caffeine on different electrode materials have been extensively reviewed and discussed [14-17]. These inlcude potentiometric, voltammetric and amperometric sensors and techniques.

II. Experimental

A. Materials

All chemicals were of analytical grade and were used as received from Sigma Aldrich, Ireland. The soft drink concentrate solution was received from a food and beverage company.

B. Instrumentation and Electrodes

Electrochemical measurements were carried out using a PalmSens handheld potentiostat/galvanostat (Netherlands) and a CH Instrument. The commercial Screen Printed Carbon Electrode used was purchased from Kanichi Research Ltd (Manchester, UK). It consisted of a graphite working electrode (3mm Ø) and an on-chip graphite counter electrode and silver/silver chloride pseudo reference electrode.

C. Electrode Modification

Prior to modification, an electrochemically active and hydrophilic working electrode surface was produced by sweeping the electrode from -0.5 V to +1.5 V in 0.1M Phosphoric Acid for 10 scans. Nafion (a perfluorosulfonated derivative of Teflon) is a cation-exchange polymer with properties of excellent antifouling capacity, chemical inertness and high permeability to cations [13]. It was used in this research as an electrode modifying material [18-21], to increase the sensor selectivity through the electrostatic repulsion of unwanted species, especially anions as well as reducing chemical adsorption of other components in the matrix, particularly commercial samples.

5 % Nafion solution (Sigma Aldrich) was diluted to 0.25% as per [19, 20].

D. Method of Electrochemical Characterisation

Characterisation of the electrodes was carried out by Cyclic Voltammetry (CV) and Square Wave Voltammetry (SWV). All electrochemical measurements were carried out with a PalmSens potentiostat. The electrode was inserted into a connector (DropSens) and connected in a three electrode system.

E. Electrode Pre-Treatment

Pre-treatment procedures were carried out using Cyclic Voltammetry and Pre-Anodisation. The procedures carried out were as follows:

- The electrode was placed into a solution of 0.2 M Sulphuric acid and CV scans were carried out between -1.2 and +1.5 V [22]. This was done both as a single scan and 5 scans for comparison.
- The electrode was placed in a solution of 0.1M Sodium Hydroxide and CV scans were carried out between -1 and +1 V for ten minutes [23].
- The electrode was placed in a 0.05 M Phosphate Buffer solution and CV scans were carried out between -1 and +1 V for 25 scans.
- The electrode was pre-anodised in 0.05 M Phosphate buffer at +1.5 V for two minutes [24]
- The electrode was pre-anodised in saturated Sodium Carbonate at +1.2 V for five minutes.

After the electrodes were pre-treated they were then analysed in a 1 mM Ferri/Ferrocyanide in 1 M KCl solution.

III. Results and Discussion

A. Scanning Electron Microscopy

The Screen Printed Carbon (SPC) electrode surface was analysed using Scanning Electron Microscopy (SEM). The surface morphology can be seen in Fig. 1. The images show a rough, unhomogenous blanket-like layer of graphite, as is expected from the untreated electrode surface.

B. Effect of Surface Pre-treatment on Electrode Performance

Pre-treatment procedures are commonly carried out on electrodes to increase their sensitivity. In the case of carbon electrodes, pre-treatment can expose the graphite edge-plane sites in the material, leading to higher sensitivity. The pre-treatment procedures were carried out, as described in the Experimental section. After pre-treatment, the electrodes were analysed in a 1 mM Ferri/Ferrocyanide in 1 M KCl solution. The resulting graphs were analysed based on the potential differences between the anodic and cathodic peaks and the anodic and cathodic peak ratios. The anodic and cathodic potential difference is an indication of how electrochemically clean an electrode surface is. The smaller the difference, the cleaner the surface and the better the electron transfer. Table 1 shows the results of the pre-treatment procedures. In all cases, pre-treating the electrodes gave an improved performance over the untreated electrodes. From the table, it can be seen that the pre-anodisation techniques gave the lowest peak potential difference. The pre-treatment using sodium carbonate, however, showed a higher deviation between electrodes. The technique with the highest reproducibility between electrodes was the 5 CV scans in Sulphuric Acid, which also showed a high anodic current. Taking into consideration these factors, along with the simple and fast method of treating the electrodes, it was decided to use 5 scans in Sulphuric Acid as the method for further electrode pre-treatment.

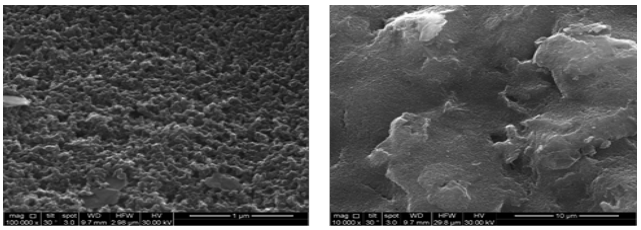

Fig. 1. Scanning Electron Micrscopy images of Bare Screen Printed Graphite Electrode at a magnification of 100,000 and 10,000.

TABLE I. THE EFFECT OF PRE-TREATMENT PROCEDURES ON SCREEN PRINTED ELECTRODE PERFORMANCE

Electrode	*Pre-treatment*	*ΔE (mV)*	i_a / i_c	*Anodic Current (μA)*	*Anodic Current STDEV (%)*
SPC (n=10)	Untreated	214	0.92	8.04	7.22
	H_2SO_4 (1 scan)	169	0.93	9.96	1.24
	H_2SO_4 (5 scans)	178	0.95	9.75	0.41
	NaOH	183	0.98	10.91	0.26
	PBS	184	0.91	8.60	2.78
	PBS Anodised	148	0.99	9.789	0.53
	Na_2CO_3 Anodised	145	0.96	10.14	1.64

C. *Electrochemical Behaviour of Caffeine at Screen Printed Carbon Electrode*

The electrochemical behavior of caffeine at the SPCE was investigated using cyclic voltammetry. In order to analyse the potential sensitivity-enhancing capabilities of a surface modification, a bare SPC and a Nafion-modified SPC electrode were compared for performance. Fig. 2 shows the cyclic voltammogram obtained for 300μM caffeine in 0.1M phosphoric acid with a scan rate of 0.1 V/s at both types of SPC electrode. From Fig. 2 it can be seen that there is a clear increase in the anodic current of caffeine oxidation for the Nafion electrode, compared to the bare. The current is 2.13 times as high with the Nafion modification due to the repulsion of unwanted species in the solution. Based on these results, a Nafion-modified SPCE was used for futher analysis.

D. *Effect of pH on the Detection of Caffeine*

The pH value of an electrolyte solution is an important factor that affects the redox behavior of electroactive species [25] and, in food production, how a product tastes. The effect of variation of pH for the oxidation of 300 μM caffeine was studied, employing CV technique, using Britton-Robinson (pH 2-8), and adjusting the solutions to the desired pH using NaOH (0.2 M). The resulting anodic current at each pH is seen in Fig. 3.

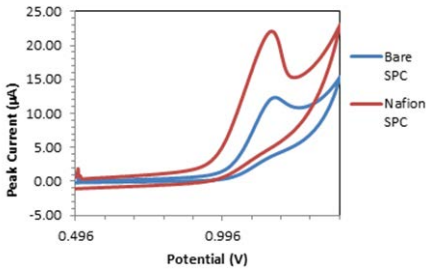

Fig. 2. Comparison of electrochemical behaviour of 300μM Caffeine in 0.1M H_3PO_4 at Bare (blue) and Nafion (red) Screen Printed Graphite Electrodes, at a scan rate of 0.1 V/s.

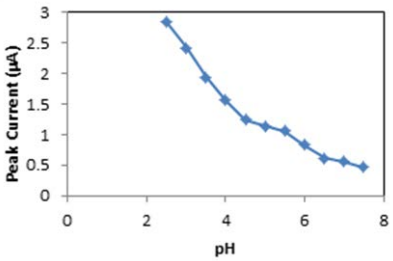

Fig. 3. Effect of pH on the oxidation of 300μM Caffeine in Britton-Robinson Buffer (pH 2-8) at a scan rate of 0.1 V/s.

In Fig. 3, the anodic peak current of caffeine decreased linearly as the solution pH increased. Based on the shape of the voltammogram and high anodic current, it is clear that the electrode performance improves in more acidic conditions, ideal for use in acidic soft drink beverage solutions.

E. *Real Sample Analysis*

The caffeine content of an acidified beverage sample containing caramel was analysed. This was done using the SPC electrode, pre-treated with CV scans in H_2SO_4 followed by modification with Nafion. Prior to analysis, the sample was diluted to beverage level with 0.1M Phosphoric acid in order to bring the caffeine concentration into the linear range readable by the sensor. For real sample analysis the electrochemical technique used was Square Wave Voltammetry. Over approximately 150 sensors, a recovered caffeine range of 96-102% was obtained, with high reproducibility between batches. The results are an indication that the developed sensors are extremely efficient for the detection of caffeine in soft drink concentrate solutions.

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REFERENCES

[1] United States Food and Drug Administration (FDA), Guidance for industry PAT-A framework for innovative pharmaceutical development, manufacturing and quality assurance, FDA, September 2004

[2] Kuswandi, Bambang; Wicaksono, Yudi; Aminah Abdullah, Jayus; Yook Heng, Lee; Ahmad, Musa; Smart packaging: sensors for monitoring of food quality and safety, Sens. & Instrumen. Food Qual. (2011) 5:137–146

[3] San Martín, Ricardo; Briones, Reinaldo; Quality control of commercial quillaja (Quillaja saponaria Molina) extracts by reverse phase HPLC, Sci Food Agric 80:2063-2068

[4] Ibánez, María; Sancho, Juan V.; Hernández, Félix; Determination of melamine in milk-based products and other food and beverage products by ion-pair liquid chromatography–tandem mass spectrometry, Analytica Chimica Acta 649 (2009) 91–97

[5] Lachenmeier, Dirk W.; Rapid quality control of spirit drinks and beer using multivariate data analysis of fourier transform infrared spectra, Food Chemistry 101 (2007) 825–832

[6] Martínez-Máñez, Ramon; Soto, Juan; García-Breijo, Eduardo; Gil, Luis; Ibáñez, Javier; Gadea, Elena; A multisensor in thick-film technology for water quality control, Sensors and Actuators A 120 (2005) 589–595

[7] Escuder-Gilabert, Laura; Peris, Miguel; Review: Highlights in recent applications of electronic tongues in food analysis, Analytica Chimica Acta 665 (2010) 15–25

[8] Dias, L.G.; Peres, A.M.; Barcelos, T.P.; Morais, J. Sá; Machado, A.A.S.C.; Semi-quantitative and quantitative analysis of soft drinks using an electronic tongue, Sensors and Actuators B 154 (2011) 111–118

[9] Peris, Miguel; Escuder-Gilabert, Laura; A 21st century technique for food control: Electronic noses, Analytica Chimica Acta 638 (2009) 1–15

[10]Centi, Gabriele; Perathoner, Siglinda; Problems and perspectives in nanostructured carbon-based electrodes for clean and sustainable energy, Catalysis Today, 150 (2010) 151-162

[11] Švorc, L'ubomír; Sochr, Jozef; Tomčík, Peter; Rievaj, Miroslav; Bustin, Dušan; Simultaneous determination of paracetamol and penicillin V by square-wave voltammetry at a bare boron-doped diamond electrode, Electrochimica Acta 68 (2012) 227–234

[12] Švorc, L'ubomír; Sochr, Jozef; Rievaj, Miroslav; Tomčík, Peter; Bustin, Dušan; Voltammetric determination of penicillin V in pharmaceutical formulations and human urine using a boron-doped diamond electrode, Bioelectrochemistry 88 (2012) 36–41

[13] Švorc, L'ubomír; Sochr, Jozef; Svítková, Jana; Rievaj, Miroslav; Bustin, Dušan; Rapid and sensitive electrochemical determination of codeine in pharmaceutical formulations and human urine using a boron-doped diamond film electrode, Electrochimica Acta 87 (2013) 503–510

[14]Švorc, L'ubomír; Determination of Caffeine: a comprehensive review on electrochemical methods, Int. J. Electrochem. Sci., 8 (2013) 5755-577 caffeine, Colloids and Surfaces B: Biointerfaces 84 (2011) 421–426

[15]Lourenção, Bruna Cláudia; Medeiros, Roberta Antigo; Rocha-Filho, Romeu C.; Fatibello-Filho, Orlando; Simultaneous differential pulse voltammetric determination of ascorbic acid and caffeine in pharmaceutical formulations Using a boron-doped diamond electrode, Electroanalysis 2010, 22, No. 15, 1717 – 1723

[16]Jeevagan, A. John; John, S. Abraham; Electrochemical determination of caffeine in the presence of paracetamol using a self-assembled monolayer of non-peripheral amine substituted copper(II) phthalocyanine, Electrochimica Acta, Volume 77, 30 August 2012, Pages 137–142

[17]Svítková, Jana; Machková, Martina; Šatkovská, Petra; Cinková, Kristína; Švorc, Ľubomír; Utilization of electrochemical methods in determination of trace elements in beverages, Acta Chimica Slovaca, Vol. 5, No. 1, 2012, pp. 42—46

[18]Torres, A. Carolina; Barsan, Madalina M.; Brett, Christopher M.A.; Simple electrochemical sensor for caffeine based on carbon and Nafion-modified carbon electrodes, Food Chemistry 149 (2014) 215–220

[19]Brunetti, Barbara; Desimoni, Elio; Casati, Paolo; Determination of caffeine at a Nafion-covered glassy carbon electrode, Electroanalysis, 19 (2007), No 2-3, 385-388

[20] Martínez-Huitle, C.A.; Fernandes, N. Suely; Ferro, S.; De Battisti, A.; Quiroz, M.A.; Fabrication and application of Nafion®-modified boron-doped diamond electrode as sensor for detecting caffeine, Diamond & Related Materials 19 (2010) 1188–1193

[21]Brunetti, Barbara; Desimoni, Elio; Determination of theophylline at a cysteic acid modified glassy carbon electrode, Electroanalysis 2009, 21, No. 6, 772 – 778

.[22]Killard, A.J.; Zhang, S.; Zhao, H.; John, R.; Iwuoha, E.I.; Smyth, M.R. Development of an electrochemical flow injection immunoassay (FIIA) for the real-time monitoring of biospecific interactions. Anal. Chim. Acta 1999, 400 (1–3), 109–119

[23]Kadara, Rashid O.; Jenkinson, Norman; Banks, Craig E.; Characterisation of commercially available electrochemical sensing platforms, Sensors and Actuators B 138 (2009) 556–562

[24]Wang, Joseph; Pedrero, Maria; Sakslund, Henning; Hammerich, Ole; Pingarron, Jose; Electrochemical activation of screen-printed carbon strips, Analyst, March 1996, Vol. I21 (345-350)

[25]B. Habibi, M. Abazari, and M. P. A. Hossein, "A carbon nanotube modified electrode for determination of caffeine by differential pulse voltammetry," Chinese Journal of Catalysis, vol. 33, no. 11-12, pp. 1783–1790, 2012