



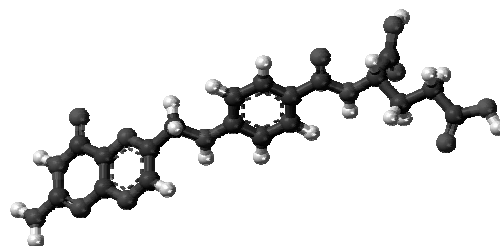
DETECTION OF FOLIC ACID FROM ORANGE JUICE USING AMPEROMETRIC DOT MICROSENSORS BASED ON GRAPHITE AND GRAPHENE

Ramona GEORGESCU,^{a,b} Jacobus Frederick VAN STADEN,^{a,*}
and Raluca-Ioana STEFAN-VAN STADEN^a

^aLaboratory of Electrochemistry and PATLAB Bucharest,
National Institute of Research for Electrochemistry and Condensed Matter, Bucharest 060021, Roumania
^bDepartment of Bioresources and Polymer Science, Faculty of Applied Chemistry and Materials Science,
University Politehnica of Bucharest, Roumania

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Nineteen amperometric dot microsensors based on graphite (G) modified with iron(III) porphyrin (Fe(III)P), tetraphenylporphine (TPP), tetraphenylporphine cobalt(II) (Co(II)TPP), iron(II) phthalocyanine (Fe(II)Pc), iron(III) phthalocyanine (Fe(III)Pc), tetraamino cobalt(II) phthalocyanine (CoTAPc), tetraamino zinc(II) phthalocyanine (ZnTAPc), tetraamino nickel(II) phthalocyanine (NiTAPc), tetraamino manganese(II) phthalocyanine (MnTAPc), tetranitro cobalt(II) phthalocyanine (CoTNPc), tetranitro zinc(II) phthalocyanine (ZnTNPc), tetranitro nickel(II) phthalocyanine (NiTNPc), tetranitro manganese(II) phthalocyanine (MnTNPc) and graphene (GR) modified with Fe(III)P, TPP, Co(II)TPP, Fe(II)Pc, Fe(III)Pc, Co(II)Pc were tested for their ability to detect folic acid (FA) from orange juice. Cyclic voltammetry (CV) was used to determine the optimum working conditions. The optimum working pH was 7.0 (phosphate buffer), with a 0.1 mol L⁻¹ KCl supporting electrolyte. Folic acid was recovered reliably from orange juice samples in percentages higher than 96.00.



INTRODUCTION

Folic acid (FA), (vitamin B9) is a water-soluble vitamin¹ and is usually employed in the treatment or prevention of megaloblastic anaemia during pregnancy, childhood and other clinical situations often associated with alcoholism and liver diseases.² Foods rich in FA are especially yeast, green vegetables, oranges, nuts, liver and kidney.³

A number of methods have consequently been reported for the determination of FA in different

samples. The most widely used are those based on HPLC with absorbance⁴⁻⁷ or fluorescence detection,⁸ chemiluminescence,⁹⁻¹¹ spectrophotometric,¹² fluorometric¹ and electroanalytical^{13,14} methods.

In this work, we describe the design^{15,16,17} of nineteen amperometric dot microsensors based on graphite (G) modified with iron(III) porphyrin (Fe(III)P), tetraphenylporphine (TPP), tetraphenylporphine cobalt(II) (Co(II)TPP), iron(II) phthalocyanine (Fe(II)Pc), iron(III) phthalocyanine (Fe(III)Pc), tetraamino cobalt(II) phthalocyanine (CoTAPc),

* Corresponding author: koosvanstaden2012@yahoo.com; website: www.patlab.ro

tetraamino zinc(II) phthalocyanine (ZnTAPc), tetraamino nickel(II) phthalocyanine (NiTAPc), tetraamino manganese(II) phthalocyanine (MnTAPc), tetranitro cobalt(II) phthalocyanine (CoTNPc), tetranitro zinc(II) phthalocyanine (ZnTNPc), tetranitro nickel(II) phthalocyanine (NiTNPc), tetranitro manganese(II) phthalocyanine (MnTNPc) and graphene (GR) modified with Fe(III)P, TPP, Co(II)TPP, Fe(II)Pc, Fe(III)Pc, Co(II)Pc, for the detection of folic acid from orange juice.

EXPERIMENTAL

1. Materials and reagents

Folic acid, dopamine, epinephrine, norepinephrine, ascorbic acid, uric acid, graphite powder (1-2 μm , synthetic) (G), 5,10,15,20-tetrakis(pentafluorophenyl)-21H,23H-porphyrin iron(III) chloride (Fe(III)P), 5,10,15,20-tetraphenyl-21H,23H-porphine (TPP), 5,10,15,20-tetraphenyl-21H,23H-porphine cobalt(II) (Co(II)TPP), iron(III) phthalocyanine-4,4',4'',4'''-tetrasulfonic acid, compound with oxygen monosodium salt hydrate (Fe(III)Pc), iron(II) phthalocyanine (Fe(II)Pc), cobalt(II) phthalocyanine (Co(II)Pc), dimethylsulfoxid (DMSO), NaH_2PO_4 , Na_2HPO_4 , KCl, NaCl, and KNO_3 were purchased from Aldrich. Paraffin oil was purchased from Fluka (Buchs, Switzerland). Tetrahydrofuran (THF) was purchased from Merck and graphene nanopowder (C, 6-8 nm) was purchased from SkySpring Nanomaterials Inc (SSNANO) Houston, USA. Tetraamino cobalt(II) phthalocyanine, tetraamino zinc(II) phthalocyanine, tetraamino nickel(II) phthalocyanine, tetraamino manganese(II) phthalocyanine, tetranitro cobalt(II) phthalocyanine, tetranitro zinc(II) phthalocyanine, tetranitro nickel(II) phthalocyanine, and tetranitro manganese(II) phthalocyanine were synthesized in house.¹⁸⁻²¹ Deionized water obtained from a Direct-Q 3 Water Purification system (Millipore Corporation, France) was used for the preparation of all solutions. Phosphate buffer solution (PBS, 0.1 mol L⁻¹) with pH = 2-8 was obtained by using different ratios between NaH_2PO_4 and Na_2HPO_4 , and adjusted with 0.1 mol L⁻¹ HCl or NaOH solutions to the required pH needed in the measurements.

The stock solutions for cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were prepared using 10⁻² mol L⁻¹ folic acid (FA). All standard solutions of FA (10⁻³ – 10⁻¹⁵ mol L⁻¹) were prepared from the stock solution by serial dilution and buffered (1:1= v/v) with phosphate buffer of different pHs containing KCl, NaCl or KNO_3 (0.1 mol L⁻¹) as electrolytes.

The orange juice was obtained daily from fresh oranges and was filtered using a 0.45 μm filter. The samples of orange juices were buffered with phosphate buffer solution (pH = 7.0) containing 0.1 mol L⁻¹ KCl. The orange juice pH was originally 3.85 and was adjusted to 7 in order to conduct the measurements.

2. Apparatus

A PGSTAT 100 potentiostat/ galvanostat and software Eco Chemie (version 4.9) were used for all amperometric measurements. A Pt electrode served as the counter electrode

and an Ag/AgCl electrode as reference electrode in the cell. A CyberScan PCD 6500 Multiparameter from Eutech Instruments was employed for all pH measurements.

3. Design of the amperometric dot microsensors

3.1. Design of graphite/graphene pastes modified with porphyrins (Fe(III)P/G, TPP/G, Co(II)TPP/G, Fe(III)P/GR, TPP/GR, Co(II)TPP/GR) based dot microsensors

Graphite or graphene pastes modified with porphyrins were prepared as follows: 100 mg of graphite or graphene powder were mixed with 30 μL paraffin oil to form the graphite or graphene pastes. 100 μL from the solution of Fe(III)P or TPP or Co(II)TPP (10⁻³ mol L⁻¹, prepared in THF) was added to the graphite or graphene pastes. The modified paste was placed into a plastic tube (Fig. 1).²²⁻²⁴ The diameter of the sensor was about 300 μm . Electrical contact was obtained by inserting an Ag/AgCl wire into the modified graphite or graphene pastes. The surface of the sensor was wetted with deionised water and polished with alumina paper before using. When not in use, the dot microsensors were stored in a dry state, away from day light and at room temperature.

3.2. Design of graphite/graphene pastes modified with phthalocyanines (Fe(II)Pc/G, Fe(III)Pc/G, Fe(II)Pc/GR, Fe(III)Pc/GR, Co(II)Pc/GR) based dot microsensors

To 100 mg of paste, obtained by mixing graphite or graphene powder with 30 μL paraffin oil, 100 μL solution of Fe(II)Pc or Fe(III)Pc or Co(II)Pc (10⁻³ mol L⁻¹, prepared in THF) was added. The resulting paste was pressed into a plastic tube (Fig. 1)²²⁻²⁴ and the diameter of the active surface of the sensor was 300 μm . Electrical contact was obtained with an Ag wire inserted into the paste. The surface of the sensor was wetted with deionised water and polished with alumina paper before using. The dot microsensors were stored in a dry state, away from day light and at room temperature.

3.3. Design of graphite paste modified with tetraamino- and tetranitro phthalocyanines (CoTAPc/G, ZnTAPc/G, NiTAPc/G, MnTAPc/G, CoTNPc/G, ZnTNPc/G, NiTNPc/G, MnTNPc/G) based dot microsensors

100 mg of paste was obtained by mixing graphite powder with 10 μL paraffin oil to give a homogenous paste and to which 25 μL solution of CoTAPc or ZnTAPc or NiTAPc or MnTAPc or CoTNPc or ZnTNPc or NiTNPc or MnTNPc (10⁻³ mol L⁻¹, prepared in DMSO) was added. The resulting paste was pressed into a plastic tube (Fig. 1)²²⁻²⁴ to obtain a sensor with an active surface of 300 μm in diameter. Electrical contact was obtained with an Ag wire inserted into the paste. The surface of the sensor was wetted with deionised water and polished with alumina paper before using. The dot microsensors were stored in a dry state, away from day light and at room temperature.

4. Recommended procedure

The cyclic voltammetry (CV) method was used for the optimization procedure and differential pulse voltammetry (DPV) was used for the reliable detection of folic acid from orange juice. The peak heights were measured at the potential given in Table 1¹⁷ and were plotted against the concentrations of standard solutions of folic acid. The unknown concentrations were calculated from the calibration graphs.

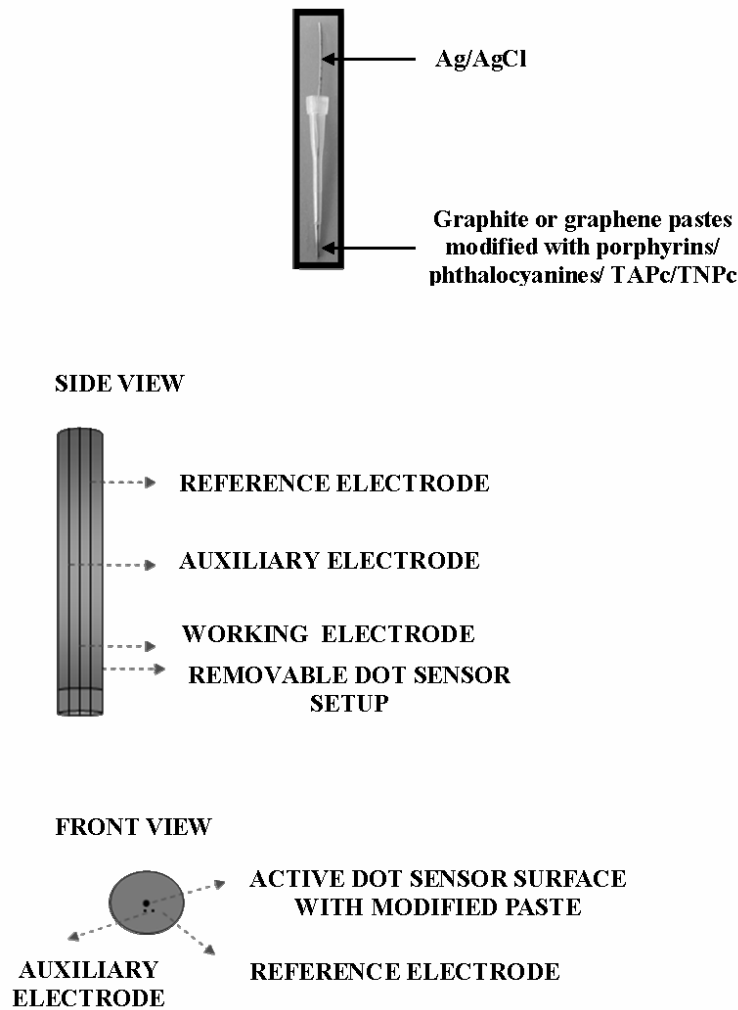


Fig. 1 – Design of amperometric dot microsensors.

Table 1

Response characteristics of the dot microsensors used for the determination of folic acid

Sensor based on	Equation of calibration*	Sensitivity (nA μmolL^{-1})	Limit of detection (mol L^{-1})	Limit of determination (mol L^{-1})	Linear conc. range (mol L^{-1})	E (mV)
Fe(III)P/G	$H = 3.14 + 0.27 \times C$ $r = 0.9997$	0.260 (± 0.009)	1.87×10^{-7}	1×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-3}$	676 \pm 25
TPP/G	$H = 5.69 + 0.20 \times C$ $r = 0.9986$	0.200 (± 0.001)	7.65×10^{-7}	1×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-3}$	676 \pm 25
Co(II)TPP/G	$H = 1.98 + 0.23 \times C$ $r = 0.9998$	0.230 (± 0.001)	1.22×10^{-7}	1×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-3}$	701 \pm 25
Fe(III)P/GR	$H = 3.92 + 0.24 \times C$ $r = 0.9996$	0.230 (± 0.005)	1.96×10^{-7}	1×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-3}$	676 \pm 25
TPP/GR	$H = 3.13 + 0.28 \times C$ $r = 0.9997$	0.270 (± 0.006)	1.40×10^{-7}	1×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-3}$	650 \pm 25
Co(II)TPP/GR	$H = 2.31 + 0.21 \times C$ $r = 0.9996$	0.200 (± 0.005)	2.20×10^{-7}	1×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-3}$	676 \pm 25
Fe(II)Pc/G	$H = 2.09 + 0.28 \times C$ $r = 0.9995$	0.270 (± 0.006)	2.57×10^{-7}	1×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-3}$	650 \pm 25
Fe(III)Pc/G	$H = 0.80 + 0.10 \times C$ $r = 0.9993$	0.100 (± 0.003)	3.92×10^{-7}	1×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-3}$	701 \pm 25

Table 1 (continued)

Fe(II)Pc/GR	$H = 2.64 + 0.22 \times C$ $r = 0.9996$	0.210 (± 0.009)	2.04×10^{-7}	1×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-3}$	676 \pm 25
Fe(III)Pc/GR	$H = 2.71 + 0.25 \times C$ $r = 0.9994$	0.240 (± 0.008)	3.35×10^{-7}	1×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-3}$	701 \pm 25
Co(II)Pc/GR	$H = 2.53 + 0.16 \times C$ $r = 0.9995$	0.160 (± 0.004)	2.82×10^{-7}	1×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-3}$	701 \pm 25
CoTAPc/G	$H = -2.34 + 0.78 \times C$ $r = 0.9975$	0.770 (± 0.007)	2.00×10^{-7}	1×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-4}$	625 \pm 25
ZnTAPc/G	$H = 1.03 + 0.22 \times C$ $r = 0.9996$	0.220 (± 0.004)	2.46×10^{-7}	1×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-3}$	650 \pm 00
NiTAPc/G	$H = 1.77 + 0.31 \times C$ $r = 0.9998$	0.310 (± 0.004)	1.22×10^{-7}	1×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-3}$	650 \pm 25
MnTAPc/G	$H = 2.06 + 0.24 \times C$ $r = 0.9995$	0.230 (± 0.007)	2.88×10^{-7}	1×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-3}$	650 \pm 25
CoTNPc/G	$H = 2.69 + 0.24 \times C$ $r = 0.9997$	0.240 (± 0.001)	1.44×10^{-7}	1×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-3}$	650 \pm 25
ZnTNPc/G	$H = 0.71 + 0.27 \times C$ $r = 0.9998$	0.260 (± 0.008)	1.14×10^{-7}	1×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-3}$	625 \pm 25
NiTNPc/G	$H = 1.05 + 0.23 \times C$ $r = 0.9995$	0.230 (± 0.003)	2.51×10^{-7}	1×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-3}$	676 \pm 25
MnTNPc/G	$H = 0.59 + 0.45 \times C$ $r = 0.9986$	0.450 (± 0.003)	1.16×10^{-7}	1×10^{-6}	$1 \times 10^{-6} - 1 \times 10^{-4}$	625 \pm 25

*H is the peak height (nA); C is the concentration of folic acid ($\mu\text{mol L}^{-1}$).

RESULTS AND DISCUSSION

1. Optimization of working conditions

Optimized working conditions were carried out for the different types of dot microsensors using 10^{-4} mol L⁻¹ solution of FA, different supporting electrolytes (0.1 mol L⁻¹ KCl, 0.1 mol L⁻¹ KNO₃ and 0.1 mol L⁻¹ NaCl) at different pHs (phosphate buffer with the pH between 2 and 8). CV was used to check the sensitivity of different sensors proposed in this article and also to observe the peak's shape. The shapes and heights of the peaks contribute in the selection of the optimum electrolyte and pH. The best sensitivities and shape of the peaks were obtained when pH = 7.0 and 0.1 mol L⁻¹ KCl solutions were used for the detection of folic acid.

2. Response characteristics of the dot microsensors

Nineteen amperometric dot microsensors were proposed to define the best microsensor for the detection of folic acid from orange juice. In Table 1¹⁷ the response characteristics of the amperometric dot microsensors are presented. Using the proposed dot microsensors one can

detect folic acid in a range of concentration from 10^{-6} to 10^{-3} mol L⁻¹ for all dot microsensors except for CoTAPc/G and MnTNPc/G which had the range of concentration from 10^{-6} to 10^{-4} mol L⁻¹ with sensitivities ranging from 0.100 nA $\mu\text{mol L}^{-1}$ to 0.770 nA $\mu\text{mol L}^{-1}$. The detection limits (DL) were calculated accordingly with the recommendation of Otto.²⁵ The lowest limit of detection was recorded for the ZnTNPc/G based sensor and the higher sensitivity was recorded for the CoTAPc/G based sensor.

3. Selectivity studies

The selectivity of the dot microsensors has been investigated using the mixed solutions method proposed by Wang²⁶ and it was tested for dopamine, epinephrine, norepinephrine, ascorbic acid and uric acid. The ratio between the concentrations of the analyte and the interfering was 1:10. The amperometric selectivity coefficients, K_{sel}^{amp} (Table 2),¹⁷ proved that dopamine, epinephrine, norepinephrine and uric acid interfere in the detection of FA when the ratio is in the favor of the interferent and ascorbic acid slightly interferes for the sensors based on Fe(III)P/G, Co(II)TPP/GR, Fe(III)Pc/GR, CoTAPc/G, ZnTAPc/G, NiTAPc/G, MnTAPc/G, CoTNPc/G, ZnTNPc/G, NiTNPc/G, and MnTNPc/G.

Table 2

Amperometric selectivity coefficients of the proposed dot microsensors

Sensor based on	K_{sel}^{amp}				
	DA	Epi	NE	AA	UA
Fe(III)P/G	9.06×10^{-1}	9.83×10^{-1}	6.39×10^{-1}	7.05×10^{-2}	4.70×10^{-1}
TPP/G	6.70×10^{-1}	1.08 x 10	6.38×10^{-1}	1.41×10^{-1}	6.21×10^{-1}
Co(II)TPP/G	3.85×10^{-1}	6.12×10^{-1}	3.71×10^{-1}	1.75×10^{-1}	5.13×10^{-1}
Fe(III)P/GR	4.96×10^{-1}	6.85×10^{-1}	4.19×10^{-1}	1.94×10^{-1}	7.75×10^{-1}
TPP/GR	4.14×10^{-1}	4.74×10^{-1}	3.45×10^{-1}	2.06×10^{-1}	6.82×10^{-1}
Co(II)TPP/GR	2.95×10^{-1}	4.94×10^{-1}	3.41×10^{-1}	7.39×10^{-2}	4.99×10^{-1}
Fe(II)Pc/G	3.27×10^{-1}	4.80×10^{-1}	2.75×10^{-1}	1.46×10^{-1}	5.89×10^{-1}
Fe(III)Pc/G	2.82×10^{-1}	3.81×10^{-1}	2.39×10^{-1}	1.00×10^{-1}	4.59×10^{-1}
Fe(II)Pc/GR	3.06×10^{-1}	3.75×10^{-1}	2.56×10^{-1}	1.03×10^{-1}	4.36×10^{-1}
Fe(III)Pc/GR	2.56×10^{-1}	3.56×10^{-1}	2.69×10^{-1}	4.93×10^{-2}	4.79×10^{-1}
Co(II)Pc/GR	3.73×10^{-1}	4.29×10^{-1}	6.69×10^{-1}	1.82×10^{-1}	1.11 x 10
CoTAPc/G	3.92×10^{-1}	3.24×10^{-1}	3.34×10^{-1}	8.92×10^{-2}	3.97×10^{-1}
ZnTAPc/G	4.83×10^{-1}	3.17×10^{-1}	2.32×10^{-1}	8.97×10^{-2}	3.32×10^{-1}
NiTAPc/G	4.14×10^{-1}	3.42×10^{-1}	2.74×10^{-1}	7.65×10^{-2}	3.14×10^{-1}
MnTAPc/G	3.75×10^{-1}	2.63×10^{-1}	2.48×10^{-1}	9.08×10^{-2}	3.11×10^{-1}
CoTNPc/G	3.47×10^{-1}	2.87×10^{-1}	2.72×10^{-1}	7.27×10^{-2}	4.62×10^{-1}
ZnTNPc/G	3.00×10^{-1}	2.63×10^{-1}	2.86×10^{-1}	7.18×10^{-2}	4.35×10^{-1}
NiTNPc/G	2.72×10^{-1}	2.42×10^{-1}	2.59×10^{-1}	6.84×10^{-2}	4.03×10^{-1}
MnTNPc/G	3.35×10^{-1}	2.98×10^{-1}	2.73×10^{-1}	6.09×10^{-2}	3.00×10^{-1}

Table 3

Recovery of folic acid from orange juice

Sensor based on	% Recovery* of FA
Fe(III)P/G	99.46 ± 1.49
TPP/G	99.00 ± 1.78
Co(II)TPP/G	99.09 ± 0.16
Fe(III)P/GR	98.70 ± 0.46
TPP/GR	99.40 ± 0.60
Co(II)TPP/GR	98.81 ± 0.66
Fe(II)Pc/G	98.72 ± 0.03
Fe(III)Pc/G	98.46 ± 1.92
Fe(II)Pc/GR	98.85 ± 1.44
Fe(III)Pc/GR	98.99 ± 0.99
Co(II)Pc/GR	98.45 ± 0.35
CoTAPc/G	99.39 ± 1.72
ZnTAPc/G	98.68 ± 0.89
NiTAPc/G	97.73 ± 1.03
MnTAPc/G	99.25 ± 0.24

Table 3 (continued)

CoTNPC/G	99.17 ± 0.82
ZnTNPC/G	99.26 ± 1.92
NiTNPC/G	98.74 ± 1.67
MnTNPC/G	96.60 ± 0.86

*All values are the average of five determinations.

4. Analytical applications

The optimum working conditions were used for the recovery test. The amperometric dot microsensors proved to be useful for the detection of folic acid from orange juice (Table 3), using differential pulse voltammetry. The added amount of folic acid was determined by calculating the difference between the amount of analyte in the spiked orange juice and in the orange juice samples before spiking.

Table 3 shows that FA can be detected from orange juice with an average value higher than 98.78% and a RSD value lower than 2.00%.

The results indicate that the sensors can be reliably used for the detection of folic acid from orange juice.

CONCLUSIONS

Nineteen amperometric dot microsensors were tested for their ability to detect folic acid from orange juice. The best dot microsensor for the detection of the folic acid from orange juice was the one based on graphite modified with porphyrin iron(III) [Fe(III)P/G].

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