Surface Analysis of Protective Films Formed by Poly(vinyl) Alcohol on Titanium in Physiological Serum

ADRIANA SAMIDE[*1]*, ADINA CIUCIU[1], CONSTANTIN LOGOFATU[2], MIRCEA PREDA[1]

[1] University of Craiova, Faculty of Chemistry, 107i Calea Bucuresti, 200515, Craiova, Romania
[2] National Institute of Materials Physics, 077125 Magurele-Bucharest, Romania

The implants surfaces investigated in the present study were modified with the films of poly (vinyl) alcohol (PVA) which were formed in physiological serum (0.9% NaCl). Surfaces evaluation included electrochemical measurements such as linear potentiometry (LP) and electrochemical impedance spectroscopy (EIS). These suggest that PVA acts by adsorption at site on the metal surface and formed a compact, adherent and uniform layer. The composition of layer was estimated using Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM/ EDX) and X-ray Photoelectron Spectroscopy (XPS) techniques, which confirm the adsorption of PVA on the surfaces, through –OH groups, with a specific affinity to the titanium sub-strate.

Keywords: titanium electrode; electrochemical measurements; poly (vinyl) alcohol; SEM/ EDX; XPS

The natural selection of titanium for implantation is determined by a combination of most favorable characteristics including immunity to corrosion, biocompatibility, strength, low modulus and density and the capacity for joining with bone and other tissues – osseointegration [1-6]. When implants are placed in bone, the bone grows around the implant in a process called osseointegration. Titanium implants come with many types of surfaces, including acid etched, plasma sprayed, acid etched and grit blasted, and hydroxyapatite coated [6,7]. Hydroxyapatite was coated on a titanium substrate over a ZrO layer by the electrolytic deposition and for the obtained biopolymeric films devoted to biomedical applications [8]. There are some alternatives to modulate the body response after implant placement. Modifying the implant surface topography has been a successful path among the scientific community. Two main types of treatment are presently available: the addition of material or coating and surface modification [3]. Porous PVA and its composites may be applied to tissue engineering as a long-term or permanent scaffold due to their good biocompatibility, elasticity and hydrophilicity [9]. It was noticed that by increasing concentration of PVA the biocompatibility increased [10]. Many compounds included in PVA, e.g. glucose, aim to improve its medical properties. There have been used aqueous concentrate solutions of PVA/starch aditivated with glycerin and urea to obtain biodegradable films [11,12]. Furthermore, it was found that PVA is very stable in the body because no degradation product was detected in the urine and feces [13]. By surface modification of the implant made of titanium, we followed two objectives: to increase the corrosion resistance, and to prepare the surface such as to be proper for stabilizing tissue-implant interface.

This study discusses the results of characterization techniques like linear potentiometry (LP), impedance spectroscopy (EIS), SEM/EDX and XPS analyses for behaviour of unmodified and modified surfaces of titanium with PVA in physiological serum (PS) solutions simulating the tissue fluid conditions.

Experimental part
Electrochemical measurements

For electrochemical measurements a standard cell was used with a plate working electrode (surface 1 cm^2) made of titanium, a platinum auxiliary electrode (surface 1 cm^2) and an Ag/AgCl reference electrode. The titanium electrode was polished with metalographic paper, washed in distilled water, degreased in acetone and dried in warm air. For each determination the samples were introduced for 30 min, at room temperature in following solutions: physiological serum (PS); PS/1% PVA; PS/ 3% PVA (molecular weight 49000 g·mol^{-1}). All reagents were obtained from Fluka. A potentiostat VoltaLab 40 connected to a computer with VoltaMaster 4 software was used in the measurements.

Surface characterization

SEM/EDX analyses were run on a Jeol JSM 35-CF instrument, resolution 60 Angstroms, magnification range: 10 X - 180 000 X, SE detector and Energy Dispersive Spectrometer Edax 9100/40 Si(Li) detector with Be window and Thompson Scientific WinEDS 3.0 microanalysis hardware and software. SEM image and EDS spectrum of detected element (titanium) in samples are presented in figure1.

The XPS spectra were recorded on a VG ESCA 3 Mk II-EUROSCAN spectrometer with a Mg Kα X-ray source (1253.6 eV photons energy) operated at 300 W (accelerating voltage 12.5 kV, emission current 24 mA).

The pressure in the analysis chamber has not exceeded the value of 5 x 10^{-9} torr during the whole period of spectra acquisition. In order to perform the surface charge compensation, a FG40 flood gun device (Specs Gmbh – Germany), with an 0.2 mA electronic current at 2 eV energy was used. The samples have been measured in an "as received" condition with no other surface cleanning treatement (chemical etching or Ar$^+$ ion beam bombardment) [14,15]. Extended spectra were recorded with a window of 1250 eV and 100 eV pass energy. High

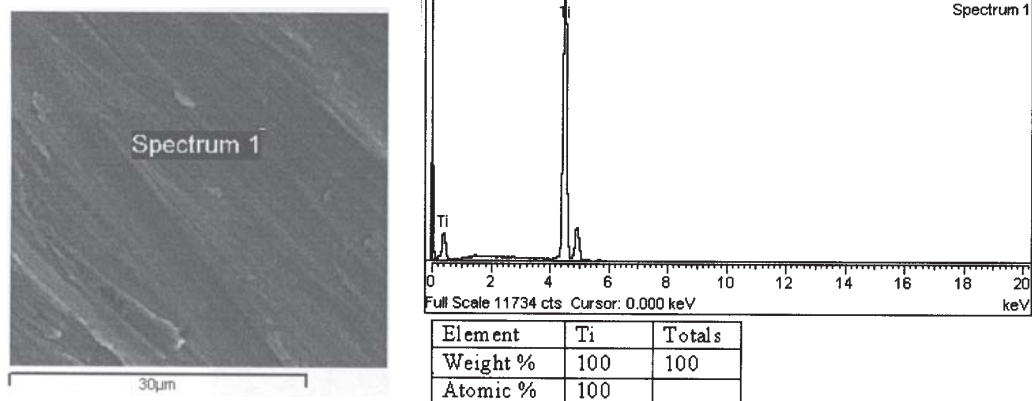* email: samide_adriana@yahoo.com; Tel: +040251597048

Fig.1. SEM/EDX analysis of titanium electrode - reference sample

Element	Ti	Totals
Weight %	100	100
Atomic %	100	

resolution spectra for C1s and O1s lines were recorded with a window of 15 eV and 20 eV pass energy, corresponding to an experimental resolution of 1.2 eV. All spectra have been deconvoluted with SDP 2.3 XPS-International software, using Gaussian profile lines for peaks fitting.

Results and discussion
Electrochemical measurements
Linear potentiometry

Potentiodinamic polarizations were recorded with a titanium electrode (surface area was 1 cm^2) immersed in physiological serum (PS) and PS containing different concentrations of PVA: 1%; 3 %. Figure 2 shows the polarization curves, in the potential range from -0.4 V to
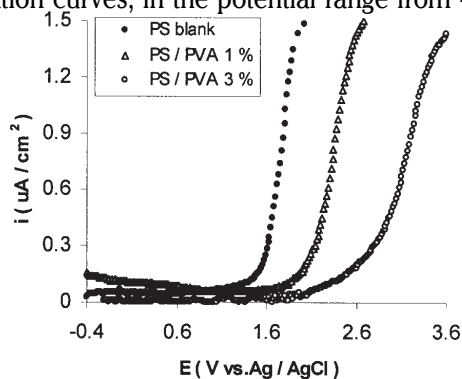

Fig.2. Polarization curves of titanium corroded in PS blank and in presence of various concentrations of PVA

3.6 V vs. Ag/AgCl reference electrode, at a scan rate of 10 mV/s.

The study of the titanium material response without and with various surface treatments given by its polarization in physiological serum (PS) showed that the addition of PVA reduces anodic dissolution. The results obtained through polarization curves indicate that critical potentials in pitting (E$_{cp}$) are shifted to higher values with the increase in PVA concentrations (fig. 2). This suggests that PVA acts by adsorption at site on the metal surface and a compact, adherent and uniform layer was formed. The polar effect of the attached groups –OH is the determining factor for adsorption process. We consider that PVA forms self-

assembled layers grown from solution and the significant feature is the adsorption of the –OH groups with a specific affinity to the sub-strate.

Electrochemical impedance measurements

The impedance measurements of a titanium electrode in PS solution and in PS containing PVA in different concentrations vs. Ag/AgCl reference electrode, were carried out at the open circuit potential (E_{ocp}) in the frequency range from 10^5 to 10^{-1} Hz, with a value of 10 mV for the amplitude. Figure 3 shows Nyquist (3a) and Bode (3b) plots for titanium in physiological serum without and with PVA. It can be seen that the impedance response of titanium in PS solution shows a change after PVA addition. This indicates that titanium impedance increases with the inhibitor concentration and consequently the inhibition efficiency increases. For the description of EIS measurements an equivalent circuit is suggested in figure 4, where (R_s) is the solution resistance of the bulk electrolyte and (C_{coat}) is the capacitance of the coating. (R_{coat}) is the resistance of the coating. Coatings often have very small pores which contain electrolyte, providing a conduction path through the coating. (C_{dl}) represents the double layer capacitance of the electrolyte at the metal surface. (R_{corr}) is the corrosion resistance of the metal. The impedance parameters derived from EIS measurements and respective fitting results using ZView software are given in table 1 and figure 4, respectively.

The fitting results show that C_{coat} and C_{dl} decrease, R_{coat} and R_{corr} increase suggesting that the amount of absorbed inhibitor molecules increases. The change in R_{coat}, R_{corr}, C_{coat} and C_{dl} values was caused by the gradual replacement of water molecules by the PVA molecules adsorption on the metal surface. The R_{corr} was used to calculate the inhibition efficiency from equation 1.

$$IE = \left(1 - \frac{R^0_{corr}}{R_{corr}}\right) \times 100 \qquad (1)$$

where:
R^0_{corr} is corrosion resistance in absence of PVA ;
R_{corr} - the corrosion resistance in presence of PVA .
The inhibition efficiency values increase with PVA concentration reaching an approximate value of 68.2 % at 3 % PVA (table 1).

C-PVA (%)	R$_s$ (Ω.cm^2)	C$_{coat}$ (μF/cm^2)	R$_{coat}$ (Ω.cm^2)	C$_{dl}$ (μF/cm^2)	R$_{corr}$ (Ω.cm^2)	IE (%)
0	2.897	470	218.2	128	28457	0
1	2.627	416	342.5	96	48759	41.6
3	1.498	358	689.3	78	89432	68.2

Table 1
ELECTROCHEMICAL PARAMETERS OBTAINED FROM IMPEDANCE MEASUREMENTS FOR TITANIUM IN PS SOLUTION IN ABSENCE AND IN PRESENCE OF PVA
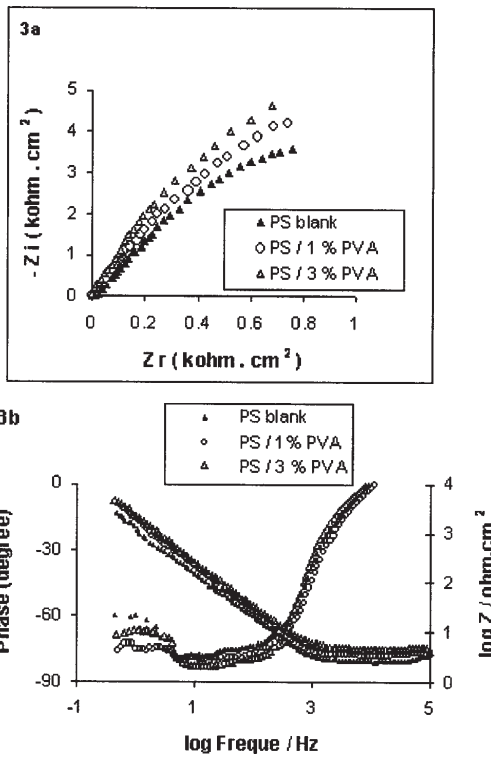
Fig.3. Electrochemical impedance measurements of titanium electrode corroded in PS in absence and in presence of PVA in different concentrations. 3a – Nyquist diagram; 3b – Bode diagram
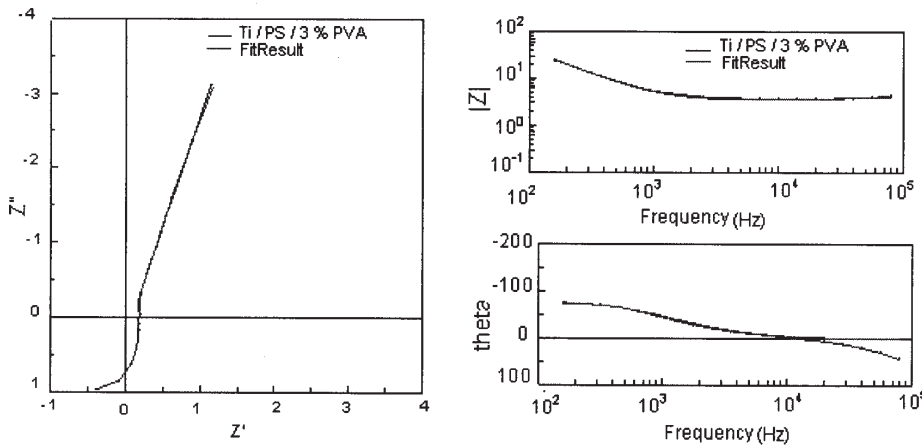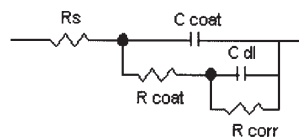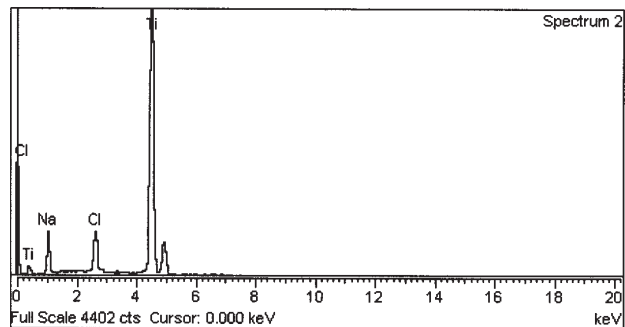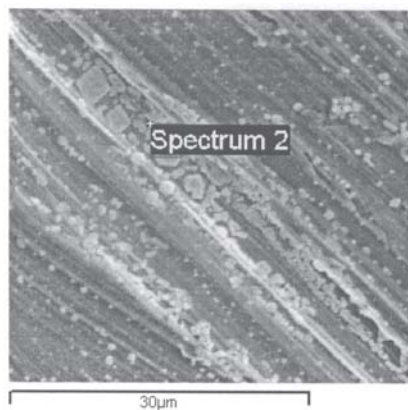

Surface characterization
SEM/EDX surface analysis

Figure 5 shows the SEM/ED X surface analysis of titanium corroded in physiological serum. It can be observed that the film includes significant amount of Na and Cl. In this regard, when the titanium is immersed in physiological serum solution a non-uniform and porous layer is formed in summary, the surface layer on titanium is not stable and the composition changes by incorporation of ions and molecules.

Surface modification techniques of titanium using PVA can be divided in two categories: thin film formation and surface-modified layer composition according to PVA concentrations. Thin film formation is used to improve the corrosion resistance and titanium biocompatibility. The increase in PVA concentration may produce a surface modified layer composition (figs. 6 and 7).

PVA film as a whole is apparently stable, but a partial destruction is taking place and, as a consequence the passive layer composition would vary with time depending on the experimental conditions. Figure 6 shows SEM/EDX analysis of modified titanium electrode in PS / 1% PVA solution.

XPS- surface analysis

The composition and stability of surface layer on titanium after corrosion in PS / 3% PVA solution were determined using XPS analysis (fig. 7). The composition of the layer is presented in figure 7. This confirms that PVA forms a stable and self-assembled layer grown from solution, which improves the surface of implant and the significant feature is the adsorption of the –OH groups, with a specific affinity to the titanium substrate.

Fig.4. Fit results for titanium in PS containing 3 % PVA and equivalent circuit model for the studied inhibitor:
■% measured: — simulated

Element	Na	Cl	Ti	Totals
Weight %	10.89	6.63	82.48	100
Atomic %	19.89	7.85	72.26	

Fig.5. SEM/EDX analysis of unmodified titanium electrode corroded in PS solution

Element	C	O	Na	Cl	Ti	Totals
Weight %	54.64	23.43	1.39	1.22	19.32	100
Atomic %	48.15	39.47	2.87	0.93	8.58	

Fig.6. SEM/EDX analysis of titanium electrode corroded in PS / 1% PVA solution

Sample Description: P4 (Ti / PS + 3 % PVA)
C1s (285eV)
Counts

Sample Description: P4 (Ti / PS + 3 % PVA)
O1s
Counts

Binding Energy, eV

--- A   285.01 eV 1.60 eV 19472.8 cts
— B   286.49 eV 1.46 eV 6636.62 cts
— C   289.12 eV 1.67 eV 1720.7 cts
··· D   287.74 eV 0.98 eV 561.312 cts
Baseline: 291.72 to 281.74 eV
Chi square: 2.59199

--- A   532.84 eV 2.01 eV 14335.9 cts
— B   534.64 eV 1.51 eV 836.748 cts
— C   530.58 eV 1.16 eV 435.679 cts
Baseline: 537.76 to 528.56 eV
Chi square: 4.22548

Sample/Element	C	O	Ti	Na	Cl
Ti/PS/PVA 3%	77.77	20.7	0.4	0.8	0.5

Sample/spectral line	BE (eV)	Bond	Atomic (%)
Ti/PS/PVA 3% / C1s	285	C-C	68.7
	286.5	C in PVA	23.3
	287.7	C=O	6.1
	289.2	O-C=O	2.0
Ti/PS/PVA 3% / O1s	530.6	O in oxides	2.8
	532.8	O in PVA	91.8
	534.6	O-C,O=C-O,OH$_2$	5.4

Fig.7. XPS spectra of titanium electrode
corroded in PS / 3% PVA solution

Conclusions

The results obtained through polarization curves indicate that critical potentials in pitting are shifted to higher values with the increase in PVA concentrations. This suggests that PVA acts by adsorption at site on the metal surface and a compact, adherent and uniform layer was formed. According to the data obtained from electrochemical impedance measurements C_{coat} and C_{dl} decrease, R_{coat} and R_{corr} increase suggesting that the amount of absorbed inhibitor molecules increases. The inhibition efficiency values increase with PVA concentration reaching an approximate value of 68.2 at 3 % PVA.

SEM/EDX and XPS techniques confirm that PVA forms a self-assembled layer grown from solution and the significant feature is the adsorption of the –OH groups, with a specific affinity to the titanium sub-strate.

References

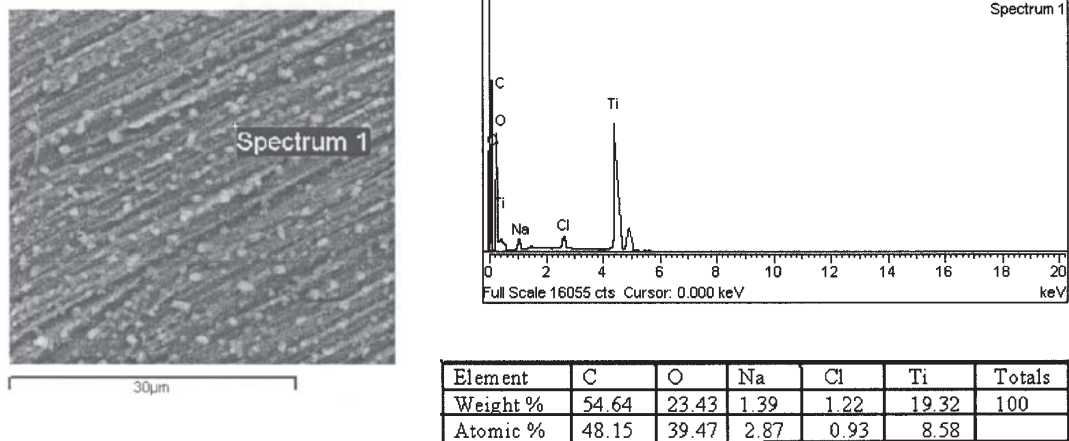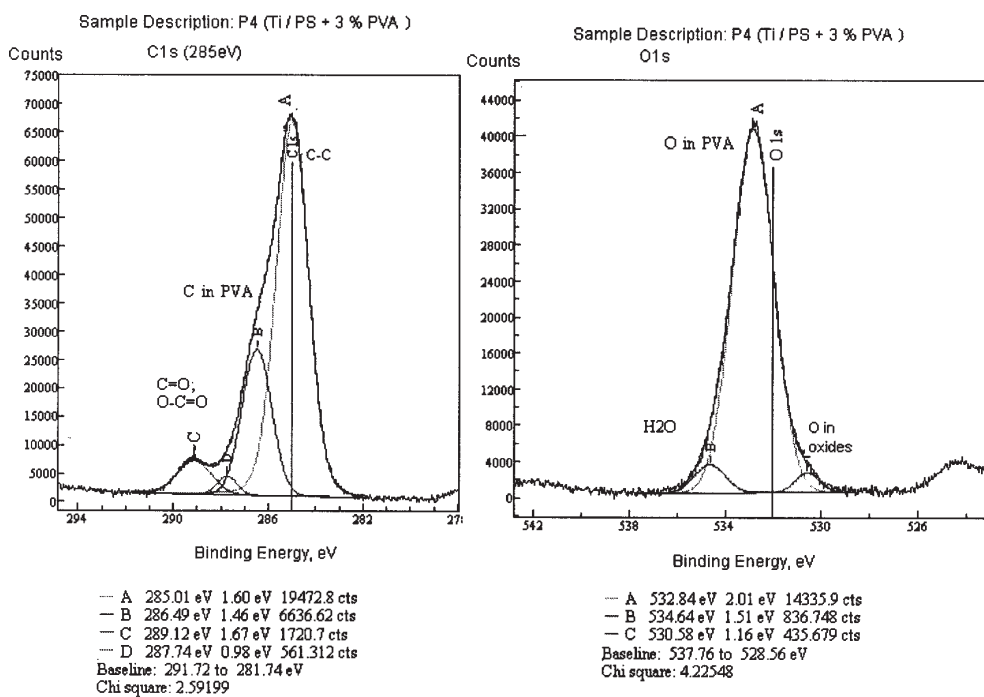1. SUL, Y.T., BYON, E., WENNERBERG, A., Int J Oral Maxillofac Implants, **23**, 2008, p.631.
2. SUL, Y.T., BYON, E., ALBREKTSSON T., **26**, 2005, p.6720.
3. De MAEZTU, M.A., ALAVAI, J.I., GAY-ESCODA, C., Clin Oral Implants Res.**14**, 2003, p.57.
4. MEIRELLES, L., CURRIE, F., JACOBSSON, M., ALBREKTSSON, T., Wennerberg A. J Oral Maxillofac Implants,**23**, 2008, p.641.
5. NASATZKY, E., GULTCHIN, J., SCHWARTZ, Z., Refuat Hapeh Vehashinayim, **20**, 2003, p.8.
6. BUSER, D., NYDEGGER, T., OXLAND, T., COCHRAN, D.L., SCHENK, R.K., HIRT, H.P., SNETIVY, D., NOLTE, L.P.**,** J Biomed Mater Res., **45**, 1999, p.75.
7. HSU, H.C., WU, S.C., YANG,J. Mater Sci. Mater Med., **20**, 2009, p.615
8. POPESCU, R., MOREGA, A., IORDACHESCU, D., DEMETRESCU, I., Mat.Plast.,**46**, no.2,2009, p.140
9. HASSAN, C.M., PEPPAS, N.A., Adv. Polym. Sci., **153**, 2000, p.37
10. BAJPA, A.K., SAINI, R., Polym. Int., **54**, 2005, p.1233
11. DUMITRASCU, I., DUMITRASCU, L., AFLORI, M., DROBOTA, M., STOICA, I., DOROHOI, D. O., Mat.Plast., **46**, no.2, 2009, p. 185
12. TUDORACHI, N., Mat.Plast., **44**, no.3, 2007, p. 208
13. KANEO,Y., HASHIHAMA, S., KAKINOKI, A., TANAKA, T., NAKANO, T., IKEDA, Y., Drug Metabolism and Pharmacokinetics, **6**, 2005, p.435
14. NEGRILA, C.C., LOGOFATU, C., GHITA, R.V., COTARLAN, C., UNGUREANU, F., MANEA, A.S., LAZARESCU, M.F., J. Crystal Growth, **310**, 2008, p.1576
15. GHITA, R.V., LOGOFATU, C.,C. , NEGRILA, C.C., COTARLAN, C., GHITA, P., MANEA, A.S., LAZARESCU, M.F., Status Solid A, **204,** 2007, p.1025