

Amperometric Determination of Hydrogen Peroxide at a Silver Electrode Fabricated from a Recycled Compact Disc

Chris Maynard, Kevin C. Honeychurch *

Centre for Research in Biosciences, Faculty of Health & Life Sciences, University of the West of England, Frenchay Campus, Bristol, UK

Abstract This present study investigates the utilisation of Ag electrodes fabricated from recycled recordable compact discs (CD-R) for the amperometric determination of hydrogen peroxide. The analytical curve was linear up to at least 30 mM hydrogen peroxide with a sensitivity of 21.89 $\mu\text{A}/\text{mM}$ over this range. A corresponding detection limit of 17.7 μM , based on a signal-to-noise ratio of three was recorded. The developed electrode represents a simple, inexpensive, reliable method for the determination of hydrogen peroxide, avoiding extended and complex multi-step fabrication as it is readily fabricated from recycled materials. It has a number of potential applications, including environmental, industrial, physiological and home security, especially where single use and disposability could be beneficial.

Keywords Compact Disc, Silver electrode, Voltammetry, Amperometry

1. Introduction

Hydrogen peroxide is widely used industrially for the bleaching of products such as paper and cloth, in chemical synthesis, metallurgy, electronics, detergents, waste water treatment [1], as a disinfectant [2] and as an oxidant source in fuel cells [3]. A number of other applications, such as fuel for rockets [4] and similar devices [5] are commonly reported. It also is a by-product of several enzyme-catalysed reactions and is used in food, environmental, pharmaceutical, clinical and industrial analyses. A great deal of interest is also focused on its detection as it is commonly employed in range of oxidase based biosensors as an indirect method to determine analytes such as blood glucose levels and lactate [6]. Recently, the detection of hydrogen peroxide has become important in other areas, such as disease diagnosis [7] the detection of peroxide based explosives [8].

Electrochemistry offers an attractive approach for the determination of hydrogen peroxide. The decomposition and reduction of hydrogen peroxide are thermodynamically favourable, but are however, kinetically unfavourable and tend to require a catalyst or a large electrochemical over-potential. Biological catalysts such as peroxidase [9] and catalase [10] enzymes have been shown to allow for the reduction of hydrogen peroxide at lower over-potentials.

However, these have a number of drawbacks as they can be difficult and expensive to isolate and purify and can be unstable. A number of different non-biological catalysts have been investigated for the reduction of hydrogen peroxide, such as Prussian blue [11], cobalt phthalocyanine [12], metallic silver [13] and platinum [14]. However, precious metals, such as Ag are particularly expensive and can become easily poisoned. A number of these more recent applications are summarised in table 1.

Previously, we have shown that silver electrodes fabricated from digital versatile discs (DVDs) can be employed for the anodic stripping voltammetric determination of Pb [15] and the cyclic voltammetric determination of hydrogen peroxide in water [16]. This was shown to be a simple, economic and green method for the fabrication of silver working electrodes. In this present study we investigate the possibility of utilising these same electrodes for the amperometry determination of hydrogen peroxide. Amperometry offers a number of advantages, such as economics as it can be undertaken on relatively simple equipment, as only a fixed potential is applied and the current is then monitored.

In the present study we have investigated a previously unpublished method for the fabrication of silver electrodes from compact discs. Initial studies are undertaken on the cyclic voltammetric behaviour of hydrogen peroxide at these silver electrodes. The effect of both pH and scan rate are investigated. Hydrodynamic voltammetric studies were then undertaken to identify the conditions necessary for the amperometric determination of hydrogen peroxide.

* Corresponding author:

kevin.honeychurch@uwe.ac.uk (Kevin C. Honeychurch)

Published online at <http://journal.sapub.org/aac>

Copyright © 2015 Scientific & Academic Publishing. All Rights Reserved

2. Materials and Methods

2.1. Apparatus

Cyclic voltammetry and amperometry in stirred solution were performed with a μ Autolab potentiostat interfaced to a PC for data acquisition via the General Purpose Electrochemical System Software Package (GPES) version 4.3 (Autolab, Windsor Scientific Limited, Slough Berkshire UK). The voltammetric cell contained a graphite rod counter electrode, a saturated calomel electrode (SCE) (Russell, Fife, UK) and a silver electrode fabricated as described in section 2.3 as the working electrode. The electrode was then connected to the potentiostat using a crocodile clip attached to coaxial cable inserted into the appropriate sockets. The cell used for the voltammetric measurements was obtained from Metrohm (Switzerland); a small magnetic stirrer bar was placed in the bottom of the cell for stirring during amperometric investigations. This was rotated at a fixed constant rate by a rotary magnetic stirrer (Hanna Instruments).

2.2. Chemical and Reagents

All chemicals were supplied from Fisher (Loughborough, UK), unless stated otherwise. A 14.7 mM hydrogen peroxide stock solution was prepared by dissolving the appropriate volume in deionised water. Working standards, for optimisation of studies, were then prepared by dilution of the primary stock solution with deionised water. Deionised water was obtained from a Purite RO200–Stillplus HP

System, (Purite Oxon, UK). Solutions of disodium, trisodium, sodium o-phosphate and o-phosphoric acid were made at a concentration of 0.2 M by dissolving the appropriate mass in deionised water. These were then titrated together, to give the desired pH. An appropriate volume was then added directly to the voltammetric cell and diluted with sufficient deionised water to give an overall phosphate concentration of 0.1 M.

2.3. Working Electrode Fabrication

The layer of silver required for the working electrode was obtained from a Verbatim recordable compact disc. The fabrication process is shown in Figure 1. The silver layer was removed by the application of sticky-backed plastic to top layer of disc. The silver layer was then cut with scissors to an appropriate size and the surface area of the electrode was defined using a plastic hole-reinforcer. This was then affixed to a piece of polycarbonate (base of compact disc) of the same size using electrical insulation tape. The remainder of the electrode was enclosed in electrical insulation tape, leaving an exposed pad at the opposite end for contact to be made to the potentiostat.

Initial experiments utilised silver working electrodes with the area of the working electrode to be in contact with solution defined using electrical tape (RS Components) with a disc of approximately 5 mm diameter removed using a hole-punch. This aspect of fabrication was later improved by utilising plastic hole-reinforcers of 5 mm diameter.

Table 1. Recent applications of silver working electrodes for the determination of hydrogen peroxide

Electrode	Technique	Linear range	Detection limit, μ M	Sample	Reference
Ink jet printed Prussian blue nanoparticles	Amperometry	0.001 – 4.5 mM	0.2	--	[11]
Dendritic Ag nanostructures electrochemically deposited at a glassy carbon electrode.	Amperometry	4 μ M to 36 μ M	0.9	Laboratory waste water.	[17]
Ag nanoparticle-decorated graphene on indium-tin-oxide electrode.	Amperometry	0.1 mM to 100 mM	5	-	[18]
Ag nanoparticle-modified glassy carbon electrode.	Cyclic voltammetry	5 to 40 μ M	2	-	[19]
Electrochemically pre-treated Ag electrode manufactured from a compact disc.	Amperometry	10.0 μ M to 22.5 mM	6	-	[20]
Electrochemically pre-treated Ag electrode manufactured from a DVD.	Amperometry	0.588 μ M to 67.3 μ M	0.2	Peroxide based disinfectant.	[21]
Dodecyl benzenesulphonic acid and KCl modified Ag screen-printed electrodes.	Amperometry	1.25 μ M to 225 μ M	5.8	--	[13]
Ag nanoparticles/multiwalled carbon nanotube-modified glassy carbon electrode.	Amperometry	0.1 mM to 10 mM	2	-	[22]
Ag nanoparticle coated glassy carbon electrode.	Amperometry	Up to 75 μ M	1.3	-	[23]
Indium-tin-oxide electrode modified with Ag nanoparticles stabilized by amine grafted mesoporous SBA-15.	Amperometry	0.3 mM to 2.5 mM	300	-	[24]
Silver nanowire (50 nm) array sensor.	Amperometry	0.1 mM to 3.1 mM	29	-	[25]
Unmodified Ag electrode manufactured from a DVD-RW.	Cyclic voltammetry	0.087 mM to 3.41 mM	78.4	Artificial swimming pool water.	[16]

2.4. Cyclic Voltammetry

Cyclic voltammograms were initially recorded in plain solutions 0.1 M of phosphate buffer, and then in the same solution containing 2 mM of hydrogen peroxide. An initial and final potential of 0.0 V and a switching potential of -1.0 V. The effect of scan rate was investigated over the range 20 to 200 mV/s.

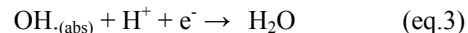
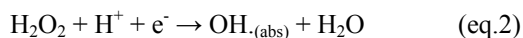
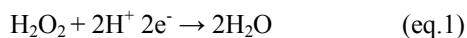
2.5. Optimisation of the Amperometric Potential

In order to deduce the optimum applied potential for calibration studies, amperometric measurements were made at various potentials in a solution containing 2.0 mM hydrogen peroxide 120 s after the application of each potential. This was achieved by transferring a 10 ml aliquot of hydrogen peroxide solution to the cell, stepping the potential from -0.2 V to -1.0 V in stepping in 100 mV steps. The resulting data was used to plot a voltammogram from which we could identify the optimum potential to be used in further amperometric studies.

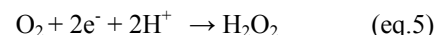
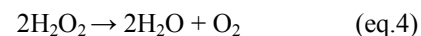
3. Results and Discussion

3.1. Cyclic Voltammetry

Previously [16], we have shown that similar cyclic voltammetric behaviour can be obtained at our Ag CD-R electrodes to that reported at conventional more expensive Ag electrodes. Figure 2 shows a typical cyclic voltammograms obtained in the presence and absence of 2 mM hydrogen peroxide, using a supporting electrolyte of 0.1 M pH 7.0 phosphate buffer. The voltammogram was predominated by reduction peak, with an E_p of -0.70 V, with a smaller more positive peak at -0.20 V. Consequently, we believe that these reduction peak results from the same $2e^-$, $2H^+$ reduction processes (eq. (1) and (2)).



This adsorbed species then undergoes a further one proton, one electron reduction (eq.3) resulting in the two waves. Alternatively, the first wave could result from the reduction of oxygen formed from the decomposition of hydrogen peroxide catalysed by the Ag (eq.4-5). The peak seen at -0.35 V results from reduction of the electrode surface and is also recorded in the absence of hydrogen peroxide.



The relationship of pH with the peak potential (E_p) of this peak was investigated over the pH range 2.0 to 10.5. A near theoretical relationship with E_p and pH was obtained between pH 4.0 and pH 10.5.

3.2. Hydrodynamic Voltammetry

Figure 3 shows the hydrodynamic voltammogram obtained in the absence and presence of 2 mM hydrogen peroxide at the Ag CD-R electrode. The background current observed in the absence of hydrogen peroxide was found to increase with increasing negative potential until a plateau was recorded at -0.5 V. In the presence of 2 mM hydrogen peroxide, the reduction currents were found to be greater than the background over the entire potential range studied and plateaued at potentials more negative than -0.6 V. As this operating potential showed a good signal to noise ratio with a short settling time, an applied potential of -0.6 V was selected for further studies.

3.3. Calibration Study

Figure 3 shows the typical amperometric response obtained in stirred solution for the addition of replicate volumes of a standard hydrogen peroxide solution. The calibration plot (Figure 4) was linear up to 30 mM hydrogen peroxide with a sensitivity of 21.89 $\mu A/mM$ over this range. A corresponding detection limit of 17.7 μM based on a signal-to-noise ratio of three was recorded.

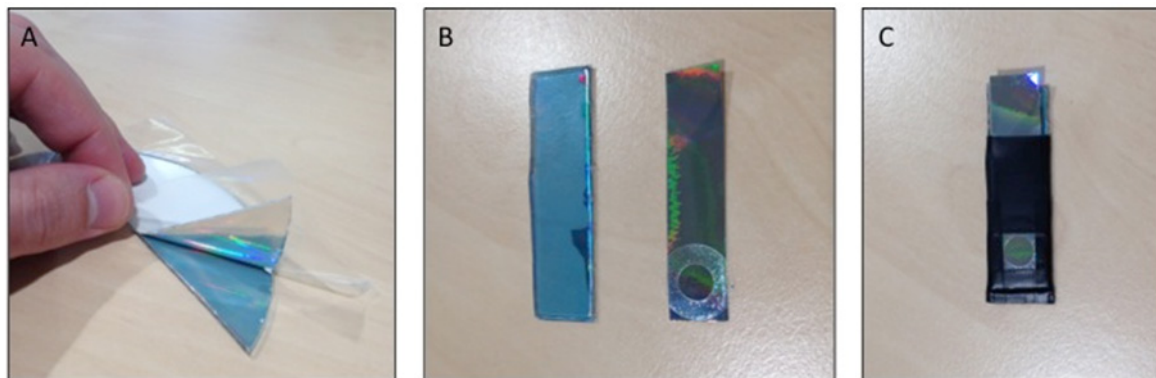


Figure 1. Silver working electrode fabrication. (A) Removal of the silver layer was facilitated by sticky-backed plastic. (B) The silver layer was then cut to an appropriate size and the surface area of the electrode to be in contact with solution was defined using a plastic hole-reinforcer. This was then affixed to a piece of polycarbonate of the same size using electrical insulation tape. (C) The remainder of the electrode was enclosed in electrical insulation tape and trimmed to yield the final product shown

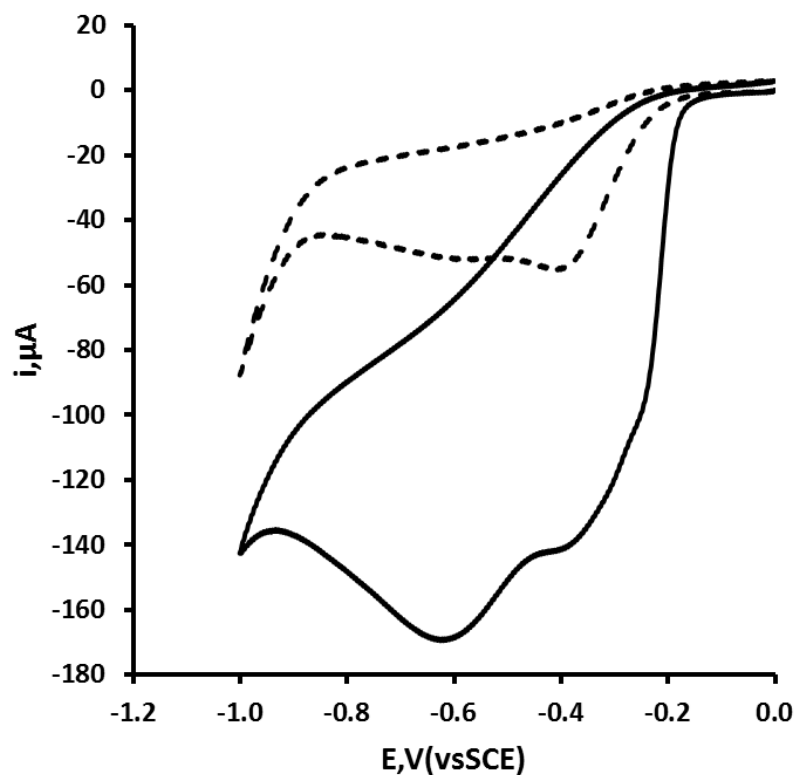


Figure 2. Cyclic voltammetric behaviour of hydrogen peroxide at Ag CD-W electrode in the absence (dashed line) and in the presence of 2.0 mM hydrogen peroxide (solid line) in 0.1 M pH 7 phosphate buffer. Voltammetric conditions: start and end potential 0.0 V; switching potential -1.0 V; scan rate 50 mV/s

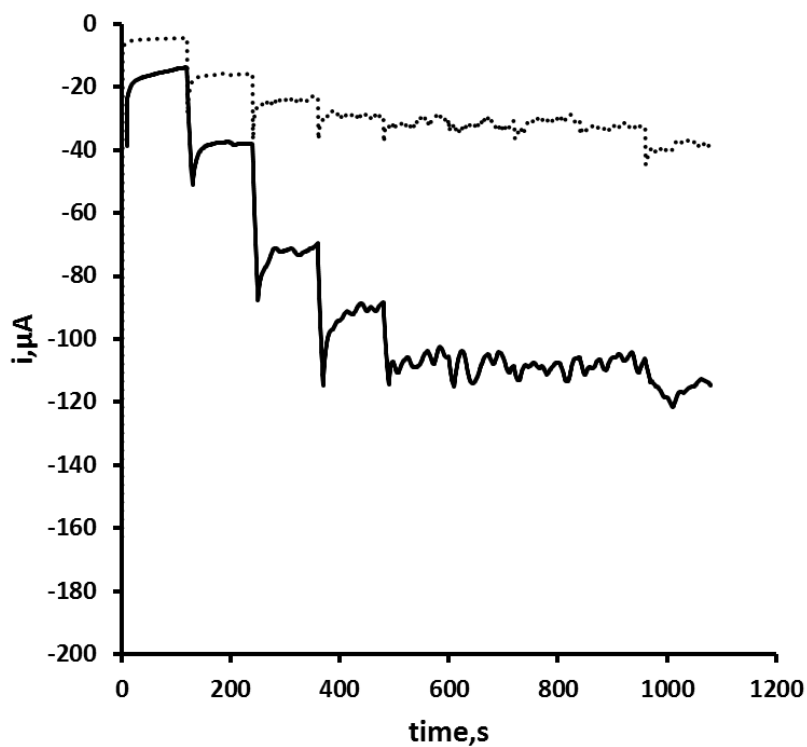


Figure 3. Hydrodynamic voltammograms undertaken in the absence (dotted line) and in the presence of 2.0 mM hydrogen peroxide (solid line) in 0.1 M pH 7 phosphate buffer. Starting potential -0.2 V; stepped in 0.1 V intervals to -1.0 V

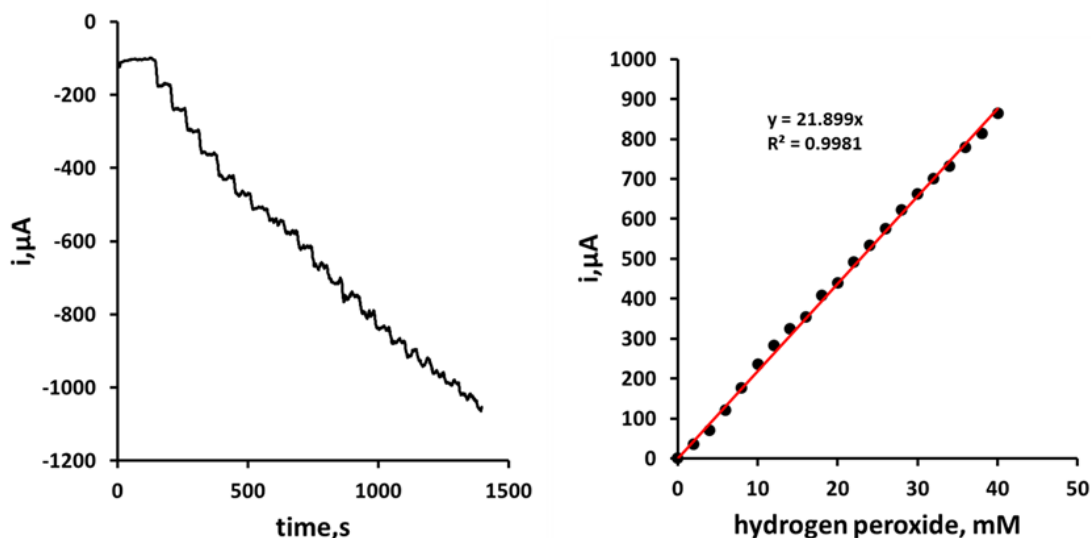


Figure 4. Amperogram obtained in stirred solution for additions of hydrogen peroxide equivalent to 2.5 mM

4. Conclusions

Amperometric quantification of hydrogen peroxide has been shown to be possible at Ag electrode manufactured from an unmodified CD-R. Amperometry in stirred solution was performed with our Ag CD-R at different concentrations of hydrogen peroxide. Steady state behaviour was observed for each concentration investigated over the range 2 to 30 mM. The steady state current was found to be linearly related with hydrogen peroxide concentration over the range 2 mM - 30 mM in 0.1 M phosphate buffer pH 7 at an applied potential of -0.6 V (vs. SCE). A limit of detection of 17.7 μ M (based on a signal-to-noise ratio of three) was recorded. These performance characteristics compare well with a number of previously reported methods (table 1). Our detection limit was over four times lower than our previous reported application of these electrodes utilising cyclic voltammetry [16]. It is also better than that obtained by some more complex approaches; such as Ag nanoparticle modified indium-tin-oxide electrodes [24] or that obtained at Ag nanowire array sensors [25]. The developed electrode represents a simple, inexpensive and reliable method for the determination of hydrogen peroxide, avoiding long and complicated multi-step fabrication procedures which are commonly reported (table 1) for these devices. It has a number of potential applications, such as for environmental, industrial, physiological and homeland security analysis, especially where single use and disposability are beneficial.

ACKNOWLEDGEMENTS

We would like to thank the University of the West of England for funding.

REFERENCES

- [1] J.M. Campos-Martin, G. Blanco-Brieva, J.L.G. Fierro, *Angew. Chem. Int. Ed.* 2006, 45, 6962-6984.
- [2] M.E. Falagas, P.C. Thomaidis, I.K. Kotsantis, K. Sgouros, G. Samonis, D.E. Karageorgopoulos, *J. Hosp. Infect.* 2011, 78, 171-177.
- [3] P.S. Khadke, P. Sethuraman, P. Kandasamy, S. Parthasarathi, A.K. Shukla, *Energies*, 2009, 2, 190-201.
- [4] A. Ingemar Skoog, *Acta Astronaut.* 2013, 85, 155-168.
- [5] Ø. Hasvold, K. Havard Johansen, O. Mollestad, S. Forseth, N. Størkersen, *J. Power Sources*, 1999, 80, 254-260.
- [6] K.C. Honeychurch, *Thick-film Biosensors*, in *Printed Films: Materials Science and Applications*, ed. M. Prudenziati and J. Hormadaly, Woodhead Publishing Ltd, Oxford, 2012, Chapter 13.
- [7] R. Stolarek, P. Bialasiewicz, M. Krol, D. Nowak, *Clin. Chim. Acta*, 2010, 411, 1849-1861.
- [8] R.M. Burks, D.S. Hage, *Anal. Bioanal. Chem.* 2009, 395, 301-313.
- [9] P. George, *Biochem. J.* 1953, 55, 220-230.
- [10] J. Williams, *J. Gen. Physiol.* 1928, 11, 309-337.
- [11] S. Cinti, F. Arduini, D. Moscone, G. Palleschi, A. Killard, *Sensors*, 2014, 14, 14222-14234.
- [12] M.A.T. Gilmarin, R.J. Ewen, J.P. Hart, C.L. Honeybourne, *Electroanalysis*, 1995, 7, 547-555.
- [13] L. Gonzalez-Macia, M. Smyth, A. Killard, *Electroanalysis*, 2012, 24, 609-614.
- [14] S.B. Hall, E.A. Khudaisha, A.L. Hart, *Electrochim. Acta*, 1998, 43, 579-588.
- [15] K.C. Honeychurch, *Adv. Anal. Chem.* 2013, 3A, 28-33.

- [16] M. Shafei, K.C. Honeychurch, *Anal. Methods*, 2013, 5, 6631-6636.
- [17] B. Liu and M. Wang, *Int. J. Electrochem. Sci.* 2013, 8, 8572-8578.
- [18] A.M. Golsheikh, N.M. Huang, H.N. Lim, R. Zakaria, C.-Y. Yin, *Carbon*, 2013, 62, 405-412.
- [19] C.M. Welch, C.E. Banks, A.O. Simm, R.G. Compton, *Anal. Bioanal. Chem.* 2005, 382, 12-21.
- [20] W. Lian, L. Wang, Y. Song, H. Yuan, S. Zhao, P. Li, L. Chen, *Electrochim. Acta*, 2009, 54, 4334-4339.
- [21] Y. Wenn, A.-J. Lin, H.-F. Chen, Y.-Z. Jiao, H.-F. Yang, *Biosens. Bioelectron.* 2013, 41, 857-861.
- [22] A. Afraz, A.A. Rafati, A. Hajian, *J. Solid State Electrochem.* 2013, 17, 2017-2025.
- [23] K. Liao, P. Mao, Y. Li, Y. Nan, F. Song, G. Wang, M. Han, *Sensor. Actuat. B-Chem.* 2013, 181, 125-129.
- [24] M. Vinoba, S. Kwan Jeong, M. Bhagiyalakshmi, M. Alagar, *Bull. Korean Chem. Soc.* 2010, 31, 3668-3674.
- [25] E. Kurowska, A. Brzozka, M. Jarosz, G.D. Sulka, M. Jaskula, *Electrochim. Acta* 2013, 104, 439-447.